

## SYNTHESIS AND CHARACTERIZATION OF POLYEPICHLOROHYDRIN DIOLS

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### Abstract

Polyepichlorohydrin (PECH) is a functional polymer with high value in energy materials. Cationic ring-opening polymerization of epichlorohydrin (ECH) with a diol initiator and Lewis or protic acids catalyst, proceeds through an activated monomer mechanism (AM) allowing control of the polymer's average molecular weight and polydispersity index. In the present investigation, PECH diol was synthesized under the catalysis of boron trifluoride etherate, with the ECH monomer:ethylene glycol as an initiator molar ratio of 1:0.045, achieving a low molecular weight  $\bar{M}_n = 1935$  g/mol, low polydispersity index PDI = 1.25, predominantly in the linear chain configuration with the terminal hydroxyl group.

**Keywords:** Polyepichlorohydrin; epichlorohydrin; CROP; characterization polymer.

### 1. Introduction

Polyepichlorohydrin (PECH) is a polyether with a functional alkyl chloride pendant that is used in a bevy of commercial materials, like fuel hoses, seals, and air ducts. In the intervening decades recently, PECH and PECH-derived materials have been increasingly utilized in a broad array of applications like polymer electrolytes [1-4], gas separation [5, 6], and ion exchange membranes [7, 8], especially as a raw material for the synthesis of energetic polymers, owing to its cheap cost, functionality, and chemically stable and flexible ether backbone. PECH is derived through the process of ring-opening polymerization of its cost-effective, functional monomer precursor, epichlorohydrin (ECH). The isotactic, semi-crystalline form of PECH was initially produced in 1954 by Pruitt and Baggett [9] for Dow Chemical, while the atactic amorphous version was created by E. J. Vandenberg in 1957 for Hercules, Inc. Subsequently, BF Goodrich commercialized these materials and their copolymers under the trademark Hydrin® elastomers.

ECH presents significant challenges for polymerization owing to the presence of alkyl chloride pendants, which are not compatible with conventional epoxide polymerization techniques. The methodologies developed by Vandenberg in the 1950s

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facilitated the formation of elastomeric copolymers utilizing ECH, thereby engendering novel materials. The catalytic system introduced by Vandenberg has been pivotal in defining the synthesis of PECH; however, this approach is not devoid of limitations. Polymerizations of epoxides employing Vandenberg's catalyst are characterized by a restricted capacity to regulate both average number molecular weight ( $\bar{M}_n$ ) and polydispersity index (PDI); the resultant polymers consistently exhibit elevated molecular weights ( $\bar{M}_n > 10^6$  g/mol) coupled with a generally high dispersity (PDI > 2) [10, 11]. Consequently, low ( $\bar{M}_n < 10^4$  g/mol) and intermediate ( $10^6 > \bar{M}_n > 10^4$  g/mol)  $\bar{M}_n$  polymers were unachievable. The underlying cause for the lack of control over  $\bar{M}_n$  can be attributed, at least in part, to an insufficient understanding of the initiating and catalytic species constituting the Vandenberg catalyst [11, 12]. Recent synthetic approaches, published within the last decade, are approaching the ease of synthesis of classical techniques, but with newfound control over molecular weight, polydispersity index, terminal group. These are broken down into several categories: cationic ring-opening polymerization (CROP), double metal cyanide (DMC) catalyst, monomer-activated ring-opening polymerization (MAROP), and coordination polymerization [13].

The present study synthesized and investigated the effect of the molar ratio of monomer to initiator on the properties of PECH to obtain PECH with low  $\bar{M}_n \sim 2000$ , PDI < 1.4 by CROP method according to AM mechanism for high-energy polymers for applications in the aerospace. This mechanism involves successive additions of protonated monomer molecules to the terminal hydroxyl groups of the developing chain.

## 2. Experiment

### 2.1. Chemicals, materials

Epichlorohydrin (ECH), ethylene glycol (EG), purity > 99%, China, boron trifluoride etherate (BF<sub>3</sub>·OEt<sub>2</sub>), pyridine (C<sub>5</sub>H<sub>5</sub>N), purity > 98%, Macklin, China, anhydride acetic (CH<sub>3</sub>CO)<sub>2</sub>O, purity > 99%, Merck, toluene, dichloromethane (DCM), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), potassium hydroxide (KOH), sodium bicarbonate (Na<sub>2</sub>CO<sub>3</sub>), calcium chloride (CaCl<sub>2</sub>), purity > 99%, China, Argon gas, purity > 99.999%, Vietnam, used without further purification.

### 2.2. Research methods

Spectroscopic analysis in IR (FT-IR) was performed on the Perkin Elmer Spectrum Two with the applied ATR attachment (Attenuated Total Reflectance method). The spectroscopic analysis of the magnetic nuclear resonance <sup>1</sup>H NMR was

performed on the Bruker NMR System 600 MHz using the internal pattern - tetramethylsilane (TMS). As a solvent, the deuterated chloroform ( $\text{CDCl}_3$ ) was used. The measurements were made at a temperature of  $25^\circ\text{C}$ . The molecular masses ( $\bar{M}_w$  and  $\bar{M}_n$ ) and the polydispersion index (PDI) were determined using the Gel Permeation Chromatography (GPC). The investigations were carried out on the Agilent 1260 Infinity chromatograph with RID detector on the column filled with PL Gel 5  $\mu\text{m}$  miniMix-C  $250 \times 4.6$  mm, molecular weight limit: 200 - 2,000,000 Da, using the polystyrene pattern ( $500 - 2.10^6$  g/mol). A mobile phase was the tetrahydrofuran (THF).

The viscosity measurements of the obtained samples were carried out on the Brookfield LVDV-II + Pro viscometer with the attachment for small samples. The spindle type: S62, rotation speed: 1 rpm. Density determination was performed by the pycnometer method, according to ISO 2811-4:2011. The hydroxyl value was determined according to ASTM-E222-17.

### **2.3. Synthesis and purification PECH**

2.5 ml of diethylene glycol (0.045 mol) was added to 100 ml of dichloromethane (DCM) in a flask connected with a thermometer and argon gas inlet 0.5 ml of cationic initiator  $\text{BF}_3 \cdot \text{OEt}_2$  (boron trifluoride diethyletherate) (0.004 mol) was then injected. After 30 minutes of mixing at room temperature, the solution was cooled by a mixture of water, ice, and NaCl crystals to  $0^\circ\text{C}$ , after which the slow dropwise addition of epichlorohydrin (ECH) (92.5g; 1 mol). These operations and our own polymerization were conducted under an argon atmosphere. This dropping was continued for more than 10 hours at 0 to  $+5^\circ\text{C}$  to ensure a constant temperature and to minimize the amount of ECH in the reaction mixture. Then the mixture was left to reach room temperature. The mixing process was continued for another 6 hours. Then 200 ml of distilled water was added with  $\sim 2$  g of  $\text{Na}_2\text{CO}_3$  to the mixture and was mixed for 1 hour. The organic phase containing PECH was extracted into DCM using a separating funnel and was washed several times with distilled water until the pH was neutral. The washed organic phase was dried by adding sodium sulphate ( $\text{Na}_2\text{SO}_4$ ), then filtered, and evaporated under vacuum (100 mbar,  $40^\circ\text{C}$ ) to obtain 89 g of poly-epichlorohydrin (colorless, viscous liquid), yield 96.2%.

### **2.4. Investigation of the effect of reaction mole ratio on the properties of PECH**

Carrying out the process of PECH synthesis reaction using DCM as a solvent and  $\text{BF}_3 \cdot \text{OEt}_2$  as a catalyst with different molar ratios of monomer and initiator (ECH : EG). The composition of substances participating in the reaction is given in Table 1.

Table 1. List of data on ECH polymerization reaction

	<b>ECH (gram)</b>	<b>EG (ml)</b>	<b>ECH:EG (mol/mol)</b>	<b>BF<sub>3</sub>.OEt<sub>2</sub> (mol)</b>	<b>DCM (ml)</b>
PECH 01	92.5	3	1:0.054	0.004	200
PECH 02	92.5	2.5	1:0.045	0.004	200
PECH 03	92.5	2	1:0.036	0.004	200
PECH 04	92.5	1.5	1:0.027	0.004	200

PECH 01-04 samples were measured for average molecular weight, PDI, viscosity, density, and hydroxyl value.



Fig. 1. Experimental diagram of PECH synthesis.

### 3. Results and discussion

The primary aim of the research was to synthesize PECH achieved  $\overline{M}_n \sim 2000$  g/mol and PDI < 1.4; therefore, we synthesized and investigated the effect of the ECH: EG molar ratio on the properties of PECH.

#### 3.1. Polymerisation of epichlorohydrin

Polymerization of epichlorohydrin (ECH) in the presence of diols (EG), catalyzed by Lewis acids BF<sub>3</sub>.OEt<sub>2</sub> (Diagram 1).

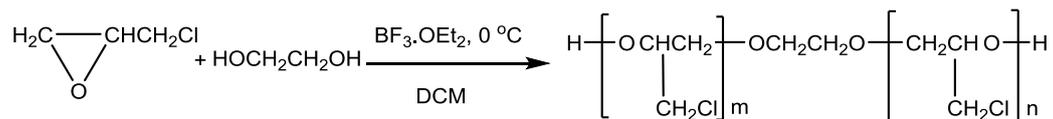


Diagram 1. Synthesis PECH

The obtained PECHs of various molecular masses were subjected to the FT-IR analysis that allows for the determination of the presence of characteristic bands in the

investigated compound. Images of FTIR spectra are the same for all obtained polymers, independently of the obtained molecular mass. Figure 2 presents the exemplary spectrum of PECH 02. IR (ATR) spectrum of ECH: 1266.55; 926.26; 852.67; 760.08 722.02; 441.21  $\text{cm}^{-1}$ . IR (ATR) spectrum of polyepichlorohydrin PECH: 3459.08; 2875.75; 1429.81; 1345.45; 1258.12; 1091.80; 839.40; 740.25; 703.38  $\text{cm}^{-1}$ .

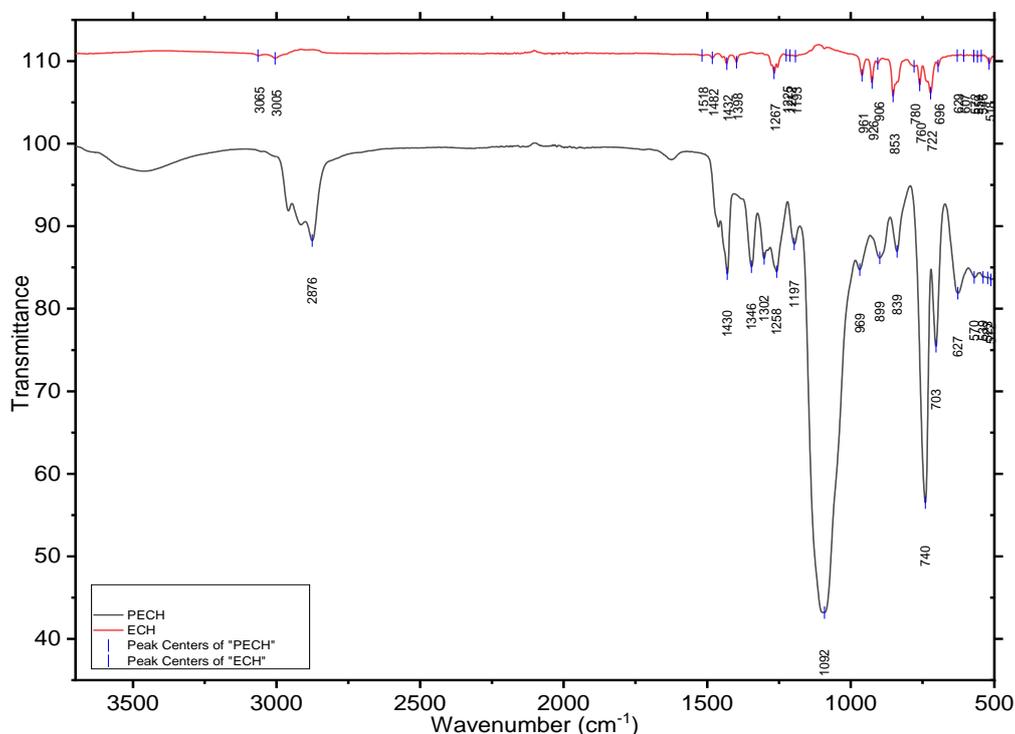


Fig. 2. The IR spectrum of ECH and PECH 02.

The FT-IR spectrum of PECH shows a broadened peak at about  $3459.08 \text{ cm}^{-1}$  which is attributed to OH group stretching vibrations. The peaks at  $2875.75 \text{ cm}^{-1}$  originate from C-H symmetrical and asymmetrical stretching vibrations of the methylene group ( $-\text{CH}_2$ ) observed for PECH. Corresponding bending vibrations are observed at about peak  $1429.81; 1345.45 \text{ cm}^{-1}$ . The strong vibration band at  $1091.80 \text{ cm}^{-1}$  corresponds to the C-O-C stretching vibrations of the ethylene glycol group in PECH. Especially, the peaks at  $740.25 \text{ cm}^{-1}$  originate from C-Cl symmetrical and asymmetrical stretching vibrations. Similar results were obtained for the samples PECH 01, PECH 03 and PECH 04. FT-IR spectral results are consistent with references [14, 15].

#### Spectral analysis - $^1\text{H}$ NMR spectra

$^1\text{H}$ -NMR (600 MHz;  $\text{CDCl}_3$ ),  $\delta$  (ppm): 3.98 (2H, s,  $\text{OH}$ ); 3.86 (4H, m,  $\text{OCH}_2\text{CH}_2\text{O}$ ); 3.77 - 3.69 (3H, m,  $\text{CH}_2\text{CH}$ ); 3.62 (2H, m,  $\text{CH}_2\text{Cl}$ ).

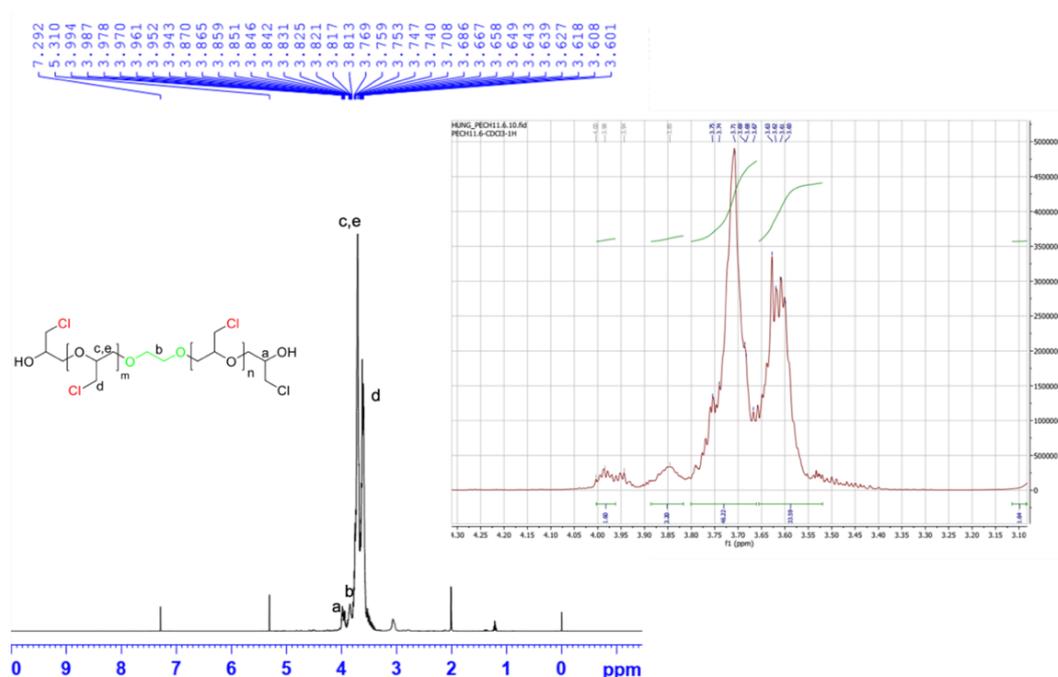


Fig. 3.  $^1\text{H-NMR}$  spectra of PECH 02.

The structures of polyepichlorohydrin were also characterized by  $^1\text{H-NMR}$  spectra as presented in Fig. 3. Characteristic peak observed at  $\delta = 3.98$  ppm (2H, s, 2OH) attributed to hydroxyl group (denoted *a*) at the end of the chain,  $\delta = 3.86$  ppm (m,  $\text{OCH}_2\text{CH}_2\text{O}$ ) attributed to  $-\text{CH}_2\text{CH}_2-$  of the initiator ethylene glycol (denoted *b*),  $\delta = 3.77 - 3.69$  ppm (3H, m,  $\text{CH}_2\text{CH}$ ) related to methyne and methylene protons in polyether backbone of polyepichlorohydrin (denoted *c*, *e*), and characteristic peak observed at 3.62 ppm (2H, m,  $\text{CH}_2\text{Cl}$ ) is the signal of 2 protons of the alkyl chloride group (denoted *d*). NMR spectral results are consistent with references [15-17]. Similar results were obtained for the samples PECH 01-04.

There are two ECH CROP mechanisms in the presence of diols (EG), catalyzed by the binary Lewis acids/protic compounds ( $\text{BF}_3 \cdot \text{OEt}_2$ ): activated monomer (AM) mechanism, and activated chain end (ACE) mechanism, as shown in Fig. 4. Initially, the alcohol interacts with the Lewis acid catalyst to yield oxonium salt, which subsequently engages with ECH to generate the activated monomer (AM). In this context, should AM react with EG, a hydroxyl-terminated macro-monomer would be synthesized, which could further react with AM to produce a PECH diol of increased molecular weight, and well-defined linear products are obtained [18].

#### *Activated monomer initiation*

Conversely, given that AM constitutes a secondary oxonium ion, it possesses the ability to react with the oxygen atom present in the neutral ECH monomer, thereby

forming an activated chain end (ACE). The ACE can undergo termination through reactions with protic compounds such as water and alcohol, culminating in the formation of PECH characterized by terminal hydroxyl groups. Nonetheless, in the absence of sufficient protic compounds, the ACE, as an oxonium ion, may engage in an intramolecular back-biting reaction with any oxygen atom within the polymer chain, leading to the production of cyclic or oligomeric by-products [18]. Therefore, it follows from kinetic considerations, that to achieve the high contribution of AMM, the reaction should be carried out at a low instantaneous concentration of monomer, and this can be accomplished by slowly adding ECH to the reaction mixture [19, 20]. The instantaneous molar ratio of [ECH] to [HO-] was < 0.5 throughout the reaction.

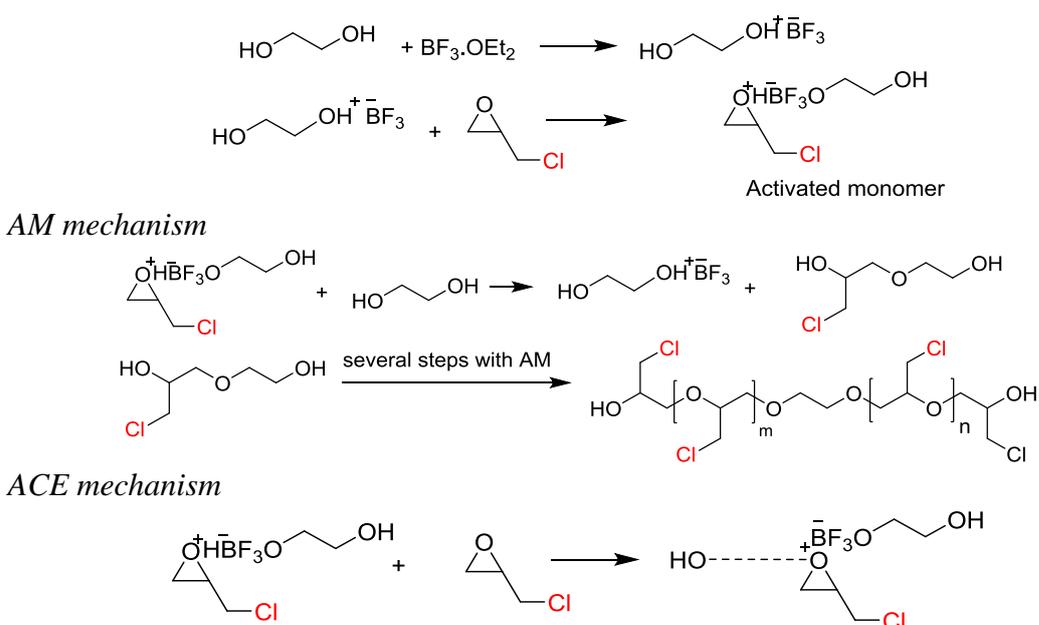


Fig. 4. Polymerization of epichlorohydrin by AM and ACE mechanism [18].

### 3.2. Effect of molar ratio on properties of PECH

#### 3.2.1. Average molecular weight

The molecular weight of a polymer serves as a representative average of the distribution of its diverse constituent molecules characterized by varying chain lengths. This parameter is critical, as it has a direct correlation to the physical properties exhibited by the polymer. In theory, the number average molecular weight of PECH can be controlled by the molar ratio of the reactants according to the following formula (1), in the case of using ethylene glycol (EG) as the initiator [19].

$$\overline{M}_n = \frac{[\text{ECH}]_0 - [\text{ECH}]_t}{[\text{EG}]_0} \times 92 + 62 \quad (1)$$

where  $[ECH]_0$  = a number of moles of ECH introduced into the system,  $[ECH]_t$  = a number of moles of ECH unreacted at the given time  $t$ ,  $[EG]$  = a number of moles of EG introduced into the system,  $92$  = molecular weight of ECH, and  $62$  = molecular weight of EG.

The outcomes of the GPC analysis of the PECH samples are presented in Table 2.

Table 2. The average molecular weight of PECH

Sample	$\overline{M}_n$ , g/mol (Calc)	$\overline{M}_n$ , g/mol (GPC)	$\overline{M}_w$ , g/mol (GPC)	PDI (GPC)
PECH 01	1740	1688	2025	1.2
<b>PECH 02</b>	<b>2106</b>	<b>1935</b>	<b>2418</b>	<b>1.25</b>
PECH 03	2618	2371	3153	1.33
PECH 04	3469	2996	4014	1.34

Based on the results obtained, it can be concluded that with an increase in the ECH ratio to the initiator, the obtained polymer (PECH) has a higher molecular mass. The number average molecular weight determined by the GPC method is lower than the theoretical calculation. Because it was polymerized by the cationic ring-opening method,  $PDI < 1.4$  was obtained, this result is consistent with theory and reference documents [13]. All PECH samples have a retention time of about 6.9 min. The GPC chromatogram of the sample PECH 02 is shown in Fig. 5.

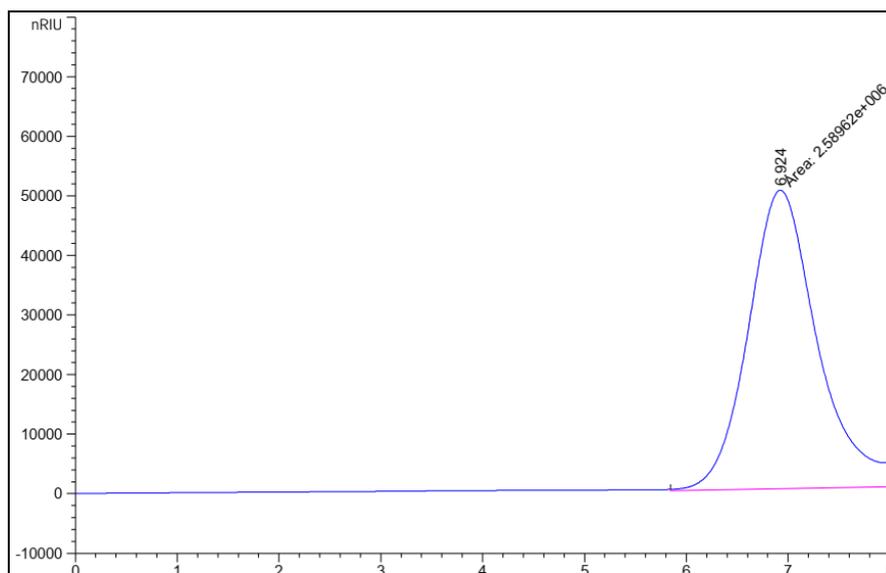


Fig. 5. GPC chromatogram of the sample PECH 02.

The findings presented in Table 2 indicate that the sample PECH 02, characterized by  $\overline{M}_n = 1935$  g/mol and  $PDI = 1.25$ , fulfills the criteria for PECH delineated in the research objective.

### 3.2.2. Viscosity, density

The dynamic viscosity of PECH samples was measured on a Brookfield LVDV-II+Pro liquid viscometer, at 30°C, and determination of density was carried out by the pycnometer method, at 25°C. The results in Table 3 also show that the viscosity and density of PECH samples are comparable to previous research [14].

Table 3. The results of viscosity, and density measurement for PECH

Entry	Sample	ECH:EG	Viscosity, cPs	Density, g/cm <sup>3</sup>
1	PECH 01	1:0.054	5807	1.3839
2	<b>PECH 02</b>	<b>1:0.045</b>	<b>11576</b>	<b>1.3909</b>
3	PECH 03	1:0.036	17860	1.3944
4	PECH 04	1:0.027	23365	1.3998

The dynamic viscosity and density of PECH increase with increasing monomer: initiator molar ratio. Increasing the ECH:EG molar ratio leads to an increase in average molecular weight (total m + n increases) linearly with PECH density, while the intramolecular and intermolecular interaction forces between PECH molecules increase, causing the dynamic viscosity to increase.

### 3.2.3. Hydroxyl value ( $H_v$ ), functionalities ( $f_n$ )

Hydroxyl value is calculated according to the following formula (2):

$$H_v = A_v + \frac{56.1x(V_0 - V_1)c}{W} \quad (2)$$

where  $A_v$  is acid value = 0 mgKOH/g;  $c = 0.54$  N ( $C_N$  KOH); anhydride acetic: 5 ml, pyridine: 5 ml;  $W$  is sample weight: 2.4 - 2.7 gram;  $\bar{V}_0$ : 192.1 ml.

Terminal functionalities (the number of reactive hydroxyl groups per molecule) are calculated according to the following formula (3):

$$f_n = \frac{H_v \bar{M}_n}{56100} \quad (3)$$

The results of the hydroxyl index analysis of PECH samples are shown in Table 4.

Table 4. Hydroxyl value and functionalities of PECH samples

	PECH 01	<b>PECH 02</b>	PECH 03	PECH 04
<b>H<sub>v</sub></b>	64.1	<b>56.8</b>	48.0	40.3
<b>f<sub>n</sub></b>	1.93	<b>1.96</b>	2.03	2.15

$H_v$  decreases as number molecular weight of PECH increases. From the results of  $H_v$  and  $f_n$ , it can be predicted that the synthesized PECH samples are mainly in the linear chain form with the terminal hydroxyl group  $f_n \sim 2$ . This result is consistent with the characteristics of ECH polymerization by AM mechanism.

#### 4. Conclusion

PECH was successfully synthesized by the cationic ring-opening polymerization method CROP. The structure of the product was demonstrated by FT-IR and  $^1\text{H}$ NMR spectroscopy and gel permeation chromatography. The polymerization process occurs by the activated monomer mechanism, which is carried out by maintaining a low instantaneous monomer concentration  $[\text{ECH}]:[\text{HO-}] < 0.5$ , creating conditions for good control of the synthesis of PECH with a high yield  $> 90\%$ . PECH synthesized with the ratio  $\text{ECH}:\text{EG} = 1:0.045$  achieved a number average molecular weight  $\overline{M}_n = 1935$  g/mol, polydispersity index  $\text{PDI} = 1.25$ , terminal functionalities  $f_n \sim 2$ , suitable for use as a raw material for synthesizing high-energy polymers for applications in the aerospace and military industries.

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## TỔNG HỢP VÀ TÍNH CHẤT CỦA POLYEPICLHYDRIN DIOL

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**Tóm tắt:** Polyepichlorohydrin (PECH) là một loại polyme chức năng có giá trị cao lĩnh vực ngành vật liệu năng lượng. Quá trình trùng hợp mở vòng cation epichlorohydrin (ECH) với diol và xúc tác axit Lewis hoặc axit protic tiến hành qua cơ chế monome hoạt hóa (AM) cho phép kiểm soát khối lượng phân tử trung bình và hệ số đa phân tán của polyme. Trong nghiên cứu hiện tại, PECH diol được tổng hợp theo phương pháp trùng hợp mở vòng cation (CROP), cơ chế monome hoạt hóa (AMM) sử dụng xúc tác boron trifluoride etherat, với tỉ lệ monome ECH: chất khơi mào ethylen glycol là 1:0,045 đạt được khối lượng phân tử trung bình số thấp  $\bar{M}_n = 1935$  g/mol, hệ số đa phân tán nhỏ PDI = 1,25, tồn tại chủ yếu ở dạng mạch thẳng với số nhóm hydroxyl cuối mạch.

**Từ khoá:** Polyepichlorohydrin; epichlorohydrin; CROP; tính chất polyme.

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