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2-Biopolymers

Poly(D-lactide)–Poly(menthide)–Poly(D-lactide) Triblock Copolymers as Crystal Nucleating Agents for Poly(L-lactide)

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Summary: Poly(*d*-lactide)–poly(menthide)–poly(*d*-lactide) (PDLA–PM–PDLA) triblock copolymers were explored as novel nucleating agents for the crystallization of poly(*l*-lactide) (PLLA). PLLA/PDLA-PM-PDLA blends containing $\geq$85 wt% PLLA were prepared in a batch melt mixer. SAXS analysis was consistent with the ability of PDLA–PM–PDLA to form micelles when mixed with atactic polylactide. The presence of the stereocomplex in the PLLA matrix was confirmed by differential scanning calorimetry (DSC). The effectiveness of the putative stereocomplexed micelle crystallites for nucleating PLLA crystallization was also confirmed by DSC. Nucleation efficiencies near 100% were obtained when using a triblock copolymer with 15 kg/mol PDLA end blocks. In addition, fast crystallization kinetics were observed in isothermal crystallization experiments at 140 °C. Compared to PLLA/PDLA homopolymer blends, improvements in nucleation efficiency were observed when blending PLLA with PDLA-containing triblock copolymers.

Keywords: crystallization; differential scanning calorimetry (DSC); nucleation; polylactide; stereocomplex

Introduction

Polylactide is a biorenewable and biodegradable polyester[1] synthesized by the ring-opening polymerization of racemic *d,l*-lactide, *l*-lactide or *d*-lactide. Isotactic poly(*l*-lactide) (PLLA) and poly(*d*-lactide) (PDLA) are semi-crystalline ($T_m \approx 180\,^{\circ}$C) with identical physical properties.[2] Blends of PLLA and PDLA form stereocomplex crystallites with a distinct crystal structure that melt at approximately 230 °C.[3,4] The high melting temperature is attributed to strong van der Waals interactions that cause a specific energetic interaction-driven packing.[5] Ikada and Tsuji et al. were the first to report the formation of the polylactide stereocomplex, and they have investigated the influences of blending ratio,[6] molecular weight,[6,7] optical purity,[8,9] and blending protocol[6–9] on formation and properties[10] of the stereocomplex. More recently, efforts have focussed on the mechanism of formation,[11] spherulite growth,[12,13] and crystal density[12,14] of stereocomplex crystallites.

Pure PLLA is slow to crystallize and nucleating agents are required in order to make use of industrially relevant processing techniques.[15] Common PLLA nucleating agents such as talc[15] and clay[16] increase the rate of crystallization, but reduce the toughness in some systems.[17] In 1995 Brochu et al. found that PLLA crystallization can take place epitaxially on PLLA/PDLA stereocomplex crystallites,[18] suggesting that stereocomplex crystallites could act as nucleation sites for the crystallization of PLLA. This notion has been confirmed through studies of the ability

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of PDLA/PLLA stereocomplex crystallites to nucleate the crystallization of PLLA.[18–24] For example, Schmidt and Hillmyer[19] and Yamane and Sasai[21] confirmed that the addition of PDLA is effective in increasing the crystallite number density, which results in an increase in the overall crystallization rate. Schmidt and Hillmyer also observed significant enhancement in the crystallization rate of PLLA when only 0.5 wt% of PDLA was present[19] and found that the nucleation efficiency was the highest when PDLA of moderate molecular weight (15 kg mol^{-1}) was employed.[20] Anderson and Hillmyer investigated the nucleation efficiencies of polylactide stereocomplex crystallites prepared in the melt.[23] Nucleation efficiencies near 100% and fast isothermal (140 °C) crystallization rates were observed.[23]

We recently prepared biorenewable ABA triblock copolymers containing atactic, amorphous poly(*d*,*l*-lactide) end blocks and amorphous, low glass transition temperature poly(menthide) [PM] midblocks that microphase separate and behave as thermoplastic elastomers.[25] More recently, we have expanded that work to include triblocks that contain semicrystalline PDLA endblocks.[26] We hypothesize that melt blending (at 190 °C) a small fraction of PDLA–PM–PDLA triblock copolymers with PLLA will result in the formation of stereocomplex crystallites at the corona of in-situ formed PDLA–PM–PDLA micelles, and cooling will lead to nucleation of the PLLA matrix by the stereocomplex crystallite corona (Figure 1). Schmidt has demonstrated that mixing 1 wt% of polyisoprene(PI)–PLLA diblock copolymer in a melt of atactic polylactide leads to PI micelles with core radii of approximately 13 nm and micelle densities of about 10^{15} micelles cm^{-3}.[20] Because of the small size and high number density of block copolymer micelles at low concentrations, PDLA block copolymer micelles could dramatically enhance the crystallization of PLLA.

In this paper we explore the ability of the PDLA–PM–PDLA triblock copolymers to act as nucleating agents for PLLA. First, we evaluated the ability of the triblocks to form micelles when mixed with atactic, noncrystalline PLA by small-angle x-ray scattering (SAXS). The nucleation efficiency of the stereocomplexed micelles in a PLLA matrix was then assessed.[20,23,27,28] In addition, isothermal crystallization experiments were performed at 140 °C to determine the ability of the all-biorenewable block copolymer to increase the crystallization rate of PLLA. Quantifiable improvements in nucleation efficiency were observed when blending PLLA with PDLA-containing triblock copolymers as compared to PDLA homopolymer. This new approach to the nucleation of PLLA with all-biorenewable PDLA block copolymers significantly increases the nucleation efficiency at relatively low levels of nucleating agent.

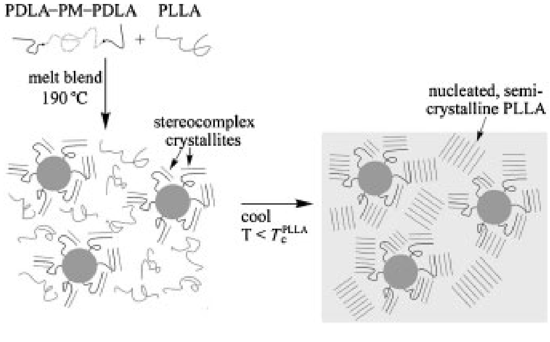

Figure 1.
Schematic representation of the nucleation of PLLA using PDLA–PM–PDLA triblock copolymers.

Experimental Part

Materials

All triblock copolymers were synthesized and characterized using methods previously reported for atactic PLA-PM-PLA triblocks.[25,26] Commercial grade poly(*l*-lactide) was supplied by the Toyota Motor Corporation.

Blend Preparation

Prior to blending, the PLLA pellets and the triblock copolymer (4 g total) were manually pre-mixed in the desired compositions in a 20 mL vial. Melt blending was performed in a DACA mixer. The pre-mixed material was added to the chamber of the mixer, which was heated to 190 °C (under a constant stream of nitrogen gas) at a mixer speed of 100 rpm. After 15 min the mixing was stopped and the blends were removed from the chamber using a spatula and allowed to cool to room temperature on the bench top.

SAXS Analysis

Measurements for small angle x-ray scattering (SAXS) were performed at the University of Minnesota Twin Cities Characterization Facility beamline. Cu Kα x-rays were generated by a Rigaku Ultrex 18 kW generator. Temperature control inside the evacuated sample chamber was accomplished with water-cooling and electrically heating the brass-block sample holder. All samples were heated to 180 °C and annealed for 5 min in the sample chamber prior to SAXS measurements at 180 °C. Two-dimensional diffraction images were recorded using a Bruker Hi-Star multiwire area detector located at the end of a 4.38 m evacuated flight tube and corrected for detector response before analysis. The two-dimensional images were azimuthally integrated and reduced to the one-dimensional form of scattered intensity versus the spatial frequency q.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Q1000 with nitrogen as the purge gas and an indium calibration standard. Samples weighing 4.0–7.0 mg were loaded into aluminum hermetic pans and the pans were sealed prior to measurement. The melting and glass transition temperatures were determined by heating the sample from $-60\,^{\circ}\mathrm{C}$ at $10\,^{\circ}\mathrm{C\,min^{-1}}$. The percent crystallinity was calculated using the equation

$$\%\ \mathrm{Crystallinity} = 100 * \frac{\Delta H_\mathrm{f}}{f \Delta H_\mathrm{f}^{\infty}} \qquad (1)$$

where ΔH_f is the measured heat of fusion, f is the weight fraction of the component in question and $\Delta H_\mathrm{f}^{\infty}$ is the enthalpy of fusion for a crystal having infinite crystal thickness. Values of $\Delta H_\mathrm{f}^{\infty}$(PLLA) of 94 J g^{-1} and $\Delta H_\mathrm{f}^{\infty}$(stereocomplex) = 142 J g^{-1} were used to make direct comparisons with the literature.[23,29,30]

Nonisothermal temperature programs were used to evaluate PLLA nucleation. First, a temperature program, modeled after the program used by Schmidt and Hillmyer, was used to determine the nucleation efficiency scale with self-nucleated PLLA.[19] A second temperature program was used to determine the nucleation efficiency of the PLLA/triblock copolymer blends. In this program, the samples were heated to 185 °C at 200 °C min^{-1}, held at 185 °C for 5 min, and cooled to 60 °C at 5 °C min^{-1}. The temperature of crystallization (T_c) and the corresponding heat of crystallization (ΔH_c) values were acquired directly from the final step. An isothermal temperature program was used to evaluate the crystallization half-time ($t_{1/2}$). Here, the samples were directly heated to 185 °C at 200 °C min^{-1}, held at 185 °C for 5 min, then quenched to 140 °C at 200 °C min^{-1}. The samples were held at 140 °C for 15 to 90 min.

Results and Discussion

Formation of PDLA–PM–PDLA/PLLA Stereocomplex Crystallites

Characterization data for the PDLA–PM–PDLA triblock copolymers and PLLA homopolymer used to prepare the melt

Table 1.
Characterization of polylactide homopolymer and polylactide-containing triblock copolymer samples

Sample	$T_{g,\ PM}$[a] (°C)	$T_{g,\ PLA}$[a] (°C)	$T_{m,\ PLA}$[a] (°C)	X_{PLA} (%)[a]	M_n[b] (kg/mol)	PDI[b]
PLLA		53	174	43	65	1.95
PDLA-PM-PDLA (3.8–34–3.8)	−23		143	58	50	1.18
PDLA-PM-PDLA (6.8–28–6.8)	−21	52	149, 154	57	71	1.28
PDLA-PM-PDLA (11–33–11)	−21		151, 160	48	74	1.16
PDLA-PM-PDLA (15–33–15)	−21	59	165	49	68	1.23
PLLA-PM-PLLA (15–31–15)	−21	61	166	43	65	1.31

[a] Determined by DSC.
[b] Determined by SEC versus polystyrene standards.

blends are given in Table 1. Additionally, we investigated blends containing PLLA homopolymer and a PLLA–PM–PLLA triblock copolymer (Table 1). All triblock copolymers listed in Table 1 are labeled according to the stereochemistry of the polylactide blocks followed in parentheses by the number average molecular weights (determined by ^{1}H NMR spectroscopy) of each block in kg mol^{-1}. PLLA blends containing 0.5% to 15% PDLA–PM–PDLA triblock copolymer were prepared by hand mixing the polymers at room temperature followed by melt blending in a DACA mixer at 190 °C.

The formation of the stereocomplex was confirmed by DSC traces obtained on the as-prepared melt blended samples that were cooled to –60 °C and heated at 10 °C min^{-1} to 250 °C (Figure 2). In most cases, the DSC signal corresponding to the glass transition temperature for polymenthide was not intense enough to accurately measure. The glass transition temperature for PLLA was between 52 and 61 °C for all samples. Endotherms indicative of both PLLA homopolymer and stereocomplex melting were observed for all PLLA/PDLA–PM–PDLA melt blends except the 99/1 wt% PLLA/PDLA-PM-PDLA (11–33–11) blend (Table 2). The melting peak from the PLLA homopolymer is present around 174 °C, while the stereocomplex melting peak is around 215 °C. For all of the blends, the level of crystallinity (Equation 1) was around 55% for the PLLA (accounting for cold crystallization) and 16 to 60% for the stereocomplex.

SAXS Characterization of PLA/PDLA–PM–PDLA Micelles

A/A-B-A blends containing low levels of the triblock copolymers in Table 1 are expected to form spherical micelles comprised of a B block core and A block corona swollen by a matrix of A (see Figure 1). Poly(*d*,*l*-lactide)/PLLA-PM-PLLA (15–31–15) melt blends containing 0.5 to 15 wt% triblock copolymer were prepared to explore the micellization behavior of the PLLA/PDLA–PM–PDLA blends in the melt. Each sample was transparent, consistent with microphase separation. Using a Percus-Yevick (PY) analysis, the characteristic

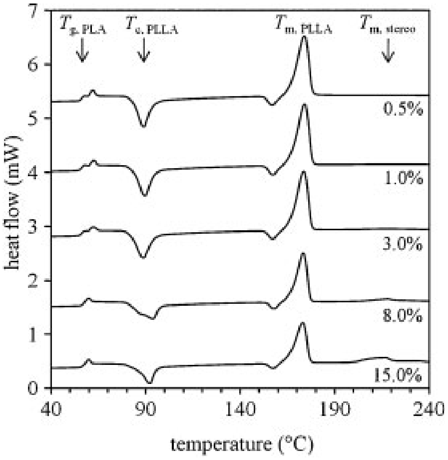

Figure 2.
DSC heating scans of PLLA melt blended with varying weight percents of PDLA-PM-PDLA (15–33–15). DSC program: samples were cooled to −60 °C from room temperature and heated at 10 °C min^{-1} to 250 °C. Data shown is from the heating scan. The data have been shifted vertically for clarity.

Table 2.
PLA/PLLA–PM–PLLA (15–33–15) SAXS analysis

Additive	Additive wt %	R_c (nm)[a]	micelle density (# micelles cm^{-3})
PDLA-PM-PDLA (15–33–15)	0.5	17.1	1.3×10^{14}
PDLA-PM-PDLA (15–33–15)	1.0	17.2	2.4×10^{14}
PDLA-PM-PDLA (15–33–15)	3.0	17.2	7.3×10^{14}
PDLA-PM-PDLA (15–33–15)	8.0	17.6	1.8×10^{15}
PDLA-PM-PDLA (15–33–15)	15.0	18.2	3.1×10^{15}

[a] Calculated from the principal peak in the SAXS data and $qR_c = 5.76$.

scattering obtained from these systems can be modeled.[31] The use of SAXS and the PY analysis to obtain quantitative information on spherical micelles in a homopolymer matrix has been demonstrated previously.[20,32]

Equation 2 describes the scattering intensity of radiation, I(q), from an array of particles,

$$I(q) = (\Delta\rho)^2 \, N \, P(q) \, S(q) \qquad (2)$$

where q is the scattering wavevector, $\Delta\rho$ is the electron density difference between the particles and their surroundings, N is the number of scattering particles, P(q) is the form factor, and S(q) is the interference (structure) factor.[31] The electron density of the corona and the matrix in a PLA/PDLA–PM–PDLA melt blend are equivalent at 180 °C (i.e., both are amorphous polylactide) so the scattering will stem entirely from the micelle cores. The intraparticle scattering for a dilute array of spheres is dependent on the size of the particles and can be expressed by a spherical form factor. The first maxima in the spherical form factor occurs at $qR_c = 5.76$, where R_c is the sphere (core) radius.[20,31] The SAXS patterns at 180 °C for the PLA/PDLA–PM–PDLA melt blends (Figure 3) contain broad peaks and have a narrow range of q due to the limitations of the instrument. Assuming that the observed peaks correspond to the first intraparticle scattering peak maxima (i.e., $qR_c = 5.76$), R_c values at 180 °C were calculated and are given in Table 2. The micelle densities of the blends were calculated based on the R_c and the amount of polymenthide in the blend (Table 2),[33] and ranged from 10^{14} to 10^{15} micelles cm^{-3}, values much higher than the PLLA/PDLA stereocomplex crystallite densities of 10^7 to 10^9 micelles cm^{-3} inferred in previous work.[20] The higher nucleation densities of the micelles suggest that the micelles could have higher nucleation efficiencies relative to the PLLA/PDLA crystallites.

Nucleation Efficiency in PLLA/PDLA–PM–PDLA Blends

To determine the effectiveness of a nucleating agent, we first need to create a nucleation efficiency scale by examining the melting behavior of pure PLLA. Following the example set forth by Wittman et al.,[27,28] Schmidt and Hillmyer constructed a calorimetric nucleation efficiency (NE) scale for PLLA, employing nonisothermal DSC experiments.[19] A nucleation efficiency scale for a polymer is determined by cooling a

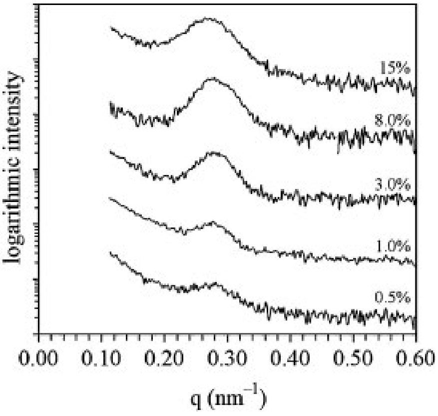

Figure 3.
SAXS data from PLA/PLLA-PM-PLLA (15–31–15) blends containing between 0.5 and 15 wt% triblock copolymer acquired at 180 °C.

polymer sample from the melt and observing the temperature at which the sample crystallizes. Minimum nucleation efficiency occurs when there is an absence of nucleation sites in the melt. Upon cooling pure PLLA from the melt, the minimum efficiency crystallization temperature, T_c^{min}, is obtained. The range of temperatures in which there exists both melted PLLA and semicrystalline PLLA is called the partial melting zone (pmz). Maximum efficiency occurs at the the highest nucleation concentration, which occurs at the lowest temperature in the pmz. Cooling the polymer from this lowest temperature would give us the maximum efficiency crystallization temperature, T_c^{max}. Using a temperature program modeled after Anderson and Hillmyer,[23] we determined $T_c^{min} = 105.5\,°C$ and $T_c^{max} = 136.6\,°C$ for the pure PLLA used in this study. The NE of a nucleating agent is calculated using the following equation[27,28]

$$\mathrm{NE} = \frac{T_c - T_c^{min}}{T_c^{max} - T_c^{min}} * 100 \qquad (3)$$

where T_c is the crystallization temperature of the blend.

The nucleation efficiency of the PLLA/PDLA–PM–PDLA stereocomplexed micelles was determined using a temperature program also modeled after the program used by Anderson and Hillmyer.[23] First, the samples were quickly heated to 185 °C (well above T_m for PLLA). At 185 °C the homopolymer PLLA is completely melted and any stereocomplex crystallites that formed from the PDLA blocks of the triblock copolymer during melt blending would still be present ($T_m > 185\,°C$). After 5 min at 185 °C the samples were cooled at 5 °C min^{-1} and the T_c and area of the crystallization exotherm (ΔH_c) were recorded (Table 3). The DSC cooling scans for PLLA homopolymer and selected PLLA/PDLA-PM-PDLA (15–33–15) melt blends are shown in Figure 4.

We observed an increase in T_c values for all blends compared to the pure PLLA, indicative of enhanced nucleation (Table 3). The lowest NE value (Equation 3) obtained was 35% for the 95.5/0.5 wt% PLLA/PDLA-PM-PDLA (3.8–34–3.8) melt blend that contained less than 0.1 wt% PDLA. By increasing the triblock copolymer content to 99/1 wt% (less than 0.2 wt% PDLA) a nearly two-fold increase in NE was observed. Increases in NE were observed with increasing additive content for the PLLA/PDLA–PM–PDLA as illustrated in Figure 4. A gradual increase in NE was observed when the additive was further increased to 3% and 8%, and a slight change in NE was observed when increasing the additive to 15 wt%.

Similar to previous findings, the nucleation efficiency is dependent on the molecular weight of the PDLA in the PLLA blends.[20,23] All PLLA/PDLA-PM-PDLA (3.8–34–3.8) blends have lower NE values than the blends containing triblock copolymers of higher PDLA-block molecular weight at identical wt% (Table 3). PLLA/PDLA-PM-PDLA (15–33–15) melt blends have the highest nucleation efficiencies at all compositions. The NE of the melt blend containing 0.5% triblock copolymer was 72% and increased to nearly 100% for the sample containing 15 wt% triblock copolymer, suggesting that the putative stereocomplex micelles behave as a nearly ideal nucleating agents. Schmidt and Hillmyer[20] and Anderson and Hillmyer[23] also observed increases in the NE values when using approximately 15 kg mol^{-1} PDLA compared to molecular weights of approximately 5 and 50 kg mol^{-1}. At low PDLA–PM–PDLA block copolymer concentrations, the NE of PLLA/PDLA–PM–PDLA melt blends are similar to those observed for PLLA/PDLA at higher levels of PDLA. For example, a nucleation efficiency of 67% was obtained for a PLLA/PDLA melt blend containing 0.5 wt% of low molecular weight (4.8 kg mol^{-1}) PDLA.[23] The 99/1 wt% PLLA/PDLA-PM-PDLA (3.8–34–3.8) blend containing a significantly lower fraction of PDLA (0.18 wt% PDLA) has a nucleation efficiency of 65%. We attribute this enhancement in NE with lower wt% PDLA in the blends to the superior nucleating ability of stereocomplexed triblock copolymer micelles over the dis-

Table 3.
Nonisothermal DSC results for self-nucleated PDLA–PM–PDLA/PLLA melt blends (cool rate = 5 °C min^{-1}).

Additive	Add. wt %	PDLA wt%	T_c (°C)	NE^a (%)	ΔH_c (J/g)	X^b_{PLLA} (%)	$t_{(1/2)}$ (min)
None	0.0	0.0	105	0	35	37	44.3
PDLA-PM-PDLA (3.8–34–3.8)	0.5	0.1	117	35	41	44	9.5
PDLA-PM-PDLA (3.8–34–3.8)	1.0	0.2	126	65	41	45	3.4
PDLA-PM-PDLA (3.8–34–3.8)	3.0	0.6	128	72	43	48	2.9
PDLA-PM-PDLA (3.8–34–3.8)	8.0	1.5	132	84	45	53	2.0
PDLA-PM-PDLA (3.8–34–3.8)	15.0	2.8	129	75	39	50	2.3
PDLA-PM-PDLA (6.8–28–6.8)	0.5	0.2	126	65	43	46	3.9
PDLA-PM-PDLA (6.8–28–6.8)	1.0	0.3	127	69	43	46	3.4
PDLA-PM-PDLA (6.8–28–6.8)	3.0	1.0	130	78	43	47	2.6
PDLA-PM-PDLA (11–33–11)	0.5	0.2	124	58	43	46	4.1
PDLA-PM-PDLA (11–33–11)	1.0	0.4	128	72	50	54	2.9
PDLA-PM-PDLA (11–33–11)	3.0	1.2	129	76	42	47	2.7
PDLA-PM-PDLA (11–33–11)	8.0	3.2	133	88	43	51	1.9
PDLA-PM-PDLA (11–33–11)	15.0	6.0	132	86	37	49	1.9
PDLA-PM-PDLA (15–33–15)	0.5	0.2	128	72	43	46	2.7
PDLA-PM-PDLA (15–33–15)	1.0	0.5	131	81	42	46	2.4
PDLA-PM-PDLA (15–33–15)	3.0	1.4	131	82	45	59	2.4
PDLA-PM-PDLA (15–33–15)	8.0	3.9	134	91	40	48	1.7
PDLA-PM-PDLA (15–33–15)	15.0	7.2	136	98	36	50	1.3
PLLA-PM-PLLA (15–31–15)	0.5	104	104	−4	31	33	13.6
PLLA-PM-PLLA (15–31–15)	1.0	102	102	−10	28	30	23.5
PLLA-PM-PLLA (15–31–15)	3.0	101	101	−14	26	28	30.7

[a] NE values obtained from Equation 3.
[b] Calculated according to Equation 1 with ΔH_f^{∞}(PLLA) = 94 J g^{-1}.

persed PLLA/PDLA stereocrystallites. Interestingly, addition of the triblock PLLA-PM-PLLA (15–31–15) to PLLA lowered the T_c when compared to melt blended PLLA, resulting in NE values of less than zero (see Table 3).

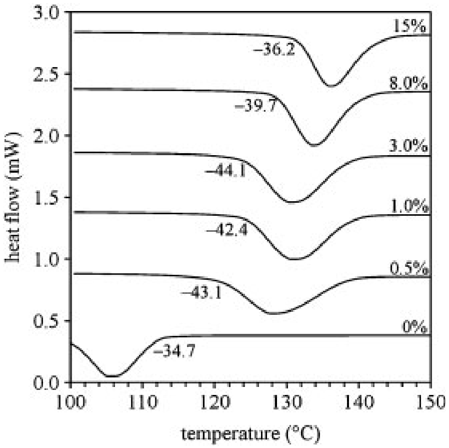

Figure 4.
Selected crystallization exotherms of PLLA/PDLA-PM-PDLA (15–33–15) melt blends cooled (5 °C min^{-1}) from 185 °C. The composition of triblock copolymer is listed on the right, and the ΔH_c values (J g^{-1}) are recorded next to each exotherm. The data have been shifted vertically for clarity.

The PLLA ΔH_c values for all of the PLLA/PDLA–PM–PDLA melt blends were higher than for the homopolymer PLLA. The ΔH_c of the melt processed PLLA was 35 J g^{-1}, corresponding to a fractional PLLA crystallinity of 37% (Equation 1). For the 99.5/0.5 wt% PLLA/PDLA-PM-PDLA(11–33–11) blend, the ΔH_c was determined to be 43 J g^{-1} resulting in a PLLA crystallinity of 46% after accounting for a loss of 0.70% of the sample due to the triblock copolymer and stereocomplex formation. Therefore, crystallinity increased by approximately 15% upon addition of the stereocomplexed nucleating micelles. This is consistent with the melt blend data of Anderson and Hillmyer and solution blend data of Yamane et al.[21,23]

Isothermal Crystallization

The effectiveness of a nucleating agent can also be assessed by measuring the crystallization half-time in an isothermal crystallization experiment. In this experiment, the

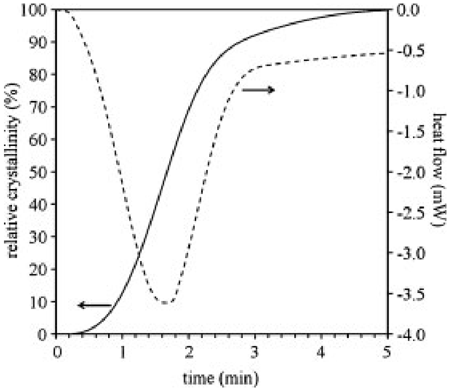

Figure 5.
Representative isothermal DSC trace taken at 140 °C (dashed line) and corresponding curve (solid line) for determining the crystallization half-time, $t_{1/2}$.

polylactide melt blends were held for 5 minutes at 185 °C and quenched to 140 °C. Crystallization at 140 °C was monitored by DSC. From the integration of the resultant crystallization exotherms, a relative crystallinity based on the total area of the crystallization exotherm can be calculated at a given time. Figure 5 gives a representative example of the observed crystallization exotherm and the calculated relative crystallinity. From the relative crystallinity curve, the time it takes to reach 50% crystallinity, the $t_{1/2}$, can be determined. For example, from Figure 5, the $t_{1/2}$ is approximately 1.7 min. The $t_{1/2}$ values are given in Table 3 for PLLA and the melt blends.

A significant decrease in the $t_{1/2}$ values was observed in the melt blends when PDLA–PM–PDLA triblock copolymers were added. As the wt% of additive in the melt blends increased, the $t_{1/2}$ values decreased. The $t_{1/2}$ values for the PLLA/PDLA-PM-PDLA (15–33–15) melt blends were significantly smaller than the other blends, in agreement with NE data (Table 3). The shortest $t_{1/2}$ value of 1.3 minutes was obtained with the 85/15 wt% PLLA/PDLA-PM-PDLA (15–33–15) melt blend. The $t_{1/2}$ values obtained were very similar to those seen by Schmidt and Hillmyer.[19] The smallest $t_{1/2}$ at 140 °C was 75 seconds for a solution blend with 10% PDLA incorporation. However, even lower values (less than 1 min) were observed for PLLA/PDLA melt blends by Anderson and Hillmyer.[23]

Conclusions

We have demonstrated that PDLA–PM–PDLA triblock copolymers act as novel crystallization nucleating agents for PLLA. Our data suggest that melt blends of 0.5 to 15 wt% PDLA–PM–PDLA triblock copolymers with PLLA formed triblock copolymer micelles in which the PDLA corona formed stereocomplexes with PLLA. In related PDLA-PM-PDLA/PLA belends the PM core radius was approximately 18 nm with micelle number densities of approximately 10^{15} micelles cm^{-3}. These number densities are much higher than those obtained using the PLLA/PDLA homopolymer blend approach (10^{7}–10^{9} cm^{-3}). The nucleation efficiency of the putative stereocomplexed micelles was evaluated and remarkable increases in the nucleation efficiencies were observed. In addition, in isothermal experiments the $t_{1/2}$ values were low, indicating a significant enhancement in the PLLA crystallization rate. The blends containing PDLA-PM-PDLA (15–31–15) stood out as having the highest nucleation efficiencies and the lowest $t_{1/2}$ values. Blends containing low molecular weight PDLA blocks at low concentrations (ex. 99/1 wt% PDLA-PM-PDLA (3.8–34–3.8)) successfully nucleated PLLA with high NE values. This study demonstrates the feasibility of using PDLA block copolymers at low levels as effective nucleating agents for PLLA.

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