



New aromatic-aliphatic co-polyesters: Effect of the Structural Characteristic on the thermal Properties

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Abstract

Despite progress in the development of biodegradable polyesters, little attention has been given to aliphatic/aromatic co-polyesters. Therefore, a series of such co-polyesters has been synthesized by polycondensation of hydroxytelechelic poly(ϵ -caprolactone) and bis(2-hydroxyethyl) terephthalate, using a two-step method and a one-step method providing regular and random distributions of starting co-monomers in the co-polyester chains, respectively. The co-polyesters have been characterized by ^1H and ^{13}C NMR, UV-visible absorption spectroscopy and SEC measurements. The chemical composition of the aliphatic/aromatic co-polyesters strongly influences the material characteristics. Even with an identical molar co-monomer composition, the properties of the obtained co-polyesters depended on the synthesis method and therefore on the co-monomer distribution along the polymer chain. The thermal properties of synthesized co-polyesters were studied using DSC and TGA, demonstrating the influence of aromatic rings spread along the macromolecular polyester chain..

Keywords: Steel, Acid solution, Thermal properties, Polycondensation, Aromatic-aliphatic polyester, BHET, Polycaprolactone.

1. Introduction

A great push is currently ongoing to develop biodegradable polyesters for use in various applications because of their versatility, ability to be mass-produced, waste management and carbon emissions [1, 2]. Numerous biodegradable polyesters have been developed, and some of them are commercially available (e.g., poly (ϵ -hydroxy butyrate) (PHB), poly (ϵ -caprolactone) (PCL), polybutylene succinate (PBS), polylactide (PLA),...). These polyesters based exclusively on aliphatic monomers are prepared for various purposes, and they exhibit some disadvantages. However, several properties of the aliphatic polyesters such as high cost, poor thermal and mechanical properties limited the realistic applications of these materials. Therefore, the polymer characteristics are either unsuitable for certain applications or insufficiently adaptable to specific product requirements. For instance, the PCL melting point of 60 °C is relatively low [3-5]. In contrast, the aromatic polyesters, such as polyethylene terephthalate (PET), have excellent thermal and mechanical properties and are relatively inexpensive. Nevertheless, they are not biodegraded in most natural environments thus increasing their resistance toward the microbial attack [6-9]. According to the literature [10-16], the introduction of a terephthalic unit in the polyester structure improves the physical properties. Indeed, many researchers have synthesized aliphatic-co-aromatic co-polyesters [10, 11] to generate biodegradable polymers with satisfactory mechanical properties. Witt et al [12, 13] showed that the biodegradation rate of co-polyesters made from the aliphatic and aromatic polyesters can be regulated by controlling the composition in aromatic segments. Poly (butylenes adipate-co-terephthalate) (PBAT, Ecoflex®) are a commercialized aliphatic-aromatic, biodegradable co-polymer, their mechanical and biodegradation properties were extensively studied [17-19]. An optimal equilibrium between the biodegradability and the physical properties [20] is attained with aliphatic–aromatic co-polyesters composed of 35-55 mol% aromatic units. PBAT and other polymers were used as packaging materials. Other works [21, 22] proposed the use of these products in agricultural applications

including plastic bags, greenhouse films, and mulch films. It is ideal for disposable packaging as it decomposes in compost within a few weeks or in soil without leaving any residue [23]. As with other aliphatic polyesters, the biocompatibility of PBAT and its copolymers has led to several commercially successful applications [24, 25]. Bis(2-hydroxyethylene) terephthalate (BHET) is a commercial low molecular weight diol based on terephthalic unit and can be used to synthesis polyester materials. Recently, in our laboratory, we have used BHET to prepare polyurethanes based on PCL. The obtained polymers possess good thermal and mechanical properties [26- 29].

In this study, we tune the thermal performance of PCL by synthesizing poly condensates containing in their structure ester links and aromatic rigid segments in limited quantities in order to preserve their biodegradability. The work presented in this article is innovative for two reasons. First, we have mastered a simple and quantitative method for to transform BHET into carboxytelechelic derivative (BHET diacide), by an esterification reaction between succinic anhydride and the commercially available BHET. Second, we report the synthesis of two types of polycondensates : i) so-called "regular" polyesters prepared by direct polycondensation of hydroxytelechelic PCL with BHET diacide and ii) "random" polyesters by polycondensation of alkoxytelechelic PCL/BHET and succinic anhydride in defined relative quantity. These conditions enabled us to obtain various polyesters with different structures and thermal properties.

All the obtained copolyesters have been characterized by high-field nuclear magnetic resonance (^1H and ^{13}C NMR), UV-Visible Absorption Spectroscopy, size exclusion chromatography (SEC), differential scanning calorimetry (DSC) and Thermogravimetric Analysis (TGA).

2. Materials and methods

2.1. Reagents

Bis(2-hydroxyethyl) terephthalate (BHET) and poly(ϵ -caprolactone) diol (α,ω -OH oligo-PCL) (number average molecular weight $2000 \text{ g}\cdot\text{mol}^{-1}$) were purchased from Aldrich and kept in a vacuum desiccator in the presence of P_2O_5 . Succinic anhydride (AS), chloroform, 1,4-dioxane, methanol, 4-dimethyl aminopyridine (DMAP) and dibutyl tin dilaurate (DBTDL) were also supplied by Aldrich. All reagents were used without further purification.

2.2. Techniques

2.2.1. Nuclear Magnetic Resonance (NMR)

^1H and ^{13}C -NMR spectra were recorded on a Bruker spectrometer 250 MHz, at room temperature. The solvents used are CDCl_3 and DMSO-d_6 . Chemical shifts are given in ppm relative to TMS as an internal reference.

2.2.2. UV-Visible Absorption Spectroscopy

Measurements were carried out using an UV-Visible absorption spectrometer UVIKON 932 with double beam, deuterium and tungsten lamps. It can operate on a range of wavelengths between 190 and 900 nm. Parallelepiped quartz cells with a length and width of 1cm and a height of 5 cm were used. Dilute solutions (1 g/L) in chloroform were prepared and placed in measurement cells. The measurements were carried out within a wavelength range of 200-400 nm. The maximum absorption of BHET is at 285 nm. The terephthalic unit percentage (TU%) in polyesters was calculated using a calibration curve performed with solutions of different concentrations in BHET (0.1, 0.2, 0.3 and 0.4 g/L) and the absorption intensity at 285 nm.

2.2.3. Size Exclusion Chromatography (SEC)

The size exclusion chromatograms were recorded on an IOTA2 apparatus supplied by JASCO with a PU-980 Intelligent HPLC pump. The columns employed were PLgel $5\mu\text{m}$ Mixed-D 300×7.5 mm, VARIAN INC. The mobile phase was chloroform and the flow rate was 1 mL/min. Samples were injected using an injector of the Agilent 100 Series. Molar masses were determined in relation to monodisperse polystyrene standards.

2.2.1. Differential Scanning Calorimetry (DSC)

DSC analyses were performed with a 204 F1 NETZSCH. Experiments were carried out under nitrogen with samples ranging from 15 to 20 mg. The temperature range of the first heating scan was between -80 to 250 $^\circ\text{C}$, with a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$, followed by a cooling at $20 \text{ K}\cdot\text{min}^{-1}$. A second scan was immediately performed with a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$. Glass transition temperature was taken at the midpoint of change in heat capacity.

2.2.4. Thermogravimetric Analysis (TGA)

These tests provide the mass loss of samples during heating. Measurements were performed on a TG 209 F3 NETZSCH 51. About 15 mg of samples were put in ceramic pan and heated from 30 to 600 °C under nitrogen purge with a temperature ramp of 10 K.min⁻¹.

2.3. Synthesis of regular copolyester P₀

2.3.1. Synthesis of carboxytelechelic BHEToligomers

In a 1 L two-necked flask equipped with a condenser, a nitrogen inlet and a magnetic stirrer, 15 g (0.059 mol) of BHET, 13 g (0.13 mol) of succinic anhydride and 1 mol% of DMAP with 500 mL of 1,4-dioxan as solvent were introduced. The reaction occurred at 50 °C. After 12 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 acid water (pH = 1) in order to remove residual succinic acid. After drying on Na₂SO₄, the solvent was removed by evaporation and under vacuum at 60 °C. We obtain a white solid with a 85% yield. mp: 83 - 85 °C (C₂H₅-O- C₂H₅); ¹H NMR (250 MHz, DMSO-d₆): δ = 4,40 (m, 4H); 4,55 (m, 4H); 2,55(t, 8H); 8,10(s, 4H); ¹³C NMR (DMSO-d₆): δ(ppm) = 28,5(CO -(C₂H₅)₂-CO); 61,4(C₂H₅-OCO); 62,85(Ph-CO₂-C₂H₅); 130(C₂H₅); 133(C₂H₅); 165(CO₂H); 172(CH₂-CO₂-); 173(Ph-CO). Anal. Calcd for C₂₀H₂₂O₁₂: C, 52.86; H, 4.84; O, 42.29. Found: C, 52.75, H, 4.78; O, 42.47.

The titration of the oligomer carboxylic functions is carried out by following a classical method: a known mass of the product is titrated by a solution of KOH in MeOH using phenolphthalein as color indicator. The carboxylic ratio is given by the equation:

$$I_{COOH} = \frac{C_{KOH} \times V_{KOH}}{m}$$

Where C_{KOH} represents the concentration of KOH solution, V_{KOH} the equivalent volume and m the mass of the titrated oligomer. The determined value is 1.98.

2.3.2. Copolyesterification of hydroxytelechelic poly(ε-caprolactone) oligomers and BHET diacide

In a 250 mL reactor, equipped with a mechanical agitation and a supply of nitrogen, 20 g (0.01 mol) of hydroxytelechelic poly(ε-caprolactone) oligomers, 4.54 g (0.01 mol) of BHET diacide and 0.3 wt% of DBTDL were introduced. The mixture was heated under nitrogen at 220 °C and the pressure was set at 1000 mbar in the reactor in order to remove the formed water. After 5 hours, the mixture was cooled down, solubilized in acetone and precipitated in a large excess of methanol. The obtained copolyester was dried under vacuum at 60 °C for 72 hours.

2.3.3. Synthesis of random copolyester P_i

A mixture of PCL, BHET and AS were simultaneously introduced in a reactor of 250 mL and then heated to 100°C until all products fused. The catalyst (DBTDL) was then introduced and the temperature of the solution was increased until 220°C. After 5 hours, the mixture was cooled down, solubilized in acetone and precipitated in a large excess of methanol. The obtained co-polyesters were dried under vacuum at 60 °C for 72 hours.

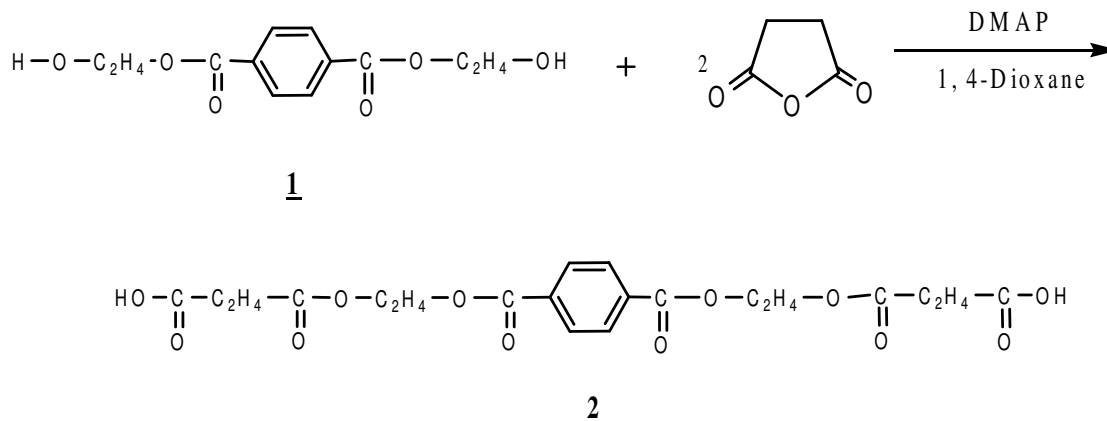
3. Results and discussion

3.1. Syntheses of PCL-based copolyesters and determining their TU%

3.1.1. Synthesis of carboxytelechelic BHET oligomers

Bis(2-hydroxyethyl)terephthalate is transformed with succinic anhydride to give carboxytelechelic oligomers which are not commercially available (Scheme 1). The analysis of the purified product show that the ring opening reaction of succinic anhydride occurred effectively. The mass yield of reaction was 85%.

In the ¹H NMR spectrums (Figure 1), we note a deshielding of the two α-protons to the alcohol of 3.75 to 4.40 ppm, and appear as a triplet. The β-protons appear at 4.55 ppm and the aromatic protons resonate at 8.10 ppm as a singlet. We note also the presence of a multiplet centred at 2.5 ppm corresponding to α- and β protons of the acid function. The ratio of the peak integration of different signals attests that the esterification reaction between succinic anhydride and BHET is quantitative. This interpretation is confirmed by ¹³C NMR, elemental analysis and carbonyl titrimetry. The latter method allowed us to calculate of the PCL carboxylic functionality of 1.98 as described in experimental part. According to the recorded results, we conclude that the opening ring reaction of succinic anhydride is quantitative.



Scheme 1. Synthesis of the BHET carboxytelechelic oligomers.

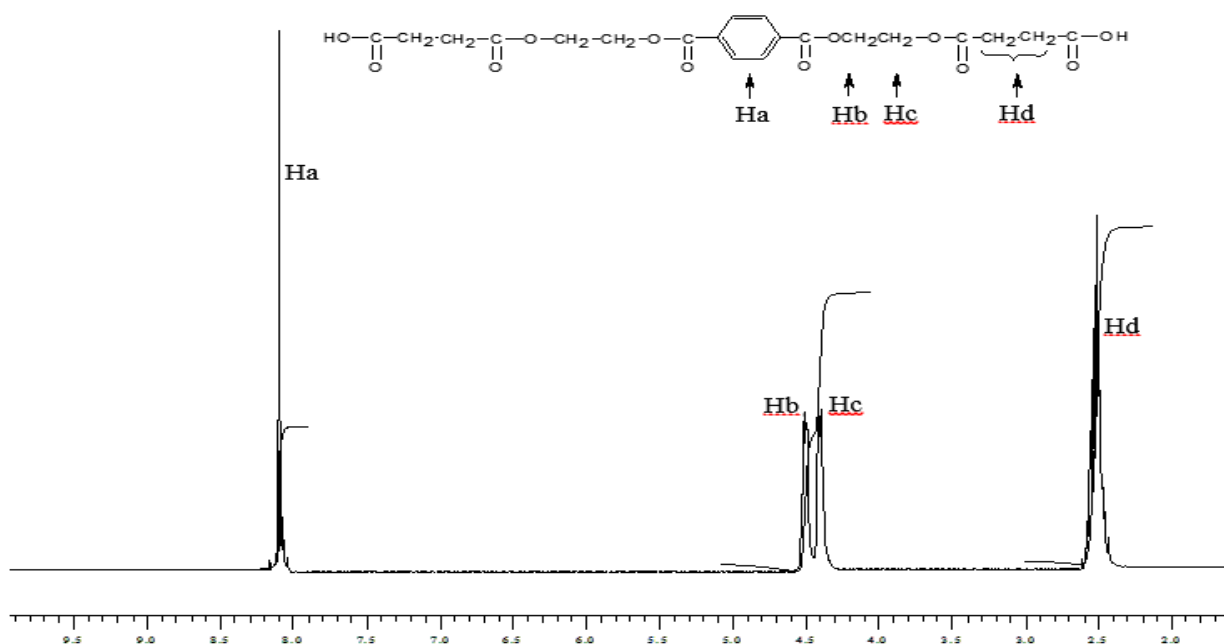
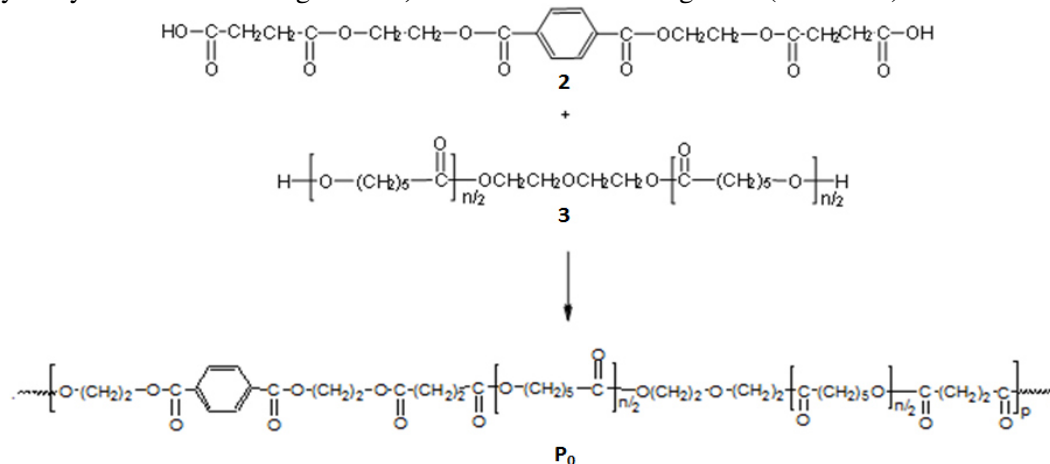


Figure 1: ^1H NMR (250 MHz, CDCl_3) spectrum of BHET carboxytelechelic oligomers

3.1.2. Synthesis of regular copolyesters In order to control the distribution of PCL and BHET units along the polymer chain, a regular copolyester (P_0) has been synthesized by a condensation reaction between the diacid **2** and the hydroxytelechelic PCL oligomers **3**, of a molar mass $2000 \text{ g}\cdot\text{mol}^{-1}$ (Scheme 2).



Scheme 2: Synthesis of the regular copolyester P_0

Figures 2 and 3 respectively show the ^1H NMR and ^{13}C NMR of the copolyester P_0 and the assignment of all resonance signals confirming the expected incorporation of terephthalic ester units within the polycondensated chains. For instance in the ^1H NMR spectrum, a shift of terminal PCL protons is observed from 4.04 to 4.53 ppm as well as the presence of 4 protons at 2.63 ppm assigned to the succinic ester moiety. Also, the composition of terephthalic ester units within the polymer chains (expressed as TU%) could be assessed from the integration peak of aromatic (8.1 ppm) and PCL central protons segments (3.7 ppm). The TU% value found for P_0 ,

$$TU\% = \frac{I_{8.10}}{I_{3.70} + I_{8.10}} \times 100 \quad (1)$$

Where I_x is the integration peak value of the signal located at x ppm.

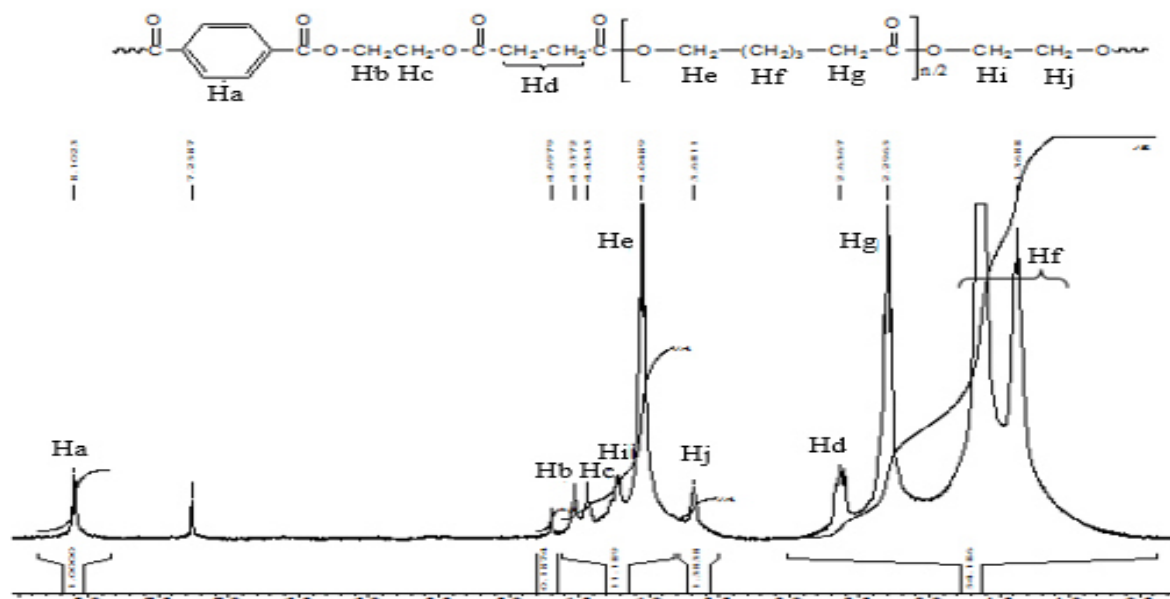


Figure 2. ^1H NMR (250 MHz, CDCl_3) spectrum of the regular copolyester P_0

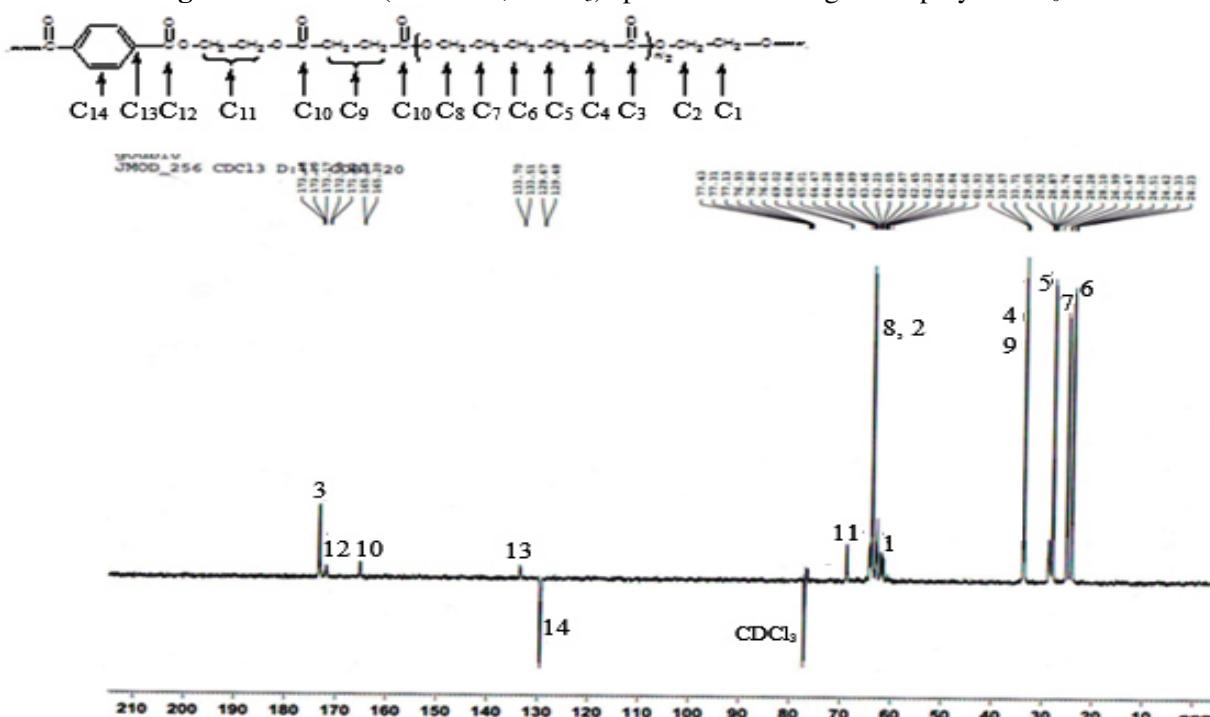
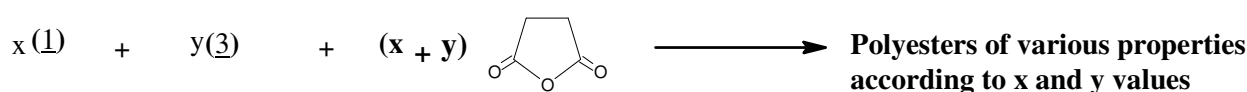


Figure 3. ^{13}C NMR (CDCl_3) spectrum of the regular copolyester P_0

The P₀TU% was also determined by UV-visible spectroscopy from the absorption intensity at 285 nm. The value of 48% is consistent with the theoretical and the values determined by ¹H NMR. Moreover, the molecular average number weight is determined by size exclusion chromatography (SEC), using polystyrene standards. The results of 29700 g.mol⁻¹ and 1.80 correspond to M_n and I_p (Table 1). All results show a good coherence and attest a successful synthesis of the P₀ regular co-polyester.

3.1.3. Synthesis of random copolyesters with different terephthalic ester contents

In order to synthesize the random polymers, we have used the strategy illustrated in Scheme 3. The target polyesters P_i possessing different structures and properties are prepared from various initial molar mixtures of BHET (**1**), PCL (**3**) and succinic anhydride. Both ¹H NMR and ¹³C NMR spectra show several similarities to our previously discussed regular co-polyester P₀. Therefore, the analysis of all resonance signals in ¹H NMR spectra, show the same chemical shift with different integration peaks. Table 1 collects the initial molar ratios of reagents, composition of polyester in terephthalic units, i.e., TU% as determined by ¹H NMR and UV-visible spectroscopies, and the number- weight-average molar masses as recorded by SEC.



Scheme 3: Synthesis of random polyester PE_i

The values of the polyesters composition determined by ¹H NMR and UV-Visible spectroscopies are consistent and show that the composition in terephthalic ester units is almost equal to the molar ratio of BHET / PCL initially introduced in the reaction mixture.

Table 1: Composition and average molar masses of different copolyesters P₀-P

Polyester	BHET/PCL/SA	(TU%) _{the}	(TU%) _{exp}		\overline{M}_n	\overline{M}_w	I _p
			¹ H NMR	UV-visible			
P ₀	1 / 1 / 2	50	52	48	29700	53400	1.80
P ₁	1 / 1 / 2	50	48	47	23000	43700	1.90
P ₂	2 / 1 / 3	67	60	68	19000	34200	1.80
P ₃	3 / 1 / 4	75	79	71	16000	33600	2.10
P ₄	1 / 2 / 3	33	33	30	39500	69000	1.75
P ₅	1 / 3 / 4	25	20	23	44500	75600	1.70

(TU%)_{the}: theoretical value

(TU%)_{exp}: experimental value

Therefore, we conclude that the strategy concerning the introduction of terephthalic ester units in the polycondensate structure is efficient and leads to copolyesters whose composition is equal to the theoretical stoichiometry. On the other hand, as can be seen from table 1, the molecular masses of the random copolyesters depend strongly on the TU% values. The molecular masses decrease as their composition TU% increases. Also, P₅ is the copolyester having the lower TU% of 25% and presents molecular average weights three times higher than that the value obtained for P₃.

This result may be due to the high reactivity of succinic anhydride, which also reacts with the hydroxyl end-groups of the α,ω-OH oligo-PCL giving carboxytelechelic PCL. Then these carboxylic groups react with OH groups of BHET and PCL diol. The succinic anhydride reacts well with both diols **1** and **3**. This explanation agrees with the observations with other samples. Moreover, the molar masses particularly increase as the concentration of PCL increases, as a result of its inherent higher number-average molar weight.

Furthermore, different molar masses have been determined for P₀ and P₁, possessing a similar chemical composition but produced in two different ways. P₀ synthesized in two-step method has a number-average molar weight (29700 g/mol) higher than that one of P₂ (23000 g/mol) which was obtained in one-step approach.

This result may be explained by the high reactivity of the hydroxytelechelic PCL with respect to the acid groups of product 2, which supports our previous hypothesis. Furthermore, the dispersity index is close to 2 for all obtained copolyesters, characteristic value for polycondensation reactions.

3.2. Thermal properties

3.2.1. Analysis by Differential Scanning Calorimetry (DSC)

Figure 4 shows the thermograms obtained during the first heating scan (see experimental part). We observe a slight displacement of the melting peak of soft segments and the glass transition temperature to higher temperatures as TU% in co-polyesters increases. This result may be explained by the strong interactions between terephthalic ester units and PCL segments [20, 30]

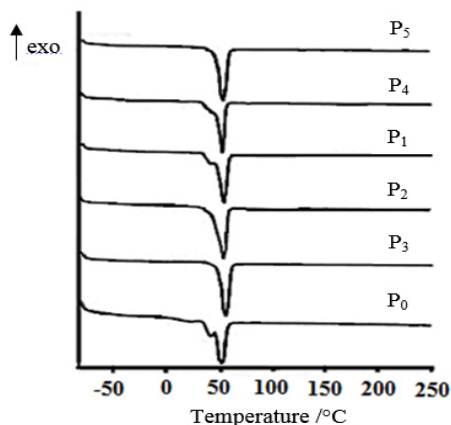


Figure 4: DSC thermograms of different co-polyesters P₀-P₅ as recorded during the first scan.

Table 2 reports some thermodynamic properties such as glass transition temperatures, melting temperatures and melting enthalpies of the investigated co-polyesters as recorded during the first heating scan. An significant decrease of the melting enthalpies from P₅ (TU% equal to 25) to P₄ (TU% equal to 33) is noted. Afterwards they increase very slightly with the increasing of TU%. These results show clearly that strong interactions of terephthalic ester units prevent soft segment from crystallizing.

Table 2: Glass transition temperature T_g , melting temperature T_m , and melting enthalpies (ΔH_m) of the polyesters P₀-P₅ recorded during the first scan

<i>Polyester</i>	T_g (°C)	T_m (°C)	ΔH_m (J/g)
P₅	-55.8	55.2	102.6
P₄	-44.6	55.3	75.4
P₁	-42.3	55.6	79.3
P₂	-40.8	55.8	79.3
P₃	-37.7	57.2	86.1
P₀	-42.0	57.3	39.8

By comparing the thermal transitions of P₀ and P₁, both containing the same TU composition but prepared with different synthesis methods, the enthalpy of fusion of the soft segments of P₀ (regular structure) is found to be much lower than the value recorded for P₁ (random structure), this is probably due to the order of arrangement of hard segments in the structural chain of the regular copolyester P₀, which diminishes the crystallization of soft segments, as previously discussed. After rapid cooling, the samples underwent a second rise in temperature. The thermograms presented in figure 5 show two endothermic melting temperatures, indicating the presence of two distinct crystalline forms in various co-polyesters. This observation is attributed to different degrees of arrangement or size of crystallites [15]. We also detected a slight increase in glass transition temperatures and a decrease in both melting temperatures and melting enthalpies of soft segments with increasing the percentage in TU (Table 3). Such an observation more likely results from the rapid cooling of the samples, which did not have enough time to crystallize.

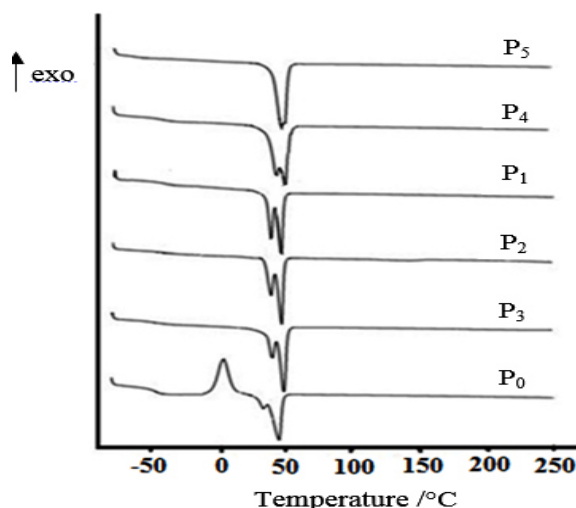


Figure 5: DSC thermograms of different co-polyesters P₀-P₅ as recorded during the second scan.

The above described thermal behavior is often observed for copolymers derived from PCL and is attributed to a more restricted mobility of soft segments (or higher viscosity) when PCL is covalently linked to a polymer chain. This chemical bond between the PCL segments and other blocks restricts the phase separation and consequently the crystallization of PCL segments. By comparing the thermal transitions of the polyesters P₀ and P₁ containing the same composition in TU, only P₀ shows the presence of an exothermic crystallization peak of PCL segments at ca. 1.5 °C. Therefore, the thermal properties of the copolyesters are strongly influenced by the method of synthesis, hence the comonomer repartition along the polymer chain.

3.2.2. Analysis by thermogravimetric Analysis (TGA)

The recorded TGA thermograms (Figure 6) show that all investigated copolyesters decompose through the same process. The degradation always starts around 270 °C and depends on the polyester composition in terephthalic ester units. So any increase in TU within the copolymer composition tends to increase the thermal stability of the materials.

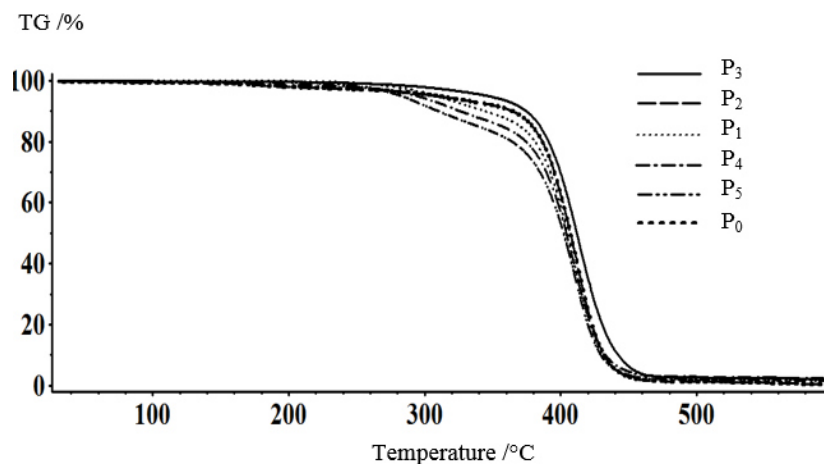


Figure 6: TGA thermograms of co-polyesters P₀-P₅.

The results demonstrate that P₃ is the most resistant polymer towards thermo-oxidative degradation, due to its higher TU%. The thermograms of copolyesters P₀ and P₂ are superimposed, so these two copolyesters have the same thermal stability even though they are characterized by different structures and relative compositions. At this stage of the study no clear-cut explanation is possible. Besides, the first stage of decomposition of the regular copolyester P₀ is observed at a higher temperature when compared to that one of P₁ containing the same chemical composition. This result may be able to be explained by the fact that terephthalic ester units are alternately arranged with PCL segments in the copolymer chains of P₀, so their influence in thermal stability is more effective.

Conclusion

In this work, we first developed a simple and quantitative way to transform BHET into the corresponding carboxytelechelic oligomer. The ring opening by addition with the hydroxyl functions of BHET is involved in this reaction. In a second step, we have introduced as defined quantity of terephthalic units in the PCL structure. Regular copolyester has been synthesized by direct polyesterification of hydroxytelechelic PCL oligomers with BHET diacide. Random copolyesters with various amounts of terephthalic ester units have then been prepared via a polycondensation reaction by varying the molar ratio of PCL diol, BHET and succinic anhydride in the initial reaction mixture. We obtained a variety of co-polyesters possessing a variable composition ranging from a high of 75% to a weak of 25% in terephthalic ester units. The study of thermal properties using differential scanning calorimetric analysis shows that they are influenced by the synthesis method and the relative amount of incorporated terephthalic ester units. The increasing of TU% in polyester chains increases the glass transition temperature and allows restricting phase separation and crystallization of PCL segments. Thermogravimetric analyses indicate that the thermal stability of the polyesters is highly depends on the synthesis method and the TU%. All co-polyesters decompose by the same process. The temperature of starting decomposition/weight loss increases with increasing terephthalic ester units within the polyesters.

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