Poly(butylene succinate-*ran*-ε-caprolactone) copolyesters:

Enzymatic synthesis and crystalline isodimorphic character

Claudio Ciulik,[1] Maryam Safari,[2] Antxon Martínez de Ilarduya,[1*] Juan Carlos Morales-Huerta,[1] Amaia Iturrospe,[3] Arantxa Arbe,[3] Alejandro J. Müller,[2,4*] and Sebastián Muñoz-Guerra[1]

[1]*Departament d'Enginyeria Química, Universitat Politècnica de Catalunya, ETSEIB, Diagonal 647, 08028 Barcelona, Spain*

[2]*POLYMAT and Polymer Science and Technology Department, Faculty of Chemistry, University of the Basque Country UPV/EHU, Paseo Manuel de Lardizabal 3, 20018 Donostia-San Sebastián, Spain*

[3]*Centro de Física de Materiales (CFM) (CSIC-UPV/EHU) - Materials Physics Center (MPC), Paseo Manuel de Lardizabal 5, 20018 San Sebastián, Spain*

[4]*IKERBASQUE, Basque Foundation for Science, Bilbao, Spain*

Corresponding authors: antxon.martinez.de.ilarduia@upc.edu and
alejandrojesus.muller@ehu.es

Abstract:

In this paper, the preparation of PBS-*ran*-PCL copolyesters by enzymatic ring opening polymerization is presented for the first time. The copolyesters were produced in a wide composition range and free of metallic contaminants, so they may be regarded as potential biomaterials. The copolymers have been characterized by proton and carbon nuclear magnetic resonance (^{1}H and ^{13}C NMR), gel permeation chromatography (GPC), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), polarized light optical microscopy (PLOM) and wide angle X-ray scattering (WAXS). The PBS-*ran*-PCL copolyesters were able to crystallize in the entire composition range and displayed a pseudo-eutectic region. Most copolymers away from the pseudo-eutectic region exhibited a single crystalline phase (PBS-rich or PCL-rich crystalline phase), while within the pseudo-eutectic region the copolymers were double crystalline. Observations by PLOM, during isothermal crystallization showed that both nucleation density and spherulitic growth rate of the copolyesters are determined by the component that constitutes the majority phase. WAXS studies revealed that *d* spacings of selected crystallographic planes depend on composition. Therefore, both DSC and WAXS results suggest that the copolymers are probably isodimorphic, as the PBS-rich crystalline phase may contain small inclusions of PCL *co*-units, while the PCL-rich crystalline domains may also contain a minor quantity of PBS *co*-units inside.

INTRODUCTION

Aliphatic polyesters have achieved an outstanding position among bio-based polymers intended for biodegradable applications [1]. Many of these polyesters can be easily synthesized from bio-based monomers and display a remarkable sensitivity to biodegradation that can be controlled by adjusting the composition. Nevertheless, it is true that thermal and mechanical properties of aliphatic polyesters are not always in agreement with expectations, and copolymerization has been an approach frequently used to overcome such limitation. Poly(ε-caprolactone) (PCL) is a polyester that exemplifies well this issue (see Scheme 1) [2]. PCL is inexpensively produced, shows both high biodegradability and good biocompatibility, and counts with FDA approval. However PCL melts around 60 ºC and its glass transition temperature (T_g) is near -60 ºC. On the other hand, poly(butylene succinate) (PBS) is another aliphatic polyester (see Scheme 1) with T_m ~120 ºC and T_g~ -30 ºC that is accessible from bio-based 1,4-butanediol and succinic acid, and that has mechanical properties comparable to those of polypropylene [3]. The combination of PCL and PBS either as blends or as copolyesters, both random and blocks, has been used in several occasions to render new materials with improved behavior [4-7].
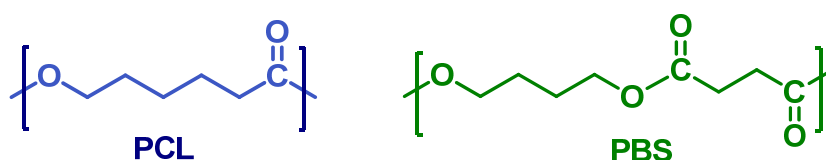
Scheme 1. Chemical repeating units of PCL and PBS homopolyesters.

Copolyesters made of butylene succinate and caprolactone have been synthesized so far using compounds of petrochemical origin, however, they could be made employing fully biobased chemicals in the near future. 1,4-butanediol and succinic acid are today readily available by sugar fermentations at industrial scale [8] and caprolactone can be prepared with high selectivity from 1,6-hexanediol produced from lignocelluloses *via* 5-hydroxymetyl furfural [9]. These copolyesters are gaining therefore relevance in the biomaterial field since they are able to combine sustainability with satisfactory bio related properties. Ideal polymers designed to be used as biomaterials should be exempted of metallic compounds. However, all synyheses reported so far to prepare poly(butylene succinate-*ran*-caprolactone) copolyesters have been performed with the concourse of organometallic catalysts. Cao et al. [5] have reported mechanical and thermal characterization of PBS-*ran*-PCL random copolymers synthesized this way.

In this paper, we present for the first time the preparation of these copolyesters by enzymatic ring opening polymerization (*e*ROP). Although PBS is prepared at industrial scale by melt polycondensation [10], the successful synthesis of this homopolyester by *e*ROP has been reported in several occasions by using cyclic (butylene succinate) oligomers $c(BS)_n$ which were previously prepared by enzymatic cyclization [11,12]. On the other hand, PCL is usually synthesized by chemically catalyzed ROP making use of a wide variety of organometallic catalysts but the enzymatic procedure is gaining importance in these last years [13]. The copolymerization of the oligomeric $c(BS)_n$ with CL has allowed us the preparation of a series of random copolyesters, abbreviated $coP(BS_xCL_y)$ (with x and y indicating the molar contents in BS and CL units, respectively), exempted of metallic contaminants and with additional merits to be

4

considered as potential candidates for biomaterials. In addition to the organocatalyzed (enzymatically) synthesis, the copolyesters prepared here have been characterized by Differential Scanning Calorimetry (DSC), Polarized Light Optical Microscopy (PLOM) and Wide Angle X-ray Scattering (WAXS). With these techniques we were able to determine their thermal properties, morphology and structure and we have found that they display isodimorphic properties.

EXPERIMENTAL SECTION

General Methods. The ^{1}H NMR and ^{13}C NMR spectra were registered at 300.1 and 75.5 MHz respectively, on a Bruker AMX-300 NMR instrument. The samples were dissolved in deuterated chloroform or deuterated trifluoroacetic acid, and TMS was used as internal reference. About 10 and 50 mg of sample in 1 mL were used for ^{1}H and ^{13}C NMR, respectively. Sixty-four scans were acquired for ^{1}H and 1000-10,000 for ^{13}C with 32-K and 64-K data points, respectively. Quantitative ^{13}C NMR spectra were recorded applying an inverse gated decoupling pulse sequence to avoid nuclear Overhauser effect (NOE) enhancement of the ^{13}C NMR signals, and using long delay times.

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) was performed using an ABSciex 4800 plus MALDI-TOF/TOF spectrometer equipped with a Nd:YAG laser. Detection was made in the reflection mode and positive ionization was used. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGA6 thermobalance. Data were collected under a constant nitrogen flow at a heating rate of 10 °C·min^{-1} within the 30 to 600 °C temperature interval.

Gel permeation chromatograms were acquired at 35 °C with a Waters equipment provided with a refraction index detector. The samples were chromatographed with 0.05 M sodium trifluoroacetate-hexafluoroisopropanol (NaTFA-HFIP) using a polystyrene-divinylbenzene packed linear column at a flow rate of 0.5 mL·min^{-1}. Chromatograms were calibrated against poly(methyl methacrylate) (PMMA) standards.

The crystalline morphology of coP(BS$_x$CL$_y$) copolyesters and PBS and PCL homopolyesters was examined with an OLYMPUS BX51 polarized light microscope connected to an OLYMPUS SC50 camera and a Mettler FP82HT hot stage provided with a liquid nitrogen flow. Samples were placed between glass covers and heated 30 °C above their melting temperature T_m (given by the melting peak observed by DSC), and kept at this temperature for 5 min in order to erase their thermal history. Samples were then cooled at 10 °C·min^{-1} to a temperature at which spherulites started to appear (denoted as ^oT_c) in the microscope field and left to crystallize at such temperature until saturation, $i.e.,$ until spherulites impinged on one another. The difference between T_m and ^oT_c was taken as the apparent supercooling (ΔT).

The non-isothermal crystallization behavior of the homopolyesters and copolyesters was examined by differential scanning calorimetry (DSC) using a Perkin Elmer Pyris 1 calorimeter equipped with a refrigerated cooling system Intracooler 2P and under a nitrogen atmosphere flow of 20 mL·min^{-1}. Indium was used as standard for calibration. Samples were heated from room temperature to 150 °C and held at this temperature for 3 min to erase thermal history. They were then cooled to -60 °C and reheated to 150 °C. Measurements were done at two different scan rates, 20°C·min^{-1} and also 10°C·min^{-1}, in order to evaluate scan rate

effect on DSC curves and crystalinity. To determine the glass transition temperature (T_g), samples were heated from room temperature to 140°C (for PBS-rich samples) or 90 °C (for PCL-rich samples) at a rate of 40 °C·min^{-1}. They were then subjected to ballistic cooling down to -90°C at an approximately rate of 100 ºC·min^{-1} and finally heated to 140 °C (for PBS-rich samples) or 90 °C (for PCL-rich samples) at a rate of 20 °C·min^{-1}.

Wide angle X-ray scattering measurements were performed with a Bruker D8 Advance diffractometer using parallel beam geometry and a line focus X-ray tube operating at 40 kV and 40 mA with filtered Cu-K$_\alpha$ radiation (0.154 nm). Experiments were carried out under vacuum at both 25°C and -60°C with the temperature controlled at ±0.1ºC by an Anton Paar TTK 450 low-temperature chamber. Measurements were made in the reflection mode with 2θ varying from 4º to 30° at steps of 0.05°.

Synthesis of *co*P(BS$_x$CL$_y$) copolyesters. The cyclic butylene succinate oligomers were synthesized according to the procedure described by Sugihara et al. [11]. In brief, 0.65 mL (0.726 g, 4.97 mmol) of dimethyl succinate and 0.45 mL (0.457 g, 5.07 mmol) of 1,4-butanediol were placed in 250 mL of toluene in a three-necked flask. The mixture was left under magnetic stirring in a thermostatized oil bath until the temperature stabilized at 96.5°C and the medium became homogeneous. Then 1.184 g (100 w% relative to the total monomer concentration) of immobilized lipase CALB were added. The cyclization reaction was left to proceed for 48 h under a low steady stream of nitrogen with 4 Å molecular sieves placed at the top of the flask to absorb the released methanol. The reaction mixture was then dispersed in chloroform and the enzyme was removed by

filtration through a fritted filter. The clean filtrate was evaporated to dryness under reduced pressure to obtain the oligomer mixture of $c(BS)_n$.

The enzymatic ring opening polymerization reaction leading to $coP(BS_xCL_y)$ copolyesters was carried out in the bulk, using $c(BS)_n$/CL mixtures at molar ratios of 90/10, 70/30, 60/40, 50/50, 40/60, 30/70 and 10/90, so that the whole copolyesters composition range was essentially covered. The experimental procedure was as follows: Predetermined relative amounts of the cyclic reactants were placed in a one-necked flask introduced in a thermostatized oil bath at 130 °C, and the mixture was mechanically stirred until complete melting and homogenization. Then immobilized lipase CALB (50% w/w relative to the total reactants mass) was added and the reaction was left to proceed for 24 h under a nitrogen atmosphere. The reaction mass was then dissolved in chloroform and the insolubilized enzyme was removed by filtration through a fritted filter. The filtrate was then evaporated to dryness under reduced pressure to obtain the corresponding copolyester. The same procedure was followed for the synthesis of the parent homopolyesters PBS and PCL using $c(BS)_n$ and CL as respective feeds.

RESULTS AND DISCUSSION

Synthesis of $coP(BS_xCL_y)$ copolyesters by enzymatic ROP

The route followed in this work for the preparation of the poly(butylene succinate-*ran*-caprolactone) copolyesters is depicted in Scheme 2.

The cyclic oligomers $c(BS)_n$ needed for ROP were firstly synthesized by enzymatic cyclization of an approximate equimolar mixture of 1,4-butanediol (BD) and dimethyl succinate (DMS) in toluene, following the method described by Sugihara *et al.* [11]. The resulting cyclic oligomeric mixture was analyzed by MALDI-Tof MS and NMR (see Supporting Information) which demonstrated that its

composition is in agreement with previously reported results. Dimer, trimer and tetramers were the main components in the mixture whereas higher size cycles as well as the monomer were present in much smaller amounts.
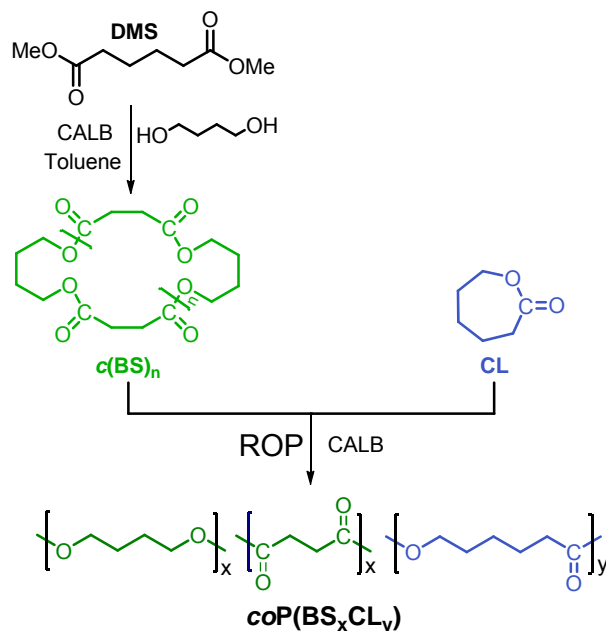
Scheme 2. Route leading to $coP(BS_xCL_y)$ copolyesters by enzymatically ROP of mixtures of cyclic butylene succinate oligomers and caprolactone.

^{13}C NMR under quantitative conditions was used for the first time to determine the content of these cyclic species. As it can be observed in Figure 1, signals from succinate methylene carbon split into four well resolved peaks that appeared upfield shifted as the size of the cycle increased. These peaks correspond to cyclic monomer (n=0), dimer (n=1), trimer (n=2) and tretramer (n=3) respectively and they appear with 5.5, 46.2 and 21.7 and 10 wt% ratio respectively. As the cycles became bigger the differences in chemical shifts reduced and then, the cyclic pentamer, hexamer and cycles of higher sizes appear partially overlapped whose content is around 16.6 % wt%.
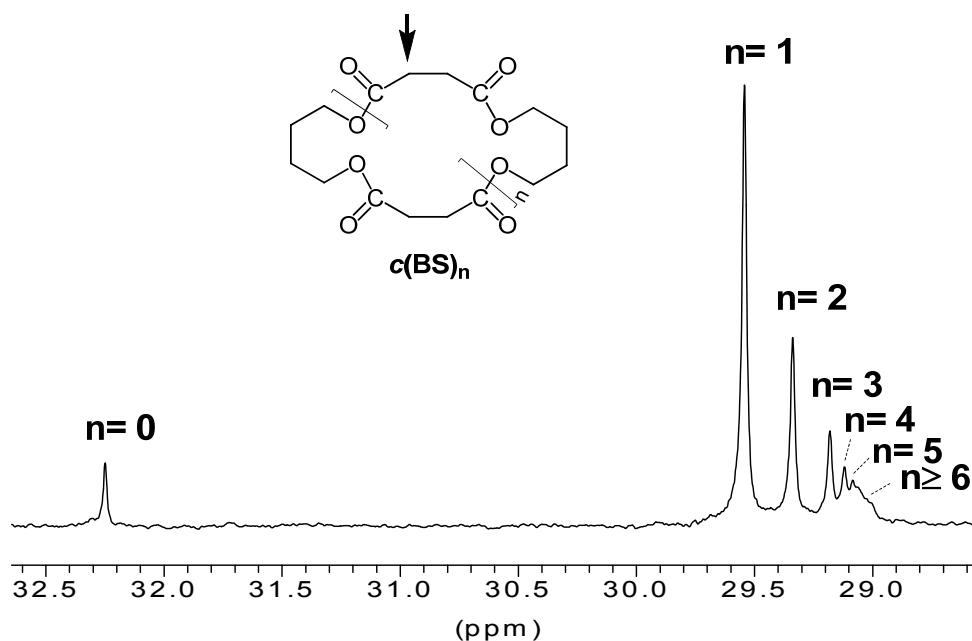
Figure 1. Quantitative ^{13}C NMR spectrum of $c(BS)_n$ cyclic oligomers in the region of the succinate methylene carbon (indicated with an arrow).

Table 1. Synthesis results of the enzymatic ROP copolymerization of cyclic oligo(butylene succinate) oligomers and caprolactone.

Polyester	Composition[a] (BS/CL mol/mol)		Molecular weight[b] (g·mol^{-1})			Microstructure[c] (S-centered triads content)			
	Feed	Polymer	M_n	M_w	$Đ$	BSB	BSCL/CLSB	CLSCL	R
PBS	100/0	100/0	4700	6100	1.3	-	-	-	-
$coP(BS_{85}CL_{15})$	90/10	84.6/15.4	2100	5000	2.3	84.0	16.0	0	0.96
$coP(BS_{64}CL_{36})$	70/30	64.3/35.7	2200	4100	1.9	59.6	36.0	4.4	1.03
$coP(BS_{54}CL_{46})$	60/40	53.6/46.4	2000	4300	2.2	46.5	45.1	8.4	1.02
$coP(BS_{48}CL_{52})$	50/50	47.7/52.3	6600	13500	2.1	38.1	49.0	13.0	1.06
$coP(BS_{45}CL_{55})$	50/50	44.7/55.3	3200	6100	1.9	35.9	46.2	17.9	1.07
$coP(BS_{36}CL_{64})$	40/60	35.6/64.4	2600	5300	2.0	31.2	49.7	19.1	0.93
$coP(BS_{26}CL_{74})$	30/70	25.8/74.2	2600	6300	2.4	10.4	62.1	27.6	0.99
$coP(BS_9CL_{91})$	10/90	8.5/91.5	4500	11800	2.6	6.6	29.7	63.7	0.93
PCL	0/100	0/100	6500	16300	2.0	-	-	-	-

[a]Composition of the feed and the resulting polymer as determined by ^1H NMR.
[b]Number and weight average molecular weights and dispersities estimated by GPC against PMMA standards.
[c]Copolyester microstructure determined by NMR; R is the degree of randomness which should be 1 for a fully statistical distribution of the comonomeric units.

A study carried out on the efficiency of the BS cycles in enzymatic ROP as a function of size has shown that no important differences in either reactivity or molecular weight of the resulting PBS are observed if cycles higher than dimer are polymerized [12]. Accordingly, the $c(BS)_n$ mixture obtained by high dilution cyclization was used directly for the copolyester synthesis without further fractionation. Thus mixtures of crude $c(BS)_n$ and CL at preselected molar ratios were subjected to ROP in the presence of CALB to produce the poly(butylene succinate-*ran*-caprolactone) copolyesters. Additionally the homopolyesters PBS and PCL to be used as references were obtained under similar conditions.

The results obtained by these polymerizations are gathered in Table 1. The chemical constitution of the polyesters was determined by NMR. Both the ^{1}H and ^{13}C NMR of the $PBS_{48}CL_{52}$ copolyester are shown in Figure 2 for illustration, whereas the spectra of the whole series are compared in the Supporting Information. As it can be seen in Table 1, weight average molecular weights of the $coP(BS_xCL_y)$ copolyesters were found to range between 4,000 and 14,000 g·mol^{-1} with dispersities oscillating between 1.9 and 2.6 and showing no apparent correlation with copolymer composition. The homopolyesters were obtained with molecular weights comparable to those found for the copolyesters although the M_w of PCL was nearly three times higher than that of PBS. It should be noted that other authors [11, 12] have reported the preparation of these homopolyesters by the same procedure with much higher molecular weight, *i.e.*, about 150,000 for PBS and 80,000 for PCL. It is known that the molecular weight of polyesters generated by enzymatic ROP is strongly influenced by polymerization conditions, such as monomers and enzyme concentrations, and reaction temperature as well. Also, the presence of small amounts of water is a critical factor in determining the

resulting polyester size, which has to be rigorously avoided if high molecular weights are desired. In the experimental practice, the CALB used for catalyzing the reaction is frequently the main source of water but it may be readily removed by subjecting the enzyme to a severe drying just before using. In the present work, no special precautions for water removal were taken, since moderate to low polymer molecular weights were quite convenient for the calorimetric study that was intended to be carried out with $coP(BS_xCL_y)$ copolyesters.

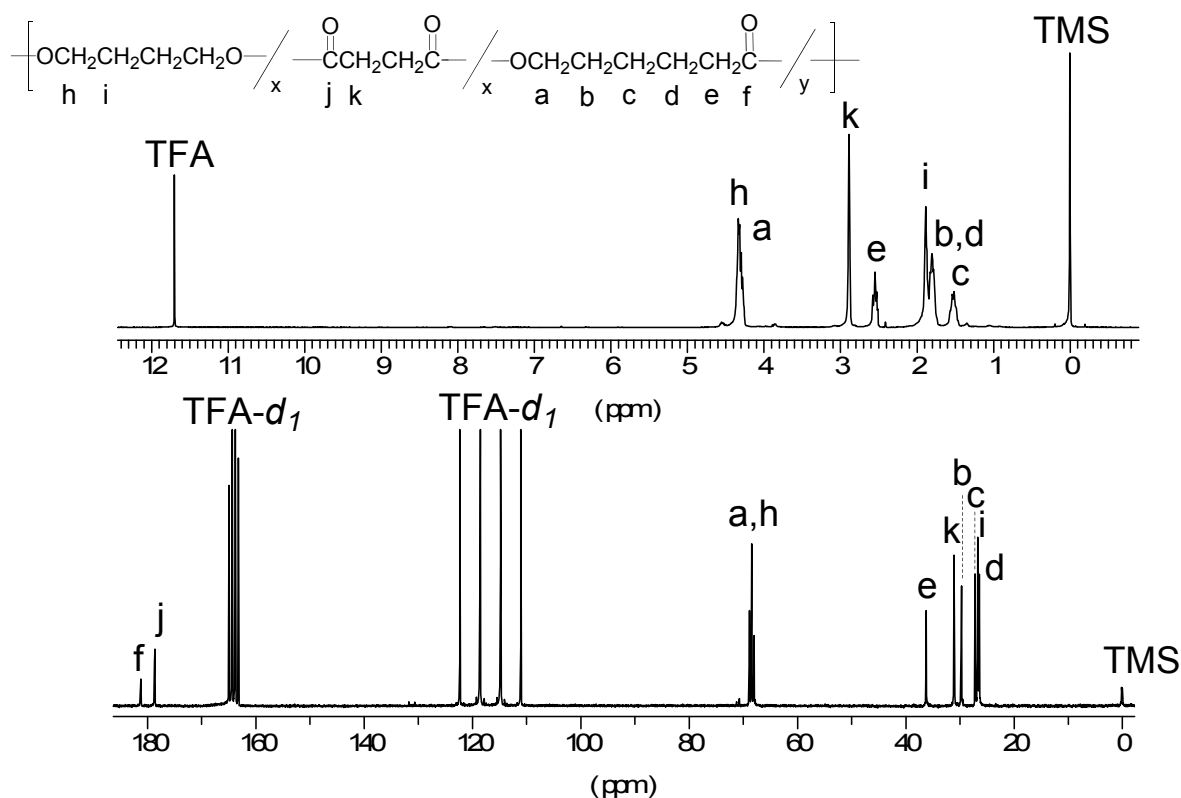**Figure 2**. ^{1}H (top) and ^{13}C NMR (bottom) spectra of $coP(BS_{48}CL_{52})$ as representative of the $coP(BS_xCL_y)$ copolyesters series recorded in TFA-d. Peaks were assigned according to the expected copolyester constitution depicted in the attached formula.

Composition and microstructure of $coP(BS_xCL_y)$ copolyesters

The composition of the $coP(BS_xCL_y)$ copolyesters regarding BS and CL units was determined by comparing the areas of ^{1}H NMR signals specifically arising

from each of these two units. As it can be seen in Table 1 the copolyester compositions are in general consistent with the BS/CL ratios used for feeding although some noticeable differences are observed between them. Deviations are in general around 10%, with the content of BS in the copolyesters found to be lower than expected from the composition of the feed, where a small amount of cyclic BS oligomers were removed by volatilization during polymerization. It can be inferred from these results that CL is more prone to react than the BS oligomeric cycles, which is indeed a reasonable fact, taking into account that larger ring opening driving forces must be operating in the relatively more strained CL cycles.

The microstructure of the copolyesters was analyzed by ^{13}C NMR by taking benefit from the splitting of the methylene signals of the succinate moiety located around 31 ppm. As it is shown in Figure 3, these signals are sensitive to sequence effects so that three peaks corresponding to the four succinate-centered triads, BSB, BSCL/CLSB and CLSCL, became observed and used for quantification. The relative contents in the four triads for every copolymer composition and the application of the statistical method previously used by us for other copolyesters of AABB-co-AB type [14], led to determine the degree of randomness R for the coP(BS$_x$CL$_y$) copolyesters.

Triads contents and R values are given in Table 1 indicating that the microstructure of these copolyesters is essentially random. Given the oligomeric size of c(BS)$_n$ and the monomeric constitution of CL, the statistical distribution of BS and CL units observed in the copolyesters implies the occurrence of randomization reactions during ROP. Transesterification reactions catalyzed by organometallic compounds and leading to randomization are known to be common in polyesterifications carried out at high temperatures, usually above 150 ºC. In the

present case, although reaction temperature is rather low, transesterification reactions may be feasible due to the probable enhancing effect exerted by the lipase used for polymerization. This fact is supported by the presence of high contents of CLSCL triads that are only present in the copolymers if these reactions take place.
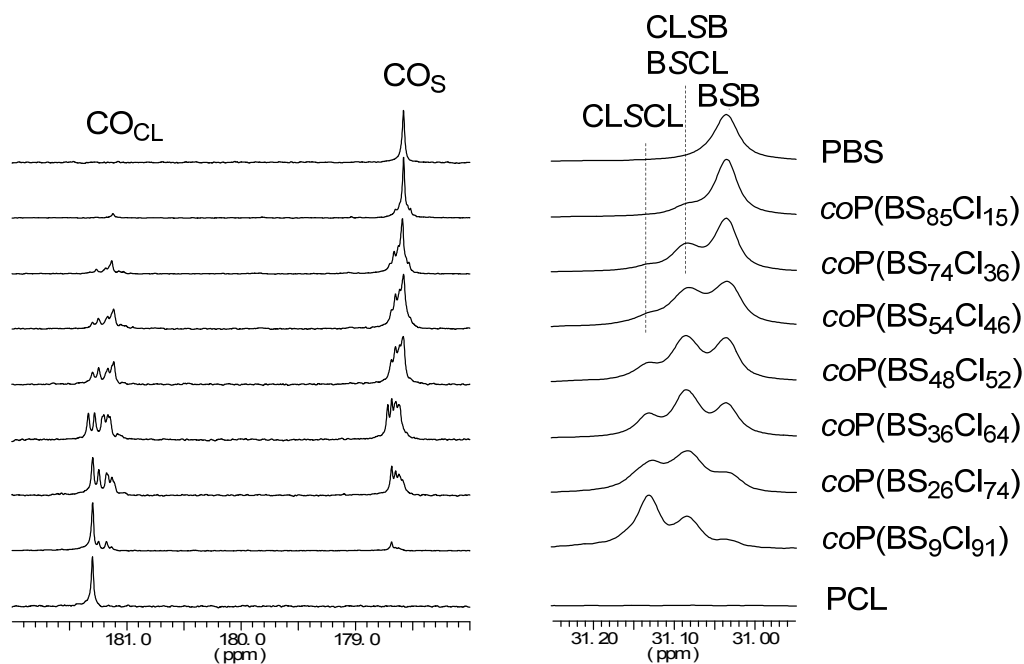

Figure 3. Carbonyls and succinate methylene carbon regions of the ^{13}C NMR spectra of PBS, PCL and $coP(BS_xCL_y)$ copolyesters recorded in TFA-d. Peaks generated by splitting of the signals due to sequence effects are assigned to the four succinate-centered triads that are feasible for these copolyesters.

Thermal stability

The thermal stability of $coP(BS_xCL_y)$ copolyesters was evaluated by thermogravimetry analysis conducted under an inert atmosphere. The TGA traces recorded for the whole series in the 50-600 ºC range are represented together in Figure 4, including an inset in which the 300-360 ºC region is enlarged in order to illustrate more clearly the differences in the onset decomposition temperatures.

Thermal decomposition parameters, for $coP(BS_xCL_y)$ in addition to those recorded for the PBS and PCL homopolyesters used as references are listed in Table 2.
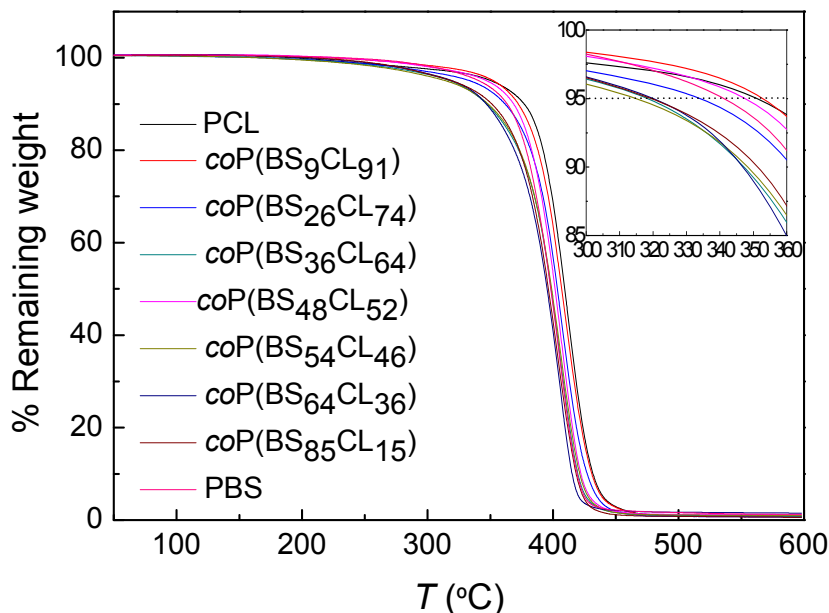

Figure 4. TGA traces of the $coP(BS_xCL_y)$ series recorded under a nitrogen atmosphere. Inset: Enlarged onset temperature region.

All the copolyesters start to decompose well above 300 ºC, but at lower values than the parent homopolyesters, a behavior which is different to what it was described for blocky CL related copolyesters, where CL was observed to enhance the thermal stability of these copolymers [15]. Both the different microstructure and the presence of residual Ti catalyst can be the factors for this different behavior. In all cases, decomposition takes place in a single step with a maximum rate at temperatures near 400 ºC, a value very close to those of both PBS and PCL. The remaining weight after heating to 600 ºC is about 1% with no significant variations in between samples. The useful conclusion that can be drawn from the TGA analysis is that these copolyesters are well resistant to heat so that, as it will be seen below, they display a wide T_d-T_m window that will allow carrying out a safety

melting-crystallization study, as well as comfortable thermal processing in the eventual case that they were to be subjected to transformation.

Table 2. Thermal parameters obtained by TGA in this work.

Copolyester	${}^{o}T_d{}^{a}$ (°C)	${}^{max}T_d$ (°C)	$R_w{}^{b}$ (%)
PBS	341	403	1.2
coP(BS$_{85}$CL$_{15}$)	320	399	0.6
coP(BS$_{64}$CL$_{36}$)	320	402	1.5
coP(BS$_{54}$CL$_{46}$)	315	403	1.0
coP(BS$_{48}$CL$_{52}$)	320	404	1.1
coP(BS$_{36}$CL$_{64}$)	318	402	0.8
coP(BS$_{26}$CL$_{74}$)	334	405	0.6
coP(BS$_{9}$CL$_{91}$)	353	406	0.7
PCL	351	410	0.6

[a] ${}^{o}T_d$, onset temperature corresponding to 5% of weight lost.
[b] Remaining weight at 600 °C.

Glass transition temperatures

All copolymers exhibited a single glass transition temperature, as expected for random copolymers that are characterized by a miscible amorphous phase. The T_g values of the random copolymers are between the T_g values of two parent homopolymers and depend on composition. As it can be seen in Figure 5, the composition dependence was found to follow closely, the well-known Gordon-Taylor equation (equation 1) with k_{GT} = 0.23:

$$T_{g,copolymer} = \frac{w_1\,T_{g,1} + k(1-w_1)\,T_{g,2}}{w_1 + k(1-w_1)} \qquad \text{Eq.1}$$

where $T_{g,1}$ and $T_{g,2}$ are the glass transition temperatures of homopolymers 1 and 2 ($T_{g,1} < T_{g,2}$), w_1 the mass fraction of homopolymer 1 and k is the Gordon-Taylor parameter [16]. These results are consistent with the random character of the copolyesters, as demonstrated above by NMR (see Table 1).
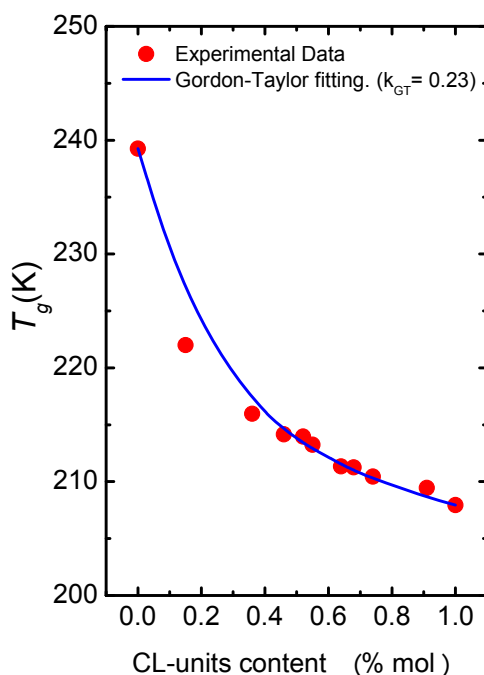

Figure 5. T_g values of coP(BS$_x$CL$_y$) copolyesters as a function of the content in CL units and their fitting in the Gordon-Taylor equation.

Melting-crystallization of coP(BS$_x$CL$_y$) copolyesters

The non-isothermal crystallization and melting of neat homopolymers and coP(BS$_x$CL$_y$) copolymers are illustrated in the DSC scans presented in Figure 6. In Table 3, extracted data from DSC traces are collected.

Figure 6a shows that all copolyesters exhibit a sharp crystallization peak during cooling from the melt, except in the case of three copolymers (coP(BS$_{45}$CL$_{55}$), coP(BS$_{48}$CL$_{52}$), and coP(BS$_{54}$CL$_{46}$)) that exhibit two broad

crystallization peaks, which are not very clear at the scale employed in Figure 6a. A close up from these DSC curves is shown in Figure SI-4 (see Supplementary Information), while the corresponding two peak crystallization temperature values for these three cases are reported in Table 3. In the Supplementary Information, analogous DSC curves, but performed at $10°C·min^{-1}$ are included for comparison purposes, as WAXS studies were performed below also at $10°C·min^{-1}$ (figure SI-5).

The copolymers are capable of crystallization in the entire composition range. This behavior indicates that frequent interruption of the crystallizable sequences of one component by the other (for example in copolymers with compositions close to 50/50) cannot frustrate crystallization, as it happens for instance in ethylene/alfa-olefin copolymers. When the comonomer units are linear and have very similar chemical structures, then crystallization can occur in the entire composition range, especially for copolyesters [16,17]. Figure 6b shows the subsequent DSC heating scans, where melting transitions can be also observed for all samples. For copolymers with close to symmetric compositions (i.e., $coP(BS_{45}CL_{55})$, $coP(BS_{48}CL_{52})$, and $coP(BS_{54}CL_{46})$), two characteristic melting points can be observed preceded by cold-crystallization processes.

As can be seen in Table 3, T_c, ΔH_c, T_m, and ΔH_m strongly depend on copolymer composition. In a previous study about thermal properties of $coP(BS_xCL_y)$, T_m and T_c of the copolyesters shifted toward a lower temperature with an increase in the CL/BS molar ratio, however, no double crystallization or melting peaks where reported, as the composition range explored was limited [5]. On the other hand, PBS/PCL blends have been found to be immiscible with two separated melting peaks observed at temperatures very close to those of the neat PBS and PCL components [18].

These two melting peaks (Fig. 6b) can be attributed to the previous crystallization (Fig. 6a) of a PBS-rich phase (higher T_c peak) and the crystallization of the PCL-rich phase (lower T_c peak). As we will show by WAXS below, a small degree of cocrystallization may have occurred in these phases, as these copolyesters probably display an isodimorphic character. In isodimorphic copolymers [19-21], the comonomer that constitutes the major phase typically crystallizes in the unit cell of the corresponding homopolymer but can include a small amount of comonomer units of the minor second component in the crystal lattice.

PBS and the two copolymers with 85 and 64 mol% BS units exhibit cold crystallization during heating (Fig. 6b), followed by a double melting peak, which indicates that PBS probably undergoes melting and recrystallization. The PCL homopolymer and also CL-rich phase copolymers (with CL contents between 91 and 40 mol%) display a single or double sharp melting peaks.

Figure 7a and 7b show plots of peak crystallization and melting temperatures respectively for the coP(BS$_x$CL$_y$) copolyesters as a function of composition (CL-units content in mol%), with legends identifying the crystalline phases present according to WAXS experiments (presented below) and corresponding scan rates. In the case of Figure 7a, it is noteworthy how composition can shift the melting point of the copolymers by as much as 100 ºC, thus providing an easy way to tailor the properties of the copolymers. On the other hand, T_g values only change by about 30 ºC and their composition dependence is very different than that exhibited by T_m values. Random copolymers are one of the few families of polymeric materials where a separate control of T_g and T_m can be obtained by regulating

composition, while for other polymeric systems, a linear correlation between T_g and T_m generally exists.

Figure 7a, shows how the melting point of the copolymers exhibit a pseudo-eutectic region in between 46-55 mol% CL content. To the left of the eutectic region, only PBS like crystals are formed (i.e., with unit cells that are very similar to that of neat PBS), and to the right of it, only PCL like crystals are obtained (according to WAXS). The pseudo-eutectic compositions have been shaded in Figure 7. For those three specific compositions, two crystalline phases were detected with distinct crystallization and melting temperatures. These two phases correspond to PBS like and PCL like crystals according to WAXS. A similar behavior was found for DSC scans performed at 20ºC·min^{-1} and 10ºC·min^{-1}.

Figure 7b shows how cooling the samples from the melt, their crystallization temperatures also exhibit a pseudo-eutectic like behavior that resembles Figure 7a, except that temperatures are displaced to lower values, as supercooling is needed for crystallization. It is interesting to observe that if samples are cooled from the melt to room temperature (20-25 ºC), only PBS and the copolymer with 85 mol% BS units can crystallize. All other samples need to be cooled down to much lower temperatures in order to become semi-crystalline. This behavior also provides control over the physical state of the copolymers depending on composition, which could be useful for specific applications. The lower scan rate (10ºC·min^{-1}) led to a slight increase in T_c values as expected.

Figure 7c shows how the enthalpy of crystallization (normalized by the content of the crystallizable phase) depends on copolymer composition. The degrees of crystallinity (X_c) of the random copolymers were calculated from these normalized enthalpies of crystallization, and the values are summarized in Table 3

and plotted in Figure 7d. The values of the enthalpy of crystallization for 100% crystalline samples $(\Delta H_m°)$ were taken as 110.3 J·g^{-1} and 139.5 J·g^{-1} [16, 22] for PBS and PCL respectively. As shown in both Figures 7c and 7d, the enthalpy of crystallization and degree of crystallinity derived from it also display a pseudo-eutectic point with composition that matches those exhibited by T_m and T_c versus composition. The reduction in crystallinity of the phases as their composition approaches the pseudo-eutectic point is a reflection of the increase difficulty in crystallization experienced by the copolymers when there is an abundance or similar amount of both comonomer units. As only a rather small amount of the second comonomer units can be included in the crystal lattice of each phase (as indicated by the WAXS results below), as the amount of the second comonomer increases, the capacity of crystallization decreases as increasingly higher amounts of the second comonomer are excluded from the crystal lattice. As polymers with reduced crystallinity tend to have faster biodegradation, we expect that copolyesters within the pseudo-eutectic region could be potentially biodegraded faster than other compositions. As expected, copolyesters cooled at a slower rate (10ºC·min^{-1}) exhibit higher ΔH_c and Xc values as they have a longer time span at their respective crystallization window during non-isothermal crystallization.

In summary, the calorimetric behavior of the coP(BS$_x$CL$_y$) random copolyesters is characteristic of isodimorphic random copolymers, as they display a pseudo-eutectic behavior and exhibit crystallization in their entire composition range [18, 21], a fact that has not been previously recognized in the literature [5]. These results indicate that a certain level of co-monomer inclusion can occur in the entire composition range. Therefore two distinct crystalline phases can be formed: a PBS rich crystalline phase, where the crystals contain a small amount of CL units

and a PCL rich crystalline phase, where small amounts of PBS units are included. The small content of the second monomer implies that the unit cells will remain very similar to those corresponding to neat PBS and neat PCL. In the special case of the pseudo-eutectic compositions the materials are double crystalline, with the two types of crystalline phases coexisting with a mixed amorphous phase. Such double crystalline character is reported in this work for the first time in $coP(BS_xCL_y)$ random copolyesters.

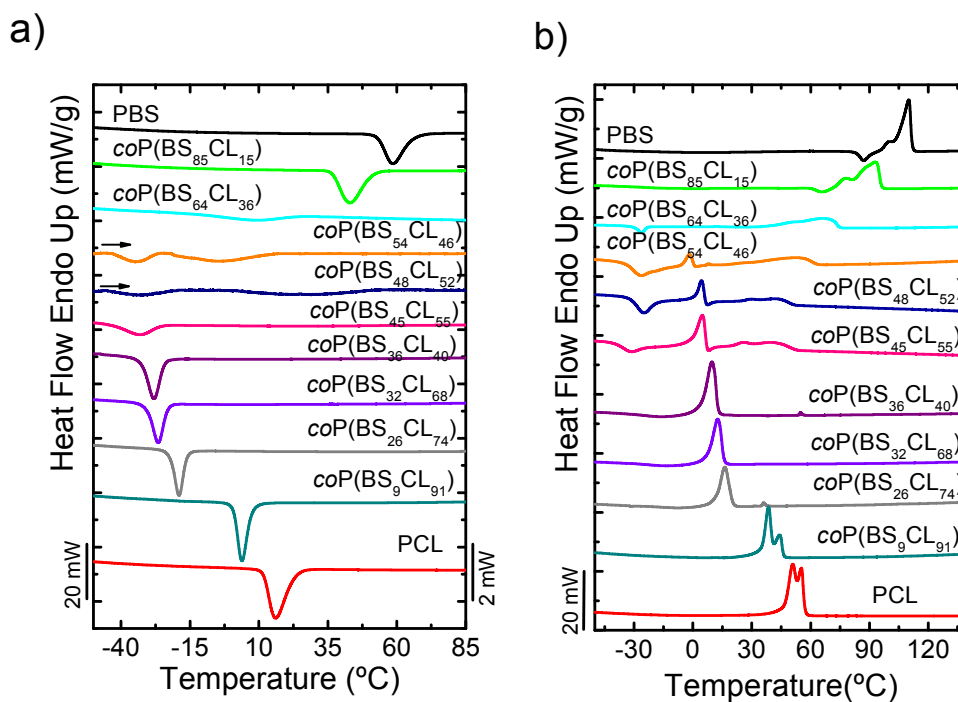**Figure 6.** DSC scans ($20^{\circ}C \cdot min^{-1}$) of the $coP(BS_xCL_y)$ copolyester series and the parent homopolyesters PBS and PCL. Traces recorded during cooling from the melt (a) and subsequent heating (b).

Table 3. A. Thermal parameters obtained by DSC for the investigated samples at 20ºC·min^{-1}.

| Copolyester | T_g (°C) | BS-rich copolyesters | | | | | | | CL-rich copolyesters | | | | |
| | | Cooling | | | | | Heating | | Cooling | | | Heating | |
		T_{c1} (°C)	ΔH_{c1} (J/g)	X_{c1} (%)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_{m1} (°C)	ΔH_{m1} (J/g)	T_{c2} (°C)	ΔH_{c2} (J/g)	X_{c2} (%)	T_{m2} (°C)	ΔH_{m2} (J/g)
PBS	-33.9	58	-61	55	87.1	-11	110.0	64	-	-	-	-	-
coP(BS$_{85}$CL$_{15}$)	-54.5	43	-59	53	-25.2	-7	93.0	72	-	-	-	-	-
coP(BS$_{64}$CL$_{36}$)	-57.2	8.3	-49	44	-25.8	-31	66.8	81	-	-	-	-	-
coP(BS$_{54}$CL$_{46}$)	-58.8	-3.0	-4	4	-25.4	-58	52.7	68	-35.0	-2	1	-1.0	20
coP(BS$_{48}$CL$_{52}$)	-59.2	16.1	-6	5	-26.5	-63	40.5	56	-34.0	-4	3	4.0	29
coP(BS$_{45}$CL$_{55}$)	-59.9	23.4	-6	5	-31.4	-27	39.0	58	-33.1	-18	12	4.8	53
coP(BS$_{36}$CL$_{64}$)	-61.6	-	-	-	-	-	-	-	-28.3	-45	32	9.7	78
coP(BS$_{26}$CL$_{74}$)	-62.7	-	-	-	-	-	-	-	-18.0	-52	37	16.3	77
coP(BS$_{9}$CL$_{91}$)	-63.2	-	-	-	-	-	-	-	3.2	-64	45	38.5	74
PCL	-65.2	-	-	-	-	-	-	-	16.1	-72	52	55.4	75

Table 3. B. Thermal parameters obtained by DSC for the investigated samples at 10ºC·min^{-1}.

| Copolyester | T_g (°C) | BS-rich copolyesters | | | | | | | CL-rich copolyesters | | | | |
| | | Cooling | | | | | Heating | | Cooling | | | Heating | |
		T_{c1} (°C)	ΔH_{c1} (J/g)	X_{c1} (%)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_{m1} (°C)	ΔH_{m1} (J/g)	T_{c2} (°C)	ΔH_{c2} (J/g)	X_{c2} (%)	T_{m2} (°C)	ΔH_{m2} (J/g)
PBS	-33.9	61.7	-71	64	86.1	-8	109.9	78	-	-	-	-	-
coP(BS$_{85}$CL$_{15}$)	-54.5	47.8	-66	60	67.6	-5	94.3	70	-	-	-	-	-
coP(BS$_{64}$CL$_{36}$)	-57.2	18.9	-51	46	18.1	-3	67.7	35	-	-	-	-	-
coP(BS$_{54}$CL$_{46}$)	-58.8	-0.5	-17	15	-31.5	-8	54.2	12	-32.0	-6	4	-4.0	9
coP(BS$_{48}$CL$_{52}$)	-59.2	-	-	-	-30.1	-9	45.8	18	-29.2	-14	10	4.8	15
coP(BS$_{45}$CL$_{55}$)	-59.9	-	-	-	-	-	43.1	21	-27.5	-30	21	5.0	20
coP(BS$_{36}$CL$_{64}$)	-61.6	-	-	-	-	-	-	-	-22.4	-51	36	7.5	49
coP(BS$_{26}$CL$_{74}$)	-62.7	-	-	-	-	-	-	-	-5.2	-60	43	22.7	61
coP(BS$_{9}$CL$_{91}$)	-63.2	-	-	-	-	-	-	-	7.0	-67	49	40.6	70
PCL	-65.2	-	-	-	-	-	-	-	24.1	-80	57	53.1	78
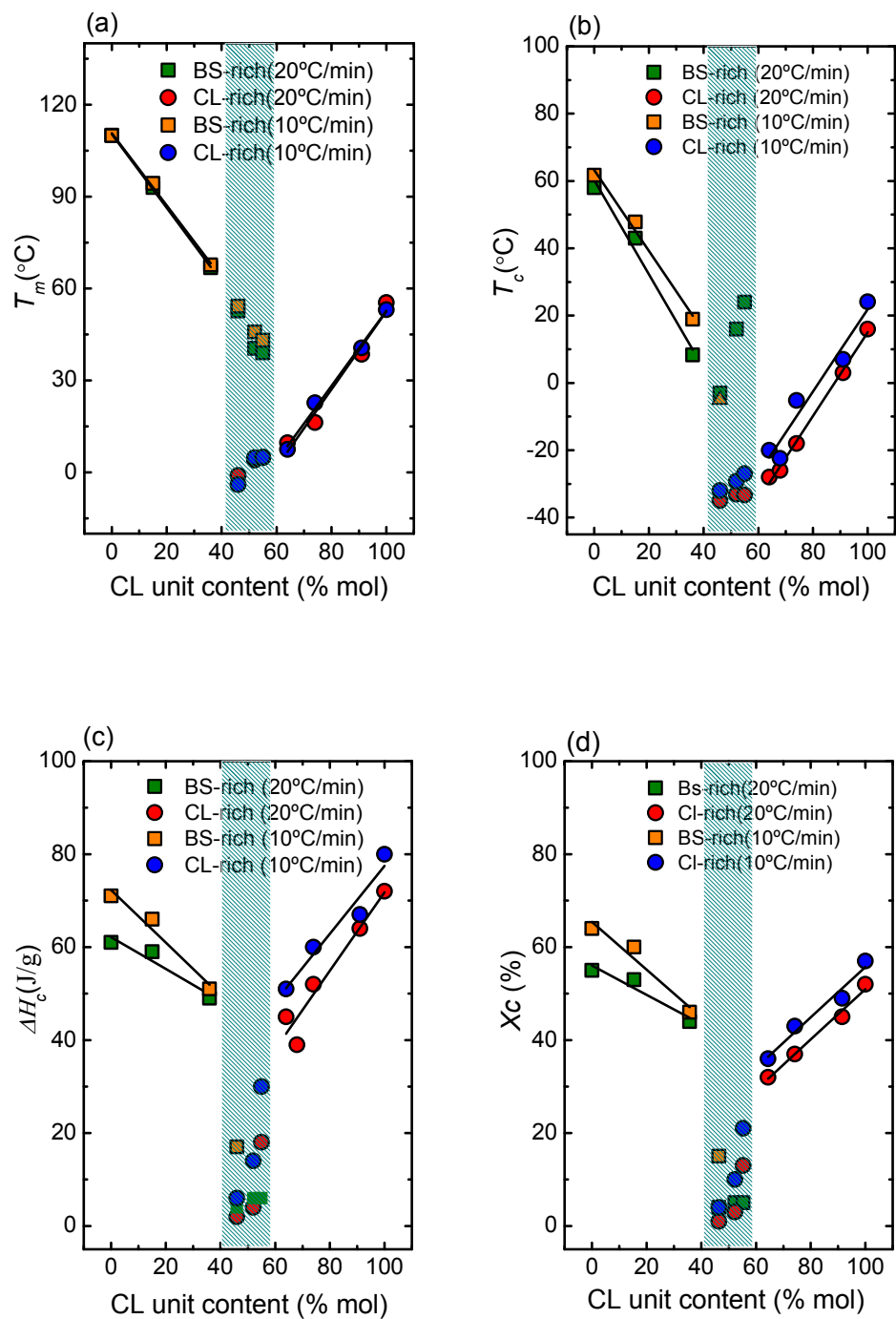
Figure 7. Peak melting temperature (a), peak crystallization temperature (b), enthalpy of crystallization (ΔH_c) (c) and degree of crystallinity (d) for the *co*P(BS$_x$CL$_y$) series as a function of composition at two different scan rates.

Crystalline morphology

We studied the effect of copolymer composition and crystallization temperature on the spherulitic morphologies of *co*P(BS$_x$CL$_y$) copolymers. Figure 8a and Figure 8b show PLOM micrographs for BS-rich samples and CL-rich samples during isothermal crystallization at the indicated temperatures and times, respectively. In general, the spherulitic morphology of all samples shows the classical Maltese cross patterns. Using a red tint plate, the colors of the first and third quadrant of the spherulites indicate a negative sign (i.e., the tangential refractive index is longer than the radial one).

The isothermal crystallization temperature values were chosen, so that for each group of materials, a constant apparent supercooling was applied (see experimental section). In the case of PBS and PBS-rich copolymers, a supercooling of 40 ºC was applied. In the case of PCL and PCL rich copolymers, in view of the intrinsically higher nucleation density of PCL as compared to PBS, a lower supercooling degree had to be employed (i.e., 20 ºC), otherwise, the nucleation density was so high, that the spherulitic size was too small in most of the PCL-rich samples.

Figure 8 shows that both spherulitic texture and nucleation density are affected by copolymerization. In Figure 8a, increasing the amount of PCL in the BS-rich copolymers leads to an increase in nucleation density and a reduction in spherulitic size. In obvious contrast, in Figure 8b, increasing the amount of PBS in the copolymer causes a reduction in nucleation density and hence an increase in spherulitic size. Therefore, composition can dramatically influence the superstructure of the copolymers, a factor that could be potentially interesting, as it can influence the mechanical properties of the samples. In a previous study of PBS/PCL blends, the

individual spherulitic morphology of each phase remains unaltered, while their size depended on composition, as the blends are reported to be immiscible [18].

Figure 8 also shows that the spherulitic growth rate in the homopolymers (at constant supercooling) is much faster (as judged by the time needed for spherulite impingement, given in the inner legend above each micrograph in Figure 8) than in the copolymers. As these copolymers are isodimorphic, only a small amount of the second comonomer is incorporated inside the unit cell of the crystallizing phase. In Figure 8, the crystallization temperatures chosen for PBS and PBS rich copolymers are so high, that only PBS spherulites (in the homopolymer) or PBS rich spherulites (in the copolymers) are formed. The majority of the PCL phase is amorphous at such high temperatures (except for those few PCL comonomer units that co-crystallized with PBS segments in the co-crystals formed in the copolymers) and lies in the interlamellar regions of the formed spherulites. A similar situation occurs as far as PCL rich copolymers are concerned. According to Figure 8, the incorporation of the comonomer units has important consequences for both the nucleation and the growth of the majority phase spherulites.

(a), ΔT= 40ºC

PBS, 70ºC, 2 min	coP(BS₈₅CL₁₅), 53°C, 4 min

50µ

50µ

coP(BS₆₄CL₃₆), 27°C, 12min	coP(BS₅₄CL₄₆), 13°C, 28min

50µ

20µ

(b), ΔT= 20ºC

PCL, 35ºC, 4 min	coP(BS₉CL₉₁), 19°C, 6 min

20µ

20µ

coP(BS₂₆CL₇₄), -4°C, 27min	coP(BS₃₂CL₆₈), -7°C, 34min

20µ

20µ
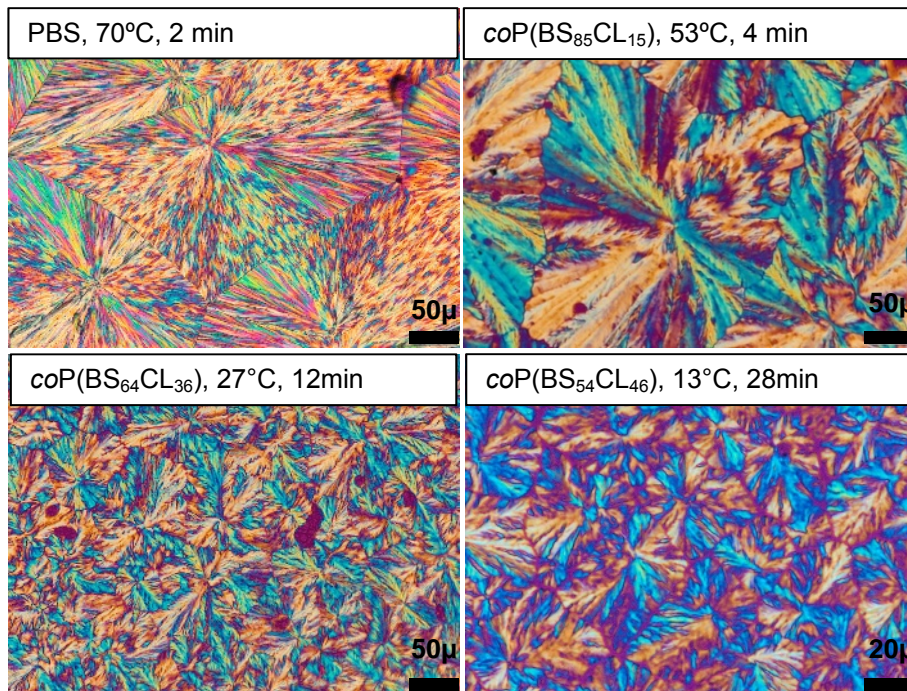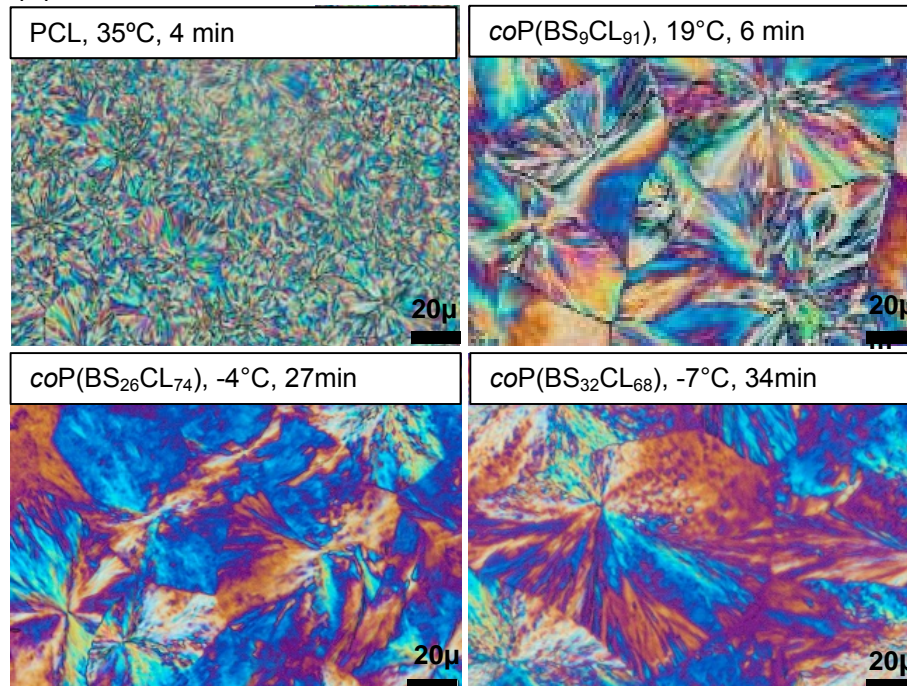
Figure 8. Polarized optical micrographs of $coP(BS_xCL_y)$ copolymers with different compositions, after isothermal crystallization at the indicated temperatures and times.

Wide Angle X-ray scattering (WAXS).

For the WAXS study, the $coP(BS_xCL_y)$ samples were cooled down to -60 ºC at a rate of 10 ºC·min^{-1} to promote crystallization, and afterward they were heated up to 25 °C at a rate of 20 ºC·min^{-1}. The WAXS patterns were registered at -60 ºC and 25 ºC and they are comparatively shown in Figures 9a and 9b, respectively. All the reflections and the calculated d values are collected in a table included in the Supporting Information document.

The WAXS diffractogram registered for PBS is consistent with the most common α form of PBS, whose monoclinic unit cell dimensions are: a = 5.23 Å, b = 9.08−9.12 Å, c = 10.79−10.90 Å and and $β$= 123.87º. Three distinct diffraction peaks are observable for PBS at 4.53, 4.05, and 3.92 Å, which are indexed as (020), (021) and (110) [23, 24], as shown in Figure 9. Neat PCL shows peaks attributed to its orthorhombic unit cell [25]: a = 7.48 Å, b = 4.98 Å, and c = 17.26 Å. The most intense reflections (4.16, 4.04, and 3.74 Å) for PCL can be assigned to (110), (111), and (200) planes [26-28], respectively. In the WAXS patterns at -60 ºC (see Figure 9a), samples with more than 60 mol% BS display distinctive PBS reflections and samples with more than 60 mol% CL show PCL reflections. Only the samples in the pseudo-eutectic region (e.g., $coP(BS_{54}CL_{46})$ in this case) display reflections of both combined crystal types, and some PCL reflections are overlapped with PBS reflections.

As it could be expected from DSC results, WAXS patterns depicted in Figure 9b indicate that some copolyester samples are amorphous at 25 ºC because their T_m values are below such temperature (see Figure 7a). The samples with more than 54 mol% of BS only display reflections attributable to the PBS unit cell, whereas $coP(BS_9CL_{91})$ exhibits the characteristic scattering of neat PCL. The

WAXS profile measured at 25 °C for *co*P(BS$_{26}$CL$_{74}$) shows a couple of weak reflections that are characteristic of PCL revealing that this copolyester contains a small amount of PCL-rich crystalline phase at this temperature.
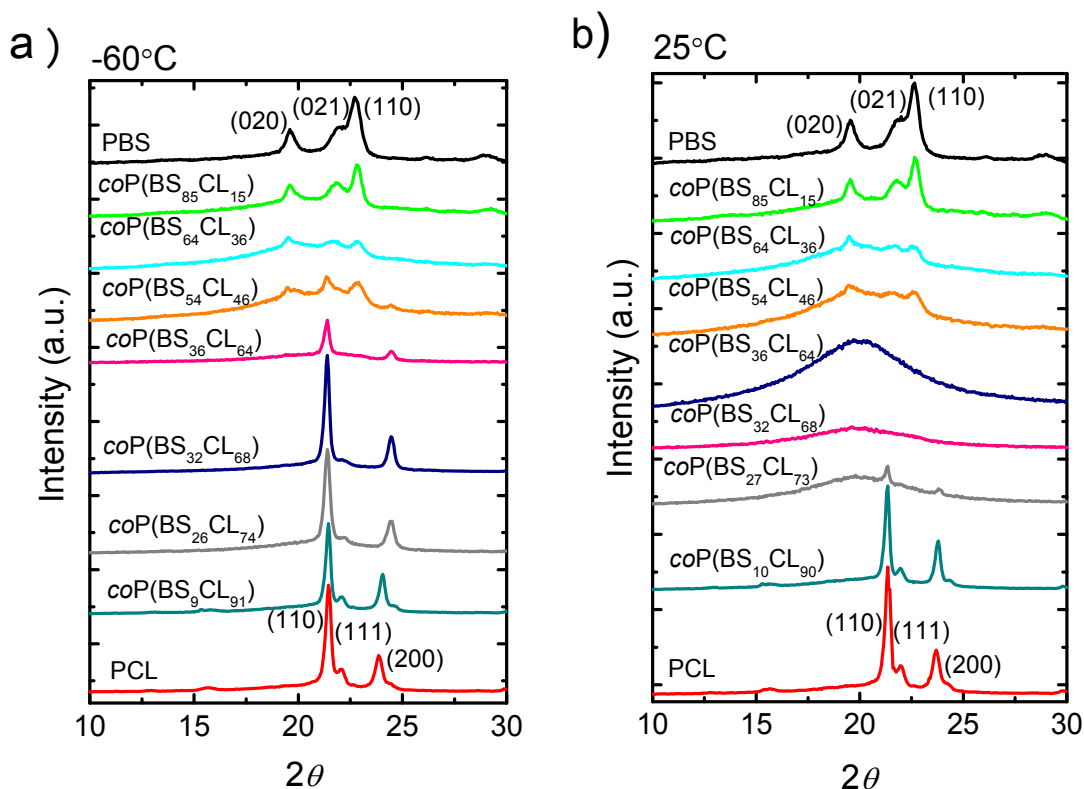

Figure 9. Powder WAXS diffraction patterns of *co*P(BS$_x$CL$_y$) registered at -60 ºC (a) and 25 ºC (b). The profiles produced by the homopolyesters PBS and PCL are included for comparison.

The *d*-spacings observed in the WAXS profiles registered at -60 ºC versus CL content are plotted in Figure 10. We have chosen -60 ºC, as at this temperature all samples were able to crystallize during the previous cooling (at 10 ºC·min^{-1}) from the melt. At -60 ºC, *d*-spacings for PBS-rich samples arising from (020) planes, as well as those for PCL-rich copolymers corresponding to (200) planes, display an increasing trend with the content in CL-units. These increases correspond to changes in unit cell sizes that can be attributed to the limited incorporation of comonomer units. The changes in *d* values shown in Figure 10 are very small,

indicating that the degree of comonomer inclusion in each phase is also limited. The degree of comonomer inclusion is a function of how the two repeating units resemble each other chemically and in size. In view of the differences in chemical repeat units between PBS and PCL (see Scheme 1), it is remarkable that a certain degree of isodimorphism can take place in their random copolymers.

Three pieces of evidences are gathered here that support some degree of isodimorphism:

(1) The fact that all copolymers are capable of crystallization regardless of their composition.

(2) The trend exhibited by the melting point as a function of composition, which displays a clear pseudo-eutectic behavior.

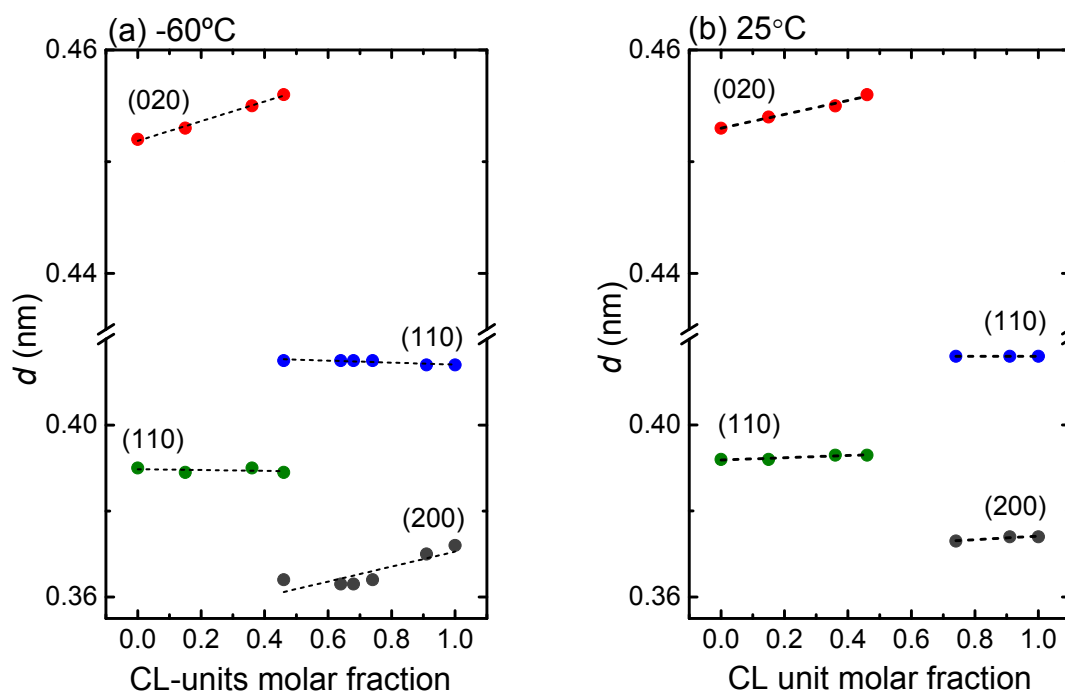(3) A small dependence of unit cell parameters with copolymer composition.

Figure 10. Plot of the most characteristic Bragg spacings observed by WAXS of *co*P(BS$_x$CL$_y$) registered at -60 °C (a) and 25 °C (b). Indexing has been made on the basis of the monoclinic and rhombic unit cells respectively reported for PBS and PCL.

CONCLUSIONS

For the first time potentially biobased and biodegradable PBS-*ran*-PCL random copolymers have been synthesized employing organocatalysis (enzymatic ring opening polymerization). The random microstructure of the copolymers was demonstrated by NMR. The copolymers are capable of displaying spherulitic superstructures whose nucleation and growth rate depend on copolymer composition, according to polarized optical microscopy observations.

The copolymers were able to crystallize in the entire composition range, their calorimetric properties exhibited a well-defined pseudo-eutectic region, and WAXS measurements demonstrated that small shifts of unit cell parameters occur as a result of minor comonomer inclusion. These results indicate that the copolymers probably exhibit some degree of isodimorphism. Additionally, the compositions within the pseudo-eutectic region were found to be double crystalline with both PBS-rich and PCL-rich crystalline phases coexisting with a mixed amorphous phase.

ACKNOWLEDGEMENTS

REFERENCES

[1] A. Lendlein, A. Sisson, Handbook of biodegradable polymers: isolation, synthesis, characterization and applications, first ed., Wiley-VCH, Weinheim, 2011.

[2] M.A. Woodruff, D.W. Hutmacher, The return of a forgotten polymer-Polycaprolactone in the 21st century, Prog. Polym. Sci. 35 (2010) 1217–1256.

[3] G.M. Matteo, M. Fabbri, N. Lotti, R. Gamberini, B. Rimini, A. Munari, Poly(butylene succinate)-based polyesters for biomedical applications: A review, Eur. Polym. J. 75 (2016) 431-460.

[4] Z. Qiu, M. Komura, T. Ikehara, T. Nishi, Miscibility and crystallization behavior of biodegradable blends of two aliphatic polyesters. Poly(butylene succinate) and poly(ε-caprolactone), Polymer 44 (2003) 7749-7756.

[5] A. Cao, T. Okamurac, C. Ishiguroc, K. Nakayamab, Y. Inoued, T. Masudab, Studies on syntheses and physical characterization of biodegradable aliphatic poly(butylene succinate-co-ε-caprolactone)s, Polymer 43 (2002) 671-679.

[6] L. Zheng, C. Li, Z. Wang, J. Wang, Y. Xiao, D. Zhang, G. Guan, Novel biodegradable and double crystalline multiblock copolymers comprising of poly(butylene succinate) and poly(ε-caprolactone): Synthesis, characterization, and properties, Ind. Eng. Chem. Res. 51 (2012) 7264−7272.

[7] Q. Liu, X. Zhou, Preparation of poly(butylene succinate)/poly(ε-caprolactone) blends compatibilized with poly(butylene succinate-co-ε-caprolactone) copolymer, J. Macromol. Sci. A 52 (2015) 625-629.

[8] I. Bechthold, K. Bretz, S. Kabasci, R. Kopitzky, A. Springer, Succinic acid: A new platform chemical for biobased polymers from renewable resources, Chem. Eng. Technol. 31 (2008) 647–654.

[9] T. Buntara, S. Noel, P. Huat Phua, I. Melián-Cabrera, J.G. de Vries, H.J. Heeres, Caprolactam from renewable resources: Catalytic conversion of 5-hydroxymethylfurfural into caprolactone, Angew. Chem. 50 (2011) 7083–7087.

[10] J. Xu, B.H. Guo, Poly(butylene succinate) and its copolymers: Research, development and industrialization, Biotechnol. J. 5 (2010) 1149-1163.

[11] S. Sugihara, K. Toshima, S. Matsumura, New strategy for enzymatic synthesis of high-molecular-weight poly(butylene succinate) via cyclic oligomers, Macromol. Rapid Commun. 27 (2006) 203–207.

[12] A. Kondo, S. Sugihara, M. Kuwahara, K. Toshima, S. Matsumura, Lipase-catalyzed ring-opening polymerization of molecularly pure cyclic oligomers for use in synthesis and chemical recycling of aliphatic polyesters, Macromol. Biosci. 8 (2008) 533–539.

[13] M. Labet, W. Thielemans, Synthesis of polycaprolactone: a review, Chem. Soc. Rev. 38 (2009) 3484–3504.

[14] G. Giammanco, A. Martínez de Ilarduya, A. Alla, S. Munoz-Guerra, Hydrolyzable aromatic copolyesters of *p*-dioxanone, Biomacromolecules 11 (2010) 2512-2520.

[15] S.G. Nanaki, K. Chrissafis, D.N. Bikiaris, Effect of molar ratio on thermal mass loss kinetics of poly(ε-caprolactone-b-propylene adipate), Thermochim Acta 517 (2011) 45-52.

[16] D.W. van Krevelen, K. te Nijenhuis, Properties of polymers: their correlation with chemical structure; their numerical estimation and prediction from additive group contributions, fourth ed., Elsevier, Oxford, 2009.

[17] L. Mandelkern, The crystalline state, in: J.E. Mark, A. Eisenberg, W.W. Graessley, L. Mandelkern, E.T. Samulski, J.L. Koenig, G.D. Wignall (Eds.), The crystalline state in physical properties of polymers, second ed., American Chemical Society, Washington DC, 1993, pp. 145-200.

[18] E. Can, S. Bucak, E. Kınacı, A.C. Çalıkoğlu, G.T. Köse, Polybutylene succinate (PBS)–Polycaprolactone (PCL) blends compatibilized with poly (ethylene oxide)-block-poly (propylene oxide)-block-poly (ethylene oxide) (PEO-PPO-PEO) copolymer for biomaterial applications, Polym. Plast. Technol. Eng. 53 (2014) 1178-1193.

[19] I. Arandia, A. Mugica, M. Zubitur, A. Arbe, G. Liu, D. Wang, R. Mincheva, P. Dubois, A.J. Müller, How composition determines the properties of isodimorphic poly(butylene succinate-ran-butylene azelate) random biobased copolymers: from single to double crystalline random copolymers, Macromolecules 48 (2014) 43-57.

[20] P. Pan, Y. Inoue, Polymorphism and isomorphism in biodegradable polyesters, Prog. Polym. Sci. 34 (2009) 605-640.

[21] R.A. Pérez-Camargo, D.C. Borja Fernández-d'Arlas, T. Debuissy, E. Pollet, L. Avérous, A.J. Müller, Tailoring the structure, morphology, and crystallization of isodimorphic poly (butylene succinate-ran-butylene adipate) random copolymers by changing composition and thermal history. Macromolecules 50 (2017) 597-608.

[22] C.G. Pitt, F.I. Chasalow, Y.M. Hibionada, D.M. Klimas, A. Schindler, Aliphatic polyesters. I. The degradation of poly (ε-caprolactone) in vivo, J. Appl. Polym. Sci. 26 (1981) 3779-3787.

[23] X. Wang, J. Zhou, L. Li., Multiple melting behavior of poly (butylene succinate), Eur. Polym. J. 43 (2007) 3163-3170.

[24] Y. Ichikawa, J. Suzuki, J. Washiyama, Y. Moteki, K. Noguchi, K. Okuyama, Strain-induced crystal modification in poly (tetramethylene succinate), Polymer 35 (1994) 3338-3339.

[25] J. Sun, X. Chen, C. He, X. Jing, Morphology and Structure of Single Crystals of Poly (ethylene glycol)−Poly(ε-caprolactone) diblock copolymers, Macromolecules 39 (2006) 3717-3719.

[26] H. Hu, D.L. Dorset, Crystal structure of poly (ε-caprolactone), Macromolecules 23 (1990) 4604-4607.

[27] D. Kołbuk, P. Sajkiewicz, K. Maniura-Weber, G. Fortunato, Structure and morphology of electrospun polycaprolactone/gelatine nanofibers, Eur. Polym. J. 49 (2013) 2052-2061.

[28] H. Bittiger, R.H. Marchessault, W.D. Niegisch, Crystal structure of poly-ε-caprolactone, Acta Cryst. 26 (1970) 1923-1927.