



Efficient and Faster Green Synthesis of GAP-Triol as a Potential Application in The Energetic Binders

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ABSTRACT

The green route protocol of synthesized glycidyl azide-triol polymer from polyepichlorohydrin-triol polymer was achieved by microwave irradiation technique. The conversion of $-\text{CH}_2\text{-Cl}$ groups of polyepichlorohydrin-triol (PECH-triol) polymer to $-\text{CH}_2\text{-N}_3$ groups of glycidyl azide-triol polymer (GAP-triol) was in very short time. The synthesized glycidyl azide-triol polymer and their precursor of polyepichlorohydrin-triol were characterized by various spectral analyses. The thermal behavior of GAP-triol was studied by thermogravimetry analysis and differential scanning calorimetric.

Keywords: Glycidyl azide Polymers, Microwave, Polyepichlorohydrins, Thermal Property, Binders

I. INTRODUCTION

Use of polymeric energetic binders in the formulation of cast cured composite solids has presented growing interest. Hydroxyl-terminated polyethers with azido or nitro group polymers of low molecular weight are able to hold the fuel and oxidizer for propellants technology [1]. Glycidyl azide polymer is one of the most renowned and well-known azide polymers and is characterized as a low molecular weight, hydroxyl terminated difunctional liquid prepolymer with pendant azidomethyl groups on the main polyether chain.

In fact, energetic polymers are a potential high energy material with a high positive heat of formation and low detonation sensitivity and therefore it is considered both as a monopropellant and as a polymeric binder [2, 3]. Numerous energetic polymers including azide or nitro polymers, such as poly(3-azidomethyl-3-methyloxetane) [poly(AMMO)], poly[3,3-is(azidomethyl)methyloxetane] [poly-(BAMO)], poly(3-nitromethyl-3-methyloxetane) [poly(NMMO)], poly[3,3-(nitratomethyl)methyloxetane] [poly(NIMMO)], and poly(glycidyl nitrate) [poly(GLYN)], have attracted the attention of researchers [4]. Poly(ethylene glycol) is widely used as a polymeric binder in solid rocket propellants [5, 6]. PEG and its two-component networks with urethane linkages

between PEG and isocyanates have also been used as the binder in rocket propellants, *i.e.* nitrate ester plasticized propellants [7].

Microwave irradiation has been used in various synthesis processes, like organic synthesis, polymer synthesis, pharmaceuticals, waste treatment, *etc.*, and now a new area such as high energy materials [8, 9]. Especially when heating is necessary, oil baths and heating jackets are the main tools used and such types of heating techniques are slow and time-consuming, and sometimes can lead to overheating and decomposition of the substrate and product. To this end, microwaves have been employed in chemistry to decrease the reaction times from hours to minutes, and to also increase yields and selectivity [10].

Therefore, the considering the importance of GAPs and greener synthetic approaches, we have attempted the synthesis of GAP-triol from PECH-triol under microwave irradiation. The structures of the polymers were confirmed by various spectral analyses. The thermal property of the GAP-triol was studied using thermogravimetry analysis (TGA) differential scanning calorimetry (DSC).

II. METHODS AND MATERIAL

The ring opening polymerization of epichlorohydrin was carried out in a 250 mL three-neck flask containing a magnetic needle, calcium chloride guard tube, nitrogen All chemicals used were of synthetic grade and used without further purification. The SINEO Industrial microwave MAS II was used to perform reaction by irradiating with a reflux system, temperature digital display, temperature IR sensor and magnetic stirring. The IR spectra were recorded with a SHIMADZU DRS 8000 spectrophotometer in KBr matrix. ¹H-NMR and ¹³C-NMR spectra were recorded in CDCl₃ using TMS as an internal standard with Varian-300 spectrometer, at 300 MHz and 75 MHz respectively. The DSC analyses of the polymers were performed by a DSC-200F3 SISIS Nano Technology instrument with the heating rate of 5^oC / minute under nitrogen atmosphere. The TGA analysis of the polymers was performed Perkin Elmer-4000 instrument, with the heating rate of 10^oC / minute under nitrogen atmosphere.

Synthesis of PECH-triol polymer [11]

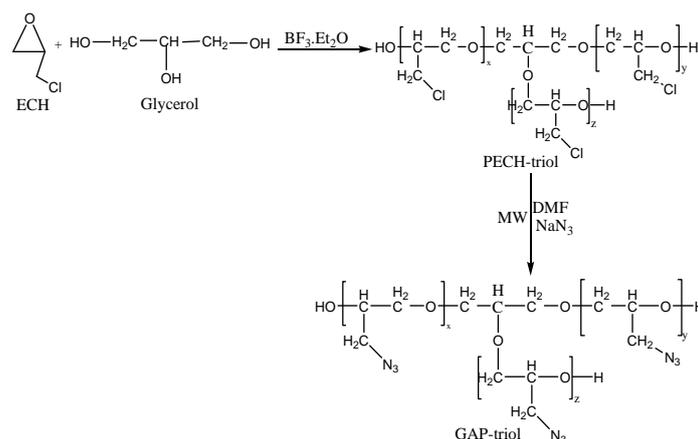
The ring opening polymerization of epichlorohydrin was carried out in a 250 mL three-neck flask containing a magnetic needle, calcium chloride guard tube, nitrogen line, and a dropping funnel. Stirred the solution of 1.194 g (0.013 mol) glycerol in 10 mL dichloromethane, and small amount of borontrifluoride etherate (1 mL) was added at room temperature with passing nitrogen gas into the flask with continue stirring. The reaction flask was then brought to 0^oC using an ice-salt mixture. Then, 12 g (0.130 mol) of epichlorohydrins dissolved in dichloromethane (25 mL) was slowly added to the reaction mixture drop by drop. The reaction was continued for 4 to 5 h at the same temperature and then stirred overnight at room temperature. The reaction was quenched by adding 50 mL of distilled water. The polymer solution was separated from water and then treated with distilled water to remove unreacted glycerol and the catalyst. The pure polymer was obtained by removing the solvent by vacuum distillation. The yield of polymer was 12 g (90 %).

Synthesis of GAP-triol

GAP-triol polymers were synthesized by reacting 2 g (0.022 mole) PECH-triol with 1.7 g (0.026 mol) sodium azide in DMF (5 mL) under microwave irradiation with power level of 800 W at 90^oC for 10 min. The reaction

mixture was cooled to room temperature to obtain the polymer solution. Then distilled water and chloroform were added to the same. The chloroform layer was separated and the product was washed several times with hot distilled water. The pure GAPs-triol polymer was obtained after evaporation of chloroform. The yield of GAPs-triol was 1.94 (91%).

The schematic representation of synthesis of glycidyl azide polymers-triol is shown in scheme 1.



Scheme 1. Synthesis of glycidyl azide polymers-triol (GAP-triol)

III. RESULTS AND DISCUSSION

The FT-IR spectrum of PECH-triol (Fig. 1) showed the main characteristic bands at 746 cm⁻¹ due to the presence of chloromethylene groups (-CH₂Cl) present in polymers chain. The formation of azide groups in the GAP-triol was clearly seen from the Fig. 2. The broad bands at 1280 and 2090 cm⁻¹ were due to the presence of -CH₂N₃ (azide group) in the polymer chain with complete disappearance of the -CH₂Cl peak at 746 cm⁻¹. The other bands appeared at 1190, 2845, and 3380 cm⁻¹ were assigned to the presences of ether linkage, -CH, -CH₂, and terminal -OH groups in polymers chain, respectively. FT-IR spectral analysis proved the complete conversion of poly(epichlorohydrin)-triol to glycidyl azide polymer-triol.

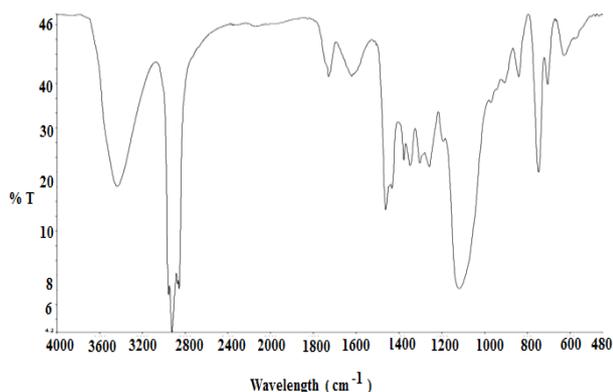


Figure 1. FT-IR spectrum of PECH-triol

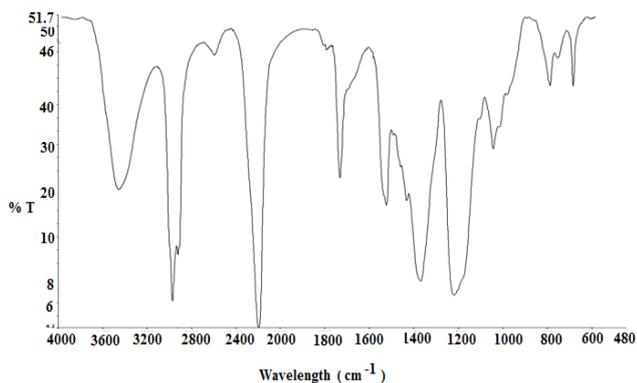


Figure 2. FT-IR spectrum of GAP-triol

In the $^1\text{H-NMR}$ spectrum of PECH-triol polymer (Fig. 3) peaks were observed at δ 3.42 ppm due to $-\text{CH}_2\text{Cl}$ protons of the pendant PECH-triol. The $^1\text{H-NMR}$ spectrum of GAP-triol is represented in Fig. 4. The $^1\text{H-NMR}$ spectrum of GAP-triol polymer showed peaks at δ 3.25 ppm, which were assigned to azido methylene protons of the GAP-triol. Other peaks appeared at δ 3.8 ppm were assigned to the protons of CH_2 , CH group's main chain of PECH-triol and GAP-triol. Thus the $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra given sufficient information associated with confirmed formation of PECH-triol and GAP-triol.

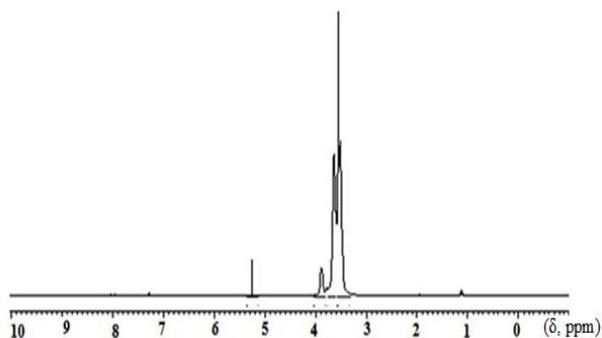


Figure 3. $^1\text{H-NMR}$ spectrum of PECH-triol

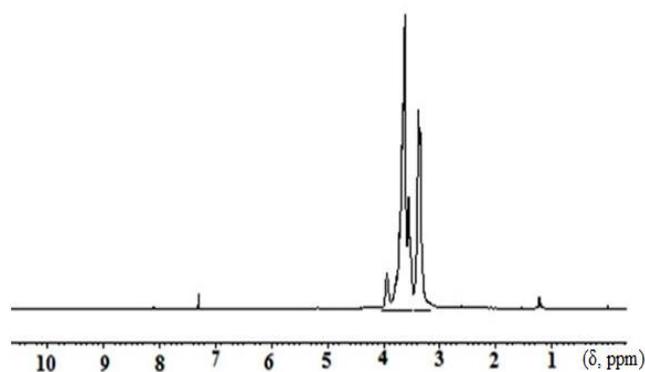


Figure 4. $^1\text{H-NMR}$ spectrum of GAP-triol

The $^{13}\text{C-NMR}$ spectra of the PECH-triol and GAP-triol are represented in the Fig. 5 and 6, respectively. The $^{13}\text{C-NMR}$ spectrum of the GAP-triol polymer showed the azidomethylcarbon signals of GAP at δ 52–54 ppm. The complete disappearance of the resonance signals at δ 42–47 ppm confirmed the completion of azidation reaction. The common peaks at δ 70.00 and 80.00 ppm were observed due to the presences of strong methylene carbon resonance and $-\text{CH}-$ signals of PECH-triol and GAP-triol. Overall spectral analysis indicated that the formation of PECH-triol and GAP-triol.

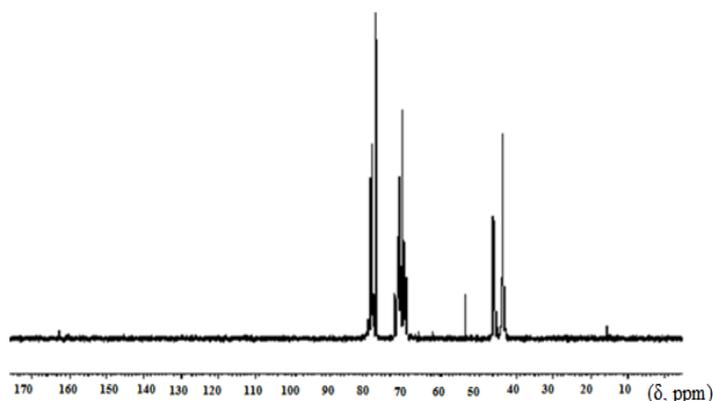


Figure 5. $^{13}\text{C-NMR}$ spectrum of PECH-triol

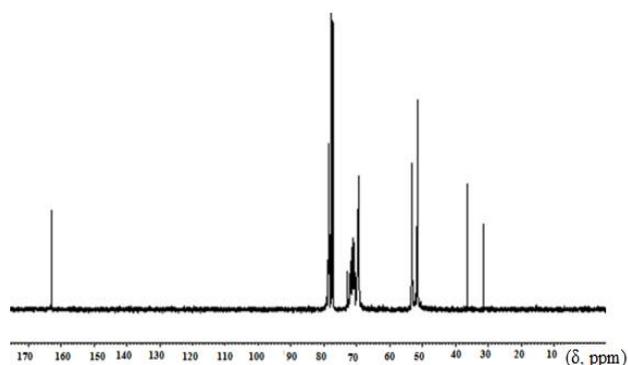


Figure 6. $^{13}\text{C-NMR}$ spectrum of GAP-triol

Thermal study

The thermal study of the synthesized GAP-triol polymer was performed using TGA and DSC analysis. The TGA analysis of GAP-triol (Fig. 7) clearly showed two steps degradation behaviour. The GAP-triol shown thermal stability up to 190 °C. Then, the first step of thermal degradation was seen in between 190-270 °C, which would have appeared due to the elimination of nitrogen from the azide group of the GAP-triol units. The second thermal degradation step was observed in between 280-450 °C might be due to the breakdown of polyether main chain of the GAP-triol units.

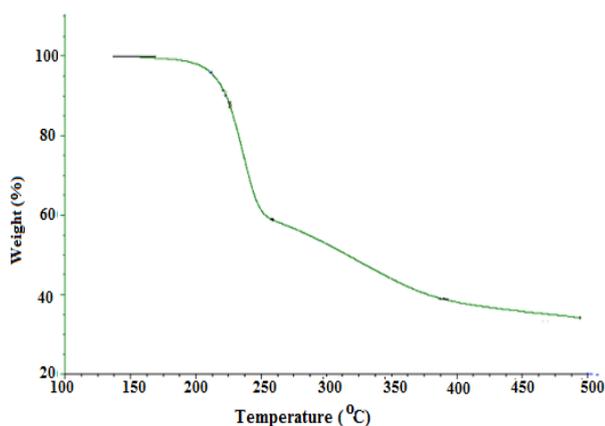


Figure 7. TGA curve of GAP-triol

The DSC curve of GAP-triol (Fig. 8) demonstrated that the polymer exhibited exothermic peak due to the presence of energetic azide group in the polymer chain of GAP-triol. The GAP-triol polymer is thermally stable upto 210 °C where the exothermic degradation starts. The maximum degradation of polymer was found at 239.62 °C due to the decomposition of the azide group of GAP unit of GAP-triol polymer.

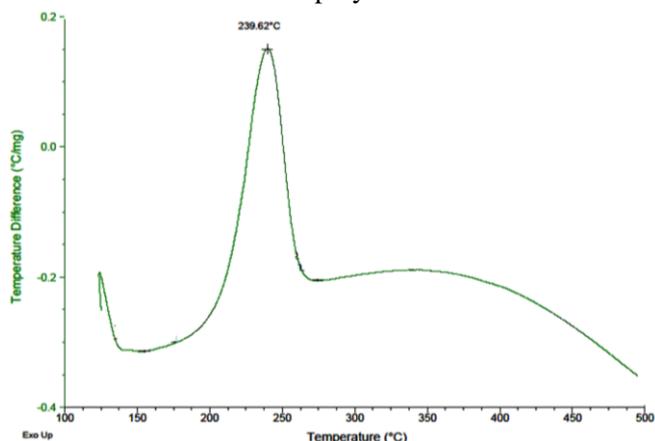


Figure 8. DSC curve of GAP-triol

III. CONCLUSION

The microwave assisted synthesis of GAP-triol completed in a short reaction time and at a low temperature, with high yields by treating the corresponding PECH-triol, with sodium azide under microwave irradiation. The structures of the synthesized polymers were confirmed by spectral analysis. The thermal property of the polymer was studied using DSC as well as TGA. The azidation method used in the present study is of particular interest for scientists and technologists working in the field of high energy materials, in terms of economy of time and safer synthesis, with increased yield and also purity of the products

IV. REFERENCES

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