

Preparation of 2, 3-Epoxypropyl Neodecanoate: Process Optimization and Mechanism Discussion

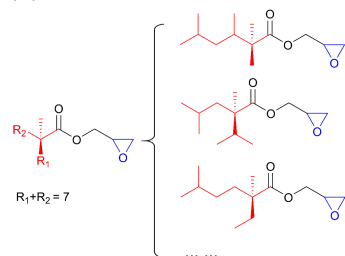
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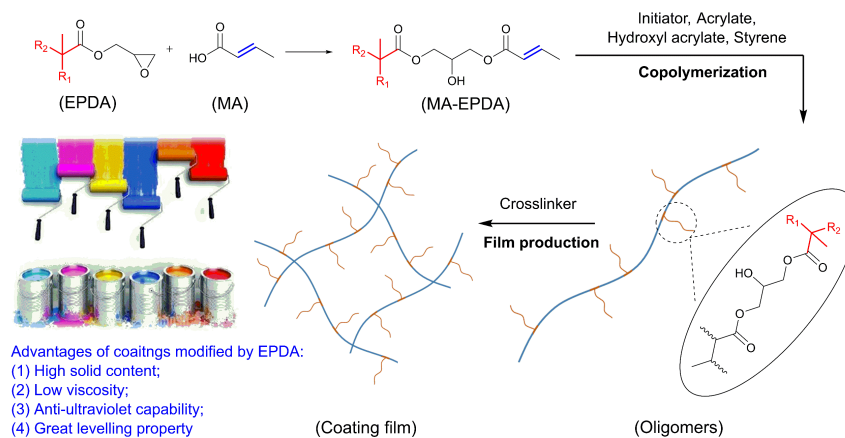
(A) Structure of EPDA

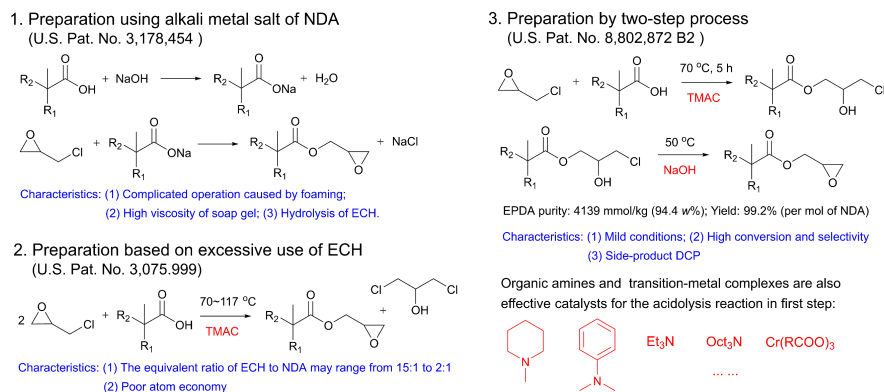


(B) Physi-chemical properties of EPDA

Property	Test Method	Value
Epoxy content	STYM 06	3906~4250 mmol/kg
Viscosity (25 °C)	ASTM D445	7.13 mPa · s
Density (25 °C)	ASTM D4052	0.945~0.965 kg/L
Saturated vapor pressure (37.8 °C)	ASTM D323	0.9 kPa
Solubility in water (20 °C)	/	70 mg/L
Distribution coefficient (octanol/water) $\log(K_{OW})$	/	4.4 (pH = 6.7)

(C) Modification process of methacrylic water-based coating by EPDA





Generally, EPDA is produced through the chemical reactions of epichlorohydrin (ECH) with neodecanoic acid (NDA), and three typical synthetic processes have been developed according to the published literatures and patents (see **Scheme 1**).¹⁰ The first preparation method is carried out by using the alkali metal salt of NDA. The specific operations can be summarized as: (1) NDA reacts with sodium hydroxide aqueous solution to generate neodecanoate, (2) then the salt solution is dripped into the reactor with ECH heated reflux in it. This organic-aqueous reaction system has high viscosity and low interfacial tension because the neodecanoate, whose chemical structure consists of a polar head and a hydrophobic tail, can function as a surfactant. Hence, the emulsification can be rather serious for this system. Besides, the alkaline environment can cause the hydrolysis of ECH to produce dichloropropanol and glycerol, leading to the waste of reactant and posing difficulties for waste water treatment. The second synthetic process is based on the largely excessive use of ECH, the by-product dichloropropanol can be converted into ECH and recycled through the reaction with alkalis. However, the atom economy is poor, and the relatively low purity of EPDA increases the cost in the downstream purification processes.

At present, the two-step process is the most widespread path for EPDA production, including the initial acidolysis ring-opening reaction of ECH with neodecanoic acid to produce chlorohydrin ester intermediate (EPDA-M), and the following ring-closure step by alkali treatment. The acidolysis reactions of ECH with organic acids can be catalyzed by a series of nitrogenous catalyst¹¹⁻¹³ and complexes of transition metal^{14, 15}. Tetramethylammonium chloride (TMAC) has been recognized as a high-performance catalyst because of its high catalytic activity and ease of separation and recovery.¹⁶ The significant advances have been made to explore the catalytic mechanism and the interaction effect between TMAC and the reactants¹⁷, providing theoretical support for process optimization. The following ring-closure reaction by dehydrochlorination is a relatively mature process involved in some practical industrial applications, such as the production of propylene oxide through the chlorohydrin approach^{18, 19} and the production of ECH from dichloropropanol (DCP)^{20, 21}.

The advantages, including the mild conditions applied in the whole process, the high conversion of neodecanoic acid and high selectivity towards EPDA, determine the great applicability of this two-step process. However, there are few researches to optimize the process conditions. Besides, the complete catalytic reaction pathways and the mechanism to explain the formation of the side product dichloropropanol (DCP) are still not clear. The lack of these studies leads to the unclarity of the strategies to improve the effective utilization rate of ECH and reduce the organic waste.

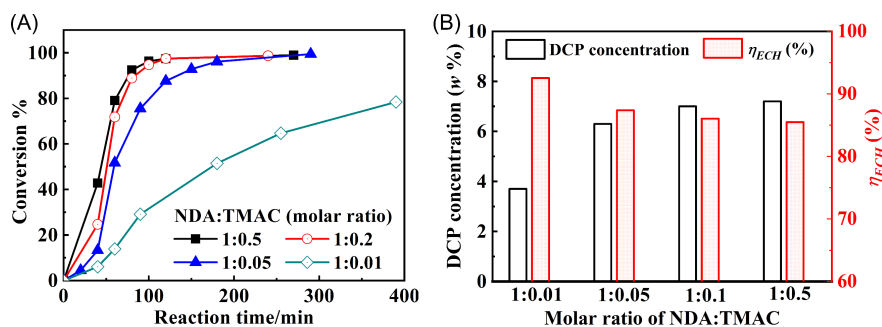
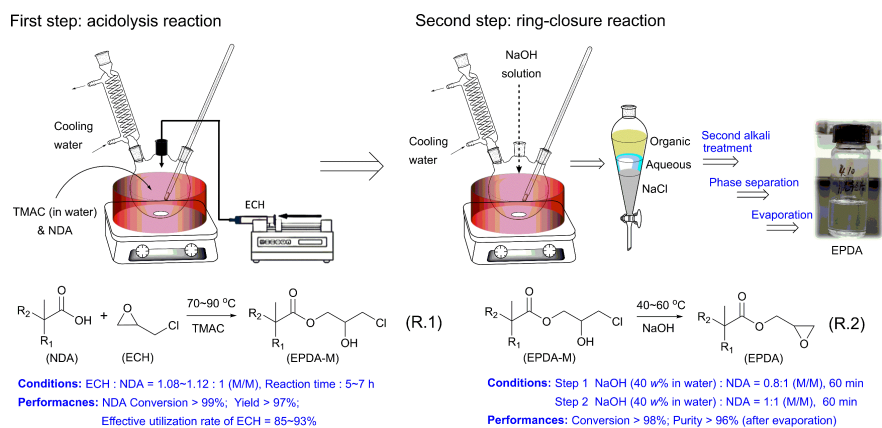
The essential objective of this work is to optimize the two-step production process of EPDA catalyzed by TMAC in batch condition. Moreover, some reliable experiments are conducted to verify the catalytic mechanism of the main acidolysis reaction and demonstrate the side reactions, as well as its occurrence conditions and control methods. Hopefully, the study methods and the obtained mechanisms can be successfully applied for other production processes of glycidyl esters, such as glycidyl acrylate and glycidyl methacrylate.

Experiment

Reagents and materials

All reagents used in the experiments were classified as analytical grade and purchased from commercial reagent company. Neodecanoic acid was purchased from Shanghai Ethyl Chemical Co., LTD, with the purity of 99% tested by titration. The rest of chemicals were routinely used in our laboratory, and all purchased from Aladdin Chemistry Co., LTD. The purities of all reagents could meet the experimental requirements, hence the further purification steps were not required.

Experimental procedures



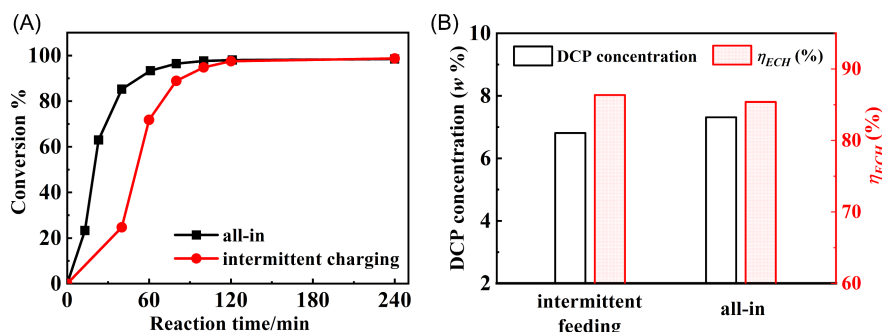
The ring-opening of ECH from the acidolysis reaction with neodecanoic acid (NDA), which was catalyzed by tetramethylammonium chloride (TMAC) in our experiments, is shown in **Scheme 2**. Different amounts of TMAC were added to study the effect of catalyst content on the reaction performances (see **Figure 2**). Figure 2(A) shows the curves of NDA conversion versus reaction time. It is acceptable that the reaction rate, especially at the early stage, increases when more TMAC is used. To be more detailed, as the amount of TMAC increases to 5% (molar ratio to NDA), the reaction time for 99% conversion of NDA basically doesn't change with the further increment of TMAC. And when using 1% TMAC, the reaction time of 20 hours is needed, which is too long to be accepted. Therefore, it is a better option to add TMAC in the molar ratio of 0.05:1 to NDA. Figure 2(B) shows the GC analysis results of the samples taken at the end of the reactions. Because of the increment of TMAC, the concentration of dichloropropanol (DCP) greatly increases from 3.7% to 7.2%, resulting in the decline of η_{ECH} by 7.1%.

Temperature is another factor that greatly influences the reaction performances (see **Table 1**). As the temperature rises from 50°C to 110 °C, the required reaction time is reduced from 1200 min to 90 min, however, the concentration of side-product dichloropropanol (DCP) in the final reaction system rises from 3.7 w % to 8.5 w %, leading to the decline of η_{ECH} by 9%. Taking both the factors of reaction time and selectivity into consideration, it is a better option to apply the temperature condition in the range of 70~90°C.

Table. 1 Effect of temperature on the reaction performances.

Temperature (°C)	Reaction time (min)	NDA conversion (%)	ECH conversion (%)	DCP concentration (w %)	η_{ECH} (%)
50	1200	98.7	95.9	3.7	93
70	290	99.5	97.7	4.9	90
90	180	99.5	98.7	6.0	88
110	90	98.2	99.9	8.5	84

Reaction conditions: NDA:TMAC:ECH = 1:0.05:1.12. ECH was fed at a constant rate in 1 hour.



¹ Referring to the molar ratio to neodecanoic acid

² The feeding speed depends on the temperature rise, so as to ensure that the reaction is conducted in the appropriate temperature range.

3.2 Mechanisms of side reactions and control strategies

According to the results listed above, it has been found that the concentration of side-product dichloropropanol (DCP) is hard to be lower than 5%, and it always increases as the reaction proceeds. The results in Figure 3 and Figure 2 suggest a hint that the side reactions leading to the generation of DCP is mainly related to the concentration of ECH and the addition of tetramethylammonium chloride (TMAC). In order to illustrate the influence of these two factors more cogent, the experiments shown in **Table 3** were designed.

Table 3. Effect of ECH concentration on the side reactions leading to the formation of DCP

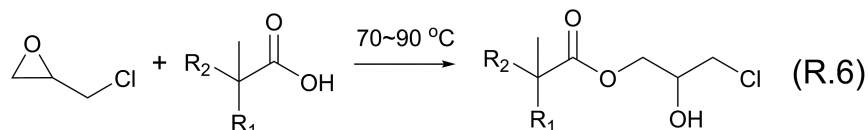
ECH : NDA (M/M)	ECH conversion (%)	NDA conversion (%)	DCP concentration (w %)	η_{Acid} (%)	η_{ECH} (%)
0.1	100	11	3.4	55	50
0.2	100	16	3.7	66	70
0.5	100	46	4.5	83	85
0.8	100	78	4.4	89	89
1	100	96	5.5	95	90

Reaction conditions: 70 °C, the molar ratio of TMAC to NDA was 0.05:1.

As the feeding amount of ECH increases, the reactions of the initial, middle and late stages were conducted under the conditions of excessive neodecanoic acid (NDA). The results indicate that DCP noticeably exists in the reaction system, even only a little amount of ECH (with molar ratio of 10%) was added. With the amount of ECH increasing from 10% to 100%, the DCP concentration only increases by 2.1%, however, the value of η_{ECH} greatly rises from 50% to 90%. A reasonable interpretation of these results is that the side

reaction causing the formation of DCP precedes the main reaction of ECH with NDA. There have been some studies^{16, 17, 23} about the mechanism of the acidolysis reaction of ECH with organic acid catalyzed by quaternary ammonium salts (shown in **Scheme 3**). The formation of quaternary ammonium carboxylate with the aid of TMAC is presumed to be the first step (R.3 and R.4), and the generated carboxylate would be the functional substance to catalyze the acidolysis reaction (R.5). The results listed in Table 2 completely comply with this catalytic mechanism. The relatively low values of η_{Acid} and η_{ECH} in the early stage can be explained by the formation of tetramethylammonium neodecanoate (TMAN), which involves the interaction of TMAC, ECH and NDA. And the subsequent increase of η_{Acid} and η_{ECH} is due to the ongoing main reaction of ECH with NDA catalyzed by TMAN.

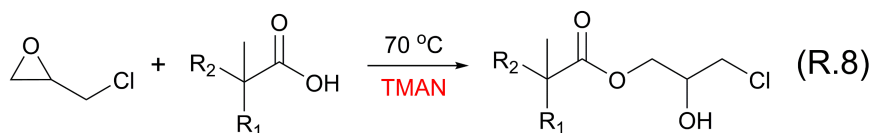
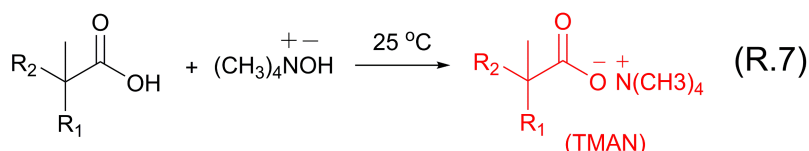
Acidolysis reaction without catalyst



Conditions: ECH:NDA = 1.10:1, Reaction time = 6 h;

Results: NDA conversion < 3%

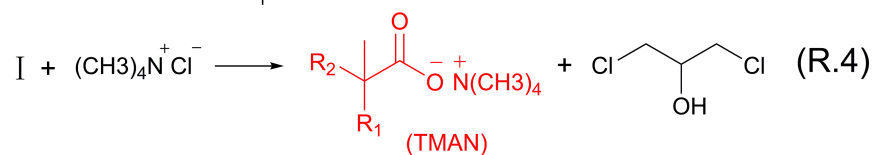
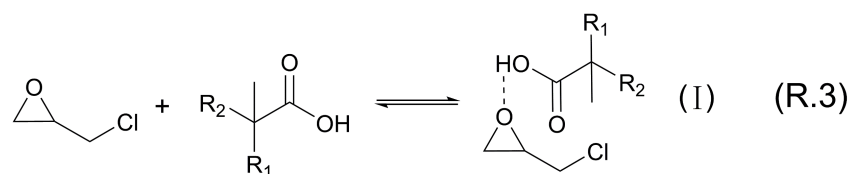
Acidolysis reaction catalyzed by TMAN



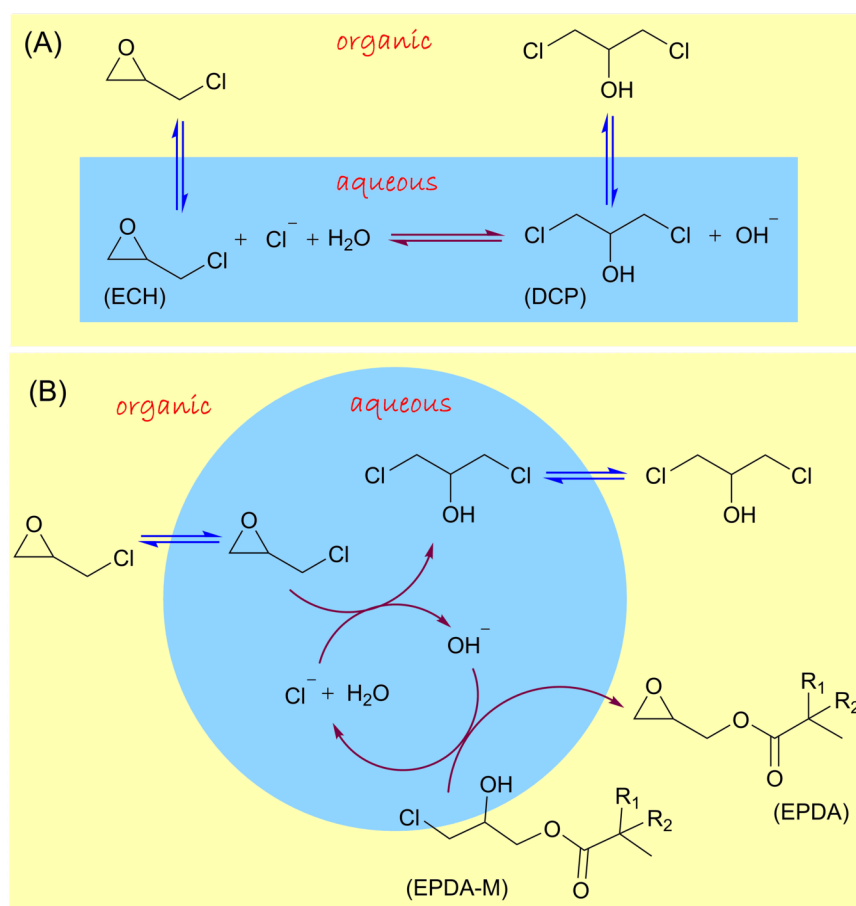
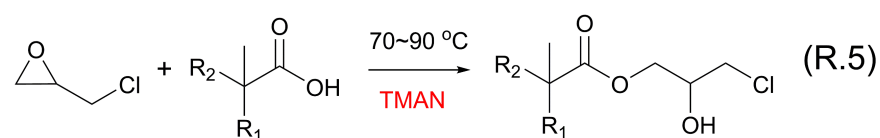
Conditions: ECH:NDA:TMAN = 1.08:1:0.05, Reaction time = 6 h;

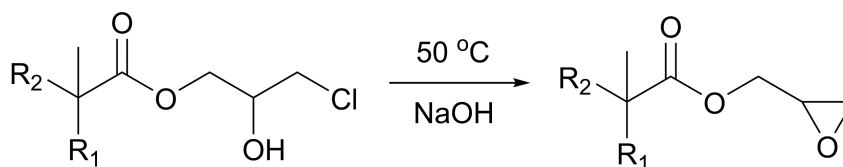
Results: NDA conversion > 99%, yield > 98%

1. Formation of quaternary ammonium carboxylate



2. Acidolysis reaction catalyzed by the carboxylate





Conditions: 40 w% NaOH in water, EPDA-M : NaOH (M/M) = 1:1.8

Performances: Reaction time = 60 min, Conversion = 89 %;

Reaction time = 120 min, Conversion = 92 %;

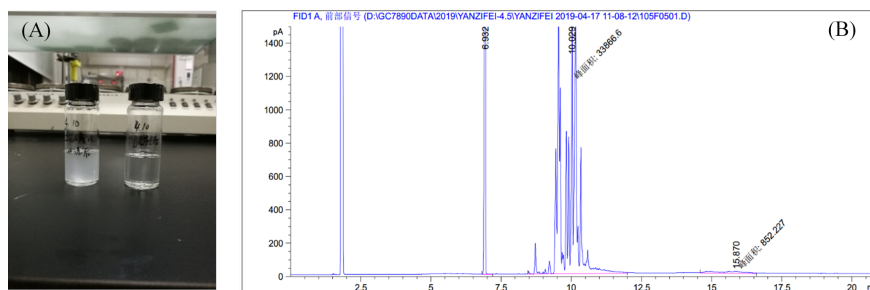
Reaction time = 180 min, Conversion = 94 %;

Reaction time = 240 min, Conversion = 94 %.

Chlorohydrin process is one of the widely used production methods of ECH, in which dehydrochlorination reaction of dichloropropanol (DCP) with hydrated lime is an essential step,²⁷ and it can be a great reference for the ring-closure process of chlorohydrin ester intermediate (EPDA-M) to produce EPDA by dehydrochlorination reaction with sodium hydroxide. The temperature and alkali concentration are two most important factors of the reaction. When the temperature higher than 70 °C was applied, EPDA degradation caused by the hydrolysis of ester bonds became obvious. Therefore, it is a better option to carry out the reaction in the temperature range of 40~60 °C. According to the experimental results shown in **Scheme 6**, it is hard to completely convert EPDA-M when excessive alkali was fed in one-time. This is because the alkali concentration, more specifically referring to the concentration at the organic-aqueous interface, decreases as the reaction proceeds, leading to the significantly reduction of the ring-closure reaction rate.

In order to maintain relatively high concentration of the alkali in the late stage of the ring-closure reaction, we adopted a two-step alkali treatment process which is introduced in the **Experiment** section. The first alkali treatment process was carried out by adding 40 w % NaOH solution (0.8 equiv). The conversion of 60~65% can be achieved after 1 hour at 50°C. Then, the secondary alkali treatment was applied by adding 40 w % NaOH (1 equiv) after phase separation. The total addition of 1.8 equivalent NaOH is the same as the one-time experiment, but the final conversion of EPDA-M can exceed 97% within 2 hours' treatment (including two steps).

Table 5 . Effects of alkali concentration and treatment time in the second step on the ring-closure reaction.



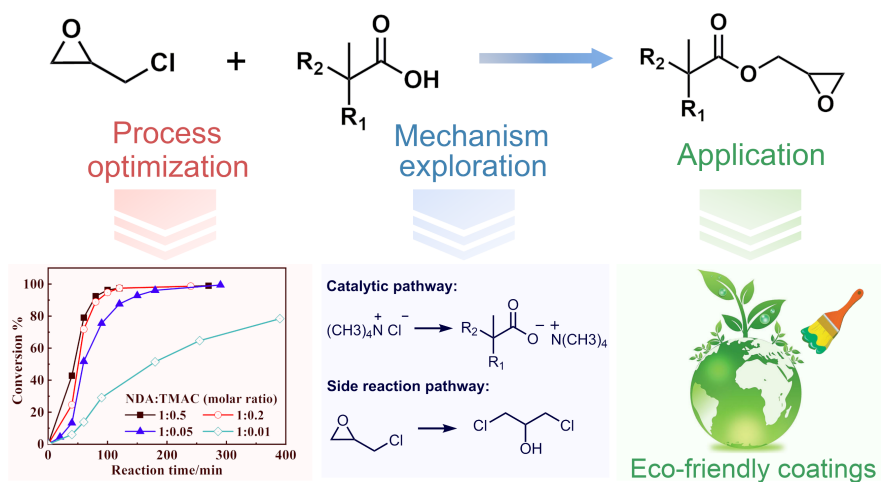


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