



One-Pot Depolymerization and Polycondensation of PET Based Random Oligo- and Polyesters

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Abstract

The glycolysis of PET is a promising well-developed technique that could be utilized in a wide range of processes. Due to its equilibrational nature, the high ratio of reagents and the purification steps it is an expensive process. In this study our goal was to modify the standard glycolysis to an easily modulateable method (acido-alcoholysis) suited for one-pot oligoester, polyester synthesis. Adipic acid was added to the depolymerization reaction to connect low molecular weighed components into oligoesters. PET depolymerization reaction series were carried out with ethylene-glycol/adipic acid and butane-1,4-diol/adipic acid to demonstrate the tuneability of these systems. The reaction products were thoroughly characterized with NMR, FTIR, TGA, DSC and functional group analysis. One-pot depolymerization-polycondensation reactions were engineered to produce unsaturated and saturated polyesters. The unsaturated polyesters were dissolved in styrene, cross-linked and moulded to be characterized with DMA. A decreasing tendency of the glass transition temperature and cross-link density were found in the function of the ratio of adipic acid used during the depolymerization step. Acido-alcoholysis proved to be a versatile technique that could be used to engineer oligoesters and polyesters. The reagent use can be minimalized, and the raw reaction products can be directly applied as mid-products.

Keywords One-pot reaction · Polyesters · Acido-alcoholysis · NMR

Introduction

The glycolysis of poly(ethylene-terephthalate) (PET) has been the focus of numerous researches for the past 40 years. A wide range of studies have been made to optimize this reaction and gain yields as high as possible of bis(2-hydroxyethyl)-terephthalate (BHET) or other terephthalic-acid derivate diesters [1–18]. This technique allowed the recycling of PET waste that could not be further used and recycled by mechanical techniques like extrusion or injection moulding [19–22]. In most cases, the primary goal of glycolysis and other techniques such as methanolysis or hydrolysis was to reproduce PET and gain a new virgin

material with identical or better properties than the original material [23–28]. Several methods like chain-extension during a reactive extrusion process were introduced the elongate the lifetime of the PET polymer were studied and developed [29–31]. But the hydrolytic or thermal degradation processes during use and mechanical recycling inevitably degrade the polyester to a level it cannot be used further [32–36]. Thus, the solvolysis of PET, chemical recycling, in general, should be used in a greater extent, in an industrial scale. The glycolysis of PET is an equilibrational reaction that requires a high ratio of diol reagent and advanced catalysts to push it towards BHET production to gain high yields (Fig. 1). Depending on the goal of the solvolysis the reaction parameters can be tailored to produce BHET or oligomers that could be further used in new reactions [5, 18, 37–43]. Usually, oligomers are discarded during the purification processes, only a few studies used these or the raw solvolysis product [44–48]. In most of the cases, the purpose of glycolysis is the reproduction PET via BHET. As a result, the development of new, more efficient and recyclable catalyst become the focus of several research groups. Renewable heterogenous catalyst can be easily removed from the reaction mixture,

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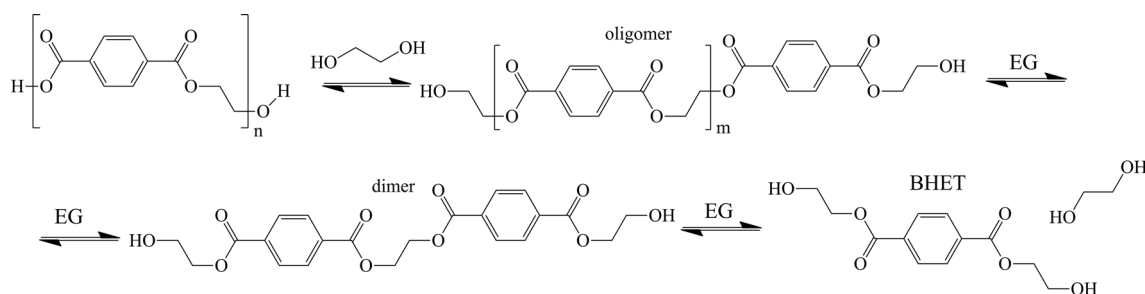


Fig. 1 The reaction route of PET glycolysis with ethylene-glycol

they have a high catalytic activity that easily rival and could exceed traditional transesterification catalysts, such as metal salts. [2, 4, 8–10, 15] The use of Fe_3O_4 and Fe_2O_3 particle based catalyst reached over 90% selective BHET yields even after several uses. [8, 15] The increasing efficiency of these processes maintains, or rather furthers the sustainability of plastics. Despite these advances, chemical recycling is still considered an expensive method due to the high volumes of chemicals and the necessary purification steps.

Solvolytic products of PET have been considered as feedstock for other plastic types, especially for unsaturated resins (USR). The synthesis of such materials consists of several steps beginning with the solvolysis of PET. The terephthalic acid derivatives further processed, modified even with bio-based compounds such as oleic acid and cellulose derivatives in separate reactions. [49–55] The omission of monomer extraction and utilizing oligomers that are mostly perceived as side products could considerably reduce the cost of PET derived unsaturated resins. One-pot type resin production has been considered before and it could prove to be an ideal solution to cut expenses. The control of condensation time allows the fine-tuning of cross-link density. The lower the molar weight of the resin the lower the T_g and the looser the network becomes [49]. The modification of unsaturated polyesters has been widely carried out with saturated diacids. They have been shown to be able to tune cross-link density and increase impact strength. [50].

Diacid components have been rarely introduced into depolymerization reactions. In our previous work, we experimented with the simultaneous use of diacids and diols during solvolysis (acido-alcoholysis) and compared it to glycolysis and acidolysis. The simultaneous use of diacids and diols resulted in higher molar weight and the complete absence of reagents in the reaction. [47].

In this study, we have introduced a dicarboxylic-acid component into the glycolysis system to make oligomers and to use the raw solvolysis product to produce polymeric materials (Fig. 2). Our goal was to design a multiple-step reaction process, that can be easily modified to gain different, fine-tuned products and can be implemented as a one-pot type process. The diacid component was intended

to react with the lower molar weight components, thus the low molar weight components are incorporated into the reaction product. These carboxyl and hydroxyl terminated oligoesters could be further used in polyurethanes or resinous crosslinked systems. As a result, the reaction product (oligomers) can be used without any purification steps and there is no need to use high amounts of diols to gain pure BHET.

Experimental

Materials

Arnite[®] D00301 PET homopolymer granules from DSM were used for chemical recycling. Adipic acid (99%) was purchased from TCI (Tokyo Chemicals Industry). Ethylene-glycol (99%), concentrated hydrochloric acid (37%), sodium-hydroxide (99%), methanol (99.18%) and pyridine (99%) were purchased from Molar Chemicals (Halásztelek, Hungary). Zinc-acetate-dihydrate [$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ AnalR Normapur[®]] was purchased from BDH chemicals. Maleic-anhydride (98 + %) and phthalic-anhydride (99%) was purchased from AlfaAesar. Deuterated chloroform (DCCl_3 99%), butane-1,4-diol (99%), styrene (99%), titanium^{IV}-butoxide (97%) and cobalt^{II}-2-ethylhexanoate solution (65% in mineral spirits) was purchased from Sigma-Aldrich. Butanox M50 (33% methyl-ethyl-ketone-peroxide solution, Akzo Nobel GmbH) commercial initiator solution was purchased from Novia Kft. (Halásztelek, Hungary).

Depolymerization of PET

The chemical recycling, depolymerisation of PET was carried out in a 250 cm³ four-necked glass flask equipped with a mechanical stirrer, a gas inlet (inert Ar atmosphere) and a thermometer. The PET granules (80 g), the ethylene-glycol (EG) (25.8 g) and the adipic acid (AdAc) were weighed in according to the calculated 1:1:x molar ratio (Table 1). The ratio of the PET repeating units, EG and the adipic acid was 1:1:0; 1:1:0.1; 1:1:0.2; 1:1:0.3; 1:1:0.4 and 1:1:0.5. 0.8 g

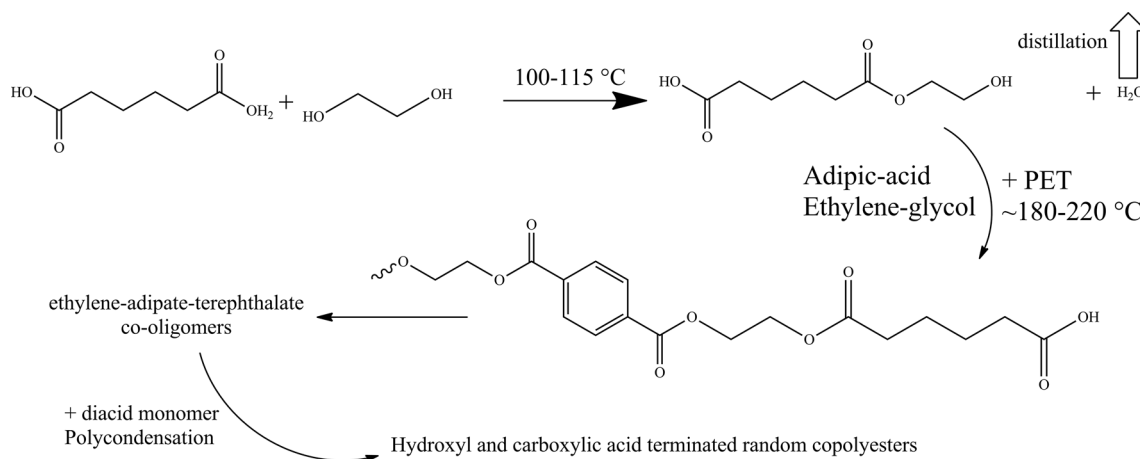


Fig. 2 The reaction route of acido-alcoholysis depolymerization reaction and one-pot polycondensation with ethylene glycol and adipic -acid

Table 1 Feed data table of the depolymerization and the unsaturated polyester condensation reactions. The weight percentages are calculated from the weight of PET (depolymerization) depolymerization product (PET:But:Adac x)

	Adac 0	Adac 0.1	Adac 0.2	Adac 0.3	Adac 0.4	Adac 0.5
PET:EG:Adac system						
PET	80 g					
Zn(OAc) ₂	0.8 g/1 m/m% of PET					
EG	25.83 g/32.9 m/m% of PET					
AdAc	0 g	6.09 g	12.17 g	18.27 g	24.37 g	30.43 g
	0%	7.61%	15.21%	22.83	30.46%	38.04%
PET:But:Adac system						
PET	80 g					
Zn(OAc) ₂	0.8 g/1 m/m% of PET					
But	37.53 g/46.91 m/m% of PET					
AdAc	0 g	6.09 g	12.17 g	18.27 g	24.37 g	30.43 g
	0%	7.61%	15.21%	22.83	30.46%	38.04%
Condensation of unsaturated polyesters						
PET:But:Adac x	80 g					
MA	22.38 g	12.90 g	12.80 g	10.50 g	8.60 g	7.09 g
	27.90%	16.12%	16.00%	13.12%	10.74%	8.87%

of zinc-acetate (1% of PET) was used as a transesterification catalyst. The reaction mixture was first heated up to 130–150 °C, during this phase the esterification reaction of the EG and adipic acid took place. The reactions were followed with the temperature of the distilling apparatus equipped to the reactor. After 30 min the distillation stopped, and a reflux condenser was equipped to the reactor. Then the reaction mixture was heated up to 220 °C and was kept at that temperature for 4 h. At the end of the reaction, the transparent/semi-transparent reaction mixture was poured into an alumina pan. Functional group analysis (hydroxyl and acid content) was done to determine the amount of excess amount of diacid for the one-pot depolymerization and polymerization reaction. The reaction products were white, soap-like materials at room temperature.

The depolymerization reaction was also carried out with butane-1,4-diol (But) with the same molar ratios as listed before [80 g PET, 37.5 g But, x AdAc, 0.8 g Zn(OAc)₂·2H₂O] and conditions as described previously. This depolymerization series was further reacted with maleic-anhydride to gain unsaturated polyesters. The functional group content of these products was measured. The amount of maleic-anhydride was added to reach 1:0.9 hydroxyl:acid group ratio (Table 1). The acid ratio was calculated from the sum of the residual acid groups and the anhydride, that was counted as two acid groups. 80 g of the raw depolymerization product was weighed in a four-necked 100 cm³ glass flask. The reaction product was heated to 150 °C to melt it, then the calculated amount of maleic-anhydride was added to the reaction mixture. The reactor was equipped with a gas inlet (argon gas bubbling),

thermometer, distillation inlet and a mechanical mixer. The reaction mixture was heated to 180 °C and was kept there for 1 h. The condensation was followed via the thermometer of the distilling apparatus. The distillation usually stopped after 30 min. At the end of the reaction the reaction mixture was poured into an alumina pan. It was stored in a plastic container in argon atmosphere at 5 °C until further use.

One-Pot Synthesis of Saturated Random Polyester

The depolymerization part of the one-pot reaction was carried out as explained previously. A 1:1:0.3 ratio of PET (118.5 g), EG (38.30 g) and adipic acid (27.03 g) was used for this reaction. The required amount of excess adipic acid was calculated from the depolymerization reaction series. The excess adipic acid amount was calculated so a stoichiometric (1:1) ratio of acid and hydroxyl groups is present during the polycondensation. After the end of the 4 hour-long isothermal depolymerization period, the reaction mixture was cooled to 110–120 °C. Then 2 cm³ of Ti^{IV}-butoxide catalyst and 43.5 g of adipic acid was added to the mixture. A distilling inlet was equipped to the reactor and the mixture was heated to 220 °C. Distillation (1 h) was used to remove the water from the reaction mixture. After the distillation stopped a vacuum apparatus was connected to the reactor through a dry ice-acetone bath trap. The polycondensation reaction in a vacuum (100 mbar pressure) with constant argon bubbling was maintained for 4 h. At the end of the reaction, the reaction mixture was poured into an alumina pan.

One-Pot Synthesis of Unsaturated Random Polyester

The depolymerization part of the one-pot reaction was carried out as explained previously. A 1:1:0.4 ratio of PET (80 g), butane-1,4-diol (37.5 g) and adipic acid (6.08 g) were used for this reaction. The required amount of excess maleic-anhydride (15.11 g) was calculated from the depolymerization reaction series. The excess maleic-anhydride amount was calculated so a near stoichiometric (1:0.9) ratio of acid and hydroxyl groups is present during the polycondensation. After the end of the 4 hour-long isothermal depolymerization period, the reaction mixture was cooled to 110–120 °C. Then 15.11 g of maleic-anhydride was added to the mixture. A distilling inlet was equipped to the reactor and the mixture was heated to 180 °C. Distillation (1 h) was used to remove the water from the reaction mixture. At the end of the reaction, the reaction mixture was poured into an alumina pan. The reaction mixture was

kept in a closed plastic container in argon atmosphere at 5 °C until further use.

Preparation and Moulding of Unsaturated Resins

The unsaturated polyester (PET:But:AdAc + MA) was weighed in a 50 cm³ four-necked glass flask equipped with a reflux condenser, thermometer, a gas inlet (Ar atmosphere) and mechanical stirrer. The unsaturated polyester was heated to 180 °C to gain a homogenous melt, then it was let to cool down to 80 °C. Hydroquinone (0.01%) was added as an inhibitor and styrene (40%) were added as a reactive-solvent and cross-linker. Cobalt^{II}-2-ethylhexanoate solution (0.03%) was used as an activator during the crosslinking reaction. The mixture was vigorously mixed for 30 min to dissolve the unsaturated polyester in the styrene. The clear mildly pink solution was let to cool down to room temperature. The resin solution was immediately used to mould “dogbone” shaped specimens for DMA (dynamic mechanical analysis) measurements. Butanox M50 (3%) (~33% methyl-ethyl-ketone peroxide solution) solution was used as initiator. The specimens were cross-linked in a Heraeus® UT series drying oven at 90 °C for 3 h, then they were heat-treated at 175 °C for 1 h.

Characterization

Functional Group Analysis, Solution Viscosimetry

The acid content of the depolymerization products was determined with a standard titration method. Three samples (1.5 g) were weighed into Erlenmeyer flasks on an analytical balance. 25 cm³ pyridine was used to dissolve the samples. The solutions were heated in an oil bath (110–120 °C) to dissolve the reaction products. The solutions were let to reflux for 30 min. Then the samples were titrated with 0.1 M methanolic sodium-hydroxide solution in the presence of phenolphthalein indicator. Three samples and a blank-sample were titrated to calculate the residual acid content.

Hydroxyl group content of the depolymerization products was measured with a back-titration method. 80 g of phthalic-anhydride was weighed and 500 cm³ in pyridine in a brown-glass flask to produce 1 M reagent solution. The mixture was stirred with a magnetic stirrer until the phthalic-anhydride completely dissolved. The reagent solution was let to rest for a day before use. Three samples (1.3–1.4 g) were weighed in into Erlenmeyer flasks. 25 cm³ 1 M phthalic-anhydride in pyridine reagent solution was added to the samples. Then the samples were heated in an oil bath (115 °C) and let to reflux for 2 h. 50 cm³ pure pyridine was added to the samples through the condensers. The samples and a blank sample were titrated with 0.5 M aqueous sodium-hydroxide

solution. Three samples and a blank-sample were titrated to calculate the residual hydroxyl content.

An Ubbelohde type capillary viscosimeter was used to compare the intrinsic viscosity of the depolymerization and the polymerization reaction products. Three samples with 0.05 g cm^{-1} , 0.075 g cm^{-1} and 0.10 g cm^{-1} were prepared. The samples were dissolved in pyridine and were let to reflux at $115 \text{ }^\circ\text{C}$ until the solutions were clear. The capillary viscosimeter was thermostated at $75 \text{ }^\circ\text{C}$ during the measurements. Intrinsic viscosity was calculated from extrapolating the relative and reduced viscosity functions to zero concentration.

Molecular Structure Identification

Bruker Tensor 27 FTIR spectrometer (ATR, 28 scans) was used to characterize the general molecular structure of the depolymerization and the polymer samples. Bruker Avance 500 spectrometer was used to measure the ^1H NMR spectra of all the reaction products. Bruker Avance 300 spectrometer was used to measure the ^{13}C , DEPT, ^1H - ^{13}C COSY, ^1H - ^1H NOESY, ^1H - ^{13}C HSQC and ^1H - ^{13}C HMBC spectra. The reaction products were dissolved in deuterated chloroform (DCCl_3 , $\sim 30 \text{ mg cm}^{-3}$ concentration). The temperature of acquisition was $30 \text{ }^\circ\text{C}$. The PET:EG:AdAc depolymerization series products showed limited solubility on the chloroform solvent at room temperature, only ^1H spectrum were recorded. The 2D correlative measurements were done on the one-pot polyester product. The solubility of these products increased with the increasing amount of adipic acid used during depolymerization. The one-pot polyester (PET:EG:AdAc) product was easily soluble in chloroform at room temperature. The PET:But:AdAc depolymerization series and its polycondensates showed reasonable solubility in chloroform. The PET:But:AdAc0.4 and PET:But:AdAc0.4 + MA were measured with the 2D correlative measurements.

Thermal Analytics

PerkinElmer TGA 6 was used to characterize the thermal stability of the samples. 10 mg of the samples were weighed in the ceramic crucible. The sample was heated from 30 to $700 \text{ }^\circ\text{C}$ at $10 \text{ }^\circ\text{C min}^{-1}$ heating rate in purging nitrogen atmosphere. Then the sample was kept at $700 \text{ }^\circ\text{C}$ for 10 min and the atmosphere was changed to oxygen to clean the ceramic crucible.

PerkinElmer DSC 7 was used to determine the glass transition temperature and crystallinity of the samples. Glass transition temperature was determined with a dynamic measurement. A 3–5 mg sample was kept at $-40 \text{ }^\circ\text{C}$ for 1 min, then it was heated to $150 \text{ }^\circ\text{C}$ with $20 \text{ }^\circ\text{C min}^{-1}$ heating rate. The sample was kept at $150 \text{ }^\circ\text{C}$ for 1 min, then it

was cooled to $-40 \text{ }^\circ\text{C}$ with $20 \text{ }^\circ\text{C min}^{-1}$. The sample was kept at $-40 \text{ }^\circ\text{C}$ for 1 min, then it was heated to $150 \text{ }^\circ\text{C}$ with $20 \text{ }^\circ\text{C min}^{-1}$. Glass transition temperature was determined from the last heating period.

PerkinElmer DMA was used to characterize the glass transition and viscoelastic properties of the cross-linked unsaturated resin samples. The “dogbone” shaped specimen ($70 \times 1.4 \times 4 \text{ mm}$) were cut to prismatic shape before measurements. The samples were heated with $2 \text{ }^\circ\text{C min}^{-1}$ heating rate from -50 to $200 \text{ }^\circ\text{C}$. $10 \text{ }\mu\text{m}$ amplitude and 1 Hz frequency was used during the measurements. The glass transition temperature was determined from the peak of the $\tan\delta$ function.

Results and Discussion

Mixed oligoesters of the terephthalic acid (TpAc), EG and the reagent diol and dicarboxylic acid are produced at the end of the depolymerization reactions (Fig. 3). Two separate reaction series were designed to explore this reaction route. In both cases adipic acid (AdAc) used as the dicarboxylic acid component. EG and butane-1,4-diol (But) were used as diol reagents. All the reagent ratios were calculated to the number of repeating units of the weighed in PET. The diols were used in a 1:2 ratio to minimize the reagent use. A 5 + 1 reactions were carried out with increasing amount if adipic acid. The ratio of adipic acid was increased from 0.1 to 0.5. The reaction products were thoroughly characterized with functional group analysis, FTIR, NMR, TGA and DSC measurements to follow the effects of the acid component on the reaction product. Standard glycolysis with only the diols present were carried out to be used as a reference points. Based on the characterization of the reaction series one-pot type reactions were designed to produce saturated and unsaturated polyesters. The PET:EG:Adac reaction series was used to produce a random copolyester poly(ethylene terephthalate co adipate). The PET:But:Adac reaction series products were reacted with maleic-anhydride in separate steps and also in a one-pot reaction to produce unsaturated polyesters. The ratio of maleic-anhydride decreased with the increasing ratio of adipic acid during the depolymerization steps. The unsaturated-polyester products were dissolved in styrene (40 m/m%) and were cross-linked to produce “dogbone” shaped resin samples for thermomechanical testing.

Functional Group Analysis and Solution Viscosity Measurements

Functional group analysis was used to initiatively characterize the depolymerization reactions and to determine the needed amount of excess diacid or anhydride for the polycondensation reactions (Fig. 4). The used acid components

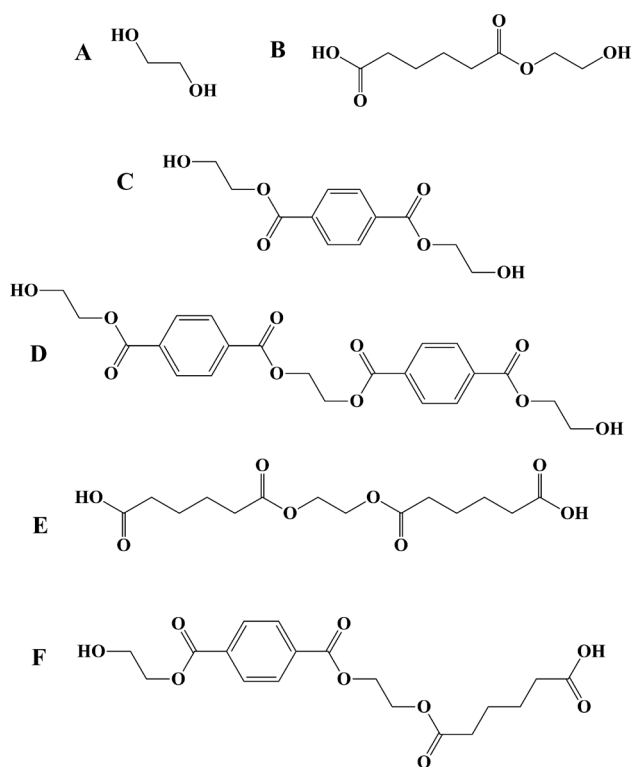


Fig. 3 Possible diol, mono-ester and diester forms of ethylene-glycol in the acido alcoholysis depolymerization reaction product

(adipic acid) were expected to react with any diol component during the depolymerization stage. Any lower molecular weighed components, such as EG are integrated into the oligomer molecules. The residual acid content scattered with

the amount of adipic acid used during the depolymerization step. In case of the PET:EG:AdAc series a slight increase, in case of the PET:But:AdAc series a slight decrease was observed. The PET:But:AdAc series had one order of magnitude higher residual acid content than the PET:EG:AdAc series. The differences of EG and butane-1,4-diol might have influenced this. Butane-1,4-diol is more likely to engage in side reactions (acid catalyzed cyclization to tetrahydrofuran) during transesterification reactions [56]. This may also explain the increase of hydroxyl and acid content at the PET:But:AdAc0.5 point, the ratio of adipic acid might have been too high for the system. The AdAc0 and AdAc0.1 point showed only a slight difference in their hydroxyl value. The AdAc0.1 had higher hydroxyl content then implied near linear decrease in both series. The observed decrease in hydroxyl groups suggest an increase in molecular weight as well.

The intrinsic viscosity of the depolymerization series and the polycondensation products was measured with solution viscosimetry. The intrinsic viscosity of the depolymerization series was between 0 and 0.06 cm³ g⁻¹ (Fig. 5). Both depolymerization series showed an increasing trend, that suggest an increase in molecular weight. It can, therefore, be assumed that our hypothesis was correct and adipic acid acted as a chain-lengthening agent during the depolymerization step. The polycondensation reaction in both cases significantly increased the intrinsic viscosity of the samples with one order of magnitude. The unsaturated polyesters (PET:But:AdAc + MA) had a higher intrinsic viscosity than the saturated polyester (PET:EG:AdAc one-pot). The one-pot unsaturated polyester (PET:But:AdAc0.4 + MA) had

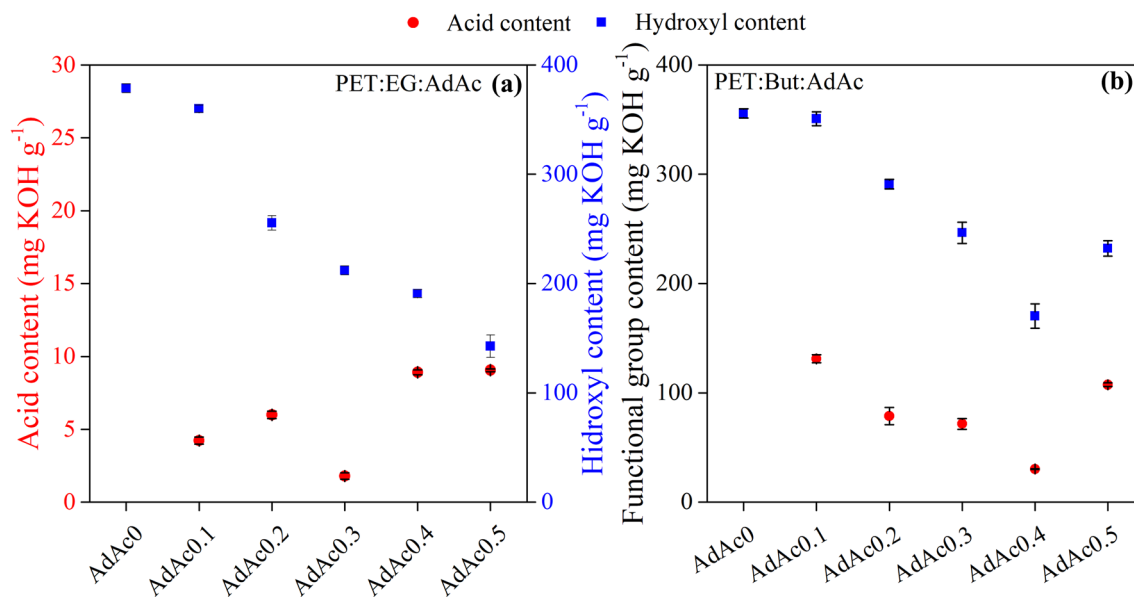


Fig. 4 Functional group content of the depolymerization products: ethylene-glycol and adipic -acid (a); butane-1,4-diol and adipic -acid (b)

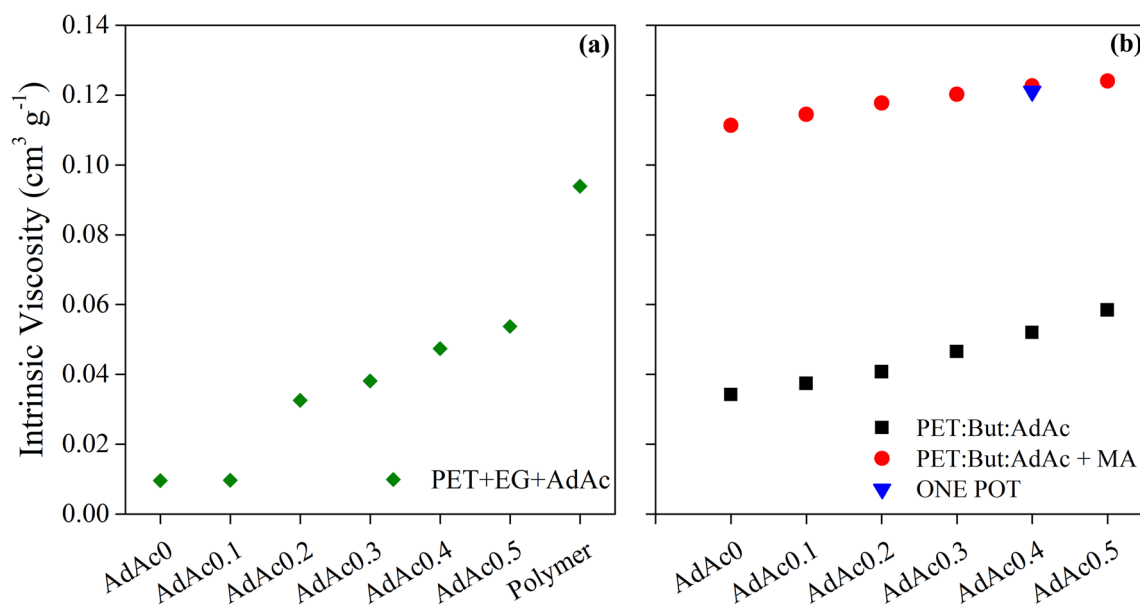


Fig. 5 Intrinsic viscosity of the depolymerization and one-pot synthesis products: PET:EG:Adac series (a), PET:But:Adac series (b)

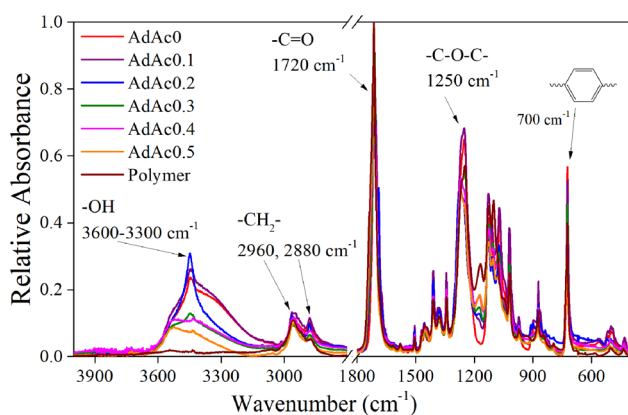


Fig. 6 FTIR ATR spectra of depolymerization reaction products (PET:EG:AdAc 1:1:x and one-pot polymer)

almost identical intrinsic viscosity to its respective pair in the depolymerization series. It is therefore likely that the acido-alcoholysis method is reproducible and can be engineered to synthesize oligo- and polyesters in a one-pot way.

Molecular Structure Identification

The FTIR and NMR studies further supported the previously described trends. Several characteristic peaks typical of polyesters were found in the FTIR spectra (Fig. 6). Ester characteristic peaks, 1720 cm^{-1} carbonyl valence vibration and 1250 cm^{-1} -C-O-C- stretching vibrations were found. C–H valence vibration characteristic peaks were found at 2960 and 2880 cm^{-1} , aromatic ring stretching vibration

characteristic peak was found at 700 cm^{-1} . The usually wide peak attributed to the valence vibrations of hydroxyl groups was found between the 3600 and 3300 cm^{-1} interval. This peak showed a decrease in intensity with the increasing concentration of the adipic acid. In case of the one-pot synthesis product, this -OH groups attributed peak completely disappeared. The PET:But:AdAc depolymerization series showed similar peaks, and the similar decreasing tendency was found for the hydroxyl related valence vibration peak at the $3600\text{--}3300\text{ cm}^{-1}$ interval.

NMR measurements allowed us to thoroughly characterize the depolymerization, and the following polycondensation reaction products. 2D correlative measurements on the one-pot polymer product were used to fully assign the peaks of the depolymerization (PET:EG:AdAc) series ^1H spectra. Adipic acid and terephthalic acid related carbonyl, aliphatic and aromatic carbon atom signals were found in the ^{13}C and DEPT spectra. EG related peaks were found in the $70\text{--}60$ ppm chemical shift range. 4 separate peaks were found that could be attributed to the diesters and mixed esters of ethylene glycol with terephthalic acid and adipic acid (Fig. 7). ^1H spectra were quantitatively evaluated by integrating the peaks derived from the various mono- and diester forms of EG (Figs. 8, 9). All the possible molecular structures and connections are represented in. All these structures were organized into three groups: diols (EG), monoesters ($\text{Ad-CH}_2\text{-CH}_2\text{-OH}$; $\text{Tp-CH}_2\text{-CH}_2\text{-OH}$) and diesters ($\text{Ad-CH}_2\text{-CH}_2\text{-Ad}$; $\text{Tp-CH}_2\text{-CH}_2\text{-Tp}$; $\text{Ad-CH}_2\text{-CH}_2\text{-Tp}$). Increasing the adipic acid content during the depolymerization stage, higher molecular weighed products were expected to appear. Inasmuch as the relative integral of diols and

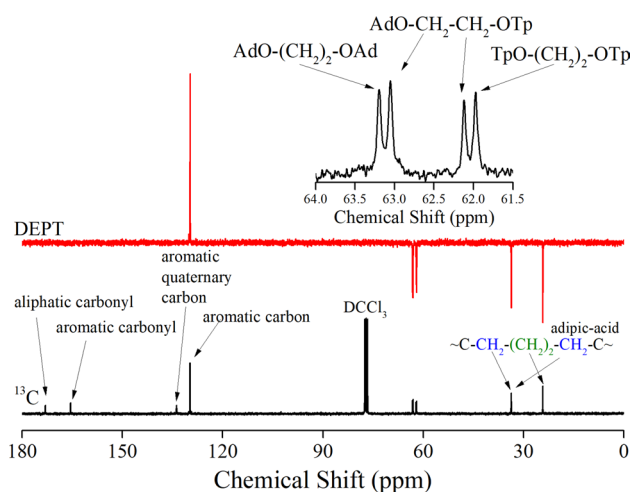


Fig. 7 ^{13}C and DEPT spectra of the PET:EG:AdAc 1:1:0.3 depolymerization product

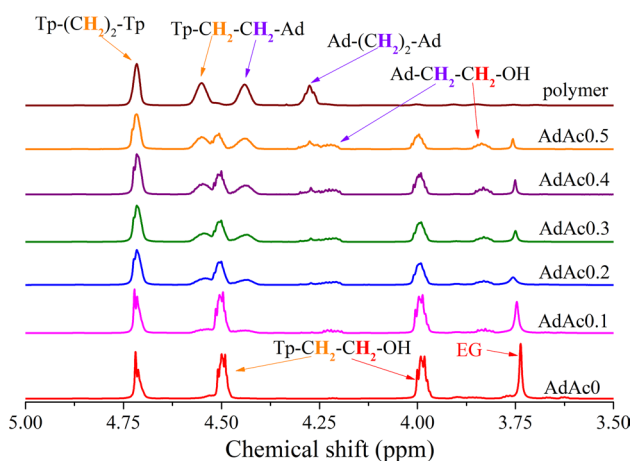


Fig. 8 ^1H NMR spectra of the PET:EG:AdAc depolymerization reaction series

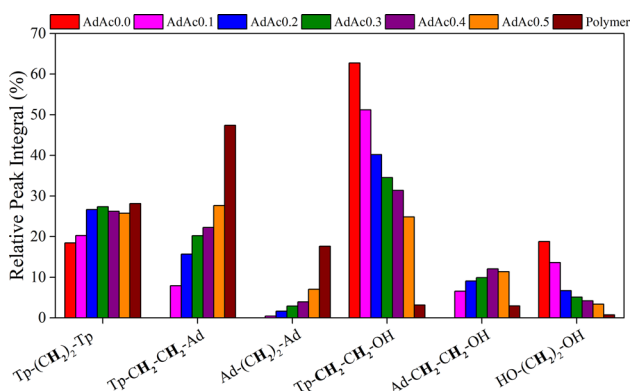


Fig. 9 ^1H NMR spectra of the PET:EG:AdAc depolymerization relative peak integrals

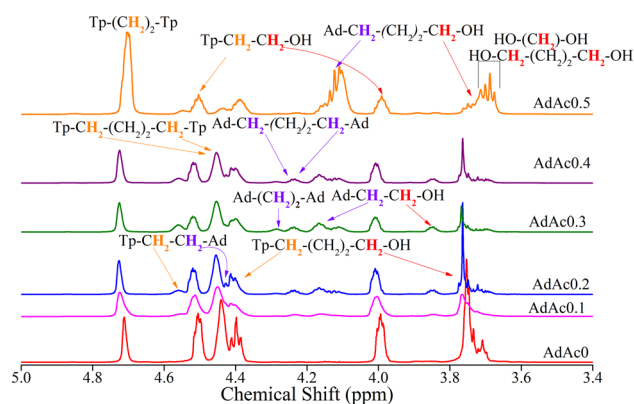


Fig. 10 ^1H NMR spectra of the PET:But:AdAc depolymerization series

monoesters related peaks showed a decreasing trend and the diester related peaks showed an increasing trend. The slightly increasing trend of the $\text{Tp-CH}_2\text{-CH}_2\text{-Tp}$ connection indicates that the use of adipic acid caused a setback in the depolymerization step. The acid component reacted with the diol and lowered its concentration. Despite that, we were able to achieve a decent rate of depolymerization the ratio of the $\text{Tp-CH}_2\text{-CH}_2\text{-Tp}$ only raised with 10%. The appearance of adipic acid monoesters confirms our theory on the adipic acid reacting with the EG at a certain degree during the first stage of the depolymerization reaction. Comparison of “ $\text{Ad-CH}_2\text{-CH}_2\text{-Tp}$ ” “ $\text{Ad-CH}_2\text{-CH}_2\text{-Ad}$ ” relative integrals shows that the BHET derivatives have a higher reactivity than EG and its aliphatic monoesters. The major decrease in the ratio of “ $\text{Tp-CH}_2\text{-CH}_2\text{-OH}$ ” structure after the polycondensation reaction further supports this.

These findings have an interesting implication in developing the one-pot type reactions of this method. The quantitative analysis of the PET:EG:AdAc reaction series clearly indicates that the depolymerization with EG and the condensation with adipic acid can occur in the same system. Thus these reaction can be engineered to reach a certain, desired functional group content and molecular weight.

PET:EG:AdAc and PET:But:AdAc reaction series showed many similarities in their characterization. The NMR spectra and characterization of the PET:EG:AdAc series clearly showed and supported the observed tendency with functional group analysis and FTIR. Strong evidence of the same type of tendencies was also found in the PET:But:AdAc series with FTIR and functional group analysis. The ^1H NMR spectra were fully assigned (Fig. 10) and integrated to qualitatively and quantitatively characterize the spectra (Fig. 11). In accordance with the PET:EG:AdAc series, the PET:But:AdAc series showed the same type of trends. Due to the introduction of butane-1,4-diol the NMR spectra became complicated and caused overlapping in the peaks. This caused these trends to be less straightforward.

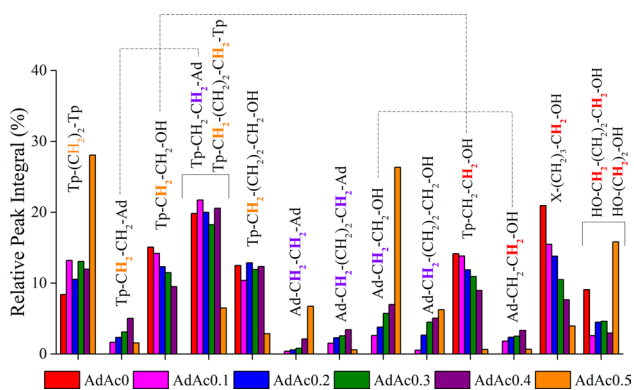


Fig. 11 ^1H NMR spectra relative integral of the PET:But:AdAc depolymerization series

Nevertheless, a declining tendency for most of the monoesters correlated peaks and an increasing tendency for the diester correlated peaks was found. The ^1H NMR spectra of the PET:But:AdAc0.5 considerably differed from the rest of the series. The sample barely dissolved in the deuterated solvent. The relative integral of the Tp-EG-Tp linkages (BHET dimer or oligomers) is almost three times higher than the rest of the series. This suggests the presence of longer PET derivative oligomers in the reaction product. High-intensity peaks at the 3.7–3.6 ppm interval imply the presence of alcohol (EG and/or But) components. These results could explain the higher than expected residual functional group content (Fig. 4). The quantitative analysis suggests, that in this case the ratio of adipic acid was too high. As a result, the depolymerization step couldn't reach the same level as the other ratios. Nevertheless, this reaction series shows that the acido-alcoholysis concept could be applied to other systems as well. In any given combination

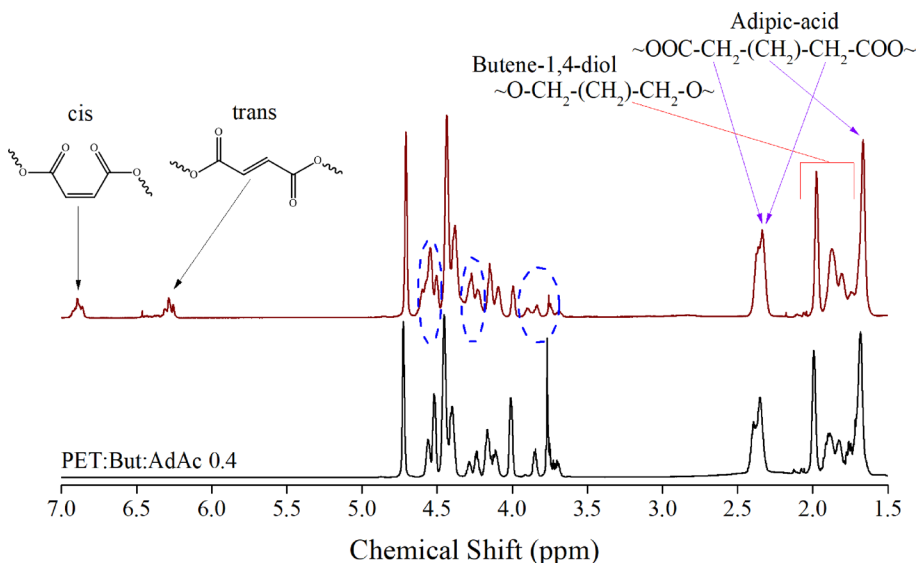
of diol and diacid and PET the reaction must be tested to find the interval of applicable reagent ratios.

The introduction of maleic-anhydride into the products (PET:But:AdAc depolymerization series) further complicated the molecular structure and the NMR spectra. Due to the relatively low amount of used maleic-anhydride only slight changes were observable in the ^1H spectra between the 5–3.5 ppm interval (Fig. 12). 2D correlative measurements were used on the PET:But:AdAc04 + MA sample. Despite this, we were unable to resolve the new connections made by the maleic-anhydride in the 5–3.5 ppm interval (^1H spectra). Certain parts of the ^1H spectrum (PET:But:AdAc04 + MA sample) were circled to show the changes derived from the condensation reaction. Those peaks were attributed to mono-ester linkages in the depolymerization products (Fig. 10). The peaks at the 3.8–3.7 ppm interval showed a significant decrease in intensity. These peaks are attributed to the hydroxyl terminated chain ends, thus these indicate an increase in molecular weight. Only the two unsaturation related peaks could be directly linked to the maleic-anhydride in the 7–6 ppm interval. The relatively high temperature of the reaction caused the maleic-acid to change from its cis isomer state to the trans isomer form.

Thermal Properties

The thermal stability of the depolymerization series samples was considerably affected by the amount of adipic acid used during the depolymerization step (Fig. 13). As it was previously stated the adipic acid component was used to connect the low molar weighed components to form oligomers. The TGA curves of the PET:EG:AdAc series support this statement. At lower temperatures (100–300 °C) the weight of the samples significantly decreased due to the evaporation of

Fig. 12 ^1H NMR spectra of the PET:But:AdAc 1:1:0.4 and its reaction product with maleic anhydride



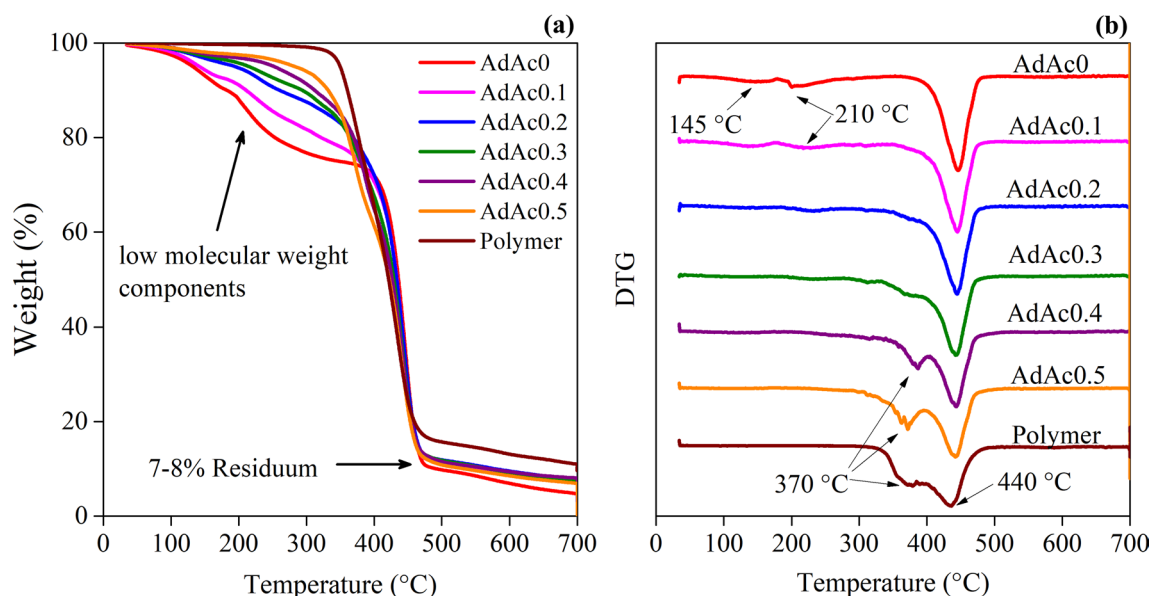


Fig. 13 The TGA (a) and DTG (b) curves of the PET:EG:AdAc reaction series

low molar weighed components like EG. With the increasing amount of adipic acid these components reacted with the adipic acid and formed oligomers. As a result, a more uniform product was gained and the amount of these easily evaporating components was minimalized. The peaks attributed to such components progressively smoothed on the DTG curves as the ratio of the adipic acid was increased. A new peak/shoulder appeared with increasing the amount of adipic acid at 375 °C. The shoulder's increase could be explained by the fact that the adipic-esters showed an increasing tendency in the reaction product. Aliphatic polyesters have lower thermal stability than aromatic polyesters. They were shown to be able decrease the thermal stability of copolyesters. [57].

The PET:But:AdAc depolymerization series showed a similar, but less distinct trend with the increasing amount of adipic acid. The thermal stability of this reaction series showed no significant change with the polycondensation reaction with maleic-anhydride (Fig. 14). A shoulder can be identified on all the DTG curves at 445 °C that became well-defined increasing the amount of used adipic acid. Especially in the case of PET:But:AdAc0.5. McNeil and his coworkers have shown that longer alkyl chains in poly(alkylene-terephthalate)s decrease the thermal stability, doing so butylene-terephthalate esters are less stable than EG esters. [58] The high ratio of adipic acid increased the ratio of residual Tp-CH₂-Tp connections in the depolymerization products (Fig. 11). Thus, certain segments of the random copolyester have higher thermal stability than the butane-1,4-diol ester rich segments.

The AdAc0 and AdAc0.1 depolymerization products in both series showed low crystallinity with a relatively fast crystallization rate. All the depolymerization products above 0.2 adipic acid ratio showed almost no or minor melt peaks that could be detected with our DSC instrument (Fig. 15). None of the depolymerization samples showed glass transition temperature, only the further polymerized samples showed the distinctive step-like shape that characterizes the glass transition of a polymer. The T_g of the polymeric samples was found to be below room temperature, easily malleable materials became rigid when stored in a freezer. The T_g value of the PET:But:AdAc + MA unsaturated polyester series roughly decreased with the increasing ratio of adipic acid (Fig. 16). Since the intrinsic viscosity of these samples was found to be similar to the decrease in T_g , it should be related to the amount of used adipic acid. Since butane-1,4-diol and adipic acid have longer saturated aliphatic chains (compared to EG, terephthalic acid and maleic-acid) they act as “soft” components and lower the T_g of the polymer.

Unsaturated Resin Characterization

Significant changes can be observed in the FTIR spectra of USR in comparison to the depolymerization and polycondensation products (Fig. 17). The spectra were normalized so the carbonyl vibration related peaks at 1720 cm⁻¹ could have a relative intensity of 1. The two new peaks at 797 cm⁻¹ and 699 cm⁻¹ can be attributed to the breathing vibration of aromatic phenyl groups. Major increases between the 3000–2800 cm⁻¹ interval can be attributed to the valence vibration of the phenyl groups. The peaks

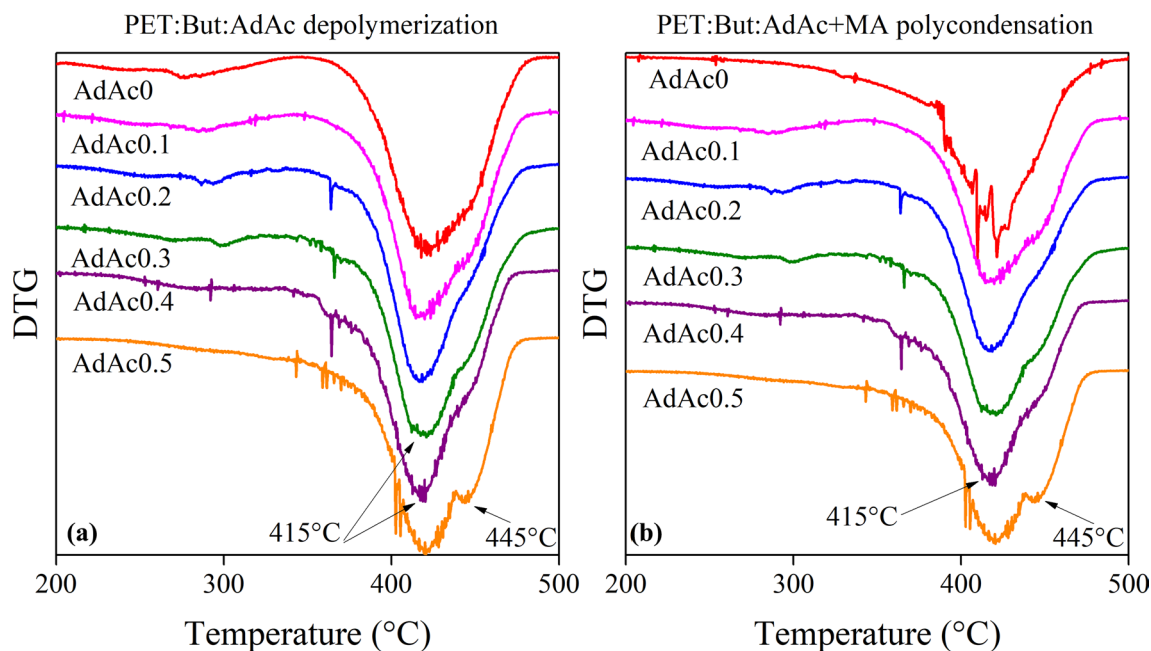


Fig. 14 The DTG curves of the PET:But:AdAc depolymerization (a) and unsaturated polyester polycondensation (b) reaction series

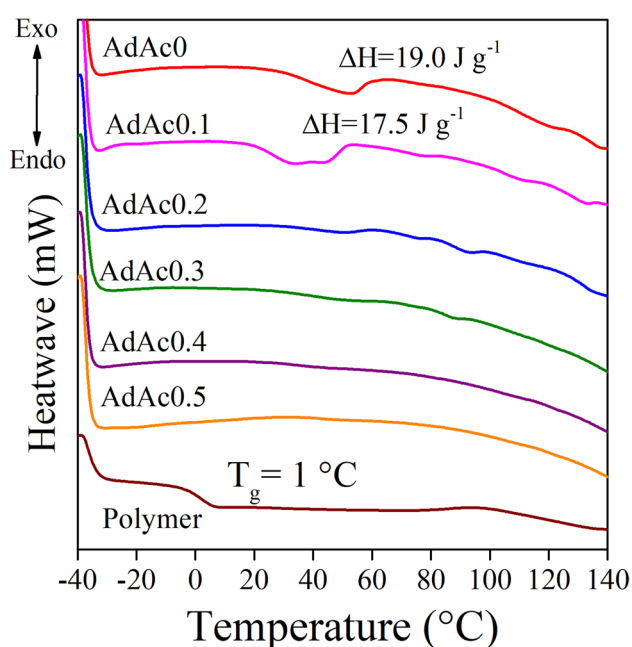


Fig. 15 DSC curves of the PET:EG:AdAc reaction series (2nd heating)

at the $1300\text{--}1000\text{ cm}^{-1}$ interval are mostly related to the vibrations of the C–O–C ester groups. The intensity of the peaks at 1258 cm^{-1} , 1099 cm^{-1} and 1020 cm^{-1} are present in the depolymerization and the polycondensation product as well. The observed increase in intensity can

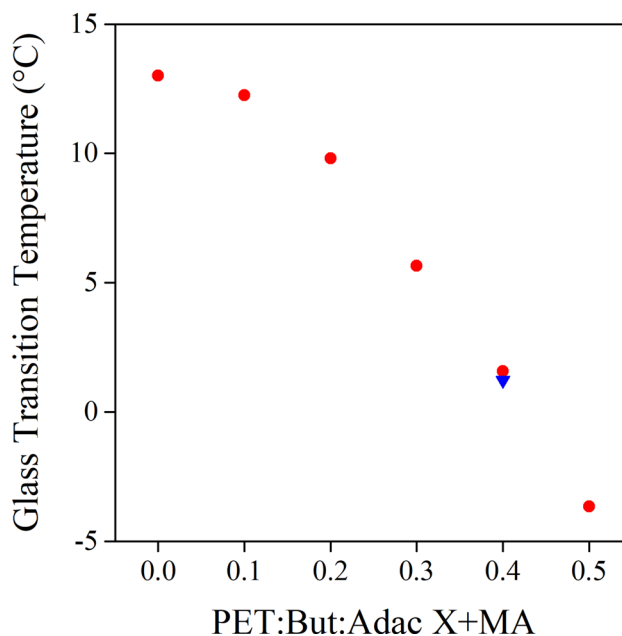


Fig. 16 The glass transition temperature of the PET:But:AdAc + MA reaction series (determined with DSC). Blue triangle represents the one-pot reaction product

be explained by the radical reaction of the vinyl group of the styrene and the unsaturation in the ester chain. Due to the cross-linking reaction, the specific vibrations of the carbonyl and C–O–C groups derived originally from the maleic-anhydride may change.

Fig. 17 FTIR spectra comparison of the depolymerization, condensation and the final unsaturated resin product

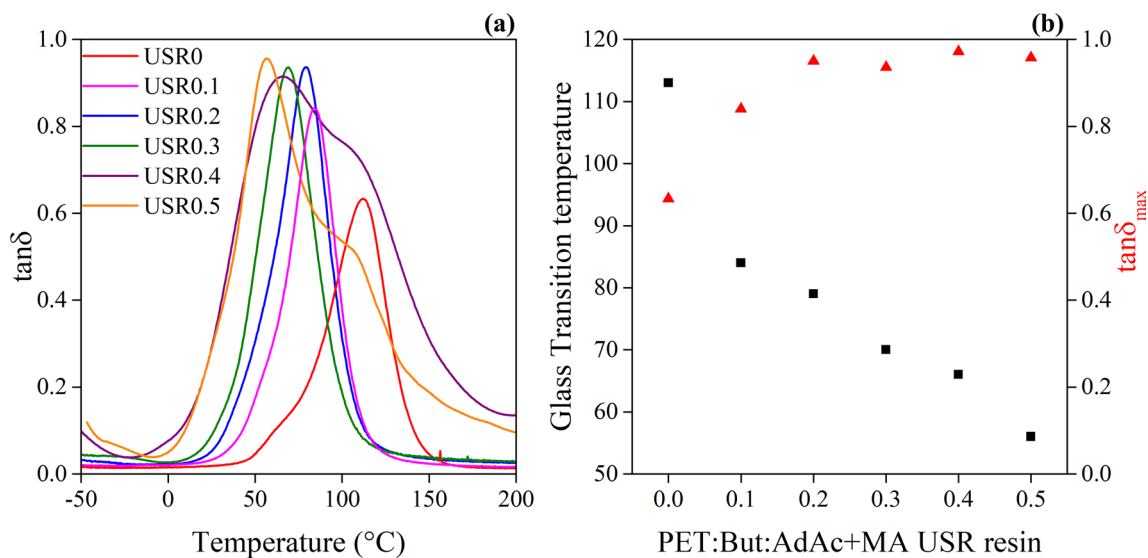
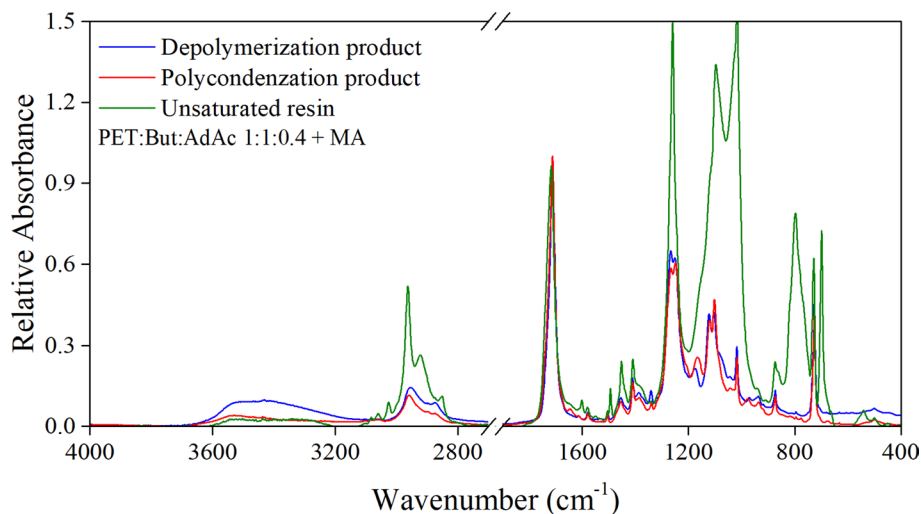


Fig. 18 A $\tan\delta$ curves (a) and $\tan\delta_{\max}$ and glass transition temperature (b) of the unsaturated resin samples

The low condensation time was utilized to keep the molecular weight of the unsaturated polyesters relatively low and only allow the terminal hydroxyl groups to react with the anhydride via ring-opening. This way a looser cross-linked network will be produced and the glass transition temperature will sensitively depend on the constitution of the ester chains. [49] Since an increase in molecular weight in the function of the adipic acid ratio the cross-link density should decrease in the function the utilized amount of adipic acid. To test this theory the thermomechanical properties of the USR were studied with dynamic mechanical analysis (Fig. 18, Table 2). The unsaturated resin samples were found to be rather elastic at room temperature. The glass transition temperature of the samples is relatively low, the onset of the glass transition starts below room temperature, thus their properties considerably change in that temperature

Table 2 Storage modulus, cross-link density of the USR samples

	Storage modulus (MPa)		Cross-link density (mol m ⁻³)
	25 °C	180 °C	
USR0	2459.7	10.18	2673
USR0.1	1629.9	7.08	1858
USR0.2	1483.3	3.13	823
USR0.3	1320.4	2.03	533
USR0.4	856.6	0.41	107
USR0.5	693.3	0.51	135

interval. The measured T_g values decreased with the increasing amount of adipic acid used during the depolymerization. The maximum of the $\tan\delta$ functions shifted to lower

temperatures with the increasing ratio of the adipic acid. A shoulder could be observed at 100–120 °C temperature range at the 0.4 and 0.5 ratios that might indicate the presence of more densely cross-linked parts in the resins. The higher amount of adipic acid also could have caused segregation of softer (adipic ester rich) and harder (terephthalic ester rich) segments in the copolyester chains. Just as the intrinsic viscosity measurements suggested higher molecular weighed products were gained that, as a result, causes a decrease in glass transition temperature and cross-link density. The cross-link density values were calculated from the storage modulus data at 150 °C, the calculated values proved to be particularly low. The higher amount of adipic acid directly influenced the needed amount of maleic-anhydride and caused a decrease in cross-link density.

Conclusions

In this study, we have investigated the use of diacid components and their effects on the depolymerization products of PET solvolysis. Our results have shown that diacids can be utilized during PET solvolysis and their use results in the production of oligoesters. The volatile, low molar weighed components are incorporated into the oligomer chains, thus a more uniform product is achieved at the end of the depolymerization. The reaction has no side-products and the produced oligomers could be directly used without any or minimal purification. The molecular structure of the depolymerization product can be finely tuned via selecting the diol and diacid reagents, thus engineering the thermal, mechanical and chemical properties of its final derivative product. The increasing ratio of the diacid results in increasing the molecular weight of the produced oligomers. We have successfully utilized and characterized acido-alcoholysis so it can be used in one-pot type reactions. Compared to traditional chemical recycling (depolymerization, then polycondensation), acido-alcoholysis combines depolymerization and condensation techniques into a single step. Excess chemical use is not necessary, and purification of the end-product is not needed or minimal. Via acido-alcoholysis oligoesters can be produced that can act as hydroxyl and acid functional mid-products. Due to their reactive terminal groups, they could be tailored to be used as polyols in polyurethanes as well. Thus, the most expensive steps of solvolysis, the purification of products can be completely avoided, and the product properties can be fine-tuned. The authors believe that this technique could be applied with a wide range and combination of diol and diacid components. Although the systems must be tested to find the optimal interval of reagent ratios. The reaction process proved to be quite modular and could be utilized in various fields.

The practicality of the method considerable depends on the purity of the feed-stock waste material. The effects of contaminants (other polymers, adhesives, metal salts) must be investigated thoroughly in the future. Further enhancements could be made in the depolymerization step with the use of new, heterogeneous, recyclable catalyst.

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