Synthesis and thermal properties of new copolyesters based on polycaprolactone

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Abstract: Several copolyesters were synthesized from carboxytelechelic poly(ϵ -caprolactone) and bis(2-hydroxyethyl)terephthalate (BHET), using a two-step method and a one-step method providing regular and random distributions of starting comonomers in the copolyester chains, respectively. Even with an identical molar comonomer composition, the properties of obtained copolyesters depended on the synthesis method, therefore the comonomer distribution along the polymer chain. The copolyester structure was characterized by ^1H and ^{13}C NMR and FTIR spectroscopy. The thermal properties of synthesized copolyesters were also studied by DSC and TGA demonstrating the influence of aromatic rings spread along the macromolecular polyester chain.

Keywords : polyester, polycaprolactone, polycondensation, thermal properties.

Introduction

Presently, increasing volumes of plastics are manufactured and used for various applications because of their versatility and ability to be mass-produced. However, they are usually not naturally decomposed, thus they are considered to cause some environmental problems. For this reason, many scientists have worked to develop new biodegradable polymers. A number of biodegradable polyesters have been developed, and some of them are commercially available (e.g., poly(β -hydroxybutyrate) (PHB), poly(ϵ -caprolactone) (PCL), polybutylene succinate (PBS), polylactide (PLA), ...). All these polyesters are based exclusively on aliphatic monomers. Although these aliphatic polyesters are applicable for various purposes, they exhibit some disadvantages. The polymer characteristics are either unsuitable for certain applications or insufficiently adaptable to specific product requirements, for instance, the melting point of PCL is relatively low, about 60 °C [1-4]. In contrast, pure aromatic polyesters, such as polyethyleneterephthalate (PET), which are

produced on a large industrial scale, display satisfactory properties, but are resistant to microbial attack [5-9].

According to the literature [10-20], the introduction of terephthalic units in the structure of polyester improves its physical properties. Tokiwa and Suzuki [12, 13] indicated that the physical properties of aliphatic polyesters are improved by adding aromatic (poly)esters into the polymer chains. They also suggested that the biodegradation rate of copolyesters made from aliphatic and aromatic polyesters can be regulated by controlling the composition in aromatic segments. Copolyesters, particularly those obtained from 1,4-butanediol, adipic acid and terephthalic acid (PBAT copolyesters), look promising as biodegradable materials in packaging and other applications.

Indeed, PBAT is now marketed under the trade name of Ecoflex[®]. Witt et al [19,20] showed that this copolyester display good mechanical and thermal properties when the molar concentration of terephthalic acid is superior to 25%, but its rate of biodegradation declines sharply at a concentration higher than 50%. Therefore, the ratio of aliphatic and aromatic comonomers must be chosen judiciously. For a terephthalic acid molar concentration between 25 and 50% in maximum, the copolyesters reach a good compromise between biodegradability and properties of use.

Bis(2-hydroxyethylene) terephthalate (BHET) is a commercial low molecular weight diol based on one terephthalic unit and can be used in the development of polyester materials. Recently, some of us have used BHET to synthesize polyurethanes based on PCL, the obtained polymers possess good thermal and mechanical properties [21- 23].

In this study, it is aimed to tune the thermal performance of PCL by synthesizing polycondensates containing in their structure ester links and aromatic rigid segments in limited quantities in order to preserve their biodegradability. We report the syntheses of two types of polycondensates : i) so-called “regular” polyesters elaborated by direct polycondensation of carboxytelechelic PCL with BHET and ii) “random” polyesters by polycondensation of alkoxytelechelic PCL/BHET and succinic anhydride in selected relative quantity. The carboxytelechelic PCL is first synthesized by esterification reaction between commercially available α,ω -OH oligo-PCL and succinic anhydride. These conditions enabled us to obtain various polyesters with different structures and thermal properties.

Results and discussions

Syntheses of PCL-based copolyesters

-Synthesis of carboxytelechelic PCL oligomers

Firstly, α,ω -OH oligo-PCL reacted with succinic anhydride giving carboxytelechelic PCL oligomers which are not commercially available. Secondly, the copolyesters were obtained by reaction between the obtained carboxytelechelic PCL and BHET (Scheme 1).

In order to control this reaction when using the PCL of molar mass 2000 g.mol^{-1} , the reaction was first studied with PCL oligomers of lower molar mass (530 g.mol^{-1}) used as model. The analyses of the purified product by FTIR and ^1H NMR show that the

ring opening reaction of succinic anhydride occurred effectively. The mass yield of reaction was 80%.

Scheme 1. Synthesis of carboxytelechelic poly (ϵ -caprolactone) oligomers.

In the ^1H NMR spectrum (Figure 1), we note the presence of a broad signal at 8.4 ppm corresponding to the acid proton. The α - and β -protons of the acid function appear as a multiplet centred at 2.55 ppm. Other peaks correspond to the protons of the aliphatic chain of PCL. The ratio of the peak integration of different signals attests for quantitative esterification reaction between succinic anhydride and PCL diol.

Fig. 1. ^1H NMR(250 MHz, CDCl_3) spectrum of carboxytelechelic poly(ϵ -caprolactone).

We repeated the same reactions with α,ω - PCL diol of higher molar mass, i.e., 2000 $\text{g}\cdot\text{mol}^{-1}$. The analyses of the purified product by ^1H NMR and FTIR show that the

reaction took place. We obtained spectra identical to the preceding ones with the same signals at the same chemical shifts.

The comparison of size exclusion chromatograms (SEC) -before and after esterification reaction- shows a slight increase in molar mass, but the obtained product displays the same polydispersity index as that of the starting product and shows no formation of by-products. The molar mass of PCL diol measured by SEC is close to the value announced by the supplier (2100 g.mol^{-1} instead of 2000 g.mol^{-1}) with a dispersity index of 1.47. After reaction, the obtained carboxytelechelic PCL oligomers have a molar mass of 2360 g.mol^{-1} and a dispersity index of 1.45.

According to the recorded results, we can conclude that the reactivity of terminal OH functions of α,ω -OH PCL is independent of its length (at least within the range of investigated molecular weight) and the ring opening reaction of succinic anhydride by these hydroxyl groups is quantitative.

-Synthesis of regular copolyesters

In order to control the distribution of PCL and BHET units along the polymer chain, a regular copolyester (P_1) has been synthesized by condensation between the carboxytelechelic PCL oligomers **2** and BHET **3** (Scheme 2).

Figures 2 and 3 respectively show the ^1H NMR and ^{13}C NMR of the obtained copolyester 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 protons of BHET is observed from 3.8 to 4.4 ppm as well as the presence of 4 protons at 2.63 ppm assigned to the succinic ester moiety.

Fig. 2. ^1H NMR (250 MHz, CDCl_3) spectrum of regular copolyester P_1 .

Fig. 3. ^{13}C NMR (CDCl_3) spectrum of regular copolyester P_1 .

From the ^1H NMR spectrum the composition of terephthalic ester units within the polymer chains (expressed as TU%) could be assessed from the peak integration of aromatic protons (8.1 ppm), and central protons of PCL segments (3.7 ppm). The TU% value found for P_1 , using the equation (1), was 53%.

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

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

Scheme 2. Synthesis of regular copolyester P_1 .

The TU% of P_1 was also determined by UV-visible spectroscopy from the absorption intensity at 285 nm, the obtained value was 48%. This result is consistent with the theoretical and the ^1H NMR determined values. Moreover, the number average molecular weight as determined by size exclusion chromatography (SEC), using polystyrene standards, was $29650 \text{ g}\cdot\text{mol}^{-1}$ with a dispersity index equal to 1.85 (Table 1). All gathered results show a good coherence and attested a successful synthesis of the regular copolyester P_1 .

-Synthesis of random copolyesters with different terephthalic ester contents

For the synthesis of these random polymers, the strategy illustrated in Scheme 3 has been adopted. In order to obtain polyester P_i with different structures and properties, various initial molar mixtures of PCL (II), BHET (III) and succinic anhydride have been investigated.

Scheme 3. Synthesis of random copolyester P_i .

The ^1H NMR and ^{13}C NMR spectra show several similarities to previously discussed regular copolyester P_1 . On ^1H NMR spectra, the resonance signals show up at the same chemical shifts but they differ in the values of peak integration.

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- and weight-average molar masses as recorded by SEC.

Tab. 1. Composition and average molar masses of different copolyesters P_1 - P_6

Polyester	BHET/PCL/SA	(TU%) _{the}	(TU%) _{exp}		$\overline{M}_n$	$\overline{M}_w$	I_p
			^1H NMR	UV- visible			
P₁	1 / 1 / 2	50	53	48.0	29650	54900	1.85
P₂	1 / 1 / 2	50	48	47.8	23050	44050	1.91
P₃	2 / 1 / 3	67	60	68.8	19100	34450	1.80
P₄	3 / 1 / 4	75	79	71.0	15300	32700	2.14
P₅	1 / 2 / 3	33	33	29.3	39650	69400	1.75
P₆	1 / 3 / 4	25	20	22.4	44500	77450	1.74

(TU%)_{the}: theoretical value

(TU%)_{exp}: experimental value

The values of the composition of polyesters 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 introduced initially in the reaction mixture. Therefore, we can conclude that the introduction strategy of terephthalic ester units in the polycondensate structure is efficient and leads to copolyesters whose composition is equal to the theoretical stoichiometry.

If we compare the molecular masses of random copolyesters, we find that they decrease as their composition in TU% increases (Table 1). P_6 is the copolyester having the lower TU%, and presents average molecular weights three-fold higher than that of P_4 having the higher TU%. This result may be due to the high reactivity of succinic anhydride with respect to the hydroxyl end-groups of the α,ω -OH oligo-PCL giving carboxytelechelic PCL. Then these carboxylic groups react promptly with OH groups of BHET. In other words, anhydride succinic reacts better with PCL diol than with BHET. This explanation can be applied to other samples. Moreover, the molar masses become particularly important as the concentration of PCL increases, as a result of its inherent higher number-average molar weight.

Furthermore, if one compares the molar masses of P_1 and P_2 , both have the same chemical composition but have been produced by two different synthesis pathways. P_1 synthesized by the two-step method displays a number-average molar weight (29650 g/mol) higher than that of P_2 (23050 g/mol) as obtained by the one-step approach. This result can be explained by the high reactivity of the carboxytelechelic PCL with respect to the hydroxyl groups of BHET, which strengthens our previous hypothesis. Besides, the dispersity index is close to 2 for all obtained copolyesters, characteristic value for polycondensation reactions.

Thermal properties

- Analysis by Differential Scanning Calorimetry (DSC)

Figure 4 shows the thermograms obtained during the first heating scan (see experimentals).

Fig. 4. DSC thermograms of different copolyesters P_1 - P_6 as recorded during the first scan.

There is a slight displacement of the melting peak of soft segments and glass transition temperature to higher temperatures as TU% in copolyesters increases. This result can be explained by strong interactions between terephthalic ester units and PCL segments [25, 26].

Tab. 2. Glass transition temperature T_g , melting temperature T_m , and enthalpies of fusion (ΔH_m) of polyesters P₁-P₆ recorded during the first scan.

Polyester	T_g (°C)	T_m (°C)	ΔH_m (J/g)
P₆	-55.8	55.2	102.6
P₅	-44.6	55.3	75.4
P₂	-42.3	55.6	79.3
P₃	-40.8	55.8	79.3
P₄	-37.7	57.2	86.1
P₁	-42.0	57.3	39.8

In Table 2, we report the glass transition temperatures, melting temperatures and melting enthalpies of the investigated copolyesters as recorded during the first heating scan. There is an important decrease in melting enthalpies from P₆ (TU% equal to 25) to P₅ (TU% equal to 33). Afterwards they increase very slightly with increasing TU%. These results show clearly that strong interactions with terephthalic ester units prevent soft segment from crystallizing.

Fig. 5. DSC thermograms of different copolyesters P₁-P₆ as recorded during the second scan.

By comparing the thermal transitions of P₁ and P₂, both containing the same TU composition but differing from the synthesis method, the enthalpy of fusion of soft segments of P₁ (regular structure) is found much lower than the value recorded for P₂

(random structure), this is probably due to the order of arrangement of hard segments in the structural chain of regular copolyester P₁, which restricts the crystallization of soft segments, as previously discussed.

After rapid cooling, the samples underwent a second rise in temperature. The thermograms obtained (Figure 5) show the presence of two melting endotherms, indicating the presence of two distinct crystalline forms in various copolyesters that can be attributed to different degrees of arrangement or size of crystallites [16]. There are also 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.

Tab. 3. Glass transition temperature T_g , melting temperature T_m , and enthalpies of fusion (ΔH_m) of polyesters P₁-P₆ recorded during the second scan.

Polyester	T_g (°C)	T_c (°C)	T_f (°C)	Tf (°C)	ΔH_f (J/g)
P₆	-53.4	-	47.3	50.7	70.2
P₅	-44.5	-	44.8	49.0	61.5
P₂	-41.7	-	41.2	49.1	56.3
P₃	-40.2	-	40.3	48.2	55.0
P₄	-39.6	-	40.0	47.1	54.6
P₁	-40.1	1.5	41.2	46.0	41.3

The thermal behavior above described is often observed for all copolymers derived from PCL and is attributed to a more limited mobility of soft segments (or higher viscosity) when PCL is linked covalently 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 P₁ and P₂ containing the same composition in TU, only P₁ displays 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.

-Thermogravimetric Analysis (TGA)

The recorded TGA thermograms (Figure 6) show that all investigated copolyesters decompose through the same process. The degradation starts only around 270 °C and depends on the polyester composition in terephthalic ester units. The temperature of starting decomposition/weight loss increases with increasing the terephthalic ester units. So any increase in TU within the copolymer composition tends to endow the materials with a better thermal stability.

We can also observe that P₄ is the most resistant towards thermo-oxidative degradation, due to its higher TU%. The thermograms of copolyesters P₁ and P₃ can be 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 has been found out. Besides, the first stage of decomposition of the regular copolyester P₁ is shifted towards higher temperature compared to that of P₂ containing the same chemical composition. This result could be explained by the fact that terephthalic ester units are distributed alternately with PCL segments in the copolymer chains of P₁, so their influence in thermal stability is more effective.

Fig. 6. TGA thermograms of copolyesters P₁-P₆.

Conclusions

In this work, we first mastered a simple and quantitative way to transform hydroxytelechelic PCL oligomers into carboxytelechelic PCL oligomers. This reaction was achieved by ring opening of succinic anhydride on the PCL diol. In a second step, we have also managed to introduce terephthalic units within the PCL structure according to the expected percentage and synthetic pathway. Firstly, a regular copolyester has been synthesized by direct polyesterification of carboxytelechelic PCL oligomers with BHET. Secondly, random copolyesters with various amounts of terephthalic ester units have been made available via polycondensation reaction by varying the molar ratio of PCL diol, BHET and succinic anhydride in the initial reaction mixture. We obtained a variety of copolyesters of variable composition ranging from 25-75% in terephthalic ester units.

The study of thermal properties by differential scanning calorimetry analysis shows that the thermal properties of the so-obtained copolyesters are influenced by the method of synthesis and relative amount of incorporated terephthalic ester units. Increasing TU% in polyester chains improves the glass transition temperature and restricts phase separation and crystallization of PCL segments.

Thermogravimetric analysis shows that the thermal stability of polyesters strongly depends on the synthesis method and TU%. All copolyesters decompose by the same process. The temperature of starting decomposition/weight loss increases with increasing terephthalic ester units within the polyesters.

Experimental part

Reagents

Two poly(ϵ -caprolactone) diol (α,ω -OH oligo-PCL) (number average molecular weights 530 and 2000 g/mol) and bis(2-hydroxyethyl) terephthalate (BHET) 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.

Synthesis of regular copolyester P1

-First step: Synthesis of carboxytelechelic poly(ϵ -caprolactone) oligomers

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-dioxane as solvent were introduced. The reaction 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 acid water (pH = 1) in order to remove residual succinic acid [24]. After drying on Na_2SO_4 , the solvent was removed by evaporation and under vacuum at 60 °C. The products were characterized by 1H NMR spectroscopy and SEC.

-Second step: Copolyesterification of carboxytelechelic poly(ϵ -caprolactone) oligomers and BHET

In a 250 mL reactor, equipped with a mechanical agitation and a supply of nitrogen, 22 g (0.01 mol) of carboxytelechelic poly(ϵ -caprolactone) oligomers, 2.54 g (0.01 mol) of BHET and 0.3 wt% of DBTDL were introduced. The reaction 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 of reaction, the reaction 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.

-Synthesis of random copolyester Pi

In a 250 mL reactor, equipped with a mechanical agitation and a supply of nitrogen, PCL, BHET and AS were simultaneously introduced. The mixture was heated to 100 °C until all products fused. The catalyst (DBTDL) was then introduced. The reaction mixture was heated under nitrogen at 220 °C and the pressure was set at 1000 mbar in the reactor. After 5 hours of reaction, the reaction mixture was cooled down, solubilized in acetone and precipitated in a large excess of methanol. The obtained copolyesters were dried under vacuum at 60 °C for 72 hours.

Techniques

-Nuclear Magnetic Resonance (NMR)

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

-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 1 cm 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.

-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 μ m Mixed-D 300x7.5 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.

-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 °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.

-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.

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