

# Acidolysis of Poly(ethylene terephthalate) Waste Using Succinic Acid under Microwave Irradiation as a New Chemical Upcycling Method

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**ABSTRACT:** A novel method of chemical upcycling of used poly(ethylene terephthalate) (PET) bottles by acidolysis with succinic acid (SA) was performed under microwave irradiation. The long polyester chain of PET was efficiently fragmented into small molecules and oligomers, such as terephthalic acid and  $\alpha,\omega$ -dicarboxylic acid oligo(ethylene succinate-co-terephthalate) (OEST). Various input molar ratios of SA/PET from 1.0 to 2.5 were used, and the product mixtures were separated successfully. The recovered terephthalic acid can be reused as a basic chemical. The  $\alpha,\omega$ -dicarboxylic acid OEST was used as a curing agent for epoxy resin. The recovered SA can be reused for further PET acidolysis. Structures of OEST were identified by Fourier transform infrared (FTIR) spectroscopy,  $^1\text{H}$  NMR spectroscopy, and electrospray ionization–mass spectrometry (ESI–MS). The presence of succinic anhydride as a side product was confirmed by FTIR and ESI–MS analyses. The evaporation of SA and the formation of volatile succinic anhydride compete with the acidolysis of PET. The minimum SA/PET ratio of 1.0 was selected so that the acidolysis was effective and without the SA recovery step by MEK treatment. OEST-1.0 was used for curing diglycidyl ether of bisphenol A. The structures and thermal properties of cured adducts were confirmed by FTIR and differential scanning calorimetry (DSC). This chemical upcycling method of PET is eco-friendly without the use of a solvent and a catalyst for the reaction, and all materials were recovered and they could be reused for novel polymer preparation.



## 1. INTRODUCTION

Poly(ethylene terephthalate) (PET) bottles were invented 50 years ago. Since then, it has become an important packaging material and its production worldwide has increased rapidly in recent years. The elevation of production and consumption generates large amounts of PET waste. Consequently, the policy and laws of many countries demand to recycle materials for sustainable development. PET can be recycled successfully by both physical and chemical methods. The advantage of chemical recycling is that it does not require high purity of waste sources that contribute to the high cost of recycling. Various chemical reactions have been applied for the recovery of monomers/oligomers from PET based on the versatile chemistry of the ester group. For instance, hydrolysis,<sup>1</sup> methanolysis,<sup>2</sup> glycolysis,<sup>3</sup> and aminolysis<sup>4,5</sup> of PET have recently been reported. These chemical methods are considered as an upcycling approach to convert waste plastic into intermediates that can be used as virgin-like materials for value-added product preparation.<sup>6–11</sup> The chemical recycling of PET has been intensively reviewed.<sup>12–19</sup> Metal–organic framework materials were prepared by using terephthalic acid obtained from the hydrolysis of waste PET.<sup>20</sup>

The exchange reaction of small molecules between an ester group and a carboxylic acid, called carboxylic acidolysis or briefly acidolysis, is rarely reported. As early as 1944, the acidolysis of esters with acetic acid was investigated for small

molecules.<sup>21</sup> The reactivity of the ester depends on the order of the alcohol, for example, the reaction rates of *t*-butyl > isopropyl >> methyl/ethyl benzoates toward the reaction with acetic acid in the presence of *para*-toluene sulfonic acid as a catalyst. The reactions of benzoate esters of primary alcohols with acetic acid under the same conditions did not occur.

The exchange of the carboxyl group in acidolysis can be described by the following reaction:  $\text{R}_1\text{COOH} + \text{R}_2\text{COOR}_3 \rightarrow \text{R}_2\text{COOH} + \text{R}_1\text{COOR}_3$ .

Because of the similarity in the chemical structures of reactants and products, this reaction is regarded as a reversible process. To shift the reaction toward the side of the products, it requires that one of the products must be easily removed from the reaction mixture or a volatile material. For this reason, esters of acetate are more selected than esters of benzoate.<sup>22</sup>

Up to now, there is only one study on the acid alcoholysis of waste PET. Kárpáti et al.<sup>23</sup> combined both acidolysis with adipic, succinic, and sebacic acids and alcoholysis with 1,4-

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Scheme 1. Purification Procedure for the Products Obtained from the Reaction of PET with SA

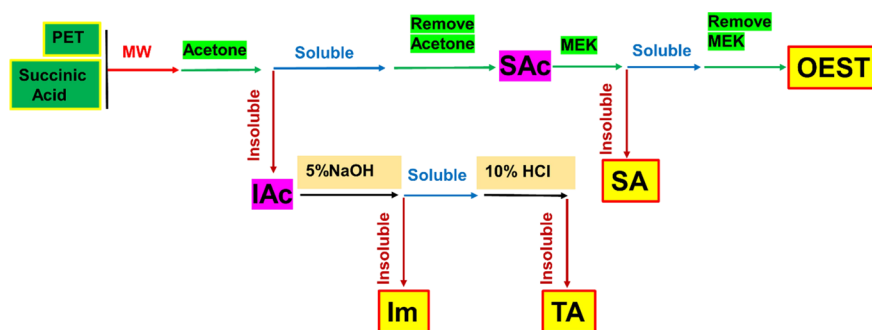


Table 1. Quantities of Reagents for the DGEBA Curing Reaction

experiment	molar ratio of DGEBA/OEST-1.0	DGEBA (400 g/mol)	OEST-1.0 (310 g/mol)
EP-OEST12	1/2	0.400 g (1.0 mmol)	0.620 g (2.0 mmol)
EP-OEST11	1/1	0.600 g (1.5 mmol)	0.465 g (1.5 mmol)
EP-OEST21	2/1	0.800 g (2.0 mmol)	0.310 g (1.0 mmol)

butanediol. The combination of both acidolysis and alcoholysis in one reaction flask makes the system complex. At least three different reactions occurred concurrently, namely, acidolysis of PET by a dicarboxylic acid, glycolysis of PET by 1,4-butanediol, and esterification between dicarboxylic acids with 1,4-butanediol.

Here in this study, we report our novel research results of the acidolysis of PET by succinic acid (SA) under microwave (MW) irradiation. From this reaction, we obtain a new oligomer oligo(ethylene succinate-co-terephthalate) (OEST) that is composed of rigid aromatic rings of the terephthalate group and flexible chains of succinate moieties. Especially, this oligomer contains carboxylic acid groups at both ends of the linear chain; therefore, these reactive groups can further react with an epoxy or alcohol to form a novel polymer.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** Used PET bottles were collected, caps and labels were removed, and then they were rinsed with water, dried at 80 °C, and cut into flakes of 5 mm × 10 mm size. SA from Merck was used as received. Acetone, methyl ethyl ketone, NaOH, and HCl used were of reagent grade from Xilong Scientific Co.

The structure and molecular weight of technical diglycidyl ether of bisphenol A (DGEBA) from CCP Taiwan were determined by a <sup>1</sup>H nuclear magnetic resonance (NMR) analysis.<sup>24</sup>

**2.2. Reaction of PET with SA under MW Irradiation.** PET flakes (9.60 g, 50 mmol) and 14.76 g of SA (125 mmol, molar ratio of SA/PET of 2.5) were added to a 100 mL Erlenmeyer flask, and it was covered with a beaker. The reaction mixture was irradiated by a MW oven at a power of 180 W (medium level) for 15 min, and then heating was controlled by the periodic on (for 2.5 min) and off (for 0.5 min) powering of a magnetron at a power of 120 W (medium to low level) for 10 cycles. At the pause time between the irradiation periods, the reaction mixture was carefully agitated to evenly distribute the PET flakes in molten SA. The reaction proceeded successfully by observing the disappearance of PET flakes.

When the reaction mixture was cooled to room temperature, it became an orange opaque paste. Next, 80 mL of acetone was

added, and the mixture was refluxed for 20 min and then cooled to room temperature. The insoluble part was separated by centrifugation and treated again with another 40 mL of acetone. This treatment was repeated one more time with 40 mL of acetone to get a solid IAc (insoluble in acetone part). The volatile materials in the combined acetone solution were removed by a rotary evaporator, and the nonvolatile part was dried at 80 °C for 10 h to get a paste, labeled SAc (soluble in acetone part).

The IAc part was dissolved in 5% NaOH solution and the pH was adjusted up to 10. After filtration under a reduced pressure to remove the insoluble part or Im (impurities), the collected filtrate was neutralized with 10% HCl solution until the pH value reached 2. A white solid appeared, and it was filtered and rinsed several times with distilled water. After drying at 80 °C in a vacuum oven for 12 h, a white solid, labeled TA (terephthalic acid), was obtained and its weight was recorded.

The SAc part was dissolved in MEK at reflux temperature. After cooling down to room temperature and then at −20 °C in a refrigerator for 12 h to solidify, the solid was filtered and dried at 80 °C under vacuum for 12 h to get the SA part. The volatile material in the MEK solution was removed, and after drying at 80 °C under vacuum, a paste was obtained and labeled OEST and its weight was recorded. The overall procedure is shown in Scheme 1.

Similar experiments with other input molar ratios of 1.0, 1.5, and 2.0 were also performed using the same procedure.

**2.3. Reaction of OEST-1.0 with DGEBA.** OEST-1.0 is the oligomer prepared using an input molar ratio of SA/PET of 1.0 by the procedure described in Section 2.2 without the MEK treatment step.

Mixtures of commercial epoxy resin (DGEBA) and OEST-1.0 with different molar ratios of 2:1, 1:1, and 1:2 (Table 1) were heated at 170 °C for 2 min. The mixtures melted and became transparent. They were further heated at 220 °C for 3 h to obtain hard, transparent thin films.

**2.4. Characterization Equipment.** MW oven: The reaction was conducted by using a MW oven at a medium power of 180 W or a medium-low power of 120 W.

The Fourier transform infrared (FTIR) spectra were recorded using a Nicolet 6700 spectrophotometer (Thermo

**Table 2.** Quantities of Reactants and Products from the Acidolysis of PET with SA<sup>a,b</sup>

input molar ratio of SA/PET	input SA, g (mmol)	sub. lost, g (%)	rec. TA, g (%)	rec. SA, g (%)	OEST, g (%)	change $\Delta m$ g (%)
1.0	5.90 (50)	0.59 (10.0)	3.17 (38.1)	1.45 (24.6)	8.64 (55.7)	-1.65(-10.6)
1.5	8.86 (75)	0.90 (10.2)	3.31 (39.8)	2.31 (26.1)	11.05 (59.9)	-0.89 (-5.4)
2.0	11.81 (100)	1.24 (10.5)	3.72 (44.8)	3.01 (25.5)	13.16 (61.5)	-0.28 (-1.3)
2.5	14.76 (125)	1.52 (10.3)	4.26 (51.3)	4.15 (28.1)	12.64 (51.9)	-1.79 (-7.3)

<sup>a</sup>All experiments were performed using 9.60 g (50 mmol of repeating units) of PET. <sup>b</sup>sub. lost: weight and percentage of lost SA during the reaction; rec. TA: weight and percentage of recovered TA; rec. SA: weight and percentage of recovered SA; and change  $\Delta m$ : weight and percentage of materials lost during purification.

Fisher). The <sup>1</sup>H NMR experiments were performed using a Bruker ARX-500 NMR spectrometer operated in dimethyl sulfoxide-*d*<sub>6</sub> (DMSO-*d*<sub>6</sub>) at 500 MHz. The electrospray ionization–mass spectrometry (ESI–MS) analysis was conducted using an Agilent LC 1290 coupled to a microTOF-Q2 Bruker Daltonics. An ACE3-C18 column (4.6 mm × 150 mm i.d. and 3.5 μm particle size) was used. Elution was performed at 40 °C using acetonitrile (50 mM ammonium formate) at a flow rate of 0.500 mL/min. A mass spectrometric analysis was carried out using a TOF/Q-TOF mass spectrometer model G6545A. ESI was performed in the negative ion mode. For the analysis, the gas temperature was set to 300 °C, the gas flow was 8 L/minute, and the nebulizer was set to 35 psig.

Differential scanning calorimetry (DSC) experiments were performed on a NETZSCH DSC 214 Polyma DSC21400A-0917-L.

Acid–base titration method: The number average molecular weights of the oligomers were determined by carboxyl end group titration with the NaOH solution. The samples were dissolved in acetone, and they were titrated with NaOH solution in EtOH using phenolphthalein as an indicator. The concentration of NaOH was determined by titrating it to a weighed sample of potassium hydrophthalate as a primary standard. For each sample, three different measurements were performed, and the average molecular weights were calculated.

### 3. RESULTS AND DISCUSSION

The acidolysis reaction of PET was performed without a solvent and a catalyst using the MW heating system. From the beginning of the reaction, both PET and SA existed in the solid state. SA started to melt first when the temperature reached its melting point of 188 °C, and SA became a continuous medium of the reaction. The reaction conducted at higher than 188 °C was satisfactory for PET transformation. The PET flakes turned into a soft material and gradually dissolved in the reaction medium. The reaction was complete when all PET flakes disappeared. However, the high temperature was a detriment to SA. At the boiling point, SA quickly melted and evaporated or dehydrated to form volatile succinic anhydride, leading to the high loss quantity of SA during the reaction. Therefore, the reaction under MW required the periodic on and off powering of the magnetron so that it was kept from intensive boiling.

After the reaction finished, the mixture was first treated with acetone. This is a good solvent for SA and OEST, but TA and PET were almost insoluble; therefore, TA and PET were removed from the solution. TA was further purified by dissolving in a NaOH solution at room temperature, and PET or some impurities were removed by filtration. All experiments showed that the quantities of PET and impurities were negligible. This was a good proof of high conversion of PET. The neutralization reaction with 5% NaOH solution trans-

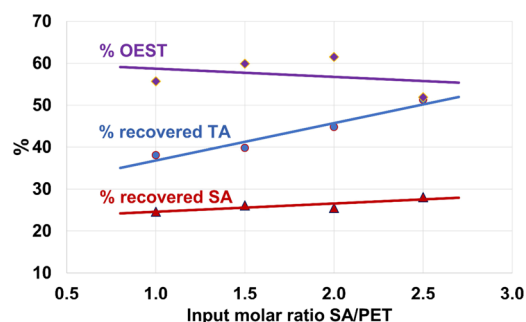
formed TA into sodium salt and then it was soluble in water. The filtrate was neutralized with 10% HCl solution to get back insoluble TA. The structure of TA was confirmed by FTIR and comparable with the standard spectrum.

The volatile materials in the acetone solution were removed and we obtained the SAc part. This half solid SAc was further treated with MEK. At -20 °C, SA crystallized and separated from the mixture. The volatile materials in MEK solution were removed to obtain OEST. The structures of these oligomers were confirmed by FTIR and <sup>1</sup>H NMR. Pictures of PET flakes, recovered TA, and OEST-1.0 products are shown in Figure S1.

The input molar ratio of SA/PET changed from 1.0 to 2.5, and the recorded weights of the reactants and products are given in Table 2. The percentage of lost SA during the reaction was calculated based on the used weight of SA. The reacted weight of PET was 9.60 g or 50 mmol of repeating units. If terephthalate ester in PET was completely converted into TA, the theoretical quantity of TA would be 8.31 g. The percentage of recovered TA (rec. TA) from chemical recycling was calculated based on this value. The percentage of recovered SA (rec. SA) was calculated according to the used SA quantity. The percentage of OEST was estimated on the basis of total reactant weights.

As the input molar ratio of SA/PET increased from 1.0 to 2.5, the percent of lost SA (sub. lost) due to sublimation was around 10.2% (Table 2). When larger quantities of SA were used, larger amounts of SA were lost under MW irradiation. Therefore, the real quantity of SA reacted with PET was only about 89.8% of the input value. The similarity of the lost percentage, as the input molar ratio of SA/PET increased, was a good proof for the high reproducibility of our experiments.

When the used SA quantity was larger, the reaction shifted forward, and more products were obtained as evidenced by the larger percentage of recovered TA from 38.1 to 51.3% (Table 2 and Figure 1). This was the nature of reversible reactions. Even though a large excess of SA was used, up to a SA/PET ratio of 2.5, only 51.3% TA was recovered and the remaining still



**Figure 1.** Percentages of recovered TA, SA, and OEST depending on the input molar ratio of SA/PET.



existed in the oligomer structures. The TA recovered from the reaction could be used as a basic reagent for new PET preparation.

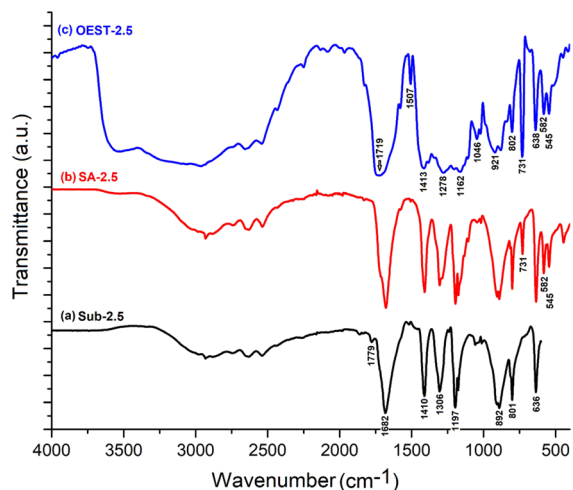
As more SA was used, more SA was recovered by MEK treatment. The structure of recovered SA will be discussed later.

The percentages of isolated OEST were from 51.9 to 61.5% and they could depend on the lost quantity (change  $\Delta m$  in Table 2) during product isolation. The change  $\Delta m$  quantities were the difference in the weights of the products, including sublimed SA quantities, recovered TA, SA, and OEST, and the reactants made up of PET and SA. These quantities were lost amounts during isolation, from 1.3 to 10.6%, and they strongly influenced the percentages of isolated OEST.

Recovered SA and TA were solid powders at room temperature, and they were quickly dried under vacuum at 80 °C. However, OEST existed in a sticky paste form, so the drying process required much longer time, and it was extremely hard to decide when the sample was dried enough. During this long drying period, not only volatile materials, like solvents, were removed but sublimed SA was also detected in the vacuum chamber. Consequently, the percentage of obtained OEST was strongly dependent on the drying process. This conclusion is quite consistent with the change  $\Delta m$  data in Table 2. As the percentage of change  $\Delta m$  in the experiments of SA/PET of 1.0 and 2.5 became larger, the percentage of OEST became lower.

Even though the weight percentages of OEST were almost independent of the input SA/PET ratio, the structures of OEST samples were different as confirmed by  $^1\text{H}$  NMR and MS characterizations.

After the reaction with an input molar ratio of SA/PET of 2.5, the sublimed part (Sub) and other products were isolated and characterized by FTIR (Figure 2). The FTIR spectrum of



**Figure 2.** FTIR spectra of (a) Sub-2.5: sublimed part during the reaction, (b) SA-2.5: recovered SA, and (c) OEST-2.5.

the sublimed part (Sub-2.5) shows typical absorptions of major SA and minor succinic anhydride. The stretching vibrations of C=O and C–O show signals at 1682 and 1306  $\text{cm}^{-1}$ , respectively. The  $\text{CH}_2$  and O–C=O deformations appear at 1410 and 636  $\text{cm}^{-1}$ , respectively. The signals of the MEK insoluble part (SA-2.5) are quite similar to SA with the exception that three minor peaks at low wavelengths at 731, 582, and 545  $\text{cm}^{-1}$  (C–C=O bending) were observed.

The OEST-2.5 sample shows a very broad peak from 2200 to 3700  $\text{cm}^{-1}$  of the OH stretching of various aromatic (terephthalic) and aliphatic (succinic) carboxylic acids. The strong and broad band at 1719  $\text{cm}^{-1}$  is a combination of various C=O stretching vibrations of esters/acids of terephthalate ring appears as a weak band at 1507  $\text{cm}^{-1}$ . A strong signal at 731  $\text{cm}^{-1}$  is due to the wagging vibration of the aromatic ring CH.

The  $^1\text{H}$  NMR spectrum of SA-2.5 (Figure 3) shows multiple peaks from 2.455 to 2.596 ppm of methylene protons of succinic units  $-\text{COCH}_2\text{CH}_2\text{CO}-$ . These peaks were overshadowed by the peak of DMSO at 2.500 ppm; therefore, the quantitative analysis of succinic units (S) based on these peak integrations was strongly influenced. DMSO- $d_6$  was selected for the NMR experiment because it was a good solvent for this substance, and the quintet of DMSO at 2.500 ppm was selected as a reference signal. Four multiple peaks at 4.673, 4.490, 4.386, and 4.205 belong to ethylene units  $-\text{OCH}_2\text{CH}_2\text{O}-$ . Each symmetrical ethylene group of TET and SES triads gives the only signals at 4.673 and 4.205 ppm, respectively. Two methylene protons in the ethylene group of unsymmetrical TES triads give two signals with nearly the same integral at 4.490 and 4.386 ppm. Our  $^1\text{H}$  NMR data matched quite well with the published data.<sup>25</sup> The methylene protons of the reactant SA give the strongest singlet signal at 2.418 ppm. Aromatic protons on terephthalate units give multiple peaks at 8.062 ppm. Carboxylic acid protons appear at 12.216 ppm as a broad peak.

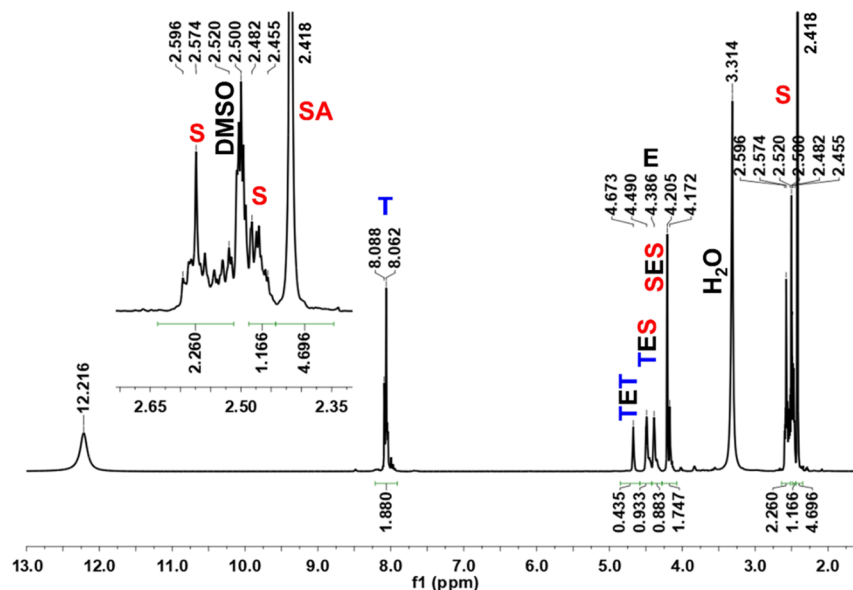
In the acidolysis of PET by SA, the ethylene units (E) in PET were transformed into OEST; consequently, the ethylene units (E) were supposed to be unchanged during the reaction. Therefore, the relative numbers of protons in OEST based on the integrations of  $^1\text{H}$  NMR resonances were normalized against the intensity of one ethylene unit (E) or 4.00 protons at 4.172–4.673 ppm. From the integration, the molar ratios of units were calculated  $\text{T/E/S/SA} = (1.880/4):[(0.435 + 0.933 + 0.883 + 1.747)/4]:[(2.260 + 1.166)/4]:(4.696/4) = 0.470:1.000:0.856:1.174$ .

The ratio of three triads was also calculated  $\text{TET/SES/SES} = (0.435/4):[(0.933 + 0.883)/4]:(1.747/4) = 0.109:0.454:0.437$ .

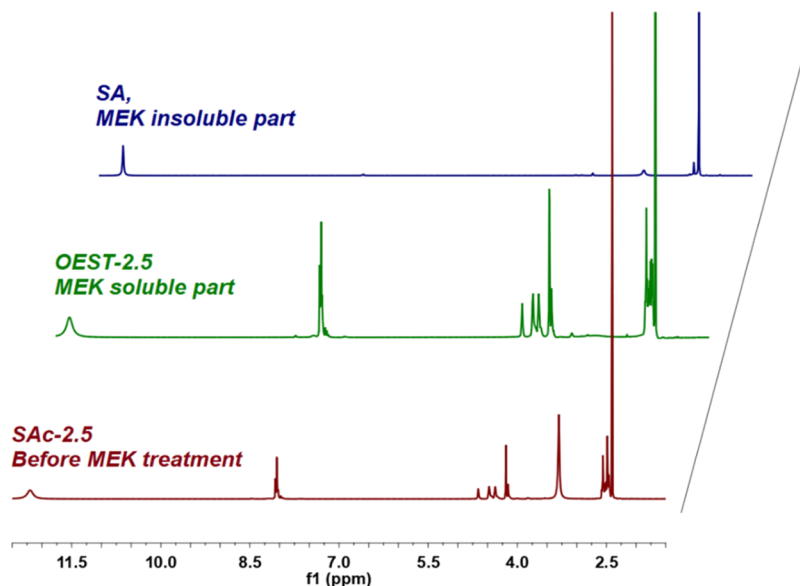
After MEK treatment, we obtained the insoluble part (SA) and MEK soluble part (named OEST-2.5). Their  $^1\text{H}$  NMR spectra are shown in Figures 4, S2, and S3.

The  $^1\text{H}$  NMR spectrum of SA, or the MEK insoluble part, gives a strong signal of symmetrical ethylene protons of SA at 2.418 ppm and very weak signals of OEST. Therefore, by MEK treatment, we can separate unreacted SA from OEST. However, SA was not completely removed from OEST-2.5 as evidenced by the existence of the same peak in the  $^1\text{H}$  NMR spectrum of the OEST-2.5 sample. Due to the similarity in the structure, polarity, and solubility of SA and the oligomer, it is very difficult to separate SA completely from OEST-2.5 by solvent treatment.

Applying similar calculations, we can obtain the molar ratio of units of T/E/S/SA in OEST-2.5 as  $(1.760/4):[(0.431 + 0.932 + 0.864 + 1.772)/4]:[(1.908 + 1.043)/4]:(2.404/4) = 0.440:1.000:0.738:0.601$ . The molar ratio of SA reduced from 1.174 in SA-2.5 to 0.601 in the OEST-2.5 sample. Therefore, the recovery rate of SA by MEK treatment was  $[(1.174 - 0.601)/1.174]100\% = 48.8\%$ , and 51.2% of SA remained as a mixture with oligomers in OEST-2.5.



**Figure 3.**  $^1\text{H}$  NMR spectrum of Sac-2.5 in  $\text{DMSO-}d_6$  before MEK treatment. The inset shows the expanded region from 2.4 to 2.6 ppm. S, T, and E stand for succinic, terephthalic, and ethylene units in OEST, and SA is free succinic acid.



**Figure 4.**  $^1\text{H}$  NMR spectra of the OEST-2.5 sample in  $\text{DMSO-}d_6$  before and after MEK treatment.

The ratio of three triads in OEST-2.5 was also calculated as  $\text{TET/SES} = (0.431/4) : [(0.932 + 0.864)/4] : (1.772/4) = 0.108:0.449:0.443$ . This ratio was almost unchanged after MEK treatment.

**3.1. Influence of the Input Molar Ratio of SA/PET.** The experiments of PET acidolysis with SA were performed with the input molar ratio of SA/PET from 1.0 to 2.5. The OEST samples were characterized by  $^1\text{H}$  NMR and volumetric analyses. The  $^1\text{H}$  NMR spectra are shown in Figure 5.

Figure 6 shows that as the input molar ratio of SA/PET increased from 1.0 to 2.5, the relative number of T units in OEST decreased, but the number of S units increased. This is true because as the larger the input molar ratio of SA/PET used, the reversible reaction shifted toward more products, so that more S and less T units contributed to OEST.

Three TET, TES, and SES triads in the OEST-2.5 sample were identified and quantified from the  $^1\text{H}$  NMR spectra. Mole

fractions of these triads were calculated and are presented in Figure 7.

As more SA was used, the SES triad content increased, but that of TET triads decreased. This result again confirmed the nature of reversible character of the reaction. When more SA was added, more T units in PET were displaced by S units and smaller oligomers were obtained.

By volumetric analysis, the OEST samples were considered as dicarboxylic acids and they were titrated with a standardized NaOH solution; then, the average molecular weights were calculated and are given in Table 3.

As a larger SA/PET ratio was used, a smaller molecular weight of OEST was obtained.

The acid–base titration method was also verified using SA as a control sample. The molecular weight of SA determined by titration was 117.14 g/mol, compared to the standard molar mass of 118.09 g/mol with an error of  $-0.8\%$ .

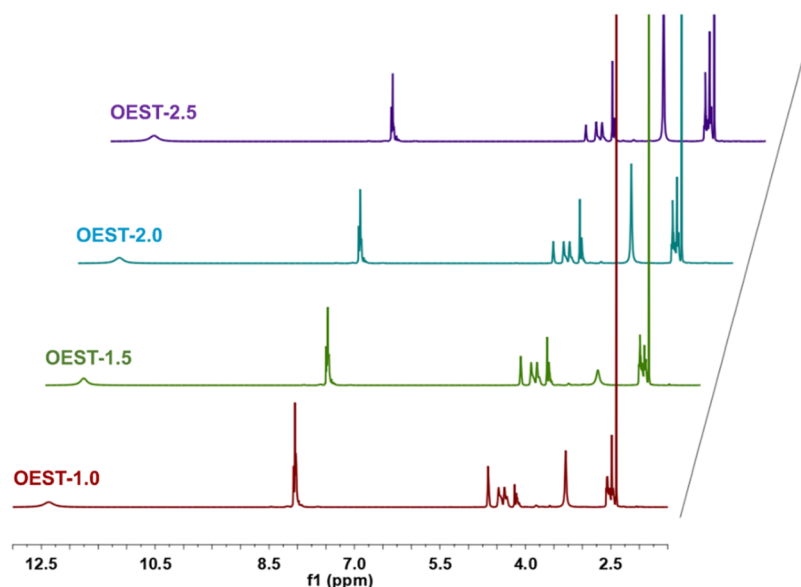


Figure 5.  $^1\text{H}$  NMR spectra of OEST prepared with an SA/PET molar ratio from 1.0 to 2.5.

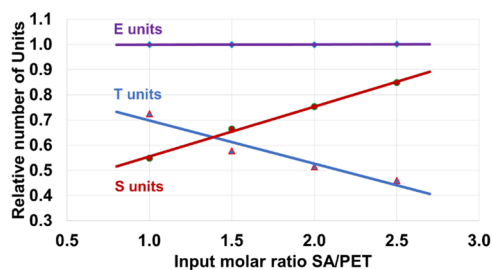


Figure 6. Dependence of the relative numbers of T, S, and E units calculated from the  $^1\text{H}$  NMR spectra on the input molar ratio of SA/PET.

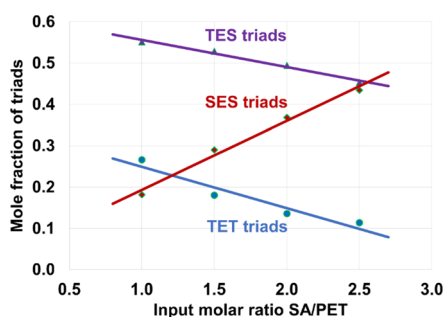


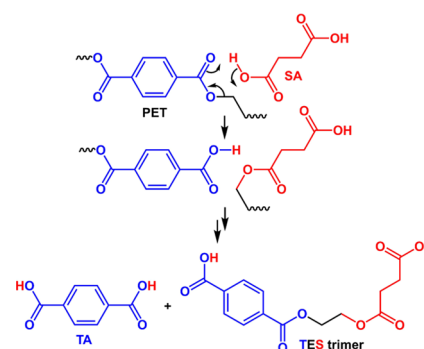
Figure 7. Mole fractions of TET, TES, and SES triads calculated from the  $^1\text{H}$  NMR spectra depending on the input molar ratio of SA/PET.

Table 3. Molecular Weights of Various OEST Samples as Determined by Volumetric Analysis

sample	OEST-1.0	OEST-1.5	OEST-2.0	OEST-2.5
molecular weight (g/mol)	397	329	289	254

**3.2. Reaction Mechanism.** The reaction of an aliphatic carboxylic acid group of SA with an ester of aromatic acid (PET) can be proposed by using the mechanism in Scheme 2. The OH group of carboxylic acid SA can form a six-membered ring intermediate with the ester group of PET, so that three pairs of electrons including two sigma bonds and one  $\pi$  bond

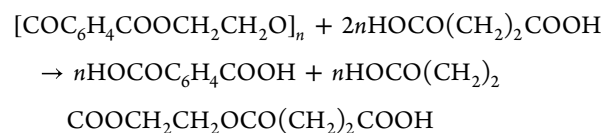
Scheme 2. Proposed Mechanism of the Reaction between Terephthalate Ester and SA



can transfer concurrently to break the ester bond of PET and form a new ester bond with SA. At the same time, the protons of SA can transfer to TA.

Although the acidity of TA is stronger than that of SA ( $\text{p}K_a$  values of 3.51 and 4.91, respectively) or TA is more effective in promoting proton transfer, however the strength of conjugate bases of these acids is reversed. Therefore, TA is a weaker conjugate base than SA, and it is less reactive toward a nucleophilic attack on the methylene carbon. Because of the two opposite effects, the reaction only reaches an equilibrium state.

The theoretical transesterification by SA can be written with the assumption of complete conversion:



In order to displace terephthalate ester completely from PET and produce free TA, the above theoretical reaction requires a minimum molar ratio of SA/PET of 2.0.

When a minimum input molar ratio of SA/PET of 1.0 is used, the following theoretical reaction will take place, and

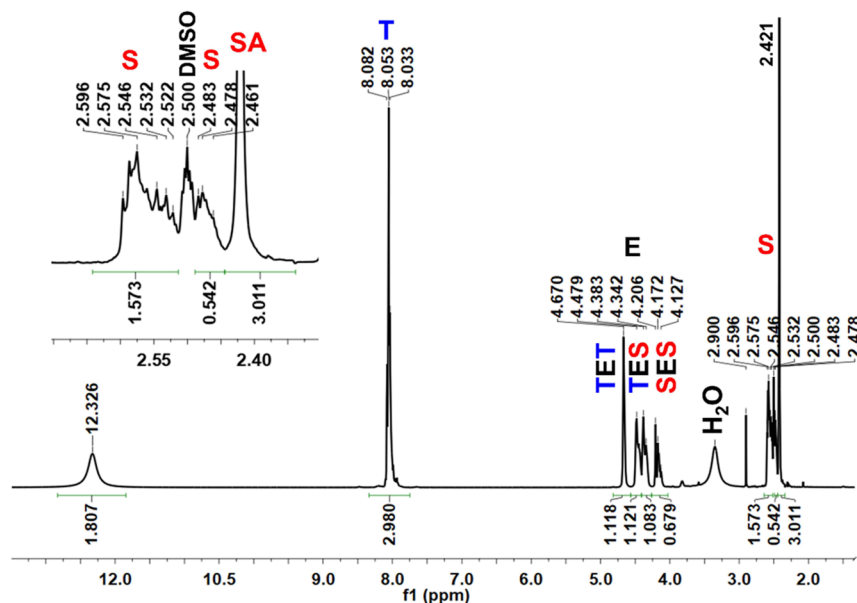


Figure 8.  $^1\text{H}$  NMR spectrum of OEST-1.0 in  $\text{DMSO-}d_6$ .

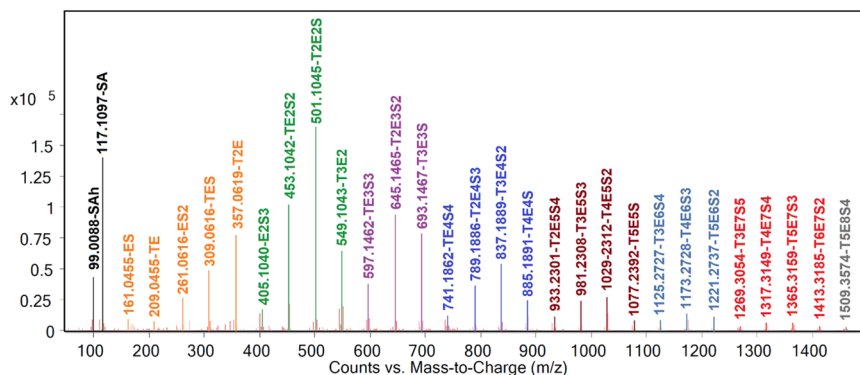
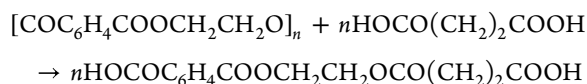


Figure 9. ESI-MS spectrum of OEST-1.0 in the negative mode. The negative ions having the same number of E units are highlighted with the same color.

then TA will contribute only in the OEST structure and no free TA was formed.



However, in practice, the reaction of PET with SA produces more complex product mixtures due to the reversible characteristic of the reaction. The forward reaction between PET ester and SA and the backward reaction between TA and OEST ester occur simultaneously until the system reaches an equilibrium state.

Our experimental data showed that when an SA/PET ratio of 1.0 was used, still we get 38.1% of TA (Table 2) and not 0% as expected by the assumption. However, when the input molar ratio of SA/PET was 2.5/1, only 51.3% TA was recovered and not 100% as proposed by the above theoretical reactions.

**3.3. Characterization of the OEST-1.0 Sample and Its Curing Reaction with DGEBA.** In the acidolysis of the PET reaction, when the input molar ratio of SA/PET was reduced to 0.7 and 0.5, however the reaction was unsuccessful, PET flakes still existed because the quantity of used SA was too small to cover all PET flakes. Finally, we found that the

acidolysis of PET by SA required a minimum ratio of SA/PET of 1.0. When a low quantity of SA was used in the reaction, the isolated excess quantity of SA was also small, and we approximated the change  $\Delta$  (1.45 and 1.65 g, respectively, in Table 2); therefore, the recovery step of SA by treatment with MEK was excluded. Consequently, the purification process became simpler. In this case, the name of the product SAC-1.0 was changed to OEST-1.0.

The OEST-1.0 sample is soluble in acetone, tetrahydrofuran, dimethylformamide, and dimethyl sulfoxide but insoluble in methanol and ethanol.

The  $^1\text{H}$  NMR spectrum of the OEST-1.0 sample (Figure 8) shows the same features as the spectrum of SAC-2.5 (Figure 3), except for the peak integration due to the difference in the microstructure.

The molar ratio was calculated from the  $^1\text{H}$  NMR spectrum as T/E/S/SA = (2.980:4):(1.118 + 1.121 + 1.083 + 0.679):4/(1.573 + 0.542):4/(3.011:4) = 0.745/1.000/0.529/0.753.

The integration of S units in the 2.45–2.60 ppm range was not accurate because these peaks were overlapped with the quintet signal of the DMSO solvent centered at 2.500 ppm.

In theory, an oligomer prepared from an excess diacid with a diol will have carboxylic acid groups at both ends and in one



polymer chain, and the number of diacid units is larger than that of the diol units by one. Based on this principle, the ratio of diacid/diol of OEST-1.0 was  $1.274/1.000 = 1.274k/1.000k$ , then  $(1.274k - 1.000k) = 1$  or  $k = 3.650$  or the average ratio of 1 mol of OEST was T/E/S/SA =  $0.745 \times 3.650/1.000 \times 3.650/0.529 \times 3.650/0.753 \times 3.650 = 2.719/3.650/1.931/2.748$ .

The average molecular weight of OEST-1.0 was calculated from the number of T, E, and S units in 1 mol of oligomer as 775 g/mol.

If there are 1 mol of OEST-1.0 (775 g/mol) and 2.748 mol of SA (118.1 g/mol), then the average  $M_n$  (eq 1) must be

$$M_n = \frac{1 \times 775 + 2.748 \times 118.1}{1 + 2.748} = 293 \text{ g/mol} \quad (1)$$

The volumetric analysis gave  $M_n = 310$  g/mol with a difference of 5.5%. This error could come from the inaccuracy of overlapped signals of S units as reported above.

The structure of the OEST-1.0 sample was further identified by ESI-MS. The molecular ions were found in the negative ion MSI-MS mode (Figure 9). The structures of oligomers were proposed by combining terephthalate [COC<sub>6</sub>H<sub>4</sub>COO] (T), ethylene glycol [CH<sub>2</sub>CH<sub>2</sub>O] (E), and succinate [CO-(CH<sub>2</sub>)<sub>2</sub>COO] (S) units. The masses of the parent negative ions were then calculated and compared with the experimental  $m/z$  data. Totally 91 structures, from SA monomer to heptadecamer TSE8S4 with an  $m/z$  value of 1509.3574 Da, were identified from the MS signals (Figure S4).

In the lower  $m/z$  range, the signals of SA and succinic anhydride (SAh) appear at 117.1097 and 99.0088 Da, respectively. SAh is a dehydrated product of SA during the reaction.

The most intensive peak at 501.1045 Da of the MS is called the base peak and the intensities of the other peaks are represented in relation to this base peak. This base peak is identified as a general structure of T2E2S or TETES in the order of units. In addition to this base peak, two other isotopic peaks of the same structure were also detected at 502.1072 and 503.1094 Da. The experimental relative abundances of the three anions are 100.00, 27.02, and 5.48. These values are very close to the calculated values of 100.0, 26.0, and 5.2. These data strongly confirmed the TETES structure in the OEST-1.0 sample.

The pentamer group with two E units contains not only the strongest signal of T2E2S but also other weaker signals of other pentamers having different T and S units, namely, E2S3 (405.1040 Da), TE2S2 (453.1042 Da), and T3E2 (549.1043 Da).

Other MS peaks of various oligomers were similarly identified and the molecular structures of totally 91 oligomers/monomers/isotopic species are shown in Figures 9 and S4. The molecular weights for OEST-1.0 are between 100.07 and 1511.32 g/mol.

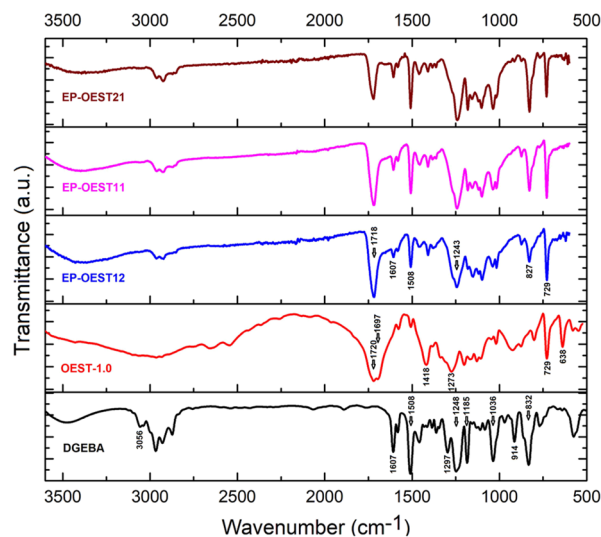
The number average molecular weight of OEST-1.0 can be calculated from the ESI-MS data using the equation  $M_n = \sum X_i M_i$ , where  $X_i$  values are mole fraction calculated from relative abundances and  $M_i$  values are molecular weights. The result gave  $M_n = 584$  g/mol. This value is much larger than 310 g/mol as determined by volumetric analysis and <sup>1</sup>H NMR. The difference also proves that in the mass spectrum, the relative abundances of peaks do not always reflect the mole fraction.

The thermal behavior of OEST-1.0 was investigated by DSC. A very broad endothermic peak from 95 to 185 °C was

observed in the first heating curve (Figure S5) of the OEST-1.0 sample due to the melting of the crystal structure polymorphism. The OEST-1.0 sample contains various oligomers with different molecular weights and hence different crystalline forms and sizes. The cooling curve showed one sharp exothermic peak at 121.0 °C for recrystallization of the principal oligomeric component. A broad endothermic melting peak appeared at 160.3 °C in the reheating curve. SA melts at 188.6 °C.<sup>26</sup> The melting ranges of OEST are lower than the melting point of SA. In the OEST sample, the T and S units distribute randomly in the chain; therefore, it is hard to pack them into a perfect crystalline lattice. These poorly packed crystals have weaker dipole–dipole interactions, and therefore, have lower crystal binding energies and then lower melting point.

**3.4. Application of OEST-1.0 for Epoxy Curing.** Mixtures of DGEBA and OEST-1.0 at 1:2, 1:1, and 2:1 molar ratios were heated to 170 °C for 2 min and 220 °C for 3 h. The obtained adducts were a transparent rigid solid.

The FTIR spectra showed that as the quantity of DGEBA in the cured adducts increased, the signals of DGEBA structures (Figure 10) became stronger, for example, typical peaks at

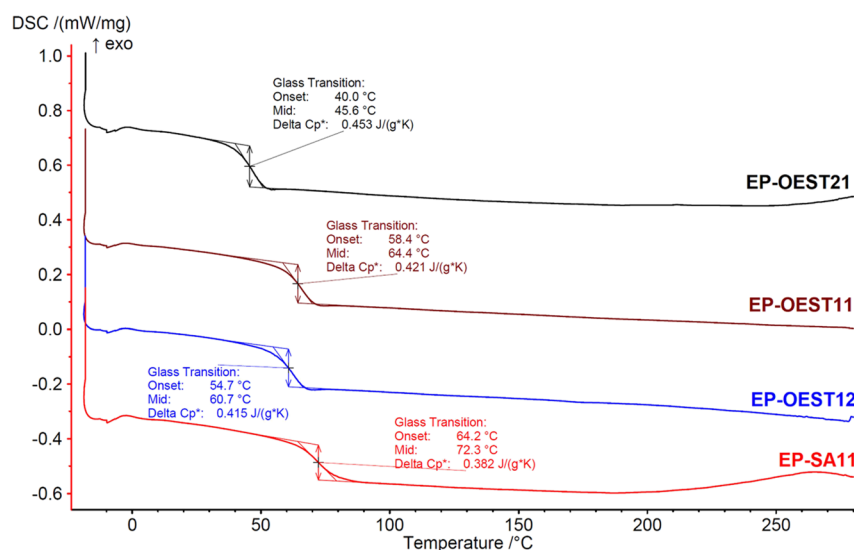


**Figure 10.** FTIR spectra of the reactants DGEBA and OEST-1.0 and the product EP-OEST with various molar ratios of 1:2, 1:1, and 2:1.

1607 and 1508  $\text{cm}^{-1}$  of the aromatic ring of bisphenol A and a strong signal at 832  $\text{cm}^{-1}$  of the out-of-plane deformation band of the para-substituted aromatic C–H. The asymmetrical deformation band of the oxirane ring of DGEBA at 914  $\text{cm}^{-1}$  and the weak signal at 3056  $\text{cm}^{-1}$  due to the oxirane C–H stretching disappeared in the cured adducts. The strong and broad signal at 1243  $\text{cm}^{-1}$  is a blend of the aromatic C–O and ester C(O)–O stretching bands. The aliphatic C–O ether stretching vibration appears as a peak at 1036  $\text{cm}^{-1}$ . The presence of the terephthalate moiety was only confirmed by a strong peak at 729  $\text{cm}^{-1}$  due to the out-of-plane deformation of para-substituted aromatic C–H. Ester C=O stretching in terephthalate showed a strong peak at 1718  $\text{cm}^{-1}$ .

Thermal properties of the cured products were investigated by DSC. The heating/cooling/reheating curves of EP-OEST11 (Figure S6) showed the only glass transition of the cured adduct. No other thermal effect was detected as the sample was





**Figure 11.** DSC curves of cured adducts of DGEBA with SA (molar ratio 1:1, EP-SA11) and OEST molar ratios of 1:2, 1:1, and 2:1 (EP-OEST12, 11, and 21). Samples were heated from  $-20$  to  $180$  °C and then cooled to  $-20$  °C and reheated to  $280$  °C. Data were extracted from the second heating from  $-20$  to  $280$  °C.

heated to  $280$  °C. This is a good evidence for the complete curing process of epoxy.

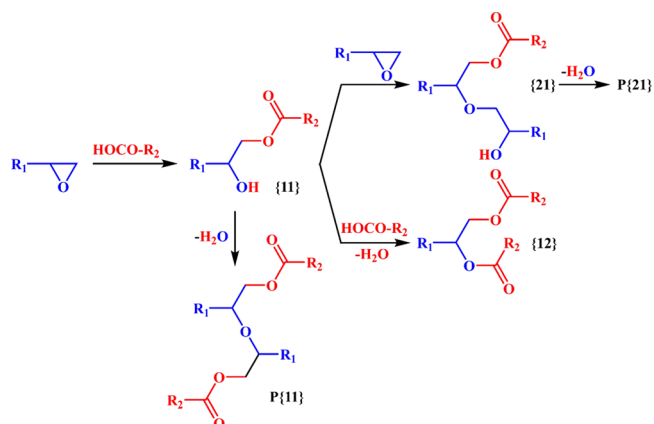
The DSC curves (Figure 11) show mainly the glass transitions of the cured adducts of DGEBA with SA and OEST. When DGEBA was cured with SA as a short dicarboxylic acid to produce an adduct with a high crosslink density, the  $T_g$  reached the highest value at  $72.3$  °C (midpoint).

When equimolar quantities of DGEBA and OEST were mixed and cured, the  $T_g$  of the adduct ( $64.4$  °C) was higher than that of the system using an excess of DGEBA (EP-OEST21 sample,  $45.6$  °C) or an excess of OEST (EP-OEST12 sample,  $60.7$  °C).

The swelling test was performed by soaking the cured samples in  $20$  mL of acetone for  $24$  h at room temperature. After the solution was separated, the weights of the swollen samples were measured. These swollen samples were dried in an oven at  $70$  °C for  $12$  h. The weights of the dried samples were recorded, and then the swelling ratios (SR) and gel contents (GC) were calculated and are given in Table S1. Acetone was selected for testing because both DGEBA and OEST-1.0 were soluble in this solvent. If the cross-linking reaction occurred, then the cured products became insoluble. The usage of the equimolar ratio of DGEBA and OEST-1.0 (sample EP-OEST11) produced a highly cross-linked system with the lowest swellability and the highest gel content.

The reaction mechanism between OEST and DGEBA is proposed in Scheme 3. The equimolar reaction (EP-OEST11 sample) gives a product of oxirane ring opening by a carboxylic acid {11}. The alcohol group of {11} can further react with an extra oxirane ring to form the {21} adduct (EP-OEST21 sample). The hydroxyl group of {21} can further self-condense to form an ether bond of P{21}. The alcohol group of {11} can also react with an excess of carboxylic acid to form an ester {12} (EP-OEST12 sample). The alcohol group of {11} can also condense to form a polyether chain P{11}. The structure of P{21} has more ether bonds than P{11}, and the ether bonds are more flexible than the ester bonds; therefore, P{21} is more flexible than P{11}. Consequently,  $T_g$  of EP-OEST11 is higher than that of EP-OEST21.

### Scheme 3. Plausible Reactions of DGEBA with OEST



## 4. CONCLUSIONS

The transesterification of PET with SA was performed without a solvent and a catalyst using an MW heating system for  $40$  min. In order to avoid losing of SA, the magnetron of the MW oven was switched on and off periodically.

The reaction mixture was treated with common solvents, namely, acetone, MEK, NaOH, and HCl solution to obtain TA, OEST, and SA. The excess of SA was separated from OEST-2.5 by MEK treatment as confirmed by the  $^1\text{H}$  NMR analysis. However, it was impossible to completely remove SA from OEST due to the similarity in the structures and polarities.

When a minimum input molar ratio of SA/PET of  $1.0$  was used, the purification was simplified by excluding the MEK treatment step.

Structures of OEST-1.0 were verified by FTIR,  $^1\text{H}$  NMR, ESI-MS, and DSC analyses. Especially, via ESI-MS characterization, molecular structures of totally  $91$  oligomers/monomers/isotopic species in OEST-1.0 were identified and the molecular weights ranged from  $100.07$  to  $1511.32$  g/mol.

The curing reactions of DGEBA with OEST-1.0 using three input molar ratios were performed. FTIR spectra showed that

the oxirane rings of DGEBA were completely opened by carboxylic acid groups of OEST-1.0. The mechanism of the curing reaction was proposed. The maximum  $T_g$  value of the adduct obtained from a 1:1 molar ratio of DGEBA/OEST was 64.4 °C. The gel content of EP-OEST11 was 86.3%, which was the highest value of three samples.

The obtained reactive oligomers OEST with carboxylic acid end groups were not only used for epoxy curing but also for other novel polymer preparation. Therefore, the acidolysis of PET is an efficient upcycling method.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c06642>.

Swelling ratios and gel contents of cured samples;  $^1\text{H}$  NMR spectrum in  $\text{DMSO-}d_6$  of SA (MEK insoluble part);  $^1\text{H}$  NMR spectrum in  $\text{DMSO-}d_6$  of OEST-2.5 (MEK soluble part); structure elucidation of the OEST-1.0 sample using ESI-MS; DSC curve of OEST-1.0; and DSC curves of EP-OEST11 (PDF)

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### Notes

The authors declare no competing financial interest.

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