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Microwave Assisted Closed-Loop Chemical Recycling of Multi-block PET-based Copolyesters

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Abstract

Thermoplastic copolyesters (TPCs), comprising segmented multiblock architectures, are frequently employed in high performance applications requiring enhanced mechanical and thermal properties. Among the various types of TPCs, poly(ethylene terephthalate) (PET) can be utilized as the rigid, semicrystalline block in the copolyester structure. These segmented copolyesters play an important role in engineering applications due to their outstanding physical properties and processability via injection molding. They are produced in various forms on the order of 100s of kilotons per year. Therefore, proposing an efficient chemical recycling method to address the accumulation of post-consumer TPCs is crucial. In this work, we demonstrate the straightforward and relatively fast methanolysis and glycolysis depolymerization of TPCs assisted by microwave radiation. Following microwave assisted depolymerization, sequential one-pot transesterification/polycondensation reactions were performed on either small scale (~3 g) or large scale (~ 40 g) to generate chemically recycled PET-based copolyesters. The depolymerization and sequential repolymerization approach applied to TPCs provides a new avenue for chemical recycling of relatively complex polymeric waste. Molecular, thermal and mechanical characteristics of the precursor copolyester and recycled structures were investigated through ^{1}H and ^{13}C NMR spectroscopy, SEC measurements, differential scanning calorimetry (DSC) and tensile testing, revealing that nearly identical material properties could be achieved.

Keywords: *Thermoplastic copolyester; microwave reaction; depolymerization; chemical recycling; methanolysis; glycolysis*

INTRODUCTION

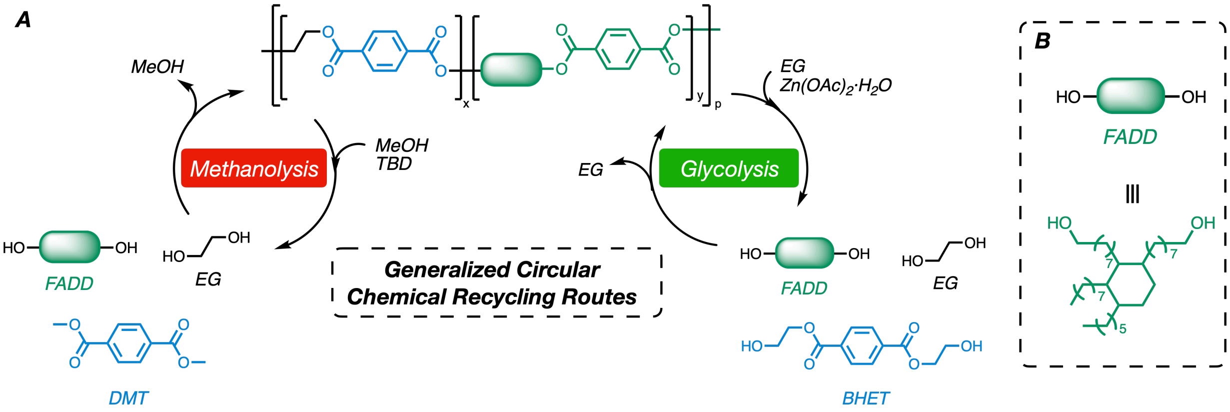
Enormous quantities of plastic are manufactured each year and there are very few end-of-life solutions in place to handle the associated waste streams.[1, 2] Annual global plastic waste generation is estimated to reach 460 million tons (MT) by 2030.[3] Mismanaged plastic waste has devastating consequences on the ecosystem and human health.[4] Circularity through recycling represents one of the most effective routes toward reducing the negative impacts associated with the current status quo.[5] Although plastic recycling toward circularity has made impressive progress with respect to commodity polymers, the technology enabling chemical recycling of more complex polymer constructs is still lagging far behind.[6]

Polyesters are promising candidates for chemical recycling via solvolysis, as the carbonyl groups are susceptible to nucleophilic attack.[7-9] Moreover, polyesters are pivotal in the current plastic industry, and their efficient chemical recycling plays a significant role in promoting a sustainable circular economy.[10] As a commodity thermoplastic polyester, poly(ethylene terephthalate) (PET) is in various applications and produced over 70 million tons annually, leading to significant accumulation of plastic waste.[11] Aside from the widespread utilization of PET in packaging and textiles, PET-based copolymers constitute a broad range of applications as well, including thermoplastic copolyesters (TPCs).[12, 13] TPCs are multiblock copolymers consisting of alternating hard and soft segments, in which the hard block is typically a semicrystalline polyester like PET or poly(butylene terephthalate). On the other hand, the soft block in TPCs contains a long chain, flexible polyol. Several efforts have been made to improve the sustainability of TPCs, for example by utilizing biobased components as feedstocks.[14] PET-based TPCs have been widely described, combined with several different soft blocks.[15-19] Owing to the relatively facile manner in which PET can be chemically transformed via esterification, several routes to upcycling post-consumer PET to various value-added products have been demonstrated.[20-25] In fact, several instances of upcycling *r*PET directly to high performance TPCs have been reported recently.[26-31] However, none of these examples demonstrate the chemical recycling of the complex upcycled products. Realizing full circularity in upcycled products remains a challenge.

Although conventional chemical recycling routes are frequently used for the depolymerization of PET, emerging technologies offer some advantages such as lower reaction temperatures.[32] In line with this idea, microwave-assisted depolymerization offers an efficient approach to PET deconstruction in the presence of various catalysts, utilizing lower temperature, and shorter reaction times.[33-36] In this scope, PET depolymerization via glycolysis was conducted utilizing microwave radiation for 5-40 min in the presence of various catalyst systems, including t-BuNH$_2$/Lewis acids, zinc acetate, and TBD.[37] In other work, microwave-assisted glycolysis of PET was accomplished utilizing ZnO catalyst, yielding 95% of BHET in 45 min.[38] Achilias and coworkers demonstrated the aminolytic depolymerization of PET under microwave irradiation, without using any external catalyst.[39] Zinc acetate, as a promising transesterification catalyst, was also used for the microwave assisted glycolytic depolymerization of PET, yielding 78% BHET in ~35 min.[40]

We have previously described the synthesis of TPCs from the conversion of bottle-grade post-consumer PET waste in the presence of complementary fatty acid dimer (FAD) soft blocks.[29, 30] This strategy proved effective for making a variety of different multiblock TPCs exhibiting a broad range of mechanical properties. Critically, these materials were constructed from post-consumer polyester feedstocks. However, we previously neglected to address end-of-life considerations for the upcycled TPCs themselves. Here, we demonstrate an efficient chemical recycling method for such multi-block PET-based copolyesters through microwave assisted depolymerization and subsequent repolymerization. We explored complementary depolymerization routes to find optimal conditions, including methanolysis and glycolysis as well as small (~ 3 g) and large (~40 g) scales. Ultimately, we were able to achieve mechanical properties matching those of the virgin copolymer. The circularity demonstrated here utilizes well-established and scalable depolymerization strategies (i.e., microwave), which have crucially never been applied to complex, high performance TPCs. This marks an important step toward expanding chemical recycling to a significantly wider swath of polymer waste streams. **Scheme 1** provides an overview of both the depolymerization and repolymerization steps explored in this work.

Scheme 1. Schematic illustration of microwave-assisted depolymerization of TPC composed of 50% PET (hard block) and 50% soft block via either methanolysis or glycolysis and subsequent repolymerization of the depolymerized mixture to achieve a closed-loop chemical recycling.



RESULTS AND DISCUSSION

We previously described the synthesis of mechanically robust TPCs with various compositions (i.e., ratio of soft- to hard-block), constructed from a combination of biobased and post-consumer recyclate feedstocks. In this work, we focus on one single multi-block composition, assuming that the conditions uncovered can be universally applied to polymers with similar molecular makeup. We started by exploring the optimal conditions for *r*PET homopolymer depolymerization, which we subsequently apply to the chemical recycling of more complex TPCs. Microwave-assisted depolymerization of *r*PET via methanolysis was carried out under various reaction conditions (**See Supporting Information, Table S1**). The conversion of *r*PET was found to be low (56–58%) after depolymerization reactions performed in the presence of 1 mol % (with respect to the *r*PET repeating unit) of zinc acetate catalyst at 160 °C for 1 h. Nearly complete conversion (93%) was achieved when the catalyst concentration and the temperature was increased to 2% and 185 °C, respectively. Nonetheless, the isolated depolymerization product, presumed to be DMT, was only slightly soluble in chloroform. This suggests that the depolymerization reaction of *r*PET may have remained at oligomer level or resulted in a mixture of oligomers and DMT. Since zinc acetate was not completely effective under the conditions we explored for depolymerization via methanolysis, an organometallic catalyst, TBD was utilized and almost complete conversion of *r*PET was accomplished even at lower temperature and catalyst concentration (**Figure 1A, left**). Still, the product obtained after depolymerization reaction at 160 °C for 60 min using TBD was not completely soluble in chloroform, suggesting incomplete transformation to the monomer DMT. Increasing the temperature to 185 °C enabled almost complete conversion of *r*PET in the presence of 2 mol % TBD after only 15 min and the resulting product was fully soluble in organic solvents. The integral ratios of the characteristic signals from ^{1}H NMR spectroscopy were consistent with the formation of DMT resulting from methanolysis of *r*PET (**Figure 1B and Figure S1**).

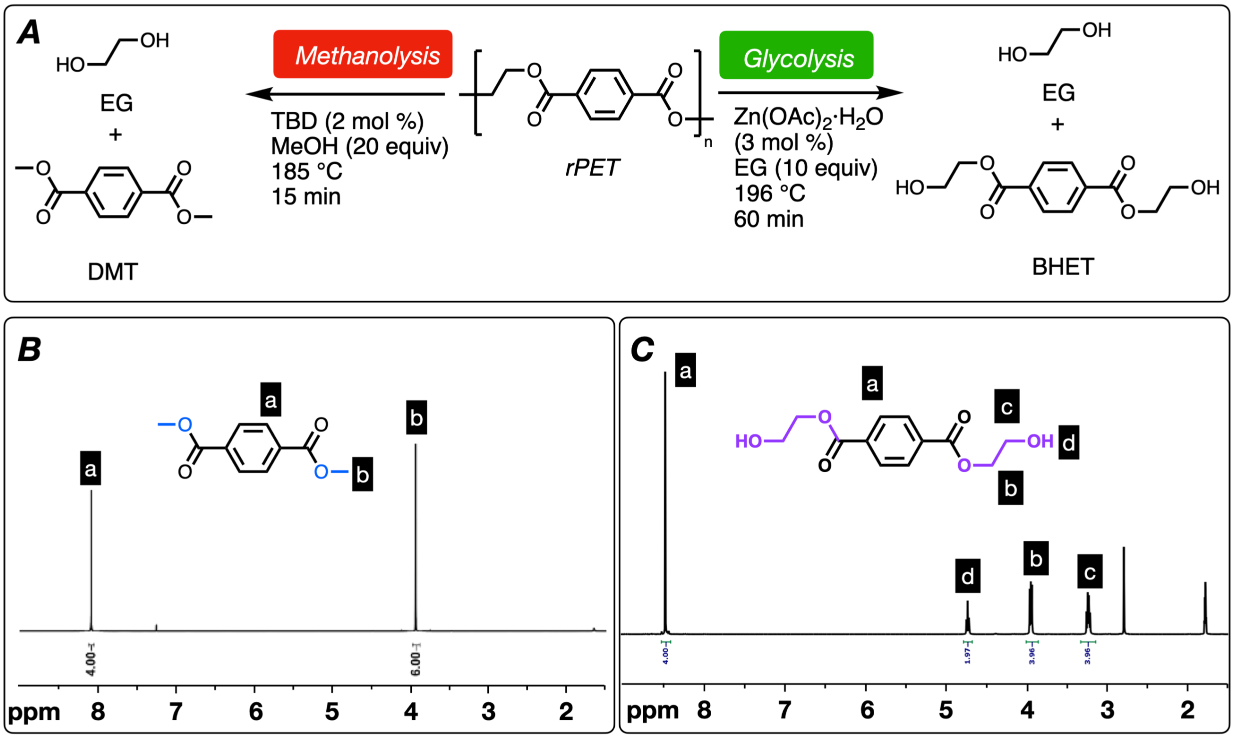


Figure 1. (A) Reaction conditions explored for the microwave assisted depolymerization of rPET via either methanolysis or glycolysis. ^{1}H NMR spectra for (B) isolated DMT after methanolysis in $CDCl_3$ and (C) isolated BHET after glycolysis in DMSO-d_6.

Although methanolysis-assisted depolymerization proved to be a fast and efficient method for depolymerization of rPET, the optimal depolymerization temperature (185 ºC) was well above the boiling temperature of methanol (b.p. = 65 ºC), leading to a rapid rise in pressure in the microwave reactor. This limitation prevented the upscaling of methanolysis depolymerization, and we anticipated this would compromise the implementation of such a method. In an effort to establish pathways that are more amenable to upscaling, microwave-assisted glycolysis using ethylene glycol (EG) was explored in parallel. Our aim with the alternative was primarily to avoid the pressure buildup associated with methanolysis.

Initially, microwave-assisted depolymerization of *r*PET via glycolysis was explored using $Zn(OAc)_2.2H_2O$ under various reaction conditions (**Figure 1A right**, **Table S2**). Based on the outcomes, glycolysis at 196 °C for 60 min using 3 mol % catalyst was selected as the optimal condition for *r*PET depolymerization (81% PET conversion). The ^{1}H NMR spectrum of the depolymerized mixture and of the isolated product after crystallization are consistent with BHET and EG in (**Figures 1C, S2** and **S3)**.

Chemical Recycling of TPCs via Methanolysis

In this study, we set out to investigate circular chemical recycling of TPCs by conducting microwave-assisted depolymerization of multi-block copolyesters, followed by direct repolymerization of the product mixture via conventional one-pot, two-step transesterification/polycondensation reactions. The conditions uncovered for *r*PET homopolymer deconstruction were translated to the TPCs in order to compare the potential for realizing full circularity. Two separate TPCs were synthesized using the previously described protocol (see Supporting Information). The source sample examined in the methanolysis experiments (TPC-A) had a molar mass consistent with samples previously described (M_n = 41.2 g/mol, M_w = 93.7 g/mol). The composition determined by NMR spectroscopy was approximately 51.1 wt % soft-block and 48.9 wt % hard-block. Microwave-assisted depolymerization of the segmented *r*PET-based copolyester was accomplished using catalyst concentrations ranging from 2 – 4 mol % at 185 °C for 15 minutes with supplemental methanol for transesterification deconstruction (**Figure 2A**). Overlaid ^{1}H NMR spectra revealed that each catalyst concentration was sufficient for nearly complete depolymerization of the TPC and the conversion of the terephthalate to DMT increased as the catalyst concentration increased (**Figure S4**). The conversion was determined from the aromatic protons associated with DMT at 8.09 ppm and the characteristic signal of methyl ester protons in DMT structure at 3.93 ppm. Additionally, methylene protons associated with EG and $–CH_2OH$ protons adjacent to the hydroxyl group in FADD were detected at 3.73 ppm and 3.62 ppm, respectively. The ^1H NMR spectra also exhibit signals associated with EG, which is liberated from the PET segments upon transesterification. The overall conversion was highest when 3 mol % TBD was used. To this end, 3% of TBD was chosen as the optimum catalyst concentration for the microwave-assisted methanolysis depolymerization of TPC (**Table 1, Figure S5**).

Table 1. Optimization of catalyst concentration for the depolymerization of TPC via methanolysis.

Entry	Catalyst Concentration[a] (*mol %*)	$\text{Conversion}_{\text{DMT}}$[b] (*%*)	$\text{Conversion}_{\text{EG}}$[b] (*%*)
TPCd1	2	85	37
TPCd2	3	88.5	49.2
TPCd3	4	96.1	36.7

[a]Per repeating unit in the precursor copolyester, TPC. [b]DMT and EG conversions were determined via ^1H NMR spectroscopy.

Initially, repolymerization reactions were carried out on a small scale (~ 3 g) using TPCd2 (**Figure 2A**; **Table 1**; from methanolysis). Notably, the small-scale (SS) reaction setup employs a small round bottom flask (25 mL) with a magnetic stir-bar, high temperature condenser, and a high vacuum with controller (**Figure S6**). We use the terms small and large scale here to differentiate between different reaction setups employed, acknowledging that all of the reactions performed in this work fit firmly into the category of laboratory scale. This allowed us to screen certain conditions for suitability in melt-phase polycondensation. Our strategy involved three main routes to determine the optimum repolymerization conditions for efficient chemical recycling. In the first scenario, the depolymerized product mixture, which was estimated to contain mainly DMT, EG and FADD according to the NMR spectrum, was directly repolymerized without adding any external reagent (i.e., nucleophile) or catalyst (*r*TPC-MeOH-SS-1). In a second trajectory, titanium (IV) tetrabutoxide/magnesium acetate (TBT/Mg-$(OAc)_2$), an industrial catalytic system, was added to the depolymerization mixture to investigate the effect of titanium-based catalyst on enhancing repolymerization efficiency (*r*TPC-MeOH-SS-2). Lastly, ethylene glycol, one of the main constituents of PET-based copolyesters, was incorporated excessively into the reaction mixture to accelerate the transesterification step, which leads to oligomerization (*r*TPC-MeOH-SS-3). In all cases, the transesterification step was completed at 200 °C in 2 hours, whereas the polycondensation step required 4 hours and the temperature was increased to 250 °C as the pressure gradually decreased to approximately 10^{-1} mbar. It should be noted that since DMT was used as the terephthalate derivative in the copolymer structure, methanol was generated as a condensate and could be easily removed at elevated temperatures (150–180 °C) and reduced pressure (**See Supporting Information for detailed procedure**). Moreover, EG, being a volatile diol, was driven off as a condensate during the repolymerization, resulting in molar mass buildup in the *r*TPCs. The resulting recycled copolyesters were evaluated for molecular, thermal and mechanical characteristics.

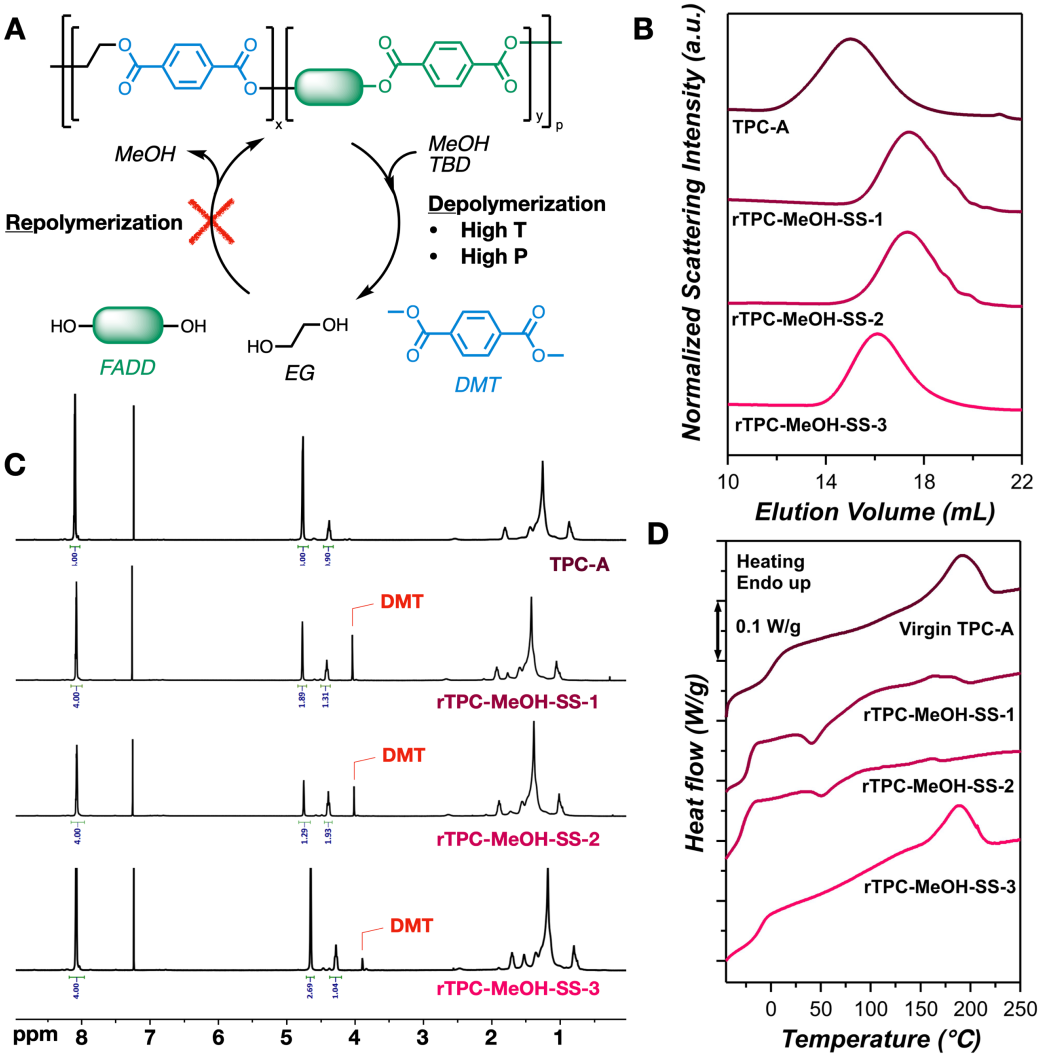


Figure 2. (A) Circular chemical recycling route via methanolysis. (B) SEC chromatograms (C) ^{1}H NMR spectra and (D) DSC heating thermograms of feedstock TPC-A and repolymerized small scale TPCs.

For the small-scale reactions, in which the depolymerized product was directly repolymerized without the addition of external reagents or catalysts, the recycled copolyester *r*TPC-MeOH-SS-1 was a viscous liquid after isolation. This observation strongly suggests low conversion and thus very low molar mass, which was consistent with SEC measurements (**Figure 2B**). Although the reaction efficiency improved with the use of a titanium-based catalyst (*r*TPC-MeOH-SS-2), the molar mass remained low compared with the original material. The addition of ethylene glycol was presumed to aid mobility and diffusion during repolymerization (*r*TPC-MeOH-SS-3). *r*TPC-MeOH-SS-3 exhibited the most comparable molecular weight (M_n = 13.6 kg/mol, M_w = 25.6 kg/mol) and dispersity ($Đ$) values to the precursor copolyester, TPC-A (M_n = 41.2 kg/mol, M_w = 93.7 kg/mol). Dispersities ranged from 2.3 to 1.9, consistent with the step-growth polymerization mechanism. These findings highlight the critical role of EG in facilitating effective polymerization and ensuring successful chemical recycling. However, although *r*TPC-MeOH-SS-3 has the most comparable molar mass with virgin TPC-A, the difference is still significant.

The chemically recycled copolyesters were investigated by ^{1}H NMR spectroscopy, and the polymer compositions were determined from the overlaid spectra (**Figure 2C**) and are tabulated in **Table 2**. The feedstock sample utilized here was TPC-A, which consists of approximately 50 wt % hard block and 50 wt % soft block. Among the recycled polyesters synthesized at small scale, *r*TPC-MeOH-SS-3 exhibited the most comparable composition to the original TPC-A, with 57.3 wt % soft block and 42.7 wt % hard-block. The same compositional analysis was performed for the other recycled structures, and *r*TPC-MeOH-SS-3 was found to be the most structurally consistent with the virgin copolyester. Specifically, the $–CH_2OH$ protons adjacent to the hydroxyl groups on the FADD polyol monomer, which comprises the soft block segment of the PET-based copolyester, shifted to δ 4.32 ppm after repolymerization. The $–CH_2$ protons associated with the enchained EG units were detected at δ 4.68 ppm. These characteristic signals were present in all recycled structures, suggesting at least partial repolymerization. However, signals corresponding to the methyl ester protons from the monomeric DMT units were detected at δ 3.93 ppm in both *r*TPC-MeOH-SS-1 and *r*TPC-MeOH-SS-2, consistent with incomplete incorporation into the polymer. The signal from DMT was substantially less intense in *r*TPC-MeOH-SS-3, highlighting the critical role of excess EG in driving the polycondensation and reducing unreacted end groups. This role was also highlighted as being crucial in the original recycling-based synthesis of the original TPCs. The exact extent of conversion is difficult to ascertain from the ^{1}H NMR spectra alone (*vide infra*).

Table 2. Molecular characteristics of the virgin TPC-A and chemically recycled copolyesters from ^{1}H NMR spectroscopy and SEC measurements.

Entry	mol % SB[a]	wt % SB[b]	wt % HB[c]	RI Detection[d]		
				M_n (kg/mol)	M_w (kg/mol)	Đ
Virgin TPC-A	23.1	51.1	48.9	41.2	93.7	2.3
*r*TPC-MeOH-SS-1	40.9	70.6	29.4	4.5	7.4	1.6
*r*TPC-MeOH-SS-2	59.9	83.8	16.2	6.3	11.8	1.8
*r*TPC-MeOH-SS-3	27.9	57.3	42.7	13.6	25.6	1.9

[a] Mol % soft block from FADD flexible diol determined from the integration of signals attributed to FADD compared with those from EG ^{1}H NMR spectra.

[b] Experimental wt % determined from relative integration of the FADD repeat units and the hard block (PET) repeat units in ^{1}H NMR spectra.

[c] Experimental wt % determined from relative integration of the hard block (PET) repeat units and FADD repeat units in ^{1}H NMR spectra.

[d] Determined by SEC, relative to polystyrene standards in chloroform.

Samples were examined using differential scanning calorimetry (DSC) to investigate their thermal characteristics (**Figure 2D**, **Table S4**). Both the glass transition temperature (T_g) and melting temperature (T_m) of *r*TPC-MeOH-SS-3 were lower than those of the feedstock TPC-A, which is likely attributed to the increased proportion of the aliphatic FADD-based soft block. The composition of soft block in the recycled *r*TPC-MeOH-SS-3 was 57.3 wt %, compared with 51.1 wt % in the original TPC-A. The T_g of the virgin TPC-A was determined to be 1 °C, whereas *r*TPC-MeOH-SS-3 exhibited a lower T_g. In line with expectations, the melting temperature also decreased from 191 °C to 188 °C due to the higher aliphatic content introduced by the FADD units in the recycled copolyester. The degree of crystallinity, X_c, was calculated from the melting enthalpy (ΔH_m), which was found to be 34% for the chemically recycled polymer, *r*TPC-MeOH-SS-3, compared to 31% for the virgin TPC-A. These thermal properties are consistent with the chemical compositions revealed by ^{1}H NMR spectroscopy. Among all samples, the virgin TPC-A and chemically recycled copolyester exhibited distinct crystallization temperatures (T_c) of 127 °C and 144 °C, respectively, upon cooling. Despite its higher content of flexible aliphatic segments, *r*TPC-MeOH-SS-3 displayed a higher crystallization temperature than the virgin TPC-A (**Figure S7**).

Lower total molar mass in the recycled sample may explain the crystallization at higher temperatures. However, cold crystallization was observed in samples where the crystallization temperature could not be clearly assessed, implying that enhanced chain mobility upon heating facilitates crystallization.

Chemical Recycling of TPCs via Glycolysis

Owing to the limitations associated with methanolysis, glycolysis was selected as an alternative depolymerization strategy for carrying out the TPC recycling (**Figure 3A**). The optimized condition established during rPET glycolysis was also translated to the depolymerization of the TPCs. **Table 3** summarizes the different conditions tested for depolymerization with EG. The ^{1}H NMR spectrum of the depolymerized TPC mixture (**Figure S8**) confirmed the presence of EG, FADD, and BHET. Microwave-assisted glycolysis depolymerization of these TPCs were also carried out using the optimal conditions using 5 g and 8 g TPC (**Figure S9**), demonstrating the potential for scalability of the process, at least within the limitations of the microwave equipment employed for this work.

Table 3. Optimization of catalyst concentration for the depolymerization of TPC via glycolysis.

Entry	Catalyst Concentration[a] (*mol %*)	V_{EG} (*mL*)	Temperature (*ºC*)	Time (*min*)	Conversion_{PET}[b] (*%*)
TPCd4	3	1.3	196	60	93.8
TPCd5	3	2.9	196	60	88.8
TPCd6	3	1.94	196	60	94.3
TPCd7	3	1.94	196	30	98.8

[a]Per repeating unit in the precursor copolyester, TPC. [b] PET conversion was calculated utilizing mass balance, $X_{PET} = (W_0 - W) / W_0$ where W_0 and W are the initial weight of PET and the unreacted PET weights obtained via filtration, respectively.

In the case of repolymerization, a large-scale reaction setup was employed for the repolymerization (**Figure S10**). Notably, this is the same reactor setup that was utilized to prepare the virgin TPCs, as described in our previous work.[29, 30] To guarantee that the helical impeller could be sufficiently submerged in the reaction mixture and provide efficient stirring, more material was needed for the large-scale (LS) repolymerization than for the small-scale setup. Since EG was already added in excess during glycolysis as the depolymerization agent, no additional EG was necessary for the subsequent repolymerization reaction, which simplifies the procedure. Two sets of repolymerization experiments were performed using the large-scale reactor. For rTPC-EG-LS-1, 15 g of the depolymerization mixture was used, while for rTPC-EG-LS-2, approximately 40 g was employed. All the other parameters were kept constant for both experiments. In each case, the depolymerized mixture was transferred to the reaction vessel along with antioxidant and TBT. The temperature was maintained at 200 °C for 2 h. Then, excess EG was removed by distillation under a progressive pressure reduction while the temperature gradually increased to 250 °C for the polycondensation step. When no further EG condensed at 250 °C under high vacuum, the torque reading of the overhead stirrer was reset to zero. The stirring speed was gradually reduced (**for more details see the Supporting Information**). The molecular, thermal, and mechanical properties of these TPCs generated via glycolysis are described in the following sections and compared with the previous experiments.

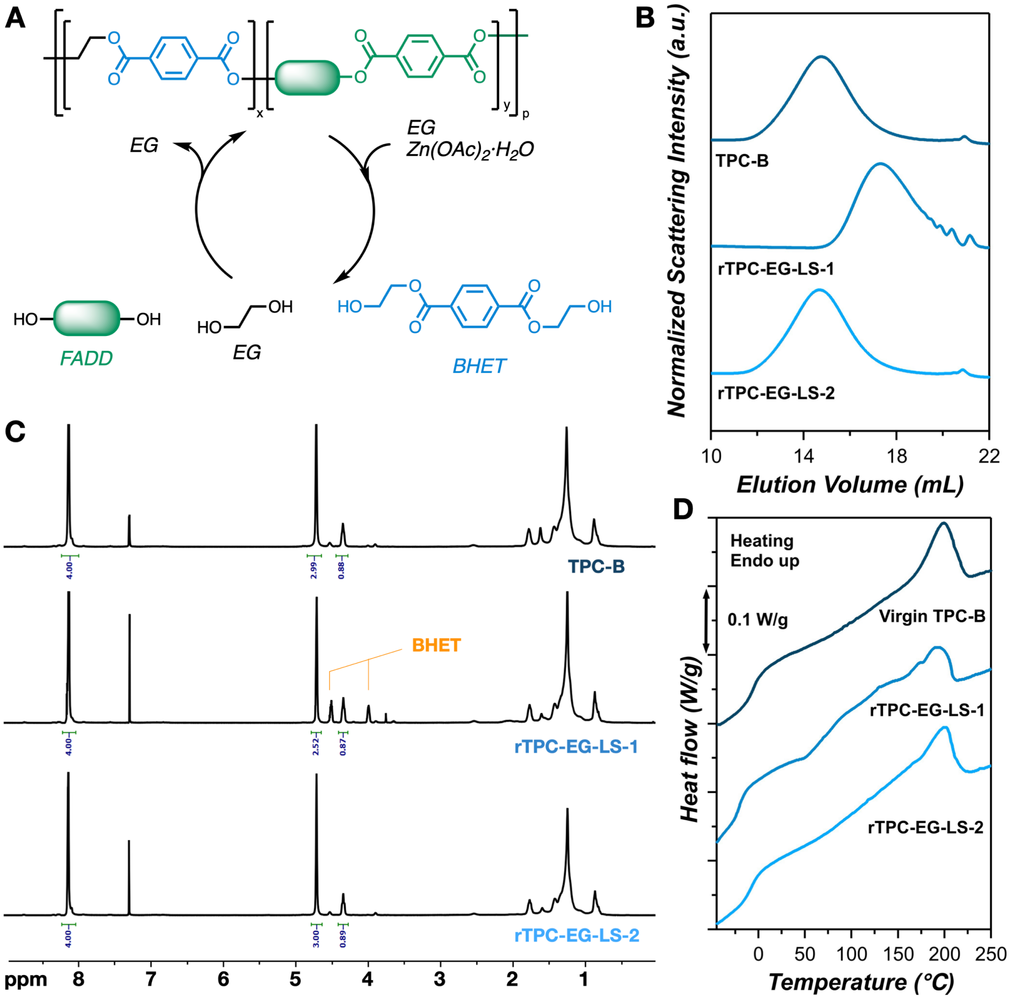


Figure 3. (A) Circular chemical recycling route via glycolysis. (B) SEC chromatograms (C) ^{1}H NMR spectra and (D) DSC heating thermograms of feedstock TPC-B and repolymerized large scale TPCs.

TPC-B and the recycled copolyesters produced using the large-scale reaction setup show dramatically different outcomes with respect to molar mass (**Figure 3B; Table 4**). Repolymerization reactions using the large-scale reactor were carried out with 15 g (*r*TPC-EG-LS-1) and 38 g (*r*TPC-EG-LS-2) of the depolymerized mixture. GPC results indicated that *r*TPC-EG-LS-1 had a relatively low molar mass (M_n = 2.43 kg/mol, M_w = 6.35 kg/mol). During the reaction, nearing complete distillation of excess EG, the impeller was no longer immersed in the reaction mixture and failed to stir it effectively. This essentially halted the reaction and prevented high molecular weight from being reached (see **video 1**, Supplementary Information). In contrast, during the synthesis of *r*TPC-EG-LS-2, the impeller remained immersed and was able to effectively stir the reaction mixture even after complete removal of EG (see **video 2**, Supplementary Information). This enabled proper mixing during the polycondensation stage and resulted in a high molecular weight TPC (M_n = 39.4 kg/mol, M_w = 109.4 kg/mol) comparable to and even surpassing that of feedstock TPC-B (M_n = 35 kg/mol, M_w = 82.2 kg/mol).

^{1}H NMR spectra of the virgin TPC-B, *r*TPC-EG-LS-1, and *r*TPC-EG-LS-2 indicate relative compositions in the starting material and final products (**Figure 3C)**. The soft and hard block contents for both virgin and repolymerized TPCs were calculated from the ^{1}H NMR spectra and are summarized in **Table 4**. The results indicate that *r*TPC-EG-LS-2 has a comparable soft and hard block composition to virgin TPC-B. For virgin TPC-B, the soft and hard block contents are 50.5% and 49.4%, respectively, and for *r*TPC-EG-LS-2, they are 50.7% and 49.2%, respectively. On the other hand, the soft and hard block contents for *r*TPC-EG-LS-1 are 54.5 and 45.5, respectively. Moreover, BHET peaks are still present in the NMR spectrum of *r*TPC-EG-LS-1 sample, further indicating incomplete repolymerization under this condition. We attribute this to insufficient stirring of the reaction mixture by the impeller if not sufficiently submerged in the melt.

Further insight into the segmental composition was obtained via ^{13}C NMR spectroscopy, which revealed the distribution of dyad sequences for both the precursor and recycled PET-based copolyesters (**Figure S11 and Table S3**). Notably, the average sequence length of the soft and hard blocks in a segmented copolyester significantly influences its mechanical properties. In a fully randomized copolymer, these segments reach their minimum average length. The degree of randomness (R) was calculated using an established equation (**see Supporting Information**) and found to be close to unity for both the precursors and recycled copolyesters, consistent with a nearly random distribution of segments.

Table 4. Molecular characteristics of the virgin TPC-B and chemically recycled copolyesters from ^{1}H NMR Spectroscopy and SEC measurements.

Entry	mol % SB[a]	wt % SB[b]	wt % HB[c]	RI Detection[d]		
				M_n (kg/mol)	M_w (kg/mol)	Đ
Virgin TPC-B	22.7	50.5	49.4	35	82	2.35
*r*TPC-EG-LS-1	25.6	54.5	45.5	2.4	6.4	2.61
*r*TPC-EG-LS-2	22.9	50.7	49.2	39	109	2.78

[a] Mol % soft block from FADD flexible diol determined from the integration of signals attributed to FADD compared with those from EG ^{1}H NMR spectra. [b] Experimental wt % determined from relative integration of the FADD repeat units and the hard block (PET) repeat units in ^{1}H NMR spectra. [c] Experimental wt % determined from relative integration of the hard block (PET) repeat units and FADD repeat units in ^{1}H NMR spectra. [d] Determined by SEC, relative to polystyrene standards in chloroform.

For the synthesized materials using the large-scale reactor, *r*TPC-EG-LS-1 exhibited lower T_g and T_m values (–24 ºC and +191 ºC) compared to virgin TPC-B (–11 ºC and +199 ºC) (**Figure 3D; Table S4**). In contrast, T_g and T_m values for *r*TPC-EG-LS-2 (-13 ºC and 200 ºC) were comparable to those of virgin TPC-B, demonstrating the potential of the large-scale method in successfully repolymerize the depolymerized mixture into TPCs with thermal properties like the virgin material. However, the calculated X_c for *r*TPC-EG-LS-2 was 20%, which is lower than that of virgin TPC-B which is (29%).

Mechanical properties of recycled TPCs

In terms of physical/mechanical properties, it was visually evident that the materials made in a small-scale via the methanolysis route may be limited in terms of molar mass. Stirring of the reaction mixture – with a magnetic stir-bar – continued throughout the reaction at high temperature, consistent with a relatively low viscosity. The isolated, repolymerized materials were qualitatively brittle and had a consistency in line with low molar mass compared with the very tough starting TPC-A and TPC-B (**Figure 4A and 4B**). In contrast, the samples made in parallel employing a more powerful mechanical stirrer (i.e., large scale) was visually very different. The final isolated materials produced on large scale, while differing substantially in color, had the mechanical feel similar to the starting TPC, most especially the *r*TPC-EG-LS-2 (**Figure 4C and 4D**).

The mechanical characteristics of virgin TPCs and chemically recycled PET-based copolyesters were assessed quantitatively at room temperature using uniaxial tensile testing at a strain rate of 50 mm/min. Dumbbell-shape specimens were first prepared by melt pressing at 220 °C (See the Supporting Information). Both virgin TPCs and chemically recycled copolyesters exhibited discoloration (i.e., yellowing) after melt pressing, likely due to thermal degradation; however, the color was more pronounced in the repolymerized samples. The mechanical properties of copolyesters were evaluated in terms of elastic modulus (E), stress at break, and strain at break. The starting material TPC-A and the repolymerized sample *r*TPC-MeOH-SS-3 exhibited markedly different responses (**Figure 4E**). While TPC-A is ductile and tough, *r*TPC-MeOH-SS-3 was very brittle, albeit with similar elastic modulus. This behavior is in line with the incomplete conversion during repolymerization and the low molar mass measured by SEC. This highlights the limitations of the experimental setup employing methanolysis combined with magnetic stirring.

Although dog-bone samples could be prepared by melt pressing the *r*TPC-EG-LS-1 material, the samples were extremely brittle owing to the relatively low molecular mass. We focused instead on *r*TPC-EG-LS-2 compared with the starting TPC-B (**Figure 4F**). According to the stress-strain curves, the Young's modulus was 37.0 ± 4.0 MPa for virgin TPC-B and 30.2 ± 1.0 for *r*TPC-EG-LS-2, exhibiting comparable stiffness. The maximum stress values were 31.2 ± 3.4 MPa for virgin TPC-B and 29.3 ± 3.5 MPa for *r*TPC-EG-LS-2, respectively. The strain at break was 1090 ± 84% and 1300 ± 170% for virgin TPC-B and *r*TPC-EG-LS-2, respectively. These findings imply that mechanical properties comparable to those of virgin TPCs can be attained by the chemically recycled copolyester produced using the large-scale setup.

This is explained by the setup's capacity to guarantee efficient mixing of the reaction mixture, especially during the polycondensation stage, when the viscosity dramatically rises. In particular, the use of an impeller helps to achieve this. To attain a high molecular weight and mechanical performance comparable to that of virgin TPCs, proper mixing is crucial at the polycondensation stage. In contrast, the small-scale synthesis, which relies on a simple stirring bar, is only effective during the initial stages of the reaction. During polycondensation, the inadequate mixing prevents the system from reaching a high molecular weight, resulting in deteriorated mechanics compared to virgin TPCs.

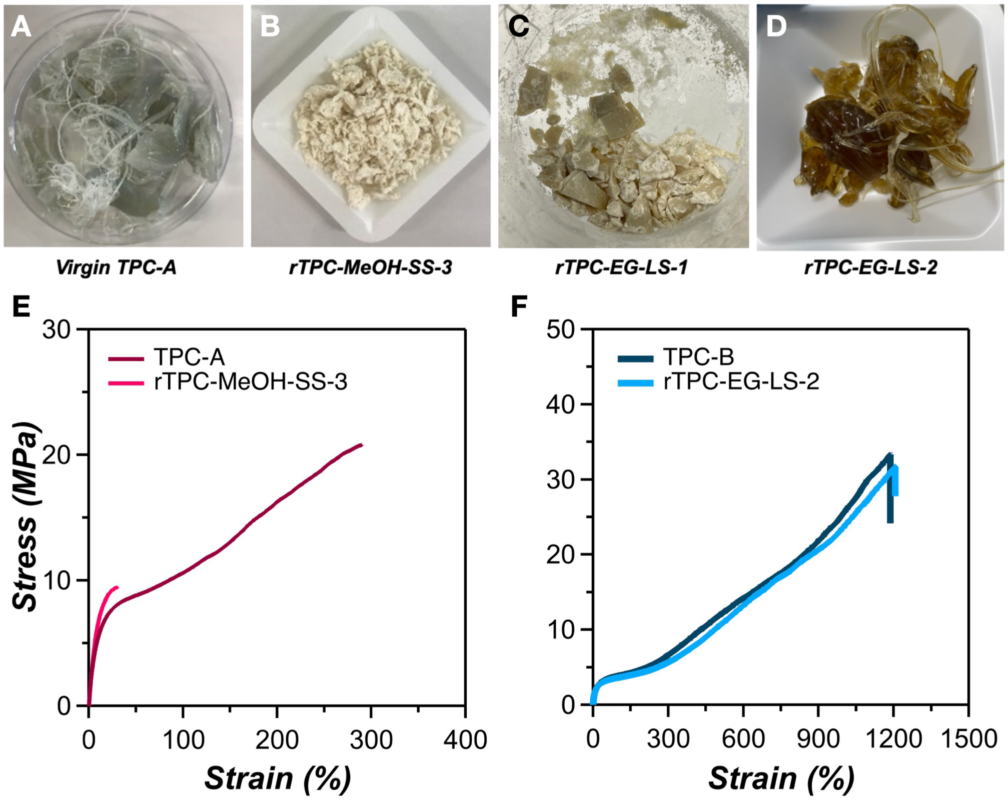


Figure 4. (A) Photograph of starting material TPC-A and additional photographs of (B) *r*TPC-MeOH-SS-3 (C) *r*TPC-EG-LS-1 and (D) *r*TPC-EG-LS-2. (E) Tensile stress-strain measurements for TPC-A and *r*TPC-MeOH-SS-3 and (F) TPC-B and *r*TPC-EG-LS-2.

Green Chemistry metrics

This research is part of a broader investigation into establishing more sustainable practices to generate already existing, commercial materials platforms, such as polyester-based TPCs. We have therefore taken measures to try to ensure that sustainability driven principles are employed at the various steps.[41] It is worthwhile to consider the different aspects here, at least in a qualitative way to compare the upcycling approach with the standard manufacturing of segmented thermoplastic copolyesters.[42] First, the inputs/monomers for the first-generation TPCs used in this work came from a combination of post-consumer recycled streams (rPET) and renewable streams (FAD). There has been detailed life-cycle analysis (LCA) performed for a variety of PET recycling protocols, with the general conclusion pointing toward lower fossil fuel depletion for rPET.[43-45] There are also important aspects of the LCA that point toward areas that need improvement to make serious gains in terms of energy inputs, water usage, and others. The process for commercial manufacturing of FAD is proprietary, but LCA suggests several strong incentives especially in the non-renewable resource for building blocks with comparable properties.[46] For example, formulations for polyester resins containing renewable FAD showed significantly improvements in climate change total and ozone depletion categories, while suffering in categories related to acidification, eutrophication, and renewable primary energy categories.[47]

The E-factor (kg waste/kg product) and reaction mass efficiency (RME) reflect the amount of products generated compared with inputs.[48, 49] For our process, the E-factor is relatively low, considering that there are no solvents employed and the ethylene glycol is recovered > 90%. Therefore, the E-factor is estimated to be less than 1, which is comparable to estimates for chemical recycling routes for polyesters having similar structures.[50, 51] The energy efficiency in our process is likely very similar to the industrial process, which is difficult to escape since in all cases the polymerization is performed in the melt ($> T_{m,PET}$), and the polycondensation requires hours due to mass transfer limitations in a viscous polymerization fluid. This is also reflected in several LCAs. However, there is a significant advantage to developing processes that fit seamlessly into existing commercial infrastructure, as new plants do not need to be constructed to implement these recycling routes.[52] Therefore, the largest gains in this approach appear to be in fossil fuel depletion, where the principles of circularity suggest significant savings by avoiding the use of virgin fossil-based carbon sources.

CONCLUSION

We successfully demonstrated the closed-loop chemical recycling for a multi-block TPC comprised of PET and dimer fatty acid segments. The depolymerization of the TPC was achieved using two different catalyst-reactive diluent systems and assisted by a microwave reactor. The first conditions involved methanolysis of the PET segments via transesterification catalyzed by TBD. While this was an effective strategy for depolymerizing the mixture fully to monomers, the conditions were not amenable to scale-up owing to pressure buildup at relatively high temperatures. Therefore, the second depolymerization strategy was pursued, wherein glycolysis was performed with a $Zn(OAc)_2$ catalyst system. This pathway was also successful at depolymerization, leading to a monomeric mixture containing almost exclusively fatty acid dimer diol and BHET. This second pathway was possible to perform on a larger scale (> 15 g), enabling the repolymerization/polycondensation to be performed at a larger scale as well (>40 g). Several different circular recycling polycondensation attempts were made, ranging from a small scale (~ 25 mL) reactor employing a magnetic stir-bar to a customized large scale (1 L) reactor equipped with a high-powered mechanical overhead stirrer. Consistent with the industrial production of condensation polymer, all repolymerizations were conducted in the melt (i.e., solvent-free). As such, the reaction mixture becomes highly viscous even at relatively low conversion, requiring significant torque to maintain efficient mixing. Furthermore, the step-growth mechanism requires very high end-group conversion to reach meaningfully high molar mass. As is typical for commercial-scale melt polycondensations with low concentrations of reactive end-groups toward the end of the reaction, driving the reaction to high conversions requires continuous renewal of the surface area via strenuous mixing. Left to diffusion alone (i.e., with no mechanical agitation), the small-scale reactions in our case yielded samples with only modest molar mass. This points to the critical importance of efficient mass transfer in achieving circularity in such polycondensations. By demonstrating that multi-block materials containing polyester as a component can be chemically recycled, we have significantly expanded the potential for materials recycling in general. Even materials with relatively complex molecular makeup are capable of being efficiently deconstructed. This represents just one piece of the recycling value chain, and this technology should be complemented by suitable collection and sorting activities. With proper organization, this approach would allow a much wider swath of high performance TPCs already on the market to be captured and reconstructed, saving precious fossil-based virgin feedstocks.

ASSOCIATED CONTENT

Supporting Information

Additional experimental details, materials, and methods, including photographs of experimental setup and reaction product mixtures, ^{1}H NMR spectra of all compounds, and tables of supplemental data. This material is available free of charge via http://pubs.acs.org.

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