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Chemical recycling of poly(ethylene terephthalate). Application to the synthesis of multiblock copolyesters

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Abstract. The chemical recycling of the poly(ethylene terephthalate), (PET), has been successfully carried out by glycolysis in the presence of bis (2-hydroxyethyl) terephthalate (BHET) resulting in the formation of hydroxytelechelic oligomers. These oligomers were then treated with carboxytelechelic poly(ε-caprolactone) oligomers of $\overline{M}_n$ = 2300 and $\overline{M}_n$ = 730 g·mol^{-1} molecular weight, in the absence or presence of the titanium tetrabutyloxide ($Ti(OBu)_4$) as a catalyst to get multiblock copolyesters. The chemical structure of the synthesized copolyesters was investigated by size exclusion chromatography (SEC) and proton Nuclear Magnetic Resonance (^{1}H NMR) spectroscopy. Moreover the differential scanning calorimetry (DSC) was used to explore their thermal properties. The ester-ester interchange reaction was observed between the two oligopolyesters, was studied and discussed in detail.

Keywords: *recycling, poly(ethylene terephthalate), polyesterification, thermal analysis*

1. Introduction

Poly(ethylene terephthalate), (PET), is a thermoplastic semi-crystalline polyester with excellent tensile and impact strength, chemical resistance, clarity, process ability, transparency, and appropriate thermal stability [1]. It is mainly used in the textile industry, to manufacture of video and audio tapes, X-ray films, food packaging, water and soft-drink bottles. The global consumption of PET packaging was almost 15.5 Mt in 2009, while it is expected to reach 19.1 Mt by 2017, a 5.2% increase per annum [2, 3]. The increased consumption of PET is creating serious environmental problems as vast waste stream reaches every year due to short life duration of PET etc. Disposing of the waste to the landfill is becoming undesirable due to legislation pressures, rising costs and the poor biodegradability of such polymers. Therefore, other ways of PET waste treatment, such as recycling is highly desired.

Polymer wastes can be recycled in many ways for example, the energetic valorization which consists of using energy emanating from PET burning. Another method called mechanical recycling where the polymers are transformed into other objects after a step in the molten state. The recycled PET is used in different applications which do not require very high quality standards [4, 5]. Among all polymer recycling methods, chemical method has attracted more attention due to sustainable development principles. This method is very useful for the condensation of polymers, such as polyamides, polyurethanes and polyesters, which are vulnerable to solvolytic chain

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cleavage. The key advantage of this method includes the huge availability of the different chemical products which can be obtained with different reagents [6–9].

Recently, several processes such as alcoholysis, aminolysis, hydrolysis, and glycolysis have been used for PET chemical recycling. Glycolysis reaction is more interesting, and can be described as a molecular depolymerisation by transesterification between PET ester groups and a diol. The ester linkages are therefore broken and replaced with hydroxyl terminals. The monomers or higher oligomers obtained can be used as building blocks to synthesize other polymers with higher economical values. For example, saturated and unsaturated polyesters [10–12], polyurethanes [13–15], coating materials [16–19] and additives [20–22] have been synthesized from such building blocks in recent years.

A large number of reagents have been used for glycolysis of PET such as ethylene glycol [23–26], diethylene glycol [27, 28], propylene glycol [29], neopentyl glycol [14], 1,4-butanediol [30, 31], and some synthetic oligoesters [32, 33]. To the best of our knowledge, no one has ever been used BHET as diol for the PET glycolysis. Similarly, several studies have been carried out on the reaction of PET and ethylene glycol for the synthesis of hydroxytelechelic oligomers of PET [34–36] which were mainly used for producing unsatured polyester resins [34, 35] and very few polycondensations have been carried out by using hydroxytelechelic oligomers of PET with ε-caprolactone [37]. Copolyesters with PET and ε-caprolactone units are mainly synthesized by polycondensation of dimethyl terephthalate, ethylene glycol and ε-caprolactone [38], or by transesterification in copolyester blend [39, 40].

In this context, in order to explore a new method for PET recycling herein, the glycolysis of the PET performed with its structural units BHET was reported. This paper presents a continuous reactive extrusion process and evaluates the potentiality of the polyesterification of hydroxytelechelic oligomers resulting from the glycolysis of PET with the carboxytelechelic PCL oligomers as a new method for valorization of PET wastes. All the obtained products are investigated by proton nuclear magnetic resonance spectroscopy (^{1}H NMR), size exclusion chromatography (SEC) and differential scanning calorimetry (DSC).

2. Experimental part

2.1. Reagents

Poly(ethylene terephtalate) (PET) ($\overline{M}_n$ = 26 000 g·mol^{-1}), bis(2-hydroxyethyl) terephthalate (BHET), poly(ε-caprolactone) diol (PCL) ($\overline{M}_n$ = 530 and 2000 g·mol^{-1}), zinc acetate (Ac_2Zn), and titanium tetrabutyl oxide (Ti(OBu)4), are obtained from Sigma-Aldrich (St Quentin Fallavier, France). All other chemicals (solvents and reagents) were used of analytical grade and were obtained from Somaprol (Casablanca, Morocco).

2.2. Glycolysis of PET by BHET

PET pellets (20.03 g; 0.104 mol (PET monomer unit)), BHET (26.50 g; 0.208 mol of hydroxyl equivalent), and 0.20 g of zinc acetate (Ac_2Zn) were put into a 500 mL reactor equipped with a mechanic stirrer, a nitrogen inlet and a vacuum outlet. The reactor was heated under nitrogen at 250°C for 2 h. After the die, the modified PET crystallized in bulk and it is grinded into powder, and the residual BHET is removed by precipitation in hot water. The white product was dried under a vacuum at 80°C for 48 h. The powder was obtained in an 85% yield and characterized by ^{1}H NMR spectroscopy with trifluoroacetic acid (TFA) and Deuterated chloroform ($CDCl_3$) as the solvent.

^{1}H NMR: δ (ppm): 8.10 (aromatic protons) 4.70 ($C\underline{H}_2$ between two esters functions); 4.55 ($C\underline{H}_2CH_2OH$); 4,15 ($C\underline{H}_2OH$).

2.3. Synthesis of carboxytelechelic poly(ε-caprolactone) oligomers

The carboxytelechelic poly(ε-caprolactone) oligomers of molecular weight $\overline{M}_n$ = 2300 g·mol^{-1} and $\overline{M}_n$ = 730 g·mol^{-1} are prepared from hydroxytelechelic oligomers of molecular weight 2000 and 530 g·mol^{-1} respectively, according to the procedure described in the literature [41].

In a 500 mL two-necked flask equipped with a condenser, a nitrogen inlet and a magnetic stirrer, 20 g (0.01 mol) of PCL, 2.2 g (0.022 mol) of succinic anhydride and 1 mol % of DMAP with 200 mL of 1,4-dioxan solvent were introduced. The reaction has occurred at 50°C. After 10 hours of reaction, the solvent was removed by evaporation under vacuum at 100°C and the residual product was solubilized in chloroform. The reaction mixture was washed with acidic water (pH = 1) in order to remove residual succinic acid. After drying on Na_2SO_4, the solvent was removed by evaporation and under vacuum at 60°C. The mass yield of the reaction was 80%. The products are characterized by pH titration of carboxylic functions, ^{1}H NMR spectroscopy and SEC.

The titration of carboxylic functions of the products (of the addition of succinic acid onto hydroxyl function) is carried out by following a classic method: a known mass of the product is titrated by a solution of KOH in methanol (MeOH) solvent with tetrahydrofuran (THF) as solvent and phenolphthalein as color indicator. The carboxyl ratio is given by the Equation (1):

$$I_{\mathrm{COOH}} = \frac{C_{\mathrm{KOH}} \cdot V_{\mathrm{KOH}}}{m} \tag{1}$$

where C_{KOH} represents the concentration of KOH solution, V_{KOH} is the equivalent volume and m is the mass of oligomer titrated. These tests were performed at least in duplicate, and the difference between the various obtained values was within the experimental error of 5%.

^{1}H NMR: δ (ppm): 8.4 (acid proton); 4.1 (CH_2 between two ester functions, one linked to caprolactone unit (in α) and one linked to succinic unit (in β)); 4.0 (CH_2 of caprolactone unit in α of ester function); 3.6 (CH_2 between two ester functions, one linked to caprolactone unit (in β) and another linked to succinic unit (in α)); 2.6 (CH_2 between an ester and a carboxylic function); 2.3 (CH_2 in α of a carboxyl group and methylenic carbon); 1.1–1.7 (Internal CH_2 of caprolactone unit).

2.4. Copolyesterification of hydroxytelechelic PET oligomers and carboxytelechelic poly(ε-caprolactone) oligomers

The reaction of copolyesterification of carboxytelechelic oligomers with hydroxytelechelic oligomers of PET is performed in a bulk, in a four-necked flask, with a condenser, a nitrogen inlet, a mechanical stirrer and a high vacuum inlet.

The hydroxytelechelic PET oligomers, the carboxytelechelic poly(ε-caprolactone) oligomers ($\overline{M}_n$ = 730 or 2300 g·mol^{-1}) and 1 wt% of catalyst ($Ti(OBu)_4$) (or without catalyst) are introduced and the reaction mixer is heated at 240°C under nitrogen until the complete fusion of oligomers of PET. After, the pressure is led to 10^{-1} mbar in the reactor and the reaction temperature is kept constant at 240°C. The copolyesters are obtained with yield ranging from 85 to 90%. Subsequently the products are characterized by SEC, ^{1}H NMR as well by DSC.

^{1}H NMR: δ (ppm) 8.1 (aromatic protons); 4.2 (CH_2 between two ester functions, one linked to caprolactone unit (in α) and another linked to succinic unit (in β)); 4.0 (CH_2 of caprolactone unit in α of ester function); 3.6 (CH_2 between two ester functions, one linked to caprolactone unit (in β) and one linked to succinic unit (in α)); 2.65 (CH_2 between an ester and a carboxylic function); 2.3 (CH_2 in α of a carboxyl group and methylenic carbon) ; 1.0–1.7 (internal CH_2 of caprolactone unit).

2.5. Apparatus

2.5.1. Nuclear magnetic resonance (NMR)

The ^{1}H NMR spectra are recorded on a Bruker spectrometer 250 MHz at room temperature. The solvent used for oligomers of PET is $CDCl_3$/TFA (20:1). The solvent for the other products is $CDCl_3$. Chemical shifts are given in ppm relative to Tetramethylsilane as an internal reference.

2.5.2. Size exclusion chromatography (SEC)

The size exclusion chromatograms are recorded on an IOTA2 apparatus supplied by JASCO with a PU-980 Intelligent HPLC pump. The columns employed were PLgel 5 µm Mixed-D 300×7.5 mm, VARIAN INC. The molecular weights of poly(ε-caprolactone) oligomers and of copolyesters are measured respectively with THF or chloroform/ hexafluoropropan-2-ol ($CHCl_3$/HFIP) (98/2 wt) as solvent at a flow rate of 1 mL·min^{-1}. Samples are injected using an injector of the Agilent 100 Series. The calibration curves are obtained from polystyrene (PS) standards. These tests were performed at least in duplicate, and the difference between the various obtained values was within the experimental error of 5%.

2.5.3. Differential scanning calorimetry (DSC)

DSC analyses were performed with a 204 F1 NETZSCH. Experiments are carried out under nitrogen with samples ranging from 7 to 15 mg. The temperature was calibrated with ultra-pure indium, octane and dodecyloctane. The temperature range of the first heating scan was between –80 to 280°C, with a heating rate of 10 K·min^{-1}, followed by a cooling at 20 K·min^{-1}. A second scan was immediately performed with a heating rate of 10 K·min^{-1}. Glass transition temperature was taken at the midpoint of change in heat capacity. These measurements were performed at least in duplicate.

3. Results and discussion

3.1. Synthesis of PET oligomers

The synthesis of hydroxytelechelic oligomers of PET was performed by glycolysis of PET with its monomer BHET using zinc acetate (Ac_2Zn) as the catalyst. This reaction of depolymerization is described in Figure 1.

As described in several previous studies [32, 35, 36] the PET glycolysis products are α, ω-hydroxyl oligomers. Indeed, different SEC analysis, ^{1}H NMR spectroscopy, and matrix-assisted laser desorption ionization time-of-flight mass spectrometry was established; these studies show a good correlation in the determination of hydroxyl end groups and molecular weights below 4000 g·mol^{-1}.

The four peaks of the ^{1}H NMR spectrum as reported in Figure 2, correspond to the signals of PET oligomer protons. The average molecular weight of the oligomers is calculated from ^{1}H NMR spectroscopy using the integrations of the aromatic protons and the methylene protons adjacent to the hydroxyl end functions. The integration ratio of these signals allowed the calculation of the number of terephthalic base units in the oligomers through Equation (2):

$$m = \frac{I_{8.10\,\text{ppm}}}{I_{4.15\,\text{ppm}}} \qquad (2)$$

where $I_{x\,\text{ppm}}$ represents the integral value of the peak centered at x ppm.

So it is easy to determine the average molecular weight of the oligomers. The m value is about 100/14.7 = 6.8. The PET oligomer has an average molecular mass of 1360 g·mol^{-1}, with an average polymerization number ($\overline{DP_n}$) of 13.6.

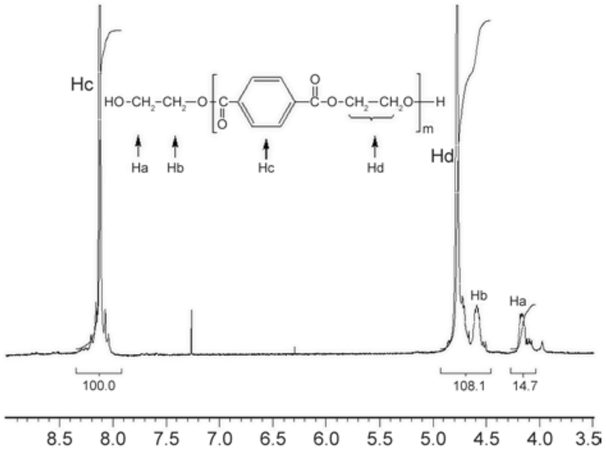


Figure 2. ^{1}H NMR spectrum of hydroxytelechelic oligomers of PET

In these conditions, the molar weight of the obtained glycosilation products were lower than the products reported in the literature (about 1450 g·mol^{-1} [35] and 1800 g·mol^{-1} [36]), these values were obtained during the PET glycolysis with the ethylene glycol, using dibutyl tin oxide as the catalyst.

The PET oligomer is soluble only in few solvents, for this reason, it is used in the molten state for further polyaddition. The differential scanning calorimetry (DSC) analysis gives the glass transition temperature (T_g = 78°C), melting point (T_m = 235°C) and crystallization temperature (T_c = 175°C) of the glycolysed PET oligomers.

The product has a melting temperature close to that of PET, but slightly lower. This is in good agreement with the literature data [5, 35], which shows that the melting temperature depends on and varies from 110 up to 220°C when $\overline{DP_n}$ varies from one to five. For $\overline{DP_n}$ above five, the melting temperature is very close to that of PET.

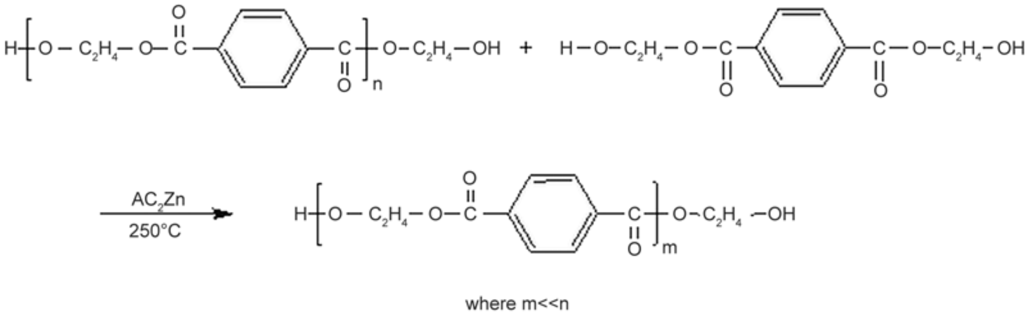


Figure 1. Depolymerization of PET by BHET

3.2. Synthesis of carboxytelechelic of poly(ε-caprolactone) oligomers

The carboxytelechelic PCL oligomers are not commercially available.Their synthesis was performed by reacting succinic anhydride with the hydroxyl functions of the commercial PCL oligomers using dimethylaminopyridine (DMAP) as a catalyst, as shown in Figure 3.

The synthesis and characterization of the carboxytelechelic poly(ε-caprolactone) oligomers of molecular weight $\overline{M}_n = 2300$ g·mol^{-1} and $\overline{M}_n = 730$ g·mol^{-1} from hydroxytelechelic oligomers of molecular weight 2000 and 530 g·mol^{-1} respectively [41] has been described. The structure of these oligomers is confirmed by ^{1}H NMR, pH titration of carboxylic functions and size exclusion chromatography. In their ^{1}H NMR spectra, it can be noticed that the presence of a broad signal at 8.4 ppm corresponding to the acid proton. The α- and β-protons of the acid function appears as a multiplet centred at 2.6 ppm. Other peaks correspond to the protons of the aliphatic chain of PCL. The peak integration ratios of different signals confirmed clearly the esterification reaction between the succinic anhydride and the PCL diol. The titration of the carboxyl functions allowed us the calculation of the carboxylic functionality of PCL, which has been determined to be 1.98 in both cases, as described in the experimental part.

3.3. Synthesis and characterization of copolyesters

The copolyesterification of hydroxytelechelic PET oligomers and carboxytelechelic PCL oligomers was performed in the molten state, under vacuum (10^{-1} mbar) and high temperature so as to get rid of water formed, to shift the esterification equilibrium. The reaction is performed at 240°C because of the high melting point of PET oligomers, using $Ti(OBu)_4$ as a catalyst, as shown in Figure 4.

As reported in the literature, the $Ti(OBu)_4$ is more reactive when being used at a reaction temperature of 240°C and enhances somewhat the $\overline{M}_n$ obtained [42]. For titanium catalytic system, studied by Fradet and Marechal [43], the acid function coordinates with Ti, and some experiments of Fradet and Marechal show that the system follows thermodynamic laws. Indeed, the rate constant of the reaction increases with increasing of the temperature. Other works enlighten the same phenomenon and give further explanations onto titanium alkoxide activity for esterification or transesterification reactions [42, 44].

To study the influence of the molecular weight of PCL carboxytelechelic on the properties of co-polyesters, the polyesterification reactions were established with the PCL oligomers of $\overline{M}_n = 2300$ g·mol^{-1} and $\overline{M}_n = 730$ g·mol^{-1}. In the same way, in order to evaluate the influence of the catalyst on these prop-

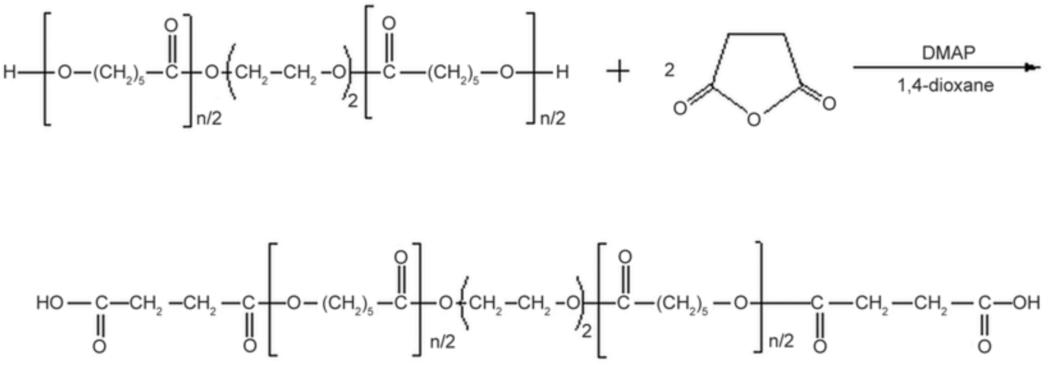


Figure 3. Synthesis of carboxytelechelic PCL oligomers

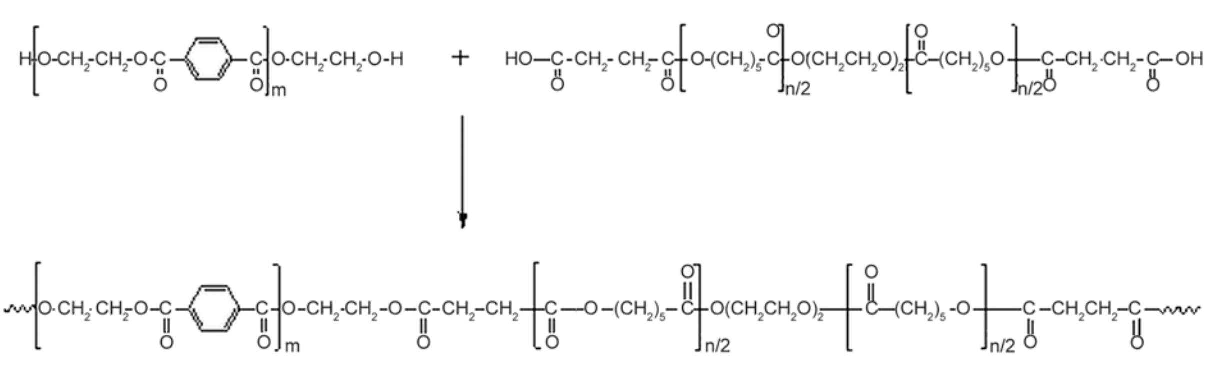


Figure 4. Copolyesterification of hydroxytelechelic PET oligomers and carboxytelechelic PCL oligomers

Table 1. Properties of products of copolyesterification

Copolyester	PET [g]	PCL [g]	$Ti(OBu)_4$ [wt%]	$\overline{M}_n$ [g·mol^{-1}][c]	$\overline{M}_w$ [g·mol^{-1}][c]	I_p[c]	T_g[d] [°C]	T_m[d] [°C]	Ester-ester reaction [%][e]
1	25	40[a]	1	21 000	38 800	1.85	–20	–	35
2	25	13[b]	1	22 500	38 200	1.70	–10	200	15
3	25	13[b]	0	19 500	37 000	1.90	–6	208	8

[a] Experiments led by using carboxytelechelic poly(ε-caprolactone) oligomers with molecular weight of 2300 g·mol^{-1}.

[b] Experiments led by using carboxytelechelic poly(ε-caprolactone) oligomers of molecular weight of 730 g·mol^{-1}.

[c] Determined by size exclusion chromatography in $CHCl_3$/HFIP (98/2 wt) with monodisperse PS standards

[d] Determined by DSC at 20°C·min^{-1}.

[e] Determined by ^1H NMR spectroscopy.

erties, an uncatalyzed reaction with the oligomers of $\overline{M}_n$ = 730 g·mol^{-1} was accomplished. All the characterization results of the obtained copolyesters are reported in Table 1.

The molecular weights of the obtained copolyesters are comprised between 19 500 and 22 500 g·mol^{-1} and the polydispersity index is close to 2. This value is characteristic for the polycondensation reactions. The molecular weight of the copolyester **1** is lower than the copolyester **2**. This can be easily explained by the lower reactivity of terminal carboxylic functions of the high molecular weights oligomers as well as by the steric environment, which prevents hydroxyl functions of PET oligomers to reacting with the carboxylic functions. It can be also noticed that the uncatalyzed reaction gives molar mass polyester (copolyester **3**) slightly lower. The obtained result is in good agreement with the literature [42, 43].

The ^1H NMR spectrum of polyesterification products (Figure 5) showed the main conventional spectroscopic fingerprints of PET and PCL blocks, respectively, and the chemical linkage between the different blocks.

From the spectra, some signals coming from ester–ester interchange reaction between base monomers units are represented in Table 2. The ester-ester exchange reaction is a well-known phenomenon that occurs in a polyester chain [45–47]. This reaction comes from internal trans-esterification reactions, leading to inversion of monomers base units into the polyester chain. Their study focused on the polymers blends, but not on a chemical reaction between PET oligomers and the PCL.

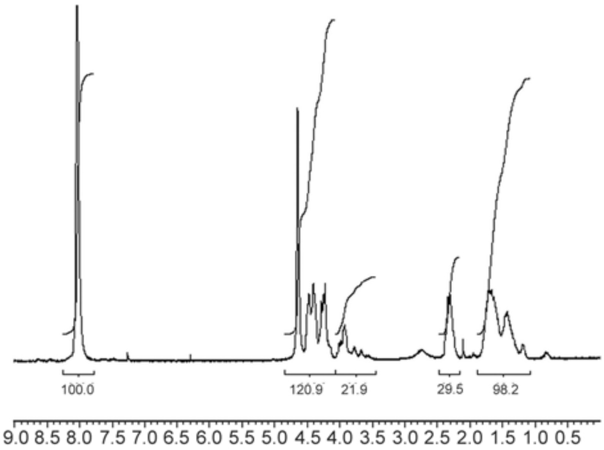
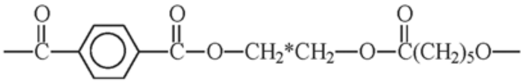
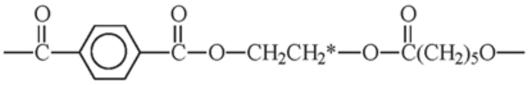
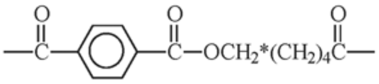
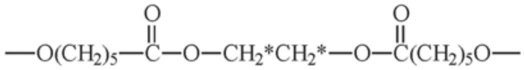


Figure 5. ^1H NMR spectroscopy of copolyesters

The ^1H NMR spectroscopy allows then the calculation of the percentage of ester–ester interchange reaction. This side reaction rate can be determined by using the value of the integration of the peaks at 4.6 and 8.0 ppm (named respectively, $I_{4.6}$ and $I_{8.0}$). If the trans-esterification reaction had not occurred, the ratio I4.6/I8 would not have been modified between the spectrum of oligomers of PET and the copolyesters. The percentage of transesterification phenomenon can be easily determined when comparing the ratio of the integration of the signals at 8 and 4.6 ppm of the PET precursor oligomers and the one of the copolyester. As a result the percentage of transesterification is given by the Equation (3):

$$\%\,\text{transesterification} = \left[1 - \frac{\left(\dfrac{I_{4.6\,\text{ppm}}}{I_{8.0\,\text{ppm}}}\right)\text{in copolyester}}{\left(\dfrac{I_{4.6\,\text{ppm}}}{I_{8.0\,\text{ppm}}}\right)\text{in PET oligomer}}\right] \tag{3}$$

Table 2. ^{1}H NMR study of transesterification products

Chemical shift [ppm]	Coming from	Chemical structure
4.50	Esterification	
4.40	Esterification	
4.25	Transesterification	
4.20	Transesterification	 $-O(CH_2)_5-\overset{O}{\overset{\Vert}{C}}-O-CH_2^*CH_2^*-O-\overset{O}{\overset{\Vert}{C}}(CH_2)_5O-$

This percentage has been calculated for each experiment (Table 1) and a correlation between the ester–ester interchange reaction and the thermal behaviour of the copolyesters has been investigated.

When the copolyesters are synthesized from PCL of $\overline{M}_n$ = 730 g·mol^{-1}, the non-catalyzed reaction gave polyester with about 8% of transesterification reaction, and the ester-ester interchange reaction with titanium-catalyzed copolyester is quantified at about 15%. The results show a link between titanium and ester-ester interchange reaction. It can be a remark also, that the exchange percentage of ester-ester is higher for the copolyester **1** (35%). This is probably due to the low reactivity of PCL used with higher molecular weight. Therefore, the low amount of ester–ester interchange reaction in the copolyester **2** is clear and it can be attributed to the utilization of PCL with low molecular weight.

The DSC thermogram shows that the copolyester **1** does not present a crystalline phase and has only one glass transition temperature (T_g), comprised between the T_g of the PET oligomers and the PCL. The intermediate T_g shows that this copolyester does not present phase segregation phenomenon. It can be explained by the ester-ester interchange reaction. This reaction prevents the copolyester from having thermoplastic elastomer behaviour because length of soft and hard segments decreases and phase segregation is then defavorized.

The immiscibility of PET and PCL was shown by Ma and Prud'homme [46]. However, in our case, the obtained DSC analysis showed that this polyester is constituted by only one phase. This can be linked to the secondary reaction, occurring during polyesterification, which leads to a homogenous mixture.

The use of the Fox-Flory law for blends of miscible polymers could be interesting in order to verify the miscibility of the two phases present in the copolyester **1**. If the glass transition temperature of the copolyester, determined by DSC analysis, is close to the calculated one, the hypothesis of non-phase segregation is confirmed. The Fox-Flory equation (Equation (4)) gives the theoretical value of glass transition temperature of –24°C for this copolyester:

$$\frac{1}{T_g} = \sum \frac{\omega_i}{T_{gi}} \tag{4}$$

where ω_i is the fraction weight of polymer i in the blend and T_gi the glass transition temperature of the polymer i.

The comparison between this value and the experimental value obtained by DSC analysis (Table 1) shows that this co-polyester approaches a mono phase compound behaviour. It can be linked with the ester-ester exchange reaction that produces random co-polyester in which phase segregation phenomenon cannot occur.

The co-polyesters **2** and **3** present only one glass transition temperature (about –6°C with non-catalyzed reaction and –10°C with titanium catalyzed reaction) and only one melting point (T_m) ranging between 200 and 208°C (Table 1). However no crystallization temperature (T_c) can be observed. These obtained co-polyesters are phase segregated. They present amorphous and crystalline phases. The T_g of each co-polyester was different if compared to the theoretical one, calculated using the Fox-Flory law, and which confirms the coexistence of crystalline and amorphous phases in these co-polyesters. Thus, it proves the immiscibility of the two phases. Therefore, it seems that when the ester-ester exchange reaction ratio is not high, the trans-esterification reactions do not prevent the co-polyester from being a segregated product.

The decreasing of the co-polyesters T_m shows also an evolution in the phase segregation. This phenomenon could be explained by the coexistence of a crystalline phase with a high content of PET and a low content of PCL, and an amorphous phase with a high content of PCL and a low amount of PET. The decreasing of PET amount in the crystalline phase can be explained by the loss of the crystallizing point. However T_m and T_c of the PCL have not been detected in the crystalline phase. This hypothesis is in accordance with the work of Ma and Prud'homme [46] which showed the immiscibility of PET and PCL.

4. Conclusions

In the present work, PET is depolymerized by its BHET monomer. Hydroxytelechelic oligomers were obtained in good yield with a molecular weight of $\overline{M}_n$ = 1360 g·mol^{-1}. The thermal properties of the obtained oligomers were found comparable to the properties of the starting PET.

Further, the synthesis of co-polyesters was achieved by polyesterification of the reactive α–ω, hydroxy oligomers of the PET and α–ω, carboxy PCL. The chemical structure of the synthesized co-polyesters was established by SEC and ^{1}H NMR spectroscopy. The comparison of the molecular weights of the obtained co-polyesters showed that the catalyst enhances the molecular weight of the obtained co-polyesters, and the use of carboxytelechelic PCL oligomers with high molecular weight ($\overline{M}_n$ = 2300 g·mol^{-1}) gives a co-polyester with a lower molecular weight. This may be due to the low reactivity of the terminal carboxylic functions.

Furthermore, the presence of the titanium catalyst improves both the polyesterification and the ester–ester exchange reaction. This phenomenon also affects the thermoplastic properties of the obtained co-polyesters. The phase segregation is limited at high ester-ester exchange reaction ratio. However, when the ester-ester exchange reaction ratio is not high, the trans-esterification reactions do not prevent the co-polyester from being a segregated product. The phase segregation permits, in this case, to obtain a thermoplastic elastomer compound. This may be achieved using oligomers carboxytelechelic PCL with a lower $\overline{M}_n$ (e.g. $\overline{M}_n$ = 730 g.mol-1).

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