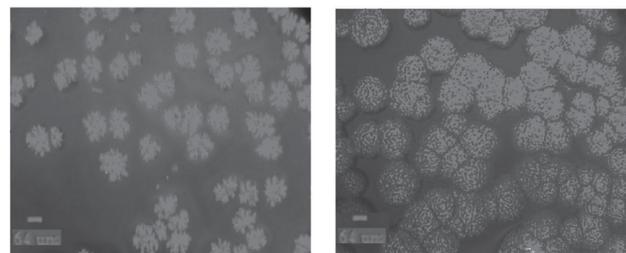


Effects of Molecular Architecture on the Stereocomplex Crystallization in Poly(lactic acid) Blends

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The crystallization behavior of two chemically identical but physically different co-crystallizing poly(L-lactic acid) (PLLA)-based blends is studied. The first set studied involves an all-L unit polymer (PLLA) co-crystallizing with a PDLA-miscible soft polyether-PDLA triblock copolymer, where D refers to the D isomer. The second set studied involves homopolymer blends of PLLA/miscible soft polyether/PDLA with compositions identical to the first set. Crystallization is performed under isothermal and non-isothermal crystallization conditions and the crystallization kinetics, crystal perfection, and the blend morphology are investigated. It is clear that the stereocomplex crystallization is significantly slower in the triblock copolymer blends in comparison with the homopolymer blends. Furthermore, based on diffraction, spectroscopic, and thermal data, it is found that the stereocomplex crystals formed in the homopolymer blends achieve higher order and perfection, with a melting temperature 15–20 °C higher than those formed in the triblock blends.



triblock copolymer blend

homopolymer blend

1. Introduction

Poly(lactic acid) (PLA), which is being considered as a “green” alternative to a number of specialty and commodity polymers, has attracted a considerable amount of attention from both academics and commercial entities. Our previous studies have focused on controlling the morphological features of the semicrystalline PLA, especially the degree of crystallinity, crystalline size, and the transformation associated with the metastable phases.^[1–6] These studies have involved both the analysis of the chain conformation distribution of the amorphous phase, the onset of crystallization, the kinetics involved, the presence

and perfection of the crystalline phases formed, and the transformation mechanisms between the mesophases as a function of time and temperature. It is well established that although the quiescent crystallization speed of PLA is slow, the increase in the degree of crystallinity can be exceedingly fast under flow, presenting significant challenges when PLA is processed by extrusion or drawing.^[7–10] In fact, the crystallization process can be so fast that the overall sample can be considered weak due to the overall sample brittleness.^[11] Therefore, we have initiated a project to limit the degree of crystallinity in PLA and to modify its overall mechanical properties by blending with triblock copolymers involving PDLA units as end-blocks and polyether units as the soft mid-block, which is compatible with PLLA.^[2,3]

In order to limit the degree of crystallinity, the use of the triblock concept incorporating stereocomplex crystals originates from earlier studies dealing with morphology control in diverse topics such as polyurethanes and crystalline polyolefins.^[12,13] Because of the tremendously large difference, $\Delta T = 50\text{--}70$ °C, in the melting temperatures

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between stereocomplex (as high as 250 °C) and either all-*l*- or all-*d*- crystals (180 °C), crystallization at any temperature between the two or even lower will result in preferential crystallization of stereocomplex crystals. It has also been recognized that a relatively low level of ordered structures formed, not necessarily crystalline, can “quench” the segmental mobility of the system thus limiting the degree of ordered structures achieved.^[13] Based on the fundamental studies first carried out,^[14–24] the deployment of various block copolymers to achieve the *d/l* stereocomplex crystallization is well documented.^[25–27] Examples of systems investigated are PDLA-blockB-PDLA/ PLLA-blockB-PLLA blends or PDLA-blockB/PLLA blends.

In our previous publications involving the co-crystallizing blends of PDLA-soft block-PDLA triblock copolymer with PLLA, it was shown that on isothermal crystallization, a morphology consisting of stereocomplex crystals dispersed in a continuous amorphous phase, containing the non-crystallized triblock copolymer and amorphous PLLA, was formed when the midblock used was miscible with PLLA.^[2,3] A small difference in the stereocomplex crystals formed due to the PDLA length and the miscibility of the soft mid-block seem to affect the overall crystallization kinetics significantly.^[2,3] In order to clarify some of these observed differences in the crystallization kinetics, two separate blends are studied. The first system involves PLLA/miscible soft block/PDLA homopolymer blends, which are chemically identical to the triblock blends. However, in this system, the connectivity between the PDLA and the soft mid-block is eliminated. With this homopolymer blend, it is possible to examine the difference in the crystallization behavior of a simpler system as compared to the triblock copolymer blends studied previously. Using both isothermal and non-isothermal crystallization techniques, the crystallization kinetics, crystal perfection, and the resultant blend morphology formed in the two sets of blends have been found to be dramatically different and are reported here.

2. Experimental Section

2.1. Materials

D-Lactide ((3*R*-*cis*)-3,6-dimethyl-1,4-dioxane-2,5-dione) was obtained from Purac Biochem BV (Gorinchem, The Netherlands) and used as received. PLLA (4.2% *D*) (PLA2002D) was obtained from Natureworks. Poly(ethylene glycol-co-propylene glycol) (PEPG12000) (UCON Lubricant 75-H-90000; functionality 2, *D* = 1.10) was obtained from Dow Chemicals, USA. The PEPG12000 has a *T*_g of –68 °C and a melting point of –2 °C and is miscible with PLLA. The triblock copolymer and the PDLA oligomer were synthesized and characterized as described previously.^[3,6] The PLLA/PDLA blend pellets used for preparing the stereocomplex reference sample were obtained from Natureworks. The pellets were annealed at 200 °C for 4 h to prepare the reference stereocomplex

Table 1. Compositions of PDLA2800-PEPG12000-PDLA2800 triblock copolymer/PLLA blends.

Composition	PLLA/triblock copolymer blends			
	Triblock [%]	PLLA [%]	PEPG ^{a)} [%]	PDLA ^{a)} [%]
A	0	100	0	0
B	15	85	10	5
C	25	75	17	8
D	35	65	24	11

^{a)}Present as part of the triblock copolymer.

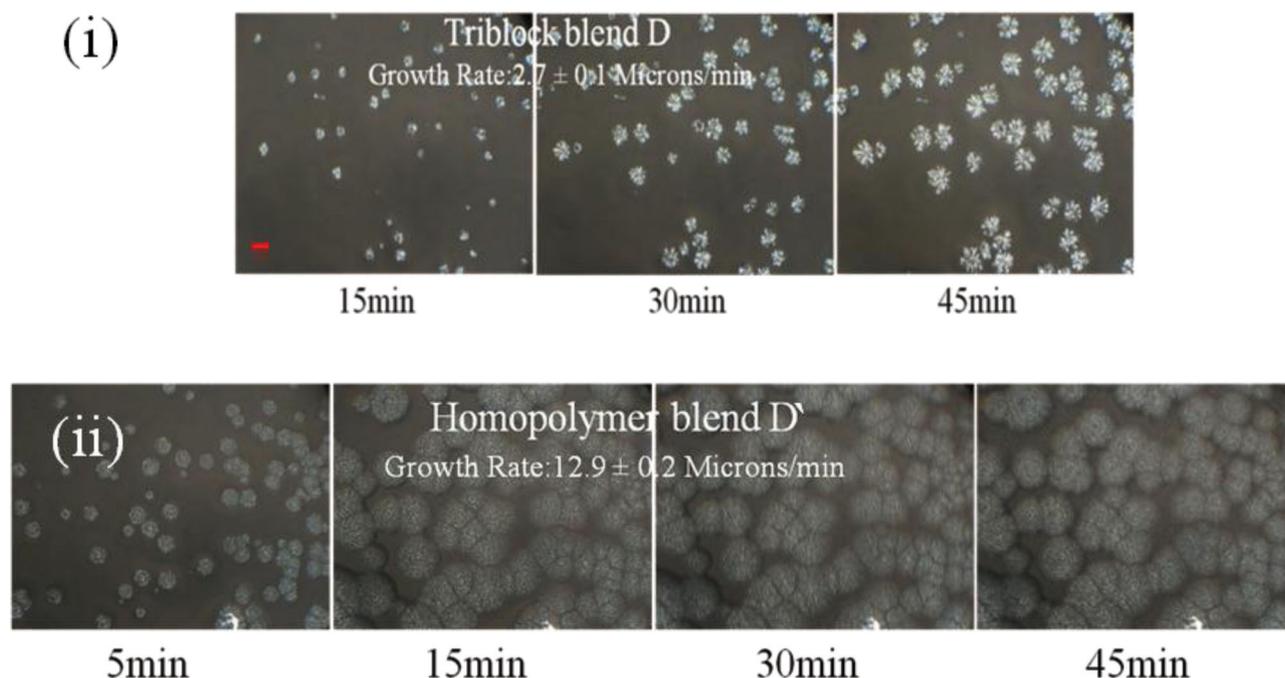
sample. Two sets of blends were prepared. The first set (Table 1) was PDLA2800-PEPG12000-PDLA2800 triblock copolymer blended with PLLA. The numbers indicate the number-average molecular weight of each block as determined by ¹H NMR spectroscopy. The compositions range from 15 to 35 wt% triblock copolymer. The triblock copolymer has a composition of 33 wt% PDLA and 67 wt% PEPG12000. The second set (Table 2) was PLLA/PDLA2500/PEPG12000 homopolymer blends with compositions matching the PLLA/triblock copolymer blends. Blends were prepared by using a 15 cc DSM twin screw mini-extruder using the following thermal profile. The blend constituents were introduced into the extruder and mixed for 5 min at a temperature *T*_b = 190 °C at 100 rpm. The melt is collected in an injection molding collection gun, maintained at 185 °C, and rapidly cooled in the mold maintained at 30 °C to form the blend specimen.

2.2. Characterization Techniques Used

Crystal growth in the prepared blends during the isothermal crystallization experiments was observed using an Olympus (Tokyo, Japan) polarized optical microscope (BH-2) equipped with a heating stage. The samples were prepared using the following procedure. First, a sample of ≈0.5 mg was placed between a glass slide and a Kapton film and was heated to completely melt the sample; it was then pressed to obtain a thin film and then cooled to room temperature. Subsequently, the sample was again heated to a temperature above the melting temperature of the stereocomplex crystals (≈220 °C) and transferred to a hot stage, which was maintained at 155 °C. All the crystallization experiments were followed using the birefringence developed for samples between crossed polarizers. Images were taken with a Canon digital camera. The growth rate of the crystals was

Table 2. Compositions of PDLA2500/PEPG12000/PLLA homopolymer blends.

Composition	PLLA/PDLA/PEPG12k blends		
	PLLA [%]	PEPG [%]	PDLA [%]
A'	100	0	0
B'	85	10	5
C'	75	17	8
D'	65	24	11



■ Figure 1. Isothermal crystallization at 155 °C: i) triblock/PLLA blend D; ii) homopolymer blend D'. The scale bar is 64 μm in all the images.

determined using the image analysis software Image J. Non-isothermal crystallization experiments were performed in a TA Q100 differential scanning calorimeter (DSC) (TA Instruments), which was calibrated against an indium standard. The samples (5–10 mg) were heated at the rate of 20 °C min^{-1} in the first cycle to study the morphology of the as-prepared samples. The samples were then cooled at 20 °C min^{-1} and then heated back at 10 °C min^{-1} to study the morphology formed during the non-isothermal cooling scan. All the DSC experiments were done under nitrogen purge. To study the crystal structure, wide-angle X-ray scattering (WAXS) (Rigaku Molecular Metrology) and Raman scattering (Jobin–Yvon Horiba LabRam HR800) were used.

3. Results and Discussion

3.1. Isothermal Crystallization

The crystallization kinetics of the two sets of blends can be conveniently differentiated using optical microscopy as shown in Figure 1. In order to suppress crystallization of either all L or all D PLA chains, an isothermal crystallization temperature of 155 °C was chosen to study the crystallization kinetics and morphology of the stereocomplex crystals. At this temperature, stereocomplex crystals all formed readily, yet few PLLA crystals are formed.

As seen in Figure 1i and ii, judging by the diameters of the birefringent crystals observed, the rate of stereocomplex crystallization in the homopolymer blend is approximately five times higher than that in the corresponding triblock copolymer/PLLA blend. The higher rate of stereo-

complex crystallization in the homopolymer blends can be explained by the following reasons: i) the mobility of the PDLA molecules in the triblock copolymer blends is lower as they are attached to the miscible PEPG midblock chains, which hinders the segregation of PDLA and PLLA chains thus reducing the rate of stereocomplex crystallization; ii) because of the absence of the covalent linkage between PDLA and PEPG in the homopolymer blends, the PDLA molecules exist as low-molecular-weight chains, thus increasing their mobility and the extent of segregation with PLLA leading to a higher rate of stereocomplex crystallization. In addition, it can be seen that the mode of segregation of the amorphous component is different in the two sets of blends. In crystalline-amorphous polymer blends, the segregation of the amorphous component can occur either in the interspherulitic or in the intraspherulitic regions, depending on the relative kinetics. The type of segregation can be evaluated based on the “segregation distance,” $\delta = D/G$, where D is the diffusion coefficient of the amorphous component and G is the growth rate of the crystalline component.^[28] Higher growth rate of crystalline component and a smaller diffusion coefficient of the amorphous component lead to a lower segregation distance and thus intra-spherulitic segregation.^[28,29] In contrast, slower growth rate and higher diffusion coefficient will lead to a higher segregation distance and thus inter-spherulitic segregation of the amorphous component.^[30,31] It is found that in the homopolymer blends, because of the faster crystallization rate (high G), the amorphous component, PEPG, is trapped

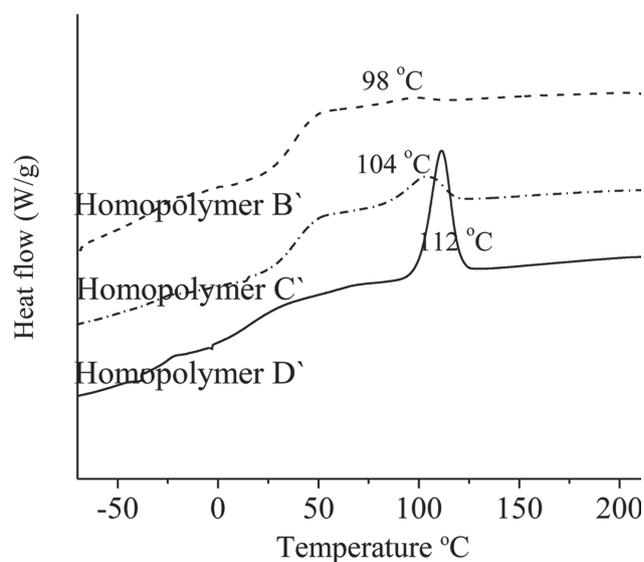
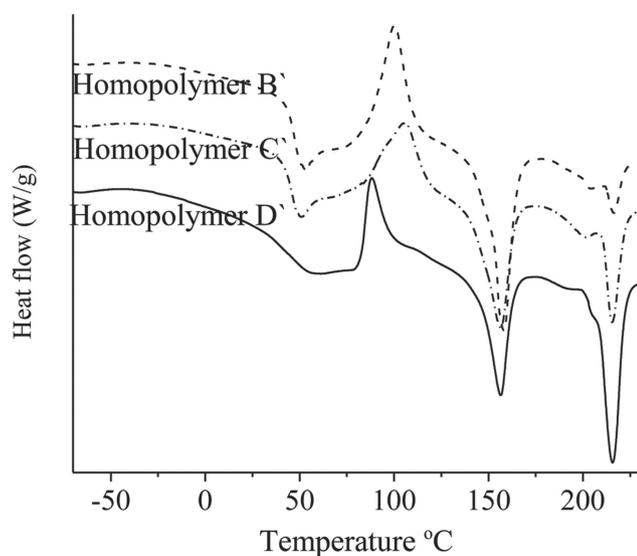
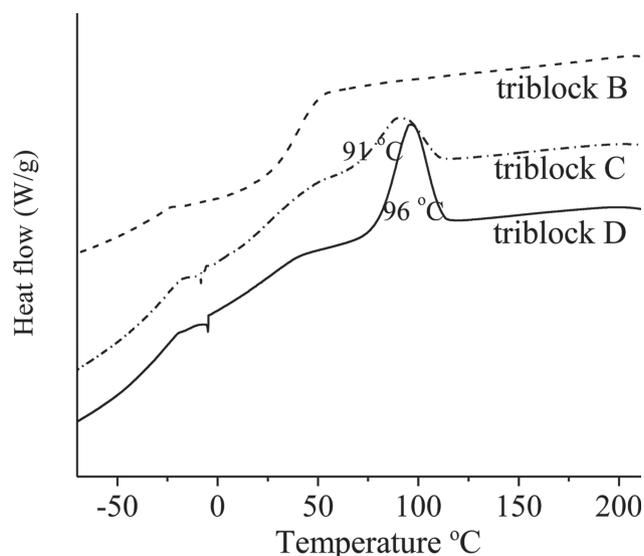
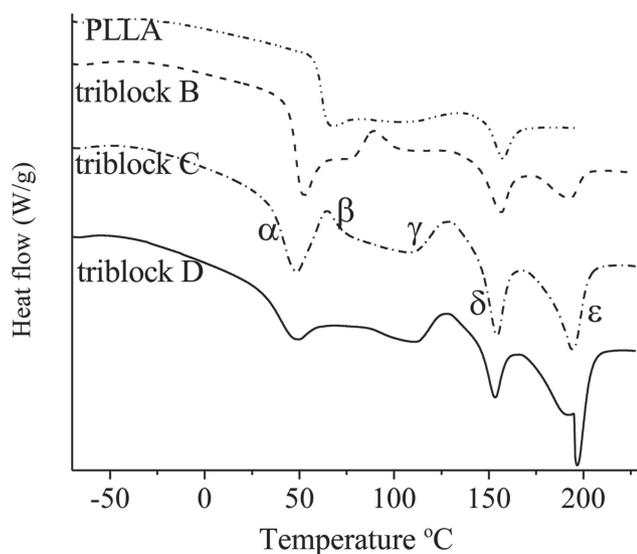


Figure 2. First DSC heating scan of the triblock and homopolymer blends (20 °C min^{-1}) [triblock C shows the nomenclature used for the various transitions].

Figure 3. Non-isothermal crystallization of triblock and homopolymer blends (cooling 20 °C min^{-1}).

in the intra-spherulitic amorphous regions. In the case of the triblock copolymer/PLLA blend, as the growth rate is much slower, the amorphous component can segregate to the inter-spherulitic region (Figure 2). Raman mapping on the continuous amorphous region in the triblock copolymer/PLLA blend has already established the presence of both amorphous PLLA and the non-crystallized triblock copolymer.^[3]

3.2. Non-isothermal Crystallization

The differences in the crystallization kinetics of the two sets of blends can also be captured expediently in non-isothermal crystallization experiments as follows: First, the blends were rapidly cooled to room

temperature from a blending temperature T_b , such that $T_{m,PLLA} < T_b < T_{m,sterocomplex}$. The morphology formed during this non-isothermal crystallization process can then be analyzed in the subsequent first heating cycle in DSC (Figure 2). Then, the second isothermal crystallization experiment is performed during the subsequent cooling cycle from a temperature T , such that $T > T_{m,sterocomplex}$ (Figure 3). The morphology formed during this non-isothermal crystallization process is analyzed based on the second heating cycle in the DSC (Figure 4) and discussed below.

Several transitions can be seen in Figure 2. These transitions are: (α) the glass transition of the amorphous phase, (β) the cold crystallization of stereocomplex crystals (present only in some blends), (γ) the cold crystallization of the PLLA crystals, (δ) the melting of PLLA crystals,

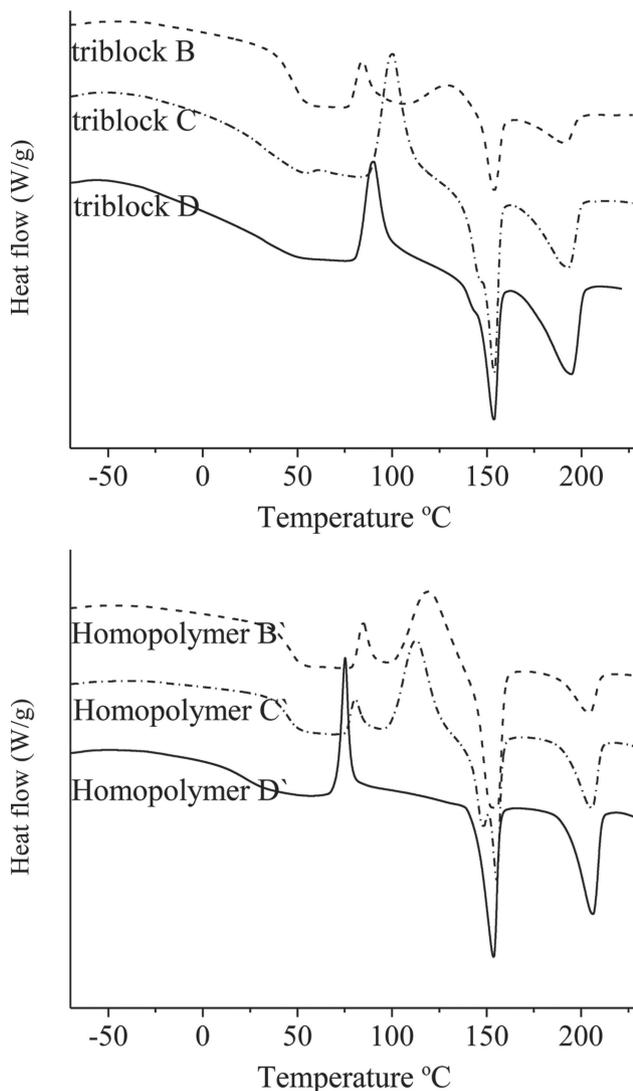


Figure 4. Second heating cycle of the triblock blends and homopolymer blends.

and (ϵ) the melting of stereocomplex crystals. The drop in the glass transition of the amorphous phase (transition α) is expected since PEPG is miscible with PLLA.

The transition (β), present only in the triblock blends B and C, is assignable to the stereocomplex crystals that could not be formed in the first cooling cycle from temperature T_b ($T_{m,PLLA} < T_b < T_{m,stereocomplex}$) to room temperature. These additional stereocomplex crystals are absent in the triblock blend D and all the homopolymer blends. As assigned previously, the transition (ϵ) corresponds to the melting of the stereocomplex crystals. The difference between the enthalpy of transitions (ϵ) and (β) corresponds to the degree of stereocomplex crystallinity in the as-prepared samples and is tabulated in Table 3. It can be seen that the degree of crystallinity is higher in the homopolymer blends. On subsequent cooling from $T > T_{m,stereocomplex}$ (Figure 3) stereocomplex crystallization occurs in all the homopolymer blends. In contrast, a smaller amount of crystallization occurs in triblock blends C and D while no crystallization occurs in triblock blend B during the cooling cycle. In addition, it is also found that the stereocomplex crystallization temperature, T_c , is 13–16 °C higher in case of the homopolymer blends when compared to the triblock blends. In samples where stereocomplex crystallization remains incomplete or does not take place at all during the cooling scan, a stereocomplex crystallization transition occurs during the second heating scan (triblock B, homopolymer B', C', Figure 4). These data unambiguously show that the stereocomplex crystallization under the non-isothermal crystallization conditions, is considerably easier in the homopolymer blends as compared to the triblock blends leading to a higher degree of crystallinity, consistent with the results obtained from the isothermal crystallization experiments.

The transitions (γ) and (δ) have identical crystallization and melting enthalpy values, which proves that all

Table 3. Enthalpy of the stereocomplex crystallization and melting transitions (first and second heating cycles).

Sample	First heating				Second heating
	Transition β ΔH [J g ⁻¹]	Transition ϵ ΔH [J g ⁻¹]	Difference ($\epsilon-\beta$) ΔH [J g ⁻¹]	Crystallinity ($\epsilon-\beta$)*100/142 [%]	Melting (scomplex) ΔH [J g ⁻¹]
Triblock B	3	3.5	0.5	0.4	3.5
Triblock C	6	11	5	3.5	10
Triblock D	0	15	15	10.6	14
Homopolymer B'	0	9	9	6.3	7
Homopolymer C'	0	15	15	10.6	11
Homopolymer D'	0	22	22	15.5	15

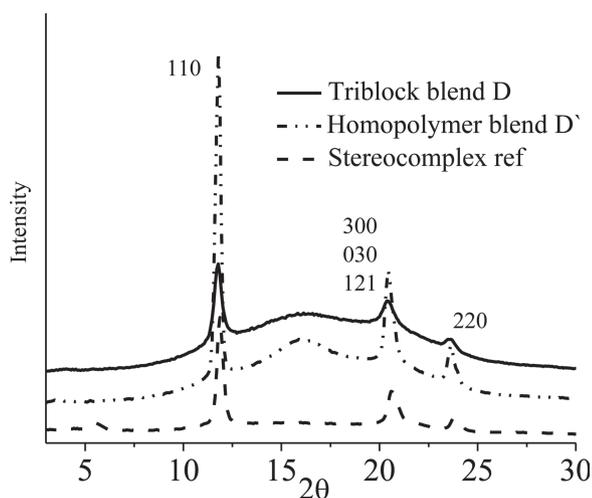


Figure 5. WAXS profiles of as-prepared composition D blends.

the PLLA crystallization occurs during the DSC heating scan and negligible PLLA crystals are present in the as-prepared blends.

3.3. Characterization of Stereocomplex Crystals Formed in the Homopolymer and Triblock Blends

WAXS and Raman scattering have been used to characterize the crystals formed in the two sets of as-prepared PLLA blends. As seen from Figure 5, the samples exhibit diffraction peaks characteristic of the PLA stereocomplex.^[14,17,32] In addition, a weak peak is observed at 16.5° indicating the presence of a small amount of PLLA crystals.^[33] It can be seen that the diffraction peaks in the triblock blend samples are less intense and broader when compared to the sharp and narrower peaks present in the homopolymer blends (FWHM_{110} triblock blend = $1.5 \times \text{FWHM}_{110}$ homopolymer blend) (Table 4). The crystal size is determined from the WAXS data using the Scherrer equation as described below:

$$\tau = \frac{K\lambda}{\beta \cos \theta}$$

where, τ is the mean crystal size, K is a dimensionless shape factor with a typical value of 0.9, β is the full width at half maxima (FWHM), and θ is the Bragg angle. This shows that the stereocomplex crystals formed in the triblock copolymer blends are smaller and less-perfect

Table 4. Crystal size characterization in the triblock blend D and homopolymer blend D'.

Blend	FWHM_{110} [°]	Size [nm]	$\text{FWHM}_{300/003/121}$ [°]	Size [nm]
Triblock D	0.5	17	0.83	10.7
Homopolymer D'	0.33	25.7	0.496	18

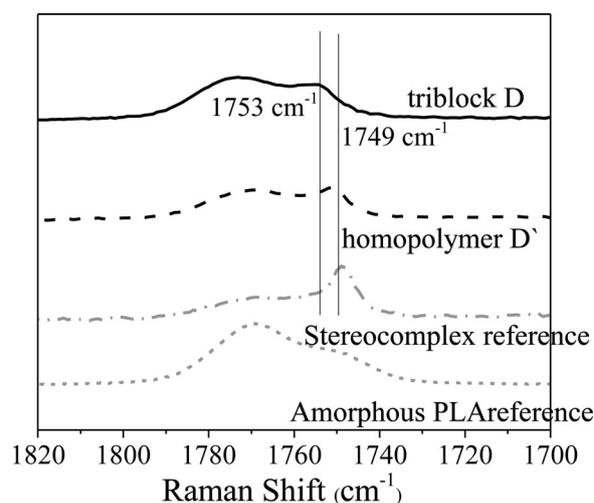


Figure 6. Raman spectra of the as-prepared composition D blends (Carbonyl region).

than those present in the homopolymer blends. This is consistent with the difference in the melting temperatures observed. The melting temperatures of the stereocomplex crystals formed in the homopolymer blends are 20° higher than those in the triblock blends.

Similar results are obtained from the Raman data. As shown in Figure 6 the Raman spectra in the carbonyl region, for both the homopolymer and triblock blends exhibit features expected for stereocomplex crystals.^[34,35] However, there is a blue shift in the stereocomplex component in the triblock copolymer/PLLA blends indicating weaker dipole-dipole interactions and hence a less perfect stereocomplex crystal.^[36] This is consistent with the X-ray and DSC data.

4. Conclusion

In this paper, the crystallization of two chemically identical but physically different co-crystallizing polymer blends is studied. The first set studied is PLLA/PDLA-PEPG-PDLA triblock copolymer blends, while the second set studied is homopolymer blends of PLLA/PEPG/PDLA with compositions identical to the triblock copolymer/PLLA blends. All the crystallization data obtained under isothermal and non-isothermal crystallization conditions have shown that attachment of PDLA to the miscible softblock slows the stereocomplex crystallization. It is established that in the homopolymer blends, rapid stereocomplex crystallization occurred because of the high mobility of the low-molecular-weight PDLA, which resulted in the amorphous miscible soft polymer being trapped in the intraspherulitic amorphous regions. The slowness of the crystallization kinetics in triblock blends led to the formation of a

continuous amorphous phase with dispersed stereocomplex crystallites. Analysis of the resultant stereocomplex crystals in the two sets of blends using WAXS, Raman scattering, and DSC revealed that the stereocomplex crystals formed by the homopolymer blends were more perfect with a melting temperature 15–20 °C higher than those formed by the triblock blends. From these studies, it can be concluded that the attachment of PDLA to a miscible mid-block significantly affects its co-crystallization with PLLA. These effects can be ascribed to the restricted mobility of the PDLA chains leading to reduced segregation of PLLA and PDLA, thus reducing both the rate and degree of stereocomplex crystallization.

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