

Supporting Information

Bio-Based Upcycling of Poly(ethylene terephthalate) Waste to UV-curable Polyurethane Acrylate

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1. Materials

All the chemicals including cardanol, 1,4-dibromobutane, diethanolamine, potassium carbonate, potassium iodide, phenol, tetrabutyl titanate, tetraisopropyl titanate, zinc acetate, dibutyltin oxide, isophorone diisocyanate (IPDI), dibutyltin dilaurate (DBTDL), pentaerythritol triacrylate (PETA), 2-hydroxy-2-methylpropiophenone (UV1173) are commercially available and could be used without further purification if not mentioned. Polyethylene terephthalate (PET) are 5 mm particle size pellets obtained by crushing PET bottle scraps ($M_n=20799$ g/mol, $M_w=44834$ g/mol, measured by GPC with hexafluoroisopropanol as mobile phase).

2. Characterization methods

NMR: ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX-300, ARX-400 and ARX-500 spectrometer at ambient temperature in deuterated chloroform (CDCl_3) or dimethylsulfoxide (DMSO) with tetramethylsilane (TMS) as the internal reference. Chemical shifts were reported in ppm from the internal standard, tetramethylsilane (0 ppm) for ^1H NMR, solvent proton shifts (ppm): CDCl_3 , 7.26 (s); DMSO- d_6 , 2.50 (s).

ESI-MS: Electro spray ionization mass spectroscopy was conducted on a system composed of a Waters Quattro, Premier XE. The system was operated with full scan function type, 3.0kV Capillary, 20V Cone, 110 °C source temperature, 80 L/Hr cone gas flow, 380 °C desolvation temperature and 600 L/Hr desolvation gas flow.

MALDI-ToF-MS: Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy was carried out on a Bruker auto flex III Mass spectrometer. The samples were dissolved in CHCl_3 at a concentration of 10 mg·mL⁻¹. The matrix was trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB).

GPC: The molecular weight and its distribution of the products were determined by gel permeation chromatography at 35 °C against polystyrene standard on Waters 410 GPC instrument with dichloromethane as eluent, where the flow rate was set at 1.0 mL/min.

LC-MS: Liquid chromatography-mass spectrometry was carried out on a Waters Synapt G2 ultra high-performance liquid chromatography quadrupole time-of-flight mass spectrometer. The total run time per sample was 15 min. The injection volume for all samples was 10 μL . The flow rate was set to 0.5 mL/min. The mobile phase was acetonitrile and water, and the elution method was gradient elution. The gradient elution conditions were as follows: the proportion of acetonitrile in the mobile phase changed from 10%

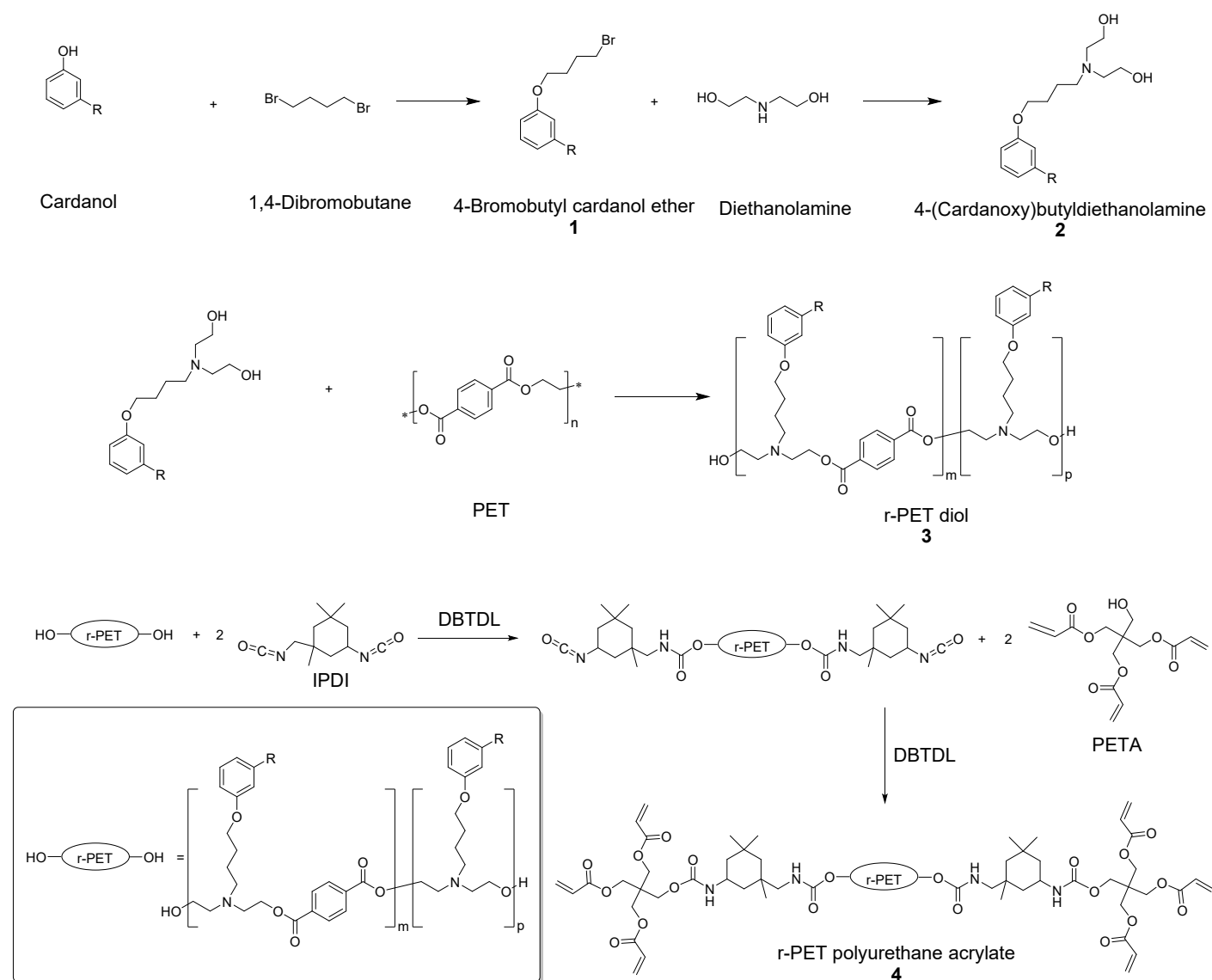
to 90% from 0 to 10 min, and then remained at 90% for 10 to 15 min.

IR: FT-IR spectra of the samples were recorded on a VERTEX-70 IR spectrometer (Bruker) with a scanning range from 4000 to 500 cm^{-1} . ATR spectra of the samples were recorded on a INVENIO-R IR spectrometer (Bruker) with a scanning range from 4000 to 500 cm^{-1} .

Coating properties of the UV-cured coatings including adhesion, pencil hardness, and flexibility were evaluated according to GB/T 9286-1998, GB/T 6739-2006, and GB/T 1731-93, respectively. Adhesion tests of the UV-cured coatings were measured by adhesion cross-cut test following the methods described in GB/T 9286-1998. Adhesion levels include grades 0 to 5, where grade 0 is the best. Pencil hardness tests of the UV-cured coatings were carried out on a QHQ-A pencil hardness tester according to the procedures listed in GB/T 6739-2006. Pencil hardness includes 6H (the hardest) to H, HB, and B to 6B (the softest). Flexibility of the UV-cured coatings were measured using a QTX paint film flexibility tester based on the methods outlined in GB/T 1731-93. The flexibility ranged from grades 1 to 7, with 7 being the best.

3. Experimental Procedures and Discussion

3.1. Synthesis of cardanol-based glycolysis agent



Synthesis of 1: In a 1000 mL flask, cardanol (60.0 g, 0.20 mol), 1,4-dibromobutane (215.6 g, 1.00 mol), K_2CO_3 (27.6 g, 0.20 mol) and KI (1.0 g, 0.03 mol) were mixed with 500 mL acetone and then reacted at 60 °C for 48 h under magnetic stirring and nitrogen protection. The crude product was purified on a silica gel column with petroleum ether/dichloromethane (6: 1, v/v) as eluent and then vacuum distillation with oil pump at 105 °C to remove the residual 1,4-dibromobutane. The yield was 88%.

Synthesis of 2: In a 1000 mL flask, 4-bromobutyl cardanol ether (76.3 g, 0.175 mol), diethanolamine (36.8 g, 0.350 mol), K_2CO_3 (48.43 g, 0.350 mol) and KI (1.0 g, 0.03 mol) were mixed with 500 mL acetonitrile and then reacted at 85 °C for 24 h under magnetic stirring and nitrogen protection. The crude product was purified on a silica gel column with dichloromethane/methanol (10: 1, v/v) as eluent. The yield was 78%.

Synthesis of 3 (r-PET diol): In a 25 mL schlenk flask, 4-(cardanoxy)butyldiethanolamine (2.0 g, 4.35 mmol), PET (0.42 g, 2.18 mmol repeating units) and catalyst (20.0 mg) were added and reacted at 230 °C with magnetic stirring for different time under nitrogen protection.

Synthesis of 4 (r-PET PUA): In a 500 mL three-necked flask, IPDI (2.89 g, 13.0 mmol) and DBTDL(0.02 g, 0.03 mmol) were mixed with 70 mL acetone and then added r-PET diol acetone solution (10.0 g, 6.50 mmol, hydroxyl value = 72.86 mgKOH/g, in 70 mL acetone) with a drop funnel in 3 hours. The reaction was carried out at 60 °C for 6 h under mechanical stirring and nitrogen protection. Then PETA (3.87 g, 13.0 mmol) was dissolved in 60 mL acetone and added into flask with a drop funnel in 3 hours. The reaction was carried out at 60 °C for 12 h with mechanical stirring and nitrogen protection. Acetone was removed by rotary evaporation after reaction.¹ Hydroxyl value were evaluated according to GB/T 12008.3-2009. The hydroxyl group in the sample was esterified in the pyridine solution of phthalic anhydride by reflux, using imidazole as catalyst. The excess phthalic anhydride was hydrolyzed with water, and the generated phthalic acid is titrated with sodium hydroxide standard solution. The hydroxyl value was calculated by the difference between the sample and the blank group.

UV curing of 4 (r-PET PUA): Added 5 wt% UV1173 (2-hydroxy-2-methylhydrophenonone) into r-PET diol, then added 50 wt% acetone and fully mixed. The mixture was coated on the metal substrate with a film applicator and then dried in a 40 °C blast oven for three days to remove acetone. The coating was cured by ultraviolet light and the ultraviolet radiation dose was measured with a UV-integrator.

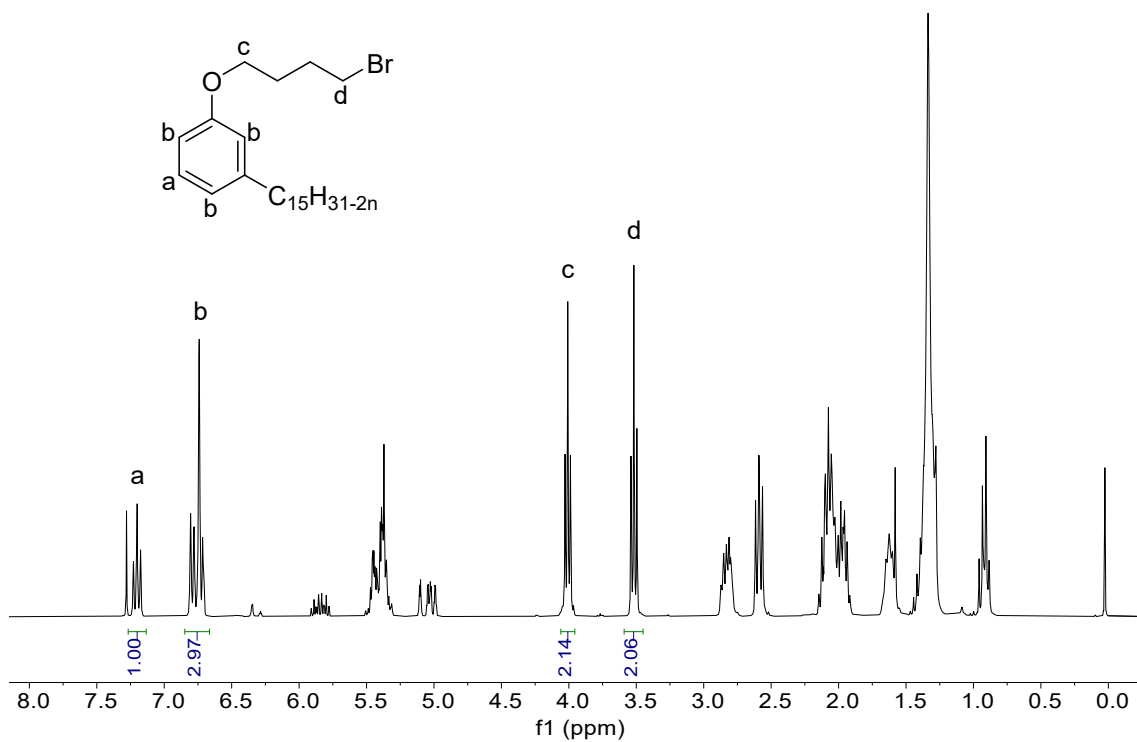


Figure S1. ¹H NMR spectrum of 1 in CDCl₃ at 25 °C (300 MHz).

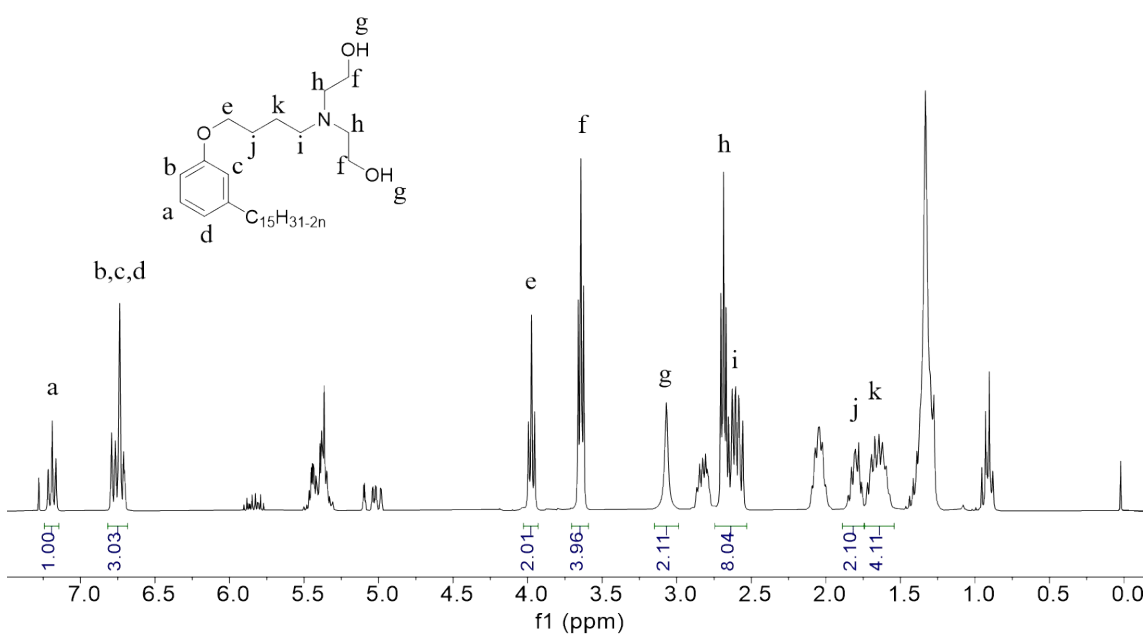


Figure S2. ¹H NMR spectrum of 2 in CDCl₃ at 25 °C (300 MHz).

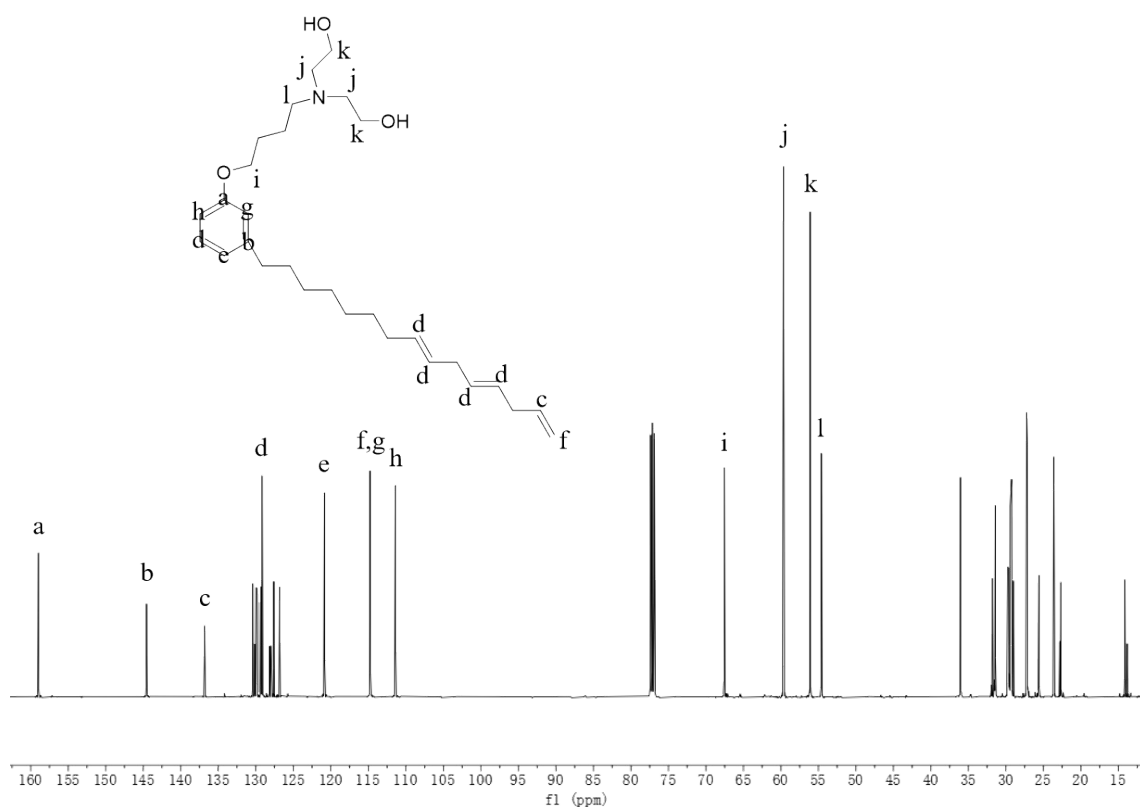


Figure S3. ^{13}C NMR spectrum of 2 in CDCl_3 at $25\text{ }^\circ\text{C}$ (500 MHz).

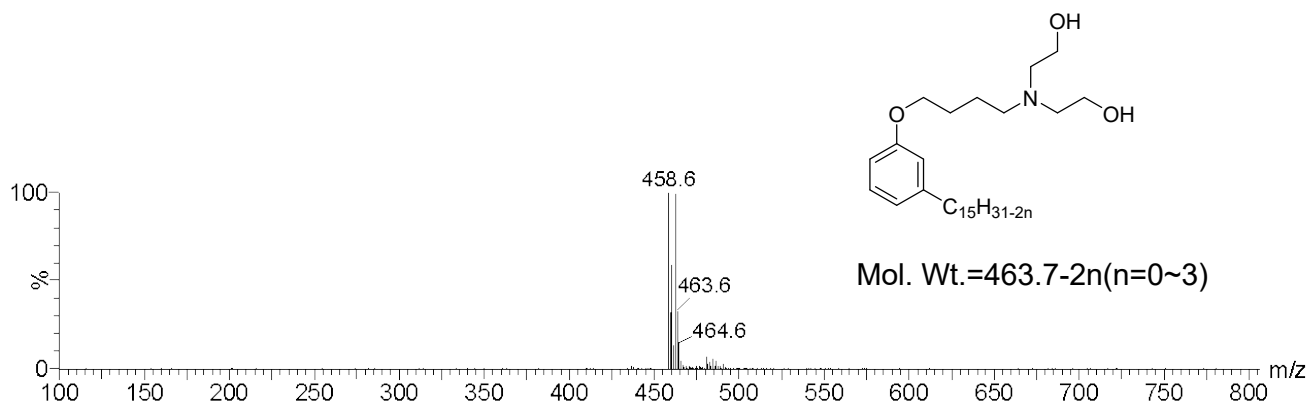


Figure S4. ESI-MS of 2. n equals to the degree of unsaturation on the side chain of 2.

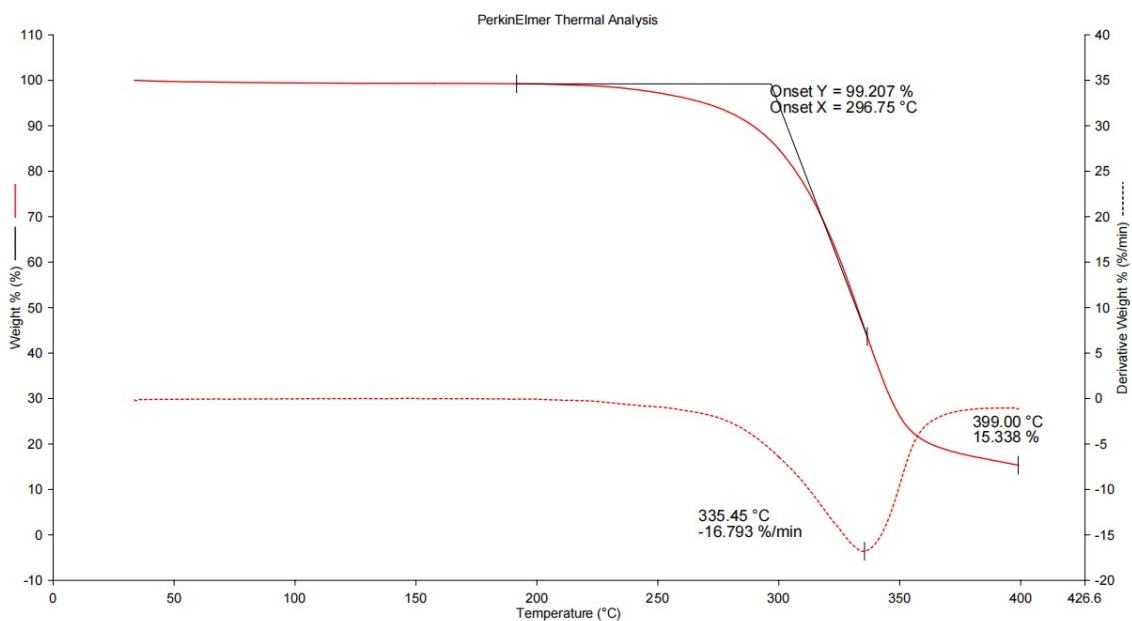


Figure S5. The TGA result of 2. (Atmosphere: N₂, Heating rate: 10 °C/min)

Table S1. Screening of glycolysis temperature^a.

Entry	Temperature/°C	Time/h	Extent of PET glycolysis ^b
1	210	1	Almost no reaction
2	210	2	Almost no reaction
3	220	1	Almost no reaction
4	220	2	The particle size of PET decreases slightly
5	230	1	The particle size of PET decreases obviously
6	230	2	The particle size of PET decreases obviously

^a Glycolysis reaction was carried out in a 25 mL schlenk flask in bulk with $m_{\text{Cardanol diol}} = 2.0$ g (4.35 mmol) and $m_{\text{PET}} = 0.84$ g (4.35 mmol repeating units).

^b The PET pellets used in this work were 5 mm in size. Therefore, the extent of PET glycolysis can be apparently judged by observing the change of particle size after reaction.

Table S2. Screening of glycolysis molar ratio^a.

Entry	Molar ratio (diol: PET)	Extent of PET glycolysis ^b
1	1: 1	The particle size of PET decreases obviously, but there are still PET solid residues
2	1.5: 1	The particle size of PET decreases obviously, but there are still PET solid residues
3	1.8: 1	The particle size of PET decreases obviously, but there are still PET solid residues
4	2: 1	Complete glycolysis of PET pellets

^a Glycolysis reaction was carried out at 230 °C for 2 hours in a 25 mL schlenk flask with $m_{\text{Cardanol diol}} = 2.0$ g (4.35 mmol) and $m_{\text{PET}} = 0.42\text{-}0.84$ g (2.18-4.35 mmol repeating units).

^b The PET pellets used in this work were 5 mm in size. Therefore, the extent of PET glycolysis can be apparently judged by observing the change of particle size after reaction.

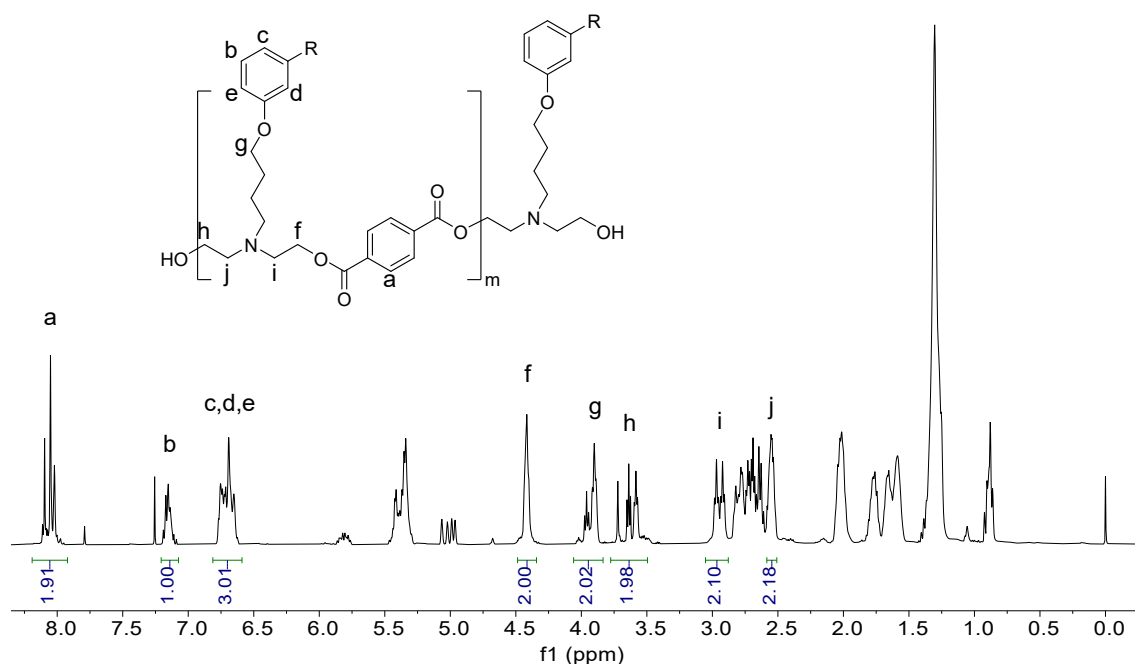


Figure S6. ¹H NMR spectrum of 3 (r-PET diol) in CDCl₃ at 25 °C (500 MHz). Glycolysis reaction was carried out at 230 °C for 2 hours in a 25 mL schlenk flask with $m_{\text{Cardanol diol}} = 2.0$ g (4.35 mmol) and $m_{\text{PET}} = 0.42$ g (2.18 mmol repeating units). The emerging proton peaks at 4.45 ppm are assigned to methylene units linked to ester group, indicating the full conversion of the PTA linkages in the parent PET polymer. And the peak at 4.7 ppm is assigned to the remaining glycol units.

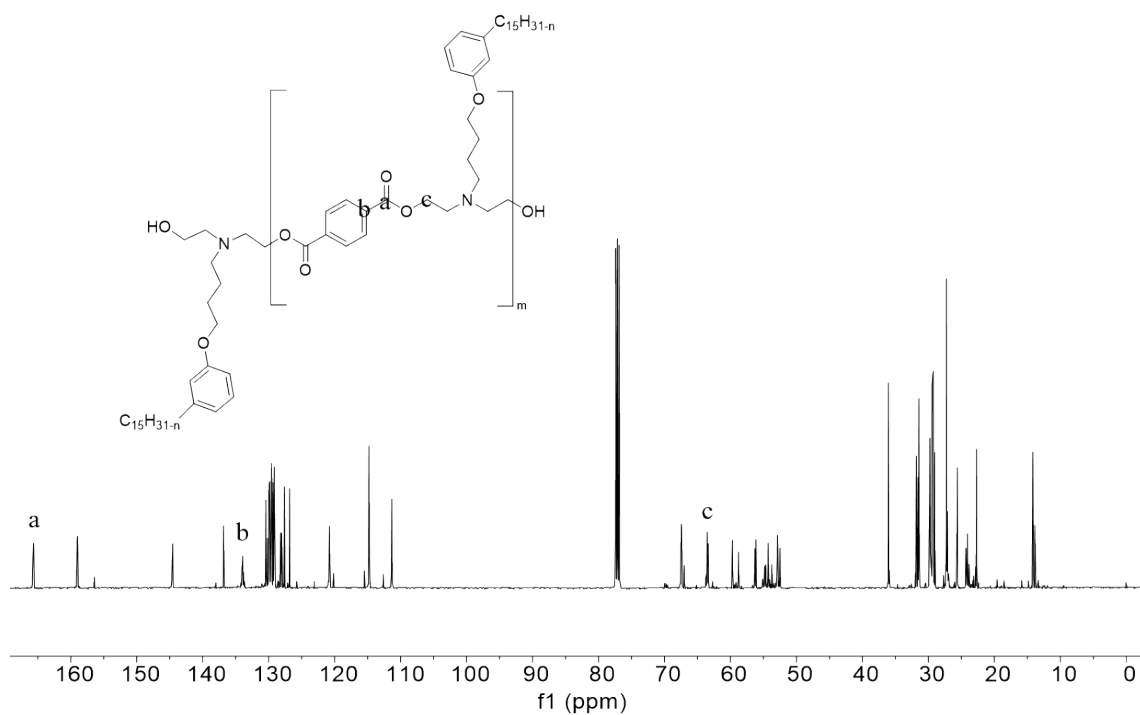


Figure S7. ^{13}C NMR spectrum of 3 (r-PET diol) in CDCl_3 at 25°C (500 MHz). Glycolysis reaction was carried out at 230°C for 2 hours in a 25 mL schlenk flask with $m_{\text{Cardanol diol}} = 2.0$ g (4.35 mmol) and $m_{\text{PET}} = 0.42$ g (2.18 mmol repeating units).

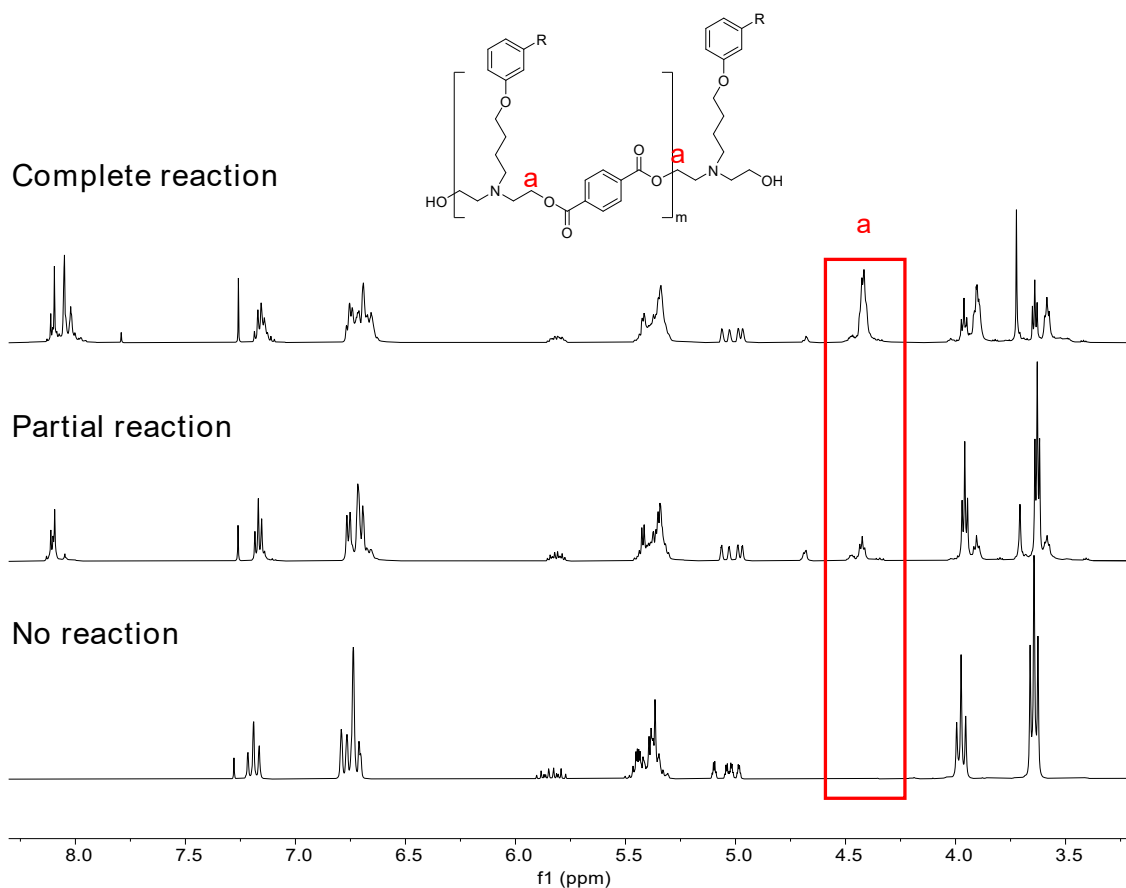


Figure S8. Comparison diagram of ^1H NMR spectrum when PET did not react, partially reacted and fully reacted (CDCl_3 at $25\text{ }^\circ\text{C}$, 500 MHz). The gradual increase of methylene peak linked to ester group at 4.45 ppm indicated the occurrence of glycolysis reaction. Glycolysis reaction was carried out in a 25 mL schlenk flask at $230\text{ }^\circ\text{C}$ for 0 min , 20 min , and 120 min with $m_{\text{Cardanol diol}} = 2.0\text{ g}$ (4.35 mmol) and $m_{\text{PET}} = 0.42\text{ g}$ ($2.18\text{ mmol repeating units}$).

3.2. Study of the glycolytic reaction of PET

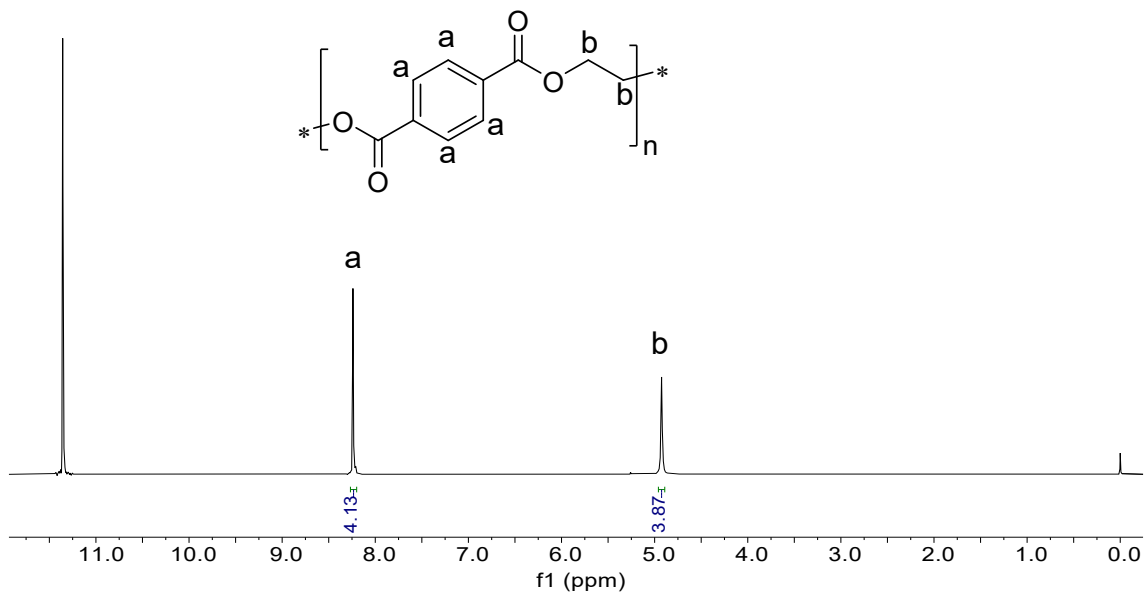


Figure S9. ¹H NMR spectrum of PET in CF₃COOD at 25 °C (300 MHz).

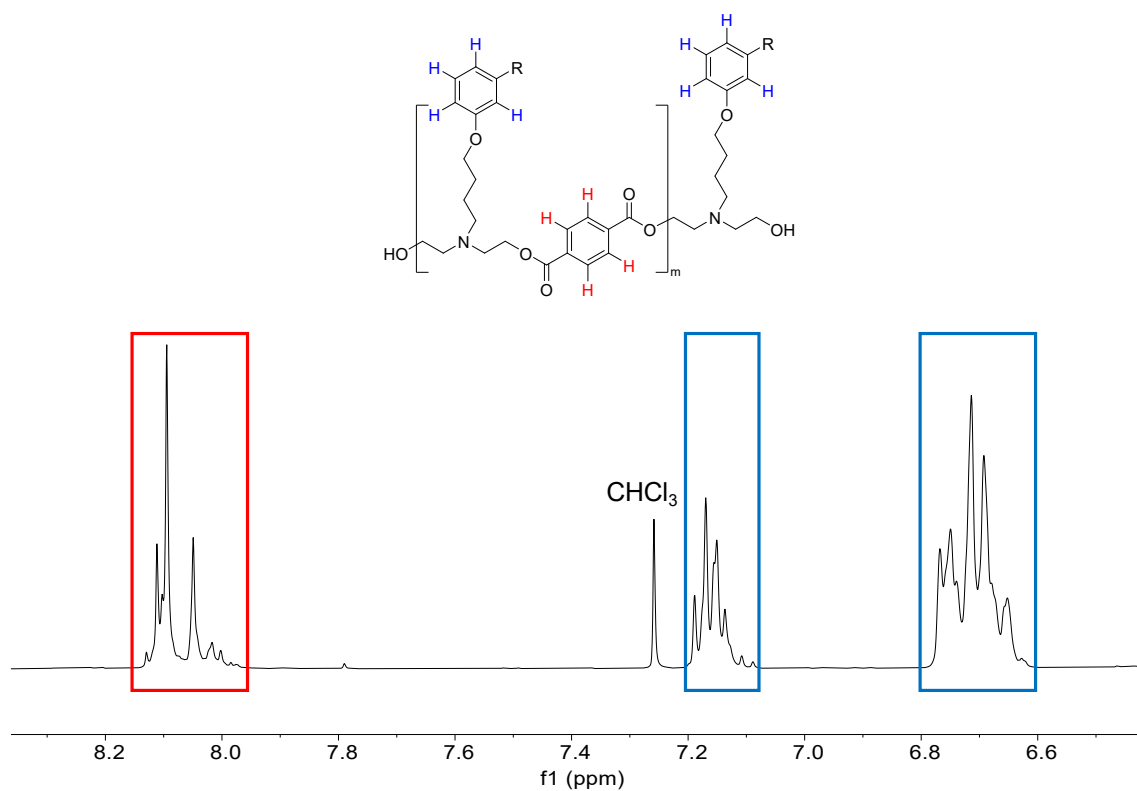


Figure S10. Calculation method of PET conversion rate. (230 °C, molar ratio of cardanol diol: PET repeating units of 2: 1) PET conversion rate is calculated by the ratio of the integral areas of the aromatic regions in the ¹H NMR according to the following formula:

$$\begin{aligned}
 \text{PET conversion rate} &= \frac{n_{\text{reacted PET}}}{n_{\text{PET}}} \\
 &= \frac{n_{\text{reacted PET}}}{n_{\text{cardanol diol}} \times \frac{1}{2}} \\
 &= \frac{\delta(7.92\sim 8.15)}{[\delta(7.07\sim 7.21) + \delta(6.60\sim 6.81)] \times \frac{1}{2}} \times 100\%
 \end{aligned}$$

Table S3. Conversion^a of PET glycolysis^b over time with different catalyst.

Entry	Time/ min	Conversion of PET				
		Blank ^c	Tetrabutyl titanate	Dibutyltin oxide	Tetraiso-propyl titanate	Zinc acetate
1	5	/	0.40	0.27	0.03	0.25
2	10	0.14	0.88	0.80	0.36	0.47
3	15	/	0.99	0.95	0.60	0.56
4	20	0.46	1.00	0.96	0.76	0.62
5	25	/	1.00	0.98	0.84	0.66
6	30	0.71	0.99	0.96	0.89	0.71
7	35	/	0.99	0.97	0.93	0.74
8	40	0.88	0.99	0.97	0.96	0.77
9	50	0.93	0.99	0.96	0.98	0.79
10	60	0.98	0.99	0.95	1.00	0.81
11	70	1.00	0.99	0.95	1.00	0.83
12	80	1.00	0.99	0.92	0.99	0.84

^a Conversion of PET was calculated by the ratio of the integral areas of the aromatic regions in the ¹H NMR of PTA units and cardanol units in glycolysis products (Fig. S10).

^b Glycolysis reaction was carried out at 230 °C in a 25 mL schlenk flask with $m_{\text{Cardanol diol}} = 2.0$ g (4.35 mmol), $m_{\text{PET}} = 0.42$ g (2.18 mmol repeating units) and $m_{\text{Cat}} = 20.0$ mg.

^c Glycolysis products were sampled every 10 minutes for blank group, while every 5 minutes for catalyst groups (within 40 min).

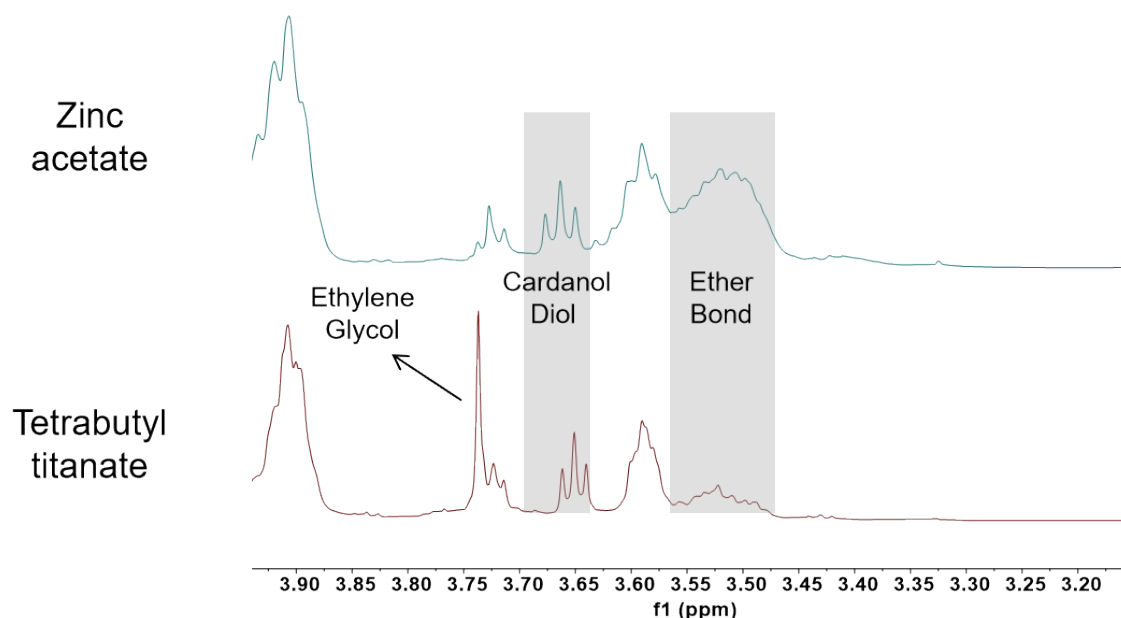


Figure S11. ¹H NMR spectrum of glycolysis products catalyzed by zinc acetate and tetrabutyl titanate, respectively. The result showed that product catalyzed by zinc acetate contained more ether bond (molar ratio) than that of tetrabutyl titanate group (11% vs 25%). Notably, the molar ratio of ether bond is calculated based on the molar amount of r-PET diol. The experiments were carried out at 230 °C for 80 minutes with molar ratio of Cardanol diol: PET repeating units of 2: 1 and 1 wt% catalyst.

Table S4. Ether bond content in r-PET diol under different catalyst conditions^a.

Entry	catalyst	Ether bond content ^b
1	blank	0.10 ^c
2	tetraisopropyl titanate	0.07
3	dibutyltin oxide	0.10
4	tetrabutyl titanate	0.11
5	zinc acetate	0.25

^a Reaction was carried out at 230 °C for 40min in a 25 mL schlenk flask with $m_{\text{Cardanol diol}} = 2.0$ g (4.35 mmol), $m_{\text{PET}} = 0.42$ g (2.18 mmol repeating units) and $m_{\text{Cat}} = 20.0$ mg.

^b Ether bond content is calculated from the integral area of the peak with chemical shift of 3.5 ppm in ¹H NMR.

^c 0.10 indicates that the molar amount of ether bond is 10% relative to the molar amount of r-PET diol.

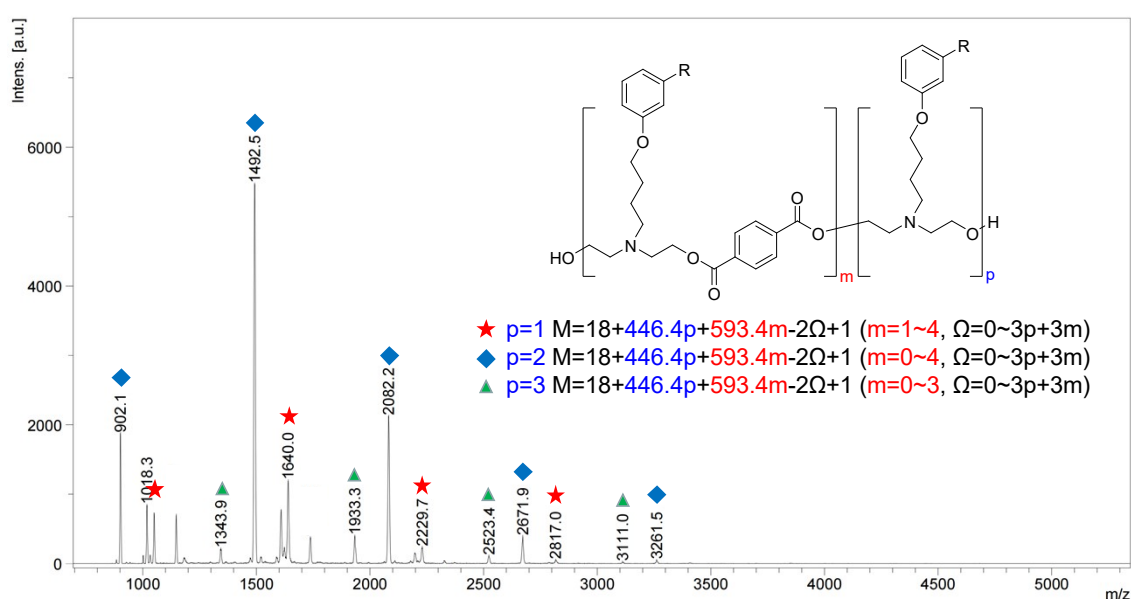


Figure S12. MALDI-ToF-MS result of r-PET diol. The results showed that glycolysis products were a series of oligomers with two different repeating units (polyester and polyether repeating units) in the glycolysis products. The experiments were carried out at 230 °C for 20 minutes with molar ratio of Cardanol diol: PET repeating units of 2: 1 and 1 wt% catalyst.

3.3. Study on glycolysis reaction through model compounds

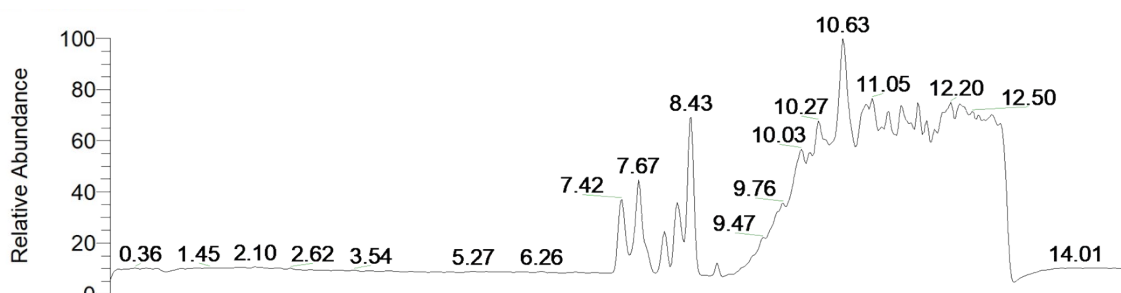
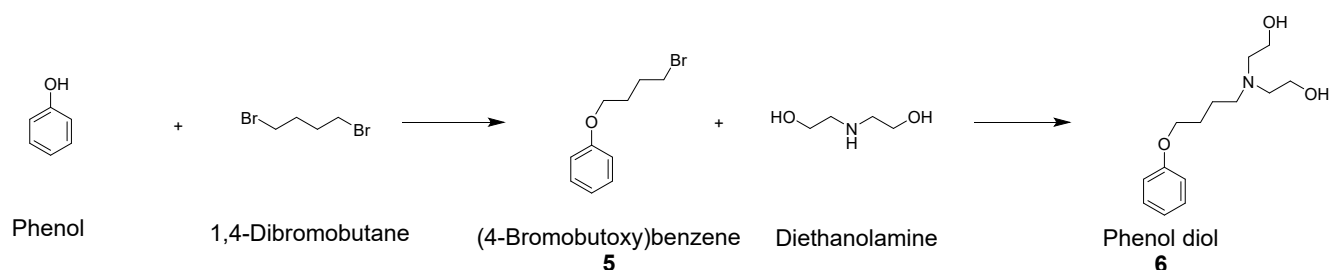


Figure S13. LC-MS result of glycolysis products (230 °C, 2 molar ratio of Cardanol diol: PET repeat units of 2: 1, 1 wt% tetrabutyl titanate, reaction time of 20 minutes). Because of the different unsaturation of cardanol side chains, the separation of glycolysis products by LC failed.²



Synthesis of 5: In a 1000 mL flask, phenol (20.0 g, 0.21 mol), 1,4-dibromobutane (229.4 g, 1.06 mol), K_2CO_3 (29.37 g, 0.21 mol) and KI (1.0 g, 0.03 mol) were mixed with 500 mL acetone and then reacted at 60 °C for 48 h under magnetic stirring and nitrogen protection. The crude product was purified on a silica gel column with petroleum ether as eluent and then vacuum distilled with oil pump at 105 °C to remove the residual 1,4-dibromobutane. The yield was 42%.

Synthesis of 6 (phenol diol): In a 1000 mL flask, (4-bromobutoxy)benzene (20.0 g, 0.873 mol), diethanolamine (18.4 g, 0.175 mol), K_2CO_3 (24.1 g, 0.175 mol) and KI (1.0 g, 0.03 mol) were mixed with 500 mL acetonitrile and then reacted at 85 °C for 24 h under magnetic stirring and nitrogen protection. The crude product was purified on a silica gel column with first dichloromethane and then dichloromethane/methanol (8: 1, v/v) as eluent. The yield was 70%.

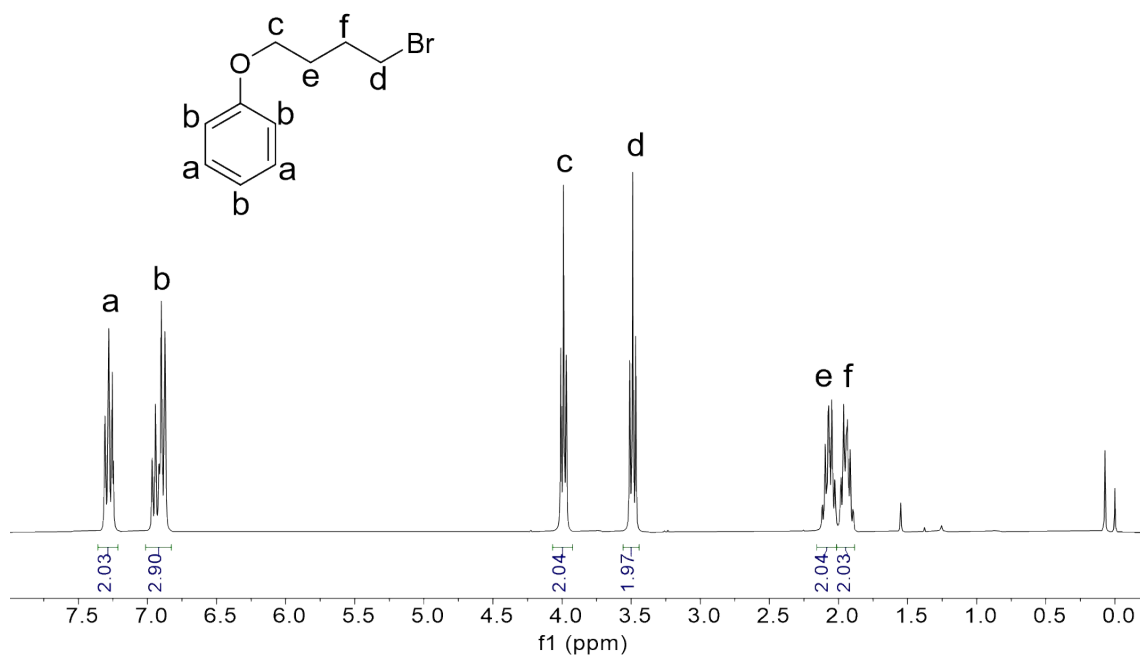


Figure S14. ¹H NMR spectrum of 5 in CDCl₃ at 25 °C (400 MHz).

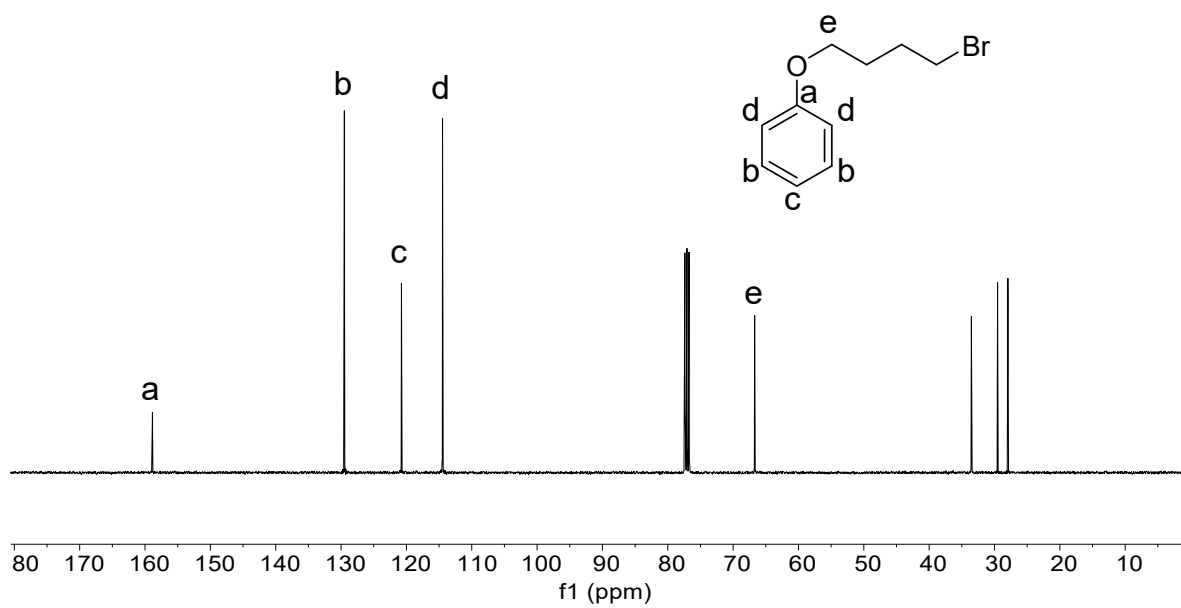


Figure S15. ¹³C NMR spectrum of 5 in CDCl₃ at 25 °C (400 MHz).

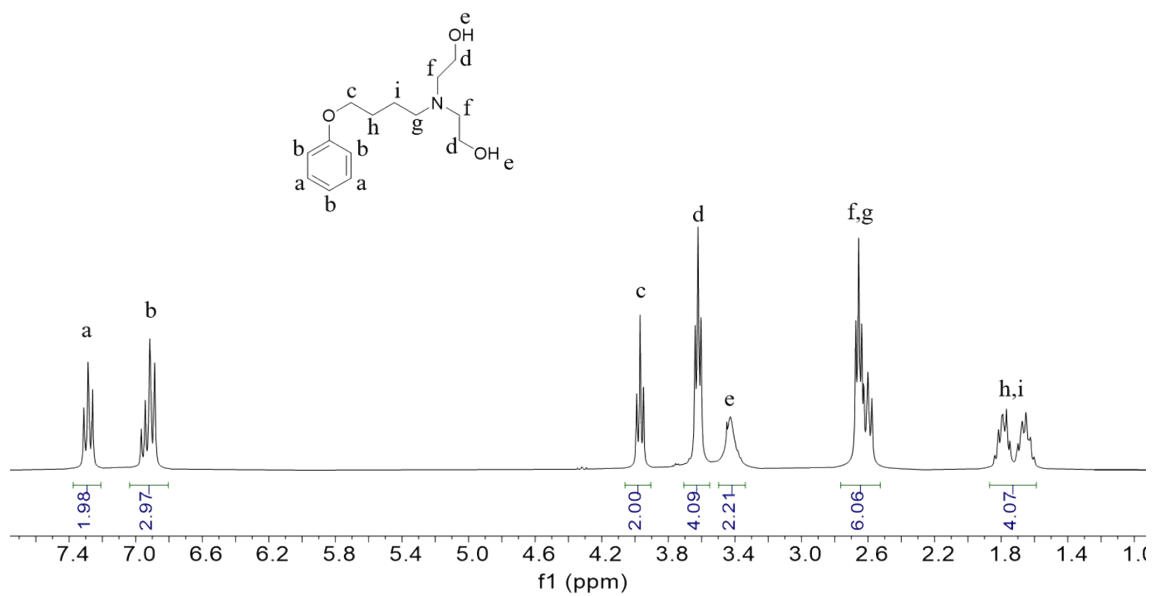


Figure S16. ¹H NMR spectrum of 6 (phenol diol) in CDCl₃ at 25 °C (400 MHz).

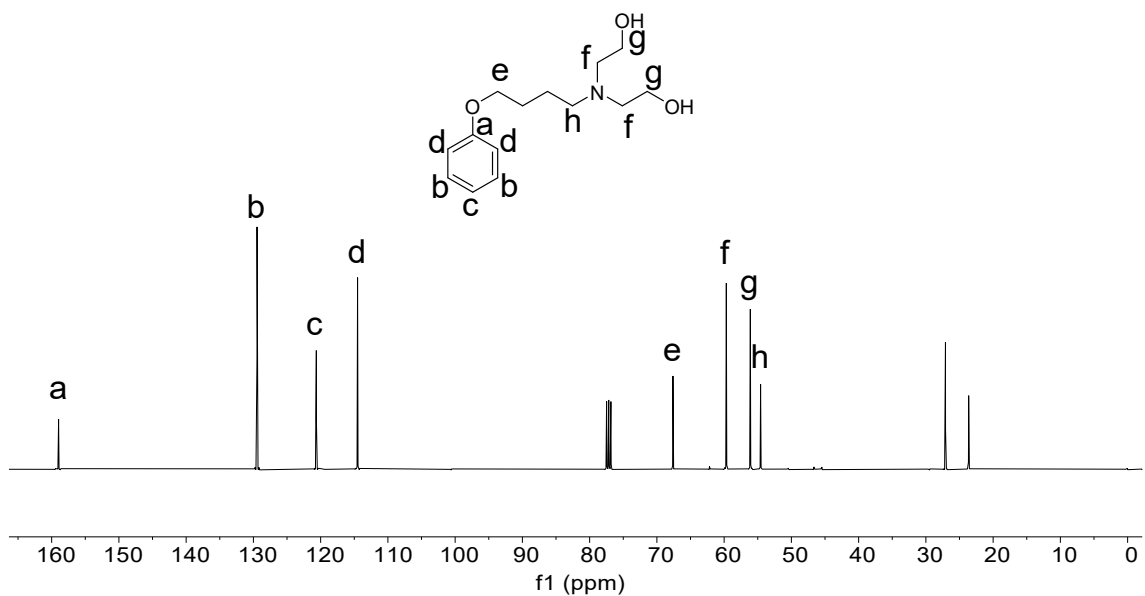


Figure S17. ¹³C NMR spectrum of 6 (phenol diol) in CDCl₃ at 25 °C (400 MHz).

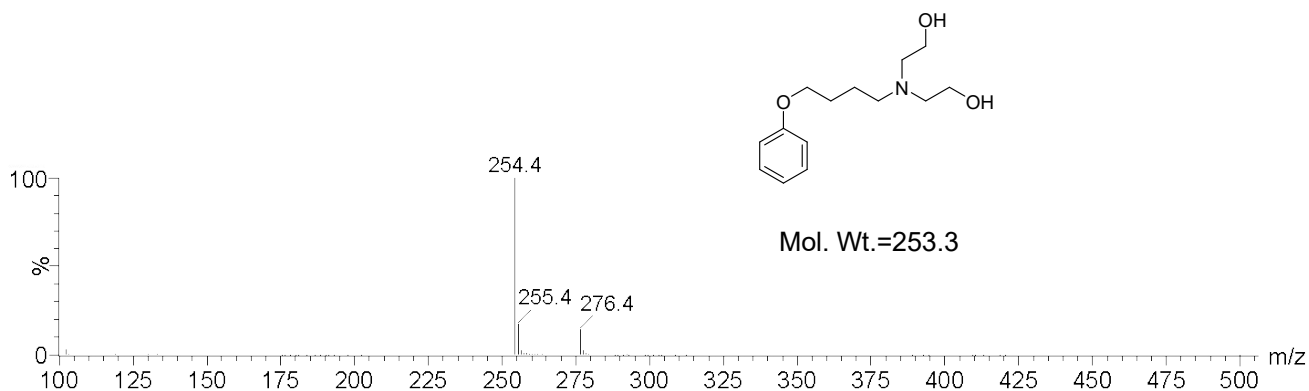


Figure S18. ESI-MS of 6 (phenol diol).

T: FTMS + p ESI Full ms [200.0000-3000.0000]

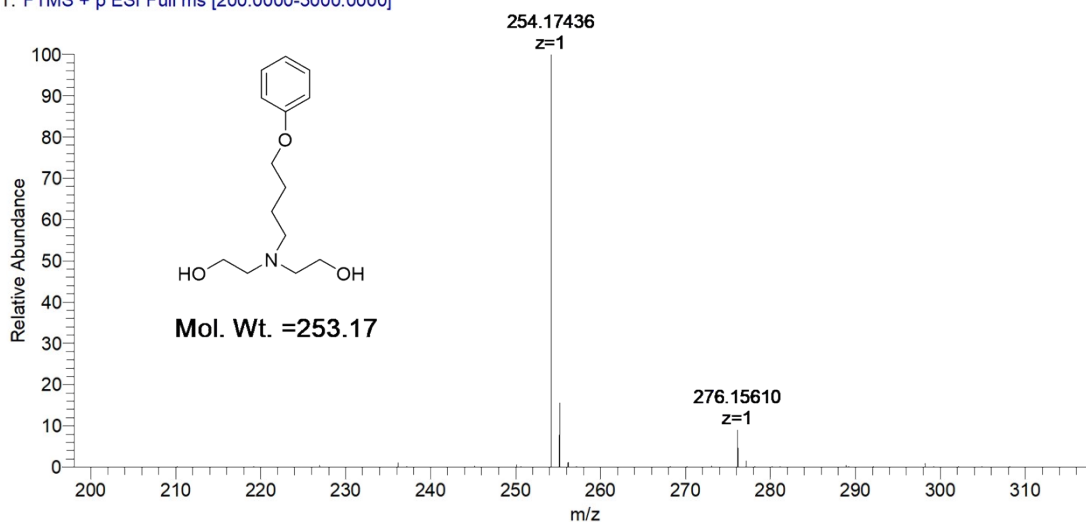


Figure S19. Mass spectrometry signals of phenol diol glycolysis products G_0 in LC-MS results.

T: FTMS + p ESI Full ms [200.0000-3000.0000]

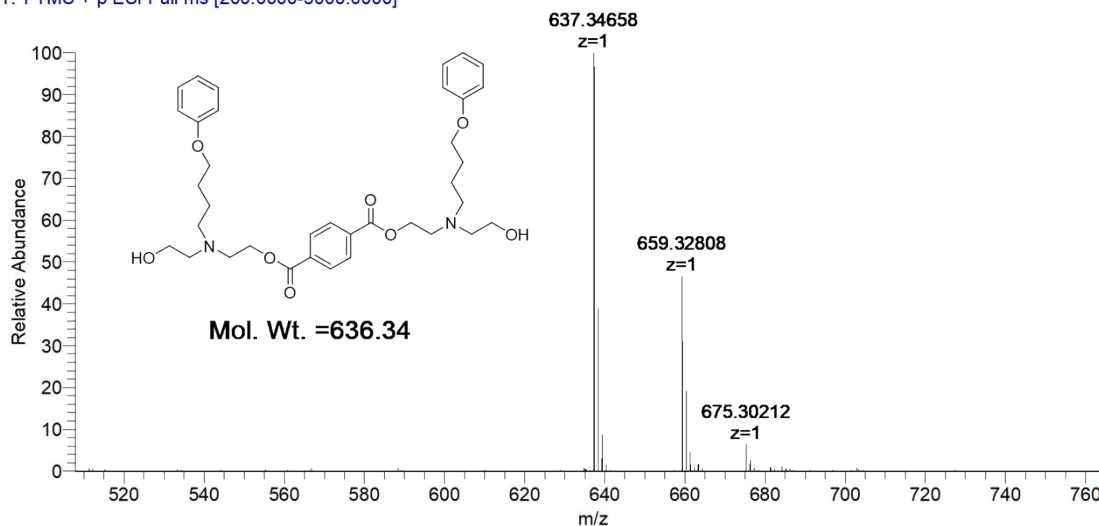


Figure S20. Mass spectrometry signals of transesterification products Tr_1 in LC-MS results.

T: FTMS + p ESI Full ms [200.0000-3000.0000]

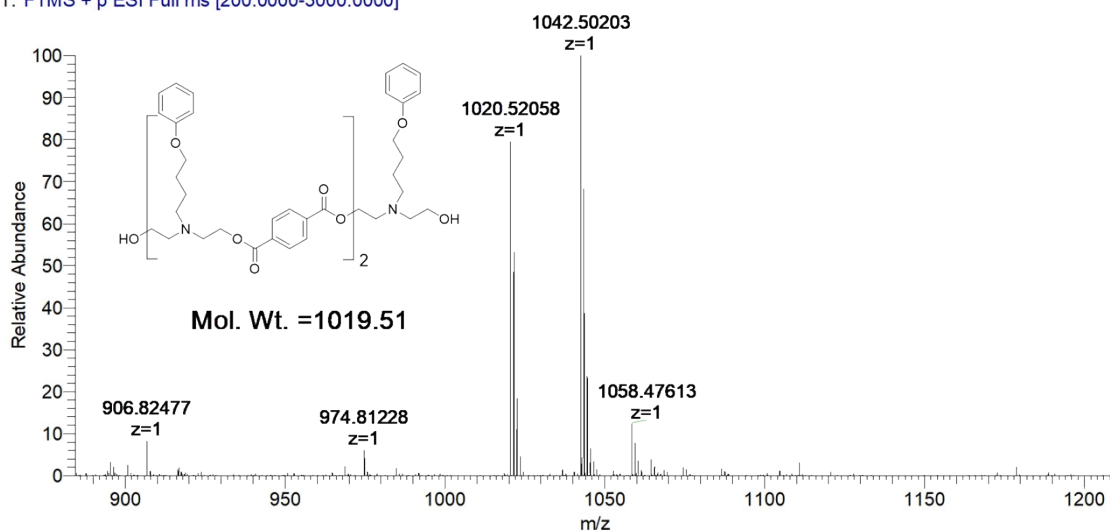


Figure S21. Mass spectrometry signals of transesterification products Tr₂ in LC-MS results.

T: FTMS + p ESI Full ms [200.0000-3000.0000]

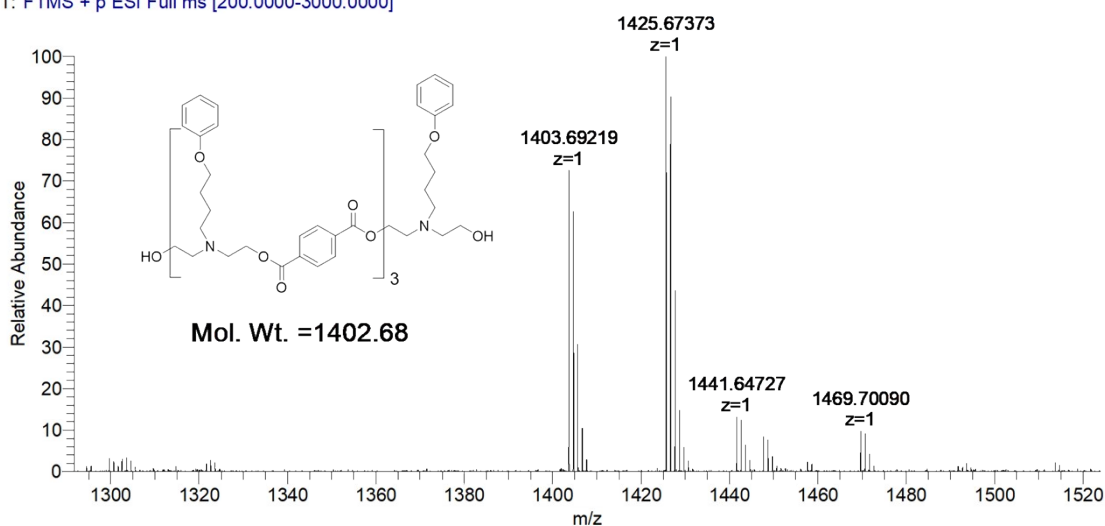


Figure S22. Mass spectrometry signals of transesterification products Tr₃ in LC-MS results.

I: FTMS + p ESI Full ms [200.0000-3000.0000]

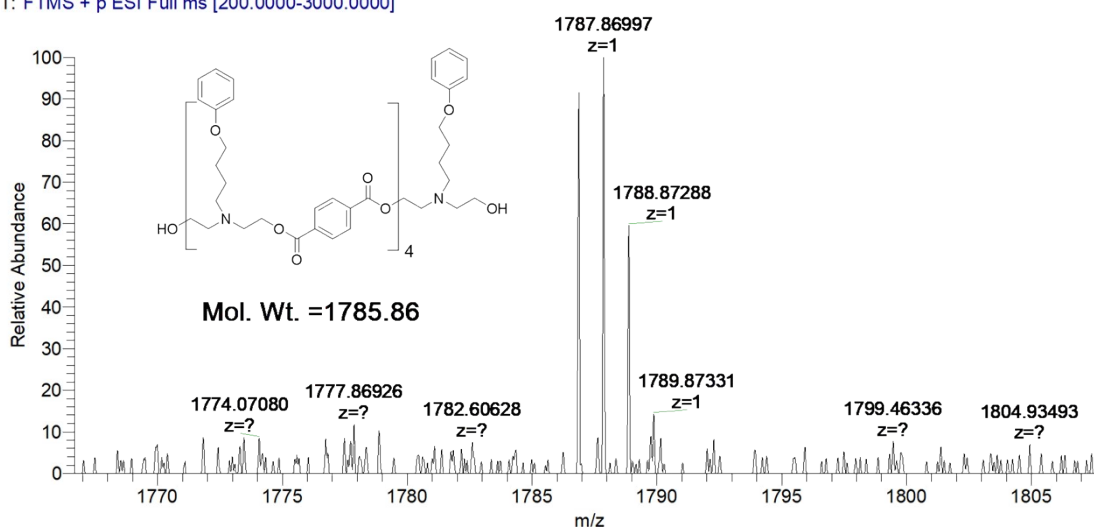


Figure S23. Mass spectrometry signals of transesterification products Tr₄ in LC-MS results.

T: FTMS + p ESI Full ms [200.0000-3000.0000]

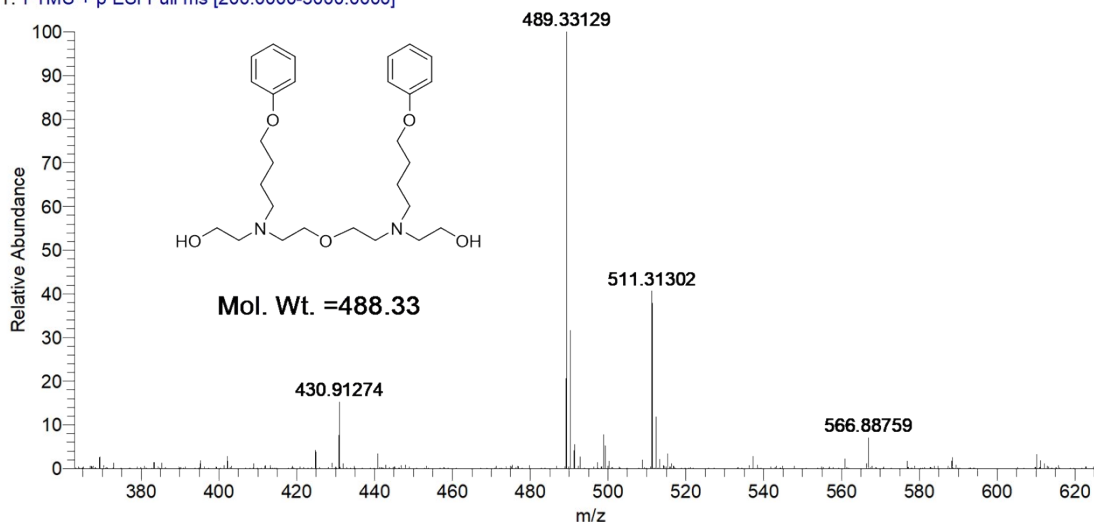


Figure S24. Mass spectrometry signals of etherification products E_{0,2} in LC-MS results.

T: FTMS + p ESI Full ms [200.0000-3000.0000]

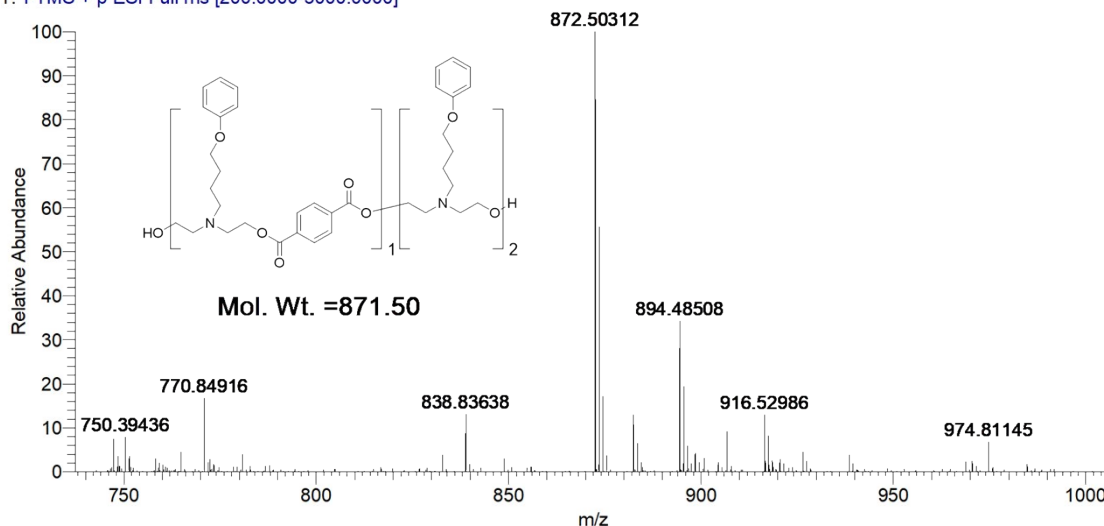


Figure S25. Mass spectrometry signals of etherification products E_{1,2} in LC-MS results.

T: FTMS + p ESI Full ms [200.0000-3000.0000]

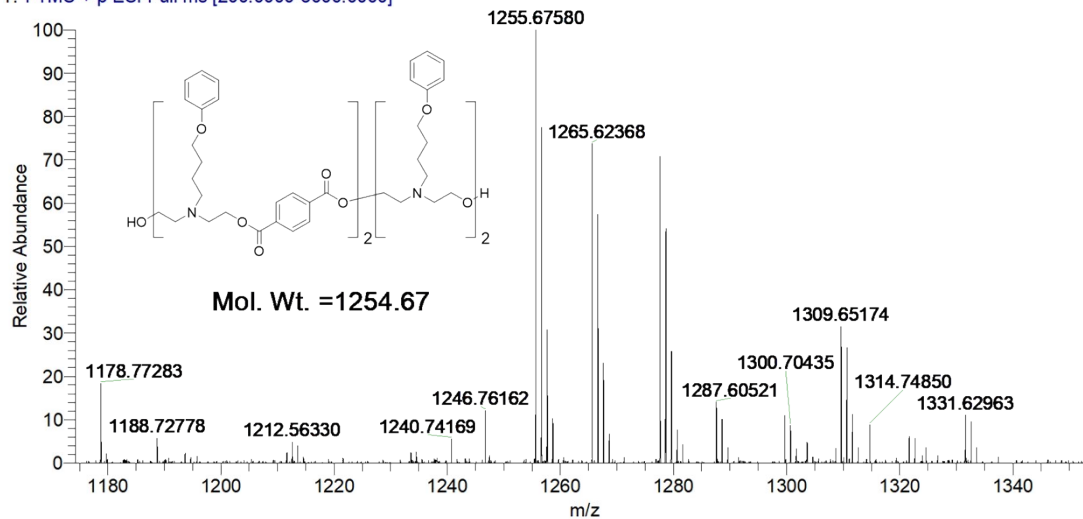


Figure S26. Mass spectrometry signals of etherification products E_{2,2} in LC-MS results.

T: FTMS + p ESI Full ms [200.0000-3000.0000]

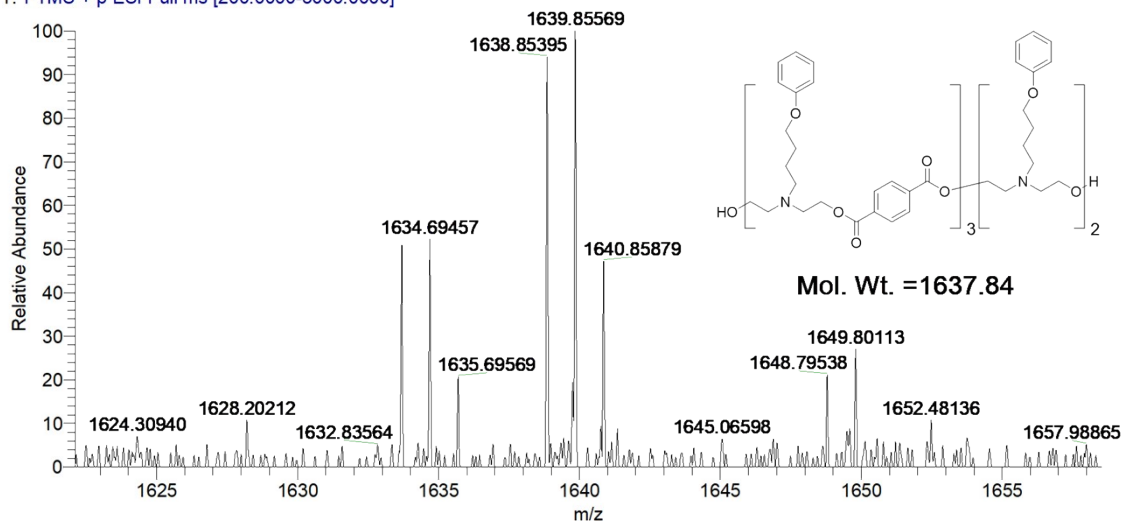


Figure S27. Mass spectrometry signals of etherification products E_{3,2} in LC-MS results.

Table S5. Transesterification and etherification products detected in the mass spectrometry results of LC-MS

Time ^a /min	Transesterification products					etherification products				
	Tr ₁	Tr ₂	Tr ₃	Tr ₄	Tr ₅	E _{0,2}	E _{1,2}	E _{2,2}	E _{3,2}	E _{4,2}
5	O ^b	O	X ^b	X	X	O	O	X	X	X
10	O	O	O	O	X	O	O	O	X	X
15	O	O	O	O	X	O	O	O	O	X
20	O	O	O	O	X	O	O	O	O	X

^a Reaction was carried out at 230 °C in a 25 mL schlenk flask with $m_{\text{Phenol Diol}} = 2.0$ g (7.89 mmol), $m_{\text{PET}} = 0.76$ g (3.95 mmol repeating units) and $m_{\text{Cat}} = 20.0$ mg.

^b “O” means product signal can be detected in LC-MS results. “X” means product signal can’t be detected in LC-MS results.

3.4. Synthesis and characterization of polyurethane acrylate

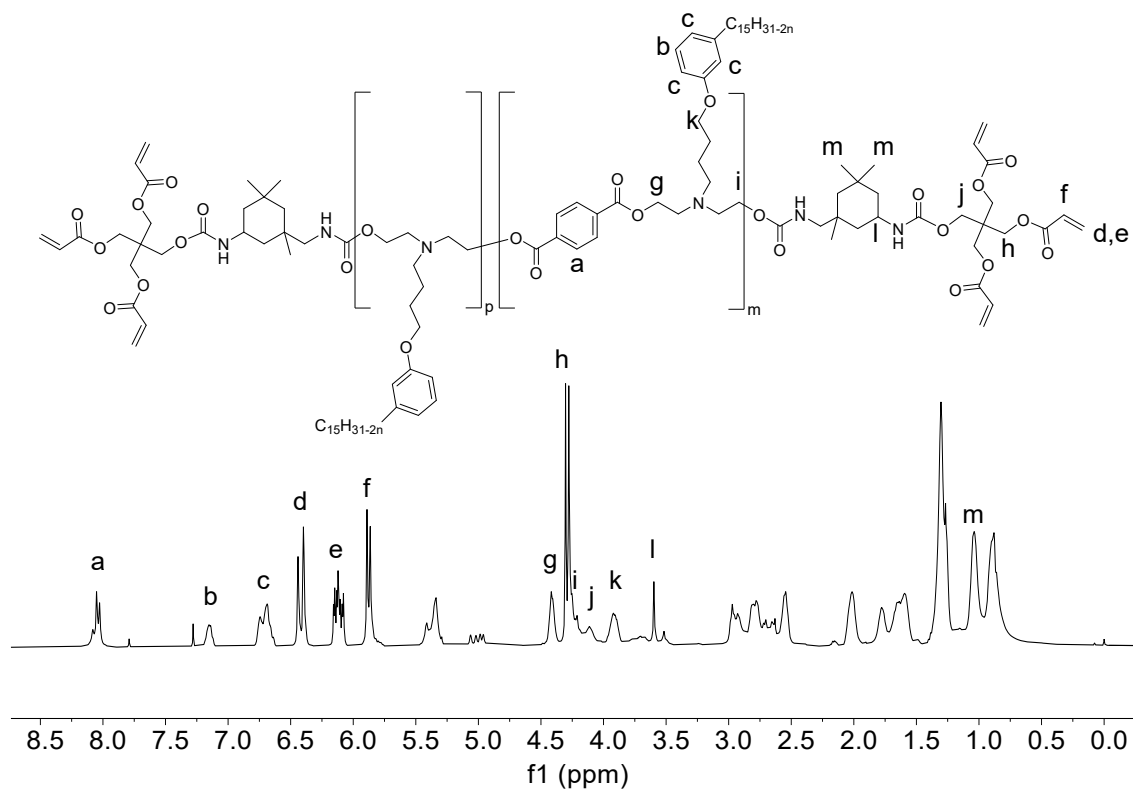


Figure S28. ¹H NMR spectrum of 4 (r-PET PUA) in CDCl₃ at 25 °C (500 MHz).

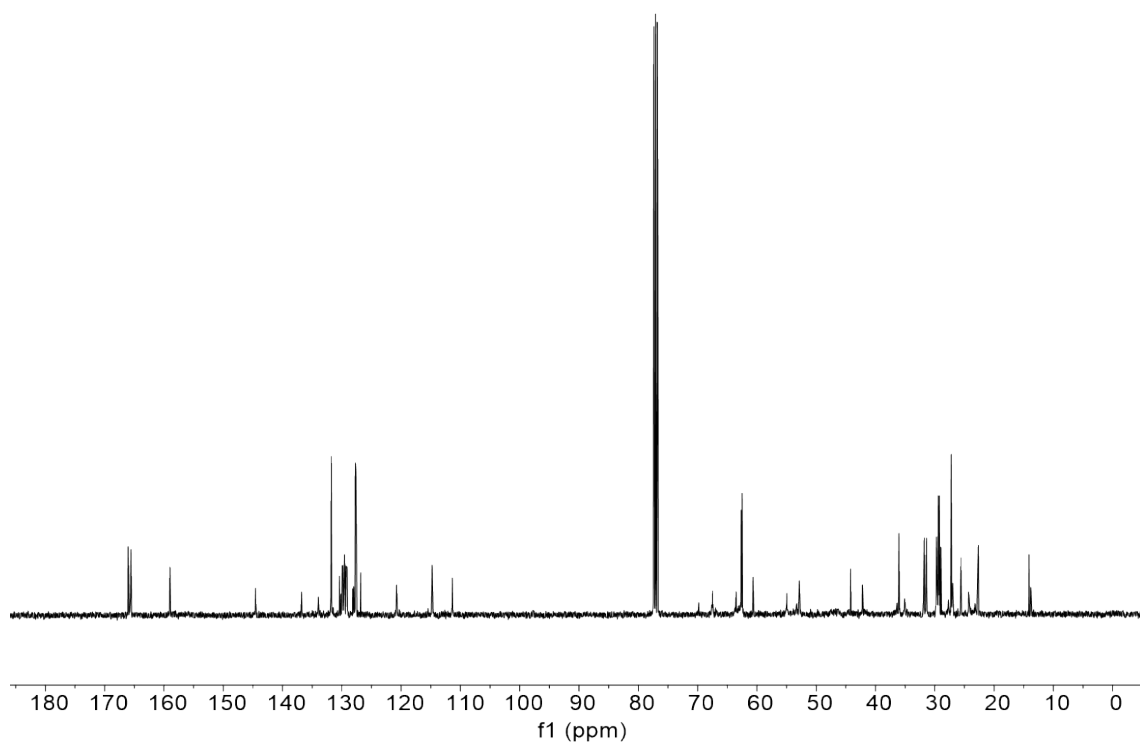


Figure S29. ^{13}C NMR spectrum of 4 (r-PET PUA) in CDCl_3 at 25 °C (500 MHz).

Table S6. Influence of UV-dose on C=C peak intensity of r-PET PUA.

UV-dose ($\text{J}\cdot\text{cm}^{-2}$)	A_{809}^{a}	A_{1725}^{a}	$A_{809}/A_{1725}^{\text{b}}$	Conversion of double bond (%) $^{\text{c}}$
0	0.969	34.298	0.0283	0
1	1.047	37.652	0.0278	1.8
5	0.627	38.435	0.0163	42.4
10	0.506	39.237	0.0129	54.4
15	0.312	37.704	0.0083	70.7
30	0.221	37.162	0.0059	79.2

^a A_{809} and A_{1725} are the integration area at 809 and 1725 cm^{-1} , which are obtained from infrared spectrum (Fig. 5b).

^b Carbonyl peak A_{1725} is used as a reference to calculate the carbon carbon double bond conversion by comparing with double bond peak A_{809} .

^c Conversion of double bond is calculated according to the following formula:

Conversion of double bond

$$\begin{aligned}
 &= \frac{n_{\text{reacted double bond}}}{n_{\text{double bond}}} \\
 &= \frac{\left(\frac{A_{809}}{A_{1725}}\right)_0 - \left(\frac{A_{809}}{A_{1725}}\right)_{UV-dose}}{\left(\frac{A_{809}}{A_{1725}}\right)_0} \\
 &= \frac{0.0283 - \left(\frac{A_{809}}{A_{1725}}\right)_{UV-dose}}{0.0283} \times 100\%
 \end{aligned}$$

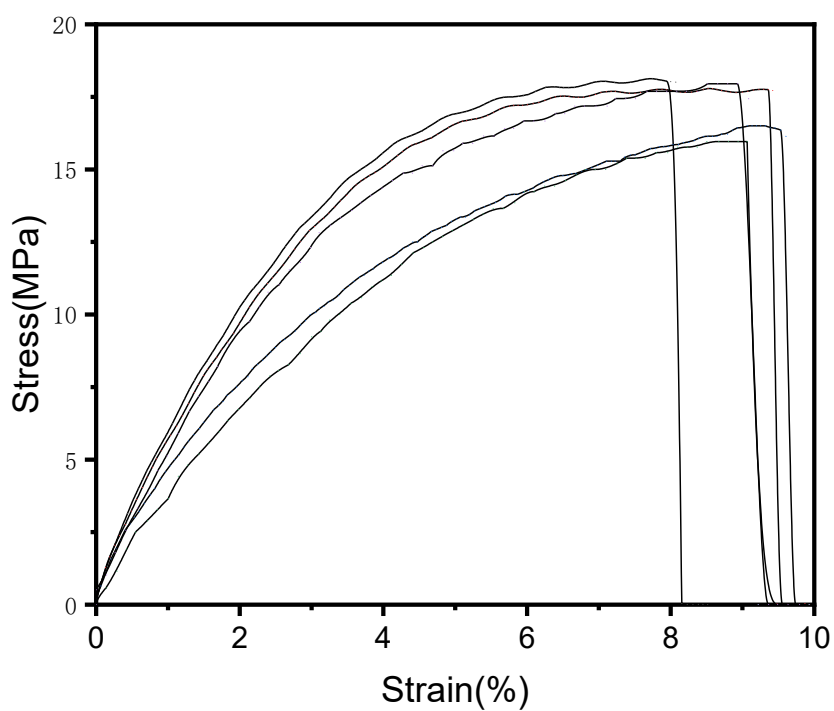


Figure S30. Stress-strain curve of r-PET PUA film (Cross-head speed: 5 mm/min).

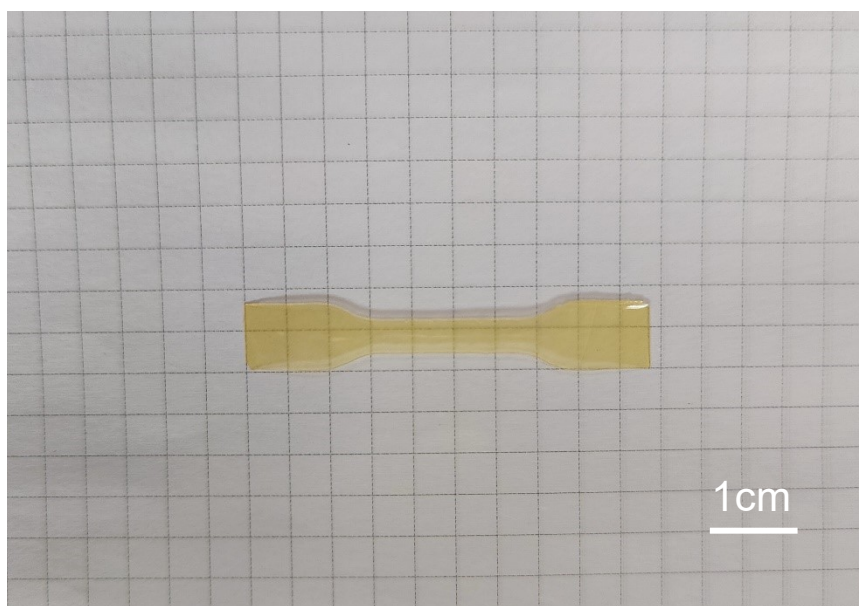


Figure S31. The r-PET PUA dumbbell-shaped spline for mechanical property test. The spline was yellow, transparent with a thickness of 0.2 mm.

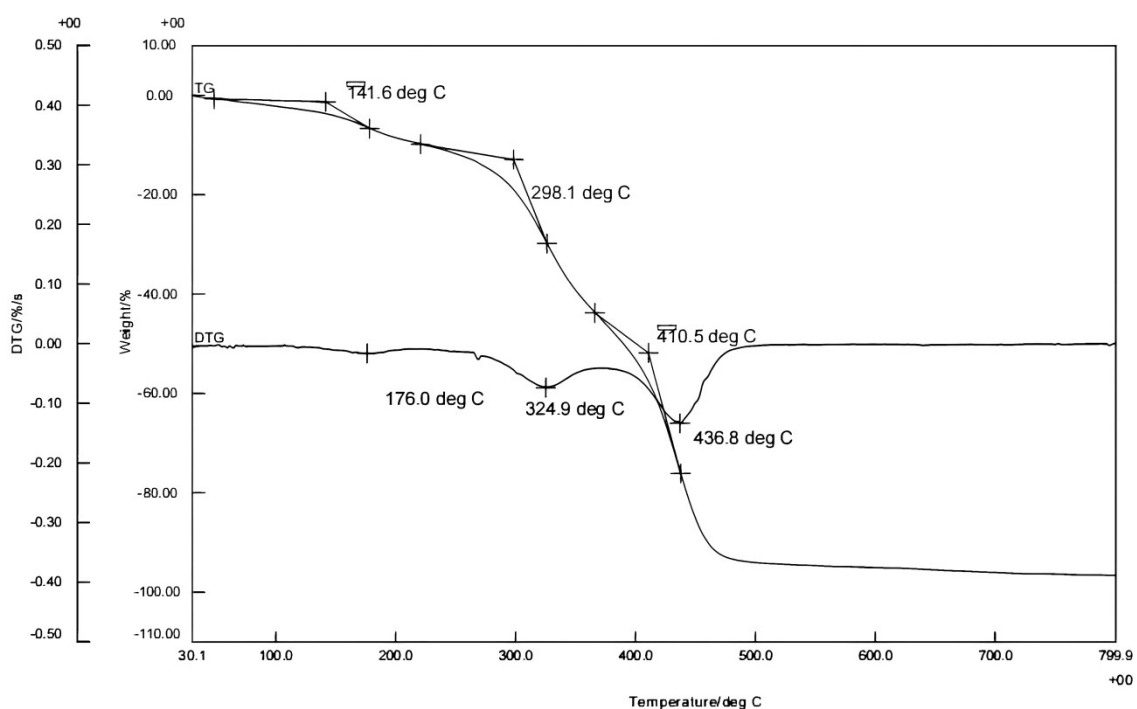


Figure S32. TGA result of r-PET PUA film (atmosphere: N₂, rate: 10 °C/min). The degradation of UV-cured r-PET PUA film can be divided into four stages. The first stage (<200 °C) is to remove the residual low molecular weight components. The second stage (200-380 °C) can be assigned to the composition of the hard segment in the urethane structures. The third stage (380-500 °C) was the quickest and can be described as the degradation of the cross-linked bonds and char formation. The fourth stage (>510 °C) corresponds to the gradient degradation of char residue.

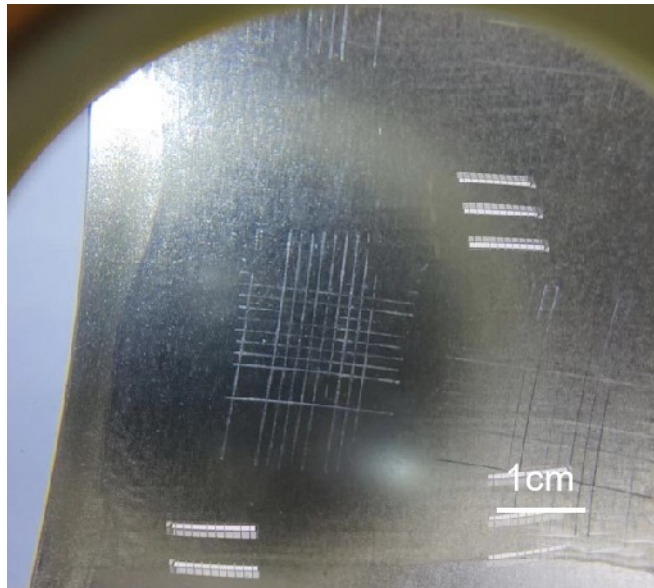


Figure S33. The adhesive property of r-PET PUA coating measured with cross cut test.



Figure S34. The hardness property of r-PET PUA coating measured with Pencil Hardness test.

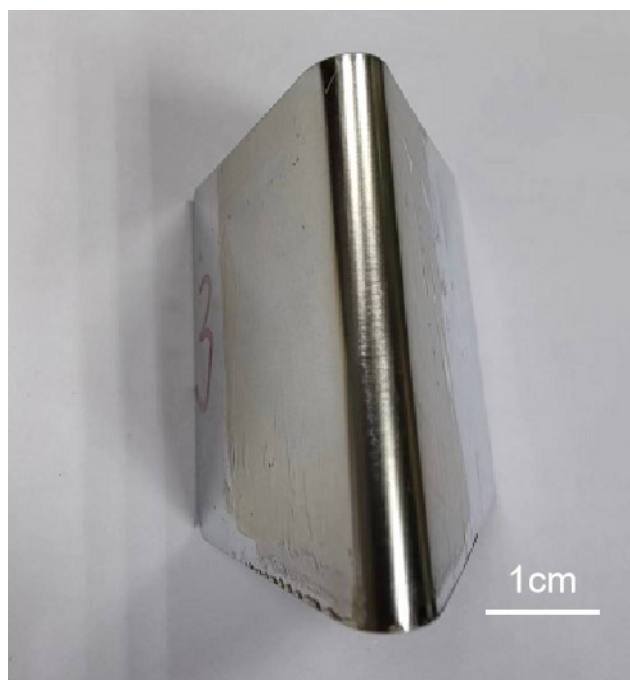


Figure S35. The flexibility property of r-PET PUA coating measured with Bend test.

Table S7. Mechanical and Coating Properties of the r-PET PUA coating^a.

	σ (MPa)	ε (%)	Adhesion	Pencil Hardness	Flexibility
r-PET PUA	17.3	8.7	1	HB	3

^a Coating properties of the UV-cured coatings including adhesion, pencil hardness, and flexibility were evaluated according to GB/T 9286-1998, GB/T 6739-2006, and GB/T 1731-93, respectively.



Figure S36. Color of main reactants and products. (a) Cardanol (b) Cardanol diol (c) r-PET diol (d) r-PET PUA

4. Reference

1. Y. Hu, Q. Shang, C. Bo, P. Jia, G. Feng, F. Zhang, C. Liu and Y. Zhou, *ACS Omega*, 2019, **4**, 12505-12511.
2. C. N. Hoang, C. T. Pham, T. M. Dang, D. Hoang, P. C. Lee, S. J. Kang and J. Kim, *Polymers (Basel)*, 2019, **11**, 236.