Synthesis and Characterization of GAP-THF Copolymers
4.1. INTRODUCTION

New type of high energetic binders/plasticizers are used in high energy materials formulations in order to modify the mechanical properties, to increase in the energy output and to improve the safety characteristics as well as to reduce the viscosity of the mixture for easier processing, maintenance of oxygen balance, and to improve the burn rate characteristics for solid propellant and explosive systems\textsuperscript{1,2}. To improve the performance of propellant/explosive systems, various workers have developed new binders/plasticizers containing high energetic groups like azido, nitramine, nitro, nitrato, and fluoroamino in the polymeric chain\textsuperscript{2}. The recent approach in this filed is to increase the structural similarity of the polymeric binder and hence the miscibility by using low molecular weight oligomers of the polymer matrix as plasticizers. Among such polymeric binders, glycidyl azide polymer (GAP) or poly(glycidyl azide) (PGA), containing terminal hydroxyl groups in their polyether backbone with alkyl azide substitutes is found to be a great promising material for high energetic applications\textsuperscript{3-14}. This polymer can be used as energetic binder (Molecular weight 2000-6000) as well as plasticizer (M.W. 500) in solid rocket propellants and explosive systems. GAP is widely used to increase the burn rate (BR) and specific impulse in the propellant systems. These facile properties are obtained to GAP due to its positive heat of formation (+ 957 kJ/kg), high oxygen balance (121.1 g O\textsubscript{2}/100g), low glass transition temperature (-48\textdegree{}C), low viscosity (2.4 x 10\textsuperscript{3} cps at 25\textdegree{}C), high density (1.3 g/cm\textsuperscript{3}), etc\textsuperscript{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 less energetic plasticizer like di-octyl phthalate (DOP) or diethyl phthalate (DEP) with GAP$^{18,19}$. Further GAP has good compatibility with high energetic chlorine free oxidizers like, ammonium nitrate (AN), ammonium dinitramide (ADN), and hydrazinium nitroformate (HNF).

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

Therefore, the present work involves the synthesis of GAP-THF copolymers by simultaneous ring opening polymerization of epichlorohydrin with tetrahydrofuran in presence of ethylene glycol/BF$_3$-etherate initiating system to produce PECH-THF copolymers and their subsequent azidation with sodium azide in a polar aprotic solvent (DMF) at 120°C for 10-12 hrs to obtain GAP-THF copolymer. The copolymers obtained were characterized by UV, IR, $^1$H-NMR and $^{13}$C-NMR spectral studies as well as by TGA, DSC, VPO and GPC. These new binders/plasticizers having high energetic azide groups as well as flexible repeating units were developed to impart better characteristics than the conventional binders.

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4.2. EXPERIMENTAL

4.2.1. 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. Boron trifluoride etherate (BF\textsubscript{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\textsubscript{2}O\textsubscript{5} towers.

4.2.2. Synthesis of PECH-THF copolymer\textsuperscript{26,27}

The bulk copolymerization reactions of epichlorohydrin and tetrahydrofuran were carried out in a 50-ml polymerization tube at 0\textdegree C for 4 hrs 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 boron trifluoride etherate (catalyst) was added drop wise to the ethylene glycol for 5 minutes and allowed stirring for 10-20 minutes at room temperature. After the reaction flask was brought to 0\textdegree C using ice-salt mixture, the monomer mixture ECH/THF was added drop wise to the reaction mixture for a period of 20-30 minutes. 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 un-reacted compounds and finally the same was dried over sodium sulphate. The copolymer was obtained after removing the solvent and the un-reacted tetrahydrofuran by distillation under vacuum.
4.2.3. Synthesis of GAP-THF copolymer

The GAP-THF copolymers were obtained by reacting ECH-THF copolymers with sodium azide in dimethylformamide at 120°C for 10 hrs. The reaction was carried out in 250-ml two-necked flask equipped with a magnetic bar and a condenser having calcium chloride guard tube. Equal weights of ECH-THF copolymer and sodium azide were taken in 50 ml of DMF and stirred the reaction mixture for 10 hrs at 120°C. Then the reaction mixture was cooled to room temperature, to obtain the copolymer solution which was filtered to remove the 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 was depicted in Scheme 4.1.

Scheme 4.1. Synthesis of GAP-THF copolymer
4.2.4. Characterization

UV spectra of the copolymers (1 mg/1 ml in chloroform) were obtained using Shimadzu 160 A UV spectrophotometer. IR spectra of the copolymers were taken with a Perkin Elmer - 882 IR spectrophotometer. Molecular weight measurements were carried out on a Thermoquest gel permeation chromatography connected with spectra series P 100 pump; RI 150 and UV 100 detectors. Number average molecular weight (Mn) was determined 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 copolymers were determined by Perkin Elemental Analyzer EA 1110. DSC analysis of copolymer was performed on a NETZSCH DSC 204 instrument with a heating rate of $5^\circ$C/min under nitrogen flow. TGA analysis of the copolymers was performed on a Dupont 2100 TGA instrument with a heating rate of $10^\circ$C/min under 60 ml/min nitrogen flow.

4.3. RESULTS AND DISCUSSION

Saegusa reported$^{26}$ the copolymerization of tetrahydrofuran with cyclic ethers of different ring sizes and also found that even very small amounts of ECH promoted the polymerization of THF in presence of small amounts of diol. Generally, three or four membered cyclic ethers act as promoters, by reacting with Lewis acid in the initiation step of the polymerization to form a highly reactive cyclicoxonium ion to induce the polymerization of tetrahydrofuran$^{26-29}$ as shown in Scheme 4.2. 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 boron trifluoride etherate and epoxide in presence of a low molecular weight polyhydroxylic compounds\textsuperscript{27,29}.

\begin{center}
\begin{tikzpicture}
  \node (p1) [draw, shape=ellipse, minimum height=1.5em, minimum width=1.5em] at (0,0) {ECH};
  \node (p2) [draw, shape=ellipse, minimum height=1.5em, minimum width=1.5em] at (1.5,0) {\text{Cat\textcdotO\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\textcdotCH\text·
Figure 4.1. GPC curve of PECH-THF copolymers

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PECH-THF copolymers obtained were treated with sodium azide to convert them into corresponding GAP-THF copolymers. The molecular weights of GAP-THF copolymers were determined by VPO and the results are presented in Table 4.1.

**Table 4.1.** Polymerization details of PECH-THF copolymers; and molecular weight data of PECH-THF and GAP-THF copolymers

<table>
<thead>
<tr>
<th>Copolymer code</th>
<th>ECH (mol) (g)</th>
<th>THF (mol) (g)</th>
<th>Copolymer yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>PECH-THF 1</td>
<td>0.108 (10.00)</td>
<td>1.108 (7.792)</td>
<td>89</td>
</tr>
<tr>
<td>PECH-THF 2</td>
<td>0.108 (10.00)</td>
<td>0.081 (5.844)</td>
<td>92</td>
</tr>
<tr>
<td>PECH-THF 3</td>
<td>0.108 (10.00)</td>
<td>0.054 (3.896)</td>
<td>93</td>
</tr>
<tr>
<td>PECH-THF 4</td>
<td>0.108 (10.00)</td>
<td>0.027 (1.948)</td>
<td>95</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PECH-THF copolymers&lt;sup&gt;b&lt;/sup&gt;</th>
<th>GAP-THF copolymers&lt;sup&gt;d&lt;/sup&gt; VPO</th>
</tr>
</thead>
<tbody>
<tr>
<td>GPC</td>
<td>VPO</td>
</tr>
<tr>
<td>$\overline{M}_n$</td>
<td>$\overline{M}_w$</td>
</tr>
<tr>
<td>570</td>
<td>1554</td>
</tr>
<tr>
<td>568</td>
<td>1426</td>
</tr>
<tr>
<td>572</td>
<td>1372</td>
</tr>
<tr>
<td>571</td>
<td>1286</td>
</tr>
</tbody>
</table>

<sup>a</sup>- copolymer yield = \([\text{copolymer weight}/(\text{weight of glycol + weight of epichlorohydrin})] \times 100 \)

<sup>b</sup>- PECH-THF copolymers prepared using 1.00 ml of boron trifluoride etherate and 1.40 ml ethylene glycol;<br>
<sup>c</sup>- Polydispersity Index ($P_I$) = $\overline{M}_w/\overline{M}_n$.<br>
<sup>d</sup>- $\overline{M}_n$ of GAP-THF copolymers derived from their corresponding PECH-THF copolymers.
The scheme of the formation of GAP-THF copolymer is depicted in Scheme 4.1. Yasuda et al.\textsuperscript{27} found the presence of secondary hydroxyl end groups in the PECH-THF copolymer by proton NMR analysis of the derivative of PECH-THF with trichloroacetylisocyanate adduct. This analysis suggests that the THF repeating units were in the centre of the polymer chain as shown in Scheme 4.1.

The GAP-THF copolymers and their precursors were characterized by the usual analytical techniques and the details are given below.

4.3.1. Spectral analysis

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 4.2 and 4.3, respectively.

\textbf{Figure 4.2.} UV spectra PECH-THF copolymers  \quad \textbf{Figure 4.3.} UV spectra GAP-THF copolymers

In Figure 4.2, no absorbance peaks were found in the UV region, showing it like 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., \(-CH_2-N^\dagger-N=\dagger\) and \(-CH_2-N^\dagger'-N^\dagger=\dagger\)) of GAP\textsuperscript{10-12}.

The IR spectra of the PECH-THF copolymers showed strong broad band at 3378 cm\(^{-1}\) corresponding to \(-OH\) group; asymmetric and symmetric CH\(_2\) and CH stretching bands in the region of 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, the peak corresponding to C-Cl of PECH at 746 cm\(^{-1}\) was totally absent and two prominent peaks corresponding to azide units were appeared at 2106 cm\(^{-1}\) and 1275 cm\(^{-1}\) indicating the complete replacement of chlorine atoms by azide groups\textsuperscript{4,10-12}. The representative Infrared spectra of PECH-THF and GAP-THF copolymers are presented in Figures 4.4 and 4.5, respectively. The IR spectra is unable to provide the information regarding the presence of THF units in the copolymer chains due to similarity of THF, ECH and GAP units in the copolymer chain.

![Representative IR spectrum of PECH-THF copolymer 1](image)

**Figure 4.4.** Representative IR spectrum of PECH-THF copolymer 1
Figure 4.5. IR spectra of GAP-THF copolymers
The proton NMR spectra of copolymers further confirm the structural information gained by UV and IR spectra. The proton NMR spectra of ECH-THF copolymers exhibited peaks at 1.5 ppm (\(-\text{CH}_2\), THF), 3.6 (\(-\text{CH}_2\text{Cl}\)), and 3.7 (\(-\text{O-CH}_2\), \(-\text{O-CH}\)). The presence of resonance signals at 3.4 ppm corresponding to the \(\text{CH}_2\text{N}_3\) protons of GAP in the NMR spectrum of GAP-THF copolymer indicates the conversion of PECH units into GAP units\(^4,10,30\). The representative proton NMR spectra of the PECH-THF and GAP-THF copolymers are presented in Figures 4.6 and 4.7, respectively.
Figure 4.6. $^1$H-NMR spectra of PECH-THF copolymers
The $^{13}$C-NMR spectra of the ECH-THF and GAP-THF copolymers shown in Figures 4.8 and 4.9, provides further subsidiary structural information complementing the information gained by UV, IR, and $^1$H-NMR spectral analysis. The peaks observed in the spectra in between 60-85 ppm corresponds to methine or methylene carbons present in the copolymer chains, either attached to hydroxyl or ether oxygen. The chloromethyl peak of ECH units of ECH-THF copolymer were observed as a pair of peaks at 43.7 and 45.7 ppm. Peaks 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 comonomer units are present in the copolymer. The GAP-THF copolymer shows the azidomethyl carbon resonance peak of GAP unit at 54.48 ppm 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\textsuperscript{30}.

Figure 4.7. $^1$H-NMR spectra of GAP-THF copolymers
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PECH-THF 1

PECH-THF 2

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Figure 4.8. $^{13}$C NMR spectra of PECH-THF copolymers
In summary, the spectral data of UV, IR, $^1$H-NMR and $^{13}$C-NMR confirms the presence of two repeating units in the copolymer chain.

4.3.2. Thermal analysis

The work is not only focused on the synthesis and characterization of polymers containing pendant azide groups but also involves the thermal decomposition behaviour of the binders which is an important factor and significantly differs from the conventional used HTPB binder$^{31,32}$. Therefore, in the present investigation, a detailed study was carried out on the thermal behaviour of GAP-THF copolymer 1.
The DSC curve presented in Figure 4.10 demonstrates that the copolymer exhibited an exothermic peak due to the decomposition of the energetic azide groups in the GAP block of the copolymer.

**Figure 4.10. DSC thermogram of GAP-THF copolymer 1**

The copolymer is thermally stable up to 180°C while the exothermic degradation starts at 180°C and maximum degradation is found at 238°C due to the decomposition of the azide groups of GAP units of GAP-THF copolymer. The energy liberation in the decomposition of azide group of GAP block is quantified as 1166 J/g. Pure glycidyl azide polymer (nitrogen content 42.42%) shows heat of degradation value of 1828 J/g. From the DSC analysis heat of degradation value of GAP-THF, the nitrogen content found is 27.05% by comparing with pure GAP value. Further, the amount of nitrogen...
The content of GAP-THF copolymer as determined by elemental analysis is found to be 27.18, which is in close agreement with the DSC value.

The TGA analysis of GAP-THF 1 (Figure 4.11) showed two-step degradation behaviour. The first degradation starts around 180°C and the second degradation step starts around 290°C. These degradation steps are due to the elimination of nitrogen from the azide groups of the GAP units in the copolymers as well as by the degradation of the polyether main chain of the GAP and THF repeating units, respectively. The initial and maximum decomposition temperatures were observed at 225°C and 256°C, respectively. Whereas its precursor PECH-THF 1 showed maximum decomposition temperature at 338°C.

Figure 4.11. TGA curve of GAP-THF 1

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Low glass transition temperature (Tg) is an important parameter to obtain favourable low temperature mechanical properties to the propellant binder. GAP has somewhat higher Tg (−48°C) compared to HTPB (−72°C), shows inferior mechano-chemical properties. In the present investigation, GAP-THF 1 showed low glass transition temperature like glycidyl azide-ethylene oxide (GAP-EO) copolymer, branched GAP, low molecular weight GAP, and its copolymers. As expected previously, a prominent single glass transition temperature (Tg) peak is identified in the DSC thermogram as shown in Figure 4.12 for GAP-THF copolymer 1, which is due to the compatibility of the GAP and THF repeating units in the copolymer. The glass transition temperature is found at −64°C, which is very low when compared to pure GAP.

![DSC glass transition curve of GAP-THF 1](image)

**Figure 4.12.** DSC glass transition curve of GAP-THF 1
4.4. CONCLUSION

The GAP-THF copolymers were synthesized in a conventional two-step process, involving the bulk polymerization of ECH and THF in the presence of small amount of ethylene glycol and boron trifluoride etherate and their subsequent azidation using sodium azide. The synthesized PECH-THF and GAP-THF copolymers were 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 behaviour of GAP-THF copolymer (1) was fully characterized by DSC and TGA.

4.5. REFERENCES


