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Structural evolution of poly(L-lactide) block upon heating of the glassy ABA triblock copolymers containing poly(L-lactide) A blocks

S. Nagarajan [a], Krishnan Deepthi [a, b], E. Bhoje Gowd [a, b, *]

[a] Materials Science and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology, Trivandrum 695 019, Kerala, India
[b] Academy of Scientific and Innovative Research (AcSIR), New Delhi 110 001, India

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ABSTRACT

Two triblock ABA copolymers poly(L-lactide-*b*-dimethylsiloxane-*b*-L-lactide) (PLLA-*b*-PDMS-*b*-PLLA) and poly(L-lactide-*b*-ethylene glycol-*b*-L-lactide) (PLLA-*b*-PEG-*b*-PLLA) containing poly(L-lactide) were synthesized by ring opening polymerization of L-lactide using bis(hydroxyalkyl) terminated PDMS and hydroxyl end-capped polyethylene glycol as macroinitiators, respectively. Both the triblock copolymers were melt-quenched to −40 °C to prepare the amorphous samples. The melt morphology of the triblock copolymers was preserved upon cooling the melt to −40 °C. PLLA and PDMS blocks are immiscible in the melt, and the amorphous triblock copolymer shows two distinct glass transition temperatures (T_g) on heating. On the other hand, PLLA and PEG segments are miscible and the triblock copolymer shows the single T_g. Structural evolution of PLLA during heating of the amorphous ABA triblock copolymers has been investigated by measuring the variable temperature small-angle and wide-angle X-ray scattering (SAXS and WAXS) and FTIR spectra. In the case of PLLA-*b*-PDMS-*b*-PLLA triblock copolymer (immiscible system), the mesophase of PLLA was found to appear just above the T_g of PLLA block (~45 °C), and on further heating the mesophase changed to the regular α form at around 90 °C. On the other hand, in PLLA-*b*-PEG-*b*-PLLA (miscible system), the mesophase of PLLA was found to appear at lower temperature i.e. −20 °C, because of the enhanced molecular mobility of PLLA chains in the presence of PEG. However, irrespective of the mesophase formation temperature, the ordered α form has appeared at around 90 °C. In this way, during heating of the amorphous triblock copolymers, the PLLA block was found to crystallize into the ordered α form always through the mesophase just above the T_g of PLLA. These results are helpful in understanding the regularization process of semicrystalline polymers in different environments.

1. Introduction

Poly (L-lactide) (PLLA) is an eco-friendly thermoplastic polymer derived from the renewable resources, such as corn [1,2]. Due to its biodegradability and biocompatibility, PLLA has been widely used in the industrial and medical fields, such as packaging and biomedical devices [3–7]. However, the slow crystallization rate and the precise control of its crystallization during processing have limited the practical incorporation of PLLA into commercial applications [8–11]. Therefore, a great deal of effort is needed to understand the crystallization process and crystal structure of PLLA for controlling the properties of this semicrystalline polymer. Five major crystalline forms α, β, γ, δ (α'), and ε have been reported for PLLA so far [12–22]. Besides these crystalline forms, a mesophase was also reported for PLLA [23–30]. The formation of mesophase in semicrystalline polymers is an interesting subject, and it is needed to understand the structure regularization of semicrystalline polymers both from melt state and glassy state. According to Strobl, the formation and growth of the lamellar crystallites in polymer crystallization is a multi-step process, and the polymer crystallization takes place through a metastable intermediate structure [31,32]. It has been reported that in semicrystalline polymers a mesophase originally exists in the melt-quenched samples or appeared prior to the cold crystallization of the glassy polymer during heating [33–40]. For example, the mesophase of semicrystalline polymers can be

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* Corresponding author. Materials Science and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology, Trivandrum 695 019, Kerala, India.
E-mail address: bhojegowd@niist.res.in (E.B. Gowd).

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formed by rapid quenching of fast crystallizing polymers such as isotactic polypropylene, syndiotactic polystyrene and poly(-butylene naphthalate) [33–36]. On the other hand, in the case of slow crystallizing polymers such as poly(ethylene terephthalate) and poly(ethylene naphthalate), the mesophase can be formed by stretching or annealing of the glassy polymers [37–39]. Stoclet et al. reported the mesophase of PLLA by stretching the amorphous polymer over the temperature range from 45 to 70 °C [23]. Zhang et al. showed that physically aging of glassy PLLA below the glass transition temperature (T_g) resulted in the formation of mesophase [24]. Tashiro and co-workers reported that the isothermal crystallization of PLLA both from glassy and melt state occur through the mesophase [40]. They also reported that melt-quenched PLLA is not perfectly amorphous phase, but it contains the mesophase [40].

Generally, plasticizers are often added as chain mobility accelerators to reduce brittleness and improve the toughness of polymers by lowering T_g [26,41–43]. The acceleration of chain mobility was also found to facilitate the crystallization kinetics of the semicrystalline polymers [29,44,45]. It has been reported that the mesophase can be formed by the addition of other components to PLLA such as polyethylene glycol and carbon dioxide (CO_2), which are known to reduce the T_g of PLLA [27,29,46]. Koido et al. observed the amorphous phase to mesophase transition at 40 °C during heating of the amorphous blend of PLLA and 26 wt% of succinic acid-bis[2-[2-(2-methoxyethoxy)ethoxy]ethyl] ester (SAE) [26]. Recently, it was shown that the mesophase formation in glassy PLLA was significantly improved at a lower temperature (0 °C) in the presence of CO_2 due to the enhanced molecular mobility of PLLA chains [29].

Several authors studied the structural development in PLLA containing polymers from the melt state and showed that segregation strength of the blocks in the melt state determines the morphological development in the crystalline block copolymers [47–51]. Recently, few reports appeared on the mesophase formation in PLLA containing block copolymer systems. Zhang et al. reported the formation of the PLLA mesophase in the melt-quenched poly(L-lactide-*b*-ethylene glycol-*b*-L-lactide) (PLLA-*b*-PEG-*b*-PLLA) triblock copolymer by means of Fourier transform infrared spectroscopy (FTIR) [48]. In our previous work, it has been shown that upon heating the melt-quenched (glassy) poly(L-lactide-*b*-dimethylsiloxane-*b*-L-lactide) (PLLA-*b*-PDMS-*b*-PLLA) triblock copolymer, the amorphous PLLA domains transiently transforms to the mesophase before transforming into the stable α crystalline form [47]. Though the PLLA mesophase formation was known in the aforementioned systems in this way, still many questions are left unanswered. What is the role of miscibility/immiscibility of the blocks in block copolymers in the formation of mesophase? Is the mesophase formation is facilitated by the segmental mobility of the PLLA chains? Though the formation of mesophase in PLLA was reported by many authors including us, no one clarified the above questions. To clarify these questions, we have chosen two block copolymer systems, PLLA-*b*-PDMS-*b*-PLLA triblock copolymer as an immiscible system and PLLA-*b*-PEG-*b*-PLLA triblock copolymer as a miscible system.

In the present work, the formation of PLLA mesophase is studied in miscible and immiscible triblock copolymers by using temperature-dependent small-angle and wide-angle X-ray scattering (SAXS and WAXS) and temperature-dependent FTIR. It is found that the PLLA mesophase is formed at a lower temperature in miscible triblock copolymers compared to that of the immiscible triblock copolymers due to the enhanced segmental mobility of the PLLA chains in the presence of miscible PEG chains.

2. Experimental

2.1. Materials

L-lactide, bis(hydroxyl) terminated poly(ethylene glycol) ($\overline{M}_n = 6000$), tin(II) 2-ethylhexanote $Sn(Oct)_2$, hexane and dry-toluene were purchased from Sigma-Aldrich. The chemicals were used as received without further purification. $PLLA_{74}$-*b*-$PDMS_{92}$-*b*-$PLLA_{74}$ used in this study was synthesized according to the procedure reported in our previous paper [47].

2.2. Synthesis of PLLA-b-PEG-b-PLLA

In a typical procedure, desired amount of poly(ethylene glycol) ($\overline{M}_n = 6000$ g/mol) and $Sn(Oct)_2$ were added to a round-bottom flask containing dry toluene (50 ml). The flask was purged with dry nitrogen and immersed in an oil bath at 60 °C for 30 min. To that reaction mixture, required amount of L-Lactide was added slowly, and the temperature of the oil bath was raised to 115 °C. After approximately 72 h at 115 °C, the solution was cooled to room temperature. The obtained polymer was reprecipitated in 500 ml of cold hexane. The filtered polymer was dried under vacuum for 48 h at 60 °C. The number average molecular weight and polydispersity of the PLLA-*b*-PEG-*b*-PLLA triblock copolymer estimated to be $\overline{M}_n$ = 18,500 g/mol and $\overline{M}_w/\overline{M}_n = 1.2$, respectively. The structure of triblock copolymer was confirmed by ^{1}H NMR using Bruker NMR spectrometer operating at 500 MHz (Fig. S1). ^{1}H NMR: $\delta = 1.59$ (CH_3 PLLA); $\delta = 3.61$ (CH_2 PEG); $\delta = 5.17$ (CH PLLA). The number average molecular weight of the $PLLA_{87}$-*b*-PEG_{136}-*b*-$PLLA_{87}$ triblock copolymer was estimated based on the integrated ratio of PEG block at 3.61 ppm and PLLA block at 5.17 ppm [52].

2.3. Characterization

2.3.1. Size exclusion chromatography (SEC)

SEC was performed at room temperature to determine the molecular weight distribution profiles by using Agilent Technologies-1260 instrument. This instrument is equipped with a PL-gel 20 μm MIXED-B column and RI detector. The molecular weight was determined using a universal calibration curve based on standard polystyrene samples.

2.3.2. Differential scanning calorimetry (DSC)

Thermal analysis of triblock copolymer was carried out using a differential scanning calorimeter (Perkin-Elmer Pyris 6 DSC) in a dry nitrogen atmosphere. The instrument was calibrated by the melting of indium prior to the DSC experiments. Around 8 mg of triblock copolymer was sealed in aluminum pans and the sample in the DSC pan was melt-quenched in liquid nitrogen. Such melt-quenched sample was scanned from −50 to 180 °C at a heating rate of 10 °C/min.

2.3.3. X-ray diffraction measurements

Wide-angle and small-angle X-ray scattering measurements (WAXS/SAXS) were carried out on XEUSS SAXS/WAXS system using a Genixmicro source from Xenocs. The generator was operated at 50 kV and 0.6 mA. The X-ray beam was collimated with FOX2D mirror and two pairs of scatterless slits from Xenocs. The fiber diagrams were recorded on a Mar345 image plate and processed using Fit2D software. All the measurements were performed in the transmission mode. Silicon powder and silver behenate were used as standard samples for calibration of the scattering vectors of WAXS and SAXS, respectively. The sample-detector distance was set at 221.75 mm and 1050 mm in the direction of the beam for WAXS and SAXS data collections, respectively. Linkam THMS 600

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