

Preparation and Characterization of Gemini Surfactant Intermedium

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Abstract

This paper studies the preparation process and characterization of gemini-diol, an intermedium compound for synthesizing anionic gemini surfactant. Firstly, as a material to synthesize anionic gemini surfactant, high purity ethylene glycol diglycidyl ether (EGDGE) is obtained by distill epoxy resin thinner at a reduced pressure. Based on gas chromatogram, 94.51 percent of liquid at cut points of 116-119°C/5mmHg is EGDGE. Then the effects of catalyst and reaction time on the reaction of nonylphenol and EGDGE are investigated. The results show the optimized conditions to synthesize gemini-diol are as following: using 0.25%KOH and 0.25% phosphorus triphenyl as catalyst to keep the reaction of nonylphenol and EGDGE at 110°C for 3-5h. The yield of gemini-diol is 88.2% under these conditions.

Key words: Ethylene glycol diglycidyl ether; Epoxy resin thinner; Gemini surfactant; Gemini-diol

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INTRODUCTION

Gemini surfactants, a new class of amphiphilic molecules, are constructed by two hydrophilic head groups and two hydrocarbon chains covalently connected by a spacer^[1-6], and were firstly reported in USP 2524218. Due to the excellent solubility, interfacial properties and improved performance in applications comparing with conventional single-chain surfactants^[7], gemini surfactants are attracting considerable interest in both academic and industrial areas. Owing to the significant advantages such as high interfacial activity, excellent solubilization capacity^[2], lower adsorption on rock surfaces and good heat resistance, Gemini surfactants also present a great potential in the realm of enhanced oil recovery.

According to the differences of hydrophilic groups, Gemini surfactant are divided to cationic, anionic, nonionic surfactant, etc.. The synthesis of cationic gemini surfactants (mostly is bis-quaternary ammonium salt) is relatively easy and is mainly studied in recent years^[8-9]. In contrast, the synthesis, separation and purification of anionic gemini surfactants are less studied because of the complexity. Since the surface of sandstone, a primary rock type of oil bearing reservoirs are negative charged, the synthesis and investigation on anionic gemini surfactants have more practical significances for EOR.

There are primarily three types of anionic gemini surfactants: phosphate, carboxylate, and sulfonate. The synthesis and characterization of these anionic gemini surfactants have been reported by many reports in the 1990s^[10-13]. Zhu YP obtained double dodecyl dihydroxy compound by the reaction between various two epoxy compounds and long-chain fatty alcohol. Then the synthesized double dodecyl dihydroxy compound will be used to produce carboxylate, phosphate, sulfate and sulfonate type anionic gemini surfactants by reacting with chloroacetic acid, phosphorus pentoxide, chlorosulfonic acid or propyl sultone, respectively^[14-15]. These papers found that the double dodecyl dihydroxy compound,

known as gemini diol, is an important intermedium for the preparation of anionic gemini surfactants. Previous studies showed that there were mainly two types of methods to synthesize this intermedium: first method was to obtain by the reaction between long-chain epoxide compound and short-chain diol; second method was by the reaction between short-chain two epoxy compounds and long chain alcohols (or phenol). The second way was developed earlier and widely used.

Ethylene Glycol Diglycidyl Ether (EGDGE) is a two epoxy compound widely used in preparing gemini diol. Although EGDGE is widely produced and sold in China, the purity and the epoxy value (0.5-0.7eq/100g) are very low. So it is mostly used for the diluents of epoxy resin. The EGDGE produced by U.S. Fluka Company is of high purity, but the price is correspondingly high. Therefore, this paper purify EGDGE from diluents of epoxy resin produced in China as raw materials, and then synthesize gemini diol by reacting with nonyl phenol.

1. EXPERIMENTAL

1.1 Materials and Apparatus

Reagents used in this paper including industrial nonyl phenol, EGDGE, and CT epoxy resin catalyst, chromatographic methyl alcohol, and tetrabutyl ammonium bromide (TBAB, CP), tetraethyl ammonium

chloride (TEAC, CP), triphenylphosphine (TPP, CP) and KOH(CP).

Instruments used in this paper including gas chromatograph, LC/MS and HPLC.

1.2 Experimental Procedure

1.2.1 The purification of EGDGE

The EGDGE is purified by vacuum distillation. The epoxy value of distillates is measured by HCl-Acetone Method, and the compositions of distillates are analyzed by GC and LC/MS. The analysis conditions of GC are: hand injection, the sample size is 0.1 μ l, HP-5M chromatographic column, the column temperature is 50~280 $^{\circ}$ C, the heating speed is 5 $^{\circ}$ C/min, and FID detector. The analysis conditions of LC/MS are: hand injection, the sample size is 0.1 μ l, the fractionation ratio is 50 : 1; HP-5M chromatographic column, the column temperature is 50-280 $^{\circ}$ C; Agilent 5973 MS detector; full scan mode, the temperature of injection port, quadrupole and ion source are 290 $^{\circ}$ C, 150 $^{\circ}$ C and 230 $^{\circ}$ C, respectively.

1.2.2 The Preparation of Gemini-Diol

A certain mass of nonyl phenol is added in to a 4-mouth flask equipped with thermometer, condenser pipe, dropping funnel and moto stirrer, and a certain amount (subjected to the mass of nonyl phenol) of catalysis is also added. Then the EGDGE is slowly dripped until the temperature rose to a certain value. The reaction equation is as Figure 1.

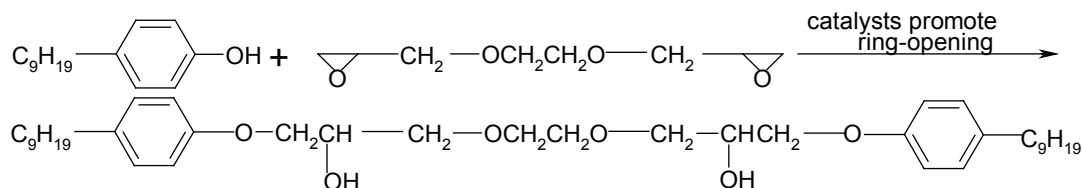


Figure 1
The Synthesis Reaction of EGDGE

Then the synthesized sample is dissolved into methyl alcohol to mass fraction of 1%. And the content of gemini diol is by LC-10 HPLC with area normalization method. The structure of gemini-diol is further characterized by LC/MS. The analysis conditions of LC are as follows: XOB-C18 chromatographic column (250mm \times 4.6mm); mobile phase chromatographic grade methanol; flow rate 1ml/min. And the analysis conditions of LC/MS are as follows: XOB-C18 chromatographic column (250mm \times 4.6mm); mobile phase chromatographic grade methanol; flow rate 1ml/min; scan wavelength 254nm; atomizing pressure 30psi, fragmentation voltage 150V; temperature of quadrupole rods 100 $^{\circ}$ C; quality range 100-1,500amu; EI and APCI ion source; dry gas flow rate 10L/min.

2. RESULTS AND DISCUSSION

2.1 Boiling Point Determination of EGDGE

Prices of the EGDGE are greatly varied from different suppliers. For example, EGDGE is 100\$/500mL from Japan and 150\$/100mL from FLUKER compared with 20\$/500mL from China. However, the concentration of EGDGE is low and there are many impurities existing, that's why it is usually served as resin diluents in China. Figure 1 shows the gas chromatogram of EGDGE offered by Jiafa Chemistry Company from China (Trade name epoxy resin diluents, Code name D-669). The peak value is disordered and there is no obvious main peak in the figure, indicating low purity and high impurities of D-669.

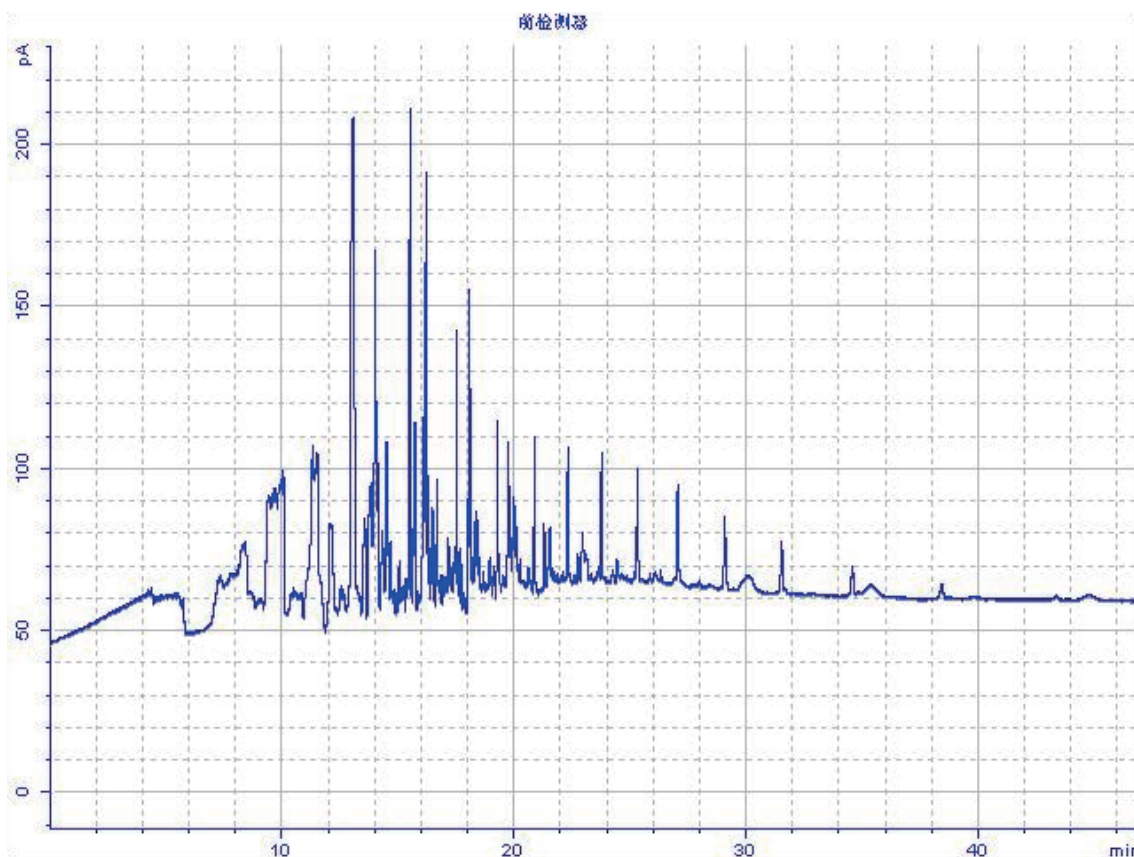


Figure 2
Gas Chromatogram of D-669

The EGDGE can be purified by distillation. The boiling point of EGDGE is varied in different documents. For example, 118-121°C/799.93Pa (*Guangxi Chemical Engineering*, 1996, 3(25), 13-19), 187-189°C/1550Pa

(*Fine Chemical Engineering*, 2005, 12(22)), 99-101°C/1010Pa and etc.. In light of the foregoing, this paper vacuum distilled the D-669 cut the different fraction, with the results shown in Table 1.

Table 1
Epoxy Value and Dropping Rate of the Fraction in Different Temperature Range

Reduced pressure distillation pressure/mmHg	Distillation temperature/°C	Epoxy number/(eq/100g)	Dropping rate
5	50-70	0.279	Slow
5	70-90	0.820	Slow
5	90-110	1.072	Slow
5	110-115	1.091	Slow
5	116-119	1.084	Fast
5	120-130	0.857	Slow

Theoretic epoxy value of EGDGE is 1.149 (eq/100g). Comparing with the results shown in Table 1, the boiling point is preliminary estimated between 90-110°C, 110-115°C and 116-119°C. Components of the

three temperature range are further analyzed by gas chromatograph, and the results are presented from Figure 3 to Figure 5.

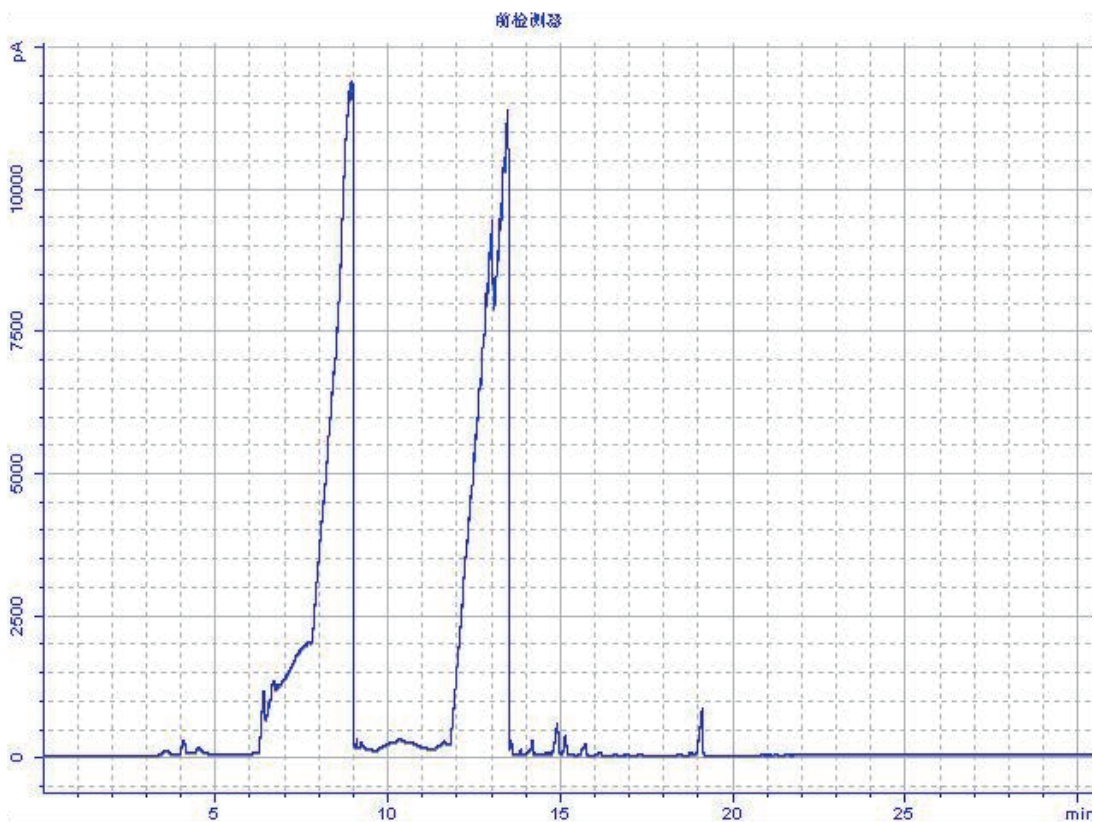


Figure 3
Gas Chromatogram of the Fraction in 90-110°C Range

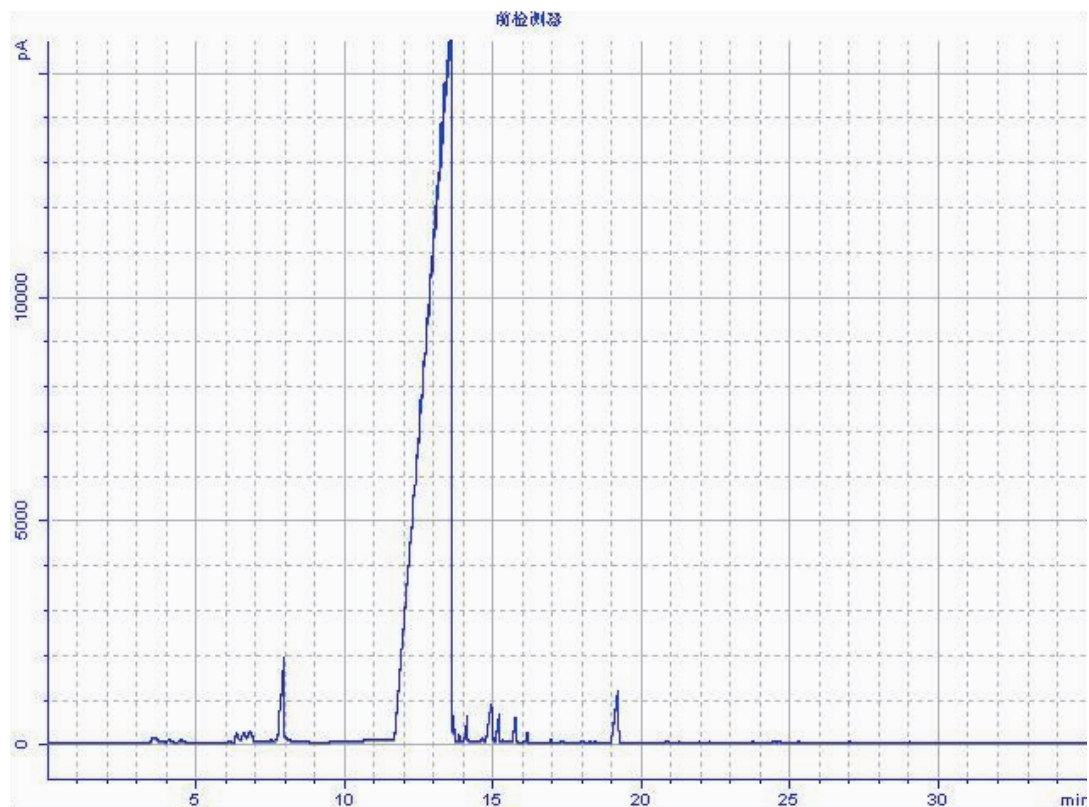


Figure 4
Gas Chromatogram of the Fraction in 110-115°C Range

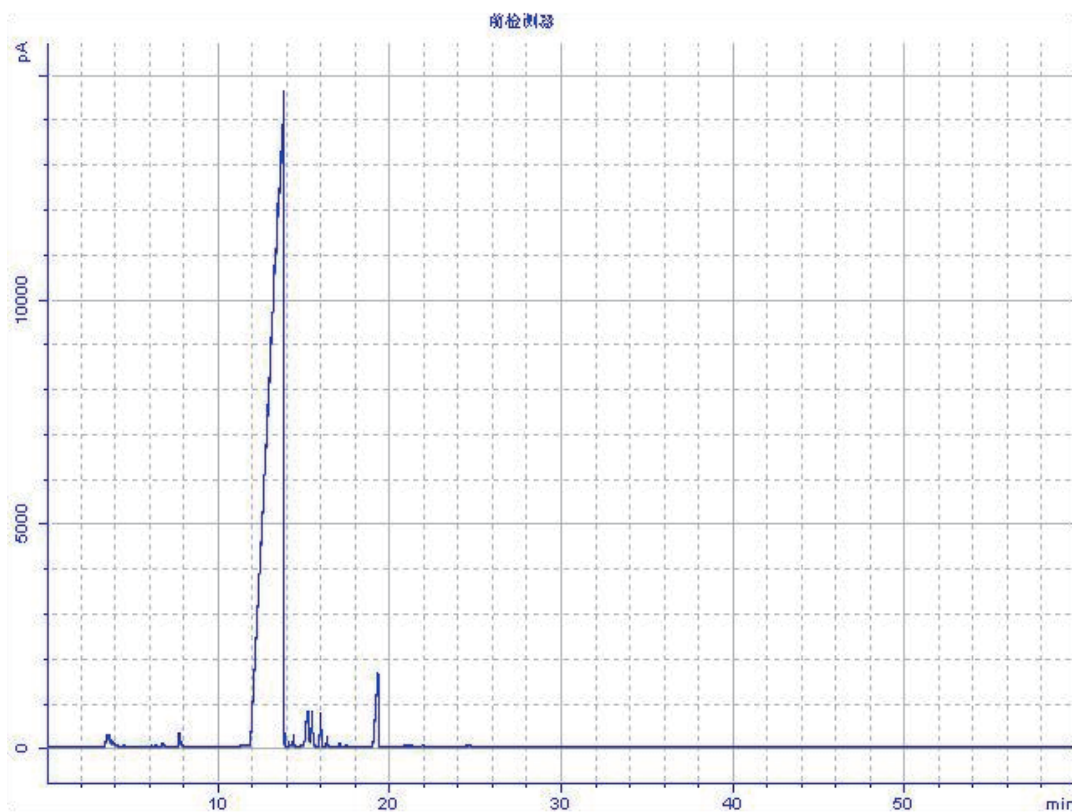


Figure 5
Gas Chromatogram of the Fraction in 116-119°C Range

There is main peak in both of the 110-115°C and 116-119°C ranges from the figures, and retention time is all 14.71min. Therefore, it is supposed that the boiling point of EGDGE lies in the two temperature ranges. Coupled with the temperature rising rate and the dropping rate of

the fraction, the boiling point of EGDGE is determined as 116-119°C. The content of EGDGE in that fraction is 94.51% from Figure 4 by using area normalization method.

Components of the main peak in 116-119°C boiling range are then MS scanned as shown in Figure 6.

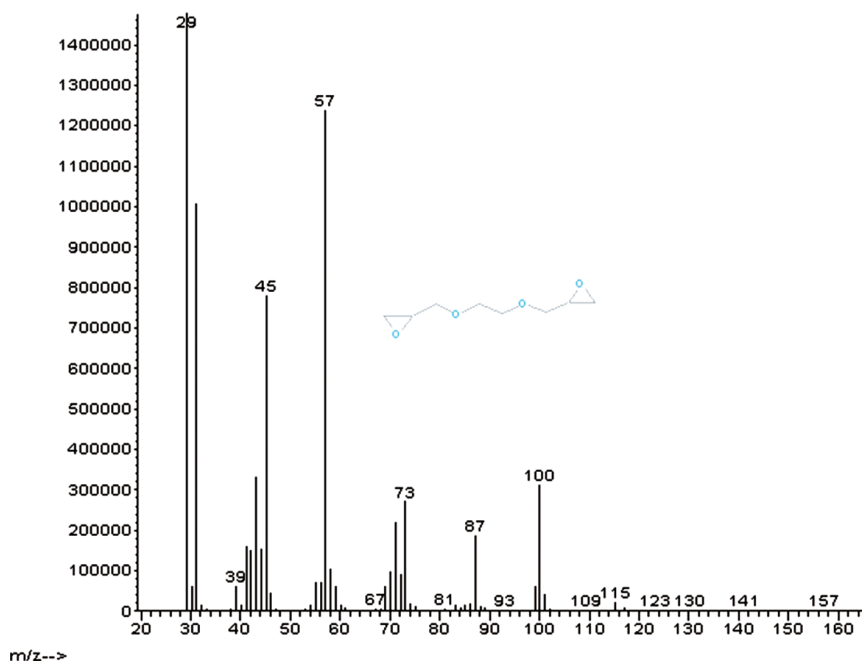


Figure 6
MS of Main Peak for EGDGE After Distillation

Compared this MS spectrogram with the standard EGDGE spectrogram from MS library the analysis results are obtained and summarized in Table 2.

Table 2
Analysis of MS(EGDGE)

Mass to charge ratio m/z	Peak categorized
$m/z=29$	EGDGE fracture fragments double hydrogen rearrangement formed $\cdot\overset{\text{O}}{\parallel}\text{CH}$ peak
$m/z=45$	EGDGE fracture fragments double hydrogen rearrangement formed $^+\text{CH}_2\text{CH}_2\text{OH}$ peak
$m/z=57$	EGDGE glycidyl ion $\text{CH}_2\text{-}\overset{\text{O}}{\text{C}}\text{-CHCH}_2$ $^+$ peak
$m/z=73$	EGDGE glycidyl ether ion $\text{CH}_2\text{-}\overset{\text{O}}{\text{C}}\text{-CHCH}_2\text{O}^+$ peak
$m/z=87$	EGDGE fracture fragments $\text{CH}_2\text{-}\overset{\text{O}}{\text{C}}\text{-CHCH}_2\text{OCH}_2$ $^+$ peak
$m/z=100$	EGDGE fracture fragments double hydrogen rearrangement formed $\cdot\text{CH}_2\text{-}\overset{\text{O}^+\text{H}}{\text{C}}\text{-CH}_2\text{-}\overset{\text{O}}{\text{C}}\text{-CH}_2$ peak

2.2 Investigation on Synthesis Conditions

Considering the following reasons, this paper choose EGDGE and nonyl phenol rather than long-chain alcohol to synthesize gemini-diol: (a) the compatibility between oil phase and the lipophilic group of surfactant constructed by dinonyl phenol is better than surfactant constructed by long-chain alcohol; (b) the reactivity of dinonyl phenol and EGDGE is higher than long-chain alcohol and EGDGE. Selecting the correct catalyst with high activity is the key for the success of this reaction. Four types of catalysts, CT epoxy resin catalyst, TEAC ($\text{C}_8\text{H}_{20}\text{ClN}$), TBAB ($\text{C}_{16}\text{H}_{36}\text{BrN}$) and TPP ($\text{C}_{18}\text{H}_{15}\text{P}$) are studied in this paper. Under the conditions of 110°C and 1% nonyl phenol mass of catalyst amounts, the effect of reaction time on the productivity for different catalysts is studied and the results are presented in Figure 7.

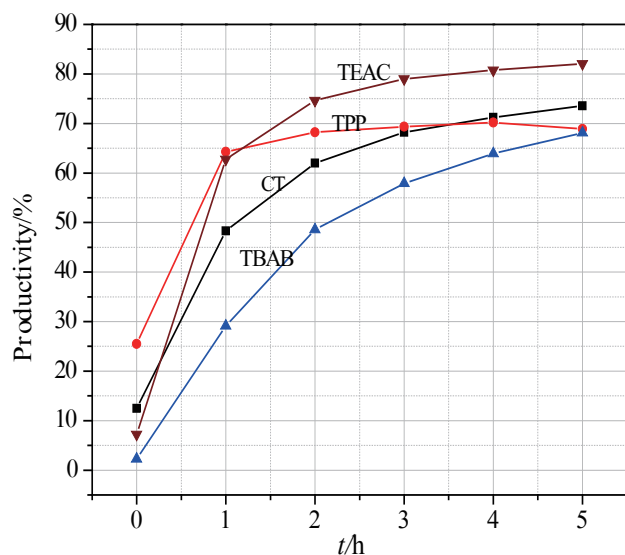


Figure 7
Effect of Reaction Time on Yield of Gemini-Diol at Different Catalyst

Figure 7 shows the productivity of gemini-diol increase in the reaction time for all catalysts. When the time is over 3 h, the productivity increases slower. TEAC

has the most best catalytic effect among the four catalysts. And the dosage of TEAC is further studied at 110°C , as shown in Figure 8. The results indicate 1% of TEAC has the highest catalytic effect.

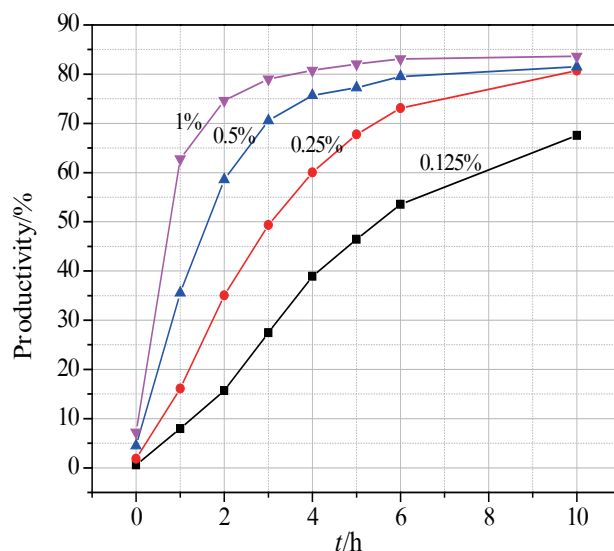


Figure 8
Effect of Reaction Time on Yield of Gemini-Diol at Different Amount of TEAC

The effect of mixed catalysts is also investigated at 110°C , and the results are shown in Figure 9.

It can be seen from the Figure 9 that when the catalyst is 0.25%KOH + 0.25% TEAC or 0.25%KOH + 0.25% TPP, the productivity of gemini-diol is higher. Moreover, the reaction rate is fast since the productivity almost stable after reacting 3h. Together with the fact that the color of the products with 0.25%KOH + 0.25% TEAC as the catalyst is lighter than 0.25% TPP as the catalyst, the synthesis condition of Gemini-diol is finally determined as follows: 0.25%KOH + 0.25% TEAC catalyst mixture, reacting 3-5h at 110°C . The productivity of Gemini-diol is 88.2% at this condition. LC analysis results of the products mentioned above is shown in Figure 10.

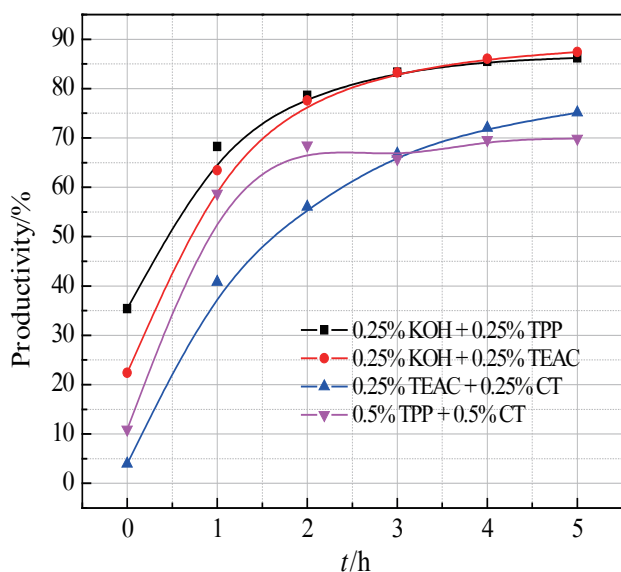


Figure 9
Effect of Reaction Time(*t*) on Yield(*x*) of Gemini-Diol at Different Combination Catalysts

In the LC spectrogram, the peak with retention time at 2.78min is the peak of nonyl phenol, the peak at 5.07 min is Gemini intermedium, and the peak at 10.31 might be polymer. The molecular weight of components at the three peaks is then analyzed by LC/MS (see Figure 11).

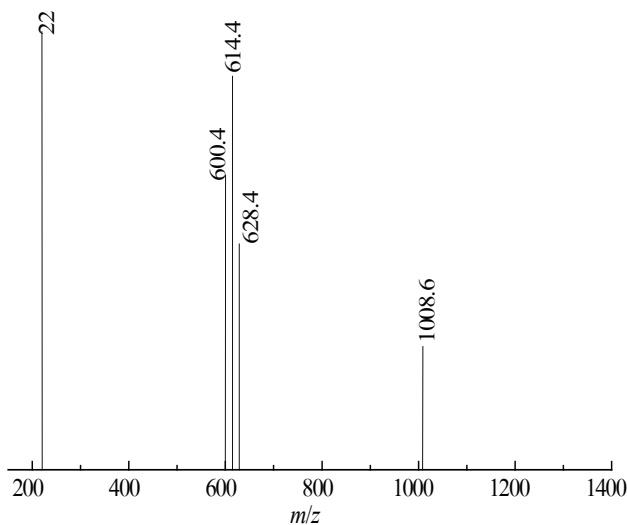


Figure 11
MS of the Synthetic Product

Figure 11 indicates the average molecular weight of peak at 2.78 min is 220.2, corresponding to nonyl phenol; the average molecular weight of peak at 5.07 min is 614.4, which equals to the molecular weight sum of two nonyl phenol and one EGDGE. Therefore, it is sure that the peak at 6.252 min corresponds to Gemini intermedium. The high molecular weight of 1008.6 at 10.31 min indicates the production of polymer byproducts with higher molecular weight from the reaction between a small amount of hydroxyl in Gemini

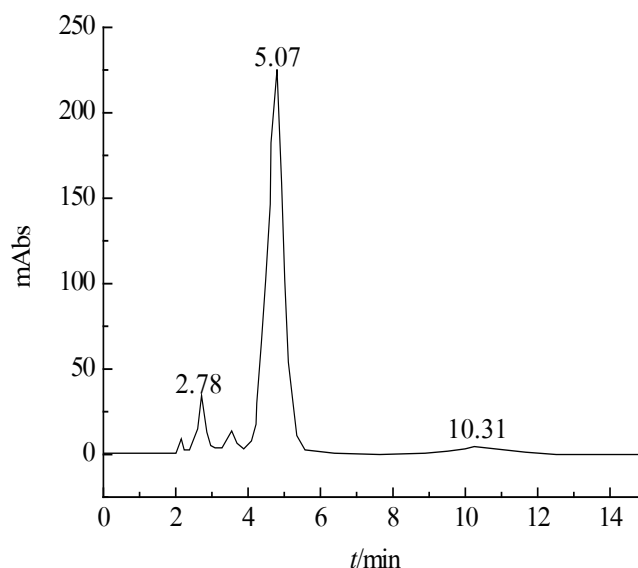


Figure 10
Liquid Chromatogram of Compound Sample

intermedium and epoxy group.

CONCLUSION

(a) Epoxy resin diluents containing EGDGE is cut into different fraction by vacuum distillation. The concentration of EGDGE is 94.51% in the fraction of 116-119°C/5mmHg.

(b) This paper has studied the effect of catalysts, reaction time on the reaction between nonyl phenol and EGDGE, the optimized synthesis conditions of Gemini-diol are: 0.25%KOH + 0.25% TEAC catalyst mixture, reacting 3-5 h at 110°C. The productivity of Gemini-diol is 88.2% in this condition.

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