Crystallization and Properties of Poly(lactide)/Poly(δ-valerolactone) Alternating Supramolecular Copolymers Adjusted by Stereocomplexation

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Supporting Information

ABSTRACT: The crystallization behavior of a series of synthesized polylactide (PLA)/poly(δ-valerolactone) (PVL) supramolecular copolymers with 2-ureido-4[1H]-pyrimidinone (UPy) groups is investigated by differential scanning calorimetry and X-ray diffraction. The stereocomplexation of PLA-based supramolecular polymers (SMPs) is strongly related to the block length, L/D ratios, and the UPy groups. Both the increase of the PLA block length and the self-complementary hydrogen bonding of the UPy end groups restrain the crystallization of the PVL blocks. The stereocomplexation of PLA-SMPs is greatly promoted by UPy groups, while the homocrystallization of PLA is constrained. The dynamic mechanical analysis indicated that the enhanced stereocomplexation would lead to higher thermal resistance and mechanical properties of PLA-based SMPs.

INTRODUCTION

Supramolecular polymers (SMPs), assembled by weak intermolecular interaction such as metal coordination, hydrogen bonding, electrostatic interaction, van der Waals force, and hydrophobic forces, are new materials with a variety of reversible features.1−5 SMPs integrate not only the excellent properties of polymers but also have the reversibility of the bond and the responsiveness to the external environment. Because the bond energy and the bond life of the noncovalent bond can be controlled by changing the temperature or other environmental conditions, the noncovalent bond possesses dynamic reversible characteristics. So far, the SMPs based on multiple hydrogen bonds have received extensive attention because the multioverlap and synergy among the multiple hydrogen bonds can produce a strong binding energy. 2-Ureido-4[1H]-pyrimidinone (UPy) is a representative multiple hydrogen-bonded motif formed by the self-complementary quadruple hydrogen bonds.6,7 The dimerization constant of UPy can reach 6 × 10⁷ mol/L, which is close to the strength of covalent linkages. However, the introduction of UPy groups disrupts the structural symmetry of the polymer chains, and consequently the mobility and regular folding of the polymer segments.8,9 A lower crystallinity would decrease the thermal and mechanical properties of SMPs, which limits the wider application.

Stereocomplexation (SC) is a unique mechanism between the stereoisomeric polymers driven by the intermolecular hydrogen bonding, resulting in strong crystallization capability.10,11 Therefore, stereocomplexation technology provides a new approach to improve the crystallization capacity of the difficult-to-crystallize or amorphous polymer with different enantiomers. Polylactide (PLA) has two stereoisomers poly(l-lactide) (PLLA) and poly(d-lactide) (PDLA), and the racemic helical pairs are generated prior to the nucleation of homopolymorph in PLLA/PDLA blends.12,13 However, the PLA stereocomplexation is greatly limited by the molecular weight, L/D ratio, with limited probability for the intermolecular interaction between PLLA and PDLA. Our former work presented enhanced stereocomplexation by introducing soft segments, UPy end groups, and nanoparticles into the PLA molecules.14−16 Therefore, enhancing the intermolecular interactions between complementary enantiomers would facilitate the nucleation and growth of SC crystallites. Pan and coauthors7,17 have reported research work about UPy-functionalized PLA, showing that the hydrogen-bonding interactions formed between the terminal UPy groups of PLLA- and PDLA-enhanced SC crystallization ability and crystallization rate. Furthermore, the dimerization of UPy groups shows good thermally responsibility, and the dimerization is reported to dissociate at about 80 °C.18,19 This thermal reversible behavior provides the UPy-based SMPs shape-memory behavior and self-healing performance, which are research interests in polymer functionalization.20 Li et al. also found that the formed network by stereocomplex crystal as
the physical cross-linking points obviously improved the shape-memory properties of the resulting materials. Therefore, the preparation of PLA-based SMPs with UPy groups could be the strategy to promote stereocomplexation.

Herein, a series of PLA-based triblock copolymer consisting of poly(δ-valerolactone) (PVL) segment in the middle were synthesized by sequential ring-opening polymerization. The UPy-functionalized PLA−PVL−PLA SMPs were then synthesized by the coupling reaction of PLA−PVL−PLA with UPy-NCO. This work focuses on the stereocomplexation of those SMPs, compared with the stereocomplexation behavior of stereoisomers without UPy functionalization. The influence of the length of PLA blocks and the L/D mixing ratios of stereoisomers on the crystallization behaviors and thermal dynamical properties was investigated.

**RESULTS AND DISCUSSION**

PLA−PVL−PLA triblock copolymers and UPy end-functionalized PLA−PVL−PLA with different stereostructures of PLA blocks were synthesized as shown in Scheme 1a. Table S1 lists the compositions and molecular weights of PLA−PVL−PLA triblock copolymers. In Figure S1, the 1H NMR spectra of L-SMPs show peaks at 13.1, 11.9, and 10.2 ppm assigned to UPy groups. In Figure S2, PLA-based SMPs possess excellent elasticity as transparent film compared to the related triblock copolymers as white brittle films. Different physical states can be explained by the mechanical flexibility induced by the UPy groups with the self-complementary hydrogen bond as shown in Scheme 1c. The supramolecular multiblock copolymer with alternating PVL and PLA blocks as stereo-multiblock SMPs was then formed as shown in Scheme 1b. In Figure S3, the sc-SMPs with shorter PLA blocks are transparent and elastic solids under all mixing ratios. However, the sc-SMPs with longer PLA blocks are transparent and elastic solids with low D-SMPs content (<20 wt %), while those with smaller PLA blocks are opaque and brittle solids with high D-SMPs content (>20 wt %). Therefore, the length of the PLA blocks and the content of the D-SMPs are both key factors affecting the physical states of the sc-SMPs and, consequently, the crystallization and mechanical properties.

The influence of PLA block length and L/D ratios on the crystallization behavior of sc-SMPs was investigated. For comparison, differential scanning calorimetry (DSC) curves of the triblock polymeric blends without UPy functionalization are also shown in Supporting Information. The heating—cooling—reheating curves of solvent-casting sc-SMPs are shown in Figure 1. In Figure 1a, the DSC curve of L-SMPs1.8 displays two endothermic processes at 24−60 and 100 °C, assigned to the melting of the PVL block and the PLLA block, respectively. With increasing D-SMPs, the endothermic peak of PVL decreases. In Figure 1b (L-SMPs6.7), the melting peak of PVL block disappears and the melting peak of hc-PLA at 150 °C decreases, while that of sc-PLA at 210 °C increases with the increase of the D-SMPs ratio. The increase of the PLA length and the enhanced stereocomplexation would constrain the crystallization of the PVL blocks. More interesting, complete stereocomplexation could be achieved when D-SMPs7.2 is more than 30%, which is attributed to the flexibility of the introduced PVL blocks. For comparison, all L-VL-L1.6/D-VL-D1.8 blends show a melting process of the PVL blocks at 30−60 °C in Figure S4a. For L-VL-L6.7/D-VL-D7.2 blends in Figure S4b, two melting peaks at 160 and 210 °C are assigned to the melting of the hc-crystal and sc-crystal, respectively. When the D content is higher than 40 wt %, complete stereocomplexation is achieved. The comparison demonstrates that UPy-functionalization enhances the intermolecular interactions between complementary enantiomers, which facilitate the formation of sc-crystallites.

Figure 1c,e shows the DSC cooling and subsequent heating curves of L-SMPs1.8/D-SMPs1.6. For comparison, the L-VL-
L1.6/D-VL-D1.8 blends are investigated in Figure S4c,e. The main differences were the crystallization peak at 110 °C during cooling and then the melting peaks of PVL at 40 °C in the second heating process, which were not obvious in the SMPs but clear in the blends without UPy systems. On the contrary, the melting peaks of sc-PLAs at 160 °C in the SMPS was much weaker.

Figure 1. DSC heating–cooling–reheating curves of L-SMPs/D-SMPs blends: (a, c, e) for L-SMPs1.8/D-SMPs1.6 and (b, d, f) for L-SMPs6.7/D-SMPs7.2.
obvious and also increase with the increasing D content. The hydrogen bond between the UPy end groups behaved as cross-linking point and then constrained the PVL crystallization, while the formed PLA sc-crystals in the L-VL-L/D-VL-D blends acted as heterogeneous nucleating agents for PVL crystallization.

Figure 1d,f displays the DSC cooling and reheating curves of L6.7/D-7.2-SMPs. The two melting peaks at 130 and 190 °C (Figure 1f) are attributed to the melting of the hc-crystal and sc-crystal, respectively. When the D-SMPs content exceeds 30 wt %, only the characteristic peaks of sc-crystal are present. For L-VL-L6.7 triblock copolymer in Figure S4d, a crystallization peak is observed at 80 °C upon cooling, assigned to the crystallization of the PLLA blocks. When with D-VL-D7.2 triblock copolymer, its crystallization rate increases due to stereocomplexation between PLLA and PDLA blocks. This indicates that the crystallization capacity of L-VL-L/D-VL-D blends is increased upon stereocomplexation. However, the stereocomplexation plays different roles in the triblock copolymeric blends with or without UPy-functionalized groups.

Based on the above DSC, the melting enthalpies of either PVL or sc-PLA in different blends could be calculated from the area of the related melting peaks as shown in Figure 2 versus the D-SMPs contents. When the PLA length is short, the PVL melting enthalpies first increases and then decrease with more D-SMPs introduced in the blends. A small amount of physical intermolecular bondings could act as nucleating agents for PVL, and the enhanced crystallinity results in the increase of melting enthalpies. While more PLA block are involved in stereocomplexation, the PVL molecular mobility is greatly constrained, which leads to the decrease of the PVL melting enthalpies. In Figure 2b, as the D-SMPs contents increases, the melting enthalpies of sc-PLA gradually increase. This indicated that the stereocomplexation was greatly improved when the L/D ratio is close to 1.

Wide-angle X-ray diffraction (WAXD) patterns of sc-SMPs and L-VL-L/D-VL-D blends are discussed for the effect of UPy groups on the crystalline structure. In Figure 3a, the neat L1.8-SMPs show obvious patterns at 16.8, 21.8, and 24.5°, attributed to the (110)/(200) plane of the α crystal of PLLA and diffraction from the (110) and (200) lattice planes.
of the orthorhombic unit cell structure formed from PVL blocks, respectively. A novel diffraction peak arises at 12.0° when the L1.8-SMPs blend with complementary D1.6-SMPs. The peak at 12.0° is assigned to the (110) plane of the PLLA β crystal owing to the PLA stereocomplexation. With the increasing D-SMPs amount, the peaks at 21.8 and 24.5° decrease but that at 12.0° increases. In other words, the crystallinity of the PVL blocks decreases, while the stereocomplex crystallization increases in the L1.8/D1.6-SMPs. In Figure 3b, for the neat L6.7-SMPs, obvious diffraction peaks at 16.8, 19.1, and 22.3° are assigned to the (110)/(200), (203), and (210) planes of the PLLA α crystal, respectively. The diffraction peaks at 12.0 and 20.8° are assigned to the 110 and 300/030 planes of the β crystal, respectively. Moreover, these peaks increase as the L-SMPs/D-SMPs mixing ratios approach 5/5.

To further elaborate the role of UPy end groups, the WAXD patterns of L-VL-L/D-VL-D blends are measured in Figure S5a. The L-VL-L1.6/D-VL-D1.8 blends show the diffraction peak of β crystal, and the peak strength increases with increasing D-VL-D amount. Figure S5b displays the WAXD patterns of L-VL-L6.7/D-VL-D7.2 blends. The triblock copolymer L-VL-L6.7 shows the WAXD pattern similar to that of L6.7-SMPs. However, the characteristic patterns of both sc-PLA and hc-PLA are detected for the L-VL-L6.7/D-VL-D7.2 blends. However, the related sc-SMPs blends only present the stereocomplexes regardless of the content of D7.2-SMPs. These results indicate that the self-complementary hydrogen-bonding of UPy units facilitates the complete stereocomplexation of sc-SMPs.

The storage modulus and loss tangent (tan δ) of sc-SMPs of L1.8/D1.6-SMPs are displayed in Figure 4. The storage modulus of sc-SMPs decreases in the ranges from ~50 to 0, 0 to 60, and >80 °C, attributed to the glass transitions of PVL and PLA and softening PLA (or dissociation of UPy dimers), respectively. The storage modulus of sc-SMPs at lower range (<50 °C) first decreases and then increases with more D content. This is because the strong hydrogen bonding of both stereocomplexation and the UPy end groups limits the movement of the PVL chains. The consequent crystallization capacity of the PVL blocks in sc-SMPs decreases. However, a large number of stereocomplex crystals were formed with further increasing of the mixing ratios (>30%), enhancing the storage modulus. At higher temperature range (>50 °C, higher than Tm of PVL blocks), the storage modulus of sc-SMP increases with increasing of the D-SMPs/L-SMPs mixing ratios. Therefore, the stereocomplex crystalization of PLLA and PDLA blocks obviously improves thermal resistance.

In Figure 4b, two relaxation peaks at ~50 to 50 °C and 50 to 80 °C are assigned to the glass transitions of the PVL and PLA blocks, respectively. The relaxation peak of PVL at lower temperature range first shifts to the lower- and then higher-temperature regions with increasing of D-SMPs content. Meanwhile, the area of PVL relaxation peak first increases and then decreases with more D-SMPs content. This can be explained by the first enhanced chain mobility of PVL and then increased PVL crystallinity with more D-SMPs and also higher degree of stereocomplexation. When the PVL block length is much longer than the PLA length, the PVL molecule mobility was first increased and then decreased when the D-SMPs contents increased. This result is similar with the trend of PVL melting enthalpies against D-SMPs content. In addition, the area of relaxation peak corresponding to the PLA block shows a decreasing trend, attributed to the increased crystallinity and the decreased amorphous content of PLA. This result can also be reflected by the shift of the PLLA glass transition peak to high-temperature range by enhanced stereocomplexation. The thermal dynamic mechanical study indicated that the mechanical properties of sc-SMPs can be adjusted by varying the L-SMPs/D-SMPs mixing ratios.

**CONCLUSIONS**

A series of UPy end-functionalized PLA–PVL–PLA with different stereostructure and molecular weight were synthesized. The stereocomplexation of PLA-based SMPs was further prepared by the blending UPy end-functionalized PLLA–PVL–PLA and PDLA–PVL–PDLA. The crystallization behavior of sc-SMPs is strongly influenced by the block lengths and the L/D mixing ratios, with the comparison of sc-triblock copolymers. The sc-SMPs presented enhanced stereocomplexation even at unequal L/D ratio, which is attributed to the hydrogen bonding of the UPy groups. This study presents the tailored crystallization by introducing stereocomplexation as well as promoted stereocomplexation by noncovalent UPy groups.
EXPERIMENTAL SECTION

Materials Details. L- and D-Lactide (≥99.5%) (Changchun Shengboma Biological Co., LTD) were recrystallized in dried toluene. Diethylene glycol (DEG, 99%) and d-valerolactone (VL, 99%) were purchased from J&K Chemical. Dihydroxyl-terminated PVL macroinitiator was prepared as reported in the literature. 2

2(6-Isocyanatohexylaminocarbonylamino)-6-methyl-[1H]-pyrimidinone (UPy-NCO) was produced by J&K Chemical and 2-amino-4-hydroxyl-6-methyl pyrimidine (J&K Chemical) according to the previous literature. 27

Stannous octoate (Sn(Oct)2) and dibutyltin dilaurate under 60 °C were used as solvent.

Synthesis of PLA−PVL−PLA Copolymers. PLA−PVL−PLA triblock oligomers were first synthesized using dihydroxyl-terminated PVL macroinitiator to initiate the polymerization of lactide monomer with Sn(Oct)2 as catalyst. The ring-opening polymerization of lactide was carried out in a Schlenk flask under nitrogen at 130 °C overnight. The product was dissolved in dichloromethane and precipitated in methanol three times. Then, the products were dried in vacuum oven. The enantiomers of PLA−PVL−PLA triblock copolymers were marked as L-VL-Lx or D-VL-Dx, where x represents the average number molecular weight of the PLA end block based on the 1H NMR spectra.

Synthesis of PLA−PVL−PLA Copolymers with UPy End Groups. PLA−PVL−PLA copolymers were functionalized with UPy as end groups by their reaction with excess of UPy-NCO. Excess UPy-NCO was reacted with the synthesized PLA−PVL−PLA in Schlenk flask in vacuum line. Dry toluene was chosen as a solvent and Sn(Oct)3 as a catalyst. The whole reaction was carried out under nitrogen at 110 °C for 20 h. Excess UPy-NCO and solvent were removed by filtration and reduced pressure distillation, respectively. The products were first dissolved in chloroform and then with the addition of silica and dibutyltin dilaurate under 60 °C for 2 h. Then, the final products were collected by the filtration of silica and solvent evaporation.

Preparation of sc-SMPs. The UPy end-functionalized PLLA−PVL−PLLA and PDLA−PVL−PDLA blends (as L-SMPs and D-SMPs, respectively) were mixed together in a solvent. The L/D ratios of the L-SMPs/D-SMPs blends were chosen to be 9/1, 8/2, 7/3, 6/4, or 5/5. The blending solution was cast in PTFE mold and dried in a vacuum oven. For comparison, PLLA−PVL−PLLA/PDLA−PVL−PDLA blends with different L/D ratios were also prepared by solution casting. In this work, Lx/Dy-SMPs m/n and Lx/Dy m/n represent the L-SMPs/D-SMPs and PLLA−PVL−PLLA/PDLA−PVL−PDLA blends, respectively, where x and y are the length of the PLLA and PDLA block, respectively, and m/n means the L/D ratio.

Measurement. 1H NMR measurements were carried out for the chemical structure characterization by a 400 MHz Bruker AVANCE II nuclear magnetic resonance spectrometer (Bruker BioSpin Co., Switzerland) in deuterated chloroform (CDCl3) as solvent and tetramethylsilane as an internal reference. The molecular weight of the synthesized product was determined by a Waters gel permeation chromatography instrument with polystyrene as standard materials.

Differential scanning calorimetry (DSC, METTLER) was chosen for the measurement of the thermal properties and the crystallization behavior of PLA copolymers and their blends. The measurement program was cooling−heating−recooling−reheating cycle in which the sample was cooled to −80 °C, heated to 190 or 230 °C and then kept for 5 min. The second cooling was back to −80 °C and then reheating to 190 or 230 °C. The heating or cooling rate was kept at 10 °C/min for all DSC cycles.

Wide-angle X-ray diffraction (XRD) was tested on a Brucker D8 X-ray diffractometer at a scanning rate of 2°/min using Cu Kα radiation (λ = 0.154 nm) at 40 kV and 200 mA. The samples were scanned at the range from 5 to 35°.

Dynamic mechanical analysis (DMA) measurement of the prepared PLA copolymers blends were carried out by a Q800 DMA instrument with a liquid nitrogen cooling system with tension mode. The samples were prepared with length × width × thickness of 30 × 5.0 × 0.3 mm3. The frequency was 1 Hz and the temperature range was between −100 and 150 °C, with a rate of 3 °C/min.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00380.

Compositions and molecular weights of PLLA−PVL−PLLA and PDLA−PVL−PDLA triblock copolymers; photo images for solvent-cast films of PLA−PVL−PLA triblock copolymer and the corresponding supramolecular polymers; DSC heating−cooling−reheating curves and WAXD patterns of PLLA−PVL−PLLA/PDLA−PVL−PDLA blends with different mixing ratios (PDF)

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Author Contributions

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Notes

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