Copolymers of ω-Pentadecalactone and Trimethylene Carbonate from Lipase Catalysis: Influence of Microstructure on Solid-State Properties

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ABSTRACT: Unusual copolymers were prepared by *Candida antarctica* Lipase B (Novozyme-435) catalyzed copolymerization of ω-pentadecalactone (PDL) with trimethylene carbonate (TMC). Atypical solid-state properties were revealed by thermogravimetric analysis, differential scanning calorimetry (DSC), and X-ray diffraction analyses. Thermal degradation of poly(PDL−TMC) occurs in two steps: the first well above the degradation range of poly(TMC) and the other at a temperature (430 °C) comparable with that of poly(PDL) decomposition. Thermal stability of PDL−TMC copolymers increases with randomization of comonomer distribution. All poly(PDL−TMC) investigated are highly crystalline, even those with equimolar comonomer content and close-to-random distribution. This result indicates that PDL and TMC units cocrystallize. The copolymers show two melting processes: the higher one at about 90 °C, i.e., close to poly(PDL) melting, and the other 30 °C lower. The relative intensity of the two phenomena changes with copolymer microstructure. The X-ray diffraction patterns of poly(PDL−TMC) are practically identical to that of poly(PDL) in the range $10° < 2\theta < 80°$. Significant differences appear in the low-angle region below $2\theta = 10°$, indicating in some copolymers the presence of crystals with higher periodicity than poly(PDL) along the chain direction. Comparison of DSC and X-ray results with copolymer microstructure shows that two crystal phases can develop in poly(PDL−TMC): poly(PDL) crystals and—whenever a significant amount of heterodiads are present—another lower melting crystal phase, characterized by a larger fiber axis periodicity and possibly associated with crystallization of alternate PDL−TMC sequences.

Introduction

Aliphatic polycarbonates and their copolymers with polyesters are of interest for use in bioresorbable suture filament, artificial skin, prostheses, bone fixation plates, ligature clamps, and galenic formulations.[1,2] The copolymerization of ω-pentadecalactone (PDL) and trimethylene carbonate (TMC) was recently reported.[3] Using immobilized lipase B from *Candida antarctica* (Novozyme-435), poly(PDL−TMC) of high molar mass was prepared. By lipases catalysis, the reactivity of PDL was higher than that of TMC.[3] Lipase promotes the formation of mixed ester/carbonate linkages through transesterification/transacylation reactions, and as a consequence, the repeating unit distribution changes with reaction time from blocky to close-to-random. Similar close-to-random distributions can also be obtained by starting with preformed poly(PDL) and TMC monomer and conducting the lipase-catalyzed reaction for a sufficient time.

The homopolymer poly(PDL) synthesized by Novozyme-435 has been recently characterized.[4] Poly(PDL) is a highly crystalline polyester that melts at about 100 °C and, due to its long methylene sequence, shows structural similarities to polyethylene. The crystal structure of poly(PDL) has been thoroughly investigated,[5] and its unit cell was found to be pseudo-orthorhombic, with $a = 7.49$ Å, $b = 5.034$ Å, $c = 20.00$ Å (fiber axis), and $\alpha = 90.06°$. In contrast, poly(trimethylene carbonate), poly(TMC), is an essentially amorphous polymer[1,6,7] with a glass transition around −20 °C. In the literature poly(TMC) is reported to develop a crystalline phase (melting point around 30 °C) only when the molar mass is lower than 12 000.[1]

In this work we report a solid-state characterization of lipase-catalyzed poly(PDL−TMC) with the aim to correlate physical properties with copolymer composition and microstructure. Since the latter can be tuned by careful selection of reaction conditions, knowledge of microstructure−property relations allows the biosynthesis of poly(PDL−TMC) copolyesters with desired physical properties.

Experimental Section

Materials. The synthesis of poly(PDL)[4] and of PDL−TMC copolymers[3] was reported earlier. Poly(TMC) was synthesized using MAO as catalyst (0.01 M) at 90 °C. The product was fractionated in methanol, and the details of the procedure are mentioned elsewhere.[3]

Table 1 summarizes the molecular characterization of the investigated poly(PDL−TMC) copolymers.

Characterization Methods. Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded on a Bruker spectrometer model DPX300 at 300 and 75.13 MHz, respectively. The chemical shifts in parts per million (ppm) for ^{1}H and ^{13}C NMR spectra were referenced relative to tetramethylsilane (TMS) and chloroform as an internal reference at 0.00 and 77.23 ppm, respectively. Molecular weights were determined by gel permeation chromatography (GPC) using a Waters HPLC system

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Table 1. Poly(PDL−TMC)

sample[a]	feed PDL:TMC (molar ratio)	reaction time (h)	copolymer composition PDL/TMC (mol %)	diads[b] P−P	diads[b] P−T	diads[b] T−P	diads[b] T−T	M_n[c] (g/mol)	M_w/M_n[c]
E1	1:1	3	75/25	0.61	0.13	0.13	0.13	13 000	2.07
E2	1:1	15	55/45	0.33	0.17	0.17	0.33	24 500	1.68
E3	1:1	24	50/50	0.25	0.23	0.23	0.29	18 800	1.65
E4	1:1	48	49/51	0.18	0.27	0.27	0.28	12 100	2.0
E5	1:1[d]	48	47/53	0.20	0.27	0.27	0.26	5 200	1.57
C1	1:1	24	53/47	0.17	0.31	0.31	0.20	5 800	1.44

[a] E = enzyme catalysis; C = chemical catalysis (sodium ethoxide, ref 3). [b] P = PDL repeat units; T = TMC repeat units. From ^{13}C NMR. [c] From GPC in $CHCl_3$ (polystyrene standards calibration). [d] Preformed poly(PDL) ($M_n = 12 \times 10^3$, $M_w/M_n = 2.0$) and TMC monomer.

equipped with model 510 pump, a Waters model 717 autosampler, a model 410 refractive index detector, and a model T-50/T-60 detector from Viscotek Corp. with 500, 10^3, 10^4, and 10^5 Å Ultrastyragel columns in series. Trisec GPC software version 3 was used for calculations. Chloroform was used as the eluent at a flow rate of 1.0 mL/min. Sample concentrations of 0.2% w/v and injection volumes of 100 μL were used. Molecular weights were determined on the basis of a conventional calibration curve generated by narrow molecular weight polystyrene standards obtained from Aldrich Chemical Co. Thermogravimetric (TGA) measurements were carried out using a TA-TGA 2950 under N_2 flow. Sample weight was in the range 7−10 mg. The analyses were performed at 10 °C/min from room temperature to 600 °C. Differential scanning calorimetry (DSC) was carried out using a TA-DSC 2010. The temperature scale was calibrated with high-purity standards. DSC scans were performed in the temperature range from −80 to 120 °C. The heating rate was 20 °C/min (unless otherwise specified), and the cooling rate was 10 °C/min. The melting temperature (T_m) was taken at the peak of the DSC endotherm. X-ray diffraction measurements were carried out at room temperature with a Bragg/Brentano diffractometer system (PhilipsPW 1050/81-PW1710), equipped with a graphite monochromator in the diffracted beam. A Cu anode was used as X-ray source (λ_1 = 0.154 06 nm, λ_2 = 0.154 43 nm). For the WAXS data collection the instrument was equipped with 1°, 0.2 mm, 1° slits. The data were collected in the range 2.5°−80° (2θ) counting for 6 s at each 0.1° step. The degree of crystallinity (χ_c) was evaluated as the ratio of the crystalline peak areas to the total area under the scattering curve.[8] The amorphous and crystalline contributions were calculated by fitting with the WinFit program.[9] The average crystal size was evaluated by means of the Scherrer equation.[8] X-ray diffraction measurements in the range 2.5°−7.5° (2θ) were acquired with 0.1° step and 50 s counting time, employing the set of slits 0.5°, 0.2 mm, 1°. The primary beam and air scattering contribution to the incoherent scattering was considered equal to the contribution of an empty sample holder recorded in the same conditions, which was therefore subtracted from the sample diffraction profile.

Results

Calorimetric Properties. Figure 1 contains the DSC curves of PDL−TMC copolymers obtained from an equimolar PDL/TMC feed by Novozyme-435 catalysis but with increasing reaction time (E1 to E4 in Table 1). For comparison, the DSC curve of poly(PDL) homopolymer is included in Figure 1. The only appreciable thermal event in the DSC curve of poly(PDL) is melting (T_m = 97 °C, melting enthalpy ΔH_m = 166 J/g). As reported earlier,[4] the glass transition of this highly crystalline polyester is better revealed by relaxation techniques (T_g = −27 °C by dynamic mechanical analysis). The DSC curves of PDL−TMC copolymers show a complex melting behavior compared with that of poly(PDL). In E1, the main endothermal peak, located a few degrees below that of poly(PDL), is preceded by a broad shoulder. Progressing from sample E1 to samples E2, E3, and E4, the shoulder evolves into a low-temperature endotherm that progressively acquires better definition and increases in magnitude. Correspondingly, the intensity of the high-temperature peak markedly decreases being barely appreciable in the DSC curve of copolymer E4. Although the intensities of the individual endothermal phenomena change so strongly, the peak temperatures remain almost constant. The poly(PDL−TMC) thermal data are collected in Table 2 where the lower and higher melting processes are identified by subscripts 1 and 2, respectively.

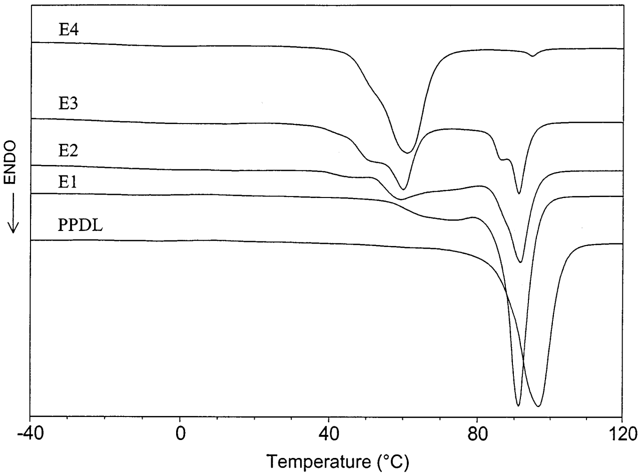

Figure 1. DSC curves (first scan) of PDL−TMC copolymers and of poly(PDL).

Copolymer E3, where the two fusion peaks are intense and well separated (Figure 1), was selected to undergo thermal treatments aimed at elucidating the nature of the observed melting phenomena. To ascertain whether melting and recrystallization processes underlie the two observed endotherms,[10−13] Figure 2 shows the DSC curves of copolymer E3 recorded at four different heating rates: 1, 2, 10, and 20 °C/min. The relative intensity of the two melting processes does not vary appreciably notwithstanding the 20-fold scan rate increase applied in the experiments. This establishes that melting−recrystallization cannot be invoked to explain the thermal behavior of poly(PDL−TMC). Figure 3 collects the DSC curves obtained during a heating/cooling/reheating cycle on E3. Both in the cooling run and in the reheating scan two separate thermal phenomena are observed, which suggests the presence of two different crystal phases that independently crystallize and melt.

Figure 4 compares the DSC curves of copolymers E4, E5, and C1. The corresponding thermal data are listed in Table 2. The curves of PDL−TMC copolymers E4 and E5 are practically identical. Thus, despite the fact that in one case prepolymerized poly(PDL) was used (E5) instead of PDL monomer (E4), after a 48 h reaction period using lipase catalysis the thermal properties of these two copolymers are nearly identical. Furthermore,

Table 2. Calorimetric and X-ray Diffraction Data of Poly(PDL−TMC) Copolymers[a]

sample	composition PDL/TMC (mol %)	T_{m1}[b] (°C)	ΔH_{m1}[b] (J/g)	T_{m2}[c] (°C)	ΔH_{m2}[c] (J/g)	$\Delta H_{m(total)}$[d] (J/g)	χ_c[e] (%)	cs[f] (Å)
E1	75/25	n.d.[g]	n.d.[g]	91	163	163	62	220
E2	55/45	59	51	91	61	112	52	91
E3	50/50	60	74	91	43	117	47	128
E4	49/51	61	118	95	5	123	54	141
E5	47/53	63	131	93	7	138	60	170
C1	53/47	64	134			134	58	191

[a] Results from first heating scan. [b] Lower temperature melting endotherm. [c] Higher temperature melting endotherm. [d] $\Delta H_{m(total)} = \Delta H_{m1} + \Delta H_{m2}$. [e] Crystallinity degree from WAXS (±5%). [f] Crystal size from WAXS. [g] Not determined.

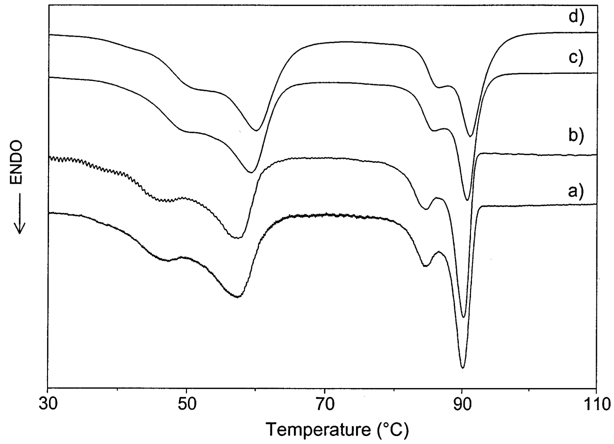

Figure 2. DSC curves (first scan) of copolymer E3 at different heating rates: (a) 1, (b) 2, (c) 10, and (d) 20 °C/min.

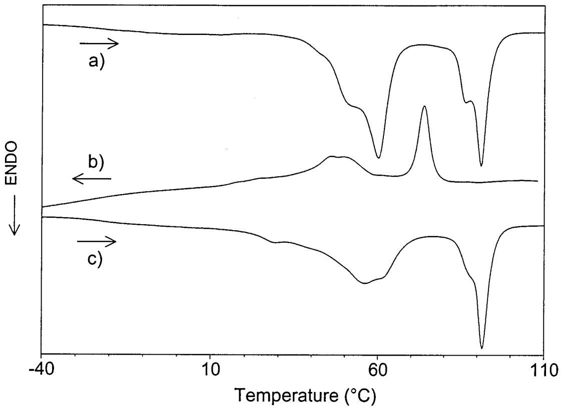

Figure 3. DSC curves of copolymer E3: (a) first heating run; (b) cooling run; (c) second heating run.

the copolymer obtained by the chemically catalyzed reaction (C1) shows a DSC curve very similar to those of E4 and E5 except for the small high-temperature endotherm that is absent in copolymer C1.

X-ray Diffraction. Figure 5 displays the diffraction profiles of copolymers E1, E3, E4, and C1 together with that of the poly(PDL) homopolymer. The diffractogram of E5 (identical to that of E4) is omitted for the sake of clarity. All diffraction profiles in Figure 5a show the polyethylene-like pattern of poly(PDL),[5] and at first sight, they look very similar. Only at very low angles can significant differences be discerned. Figure 5b shows the range from $2\theta = 2°$ to $2\theta = 7°$ containing the (001) reflection associated with the periodicity along the chain direction. Table 2 reports degree of crystallinity and average crystal size of the copolymers. The latter is the average of the values obtained from reflections (110) at $2\theta = 21.5°$ and (200) at $2\theta = 23.9°$.

Thermogravimetric Analysis. Figure 6 reports the TGA curves of PDL−TMC copolymers E1 to E5 together with the curves of the reference homopolymers. Poly(PDL) and poly(TMC) have very different thermal stability, the polycarbonate degrading about 200 °C lower than the polyester. The copolymers obtained by Novozyme-435 catalysis show a two-step degradation behavior, the second weight loss occurring at a temperature comparable with that of poly(PDL). The first degradation step in all copolymers investigated starts well above the thermal degradation range of poly(TMC) homopolymer, and its location and steepness depend on the specific PDL−TMC copolymer analyzed.

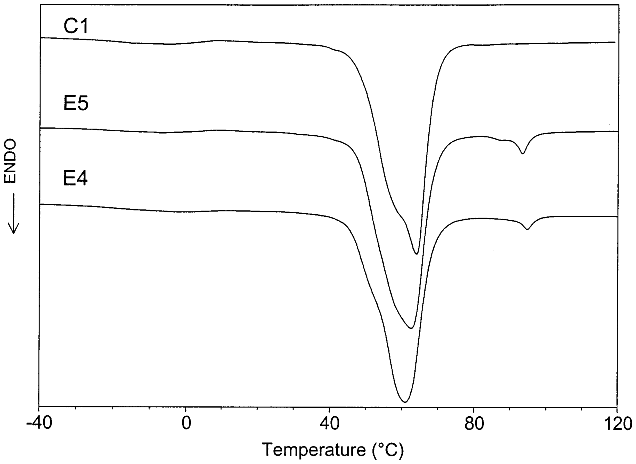

Figure 4. Comparison of DSC curves (first scan) of copolymers E4, E5, and C1.

Discussion

The homopolymer poly(TMC) is thermally unstable above 150 °C. The proposed degradation mechanism[14,15] involves decarboxylation and chain-end hydroxyl backbiting reactions, leading to loss of monomer and cyclic oligomers. Interestingly, the PDL−TMC copolymers investigated in this work show good thermal stability up to about 300 °C (Figure 6), with the exception of E2, which shows a steep weight loss around 300 °C that may be associated with degradation of trimethylene carbonate blocks (see T−T diad fraction in Table 1). With increasing reaction time, in copolymers with the same overall composition (E2, E3, E4), transesterification reactions induce changes of microstructure and thermal stability improves (Figure 6). This result suggests that the interruption of TMC sequences by PDL units hinders the degradation mechanism of poly(TMC) described in the literature.[14,15]

A remarkable feature of poly(PDL−TMC) is that, irrespective of composition and microstructure, all of the copolymers investigated were highly crystalline (Table 2). The commonly expected behavior[16−18] upon copolymerization of crystallizable polymers is a progressive decrease of crystallinity with increasing comonomer

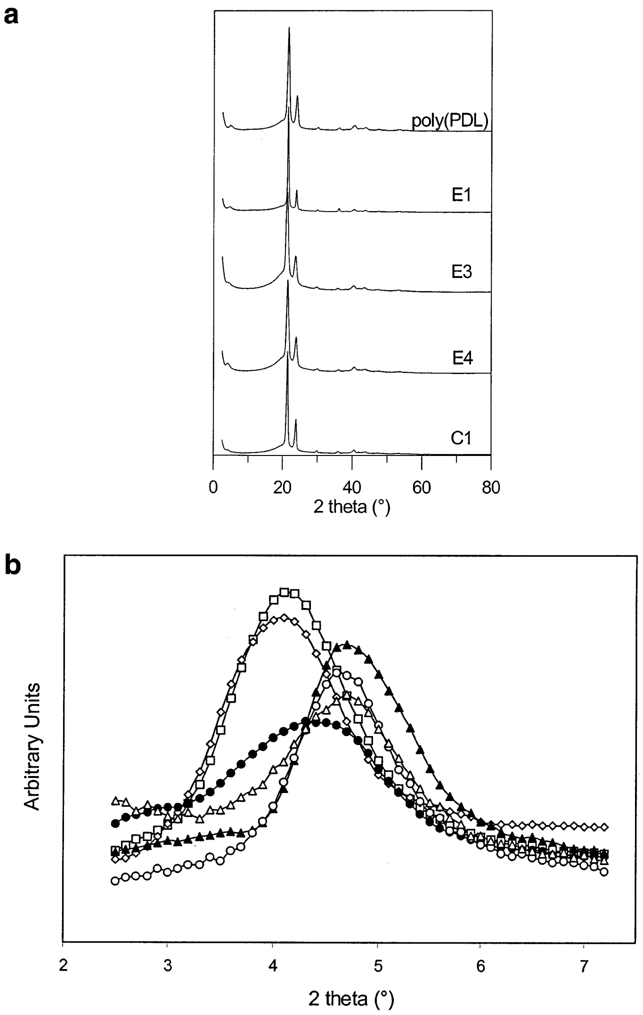

Figure 5. X-ray diffraction of poly(PDL) and PDL–TMC copolymers: (a) full angle range; (b) (001) reflection of poly(PDL) (▲), E1 (○), E2 (△), E3 (●), E4 (□), and C1 (◇).

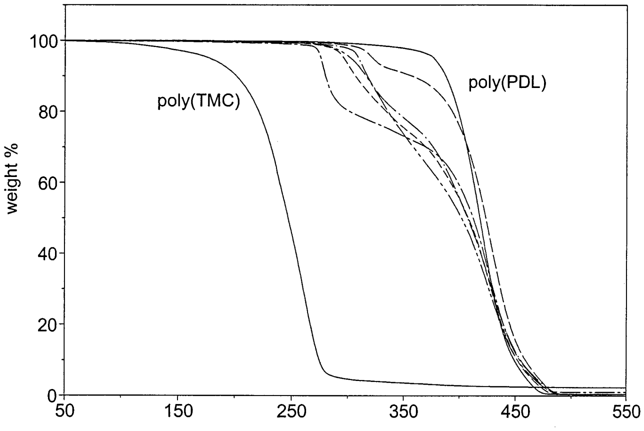

Figure 6. Thermogravimetric curves of poly(TMC), poly(PDL), and copolymers E1 (– –), E2 (– - –), E3 (– - - –), E4 (- - -), and E5 (– • –).

content and degree of randomness. Only when the repeating units undergo isomorphous substitution is high crystallinity maintained.[19] In the present system, the reference homopolymers, poly(PDL) and poly(TMC), are highly crystalline and essentially amorphous, respectively. Therefore, according to usual copolymer behavior, introduction of TMC units inside PDL sequences during copolymerization should cause a strong decrease of crystallinity compared with that of poly(PDL) ($\Delta H_m = 166$ J/g). In contrast, Table 2 shows that even equimolar copolymers with close-to-random diad distribution (E3, E4, E5) develop a considerable amount of crystallinity ($\Delta H_{m(total)} \geq 117$ J/g, $\chi_c \geq 47\%$) consisting of crystallites of remarkable size (Table 2). This result strongly suggests that some type of cocrystallization occurs in poly(PDL–TMC), i.e., that also TMC units take part in crystal formation.

The crystal fraction of the copolymers melts over two distinct temperature ranges (Figure 1), the higher one close to poly(PDL) homopolymer melting and the other about 30 °C lower. With increasing TMC content and shortening of homo-blocks (decrease of P–P and T–T diads), the relative intensity of the endotherms changes: the intensity of higher endotherm decreases while that of the lower melting endotherm increases. However, the change of composition and microstructure in copolymers E1 to E4 does not result in variation of the melting temperatures.

It is well-known[10–13] that polymers and copolymers can undergo melting and recrystallization during heating and that, under such circumstances, multiple-peak endotherms usually appear in the DSC curves. Suitable calorimetric treatments, i.e., heating rate changes, can be applied to highlight melting/recrystallization processes. Low heating rates facilitate rearrangements of the crystalline phase with formation of more ordered crystals that melt at higher temperature. In contrast, high heating rates hinder crystal reorganization. Therefore, by changing the heating rate, the relative population of low- vs high-melting crystals should vary if melting/recrystallization occurs. The results of the thermal treatments applied to E3 as an example (Figure 2) show that the two melting endotherms do not evolve as expected upon changing the heating rate. The relative magnitude of the two endotherms does not change, while the melting temperature slightly increases with scan rate according to well-known thermal lag effects.[20] It is therefore concluded that the thermal behavior of PDL–TMC copolymers is not caused by a single crystalline phase that melts and recrystallizes into more ordered crystals, but rather by the presence of two different crystal phases.

If the hypothesis of two crystal phases (low- and high-melting) in poly(PDL–TMC) is correct, X-ray diffraction results should give evidence of structural differences in copolymers that show well-diversified thermal behaviors (E1 vs E4, for example). The structural analysis of the copolymers (Figure 5) shows that, although all diffractograms in the range from $2\theta = 10°$ to $2\theta = 80°$ are practically identical to that of poly(PDL), significant differences appear in the low-angle region below $2\theta = 10°$. The mentioned E1 and E4 copolymers show the (001) reflection at different angles, corresponding to different periodicity along the chain direction (*c*-axis in the unit cell). From the reflection position (Figure 5b) E1 shows a periodicity ($d = 19.4$ Å) comparable to that of the homopolymer poly(PDL) ($d = 19.3$ Å). In contrast, for E4 $d = 21.7$ Å. Furthermore, for poly(PDL–TMC) obtained by chemical catalysis (C1), the (001) reflection is located at an angle close to that of copolymer E4 and $d = 21.9$ Å.

The foregoing discussion leads to the following conclusion. In poly(PDL–TMC) copolymers, the high-melting crystals—such as those producing the large melting endotherm in E1 (Figure 1)—are structurally identical to those of poly(PDL). Conversely, the low-melting crystals—largely present in E4 and C1—are structurally different, namely with regard to periodicity in the chain direction.

From the structural point of view, E3 and E2 represent intermediate cases with respect to the copolymers discussed above, because their (001) reflection is rather broad and encompasses the 2θ values typical of E1 and E4 (Figure 5b). This result agrees with the presence in E3 and E2 of a considerable amount of both low- and high-melting crystals (Figure 1). The different shape of the (001) reflections—symmetrical and centered at $2\theta = 4.4°$ in E3, asymmetrical with maximum at the same 2θ value as poly(PDL) and marked broadening toward lower angles in E2—reflects the different melting behavior of the two copolymers (Figure 1). In E3 two distinct clearly defined endotherms reveal the presence of well-developed crystals of both types, whereas the multiple-peak endotherm of E2 suggests that good-quality high-melting crystals coexist with poorly developed low-melting ones. This suggestion is substantiated by the relatively low value of the overall average crystal size in copolymer E2 (Table 2).

The low-melting crystal phase well developed in E4 and C1 shows a periodicity along the chain axis of about 22 Å, i.e., higher than that of poly(PDL). This suggests that a unit longer than the PDL monomer crystallizes in these copolymers. Analysis of the microstructure of the investigated poly(PDL−TMC) helps in rationalizing this point. As was previously discussed,[3] when the reaction time of Novozyme-435-catalyzed PDL/TMC copolymerization is increased, transesterification modifies the copolymer sequence (Table 1). The biosynthesized copolymer with the highest amount of heterodiads (P−T, T−P) is E4. In the copolymer C1 formed by chemical catalysis, the mixed-diad fraction is even higher than in E4. On the basis of these considerations, we believe that the long crystallizing unit is constituted by an alternate PDL−TMC diad.

Indeed, crystallization of alternate copolymers has been widely investigated in the literature.[17] Relevant to this work are the studies on alternate ethylene copolymers[21,22] that develop polyethylene-like crystal structures. In alternate copolymers of ethylene with carbon monoxide,[21] a unit cell with an elongated *c*-axis (7.52 Å compared with 2.54 Å of polyethylene) that accommodates two (CH_2-CH_2-CO) repeats has been proposed. Analogously, poly(1-methyloctamer),[22] a polyolefin regularly alternating one propylene with three ethylene units, shows a polyethylene-like structure with fiber axis periodicity that agrees with the eight-carbon repeat. While the crystal phase of poly(ethylene-*alt*-carbon monoxide) shows a very high melting point,[23] the alternate ethylene/propylene copolymer[22] melts well below the melting point of the reference homopolymer (polyethylene), a behavior similar to that of the presently proposed alternate PDL−TMC crystal phase, which melts 30 °C lower than poly(PDL).

The linear extension of an alternate planar zigzag PDL−TMC diad can be calculated using literature values for bond lengths and angles.[19,24] The obtained result (26.9 Å) exceeds by about 20% the *d* values experimentally obtained for E4 and C1 from Figure 5b. The mismatch can be sensibly reduced by slight changes of bond lengths and angles as well as by chain packing considerations. Alternatively, a monoclinic distortion of the unit cell could be invoked to explain the observed discrepancy. Differences of similar magnitude (15−20%) between experimental and calculated chain extension have been reported earlier for crystalline aromatic polycarbonates.[25]

In the presently investigated PDL−TMC copolymers three factors—(i) constancy of melting temperature, (ii) enthalpy changes that reasonably follow microstructure variations, and (iii) low-angle shift of the (001) X-ray reflection—contribute to identify the low-temperature melting crystals as a new phase, likely to be formed by alternate PDL−TMC sequences that independently crystallize and melt.

Conclusions

The PDL−TMC copolymers investigated in this work show solid-state properties that change with microstructure. Thermal stability improves with randomization of the comonomer distribution. Poly(PDL−TMC) with equimolar comonomer content and close-to-random distribution are highly crystalline, showing that PDL and TMC cocrystallize. In addition to the known poly(PDL) crystals,[5] another low-melting crystal phase is observed. Relative to the poly(PDL) crystals that melt at a higher temperature, this low-melting phase is characterized by a larger fiber axis periodicity. The long crystallizing unit is associated with crystallization of alternate PDL−TMC sequences. The low-melting crystal phase develops whenever a significant amount of heterodiads is present.

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