Electronic Supporting Information

Remarkable improvement of epoxide ring-opening reaction efficiency and selectivity with water as a green regulator

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1. Introduction of 2, 3-Epoxypropyl neodecanoate (EPDA)

The structure of EPDA is shown in **Figure S1**, and its important physical properties are listed in **Table S1**. EPDA is a mixture of isomers because its synthetic raw materials, neodecanoic acid (NDA), is a mixture of isomers.

Modified by EPDA, the coatings can have many excellent characteristics.[1-3] First, the larger steric hindrance of EPDA can increase the stability of the active groups on adjacent monomers, thereby significantly improving the chemical resistance and weather resistance. Second, the huge branched structure of EPDA can effectively weaken the interaction between polymer chains, thus reducing the viscosity of oligomers. In this way, the solvent consumption for dilution can be reduced significantly. Third, EPDA can improve the water resistance of coatings by enhancing their hydrophobicity. Fourth, the tertiary carbon structure of EPDA can effectively absorb the energy of ultraviolet rays, thus improving the anti-ultraviolet performance of the coatings.

The application of EPDA is gradually being promoted. Up to now, it has been used in acrylic coatings, polyester and alkyd resin coatings, polyurethane coatings, cathodic electrophoretic coatings, water-based coatings, room temperature solid coatings and some other products.[2]

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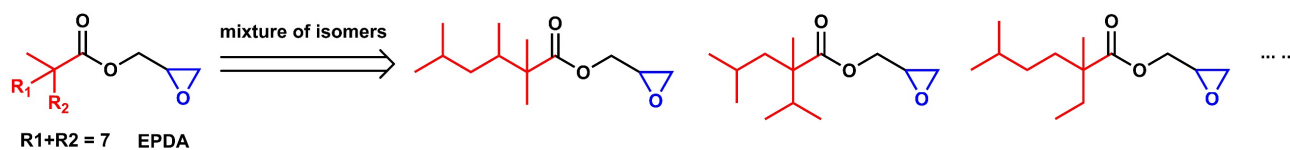
Figure S1. Structure and component of EPDA

Table S1. Physical properties of EPDA[4]

Property	Testing method	Value
Epoxy group content	STYM 06	$3906 \sim 4250\ mmol/kg$
Viscosity (25 °C)	ASTM D445	$7.13\ mPa \cdot s$
Density (25 °C)	ASTM D4052	$0.945 \sim 0.965\ kg/L$
Saturated vapor pressure (37.8 °C)	ASTM D323	$0.9\ kPa$
Boiling point (1 atm)	/	$292\ °C$
Solubility in water (20 °C)	/	$70\ mg/L$
Distribution coefficient (octanol/water) $\log\left(K_{OW}\right)$	/	$4.4\ (pH = 6.7)$

2. GC testing conditions and standard curves

The GC testing conditions are listed in **Table S2**. Under these conditions, the standard curves of ECH, EPDA, EPDA-M and diester are shown in **Figure S2**.

Table S2. GC testing conditions

Device: Agilent GC-7890A	Detector: FID
Column: HP-5 / 30 m × 0.32 mm × 0.25 μm	Injection temperature: 300 °C
Carrier gas: N_2, 1 mL/min; Split ratio: 30:1	Detection temperature: 300 °C
Column temperature: Start at 50 °C, maintain for	Sample: 1 μL
2 min; 10 °C/min to 160 °C; 5 °C/min to 200 °C;	Quantitative method: Internal standard
10 °C/min to 300 °C, maintain for 3 min	Internal standard substance: Methyl benzoate

(A)

Equation	y = a + b*x
Intercept	0.00293 ± 0.0022
Slope	2.12897 ± 0.00257
R2	0.99999

(B)

Equation	y = a + b*x
Intercept	0.0015 ± 0.00891
Slope	1.11238 ± 0.00538
R2	0.99986

(C)

Equation	y = a + b*x
Intercept	-0.00251 ± 0.00236
Slope	1.24903 ± 0.00115
R2	0.99999

(D)

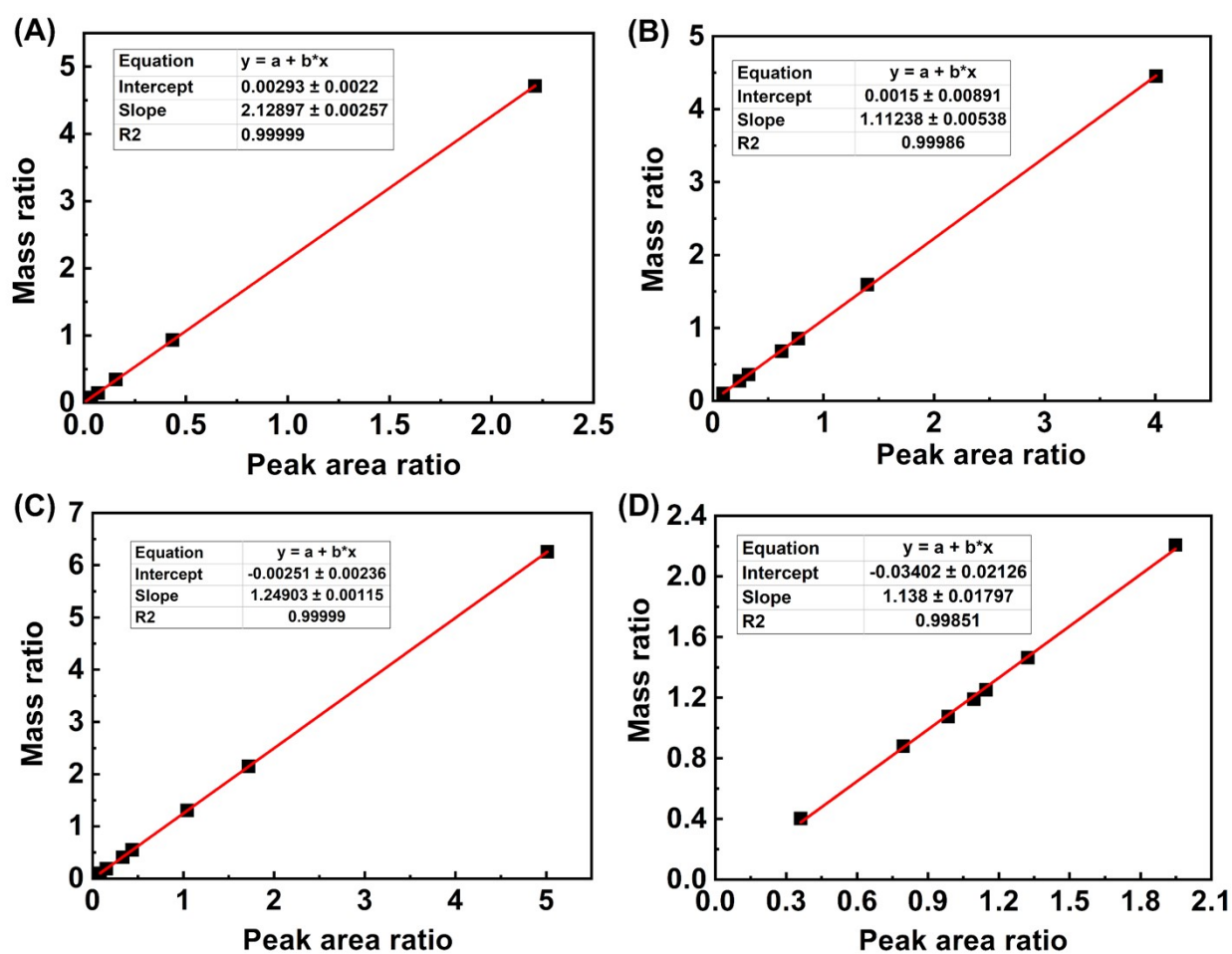| Equation	y = a + b*x
Intercept	-0.03402 ± 0.02126
Slope	1.138 ± 0.01797
R2	0.99851

Figure S2. GC internal standard curves of ECH (A), EPDA (B), EPDA-M (C) and diester (D).

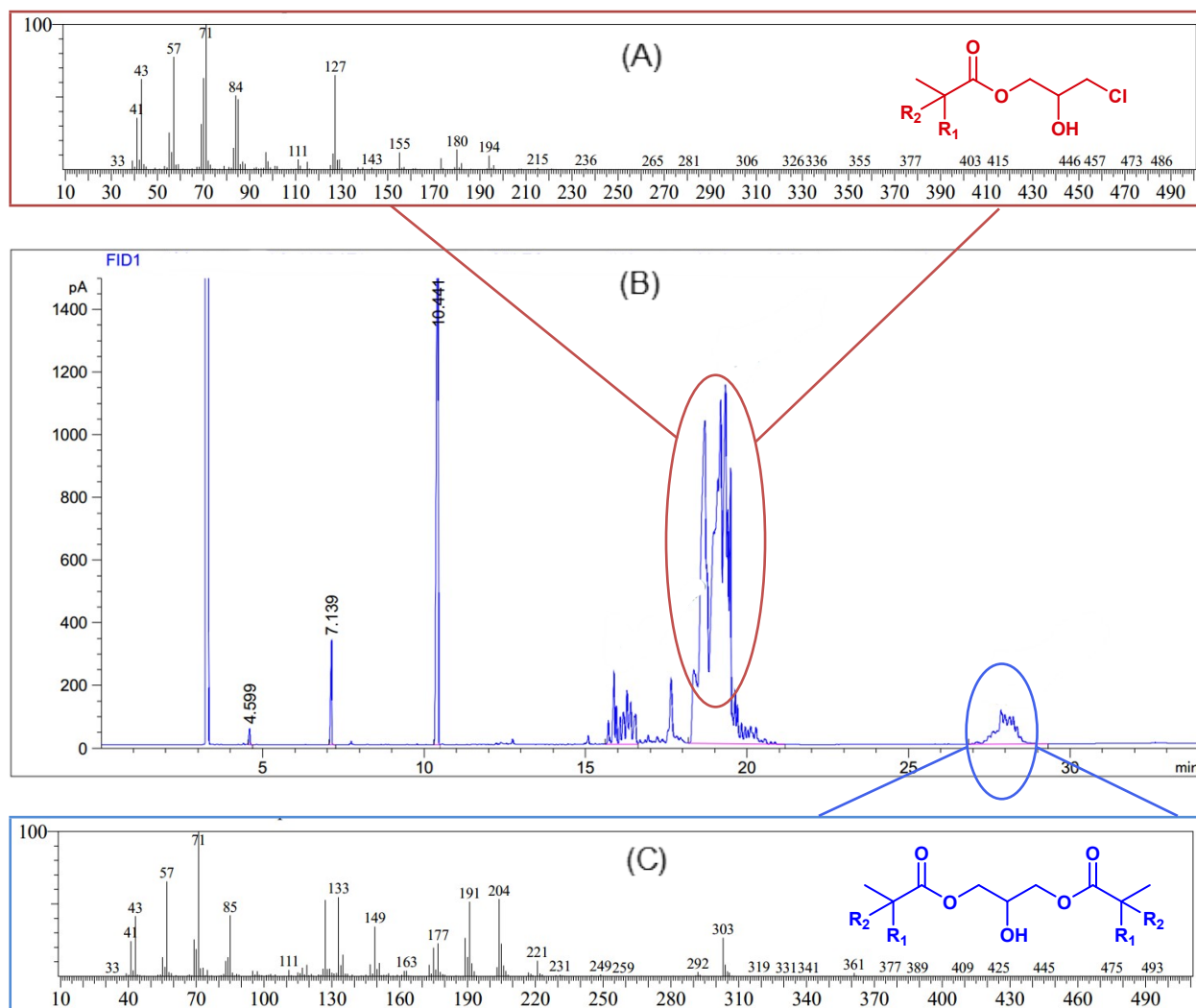3. Characterization of the side product diester

Figure S3. Characterization of the product after the acidolysis reaction of ECH with NDA by GC-MS. Reaction condition: molar ratio of ECH:NDA:TMAN(catalyst)=1.12:1:0.05, 100 °C, 60 min. (A) Mass spectrum of the peaks in the range of 17-20 min. (B) GC characterization. The peak at 3.1 min is CH_2Cl_2, using as dilution solvent for GC. The peak at 4.6 min is ECH, and the peak at 7.1 min denotes dichloropropanol. The peak at 10.4 min denotes methyl benzoate, which is the internal standard substance. The peaks in the range of 15-17 min denote EPDA. The peaks in the range of 17.5-21 min denote EPDA-M, which is the main product of the acidolysis reaction. The signal of the unknown side product is in the range of 27-29 min. (C) Mass spectrum of the peaks in the range of 27-29 min.

As shown in **Figure S3(A)**, the signals of a group of mass loss fragment peaks in the range of 0~100 represent the branched carbon structure of EPDA-M. Comparing to the results of EPDA-M, there are two groups of mass loss fragment peaks (0~100 and 130~230) of such branched carbon structure in the signals of the unknown side product (Figure S3(C)). Therefore, it can be concluded that this side product is formed by the reaction in which two molecules of neodecanoic acid (NDA) participate, and

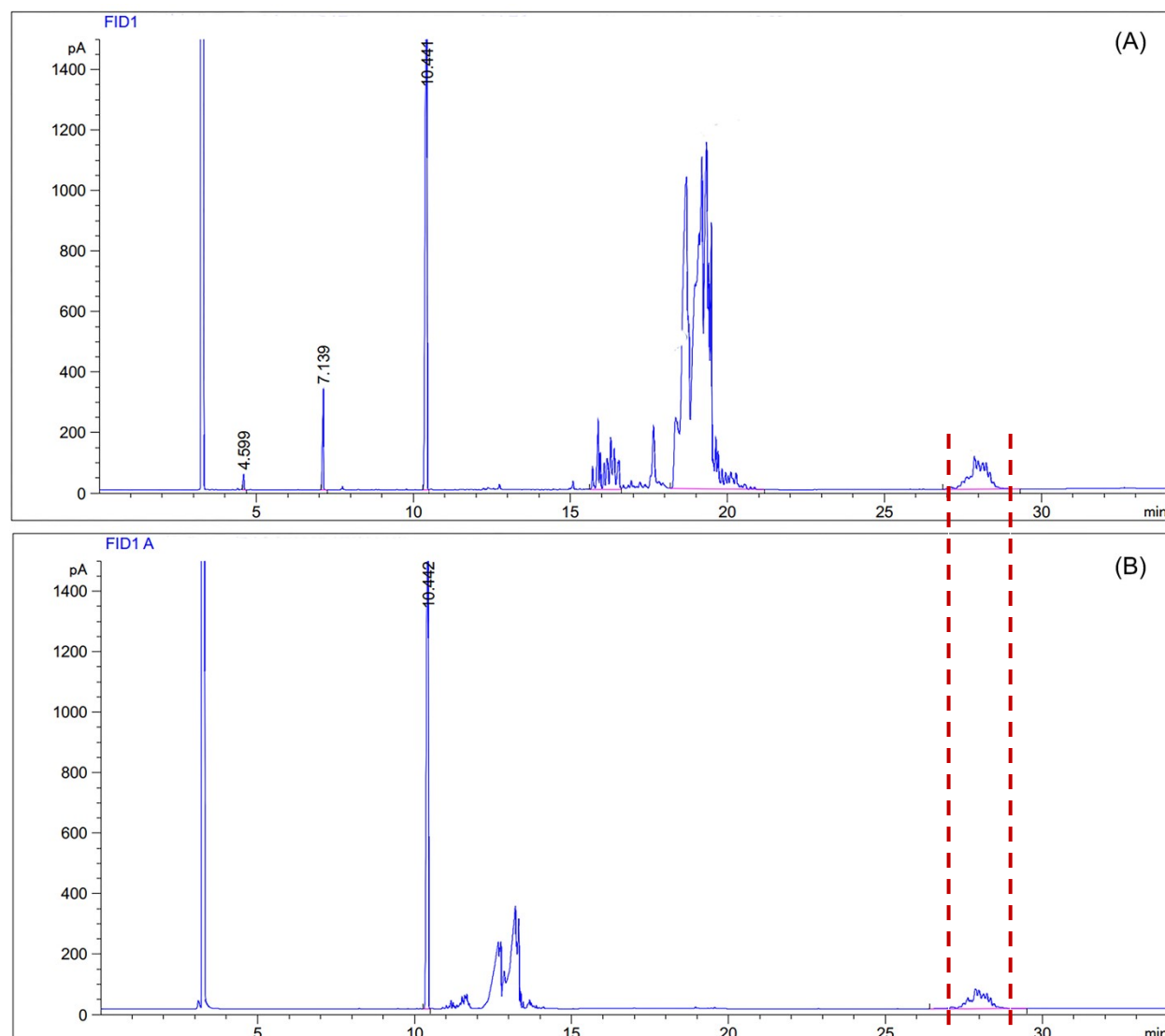most likely, by the further acidolysis reaction of EPDA with NDA.

Figure S4. Comparison of the reaction mixtures after ECH ring-opening reaction and EPDA ring-opening reaction. (A) GC characterization of the reaction mixture after the acidolysis reaction of ECH with NDA. Reaction condition: molar ratio of ECH:NDA:TMAN=1.12:1:0.05, 100 °C, 60 min. (B) GC characterization of the reaction mixture after the acidolysis reaction of EPDA with NDA. Reaction condition: molar ratio of EPDA:NDA:TMAN=0.1:1:0.05, 70 °C, 240 min.

In order to further demonstrate that the product formed in the reaction of EPDA with NDA is exactly the unknown side-product, the reaction mixtures after ECH ring-opening reaction and EPDA ring-opening reaction were characterized by GC respectively, and the results are shown in **Figure S4**. It turns out that, in Figure S4(B), the peak location and peak shape of the product, which is obtained from the reaction of EPDA with NDA, are exactly the same as the unknown side product in Figure S4(A).

Therefore, it can be concluded that the ring-opening product of EPDA is definitely the side product that causes the decline of selectivity in the acidolysis ring-opening reaction of ECH with NDA at high temperature condition.

The reaction equation of EPDA with NDA is shown in **Eq 1**, its product is a kind of diester. Unlike the acidolysis ring-opening reaction of ECH with NDA, there is basically no side product in this reaction because there is no γ-substituted chlorine in EPDA molecular structure. This peculiarity determines that the ring-opening reaction of EPDA with NDA can be used to synthesize high-purity diester for further NMR characterization.
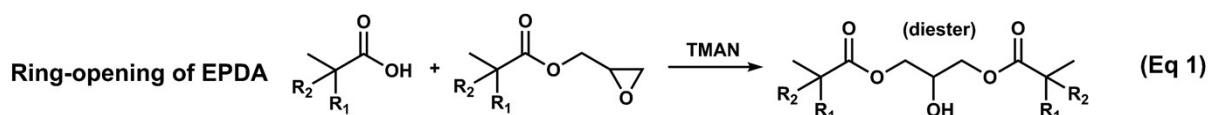
Diester with greater than 95 w% purity is synthesized via the ring-opening reaction of EPDA with NDA, and its GC characterization spectrum is shown in **Figure S5(A)**. After vacuum distillation (95 °C, vacuum degree > 0.09 MPa, 120 min) to remove light impurities like water, ^{1}H NMR characterization was applied to determine the molecular structure of diester (see Figure S5(B)). Combining the features of epoxide ring-opening reaction, it is easy to deduce the structure of diester (also shown in Figure S5). There are three groups of hydrogen signals in the ^{1}H NMR spectrum. The first one is in the range of 0.6-2 ppm, which represents the hydrogens on the branched carbon structure on both sides. The second one is a single peak signal at 2.7 ppm, which represents the hydrogen in hydroxyl group. The third one is in the range of 3-4.5 ppm, which represents the hydrogens in the structure of -O-CH$_2$-CH-CH$_2$-O- in the middle. By integrating each type of hydrogens, the obtained ratio is 1:40:4.7. The theoretical ratio of diester with 100% purity is 1:38:5, this slight difference is caused by the 5% impurities in the system, including EPDA and NDA.
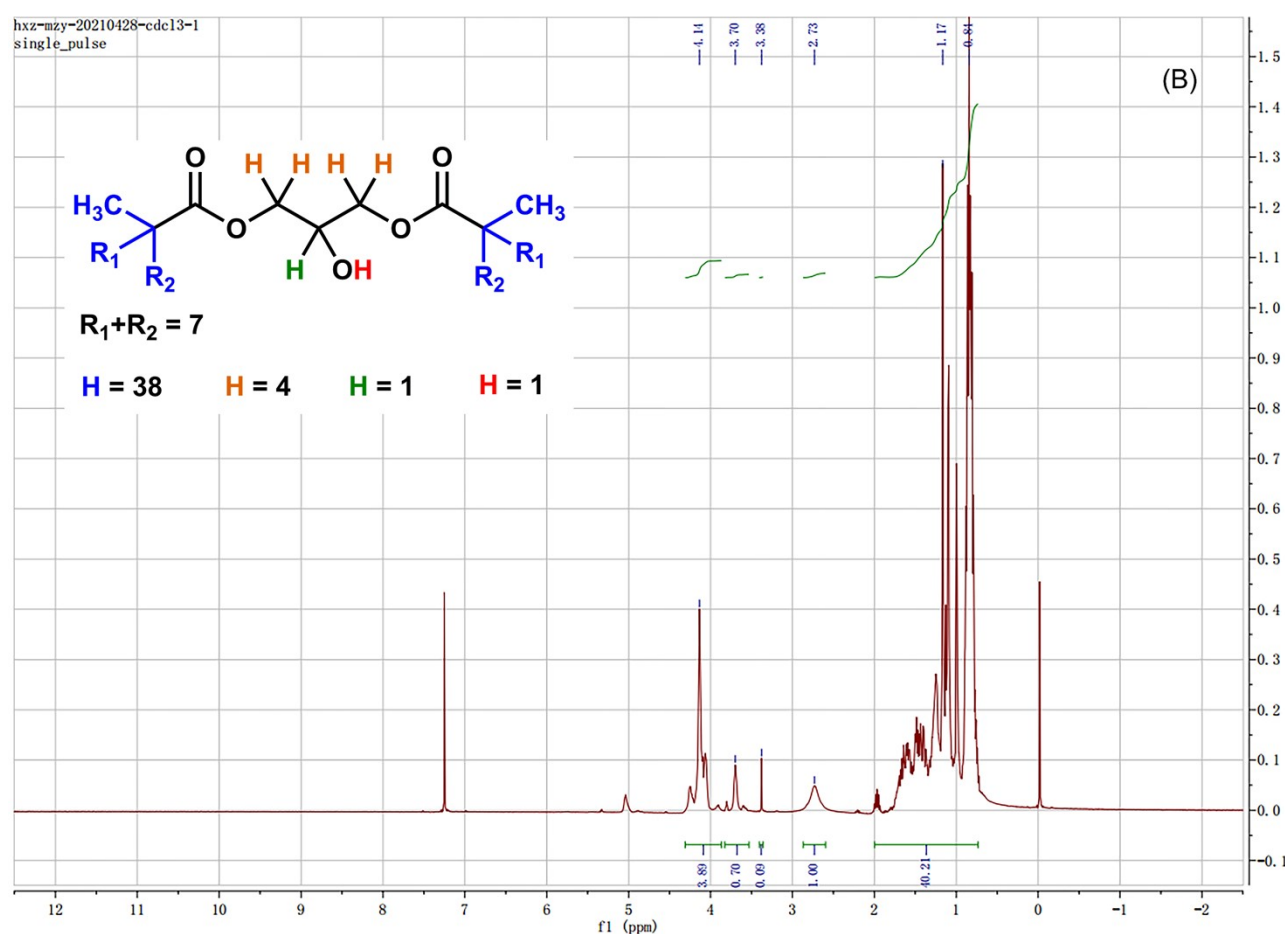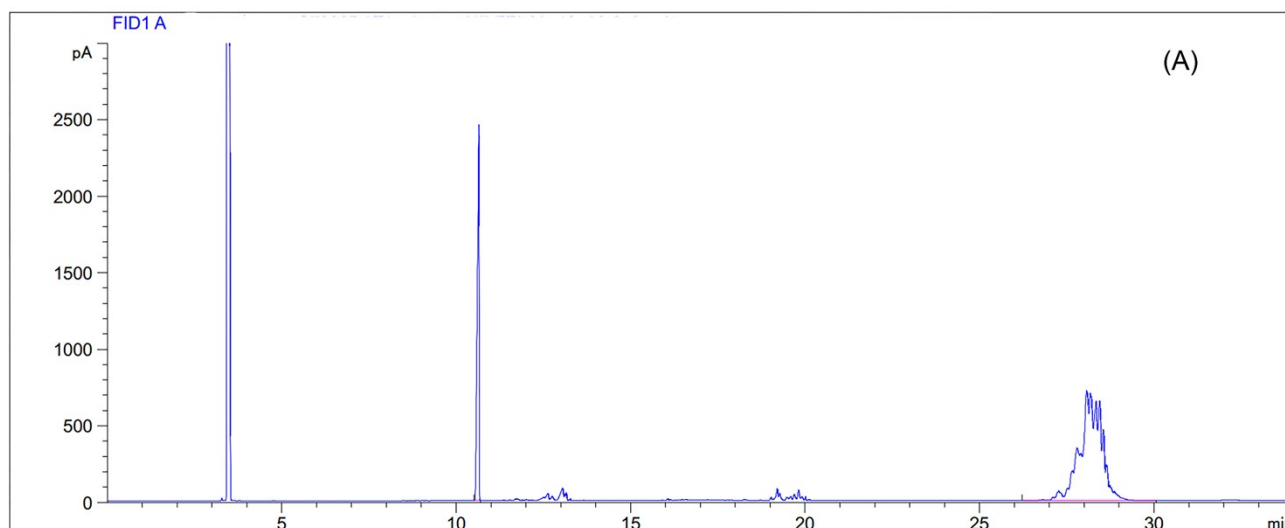
Figure S5. ^{1}H NMR characterization of diester. (A) GC spectrum of the synthesized diester via the ring-opening reaction of ECH with NDA. Reaction condition: molar ratio of EPDA:NDA:TMAN=1:1:0.01, 90 °C, 24 h. The peak at 3.4 min is CH_2Cl_2, using as dilution solvent for GC. The peak at 10.6 min is methyl benzoate, which is the internal standard substance. (B) ^{1}H NMR result of diester. Deuterated chloroform was used as solvent, and the signal at 7.3 ppm denotes it.

4. Comparison with the industrialized process for EPDA production

The high-temperature TMAN-catalytic process developed in this work is compared with the industrialized low-temperature TMAC-catalytic process,[5] and the results are listed in **Table S3**. Both of the two processes are based on two-step method to prepare EPDA. Compared with the industrialized process, the new one developed in this work can significantly reduce the reaction time from 11 hours to 1 hour, and the product purity is higher.

The catalyst properties are also shown in Table S3. As for the detailed information about tetramethylammonium neodecanoate (TMAN) catalyst, with respect to its preparation method, characterization, catalytic activity and repeatability, please refer to our previous study.[6] This study optimized the catalyst for the acidolysis ring-opening reaction of ECH with NDA, and demonstrated that TMAN had better performances than traditional industrial catalyst TMAC with respect to activity and selectivity. Moreover, TMAN is recyclable and easy to be separated from the reaction system, its catalytic activity is basically unchanged in three cycles.

Table S3. Comparisons of the process developed in this work with the industrialized one.

Entry	Preparation condition			Reaction performances		Catalyst properties				
	Preparation method	Temperature (^{o}C)	Reaction time in first step (h)	Purity (w%)	Yield (%)	Catalyst	Catalyst preparation	Activity	Selectivity	Recyclability
Industrialized process	Two-step	70	6	94.4	98.1	TMAC	/	Low	Low	Recyclable
This work	Two-step	100	1	95.6	95.7	TMAN	Easily prepared from TMAC	High	High	Recyclable

Notes and references

1. L. Sun, *Modern Paint and Finishing*, 2017, **20**, 12-17, 52.
2. L. Sun, *China Coatings*, 2019, **34**, 66-74.
3. Z. Yan, J. Deng, Y. Chen and G. Luo, *Ind. Eng. Chem. Res.*, 2020, **59**, 19168-19176.
4. Y. Xiao, C. Huang and Y. Li, *Guangzhou Chemical Industrial*, 2017, **45**, 13-16.
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6. Z. Yan, Y. Hu, C. Du, J. Deng, K. Wang and G. Luo, *J. Catal*., 2020, **385**, 44-51