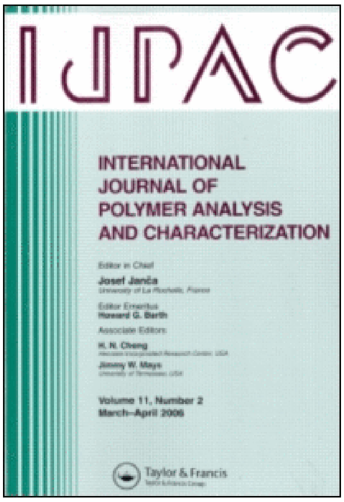

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Synthesis and Characterization of Low Molecular Weight Azido Polymers as High Energetic Plasticizers

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The present work describes a convenient process for the preparation of low molecular weight hydroxyl-terminated glycidyl azide polymers. The facile route involves the formation of glycidyl azide polymer in a single step. The polymerization of epichlorohydrin was carried out in dipolar aprotic solvent N,N^1-dimethylformamide (DMF) medium using diols as initiators in the presence of sodium azide. Various low molecular weight diols such as ethylene glycol (EG), propylene glycol (PG), diethylene glycol (DEG), 2-methylpentane-2,4-diol (MPD), and resorcinol (RS) are employed as initiators in the present investigation. The effect of initiating diols on the polymer formation was confirmed by gel permeation chromatography (GPC) and vapor pressure osmometry (VPO). The GPC analysis indicates that the glycidyl azide polymers (GAPs) contain different-sized oligomers, due, to the multimodal molecular weight distribution. The GAPs obtained in all the polymerizations by using different diols have a maximum of five to seven glycidyl azide repeating units. Further, the effect of diol on the GAP decomposition was investigated, and it was found that the GAPs obtained by using different diol units have a thermal decomposition pattern similar to that of glycidyl azide polymer. Since the glycidyl azide polymers have low molecular weights, their glass transition temperatures, are lower, betweens −70° and −72°C, due to variation in the structure of the polymers. Structural analysis of the GAPs using spectral methods revealed that the initiating diol units are present in the polyether backbone of GAPs. Nitrogen content and solubility tests were also performed.

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Keywords: Glycidyl azide polymer (GAP); Azidation; Propellant binder; Energetic plasticizer

INTRODUCTION

Telechelic polyethers having alkyl azide constituents are useful as energetic binders as well as plasticizers in composite explosives and solid propellants[1–6]. One such distinct polyether is glycidyl azide polymer (GAP) or poly(glycidyl azide) (PGA). This prominent material is used in solid rocket propellant systems and composite explosives as an energetic propellant binder (molecular weight (MW) 2000–6000) and as a plasticizer (MW 500) to improve mechanical properties, increase performance, impart additional energy, and enhance the stability of the system[7] In fact, GAP has become one of the promising potential candidate in rocket propellant technology due to its high positive heat of formation[8], low glass transition temperature (Tg)[9,10], low viscosity and high density when compared to other prepolymers[9,10], etc. GAP produces low-pollution propellants in conjunction with ammonium nitrate oxidizer[11]. It is also considered a better replacement material for diethyl phthalate (DEP) plasticizer in both cross-linked and cross-linked composite modified double-based (CMDB) propellants[12,13]. Due to its high-energy potential and low detonation sensitivity properties, it is very widely employed as a polymeric binder in propellant technology.

Because of GAP's excellent properties, extensive research work is going on all over the world for the development of different GAPs, such as hydroxyl-terminated GAPs[3], branched GAPs[4], azido-terminated GAPs[14], direct synthesis of GAPs[15], GAPs containing diol units[16], GAP-ethylene oxide copolymers (GAPs-PEO)[17], GAP-poly(ethylene glycol) copolymers (GAP-PEG)[18], GAP-tetrahydrofuran copolymers (GAP-THF)[19], GAP-hydroxyl-terminated poly(butadiene) block and graft copolymers (GAP-b-HTPB) (GAP-g-HTPB)[20,21], and other GAP copolymers[22,23] for propellant formulations as well as for superior performance[24]. The influence of GAP, hydroxyl-terminated poly (butadiene) (HTPB), and cellulose acetate butyrate (CAB) polymeric binders on properties of nitramine propellants, such as cyclotrimethylene trinitramine (RDX), cyclotetramethylene tetranitramine (HMX), nitroglycerine (NG), and triaminoguanidine nitrate (TAGN), was studied by Volk and Bathelt[24], who found that nitramine-based GAP propellants have superior specific energies when compared to other propellant binders. This is due to their more positive heat of formation and better oxygen balance when compared to HTPB. However, GAP is widely used in conjunction with HTPB. Even though GAP has many excellent properties, it suffers from poor mechanical properties. This is due to the hard and brittle nature of GAP at low temperatures because the rigid conjugated $-N_3$ groups limit the flexibility of the polymer chains. The poor mechanical properties of the GAP polymer can be improved remarkably by the incorporation of low molecular weight energetic azido plasticizers, such as GAP (MW $\approx$500).

Many reports in the literature have shown that GAP can be produced by a two-step process[3,4,9,10,16,18] involving initial preparation of poly (epichlorohydrin) (PECH) and its subsequent conversion into GAP by treatment with sodium azide in polar aprotic solvents like dimethyl sulphoxide (DMSO), N,N-dimethyl formamide (DMF), and N,N-dimethyl acetamide (DMAc). The conversion of poly(epichlorohydrin) into GAP requires longer reaction times in aqueous media[25]. Fast neutron activation analysis of glycidyl azide polymers indicates that the complete conversion of poly(epichlorohydrin) to glycidyl azide polymer was achieved after 12 h of reaction time[26]. In contrast to the above methods, a convenient single-step process was reported by Ahad[15] employing epichlorohydrin as starting material in the presence of sodium azide using ethylene glycol as initiator.

The present investigation describes a process for the preparation of telechelic glycidyl azide polymers containing five to seven ether repeating units from the epichlorohydrin monomer in the presence of sodium azide by using different diols as initiators. The formation of telechelic GAPs and their structural information was verified by spectral analysis. The effect of the presence of different diol units in the polymer main chain on the properties of GAPs was obtained from gel permeation chromatography (GPC), elemental, and thermal analysis.

EXPERIMENTAL

Materials

Epichlorohydrin (ECH), ethylene glycol (EG), propylene glycol (PG), diethylene glycol (DEG), 2-methylpentane-2,4-diol (MPD), resorcinol (RS), N,N-dimethyl formamide (DMF), dichloromethane (DCM), and sodium azide (98% purity) were purchased from S.D. Fine-Chem Limited (Bombay, India). ECH, EG, PG, DEG, MPD, and DMF were distilled before use.

Synthesis of Glycidyl Azide Polymer

Sodium azide was added slowly to the stirred mixture of epichlorohydrin, N,N^1-dimethyl formamide, and diol at 70°C. The azidation reaction started immediately as the sodium azide was added to the reaction mixture. Once the addition of sodium azide was completed and no sudden rise in temperature was noticed, the reaction temperature was maintained at 100°C for 25–30 h. After completion of the reaction, the reaction flask was brought to room temperature, and the unreacted sodium azide and the by-product (sodium chloride) were removed by filtration. The polymer solution was washed three times with 50 mL of hot water (50°C–60°C) in order to remove the unreacted diol and DMF solvent. Finally, the polymer was dissolved in dichloromethane, and the polymer solution was dried over sodium sulfate and then passed through a column containing 5 g silica gel. The dichloromethane solvent was removed by evaporating the polymer solution at 50°C and finally stripping under vacuum to yield a constant weight of a resin with an amber/brown color. The polymerization reactions were conducted by using different diols as initiators, and the results are shown in Table I.

Analysis of the Polymers

The UV spectra of polymers were measured using a Shimadzu 160 A UV spectrophotometer under dilute solutions (1 mg/1 mL of chloroform). IR spectra of polymers were recorded with a Perkin Elmer 882 IR spectrophotometer. ^{1}H-NMR spectra of polymers were carried out using a JEOL GSX 400 MHz nuclear magnetic resonance (NMR) spectrometer in $CDCl_3$ solvent using tetramethylsilane as internal standard. The GPC analysis of polymers was performed using a Thermoquest gel permeation chromatography instrument equipped with spectra series P 100 pump. GPC measurements were done using 100 Å, 500 Å, 10^3 Å, 10^4 Å, and one linear ultrastyragel columns with THF as the eluent at a flow rate of 1 mL/min at 30°C. Standard monodisperse polymethyl methacrylate (PMMA) standards (Polymer Laboratories, U.K.) were used for calibration. The molecular weight measurements were carried out using a Knauer vapor pressure osmometer (VPO) instrument using benzil as a standard. Thermal analysis of polymers was performed by a Netzsch DSC 204 instrument at a heating rate of 10°C/min under nitrogen flow. The nitrogen content of the synthesized polymers was found by a Perkin Elmer Elemental Analyzer, DSC, and redox methods.

RESULTS AND DISCUSSION

Improved mechanical properties can be imparted to GAP propellants by incorporation of energetic azido functional plasticizers, such as GAP plasticizers (molecular weight $\approx$500)[27]. Further, the GAP plasticizers are also compatible with nitrate esters, such as butanetriol trinitrate (BTTN) and trimethylol ethane trinitrate (TMETN). In the early 1990s

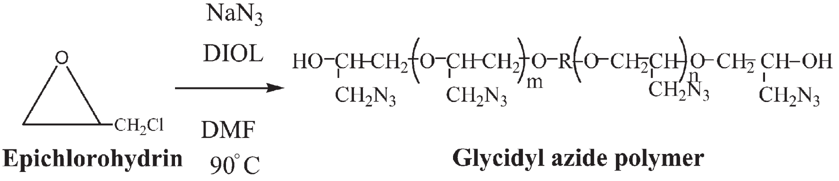
TABLE I Analytical details of glycidyl azide polymers containing low molecular weight diol units

Polymer code	ECH (mol)	LMW diol (mol)	Number average molecular weight (Mn) (g/mol)	Polymer yield (%)	LMW diol unit identified in polymeric chains	
					IR spectroscopy	UV spectroscopy
GAPEG	0.10807	0.01079	598	68.2	No peak identified	No peak identified
GAPPG	0.10807	0.00108	675	62.7	No peak identified	No peak identified
GAPDEG	0.10807	0.01079	620	64.8	No peak identified	No peak identified
GAPMPD	0.10807	0.01079	644	60.5	No peak identified	No peak identified
GAPRS	0.10807	0.01079	705	63.2	Peak observed at 1690 cm^{-1}	Peaks observed at 245 nm and 290 nm

Frankel developed a facile and improved process for the synthesis of GAP plasticizer in a single step using epichlorohydrin as starting material[15].

In the present investigation, the direct one-step synthesis of GAP plasticizers (low molecular weight GAP) was achieved using different diols as initiators in the polymerization of ECH in the presence of sodium azide, in contrast to conventional procedures involving a two-step process via the polymerization of ECH and its subsequent azidation, resulting in relatively high molecular weight polymers. The two-step GAP synthesis process is time-consuming and involves more work-up time taking up to a week. As shown in Scheme 1, the single-step polymerization process was carried out in DMF solvent at 100°C. The chlorine atom in epichlorohydrin is substituted by the azide group, and the azidation reaction was fast in polar aprotic solvent. The polymerization scheme as well as the diols employed as initiators in the polymerization reactions are presented in Scheme 1. It is expected that the formation of low molecular weight GAP involves the initial replacement of the chlorine atoms in the epichlorohydrin monomer and then undergoes ring-opening polymerization in the presence of low molecular weight diols.

Various low molecular weight diols were employed as initiators in the preparation of oligomeric (low molecular weight) GAPs, and it was found that all the diols effectively initiated the polymerization reactions[15]. The results of the direct synthesis of GAPs with linear and ring-structured diols are shown in Table I. It is noticed that there are slight



Diols used in the polymerization

$HOCH_2CH_2OH$	Ethylene glycol
$CH_3CH(OH)CH_2OH$	Propylene glcyol
$HOCH_2CH_2OCH_2CH_2OH$	Diethylene glycol
$CH_3C(CH_3)(OH)CH_2CH(OH)CH_3$	2-methylpentane,2-4-diol
HOC_6H_4OH	Resorcinol

SCHEME 1 Schematic representation of glycidyl azide polymer.

variations in the polymer yields; this may be due to variation in solubility as well as the difference in reactivity of the diols in the reaction medium. The obtained polymers are dark yellow/brown viscous resins.

GPC and VPO Analysis

Gel permeation chromatographic analysis of glycidyl azide polymers initiated by different diols showed multimodal distributions. Resorcinol-initiated GAP shows bimodal distribution in GPC analysis. The GPC results of the GAPs initiated by ethylene glycol (a), propylene glycol (b), diethylene glycol (DEG) (c), 2-methylpentane-2,4-diol (MPD) (d), and resorcinol (RS) (e) are presented in Figure 1. The multiplicity and bimodal distribution of GAPs indicate the purity of the polymers where there is no un-reactive monomer or sodium azide. The GPC molecular weight distribution pattern confirms the possibility of the presence of different-sized oligomers in the glycidyl azide polymeric chains. The GPC results further indicate that the use of different diols in the polymerizations does not markedly affect the molecular weight of the polymers. The VPO results of GAPs presented in Table I further supports the oligomeric nature of the GAP materials. The variation in the molecular weight of GAPs observed is due to the difference in the nature of diols used for the initiation. From the results shown in Table I, it is clear that the resorcinol-initiated GAP showed higher molecular weight than the GAPs initiated with other diols. VPO analysis of GAPs containing different diol units prepared by the one-step process showed number-average molecular weights between 590 and 710. This clearly indicates that the glycidyl azide polymers have five to seven GAP repeating units in the polymer chains.

Spectral Analysis

GAP plasticizer formation is confirmed by observing the corresponding characteristic peaks in their spectral analysis. The peaks characteristic of related segments present in the polymer were identified in the IR, UV, and ^{1}H-NMR spectra as shown in Figures 2, 3, and 4, respectively.

The IR spectra of GAP plasticizers showed the main characteristic peaks at about 1280 cm^{-1} and 2090 cm^{-1} corresponding to the azide group; a strong OH stretching peak at 3405 cm^{-1}; asymmetric and symmetric CH_2 and CH stretching peaks between 2895 and 2945 cm^{-1}; and broad intense stretching vibrations of the ether C$-$O$-$C system at about 1120 cm^{-1}. There are no peaks at 745 cm^{-1} corresponding to chlorine stretching vibration, indicating no more epichlorohydrin units are present in the polymer. Additional peaks corresponding to diols are not observed

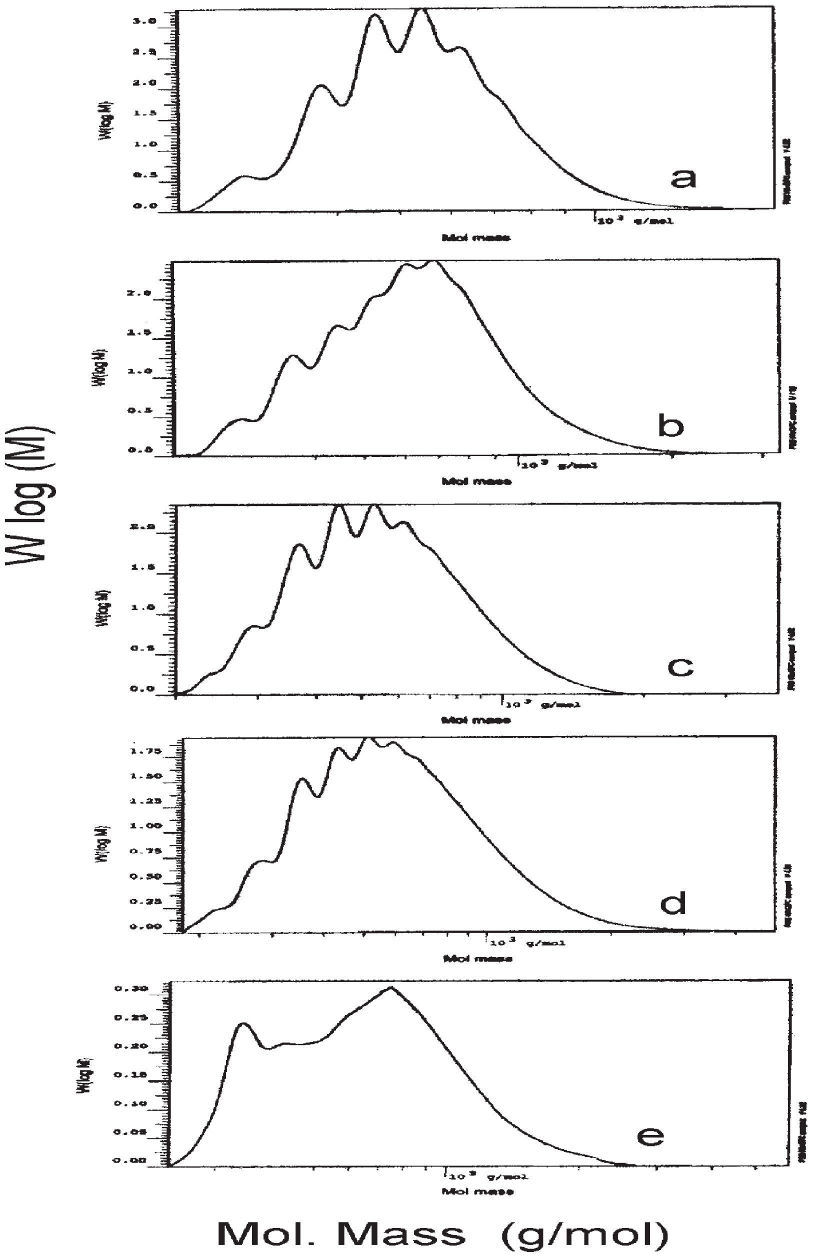


FIGURE 1 Gel permeation chromatographs of GAP containing (a) ethylene glycol; (b) propylene glycol; (c) diethylene glycol; (d) 2-methylpentane-2,4-diol; (e) resorcinol units.

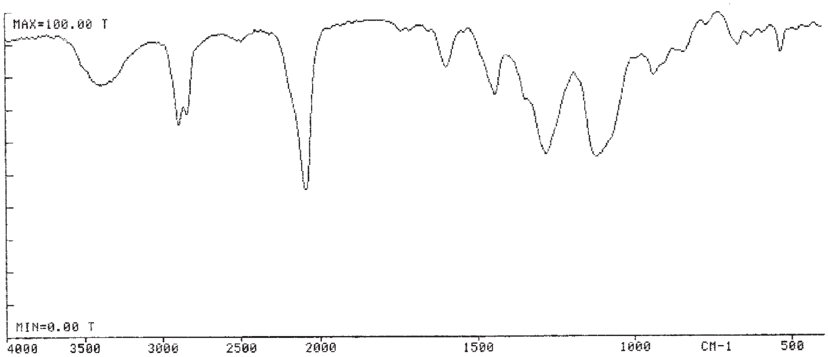


FIGURE 2 IR spectrum of GAP containing resorcinol diol units.

clearly because the diol corresponding peaks are overlapped with the peaks characteristic of GAP. However, in the case of GAP initiated by resorcinol the corresponding peaks in the IR spectrum characteristic of an aromatic ring system are observed between 1450 and 1690 cm^{-1}. The representative IR spectrum of GAP containing resorcinol diol is shown in Figure 2. Further, the azide polymer formation was also identified from UV spectroscopy. The UV spectra of glycidyl azide polymers showed two peaks at 247 nm and 278 nm due to resonance of nitrogen bonds of the azide group of the polymers, as shown in Figure 3.

^{1}H-NMR spectroscopy of the polymers further confirms the structural information obtained by IR spectroscopy. From the proton NMR

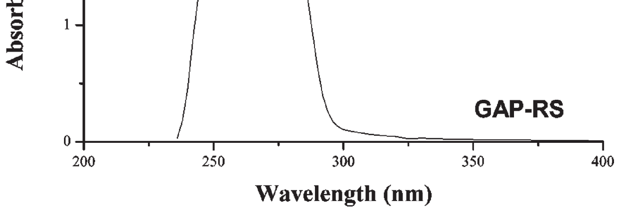


FIGURE 3 UV spectrum of GAP containing resorcinol diol units.

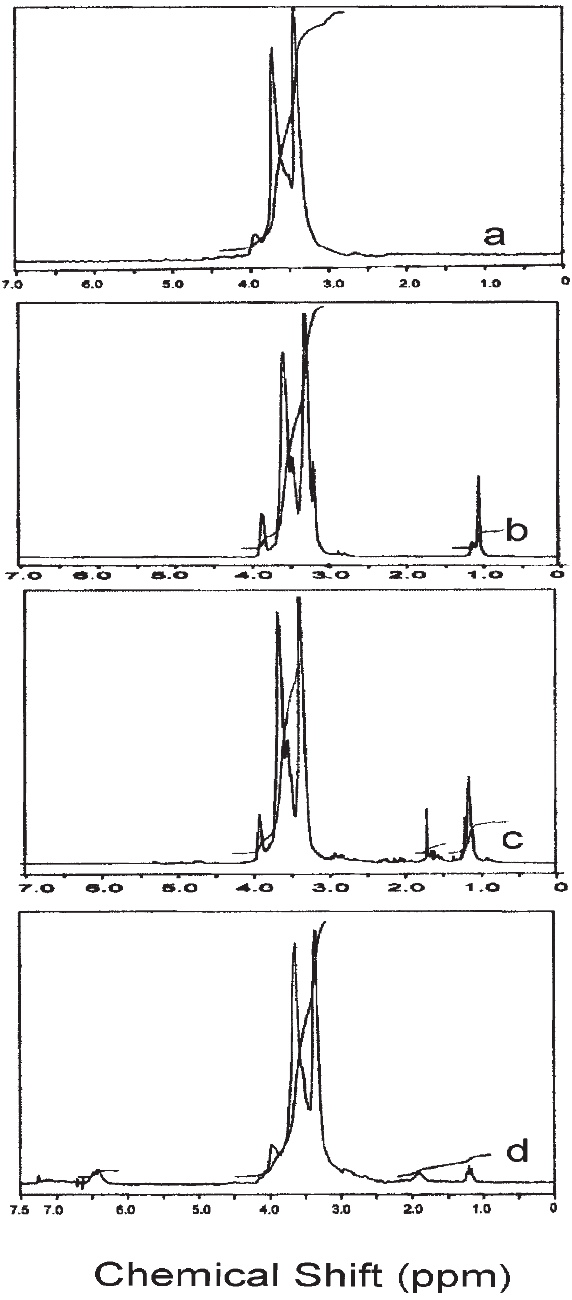


FIGURE 4 ^{1}H NMR spectra of GAP containing (a) ethylene glycol; (b) propylene glycol; (c) 2-methylpentane-2,4-diol; (d) resorcinol units.

spectra of the polymers, not only the polymer formation but also the presence of corresponding diol units in the GAP chains is clearly indicated. In the NMR spectra of the polymers the common proton resonance peaks for all the GAPs[9,10] are observed at around 3.4 ppm and 3.8 ppm due to CH_2N_3 protons of the pendant group of GAP and CH_2, CH (3H) protons of the polyether main chain respectively. Interestingly, a few prominent characteristic peaks are also observed in their NMR spectra corresponding to diol units used in the initiation of polymerization reactions. The diol peaks are observed at various regions, in addition to the above main peaks of GAPs. The characteristic peaks for the diol units observed are at (δ) 1.1–1.2 ppm, due to CH_3 protons of propylene glycol; 1.2–1.9 ppm, due to CH_3 and CH_2 protons of 2-methylpentane-2,4-diol; and 6.4–8.0 ppm, corresponding to the protons of the resorcinol as shown in Figure 4 (b), (c), and (d) respectively.

Thermal Analysis

Thermal decomposition of the propellant binders/plasticizers plays an important role in the combustion of the composite solid propellants. Therefore the decomposition behavior of the GAP plasticizers was studied using differential scanning calorimetry (DSC). As reported earlier, the azide groups of GAP have a tendency to decompose at elevated temperatures. Thermal analysis of GAP polymers clearly indicates the exothermic nature of decomposition. The DSC analysis of the polymers

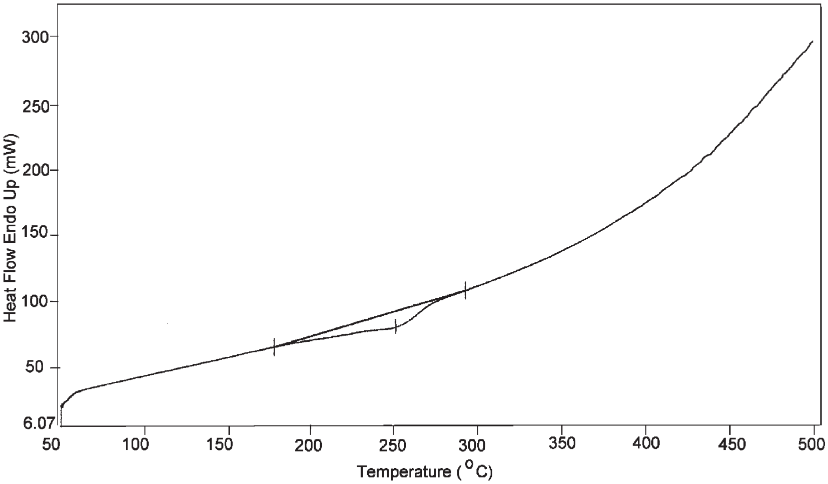


FIGURE 5 DSC thermogram of GAPDEG.

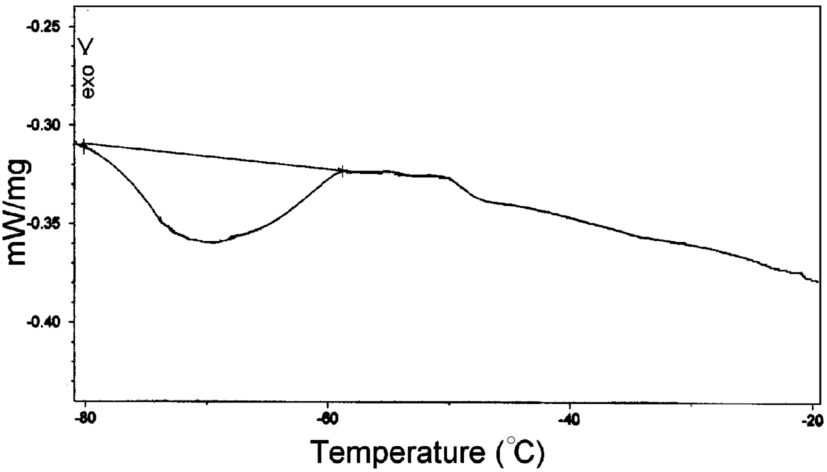


FIGURE 6 DSC glass transition temperature curve of GAPDEG.

showed an exothermic peak at 250°C due to the decomposition of the pendant azide groups of GAP. Variation in the maximum peak decomposition was observed in the GAPs due to the presence of different diol units in the GAP chains. From the exothermic peak the amount of liberated azide group in the polymer can be derived. As reported by Eroglu and Guven[10], the heat liberated in the decomposition of pure GAP was about 1828 J/g. The ratio of energy liberated at the exothermic peak decomposition to the energy value of pure GAP-diol makes it possible to calculate the azide content in the GAP plasticizer. The enthalpy of decomposition of glycidyl azide polymers containing different diol units was lower compared to the GAP values as reported by us in our previous investigations[16,18]. Here also similar phenomena were observed due to the presence of different diol units in the polymeric chains, which decreases the total number of azide groups in the polymer. A representative GAPDEG DSC thermogram is presented in Fig. 5.

Fundamentally, a low glass transition temperature (Tg) of polymeric propellant binder is an indication of its superior physico chemical properties as propellant binder. The glass transition temperatures of GAPs containing different diol units was found to be very low, from −70° to −72°C, i.e., a small variation due to the different diol units present in the polymer chains. The values are in accordance with the reported value of −70°C by direct synthesis of glycidyl azide polymer having molecular weight of 540[15]. GAPs[27] having different molecular weights, around 1700 ± 300, have Tg of −45°C. Further, in our earlier investigation we found Tg around −65° to −66°C for the GAPs having molecular weights in the range of 900–1100. In the present investigation, the low molecular

TABLE II DSC data of glycidyl azide polymers

Polymer code	Peak decomposition temperature (Td) (°C)	Delta H (J/g)	Tg (°C)
GAPEG	247.10	1656.48	−70.54
GAPPG	249.24	1677.17	−70.15
GAPDEG	250.48	1669.85	−71.42
GAPMPD	250.63	1628.91	−71.86
GAPRS	251.35	1622.43	Not detected

weight GAPs synthesized showed very low Tg when compared to GAPs with high molecular weights. This serves the objective of the present investigation to obtain low Tg to improve the flexibility of the GAPs. A representative DSC curve of GAPDEG is presented in Figure 6. The Tg values for GAPs reported in the present investigation are below −70°C, which are lower than the operational temperature (−40°C) for rocket motors. Therefore, these GAPs can be considered as mechanically safe plasticizers/binders for composite propellants. The results of thermal analysis studies of GAPs are presented in Table II.

Nitrogen Content

The nitrogen content present in the GAPs was found to be 37–39% by instrumental elemental analysis. Generally, the pure glycidyl azide polymer has nitrogen content up to 42.42%. The decrement in the nitrogen percentage in these polymers is due to the presence of low molecular weight diol units in the polymer chains, which are employed as initiators in the polymerization reactions. The nitrogen content of GAPs was estimated using DSC by comparing the enthalpy values of the polymers with pure GAP enthalpy value as reference[10]. The nitrogen

TABLE III Nitrogen content in GAP containing low molecular weight diol units

	Nitrogen content (%)		
GAP code	Elemental analyzer	Redox method	DSC method
GAPEG	39.14	38.92	38.44
GAPPG	38.45	38.82	38.92
GAPDEG	38.3	38.15	38.75
GAPMPD	38.10	37.46	37.80
GAPRS	38.25	38.17	37.65

content of the polymers was also estimated by the redox method using potassium iodide (KI)[28]. The values found both by redox and DSC methods agree with the elemental analysis values. The nitrogen contents in the GAPs are presented in Table III.

Solubility Studies

Because of the importance of GAPs in space technology, the chemical structure of these GAPs is to be modified either by producing copolymers with various vinyl/other monomers or by blending with other polymers to achieve favorable properties. To carry out the above process, it is necessary to know the solubility nature of these polymers. The solubility test for the polymers was performed with 50 mg polymer in 5 mL solvent at 30°C. The solubility results indicate that glycidyl azide polymers were soluble in dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), dimethyl acetamide (DMAc), benzene, toluene, and butanol and insoluble in hexane and methanol.

CONCLUSION

A facile route was employed for the synthesis of low molecular weight hydroxyl-terminated glycidyl azide polymers containing different diol units in the polymeric chains. The method of synthesis involves only one step, employing epichlorohydrin as starting material and diol as initiator in the presence of sodium azide in polar aprotic solvent DMF. In this investigation several diols were employed as initiators, and it was found that all the resulting GAPs had molecular weights between 590 and 710, thus containing five to seven GAP repeating units. The formation of GAPs containing different diol units in the polymer chain was confirmed by spectral, thermal, and elemental analysis. The GAPs reported in this investigation showed thermal behavior similar to pure GAP, with slight variation in their decomposition behavior due to the presence of different diol units in the polymer chains. However, the glycidyl azide polymers showed very low glass transition temperature, between $-70°$ and $-72°C$, and may find superior application as plasticizers/binders in rocket propellant technology.

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