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Tailoring the isothermal crystallization kinetics of isodimorphic Poly (butylene succinate-*ran*-butylene azelate) random copolymers by changing composition

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ABSTRACT

A detailed isothermal crystallization study of biobased and biodegradable isodimorphic poly (butylene succinate-*ran*-butylene azelate) random copolyesters (PBS-*ran*-PBAz) with a wide composition range has been carried out to determine nucleation kinetics, spherulitic growth rates and overall crystallization kinetics. Differential Scanning Calorimetry (DSC) and Polarized Light Optical Microscopy (PLOM) analysis show that for the PBS-rich phase, the incorporation of BAz comonomer leads to a significant increase in nucleation density and a decrease in spherulitic growth. On the contrary, for the PBAz-rich phase, an antinucleating effect of the incorporation of BS comonomer has been observed. Both effects agree with the thermodynamic analysis of the equilibrium melting point depression as a function of composition, which predicts that only a small amount of BAz comonomer is included within the PBS-rich crystals and a larger amount of comonomer is included in PBAz-rich crystals. In addition, the enthalpy of melting of 100% crystalline PBS and PBAz were determined by a different practical approach: extrapolating real time synchrotron Wide Angle X-ray Scattering (WAXS) isothermal crystallization data and isothermal DSC data.

Keywords: *isodimorphism; random copolymers; nucleation; crystallization; equilibrium melting enthalpy.*

INTRODUCTION

Biodegradable and biobased polymers are considered potential substitutes of traditional non-biodegradable polymeric materials. Among these, aliphatic polyesters, such as poly (lactic acid) (PLA), poly (ϵ -caprolactone) (PCL), poly (butylene succinate) (PBS), and poly (butylene azelate) (PBz), are the most promising materials. They are obtained from renewable sources and have attracted increasing interest in a large range of applications in textile and agricultural industries, packaging, and biomedical devices because of their biodegradability and biocompatibility [1-3]. Unfortunately, their applications are limited in some cases by inadequate mechanical properties and/or by a slow biodegradation rate caused by their high degree of crystallinity. Therefore, with the aim of adapting these properties, the synthesis of random copolyesters, with biobased comonomers, has been accomplished to obtain versatile random copolymers [4-9].

The properties of crystallizable random copolymers constituted by two potentially semi-crystalline parent components have been recently reviewed [10]. Depending on their miscibility and ability to share crystal lattices, three different cases have been reported [11]. The most commonly reported case is the total exclusion of the comonomer that constitutes the minor component from the crystalline regions of the major component. In this case, the copolymers are unable to crystallize in a wide composition range. Only compositions containing typically 10 mol % or less of the second comonomer are able to crystallize. This case usually arises when comonomers chemical structures are very different from one another.

On the other hand, only when the chemical structures of both comonomers are similar, two cases of co-crystallization may occur: isomorphism or isodimorphism [10,12]. In isomorphic copolymers, total comonomer inclusion inside the crystal unit cell occurs, therefore only one crystalline phase containing

both comonomer units is formed and only one crystalline structure is obtained for all compositions [9,13-15].

In isodimorphic copolymers, the random copolymers also crystallize in the whole composition range, but with two crystal structures that resemble those of the parent homopolymers depending on composition, and at least one of the two crystalline phases includes some comonomeric units of the minor component in their crystal lattice. Isodimorphic copolymers also show a pseudo-eutectic behaviour when their thermal transitions, such as melting and crystallization temperatures, are plotted as a function of composition, and the eutectic point is located at the composition at which a change in crystal structure occurs. On each side of the pseudo-eutectic point, only the crystalline phase of the major component is formed, which may contain a limited amount of the minor comonomer chains included in the crystal lattice. It is usually observed that with the addition of minor comonomer units, the crystallization and melting temperatures of the copolymers decreases [16]. Additionally, we have previously demonstrated that at the pseudo-eutectic point, two crystalline phases can form and co-exist within double crystalline spherulites [10].

In previous works, we have studied the morphology and non-isothermal crystallization of poly (butylene succinate-*ran*-butylene azelate) (PBSAz) copolyesters previously synthesized by Mincheva et al. and presented in ref. 17. Both main components of these interesting copolymers are biodegradable and their monomers are derived from biomass. Poly (butylene succinate) (PBS) is well known for its good mechanical properties, easy processability and relatively low production cost [18-20]. The copolymers are isodimorphic as poly (butylene azelate) (PBAz) has the same functional groups as PBS and they differentiate only

in the length of the corresponding dicarboxylic acid [4]. Wide Angle X-Ray Scattering (WAXS) measurements showed that due to a partial comonomer inclusion, small variations in the crystalline unit cell dimensions of the dominant crystalline phase were found. Also, Differential Scanning Calorimetry (DSC) measurements showed that the thermal transitions temperatures (i.e., T_c and T_m) went through a pseudo-eutectic point when plotted as a function of composition. Furthermore, thermal fractionation by Successive Self-nucleation and Annealing (SSA), which promotes segregation of molecular defects that interrupt crystallizable sequences, was performed and signs of co-crystallization were still detected [21]. The study of the dielectric relaxation of PBSAz copolymers was also performed [22]. In this previous work, the dynamics of the comonomers remaining in the amorphous phase were analyzed, and it was possible to quantify the comonomer fraction participating in the crystalline and amorphous phases.

Puiggali et al. [23] previously studied the crystallization of similar PBSAz copolymers. The possible co-crystallization behavior was analyzed by comparing the experimental estimations of the equilibrium melting points, with exclusion-inclusion models available in the literature [10]. They concluded that their copolymers behavior could be explained by total comonomer exclusion, in spite of the fact that their copolymers were able to crystallize in the entire composition range examined.

In the present work, we perform for the first time, detailed isothermal studies of the nucleation kinetics, spherulitic growth rates and overall crystallization kinetics of PBSAz copolymers in a wide composition range to demonstrate the dramatic influence of composition on crystallization kinetics. By measuring nucleation, growth and overall crystallization kinetics, we are able to ascertain

which factors determine the final solidification kinetics of the copolymers and assess the influence of composition. In addition, we determine the enthalpy of melting of 100% crystalline PBS and PBz by a different and practical approach: extrapolating real time synchrotron WAXS isothermal crystallization data and isothermal DSC data. Finally, by applying thermodynamic models to the equilibrium melting point data as a function of composition, we are able to calculate the amount of comonomer inclusion within each crystalline phase and correlate these results with the trends in crystallization rate with composition.

EXPERIMENTAL SECTION

Materials

The PBz copolymers were synthesized by a two-stage melt polycondensation reaction. This consisted in an esterification at atmospheric pressure of diacid (co)monomer(s) and a diol, and polycondensation of the obtained oligoesters to (co)polymers at reduced pressure. Reactions were performed in a expressly designed and adapted Inox Autoclave reactor (Autoclave-France, France). Succinic acid (SuA) and dimethyl azelate (DMAz) were copolymerized at [COOH]: [COOCH₃] = 1.0:0, 0.8:0.2, 0.6:0.4, 0.5:0.5, 0.4:0.6, 0.2:0.8, and 0:1.0 molar ratios in the presence of 1,4-butanediol (BDO). The details of the synthesis have been previously reported [17]. Samples are denoted in an abbreviated form, e.g., BS_{xx}Bz_{yy}, indicating the molar ratio of each component as subscripts (xx and yy) and are specified in Table 1.

Table 1. Molar composition determined by ^1H NMR, number-average molecular weight determined by SEC and thermal transitions determined by DSC (at 10 °C/ min) of the materials employed in this work.

Code	Composition (PBS/PBAz), mol ^1H NMR	M_n (g/mol) SEC	\bar{D}	DSC Data [4]			
				T_g (°C)	T_{m1} (°C)	T_{m2} (°C)	
1	BS	1/0	25.300	2.36	-36	115	--
2	BS ₈₂ BAz ₁₈	0.82/0.18	22.300	1.76	-50	98	--
3	BS ₆₁ BAz ₃₉	0.61/0.39	31.300	5.16	-56	72	--
4	BS ₅₈ BAz ₄₂	0.58/0.42	36.500	3.44	-57	60	--
5	BS ₄₅ BAz ₅₅	0.45/0.55	38.300	3.24	-61	46	26
6	BS ₂₅ BAz ₇₅	0.25/0.75	39.600	3.45	-62	--	34
7	BAz	0/1	42.500	2.42	-63	--	41

Estimation of errors is based on the repetition of DSC experiments; calibration and baseline drifts indicate that transition temperatures are valid within 0.5 °C (except for T_g measurements which are within 1 °C).

Polarized Light Optical Microscopy (PLOM)

An Olympus BX51 polarized light optical microscope was used with a Linkam THMS600 hot stage for accurate temperature control. The appearance of nuclei was recorded as a function of time during isothermal crystallization from the melt. Samples were first melted, at a temperature 30 °C higher than the melting point of the sample determined by DSC, to erase their thermal history for 3 min. Then they were quickly cooled down to the chosen T_c value.

Spherulite growth rate experiments were also performed by recording their growth by PLOM (Olympus BX51), incorporating a λ plate in between the polarizers at 45° to facilitate observation and determine the sign of the birefringence. The dimensions of the spherulites were periodically registered with an Olympus SC50 digital camera. The samples were placed in between of a glass slide and a glass coverslip. The conditions used for the isothermal experiments were very similar to the DSC ones, where samples were first heated to a temperature of 30 °C above their DSC melting peak to erase their thermal history

and then crystallized from the melt to a selected isothermal crystallization temperature (T_c) at 60 °C/min employing the Linkam THMS600 hot stage.

Isothermal Crystallization Kinetics

Isothermal crystallization experiments were performed with a PerkinElmer Pyris 1 differential scanning calorimetry (DSC), which contains a refrigerated cooling system (Intracooler 2P). It was calibrated with indium and tin standards. For the measurements, which were made under a nitrogen atmosphere flow, ≈ 5 mg, samples were sealed in aluminum pans and the procedure followed was that recommended by Lorenzo et al. [24]. Overall isothermal crystallization experiments were performed by directly quenching the samples from the melt at 60 °C/min. Before starting with the isothermal procedure, the minimum isothermal crystallization temperature was first determined. This was done by heating the sample directly from the chosen T_c value, after being quenched from the melt (at 60 °C/min). The lowest temperature which did not show any melting enthalpy during immediate subsequent heating was the minimum isothermal crystallization temperature employed [24].

The samples were heated to 30 °C above their melting temperature for 3 minutes in order to erase the previous thermal history, and then cooled at a rate of 60 °C/min (at which the calorimeter can control the cooling rate) to the chosen isothermal crystallization temperature T_c . At these chosen T_c values, the samples were left to crystallize until saturation, and finally they were heated up from T_c to 30 °C above their peak melting temperature at 20 °C/min.

The complimentary origin plug-in developed by Lorenzo et al. [24] was employed to perform the fittings to the Avrami equation following the

recommendations given in this paper (this plug-in is for free distribution upon request).

Simultaneous SAXS/WAXS Synchrotron measurements

Simultaneous SAXS/WAXS experiments were performed at the beamline BL11-NCD, ALBA Synchrotron facility in Barcelona, Spain. A Linkam THMS600 hot stage equipped with a liquid nitrogen cooling system was used to heat and cool the samples placed inside capillaries, and while copolymers were crystallizing SAXS/WAXS patterns were periodically recorded.

In order to calculate the heat of fusion of a 100 % crystalline polymer, $\Delta H_{m(100\%)}^0$, of each neat homopolymer (i.e., PBS and PBz), the samples were heated to 30 °C above their melting point for 3 minutes, and then cooled to a chosen temperature at 50 °C/min. At this temperature, the samples were isothermally crystallized during 30 minutes while SAXS and WAXS patterns were simultaneously registered every 10 seconds.

The Thomson-Gibbs equation is used to calculate the equilibrium melting temperature (T_m^0) of a homopolymer if the melting point and the average value of the lamellar thickness are known for a series of isothermally crystallized samples. In the case of calculating the equilibrium melting temperature, T_m^0 , all samples were isothermally crystallized at different temperatures before cooling them to room temperature at which SAXS and WAXS patterns were registered. Their melting points were separately determined by DSC.

The X-ray energy source used for WAXS/SAXS measurements was 12.4 keV ($\lambda = 1.03 \text{ \AA}$). Specifically, for the SAXS configuration the distance between the sample and the detector was 6495.0 mm with a tilt angle of 0° and was

calibrated using silver behenate (ADSC Q315r, Poway, CA, USA, with a resolution of 3070×3070 pixels, pixel size of $102 \mu\text{m}^2$). For the WAXS configuration, which was calibrated using chromium (III) oxide, the distance between the sample and the detector was 132.6 mm with a tilt angle of 21.2° . (Rayonix LX255-HS detector, Evanston, IL, USA, with resolution of 1920×5760 pixels, pixel size of $44 \mu\text{m}^2$).

The intensity profiles plot the scattering intensity as a function of the scattering vector, $q = 4\pi\sin\theta\lambda^{-1}$, where λ is the X-ray wavelength ($\lambda = 1.03 \text{ \AA}$) and 2θ is the scattering vector.

Results and Discussion

Nucleation kinetics studied by PLOM

Examples of nucleation data obtained by PLOM are plotted in Figure 1a and 1b. Both figures show the nucleation density ρ (N/mm^3) as a function of time for neat PBS and BS₅₈BAZ₄₂ copolymer respectively. Data for the other samples are reported in Figure S.1 of the Supplementary Information. On the other hand, due to the high nucleation density of the samples which contain only PBAz-rich crystals (i.e., BS₂₅BAZ₇₅ copolymer and PBAz homopolymer), it was impossible to determine their nucleation kinetics.

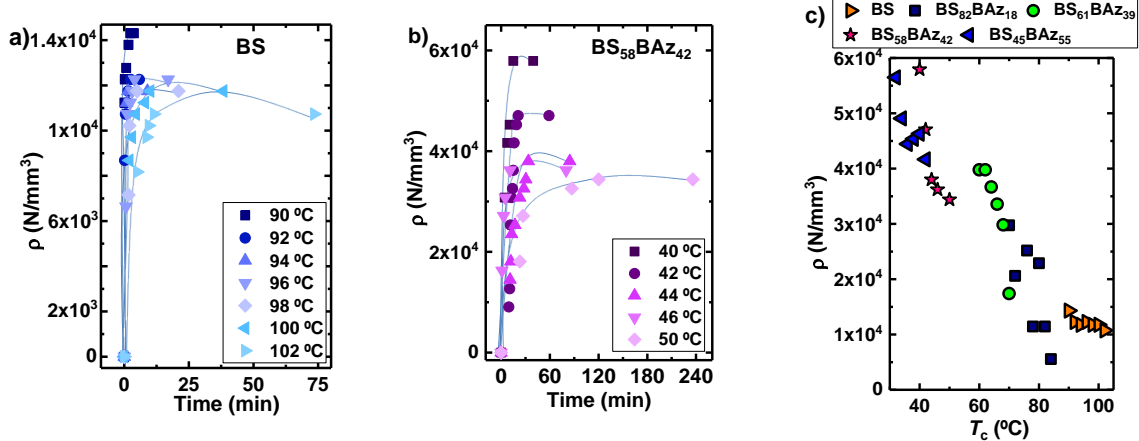


Figure 1. (a) and (b) Nucleation density as a function of time for PBS and BS₅₈BAZ₄₂ copolymer. (c) Nucleation density at saturation values as a function of crystallization temperature (T_c).

The nucleation behavior observed in all samples (e.g., Figure 1a and 1b) was close to instantaneous. A more detailed analysis indicates that two important parameters affect the nucleation density of PBS-rich copolymers (Figure 1c): (a) the chosen isothermal crystallization temperature and (b) the increase of the BAZ minor comonomer content.

At lower isothermal crystallization temperatures, the nucleation density was higher than that obtained at higher temperatures, due to the increase in the thermodynamic driving force required for nucleation as supercooling increases [25]. For example, in the case of PBS homopolymer, when the sample is measured at 90 °C, it only takes 3 minutes to fill the whole microscope field with spherulites. However, when it is measured at 102 °C, more than one hour is needed for the entire field to be completely filled with crystalline superstructures. This is the expected result, as nucleation tends to be more sporadic as temperature increases.

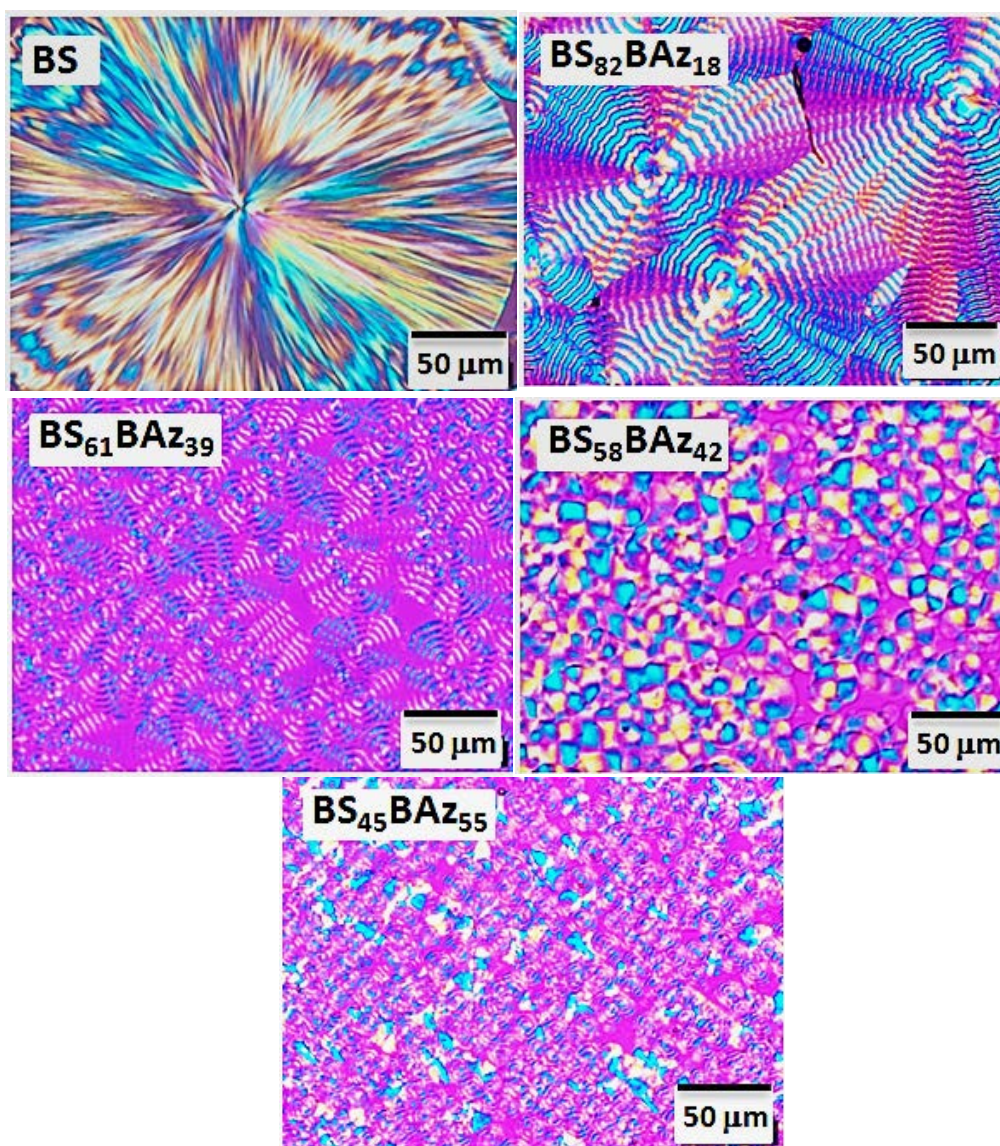


Figure 2. Polarized light optical micrographs of PBS-rich copolymers during non-isothermal crystallization from the melt at 5 °C/min. Micrographs were taken when spherulites completely covered the microscope field under observation

On the other hand, the incorporation of BAz comonomer significantly increases the nucleation density for the PBS-rich phase. This can be easily appreciated in Figure 1c, where nucleation density increases with the BAz content, and also in PLOM micrographs of PBSAz copolymers presented in Figure 2. These micrographs were taken, after the samples were cooled from the melt at 5 °C/min and had impinged on one another, completely filling the microscope observation

field (therefore, the temperature at which the images were taken varies depending on the crystallization range of the sample).

The spherulites are negative in all cases, with Maltese Cross extinction patterns. Additionally, regular banding was observed in the PBS-rich copolymer spherulites but not in neat PBS, where some highly irregular banding can only be observed near the spherulite edges in Figure 2. The addition of miscible “impurities”, such as plasticizers and miscible polymeric components is known to induce banding [26]. In the present case, the addition of comonomeric units in a random fashion within the PBS chain also causes a similar effect. The accumulation of the excluded comonomeric units near the lamellar surfaces (it has to be remembered that in these isodimorphic copolymers there are both included and excluded comonomer units within the crystals according to our own previous works) [4,21,22] may be the determining factor to induce banding in the present case.

In the case of the compositions rich in PBAz, although the density of nuclei could not be measured for both samples, the BS₂₅BAZ₇₅ copolymer and PBAz homopolymer, results showed that the incorporation of BS comonomer results in lower nucleation density, the opposite effect of what occurs in the PBS-rich samples. Figure 3 shows polarized light optical micrographs of both samples after cooling from the melt at 5 °C/min (Figure 3a and 3b) and also isothermally crystallized at same supercooling (Figure 3c and 3d). The supercooling was calculated with the equilibrium melting temperature (T_m^0) determined here, by using the Thomson-Gibbs method (see the different T_m^0 determinations below). When both compositions are cooled from the melt, much lower nucleation density is appreciated in BS₂₅BAZ₇₅ copolymer because the addition of BS comonomer

causes an unexpected antinucleation effect. This effect is better appreciated when both are isothermally crystallized at same supercooling (Figure 3d), where a reduced number of larger spherulites can be appreciated for the copolymer as compared to the PBz homopolymer.

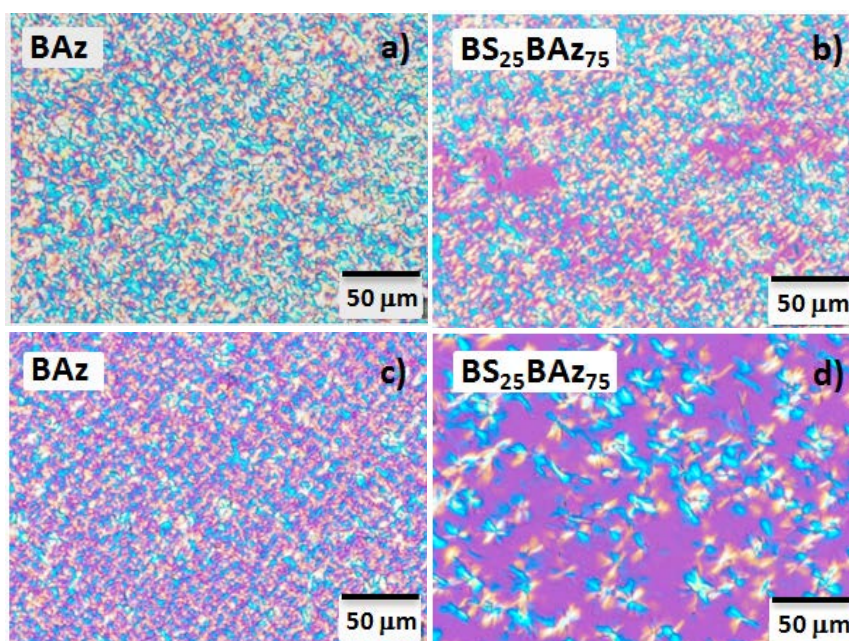


Figure 3. Polarized light optical micrographs, (a) PBAz homopolymer and (b) BS₂₅BAz₇₅ copolymer during non-isothermal crystallization from the melt at 5 °C/min. (c) PBAz homopolymer isothermally crystallized at 35°C and (d) BS₂₅BAz₇₅ copolymer isothermally crystallized at 24°C.

We speculate that the reason behind the changes in nucleation density with composition is due to the comonomer inclusion within each crystallizing phase. As will be explained below (in Figure 13), a large amount of PBS comonomer units (up to 20% or more depending on composition) can be included in the PBAz-rich crystals formed, apparently causing some small hindering of the nucleation process. On the other hand, there is a very small incorporation of PBAz (between 1 and 2% maximum, depending on composition) in the PBS-rich crystals

apparently favoring the nucleation of this phase. This may be due to a balance between inclusion and exclusion, which can affect the heterogeneous nucleation process, although the exact mechanism is still unknown.

Kinetics of superstructural growth (secondary nucleation) by PLOM

The spherulitic growth rate of PBS and PBS-rich copolymers as a function of the isothermal crystallization temperature is shown in Figure 4. As explained before, due to the high nucleation density of some samples, only compositions rich in PBS were measured. Experiments were performed by cooling the samples from the melt to a chosen crystallization temperature in the range between 100 and 32 °C. From the slope of plots of radius versus time (which were always linear), spherulitic growth rates, G ($\mu\text{m}/\text{min}$), for each composition was determined at different crystallization temperatures.

Figure 4 shows the spherulitic growth rate G ($\mu\text{m}/\text{min}$) as a function of T_c . In this case, only the right side of the typical bell-shape trend caused by the competition between thermodynamic control of secondary nucleation and diffusion is observed [27]. When lower T_c values were attempted, both the nucleation and growth rates were too high and measurements of spherulitic growth before impingement proved impossible.

The spherulitic growth rate G ($\mu\text{m}/\text{min}$) depends strongly on the copolymer composition, as G dramatically decreases with the increase of BAZ-units content. In fact, in comparison with neat PBS, copolymers with 61% PBAz or more can have values of growth rate as low as one order of magnitude lower. As a result, large differences are observed between compositions with only 18% of BAZ and compositions with more than 61% of BAZ (see Figure 4a and 4c).

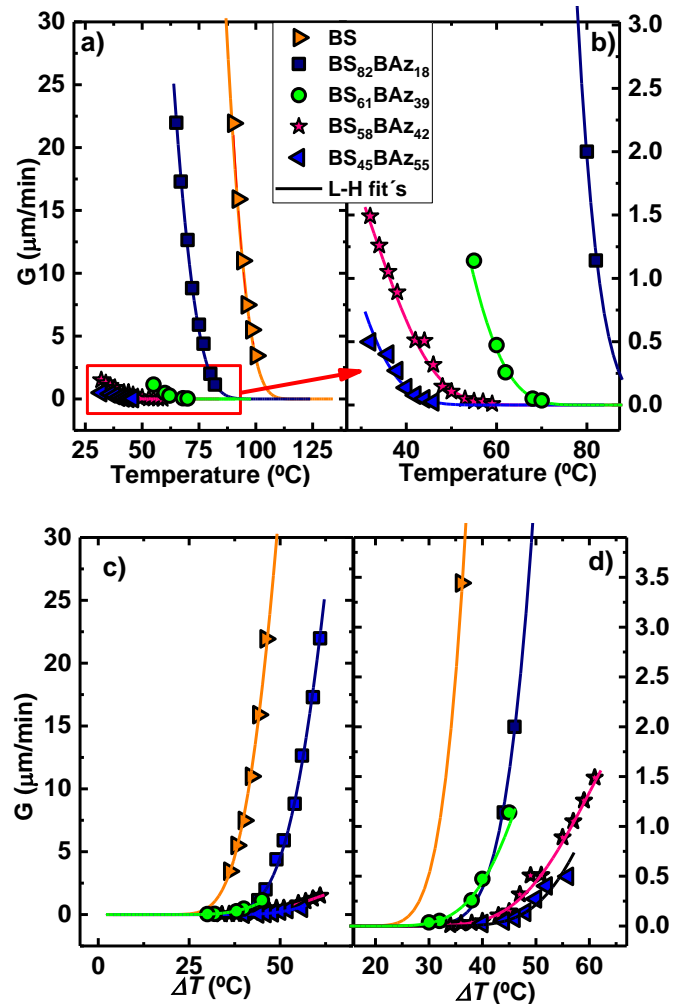


Figure 4. (a) and (b) spherulitic growth rates determined by PLOM for neat PBS and PBS-rich copolymers. The solid lines are the fits to the Lauritzen–Hoffman (LH) theory. (c) and (d) spherulitic growth rates as a function of supercooling. Note that Figures 4b and d, correspond to a close-up of the following samples: BS₆₁BAZ₃₉, BS₅₈BAZ₄₂, BS₄₅BAZ₅₅

The supercooling required for crystallization also increases with BAZ content in the copolymers, as a result of the change in equilibrium melting temperature with composition. When G is plotted as a function of supercooling ($\Delta T = T_m^0 - T_c$), using the equilibrium melting temperatures (T_m^0) determined by the Thomson-Gibbs method (see below), in Figure 4c and 4d, the curves are now shifted along the x-axis reducing the differences between the overall crystallization curves versus T_c . Nevertheless, the curves are not completely superimposed, neither on the x-axis nor on the vertical y-axis. This means that the overall crystallization

kinetic differences between PBS-rich copolymer chains cannot be normalized by just a single thermodynamic variable (i.e., T_m^0). These results indicate that apart from this thermodynamic effect (i.e., the supercooling), also kinetic effects are influencing chain diffusion of copolymers, as PBS linear sequences are frequently interrupted by BAz repeating units [4].

Summarizing the results obtained so far, the incorporation of BAz units in the random copolymers with a majority of PBS content causes two opposing trends: an increase in nucleation density and a large decrease in spherulitic growth kinetics. The competition between these two factors will determine the overall crystallization rate (that was measured by DSC and will be presented in the next section).

Overall Isothermal Crystallization.

To determine the overall crystallization rate of PBS, PBAz and PBSAz copolymers, isothermal crystallization experiments were performed by DSC. From DSC experiments, the inverse of the half-crystallization time ($1/\tau_{50\%}$) was determined and plotted against the crystallization temperature (Figure 5a). The $1/\tau_{50\%}$ value is the inverse of the time needed to achieve the 50% of the total transformation to the semi-crystalline state during the isothermal crystallization process, and with this an experimental measure of the overall crystallization rate, which includes both growth and nucleation contributions, can be quantified.

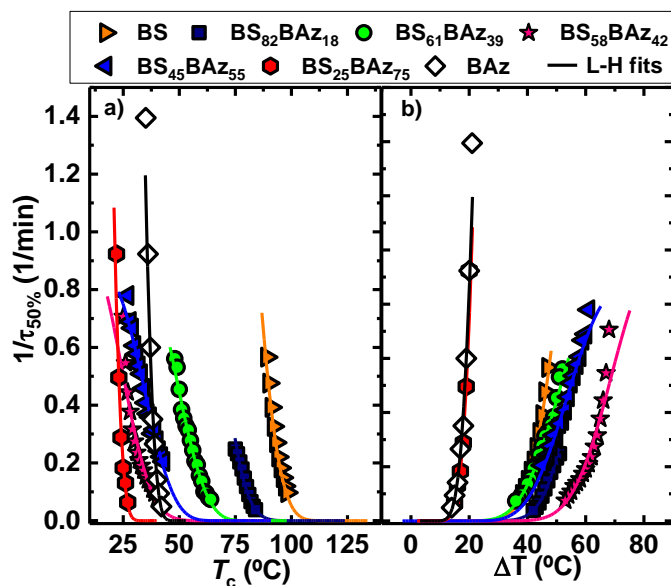


Figure 5. Inverse of half-crystallization time as a function of (a) T_c and (b) supercooling ΔT for indicated PBsAz samples.

For those compositions rich in PBS, results show that when the BAZ comonomer content increases the inverse of the half-crystallization time decreases, as well as it occurs with the spherulitic growth rate (G), explained above in the text. However, as in the overall crystallization, both nucleation and spherulitic growth rate contribute, in this case, $1/\tau_{50\%}$ does not decrease as dramatically as G with the increase of BAZ-units in the copolymer. Therefore, the changes in nucleation density strongly affect the overall crystallization rates determined by DSC, as they compensate the dramatic decrease in G values with comonomer content by increasing the nucleation rate.

On the other hand, it was not possible to measure the nucleation density of both PBsAz homopolymer and BS₂₅BAZ₇₅ by PLOM, as they were too high. However, the half-crystallization time ($1/\tau_{50\%}$), determined by DSC for both samples, showed similar behavior as a function of T_c . When these results are plotted against supercooling (ΔT) (Figure 5b), there are no differences between neat PBsAz and the copolymer, and the curves in the x-axis are shifted normalizing

the differences in crystallization temperature exhibited by both compositions. Furthermore, the curves are also superimposed on the vertical axis. Although the micrographs in Figure 3 showed that the density of nuclei decreases when 25% of BS content was added to the copolymer (BS₂₅BAZ₇₅), the overall crystallization rate is not affected, indicating that two important factors may be influencing the crystallization of PBAz-rich copolymers: (a) the addition of BS comonomer has a plasticizing effect in the PBAz-rich phase, and/or (b) the inclusion of BS-units within the PBAz crystallites is significant and the excluded units do not significantly limit crystallization. This latter behavior would be in good agreement with predictions of the Wendling-Suter model (Figure 13a), as explained below in the text. The results of fitting the T_m^0 data as a function of composition with the Wendling-Suter model indicate that the energy barrier needed in order to introduce BS comonomer units within the PBAz-rich crystalline face is much lower than in the opposite case. In addition, the estimation of the minor comonomer percentage incorporated within PBAz crystals is predicted to be a large relative number.

In the case of PBS-rich copolymers, Figure 5b shows that even though the crystallization curves are brought together when represented as a function of supercooling, there is no perfect superposition between PBS and the PBS-rich copolymers, as in the case of the PBAz-rich copolymer with PBAz. Once again, the thermodynamic parameter (i.e., supercooling) can only partially explain the reduction in crystallization rate caused by PBAz comonomer sequences in the PBS-rich phase. So, kinetic effects, related to both primary and secondary nucleation must be playing a role influenced by the different inclusion/exclusion balance of comonomeric units. In the case of PBS-rich copolymers, we believe that exclusion

dominates the behavior. This is consistent with the theoretical predictions of the Wendling-Suter model, to be presented below.

Fitting of DSC Isothermal Data to the Avrami Model

The isothermal experimental data obtained from the DSC measurements were fitted to the Avrami equation [24,28,29]:

$$1 - V_c(t - t_0) = \exp(-k(t - t_0)^n) \quad (1)$$

where $V_c(t)$ is the relative volumetric transformed fraction as a function of time, t the experimental time and t_0 is the induction time for crystallization. k is the overall crystallization rate constant and n is the Avrami index, which strongly depends on both the time dependence of the nucleation (n_n) and the crystal growth geometry (n_d) [30]. When polymers crystallize with spherulitic-type morphology (3D structure), the Avrami index value is usually in between 3 and 4, whereas when they crystallize with axialites-type morphology (2D aggregates) the Avrami index fluctuates between 2 and 3. But in both cases the final value will always depend on nucleation kinetics. Sporadic nucleation will produce values of $n=3$ (for axialites) and $n=4$ (for spherulites. or instantaneous). However, instantaneous nucleation yields n values of 2 and 3 for axialites and spherulites respectively [31,32].

The fits to the Avrami equation were calculated using the free Origin plug-in developed by Lorenzo et al. [24], and in Figure 6 an example of a representative fit of the Avrami model for the BS₂₅BAZ₇₅ copolymer crystallization at 24 °C is plotted.

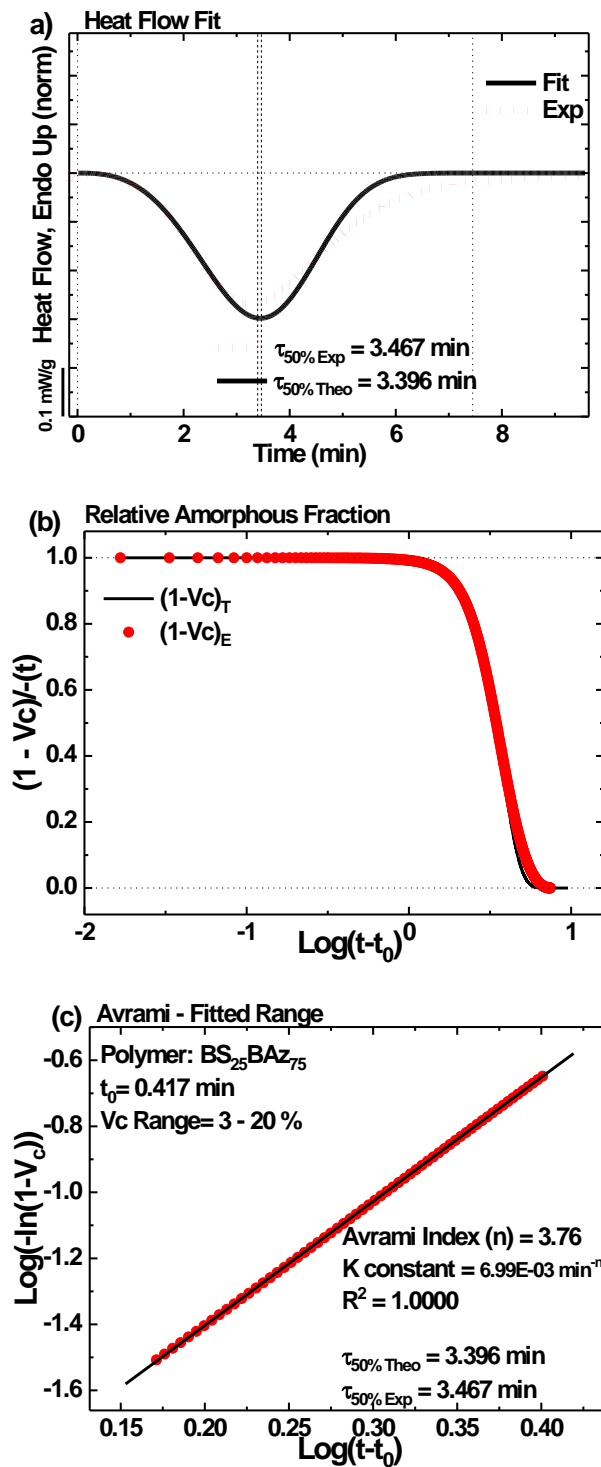


Figure 6. (a–c) The fits to the Avrami equation using the free Origin plug-in developed by Lorenzo et al. [24] and the experimental data for the BS₂₅BAZ₇₅ copolymer sample.

Even though Avrami fit estimations were made for all the compositions and at different crystallization temperatures, the result of the BS₂₅BAZ₇₅ copolymer

was taken as an example of the good fit between the Avrami model and the experimental data. In Figure 6c it can be observed how the Avrami equation can perfectly describe the overall crystallization kinetics of the chosen copolymer in the primary crystallization range, i.e., in a conversion range of 3–20%, with a correlation coefficient of 1.000. The fit of the Avrami equation was very good until at least 50% conversion (see Figure 6a and Figure 6b) and only experienced significant deviations from the experimental data beyond 75% conversion.

Figure 7 shows the Avrami index as a function of T_c for all the compositions. Most of the samples exhibited an expected Avrami index value between 2.5 and 4, since by PLOM spherulites were observed for all the samples. In addition, a general trend of increasing the Avrami index with temperature can be observed, due to a more sporadic nucleation produced at lower supercoolings (i.e., high crystallization temperatures). Nevertheless, some compositions exhibited Avrami index values close to 1.5, a value that can be approximated to $n = 2$, corresponding to instantaneously nucleated axialites (or 2D aggregates). If the nucleation density is very high, the development of 3D structures can be limited by their early impingement during growth, thereby forming axialites. The formation of axialites can be due to several reasons. It must be remembered that by adding BAz comonomer units to the PBS-rich copolymers, the nucleation density was greatly enhanced, and the samples in which PBS-rich phase crystallizes but with the highest BAz content show the lowest Avrami index values. On the other hand, the low isothermal temperatures, T_c values, used to study the overall crystallization rate by DSC, can produced an even more instantaneous nucleation. In DSC studies, the overall crystallization kinetics can be determined at lower temperatures than

those employed in determining spherulitic growth kinetics, as long as the sample does not crystallize during the cooling step to T_c (at 60 °C/min).

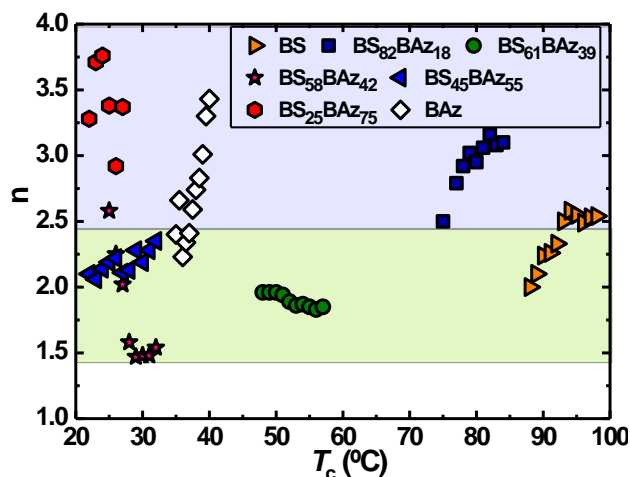


Figure 7. Avrami index as a function of T_c . The two shaded regions in the plot represent the values corresponding to Avrami indexes that can be approximated to $n=2$ and those in the upper shaded region, where the Avrami index fluctuates between 2.5 and 3.75, which can be approximated to 3 or 4 respectively.

Enthalpy of fusion of the 100% crystalline homopolymers

The heat of fusion of a 100% crystalline polymer ($\Delta H_{m(100\%)}^0$) is a required value for the estimation of crystalline fraction of polymers by DSC. In this work, we have reevaluated published values for both PBS and PBAz by employing a combined DSC and X-ray diffraction (WAXS) method.

In order to calculate the $\Delta H_{m(100\%)}^0$ of a polymer, the most commonly used method in the literature is to prepare samples with different crystallinity degrees (applying different cooling rates for instance) and then determine their crystallinities by WAXS. The experimental heats of fusion are determined by DSC, and then a plot is made of WAXS crystallinity degree versus enthalpy of fusion, that is extrapolated to 100% crystallinity. The difficulty in this method is that it is not easy to prepare fast crystallizing polymer samples (like PBS and PBAz) with

different crystallinities. In fact, if the available values from the literature are examined [33,34], they were determined by extrapolating 6 or less data points.

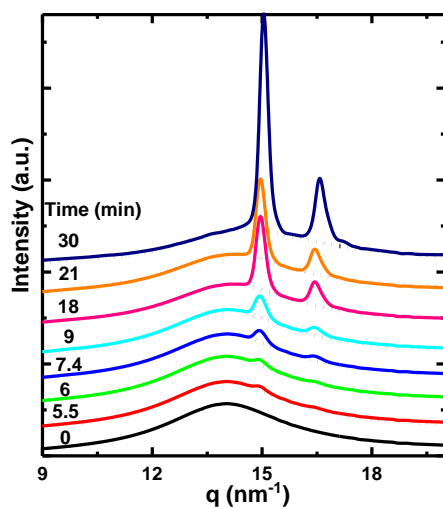


Figure 8. Selected WAXS patterns for PBAz homopolymer at different crystallization times at 34 °C. The included “dotted line” represents the amorphous halo (i.e., see curve at t=0 min).

In the present work, we propose simple method to determine the 100% enthalpy of fusion of a fast crystallizing polymer by making use of real time WAXS measurements at the synchrotron. A sample of each homopolymer was heated to erase its thermal history (at a temperature 30 °C higher than the melting peak registered by DSC at 10 °C/min) and then cooled at 50 °C/min to a selected crystallization temperature. During the isothermal crystallization process, WAXS patterns were obtained every 10 seconds until the sample completed its crystallization process. Employing the WAXS patterns, the crystallinity values were calculated using the relative areas under the crystalline peaks. Before the crystallization starts, just when the sample reaches the desired crystallization temperature after cooling from the melt, the sample is in the melt, so the WAXS pattern at time = 0 corresponds to the amorphous halo that is later used for the crystallinity calculations. Figure 8 shows an example of the WAXS patterns observed at different crystallization times at $T_c = 34$ °C for PBAz homopolymer.

The possible temperature differences that may exist between the DSC and the Linkam hot stage were taken into account by comparing the crystallization times that are measured by each technique for the same sample. Then any difference, which in the cases that were detected were always very small (less than 1 °C), can be taken into account by normalization.

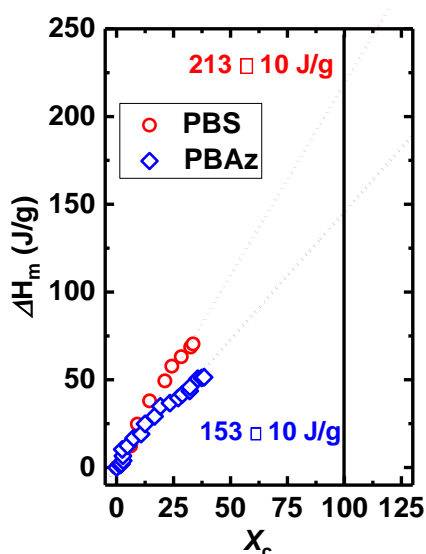


Figure 9. DSC crystallization enthalpy values as a function of crystallinity degrees obtained by WAXS.

In Figure 9, crystallinity degree values calculated by WAXS are plotted versus the crystallization enthalpy values obtained at each measured time from the respective DSC isothermal curve. Both DSC and WAXS measurements were done at 3 different isothermal temperatures for each homopolymer; however, only one example for PBAz is shown in Figure 8. The data for the other samples are reported in Figure S.2 of the Supplementary Information.

The values obtained with our method for the enthalpy of fusion of the 100% crystalline polyester were found to be $\Delta H_{m(100\%)}^0 = 213 \pm 10$ J/g for PBS and $\Delta H_{m(100\%)}^0 = 153 \pm 10$ J/g for PBAz. In the case of PBS, this value resulted higher

than $\Delta H_{m(100\%)}^0 = 110$ J/g estimated empirically by the group contribution method [35], but relatively close to the $\Delta H_{m(100\%)}^0 = 210$ J/g reported by Papagerorgiu et al. [34]. In the case of PBz, the new value resulted close to the $\Delta H_{m(100\%)}^0 = 160$ J/g estimated by the group contribution method [35] and also very close to the $\Delta H_{m(100\%)}^0 = 150$ J/g reported by Papagerorgiu et al. [33].

Equilibrium Melting Temperature (T_m^0).

The equilibrium melting temperature T_m^0 , is the melting point of lamellar crystals of infinite thickness and negligible surface effects on melting. It represents the first order transition of a hypothetical macroscopic perfect crystal [36]. It is very important to determine this parameter in order to analyze the crystallization growth kinetics, and in the case of copolymers every composition will show a different value of T_m^0 , as melting is a function of the nature, type and distribution of comonomer units [36]. In this work, several methods have been used to estimate this value.

The first method used to evaluate T_m^0 was The Thomson–Gibbs approach [27,37], which is based on the thermodynamic consideration that the melting temperature of a crystal of finite thickness is smaller than that of a crystal of infinite thickness. The Thomson–Gibbs approach is also considered a good way in order to obtain T_m^0 values of copolymers, since more than one experimental technique is used for its calculation, such as the DSC and SAXS. The method follows equation 2:

$$T_m = T_m^0 \left(1 - \frac{2\sigma_e}{l\Delta H_{m\%100}} \right) \quad (2)$$

where T_m^0 is the equilibrium melting temperature, $\Delta H_{m\%100}$ is the enthalpy per unit volume of a perfect crystal (100% crystalline), and σ_e is the fold surface free energy. Following this equation, experimental values of melting temperature obtained by DSC after isothermal crystallization are represented linearly as a function of the inverse of the lamellar thickness (l), determined by SAXS, and the intersection with the ordinate axis will represent the melting temperature of a crystal of infinite thickness, which is the equilibrium melting temperature of the defect-free crystal (Figure 10b).

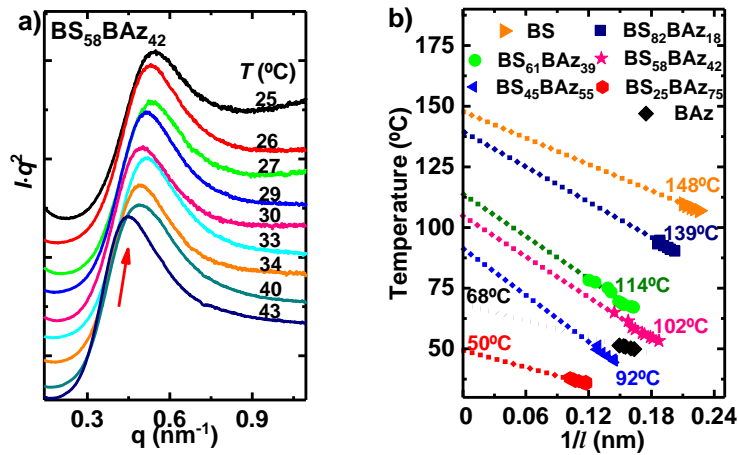


Figure 10. (a) Lorentz-corrected SAXS profiles, with $I \cdot q^2$ as a function of the scattering vector. (b) Representation of the Thomson–Gibbs plots to obtain T_m° for all PBSAz samples.

For each composition, between 5 and 9 samples were prepared and isothermally crystallized at different temperatures. For that, they were firstly heated to above 30 °C of their melting point during 3 minutes and afterwards cooled down at 60 °C/min (in order to prevent crystallization during cooling) to a chosen crystallization temperature. The samples were left at those temperatures the time required to crystallize and finally quenched to room temperature. Figure 10a shows the SAXS measurements performed to BS₅₈BAz₄₂ samples after the thermal

treatment explained above. All samples exhibit a clear intense maximum which is interpreted as the scattering caused by lamellar stacks, and from those q_{max} values, the long periods (d^*) were calculated by equation 3 from Lorentz corrected plots ($I \cdot q^2$ versus q):

$$d^* = (2\pi)/q_{max} \quad (3)$$

Lamellar thickness (l) values were calculated by employing the approximation $l = x_c \cdot d^*$, where x_c is the crystalline fraction. For that, after the SAXS measurements, DSC heating scans were also performed to the same samples in order to obtain the experimental melting points, melting enthalpies and therefore crystalline fractions [4]. Then applying the Thomson–Gibbs equation [27,37], the inverse of lamellar thickness values were plotted versus the experimental melting points of the isothermally crystallized samples (Figure 10b), and from the intercept the equilibrium melting temperatures (T_m^0) were determined (see Table2).

The second method used to estimate T_m^0 values was the Hoffman-Weeks plot [38], which involves the extrapolation of a linear region of melting temperatures (T_m) observed experimentally at various crystallization temperatures (T_c), to the thermodynamic equilibrium line $T_m = T_c$ [39,40]. From the intercept T_m^0 is calculated.

Figure 11a shows an example of the DSC heating scans after the previous isothermal crystallization at different temperatures for BS₈₂BAZ₁₈ copolymer. Despite the fact that two peaks were observed at low temperatures, only the peak which varies when the T_c increases was taken into account, since the second peak occurs after a recrystallization process during the heating scan and did not reflect

the melting of the isothermally formed crystals. In addition, the extrapolation of melting temperatures T_m to the thermodynamic equilibrium line $T_m = T_c$ of all compositions is observed in Figure 11b, and T_m^0 values of the intercept showed in Table 2.

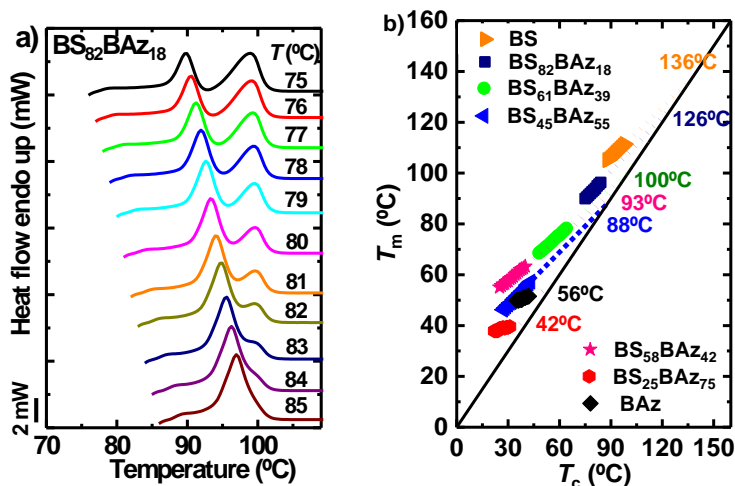


Figure 11. (a) DSC heating scans after a previous isothermal crystallization at different temperatures in BS₈₂BAZ₁₈ copolymer. (b) Hoffman–Weeks plots for all compositions (the black solid line represents the thermodynamic equilibrium line $T_m = T_c$).

Table 2 and Figure 12 report the T_m^0 obtained by both methods. For comparison purposes, we include in both Table 2 and Figure 12 the end melting temperatures determined by DSC on non-isothermally crystallized samples (previously cooled from the melt at 20 °C/min and then heated at the same rate). These are the temperatures where the endothermic signal of the DSC trace finally disappears and joins the DSC base line, i.e., when all traces of crystallinity disappear. These values represent the experimental melting points of the thickest possible lamellae in the material, even if they had reorganized during the heating DSC scans.

Table 2 and Figure 12 also show the end melting temperatures determined during the final heating DSC scans of samples submitted to Successive Self-nucleation and Annealing (SSA) thermal fractionation obtained from a previous

work [21]. The final melting temperature after SSA treatment [41] represents the melting of even thicker lamellae as this method promotes successive annealing.

Hoffman-Weeks and Gibbs-Thomson methods give extrapolated values that theoretically represent the fusion of infinite crystals, without surfaces or defects and with extended chains. Therefore, they should always be greater than any experimental value. In general terms, this expectation is corroborated in Table 2 and Figure 12.

Table 2. Experimentally obtained end melting temperatures ($T_{m(end)}$) and equilibrium melting temperatures, T_m^0 ($^{\circ}\text{C}$), obtained by different techniques

	$T_{m(end)}$ from DSC scans	$T_{m(end)}$ from SSA	T_m^0 Hoffman- Weeks (HW)	T_m^0 Gibbs- Thomson (GT)	T_m^0 (SSA/GT)
BS	118	119	136	148	148
BS₈₂BAz₁₈	100	101	126	139	129
BS₆₁BAz₃₉	79	80	100	114	108
BS₅₈BAz₄₂	68	73	93	102	101
BS₄₅BAz₅₅	58	62	88	92	90
BS₂₅BAz₇₅	41	43	42	50	63
BAz	46	48	56	68	68

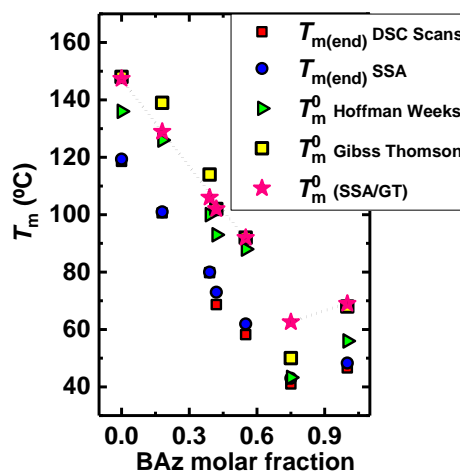


Figure 12. Experimentally obtained end melting temperatures ($T_{m(end)}$) and equilibrium melting temperatures, T_m^0 ($^{\circ}\text{C}$), versus BAz molar content.

The T_m^0 determined by Hoffman-Weeks for pure PBS (136 °C) is similar to previously reported values (125 - 134 °C) [34,42-44], and the T_m^0 measured by Gibbs-Thomson (148 °C) is also similar to reported values in the literature that have employed the same method (146.5 °C) [34,43]. In the case of PBAz, only values obtained from Hoffman-Weeks extrapolation were found in literature [23,33], 53 °C and 67 °C respectively which agree very well with the value obtained in this work (56 °C).

In the case of the extrapolated T_m^0 values for the copolymers, determined by both GT and HW methods, a significant scattering of the data as a function of composition can be seen in Figure 12, which is a consequence of both experimental errors and extrapolation errors.

In order to get a smoother trend with composition, we have performed a reasonable approximation, which is also reported in Table 2 and Figure 12. In the case of homopolymers, the T_m^0 data is usually considered more reliable than in the case of copolymers [36]. If the data related to PBS in Table 2 is examined, the differences between SSA experimental melting point and the highest T_m^0 values obtained by GT is 29 °C. In other words, the ideal crystals have an equilibrium melting temperature which is 29 °C higher than the apparent or experimentally determined melting temperature of the thickest possible crystals that can be prepared by SSA. Therefore, we have assumed that the 29 °C difference can also hold for the PBS-rich copolymers phase and we have added this constant value to the experimentally determined SSA value in order to estimate T_m^0 values (and they are labeled $T_m^0_{(SSA/GT)}$ in Figure 12) that have a smoother trend with copolymer composition and are in fact not far from the values determined by GT method as reported in Table 2. For PBAz-rich phases, the added factor was 20 °C in

correspondence with the difference between SSA experimental melting point and the highest T_m^0 values obtained by GT. Figure 12 shows straight lines fit for the values corresponding to $T_m^0_{(SSA/GT)}$ and it is observed that they can be used as an approximate representation of the variation of T_m^0 with composition, as these values are quite close to those obtained by both GT and HW methods. These $T_m^0_{(SSA/GT)}$ values are reported in Table 2 and they were employed to perform the fittings to the copolymer melting theories presented in what follows.

Using the calculated equilibrium melting temperature and following exclusion-inclusion theories, the partitioning of comonomer units between the crystalline and amorphous phase can be analyzed in random copolymers. Those models interpret the effect of exclusion and inclusion of comonomeric sequences in copolymer crystals, or the effect of composition on competition for cocrystallization when inclusion occurs.

The theories that assume comonomer exclusion from the crystal into the amorphous phase are the Flory [45] and Baur [46] exclusion theories. Subsequent theoretical works, Sanchez and Eby [47] or Wendling and Suter models [48], take into account the inclusion of the comonomer B in crystals of the A repeating unit, suggesting that when the B comonomer is partially included into the crystals of A, it acts as a defect modifying the equilibrium melting point. In order to deal with comonomer inclusions, the defect Gibbs free energy (ε) is included in comonomer inclusion models. Furthermore, Wendling and Suter proposed a more thorough treatment of the problem to account for isodimorphic behavior, employing a new parameter, which considers the comonomer fraction that is cocrystallizing, besides of the above mentioned ε parameter.

The Wendling-Suter model (equation 4) takes into account the energy required by the minor comonomer repeat units to be introduced into the crystal lattice of the major comonomer and also assumes that the free energy penalty paid to accommodate a defect in the crystal decreases while the amount of included comonomer increases:

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

where T_m^0 and ΔH_m^0 are the homopolymer equilibrium melting temperature and heat of fusion, X_B is the concentration of the minor comonomer B in the copolymer, R is the universal gas constant and X_{CB} is the concentration of B units in the crystal. If there is an equilibrium comonomer inclusion, the concentration of comonomer B units in the crystal is given by:

$$X_{CB}^{eq} = \frac{X_B e^{-\varepsilon/RT}}{1 - X_B + X_B e^{-\varepsilon/RT}} \quad (5)$$

and when X_{CB} in equation (4) is substituted by equation (5), it gives a simplified equation:

$$\frac{1}{T_m^0} - \frac{1}{T_m(X_B)} = \frac{R}{\Delta H_m^0} \{ \ln(1 - X_B + X_B e^{-\varepsilon/RT}) - \langle \xi \rangle^{-1} \} \quad (6)$$

where:

$$\langle \xi \rangle^{-1} = 2(X_B + X_B e^{-\varepsilon/RT}) \cdot (1 - X_B + X_B e^{-\varepsilon/RT}) \quad (7)$$

The ξ parameter takes into account the comonomer units that are cocrystallizing.

In the case of our experimental data we found that the models by Flory, Baur and Sanchez-Eby were not able to give good fits (see Supplementary Information), hence we only present here the fittings performed with the Wendling-Sutter model.

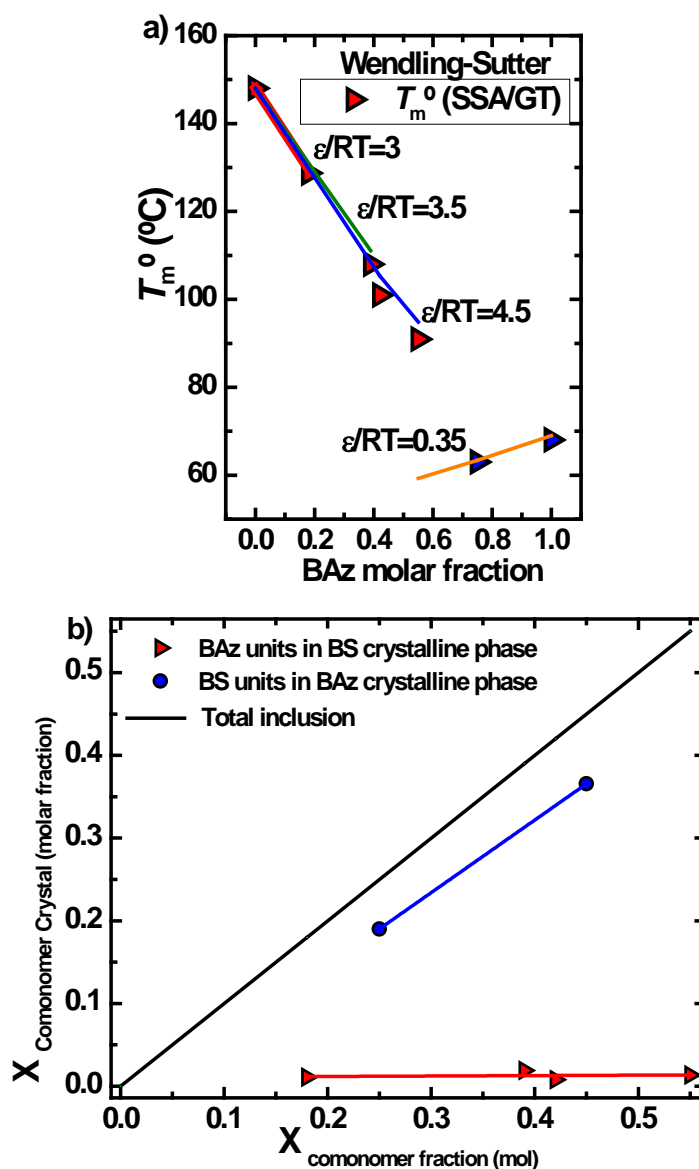


Figure 13. (a) Comparison of the experimental equilibrium melting temperatures with the theoretical melting temperatures predicted by the Wendling-Sutter equation. (b) Equilibrium concentrations of the minor comonomer units in the crystal of the homopolymer corresponding to the major comonomer, as a function of copolymer composition.

Figure 13a shows the results of employing the Wendling-Suter model to predict the equilibrium melting temperatures of PBSAz copolyesters (straight lines) in comparison with T_m^0 (SSA/GT) values previously described (data points).

The results predicted by using Flory, Baur and Sanchez-Eby models are plotted in Figure S.3 in the Supporting Information. The Flory and Sanchez-Eby models do not fit the experimental values, since they overestimate the equilibrium melting temperatures. In contrast, the predicted values by the Baur model are the lowest ones, and can partially fit some of the PBS-rich compositions data. However, the Baur model does not fit the PBaz-rich compositions data. The results of applying the Flory, Baur and Sanchez-Eby models are in line with previous works [22], in which it was found that a higher amount of comonomer exclusion dominates over inclusion in isodimorphic copolymers crystallization.

The Wendling-Suter model shows the best fit to the experimental data for lower comonomer content and allows to calculate the defect Gibbs free (ε) energy for each composition. Table 3 shows ε values, calculated from the function ε/RT which was determined as an adjustable parameter. In case of including BAZ comonomer units in PBS-rich crystals, ε values tend to increase and they are higher than in the case of incorporating BS repeating units into the PBaz-rich crystal. This ε low value indicates that BS units are much easier to include within PBaz crystal unit cells. This result together with Baur's model poor fit, leads to the conclusion that the comonomer inclusion in PBaz-rich phase is larger than expected. Therefore, this theory is in good agreement with the results obtained for the isothermal crystallization of PBaz-rich compositions (Figure 5b), which

showed that when $(1/\tau_{50\%})$ values are plotted against supercooling (ΔT), the curves in the x-axis and vertical axis are superimposed.

The Wendling-Suter model was also used to estimate the percentage of the minor comonomer units incorporated in both cases, for PBS-rich and PBAZ-rich crystalline phases. Using Eq. (5), the equilibrium concentration of minor comonomer repeat units into the crystal was calculated (see Table 3) and also plotted as a function of minor comonomer fraction in Figure 13b.

Table 3. Values of the average defect Gibbs energy (ε) and the percentage of comonomer inclusion (X_{CB}) for the PBAz inclusion into a PBS Crystal and for PBS inclusion into BAz Crystals obtained by Fitting Eq. 5 to the experimental data. Note that the subscript indicate which material is included (e.g., $X_{CB,BAz}$ is the percentage of comonomer inclusion of BAz into BS crystals)

PBAz content	ε_{BAz} (kJ/mol)	$X_{CB,BAz}$
0	0	0
0.18	10.03	0.01081
0.39	11.09	0.01894
0.42	13.99	0.00798
0.55	13.74	0.01339
PBS content	ε_{BS} (kJ/mol)	$X_{CB,BS}$
*0.45	0.68	0.37738
0.25	0.84	0.19803
0	0	0

*Value obtained from an extrapolated T_m^0 value

In the case of PBS-rich compositions, the % comonomer included in the crystal is very small. This is clear in Figure 13b when the obtained values are compared with total inclusion case ($X_{CB}=X_B$). On the contrary, for PBAZ-rich compositions, a large amount of comonomer inclusion is predicted. This latter result is in good agreement with the conclusion obtained in our previous work [22], where dielectric spectroscopy measurements were carried out with same copolymers in order to calculate the relative fractions of both comonomers

incorporated in the crystalline phase. In the case of BS₂₅BAZ₇₅ sample, dielectric spectroscopy detected a fraction of BS comonomer units being involved in the crystallization (as it was absent from the amorphous regions). However, DSC indicated for this copolymer that the PBS phase cannot crystallize, therefore it was concluded that these BS units must be incorporated in the PBaz-rich crystalline phase.

Conclusions

Two different behaviors were found when analyzing the isothermal crystallization of PBSAz random copolymers. Firstly, the incorporation of BAz-units greatly affected the crystallization of PBS-rich compositions, increasing the density of nuclei and slowing down the spherulitic growth rate due to the difficulty of incorporating units of this minor comonomer inside PBS crystals. On the other hand, a very different behavior was found in PBaz-rich compositions, where the incorporation of BS-units not only did not affect the crystallization of this copolymer significantly, but also caused an antinucleating effect.

The use of the different inclusion-exclusion models together with the calculated equilibrium melting point values allowed us to conclude that in the case of PBS-rich compositions, only a small portion of BAz comonomer units can be included within PBS crystals, while in the case of PBaz-rich compositions, a larger inclusion of BS-units is possible. Results corroborated that the crystallization behavior of isodimorphic copolymers is largely affected by the amount of comonomer inclusion in their crystal lattices, and consequently it has a direct effect in their crystallinity degree, crystallization rates and in the pseudo-eutectic composition.

Techniques such as WAXS, SAXS and DSC were successfully used in order to calculate the equilibrium melting temperature of these random copolymers. Additionally, the enthalpy of melting of 100% crystalline PBS and PBAz were determined by a different and practical approach: extrapolating real time synchrotron Wide Angle X-ray Scattering (WAXS) isothermal crystallization data and isothermal DSC data.

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