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Thermal properties of di- and triblock copolymers of poly(L-lactide) with poly(oxyethylene) or poly(ε-caprolactone)

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Abstract

High molecular weight di- and triblock copolymers of poly(L-lactide), PLLA, (80 wt%) with a crystallizable flexible second component such as poly(ε-caprolactone), PCL, or poly(oxyethylene), PEO, (20 wt%) were obtained in nearly quantitative yields by ring opening of L-lactide initiated by PCL or PEO hydroxy terminated macromers. The copolymers were characterized by ^{1}H NMR and FTIR spectroscopy and size exclusion chromatography and showed unimodal and narrow molecular weight distributions. X-ray diffraction measurements revealed high crystallinity (38–56%) of the PLLA blocks and gave no clear evidences of PCL or PEO crystallinity. DMTA and DSC techniques showed a melting behaviour of the copolymers ($T_m = 174–175$ °C; $\Delta H_m = 19–37$ J/g) quite similar to that of PLLA. PCL and PLLA segments are immiscible, while PLLA and PEO segments are partially miscible in the amorphous phase. Stress–strain measurements indicated a ductile behaviour of the copolymers, characterized by lower tensile moduli (225–961 Pa) and higher elongations at break (25–134%) with respect to PLLA.

Keywords: Block copolymers; Poly(L-lactide); Poly(ε-caprolactone); Poly(oxyethylene)

1. Introduction

Poly(L-lactide), PLLA, and PLLA-based copolymers are well established semicrystalline, biodegradable materials used for a variety of applications in the pharmaceutical and biomedical field as they are degraded by hydrolysis of ester bonds and are resorbed in living tissue with the release of products which are non-toxic for living cells [1–4]. Although high molecular weight PLLA is a relatively stiff polymer characterized by good mechanical strength, it is too brittle for applications as temporary bone fixation devices and as scaffold for tissue engineering [5,6]. One successful approach to the toughening of PLLA has been the preparation of multicomponent systems incorporating a biocompatible flexible polymer as the second component. Modification of PLLA by blending with poly(ε-caprolactone), (PCL), has been investigated by several research groups [7–10]. Although PLLA and PCL are immiscible, fine dispersions of PCL domains in the PLLA matrix were obtained by means of efficient mixing procedures and/or using block copolymers as emulsifying agents [10]. Block copolymers containing hard PLLA and soft PCL or poly(oxyethylene), (PEO), segments may also develop a microphase separation structure characterized by a stronger interphase adhesion with respect to the corresponding blends because of the chemical links at the particle-matrix interface [11–14]. Moreover, both segments are crystallizable, provided that their molecular weights (M_w) are sufficiently high, and their crystallization may influence microphase separation, water absorption and degradation rate of PLLA. Block PLLA–PEO copolymers, in particular, have been widely investigated because of the good combination of the properties of hydrophobic, stiff and degradable PLLA segments with those of hydrophilic, flexible and non-degradable PEO segments.

In previous papers, we reported the preparation, morphology and physico-chemical properties of PLLA/PCL blends [9,10]. Triblock PLLA–PCL–PLLA copolymers were found to act as an emulsifying agent leading to a fine dispersion of PCL domains in the PLLA matrix thus improving the mechanical properties of the blends. PLLA–PEO di- and triblock copolymers have also been found to enhance the compatibility of PLLA/PCL blends [15]. In this paper, we describe the synthesis and the characterization of high M_w triblock PLLA–PCL–PLLA or

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PLLA–PEO–PLLA and diblock PLLA–PEO copolymers obtained by ring opening polymerization of L-lactide (LA) in the presence of OH-terminated bifunctional PCL and PEO or monofunctional PEO macromers, respectively. The copolymer properties were investigated by differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), X-ray diffractometry and stress–strain measurements.

2. Experimental

2.1. Materials and techniques

L-lactide (LA, Aldrich) was repeatedly recrystallized from anhydrous ethyl acetate and stored over phosphorous pentoxide. Stannous-2-ethylhexanoate, $SnOct_2$, (Sigma) and α,ω-dihydroxy-poly(ε-caprolactone) (PCL–OH, Aldrich; $M_n = 10.0$ kDa, $M_w/M_n = 1.50$), were used as received. α,ω-Dihydroxy-poly(ethyleneoxide) (PEO–OH, $M_n = 10.0$ kDa, $M_w/M_n = 1.06$) and hydroxy-poly(ethyleneoxide)-monomethylether (PEO*m*, $M_n = 5.0$ kDa, $M_w/M_n = 1.07$), both purchased from Aldrich, were dehydrated by removing the water through azeotropic distillation with toluene.

The DMTA spectra were obtained using a Polymer Laboratories MKIII analyzer operating from −100 to 120 °C at 1 Hz on 0.4–0.5 mm thick films obtained by compression molding. DSC experiments were performed with a Perkin–Elmer Pyris instrument on 5–6 mg of copolymers. The samples were heated under nitrogen from −100 to 200 °C at 20 °C/min, rapidly cooled to −100 °C at 100 °C/min and heated again to 200 °C at 20 °C/min. The ^{1}H NMR spectra were recorded in chloroform-*d* at 25 °C by means of a Varian Gemini instrument operating at 250 MHz. Fourier transform infrared analysis (FTIR) was carried out on polymer film using a Jasco FTIR spectrophotometer. Wide-angle X-ray diffraction patterns (WAXS) were recorded at room temperature on a Philips PW 1711 diffractometer equipped with a continuous scan attachment and a proportional counting, using Ni-filtered Cu Kα radiation (1.5418 Å). Size exclusion chromatography (SEC) was performed at 30 °C by a Jasco PU-1580 instrument equipped with two Polymer Laboratories PL gel MIXED column and a Jasco 830 RI detector, using chloroform as solvent and polystyrene standards. Stress–strain experiments were carried out at room temperature on compression molded copolymer samples using an Instron 4505 dynamometer operating at a 2 mm/min speed. At least three experiments were performed for each copolymer.

2.2. Synthesis of the PLLA–PEO–PLLA triblock copolymer

LA (3.71 g), PEO–OH (0.93 g) and a solution of 5.3 mg of $SnOct_2$ in 0.4 ml of petroleum ether were charged under nitrogen into a flame dried vial. The mixture was heated at 50 °C in vacuum for 10 min, cooled to −20 °C and the vial was purged with nitrogen three times and sealed under high vacuum. Polymerization was carried out at 120 °C for 24 h with stirring. After cooling to room temperature, the vial was opened and the white product was dissolved in chloroform, precipitated in petroleum ether, and rapidly washed twice with distilled water. The copolymer was dried in a vacuum oven at 60 °C for 3 days (4.52 g, 97% yield; $\eta_{inh} = 0.92$ dl/g, chloroform, $c = 0.5$ g/dl at 25 °C). ^{1}H NMR: $\delta = 1.59$ (CH_3 PLLA, d); $\delta = 3.61$ (CH_2 PEO, s); $\delta = 5.17$ (CH PLLA, q). FTIR(film): 2996, 2944, 2876 cm^{-1} (CH st); 1757, cm^{-1} (C=O st); 1215, 1185, 1130, 1089 cm^{-1} (C–O–C st).

The diblock PLLA–PEO copolymer was prepared according to the above procedure using PEO*m* as initiator (94% yield; $\eta_{inh} = 0.61$ dl/g, chloroform, $c = 0.5$ g/dl at 25 °C). ^{1}H NMR: $\delta = 1.58$ (CH_3 PLLA, d); $\delta = 3.55$ (CH_2 PEO, s); $\delta = 5.16$ (CH PLLA, q). FTIR(film): 2996, 2944, 2877 cm^{-1} (CH st); 1757, cm^{-1} (C=O st); 1213, 1185, 1130, 1091 cm^{-1} (C–O–C st).

The preparation of PLLA/PCL/PLLA was reported in a previous paper (92% yield; $\eta_{inh} = 0.91$ dl/g, chloroform, $c = 0.5$ g/dl at 25 °C) [9]. ^{1}H NMR: $\delta = 1.57$ (CH_3 PLLA, d); $\delta = 1.3–1.7$ (CH_2CH_2 PCL, m); $\delta = 2.31$ (CH_2CO PCL, t); $\delta = 4.06$ (CH_2O PCL, t); $\delta = 5.16$ (CH PLLA, q). FTIR(film): 2995, 2946 cm^{-1} (CH st); 1758, 1730(shoulder) cm^{-1} (CO st);1214, 1186, 1132, 1093 cm^{-1} (OC–O–C st).

3. Results and discussion

3.1. Synthesis and characterization

Diblock PEO–PLLA and triblock PLLA–PEO–PLLA or PLLA–PCL–PLLA copolymers were synthesized by the ring-opening polymerization of LA using $SnOct_2$ as catalyst and α,ω-dihydroxy-poly(ε-caprolactone), PCL–OH, ($M_n = 10.0$ kDa), α,ω-dihydroxy-poly(oxyethylene), PEO–OH, ($M_n = 10.0$ kDa) and hydroxy-poly(oxyethylene) monomethylether, PEO*m*, ($M_n = 5.0$ kDa) as macroinitiators. Polymerizations were performed in bulk at 120 °C for 24 h. It is well known that under these experimental conditions, the conversion is almost quantitative and the LA insertion occurs without racemization [16]. Moreover, in the case of PLLA–PCL–PLLA, the formation of a random copolyester because of transesterification reactions is not expected considering the low catalyst concentration and the low polymerization temperature. The molecular weight of the PLLA blocks depends on the monomer/initiator molar ratio. The experimental condition used in the polymerization and the characterization data of the copolymers prepared are summarized in Table 1. The feed composition, 1/4 by weight of macromer/LA, used for all the copolymers should lead to an average size of PLLA blocks close to 20 kDa and to a composition close to 80 wt% of PLLA, provided that LA was completely reacted at the end of the

Table 1
Characterization data of the investigated block copolymers

Copolymer	LA/macromer (wt/wt in feed)	Yield (%)	Composition[a] (wt%)		M_n[b] (kDa)	M_w/M_n[c]	η_{inh}[d] (dl/g)
			PLLA	PEO(PCL)			
PLLA–PEO–PLLA	4	97	78	22	46 (50.0)	1.25	0.92
PLLA–PEO*m*	4	94	79	21	24 (24.9)	1.37	0.61
PLLA–PCL–PLLA	4	92	80	20	49 (50.3)	1.32	0.91

[a] Calculated from ^{1}H NMR.
[b] Number average molecular weight evaluated from ^{1}H NMR and calculated from the feed (in brackets).
[c] Polydispersity index obtained from SEC.
[d] Inherent viscosity in chloroform at 25 °C ($c = 0.5$ g/dl).

polymerization and that all the –OH end-groups of the macromer were involved in the chain growth. This hypothesis is supported by the high polymerization yields (92–97%). The copolymers are readily soluble in chloroform and their inherent viscosities lay in the range of 0.61–0.92 dl/g. Tough and flexible films were obtained by solution casting or by melt pressing.

The molecular structure of the copolymers was investigated by ^{1}H NMR and FTIR spectroscopy and by SEC. The ^{1}H NMR spectra of the copolymers are characterized by resonances at 1.57–1.59 δ and 5.16–5.17 δ due to the methyl and methyne protons of LA units in the chain, respectively. PEO containing copolymers exhibited an additional peak due to the $-OCH_2-$ protons at 3.55–3.61 δ. Well resolved PCL resonances at 4.06 δ ($-CH_2-O-CO-$) and 2.31 δ ($-CH_2-CO-O-$) were observed in the spectrum of PLLA–PCL–PLLA copolymer, whereas the other PCL resonances, at 1.3–1.7 δ, partially overlapped those of the methyl protons of LA units. It was not possible to detect resonances due to methyl groups of PLLA end units at 4.2–4.3 δ [12] as well as those of residual monomer, in agreement with the expected high M_w of PLLA blocks. The experimental composition and size of the PLLA blocks determined from the ^{1}H NMR spectra were in close agreement with those calculated from the feed assuming a complete conversion of LA. In particular, the PLLA and the copolymer molecular weights were calculated by the following equations:

$$M_n\text{PLLA} = \text{LA/EO(CL)} \times 144/44(114) \times M_n\text{PEO(PCL)}$$

$$M_n\text{copolymer} = M_n\text{PLLA} + M_n\text{PEO(PCL)}$$

where LA/EO(CL) is the molar ratio of LA units to ethylene oxide or caprolactone units obtained from ^{1}H NMR and M_nPEO(PCL) is the number average molecular weight of PEO or PCL macromers. The FTIR spectra showed the strong absorption of C=O stretching at 1757–1758 cm^{-1}, with a shoulder at $\approx$ 1730 cm^{-1} in the presence of PCL, and the C–H stretching bands at 2995–2996, 2944–2946 and 2876–2877 (PEO) cm^{-1}. Characteristic C–O–C stretching absorptions were detected at 1091–1093, 1130–1132, 1185–1186 and 1213–1214 cm^{-1}.

The M_w distributions of the copolymers were determined by SEC. The SEC chromatograms of the macroinitiators and of synthesized copolymers are shown in Fig. 1 and the polydispersity index (PI) values are summarized in Table 1. PEO–OH and PEO*m* exhibit a very narrow M_w distribution (PI = 1.06–1.07), while the PI of PCL–OH is 1.5. The copolymer molecular weight distributions are unimodal and fairly symmetric. The distribution curve of PLLA–PEO diblock copolymer shows a small lateral tail at higher M_w values, which could be attributed to the formation of some triblock chains derived from a very small fraction of α,ω-dihydroxy terminated PEO present in the macroinitiator. In all the chromatograms, the absence of peaks due to residual PEO–OH or PEO*m* indicates that PEO and PCL hydroxyl end-groups were totally esterified and that the polymers recovered from the polymerization of LA in the presence of PEO or PCL macromers can be considered as exclusively composed of OH-terminated PLLA–PEO–PLLA and

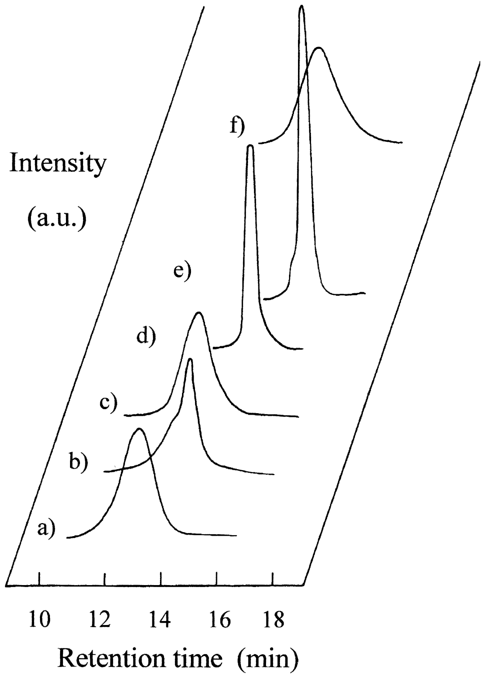

Fig. 1. SEC chromatograms of PLLA–PCL–PLLA (a), PLLA–PEO (b), PLLA–PEO–PLLA (c) block copolymers and PEO–OH (d), PEO*m* (e), PCL–OH (f) macromers.

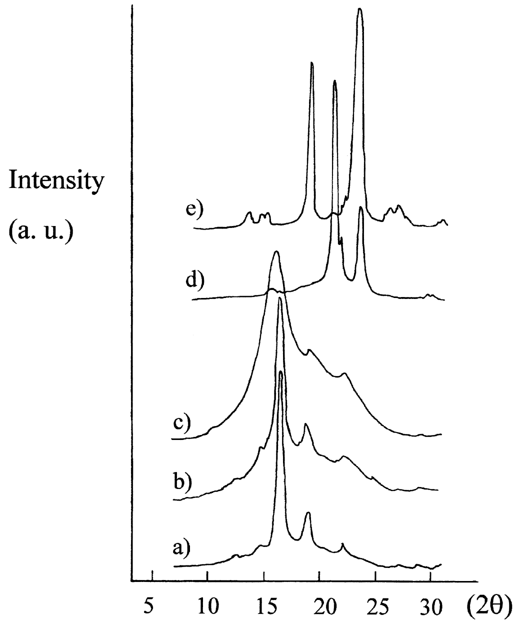

Fig. 2. X-ray diffraction diagrams of PLLA–PCL–PLLA (a), PLLA–PEO–PLLA (b), PLLA–PEO (c) block copolymers and PCL–OH (d), PEO–OH (e) macromers.

PLLA–PCL–PLLA tri-block or PLLA–PEO structures. A clear relation between the M_n values calculated from ^{1}H NMR and those obtained from SEC was not found, as the latter were systematically higher. In fact, the SEC data, obtained using polystyrene standards for calibration, allow only a limited statement on the molecular weight of the synthesized copolymers considering that the polystyrene intrinsic viscosity differs significantly from those of the copolymers [17]. Nevertheless, the PI of the copolymers indicate a fairly narrow molecular weight distribution of all polymers, as expected from the polymerization procedure employed.

3.2. X-ray diffraction experiments

X-ray diffraction diagrams of PEO and PCL macromers are shown in Fig. 2 together with those of the copolymers as obtained from the synthesis. The PEO–OH spectrum (d) exhibited two main diffraction peaks of crystalline phase at 2Θ angles of 19.2 and 23.1° and a quite similar spectrum (e) was obtained for the PEO*m* macromer. These peaks were neither detected in the spectra of the 'as polymerized' PLLA–PEO copolymers (b–c), nor when the copolymer samples were obtained as films both from their chloroform solution or by melt casting. On the other side, two diffraction maxima, characteristic of the α crystal cell of PLLA, were observed at 2Θ angles of 16.8 and 19.2°. Similar results were found for the PLLA–PCL–PLLA triblock copolymer (a). In fact, sharp diffraction peaks of crystalline PLA were easily detected in its X-ray diffraction spectrum, while those characteristic of PCL (d), at 21.4 and 23.8° of 2Θ, were absent. The crystallinity values calculated were 38% for PLLA–PEO and 43% and 56%, respectively, for PLLA–PEO–PLLA and PLLA–PCL–PLLA. These values can be considered fairly high when compared with the crystallinity of high M_w (50–100 kDa) PLLA (52–55%). The absence of clear diffraction peaks related to PEO or PCL suggests that extensive crystallization of the flexible PEO or PCL blocks does not occur in the copolymers investigated.

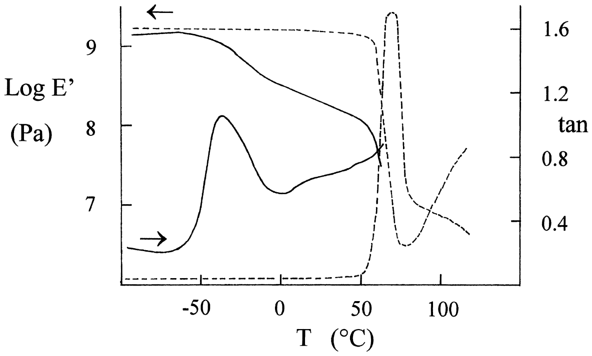

Fig. 3. DMTA spectra of PLLA (– – –) and of the PCL–OH (—) macromer.

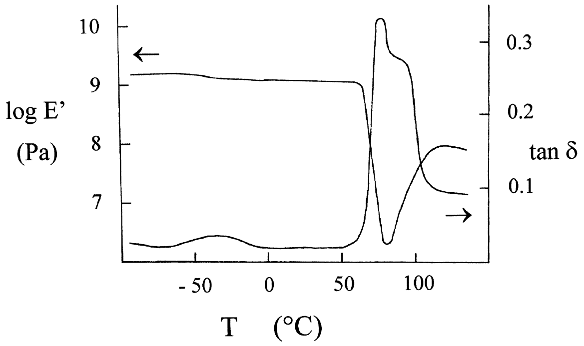

Fig. 4. DMTA spectrum of the PLLA–PCL–PLLA tri-block copolymer.

3.3. Thermal analysis

The thermal characterization of the synthesized copolymers was performed by DSC and DMTA techniques. Fig. 3 shows the DMTA spectra of PLLA and of the PCL–OH macromer. The glass transition temperatures T_g taken from the maxima of the loss tangent (tan δ) were found at 69 °C and -37 °C, respectively. In the case of PLLA, the increase in the storage modulus (E') after the glass transition is indicative of a cold crystallization of amorphous PLLA. As the PEO macromers were too brittle for dynamic mechanical experiments, the T_g value (≤ -42 °C) was taken from the literature [18]. The DMTA spectra of the copolymers are presented in Figs. 4 and 5. Two relaxation phenomena, which are indicated by a decrease in E' and by a corresponding tan δ peak, are observed for all copolymers. The corresponding T_g values are reported in Table 2 together with those found for PLLA, PEO and PCL. These data indicate a microphase separated structure in the

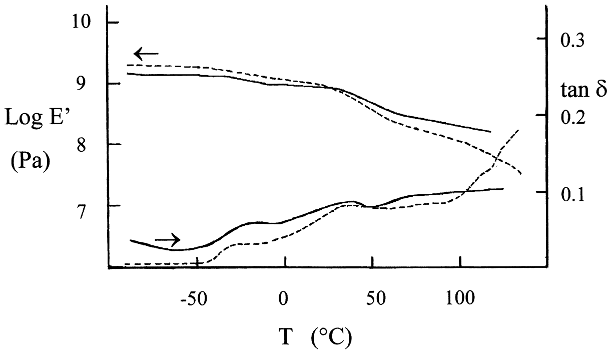

Fig. 5. DMTA spectra of the PEO containing block copolymers PLLA–PEO (—) and PLLA–PEO–PLLA (– – –).

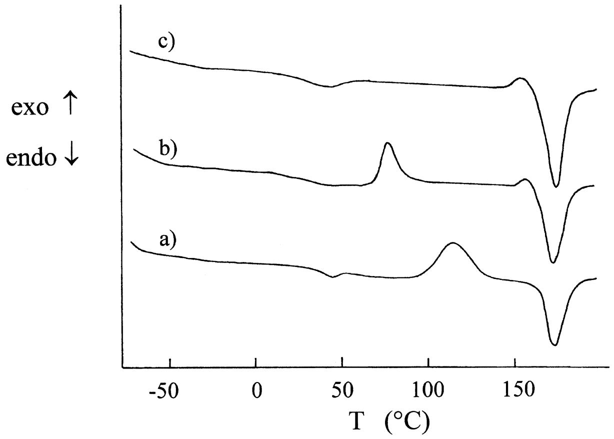

Fig. 6. Second scan DSC thermograms of PLLA–PCL–PLLA (a), PLLA–PEO–PLLA (b) and PLLA–PEO (c) block copolymers.

amorphous component of the copolymers. The low temperature transition is related to the flexible PCL or PEO segments and the high temperature transition is attributed to the PLLA segments. The PLLA and PCL blocks can be considered immiscible, as the copolymer T_gs are nearly identical to those of the homopolymers. This conclusion is in agreement with the literature data on PLLA/PCL blends [10,19]. Accordingly, the cold crystallization of PLLA is observed in the spectrum of PLLA–PCL–PLLA. PEO containing copolymers, on the contrary, exhibit a different behaviour. The T_g values obtained for the individual segments, in fact, are significantly closer to each other than those reported for pure PLLA and PEO homopolymers. The lowering of T_g for the polyester component ($\Delta T_g = 35$–39 °C) is particularly relevant. This effect is considered to be a strong indication that complete segregation of PEO and PLLA segments does not occurs and that PEO and PLLA are miscible in the amorphous phase, albeit partially. Similar conclusions were reached by Rashkov et al. for PLLA–PEO–PLLA low M_w oligomers [20]. Evidence of partial [21] or even complete miscibility [8,22] of the components was reported for PLLA/PEO blends. It is worth noting that PEO containing copolymers show low intensity tan δ peaks corresponding to the PLLA transition and do not exhibit cold crystallization phenomena. These findings could be related to an easier crystallization of PLLA chains in these copolymers with respect to PLLA–PCL–PLLA or to PLLA itself.

The melting and crystallization behaviour of the copolymers was investigated by means of DSC. Samples of copolymers, as obtained from synthesis, were first heated from −100 to 200 °C at a rate of 20 °C/min, cooled to −100 °C at 100 °C/min and heated again to 200 °C at 20 °C/min. DSC thermograms relative to second heating runs after a rapid cooling from the melt are presented in Fig. 6 and the thermal parameters are listed in Table 2. High M_w PLLA ($M_n \cong 100$ kDa), when quenched from the melt, exhibits a cold crystallization exotherm at 120 °C followed by a melting endotherm at 179 °C [10]. All copolymers show melting endotherms relative to the PLLA blocks at 174–175 °C. PLLA–PEO–PLLA and PLLA–PCL–PLLA show also exothermal crystallization peaks at 78 and 113 °C, respectively. On the contrary, a crystallization peak was not observed for the PLLA–PEO diblock copolymer. These results indicate that both the copolymer architecture and the M_w and chemical nature of the flexible blocks influence the cold crystallization of the PLLA segments. In fact, we observed that for the triblock

Table 2
Thermal parameters for the block copolymers and for the PEO, PCL and PLLA homopolymers

	T_g[a] (°C)		T_m[b] (°C)	ΔH_m[b] (J/g)	T_c[b] (°C)	ΔH_c[b] (J/g)
	PLLA	PCL(PEO)				
PLLA	70		179	35	120	35
PCL		−36	60	58	–	–
PEO		≤ −42[c]	70	84	–	–
PLLA–PCL–PLLA	69	−37	174 (44)[d]	37 (3)[d]	113	37
PLLA–PEO–PLLA	35	−30	174	34	78	17
PLLA–PEO	31	−23	175 (40)[d]	19 (4)[d]	–	–

[a] Calculated from DMTA spectra performed from −100 to 120 °C.

[b] Melting and crystallization parameters for PLLA blocks obtained from a second heating DSC run from −100 to 200 °C after rapid cooling from 200 °C.

[c] From Ref. [18].

[d] In brackets the parameters relative to the melting of the PCL or PEO blocks.

Table 3
Mechanical properties of the block copolymers and of PLLA

	E^a (MPa)	$\sigma_y{}^a$ (MPa)	$\sigma_b{}^a$ (MPa)	ε^a (%)
PLLA[b]	1720	46	–	2.9
PLLA–PCL–PLLA	961	19	11	25
PLLA–PEO–PLLA	225	–	7	134
PLLA–PEO*m*	320	–	7	49

[a] Tensile modulus (E), stress at yield (σ_y), stress at break (σ_b) and elongation at break (ε), evaluated from stress–strain measurements.
[b] $M_n = 50$ kDa; from Ref. [6].

copolymers, T_c shifts to values lower than that of PLLA. This effect can be ascribed to the enhanced flexibility of the copolymers, especially when the central block is PEO, as the glass transition temperature of PLLA blocks in PLLA–PEO–PLLA is much lower than that of pure PLLA. In fact, crystallization of amorphous PLLA can occur only at $T > T_g$ where chain mobility is sufficiently high to allow reorganization in a crystalline phase. PEO blocks, moreover, allow a partial crystallization of PLLA segments during the cooling as suggested by the finding that $\Delta H_m > \Delta H_c$. The absence of a cold crystallization phenomenon for PLLA–PEO, indicates that in the case of the diblock copolymer the PLLA segments are able to crystallize from the melt state during the rapid cooling because of the more favourable architecture and the lower M_w with respect to those of the triblock copolymers.

The DSC thermogram relative to the second heating run of PLLA–PEO–PLLA does not show an endothermic transition associated to the melting of PEO segment, and very small endothermic transitions associated to the melting of PEO and PCL segments are observed around 40 and 44 °C in the DSC traces of PLLA–PEO and PLLA–PCL–PLLA copolymers, respectively. These findings are in good agreement with the results of the X-ray diffraction experiments which gave no evidence of diffraction maxima attributable to PEO or PCL crystalline phases. It has been reported that PEO segments do not crystallize in PLLA–PEO–PLLA tri-block copolymers with long PLLA arms (5–10 kDa) and relatively low M_w polyether blocks (2 kDa) [12]. In the case of the copolymers reported in this paper, the M_w of the PEO segments are higher (5–10 kDa) and comparable with those of PLLA blocks (20 kDa). As two independent melting peaks due to the individual blocks were reported for PLLA/PEO copolymers of moderate M_w when the PEO and PLLA block lengths are quite similar [14], it appears that the crystallizability of PEO segments, even when their M_w is fairly high, is strongly reduced when they are covalently bound to long PLLA blocks at both ends, provided that $M_{w_{\mathrm{PLLA}}} > M_{w_{\mathrm{PEO(PCL)}}}$ and, consequently, the wt% of PLLA is high as in our copolymers (≈80%). Similar conclusion were reached by Nojima et al. for PCL–PEO–PCl copolymers if the amount of one component is less than 25 wt% [23]. Also in the case of a more complex copolymer architecture, such as that of a triarm star block copolymers composed of two crystallizable blocks (PEO and PCL) and one amorphous block (polystyrene), Floudas et al. found that only the longer block will crystallize when the crystallizable block length ratio is ≥3 [24]. In the case of the copolymers investigated in the present work, an additional driving force to reduce the crystallizability of the PCL and PEO segments is the high T_m of PLLA compared with those of the PCL and PEA. Therefore, we may assume that the rigid PLLA blocks partially crystallize first when cooling the melt, giving rise to a frozen structure where the mobility of the flexible segments is effectively reduced. The low intensity melting endotherm (4 J/g) observed for PLLA–PEO at 40 °C (Fig. 6) suggests that crystallization of PEO segments may occur to a very low extent during the quenching or the second heating run favoured by their higher mobility with respect to the triblock copolymer. It is interesting to remark that for a diblock PLDA–PEO copolymer, where the D,L-lactic acid blocks are amorphous, extensive crystallization of the polyether segments was highlighted both by DSC and WAXS experiments [17]. Also in the case of PLLA–PCL–PLLA the DSC trace shows a low intensity melting endotherm (3 J/g) at 44 °C. As a low temperature melting peak was not observed in the PEO containing triblock copolymer, we may hypothize that this different behaviour depends on the immiscibility of the PCL and PLLA blocks, which increases the crystallizability of PCL segments. It is conceivable that, in spite of the high flexibility of PEO and PCL segments, their crystallization was also hampered by the high cooling rate from the melt before the second heating run. We found, however, that the thermal behaviour of the copolymers was unaffected by prolonged storage (up to 1 month) at temperatures (4–5 °C) intermediate between the T_g (−42, −36 °C) and T_m (70, 60 °C) of PEO and PCL, respectively.

3.4. Mechanical properties

The tensile stress–strain properties of all the copolymers are presented in Table 3 together with those of a PLLA sample whose M_w ($M_n = 50$ kDa) is comparable to those of the copolymers. The PLLA data, reported for the sake of comparison and taken from the literature [6,7], are characteristic of a high modulus and brittle semicrystalline material with a very low elongation at break. The stress–strain curves of the copolymers, shown in Fig. 7, display typical ductile behaviours, as a consequence of the presence of highly flexible PEO or PCL segments of moderate M_w. The mechanical behaviour, however, is influenced by the nature of the flexible blocks. The PLLA–PCL–PLLA copolymer, in fact, exhibits yield deformation characteristic of a semi-crystalline thermoplastic polymer. The neck formation, however, was not observed in the case of PEO containing copolymers that behave as elastomeric-like materials. The tensile modulus of the copolymers is substantially lower than that of PLLA, mostly in the presence of highly flexible PEO blocks. A large increase in

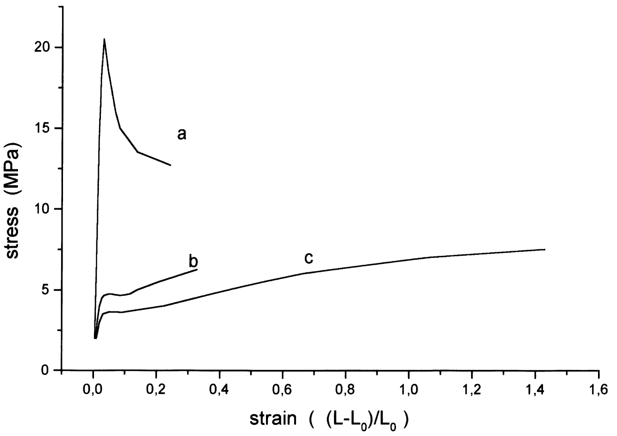

Fig. 7. Stress–strain diagrams of PLLA–PCL–PLLA (a), PLLA–PEO (b) and PLLA–PEO–PLLA (c) block copolymers.

the elongation at break (49–134%), however, can be observed especially for PEO containing copolymers that are tough yet very flexible materials.

4. Conclusions

The investigated block copolymers are highly crystalline materials that display a melting behaviour close to that of the main component, PLLA, and show a microphase separation of the two components in the amorphous phase. The partial miscibility of PLLA and PEO segments leads to a significant lowering of the PLLA T_g, thus increasing the overall chain flexibility of the PEO containing copolymers. The crystallization of the main component, PLLA, prevents a significant crystallization of the PEO or PCL blocks. The copolymers are characterized by high elongations at break and by tensile moduli much lower than that of PLLA.

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