

Crystallization of isodimorphic aliphatic random copolyesters: pseudo-eutectic behavior and double-crystalline materials

Ricardo A. Pérez-Camargo¹, Idoia Arandia¹, Maryam Safari¹, Dario Cavallo², Nadia Lotti³, Michelina Soccio³, Alejandro J Müller^{1,4*}

¹POLYMAT 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.

²Department of Chemistry and Industrial Chemistry, University of Genova, Genova, Italy.

³ Department of Civil, Chemical, Environmental, and Materials Engineering, Via Terracini 28, 40131 Bologna, Italy.

⁴IKERBASQUE, Basque Foundation for Science, Bilbao, Spain.

*Corresponding author (A.J.M.) E-mail: alejandrojesus.muller@ehu.es

Abstract

Isodimorphic random copolyesters are intriguing polymeric materials that can crystallize in their entire composition range, despite the random distribution of comonomer units along their chains. This behavior stems from the relatively similar chemical repeating units of the parent homopolymers. In this feature article, we review our recent works on isodimorphic aliphatic copolyesters, and extract general trends in the framework of the literature. Isodimorphic behavior is a complex phenomenon driven by comonomer partition within the crystalline unit cells formed. These copolyesters crystallize in the entire composition range displaying a pseudo-eutectic behavior when their melting points are plotted as a function of composition. Two crystalline phases, which resembled the crystalline structures of the parent homopolymers, are formed, depending on the considered composition range. The unit cell dimensions of the parent homopolymers change, as a consequence of the inclusion of co-units. At the pseudo eutectic point or pseudo-eutectic region, two crystalline phases can co-exist and their formation strongly depends on thermal history. In this case, double crystalline random copolyesters with two melting points and mixed double-crystalline spherulites can be obtained. The exact composition of the pseudo-eutectic point, the level of comonomer inclusion and the crystallinity degrees cannot be easily predicted by the copolyester chemical structure and composition. These are important issues for further future studies, as well as the quantitative determination of comonomer inclusion in the generated crystalline phases. The extraordinary variation of thermal properties, morphology and crystallinity that isodimorphic random copolyesters display as a function of composition, allows to conveniently tailor their biodegradation, permeability to gases and mechanical properties.

Keywords: Random aliphatic copolyesters, isodimorphism, double-crystalline random copolymers, rate-dependent crystallization, comonomer exclusion/inclusion.

1. Introduction

Copolymers are versatile materials that have been attracting academic and industrial interest for decades. There are several types of copolymers including block, graft and random amongst others [1]. This paper deals with the crystallization of the simplest possible copolymers, i.e., random copolymers.

Random copolymerization is a simple synthetic strategy of combining the properties of two distinct homopolymers. It provides random covalent links between different comonomers, therefore ensuring total melt miscibility, at variance with the typical immiscible polymer blends. Their thermal and mechanical properties can be tailored by changing the composition of the copolymer.

Random copolyesters are very important polymeric materials as many of them can be biobased and biodegradable. Their hydrolytic degradation rates strongly depend on their chemical structure, degree of crystallinity and morphology. Their morphology and crystallinity can also influence their mechanical properties, permeability to gases and thermal stability.

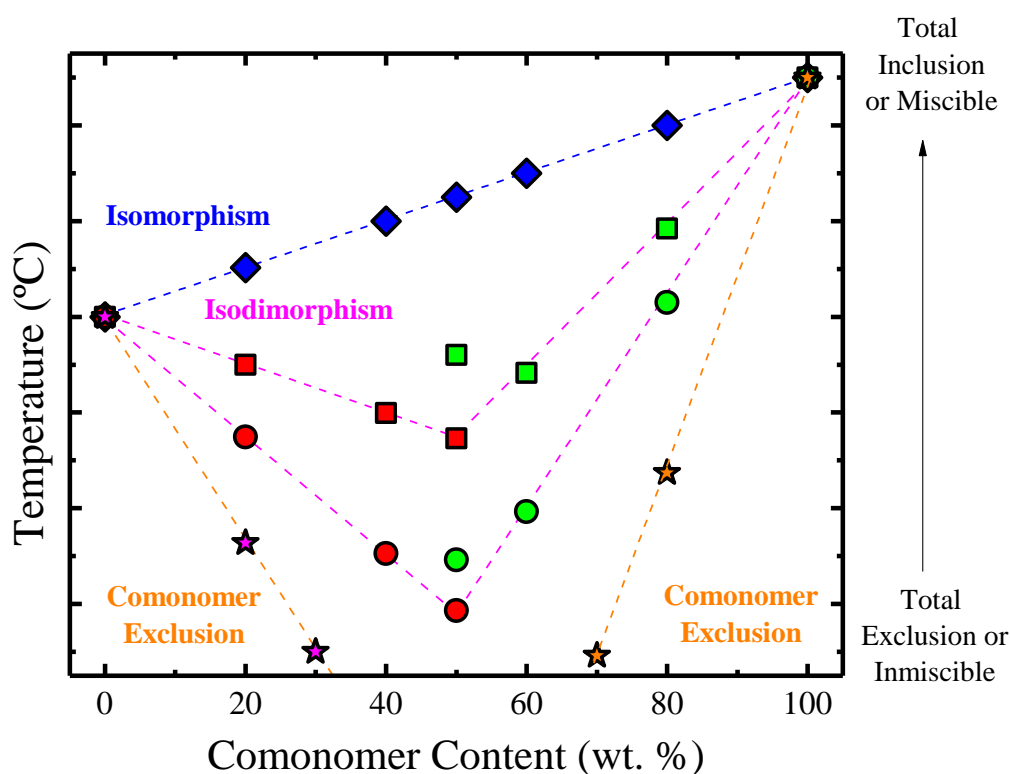
The crystallization of random copolymers is a complex function of the chemical structure of the repeating units involved, molar ratio of comonomers and molecular weight.

Scheme 1 represents the three general ways in which random copolymers can crystallize, as deduced from the trends of how the thermal transitions vary as a function of copolymer composition. The thermal transitions represented as examples in Scheme 1 are those typically determined by non-isothermal Differential Scanning Calorimetry (DSC) experiments.

Provided that the two crystallizable repeating units meet strict molecular requirements, the copolymers can crystallize in the same crystal lattice, in the entire composition range. In other words, the two comonomeric units along the chain can co-crystallize regardless of the composition. Therefore, the two comonomers can be considered miscible in the crystalline state. This case is referred to in Scheme 1 as total inclusion of comonomers in a single crystal lattice or isomorphic behavior. Thermal and structural properties, such as melting temperatures and lattice parameters, typically show linear dependence on composition (see Scheme 1).

The concept of isomorphism in the polymer field was first considered by Natta et al. [2]. According to Allegra and Bassi [3], the requirements to observe

macromolecular isomorphism in random copolymers are: (i) approximately same shape, volume and compatible conformations of the different monomer units, (ii) analogous chain conformation, lattice symmetry and dimensions of the crystalline phase of the “parent” homopolymers, (iv) total miscibility in the melt of the comonomers and (v) similar rate of crystallization of the two parent homopolymers. As a result, a total inclusion of both comonomers in the crystalline lattice occurs, and the composition of the crystal perfectly reflects the one of the polymer chain. Because of the specific conditions to be met, as far as the author are aware, only four random copolyesters have been reported to exhibit isomorphic crystallization: poly (hexamethylene gluarate-*ran*-hexamethylene azelate) (P(HG-*ran*-HA)) [4], poly (ϵ -caprolactone-*ran*-2-oxepane-1,5-dione) (P(CL-*ran*-OPD)) [5], poly (ϵ -caprolactone-*ran*- ω -pentadecalactone) (P(CL-*ran*-PDL)) [6], and poly (butylene succinate-*ran*-butylene fumarate) (P(BS-*ran*-BF)) [7].



Scheme 1. Melting (or crystallization) temperature as a function of comonomer content for different possible copolymers. From top to bottom four cases are represented: isomorphic behavior, isodimorphic behavior for copolymers with small amount of comonomer exclusion, isodimorphic behavior with a large amount of comonomer exclusion, copolymers with total exclusion of second comonomer. See text.

When the two homopolymers (A and B) do not share a common crystalline structure, but they still have similar repeating units, an isodimorphic behavior of the random copolymers (A-*ran*-B) constituted by the respective repeating units can result. A partial inclusion of comonomer A in the unit cell of homopolymer B crystals is typically observed for copolymers with composition rich in B units, and *vice versa*. However, the inclusion is only partial, i.e., the concentration of comonomer A in the B crystals is lower than its concentration in the polymer chain. Since both comonomers can be hosted in the crystals of the majority component (comonomer A in the B crystals, and comonomer B in the A crystals), a “pseudo-eutectic” trend of the thermal properties (melting and crystallization temperatures, as well as their enthalpies) is obtained (Scheme 1).

As represented in Scheme 1, isodimorphic copolymers are characterized by a homopolymer-A-rich crystalline phase in one side of the pseudo-eutectic region and a homopolymer-B-rich crystalline phase on the other side of the eutectic region. While isodimorphic copolymers can still crystallize in the entire composition range, the melting temperature of the two crystalline phases is depressed by the presence of the included second comonomer, until a minimum value is reached for an intermediate composition. As will be reported below, recently, three phases have been found at the eutectic region, i.e., mixed amorphous phase, homopolymer-A-rich crystalline phase and homopolymer-B-rich crystalline phase. This is the reason behind the double data points represented at the eutectic composition in Scheme 1. More precisely, the term pseudo-eutectic point or pseudo-eutectic region should be preferred, since the three phases are not in thermodynamic equilibrium. Hence, at the pseudo-eutectic region the copolymers can display double crystalline superstructural morphologies (see below).

As far as the authors are aware, there are no general rules that can unambiguously predict if a copolymer will display isodimorphism or not. In fact, even in those cases where the comonomers have similar chemical structures and are miscible in the amorphous phase, the possibility of forming a mixed crystalline unit cell, or in other words the efficiency of comonomer inclusion, is not easily determined. In spite of this, some features affecting isodimorphic behavior have been highlighted in the literature. For instance, a homopolymer with a large unit cell is expected to include more easily a comonomer whose respective homopolymer presents a smaller unit cell [8]. Also, a comonomer with an even number of methylene groups in the repeating unit

will most likely include similar even CH₂ comonomers in its unit cell, and exclude those with odd number of carbon atoms in their chemical structure [4, 9]. These empirical rules, related to the miscibility of the comonomers in the crystalline state are not always strictly obeyed.

It is worth noting that in Scheme 1 two curves for the isodimorphic case are shown from top to bottom, representing different degrees of inclusion of the comonomers in the homopolymer crystal lattice. With a higher degree of inclusion, the crystallization/melting behavior deviates less from the isomorphic case. In contrast, when the comonomer units are largely excluded from the crystals, even though the copolymer may still be able to crystallize in all compositions, the thermal response will be closer to that of a copolymer characterized by a complete rejection of the co-units to the amorphous phase, discussed in the following.

When comonomer B is completely rejected from the crystalline structure of the major component (comonomer A), the transition temperatures and enthalpies are strongly depressed as the content of comonomer B increases in the random copolymer, and there exists a range of copolymer compositions where the copolymer remains completely amorphous. Random copolymers with complete exclusion, where symmetrical compositions do not crystallize are very common and constitute the most commonly reported case in the literature.

In this feature article, we will focus on the crystallization of isodimorphic random aliphatic copolyesters. These polymers have recently drawn the attention of researchers because of their bio-degradability and, in some cases, bio-renewable origin. Most importantly for the present topic, many random copolymers show isodimorphism to different extents. Beside the scientific interest, this peculiarity offers a way of tailoring the copolymer properties by varying composition.

Several examples of isodimorphic copolyesters, mainly poly(hydroxyalkanoates), were reported in the review of Pan et al., in 2009 [10]. In Table 1 we summarize more recent works on random aliphatic copolyesters, indicating for each system the type of comonomers and the melting points of each homopolymer. We note that in most of the cited studies, the co-crystallization of the co-units in the whole composition range was observed, but the isodimorphic behavior of the systems is seldom discussed in detail.

Table 1. List of isodimorphic random aliphatic copolymers reported in the literature after 2009

System	Acid Group		Alcohol group	T_m (°C)	Reference
PHS	Succinid acid	+	1,6- Hexanediol	52.6	[11]
P(HS- <i>ran</i> -HA)	Adipic Acid	+	1,6- Hexanediol	54	
P(HS- <i>ran</i> -HSu)	Suberic acid	+	1,6- Hexanediol	63.3	
P(HS- <i>ran</i> -HSe)	Sebacic acid	+	1,6- Hexanediol	64.3	
P(HS- <i>ran</i> -HD)	Dodecanedioic acid	+	1,6- Hexanediol	70	
P(HS- <i>ran</i> -HA)	Succinic acid	+	1,6- Hexanediol	57	[12]
	Adipic Acid	+	1,6- Hexanediol	62	
P(HSe- <i>ran</i> -HA)	Sebacic acid	+	1,6- Hexanediol	68.9	[13, 14]
	Adipic Acid	+	1,6- Hexanediol	60	
P(PS- <i>ran</i> -ES)	Succinid acid	+	1,3-propanediol	45.4	[9]
	Succinid acid	+	ethylene glycol	105.5	
P(BS- <i>ran</i> -HS)	Succinid acid	+	1,4-butanediol	113.8	[15]
	Succinid acid	+	1,6- Hexanediol	51	
P(HG- <i>ran</i> -HP)	Glutaric acid	+	1,6- Hexanediol	30.3	[4]
	Pimelic acid	+	1,6- Hexanediol	49.9	
P(HP- <i>ran</i> -HA)	Pimelic acid	+	1,6- Hexanediol	49.9	
	Azelaic acid	+	1,6- Hexanediol	53	
P(HG- <i>ran</i> -HA) Isomorphic	Glutaric acid	+	1,6- Hexanediol	30.3	
	Azelaic acid	+	1,6- Hexanediol	53	
P(BS- <i>ran</i> -BAz)	Succinid acid	+	1,4-butanediol	115	[16-18]
	Azelaic acid	+	1,4-butanediol	41	
P(BS- <i>ran</i> -BA)	Succinid acid	+	1,4-butanediol	114	[19]
	Adipic Acid	+	1,4-butanediol	51-59	
PHSu	Suberic acid	+	1,6- Hexanediol	63.8	[20]
P(HSu- <i>ran</i> -HSe)	Sebacic acid	+	1,6- Hexanediol	65	
P(HSu- <i>ran</i> -HA)	Adipic Acid	+	1,6- Hexanediol	59.4	
P(HA- <i>ran</i> -BA)	Adipic Acid	+	1,6- Hexanediol	59.8	[21]

	Adipic Acid	+	1,4-butanediol	51.2		[22]
P(PS- <i>ran</i> -BS)	Succinid acid	+	1,3-propanediol	50		
	Succinid acid	+	1,4-butanediol	116		
P(PA- <i>ran</i> -BA)	Adipic Acid	+	1,3-propanediol	48		
	Adipic Acid	+	1,4-butanediol	58		
	Monomer A		Monomer B	<i>T_m</i> (°C)		Reference
P(LLA- <i>ran</i> -L-2HB)	L-lactic acid	+	L-2hydroxybutanoic acid	165	101	[23]
PB- <i>ran</i> -Manx	diol 2,4:3,5-di-O-methylene-D-mannitol(Manx)	+	Poly(dimethyle succinate)	111.5	125	[24]
P(BS- <i>ran</i> -CL)	Poly(butylene succinate)	+	Poly(ε-caprolactone)	110	55	[25]
P(BL- <i>ran</i> -CL)	Poly(γ-butyrolactone)	+	Poly(ε-caprolactone)	63.5	57.6	[26]
P(BL- <i>ran</i> -VL)	Poly(γ-butyrolactone)	+	Poly(σ-valerolactone)		58.6	
P(CL- <i>ran</i> -DL)	Poly(ε-caprolactone)	+	Poly(ω-pentadecalactone)	52	92	[27]

Therefore, this article will first describe the general crystallization features of isodimorphic aliphatic copolyesters, using selected examples, mainly from our own work. In particular, we will discuss how different experimental techniques can reveal the presence of isodimorphism, as well as kinetics and thermodynamics aspects of the crystallization process.

Finally, we will highlight the peculiar crystallization behavior of random copolyesters with compositions corresponding (or near) to the pseudo-eutectic point. In these systems, both types of crystals, either rich in one or the other component, can develop and coexist, often depending on the specific imposed thermal history. The crystallization of pseudo-eutectic compositions is probably the most intriguing and overlooked aspect of the crystallization of these materials.

2. Crystallization of isodimorphic random aliphatic copolyesters

The isodimorphic character of random copolyesters is reflected in various aspects of their crystallization process. Differential scanning calorimetry (DSC) characterization can efficiently highlight the pseudo-eutectic feature of the thermal transitions. Moreover, the partial inclusion of the minority co-unit in the crystalline unit cell of the major component impacts the structure and morphology at different levels, and can thus be probed with suitable techniques, such as Wide and Small Angle X-Ray Scattering (WAXS/SAXS), infrared spectroscopy (FT-IR) and Polarized Light Optical Microscopy (PLOM). However, the direct quantification of the extent of comonomer inclusion in a given crystalline lattice is not frequently reported, as it is not an easy task, while indirect estimates can be provided by the comparison of the experimentally determined equilibrium melting points with existing theories of random copolymers melting. On the other hand, the effect of isodimorphism on crystallization is seldom explored in detail and typically only in a limited range of compositions and/or undercoolings. Results on the above mentioned aspects of isodimorphic crystallization of random aliphatic copolyesters are briefly reviewed in the following.

2.1 Pseudo-eutectic behavior

The isodimorphic behavior in random copolymers is clearly manifested in non-isothermal heating and cooling experiments, since the transition temperatures show a

strong and characteristic dependence on copolymer composition. Regarding the glass transition temperature (T_g), a single value for each composition is found, in agreement with the expected random distribution of co-units along the polymer chain. The T_g lays between the values of the two relative homopolymers and depend on composition. Deviations from the linear dependence [19, 23, 25, 28] are typically described according to Fox [29] and Gordon-Taylor [30] equations.

Despite being random, these copolymers can crystallize in the entire composition range. Figure 1 shows an example, for the system poly (butylene succinate-*ran*-butylene adipate) (PBSA), of the variations of the crystallization and subsequent melting curves when changing the content of the diacid co-unit from 0 to 100%.

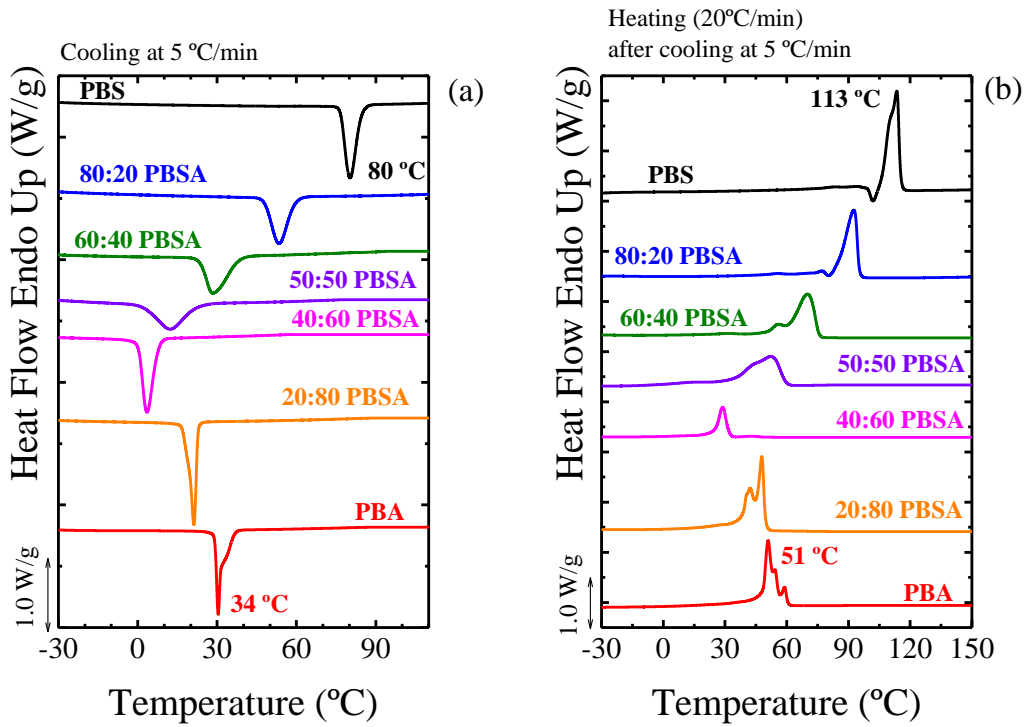


Figure 1. Non-isothermal DSC (a) cooling and (b) subsequent heating scans for PBSA random copolymer; the crystallization and melting temperatures of the parent homopolyesters are indicated. Based on ref. [19].

A change in the trend of the crystallization/melting process is observed at a certain composition, which divides the copolymer composition interval into two ranges, one with crystalline features related to “comonomer A-rich”, the other with “comonomer B-rich” phases. At intermediate compositions (close to 50:50 in the

example of Figure 1) crystallization is certainly hindered, as deduced from a minimum in the crystallization temperature and enthalpy, but not prevented.

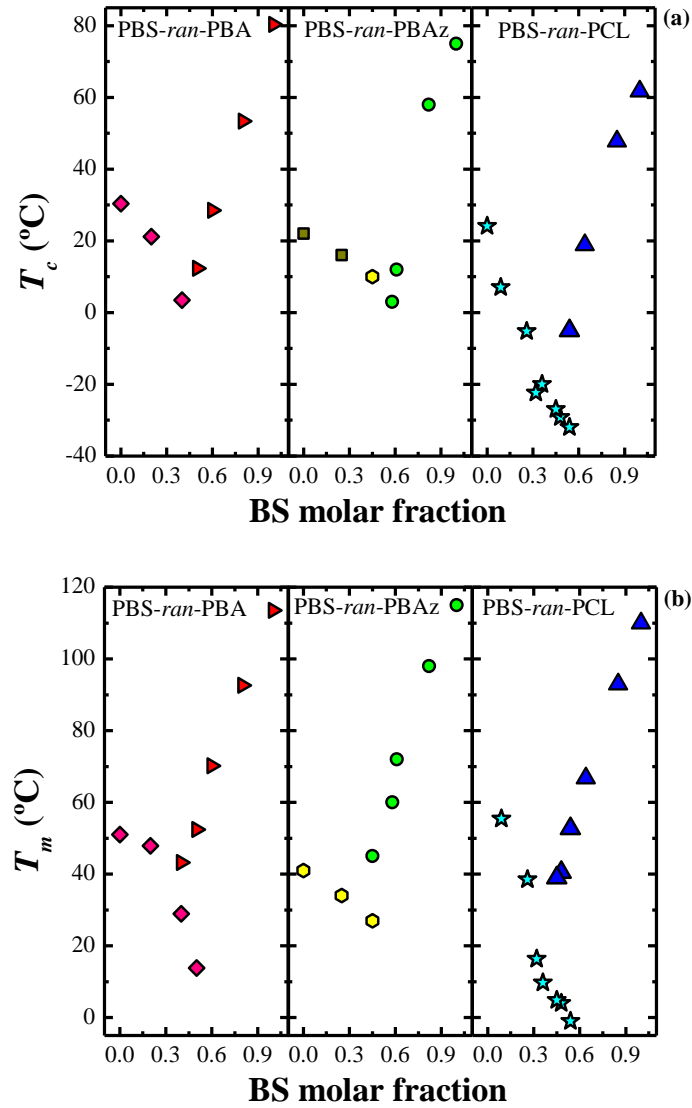


Figure 2. Peak (a) crystallization and (b) melting temperatures for poly (butylene succinate-*ran*-butylene azelate) P(BS-*ran*-BAz), poly (butylene succinate-*ran*-butylene adipate) P(BS-*ran*-BA) and poly (butylene succinate-*ran*- ϵ -caprolactone) P(BS-*ran*-CL) as a function of copolyester composition. Based on ref. [16, 19, 25].

Therefore, the thermal properties extracted from the typical non-isothermal DSC scans, i.e., crystallization and melting temperatures, as well as the respective enthalpies, follow a pseudo-eutectic behavior. Some representative examples are shown in Figure 2, which reports the crystallization and melting temperatures of three random copolyesters based on poly (butylene succinate) with different comonomers, as a function of butylene succinate (BS) molar fraction. Figure 2 also shows the tailored

control of thermal properties of isodimorphic copolymers simply selecting specific compositions.

The fact that truly random copolyesters can crystallize in all the composition range (see Figure 2a) is in itself a strong indication that both crystalline phases can incorporate at least a small amount of the minor component in the crystalline lattice of the corresponding phase. Considering for instance the PBS-rich side (right hand side of the pseudo-eutectic region) of the plots in Figure 2b, the melting of the crystalline phase is depressed to lower temperatures as the comonomer content is increased. Therefore, despite the interruption of PBS sequences by the BA, BAz or CL repeating units, which leads to lower melting point crystals, a significant degree of crystallinity of the PBS-rich phase can still be achieved in these copolymers, even when the content of comonomer is as high as 40-60 %. This indicates that co-crystallization of the two comonomers in the same crystal lattice is possible to some extent.

In the case of total exclusion of the comonomers in the amorphous regions, any given crystalline phase is formed by A units only or by B units only. In those cases, 20 % of co-units randomly distributed along the chains is usually enough to completely inhibit the crystallization. A clear example of this behavior is given by statistical ethylene/1-octene or propene/1-octene synthesized with metallocene catalysts [31, 32]. For random copolyesters, a similar behaviour has been claimed by Soccio et al. in poly (propylene isophthalate-*ran*-propylene succinate) [33] and poly (propylene isophthalate-*ran*-propylene adipate) [34].

A more direct evidence of co-crystallization of the co-units can be obtained by FT infrared spectroscopy (FT-IR). Inoue et al. studied the crystallization behavior of several aliphatic random copolyesters with this technique [12, 13, 21]. Some IR absorption bands can be assigned specifically to a given co-unit in the crystalline state. In the isodimorphic copolymers (see, for example, poly (hexamethylene adipate-*ran*-butylene adipate) (P(HA-*ran*-BA)) [21]), the intensities of these characteristic bands of both comonomers simultaneously increase with time during crystallization and decrease with temperature upon melting. This result proves the co-existence of the two units in the crystalline lattice of the different homopolymers. Furthermore, by applying Lambert-Beer's law, the content of co-unit included in the crystals can also be estimated [13, 35].

The pseudo-eutectic behavior of isodimorphic polymers is manifested by a decrease in the transition temperatures with composition departing from those of the two homopolyesters, until a minimum value is reached. The comonomer concentration at which this minimum is found is generally located around the equimolar composition [20, 21], however, some systems show pseudo-eutectic points in significantly different concentration interval (e.g., 60:40, 80:20) [4, 11, 13, 16, 19, 23, 36, 37]. For instance, in poly (hexamethylene dicarboxylate) copolymers the eutectic composition shifts from a co-unit concentration of 50 to 20 %, with increasing the length of aliphatic diacid units from 4 to 8 CH₂ units [11]. In most studies [4, 11, 16, 19, 21, 36], the minimum of crystallization/melting temperature is located at compositions shifted towards higher contents of the commoner whose respective homopolyester has the lower melting point. In order to explain this feature, several thermodynamic models that take into account the energy behind the higher or lower tendency to co-crystallize of different comonomer pairs have been applied. The main models adopted, and their application to isodimorphic random copolyesters will be summarized in a subsequent section (see section 2.5).

An intriguing aspect of copolymer crystallization at compositions close to the pseudo-eutectic one, is the presence of a double melting peak, related to the formation of two different crystalline phases, rich in one and in the other type of comonomers, respectively [15, 16, 19, 24, 25]. This observation will be discussed in more details in section 3.

Interestingly, the overall crystallinity of an isodimorphic system also exhibits a pseudo-eutectic trend with composition, as shown in Figure 3. Indeed, despite that these random copolymers can crystallize in the entire composition range, testifying the partial inclusion of both co-units in the different homopolyester crystal lattice, the degree of crystallinity attained by the copolymers typically shows a minimum around the pseudo-eutectic composition. This indicates that the co-units still represent “defects” for the crystal and their presence hinders crystallization, as such, they are preferentially excluded from the lattice (or only partially included). The extent of crystallinity depression is thus related to the easiness of comonomer co-crystallization. Note that the crystalline phase with the highest amount of a given comonomer is the one that develops a higher crystallinity degree within the pseudo-eutectic region.

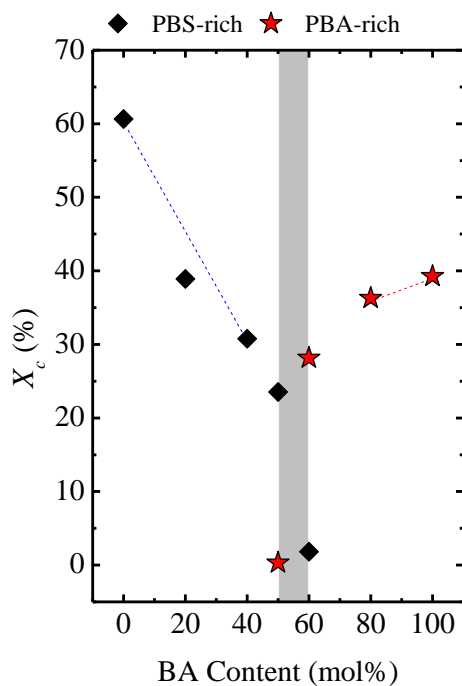


Figure 3. Percentage of crystallinity ($X_c\%$) as a function of BA content in P(BS-*ran*-BA) random copolymers. The shadowed area indicates the pseudo-eutectic compositional region. The X_c values were calculated from the data reported in reference [19].

2.1. Co-units co-crystallization: unit cell and lamellae

In many cases, the partial inclusion of a comonomer into a crystalline structure different from that of its homopolymer can be revealed by X-ray diffraction. Two typical series of WAXS patterns of PBSAz and PBSA isodimorphic random copolyesters [16, 19] of different compositions are shown in Figure 4.

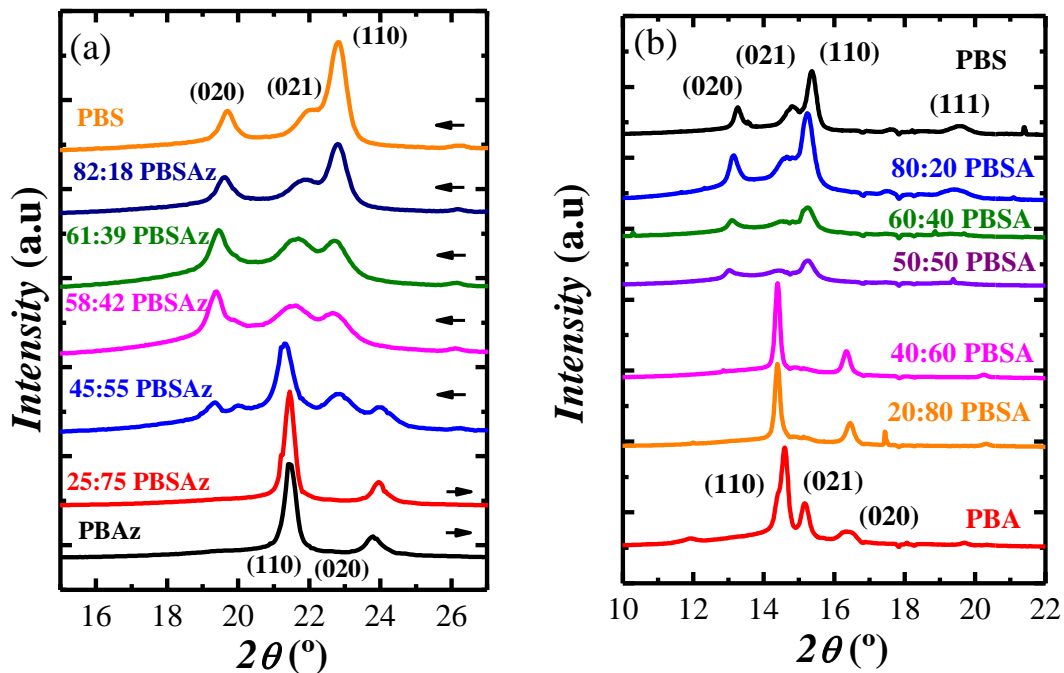


Figure 4. WAXS patterns for (a) PBzAz and (b) PBzA taken at (a) -30 and (b) -40 °C after previously cooling the samples from the molten state at (a) 10 and (b) 5 °C/min, respectively. The differences in 2θ angles are due to the different wavelengths employed: (a) $\lambda=0.154$ nm and (b) $\lambda=0.103$ nm (synchrotron experiments). Data replotted from refs. [16, 19], for (a) and (b) respectively.

Both cases illustrate the changeover from the crystalline phase of PBz to the one of PBzA (or PBz) (see Figure 4a and b, respectively), with changing the copolymer composition, as expected for isodimorphic systems. The WAXS pattern acquired after crystallization corroborate the information derived by DSC, and allow to attribute the pseudo-eutectic behavior in the crystallization/melting temperatures to the formation of crystalline phases rich in the different comonomers. At intermediate compositions, the presence of reflections typical of both crystalline phases can be clearly deduced in Figure 4a, while the diffractions peaks partially overlap in the case of PBzA (Figure 4b). However, the concurrent formation of the two phases at the pseudo-eutectic point can be promoted with specially designed thermal treatments, as later discussed in section 3.

Besides the general information on the presence of the crystalline phases, the WAXS analysis can reveal the (partial) inclusion of a co-unit in a given structure. Indeed, when the crystal hosts a repeating unit different from that which constitutes the homopolymer, several different situations can arise, depending on the specific crystallographic features of the considered systems. In particular, upon inclusion of a

comonomer, a crystalline unit cell can: (a) increase in size to accommodate the co-unit (generally bulkier although it can happen with smaller co-unit as well [38]); (b) shrink in certain directions, as a result of a lower volume occupied by the defect; (c) remain unchanged in size.

These changes can be identified by tracking the crystallographic spacings (d -spacing) of the various planes as a function of copolymer composition. Examples of the three different situations are reported in Figure 5 for different systems [4].

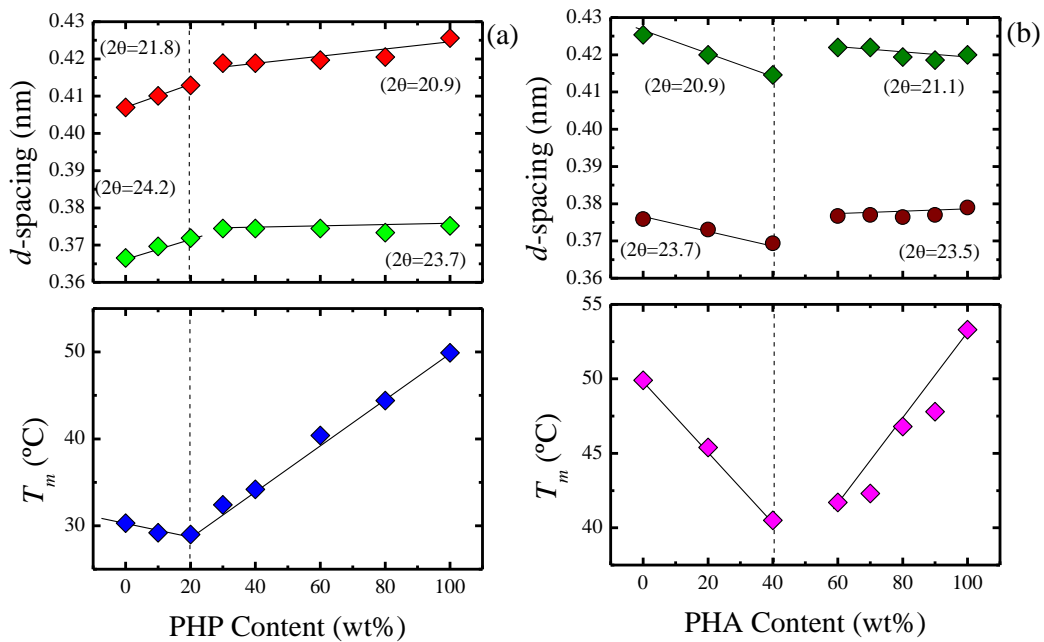


Figure 5. d -spacings values of characteristic diffraction planes and T_m as a function of comonomer content for: (a) poly (hexamethylene glutarate-*ran*-hexamethylene pimelate) P(HG-*ran*-HP) and (b) poly (hexamethylene pimelate-*ran*-hexamethylene azelate) P(HP-*ran*-HAz) . Data replotted from ref. [4].

The copolymers of Figure 5 are poly (hexamethylene dicarboxylate) copolyesters where the chain length of the aliphatic diacid is varied. It can be seen that little or no variations in the spacings is observed when comonomers with lower number of methylene units are included in the crystals of the homopolymer with longer aliphatic sequences, i.e., as in the case of glutaric acid substituting pimelic acid (3 and 5 methylene units, respectively), Figure 5a, or pimelic acid (5 methylene) copolymerized with azelaic acid (7 CH₂), Figure 5b. On the other hand, accommodating a diacid with higher number of CH₂ in the unit cell of a polyester with a shorter diacid can lead to both an increase or decrease in the distance between a given family of planes, see

P(HG-*ran*-HP) and P(HP-*ran*-HAz), Figure 5a and b, respectively. The difference may depend on the details of the specific structure, i.e., on the volume occupied by the co-unit in the acquired conformation along the considered crystallographic direction. Note that the changes in the spacings can be correlated with variations of T_m values as a function of composition (see bottom plots in Figure 5).

It should be noted that the increase in the spacings of the lattice planes has not always been attributed to the inclusion of comonomer. Tan et al. suggested that such small changes may be attributed to lattice distortions due to the accumulation of excluded comonomer at the surface of the crystals, although no specific evidences for such accumulation were provided [15]. However, this interpretation would not be in agreement with the relevant changes in the thermal properties (See Figure 2 and bottom part of Figure 5) observed in these systems, in parallel with the changes in the lattice spacings [4, 11, 16, 19, 25]. In fact, several theories of comonomer inclusion in the crystal predict the observed trend of (equilibrium) melting temperatures with composition, as it will be described in a forthcoming section.

In order to qualitatively compare different random copolymer systems, in terms of lattice distortions due to partial comonomer inclusion, we have normalized the d -spacing values of selected planes, by calculating the ratio between their value in a given copolymer and the maximum overall spacing reached in the entire composition range. The results are summarized in Figure 6, where the homopolymer of “monomer A” is the one with the highest melting point, and the vertical dashed lines indicate the position of pseudo-eutectic point for each system.

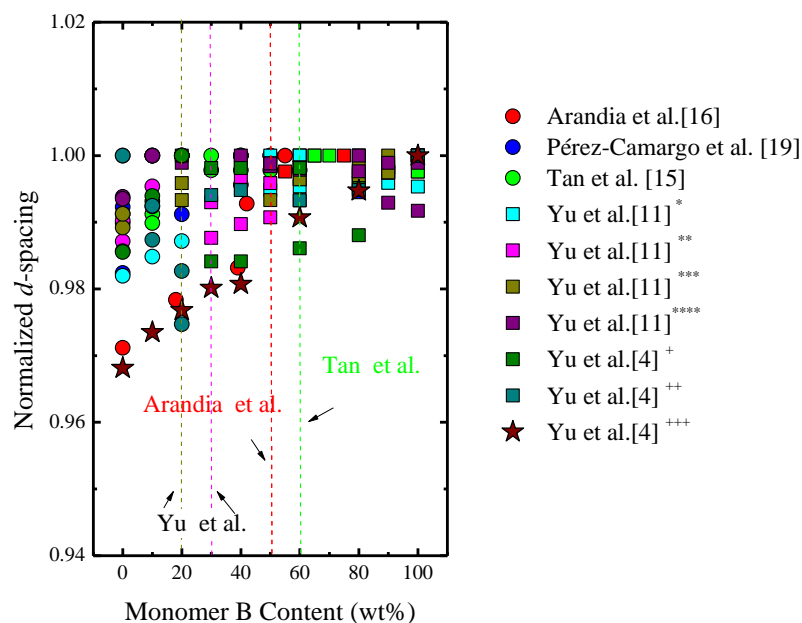


Figure 6. Normalized d -spacing as a function of copolymer composition for different isodimorphic random copolymers [4, 11, 15, 16, 19]. Note that one isomorphous random copolymer is included [4]. Circle symbols are used to indicate the spacings of the A-rich phase, whereas square symbols are used to indicate the spacings of the B-rich phase, to the right of the pseudo-eutectic points indicated with vertical dashed lines for the different copolymers reported. Note that the superscripts in the legend of the works of Yu et al. [4, 11] are used to indicate different isodimorphic random copolymers.

It is interesting to see that, although the changes in the d -spacings are typically less than 4%, these relatively small variations are associated with large depressions of crystallization capability and melting temperatures, as discussed in the previous section. Moreover, by comparing the left and the right-hand part of the dash vertical lines in the plot of Figure 6 together with the melting point data for the selected copolymers, we learn that the crystals with higher melting temperatures undergo larger distortions of their structural dimensions upon comonomer inclusion, with respect to the lower melting temperature crystals.

It appears that several factors may play a role in determining the miscibility of the comonomers in the crystalline state. The type of crystalline unit cell of a polyester is generally determined by the number of methylene groups in the glycol and diacid sub-units: polymers with an odd number of CH_2 units between the ester bond usually crystallize in an orthorhombic unit cell, whereas in the case of an even number of methylene groups, a monoclinic unit cell is obtained [9]. Polyesters with odd-chain

segments crystallize with more difficulty with respect to even-methylene segments one, as judged by their lower crystallinity [4]. In general, co-crystallization of two co-units is expected to be easier when the relative homopolymers share the same type of unit cell. However, exceptions to this rule are also reported [32]. The length of the co-units is not a universal criterium to predict co-crystallization ability. Indeed, sometimes co-units with shorter methylene sequences are easily included in the unit cell of polyesters with more CH₂ units, and *vice versa*. Clearly, the extent of co-crystallization in aliphatic copolyesters depends on subtle crystallographic details, which, at present, need to be evaluated for each particular investigated system.

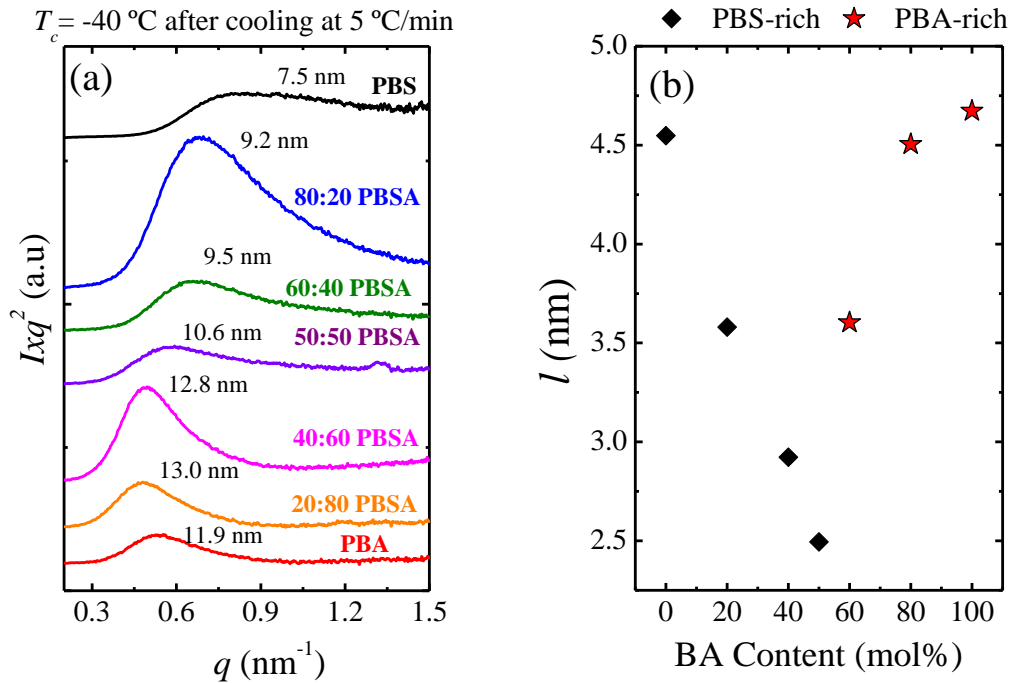


Figure 7. (a) Lorentz-corrected SAXS patterns and (b) lamellar thickness as a function of PBA content for PBSA random copolyesters. Based on ref. [19].

Moving from the crystal unit cell sizes to the mesoscale, some representative SAXS patterns of isodimorphic copolymers with different compositions are shown in Figure 7a [19]. The samples exhibit a clear intense maximum that is interpreted as the scattering produced by stacks of lamellar crystals. Depending on the composition, the lamellae correspond either to one or the other comonomer-rich crystals. (e.g., PBS or PBA rich phase crystals in Figure 7a). At intermediate compositions, the SAXS patterns

might show a single peak or double peak, related to the presence of crystal populations with different average lamellar thickness, as explained in the next section.

From the long period of the system (d^*), and knowing the crystallinity, the lamellar thickness can be estimated for each composition [16, 19]. Also the thickness of the lamellae display a pseudo-eutectic variation with composition, as shown in Figure 7b [19]. This indicates that the inclusion of the comonomer in a homopolyester lattice is not straightforward, since it causes the formation of thinner lamellae as the content of co-unit is raised.

2.2. Supramolecular morphology

Isodimorphic copolyesters usually exhibit typical spherulitic morphology, commonly identified by polarized light optical microscopy (PLOM). In one of our recent works [25], we studied the effect of copolymer composition and crystallization temperature (T_c) on the spherulitic texture of P(BS-*ran*-CL) copolyesters. Figure 8 shows PLOM micrographs for PBS and PCL-rich compositions, during isothermal crystallization at a constant nominal supercooling, i.e., at identical observed T_m - T_c values.

The incorporation of comonomer units has a strong impact on both nucleation and growth of the majority phase spherulites. Increasing amount of CL co-units content in the PBS-rich copolymers leads to the formation of a higher concentration of less perfect spherulites, indicating an increase in nucleation density. A similar effect is seen in the other end of compositions. According to studies by Gan et al. [39] on poly (butylene succinate-*ran*-ethylene succinate) (P(BS-*ran*-ES)), and Wang et al. [40] on poly (butylene succinate-*ran*-hexamethylene succinate) (P(BS-*ran*-HS)), copolymerization decreases crystal growth rate. For example, the inclusion of 14 mol% of hexamethylene succinate in PBS homopolymer decreases the spherulitic growth rate by an order of magnitude, at the same crystallization temperature. However, a more fair comparison would have to be made as a function of supercooling (at least an apparent supercooling, if the equilibrium melting temperatures are not available).

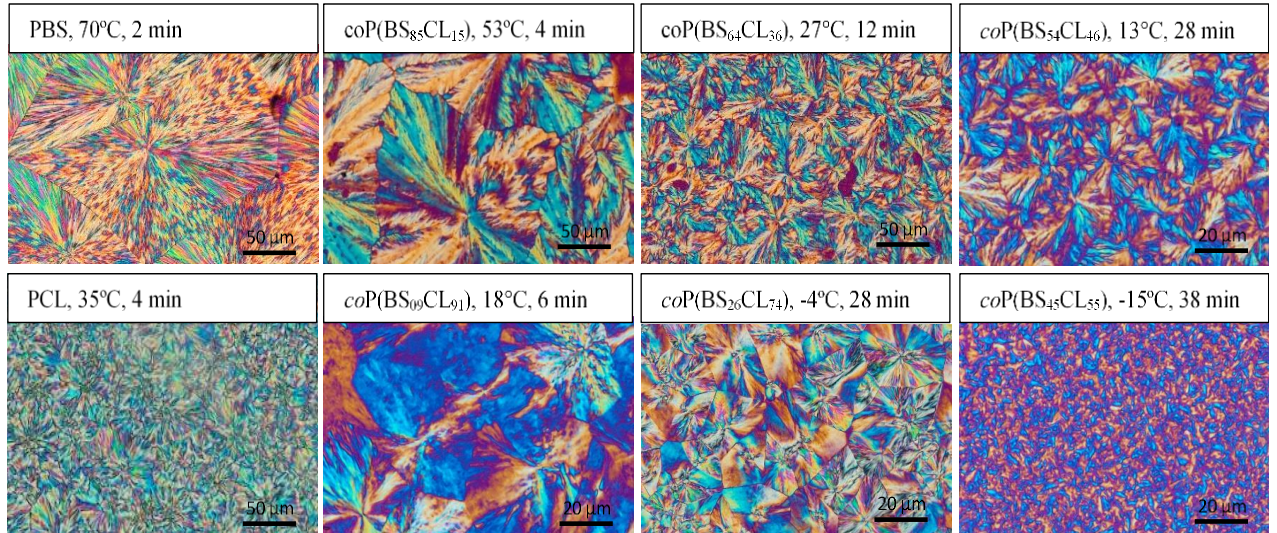


Figure 8. Polarized optical micrographs of P(BS-*ran*-CL) (coP(BS_xCL_y)) copolymers with different compositions, after isothermal crystallization at the indicated temperatures (which correspond to the same apparent supercooling for the crystallizing component, see text) and times. Based on ref. [25].

In another recent paper, the morphology of non-isothermally crystallized PBSA copolymers was analyzed [19]. The PBS and PBA-rich compositions exhibit the spherulitic morphology of the parent corresponding homopolymers, as shown in Figure 9. In both cases, the nucleation density increases with increasing co-units content, probably due to the related change in supercooling with composition, upon cooling at constant rate. Interestingly, the presence of ring-banded spherulites in PBS-rich (see Figure 9a) composition, and their absence in PBA-rich compositions (see Figure 9b), is an evidence that the superstructural morphology is dominated by the majority component in the copolymer. Similar results were obtained by Tan et al. for P(BS-*ran*-HS) copolymer [15].

The spherulitic morphology of double-crystalline copolymers of composition close to the pseudo-eutectic one will be considered in Section 3.

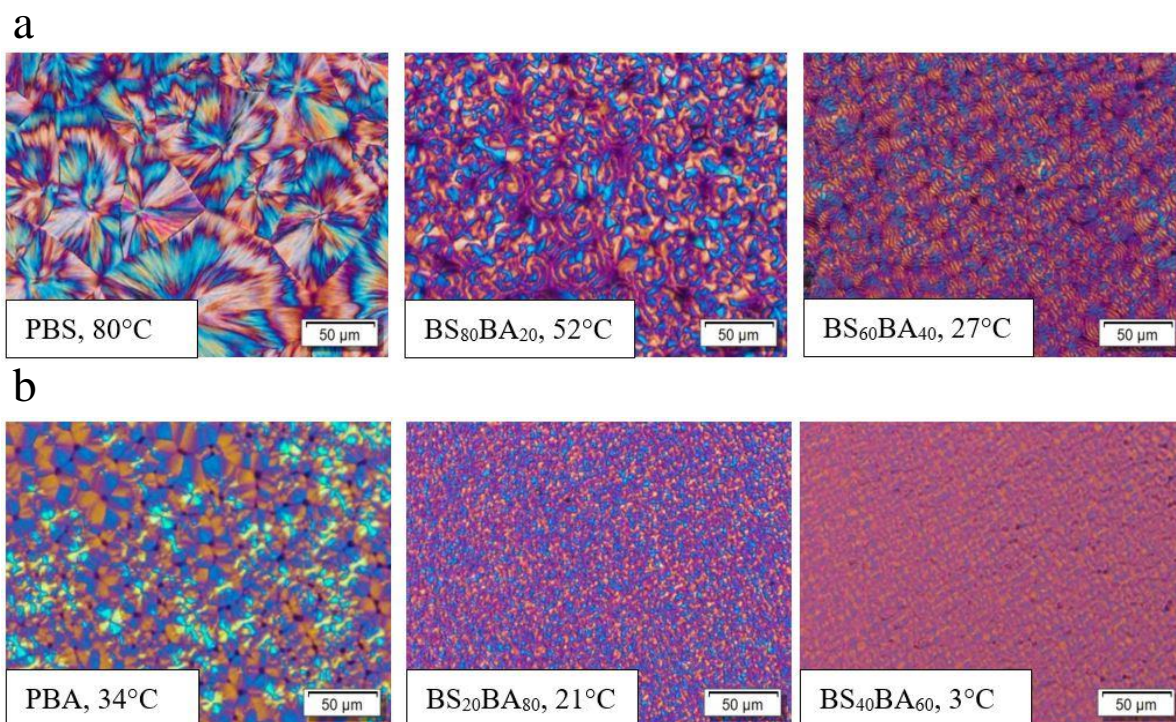


Figure 9. Polarized light optical micrographs for (a) PBS-rich phase copolymers and (b) PBA-rich phase copolymers taken at $-40\text{ }^{\circ}\text{C}$ after cooling from the melt at $5\text{ }^{\circ}\text{C}/\text{min}$. The temperature at which the first spherulites appear, i.e., onset crystallization temperature, is indicated under each micrograph, see text and ref. [19]. for details. Based on ref. [19].

2.3. Isothermal crystallization kinetics

The overall isothermal crystallization kinetics, which takes into account both nucleation and growth, can be conveniently measured by isothermal DSC experiments. For isodimorphic random copolyesters there are several literature reports dealing with DSC isothermal crystallization kinetics, however, they typically cover a limited range of compositions, i.e., close to the major components [18, 24, 41, 42]. This limitation is related to the widely different crystallization temperature range or kinetics observed when changing from one type of crystalline phase to the other. Data extracted from two recent studies on poly (hexamethylene adipate-*ran*-butylene adipate) (P(HA-*ran*-BA)) [43] and P(BS-*ran*-HS) [40] copolymers are reported in Figure 10, as an example.

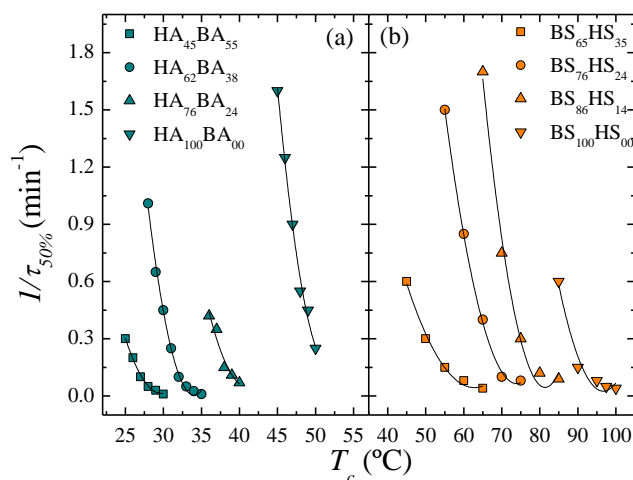


Figure 10. Isothermal crystallization of P(HA-*ran*-BA) (HA_xBA_y) (left) and P(BS-*ran*-HS) (BS_xHS_y) (right). Data replotted from ref. [40, 43].

The crystallization rate, expressed as the reciprocal of the half-crystallization time ($1/\tau_{50\%}$), decreases for all systems with increasing T_c , a common trend in the temperature range close to the melting point of the sample, where crystallization is dominated by nucleation control (in this case both primary and secondary nucleation, as the experiments are performed by DSC). The half-crystallization time curves shift to lower temperatures as the second comonomer is incorporated in the copolymers, indicating a large change in supercooling. A copolymer with 35-55 % co-units crystallizes at the same rate of the parent homopolymer if crystallization occurs at temperatures 25-40 °C lower. This behaviour is attributed to a diluting effect of the comonomer, which is preferentially not included in the crystals, and to the decrease of the equilibrium melting point with increasing comonomer content. In fact, the crystallization kinetics of different copolymers should be more rigorously compared at the same supercooling, rather than at the same crystallization temperatures. This can be done either by using nominal supercooling values (calculated with experimentally determined T_m values) or with equilibrium melting temperature values. However, the issue of equilibrium melting temperature of random copolymers is not trivial, and the extrapolation methods used for its determination are often questionable [44].

2.4. Effect of comonomer partitioning on the equilibrium melting point

As shown in previous sections, the extent of comonomer inclusion in the crystal lattice controls the crystallization behavior of isodimorphic copolymers, affecting for

instance the shape of the pseudo-eutectic curves, the degree of crystallinity and the rate of crystal formation. An indirect way to derive information on the partitioning of co-units between the crystalline and amorphous phase is to compare the experimental estimations of the equilibrium melting points with theoretical models which account for the effect of partial inclusion of the comonomer in the crystal on this thermodynamic value.

If the comonomer is totally rejected from the crystal into the amorphous phase, Flory [45, 46] and Baur [47] theory can be applied. The Flory theory was the first to treat the issue of crystallization of random copolymers. Neglecting the enthalpy of mixing for the two comonomer units, the equilibrium melting point of a copolymer containing a concentration X_B of non-crystallizable comonomer can be expressed as:

$$\frac{1}{T_m^0} - \frac{1}{T_m(X_B)} = \frac{R}{\Delta H_m^0} \ln(1 - X_B) \quad (1)$$

where T_m^0 and ΔH_m^0 are the homopolymer equilibrium melting temperature and heat of fusion, and R is the universal gas constant.

Baur modified the expression obtained by Flory, on the basis of the concept of “hindered equilibrium” introduced by Kilian [48]:

$$\frac{1}{T_m^0} - \frac{1}{T_m(X_B)} = \frac{R}{\Delta H_m^0} [\ln(1 - X_B) - \langle \xi \rangle^{-1}] \quad (2)$$

where, $\langle \xi \rangle = [2X_B(1 - X_B)]^{-1}$ is the average length of crystallizable homopolymer sequences in the melt.

Subsequent theoretical works accounted for the partial inclusion of the comonomer B in crystals of the A repeating unit [49, 50]. Sanchez and Eby proposed that if the B comonomer was partially included into the crystal of A, it could act as defect and modify the equilibrium melting point according to:

$$\frac{1}{T_m^0} - \frac{1}{T_m(X_B)} = \frac{R}{\Delta H_m^0} \ln(1 - X_B + X_B e^{-\varepsilon/RT}) \quad (3)$$

where $X_B e^{-\varepsilon/RT}$ is the equilibrium fraction of B repeating units that are able to co-crystallize, and ε is the excess free energy of a defect created by the incorporation of a single B unit into the crystal.

A more comprehensive treatment of the problem was proposed by Wendling and Suter to account for isodimorphic behavior and crystallization of copolymers with large content of co-unit [48, 51, 52], assuming that the free energy penalty paid to accommodate a defect in the crystal decreases with the increase of included comonomer. As such, the equilibrium melting point of the copolymer is then given by:

$$\frac{1}{T_m^0} - \frac{1}{T_m(X_B)} = \frac{R}{\Delta H_m^0} \ln \left(1 - X_B + X_B e^{-\frac{\varepsilon}{RT}} \right) - \langle \xi \rangle^{-1} \quad (4)$$

where:

$$\langle \xi \rangle^{-1} = 2(X_B - X_B e^{-\frac{\varepsilon}{RT}}) \cdot (1 - X_B + X_B e^{-\frac{\varepsilon}{RT}}) \quad (5)$$

The case of complete exclusion and of uniform inclusion can be obtained as particular solutions to this equation.

Flory, Baur, Sanchez-Eby and Wendling-Suter equations have been employed to describe the experimental variation of equilibrium melting temperatures of isodimorphic copolyesters in several studies [4, 9, 11, 36]. As an example, Figure 13 shows comparison performed for copolyesters of hexamethylene diol with diacids of different lengths with the different models [11]. The Wendling-Suter equation provides the best fit for the experimental results using as fitting parameter the defect free energy (ε), which is independent on composition, but is determined by the particular system and crystalline phase. Typical values of the defect free energy are comprised between 4 and 8 kJ/mol, the higher the value, the more difficult is the commoner inclusion in the lattice. From the analysis of the data in Figure 13, it can be deduced that the defect free energy values for incorporating diacid co-units with higher methylene number into the P(HS) crystals (diacid sub-unit with only two CH₂ groups) increases with the number of CH₂ moieties. On the other hand, succinic acid is in general more easily included in P(HX) crystals, where X is a diacid sub-unit characterized by a number of methylene groups higher than 2, and the inclusion is greater the longer the diacid sub-unit X [11].

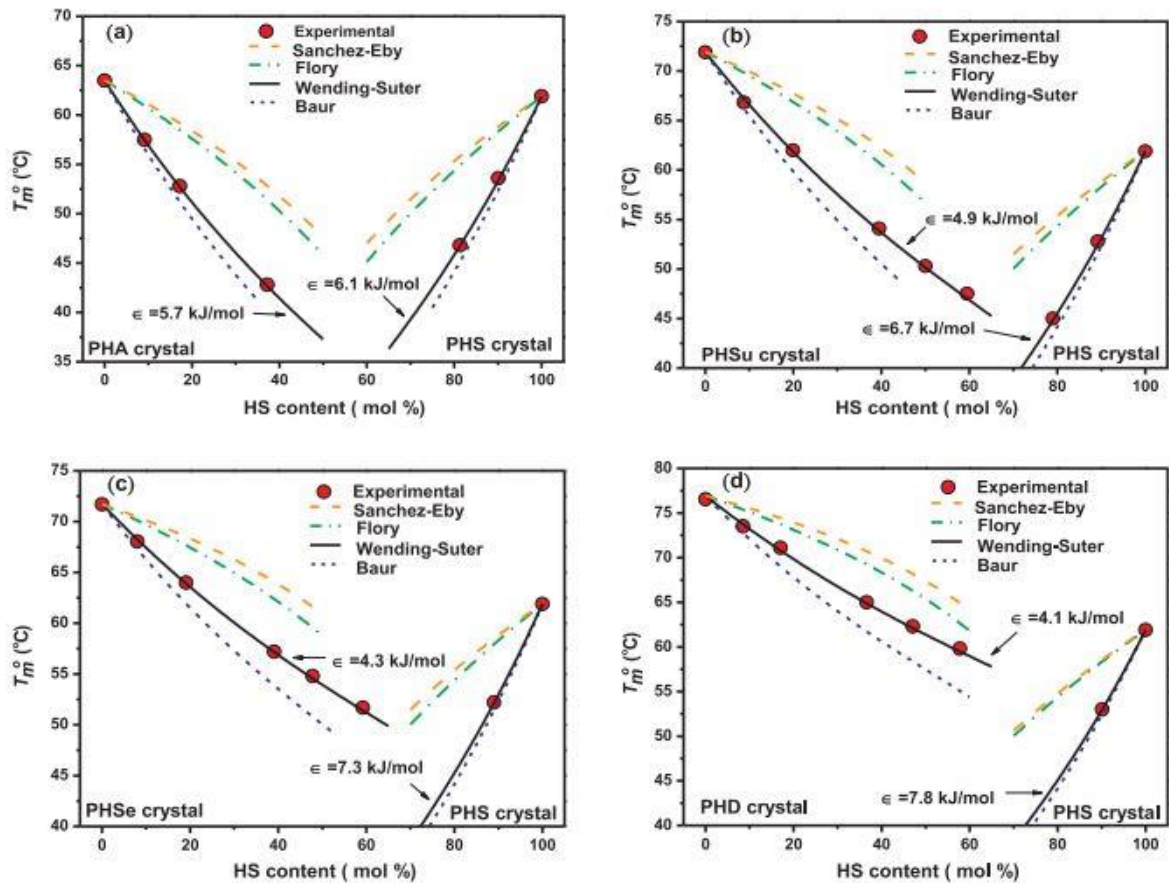


Figure 11. Comparison of the experimental equilibrium melting temperatures with the theoretical melting temperatures predicted by the Sanchez-Eby theory (orange curves), the Flory theory (green curves), Baur theory (blue curves) and the Wendling-Suter theory (black curves): (a) P(HS-ran-HA), (b) P(HS-ran-Hsu), (c) P(HS-ran-HSe) and (d) P(HS-ran-HD). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article). Reprinted with permission from [11].

It appears clear that useful information on comonomer partitioning can be derived by existing theories of copolymer melting. However, since the experimental determination of equilibrium melting temperature of random copolymers is not easy and the methods employed can yield to erroneous values, [44] the use of other empirical methods to estimate the degree of comonomer inclusion into a crystal are of importance. Successful attempts based on selective chemical etching of the amorphous phase [53] or on solid state ^{13}C -NMR [54] are known in the literature for the ethylene or propene-based copolymers. The possible extension of these methods to the family of aliphatic copolyesters is needed for the advancement of the understanding of isodimorphic crystallization, given the large variety of known co-crystallizing systems in these copolymers.

3. Crystallization process at the pseudo-eutectic composition: double crystalline random copolyesters.

Several random copolyesters exhibit coincident crystallization, manifested by a single crystallization exotherm upon cooling from the melt followed by double melting upon subsequent heating. The detailed study of this phenomenon has been performed only for a few copolymers in the literature, and it will be briefly reviewed below.

The double crystalline nature of isodimorphic random copolymers at intermediate compositions can be sometime observed only by cooling down to low temperatures or by varying the cooling rates, which reflect a strongly rate-dependent behavior.

3.1 Kinetic effects

The rate-dependent non-isothermal test is a strategy that has been used [18, 19, 55] in order to obtain more information on the isodimorphic random copolyesters at intermediate compositions.

In some cases non-isothermal DSC measurements performed at 10 or 20 °C/min only produce the crystallization of one of the phases. However, Pérez-Camargo et al. [19] were able to observed clearly the generation of two distinct crystalline phases for the PBSA copolymers, when high cooling rates (> 20 °C/min) were employed. A similar behavior was found by Arandia et al. [16] in PBSAz.

Figure 12 shows the comparison of the DSC heating scans for PBSA and PBSAz after the samples were previously cooled at two different rates (5 and 40 °C/min). The heating scans were performed at the same heating rate (20 °C/min).

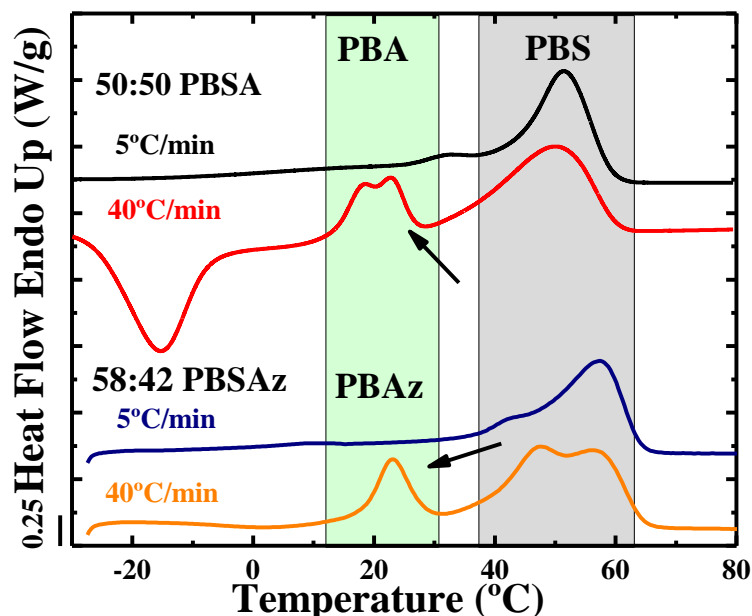


Figure 12. 50:50 PBSA and 58:42 PBSAz DSC heating scans (employing a heating rate of 20 °C/min) after having been cooled from the melt at the indicated rates.

Figure 12 shows that after cooling at 5 °C/min, the melting endotherm of the PBA-rich crystal phase (or PBz-rich one) are practically negligible. The reason for this peculiar behavior is that when the cooling rate is slow enough, the PBz-rich phase (the first one to crystallize upon cooling from the melt phase) will have ample time to develop spherulites with a relatively high degree of crystallinity [16, 19]. The second component of the copolymer would have to crystallize in the confined interlamellar spaces of the PBz-rich crystalline lamellae. However, the topologically constrained amorphous chain segments are not able to crystallize at the cooling rate of 5 °C/min.

On the other hand, when much faster cooling rates are employed (40 °C/min), the PBz-rich phase can still crystallize during cooling but up to a lower degree of crystallinity. For the PBSAz copolymer case, the PBz component is also able to crystallize during the fast cooling within the interlamellar regions of the PBz spherulitic templates, as deduced in Figure 12 by the lack of cold crystallization before melting [16]. In the case of the PBSA copolymer, the PBA-rich crystalline phase does not form during the cooling at 40 °C/min, but it develops during the subsequent heating scan, as revealed by the DSC trace, characterized by a prominent cold crystallization peak around -25 °C (more details can be found in ref. [19]).

As we mentioned before, in the majority of works a single melting point was found, however rate-dependent experiments provide an efficient strategy to detect the formation of two co-existing crystalline phases around the pseudo-eutectic point.

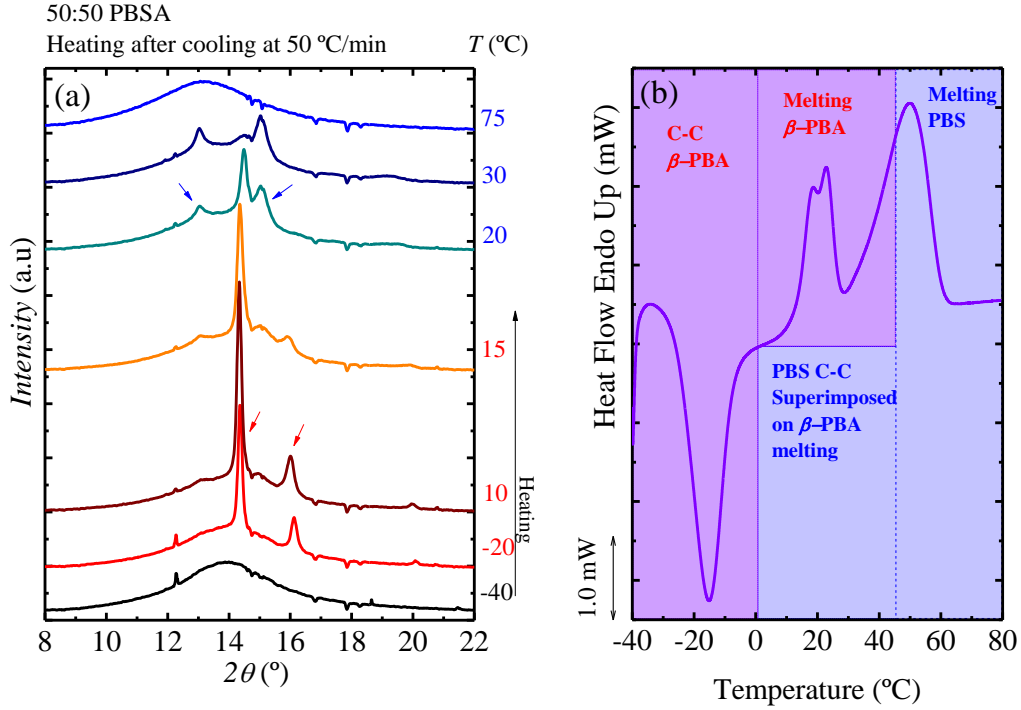


Figure 13. (a) WAXS diffractograms (at different temperatures) obtained during heating after cooling the 50:50 PBSA sample at 50 °C/min and (b) DSC heating scans, for a sample with identical thermal history. The cold-crystallization (C-C) and melting processes are indicated. The violet shadows as well as red color on the numbers are employed to highlight the PBA-rich phase thermal events while the blue shadows as well as blue color on the numbers are used for the corresponding PBS-rich phase. The heating scans (for both WAXS and DSC) were performed at 10 °C/min. The values indicated on the right of figure (a) show the temperature at which the patterns were taken. The arrows indicate the main reflections for PBA (see pattern taken at 10 °C) and PBS (see pattern taken at 20 °C). Based on ref. [19].

Pérez-Camargo et al. [19] applied different cooling rates (followed by heating at a constant heating rate) in order to generate different semicrystalline states. They found that at a cooling rate of 50 °C/min, the crystallization of both PBS and PBA-rich crystalline phases is inhibited. However, during subsequent heating, the random copolymer experiences the following sequential processes as temperature increases: (a) cold crystallization of the PBA-rich phase (b) melting of the PBA-rich crystals and simultaneous cold crystallization of the PBS-rich phase and (c) melting of

the PBS-rich crystals. The sequence of crystallization and melting of the two crystalline phases was followed by synchrotron WAXS/SAXS experiments. Figure 13 shows one illustrative example.

Another interesting result reported in ref. [19] is that even though PBA homopolymer crystallizes in the thermodynamically stable α phase (when the a thermal treatment like that of Figure 13 is applied), once it is copolymerized, the PBA-rich crystalline phase can only crystallize in the metastable β phase. This is probably a consequence of the need to accommodate a small amount of PBS co-units in the crystal lattice. So, the unit cell does not only change its dimensions but also a less stable polymorph is produced when the PBA-rich phase crystallizes. In related references, Soccio et al. reported that copolymerization can indeed be used as a strategy to tune polyesters polymorphic behavior [56, 57].

3.2 Morphology of double-crystalline random aliphatic copolyesters at different length scales

In cases where the random aliphatic copolyester can produce double crystalline spherulites, SAXS measurements can be used to probe the lamellar structure developed in the material. In PBSAz copolymers, the double crystalline samples displayed two distinct peaks in SAXS profiles. Subsidiary low intensity maxima located at higher q values can correspond to second or third order reflections, if they are located at scattering vectors equal to 2 or 3 times the q_{max} . However, when the scattering peaks have almost equivalent intensity, they can indicate that the material is constituted by two types of lamellar stacks with enough density contrast to be able to individually produce small angle scattering at discrete q values. This remarkable behaviour was found in the case of PBSAz at intermediate compositions by Arandia et al. [16].

Figure 14a shows SAXS patterns for a series of PBSAz random copolymers and corresponding homopolymers taken at -30 C after all samples were cooled at a rate at which the two types of crystalline phases could be developed. Arandia et al. [16] found that the peak located at lower q values can be assigned to the long period of the PBS lamellar stacks, whereas the one at higher q values is due to the PBaz-rich phase lamellar long period. The results were also complemented by WAXS/SAXS measurements as a function of temperature. However, finding two well defined SAXS

peaks that correspond to two different lamellar long periods is not a general rule. Pérez-Camargo et al. [19] found that PBSA double crystalline random copolymers only display a single maximum in SAXS, as the long periods of the two types of lamellae overlap, due their similar periodicities.

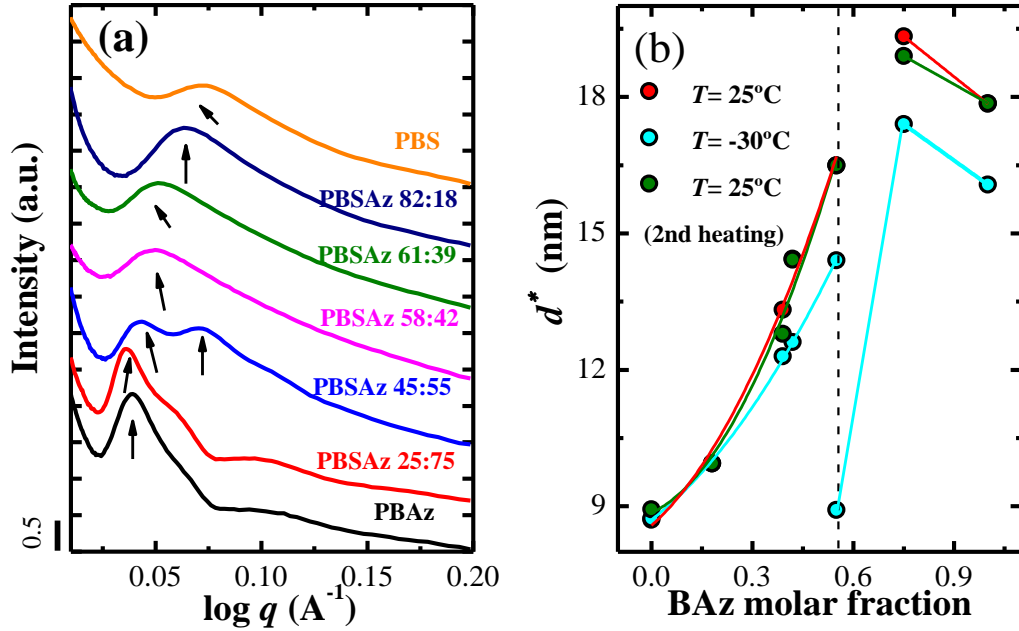


Figure 14. (a) SAXS patterns and (b) long spacing as a function of the BAz molar fraction for PBSAz isodimorphic random copolymer. Based on ref. [16].

Figure 14b shows the long spacing as a function of the BAz molar fraction. The long period of the PBS-rich crystalline phase increases as BA co-units are incorporated in the copolymer until the pseudo-eutectic composition is reached. At the pseudo-eutectic composition two long period values are clearly displayed corresponding to the PBS and PBz-rich crystalline phases. There is a sharp change or discontinuity, when the content of BA comonomer exceeds 60% molar percentage and only the PBz-rich phase can form. The double-lamellar morphology of these random copolymers is highly dependent on composition. This will have an important impact on permeation to gases and degradation properties of the materials.

Arandia et al. [16] were able to study the morphology (by PLOM and AFM) of the two crystalline phases in the double crystalline random copolymer 45:55 PBSAz. Figure 15 shows the optical micrographs of the sample at different temperatures and times, and the formation of double crystalline spherulites can be directly observed.

Upon cooling from the melt, the PBS-rich phase crystallizes first, forming PBS spherulitic templates. Figure 15a shows PBS-rich spherulites isothermally crystallized at 35 °C for 38 min. At this temperature, the PBaz-rich phase is in the molten state. If the sample is held at this temperature for long time, the whole field of view would be filled with impinged PBS-rich phase spherulites (i.e., radial lamellae), containing two phases within them: (a) a PBS crystalline phase which include a certain amount of BAz co-units; (b) an amorphous phase constituted by copolymer chains with BAz and BS repeating units in the intraspherulitic regions. Figure 16a shows a cartoon that represents in blue the PBS-rich lamellae within a spherulitic template growing at 35 °C. The amorphous regions have not been drawn for the sake of clarity, but they are located in between the crystalline lamellae.

Figures 15b and c show the development of the superstructural morphology, as the sample observed in Figure 15a is quenched to 8 °C. At this temperature, the PBaz-rich phase can crystallize very rapidly, together with the remaining PBS-rich amorphous phase (since the growth rate of the PBS-rich spherulitic templates also increases as T_c decreases). Such low temperature also enhances the nucleation and as a result a higher number of spherulites can be seen. After 2 minutes at 8 °C (Figure 15c) the microscope field of view was already filled with impinging mixed spherulites that contain lamellar crystals of both phases. The double crystalline spherulites can be represented by the cartoon shown in Figure 16b, where the red lines represent the PBaz-rich crystalline lamellae formed at 8 °C. The cartoons represented in Figure 16 are based on DSC, SAXS/WAXS, PLOM and AFM evidences.

It is worth noting that Figure 15d proofs the schematic model of Figure 16, since when the sample is heated back up to 25 °C, the field of view remains full with PBS-rich phase spherulites, after the PBaz-rich lamellar crystals are molten at 25 °C.

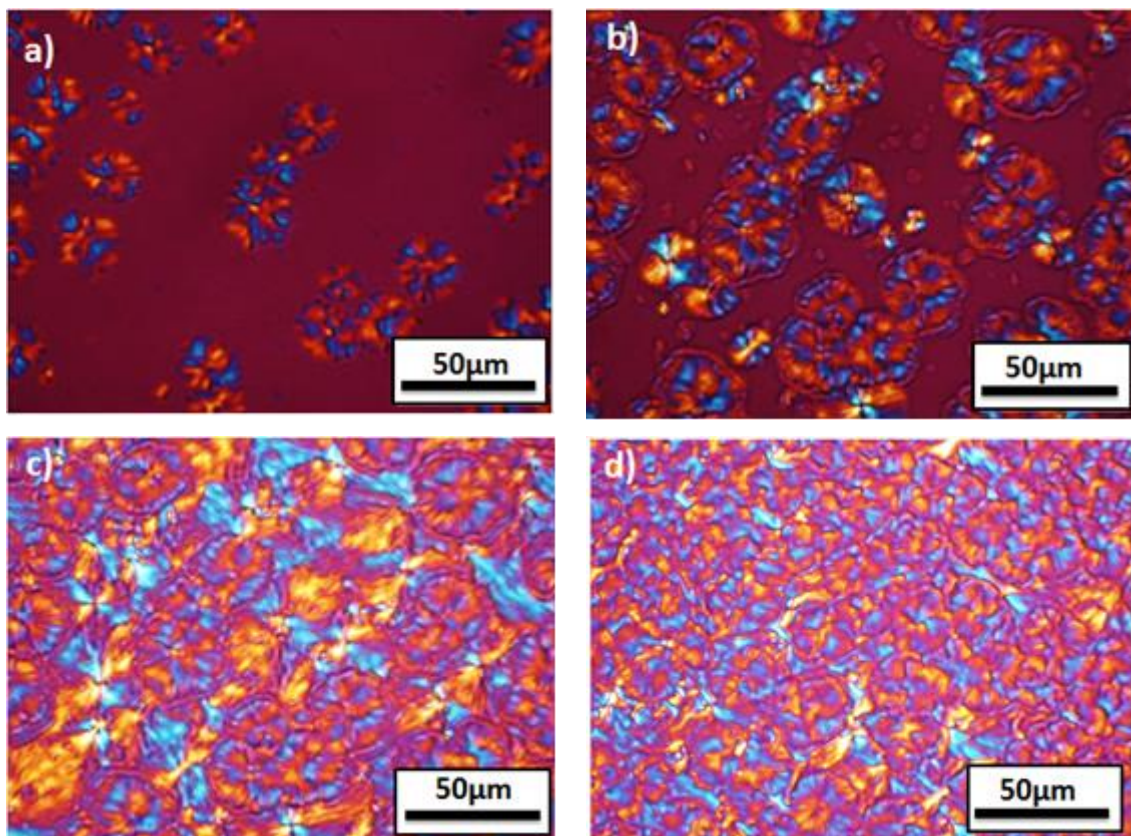


Figure 15. Polarized light optical micrographs for the 45:55 PBSAz copolymer: (a) the sample was cooled from the melt and held at 35 °C for 38 min, (b) micrograph taken after the sample in part (a) was quenched rapidly from 35 °C down to 8 °C and (c) after 2 min at 8 °C, and (d) the sample was reheated to 25 °C. Reprinted with permission from reference [16].

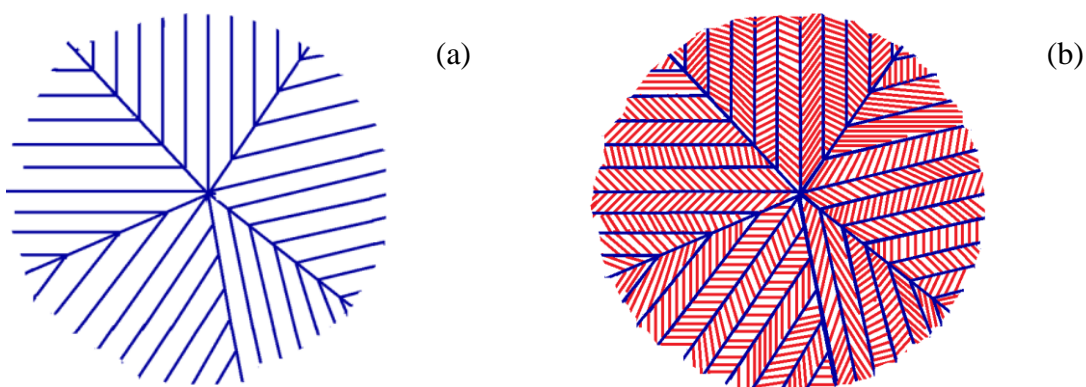


Figure 16. Schematic (not to scale) model of the superstructural morphology of the 45:55 PBSAz copolymer: (a) when only the PBS-rich phase has crystallized and a PBS-rich spherulitic template is formed at temperatures above the melting point of the PBAz-rich phase and (b) after the temperature is reduced so that the PBAz lamellae can be formed within the PBS spherulitic template. PBS-rich lamellae and PBAz-rich lamellae are represented in blue and red color respectively. Based on ref. [16].

4. Concluding Remarks

Isodimorphic random aliphatic copolyesters offer a wide range of potential applications, since they are able to crystallize in all the composition range regardless of their random distribution of comonomer units along their chains. Moreover, depending on composition, crystalline phases that resemble one and/or the other parent homopolymer are obtained. Therefore, the final properties of these materials strongly depend on composition and thermal history.

In this feature article, we show that isodimorphism is a complex phenomenon driven by comonomer partitioning within the crystalline unit cells formed. There are still many unanswered questions regarding the exact reasons that drive the easiness and extent of co-units incorporation into a particular crystalline phase. However, some general criteria can be drawn from the literature that has been reviewed in this contribution.

Several important features are common to isodimorphic aliphatic copolyesters:

- (a) They can crystallize in the entire composition range.
- (b) These isodimorphic copolymers display a pseudo-eutectic behavior when their melting points are plotted as a function of composition.
- (c) Two crystalline phases are formed in any given isodimorphic *A-ran-B* random copolymer, which resembled the crystalline structure of the parent homopolymers. One of them is constituted by A-rich phase crystals in one side of the eutectic point and the second by B-rich phase crystals on the other side of the eutectic point.
- (d) At the pseudo-eutectic point or pseudo-eutectic region, the two A-rich and B-rich phases can co-exist and their formation strongly depends on thermal history. In this case, double crystalline random copolyesters with two melting points are obtained. Their superstructural morphology is characterized by double crystalline mixed spherulites.
- (e) The unit cell dimensions can change in order to accommodate the inclusion of co-units and these changes can be determined by WAXS experiments.

The exact composition of the pseudo-eutectic point and the level of comonomer inclusion and crystallinity degrees obtained cannot be easily predicted by the copolyester chemical structure and composition. These are important factors that need

further study, especially aimed at quantitatively determine the degree of comonomer inclusion in the crystalline phases.

ACKNOWLEDGMENTS

R.A.P-C. and M.S acknowledge the support of their fellowships by POLYMAT Basque Center for Macromolecular Design and Engineering. I.A. acknowledges the fellowship granted by the University of the Basque Country UPV/EHU. The UPV/EHU team gratefully acknowledge the support of MINECO through grant MAT2017-83014-C2-1-P. We also gratefully acknowledge the support of the EU through the H2020-MSCA-RISE-2017-778092 project.

5. References

- [1] P.C. Hiemenz, T.P. Lodge, *Polymer Chemistry*, Second Edition, Taylor & Francis, 2007.
- [2] G. Natta, P. Corradini, D. Sianesi, D. Morero, Isomorphism phenomena in macromolecules, *J. Polym. Sci.* 51 (1961) 527-539.
- [3] G. Allegra, I.W. Bassi, Isomorphism in synthetic macromolecular systems, *Fortschritte der Hochpolymeren-Forschung*, Springer Berlin Heidelberg, Berlin, Heidelberg, 1969, pp. 549-574.
- [4] Y. Yu, L. Sang, Z. Wei, X. Leng, Y. Li, Unique isodimorphism and isomorphism behaviors of even-odd poly(hexamethylene dicarboxylate) aliphatic copolyesters, *Polymer* 115 (2017) 106-117.
- [5] J.-P. Latere Dwan'Isa, P. Lecomte, P. Dubois, R. Jérôme, Synthesis and Characterization of Random Copolyesters of ϵ -Caprolactone and 2-Oxepane-1,5-dione, *Macromolecules* 36 (2003) 2609-2615.
- [6] G. Ceccorulli, M. Scandola, A. Kumar, B. Kalra, R.A. Gross, Cocrystallization of Random Copolymers of ω -Pentadecalactone and ϵ -Caprolactone Synthesized by Lipase Catalysis, *Biomacromolecules* 6 (2005) 902-907.
- [7] H.-M. Ye, R.-D. Wang, J. Liu, J. Xu, B.-H. Guo, Isomorphism in Poly(butylene succinate-co-butylene fumarate) and Its Application as Polymeric Nucleating Agent for Poly(butylene succinate), *Macromolecules* 45 (2012) 5667-5675.
- [8] V. Siracusa, M. Gazzano, L. Finelli, N. Lotti, A. Munari, Cocrystallization phenomena in novel poly(diethylene terephthalate-co-thiodiethylene terephthalate) copolyesters, *J. Polym. Sci., Part B: Polym. Phys.* 44 (2006) 1562-1571.
- [9] G.Z. Papageorgiou, D.N. Bikiaris, Synthesis and Properties of Novel Biodegradable/Biocompatible Poly[propylene-co-(ethylene succinate)] Random Copolyesters, *Macromol. Chem. Phys.* 210 (2009) 1408-1421.
- [10] P. Pan, Y. Inoue, Polymorphism and isomorphism in biodegradable polyesters, *Prog. Polym. Sci.* 34 (2009) 605-640.
- [11] Y. Yu, Z. Wei, C. Zhou, L. Zheng, X. Leng, Y. Li, Miscibility and competition of cocrystallization behavior of poly(hexamethylene dicarboxylate)s aliphatic copolyesters: Effect of chain length of aliphatic diacids, *Eur. Polym. J.* 92 (2017) 71-85.

- [12] L. Xiangyang, H. Zhenfei, S. Jie, G. Yong, H. Youju, A. Haining, M. Zhe, Z. Baijin, S. Chunguang, F. Yapeng, Y. Chuanlu, L. Liangbin, Identifying the phase behavior of biodegradable poly(hexamethylene succinate-co-hexamethylene adipate) copolymers with FTIR, *J. Phys. Chem. B* 113 (2009) 2695-2704.
- [13] Z. Liang, P. Pan, B. Zhu, T. Dong, L. Hua, Y. Inoue, Crystalline Phase of Isomorphic Poly(hexamethylene sebacate-co-hexamethylene adipate) Copolyester: Effects of Comonomer Composition and Crystallization Temperature, *Macromolecules* 43 (2010) 2925-2932.
- [14] X. Li, J. Sun, Y. Huang, Y. Geng, X. Wang, Z. Ma, C. Shao, X. Zhang, C. Yang, L. Li, Inducing New Crystal Structures through Random Copolymerization of Biodegradable Aliphatic Polyester, *Macromolecules* 41 (2008) 3162-3168.
- [15] B. Tan, S. Bi, K. Emery, M.J. Sobkowicz, Bio-based poly(butylene succinate-co-hexamethylene succinate) copolyesters with tunable thermal and mechanical properties, *Eur. Polym. J.* 86 (2017) 162-172.
- [16] 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 (2015) 43-57.
- [17] R. Mincheva, A. Delangre, J.-M. Raquez, R. Narayan, P. Dubois, Biobased Polyesters with Composition-Dependent Thermomechanical Properties: Synthesis and Characterization of Poly(butylene succinate-co-butylene azelate), *Biomacromolecules* 14 (2013) 890-899.
- [18] A. Díaz, L. Franco, J. Puiggali, Study on the crystallization of poly(butylene azelate-co-butylene succinate) copolymers, *Thermochim. Acta* 575 (2014) 45-54.
- [19] R.A. Pérez-Camargo, B. Fernández-d'Arlas, D. Cavallo, 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.
- [20] Z. Liang, P. Pan, B. Zhu, Y. Inoue, Isomorphic crystallization of aliphatic copolyesters derived from 1,6-hexanediol: Effect of the chemical structure of comonomer units on the extent of cocrystallization, *Polymer* 52 (2011) 2667-2676.
- [21] Z. Liang, P. Pan, B. Zhu, Y. Inoue, Isomorphic Crystallization of Poly(hexamethylene adipate-co-butylene adipate): Regulating Crystal Modification of Polymorphic Polyester from Internal Crystalline Lattice, *Macromolecules* 43 (2010) 6429-6437.
- [22] T. Debuissy, P. Sangwan, E. Pollet, L. Avérous, Study on the structure-properties relationship of biodegradable and biobased aliphatic copolyesters based on 1,3-propanediol, 1,4-butanediol, succinic and adipic acids, *Polymer* 122 (2017) 105-116.
- [23] H. Tsuji, T. Sobue, Cocrystallization of monomer units in lactic acid-based biodegradable copolymers, poly(l-lactic acid-co-l-2-hydroxybutanoic acid)s, *Polymer* 72 (2015) 202-211.
- [24] C. Lavilla, A. Alla, A. Martínez de Ilarduya, S. Muñoz-Guerra, High Tg Bio-Based Aliphatic Polyesters from Bicyclic d-Mannitol, *Biomacromolecules* 14 (2013) 781-793.
- [25] C. Ciulik, M. Safari, A. Martínez de Ilarduya, J.C. Morales-Huerta, A. Iturrospe, A. Arbe, A.J. Müller, S. Muñoz-Guerra, Poly(butylene succinate-ran- ϵ -caprolactone) copolyesters: Enzymatic synthesis and crystalline isodimorphic character, *Eur. Polym. J.* 95 (2017) 795-808.
- [26] M. Hong, X. Tang, B.S. Newell, E.Y.X. Chen, "Nonstrained" γ -Butyrolactone-Based Copolyesters: Copolymerization Characteristics and Composition-Dependent

- (Thermal, Eutectic, Cocrystallization, and Degradation) Properties, *Macromolecules* 50 (2017) 8469-8479.
- [27] K. Wang, Y.-G. Jia, X.X. Zhu, Two-Way Reversible Shape Memory Polymers Made of Cross-Linked Cocrystallizable Random Copolymers with Tunable Actuation Temperatures, *Macromolecules* 50 (2017) 8570-8579.
- [28] M. Mochizuki, K. Mukai, K. Yamada, N. Ichise, S. Murase, Y. Iwaya, Structural effects upon enzymatic hydrolysis of poly(butylene succinate-co-ethylene succinate)s, *Macromolecules* 30 (1997) 7403-7407.
- [29] R.J. Young, P.A. Lovell, *Introduction to Polymers*, Third Edition, Taylor & Francis, 2011.
- [30] M. Gordon, J.S. Taylor, Ideal copolymers and the second-order transitions of synthetic rubbers. i. non-crystalline copolymers, *J. Appl. Chem.* 2 (1952) 493-500.
- [31] S.V. Eynde, V.B.F. Mathot, M.H.J. Koch, H. Reynaers, Thermal behaviour and morphology of homogeneous ethylene-1-octene copolymers with high comonomer contents, *Polymer* 41 (2000) 4889-4900.
- [32] B. Poon, M. Rogunova, S.P. Chum, A. Hiltner, E. Baer, Classification of homogeneous copolymers of propylene and 1-octene based on comonomer content, *J. Polym. Sci., Part B: Polym. Phys.* 42 (2004) 4357-4370.
- [33] M. Soccio, L. Finelli, N. Lotti, M. Gazzano, A. Munari, Poly(propylene isophthalate), poly(propylene succinate), and their random copolymers: Synthesis and thermal properties, *J. Polym. Sci., Part B: Polym. Phys.* 45 (2007) 310-321.
- [34] M. Soccio, L. Finelli, N. Lotti, M. Gazzano, A. Munari, Novel random poly(propylene isophthalate/adipate) copolyesters: Synthesis and characterization, *Eur. Polym. J.* 42 (2006) 2949-2958.
- [35] D.F. Swinehart, The Beer-Lambert Law, *J. Chem. Educ.* 39 (1962) 333.
- [36] M. Konstantopoulou, Z. Terzopoulou, M. Nerantzaki, J. Tsagkalias, D.S. Achilias, D.N. Bikiaris, S. Exarhopoulos, D.G. Papageorgiou, G.Z. Papageorgiou, Poly(ethylene furanoate-co-ethylene terephthalate) biobased copolymers: Synthesis, thermal properties and cocrystallization behavior, *Eur. Polym. J.* 89 (2017) 349-366.
- [37] M.P.F. Pepels, L.E. Govaert, R. Duchateau, Influence of the Main-Chain Configuration on the Mechanical Properties of Linear Aliphatic Polyesters, *Macromolecules* 48 (2015) 5845-5854.
- [38] G. Guidotti, M. Soccio, V. Siracusa, M. Gazzano, E. Salatelli, A. Munari, N. Lotti, Novel Random PBS-Based Copolymers Containing Aliphatic Side Chains for Sustainable Flexible Food Packaging, *Polymers* 9 (2017) 724.
- [39] Z. Gan, H. Abe, H. Kurokawa, Y. Doi, Solid-State Microstructures, Thermal Properties, and Crystallization of Biodegradable Poly(butylene succinate) (PBS) and Its Copolyesters, *Biomacromolecules* 2 (2001) 605-613.
- [40] G. Wang, Z. Qiu, Synthesis, Crystallization Kinetics, and Morphology of Novel Biodegradable Poly(butylene succinate-co-hexamethylene succinate) Copolyesters, *Ind. Eng. Chem. Res.* 51 (2012) 16369-16376.
- [41] Y.G. Jeong, W.H. Jo, S.C. Lee, Cocrystallization Behavior of Poly(butylene terephthalate-co-butylene 2,6-naphthalate) Random Copolymers, *Macromolecules* 33 (2000) 9705-9711.
- [42] J.C. Morales-Huerta, A. Martínez de Ilarduya, S. Muñoz-Guerra, Sustainable Aromatic Copolyesters via Ring Opening Polymerization: Poly(butylene 2,5-furandicarboxylate-co-terephthalate)s, *ACS Sustainable Chem. Eng.* 4 (2016) 4965-4973.
- [43] Z. Liang, P. Pan, B. Zhu, J. Yang, Y. Inoue, Critical role of the conformation of comonomer units in isomorphic crystallization of poly(hexamethylene adipate-co-

- butylene adipate) forming Poly(hexamethylene adipate) type crystal, *Polymer* 52 (2011) 5204-5211.
- [44] L. Mandelkern, *Crystallization of Polymers: Volume 1, Equilibrium Concepts*, Cambridge University Press, 2002.
- [45] P.J. Flory, Theory of crystallization in copolymers, *Trans. Faraday Soc.* 51 (1955) 848-857.
- [46] P.J. Flory, Thermodynamics of Crystallization in High Polymers. IV. A Theory of Crystalline States and Fusion in Polymers, Copolymers, and Their Mixtures with Diluents, *The Journal of Chemical Physics* 17 (1949) 223-240.
- [47] V.H. Baur, Einfluß der sequenzlängenverteilung auf das schmelz-ende von copolymeren, *Die Makromolekulare Chemie* 98 (1966) 297-301.
- [48] J. Wendling, U.W. Suter, A New Model Describing the Cocrystallization Behavior of Random Copolymers, *Macromolecules* 31 (1998) 2516-2520.
- [49] E. Helfand, J.I. Lauritzen, Theory of Copolymer Crystallization, *Macromolecules* 6 (1973) 631-638.
- [50] I.C. Sanchez, R.K. Eby, Thermodynamics and Crystallization of Random Copolymers, *Macromolecules* 8 (1975) 638-641.
- [51] J. Wendling, A.A. Gusev, U.W. Suter, Predicting the Cocrystallization Behavior of Random Copolymers via Free Energy Calculations, *Macromolecules* 31 (1998) 2509-2515.
- [52] J. Wendling, A.A. Gusev, U.W. Suter, A. Braam, L. Leemans, R.J. Meier, J. Aerts, J.v.d. Heuvel, M. Hottenhuis, Crystal Morphology and Thermodynamics of Poly(ethylene-4,4'-biphenyl dicarboxylate) and Related Copolymers with Ethylene-2,6-naphthalene Dicarboxylate, *Macromolecules* 32 (1999) 7866-7878.
- [53] S. Hosoda, H. Nomura, Y. Gotoh, H. Kihara, Degree of branch inclusion into the lamellar crystal for various ethylene/ α -olefin copolymers, *Polymer* 31 (1990) 1999-2005.
- [54] K. Jeon, Y.L. Chiari, R.G. Alamo, Maximum Rate of Crystallization and Morphology of Random Propylene Ethylene Copolymers as a Function of Comonomer Content up to 21 mol %, *Macromolecules* 41 (2008) 95-108.
- [55] A. Díaz, L. Franco, F. Estrany, L.J. del Valle, J. Puiggalí, Poly(butylene azelate-co-butylene succinate) copolymers: Crystalline morphologies and degradation, *Polym. Degrad. Stab.* 99 (2014) 80-91.
- [56] M. Soccio, M. Gazzano, N. Lotti, L. Finelli, A. Munari, Copolymerization: A new tool to selectively induce poly(butylene naphthalate) crystal form, *J. Polym. Sci., Part B: Polym. Phys.* 47 (2009) 1356-1367.
- [57] M. Soccio, M. Gazzano, N. Lotti, L. Finelli, A. Munari, Synthesis and characterization of novel random copolymers based on PBN: Influence of thiodiethylene naphthalate co-units on its polymorphic behaviour, *Polymer* 51 (2010) 192-200.