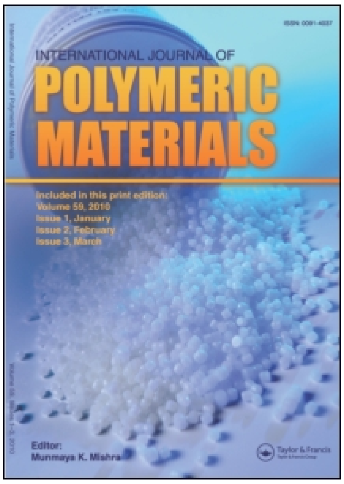

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Y. Murali Mohan[a]; K. Mohana Raju[a]
[a] Synthetic Polymer Laboratory, Department of Polymer Science & Technology, Sri Krishnadevaraya University, Anantapur, India

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Synthesis and Characterization of GAP-THF Copolymers

Y. Murali Mohan
K. Mohana Raju
Synthetic Polymer Laboratory, Department of Polymer Science & Technology, Sri Krishnadevaraya University, Anantapur, India

The present investigation describes the synthesis and characterization of poly(glycidyl azide-co-tetrahydrofuran) poly(GA-THF) or GAP-THF copolymers which are recognized as high-energy binders/plasticizers in explosive systems. GAP-THF copolymers were synthesized by copolymerization of epichlorohydrin (ECH) with tetrahydrofuran (THF) in presence of borontrifluoride etherate (BF_3-etherate) and ethylene glycol (EG) as catalyst and co-catalyst, respectively; and subsequent azidation of the product with sodium azide in dimethylformamide at 120°C. The GAP-THF copolymers and their precursors PECH-THF copolymers were well characterized by UV, IR, ^{1}H-NMR, ^{13}C-NMR spectroscopy. Molecular weights of these copolymers were determined using VPO (Vapor pressure osmometer) and GPC (Gel permeation chromatography) techniques. The synthesized GAP-THF copolymer followed a thermal decomposition behavior in its DSC and TGA analyses similar to that of pure GAP. However, the copolymer GAP-THF has shown a very low glass transition temperature (Tg) of -64°C.

Keywords: poly(epichlorohydrin) (PECH), glycidyl azide polymer (GAP), propellant binder, ring opening cationic polymerization, ECH-THF copolymer, GAP-THF copolymer

INTRODUCTION

A new type of high-energy binders and/or plasticizers are used in energy material formulations in order to modify the mechanical properties, increase the energy output, and to improve safety characteristics as well as to reduce the viscosity of the mixture for easier processing, maintenance of oxygen balance, and to improve the burn

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Address correspondence to K. Mohana Raju, Synthetic Polymer Laboratory, Department of Polymer Science & Technology, Sri Krishnadevaraya University, Anantapur, 515 003, India. E-mail: kmrmohan@yahoo.com

rate modification for solid propellant and explosive systems [1–2]. To enhance the performance of propellant/explosive systems, various workers have developed new binders/plasticizers containing high energetic groups like azido, nitramine, nitro, nitrato, and floroamino in the polymeric chain [2]. A promising recent approach is to increase the structural similarity and hence the miscibility by using low molecular weight oligomers of the polymer matrix as plasticizer. Among such polymers, azido polymer (glycidyl azide polymer (GAP)), containing terminal hydroxyl groups in its polyether backbone with alkyl azide substistuents, was found to be a great promising material for high-energy applications [3–15]. These polymer can be used as energetic binders (M.W. 2000–6000) as well as plasticizers (M.W. 500) in solid rocket propellants and explosive systems. GAP is widely used to increase the burn rate (BR) and specific impulse of the propellant systems. These facile properties are present in GAP due to its positive heat of formation (+957 kJ/kg), high oxygen balance (121.1 g O_2/100 g), low glass transition temperature (−48°C), low viscosity (2.4×10^3 cps at 25°C), high density (1.3 g/cm^3), and so on [3–4, 10–11]. GAP also led to realization of chlorine-free low pollution propellants with ammonium nitrate oxidizer [16–17]. Attempts were also made to replace the less energetic plasticizers di-octyl phthalate (DOP) or diethyl phthalate (DEP) with GAP [18–19]. Further, GAP possess good compatibility with high-energy pollution free oxidizers such as ammonium nitrate (AN), ammonium nitronitramide, or ammonium dinitramide (ADN) and hydrazinium nitroformate (HNF).

GAP is also widely used in conjunction with the conventional workhorse propellant binder, hydroxyl-terminated poly(butadiene) (HTPB). But, it is found that there is no compatibility between these two binders and their copolymers [16,20–22]. Further, GAP suffers from inferior mechanical properties when used as a binder alone. Moreover, it was noted that the critical temperature (Tc) of GAP is 6°C where the binder starts to loose its elastomeric properties under operation conditions [23]. The facile way to impart good mechanical properties to GAP is to copolymerize it with a monomer giving flexibility to the chain, like THF, ethylene oxide, or other vinyl monomers [24–25].

Therefore the present work deals with the synthesis of GAP-THF copolymer by ring opening polymerization of epichlorohydrin and tetrahydrofuran in presence of ethylene glycol/BF_3-etherate initiating system, to produce PECH-THF copolymer. Subsequently the same was azidated with sodium azide in a polar aprotic solvent (DMF) at 120°C for 10–12 h to obtain GAP-THF copolymer. The copolymers obtained were characterized by UV, IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy as well as by TGA, DSC, VPO, and GPC. These new binders/plasticizers having high energetic azide groups as well as flexible repeating units may possess better characteristics than the conventional binders.

EXPERIMENTAL

Materials

Epichlorohydrin (ECH), ethylene glycol (EG), dimethylformamide (DMF), and dichloromethane (DCM) were received from S.D. Fine-Chem Limited, Mumbai and purified by normal distillation. Borontrifluoride etherate (BF_3-etherate) obtained from Spectro Chem, Bombay was purified by distillation under reduced pressure. All the solvents and chemicals were stored over 4A molecular sieves. Nitrogen gas was purified by passing through pyrogallol solution, calcium chloride, and P_2O_5 towers.

Method of Synthesis

Synthesis of PECH-THF Copolymer [26–27]

The bulk copolymerization reactions of epichlorohydrin and tetrahydrofuran were carried out in a 50-ml polymerization tube at 0°C for 4 h under nitrogen atmosphere. After being capped with rubber septa, ethylene glycol was taken and dry nitrogen gas was passed to expel the air in the reaction tube. Then borontrifluoride etherate (catalyst) was added drop wise to the ethylene glycol for 5 min and stirring was continued for 10–20 min at room temperature. After the reaction flask was brought to 0°C using ice-salt mixture, the monomer mixture ECH/THF was added dropwise to the reaction mixture over a period of 20–30 min. After completion of the polymerization time, the viscous resin formed was dissolved in 25 ml of DCM and washed with distilled water. The polymer solution layer was washed with distilled water for several times to remove the unreacted compounds and finally the same was dried over sodium sulphate. The copolymer was obtained after distilling the solvent and tetrahydrofuran under vacuum. The reaction conditions and analytical details are presented in Table 1.

Synthesis of GAP-THF Copolymer [10,14]

The GAP-THF copolymers were obtained by reacting ECH-THF copolymers with sodium azide in dimethylformamide at 120°C for 10 h. The reaction was carried out in 250-ml two-necked flask equipped with a magnetic bar and a condenser having calcium

TABLE 1 Polymerization Details of PECH-THF and GAP-THF Copolymers

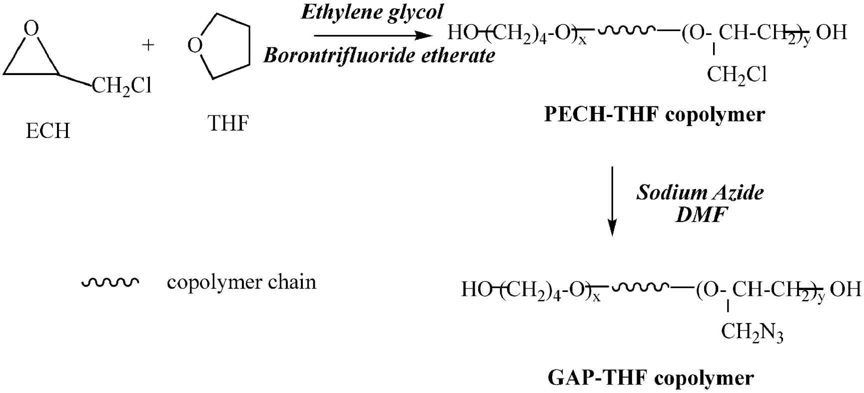
				PECH-THF molecular weight[b]				
				GPC		VPO		
Copolymer code	ECH (mol) (g)	THF (mol) (g)	Copolymer yield (%)[a]	$\overline{M}_n$	$\overline{M}_w$	PI[c]	$\overline{M}_n$	GAP-THF molecular weight VPO ($\overline{M}_n$)[d]
PECH-THF 1	0.108 (10.00)	1.108 (7.792)	89	570	1554	2.72	1425	1556
PECH-THF 2	0.108 (10.00)	0.081 (5.844)	92	568	1426	2.51	1382	1510
PECH-THF 3	0.108 (10.00)	0.054 (3.896)	93	572	1372	2.39	1315	1445
PECH-THF 4	0.108 (10.00)	0.027 (1.948)	95	571	1286	2.24	1260	1380

[a] Copolymer yield = [copolymer weight/(weight of glycol + weight of epichlorohydrin)] × 100;

[b] PECH-THF copolymer prepared using 1.00 ml of borontrifluoride etherate and 1.40 ml ethylene glycol;

[c] Polydispersity Index (PI) = $\overline{M}_w/\overline{M}_n$;

[d] $\overline{M}_n$ of GAP-THF copolymers derived from their corresponding PECH-THF copolymers.



SCHEME 1 Schematic preparative route of PECH-THF copolymer.

chloride guard tube. Equal weights of ECH-THF copolymer and sodium azide were taken in 50 ml of DMF and the reaction mixture stirred for 10 h at 120°C. Then, the reaction mixture was cooled to room temperature to obtain the copolymer solution, which was filtered to remove un-reacted sodium azide and sodium chloride (by product), and then washed several times with hot distilled water. Finally, the copolymer was dissolved in DCM and the solution was dried over anhydrous sodium sulphate. Pure GAP-THF copolymer was obtained after evaporation of DCM. The schematic representation of synthesis of GAP-THF copolymer, including the formation of PECH-THF copolymer, is depicted in Scheme 1.

Characterization

UV spectra of the copolymers (1 mg/1 ml chloroform) were obtained using a Shimadzu 160 A UV spectrophotometer. IR spectra of copolymers were taken with a Perkin Elmer 882 IR spectrophotometer. GPC measurements were carried out on a waters 501 gel permeation chromatography instrument equipped with refractive index (RI 1401) and UV detectors and three ultrastyragel columns. Number average molecular weight ($\overline{M}_n$) was measured by Knauer vapour pressure osmometer. ^{1}H-NMR and ^{13}C-NMR spectra of the copolymers were recorded using a Jeol GSX 400 MHz NMR spectrometer in $CDCl_3$ as solvent and TMS as internal standard. Elemental analysis of the copolymer was determined by Perkin Elemental Analyzer EA 1110. DSC analysis of copolymer was performed on a Netzsch DSC 204 instrument with a heating rate of 5°C/min under nitrogen flow.

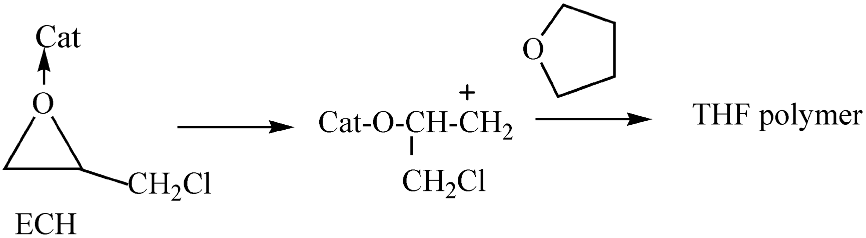
TGA analysis of the copolymers was performed on a DuPont 2100 TGA instrument with a heating rate of 10°C/min under 60 ml/min nitrogen flow. The nitrogen content of the copolymers was determined by redox method [28].

RESULTS AND DISCUSSION

T. Saegusa reported the copolymerization of tetrahydrofuran with cyclic ethers of different ring sizes and also found that even very small amounts of ECH have promoted the polymerization of THF in presence of small amounts of diol [26]. Generally, three or four membered cyclic ethers act as promoters, by reacting with the Lewis acid in the initiation step of the polymerization to form a highly reactive cyclicoxonium ion to induce the polymerization of tetrahydrofuran as shown in Scheme 2 [26–27,29]. Telechelic and multifunctional terminated polymers of tetrahydrofuran having terminal groups with symmetrical structure were prepared by the cationic ring-opening polymerization of tetrahydrofuran initiated by the combination of borontrifluoride etherate and epoxide in the presence of a low molecular weight polyhydroxylic compound [27,29] (Scheme 2).

In the present study, epichlorohydrin is employed, as a comonomer in the copolymerization of tetrahydrofuran to prepare ECH-THF copolymer, using ethylene glycol and BF_3 as initiating system. Four different monomeric ratios of ECH and THF were employed for the copolymerization and the results are presented in Table 1. It is observed that for all the monomer ratios, the copolymers were obtained within 2–3 h as brown-colored viscous resins. Nevertheless the copolymerization reaction was continued for 4 h.

The GPC curve of PECH-THF copolymer 1 is presented in Figure 1. GPC results, in Table 1 indicate that as the THF content increases in the reaction feed, this resulting polymer has a higher polydispersity. This may be due to increase total monomer concentration at a fixed



SCHEME 2 ECH initiated THF polymerization.

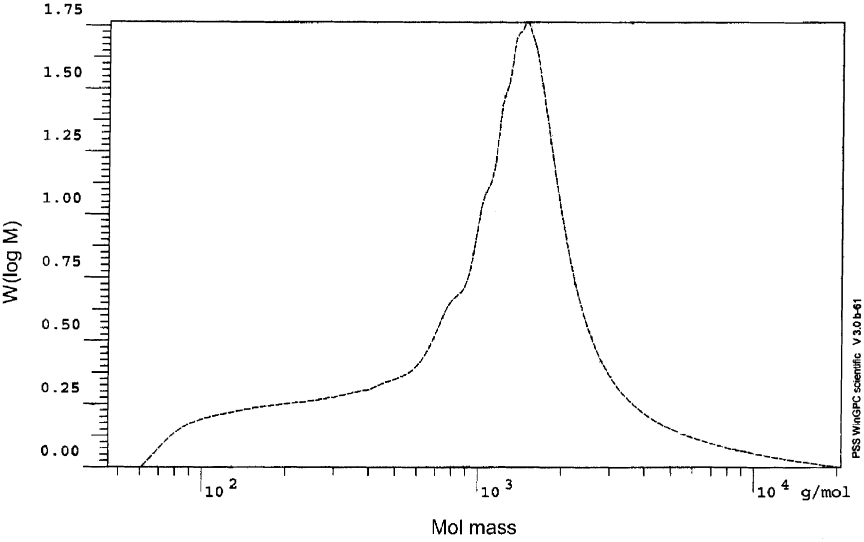


FIGURE 1 GPC curve of PECH-THF 1.

initiator concentration, and this is quite acceptable. Similar results were observed in VPO analysis of copolymers. Number average molecular weight ($\overline{M}_n$) of copolymers decreases as the total monomer concentration increases. The molecular weight details of the copolymers are presented in Table 1.

The obtained ECH-THF copolymer was treated with sodium azide to convert it into the corresponding azide copolymer. The molecular weights of GAP-THF copolymers were determined by VPO and the results are reported in Table 1. The scheme of the formation of GAP-THF copolymer is depicted in Scheme 1. Yasoda et al. found the presence of secondary hydroxyl end groups in the PECH-THF copolymer using NMR analysis of the PECH-THF and trichloroacetylisocyanate adduct [27].

The GAP-THF copolymers and its precursors were characterized by the usual analytical techniques and the details are given in what follows.

Structure

The UV spectral analysis gave sufficient information regarding the formation of PECH-THF and GAP-THF copolymers. UV spectra of PECH-THF and GAP-THF copolymers are presented in Figures 2

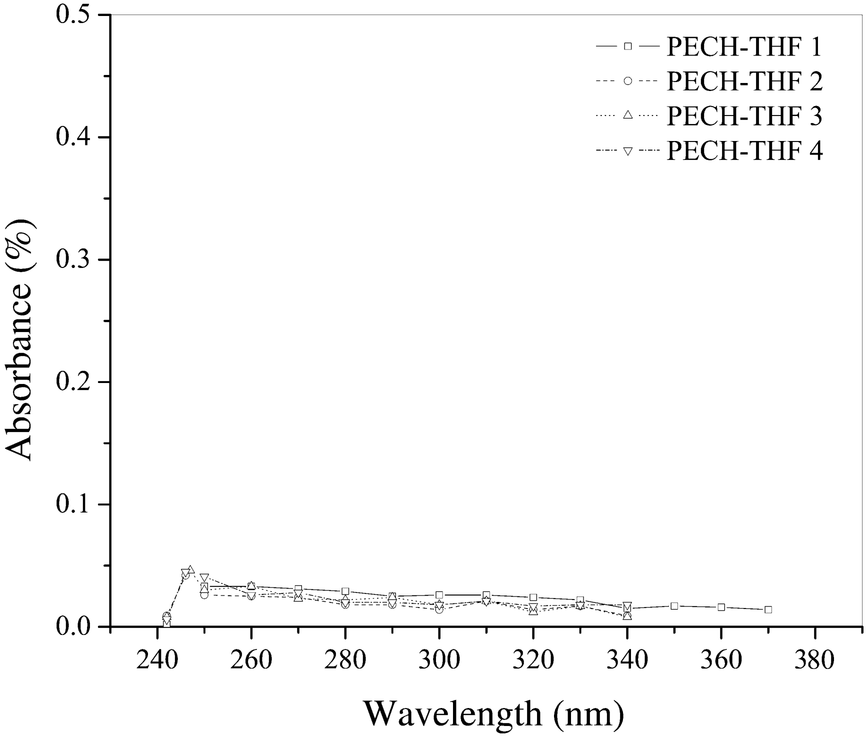


FIGURE 2 UV spectra of PECH-THF copolymers.

and 3, respectively. In Figure 2, no absorbance peaks were found in the UV region; the spectrum appears as a straight line. But clear absorption peaks were found at 247 and 278 nm in GAP-THF copolymers due to resonance peaks of nitrogen bonds in the $-N_3$ group (i.e., $-CH_2-N^{-}-N=N^{+}$ and $-CH_2-N^{-}-N^{+}\equiv N$) of GAP [10–12].

The IR spectrum of the PECH-THF copolymer showed strong broad band at 3378 cm^{-1} corresponding to –OH group; asymmetric and symmetric CH_2 and CH stretching bands at 2842 cm^{-1}, broad intense stretching vibration of C–O–C ether system at about 1110 cm^{-1}, and a strong C–Cl stretching vibration at 746 cm^{-1}. In the IR spectra of the GAP-THF copolymers, this 746 cm^{-1} peak of PECH was totally absent and two prominent peaks at 2106 cm^{-1} and 1275 cm^{-1}, corresponding to $-N_3$ of GAP units, were present, indicating the replacement of chlorine groups by azide units [4,10–12]. The representative Infrared spectra of the ECH-THF and GAP-THF copolymers are presented in Figure 4. The IR spectra could

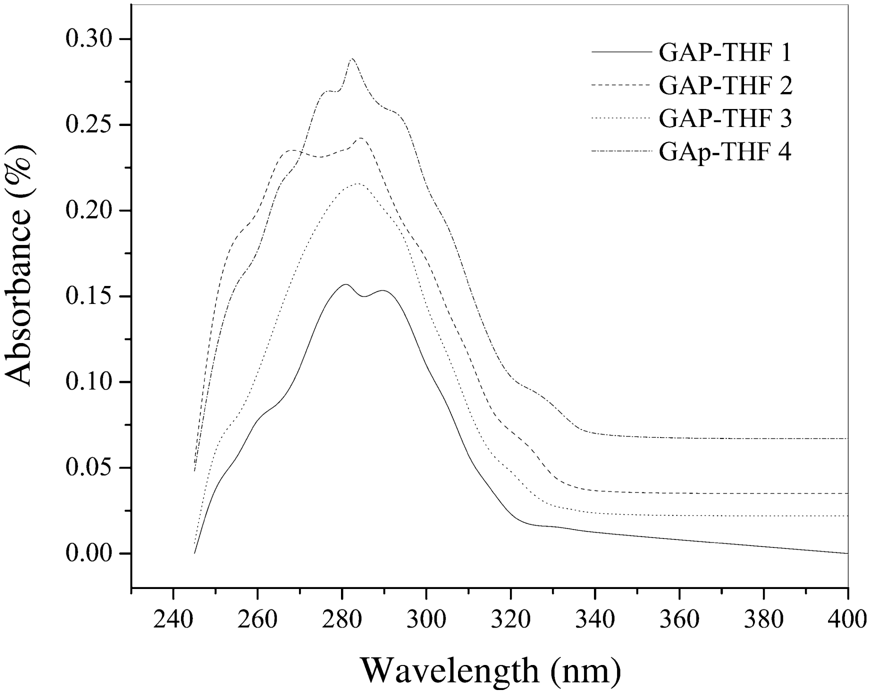


FIGURE 3 UV spectra of GAP-THF copolymers.

not give information whether the THF units are incorporated in the copolymer chains, due to similarity of THF and ECH and GAP units in the copolymer chain.

The proton NMR spectra of the copolymers further confirms the structural information gained by UV and IR spectra. The proton NMR spectra of ECH-THF copolymers exhibited peaks at 1.5 ppm ($-CH_2$, THF), 3.6 ($-CH_2Cl$), and 3.7 ($-O-CH_2$, $-O-CH$). The presence of resonance signals at 3.4 ppm corresponding to the CH_2N_3 protons of GAP in the NMR spectrum of GAP-THF copolymer indicates the conversion of PECH into GAP [4,10,30]. Representative proton NMR spectra of the copolymers are presented in Figure 5.

The ^{13}C-NMR spectra of the ECH-THF and GAP-THF copolymers shown in Figure 6 provide further subsidiary structural information complementing the information gained by UV, IR, and ^{1}H-NMR spectral analysis. The peaks observed between 60–85 ppm in the spectra correspond to methylene carbons along the copolymer chains, either attached to hydroxyl or ether oxygen. The chloromethyl peak of ECH units of ECH-THF copolymer are seen as a pair of peaks at 43.7 and 45.7 ppm.

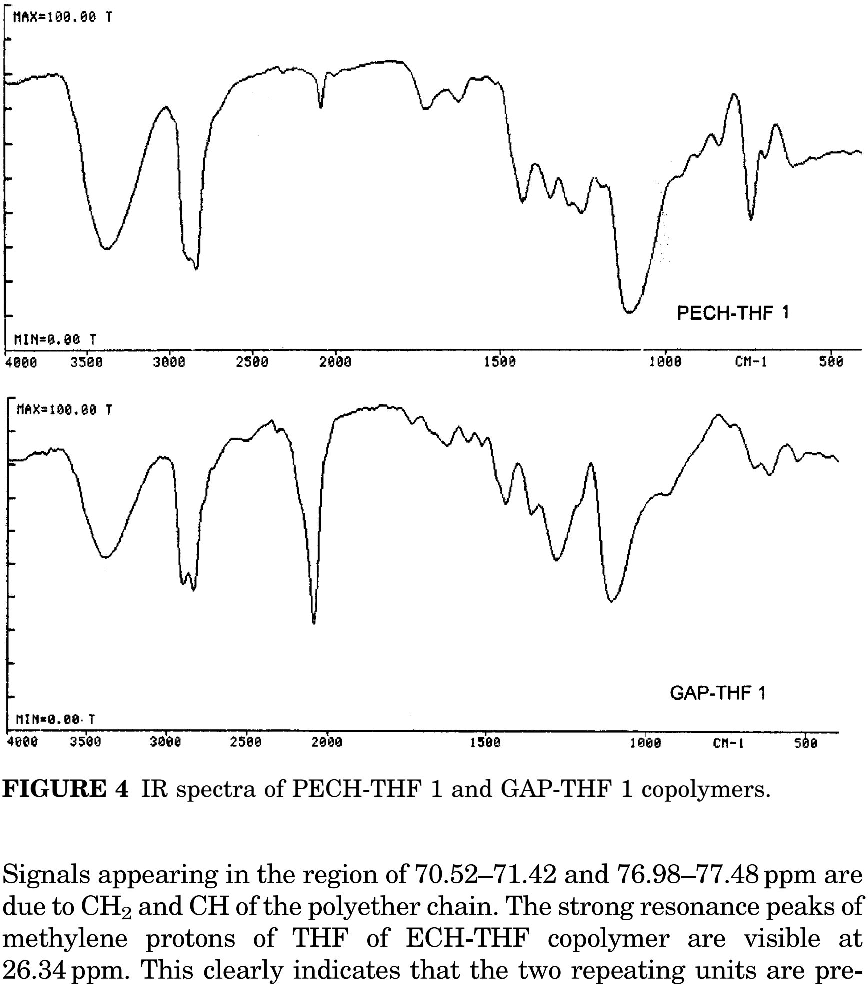


FIGURE 4 IR spectra of PECH-THF 1 and GAP-THF 1 copolymers.

Signals appearing in the region of 70.52–71.42 and 76.98–77.48 ppm are due to CH_2 and CH of the polyether chain. The strong resonance peaks of methylene protons of THF of ECH-THF copolymer are visible at 26.34 ppm. This clearly indicates that the two repeating units are presented in the copolymer. The GAP-THF copolymer shows the azidomethyl carbon resonance peak of GAP unit at 54.48 ppm along with total absence of resonance signals at 43.7–45.7 ppm corresponding to chloromethyl protons of ECH, confirming the azidation reaction was completed in the conversion reaction [30].

In summary, the spectral data of UV, IR, ^{1}H-NMR, and ^{13}C-NMR confirm the presence of two repeating units in the copolymer.

Thermal Analysis

Current research is not only focused on synthesis and characterization of polymers containing azide groups in the side chains but also on the

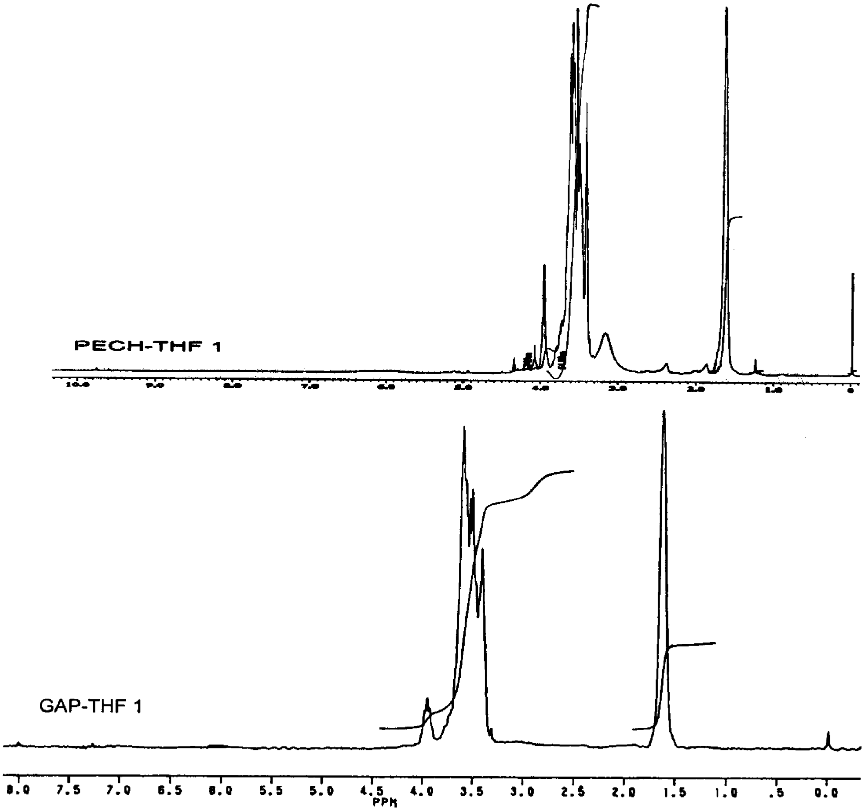


FIGURE 5 ^{1}H-NMR spectra of PECH-THF 1 and GAP-THF 1 copolymers.

thermal decomposition behavior of the binders, which significantly differs from that of the conventional used HTPB binder [3,31–32]. Therefore, in the present investigation, a detailed study was made on the thermal analysis of GAP-THF copolymer 1.

The DSC curve presented in Figure 7 demonstrates that the copolymer exhibited exothermic peak due to the presence of energetic azide group in the GAP block of the copolymer. The copolymer is thermally stable upto 180°C where the exothermic degradation starts. Maximum degradation is found at 238°C, due to the decomposition of the azide group of GAP unit of GAP-THF copolymer [4,10–12]. The energy liberation in the decomposition of azide group of GAP block is quantified as 1166 J/g. Glycidyl azide polymer (nitrogen content 42.42%) shows heat of degradation value of 1828 J/g [11–12]. From the DSC heat of degradation value of GAP-THF, the calculated nitrogen content is

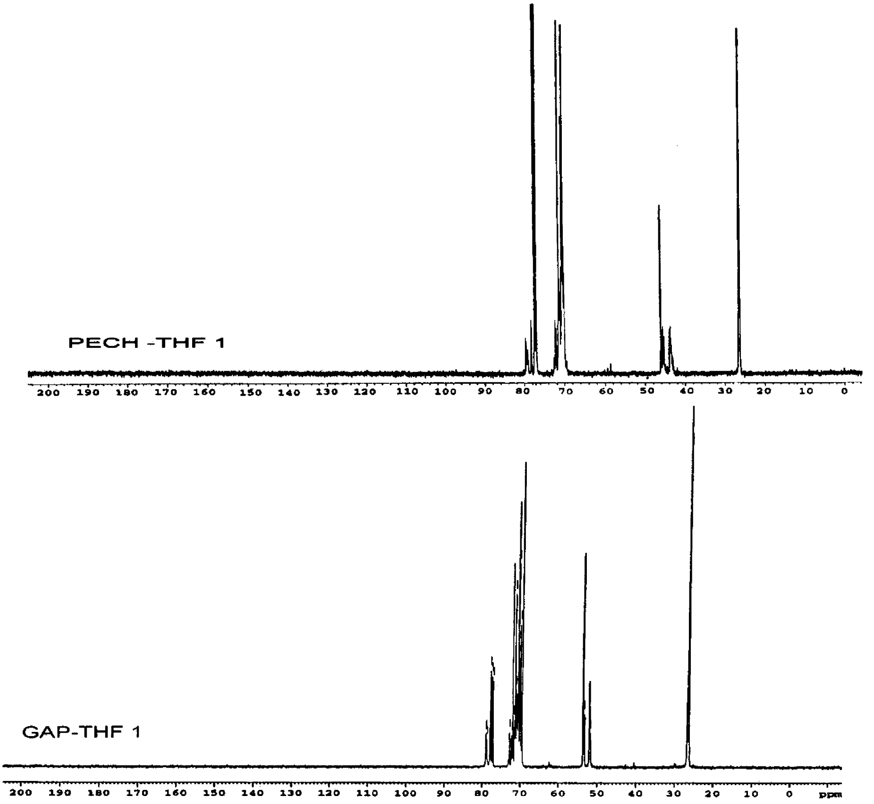


FIGURE 6 ^{13}C-NMR spectra of PECH-THF 1 and GAP-THF 1 copolymers.

27.05% by comparing with the pure GAP value. Further, the calculated nitrogen content of GAP-THF copolymer as determined by elemental analysis and redox method are 27.18 and 27.22, respectively, are in close agreement.

The TGA analysis of GAP-THF 1 (Figure 8) shows two-step degradation behavior. The first degradation starts around 180°C and the second degradation step 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 PECH repeating units, respectively [4,10–12]. The initial and maximum decomposition temperatures are observed at 225°C and 256°C, respectively. This compares with the precursor PECH-THF 1 that showed a maximum decomposition temperature at 338°C.

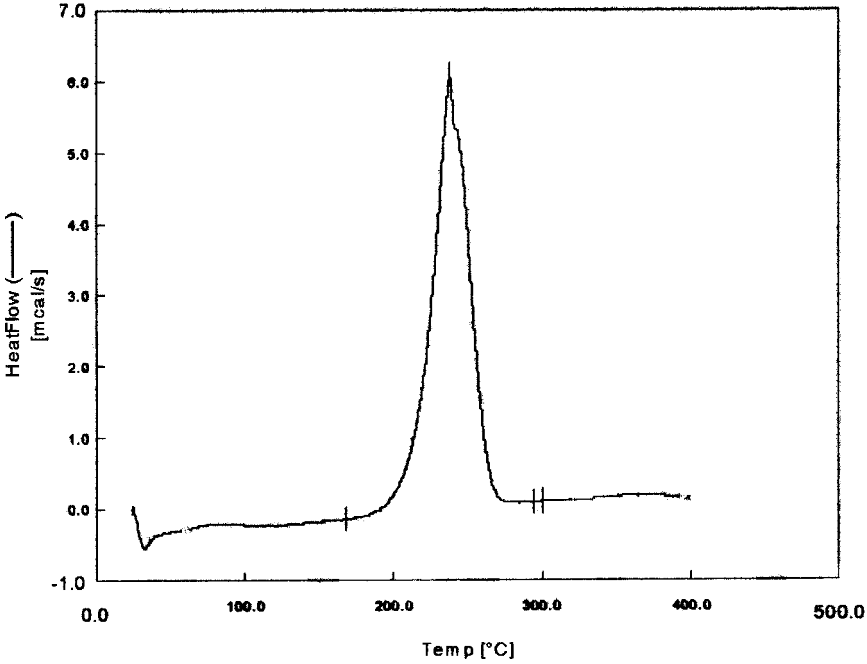


FIGURE 7 DSC curve of GAP-THF 1.

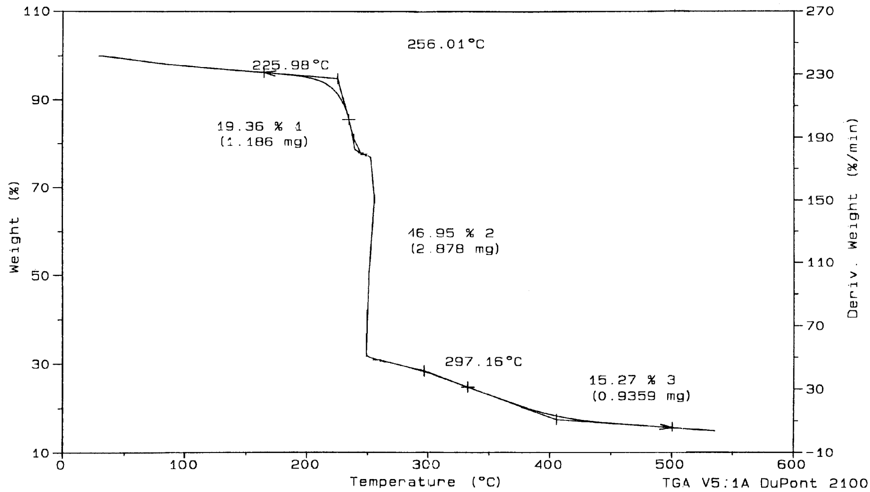


FIGURE 8 TGA curve of GAP-THF 1.

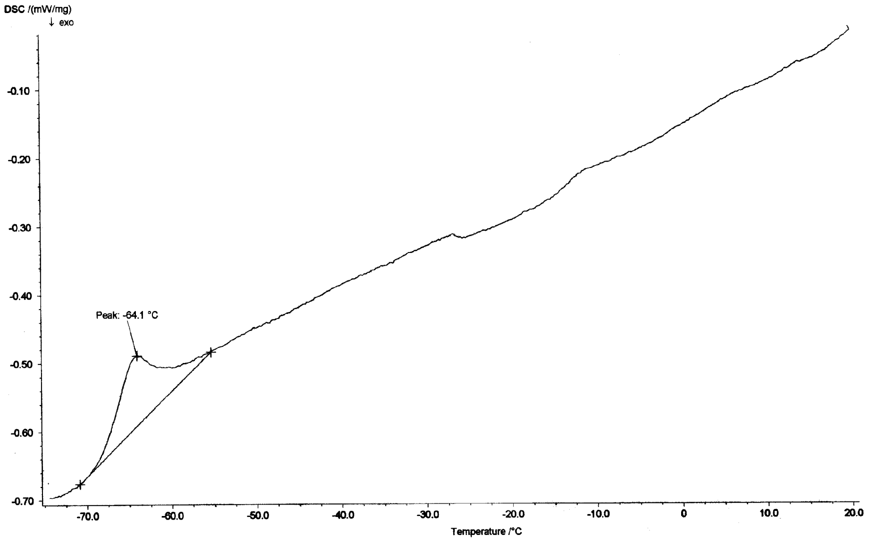


FIGURE 9 DSC glass transition curve of GAP-THF 1.

Low glass transition temperatures (Tg) is an important parameter to obtain favorable low temperature mechanical properties. Because GAP has somewhat higher T_g (−48°C) compared with HTPB (−72°C), it shows inferior mechano–chemical property. In the present investigation, GAP-THF 1 showed low glass transition temperature, is glycidyl azide-ethylene oxide (GAP-EO) copolymer, branched GAP, low molecular weight GAP, and its copolymers [8,24,33]. As expected, a prominent single glass transition temperature (T_g) peak is identified in the DSC thermogram, shown in Figure 9, for GAP-THF copolymer 1, because of compatibility of the two repeating units GAP and THF in the copolymer. The glass transition is found at −64°C, which is very low when compared to pure GAP.

CONCLUSIONS

The GAP-THF copolymers were synthesized via conventional two-step process, involving the bulk polymerization of ECH and THF, in the presence of small amount of ethylene glycol and borontrifluoride etherate, and its subsequent azidation. The synthesized PECH-THF and GAP-THF copolymers are characterized by UV, IR,^{1}H-NMR, and ^{13}C-NMR spectroscopy. The average molecular weights of the copolymers were determined using VPO and GPC. Thermal characteristics of GAP-THF copolymer (1) are fully characterized by DSC and TGA.

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