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## **SYNTHESIS AND IDENTIFICATION OF GLYCIDYLE AZIDE PREPOLYMER**

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### **ABSTRACT**

In this study, Glycidyl Azide Prepolymer was successfully prepared using the published one-step method, the published two-step method and finally by modifying the commonly known two-step procedure. The prepared samples were identified by Fourier transformer infra-red (FTIR), elemental analysis apparatus (CHNS) and Gel-permeation chromatography connected with light scattering apparatus (GPC-LS). The prepared prepolymer offers higher molecular weight and nitrogen content. The yield obtained after modification was about 98%.

### **Keywords**

Glycidyl azide polymer, Polyepichlorohydrin, Energetic materials

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## 1. INTRODUCTION

Glycidyl azide polymer (GAP), Figure 1, is a prepolymer with azide functional group which burns very rapidly and secures steady state combustion without external heating. The terminal (OH) groups of GAP can be linked with a diisocyanate such as hexamethylene diisocyanate (HMDI) or isophoron diisocyanate (IPDI) [1-3].

Glycidyl azide prepolymer (GAP), offers a unique energetic binder and plasticizer system for advanced propellants and plastic bonded explosives (PBX's) for achieving higher performance, superior structural integrity and low vulnerability. Its chief advantages are higher density and positive heat of formation as compared to widely used binder, hydroxyl terminated poly butadiene (HTPB) and non-energetic plasticizer, diethyl phthalate (DEP) [1,2].

In this paper, GAP was successfully prepared using the three different methods which includes the polymerization of epichlorohydrin (ECH) then azidation of resulted polyepichlorohydrin (PECH). Also, the characteristics of the prepared polymer were determined using FTIR, CHNS, GPC-LS and Karl-Fisher technique.

## 2. Experimental

### 2.1 Preparation of hydroxyl terminated GAP prepolymer using the one-step method

Sodium azide ( $\text{NaN}_3$ ) was added gradually to a mixture of epichlorohydrin (ECH), dimethyl formamide (DMF) and ethylene glycol (EG). The starting conditions were a temperature of about  $70^\circ\text{C}$  under nitrogen blanket and with a good agitation with 180 rpm. Then temperature was raised up to  $90^\circ\text{C}$  and the reaction was left to be completed after 24 hours. The heating and agitation were stopped and the vessel was cooled.

After that the sample was washed with 50 ml of hot water at  $60^\circ\text{C}$  for three times to remove any remaining residual of DMF, unreacted EG, sodium azide and the resulted sodium chloride. Then it was filtered and the resulted solution was placed in a vacuum oven to yield about 8 g GAP [80% conversion] with an amber color in the form of viscous liquid [3].

### 2.2 Preparation of hydroxyl terminated GAP prepolymer using the classical two-step method

The first step (polymerization step) at which ECH monomer were placed in the 2 liter conical flask (reactor) together with EG as an initiator. Then triethyl oxonium hexafluorophosphate (TEOP) was used as a catalyst. The reaction temperature maintained at  $50^\circ\text{C}$  for 10 hours in presence of good agitation and an effective nitrogen blanket to provide an inert medium. After completion of the reaction the polyepichlorohydrin (PECH) polymer was separated from the unreacted ECH in an ordinary separating funnel.

The second step was the azidation step at which a mixture of PECH,  $\text{NaN}_3$  and DMF was agitated with 180 rpm at  $90^\circ\text{C}$  for 48 hours on batches using the nitrogen blanket to provide the inert medium [3].

### **2.3 Preparation of hydroxyl terminated GAP prepolymer using the modified two-step method**

The first step (polymerization step) at which EG as an initiator were primarily placed in the 2 liter conical flask (reactor vessel). The reaction temperature maintained at 50°C for 10 hours in presence of good agitation with 180 rpm. An effective nitrogen blanket was introduced in order to decrease the exothermicity of the reaction and to provide an inert medium. Nitrogen blanket was used with a specific strategy in order to guarantee keeping the exothermicity of the reaction under control. Then ECH monomer was added together with TEOP as catalyst. TEOP was selected to be effective to catalyze the cationic polymerization of the monomer and also it works as a preinitiator for EG.

After completion of the reaction the PECH polymer was separated from the unreacted ECH in an ordinary separating funnel then it was washed using a mixture of 10% aqueous methanol with a saturated solution of sodium EDTA, then the polymer was washed three times using 10% aqueous methanol only without the addition of Sodium EDTA.

The second step was the azidation step at which a mixture of PECH with tricapryl methyl ammonium chloride (Aliquate 336) as a phase transfer catalyst was agitated at 90°C. Then NaN<sub>3</sub> was added to the reaction vessel. The whole mixture was agitated at 90°C for 48 hours on batches using the nitrogen blanket to provide the inert medium.

### **2.4 Fourier Transformer Infrared Analysis**

Shimadzu 8000 series FTIR was used to identify the presence of the azide group in the prepared GAP samples. A thin layer of the polymer was placed on the surface of the KBr tablet. The used wave number range was 500- 4000 cm<sup>-1</sup> which is the appropriate range for the most organic compounds (azide group appears at 2100 cm<sup>-1</sup>) [4,5].

### **2.5 Gel-Permeation Chromatography/Light Scattering Analysis**

Gel-Permeation Chromatography 600E (GPC) apparatus connected with light scattering DAWN EOS (LS) apparatus were used to determine the molecular weight distribution ( $M_w$ ,  $M_n$ ). Tetrahydrofuran (HPLC grade) was used as a mobile phase in this work [1,6]. The injection volume was 30 microliter, temperature was 30°C and the run time was 28 min.

### **2.6 Determination of water content using Karl-Fisher Technique**

Determination of water content had been carried out using Karl-fisher device by using titration with a standardized Karl-fisher reagent to determine the water content as % by weight.

### **2.7 Determination of nitrogen component**

Determination of nitrogen content was carried out using CHNS-device model 932 (LECO-USA). A sample was put into aluminum capsule which decomposed in the presence of oxygen at 950°C, and mainly converted to oxides of varies elements present in the sample.

## **3. Results and Discussion**

### **3.1 Preparation of hydroxyl terminated GAP prepolymer**

Linear GAP diol was prepared by the modified two-step. Then, prepared by the classical two-step method. Finally, was prepared by the one-step method as was explained in the

experimentation part. The prepared prepolymer was then separated and washed then dried with the adopted techniques. After the drying process, GAP was obtained with the characteristic viscous yellow colour.

### 3.2 Fourier Transformer Infra-Red Analysis

The results of the FTIR analysis are given in Table 1 together with standard values. From Table 1, Figure 2 of PECH and Figure 3 of GAP diol, it can be seen that, the azide group was successfully inserted into the GAP structure as it appears at  $2102.3\text{ cm}^{-1}$  and  $1280.6\text{ cm}^{-1}$ . Also, chlorine peaks appears at  $628.8\text{ cm}^{-1}$  as  $(-\text{Cl})$  group. These results are in agreement with the reference values.

### 3.3 Gel Permeation Chromatography Results

According to the GPC-LS analysis the weight average molecular weight ( $M_w$ ) of the prepared GAP samples was varied according to the preparation method. Table 2 summarizes these results.

### 3.4 Determination of water content using Karl-Fisher Technique

The value of the freshly prepared samples was found to be 0.65%, which was not satisfactory. Hence, the product was subjected to several steps in order to reach the minimum content of moisture. A value of 0.03 % moisture content was obtained which is very satisfactory.

### 3.5 Elementary analysis results

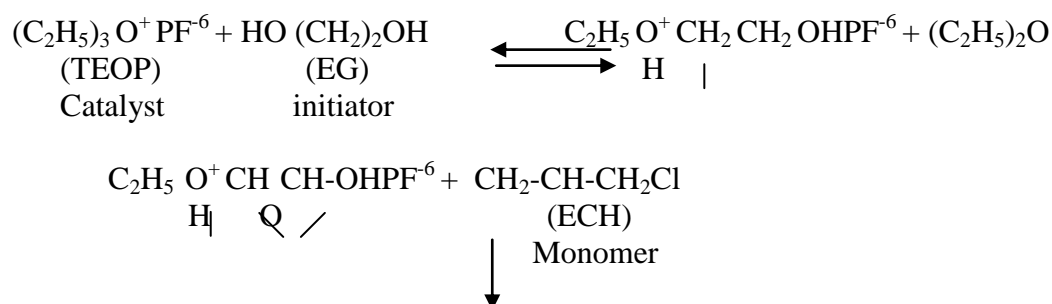
Theoretically, the nitrogen atoms represent about 42.5% weight percent from the total weight of GAP. Using CHNS 932 instrument gave the results given in Table 2. As shown in Table 2, GAP prepared using the modified two-step method gives 42.82% as nitrogen content, which coincides approximately with the theoretical value.

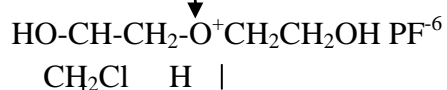
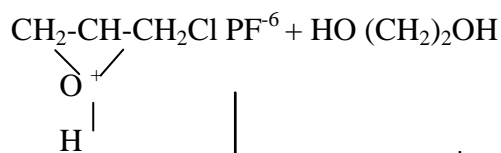
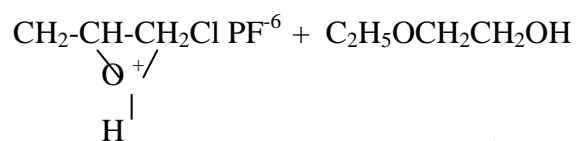
### 3.6 The Proposed Mechanism

The cationic ring opening polymerization can be proceed by two suggested general mechanisms. One mechanism involves the primary interaction of the catalyst system with the monomer to form an onium ion which acts as the initiating species. Propagation is then predominantly as  $\text{SN}_2$  type substitution reaction [7]. An alternative mechanism requires ring cleavage by the catalyst to form an ionic species. This is followed by attack of another monomer, with ring opening and regeneration of the active site.

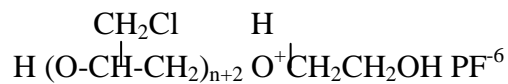
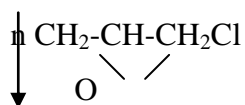
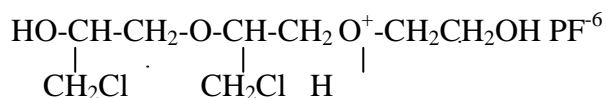
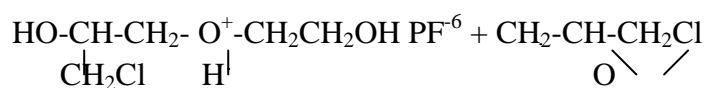
The following polymerization mechanism is postulated for ECH cationic ring opening polymerization in the presence of ethylene glycol. Since the TEOP salt is a strong alkylation agent, it properly alkylates ethylene glycol, which is a strong base than ECH monomer:

- **Initiation step**





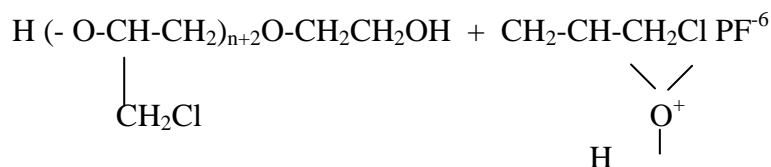
• **Propagation**



• **Termination**



Transfer of the active  
Centers to the monomer



#### 4. CONCLUSIONS

The linear hydroxyl terminated GAP prepolymer was successfully prepared using the one-step method, the two-step method and a modified two-step method. The prepared polymer was identified using the FTIR technique.

The GPC-LS technique was used to determine the weight average molecular weight ( $M_w$ ). The prepared product by the one-step method showed a value less than 500 g/mol. Moreover, GAP prepared by the two-step method showed values between 1000-2000 and GAP prepared by the modified two-step method showed values between 2000-6000 g/mol.

Finally, the elemental analysis showed that the polymer prepared by the modified two-step method has nitrogen content of 42.82 % which is very closed to the theoretical value (42%).

The introduced modification was able to prepare hydroxyl terminated GAP prepolymer with 98% polymer. The prepared prepolymer had a nitrogen content of approximately 42% and a molecular weight between (2000-6000) g/mol.

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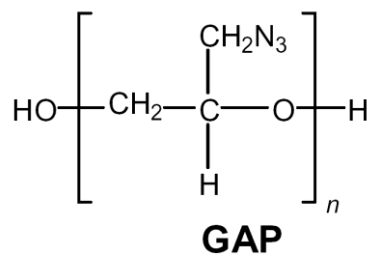


Figure 1: Chemical Structure of GAP

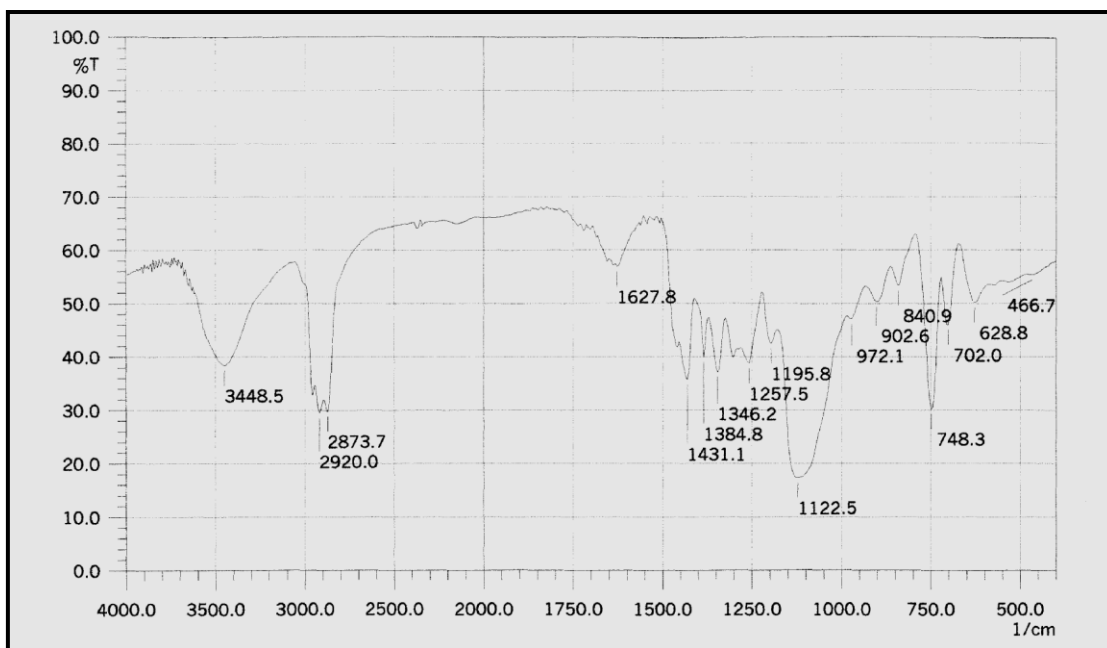


Figure 2: FTIR spectrum of PECH

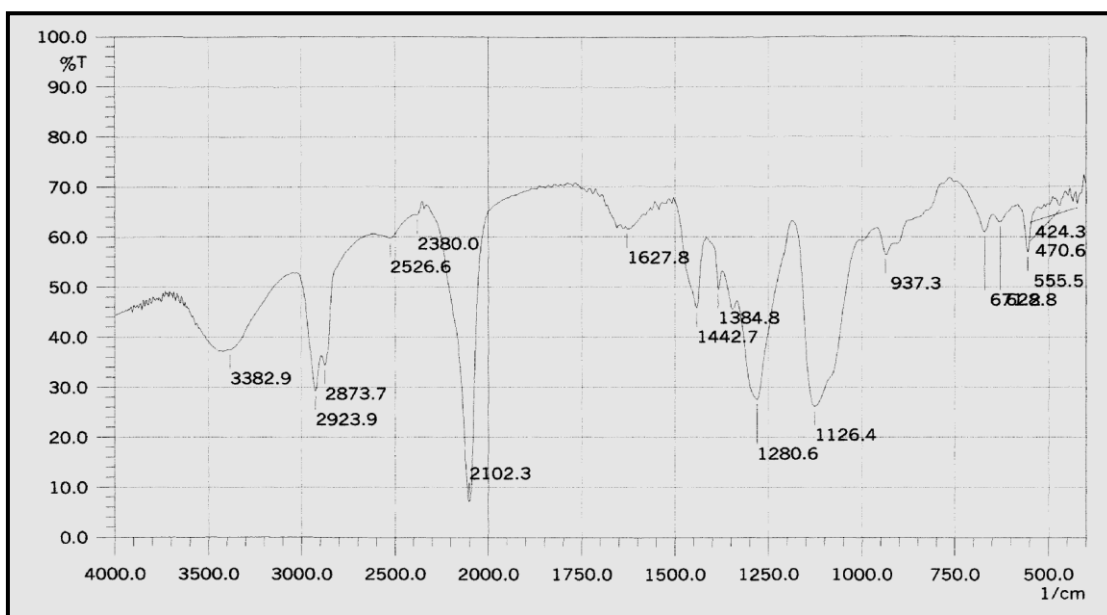


Figure 3: FTIR spectrum of GAP diol

Table1: FTIR characteristic absorption peaks.

| Function group                     | Wave number (cm <sup>-1</sup> )<br>(Reference) | Wave number (cm <sup>-1</sup> )<br>(Experimental) |
|------------------------------------|--|---|
| -OH                                | 3600-3300                                      | 3448.0  |
| C-O-H                              | near 1450                                      | 1431.1  |
| -CH <sub>2</sub> -CH               | near 3000                                      | 2920.0  |
| C-H                                | 2900-2750                                      | 2873.7  |
| C-Cl                               | 667-500  | 628.8   |
| C-O-C                              | 1300-1000                                      | 1122.5  |
| CH <sub>2</sub> -N <sub>3</sub>    | near 1280                                      | 1280.6  |
| CH <sub>2</sub> -O-CH <sub>2</sub> | 1650-1450                                      | 1627.8  |
| CH <sub>2</sub> -N <sub>3</sub>    | near 2100                                      | 2102.3  |

Table 2: GPC chromatography results

| Sample Name                        | Weight average molecular weight (M <sub>w</sub> ) |
|------------------------------------|---|
| GAP (by one-step method)           | Less than 500                                     |
| GAP (by common two-step method)    | 1000-2000   |
| GAP (by modified two -step method) | 2000-6000   |

Table 3: Results of elementary analysis

| Prepolymer                     | C (%) | H (%) | N (%) | O (%) |
|--------------------------------|-------|-------|-------|-------|
| GAP (one-step method)          | 36.48 | 4.70  | 40.14 | 18.68 |
| GAP (modified two-step method) | 35.89 | 5.22  | 42.82 | 16.07 |
| GAP (common two-step method)   | 34.98 | 12.66 | 48.98 | 3.38  |

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