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Kimikako Gradua

GRADU AMAIERAKO LANA

Synthesis and characterization of isodimorphic biodegradable poly (hexamethylene succinate-ran-ε-caprolactone) [P(HxS-ran-CL)]

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Abstract

Nowadays polymers are materials used in a wide range of applications but during their lifetime they cause high plastic pollution into the environment. Because of the importance of this issue, biodegradable polymers have acquired research interest, focused on the discovery of new biodegradable polymers and finding suitable applications for them.

So, the research of biodegradable semicrystalline copolymers is an important path because properties can be adjusted changing the composition or chemical structure. Semicrystalline copolymers can show a behaviour known as isodimorphic, a phenomenon observed in copolymers composed of two comonomers with similar repeating units and crystalline structures. Isodimorphic behaviour is based on the inclusion-exclusion balance of one comonomer in the other homopolymer's crystalline structure, where the values of melting- and crystallization temperatures vary giving a V shaped tendency. The minimum point in that V shaped thermal properties is known as the pseudo eutectic point.

However, a copolymer has to fulfill three conditions in order to be considered isodimorphic; the ability to crystallize in the entire composition range, the change of the thermal transitions with composition and the change of the unit cell dimensions with comonomer composition.

In this project the isodimorphic behaviour of poly (hexamethylene succinate-ran- ε-caprolactone) [P(HxS-ran-CL)] will be studied. For that, different compositions of copolymers will be synthesized (20, 40, 60, 80 in CL mol%). Moreover, Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) will analyze thermal properties. Structural properties will be studied by Wide-Angle X-ray Scattering (WAXS) and morphology by Polarized Light Optical Microscope (PLOM).

Laburpena

Gaur egun polimeroak aplikazio ezberdin askotarako erabiltzen diren materialak dira baina gehienek beren bizi-zikloan zehar ingurugiroaren plastiko bidezko kutsadura eragiten dute. Horren ondorioz, ikerketa kimikoaren alor garrantzitsu bilakatu da polimero biodegradagarrien aurkikuntza eta hauei aplikazio ezberdinak ematea.

Beraz, kopolimero erdi kristalino biodegradagarrien ikerketa garrantzitsua da egitura kimikoa eta konposizioa aldatuz propietateak molda daitezkeelako. Kopolimero erdi kristalinoek isodimorfismo deritzon portaera aurkeztu dezakete, hau da, unitate-errepikakor antzekoa eta kristal-egitura ezberdina duten bi komonomeroren kasuetan ikus daitekeen fenomenoa. Fenomeno hau komonomero batek bestearen kristal-egituraren gelaxka-unitatean ematen duen inklusio-esklusio prozesuan datza, konposizio-tartean kristaltze- eta urtze-puntuen balioei aldaketa V itxura hartuz, minimoa puntu pseudoeutektikoa izanik.

Hala ere, kopolimero bat isodimorfikotzat har dadin hiru baldintza bete behar ditu; lehena, konposizio-tarte osoan zehar kristaltzeko gai izatea, kopolimero isodimorfikoen bereizgarria den izaera termiko aldakorra izatea eta gelaxka-unitatearen dimentsioen aldaketa konposizioarekin aldatzea.

Lan honetan poli[hexametilen sukzinato-ran-ε-kaprolaktona] (PHxS-ran-PCL) kopolimeroaren izaera isodimorfikoa aztertuko da. Horretarako hainbat konposiziotako kopolimeroak sintetizatutako dira (20, 40, 60, 80 CL % mol). Horretaz gain, haien propietate termikoak Ekorketa Diferentzialeko Kalorimetria (DSC) eta Analisi Termograbimetriko (TGA) bidez, egiturazko-propietateak X-izpien difrakzio bidez eta morfologia argi polarizatuko mikroskopiko optiko (PLOM) bidez aztertuko dira.

Sustainable Development Goals (SDGs) identification and thought

This project is based on the synthesis and study of a biodegradable copolymer. The utilization of this type of copolymer is related to **Goal 14** which is about **conserving and sustainably using the oceans, seas, and marine resources**. It is widely known that marine pollution is reaching extreme levels, and it is expected to increase even more in the coming years, so, crucial decisions have to be made. Oceans are our planet's life support, largest ecosystems, and global climate system's regulators.

Therefore, this project **increases the scientific knowledge of prevention of marine pollution, 14.A**, of polymers and targets various objectives: **the prevention of polluting the marine ecosystems, 14.1**, because biodegradability avoids plastic accumulation in oceans, an issue that requires drastic solutions as soon as possible. Because of biodegradation, the **protection of marine and coastal ecosystems, 14.2**, can be assured due to the negligible accumulation biodegradable polymers cause into those environments.

However, this research project does also target **Goal 12, ensure sustainable consumption and production**. The specific target is **12.4, the management of chemicals and wastes throughout their life cycle reducing their release to air, water and soil** because microorganisms degrade biodegradable polymers, therefore, making waste management more environmentally sound.

1. Introduction

Polymers are synthetic or semi-synthetic high molecular mass compounds that are acquiring an increasing importance in the current society as they are being introduced to different fields of science and industry. The usage of these materials has increased abruptly due to their good specific properties and wide range of applications. That is why it is hardly possible to think about a world without any plastic product in it, which provides a wide range of characteristics compared to other materials that were used decades ago. Although the increasing use of polymeric materials is advantageous in terms of utilities, it is leading to serious environmental problems. Their accumulation is the main problem as that leads to the contamination of the environment. Contamination usually happens due to the durability of the disposed materials single-use plastics contain polymers, which have chemically resistant and strong structures. This inconvenience has led to the development of new polymers that may have equivalent properties but a better end of life-cycle due to their biodegradability, decreasing the level of pollution.

To achieve the objective of solving environmental issues biopolymers are one of the possible research paths to follow. This term refers to biobased polymers, biodegradable polymers and biodegradable and biobased polymers. Biobased polymers are those that are synthesized using renewable sources such as biomass, for example PE, PP or PET[1]. Global production of biobased polymers was 2.3 million tones in 2023 and it is expected to increase with the amount of research that is being done[2]. Biodegradable polymers are those that can be degraded by enzymatic activities even if the monomers come from fossil sources. PCL is an example of this type of biopolymers[3,4]. Apart from those, there are polymers that are both biobased and biodegradable, for example poly (lactic acid) (PLA).

Biodegradation is defined as the ability of the polymer to be decomposed by the digestion of microorganisms such as bacteria or fungi. Polymers with heteroatom linkages in their backbone show this property, usually happening by hydrolysis or oxidation reactions[5,6]. This process starts with the fragmentation of chains, converting the macromolecular chains into oligomers or monomers. Once the chains are fragmented, mineralization happens where the microorganisms absorb and digest

them to create biomass, carbon dioxide (CO_2), methane (CH_4) or water (H_2O). This entire process is defined by certain parameters that will vary depending on the environment such as the oxygen concentration, pH and temperature[7].

1.1.Polyesters

Polyesters are a class of polymers characterized by the carboxylate group or ester linkage (CO-O) in their repeating-units. Linear polyesters are usually obtained by the polycondensation reaction between a diol and a diacid or diester. If branches are desired, the functionality of the alcohol or the acid/ester must increase so it enables the cross-linking reaction[8,9]. With this reaction the ester linkage is formed in the main chain of the polymers which is key in their biodegradability. This type of polymer can be polymerized by three different polymerization-reactions: polycondensation, polyaddition or ring-opening polymerization (ROP)[10].

1.1.1. Aliphatic polyesters

Aliphatic polyesters are among the most used biodegradable polymers because the ester linkage they contain makes them potentially biodegradable under specific conditions. The biodegradation of aliphatic polyesters proceeds by hydrolysis, microbial, enzymatic or thermal degradation. Aliphatic polyesters biodegrade by hydrolysis because of the labile ester bonds in the main chain forming acidic hydrolytic by-products [10].

Even though aliphatic polyesters are already used for medical applications such as drug delivery and implants due to their biocompatibility, research is focusing on these biodegradable polymers so they can find any commodity application for them. The main reason for that is their potential biodegradability can potentially help the current environmental problems.

1.2.Copolymerization

There are two possible main ways to try enhancing the properties of biopolymers: blending and copolymerization. As polymer blends rely on their miscibility to have improved properties, copolymerization is a more suitable mechanism to improve the

biodegradability of polymers [11]. Copolymerization incorporates comonomers into the main chain by covalent bonds, overcoming the problem the miscibility causes in blends. By copolymerizing two different comonomers, the obtained properties of both homopolymers are combined and properties in between both homopolymers are obtained. Copolymerization changes certain properties regarding the initial properties of each homopolymer, such as crystallinity, transition-temperatures and mechanical properties. Four types of copolymerization can be distinguished: random, block, graft and alternating copolymerization. In this project the focus will be on random copolymerization.

1.2.1. Random Copolymerization

Random copolymerization is one of the main copolymerization techniques used in the world. In this copolymerization type comonomers will not be following any ordered entry into the chains. This type of copolymerization provides covalent bonds between different comonomers as comonomers are randomly introduced into the main chain. The introduction of all comonomers into the same macromolecular chains makes the copolymer have intermediate mechanical, thermal and crystalline properties of both copolymers[12].

Upon random copolymers, random copolyesters are one of the most important copolymer families as most of them are used to improve mechanical properties and processability. The modification of polyester properties is usually focused on biodegradability, which increases in case of copolymerizing a non-biodegradable polyester with a biodegradable polyester. This type of copolymer is synthesized by random copolymerization which will influence the crystallinity, consequently modifying the thermal stability and mechanical properties of the copolymer[12].

1.3.Crystallization of random copolymers

Polymers can be amorphous or semi-crystalline. Amorphous polymers do not have any ordered structure so macromolecular chains will not create crystalline structures. On the other hand, semi-crystalline polymers form spherulites, a structure where the macromolecular chains form lamellae, crystalline ordered structure, and amorphous regions between those crystalline structures. Each homopolymer has its exact

crystalline structure but when it is polymerized different changes can happen in the crystalline structure depending on the copolymerization technique (random, block, alternating or graft).

On the other hand, the crystallization of random copolymers does not present more than one crystalline structure when various semi-crystalline homopolymers are copolymerized. Moreover, an inclusion/exclusion of a comonomer in the other comonomer's crystalline structure phenomena can be defined. Apart from that, the chemical structure of the repeating units, molar ratio of comonomers and the molecular weight are also variables that will affect the crystallization. That means comonomers can be included or excluded from a crystalline structure, depending on the comonomer's homopolymer crystalline structure[12].

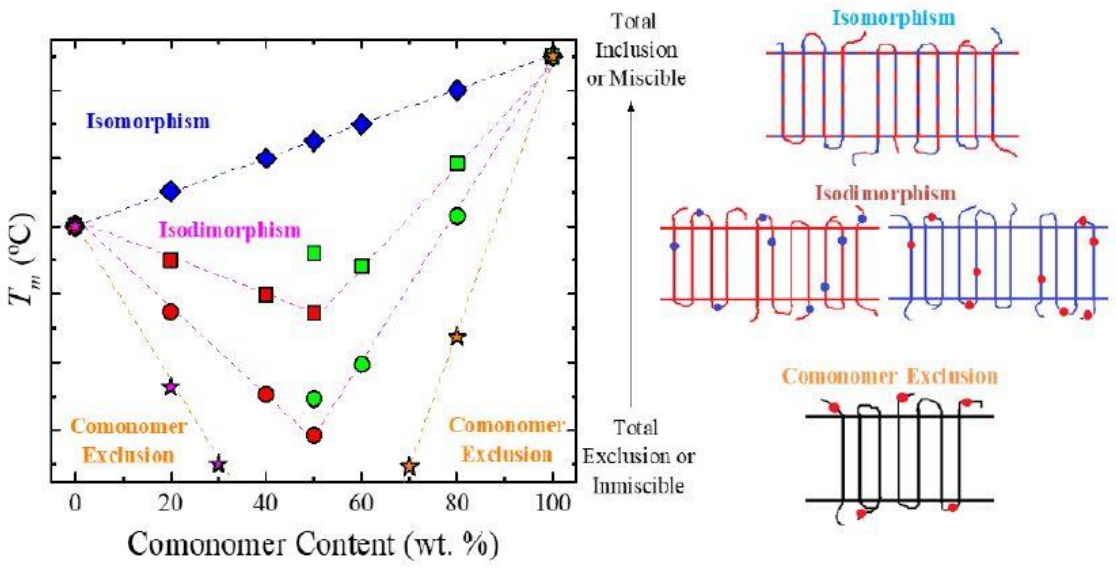


Figure 1: Melting temperature as a function of comonomer content for different copolymers. Four cases are defined: isomorphic behaviour, isodimorphic behaviour with small amount of comonomer inclusion, isodimorphic behaviour with a larger amount of inclusion and copolymers with total exclusion of comonomer.[12]

Depending on the inclusion or exclusion of each comonomer three types of crystallization types can be distinguished: total exclusion, isomorphism (or total inclusion) and isodimorphism (see figure 1). Total exclusion, also known as non-crystallization case, is characterized by the exclusion of a monomer from the crystalline structure of the comonomer's homopolymer. In the case of comonomer A and B being totally excluded, when the copolymer is richer in comonomer A crystalline structure of homopolymer A will be formed and vice versa. Furthermore, in intermediate

compositions no ordered structure will be formed because of the inability of each comonomer to form any crystallites having an amorphous structure. The tendency of all transition-temperatures will be descendant as comonomer composition increases and there will also be a composition range in which the copolymer will be completely amorphous.

On the other hand, isomorphism defines the case in which total inclusion of both A and B comonomers happens (see figure 1), in other words, both comonomers can co-crystallize forming a single crystalline structure in the entire range of composition. Isomorphic behaviour is given in comonomers that have similar repeating units and form similar crystalline structures[12]. That facilitates the crystallization of both comonomers in the same crystalline structure, which gradually changes from one homopolymer's structure to the other's depending on the composition[13]. Because the inclusion of comonomers into the crystallite is total, the transition-temperatures of the copolymers will follow a linear tendency in the whole composition range, limit values being the homopolymer transition-temperatures. An example of this type of copolymer is poly (ε-caprolactone-ran-ω-pentadecalactone) [P(CL-ran-DL)] that crystallizes in the entire composition range and the properties follow a linear tendency[13].

However, there are also random copolymers that can be viewed as an intermediate crystallizing behaviour between isomorphism and total exclusion known as isodimorphism, which is the behaviour that is going to be studied in this project. These copolymers show an inclusion-exclusion balance or competition in which comonomers A and B present a similar repeating unit but different crystal structures. In this behaviour A monomer units are partially introduced into the crystal structure of B and vice versa, crystallizing in the whole composition range. When the copolymer is rich in comonomer A, crystalline structure of homopolymer A will be formed while comonomer B is introduced and vice versa[11]. Even if there is inclusion of comonomers into crystalline structures, the concentration of it in the amorphous region will be higher than the concentration of B inside the crystallites because the inclusion of it is only partial. This means there is certain exclusion that hinders the crystallization of the major phase causing a depression of physical properties (crystallinity, crystallization-, Tc, and melting-temperatures, T_m)[14]. These inclusions can be considered as defects inside the crystal

structure and increasing the amount of them leads to the decrease of the crystalline structure's T_m and T_c.

An isodimorphic copolymer can be identified by three experimental observations. The first observation is the existence of a pseudo-eutectic region, a composition point or region in which both crystalline structures co-exist at the same time. At that range, the copolymer will have 2 different melting- and crystallizing-temperatures which will correspond to each homopolymer's crystalline structure. The second evidence is that the copolymer crystallizes in the entire composition range. And the last evidence is that the unit cell parameters of the crystallite changes gradually with comonomer composition at both sides of the pseudo eutectic region[15].

1.4.Biodegradable polyesters

In this project a random aliphatic copolyester composed of two different biodegradable aliphatic polyesters are synthesized: poly (ε-caprolactone) (PCL) and poly (hexamethylene succinate) (PHxS).

1.4.1. Poly(ε-caprolactone) (PCL)

ε-caprolactone (see figure 2) is a cyclical ester obtained by the Baeyer-Villiger oxidation of cyclohexanone with oxidating agent[16–18]. It must be said that ε-caprolactone is increasingly being obtained from natural resources by obtaining 5-hydroxymethylfurfural (HMF) from fermentation and converting it first to 1,6-hexanediol and then to ε-caprolactone[18]

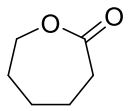


*Figure 2: **ε**-caprolactone chemical structure.*

PCL (see figure 3) is an aliphatic copolyester obtained by ring-opening polymerization of ε-caprolactone, a chain-growth polymerization mechanism. The polymerization can be done in a batch reactor because it is a polyaddition reaction in which every atom from the monomer goes into the polymeric chains without creating any by-product.

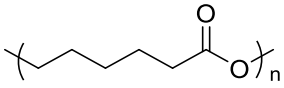


Figure 3: Chemical structure of poly (ε-caprolactone) (PCL).

PCL is a semi-crystalline polyester with a glass-transition temperature (T_g) around -60 ºC and a melting-temperature of 59 ºC, which means that in room-temperature this material has an elastic behaviour as it will be way above its T_g. PCL is a biodegradable polyester that can be biobased, miscible with other polymers and biocompatible. Due to those properties PCL has high applicability in different fields such as long-term drug delivery systems, adhesives, and packaging. But the most important aspect of PCL is the slow biodegradability because it biodegrades within months or years, depending on the crystallinity, molecular weight, and more conditions[19].

1.4.2. Poly (hexamethylene succinate) (PHxS)

Poly (hexamethylene succinate) (PHxS) is an aliphatic polyester polymerized by step growth polycondensation of dimethyl succinate (see figure 4a), DMS, and 1,6-hexanediol (see figure 4b), 1,6-Hx. In this polycondensation reaction methanol (CH_3OH) is formed as a by-product, which must be removed if high conversions are desired. So, polymerizing DMS and 1,6-Hx the repeating unit shown in figure 5 is obtained.

Figure 4: Chemical structures for dimethyl succinate (a) and 1,6-hexanediol (b).

P(HxS) is a promising semi-crystalline aliphatic polyester which presents one of the highest biodegradability in the succinate polyester family[20]. Moreover, due to its biocompatibility it can be used in biomedical applications. Because of its high biodegradability it is an interesting polymer to copolymerize to improve other polyesters' properties.

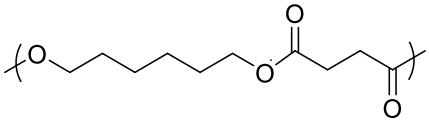


Figure 5: Chemical structure of the repeating unit of poly (hexamethylene succinate) (PHxS).

2. Objectives

The objective of this project is to study the synthesis and the characterization of the biodegradable poly (hexamethylene succinate-ran-**ε**-caprolactone) [P(HxS-ran-CL)]. Moreover, the isodimorphic behaviour of this random aliphatic copolyester is studied and the pseudo eutectic region is estimated. For that, different copolymer compositions were synthesized by ring-opening polymerization (ROP) and polycondensation, covering the whole composition range. The synthesized copolyesters are characterized by Proton Nuclear Magnetic Resonance (^{1}H-NMR) and Gel Permeation Chromatography (GPC) to obtain the exact composition of the copolymers and their average molecular weights and dispersity.

To observe the isodimorphic behaviour of the copolymer, the obtained copolymers' crystalline structures were studied. Differential Scanning Calorimetry (DSC) was used to observe the thermal-transitions and Wide-Angle X-ray Scattering (WAXS) was used to determine the crystalline structure. The variation of the crystalline structure over composition was studied using both techniques. Thermal stability was studied by Thermogravimetric Analysis (TGA), which observes thermal degradation of polymers.

Finally, Polarized Light Optical Microscope (PLOM) was used to visualize the morphology of the crystallites formed during the rearrangement of the macromolecular chains.

3. Experimental part

3.1. Materials

Dimethyl succinate (DMS), titanium tetraisopropoxyde (TTP), 1,6-hexanediol (1,6-Hx) and ε-caprolactone (CL) were used in this project. DMS was provided by Merck KGaA (synthesis grade), TTP was provided by Sigma Aldrich (97%) and 1,6-Hx and CL were provided by BLDpharm. All the reagents were directly used just as they were received.

3.2. Synthesis of random copolyester poly (hexamethylene succinate-ran-ε-caprolactone) [P(HxS-ran-CL)]

In this project copolymer [P(HxS-ran-CL)] (see structure in figure 6) was synthesized at different compositions; 0/100, 20/80, 60/40, 40/60, 20/80 and 100/0. By synthesizing the copolymer at different compositions, the variation of properties with composition can be studied as well as defining a pseudo eutectic region of composition for this copolymer.

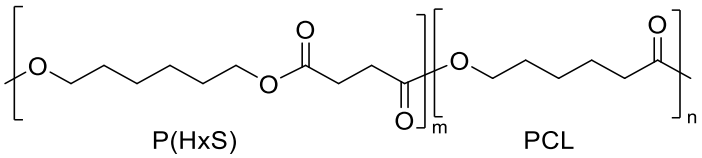


Figure 6: Chemical structure of poly (hexamethylene succinate- ε-caprolactone) [P(HxS-CL)].

To obtain the desired compositions, the amount of each monomer was calculated proportionally. The formulation is defined around 10 g of reactant and the mol percentage is calculated specifically for each case. The mol percentages that were used in the reactor were the same as the percentage of the desired copolymer composition, with a little excess 1,6-hexanediol, nearly 5 %. The excess of 1,6-Hx is added so the chain-end groups are hydroxyl groups, facilitating the polycondensation reaction, which will be explained later in this chapter.

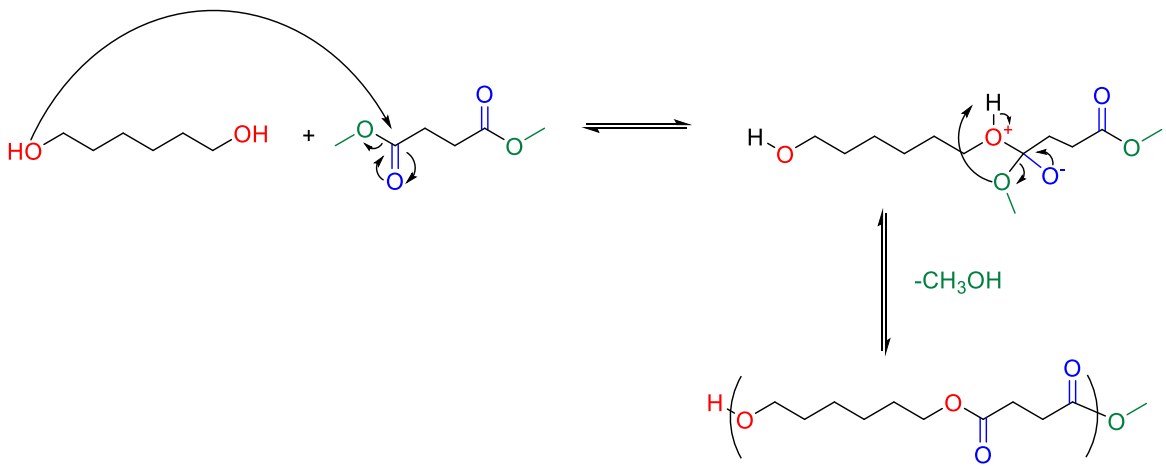
For example, to synthesize a copolymer with a composition of $HxS_{60}CL_{40}$ the following amounts were added into a 250 mL three-necked round flask: 4.1409 g DMS (28.3 mmol), 3.5161 g 1,6-Hx (29.8 mmol) and 2.1560 g CL (18.9 mmol). The objective of

this formulation composition is to obtain a final copolymer composition like the initial one.

The polymerization will be divided into 2 steps: first, the transesterification and ring-opening (ROP) step and then, the polycondensation step. Transesterification and ROP step will be conducted by a metal catalyzed melt polymerization[21]. The mix of monomer is heated in an oil bath using an IKA C-MAG HS7 heating plate and the oil bath temperature was controlled using a termopar IKA ETS-D5 up to 160 ºC. It is homogenized by a stirrer at 50 rpm. The three-necked round flask is inside the thermostated oil bath, and the monomers are mixed. Using the other two necks of the flask, a low nitrogen (N_2) flux was active during the whole polymerization process. This flux will enable an inert atmosphere inside the reactor expulsing the O_2 from it. Even if it purges the reaction media by eliminating by-products from the reactor.

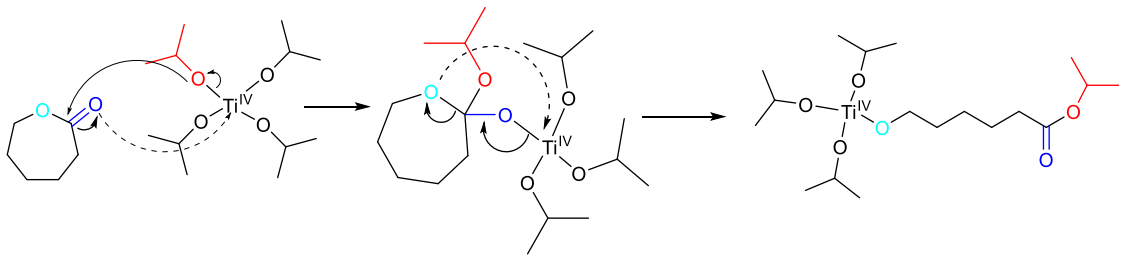
Once the reactor is thermostated at 160 ºC the catalyst TTP has to be added with a TTP/CL proportion of 0.0005 %. In this case 0.18mL (~0.2 mL) of 6.72 x 10^{-2} M TTP in tetrahydrofuran (THF) was added (0.0121 mmol TTP), which is 0.00064 % of CL. Once TTP is added, the reaction starts, and the reactor is maintained at 160 ºC for 4 hours.

In this step the transesterification reaction and ROP take place simultaneously. As it can be scheme 1, the transesterification reaction is based on the nucleophilic attack of the alcohol to the ester. This reaction will be forming the repeating unit of poly (hexamethylene succinate) and releasing methanol (CH_3OH) as by-product, which is purged from the reactor by the N_2 flux. As DMS and 1,6-Hx are bifunctional, both end-groups will react forming longer chains each time (dimers, trimers, tetramers...) but polymeric chains will be formed only at high conversions.



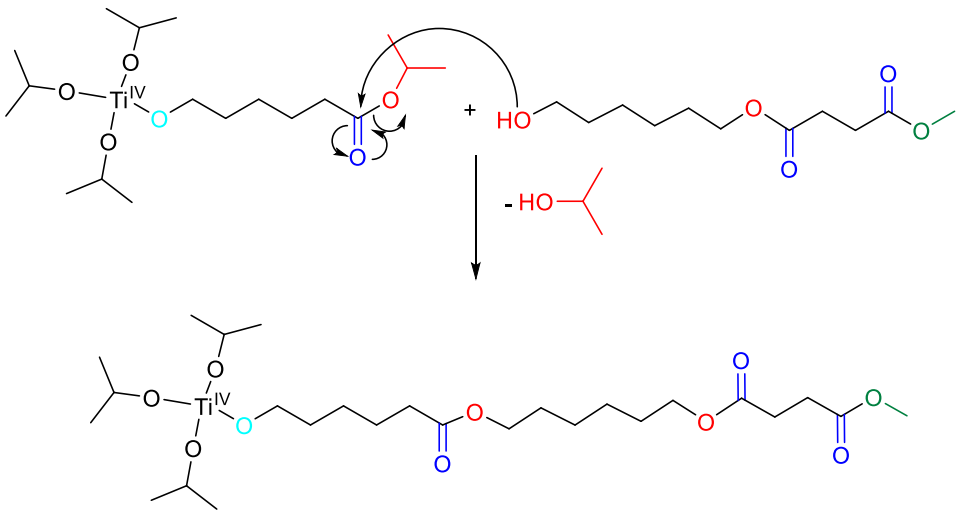
Scheme 1: Transesterification reaction mechanism to obtain poly (hexamethylene succinate) (PHxS).

When it comes to the ROP reaction, the mechanism is more complex. The opening of CL is enabled by a titanium (IV) catalyst. Titanium alkoxides are the most efficient and active metal catalyst. As scheme 2 shows, ROP reaction starts with the formation of the complex between CL and TTP because of the interactions between the metal and carbonyl of CL. Then, the rearrangement of electrons ends up by obtaining an opened cycle which can activate other CL molecules because the Ti (IV) catalyst remains in the chain, enabling the polymerization[22].



*Scheme 2: Ring-opening polymerization mechanism **of ε-**caprolactone to obtain poly(**ε-**caprolactone).*

The random copolyester is obtained by the cross reaction of the products. The alcohol of the transesterification product can attack the residual carbonyl of the ROP product with the mechanism that can be seen in scheme 2. In that mechanism the alcohol reacts with the carbonyl and the isopropoxyde group that is inserted in the ROP reaction is released as byproduct, in this case isopropanol (see scheme 3).



Scheme 3: The reaction mechanism to obtain a random PHxS-PCL copolyester.

With the mechanism that can be seen in scheme 3 random copolymers are obtained as both repeating units are combined in the same macromolecular chain, which is the objective of this project.

So, after the transesterification and ROP step finishes after 4 h at 160 ºC, low molecular weight chains, oligomers, are formed. To increase molecular weights a polycondensation step is added into the polymerization strategy. But, before the polycondensation reaction, the reactor is thermostated at 190 ºC at the same conditions of stirring and N_2 flux as in the transesterification and ROP step. This step is added to ensure that the chains have a molecular weight high enough not to be volatilized due to the elevated temperature and vacuum.

In the polycondensation step vacuum is applied by an Edwards T-Station 85 pump, which applies vacuum at 0.1 mbar. The temperature increases to 220 ºC slowly as the vacuum is increasingly applied. A trap is used to securely use the pump to avoid by-products purged from the reactor from going into the pump. Then, the molten polymerization is maintained under vacuum and thermostated at 220 ºC for around 2 h and the copolymerization is finished. The obtained copolymer is reserved in 20 mL vials and stored in the freezer until samples have to be prepared to proceed with its characterization.

In this project only copolymers will be synthesized and pure homopolymers will be obtained by data provided by Alejandro Müller's research group.

3.3. Proton Nuclear Magnetic Resonance (^{1}H-NMR)

Proton Nuclear Magnetic Resonance (^{1}H-NMR) is a technique used to verify the chemical structure of organic compounds, either small molecules or macromolecules. The basis of this technique is the differentiation of every proton due to its behaviour when an external magnetic field is applied. Depending on the functional groups around each proton, the protons will be chemically different. Their resonance varies and will lead to different chemical shift values, for each signal in the ^{1}H-NMR spectra, δ (ppm). The intensity of each signal is proportional to the concentration of that type of proton in the molecule, which will lead to an easier analysis of the chemical structure of the samples.

In the case of copolymers, not only the chemical nature can be determined but the copolymer composition can also be quantified. This quantification is based on the contribution the protons from each repeating unit have in the total area of the signals. To calculate the proton contributions (CPH) of CL $(CPH)_{CL}$) and HxS $(CPH)_{HxS}$), an isolated proton's signal has to be selected. To get the proton contribution of each repeating unit's protons, the total area of each signal has to be divided by the number of protons that give that signal, obtaining the proton contribution. Once $(CPH)_{CL}$ and $(CPH)_{HxS}$ are quantified, the copolymer composition (mol %) can be calculated (Eq 1.1 and Eq 1.2).

$$X_{CL}\ (\text{mol}\ \%) = \frac{(CPH)_{CL}}{(CPH)_{CL}+(CPH)_{HxS}} \quad \text{(Eq 1.1)} \qquad X_{Hxs}\ (\text{mol}\ \%) = \frac{(CPH)_{Hxs}}{(CPH)_{CL}+(CPH)_{HxS}} \quad \text{(Eq 1.2)}$$

Where X_{CL} and X_{HxS} are the copolymer composition of CL (Eq 1.1) and HxS (Eq 1.2).

In order to obtain the 1H-NMR spectra for the copolymers at different composition Bruker NMR Avance 300DPX at 300 MHz was used. The sample was dissolved at $CDCL_3$ and tetramethyl silane (TMS) was used as standard.

3.4. Gel permeation chromatography. (GPC)

Gel permeation chromatography is a technique that separates by size the analyzed polymer chains. That separation is controlled by using a column filled with a porous gel

that obstructs the path of the macromolecular chains. The polymer will be pumped into the column solve, in an eluent, which may cause problems depending on the solubility of the polymer, and at the end of the column a detector will record the signals. The larger chains will not interact within the porous cavities and will exit the column at low elution times. Meanwhile, short polymeric chains will interact with the porous cavities making a larger path inside the column, increasing the elution time.

The most used eluent for polymers in UPV/EHU is THF. However, due to the low solubility of the copolymer in the solvent, samples were analyzed in Universidad Politécnica de Catalunya. Molecular weights were obtained at 35 ºC using a Waters equipment with a refractive index detector and PS and PMMA standards. A 0.05 M sodium trifluoroacetate-hexafluorure-2-propapanol (NaTFA-HFIP) solution was used to measure the samples in a poly (styrene-co-divinylbenzene) gel with an eluent speed of 0.5 mL min^{-1}.

3.5.Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is a technique that studies the thermal stability of polymers. The basis of this technique is to observe how the polymer sample thermally degrades by quantifying the loss of weight (wt %) with temperature. In this equipment the sample is added into a scale and the normalized weight of the sample is measured for each temperature giving information of the thermal stability of the polymer.

The main objective of TGA is to study the thermal stability of the synthesized copolymers with parameters such as $T^d_{10\%}$, temperature at which 10 % of the weight of the sample is volatilized or T^d_{max}, temperature in which the degradation-rate is maximum. All the copolymer systems' thermal stability and degradation were studied at 20 ºC min^{-1} up to 800 ºC heating 20 ºC min^{-1}.

The equipment used in this project to study the thermal stability of the samples was a PerkinElmer Thermogravimetric Analyzer TGA 8000. This equipment has a chamber where thermal degradation happens, and its main characteristic is that there is an inert atmosphere because N_2 is introduced. As O_2 is purged from the chamber, the thermo-

oxidative degradation of the samples is avoided, and the measurements are isolated just to observe thermal degradation.

3.6. Differential Scanning Calorimeter (DSC)

Differential Scanning Calorimeter (DSC) is used to analyze the thermal behaviour of the synthesized copolymers at different compositions. This technique is used to obtain information about the thermal transitions of the sample. This equipment has two independent ovens; one is for the capsule with the sample and the other for an empty capsule. The equipment used in this research project was a PerkinElmer Differential Scanning Calorimeter DSC8500.

The basis of this technique is to heat or cool the sample and quantify the heat needed (endothermic processes) or the heat released (exothermic processes) when the temperature is changed. To quantify the heat in those processes, the equipment takes the empty capsule as a reference, and it measures the heat flow needed in the sample's oven, so it gets to the same temperature of the reference.

Those heat flow differences are the basis of the appearance of the peaks, which correspond to the thermal transitions of the polymer. In this project the focus will be the determination of T_c and T_m and their respective enthalpies, ΔH_c and ΔH_m, and to study the isodimorphic behaviour they might represent. For that, the method composed by three scans is done (see figure 7): the first scan is a heating-ramp the sample is heated up to 80 ºC in which the thermal history of the polymer is erased. Then, it is cooled to -40 ºC at a cooling-speed of 20 ºC min^{-1}. The last scan is the second heating-ramp in which the sample is heated 20 ºC min^{-1} up to 80 ºC. It has to be said that between ramps the temperature was maintained for 3 minutes to verify the sample was homogeneously thermostated at the desired temperature.

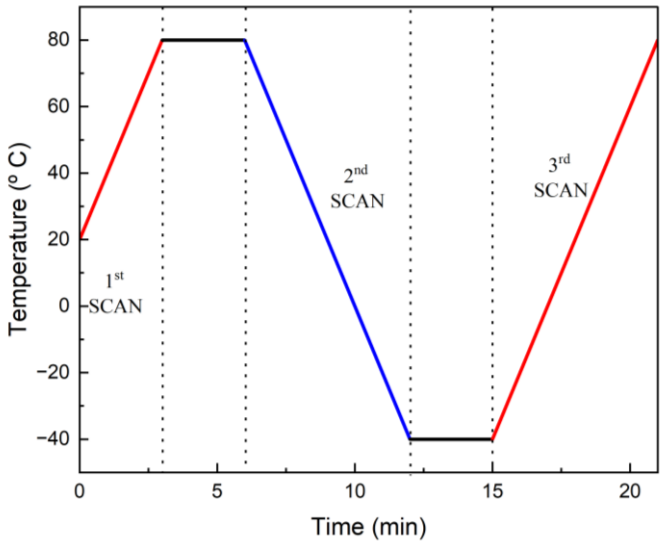


Figure 7: Graphical description of the designed method for the DSC analysis of copolymers.

The melting-temperature and melting-enthalpy will be obtained from the second heating scan and the crystallization temperature and crystallization-enthalpy will be obtained from the cooling-ramp. It is important that this method is followed equally for all the copolymers because this will enable the comparison between the obtained data. For each thermal transition, the enthalpy will be calculated as the area of the peak and the transition temperature will be defined by the maximum value of the peak. Isodimorphic behaviour will be studied with the data obtained from the explained method.

3.7.X-ray scattering

X-ray scattering is a technique used to study the crystalline structures of different compounds. The sample is irradiated with an X-ray beam, whose wavelength is the same order of the crystalline structure's intermolecular distances. Because of those similarities between the wavelength and the intermolecular distance, X-rays beams are diffracted due to the interaction between the molecules and the radiation. The scattered beams can have constructive interactions, in other words, scattered radiation may comply with Bragg's Law ($n = 2 d \sin \theta$, where n is a entire number, λ is the wavelength of the irradiated X-ray beam, d the distance between crystalline planes and θ the angle the beam has been scattered) because of the constructive interactions of scattering patterns, which give information about the crystalline structure of the analyzed semicrystalline polymer.

In this project WAXS (Wide Angle X-ray Scattering) was carried out in situ with the equipment beamline BL11-NCS and Rayonix LX225-HS detector in ALBA syncrotron radiation installations, Barcelona. DSC capsules were filled with the sample and the crystalline structure was observed while applying a 20 ºC min^{-1} temperature ramp. The measurements were obtained using an irradiation of 1.0 Å wavelength X-ray beam and the detector was a Rayonix LX225-HS.

3.8.Polarized Light Optical Microscopy (PLOM)

Polarized light optical microscopy (PLOM) is a technique used to study anisotropic materials and their optical properties. Anisotropic materials are characterized by the variation of optical properties depending on the direction of the light-material interaction. Using polarizers, selective filters that allow light to oscillate in a specific direction and block in all other directions, morphological properties of anisotropic materials are studied.

Using this technique crystallization were studied applying a 20 ºC min^{-1} cooling-ramp and capturing the structures at different temperatures. In this project an Olympues BX51 polarized light optical microscope is used equipped with the camera Olympues SC50 combined with a Linkam TP-91 heater.

4. Results and discussion

In this project the synthesis and characterization of the random copolymerization of biodegradable polyesters PHxS and PCL was done to obtain an aliphatic copolyester P(HxS-ran-CL) at different comonomer compositions. The following copolymer compositions were targeted: 20/80, 40/60, 60/40 and 80/20 (HxS/CL). Pure homopolymer values were taken from experimental data obtained beforehand by Alejandro Müller's investigation group. Using different characterization techniques, the isodimorphic behaviour of the copolyester was studied, which has been done for different random copolyesters[11,15,23].

4.1.Chemical characterization

To characterize the different composition copolymers ^{1}H-NMR and GPC were used obtaining the final copolymer composition, number average molecular weight (M_n), number average molecular weight (M_w) and the dispersity index (Đ).

First, the comonomer compositions were calculated by ^{1}H-NMR. For that, proton contribution (CPH) for each comonomer was calculated. In figure 8 can be seen the ^{1}H-NMR spectra of the copolymer $HxS_{39}CL_{61}$ where two independent signals are highlighted each one corresponding to a different repeating unit's methylene (-CH_2-). In that spectra most of signals are overlapped but there are two signals around 2.5 ppm that are isolated and each one correspond to one of the repeating units; the signal at 2.65 ppm corresponds to the 4 protons from the methylene of the succinate (proton n.1).

The signal at 2.45 ppm, on the other hand, corresponds to the 2 protons of the methylene next to the carbonyl in the repeating unit of CL. Integrating the areas of those signals and the number of protons corresponding to each signal the copolymer compositions can be obtained.

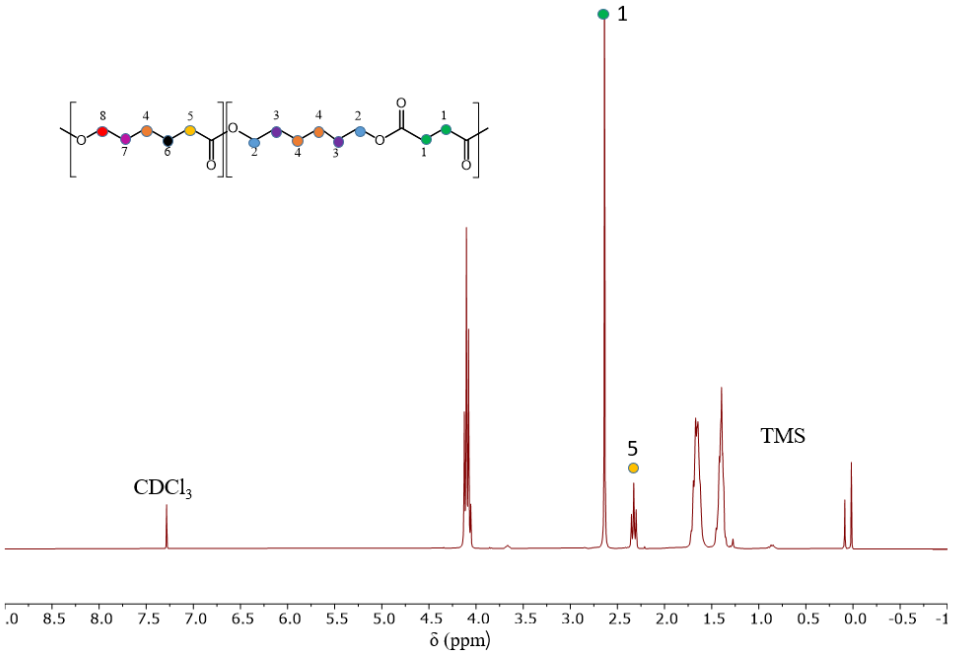


*Figure 8: ^{1}H-NMR spectra of poly (hexamethylene succinate-**ε**-caprolactone) [P(HxS-CL)] copolymer system $HxS_{39}CL_{61}$.*

In figure 9 signals of H n.1 (a) and H n.5 (b) at different comonomer compositions can be seen. The change on the composition can clearly noticed because of the variation of the areas of the signals. The increase of the area of the peak is proportional to the increase of (CPH) and, therefore, comonomer composition.

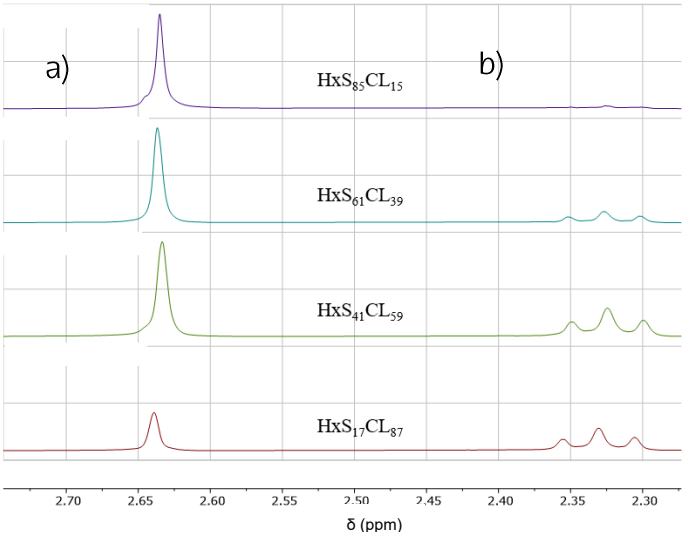


Figure 9: Variation in the areas of the peaks corresponding to HxS (H n.1) (a) and CL (H n.5) (b) with composition.

MestRenova software was used to integrate the areas from the spectra and $(CPH)_{CL}$ $(CPH)_{HxS}$ were calculated. Then, using equations 1.1 and 1.2 compositions for comonomers CL (X_{CL}) and HxS (X_{HxS}) were calculated. In table 1 the composition values before and after the polycondensation step are shown.

*Table 1: Composition (hexamethylene succinate) and **ε**-caprolactone of the initial formulation, before and after the polycondensation reaction, calculated by ^{1}H-NMR.*

Monomer composition (mol %)	Transesterification + ROP		Polycondensation		Final copolymer composition (mol %)
	X_{HxS} (mol %)	X_{CL} (mol %)	X_{HxS} (mol %)	X_{CL} (mol %)	
PHxS	100	0	100	0	PHxS
$HxS_{80}CL_{20}$	82	18	85	15	$HxS_{85}CL_{15}$
$HxS_{60}CL_{40}$	58	42	61	39	$HxS_{61}CL_{39}$
$HxS_{40}CL_{60}$	39	61	41	59	$HxS_{41}CL_{59}$
$HxS_{20}CL_{80}$	19	81	17	83	$HxS_{17}CL_{83}$
PCL	0	100	0	100	PCL

Samples were taken from the reactor before and after the polycondensation step to see if the applied vacuum caused significant changes in the composition of the copolymer. A small amount of monomer could have been volatilized because of the low pressures and high temperatures, 220 ºC, for low molecular weight organic compounds. This effect can be seen in the cases of $HxS_{85}CL_{15}$, $HxS_{61}CL_{39}$ and $HxS_{41}CL_{59}$ in which the composition of CL decreases after the polycondensation step, but the decrease of X_{CL} is 2-3 mol % for every case.

On the other hand, molecular weights and dispersity index were obtained by GPC. PS standards were used in all the samples but PCL, in which PMMA standards were used using NaTFA-HFIP 0.05 M as eluent. The values obtained for these copolymers can be seen in table 2. The obtained values are given as the equivalent molecular weight of the polymer used as standard because the detector was a refractive index detector, with did not enable the direct calculation of the specific molecular weight of the synthesized polymers.

All copolymer systems and homopolymers surpass the barrier of $\overline{M_n}$ › 5,000 g mol^{-1}, having an adequate value in order to analyze properties in the following chapters.

Table 2: Values of molecular weights and dispersity for the synthesized copolymer systems.

Sample	$\overline{M_n}$(g mol^{-1})	$\overline{M_w}$ (g mol^{-1})	Đ
PHxS	15,658	36,603	2.2
$HxS_{85}CL_{15}$	22,500	43,900	2.0
$HxS_{61}CL_{39}$	21,700	41,100	1.9
$HxS_{41}CL_{59}$	19,200	36,500	1.9
$HxS_{17}CL_{83}$	18,350	33,900	1.8
PCL	18,350	33,900	1.8

4.2.Thermal characterization

The synthesized aliphatic copolyesters were thermally analyzed by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). TGA was the first used thermal characterization technique in order to analyze the thermal stability of the synthesized copolymers. The thermal stability was studied from 40 ºC to 800 ºC with a 20 ºC min^{-1} heating-ramp and the results of the synthesized copolyesters are shown in figure 10.

From figure 10 different information can be extracted. First, it has to be remarked that all the copolymer systems were studied in the same conditions and the samples were taken directly from the vials, where the final product of the synthesis was stored. Once the conditions of the sample are defined, the low water absorption has to be highlighted. Samples that have certain water uptake show significant weight decrease in temperatures lower than 100 ºC. As the weight % remains constant from 40 ºC to 200 ºC, it can be said that these copolyesters are not hygroscopic even if the ester linkages in their main chains are polar.

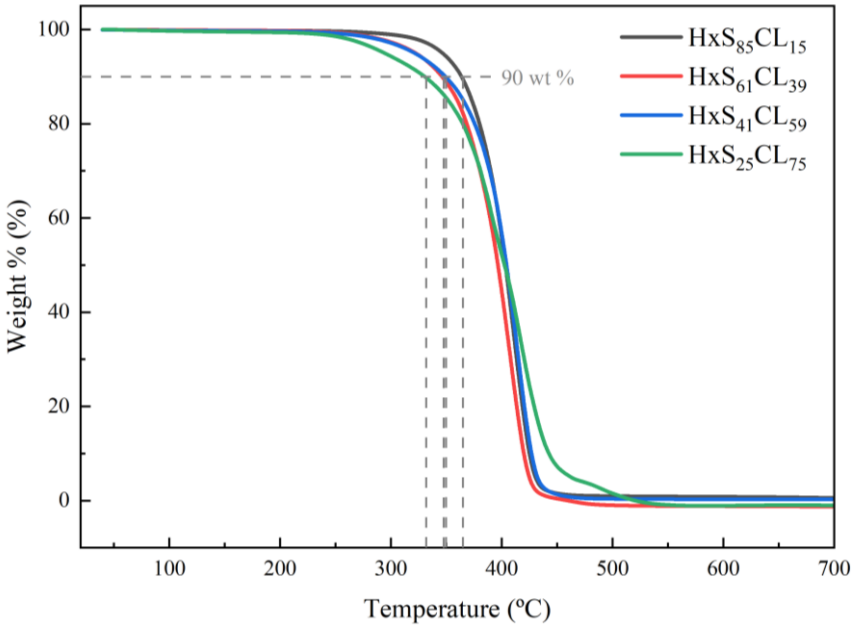


Figure 10: TGA curves of the synthesized P(HxS-CL) copolymer systems.

Apart from the hygroscopic behaviour of the copolymers, $T_d^{\%10}$ and T_d^{max} were obtained and are displayed in table 3. $T_d^{\%10}$ represents the temperature in which 10 % of the weight is lost because of the formation of volatile compounds. These values for the different copolymer systems vary in values between 330 ºC and 364 ºC. Analyzing figure 10, a noticeable tendency of $T_d^{10\%}$ can be described: $T_d^{10\%}$ decreases when the CL comonomer composition increases. Following this tendency the $T_d^{10\%}$ value of the homopolymer PCL is expected at lower temperatures than 330 ºC and the value for PHxS is expected at higher temperatures than 364 ºC. It also has to be said the residue remaining at 600 ºC is 0-1 wt %, which means that the copolymers degrade by forming volatile compounds.

Table 3: Experimental values of the 10 % weight loss ($T_d^{\%10}$) and maximum degradation-rate (T_d^{max}) temperatures.

Samples	$T_d^{\%10}$ (ºC)	T_d^{max} (ºC)
$HxS_{85}CL_{15}$	364	412
$HxS_{61}CL_{39}$	346	408
$HxS_{41}CL_{59}$	349	414
$HxS_{17}CL_{83}$	330	418

T_d^{max} was calculated by calculating the derivation of curves from figure 10. Calculating the minimum value for the derivative of the weight percentage, the temperature in

which the degradation-rate is maximum (T_d^{max}) can be determined. The derivative of the curves for each copolymer system can be seen in figure 11.

Even if $T_d^{10\%}$ does have a decreasing tendency with CL comonomer composition, T_d^{max} is maintained similar for the different copolymer systems (see values in table 3). This similarity may be since both homopolymers may have a similar T_d^{max} value, which might lead to the small variation with the change of composition.

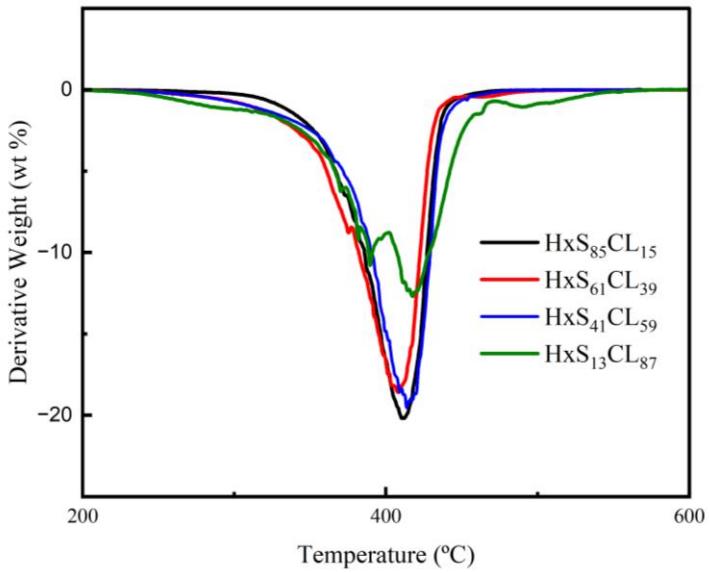


Figure 11: Derivative of the thermogravimetric curves (DTG) for each P(HxS-CL) copolymer system.

Although every curve has its minimum point at a similar temperature (see figure 11), $HxS_{13}CL_{87}$ shows two peaks while other copolymers show a single peak. This may have happened due to the contribution of the residual catalyst in the final copolymer chemical structure. All copolymers have been synthesized with the same amount of TTP but in the case of $HxS_{17}CL_{83}$ residual TTP may have hindered the degradation. That hinderance causing the separation of the peak and obtaining two different relative maximum degradation-rates, the absolute maximum being the second one.

Apart from that, random copolymers tend to show a single peak in the differential thermogravimetric analysis while block copolymers show peaks corresponding to each copolymer. In this case, all copolymers have a single decreasing slope which can be corroborated in figure 10. In that graph all copolymers show just one maximum degradation-rate, reassuring the success of the designed synthesis strategy to obtain random P(HxS-CL) copolyesters.

Overall, the synthesized copolyesters do have great thermal stability up to 200 ºC. Once that limit temperature is surpassed, the loss of weight increases abruptly causing the decrease of its properties. However, the degradation starts being significant from 300 ºC onwards as the slope of the curves has a huge increase in which the degradation-rate is maximum at around 410 ºC.

Once the copolymers are verified to be thermally stable up to 200 ºC, Differential Scanning Calorimeter DSC 8500 was used in order to study the crystallization and melting processes of the copolymers at different comonomer compositions. The method explained in figure 7 was followed, in which the temperature-ramp is 20 ºC min^{-1} so all the results could be compared.

The objective of the project is the study of the isodimorphic behaviour of this random aliphatic copolyester, melting and crystallization processes will be studied and compared. As was explained before, certain random copolymers do show a variation on their properties due to their isodimorphic nature. The inclusion of comonomers will cause a decrease of properties of both homopolymers until the pseudo eutectic region is reached.

Table 4: Experimental values for T_m, T_c, ΔH_m and ΔH_c for every P(HxS-CL) copolymer at different compositions.

Samples	T_m (ºC)	ΔH_m (J g^{-1})	T_c (ºC)	ΔH_c (J g^{-1})
PHxS	52	63	27	63
$HxS_{85}CL_{15}$	45	59	12	54
$HxS_{61}CL_{39}$	35	58	5	52
$HxS_{41}CL_{59}$	30	62	4	55
$HxS_{17}CL_{83}$	37	65	9	60
PCL	57	33	33	55

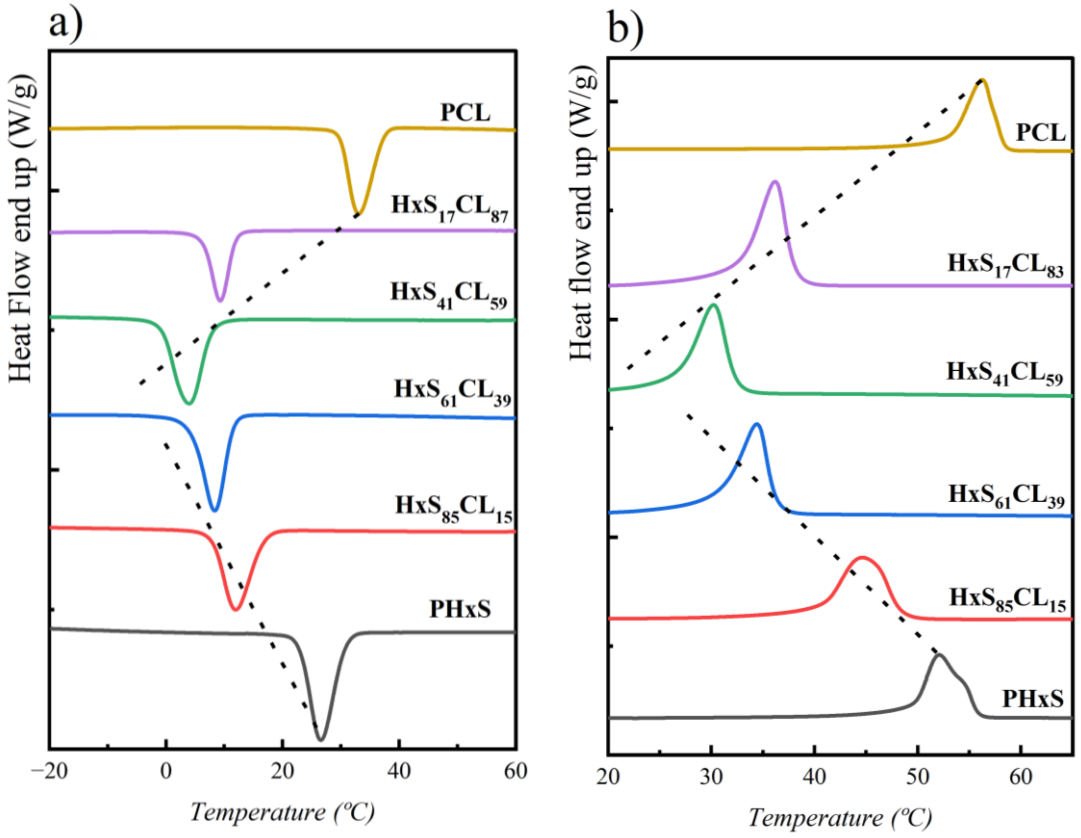


Figure 12: Crystallization (a) and melting (b) processes for all P(HxS-CL) copolymer systems.

Exothermic peaks are obtained because of the crystallization of the copolymer and in figure 12a the copolymer P(HxS-CL) crystallizes in the entire range of composition. Because of the crystallization in the entire range of composition, the copolymer studied shows one of the most common characteristics of an isodimorphic copolymer. Data obtained by crystallization and melting processes can be seen in table 4. That data was obtained by calculating the areas and taking the temperature values of the peaks of non-isothermal DSC scans (see figure 12).

The composition range can be separated into two different sections: a section rich in CL and another section rich in HxS. The first section will be characterized by a predominant crystalline structure of CL and the partial inclusion of HxS, and the second one will form HxS comonomer's crystalline structure and CL will be included partially. In the case of the CL rich section, the transition-temperatures decrease as CL composition decreases until 61/39 (HxS/CL) comonomer composition, where increasing T_c values are obtained. In that range of 50 CL mol % the pseudo eutectic region is expected as PCL and PHxS

crystalline structures are recovering their thermal properties when the copolymer composition is near to the homopolymer.

In the rich PHxS section can be seen that the temperature values of the peak corresponding to the crystallization of PHxS decrease as the CL comonomer composition of the copolymer increases. This shift of the crystallization into lower temperatures happens because of the inclusion-exclusion balance of CL into the crystalline structure of PHxS. T_c values decrease until the composition corresponding to $HxS_{41}CL_{59}$ is reached. From that composition on, thermal properties increase with CL comonomer composition. This shift of the crystallization into higher temperature values is due to the change of the predominant crystalline structure, from PHxS to PCL.

In figure 12b non-isothermal DSC heating scans of the crystalline structures formed in the cooling scans from figure 12a are shown. Endothermic peaks are obtained because the melting process requires heat to melt the crystalline structure of the copolymer. The same tendency as in the crystallization is observed where T_m values decrease when CL comonomer composition is increased until a change of tendency. At that composition, the predominant crystalline structure is changed from PHxS to PCL and T_m values start increasing until pure PCL is obtained.

To have a clearer visualization of the variation of transition temperatures with CL composition, T_m and T_c values are plotted as a function of CL comonomer composition in figure 13. In that graph PCL rich and PHxS rich sections can be differentiated clearly. In the case of crystallization (see figure 13a) T_c of PHxS decreases from 27 ºC to 5 ºC because of the inclusion of CL into the crystalline structure. That composition range will be defined as PHxS rich section. However, from 59 mol % CL to the homopolymer (PCL), T_c values increase from 4 ºC up to 33 ºC because the predominant crystalline structure was changed, therefore defining the CL rich section of the composition.

In figure 13b the variation of melting-temperature with CL comonomer composition is plotted. T_m values follow a similar tendency to the crystallization-temperatures and in both a V shaped transition temperature-CL composition correlation is obtained.

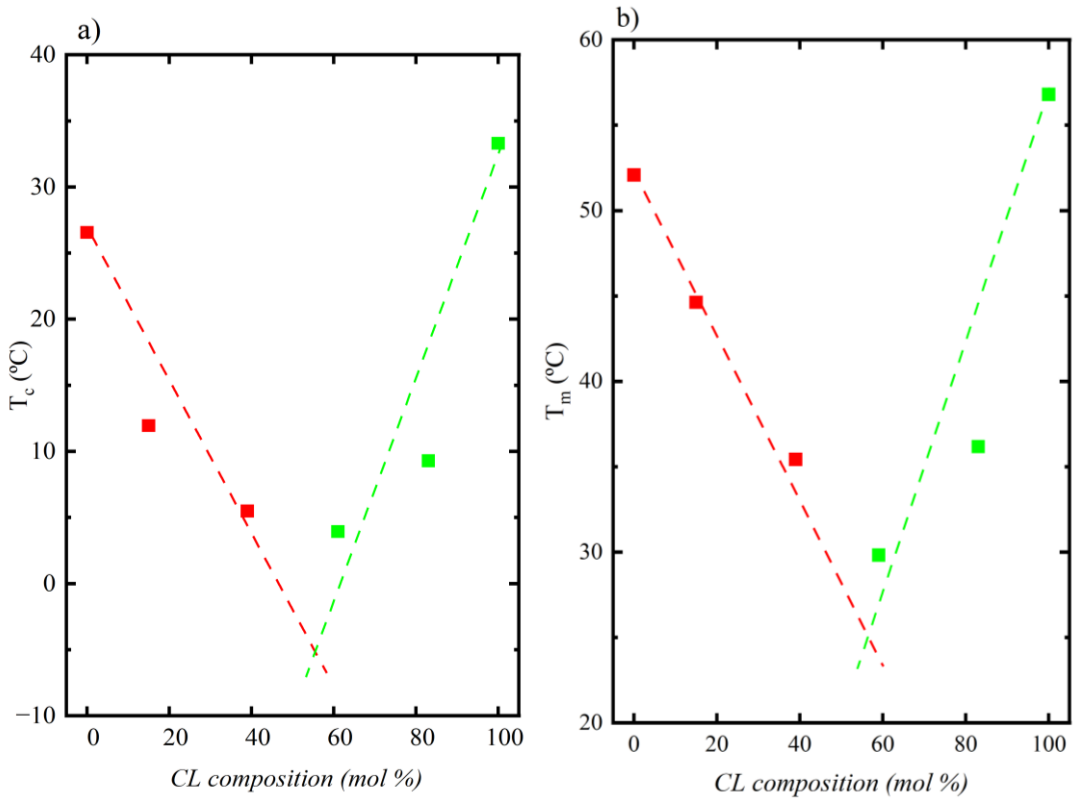


Figure 13 Crystallization- (a) and melting-temperatures (b) plotted as a function of CL composition (mol %).

This V shaped tendency is also characteristic of isodimorphic polymers in which the minimum point of the V is the pseudo eutectic region. In this project the pseudo eutectic region could not be experimentally observed but because of the two tendencies described in both figure 13a and figure 13b the pseudo eutectic region is expected to be located at CL comonomer compositions around 50 %.

4.3.Characterization of the crystalline structure

Wide Angle X-ray Scattering (WAXS) was used in order to calculate the d spacing of the crystalline structure at every composition of the copolymer. The main objective of the characterization of the crystalline structure is to quantitatively study the effect of the inclusion-exclusion balance of comonomers on the crystalline structure's dimensions, more specifically the d spacing. All the samples were measured in the same conditions. First, the thermal history was erased and then cooled to -40 ºC applying a temperature ramp of 20 ºC min^{-1}, and finally, heated up to 80 ºC.

So, the d spacing of the different crystalline planes could be compared WAXS measurements for every sample at -40 ºC were taken and plotted in figure 14. This temperature was selected because at -40 ºC every sample can crystallize having started the crystallization process from a molten state (80 ºC).

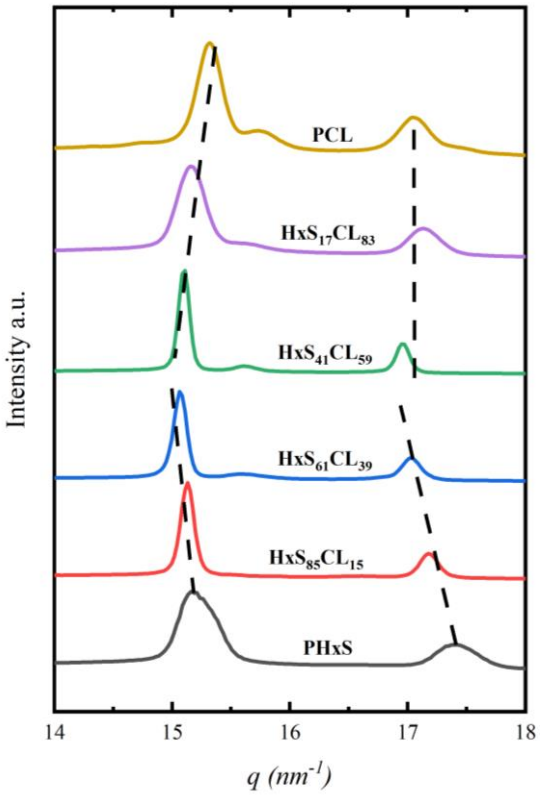


Figure 14: Signals corresponding to the crystalline structures of different comonomer composition P(HxS-CL) copolymer systems at -40 ºC.

In figure 14 both homopolymers crystalline structure's signals can be observed. Both signals have similar values, in other words, it seems both homopolymers do have similar crystalline structures. When the composition is changed, the signals vary. The value represented in the X axis in figure 14 is *q*, the scattering vector, which was calculated by introducing the measurement conditions into equation 2.

$$q = \frac{4\,\pi\,sin\,2\theta}{\lambda} \qquad (Eq.\ 2)$$

Where λ *is the wavelength of the X-ray beam and* θ *the angle of the irradiated X-ray beam.*

To calculate the d spacing for each copolymer the maximum value from each signal was taken and Bragg's law was applied which is simplified to equation 2 (Eq.2) by introducing the scattering vector defined in equation 3 (Eq.3).

$$d = \frac{2\pi}{q} \qquad (Eq.3)$$

Where q is the scattering vector defined in equation 2 (Eq.2) and d is the d spacing value for the analyzed crystalline structure

d spacing values in the PCL rich section correspond to crystal planes (110) and (200)[24]. On the other hand, *d* spacing values for PHxS rich sections correspond to crystal planes (220) and (040) [25]. These crystal planes are selected due to their similar *d* spacing values, which enables the study the effect the inclusion of a comonomer has in the unit cell dimensions focusing on a *q* range between 14-18, were all four plane's signals can be observed.

All the *d* spacing values obtained from figure 14 are shown in figure 15, where the tendency of *d* spacing values with different CL comonomer composition can be observed. The crystalline structure's dimensions increase with the comonomer inclusion. Comonomer inclusion can be considered as the introduction of defects into the crystalline structure. So, if defects are introduced, the unit cell will not be as compact as if there were no defects, which will lead to a crystalline structure with higher dimension.

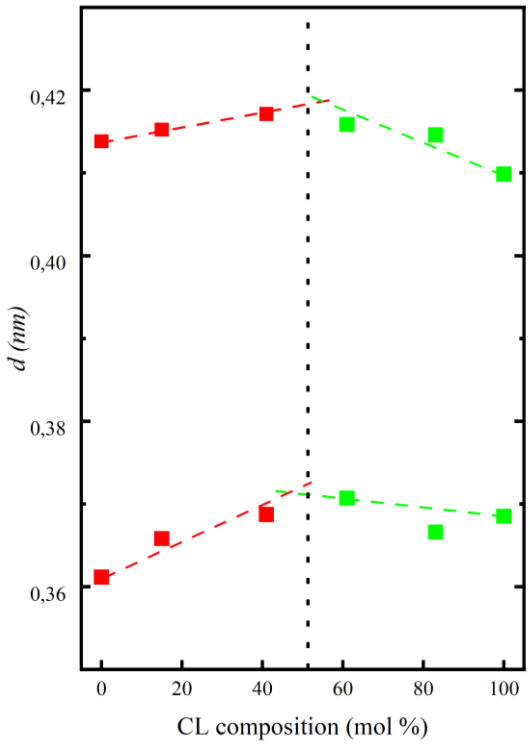


Figure 15: d spacing values of PCL and PHxS crystal planes for all the copolymer systems.

Moreover, the change of the dimensions is in the order of 0.01 nm. This means that the inclusion of the comonomer is quite good even though they function as defects in the crystalline structure. Another reason for the low increase of the *d* spacing values is that both comonomers have similar repeating-units (see chemical structure in figure 5) increasing the probability of inclusion into the predominant crystalline structure. As both comonomers present a similar repeating unit the probability of the comonomer being introduced into the crystalline structure is similar in both sections. In the PCL rich section HxS comonomer will be partially included while CL comonomer will be included in the PHxS rich section barely changing the value for *d* spacing of both sections.

This increase in the dimensions of the crystalline structures shows that the studied aliphatic copolyester presents isodimorphic behaviour as the crystalline structures of both homopolymers are represented and the inclusion of the corresponding comonomer makes the dimensions of those structures bigger.

4.4. Morphology

The morphology of the copolymers was studied by Polarized Light Optical Microscope (PLOM) applying a temperature-ramp of 20 ºC min^{-1}. The cooling process was observed focusing on the crystallization of different P(HxS-CL) systems. Every copolymer system was studied at those conditions, but temperatures depended on the crystallization kinetic of each one of them.

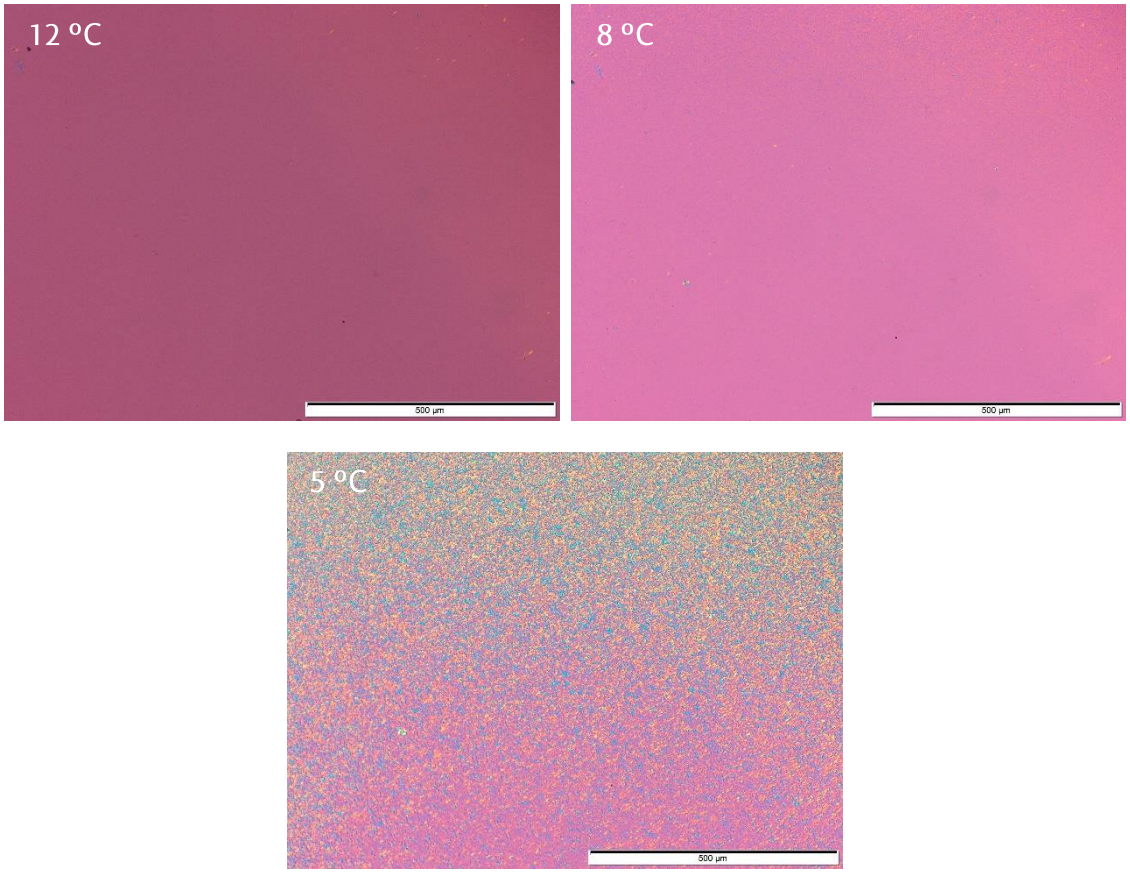


Figure 16: Morphology of crystals obtained for P(HxS-CL) copolymer system of composition $HxS_{17}CL_{83}$ applying a 20 ºC min^{-1} cooling-ramp .

In figures 16,17 and 18 the crystallization process is shown by pictures taken throughout the process. All of them show crystalline structures but the formed lamellae were too small. So, after observing the morphology of the crystallization process of P(HxS-CL) systems at different compositions it was concluded that the morphology of the formed spherulites is not big enough to analyze their structure. The crystallization process was fast, and the arrangement of chains happened in a matter of 10 seconds forming little spherulites.

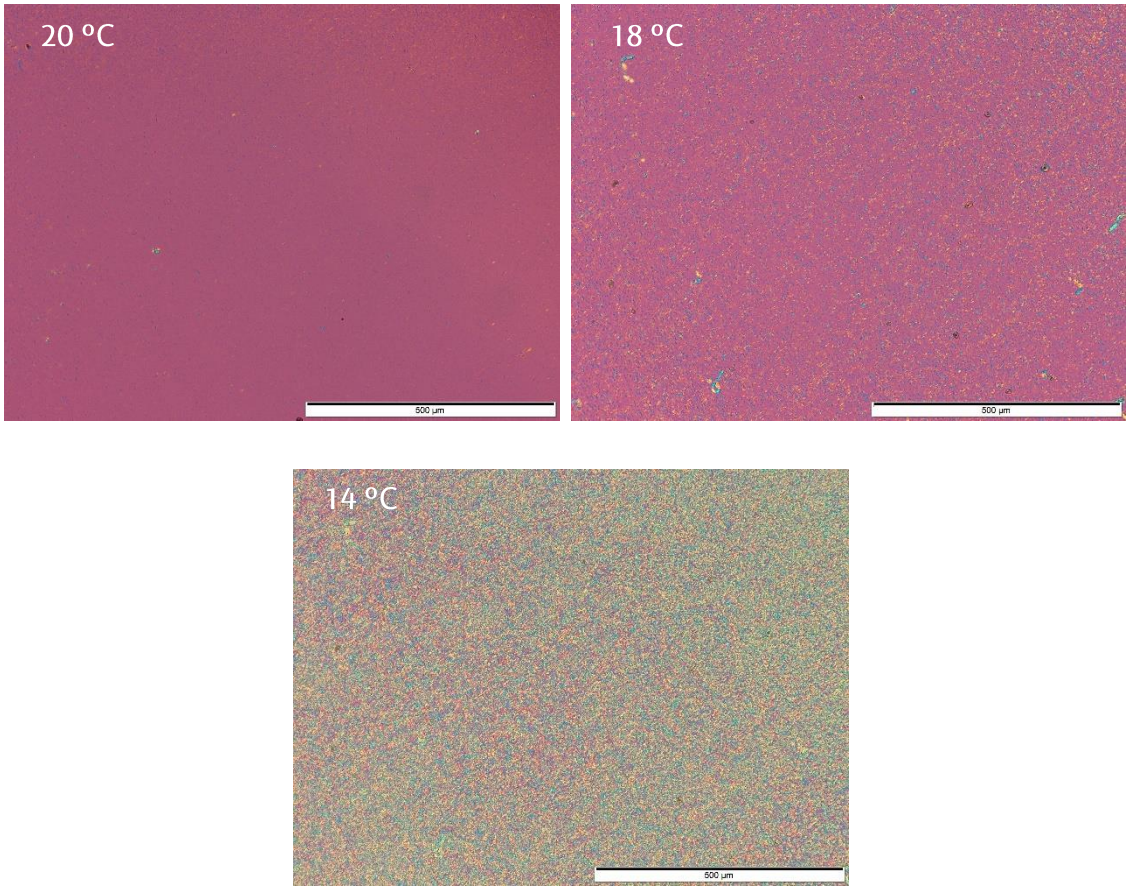


Figure 17: Morphology of crystals obtained for P(HxS-CL) copolymer system of composition $HxS_{85}CL_{15}$ applying a 20 ºC min^{-1} cooling-ramp.

However, the crystallization observed by PLOM, using the same cooling-rate as in DSC analysis, shows the same tendency in which intermediate composition $HxS_{39}CL_{61}$ crystallizes at lower temperatures than $HxS_{85}CL_{15}$ or $HxS_{17}CL_{83}$. $HxS_{85}CL_{15}$ started crystallizing at around 8 ºC (see figure 17), $HxS_{41}CL_{59}$ at around 5 ºC (see figure 18) and $HxS_{17}CL_{83}$ at 18 ºC (see figure 16). Furthermore, those temperature values are quite like the T_c values obtained from DSC cooling scan (see figure 13a). So, the isodimorphic behaviour of P(HxS-CL) systems can also be observed by PLOM.

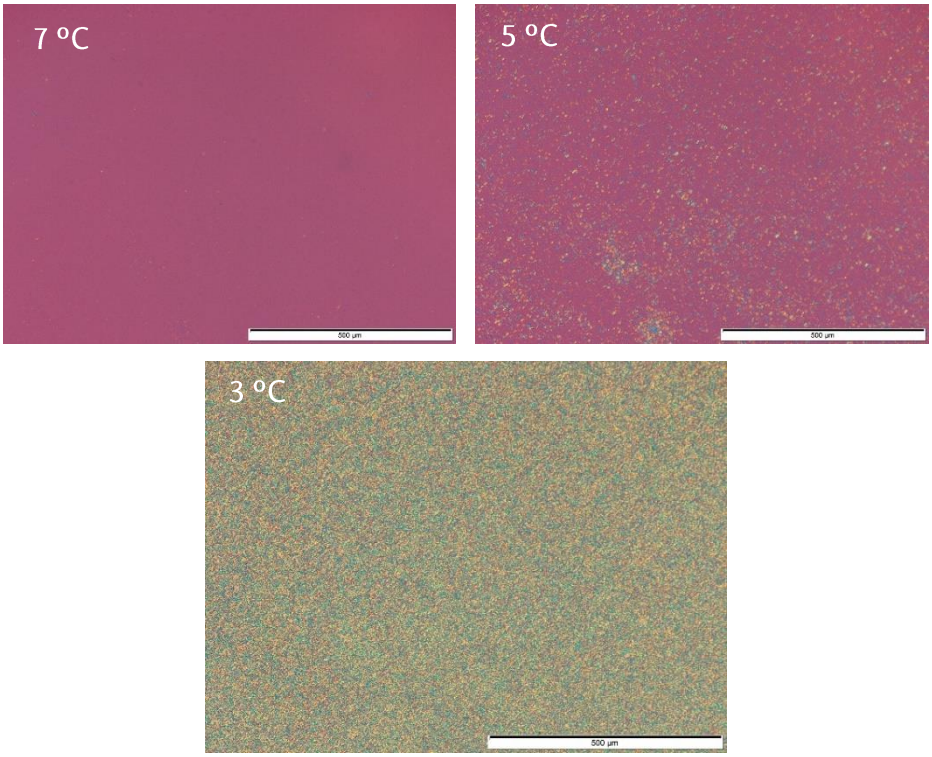


Figure 18: Morphology of crystals obtained for P(HxS-CL) copolymer system of composition $HxS_{41}CL_{59}$ applying a 20 ºC min^{-1} cooling-ramp.

Conclusions

The synthesis of the P(HxS-ran-CL) biodegradable aliphatic copolyester systems were completed correctly, the desired compositions were obtained, and average molecular weights were between the expected range[21].

Firstly, the copolymer can crystallize in the whole composition range. Moreover, thermal properties show an isodimorphic behaviour when one comonomer's composition is increased. That behaviour is defined by the inclusion-exclusion equilibrium of two comonomer's with similar repeating units and crystalline structure. Because of this decreasing tendency, around 50 % CL mol composition range has been defined as the pseudo eutectic region of this copolymer. This region has been defined because the minimum thermal properties are expected to be in that composition. From that region to both directions a predominant homopolymer crystalline structure with a partial inclusion of comonomer is defined. This inclusion is verified by measuring the *d* spacing of both crystalline structures by WAXS, where those *d* spacing values increase with the inclusion of the comonomer.

So, the discovery of the isodimorphic behaviour poly (hexamethylene succinate-ran-ε-caprolactone) can be concluded because this aliphatic random copolyester fulfills the main three characteristics of an isodimorphic polymer: the ability to crystallize in the entire range of composition, the V shaped variation of T_m and T_c values with composition and the variation of the *d* spacing. With those observations, it can be concluded that P(HxS-CL) copolymers show isodimorphic behaviour.

The main advantage of isodimorphic polymers is the ability to control such as mechanical or thermal properties by changing its comonomer composition. Furthermore, all the copolymer compositions are thermally stable up to 250-300 ºC which enables their processability by processing techniques such as extrusion or injection molding.

Ondorioak

P(HxS-CL) kopoliester alifatiko biodegradagarri sistema ezberdinen sintesia arrakastaz burutu ziren. Lortutako konposizioak esperotako balioetan lortu ziren eta masa molekularrak aurreikusitako tartean sartu ziren [21].

Lehenik, kopolimeroa konposizio-tarte osoan kristaltzeko gai dela ikusi da. Gainera, propietate termikoek izaera isodimorfikoa erakusten dute komonomero baten konposizioa handiagotzean. Izaera hori unitate errepikakor eta kristal egitura antzekoa duten bi komonomeroren inklusio-esklusio orekagatik zehaztu daiteke. Propietate termikoen joera beherakorragatik %50 CL mol komonomero konposizio balioaren inguruan definitu da P(HxS-CL)-rentzat tarte pseudoeutektikoa. Tarte hau definitu da puntu pseudoeutektikotzat propietate termikoen balio minimoak bertan espero direlako. Konposizio horretatik bi norantzetara homopolimero baten kristal egitura gailentzen da beste komonomeroren inklusioa emanez bertara. Bi egitura kristalinoentzat WAXS bidez lortutako *d* espazio balioen igoerak komonomeroen inklusioa ziurtatu daiteke, komonomeroaren konposizioa igo ahala *d* espazio balioek gorakada ematen dutelako.

Horretaz, poli (hexametilen sukzinato-ran-**ε**-kaprolaktona) kopolimeroaren izaera isodimorfikoaren aurkikuntza baiezta daiteke, ausazko kopoliester alifatiko honek polimero isodimorfikoen hiru ezaugarri nagusiak betetzen dituelako: konposizio tarte osoan kristaltzeko gaitasuna, V itxurako aldaketa T_m eta T_c balioetan konposizioa aldatzean eta *d* espazioen balioen aldaketa. Behaketa horietan oinarrituz, P(HxS-CL) kopolimeroak izaera isodimorfikoa erakusten duela ondoriozta daiteke.

Polimero isodimorfikoen abantaila nagusia konposizioak propietateengan duen eragina da, honen aldaketarekin propietate termiko zein mekanikoak alda daitezkeelako. Gainera, konposizio ezberdinetan sintetizatu diren kopolimeroak egonkorrak dira 250-300 ºC tartera arte. Horrek beren prozesatze-propietateak hobetuko ditu tenperatura altuetan degradaziorik ez duelako jasango.

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