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Synthesis of (polyethylene terephthalate/polyϵ-caprolactone) copolyesters

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Abstract

Polyethylene terephthalate (PET) was alcoholised with ethylene glycol to synthesize hydroxytelechelic oligomers of PET. On the other hand, commercial hydroxytelechelic polyϵ-caprolactone was modified in order to synthesize carboxytelechelic polyϵ-caprolactone. The chemical structure of the products was investigated by ^{1}H NMR. Multiblock copolyesters were then synthesized by polyesterification of hydroxytelechelic PET and carboxytelechelic polyϵ-caprolactone oligomers, using several catalysts and different reaction conditions, which have been linked with the average molecular weight of the obtained block copolyesters. It appeared that residual distannoxane species coming from glycolysis step are best catalyst for polyesterification reaction. The chemical structure of the synthesized copolyesters was investigated by size exclusion chromatography and ^{1}H NMR. The thermal and thermomechanical behavior of the synthesized copolyesters was investigated by differential scanning calorimetry and by dynamic mechanical analyses. The ester–ester interchange reaction between the two types of oligopolyesters has been enlightened and estimated taking in account the different reaction parameters. This side reaction led to the miscibility of the two phases of the oligomers, that can be explained by a random structure of the copolyester, and prevented to obtain multiblock copolymer.

Keywords: Polyethylene terephthalate; Chemical recycling; Polyϵ-caprolactone

1. Introduction

The growing interest of recycling of polyethylene terephthalate (PET) is due to the widespread use of packaging made of this polymer—mainly as bottles. PET does not create a direct hazard to the environment, but due to its substantial fraction by volume in the waste stream and its high resistance to the atmospheric and biological agents, it is seen as a noxious material. Ecological as well as economic considerations advocate the introduction of wide-scale PET recycling, similar to the recycling of traditional materials such as glass, paper or metals.

The recycling of polymers wastes including PET can be carried out in many ways. The energetic valorization consists in using energy coming from the incineration of polymers. Another method is the mechanical recycling where the polymers are transformed into other objects after a step in the molten state. Beside other methods of polymer recycling, chemical recycling, is mainly applied in the case of post consumer polycondensates, which are very vulnerable to solvolytic chain cleavage. Polyamides, polyurethanes and polyesters belong to this group of polymers. The availability of numerous depolymerizing agents and a large variety of obtained products, e.g. monomers for syntheses of polymers and resins and other additives for polymeric materials, are some of the advantages of PET chemical recycling [1]. Therefore, in recent years one can observe a growing interest in the use of PET waste for production of specialized products such as raw materials for the syntheses of saturated and unsaturated polyesters [2–10], polyurethanes [8,11,12], coating materials [9,10, 13–17] and additives [18–22].

The glycolysis of PET or polybutylene terephthalate (PBT) led to monomers or low $\overline{\mathrm{DP}n}$ oligomers (essentially $\overline{\mathrm{DP}n} = 2$ or 3). The main reactants used with different soft segments to synthesize a large range of PET or PBT block copolyesters are ethylene glycol (EG), terephthalic acid (TA), bis-hydroxy ethylene terephthalate (BHET) and dimethylene terephthalate (DMT).

The most common soft segments used are polyether as

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poly(tetra methylene ether) [23–29], poly (propylene oxide) [30,31] or poly(ethylene oxide) [25,32–34]. Some other compounds are copolymerized to get interesting products: mainly polyolefins [35,36], poly(dimethyl siloxanes) [37–39] and perfluoropolyether (Fomblin Z®) [40–42] in order to get multiblock copolymers.

Another interesting way for synthesizing this kind of products is based on transesterification reaction [43–45] or chemical reactions with organic compounds [46–50].

However, to our knowledge, no study has been led to synthesize block copolyesters by direct polyesterification of reactive PET and polyϵ-caprolactone oligomers.

Nevertheless, different ways exist to synthesize block polyesters from functionalized oligomers. The two mains are, on one hand, the use of a chain extender reactive onto telechelic functions of the oligomers giving multiblock copolymers with a linkage resulting from the reaction onto the chain-extender. As an example of this class of chain coupling agents, reactive functions onto carbonyl end groups as epoxides [51–55], carbodiimides [56] or bis-oxazoline [57–60] coupling agents can be mentioned. The example of diisocyanates [61–66] or bis-oxazolin-5-one [67–69] shows the use of telechelic reactive compounds as chain extender for hydroxytelechelic oligomers.

On the other hand, the direct reaction of end group functions of different oligomers can consist in an interesting method to synthesize block copolymers. A well-known example of this kind of reactions is the synthesis of Pebax® [70] by direct reaction of functionalized oligomers. An interesting way consists in using the hydrosililation in order to couple poly-imides and poly-siloxanes blocks [71].

In this paper, hydroxytelechelic oligomers of PET of $\bar{M}_n = 1800\ \mathrm{g\ mol^{-1}}$ coming from glycolysis of PET is used for synthesizing multiblock copoly(ester–ester) by polyesterification with carboxytelechelic polyϵ-caprolactone oligomers of $\bar{M}_n = 700$ and $2200\ \mathrm{g\ mol^{-1}}$.

The aim of this paper is to evaluate the potentiality of the polyesterification of hydroxytelechelic oligomers resulting from the glycolysis of PET with carboxytelechelic polyϵ-caprolactone oligomers as a new method for valorization of PET wastes.

2. Results and discussion

2.1. Synthesis of hydroxytelechelic PET oligomers

The synthesis of hydroxytelechelic oligomers of PET was performed by glycolysis (alcoholysis by ethylene glycol) of PET using dibutyl tin oxide (DBTO) as a ‘catalyst’ as shown in a recent patent [72]. This reaction of depolymerization is described in Scheme 1.

In this patent and several studies, the PET oligomers obtained by glycolysis of PET with ethylene glycol were α,ω-dihydroxyl oligomers [72].

The methylenic protons adjacent to the hydroxyl end functions permit the determination of the molecular weights of the oligomers by ^{1}H NMR spectroscopy: the four peaks of the ^{1}H NMR spectrum (Fig. 1) correspond to the signals of PET oligomers protons.

The integration ratio of different signals allows the calculation of the number of terephthalic base units in oligomers by Eq. (1):

$$n = \frac{IH_\mathrm{d}}{IH_\mathrm{a}} = \frac{I_{8.2\ \mathrm{ppm}}}{I_{4.15\ \mathrm{ppm}}} \tag{1}$$

where H_d represents the integration value of signals of aromatic protons, H_a the integration value of the signals of methylenic protons in α of an hydroxyl end group and $I_{x\ \mathrm{ppm}}$ represents the integration value of the peak centered at x ppm.

So it is easy to determine the average molecular weight of the oligomers. The product obtained by glycolysis has been determined to have an average molecular weight ($\bar{M}_n$) of 1800 g mol^{-1}, with an average polymerization number ($\overline{\mathrm{DP}n}$) of 9.

The catalytic process of the glycolysis comes from the transformation of polymeric DBTO and the creation of distannoxane species, which are the real active catalyst, as shown in Scheme 2.

The products of this reaction have been investigated by elementary analysis that showed the product contained 0.41 wt% of tin coming from residual catalyst, which is supposed to stay as distannoxane in polymer matrix. In the following study, the term DBTO will be used to stand for polymeric DBTO and the distannoxane catalyst value present in glycolysed PET oligomers is further noted ϵ.

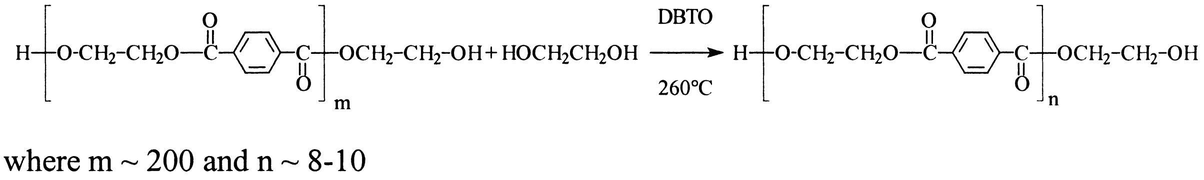
The differential scanning calorimetry (DSC) analysis permits the determination of glass transition temperature ($T_\mathrm{g} = 80\ ^\circ\mathrm{C}$), melting point ($T_\mathrm{m} = 245\ ^\circ\mathrm{C}$) and crystallization temperature ($T_\mathrm{c} = 150\ ^\circ\mathrm{C}$) of glycolysed PET oligomers.

Another hydroxytelechelic PET oligomers have been provided by Rhodia, with only traces of classical PET polycondensation catalyst. It was determined to have a $\bar{M}_n$ of 2000 g mol^{-1} and a melting point of 255 °C.

2.2. Synthesis of carboxytelechelic polyϵ-caprolactone oligomers

The synthesis of carboxytelechelic polyϵ-caprolactone oligomers was performed by reaction of succinic anhydride onto the hydroxyl functions of commercial polyϵ-caprolactone oligomers using dimethylaminopyridine (DMAP) as a catalyst, as shown in Scheme 3.

This reaction has been performed by using hydroxy telechelic polyϵ-caprolactone oligomers of molecular weights ($\bar{M}_n$) of 530 and 2000 g mol^{-1}. The products were characterized by ^{1}H NMR spectroscopy, by pH titration of carboxylic functions and by size exclusion chromatography.



Scheme 1. Depolymerization of poly(ethylene terephtalate) by ethylene glycol.

The proton chemical shifts are given in Fig. 2 and developed in experimental procedure. The diminution of the integration ratio of the peak between 3.5 and 3.6 ppm corresponding to the absence of the peak at 3.55 ppm (characteristic methylenic protons in α from a hydroxyl group in commercially available hydroxytelechelic polyϵ-caprolactone) permits to conclude that the reaction is quantitative.

The comparison of size exclusion chromatograms, before and after reaction, shows a low molecular weight increase but the products keep the same polydispersity index and does not exhibit high molecular weights products.

The titration of carbonyl functions permits the calculation of the carboxylic functionality of polyϵ-caprolactone, which has been determined to be 1.98, as described in experimental part.

All these analyses proved the synthesis of carboxytelechelic polyϵ-caprolactone by reaction of succinic anhydride onto hydroxytelechelic polyϵ-caprolactone is a quantitative reaction with a yield of 97% due to the slight loss of product during purification steps.

2.3. Copolyesterification of hydroxytelechelic PET oligomers and carboxytelechelic polyϵ-caprolactone oligomers

The copolyesterification of hydroxytelechelic PET oligomers and carboxytelechelic polyϵ-caprolactone oligomers was performed in the molten state, under vacuum (10^{-1} mbar) and high temperature so as to get rid of water, as it was formed, to shift the esterification equilibrium.

In order to work in the molten state, the reaction temperature has to stand between 255 and 260 °C in a first step of the reaction, because of the high melting point of

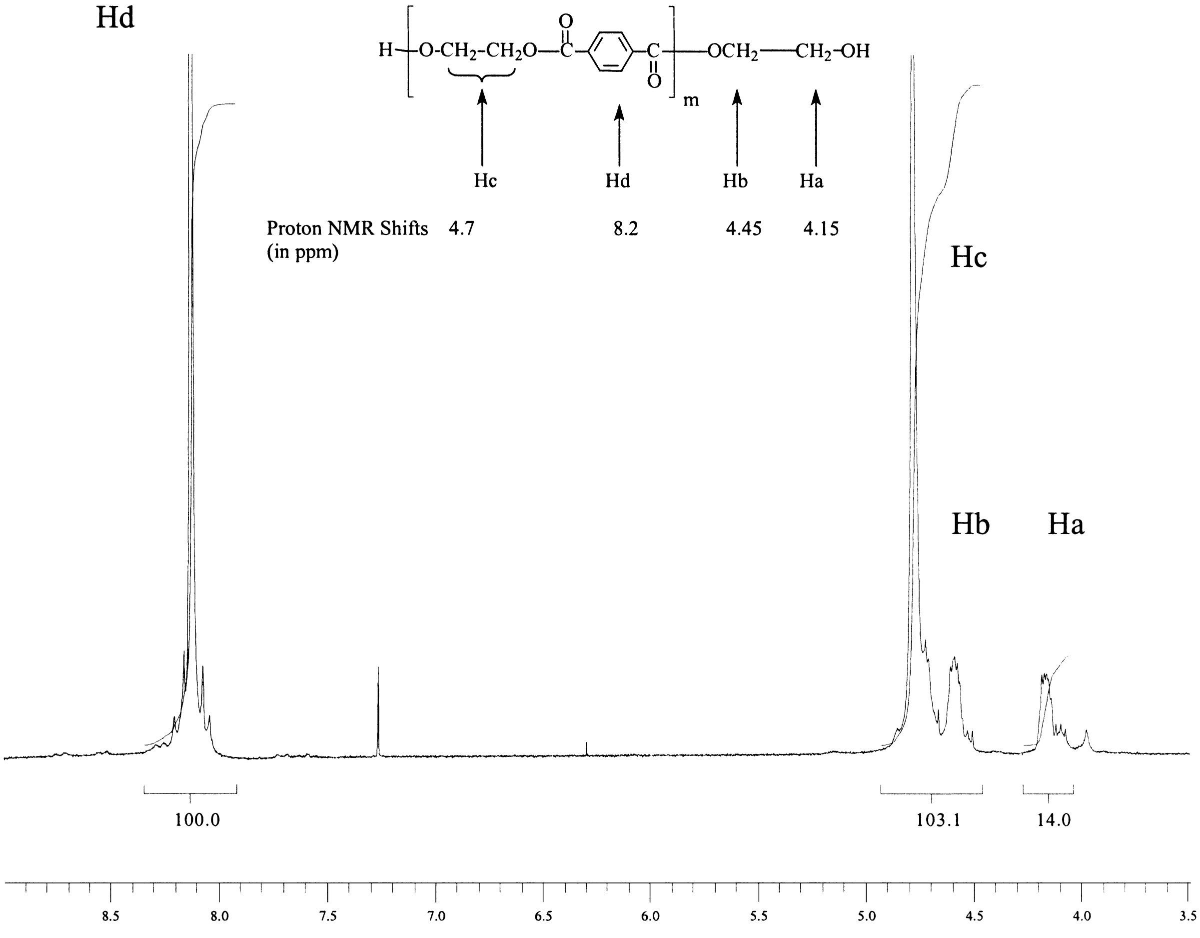
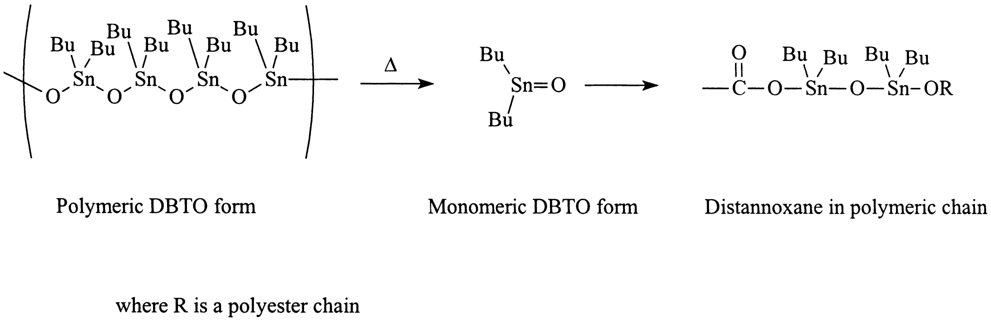


Fig. 1. ^{1}H NMR spectrum of hydroxytelechelic oligomers of PET.



Scheme 2. From DBTO to distannoxane catalyst.

PET oligomers. But at high temperature, degradation phenomena could occur, so reaction time had to be adapted in order to produce melting of PET oligomers and to avoid their degradation. The thermo gravimetric analysis permits to determine the melting step maximum time with lower degradation phenomena. It appears that PET oligomers present a weight loss about 8% after 2 h at 260 °C under nitrogen and less than 1% after 30 min. The poly϶-caprolactone oligomers (having molecular weight of 700 g mol^{-1}) present a weight loss of 15% after 2 h at 260 °C under nitrogen and fewer than 3% after 30 min.

The first reaction step is the melting of oligomers under nitrogen during 30 min where few degradation phenomena occur. The following step consisted in reaching vacuum by proceeding by stages so as to strip all water produced by the esterification at different temperatures.

This reaction is described in Scheme 4.

The influence of different reaction parameters has been investigated: the molecular weight of poly϶-caprolactone carboxytelechelic, the reaction temperature, the nature and the amount of the catalyst. All the results of characterization of the obtained copolyester were gathered in Table 1.

2.3.1. *Influence of the catalyst onto the $\bar{M}_n$ of the obtained copolyesters*

The experiments have been led by using two different PET oligomers: one coming from polyesterification of terephthalic acid and ethylene glycol ($\bar{M}_n = 2000$ g mol^{-1}.), and the other coming from tin-catalyzed glycolysis of PET ($\bar{M}_n = 1800$ g mol^{-1}) containing traces of residual distannoxane catalyst.

We have compared the highest $\bar{M}_n$ obtained by using different kinds of catalyst. As shown in Scheme 5, the comparison of the different catalysts shows that distannoxane seems to be the best catalyst. Furthermore, we noticed that the $\bar{M}_n$ of the copolyester obtained with distannoxane free PET were lower than the one with distannoxane catalyst Scheme 5.

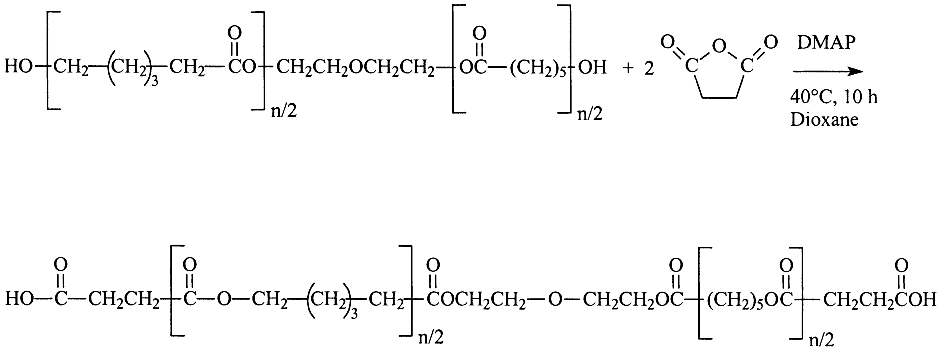
The addition of a known amount of DBTO under its polymeric form did not increase the $\bar{M}_n$ of the obtained copolyester. The best results obtained with DBTO as catalyst correspond to the residual amount of DBTO coming from the PET glycolysis step. This phenomenon could be linked to a catalytic threshold: the residual amount of distannoxane is enough to permit a good polyesterification, but the excess of this catalyst under its polymeric form partially inhibits the reaction.

The use of $Ti(OBu)_4$ catalyst enhances a little the $\bar{M}_n$ obtained. The results of molecular weight increase are the best for distannoxane catalyst alone or coupled with $Ti(OBu)_4$ catalyst.

The differences between different catalysts also come from their activity, which has been investigated.

2.3.2. *Influence of the reaction temperature onto the catalysts activity*

Reaction time and temperature are intimately linked in order to limit the degradations during the polyesterification, reaction time must be inversely proportional to reaction



Scheme 3. Synthesis of carboxytelechelic poly϶-caprolactone oligomers.

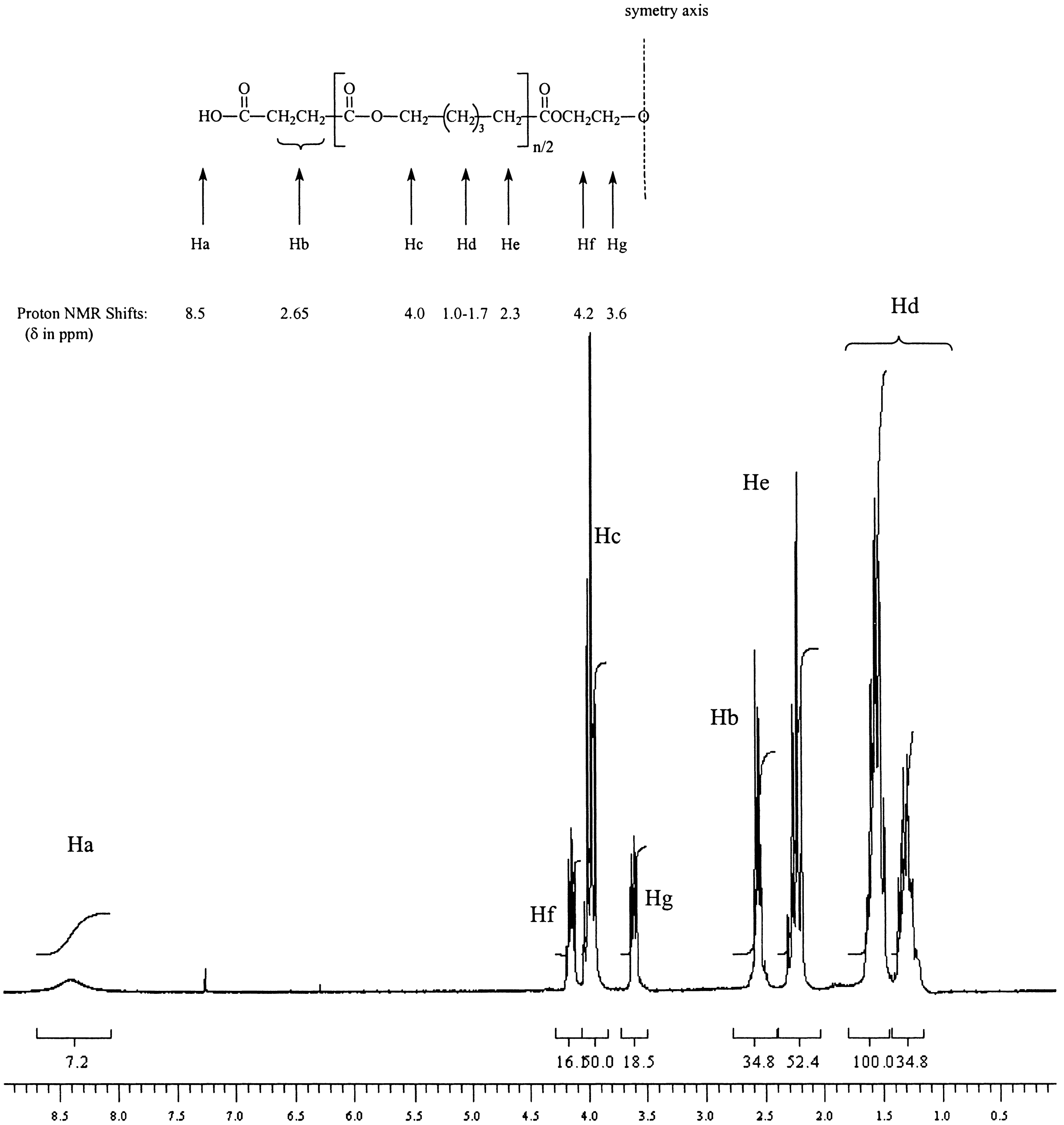
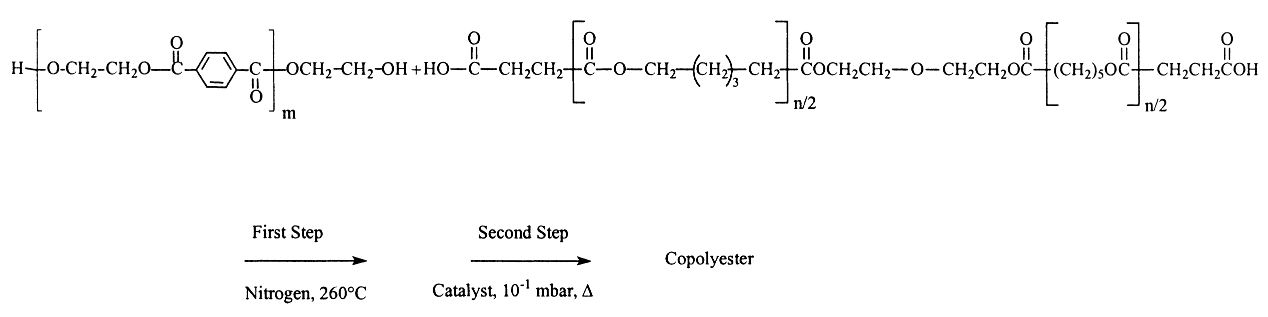


Fig. 2. ^{1}H NMR spectroscopy of carboxytelechelic polyε-caprolactone.



Scheme 4. Copolyesterification of hydroxytelechelic PET oligomers and carboxytelechelic polyε-caprolactone oligomers.

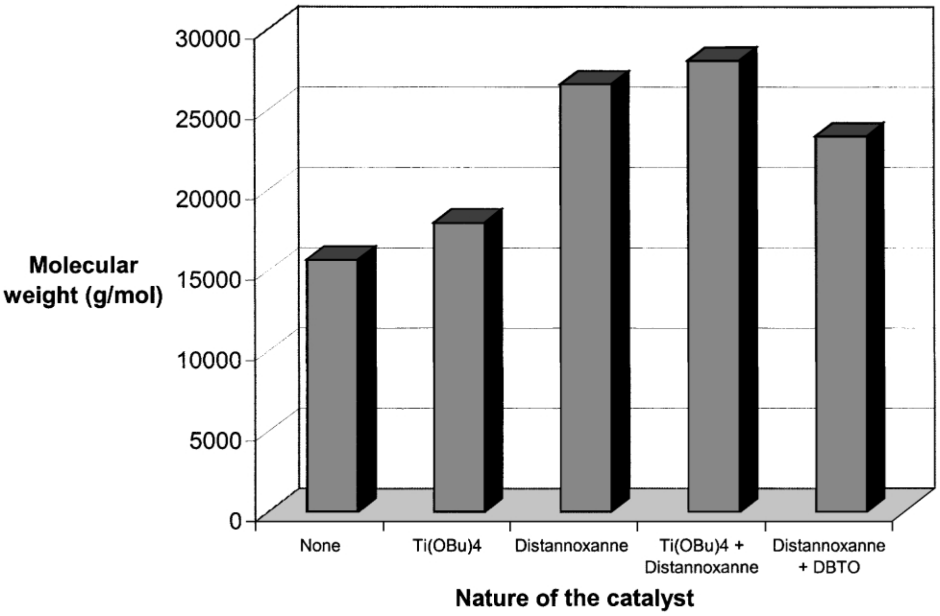
Table 1
Properties of products of copolyesterification of hydroxytelechelic PET oligomers and carboxytelechelic polyϵ-caprolactone oligomers

Exp.	PET (g)	CAPA (g)	Ti(OBu)4 (wt%)	DBTO (wt%)	T (°C)	Time (h)	$\bar{M}_n$ (g mol^{-1})[a]	$\bar{M}_w$ (g mol^{-1})[a]	I_p[a]	T_g (°C)[b]	Ester–ester reaction (%)[c]
1	30	13[d]	1	ϵ	250	1h30	28,100	53,200	1.89	25	37
2	30	13[d]	1	ϵ	220	2h30	21,000	36,600	1.74	16	40
3	30	13[d]	1	ϵ	200	3h30	18,600	33,200	1.79	21	37
4	30	13[d]	0	ϵ	250	1h30	14,700	34,700	2.35	18	45
5	30	13[d]	0	ϵ	220	2h30	25,100	46,200	1.84	18	43
6	30	13[d]	0	ϵ	200	3h30	26,600	45,700	1.72	18	37
7	30	13[d]	0	$\epsilon + 1\%$	250	1h30	20,100	44,500	2.21	30	40
8	30	13[d]	0	$\epsilon + 1\%$	220	3h30	20,900	37,800	1.81	17	39
9	30	13[d]	0	$\epsilon + 1\%$	200	3h30	23,400	40,200	1.72	20	44
10	30	13[d]	0	$\epsilon + 2\%$	220	2h30	22,600	39,200	1.73	22	40
11	30	13[d]	0	$\epsilon + 2\%$	200	3h30	23,000	43,300	1.87	23	41
12	30	13[d]	0	$\epsilon + 2\%$	180	4h30	11,500	21,000	1.82	17	36
13	30	37[e]	1	ϵ	200	3h30	20,000	39,600	2.00	− 23	78
14	30	37[e]	0	ϵ	200	3h30	26,700	45,700	1.72	− 10	74
15	30	37[e]	0	$\epsilon + 1\%$	200	3h30	17,000	35300	2.09	− 18	83
16[f]	30	13[d]	0	0	260	3h30	15,700[g]	21,400[g]	1.36[g]	$T_g = -10$; $T_f = 200$	5
17[f]	30	13[d]	1	0	260	3h30	18,000[g]	23,600[g]	1.31[g]	$T_g = 3$; $T_f = 210$	10

[a] Determined by size exclusion chromatography in THF with monodisperse PS standards.
[b] Determined by DSC at 20 °C min^{-1}.
[c] Determined by ^{1}H NMR spectroscopy.
[d] Experiments led by using carboxytelechelic polyϵ-caprolactone oligomers with molecular weight of 700 g mol^{-1}.
[e] Experiments led by using carboxytelechelic polyϵ-caprolactone oligomers of molecular weight of 2200 g mol^{-1}.
[f] Expriments led by using hydroxytelechelic PET oligomers of molecular weight of 2000 g mol^{-1}, containing no residual DBTO (non-glycolysed).
[g] Determined by size exclusion chromatography in CHCl3/HFIP (98/2 wt) with monodisperse PS standards.

temperature. But the temperature has in the same time an important influence onto the catalyst activity, as represented in Scheme 6.

The experiments 4–12 (Table 1) show that whatever the concentration of DBTO in the reaction mix is, the activity of the DBTO onto molecular weights seems to be maximal between 220 and 200 °C. The influence of the temperature can be linked to the catalytic activity of DBTO: distannoxane species are the real catalyst of the esterification reactions because of its addition onto acid functions of the polyϵ-caprolactone to easy the reaction with the hydroxyl functions of the PET oligomers [73–77]. So, the DBTO should in a first time be activated by heating so as it forms distannoxanes species and if the temperature is too high the formation of distannoxanes seemed to be not high enough to lead to high molecular weights compounds. The residual



Scheme 5. Influence of the nature of the catalyst onto the average molecular weight of the obtained copolyester.

distannoxane coming from the glycolysis of PET still gave the best results.

The comparison between reactions conditions (experiments 1–3) shows the $Ti(OBu)_4$ is more reactive when being used at a reaction temperature of 250 °C. For titanium catalytic system, studied by Marechal and Fradet [78], the acid function coordinates with Ti, and some experiments of Marechal show that the system follows thermodynamic laws. In fact, the rate constant increases with increasing temperature. Other works enlighten the same phenomenon and give further explanations onto titanium alkoxide activity for esterification or transesterification reactions [79,80].

Those results correspond to our observations. The differences between the two catalyst come from their different way of activation, the catalytic activity of the $Ti(OBu)_4$ is proportional to the temperature. For distannoxane catalyst, a catalytic threshold has been shown, linked to the thermal stability of the distannoxane species. Once more, it is shown that adding DBTO cannot improve the molecular weight of the obtained copolyester.

2.3.3. Influence of the $\bar{M}_n$ of the polyϵ-caprolactone onto the $\bar{M}_n$ of the obtained copolyesters

The molecular weights of polyesterifications products of $\bar{M}_n = 700$ and $\bar{M}_n = 2200\ \mathrm{g\ mol^{-1}}$ oligomers are close (experiments 4–6 and 13–15). The $\overline{\mathrm{DP}n}$ of products obtained by polyesterification of $\bar{M}_n = 2200\ \mathrm{g\ mol^{-1}}$ oligomers is lower than the one got by polyesterification of $\bar{M}_n = 700\ \mathrm{g\ mol^{-1}}$ oligomers. This phenomenon can easily be explained by the lower reactivity of terminal carboxylic functions of high molecular weights oligomers and by the steric environment, which prevents hydroxyl functions of PET oligomers from reacting onto carboxylic functions. Whatever the molecular weights of the oligomers used in polyesterification reaction, the molecular weights of the products are comprised between 20,000 and 30,000 $\mathrm{g\ mol^{-1}}$.

2.3.4. Characterization of the obtained copolyesters

The ^{1}H NMR spectrum of polyesterification products showed classic signals corresponding, respectively, to PET and polyϵ-caprolactone blocks and the chemical linkage between the different blocks (Fig. 3).

On this spectrum, some signals coming from ester–ester interchange reaction between base monomers units are noticed (Scheme 7). The ester–ester exchange reaction is a well-known phenomenon that occurs in a polyester chain. This reaction comes from internal transesterification reactions, leading to inversions of monomers base units in the polyester chain.

The immiscibility of PET and polyϵ-caprolactone was shown by Ma et al. [81] but it was also confirmed by DSC (Table 1). However, in our case, DSC analyses showed that the product is constituted by only one phase. This can be linked to the ester–ester interchange reaction, occurring during polyesterification, which leads to a homogenous mixture. Even if the ester–ester interchange reaction is a well-known phenomenon [81–85], it has not been described to our knowledge for PET and polyϵ-caprolactone blends until Zhang et al. [86]. Their study focused on the polymers blends, but not on a chemical reaction between PET and ϵ-caprolactone oligomers.

The ^{1}H NMR investigation effected by Zhang and by previous works [87] permits a good understanding of the transesterification side reaction that takes place in our case during the polyesterification of polyϵ-caprolactone and PET oligomers.

The ^{1}H 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 8 and 4.7 ppm (respectively, I_8 and $I_{4.7}$). If the transesterification reaction did not occur, the ratio $I4.7/I8$ would not have been modified between the spectrum of oligomers of PET and the copolyester one. The percentage of transesterification phenomenon can easily be determined when comparing the ratio of the integration of the signals at 8 and 4.7 ppm of the PET precursor oligomers and the one of the copolyester. So the percentage of transesterification is given by Eq. (2).

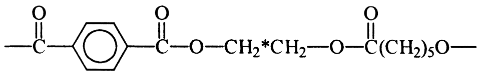
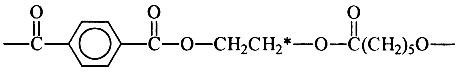
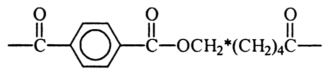
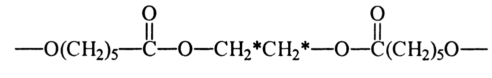
$$\%\ \text{transesterification} = \left(1 - \frac{\left(\dfrac{I_{4.7\ \text{ppm}}}{I_{8.2\ \text{ppm}}}\right)\ \text{in copolyester}}{\left(\dfrac{I_{4.7\ \text{ppm}}}{I_{8.2\ \text{ppm}}}\right)\ \text{in PET oligomers}}\right) \times 100 \qquad (2)$$

This percentage has been calculated for each experiment and a correlation between the ester–ester interchange reaction and the thermal behavior of the copolyesters has been investigated.

When tin catalyst free PET oligomers were used in polyesterification reaction, the copolyesters obtained did not show the same amount of ester–ester interchange reaction. The non-catalyzed reaction gave polyester with about 5% of transesterification reaction, and the ester–ester interchange reaction with titanium-catalyzed copolyester was quantified at about 10%. Those results showed a linkage between distannoxane presence and ester–ester interchange reaction. The high rate of ester–ester exchange reaction comes from the presence of distannoxane catalyst that easy both polyesterification and transesterification reactions thermodynamically. It is known that transesterification has an activation energy higher than polyesterification reaction. The presence of distannoxane catalyst permits the lowering of the activation energy of both reactions and the high reaction temperatures enhanced the ester–ester exchange ratio.

The results of DSC and the calculation of the percentage of ester–ester interchange reaction are gathered in Table 1.

The DSC thermogram showed only one glass transition

Chemical shift	Coming from:	Chemical structure
4.49	Ester-Ester	
4.40	Ester-Ester	
4.32	Ester-Ester	
4.25	Ester-Ester	 $—O(CH_2)_5—C(=O)—O—CH_2{}^{*}CH_2{}^{*}—O—C(=O)(CH_2)_5O—$

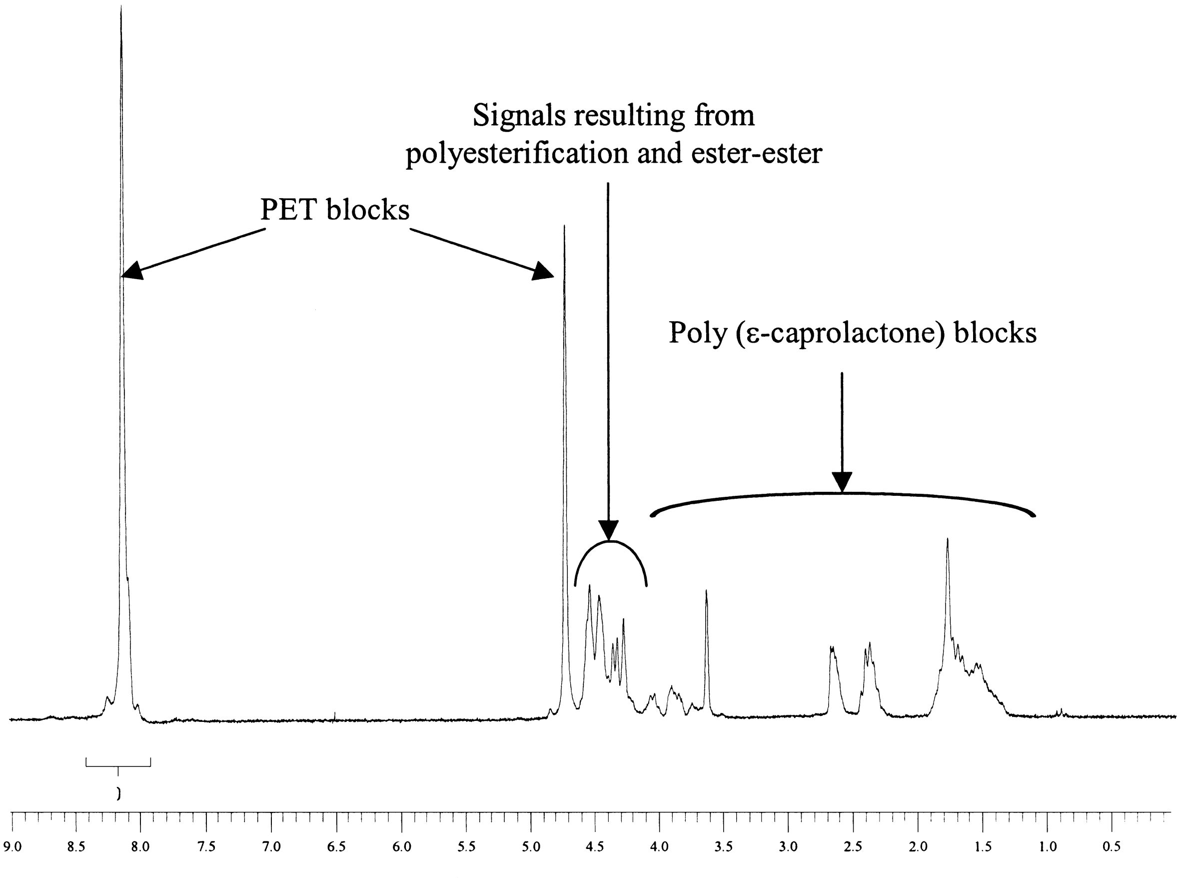
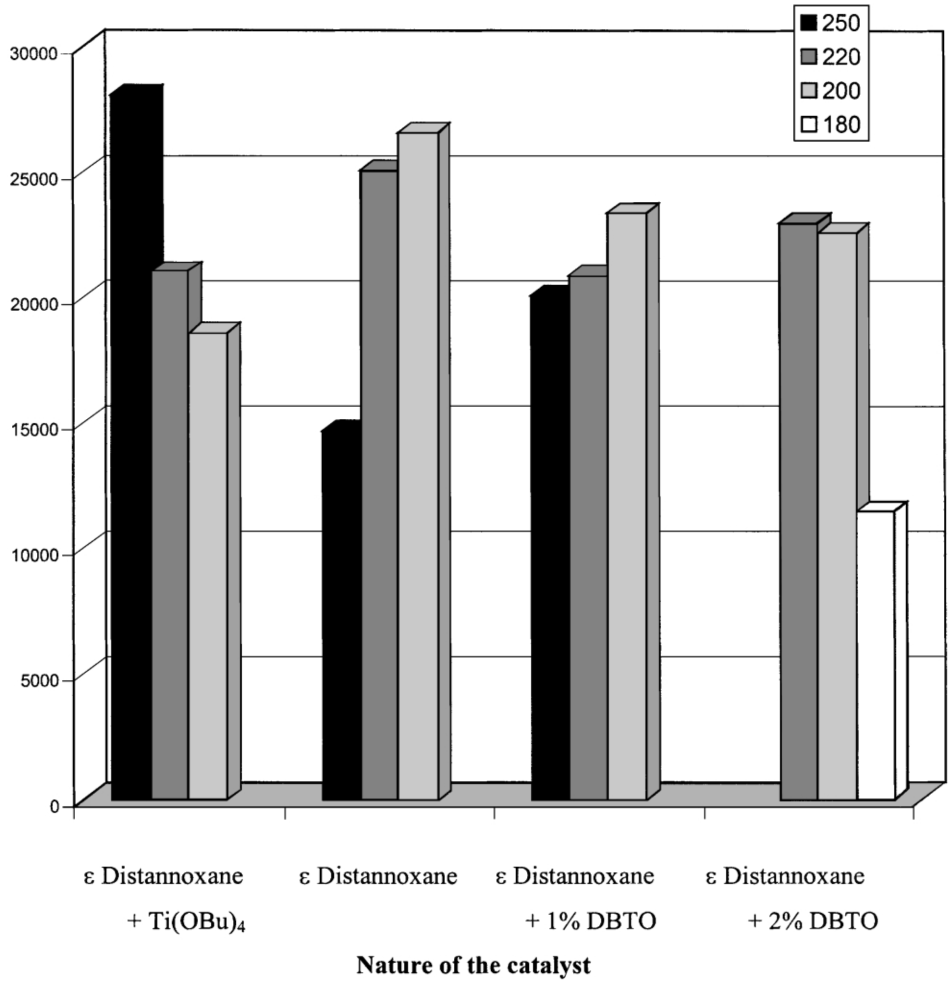


Fig. 3. ^{1}H NMR spectroscopy of copolyesters.

temperature, comprised between the T_g of the PET oligomers and the polyε-caprolactone one. The intermediate glass transition temperature shows that our copolyesters does not present phase segregation phenomenon that can be explained by the ester–ester interchange reaction. This reaction prevents the copolyester from having a thermoplastic elastomer behavior because length of soft and hard segments decreases and phase segregation is then defavorized. However, no quantitative correlation between glass transition temperature and the percentage of ester–ester interchange reaction has been enlightened: It appears that the amount of ester–ester interchange reaction cannot be directly linked to the glass transition temperature of the copolyester. 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. 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 (Eq. (3)) gives the theoretical value of glass transition temperature of 22 °C for copolyesters synthesized with polyε-caprolactone of $\bar{M}_n = 700\ \mathrm{g\ mol^{-1}}$ and of



Scheme 6. Influence of the nature of the catalyst onto the average molecular weight of the obtained copolyester.

-22 °C for copolyesters synthesized with polyϵ-caprolactone of $\bar{M}_n = 2200$ g mol^{-1}.

$$\frac{1}{T_g} = \sum \frac{\omega_i}{T_{gi}} \tag{3}$$

where ω_i is the massic fraction 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 values got by DSC analysis (Table 1) showed the multiblock copolyester approaches a mono phase compound behavior. That can be linked with the ester–ester exchange reaction that produces a random copolyester in which phase segregation phenomenon cannot occur.

When PET oligomers without distannoxanes traces were used in polyesterification reaction, the copolyesters obtained is phase segregated product. The two copolyester (experiments 16 and 17) present a low glass transition temperature (about -10 °C with non-catalyzed reaction and 3 °C with titanium catalyzed reaction) and a melting point ranging between 200 and 210 °C (Table 1). The low amount of ester–ester interchange reaction in those experiments is clearly the consequence of the absence of distannoxane catalyst. It appeared that when ester–ester exchange reaction ratio is not upper than 10%, transesterification reactions do not prevent the copolyester from being a segregated product. The phase segregation permits in the case the obtaining of a thermoplastic elastomer compound.

The DMA analyses results (Fig. 4) modified the interpretation of the DSC results: even if a main mechanical transition phenomenon associated with T_g at 37 °C (phase a) appears on the thermogram, another mechanical phenomenon showed the presence of a glass transition temperature near -40 °C (phase b) and a glass transition temperature close to 90 °C (phase c).

Those results gave the evidence that the copolyester is not composed by only one phase. The difference between the results of the thermal (DSC) and thermomechanical (DMA) analyses could be explained by the low amount of the phases b and c, under the detection threshold of the DSC.

An interpretation of the chemical nature of the phase a has been given before: phase a is an amorphous phase coming from the ester–ester exchange reaction product, composed in the same molar ratio of the two oligomers. The phase b could correspond to an amorphous phase composed essentially by polyϵ-caprolactone: the T_g determined by DMA is rather close to the T_g of the polyϵ-caprolactone

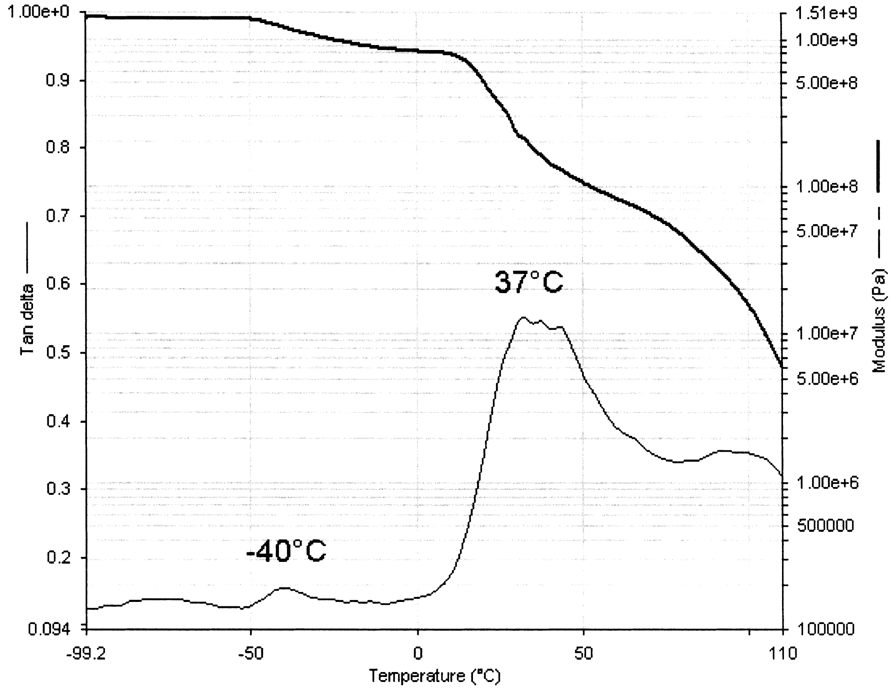


Fig. 4. DMA analysis of copolyesters.

(near $-55\,°\mathrm{C}$ for polyε-caprolactone oligomers of $\bar{M}_n = 2000\ \mathrm{g\,mol}^{-1}$).

The phase c is an amorphous phase that is mainly composed by non crystalline PET.

The DMA and DSC analyses enlighten the specific thermal behavior of the copolyester: the presence of three different phases in the copolyester is intimately linked to the ester–ester exchange phenomenon.

The main phase of the copolyester is composed by the product of the ester–ester exchange reaction that gives a random polyester with a glass transition temperature determined by Fox–Flory law. This phase is like a matrix with different nodules of two immiscible phases: one constituted mainly by poly e-caprolactone and the other mainly by PET.

3. Conclusions

The synthesis of copoly(ester–ester) has been achieved by polyesterification of reactive α–ω, hydroxy oligomers of PET and α–ω, carboxy polyε-caprolactone. Reactive PET oligomers have been synthesized by glycolysis of PET and reactive polyε-caprolactone have been obtained by chemical modification of commercially available hydroxytelechelic polyε-caprolactone. The chemical structure of the synthesized copolyesters has been investigated by size exclusion chromatography and ^{1}H NMR. The molecular weights obtained were up to about $30{,}000\ \mathrm{g\,mol}^{-1}$ with glycolysed PET oligomers.

The comparison with molecular weights of copolyester synthesized with non-glycolysed PET oligomers showed that without residual distannoxane catalyst the molecular weight increases is half-lower than with glycolysed PET oligomers. The comparison of different catalyst showed that residual distannoxane is the best catalyst for polyesterification reaction. The chemical structure of the copolyesters was well defined by ^{1}H NMR spectroscopy, showing the linkage between reactive oligomers and the presence of a side reaction. This last reaction has been determined to be the ester–ester interchange reaction, which competes with the polyesterification reaction. The presence of distannoxane favors both polyesterification and ester–ester exchange reaction, leading to a high ratio of transesterification reaction.

This phenomenon harmed to thermoplastic properties of the PET block, leading to an amorphous phase for copolyesters with more than 10% of ester–ester interchange reaction. It was also directly linked with distannoxane presence in PET oligomers because this phenomenon seemed to be catalyzed by distannoxane, and the higher molecular weight of polyε-caprolactone oligomers, the higher the rate of ester–ester interchange reaction. In the copolyester, the thermomechanical analyses show the presence of an amorphous phase resulting from ester–ester exchange reaction composed by a molar ratio of 50/50 of twice oligomers. In this matrix, some amorphous nodules composed mainly by polyε-caprolactone or by PET have been detected. However, non thermal analyses exhibit the presence of a crystalline phase in the copolyester.

So, distannoxane seems to be the best catalyst to obtain high molecular weight copolyester but is responsible for the loss of the crystallinity of PET blocks. The synthesis of a thermoplastic elastomer copoly(ester–ester) compound cannot be achieved by using glycolysed PET oligomers because of distannoxane presence leading to ester–ester interchange reaction (Scheme 7), and without distannoxane, high molecular weights copolyester cannot by prepared. This problem for synthesizing thermoplastic elastomer with glycolysed PET oligomers might be avoided by using other non-polyester oligomers as soft segments (polyether for example), which will be the subject of a further work.

4. Experimental procedure

4.1. Materials

Polyethylene terephthalate (PET) ($\bar{M}_n = 40{,}000\ \mathrm{g\ mol^{-1}}$), ethylene glycol (EG), dibutyl tin oxide (DBTO), titanium tetrabutyl oxide ($Ti(OBu)_4$), succinic anhydride, polyϵ-caprolactone ($\bar{M}_n \sim 530$ and $2000\ \mathrm{g\ mol^{-1}}$.) and dimethyl amino pyridine were obtained from Aldrich Chemical Company. All solvents used in this study were analytical grade and were used without further purification.

4.2. Polymerization procedure

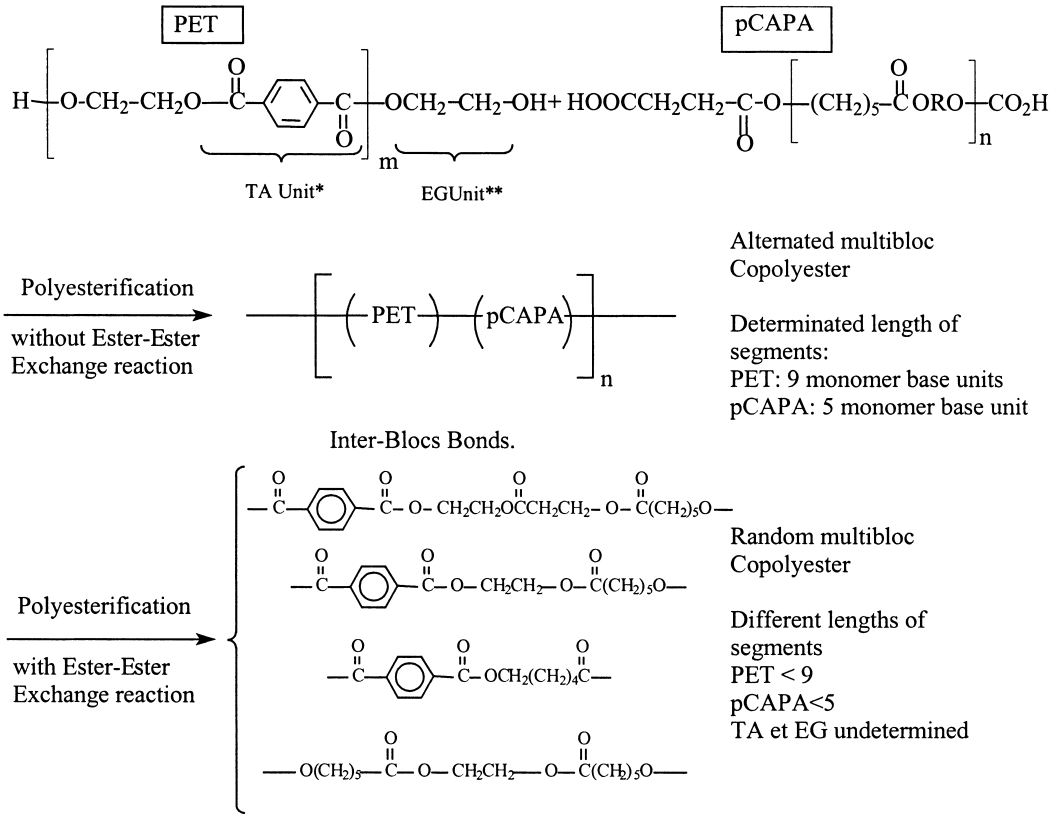
4.2.1. Glycolysis of PET by EG

The reaction of glycolysis of PET was performed by reactive extrusion at 270 °C, as described in literature [49]. The reaction mixture was grinded and the extraction of residual EG was performed by solid–liquid extraction during 24 h. The powder was then characterized by ^{1}H NMR spectroscopy with trifluoroacetic acid (TFA) and CDCl3 as the solvent.

1H NMR: δ (ppm) = 4 (CH_2OH); δ (ppm) = 4.45 (CH_2CH_2OH); δ (ppm) = 4.7 (CH_2 between two esters functions); δ (ppm) = 8.2 (aromatic protons). Integration ratio: 12:12:88:100.

4.2.2. Synthesis of carboxytelechelic polyϵ-caprolactone oligomers

The reaction of synthesis of carboxytelechelic polyϵ-caprolactone oligomers was performed in a two-necked flask, with a condenser, a nitrogen inlet and a magnetic stirrer. The polyϵ-caprolactone oligomers were introduced in the flask with succinic anhydride in excess (2.2 mol for a mole of polyϵ-caprolactone) and 1 mol% of DMAP with 1,4- dioxan as solvent. The reaction is performed at 50 °C. After 10 h of reaction, the solvent was removed and the residual product was solubilized in toluene. The reaction mixture was washed with water (pH = 1), in order to remove residual succinic acid. The solvent is then removed



*TA: Terephthalic Acid base unit
**EG: Ethylene Glycol base unit
Coming from Ester-Ester Exchange reaction.

Scheme 7. Ester–ester interchange reaction.

and the DMAP is extracted by pentane. The products were characterized by ^{1}H NMR spectroscopy and SEC.

^{1}H NMR: δ (ppm) = 1.0–1.7 (Internal CH_2 of caprolactone unit); δ (ppm) = 2.3 (CH_2 in α of a carboxyl group and methylenic carbon); δ (ppm) = 2.65 (CH_2 between an ester and a carboxylic function); δ (ppm) = 3.6 (CH_2 between two ester functions, one linked to caprolactone unit (in β) and one linked to succinic unit (in α)); δ (ppm) = 4.0 (CH2 of caprolactone unit in α of ester function); δ (ppm) = 4.2 (CH_2 between two ester functions, one linked to caprolactone unit (in α) and one linked to succinic unit (in β)); δ (ppm) = 8.5 (acid proton). Integration ratio: $6n : 2n : 4 : 2 : 2n : 2 : 1$ where $n = \overline{\mathrm{DP}n}$ of oligomer.

4.2.3. Copolyesterification of hydroxytelechelic PET oligomers and carboxytelechelic polyϵ-caprolactone oligomers

The reaction of copolyesterification of carboxytelechelic oligomers with hydroxytelechelic oligomers of PET was performed in bulk in a four-necked flask, with a condenser, a nitrogen inlet, a mechanical stirrer and a high vacuum inlet. The hydroxytelechelic PET oligomers and the carboxytelechelic polyϵ-caprolactone oligomers were introduced and the reaction mix is heated under nitrogen at 260 °C until the complete fusion of oligomers of PET. When DBTO is used as catalyst, it is introduced with oligomers before fusion of PET. After the complete fusion of PET oligomers, the pressure is led to 10^{-1} mbar in the reactor and the temperature is lowered to the reaction temperature. After reaction, the products were then characterized by size exclusion chromatography, ^{1}H NMR, DSC and dynamic mechanical analysis (DMA). The shore hardness of the copolyesters was also determined.

^{1}H NMR: δ (ppm) = 1.0–1.7 (internal CH_2 of caprolactone unit); δ (ppm) = 2.3 (CH_2 in α of a carboxyl group and methylenic carbon); δ (ppm) = 2.65 (CH_2 between an ester and a carboxylic function); δ (ppm) = 3.6 (CH_2 between two ester functions, one linked to caprolactone unit (in β) and one linked to succinic unit (in α)); δ (ppm) = 4.0 (CH_2 of caprolactone unit in α of ester function); δ (ppm) = 4.2 (CH_2 between two ester functions, one linked to caprolactone unit (in α) and one linked to succinic unit (in β)); δ (ppm) = 8.5 (acid proton).

4.3. Analyses

4.3.1. Size exclusion chromatography

The molecular weight and molecular weight distribution of polyϵ-caprolactone oligomers and of copolyesters were measured by liquid chromatography with THF or CHCL3/HFIP (98/2 wt) (for polyesters non soluble in THF) as solvent at a flow rate of 0.8 ml/min. The calibration curves were obtained from PS standards.

4.3.2. ^{1}H NMR

All the experiments were performed on a Bruker Aspect 200 MHz spectrometer at room temperature. The ^{1}H NMR spectra of oligomers of PET and of the co-oligomers were obtained on 8–10% solutions. The solvent used for oligomers of PET was deuterated chloroform and trifluoroacetic acid (20:1). The solvent for the other products was deuterated chloroform.

4.3.3. Thermogravimetric analysis

The thermogravimetric analyses have been effected using a TGA 51-thermogravimetric analyzer (TA Instruments) from room temperature to complete degradation at a rate of 20 °C/min with air or nitrogen atmosphere.

4.3.4. Titration of carboxylic functions

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 MeOH solvent with THF as solvent and phenolphthalein as color indicator. The carboxyl ratio is given by the equation:

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

where C_{B} represents the concentration of KOH solution, V_{B} the equivalent volume and m the mass of oligomer titrated.

4.3.5. Differential scanning calorimetry

DSC measurements were carried out on a Perkin–Elmer DSC. The temperature was calibrated with ultra-pure indium, octane and dodecyloctane. The samples were heated from −110 to 300 °C at a rate of 20 °C/min to record the curves. The temperature of the half-height of the corresponding heat capacity jump was defined as T_{g}, while T_{m} was the peak temperature of the melting endotherm and T_{c} the peak temperature of the crystallization exotherm.

4.3.6. Determination of hardness

The determination of hardness of copolyester has been made by using a hardness meter.

4.3.7. Dynamic mechanical analyzer

DMA measurements were carried out on a Perkin–Elmer DMA 7$^{\mathrm{e}}$, with a temperature ramp of 5 °C/min from −100 to 120 °C.

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