

# A new approach to prepare Polyethylene Glycol Allyl Glycidyl Ether

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**Abstract.** The polyethylene glycol allyl glycidyl ether (PGAGE) is an important intermediate for preparing silicone softener that can be synthesized from allyl alcohol polyoxyethylene ether and epichlorohydrin (ECH). The performance parameters including the concentration of ECH, initial boron trifluoride diethyl etherate (BFEE) as well as CaCl<sub>2</sub> quality were investigated respectively. The optimum process parameters which can get high capping and low by-product rate are as follows: the ECH concentration is 2.0 M, the initial BFEE concentration is 1.65mM, and the CaCl<sub>2</sub> dosage is 1.65g/L. Under these conditions, the maximal yield can be improved to 91.36%, the percent of capping rate is higher than 98.16%, the residual concentration of F<sup>-</sup> is only 0.63 mg/L.

## 1 Introduction

Polyethylene glycol allyl glycidyl ether (PGAGE) and the allyl polyoxyethylene ether (APEG), tethering with both alkene and epoxy groups, are widely used as fabric finishing agent [1-2], reactive diluent [3], cross-linking agent, chemical fixation of carbon dioxide [4-5], and non-ionic surfactants for detergents.[6] In addition, the PGAGE and APEG are often used to improve the properties such as viscosity of the epoxy resins.

By far the allyl glycidyl ether (AGE) is usually manufactured via two-step reactions. The typical conventional method contains two steps. The first reaction step is performed in the presence of Lewis acid. Then, the second reaction step is performed in a basic solution. Comparison with conventional one-step, the two-step reaction can significantly enhance the end-capping rate, at the same time, reduce the required concentration of ECH to a very low level. Furthermore, compared with one-step, this production process is easy to carry out, a much higher yield is obtained [6]. It is not be ignored that the product performance is fine while the reaction needs less time. Hence, the two-step reactions are suitable for commercial mass-production.

Currently, the two-step reaction has been reported to be used in preparing AGE from allyl alcohol and ECH in the presence of Lewis acid such as HClO<sub>4</sub>, SnCl<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, boron trifluoride diethyl etherate (BFEE) [6]. The synthesis of AGE using the two-step reaction has been presented by Inagi et al [7-9]. Results showed that AGE was generally prepared by treating allyl alcohol with ECH in the presence of a small amount of H<sub>2</sub>SO<sub>4</sub>/SnCl<sub>4</sub> or SnCl<sub>4</sub>/BFEE. Allyl alcohol  $\alpha$ -mono-chlorohydrin ether can convert to the APEG via the action occurring in

concentrated basic solution, in which the total yield was between 90%~91% by Matsuoka et al. [10] also use the two-step reaction to synthesize AGE based on the reaction of allyl alcohol with ECH using BFEE as the catalyst. Their results demonstrated that the yield reaches 82% under the following condition: n (ECH) : n (allyl alcohol): (catalysis) = 1: (1~3) : (0.01~0.002).

Xu et al.[11] also synthesized the APEG in the presence of BFEE. It was shown that the highest yield of APEG was about 92% when the n (NaOH): n (allyl alcohol  $\alpha$ -monochlorohydrin) is 1.2 : 1. All of these researches indicate that the two-step reactions are a useful method to prepare the AGE. Unfortunately, how to control the operating parameters to optimize the reaction performance for preparing PGAGE and a specific BFEE removal is still poorly discussed in the literature, so more systematic studies should be carried out.

Therefore, in this paper, our group has synthesized and characterized a series of PGAGE using the BFEE catalyst. The effects of different conditions, such as molar ration of reactant, the amount of catalyst, alkali and CaCl<sub>2</sub> were investigated in detail.

In the optimal condition, the maximal yield can be improved achieved to be 91.36%, the percent of capping rate is higher than 98.16%, the residual concentration of F<sup>-</sup> is only 0.63 mg/L.

## 2 Experimental

### 2.1 Materials

The Allyl polyoxyethylene ether (APEG,  $\overline{Mn}$  =550,  $\overline{DP}$  =10) was purchased from Zhejiang Huangma

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Chemical Industry Group Co. Ltd., (Zhejiang, China). BFEE (47wt% aqueous solution) was purchased from Changshu Yangyuan Chemical Engineering Co., (Jiangsu, China). NaOH was purchased from Chengdu Kelong Reagents Co. Ltd., (Chengdu, China). ECH was purchased from Tianjin Chemical Corp. (Tianjin, China)

## 2.2 Characterization

The  $^1\text{H}$  NMR spectra were recorded on a Bruker Advance DMX 400 MHz spectrometer in  $\text{CDCl}_3$  using TMS as the internal reference. The number-average molecular weight ( $\overline{M}_n$ ) were determined with respect to polystyrene standards by gel permeation chromatography (GPC, Agilent 1200), THF was used as the mobile phase (flow rate=1.0 ml/min). The chromaticity value of PGAGE was measured by spectropolarimeter (PFXi195/2, UK). The kinematic viscosity value of PGAGE was monitored by a viscometer (SYD-265D-1, China). The concentration of  $\text{F}^-$  was measured by an ion chromatograph (881 Compact IC Pro, Switzerland).

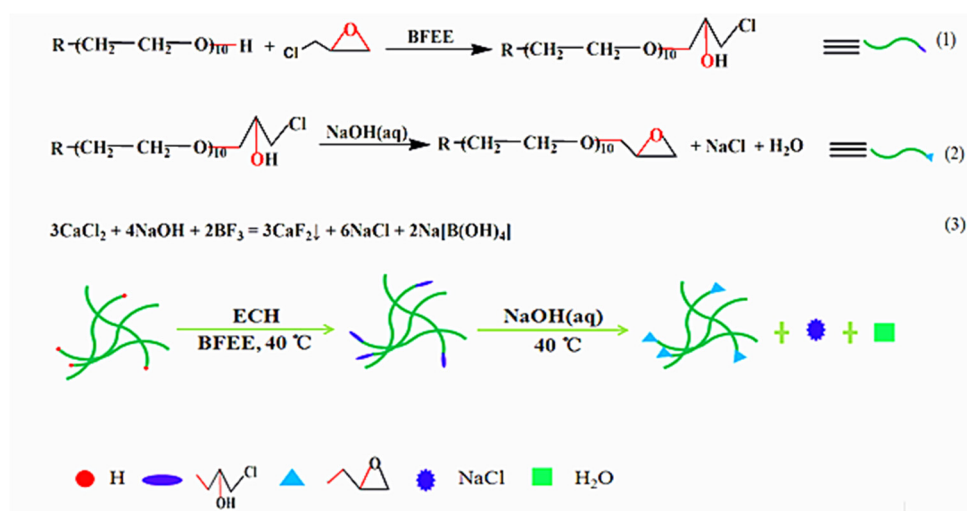
## 2.3 Synthesis of polyethylene glycol allyl glycidyl ether

The PGAGE was synthesized according to the reported

two-step reactions, as shown in (Scheme 1). Firstly, APEG (550.0 g, 1.0 M) and BFEE (1.1g, 1.55 mM) solutions were added to a 2L four-neck flask equipped with a digital agitator and a reflux condenser in a water bath. The given amount of ECH (185.04 g, 2.0 M) was added dropwise into the mixed solution over 1.5 h at  $40^\circ\text{C}$  under vigorous stirring and the resulting mixture was stirred at  $40^\circ\text{C}$  for another 1.5 h.

Then, the given amount of 50% NaOH (60.0 g, 1.5 M) aqueous solution was added to the four-neck flask and the mixture was stirred at  $40^\circ\text{C}$  for 2 h. The resulting white precipitate was separated by pressure filtration. Once again, the mixture solution was added to a 2 L four-neck flask.[12] Since  $\text{F}^-$  would cause severe environmental pollution, the aqueous solution of  $\text{CaCl}_2$  (1.65 g, 14.86 mM) was added and stirred at room temperature for 30 min following adjustment of the pH value to 4.0-4.5 by addition  $\text{H}_3\text{PO}_4$ .

Finally, the adsorbent was added to the mixture solution, and the purification was performed by distillation under reduced pressure, then the adsorbent was separated by pressure filtration. PGAGE was obtained as a colorless and transparent liquid.



Scheme 1. Schematic representation of two-step reactions

The reaction yield is the most important technical specification to examine the practical feasibility of this work. The reaction yield can be calculated by (Equation 1):

$$\text{Yield}(\%) = \frac{m_{\max} \text{ PGAGE}}{m_{\text{initial}} \text{ APEG}} \times 100 \quad (1)$$

Where  $m_{\max}$  is the maximum quality of PGAGE (g);  $m_{\text{initial}}$  is the initial quality of APEG (g).

The percent of capping rate ( $C_a$ ) is also an important technical specification for preparing PGAGE. The  $C_a$  is defined as (Equation 2):

$$C_a = \frac{E \times (\overline{M}_n + 56)}{1600} \times 100 \quad (2)$$

Where E is the measured epoxide value at  $25^\circ\text{C}$  in accordance with GB/T 1677-1981;  $\overline{M}_n$  is the number-average molecular weight of APEG.

The ring open reaction is the first-order reaction,[13] and the reaction rate is determined by using (Equation 3):

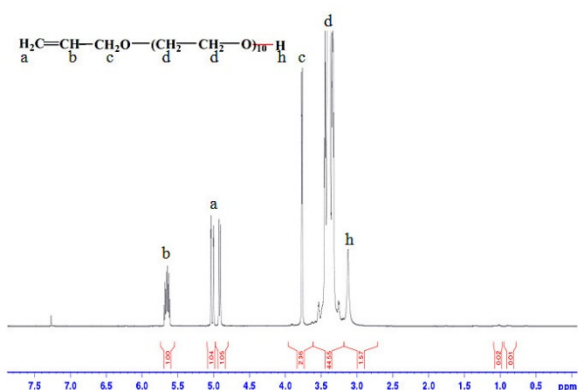
$$-\frac{d_c}{d_t} = K \cdot C_1 \cdot C_2 \quad (3)$$

Where K is the rate constant, and it is proportional to the concentration of the BFEE;  $C_1$  is the concentration of BFEE (M);  $C_2$  is the concentration of ECH (M).

All measurements were carried out three times at constant temperature ( $25^\circ\text{C}$ ) and their mean value was taken as the final result. The estimated error is about  $\pm 5\%$ .

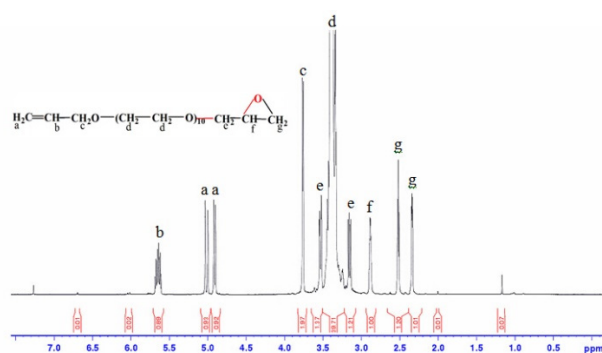
### 3 Results and Discussion

#### 3.1 Structure of polyethylene glycol allyl glycidyl ether



**Figure 1.** The <sup>1</sup>H-NMR spectrum of allyl polyoxyethylene ether

NMR was used to confirm the structure of PGAGE. <sup>1</sup>H NMR spectra of APEG and PGAGE are shown in Figure 1 and Figure 2. The average degree of polymerization ( $\overline{DP}$ ) of APEG500 is 10, therefore, the theoretical intensity ratio of methylene (APEG, 3.54 ppm) resonance to methine (glycidyl, 2.89 ppm) resonance of PGAGE in <sup>1</sup>H NMR spectrum is 40/1. From (Figure 1), the resonance at 3.1 ppm corresponds to the terminal hydroxyl groups is present, but the resonances of methylene and methine proton of the epoxy group did not appear.



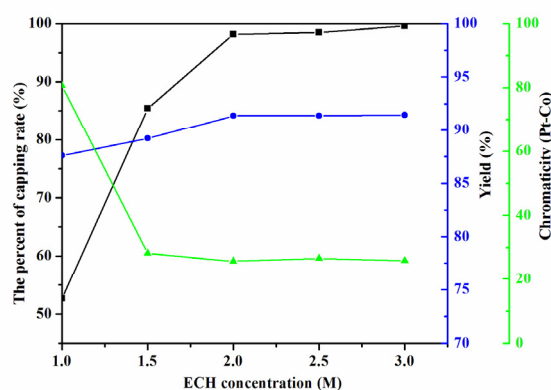
**Figure 2.** The <sup>1</sup>H-NMR spectrum of Polyethylene Glycol Allyl polyoxyethylene ether

From (Figure 2), the resonance at 3.1 ppm corresponds to the terminal hydroxyl groups is not present, but the resonances of methylene and methine proton of the epoxy group appear. Therefore, the hydroxyl group of APEG was all converted to the epoxy group, the real intensity ratio was 39.71/1, therefore, the epoxide number of PGAGE is 0.99 (converted from hydroxyl group: 0.99, the unreacted hydroxyl group of APEG:  $1 - 0.99 = 0.01$ ). The number-average molecular weight ( $\overline{M}_n$ ) of the PGAGE was 554 Da, such a result is similar to what was presented by Lu *et al.*[12] who synthesized Multi-hydroxyl end-groups poly (ethylene glycol) (PEG) from PEG and ECH.

#### 3.2 Effect of ECH Concentration

The ECH concentration plays a major role in the synthesis of PGAGE. Herein, five different ECH concentrations (1.0, 1.5, 2.0, 2.5 and 3.0 M) were investigated at 40°C respectively, while the concentration of APEG is 1.0 M, the initial concentration BFEE is 7.75 mM. The changes in percent of capping rate, yield and chromaticity of the product (PGAGE) with the different concentration values of ECH concentration are shown in (Figure 3).

The percent of capping rate and yield depended on the ECH concentration, with a significant increase being observed up to 2.0 M ECH. The chromaticity of PGAGE was decreased with the increase of ECH concentration. That is to say, increasing the ECH concentration is advantageous to prepare for PGAGE. In this work, the largest percent of capping rate can be achieved 98.16%, the yield can reach 91.36%, and the chromaticity was less than 25.6 at the 2.0 ECH concentration. However, when the ECH concentration higher than 2.0 M, the value of chromaticity remained almost unchanged while there was only a slight increase in the percent of capping and yield. The addition of extra ECH to the mixture solution leads to an increase in the overall operational cost. As a consequence, taking the percent of capping rate, yield and chromaticity into consideration, the ECH concentration of 2.0 M is regarded as the optimum value.



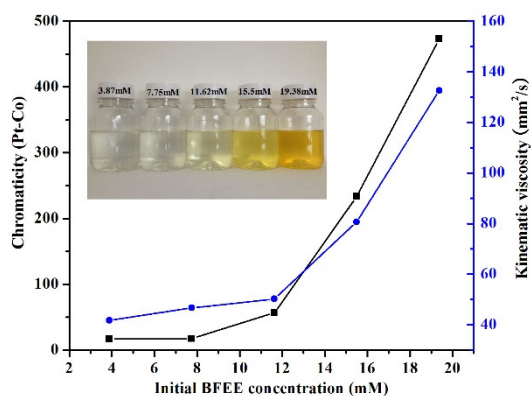
**Figure 3.** Variation of the percent of capping rate, yield, and chromaticity with ECH concentration. (APEG concentration: 1.0 M; initial BFEE concentration: 7.75mM; temperature: 40°C)

#### 3.3 Effect of Initial BFEE Concentration

In this part, the effect of the initial BFEE concentration was investigated. Initial BFEE of 3.87, 7.75, 11.63, 15.50, and 19.38 mM were chosen as samples.

The chromaticity and kinematic viscosity changed with the difference of initial BFEE concentration are depicted in (Figure 4). Obviously, the chromaticity and kinematic viscosity increased with the increase of BFEE concentration, with a significant increase being observed up to 11.63 mM BFEE. When the initial concentration is 19.38 mM, the chromaticity can reach above 473.3, meanwhile, the kinematic viscosity reaches about 132.7 mm<sup>2</sup>/S. These were possibly due to side reactions which can lead to product degradation and/or by-product

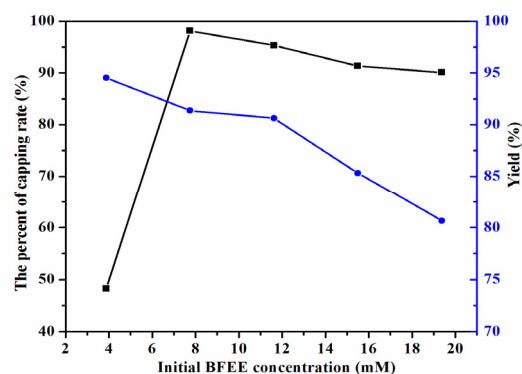
formation. Since the reaction time is fixed as 5h as mentioned previously, the rate of ring open reaction at a certain ECH concentration is mainly dependent on the BFEE concentration as can be seen from (Equation 5). Apparently, the more the initial BFEE is, the fast the reaction rate is. However, a certain amount of by-product formation could occur between the APEG and ECH or ring-opening of the epoxide group as well as subsequent reactions, [9] causing the rise of chromaticity and kinematic viscosity.



**Figure 4.** Variation of chromaticity and kinematic viscosity with initial BFEE concentration. (APEG concentration: 1.0 M; ECH concentration: 2.0 M; temperature: 40°C).

The percent of capping rate and the yield changed with the difference of initial BFEE concentration were shown in (Figure 5). As a whole, the percent of capping rate increases with initial BFEE concentration first, and then, it decreases conversely. However, the product yield was always reduced with the increase of BFEE concentration. The reasons are considered as below: The percent of capping rate depends on the epoxide value of PGAGE as can be seen from (Equation 2 and 4). When the ECH concentration is 2.0 M, more BFEE tend to stay in a four-neck flask at a constant time. The more polymerization of compounds formation, the smaller epoxide value and higher kinematic viscosity is, causing the yield to decrease evidently with a difficult recovery. Thus, the percent of capping rate of APEG is increased first and then decreased with the rising BFEE concentration. Obviously, for the yield, increasing the concentration of BFEE performed the opposite effect.

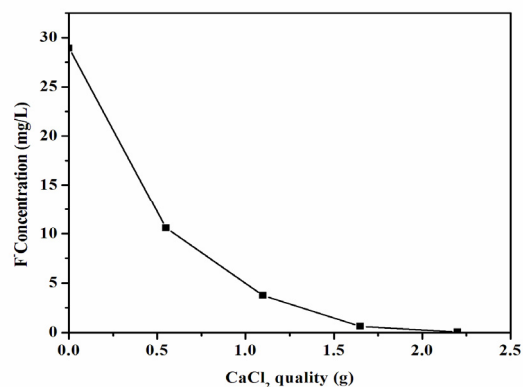
It is worth mentioning that only when the initial BFEE concentration is 7.75 mM can the percent capping rate be achieved to be higher than 98.16%, meanwhile, the yield can reach 91.36%, the chromaticity is less than 17.6, and kinematic viscosity is about 46.7 mm<sup>2</sup>/s. Taking the percent of capping rate, the yield, the chromaticity, and kinematic viscosity into consideration, the initial concentration of 7.75 mM is optimum in this work.



**Figure 5.** Variation of the percent of capping rate and yield with initial BFEE concentration. (APEG concentration: 1.0 M; ECH concentration: 2.0 M; temperature: 40°C)

### 3.4 Effect of CaCl<sub>2</sub> Quality

In this part, the effect of CaCl<sub>2</sub> dosage was investigated. Herein, the initial concentration of F<sup>-</sup> in the mixture solution is 28.93 mg/L. The change of F<sup>-</sup> concentration with varying CaCl<sub>2</sub> concentration is shown in (Figure 7).



**Figure 6.** Variation of the F<sup>-</sup> concentration with CaCl<sub>2</sub> dosage. (APEG concentration: 1.0 M; ECH concentration: 2.0 M; initial BFEE concentration: 7.75 mM; temperature: 40°C; time: 30 min).

As shown in (Figure 7), the F<sup>-</sup> concentration in the mixture solution decreases with CaCl<sub>2</sub> quality as expected. Obviously, the performance of F<sup>-</sup> removal is strongly affected by CaCl<sub>2</sub> dosage. Different from other halide ions, the concentration of F<sup>-</sup> decreases although at low CaCl<sub>2</sub>. Herein, the reason can be considered to be the generation of the CaF<sub>2</sub> sediment since CaF<sub>2</sub> is not soluble in water. That is to say, adding the CaCl<sub>2</sub> can remove F<sup>-</sup> from the mixture solution. When the stirring time is 30min, the order of F<sup>-</sup> concentration at different CaCl<sub>2</sub> quality is 2.75 > 2.2 > 1.65 > 1.1 > 0.55 g/L. Considering that the residual F<sup>-</sup> concentration should be less than 1.0 mg/L according to Sivasankar et al.[14] Apparently, when the CaCl<sub>2</sub> dosage is more than or equal to 1.65 g/L, the residual F<sup>-</sup> concentration will be low than 1.0 mg/L within 30 min. However, the addition of more CaCl<sub>2</sub> to the mixture solution leads to an increase in overall operational cost. As a consequence, considering the concentration of CaCl<sub>2</sub> is about 1.65 g/L, the residual F<sup>-</sup> concentration is close to

0.63 mg/L. Hence, the dosage of CaCl<sub>2</sub> is suggested to be 1.65 g/L for a practical application in order to save the overall cost.

## 4 Conclusions

The PGAGE was successfully synthesized through direct polycondensation of APEG and ECH. The performance parameters including ECH concentration, initial BFEE concentration, NaOH concentration, and CaCl<sub>2</sub> quality are investigated respectively. The optimum variables are as follows: the ECH concentration of 2.0 M, the initial BFEE concentration of 7.75 mM, the NaOH concentration of below 1.5 M, and the CaCl<sub>2</sub> dosage of 1.65 g/L. Under these conditions, the maximal yield can be achieved to be 91.36%, the percent of capping rate is higher than 98.16%, the residual concentration F<sup>-</sup> is 0.63 mg/L.

## Acknowledgments

Financial supports from Zhejiang Huangma Chemical Industry Group Co. Ltd., and Opening Foundation of Zhejiang Huangma Surfactant Research Institute. This work was also supported by Ministry of Education Chunhui Project (191630), Sichuan Provincial Department of Education Project (18ZB0571).

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