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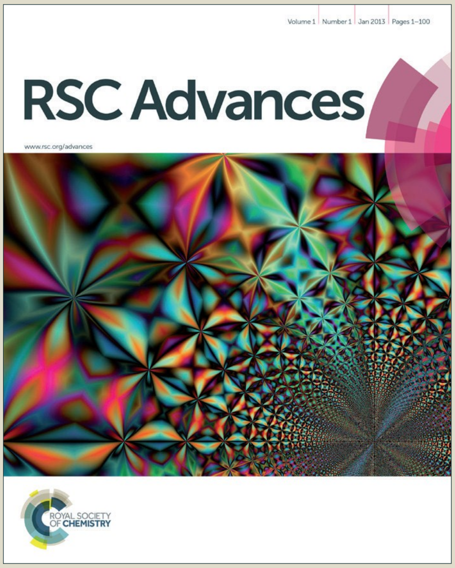

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Efficient stereocomplex crystallization in enantiomeric blends of high molecular weight Polylactides.

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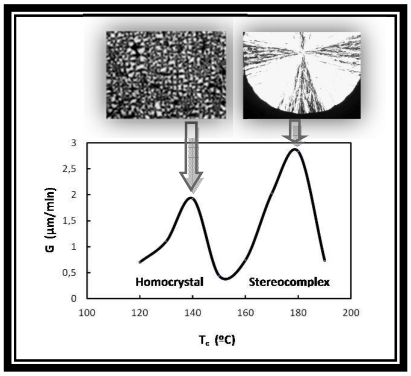
Abstract

The crystallization behavior of the high molecular weight equimolar mixture of optically pure poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) is investigated in order to analyze the factors affecting its stereocomplexation. PLLA/PDLA blend films at 1:1 molar ratio were prepared by solvent casting and isothermally crystallized from as cast samples (cold-crystallization) and from molten samples (melt-crystallization). The crystallization behavior was analyzed by means of DSC, PLOM, WAXD and FTIR. The experimental evidence indicates that stereocomplexation is much more efficient in cold crystallized samples than in melt crystallized ones. To achieve exclusive stereocomplexation with a high degree of crystallization from high molecular weight polylactides ($M_w > 2 \cdot 10^5$ g mol^{-1}) samples must be crystallized above the melting point of the homocrystals, the thermal treatment must increase the number of nucleation points and adverse transesterification reactions must be avoided.



Keywords: polylactide, blends, crystallization, stereocomplex,

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1. Introduction

Ikada et al. first published the existence of a stereocomplex in mixtures of isotactic polylactides (PLAs) with opposite configuration in 1987.[1] This particular structural organization has attracted a significant amount of research, with studies into the effects of various parameters during the formation of stereocomplex crystals, such as the mixing ratio of isomers,[2-4] the molecular weight,[5,6] optical purity (isotacticity),[2,7] mixing conditions,[8,9] and time and temperature treatments.[2,7,10]

Stereocomplexation has been observed in copolymers based on the two enantiomers of lactid acid,[11-13] and on enantiomeric mixtures of PLAs,[2,9,14-16] and is a result of the improved spatial match found between lactide units, bringing the enatiomeric chains into closer contact, improving the compact molecular packing, and the strengthening of intermolecular interactions.[10,17] The molecular weight of the PLAs and the composition of the blend are key factors regarding the stereocomplexation behaviour. The crystallization of PLLA or PDLA homocrystals usually overrides stereocomplex crystallization when the mixtures are prepared from high molecular weight polylactides.[6,18] Tsuji and Ikada reported that polylactides exclusively crystallized in the stereocomplex form can only be found below a critical molecular weight $M_w \sim 1.0 \times 10^5$.[19] Regarding the effect of composition, the study of asymmetric mixtures of PLLA/PDLA has shown that ordered regions can contain both homopolymer and stereocomplex crystals, provided that the amount of PDLA exceeds 10%.[2] But when PDLA is added in small amounts (below 10%),[20] the formation of stereocomplex crystals prompts homo-crystallization; the stereocomplex crystals act as nucleating agents inducing homocrystal formation on its surface, both crystals being in contact, a process known as epitaxial crystallization.[18,21-26]

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On the other hand, the thermal treatments usually carried out to obtain stereocomplex crystals are usually carried out at high temperatures, and it is necessary to consider the possibility of certain thermal degradation. Thermal degradation reactions in PLAs include hydrolysis, inter-chain transesterification and depolymerization by back-biting (intramolecular transesterification).[27,28] Hydrolysis is a water-based degradation mechanism of PLA in which a chain is split into two sub-chains. This process is not expected to be significant in properly dried samples, and if occurs it should increase the stereocomplexation rate because PLAs of reduced molecular weight are known to cocrystallize faster. Intramolecular transesterification, or "back-biting", leads to the formation of cyclic polylactide oligomers and the reduction of molecular weight.[27-30] On the other hand, intermolecular transesterification reactions in a blend of optically pure polylactides will reduce the optical purity (isotacticity) of the chains, reducing therefore the ability of the blend to cocrystallize.[27-30]

The present study analyzes the crystallization of racemic PLLA/PDLA blends of high molecular weight polylactides ($M_w > 200{,}000$ g mol^{-1} for both PLAs). Isothermal crystallizations were carried out at different crystallization temperatures and times directly from melt and from as cast samples in order to understand the key factors controlling the stereocomplexation process and to establish the conditions that favour cocrystallization over homocrystallization. Kinetic and morphological aspects are also described and discussed.

2. Experimental Section

2.1. Starting Materials

PLLA (Biomer® trade name) with $M_w = 2.1 \cdot 10^5$ g mol^{-1} and $M_w/M_n = 1.58$ (as determined by GPC) was supplied by the German firm *Biomer*. PDLA with M_w =

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$3.5 \cdot 10^5$ g mol^{-1} and M_w/M_n = 1.92 was obtained from Purac Biochem (The Netherlands).

2.2 Film preparation

PLLA and PDLA pellets were dried overnight in a vacuum oven at 30 ºC prior to processing. Films were prepared with an approximate thickness of 30 μm by casting into petri dishes from 1 wt % chloroform solutions at room temperature. The mixing ratio of PLLA and PDLA was fixed to 1:1 in the blend film, hereafter named B-5050. Residual solvent was further removed in a vacuum oven at 30 ºC for 24 h. Predominantly amorphous samples were obtained in all cases, as assessed by FTIR spectroscopy using the bands located in the 900-1000 cm^{-1} spectral region (see supplementary information).

2.3. Thermal treatments

Two types of thermal treatments were carried out so as to achieve different degrees of crystallinity and separate studies were made into the development of homocrystals (α) and stereocomplex crystals (η) in the racemic mixture of polylactides. On the one hand isothermal crystallizations at different temperatures between 120 and 190 ºC for 1 and 24 h were performed in an oven on the cast films (cold crystallizations). Samples were then allowed to cool into a desiccator prior to subsequent analyses. On the other hand, isothermal melt-crystallization was also performed within this same temperature range on the films molten at 250 ºC for 2 min followed by a rapid quenching in the DSC to the crystallization temperature.

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2.4. Differential Scanning Calorimetry (DSC)

Thermal analysis of the films was conducted on a DSC 2920 thermal analyzer from TA Instruments. All scans were carried out in hermetic aluminium pans under a nitrogen atmosphere for sample weights of approximately 5 mg. The analysis procedure consisted of a heating scan from 0 to 250 ºC at a heating rate of 10 ºC min^{-1}. The crystallization and melting peaks of homocrystals and stereocomplex crystals were analyzed and the structural changes resulting from the heat treatments were quantified by measuring the corresponding melting enthalpies.

The overall crystallinity degree of PLLA/PDLA blends was calculated as:[16,26]

$$X_c\,(\%) = \frac{\Delta H_H + \Delta H_S - \Delta H_c}{\Delta H_m^o} \times 100 \qquad (1)$$

ΔH_H and ΔH_S are, respectively, the experimental melting enthalpies of the α homocrystal and the η stereocomplex crystal polymorphs of polylactide, ΔH_c is the exothermic enthalpy change (cold crystallization) observed during the heating DSC scan, and ΔH_m^0 is the theoretical value of melting enthalpy for perfect crystals. This value is different from those corresponding to the pure α and η crystals (106 J g^{-1} and 142 J g^{-1} respectively[10]), and is calculated by taking into account the relative amounts of both crystalline forms according to the following equation:

$$\Delta H_m^0 = \Delta H_H^0 \cdot X_{Homo} + \Delta H_S^0 \cdot X_{Stereo} \qquad (2)$$

where X_{Homo} and X_{Stereo} are the fractions of the total crystallinity corresponding respectively to homopolymer and stereocomplex. Notice, however, that that the determination of initial crystallinities using conventional DSC is known to involves some uncertainty,[31] and the procedure outlined above only intends to provide estimate values.

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2.5. Polarized Light Optical Microscopy (PLOM)

The spherulitic morphology of PLLA/PDLA blends was studied in a Leica DMLM optical microscope operating with a Mettler-Toledo (model FP82HT) controlled heating/cooling stage system. The evolution of crystalline morphology produced at different crystallization temperatures was followed *in situ* with a warming plate connected to the microscope. Isothermal crystallizations were carried out from the melt after rapid quenching to the selected crystallization temperature: 120, 130, 140, 150, 160, 170, 180 and 190 ºC. Images were taken at different times until crystallization rates became negligible. Spherulite sizes were obtained from the PLOM images using the image analysis program "FIVE docu analysis" from Olympus Soft Imaging Solutions.

2.6. X-ray Diffraction (WAXD)

Cold-crystallized samples (isothermal crystallizations at the above mentioned temperatures for 24 h.) were analyzed by WAXD. The X-ray powder diffraction patterns were collected using a PHILIPS X'PERT PRO automatic diffractometer in theta-theta configuration, secondary monochromator with Cu-K_{α} radiation (λ = 1.5418 Å) and a PIXcel solid state detector. The sample was mounted on a zero background silicon wafer fixed in a generic sample holder. Data were collected from 10 to 25° 2θ (step size = 0.026º) at room temperature.

2.7. Infrared Spectroscopy

Melt-crystallization at 190 ºC (after melting for 2 min. at 250 °C) was analyzed by FTIR. This temperature was chosen because it ensures the stereoselective crystallization of the polylactide exclusively in the stereocomplex form since the α crystalline polylactide melts at 180 °C. Infrared spectra of the blends were recorded on a Nicolet

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AVATAR 370 Fourier transform infrared spectrophotometer (FTIR). Spectra were taken with a resolution of 2 cm^{-1} and were averaged over 64 scans. Chloroform solutions containing 0.25 wt% polylactide were cast on KBr pellets, and samples were vacuum-dried at 60 °C for 48 h. The absorbance of the samples was within the range where the Lambert-Beer law is obeyed. Second-derivative spectra were smoothed with a quartic 11-point Savitzky-Golay smoothing filter.

3. Results and discussion

3.1. Isothermal melt-crystallizations.

The isothermal melt crystallization of the B-5050 blends was studied by polarized light optical microscopy (PLOM) to gain information on the spherulitic crystallization: growth rate, induction period, the temperature range at which each type of crystal can be observed, and the crystalline morphology. For this purpose, isothermal crystallizations were performed with varying degrees of undercooling to differentiate the crystallization of α and η crystals. Upon completion of the isothermal crystallizations in the 120 - 190 ºC temperature range, the temperature was raised above the melting temperature of the α crystal, in order to verify whether the spherulites obtained are homocrystals or stereocomplex, because at first glance their appearance is very similar.

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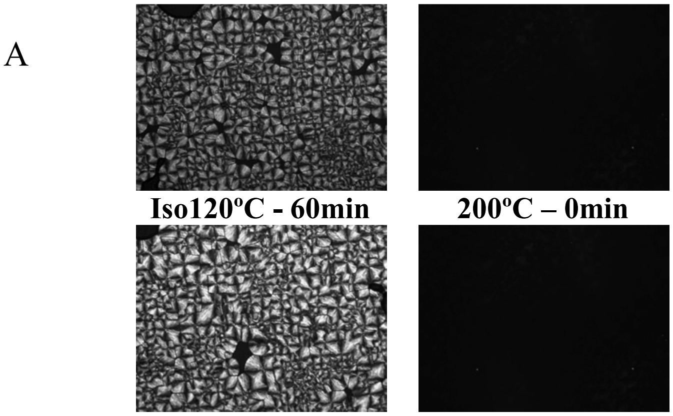

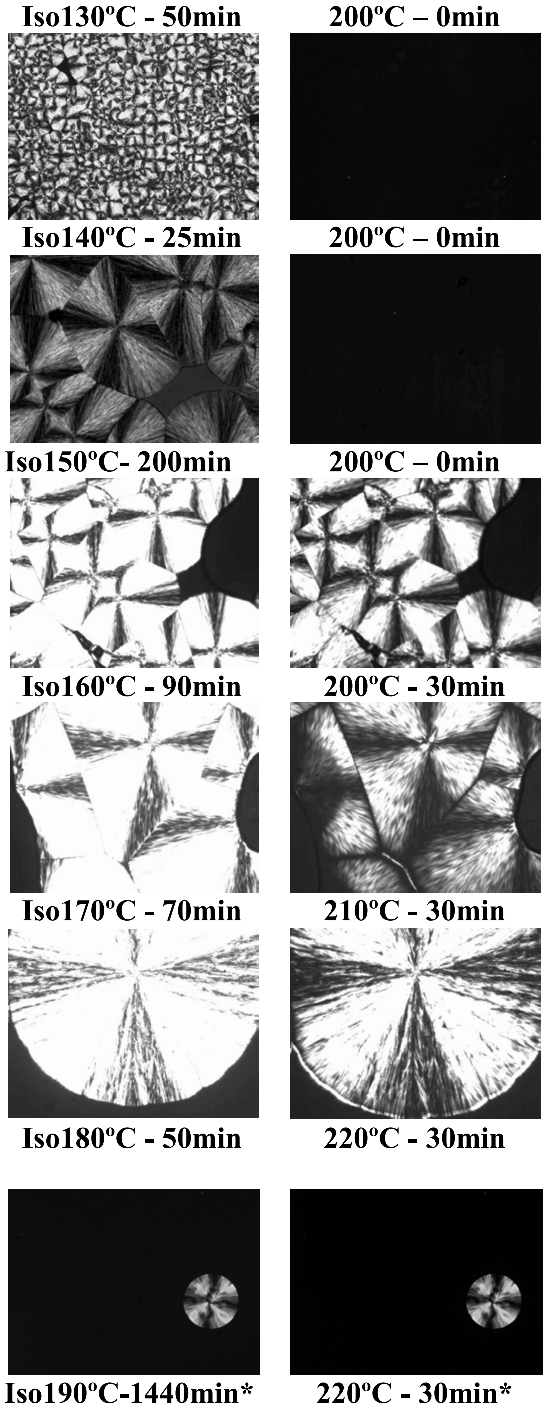

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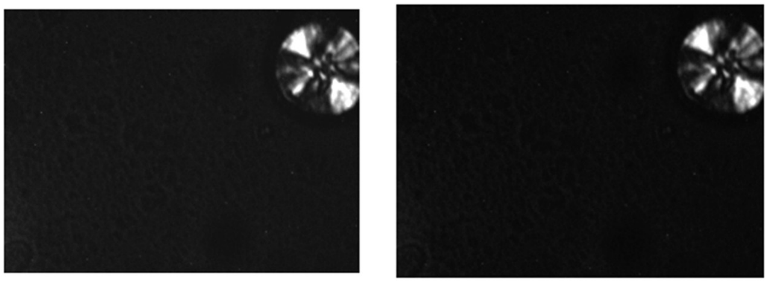
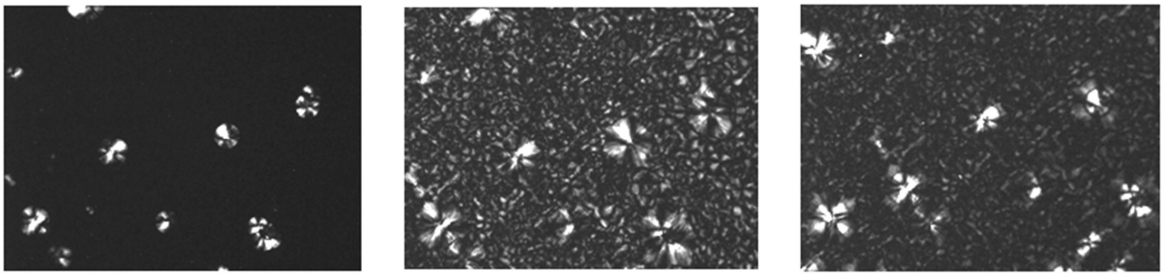
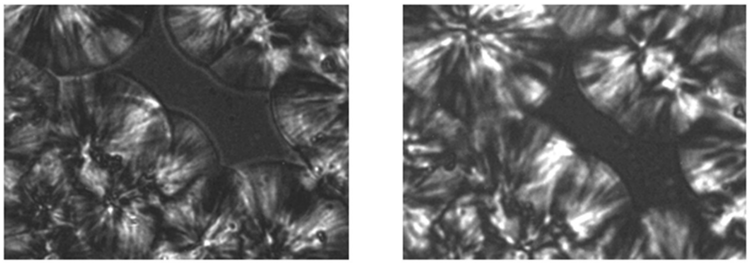


Iso190ºC-1440min* **140ºC - 120min***



Iso190ºC-120min **140ºC - 120min** **200ºC - 30min**



Iso180ºC - 65min **140ºC - 120min**

Figure 1A. Spherulitic morphology of the B-5050 blends crystallized from the melt in the 120 - 190 ºC temperature. The left-hand column shows the spherulites obtained after complete crystallization (when the full space is filled with spherulites, or when crystallization rate falls down to zero), and the right-hand column shows unmolten spherulites when temperature is raised above the melting point of the α crystal. The images represent an area at the surface of the sample of 357 x 261 μm^2 (except images marked with *, 143 x 104 μm^2). *Figure 1B.* Samples crystallized from the melt at 180 and 190 ºC and subsequently annealed at 140 ºC for 2 hours.

The left-hand column in Figure 1 shows PLOM images recorded at various isothermal crystallization temperatures for the B-5050 blend. As can be seen, the number of nucleation points decreases as the crystallization temperature increases, allowing the growth of larger spherulites at these temperatures. The crystallized samples

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were then heated to a temperature intermediate between the melting points of the homocrystal and the stereocomplex crystal (in the 200-220 ºC range) to detect the type of crystals obtained in each case. As can be seen in the right-hand column in Figure 1, samples crystallized at temperatures below 160 ºC and subsequently heated to 200 ºC show a major loss of crystallinity, indicating that homocrystallization occurs preferentially in those samples during the isothermal crystallization stage. Notice, however, that the presence of small nuclei or small remanent stereocomplex crystallites cannot be discarded from the PLOM images at 200 ºC. On the other hand, samples crystallized at temperatures starting from 160 °C show quantitative remanent crystallinity at temperatures above 200 °C, suggesting the presence of stereocomplex crystals. In particular, the spherulites formed at 180 and 190 ºC (which should not contain homopolymer since the neat PLAs used in this study melt at temperatures below 180 ºC) remain unmelted at 220 ºC (see Figure 1), as expected for stereocomplex crystals with a high melting temperature. These results along with the evidences obtained in the following sections indicate that as the crystallization temperature approaches the melting temperature of the homocrystals (Tm in the 170-180 ºC range), homocrystallization is progressively replaced by stereocomplexation. In this “transition” region (160-170 ºC) homocrystallization can compete with stereocomplexation, and might limit the growth/perfection of the stereocomplex lamellae, explaining the lower melting temperatures observed for the sterocomplex crystals obtained at these intermediate temperatures. Finally, PLOM images reveal that both types of crystals have a very similar morphology, although the stereocomplex spherulites present higher birefringence.

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In addition, it is necessary to point out that complete primary crystallization could not be obtained for the sample isothermally crystallized at 190 ºC. At this temperature the crystal growth rate remains constant during the first hour, but then decays progressively to reach zero after four hours (see supplementary information). This behaviour can be attributed to two possible reasons: the occurrence of phase separation during crystallization[9] or degradation of the blend through intermolecular transesterification reactions (see introduction). Phase separation can occur in high molecular weight samples because in these systems only small differences in chemical nature (different molecular weights or optical purities) are necessary to render immiscible systems. On the other hand, it is also true that molten enantiomeric PLAs tend to establish favourable interactions (the formation of a mesophase prior to the formation of the stereocomplex crystals has been reported),[32] that should stabilize the homogeneous melt. Regarding the intermolecular transesterification reactions, these should reduce the optical purity (isotacticity) of the chains, reducing therefore the ability of the blend to cocrystallize.[27,28] A second set of PLOM experiments (Figure 1B) has been therefore carried out to understand the crystallization stopping observed at high isothermal crystallization temperatures. In the first experiment, the B-5050 blend has been isothermally crystallized from the melt at 190 ºC for 24 hours and then isothermally crystallized at 140 ºC for 2 hours. As can be seen, the PLOM images do not show any additional crystallization during the second annealing stage, indicating a degraded sample (homocrystallization should be expected in a phase separated but non-degraded blend). In the second experiment, the sample has been isothermally crystallized from the melt at 190 ºC for 2 hours (since certain growth rate slow down can be observed after this time) and then isothermally crystallized at 140 ºC for 2 hours. During the second annealing stage additional crystallization is observed, but

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birefringent entities of significant size cannot be observed for most of the new crystals. In addition, when these crystals are heated to 200 ºC (see Fig. 1B), they do not melt indicating that they do not consist on the pure homopolymers. These crystals are not characteristic of a phase-separated amorphous system (where regular homocrystals should be expected), and can be therefore attributed to stereocrystals nucleated from the transient mesomorphic phase.[32,38,39] The partial order existing in the mesomorphic phase promotes the fast crystallization of the sample upon cooling and the formation of the non-spherulitic crystalline morphologies observed in Figure 1B. In a recent study dealing with the stereocomplex crystallization of PLAs, Yang et al. attributed about one half of the stereocomplex crystals obtained from PLA blends to the crystallization of the mesomorphic clusters formed within the amorphous phase, whilst the other half was attributed to crystal growth via the traditional route of surface nucleation of amorphous chains.[32] Finally, the sample crystallized from the melt at 180 ºC and subsequently annealed at 140 ºC also shows additional crystallization during the second annealing stage. However, since in this case crystallization at 180 ºC was carried out to completion, the new crystals grow over the already formed stereocomplex spherulites. These results suggest that stereocomplex crystallization at temperatures above the Tm of the homocrystals proceeds both by surface nucleation and clustering of a transient mesophase,[32] and that polymer degradation becomes a concern for the samples crystallized at sufficiently high temperatures and for long times.[27-30] According to these results, the growth rate slow down observed during crystallization at 190 ºC should not be attributed to phase separation during crystallization, since this hypothesis is not consistent with the nature of the observed crystals.

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Figure 2 shows the spherulite growth rate obtained from PLOM experiments against the crystallization temperature. A bimodal behavior can be observed, with maxima located at about 140 ºC and 180 ºC. According to the results discussed in the preceding paragraph, the maximum at 140 ºC is attributed to the maximum growth rate of the homocrystal (crystallized from the blend, not from the pure amorphous phase), and the maximum at 180 ºC to the maximum growth rate of the stereocomplex (at this temperature the homocrystal is molten). In agreement with recent reports,[14] the stereocomplex shows higher growth compared to the homocrytals.

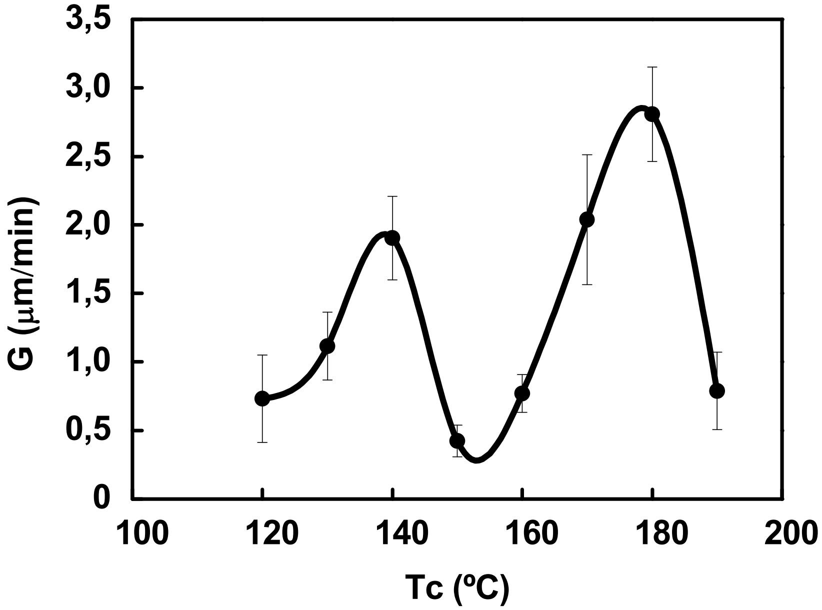

Figure 2. Radius growth rate of spherulites (G) of B-5050 blends as a function of crystallization temperature (T_c).

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Figure 3 shows the DSC thermograms of B-5050 blends melt-crystallized at temperatures between 120 and 190 ºC. Notice that these curves display features corresponding not only to the structures formed during the isothermal stage but also during the fast cooling ramp from the crystallization temperature and the subsequent heating scan. As can be seen, samples melt-crystallized at temperatures up to 150 ºC show two main endothermic signals with an exothermic deviation of the baseline between them. The signal located at about 170 ºC is actually a double peak corresponding to polylactide homocrystals, and the single peak located at about 215 ºC corresponds to the stereocomplex crystal. The multiple melting behavior observed for the homocrystals in the crystallization experiments performed up to 150 ºC can be ascribed to recrystallization during melting or to the melting of crystalline structures with different morphology.[33,34] Recrystallization during melting consists on the formation of higher melting crystals during the melting process of the initial crystals (grown during the isothermal crystallization stage). As a consequence, the melting temperature of the higher melting peak is nearly independent of the crystallization temperature.[33,34] However, since the double melting peaks corresponding to the homocrystals shift to higher temperatures with crystallization temperature (see Figure 3), the hypothesis of recrystallization during melting should be discarded. Hence, the double melting behavior observed for the samples crystallized at temperatures up to 150 ºC can be attributed the melting of morphologically different crystal structures, probably occurring as a consequence of the different molecular weights of the pure homopolymers. Referring to the single peak located at about 215 ºC, which corresponds to the stereocomplex crystal, its location remains practically unaffected by the crystallization temperature. Hence, this peak can be attributed to a stereocomplex formed during the heating scan, after the melting of the homocrystals. This explains the observed broad exothermic contribution located at about 190 ºC.

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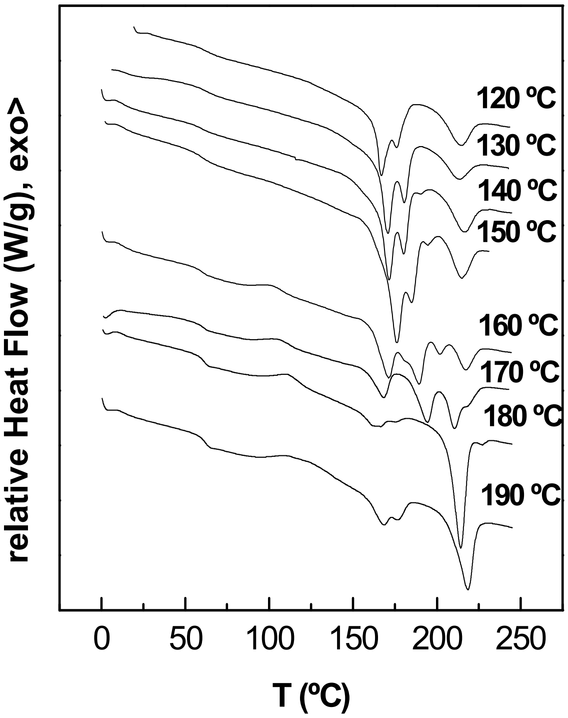

Figure 3. DSC curves of the B-5050 blends after crystallization from the melt at different temperatures for 24 h.

Samples melt-crystallized at 160 and 170 ºC show an intermediate peak between those corresponding to the homocrystal and the stereocomplex, located at about 195 ºC. which some authors attribute to a melting-recrystallization mechanism,[15] i.e., the stereocomplex may form during the isothermal crystallization stage as a result of structural reorganization that occurs when the homocrystal partially melts and recrystallizes in stereocomplex form. However, recent investigations of polymer crystallization have provided strong evidences indicating that polymer crystallization proceeds through a transient mesophase instead of the classical nucleation and growth mechanism.[35-39] The occurrence of these mesomorphic clusters has also been confirmed in blends of enantiomeric polylactides, and the peak at 195 ºC could be associated alternatively to their crystallization.[32] These samples also show a cold crystallization peak at about 100 ºC, indicating the presence of crystallizable material at

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the end of the crystallization process. This material indicates a partially phase separated system, but it is not possible to establish whether phase separation was actually present in the initial amorphous blend or if it occurs as a consequence of the crystallization process. The cold crystallization of this material accounts for a a significant fraction of the homocrystals melting at about 170 ºC. Finally, in melt-crystallizations carried out above the melting point of the homocrystals (at temperatures starting from 180 ºC), the intermediate peak disappears and the DSC trace is dominated by the stereocomplex melting peak. The heating scan also shows minor contributions corresponding to the cold crystallization and subsequent melting of homocrystals.

Table 1 summarizes the thermal features obtained by DSC during the heating scan after the isothermal melt-crystallization of the B-5050 blends at different crystallization temperatures. Glass transitions have not been included since they are located at about 70 ºC in all cases and do not show significant variations. As expected, homocrystal formation dominates over stereocomplexation in samples crystallized at the lower temperature range, but the opposite is observed in samples crystallized at higher temperatures. Regarding the percentages of crystallinity, Table 1 indicates that quite high crystallinity degrees (up to 60 wt%) can be achieved within the low temperature range, but crystallinity degrees decrease with increasing temperatures. The occurrence of (partial) phase separation and of transesterification reactions (at the highest temperatures investigated) probably plays a key role in this behavior.

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Table 1. Thermal properties of B-5050 blends after isothermal crystallization from the melt for 24 h. X_c is the overall crystallinity of the blend, X_{Stereo} is the stereocomplex crystal fraction, $\Delta H_m(H)$ and $\Delta H_m(S)$ are, respectively, the melting enthalpies of the α and η crystalline forms, $T_m(H)$ and $T_m(S)$ are their respective melting temperatures and ΔH_c and T_c are the cold crystallization enthalpy and temperature respectively.

Iso. Temp.	T_c [ºC]	ΔH_c [J/g]	$T_m(H)$ [ºC]	$\Delta H_m(H)$ [J/g]	$T_m(S)$ [ºC]	$\Delta H_m(S)$ [J/g]	X_c [%]	X_{Stereo} [%]
Iso 120ºC	-	-	166.8	35.5	213.9	13.4	42.3	27.4
Iso 130ºC	-	-	170.8	47.9	212.6	10.8	52.1	18.3
Iso 140ºC	-	-	171.6	51.9	216.1	15.0	58.7	22.4
Iso 150ºC	-	-	176.0	45.6	214.7	9.5	49.1	17.3
Iso 160ºC	102.1	3.4	171.1/189.3	35.9	217.1	9.4	37.0	20.8
Iso 170ºC	105.4	5.8	168.0/194.2	10.4/13.0	210.6	16.5	28.2	41.4
Iso 180ºC	113.4	9.2	167.3	11.7	215.4	35.8	28.8	75.4
Iso 190ºC	122.1	15.9	168.4	16.8	218.4	27.8	22.3	62.3

3.2. Isothermal crystallization from cast (cold-crystallization).

Figure 4 shows the DSC scans and WAXD profiles for samples cold-crystallized for 24 h at temperatures between 120 and 190 ºC. As can be seen in Figure 4a the DSC curves indicate that within the 120-160 ºC temperature range the homocrystal crystallizes favorably during the isothermal treatment. As in the samples analyzed in the preceding section, the small amount of stereocomplex observed in these scans is probably formed again during the heating ramp after melting of the homocrystals. Stereocomplex formation during the isothermal crystallization stage can only be observed again for the samples crystallized at temperatures approaching the melting point of the homocrystals, specifically at temperatures starting from 170 ºC. Actually, the DSC curve obtained at 170 ºC shows the presence of both homocrystal and stereocomplex crystals. At 180 ºC four thermal events can be observed: a cold crystallization peak at about 100 ºC, a homocrystal melting peak at about 170 ºC, a intermediate crystal melting peak at about 190 ºC and a stereocomplex melting peak at about 215 ºC. The location of the homocrystal melting peak clearly indicates that these

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crystals actually grow during heating in the DSC scan, hence the only crystals grown during the isothermal stage at 180 ºC are the intermediate crystals and the stereocomplex crystals. Notice also that in this sample (and particularly in samples crystallized above the Tm of the homocrystals), in addition to the cold crystallization observed during the heating scan, additional cold crystallization may have occurred during the cooling step before the DSC analysis. Moreover, the presence of crystallizable material at the end of the isothermal crystallization stage indicates the incomplete crystallization of the sample. Finally, at 190 ºC only stereocomplex formation was observed.

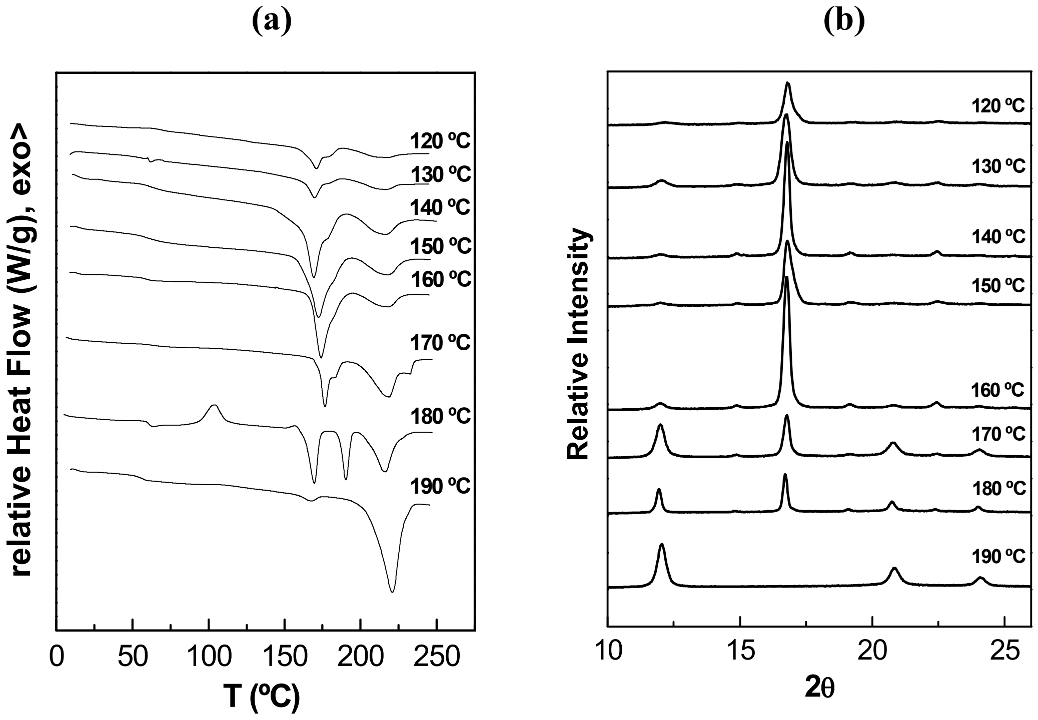

Figure 4. (a) DSC curves and (b) WAXD profiles of B-5050 blends annealed after “casting” at different crystallization temperatures for 24 h.

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All the thermal properties obtained from the DSC curves shown in Figure 4a are summarized in Table 2. As can be seen, at temperatures below 170 ºC, the melting enthalpy of the homocrystal is much larger than the melting enthalpy of the stereocomplex crystal, while when the annealing temperature reaches the melting temperature of the homocrystal, the stereocomplex crystal dominates, reaching high crystallinity degrees (~ 55 wt% at 190 ºC). This behavior is qualitatively similar to that observed for the samples annealed from the melt (see above), however; the degrees of crystallization obtained are different. At crystallization temperatures below 170 °C, the melting enthalpy of the homocrystal is higher when the samples are crystallized from melt and consequently the overall crystallinity is also larger. In contrast, when the crystallization temperature is higher than 170 °C, the melting enthalpies of the stereocomplex are much higher for the cold crystallized samples (those annealed directly after "casting"), and moreover, stereocomplexation can be exclusively achieved at 190 ºC. In fact, cold crystallized samples always show larger stereocomplex fractions regardless of the crystallization temperature. These results suggest that stereocomplex formation is more efficiently achieved through cold crystallization treatments.

Table 2. Thermal properties of B-5050 blends annealed after "casting" for 24 h. X_c is the overall crystallinity of the blend, X_{stereo} is the stereocomplex crystal fraction, $\Delta H_m(H)$ and $\Delta H_m(S)$ are, respectively, the melting enthalpies of the α and η crystalline forms, $T_m(H)$ and $T_m(S)$ are their respective melting temperatures and ΔH_c and T_c are the cold crystallization enthalpy and temperature respectively.

annealing	**T_c [ºC]**	**ΔH_c [J/g]**	**$T_m(H)$ [ºC]**	**$\Delta H_m(H)$ [J/g]**	**$T_m(S)$ [ºC]**	**$\Delta H_m(S)$ [J/g]**	**X_c [%]**	**X_{Stereo} [%]**
Iso 120ºC	-	-	171.0	23.7	211.7	13.6	28.8	36.4
Iso 130ºC	-	-	169.7	25.3	213.7	15.2	33.9	37.6
Iso 140ºC	-	-	169.2	35.9	216.1	12.9	42.2	26.4
Iso 150ºC	-	-	172.3	35.1	218.2	11.4	40.5	24.5
Iso 160ºC	-	-	174.0	37.6	218.2	12.2	43.3	24.5
Iso 170ºC	-	-	176.5	20.1	218.8	37.8	41.4	65.8
Iso 180ºC	104.3	16.1	169.5/190.3	17.5/12.0	216.2	27.5	31.3	69.3
Iso 190ºC	-	-	-	-	222.2	77.6	54.6	100.0

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Figure 4b shows the WAXD diffraction profiles of B-5050 blends cold crystallized at different crystallization temperatures over 24 h. WAXD diffraction is an accurate experimental technique allowing the elucidation of the crystalline polymorphs of polylactides. The α polymorph of optically pure PLLA has been reported to show its most intense diffraction peaks at 2θ values of 14.5º, 16.3º, 18.7º, and 21.9º.[10,40] However, the diffraction pattern of the PLLA/PDLA blends crystallized as stereocomplex is very different from that of optically pure polylactides crystallized as α polymorph and presents three main diffraction peaks at 2θ equal to 12º, 21º, and 24º.[10,40] As can be seen in Figure 4b, samples crystallized between 120 and 160 ºC display the diffraction peaks characteristic of the α crystals, with a small peak at 12º, indicating the presence of only a small stereocomplex fraction. At 170 ºC and above, the diffraction peaks corresponding to the stereocomplex gain intensity as the crystallization temperature increases, and at the same time the peaks of the homocrystal gradually lose intensity until completely vanishing at 190 ºC.

The size of crystalline domains can be also estimated from the WAXD results, since the peak width at half height decreases with increasing the crystal size. The equation that provides this value is the Scherrer equation.[41,42]

$$\tau = \frac{K\lambda}{\beta_\tau \cos\theta} \qquad (3)$$

Where: τ is the average size of crystals, λ is the wavelength of the incident radiation used, θ is the diffraction angle, K is the Scherrer constant, which has an average value of 0.9, and β_t is the peak width at half height in radians.

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Figure 5 shows the sizes estimated for the crystalline domains formed at different crystallization temperatures, calculated from the diffraction peaks 2θ = 16.8° and 12° for α and η forms, respectively. As can be seen the size of the crystalline domains increases gradually with increasing crystallization temperature for both the homocrystals and the stereocomplex. It is noteworthy that the maximum sizes for the α and η crystals occur at 140 and 180 °C respectively, coinciding with the maximum growth rates for the respective crystals. In addition, a second maximum is also observed for the α crystals at 180 ºC which corresponds to the intermediate crystals that melt at about 190 ºC in the DSC scans. These crystals may crystallize form the mesophase and may contain both enantiomeric chains instead of a single pure polymer.

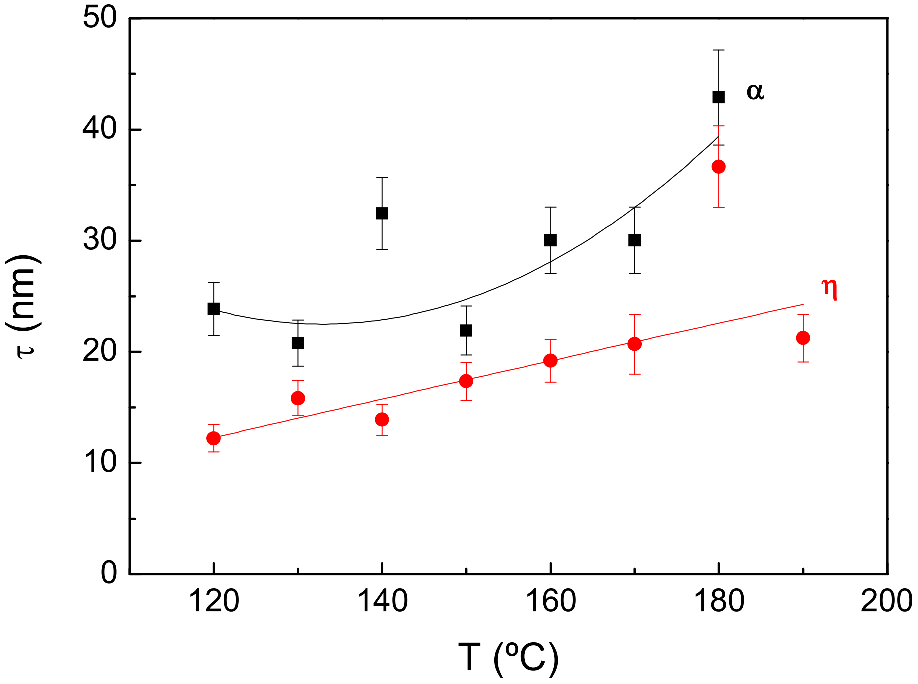

Figure 5. Evolution of crystalline domain size of B-5050 blends annealed after "casting" at different crystallization temperatures for 24 h.

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In view of the results obtained by DSC and WAXD, the B-5050 blends annealed at 180 ºC show well resolved peaks and further annealing studies at this temperature could provide insights into the structural reorganization occurring during the stereocomplexation process. Figure 6 shows the DSC curves obtained after annealing at 180 °C the cast samples for different lengths of time. The sample annealed for 30 min (Fig. 6a) shows a single peak at 177 ºC corresponding to crystals that cannot be formed during the isothermal stage at 180 ºC. In addition, the cold crystallization exotherm observed during the heating ramp only explains a minor fraction of the melting peak, hence, it must be assumed that the sample shows fast crystallization during cooling. This behavior suggests the existence of a molten mesophase for the sample annealed during 30 min., because these phases are known to exhibit fast crystallization rates during cooling, which usually lead to nodular crystallites.[38,39] The sample annealed for 1 hour (Fig. 6b) shows two peaks located at 170 ºC and 183 ºC. Referring to the first peak, its location (~170 ºC) and the occurrence of a broad exothermic peak at lower temperatures suggest that these crystals have cold crystallized from the rubbery state during the heating ramp. Therefore, the melting peak at 183 ºC may be attributed to the intermediate crystals of reduced size/perfection formed during the relatively short annealing stage (1 hour at 180 ºC), but may also crystallize from the mesophase during the cooling stage (similarly to the sample crystallized for 30 min.). In addition, only a minor amount of stereocomplex can be observed. Samples annealed for 4 hours, 8 hours and 24 hours (Fig. 6c, 6d and 6e) show very similar profiles, with three peaks located at about 170 ºC, 190 ºC and 215 ºC; these can be assigned to homocrystals, intermediate crystals and stereocomplex respectively. The similar profile of the scans in the 4h-24h range indicates that the stereocomplexation process stops after some time (about 4 hours

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for the molecular weights studied in this paper). The peak at 170 ºC indicates partial phase separation. It is not possible to know whether phase separation is present in the initial blend or if it occurs during the crystallization process due to kinetic constraints resulting from the intricate and highly entangled crystalline structure developed during the isothermal crystallization at 180 ºC. In the same way as pure crystalline materials cannot achieve complete crystallization, exclusive stereocomplexation may also be hindered in blends of high molecular weight enantiomeric PLAs due to their highly constrained nature

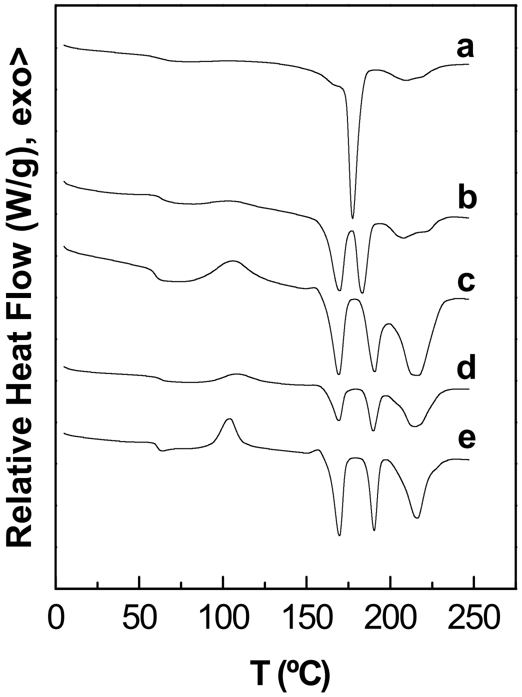

Figure 6. DSC curves of "as cast" B-5050 blends annealed at 180 ºC for: (a) 30 min (b) 1h (c) 4h (d) 8h (e) 24 h.

3.3. Improving stereocomplexation through specific thermal treatments.

The two crystallization processes studied in this paper, i.e., melt crystallization and cold crystallization, show different stereocomplexation efficiencies that can be rationalized

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as follows. At temperatures below 160 ºC, homocrystallization is always favored regardless of the crystallization process. Crystallization from the melt at 160 ºC and 170 ºC favours the nucleation and growth of intermediate crystals and of stereocomplex crystals compared to homocrystallization, but the system cannot evolve to complete stereocomplexation because of the highly entangled nature of the mixed crystalline systems obtained from polylactide blends of high molecular weight. Crystallization from the melt at 180 ºC and 190 ºC results in the exclusive formation of stereocomplex crystals, but partial phase separation and, particularly at temperatures above 180 ºC, transesterification reactions, reduce the ability of the system to crystallize in the form of stereocomplex (see Table 1).

Regarding the cold-crystallized samples, recent studies have shown that the formation of crystal nuclei is not restricted to the temperature range above the glass transition temperature and that it also occurs in the glassy state without the requirement of large-amplitude cooperative segmental mobility.[43] In addition polylactides show very fast crystallization rates at temperatures about 100 ºC, meaning that in the cold crystallization experiments a large amount of incipient homocrystal spherulites can be expected before the isothermal crystallization temperature is reached. The results in Figure 4 suggest that when the crystallization is performed at temperatures up to 170 ºC, the homopolymer crystallizes first, avoiding the crystallization of the stereocomplex. At temperatures starting from 180 ºC any homocrystal formed during the heating ramp should be molten, and exclusive stereocomplexation should be possible. However, at 180 ºC the DSC scan shows a homocrystal peak and an intermediate crystal peak in addition to the sterecomplex peak, suggesting a hindered crystallization process that results in a partially phase separated system. Finally, at 190 ºC exclusive

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stereocomplexation is observed, and the degree of crystallinity is much larger for the cold crystallized sample than for the melt crystallized one (~55 wt% vs ~14 wt% respectively), probably due to the lower degradation of the former through transesterification reactions. In addition, phase separation is not observed in the system cold crystallized at 190 ºC, suggesting that phase separation during stereocomplexation in high molecular weight PLAs may be a result of the hindered nature of the crystallization process rather than an actual feature of the initial amorphous phase.

The two main differences existing between the cold and the melt crystallized samples regarding the stereocomplexation process are therefore the amount of nucleation points (homocrystal nucleation points are present in the cold crystallized samples at temperatures up to 170 ºC and seem to influence the crystallization behavior at even higher temperatures through the "melt memory" effect[44,45]) and the loss of optical purity through transesterification reactions (larger in melt crystallized samples due to the longer crystallization times needed as a consequence of the smaller number of nucleation points). To gain insight into the relative importance of both effects, additional experiments were carried out. Figure 7 compares the DSC scans for samples that have been directly crystallized from the melt at 190 ºC with the DSC scans obtained for samples that have been cooled from the melt to 130 ºC for 10 min to allow the formation of nucleation points and which were then heated to 190 ºC to allow the isothermal crystallization of the samples. In curves 7a and 7b the isothermal crystallization time at 190 ºC is 1 hour; but the former corresponds to the directly melt crystallized sample and the latter to the sample allowed to nucleate for 10 min at 130 ºC. As can be seen, the endotherm corresponding to stereocomplex crystals is noticeably larger in curve 7b than in curve 7a. Curves 7c and 7d follow equivalent thermal

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treatments, but the isothermal crystallization time at 190 ºC is 24 h. The sample allowed to nucleate (curve 7d) shows a stereocomplex weight fraction intermediate between those obtained for the cold crystallized (~55 wt%) and the melt crystallized samples (~14 wt%) at the same temperature. The improvement in the stereocomplexation efficiency compared to the melt crystallized sample can be attributed to the occurrence of a larger number of nucleating points through the "melt memory" effect. These allow a faster crystallization of the sample, reducing the extent of the detrimental transesterification reactions.

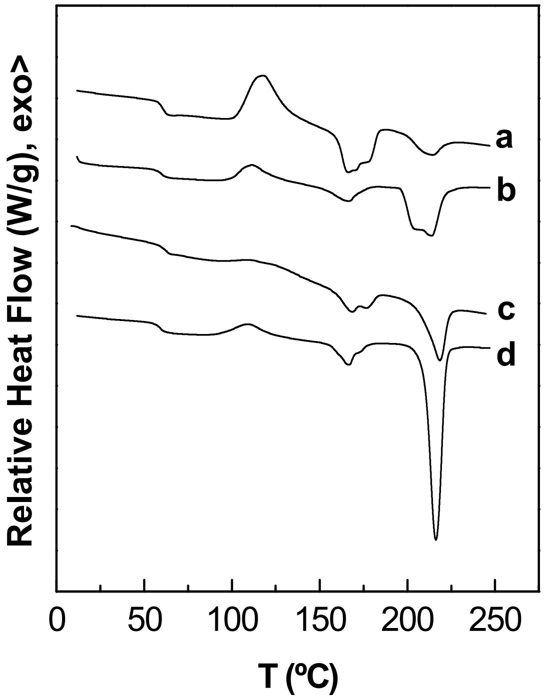

Figure 7. DSC curves of blends B-5050 after crystallization from melt with different isothermal treatments: (a) 190 ºC for 1 h, (b) 190 ºC for 1h after 130 ºC for 10 min, (c) 190 ºC for 24 h and (d) 190 ºC for 24 h after 130 ºC for 10 min.

FTIR spectroscopy can be used to follow "*in situ*" the crystallization treatments performed on the samples in Figure 7, allowing the identification of the crystalline

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forms present in the sample during the whole thermal treatment. Figure 8i shows the FTIR spectra obtained during the isothermal crystallization experiment at 190 ºC (after melting for 2 min at 250 ºC) for the stoichiometric blend B-5050. The initial spectrum recorded at room temperature for the C=O stretching band (8iA) is located at about 1759 cm^{-1} and shows the broad profile characteristic of a predominantly amorphous sample. During the isothermal crystallization at 190 ºC (spectra 8iB-8iF) a new contribution located at about 1748 cm^{-1} and attributed to crystalline B-5050 in the 3_1 helix conformation[10] gains intensity at the expense of the initial absorption. Hence, FTIR results confirm the sterocomplexation of the sample during the isothermal stage. It is worth mentioning that the change between the spectrum recorded after 6 hours (8iE) and the one recorded after 24 hours (8iF) is negligible, indicating that the crystallization rate slows down after a few hours at high temperatures. Figure 8ii shows the annealing at 190 ºC for a B-5050 sample that has been previously molten for 2 min at 250 ºC and then allowed to nucleate at 130 ºC for 10min before annealing. The initial spectrum recorded at room temperature (8iiA) once again indicates an initially amorphous sample. The spectrum recorded at the beginning of the pre-treatment at 130 ºC (8iiB) is dominated by a contribution at about 1748 cm^{-1}**,** indicating the presence of stereocomplex crystals formed during the cooling ramp (cooling rate is about 5 ºC/min). During the pre-treatment at 130 ºC (see spectrum 8iiC) the contribution at about 1759 cm^{-1} increases slightly, confirming the development of homocrystalline nuclei. Finally, during the isothermal stage at 190 ºC (spectra 8iiD-8iiH) the absorption at 1748 cm^{-1} gains again intensity at the expense of the contribution at 1759 cm^{-1}, indicating the stereocomplexation of the sample. These results are in good qualitative agreement with the DSC results discussed above.

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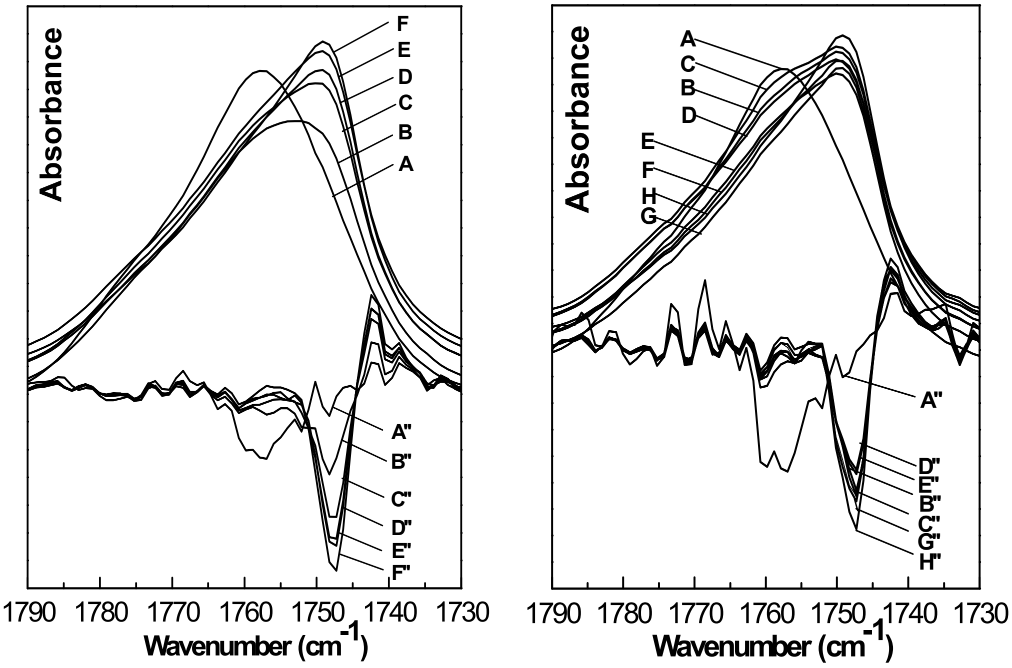

(i) (ii)

Figure 8. Carbonyl stretching region of B-5050 blends (upper side spectra) and second derivative (lower side spectra). (i) isothermal crystallization from the melt at 190 ºC: (A) initial spectrum at room temperature (B) 0 min at 190 ºC; (C) 30 min at 190 ºC, (D) 4 h at 190 ºC, (E) 6 h at 190 ºC, (F) 24 h at 190 ºC. (ii) isothermal crystallization at 190 ºC after 10 min. at 130 ºC: (A) initial spectrum at room temperature (B) 0 min at 130 ºC; (C) 10 min at 130 ºC, (D) 0 min at 190 ºC, (E) 30 min at 190 ºC, (F) 4 h at 190 ºC, (G) 6 h at 190 ºC, (H) 24 h at 190 ºC.

4. Conclusions

According to recent publications,[8,16,44,46,47] the formation of homocrystallites composed of either PLLA or PDLA prevails over stereocomplex crystallization when blends are prepared from high molecular weight polylactides, and stereocomplex form can only be crystallized when the molecular weights of both polylactides are below 1.0 x 10^5. In this paper, the PLLA/PDLA 50/50 blends are shown to be crystallizable exclusively as stereocomplex with a high degree of crystallization by performing recrystallization of the blends at 190 ºC.

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The experimental results obtained in PLLA/PDLA 50/50 blends with $M_w > 2\cdot10^5$ g mol^{-1} indicate that homocrystallization occurs preferentially at crystallization temperatures below 160 ºC. Stereocomplex formation noticeably increases in the temperature range between 160 ºC and the melting temperature of α crystals (~180 ºC). Exclusive stereocomplexation can only be achieved at temperatures above the melting temperature of the α crystals, and can be carried out much more efficiently in cold crystallized samples than in melt crystallized samples because i) cold crystallized samples contain homocrystal nucleation points that favour the nucleation/growth of stereocomplex crystals, even at temperatures above the melting temperature of the α crystals through the "melt memory" effect and ii) cold crystallized samples crystallize faster due to the larger amount of nucleation points and are therefore less prone to the loss of optical purity through transesterification reactions.

Since melt processing is the standard technique to obtain plastic parts, from the industrial point of view, this paper also analyzes how to improve stereocomplexation in the melt crystallization process. Performing a pre-treatment that allows the formation of homocrystal nuclei is shown to increase the crystallization rate of the sample during the isothermal crystallization step at temperatures above the melting temperature of the α crystals.

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References

[1] Y.Ikada, K. Jamshidi, H. Tsuji, S. H. Hyon, *Macromolecules* **1987**, *20*, 904.

[2] S. Brochu, R. E. Prud´homme, I. Barakat, R. Jérôme, *Macromolecules* **1995**, *28*, 5230.

[3] H. Yamane, K. Sasai, *Polymer* **2003**, *44*, 2569.

[4] H. Tsuji, Y. Ikada, *J. App. Polym. Sci.* **1995**, *58*, 1793.

[5] H. Tsuji, S. H. Hyon, Y. Ikada, *Macromolecules* **1991**, *24*, 5651.

[6] H. Tsuji, S. H. Hyon, Y. Ikada, *Macromolecules* **1991**, *24*, 5657.

[7] H. Tsuji, Y. Ikada, *Macromol. Chem. Phys.* **1996**, *197*, 3483.

[8] K. Fukushima, Y. Kimura, *J. Polym. Sci.* **2008**, *46*, 3713.

[9] H. Tsuji, Y. Ikada, *Polymer* **1999**, *40*, 6699.

[10] J. R. Sarasua, N. López-Rodríguez, A. López-Arraiza, E. Meaurio, *Macromolecules* **2005**, *38*, 8362.

[11] H. Xu, X. Teng, M. Yu, *Polymer* **2006**, *47*, 3922.

[12] R. T. MacDonald, S. P. McCarthy, R. A. Gross, *Macromolecules* **1996**, *29*, 7356.

[13] S. Pensec, M. LeRoy, H. Akkouche, N. Spassky, *Polymer Bulletin* **2000**, *45*, 373.

[14] H. Tsuji, Y. Tezuka, *Biomacromolecules* **2004**, *5*, 1181.

[15] M. Fujita, T. Sawayanagi, H. Abe, T. Tanaka, T. Iwata, K. Ito, T. Fujisawa, M. Maeda, *Macromolecules* **2008**, *41*, 2852.

[16] J. R. Sarasua, A. López-Arraiza, P. Balerdi, I. Maiza, *Polym. Eng. Sci.* **2005,** *45*, 745.

[17] E. Meaurio, E. Zuza, N. López-Rodríguez, J. R. Sarasua, *J. Phys. Chem. B* **2006**, *110*, 5790.

RSC Advances Accepted Manuscript

[18] H. Tsuji, M. Nakano, M. Hashimoto, K. Takashima, S. Katsura, A. Mizuno, *Biomacromolecules* **2006**, *7*, 3316.

[19] H. Tsuji, Y. Ikada, *Polymer* **1999**, *40*, 6699.

[20] H. Tsuji, H. Takai, S. K. Saha, *Polymer* **2006**, *47*, 3826.

[21] S. C. Schmidt, M. A. Hillmyer, *J. Polym. Sci. B* **2001**, *39*, 300.

[22] H. Urayama, T. Kanamori, K. Fukushima, Y. Kimura, *Polymer* **2003**, *44*, 5635.

[23] K. S. Anderson, M. A. Hillmyer, *Polymer* **2006**, *47*, 2030.

[24] N. Rahman, T. Kawai, G. Matsuba, K. Nishida, T. Kanaya, H. Watanabe, H. Okamoto, M. Kato, A. Usuki, M. Matsuda, K. Nakajima, N. Honma, *Macromolecules* **2009**, *42*, 4739.

[25] L. Cartier, T. Okihara, Y. Ikada, H. Tsuji, J. Puiggali, B. Lotz, *Polymer* **2000**, *41*, 8909.

[26] J. R. Sarasua, A. L. Arraiza, P. Balerdi, I. Maiza, *J. Mat. Sci.* **2005**, *40*, 1855-1862.

[27] F.D. Kopinke, K. Mackenzie, *J. Anal. Appl. Pyrolysis* **1997**, *40*, 43-53.

[28] Y. Fan, H. Nishida, Y. Shirai, Y. Tokiwa, T. Endo, *Polym. Degrad. Stab.* **2004**, *86*, 197–208.

[29] H. Tsuji, Y. Ikada, *Macromolecules* **1993**, *26*, 6918-6926.

[30] E. Zuza, E. Meaurio, A. Etxeberria, J. R. Sarasua, *Macromol. Rapid Commun.* **2006**, *27*, 2026-2031.

[31] Y. P. Khanna, W. P. Kuhn, *J. Polym. Sci. B* **1997**, *35*, 2219-2231.

[32] C. F. Yang, Y. F. Huang, J. Ruan, A. C. Su *Macromolecules* **2012**, *45*, 872-878.

[33] A. P. T. Pezzin, G. O. R. Alberda van Ekenstein, E. A. R. Duek, *Polymer* **2001**, *42*, 8303-8306.

[34] M. A. Sabino, J. L. Feijoo, A. J. Muller, *Macromol. Chem. Phys.* **2000**, *201*, 2687-2698.

RSC Advances Accepted Manuscript

[35] G. Strobl, *Prog. Polym. Sci.* **2006**, *31*, 398–442.

[36] E. B. Sirota, *Macromolecules* **2007**, *40*, 1043-1048.

[37] T. Zhang, J. Hu, Y. Duan, F. Pi, and J. Zhang, *J. Phys. Chem. B* **2006**, *115*, 13835–13841.

[38] C. De Rosa, F. Auriemma, R. Di Girolamo, O. Ruiz de Ballesteros, M. Pepe, O. Tarallo, A. Malafronte, *Macromolecules* **2013**, *46*, 5202−5214.

[39] D. Mileva, Q. Zia, R. Androsch, H.J. Radusch, S. Piccarolo, *Polymer* **2009**, *50*, 5482–5489.

[40] J. R. Sarasua, R. E. Prud´homme, M. Wisniewski, A. Le Borgne, N. Spassky, *Macromolecules* **1998**, *31*, 3895.

[41] M. L. Minus, H. G. Chae, S. Kumar, *Polymer* **2006**, *47*, 3705.

[42] D. Brizzolara, H. J. Cantow, K. Diederichs, E. Keller, A. J. Domb, *Macromolecules* **1996**, *29*, 191.

[43] R. Androsch, M. L. Di Lorenzo, *Macromolecules* **2013,** *46*, 6048−6056.

[44] Y. He, Y. Xu, J. Wei, Z. Fan, S. Li, *Polymer* **2008**, *49*, 5670.

[45] S. Schneider, X. Drujon, B. Lotz, J. C. Wittman, *Polymer* **2001**, *42*, 8787.

[46] P. Purnama, S. H. Kim, *Macromolecules* **2010**, *43*, 1137.

[47] L. Bouapao, H. Tsuji, *Macromol. Chem. Phys.* **2009**, *210*, 993.

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Graphical Abstract

Efficient stereocomplex crystallization in enantiomeric blends of high molecular weight Polylactides.

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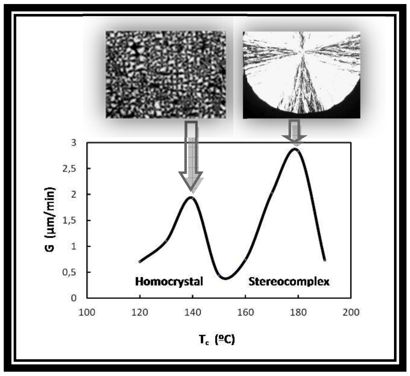
The crystallization kinetics of the equimolar PLLA/PDLA blend shows a bimodal behavior corresponding to the two main crystalline forms, being spherulite growth rates higher in the case of the stereocomplex due to higher crystallization temperatures. Crystallization conditions that reduce the loss of optical purity arising from transesterification reactions increase the stereocomplexation degree.



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