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Nucleation and Crystallization of PLDA-*b*-PE and PLLA-*b*-PE Diblock Copolymers

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Summary: The nucleation and crystallization of two types of strongly segregated poly(lactide)-*block*-polyethylene diblock copolymers with an approximate 50/50 composition has been investigated. One material contains an amorphous PLDA block (PLDA-*b*-PE) and the other contains a semicrystalline PLLA block (PLLA-*b*-PE). The overall isothermal crystallization rate of the PLLA block was slowed down as compared to homo-PLLA by the covalently bonded PE chains that were molten at the PLLA crystallization temperatures. This crystallization rate depression of the PLLA block produces a coincident crystallization process when PLLA-*b*-PE is cooled down from the melt at rates larger than 2 °C/min. The overall crystallization rate of the PE block is faster when it is covalently bonded to previously crystallized PLLA than when it is attached to a rubbery PDLA block, this results from a nucleation effect of PLLA on the PE block. Polarized Light Optical Microscopy (PLOM) confirmed the confined nature of the crystallization process within lamellar microdomains for both diblock copolymers, since neither PLLA nor PE are capable of breaking out and spherulites can not be formed.

Keywords: coincident crystallization; double crystalline diblock copolymers; PE; PLDA; PLLA

Introduction

Strongly segregated block copolymers have attracted much attention in view of their fascinating morphologies and their potential applications as nanotemplates.[1] In the case of polylactide-*block*-polyethylene, the material includes a bio-stable block (i.e., polyethylene) and a biodegradable one, an interesting combination that can provide ''contact guidance'' for cell adhesion and may be interesting for specific applications.[2] The performance of the material will be dependent of its degree of crystallinity and morphology. The morphology will be a function of the composition and the segregation strength. For strongly segregated systems, the thermodynamic repulsion between the blocks leads to stable microdomains where crystallization occurs in a confined fashion (i.e., within lamellar, gyroid, cylindrical or spherical phases).[3–5] The crystallization of AB diblock copolymers with one crystallizable block has been extensively studied in the literature[3–5] while that of double crystalline diblocks has been less studied and only recently reviewed.[6] In particular, there are not many double crystalline diblock copolymers where the low temperature melting block is polyethylene.

In this work, the thermal and morphological behaviour of PLDA-*b*-PE (poly(L, D-lactide)-*block*-polyethylene) and PLLA-*b*-PE (poly(L-lactide)-*block*-polyethylene) are studied. In the first case only the PE block can crystallize since the polylactide block is a mixture of L and D configurational isomers. In the second case, the PLLA block can also crystallize in addition to the PE block. In view of the large difference in solubility parameters between polyethylene and both types of polylactide,

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they are expected to be in the strong segregation regime. In fact, a simple calculation based on the molecular weight of the blocks employed in this work and their solubility parameters, yield values of the segregation strength parameter (i.e. χN[3]) larger than 350. The influence of the physical nature of the second block (either rubbery or semi-crystalline) on the crystallization kinetics of the PE block were examined. In the case of the PLLA block, a comparison is made with an equivalent molecular weight PLLA homopolymer (homo-PLLA).

Experimental Section

Materials

The synthesis of well defined PLDA-*b*-PE and PLLA-*b*-PE block copolymers has been previously described[7]. The PE block has been prepared by hydrogenating a high 1,4-polybutadiene and it can be considered a random copolymer of ethylene and butene (with a low butene content, of approximately 7%). Table 1 lists the molecular weight characterization data obtained by size exclusion chromatography (SEC) and by ^{1}H NMR spectroscopy. The diblock copolymer nomenclature that we have used in Table 1 denotes the PLLA block as L, PDLA block as LD and the PE block as E, subscripts indicate the approximate composition in weight % and superscripts the approximate number average molecular weight in kg/mol.

DSC

A Perkin-Elmer DSC-7 differential scanning calorimeter was employed. Samples were encapsulated in Aluminium pans (mass was approximately 5mg). The calibration was performed with indium and hexatriacontane and all tests were run employing ultra pure nitrogen as purge gas.

Isothermal crystallization experiments were also carried out by DSC. For the PLLA block within PLLA-*b*-PE and for the PE block within PLDA-*b*-PE, the samples were first heated to a temperature of approximately 20 °C higher than the melting point of either PLLA or PE blocks and kept at that temperature for 3 min in order to erase thermal history. Then the samples were cooled at 60 °C/min to the isothermal crystallization temperature and the DSC recorded the crystallization process as a function of time.

For the special case of the PE block within the PLLA-*b*-PE, the PLLA block was first crystallized until saturation. The sample was cooled from the melt to 25 °C and then heated to 130 °C in order to fully melt the PE block but not the PLLA block. The sample was then annealed at 130 °C for 15 min, with the purpose of promoting further crystallization and/or annealing of PLLA. Finally the sample was cooled at 60 °C/min to the chosen crystallization temperature of the PE block, and the isothermal crystallization of the PE block was recorded by the DSC.

Results and Discussion

Standard DSC Results

Figure 1 presents DSC cooling and subsequent heating scans at 10 °C/min for PLLA-*b*-PE, PLDA-*b*-PE and a homo-

Table 1.
Molecular Characteristics of the Block Copolymers and Homopolymers.

Sample code	PLLA/PCL exp. comp.[a)]	$\overline{M}_{n,exp}$[b)] PLLA block	$\overline{M}_{n,exp}$[b)] PE block	I[c)]
$PLLA^{24}$	100/0	24140	-	1.16
$L_{46}^{23}E_{54}^{27}$	46/54	22540	26480	
$LD_{54}^{32}E_{46}^{28}$	54/46	32419	27690	

[a)] Experimental compositions as determined by ^{1}H NMR spectroscopy.
[b)] Experimental $\overline{M}_n$ estimated by ^{1}H NMR spectroscopy.
[c)] Polydispersity index determined by SEC.

PLLA. The PLLA-*b*-PE diblock exhibits two well defined fusion endotherms, while both blocks crystallized in a single coincident exotherm upon cooling from the melt (as indicated in Figure 1). This coincident crystallization process is likely a consequence of the restrictions imposed on the crystallization of the PLLA block by the covalently bonded PE block. The crystallization kinetics of the PLLA block is slowed down and during cooling from the melt at 10 °C/min its delayed crystallization process overlaps with that of the PE block which starts at lower temperatures. Similar delayed crystallization kinetics as compared to parent homopolymers has already been reported previously for PPDX-*b*-PCL (poly(*p*-dioxanone)-*block*-poly(ε- caprolactone), PE-*b*-aPP (polyethylene-*block*-atactic polypropylene) and PEO-*b*-PB (poly-(ethylene oxide)-block- polybutadiene).[5] The crystallization kinetics study to be presented below will confirm the reduced overall crystallization rate of the PLLA block as compared to homo-PLLA. Furthermore, the crystallization process of both blocks can be separated by employing a slower cooling rate (see Figure 2) or by self-nucleating the PLLA block in a similar way to that reported previously for PPDX-*b*-PCL.[8] Additionally, WAXS experiments performed at room temperature after cooling the sample from the melt at 10 °C/min revealed reflections from both PLLA and PE indicating that both blocks had indeed crystallized.

In Figure 1 (left side), a small exothermic peak appears at lower temperatures after the main crystallization event. This small exotherm occurs in most ethylene-α-olefin copolymers at temperatures ranging from 50–75 °C and has been attributed to the crystallization of short linear sequences (that could be intramolecularly segregated) within the polymer chains.[9] Also in Figure 1 (right side), the DSC melting trace of the PLLA-*b*-PE diblock shows a bimodal endotherm at lower temperatures in the temperature range corresponding to the melting of the PE block. The bimodality arises from the interference of the PLLA block cold crystallization exotherm occurring at temperatures above its T_g (also visible in the DSC heating scan and at a temperaure almost identical to the T_g of homo-PLLA, see Table 2, as expected for a strongly

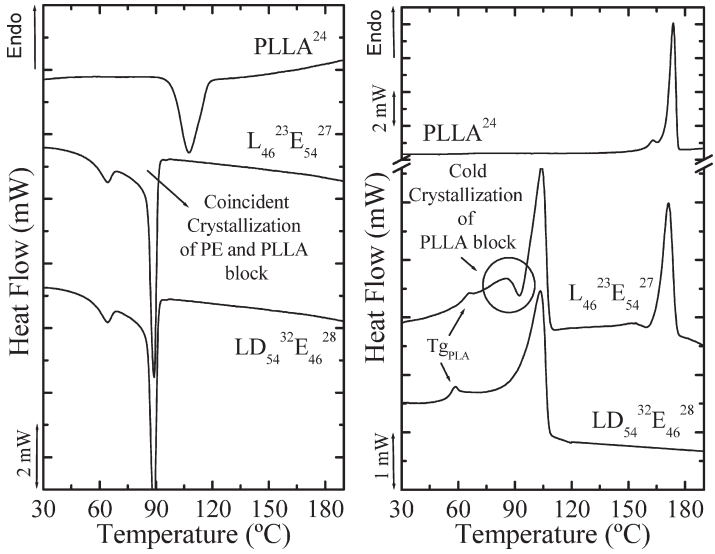

Figure 1.

Left side: DSC cooling scans at 10 °C. min^{-1}, after melting at 190 °C for 3 min. *Right side:* DSC subsequent heating scans (at 10 °C . min^{-1}) to the cooling scans presented in the left side.

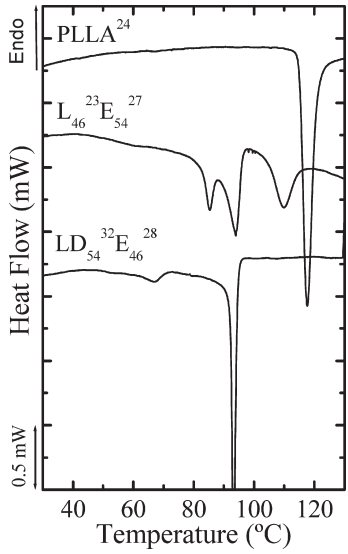

Figure 2.
DSC cooling scans at 2 °C . min^{-1}, after melting 20 °C above T_m for 3 min.

segregated copolymer.[3]. This can be easily demonstrated by partially melting the sample to 120 °C (only the PE block will melt), followed by cooling it to allow the crystallization of the PE block, then, upon reheating the melting endotherm acquires a shape very similar to that shown in Figure 1 (right side) for the melting of the PE block within PLDA-*b*-PE.

Figure 1 also shows the crystallization of the PE block within PLDA-*b*-PE diblock copolymer and its subsequent melting. Superimposed on the beginning of the melting DSC trace the T_g of the PDLA block can be clearly identified. Table 2 lists all relevant thermal transitions appreciated by DSC and the values of the crystallization and melting enthalpies.

With the intent of separating the crystallization exotherms corresponding to PLLA and PE blocks within the PLLA-*b*-PE diblock copolymer, a DSC cooling trace was recorded at 2 °C/min (see also Table 2). Figure 2 shows the cooling scan at this slower cooling rate for both diblock copolymer samples. The separate crystallization of each component in PLLA-*b*-PE can now be seen and can be compared with the crystallization of just the PE block in PLDA-*b*-PE. The crystallization of the PLLA block occurs at 109.8 °C under this cooling condition, however, even though it is now separate from that of the PE block (which now shows a bimodal distribution of crystallization temperatures whose origin is not yet clear), it is much lower than the crystallization temperature of the corresponding homo-PLLA at 117.6 °C at the same cooling rate. The results reveal the influence of the molten PE block on the overall crystallization of the covalently bonded PLLA block.

Figure 2 also shows that the PE block within PLLA-*b*-PE crystallizes at a peak temperature of 93.9 °C while the PE block within PLDA-*b*-PE does it at 93.2 °C. This

Table 2.
Thermal properties obtained from DSC scans presented in Figure 1 and 2.

Sample	Scan	PLA					PE			
		T_c	T_m	ΔH_c	ΔH_m	T_g	T_c	T_m	ΔH_c	ΔH_m
	rates	°C	°C	J . g^{-1}	J . g^{-1}	°C	°C	°C	J . g^{-1}	J . g^{-1}
PLLA^{24}	10 °C/min	107.5	173.9	31	40	63.2[a)]	-	-	-	-
$L_{46}^{23}E_{54}^{27}$		-	171.7	-	39	62.1	88.7	104.2	-[b)]	-[b)]
$LD_{54}^{32}E_{46}^{28}$		-	-	-	-	55.0	88.3	103.5	109	115
PLLA^{24}		117.6	171.7 176.5	47	70	-	-	-	-	-
$L_{46}^{23}E_{54}^{27}$	2 °C/min	109.8	172.5	34	72	-	93.9	101.6	80	85
$LD_{54}^{32}E_{46}^{28}$		-	-	-	-	-	93.2	105.0	92	109

[a)] Measured after quenching the simple to room temperature.
[b)] Signals are overlapped during cooling by coincident crystallization and during heating by PLLA cold crystallization.

rather small change was reproducible. Increasing the nucleation density of PE is usually difficult and a shift of even half a degree can be a sign of a moderate nucleating effect, in this case caused by the previously crystallized PLLA. More evidences of a nucleating effect of the PLLA block on the PE block within PLLA-*b*-PE were obtained by self-nucleation experiments not reported here.

The isothermal crystallization kinetics of the crystalline components of the block copolymers and the homo-PLLA were determined by DSC experiments and the results were analyzed in terms of the Avrami equation[10]:

$$\alpha_c(t) = 1 - \exp(-Kt^n)$$

where $\alpha_c(t)$ is the relative crystalline volume fraction as a function of time. K is an overall transformation rate constant and n is the Avrami index. The results of fitting the Avrami equation to the data are presented in Table 3 while the experimentally determined half-crystallization time is presented in Figure 3 as a function of the crystallization temperature. As expected, the inverse of the half-crystallization time correlates well with the values of the overall rate of crystallization, K, and they both decrease with increasing crystallization temperature.

Figure 3 shows that a higher supercooling is needed to crystallize the PLLA block within PLLA-*b*-PE than homo-PLLA. The values of half-crystallization time also indicate that the PLLA block crystallizes at much slower rates than homo-PLLA when similar crystallization temperatures are considered by extrapolation. Similar decreases in crystallization rate have been reported by Ho et al.[11] for the PLLA block within PLLA-*b*-PS (poly(L-lactide)-*block*-polystyrene) and were explained by a confinement effect caused by the PS block on PLLA.

The decrease in overall crystallization rate of the PLLA block is responsible for the coincident crystallization effect (see Figure 1) that can be observed when the PLLA-*b*-PE diblock copolymer is cooled down from the melt at rates larger than 2 °C/min.

The higher Avrami indices obtained for the PLLA block as compared to homo-PLLA can be interpreted as a sign of

Table 3.
Avrami parameters obtained by fitting isothermal crystallization data obtained by DSC.

					$L^{23}_{46}E^{27}_{54}$			$LD^{32}_{54}E^{28}_{46}$	
	PLLA[24]		+PLLA block			PE block		PE block	
T_c	n	K	n	K	T_c	n	K	n	K
°C		min^{-n}		min^{-n}	°C		min^{-n}		min^{-n}
106			2.72	0.0190	94			2.08	0.9640
108			2.74	0.0172	94.5			2.07	0.4971
109			2.81	0.0156	95			2.13	0.2232
110			2.88	0.0122	95.5			2.02	0.1695
111			3.04	0.0062	96	2.02	0.8035		
112			3.03	0.0053	96.5	2.03	0.5289	2.13	0.0301
113			2.76	0.0038	97	1.98	0.1266	2.04	0.0134
120	2.05	0.1394			97.5	1.96	0.0724		
121	2.04	0.0936			98	2.19	0.0102		
121.5	2.04	0.0851							
122	2.17	0.0616							
123	2.29	0.0288							
124	2.41	0.0300							
125	2.29	0.0288							
126	2.37	0.0158							

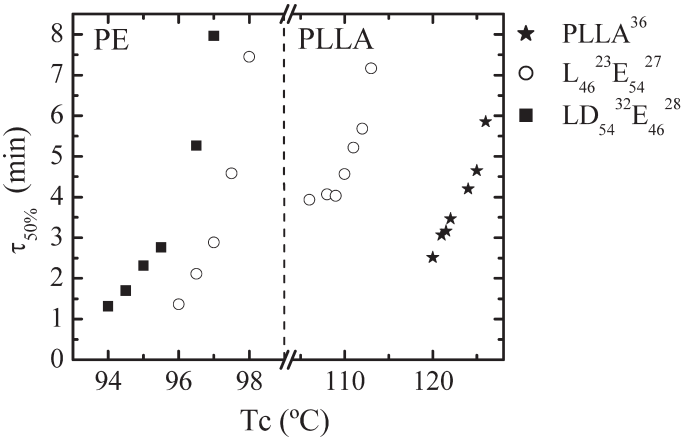

Figure 3.
Half crystallization times for the indicated copolymers and homopolymers. Left: PE block. Right: PLLA block.

nucleation restrictions on the PLLA block which renders nucleation more sporadic (and therefore increases Avrami index). The effect of the molten PE covalently bonded block is to slow down both the nucleation and the growth of PLLA crystals. The physical significance of the Avrami index for homo-PLLA is not clear since Polarized Light Optical Microscopy experiments (PLOM) reveal that homo-PLLA forms well structured spherulites with clear maltese cross extinction patterns. These structures should correspond to an Avrami index of at least 3 (if instantaneous nucleation is assumed), however, for our homo-PLLA in the range of temperatures examined a value close to 2 was obtained. Such discrepancies have been reported for a number of polymers,[12] a fact that limits the physical interpretation of the Avrami equation. It is always advisable to have an independent proof of the superstructural morphology obtained, like PLOM observations. Hamley et al.[13] reported for strongly segregated PE-*b*-PVCH (polyethylene-*block*-poly(vinylcyclohexane)) that even though PE was confined and was not able to form spherulites, the Avrami index obtained was 3.

Even though homo-PLLA readily forms spherulites at all explored crystallization temperatures reported in Table 3, the PLLA block within PLLA-*b*-PE did not form spherulites at any examined temperature. This is the expected behavior of a polymer block that is strongly segregated from its corresponding covalently bonded neighbor and in this case is forming microphase separated lamellae (since the composition is nearly 50-50) where the crystallization of each component has to occur in the confined space defined by the microdomain, i.e., no break-out can occur[4–5]. The behavior of strongly segregated PLLA-*b*- PE can be contrasted with weakly segregated PLLA-*b*-PCL double crystalline diblock copolymers where PLLA spherulites are formed in a wide composition range, even when the copolymer contains only 30% PLLA.[14–15]

With respect to the PE block within the block copolymer samples, Figure 3 shows that the crystallization kinetics is slower for the PE block covalently bonded to amorphous and rubbery PLDA (within PLDA-*b*-PE) as compared to that of the PE block attached to previously crystallized PLLA (within PLLA-*b*-PE). The slight nucleating influence of PLLA on PE is probably responsible for the acceleration of the overall crystallization kinetics. Therefore, a decrease in the Avrami index would be

expected, however, both PE blocks exhibited similar values of the Avrami index which are already quite low, see Table 3. The value obtained was close to 2 for almost all crystallization temperatures examined. This value is reasonable if confined and instantaneous two-dimensional crystallization within the lamellar microdomains is considered. In the PE block case, no spherulites were observed by PLOM as expected for confined crystallization within the phase separated lamellar microdomains[4–5].

In the case of a similarly double crystalline diblock copolymer system, i.e., PPDX-*b*-PCL, it was found that the effect of the molten PCL chains on decreasing the crystallization rate of PPDX with respect to homo-PPDX was much more pronounced than that of previously crystallized PPDX on the crystallization of PCL. In that case, a nucleation effect of PCL by PPDX was also found.[16–17] The results presented in Figure 3 also show that the effect of having a covalently bonded amorphous block on the PE block crystallization kinetics is larger than when the neighboring block has previously crystallized.

Conclusions

Strongly segregated and nearly symmetric PLA-*b*-PE diblock copolymers are most likely phase segregated in lamellar microdomains. The blocks that can crystallize have to do it within the confinement of their lamellar microdomains without forming superstructural aggregates like spherulites. In the case of PLLA-*b*-PE double crystalline diblock copolymers a coincident crystallization process was detected when they are cooled from the melt at rates exceeding 2 °C/min. This behavior is caused by the reduction in PLLA overall crystallization kinetics induced by the attached molten PE block. When the crystallization of the PE block is studied, it is found that if a rubbery PDLA block is covalently bonded to it its overall transformation rate is slower than when a previously crystallized PLLA block is attached to it. Such differences in overall crystallization rate are attributed to a nucleation effect of the PLLA block on the PE block.

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