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Synthesis and Characterization of Polyether Polyol Based on Epoxy Cyclohexane and Epichlorohydrin

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Epoxycyclohexane-epichlorohydrin polyether polyol was synthesized by using epoxy cyclohexane and epichlorohydrin as raw materials, glycerol as an initiator, dichloromethane as solvent and aluminum chloride as catalysis. The structure of the copolyether was characterized by infrared (IR) spectroscopy and nuclear magnetic resonance (NMR), and its viscosity was determined. The results showed that the structure and viscosity properties of the products prepared by using aluminum chloride as the catalyst and the boron trifluoride diethyl ether catalyst were basically the same, but the aluminum chloride was more environmentally safe and lower in cost. At the same time, the polyurethane coating film prepared by using the copolyether synthesized by using aluminum chloride as a catalyst had excellent performance.

Keywords: aluminum chloride, polyether polyol, environmentally, safety.

1. INTRODUCTION

Polyether polyol is an organic polymer containing ether bond in the main chain, and more than two hydroxyl groups in the terminal group or the side group [1]. It is synthesized by ring-opening polymerization of epoxy compounds with low molecular weight polyols or active hydrogen compounds as initiators under the action of catalysts [2]. There are many kinds of polyether polyols, and four types are commonly used: propylene oxide polyether polyols, butadiene polyether polyols, tetrahydrofuran polyether polyols and special polyether polyols [3, 4].

Polyurethane products made from polyether polyols include building coatings, synthetic fibers, adhesives, sound insulation panels, automotive glass, etc. They are widely used in construction and decoration industry, textile industry, automotive industry, aerospace materials and other aspects of the people's livelihood [5]. With the increasing consumption of polyurethane products, the demand for polyether polyols increases year by year [6].

Polyurethane synthesized by epoxy cyclohexane-epichlorohydrin copolyether has good transparency, and its six-membered ring can improve wear resistance and weather resistance of the polymer [7]. Moreover, the introduction of chlorine atom makes the polyurethane synthesized by the copolyether have some new characteristics, such as improving the flame retardancy and thermal stability, therefore, it also has potential application prospects in adhesives, coatings and other fields [8]. However, at present, there are few literatures on the synthesis of polyether polyols based on epoxy cyclohexane, and boron trifluoride-ethyl ether is often used as the catalyst, while the boron trifluoride etherate catalyst has strong toxicity and great harmfulness, so the catalyst has been improved by choosing environmental-friendly agent instead of the boron trifluoride etherate. Therefore, in this study, the relatively safe and non-toxic aluminum chloride was used as the catalyst to prepare epoxy cyclohexane-epichlorohydrin copolymer ether, and the synthetic conditions of the copolymer ether were researched and optimized [9].

2. EXPERIMENTAL

2.1. Main reagents and apparatus

Epoxycyclohexane (purity > 99.5 %) was obtained from Shenma Group. Dichloromethane (PC, purity > 99.5 %), epichlorohydrin (purity > 99.5 %), and glycerol (PC, purity > 99.5 %) were purchased from Tianjin Komeo Chemical Reagent Co., Ltd. Anhydrous aluminium chloride (AR, purity > 99.7 %) were supplied by Tianjin Tianli Chemical Reagent Co., Ltd. Sodium hydroxide (AR, purity > 99.7 %) and anhydrous ethanol (AR, purity > 99.7 %) were produced from Tianjin Chemical Reagent Plant 3. Isofarone Diisocyanate (AR, purity > 99.7 %) was purchased from Shanghai McLean Biochemical Technology Co., Ltd.

The following techniques were used in the experiment: heat collection-constant temperature type magnetic stirrer of type SZCL2, Gongyi City Yuhua Instrument Co., Ltd.; A Fourier infrared spectrometer, FT-IR200, Thermo Corporation of the United States; Nuclear magnetic resonance instrument (NMR), INOVA-400, Bruker Corporation of the United States; DSC-TGA, DTG-60 Shimadzu Corporation of Japan; Ubbelohde viscometer, Shanghai Shenli Glass Instrument Sales Co., Ltd.

2.2. Preparation of polyether polyol

A certain amount of anhydrous aluminium chloride was weighed and heated in three flasks. Appropriate amount of

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dichloromethane was used as solvent. The mixture of cyclohexane oxide and epichlorohydrin was added in ice water bath for 20 minutes at constant temperature. The temperature was controlled below 10 ℃. After the solution was dripped, glycerol initiator was added to start the react. After 5 hours, 20 ml distilled water was added to terminate the reaction, and the product was poured out and washed with sodium hydroxide solution. The purpose of washing is to separate the water-soluble oligomer from the water-insoluble crude polymer, and the aluminium ion in the solution was precipitated under the action of sodium hydroxide until the solution is neutral. The product was transferred to a single-necked flask for vacuum distillation, product was obtained by remove the solvent and unreacted materials.

2.3. Analysis and testing methods

Determination of Hydroxyl number: hydroxyl number was determined according to national standard [10] GB/T 12008-1989.

Viscosity measurement [11]: according to the national standard GB/T 1632.1-2008, polyether polyols of a certain quality were dissolved in N, N-dimethylformamide to prepare a 50 ml solution. The prepared solution was added to the Ubbelohde-type viscometer and placed in a constant temperature water bath for 30 min. At least five repetitions of each datum point obtained were reproducible to ± 0.06 s, and the results were averaged.

It can be seen that as long as the outflow time t_1 of the polymer solution at different concentration and outflow time t_0 of pure solvent were measured, then the relative viscosity η_r and Specific viscosity η_{sp} at different concentration can be calculated. According to the empirical formula [12]:

$$\frac{\eta_{sp}}{c} = [\eta] + k[\eta]^2 c; \tag{1}$$

$$\frac{\ln \eta_r}{c} = [\eta] - \beta[\eta]^2 c \tag{2}$$

Plotting the curve of $\frac{\eta_{sp}}{c}$ - c and $\frac{\ln \eta_r}{c}$ - c, and finding intersections on the two lines, that is the intrinsic viscosity $[\eta]$. The relationship between viscosity and concentration is shown in Figure 1:

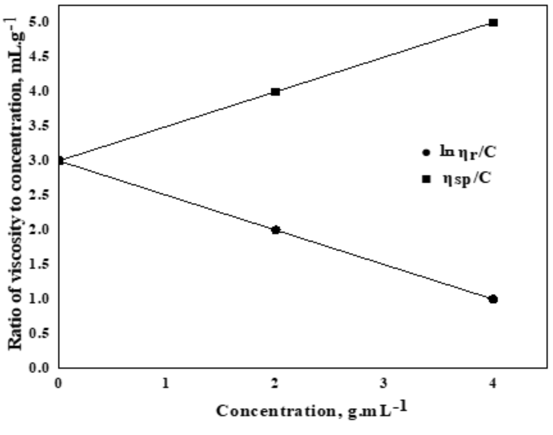


Fig. 1. The relationship between intrinsic viscosity and concentration

Testing of film properties: The paint film was prepared according to national standard [13] GB/T 1727-1992, and its appearance, gloss and acid resistance were tested.

The adhesion test was performed according to national standard [14] GB/T 9286-1998.

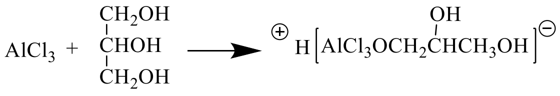
Water resistance test was performed according to the national standard [15] GB/T 1733-1993, the water resistance of the paint film was tested.

Mechanical properties test was done: hardness and tensile properties were tested according to national standard [16] GB/T 2411-2008 and national standard [17] GB/T 1040.1-2006.

Flame retardancy test was done according to the national standard [18] GB/T 1408-2008, the flame retardancy of materials was tested by horizontal method.

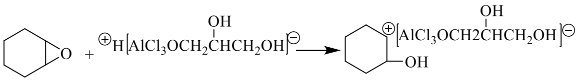
3. RESULTS AND DISCUSSION

The epoxy cyclohexane-epichlorohydrin copolyether was prepared by catalytic reaction with aluminum chloride as catalyst and glycerol as initiator. The principle of polymerization is similar to that of cationic ring-opening polymerization of epoxy compounds [19]. The reaction mechanism is as follows: Aluminum chloride reacts with propanetriol to form a complex, as shown in Eq. 3; the complex reacts with epoxy cyclohexane to form an intermediate compound, as shown in Eq. 4; the intermediate compound reacts with epichlorohydrin to form a polyether polyol, as shown in Eq. 5.

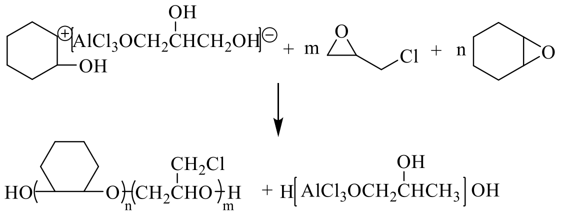


$$AlCl_3 + \begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix} \longrightarrow {}^{\oplus}H\left[AlCl_3OCH_2\overset{OH}{\overset{|}{C}}HCH_3OH\right]^{\ominus}$$

; (3)

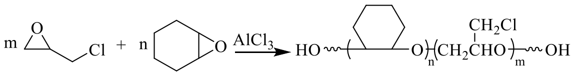


; (4)



. (5)

The total equation is as follows:



.`(6)

3.1. Orthogonal experiment

As mentioned previously, the reaction time (A), the molar ratio of initiator to total raw material (B), the amount of catalyst (C), and the molar ratio of epoxycyclohexane to epichlorohydrin (D) are the main factors the catalytic synthesis of polyether polyol. Based on the above single-factor experiments, the factors and levels for the synthesis are determined and shown in Table 1, and then the orthogonal experiment including four factors and three levels was designed and carried out. The test results based on the orthogonal array $L_9(3^4)$ are listed in Table 2. It can be concluded from Table 2 that the most important factor is starting agent (B), then in sequence is the catalyst (C) > reaction time (A) > raw material ratio (D); the optimal conditions are A2B2C3D1.

Table 1. The factors and levels for catalytic synthesis of polyether polyol with $AlCl_3$

Factor	Level		
	1	2	3
A, h	4	5	6
B	1.75：100	2.25:100	2.75:100
C, g	1.1667	1.5	1.8334
D	1.5:1	1:1	1:1.5

To further optimize the experimental conditions, A2B2C2D2, A2B2C3D2 and A2B2C4D2 (C4 = 2.0) were selected for the single factor experiment, the relative molecular weights were 1693, 2258 and 2354, respectively. The optimal conditions were as follows: reaction time 5 h, starting agent 0.69 g, catalyst 2.0 g, raw material ratio 1:1. In order to verify whether A2B2C4D2 is the optimal process condition for polymerization, epoxy cyclohexane polyether was synthesized under this condition, with a yield of 77.3 %, a relative molecular weight of 2354, and a relative molecular weight and a yield higher than that of polyether under other conditions. Therefore, A2B2C4D2 is the optimal process condition for epoxycyclohexane–epichlorohydrin polyether polyols.

3.2. Determination and comparison of IR and viscosity

The main functional groups and structures of polyether polyols catalyzed by aluminum chloride and boron trifluoride were analyzed by IR spectroscopy.

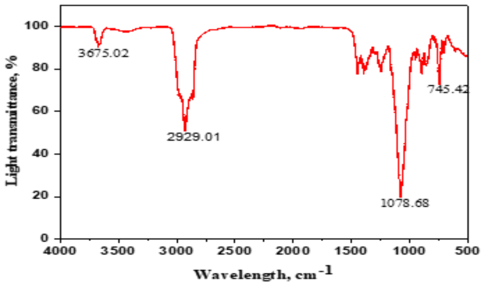


Fig. 2. IR absorption spectrum of product with aluminum chloride as catalysts

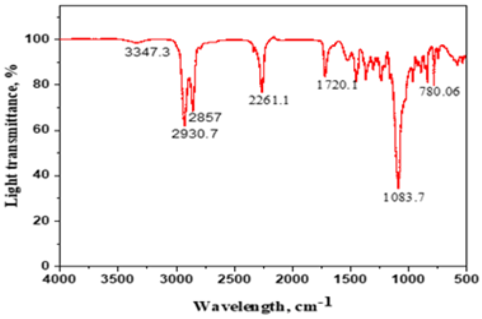


Fig. 3. IR absorption spectrum of product with boron trifluoride as catalysts

Analysis of IR spectrum based on Fig.2, the characteristic absorption peak of carbonyl group is at 3675 cm^{-1}, the strong absorption peak at 2929 cm^{-1} is the absorption peak of methylene and methine group, the strong absorption peak at 1078 cm^{-1} is the absorption peak of aliphatic ether bond, which is also the absorption peak of the iconic functional group of the product, and the absorption peak at 745 cm^{-1} is the absorption peak of carbon chlorine bond. By comparing Fig. 2 and Fig. 3, it can be seen that the structures of product with two catalysts are basically the same.

The viscosity of the above products was determined and compared with polyether polyols catalyzed by boron trifluoride. The results are shown in Table 3.

As can be seen from Table 3, the viscosity properties of products catalyzed by two catalysts are basically the same, which indicates that boron trifluoride ethyl ether catalyst can be replaced by aluminum chloride catalyst, and the cost and safety are greatly improved.

3.3. Nuclear magnetic resonance (NMR) analysis

The ^{1}H-NMR spectrum of epoxy cyclohexane-epichlorohydrin copolyether is shown in Fig. 4.

It can be seen from Fig. 4 that the resonance peaks of hydrogen atoms on methylene in epoxycyclohexane residues range from 1 to 2 ppm and the absorption peaks of protons on methine in epoxycyclohexane residues and in epichlorohydrin residues range from 3 to 4 ppm. Combined with infrared spectroscopy, it can be verified that the epoxy ring of the obtained raw material has been opened, and polymerization has occurred to form a terminal hydroxyl polymer, that is, a target product polyether polyol.

Table 2. Results of orthogonal experiment

Experiment number		A	B	C	D	Relative molecular mass	Yield, %
1		1	1	1	1	784	66.3
2		1	2	2	2	851	58.5
3		1	3	3	3	1794	79.8
4		2	1	2	3	984	77.4
5		2	2	3	1	2133	76.6
6		2	3	1	2	1721	76.2
7		3	1	3	2	1413	79.2
8		3	2	1	3	1333	65.7
9		3	3	2	1	1652	83.1
Take molecular weight as the parameter	K1	1143	1049	1280	1523		
	K2	1600	1439	1150	1329		
	K3	1466	1722	1780	1358		
	R	458	674	630	195		
Primary and secondary order		3	1	2	4		

Table 3. Comparison of products catalyzed by Aluminium chloride and boron trifluoride

	Aluminium chloride catalyst		Boron trifluoride etherate catalyst	
Relative molecular weight	2354	2258	2529	2220
Viscosity, $cm^3.g^{-1}$	3.29	3.11	3.35	3.06
Yield, %	77.3	76.8	80.5	74.0

In addition, according to the literature [20], the copolyether of cyclohexane oxide and epichlorohydrin is an irregular structure.

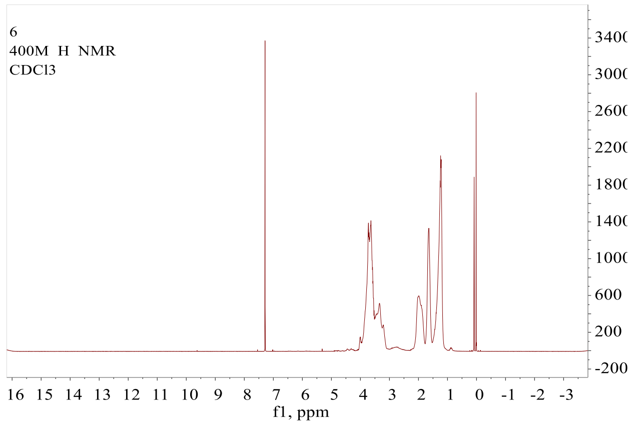


Fig. 4. ^{1}H-NMR spectra of copolyether

3.4 Thermal analysis of polyurethane material

The polyurethane was synthesized by the reaction of polyether polyols with isophorone diisocyanate. The DSC-TGA curve of the polyurethane material was shown in Fig. 5.

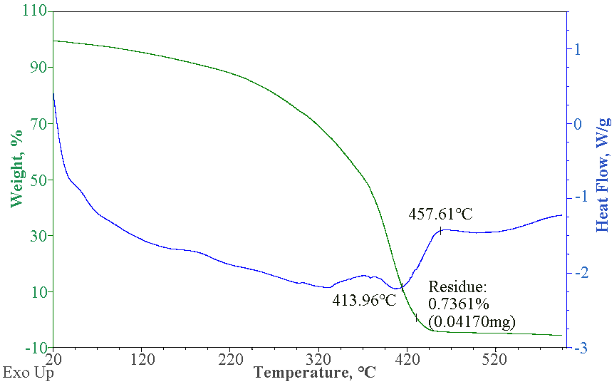


Fig. 5. DSC-TGA curve of epoxycyclohexyl polyurethane material

By Fig. 5, it can be concluded that the polyurethane materials before 320 ℃ almost no pyrolysis, thermal stability is better, when temperatures continue to rise, appeared two peaks of weightlessness, for the first time between 330 – 380 ℃, and the second between 380 – 413 ℃. This is mainly because the thermal decomposition process of the polyurethane material is divided into two stages. The first stage is the thermal decomposition of hard segment in polyurethane, and the second stage is the thermal decomposition of soft segment copolymer ether. Therefore, the polyurethane material has a high thermal decomposition temperature and is relatively stable at normal temperature.

4. PERFORMANCE TESTING

The polyurethane film of the copolyether was prepared, and its properties, adhesion, water resistance, mechanical properties and flame retardancy were tested.

The results of film properties are shown in Table 4.

Table 4. Results of film properties

Film appearance	Gloss	Acid resistance (V_{HCl} = 5 %)
Smooth, uniform, transparent	93	36 h unchanged

Adhesion test: The performance of the paint film was tested by scratch method. The results showed that the adhesion grade was 0.

Water resistance test were performed and the observation results were shown in Table 5.

Table 5. Results of water resistance

Time, h	Phenomena
24	no change
48	light loss, but no bubbles on the surface
72	obvious light loss, a small number of bubbles on the surface but no rust
96	serious light loss, the surface of a moderate number of bubbles and several rust spots, recovering 10 hours after removal

A series of polyurethane materials were prepared by changing the curing parameter *R* value, and their mechanical properties were tested. The results are as shown in Table 6.

Table 6. Influence of *R* value on mechanical properties of polyurethane materials

R value	Hardness	Tensile strength, MPa	Impact resistance, kJ/m^2
0.5	49	0.19	1.13
1	60	1.62	2.93
1.5	67	1.70	2.70
2	70	4.56	2.29
2.5	56	1.08	2.08

With the increase of *R* value of curing parameter, Shore hardness and tensile strength increase continuously, and impact resistance decrease continuously. This is mainly because the increase of *R* value will increase the hard segment content of polymer, strengthen the hydrogen bonding, and increase the physical cross-linking points. However, the increase of *R* value will increase the -NCO in the system, while the -NCO group is easy to absorb moisture and become urea group, which improves the cross-linking density of TPU, increases its Shore hardness and decreases its impact resistance.

Flame retardancy test, the horizontal method was used to measure the flame retardancy of materials. The observation results were as follows: after the sample was ignited, the sample burned stably, waxy softening appeared near the combustion end, and the sample was placed on the metal network to continue to burn until the end of the combustion. The combustion process was accompanied by strong black smoke and irritating smell. The results are shown in Table 7.

Table 7. Flame retardancy test results

Sample	Burning time, s	Burning speed, mm/min	Average burning speed, mm/min	Flame retardant grade
1	206.67	21.77	21.26	FH-3-21
2	211.03	21.32		
3	217.26	20.71		

5. CONCLUSIONS

In this study, epoxycyclohexane and epichlorohydrin were used as main raw materials, and polyether polyol was synthesized under the action of catalyst aluminum chloride. The copolymers of epoxycyclohexane and epichlorohydrin were characterized by IR and ^{1}H NMR spectra. The synthesized polyurethane was characterized by DSC-TGA. The results showed that both epoxycyclohexane and epichlorohydrin achieved ring opening, and the copolyether of epoxycyclohexane and epichlorohydrin with hydroxyl end was obtained. The structure of polyether polyols obtained by using aluminium chloride as catalyst was basically the same as that obtained by using boron trifluoride ether as catalyst. However, aluminium chloride has a wide range of sources, low cost, non-toxicity and non-volatility, and has less harm to the experimental operators. Moreover, the polyurethane material prepared by the copolyether has higher thermal decomposition temperature and is stable at room temperature, and the polyurethane film has excellent water resistance, acid resistance and alkali resistance.

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