Non-Covalent PS–SC–PI Triblock Terpolymers via Polylactide Stereocomplexation: Synthesis and Thermal Properties

Viko Ladelta, Konstantinos Ntetsikas, George Zapsas, and Nikos Hadjichristidis

ABSTRACT: Polylactide (PLA) stereocomplexes (SCs) containing amorphous block copolymers have gained enormous interest due to their unique properties and wide range of potential applications. In this work, we report the synthesis and properties of non-covalent triblock terpolymers: polystyrene−SCPLA−polyisoprene (PS−SC−PI) via the stereocomplexation of PS-b-PDLA with PI-b-PLLA diblock copolymers through the solution-precipitation method. The diblock copolymers were prepared by combining the anionic polymerization high-vacuum technique with ring-opening polymerization (ROP). First, several well-defined ω-hydroxyl polystyrenes and polyisoprenes (PS-OH and PI-OH) with varied molecular weights were synthesized by anionic polymerization using sec-BuLi as the initiator. PS-OH and PI-OH were used as the macroinitiators for the ROP of DLA and LLA catalyzed by tin(II) 2-ethyl hexanoate to afford PS-b-PDLA and PI-b-PLLA. PS−SC−PIs were prepared by mixing PS-b-PDLA and PI-b-PLLA solutions (in dichloromethane) and precipitated into methanol. The molecular characteristics of the block copolymers were determined by 1H NMR spectroscopy and size exclusion chromatography. The formation of PS−SC−PIs was evidenced by differential scanning calorimetry, X-ray diffraction, and Fourier-transform infrared, and circular dichroism spectroscopies. A preliminary study by atomic force microscopy reveals the thin-film phase behavior and the supramolecular organization of the PS−SC−PI.

INTRODUCTION

Polyesters (PLAs) have attracted significant attention in the past few decades due to their outstanding thermal and mechanical properties, biodegradability, and biocompatibility.1−4 PLAs have been widely used as biodegradable plastics, as nanocarriers in drug delivery, in tissue engineering, and in 3-D printing, among other applications.5−8

PLAs can be prepared by ring-opening polymerization (ROP) of lactide (LA).9 One of the most common catalysts for ROP of LAs is tin(II) 2-ethyl hexanoate (Sn(Oct)2), which can catalyze the ROP of LAs in bulk or solutions. Sn(Oct)2 is widely used as the catalyst for ROP of LAs and lactones because it is cheap, commercially available, has good solubility in organic solvents, is stable at high temperature, and promotes a well-controlled ROP with a high degree of stereoregularity.10 Moreover, Sn(Oct)2 has been approved as a food additive by the FDA.9

LAs possess two stereocenters and thus provide three stereoisomeric forms: (R,R)-lactide (LLA), (S,S)-lactide (DLA), and (R,S)meso-lactide (mLLA).11 The polymerization of LLA or DLA with Sn(Oct)2 leads to the formation of poly(l-lactide) (PLLA) and poly(d-lactide) (PDLA) with a high degree of isotacticity. Isotactic PLLA and PDLA undergo a stereoselective association to form a PLA stereocomplex (SC) in melt or solution.12,13 Stereocomplexation of PLAs has gained significant interest in material science because the resulting SC has improved mechanical and thermal properties compared with the corresponding homopolymers.13

A SC was first reported in 1987 by Ikada et al., who used differential scanning calorimetry (DSC) and wide-angle X-ray diffraction to study the stereocomplexation of PLLA and PDLA blends with different molar ratios.14 Ozaki et al. found that SC crystallites are stabilized by the intermolecular hydrogen bonding (CH···O=).15 The resulting SC-based PLA has improved mechanical and thermal properties compared with the corresponding homopolymers.13

Stereocomplexation of an equimolar mixture of PLLA with PDLA homo-polymers produces polymeric materials exhibiting a completely new crystalline structure (triangular instead of orthorhombic crystal lattice).17,18 The resulting SC-based PLA materials show improved mechanical properties as well as higher thermal and hydrolytic stability. These enhanced thermo-mechanical properties result from the hydrogen bonding interaction between l- and d-lactides in the PLA SCs.19−23

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*Corresponding Author.
In order to improve their properties and expand their applications, PLAs have been copolymerized with many other polymers, resulting in new polymeric materials. The presence of another polymeric block covalently linked to the PLA segment has been used to improve the thermal and mechanical properties and derive a new morphological behavior. The self-assembly of PLA-containing block copolymers has created pathways for the fabrication of various nanoparticles with optimized properties, advanced drug carriers, and drug release systems and led to the invention of new morphologies. Several polymers that have been block copolymerized with PLAs including polyethylene glycol (PEG), poly(ε-caprolactone) (PCL), poly(ethylene oxide), poly(butylene succinate), poly(2-(dimethylamino)ethyl methacrylate), polycrylic acid (PAAs), poly(3-hexyl thiophene) (P3HT), polystyrene (PS), and polyisoprene (PI) have been used to achieve the desired properties.

Furthermore, several studies have been reported on the synthesis and application of non-covalent triblock copolymers based on PLA SCs. Some examples are PEG–SC–PEG, P3HT–SC–P3HT, PDMMA–SC–PDMMA, PCL–SC–PCL, PAA–SC–PAA, and PDMS–SC–PDMS. Nevertheless, to the best of our knowledge, there is no report on the synthesis and properties of non-covalent polystyrene–SCPLA–polystyrene (PS–SC–PI) triblock terpolymers. Ho and co-workers synthesized a PS-b-PLA diblock copolymer via the combination of nitroxide-mediated polymerization (NMP) and ROP. PS was first prepared by the NMP of styrene initiated with benzyl peroxide using 2,2,6,6-tetramethylpiperidine 1-oxyl, and the radical mediator. The resulting polystyrene-TEMPO-PS was mixed with [(μ1-EEDP)Li2][[(μ1-nBu)Li(0,5Et,O)]2 to form a lithium alkoxide macroinitiator. The resulting diblock copolymer was studied extensively to understand the chiral properties of the diblock copolymers, the self-assembly of the nano-helices, and the formation of nanostructures.

EXPERIMENTAL SECTION

Materials. For Anionic Polymerization. Benzene (Sigma-Aldrich, 99%) was purified over CaH2 and subsequently distilled and stored into a glass cylinder containing living PS-Li- under a high vacuum. Styrene (Sigma-Aldrich, 99%) was purified by successive distillations over CaH2 and di-n-butylmagnesium (Sigma-Aldrich, 1 M solution in heptane) and stored at ~20 °C. Isoprene (Sigma Aldrich, 99%) was purified over CaH2, distilled twice over n-ButLi, and finally stored at ~20 °C. sec-Butylithium (1.4 M in cyclohexane, Sigma-Aldrich) was diluted to the appropriate concentration in purified benzene in a specific glass apparatus under a high vacuum. EO (Sigma-Aldrich, 99.5%) was purified by successive distillations over CaH2 and n-ButLi at 0 °C and finally stored under high vacuum. Methanol was purified by successive distillations over CaH2 and stored under a high vacuum. All the above purification methods were performed in custom-made glass apparatuses by employing high-vacuum techniques and standard procedures, based on the requirements of anionic polymerization, described in detail elsewhere.

For Ring-Opening Polymerization. Methanol (MeOH), tetrahydrofuran (THF), dichloromethane (DCM), ethyl acetate (EtOAc), and diethyl ether (Et2O) were purchased from VWR Chemicals (HiPerSolv CHROMANORM). 1,4-Dioxane (anhydrous, >99.9%), benzoic acid (99.5%), and toluene were dried by distillation over calcium hydride (CaH2, 95%) and polystryliumthyll. THF was purified by distillation over CaH2 and sodium/benzophenone. Phenylpropeno (PPA, 99.8%, Sigma-Aldrich) was distilled twice over CaH2 under vacuum. LLAs (Alfa-Aesar, 99%) and DLA (Jinan Daigang Biomaterial Co., Ltd, 299.5%) were recrystallized from EtOAc three times, cryo-evaporation from 1,4-dioxane, followed by drying under vacuum overnight. Sn(Oct)2 (95%, Sigma-Aldrich) was distilled twice over anhydrous MgSO4 and activated 4 Å molecular sieves followed by azotropic distillation with dry toluene. All monomers, solvents, and catalysts were stored under argon (Ar) in a glovebox (LABmaster®SP, MBraun, Germany).

Our group recently reported the synthesis and properties of non-covalent (supramolecular) diblock copolymers based on well-defined PS and PI functionalized with hydrogen bonding motifs. The driving force for the formation of the supramolecular copolymers is the donor–acceptor hydrogen bonding interaction at the ω-end of the PS and PI. The supramolecular block copolymers showed interesting morphologies, different from the corresponding covalent diblock copolymers in terms of the d-spacings and the microdomain size and shape.

In this work, we aim to synthesize well-defined PS–SC–PI through the stereocomplexation of PI-b-PLLA and PS-b-PDLA. The synthesis of the well-defined diblock copolymers was achieved through the combination of anionic polymerization with the ROP of LAs. α-Hydroxyl functionalized PI and PS were synthesized by the anionic polymerization high-vacuum technique and then used as the macroinitiators to promote the ROP of d/L-LA catalyzed by Sn(Oct)2. The molecular characteristics of the resulting PI-b-PLLA and PS-b-PDLA block copolymers were determined by 'H nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC). The stereocomplexation of PI-b-PLLA and PS-b-PDLA was performed by mixing PS-b-PDLA and PI-b-PLLA solutions (in dichloromethane) and precipitating it into methanol. DSC, X-ray diffraction (XRD), circular dichroism (CD), and Fourier-transform infrared (FT-IR) spectroscopies were used to prove the formation of PS–SC–PI. A preliminary study by atomic force microscopy (AFM) reveals the thin-film phase behavior and the supramolecular organization of the final PS–SC–PI non-covalent triblock terpolymer. Since, on the one hand, PLAs find different applications in biomedicine and, on the other hand, the heart of the material properties is situated at the molecular level, it will be very important to synthesize and study the properties of new non-covalent SC-based biodegradable materials with different structures (stars, combs, cyclics, etc.).
Instrumentation. NMR measurements were performed at room temperature using Bruker AVANCEIII spectrometers operating at 400 and 950 MHz. CDCl₃ was used as the solvent. ¹H NMR spectra were used to determine the number average molecular weight (Μₐ,NMR) of the polymer by calculating the integral ratio of the protons end group and the characteristics of protons on the main chain. GPC measurements were performed in an Agilent GPC instrument (Agilent Technologies) equipped with a PLgel 5 μm MIXED-C and PLgel 5 μm MIXED-D columns. THF was used as the eluent at a rate of 1 mL min⁻¹. The instrument was calibrated with PS standards. DSC measurements were performed with a Mettler Toledo DSC1/TC100 under nitrogen and calibrated with indium. The samples were heated from -80 °C to 200 °C, then cooled again, and finally heated again to 200 °C at a heating/cooling rate of 10 °C min⁻¹. This cycle was repeated two times, and the glass transition temperature (Tg), melting, and cooling temperatures (Tm and Tc) were recorded. XRD spectra were obtained using a Bruker D8 ADVANCE with Cu Kα radiation. The samples for XRD measurements were deposited on a glass substrate (from CHCl₃ solution) with an approximate size of 1.5 cm × 1 cm, pre-annealed at 170–180 °C for 10 min, and cooled down to room temperature with a cooling rate of 10 °C min⁻¹.

The PS-b-PDLA and PI-b-PLLA thin films were prepared from chloroform solution (10 mg mL⁻¹), while the SC thin film was prepared from toluene solution. The silicon (Si) substrates were treated with a mixture of 98% H₂SO₄ and 30% H₂O₂ (volume ratio 2:1). The polymer solutions were spin-coated on top of the Si substrates at 300 rpm for 15 s and 2500 rpm for 50 s.

The surface topography information for all the samples was measured by adjusting the strength of the tapping mode-AFM. A Bruker Dimension Icon AFM (scanning probe microscope) was used under air at room temperature. The measurements were performed using phosphorus-doped Si tips (TAP150A) of resonance frequency ranging between 120 and 162 Hz, with a force constant (k) of 5 N m⁻¹. Image analysis software (IA 3.5) was applied for the analysis of height images and the corresponding cross-sectional line profiles.

Synthetic Procedure. Synthesis of PS-OH. All synthetic procedures were performed using conventional high-vacuum techniques. The anionic polymerization was carried out in evacuated, n-BuLi washed custom-made glass reactors. Reagents were added via break-seals, and aliquots for characterization were taken at all steps. More details concerning the techniques and the apparatuses used are given in previous reports. As an example, the synthesis of PS-OH 5500 g mol⁻¹ is given below.

Styrene (5 g) was added to 100 mL of benzene, followed by the addition of sec-BuLi (1 mmol), and kept for 18 h at room temperature. After completion of polymerization, an aliquot was taken to verify the molecular characteristics of the synthesized PS. Subsequently, EO (~1 mL) was added to the reaction mixture and left for 12 h at room temperature, and the reaction was terminated by the addition of methanol (~0.5 mL) (Scheme 1). The polymerization solution was precipitated into an excess of methanol, and the polymer was dried in a vacuum oven for 24 h at 40 °C. The number-average molecular weight (Μₐ) and dispersity index (D) of PS-OH were calculated by GPC (Μₐ = 5500 g mol⁻¹ and D = 1.05) calibrated with PS standards. ¹H NMR PS-OH (400 MHz, CDCl₃, 25 °C): δ ppm 0.41–0.67 (8H; sec-Bu), 0.69–1.55 (2H; −CH₃–CH–Ph), 1.56–2.15 (1H; CH₂–CH–Ph(Ph)–CH₂), 3.06–3.33 (2H; −CH₂–OH), 6.28–7.25 (phenyl protons).

Synthesis of PS-b-PDLA. A dry polymerization flask equipped with a stirrer bar was charged with 440 mg of dry PS-OH 5500 g mol⁻¹ (0.08 mmol), 16.2 mg of Sn(Oct)₂ (0.04 mmol), 403 mg of D-LA (2.8 mmol), and 7 mL of dry toluene under an Ar atmosphere. The flask was sealed and placed in an oil bath at 80 °C. After 24 h, the conversion of D-LA reached 96.0%. The ROP was quenched with benzoic acid, and the solution was precipitated in cold MeOH (0 °C). PS-b-PDLA was isolated by centrifugation and dried in vacuo for 24 h at 40 °C. ¹H NMR PS-b-PDLA (400 MHz, CDCl₃, 25 °C): δ ppm 0.41–0.67 (8H; sec-Bu), 0.69–1.55 (2H; −CH₃–CH–Ph), 1.52–1.66 (d, 3H; −CH(CH₃)–COO), 1.56–2.15 (1H; CH₂–CH–Ph(Ph)–CH₂), 3.66–3.89 (2H; CH₂–CH–Ph(Ph)–COO), 4.32–4.41 (1H; −CH₂–CH(CH₃)–COO end-group), 5.05–5.31 (1H; −CH(CH₃)–COO), 6.28–7.25 (phenyl protons).

Synthesis of PI-OH. A similar procedure as above was followed for the synthesis of ω-OH functionalized polyisoprene samples. A typical example is as follows. Isoprene (9.86 g) was added to 120 mL of benzene, followed by the addition of sec-BuLi (1.812 mmol), and kept
overnight at 40 °C. The polymerization solution was precipitated into an excess of methanol, and the polymer was dried in a vacuum oven indicated by the 1H NMR analysis. 1H NMR PI-OH (950 MHz, CDCl3, δ ppm 4.90 (1H; 1,4-microstructure), 1.83–2.02 (2H; −CH2−), 3.41–3.61 (2H; −CH2−OH), 4.49–4.71 (2H; 3,3,4-microstructure), 4.90–5.08 (1H; 1,4-microstructure).

Synthesis of PI-b-PLLA. A dry polymerization flask equipped with a stirrer bar was charged with 480 mg of dry PI-OH 6000 g mol−1 (0.08 mmol), 162 mg of Sn(Oct)2 (0.04 mmol), 403 mg of L-LA (2.8 mmol), and 7 mL of dry toluene under an Ar atmosphere. The flask was sealed and placed in an oil bath at 80 °C. After 24 h, the conversion of LLA reached 96.0%, and then, the whole reaction mixture was quenched with benzoic acid and precipitated in cold methanol. PI-b-PLLA was isolated by centrifugation and dried in vacuo for 48 h.

RESULTS AND DISCUSSION
The anionic polymerizations of isoprene and styrene were carried out in benzene at room temperature using sec-BuLi as the initiator and benzene as the solvent would lead to the formation of PI having a high content of cis-1,4 microstructure, which will be discussed later in the NMR section.

Dry PI-OH and PS-OH were used as the macrorinitiators to initiate the ROP of d/L-LA using Sn(Oct)2, as a catalyst in toluene at 80 °C (Scheme 1). The reaction conditions and the results of the molecular characterization are presented in Table 1. Sn(Oct)2 was chosen as the catalyst for the ROP of LA at 80 °C or above because in this condition, LA undergoes a minimum racemization side reaction, resulting in PLAs with high isotactic content. Two PLLA homopolymers with molecular weights of 7000 and 3500 g mol−1 were also synthesized under the same conditions using phenyl propanol as the initiator to compare their physical properties with the corresponding PLAs in the block copolymers.

Table 1. Molecular Characteristics of Diblock Copolymers Prepared by ROP of d/L-LA with PS-OH/PI-OH Macrorinitiators

| entry | sample | time (h) | conv. (%) | Mw,LA,NMR (g mol−1) | Dn |
|-------|--------|---------|-----------|---------------------|-----|
| 1     | PS12-b-PLDLA5 | 24   | 100   | 9.0      | 1.08 |
| 2     | PS14-b-PLDLA5 | 24   | 98    | 5.5      | 1.04 |
| 3     | PS16-b-PLDLA5 | 24   | 100   | 11.1     | 1.08 |
| 4     | PS18-b-PLDLA5 | 24   | 98    | 10.1     | 1.04 |
| 5     | PS20-b-PLDLA5 | 24   | 100   | 11.0     | 1.08 |
| 6     | PS22-b-PLDLA5 | 24   | 98    | 10.2     | 1.04 |
| 7     | PS24-b-PLDLA5 | 24   | 99    | 10.3     | 1.04 |
| 8     | PS26-b-PLDLA5 | 24   | 99    | 10.4     | 1.04 |
| 9     | PS28-b-PLDLA5 | 24   | 99    | 10.5     | 1.04 |
| 10    | PS30-b-PLDLA5 | 24   | 99    | 10.6     | 1.04 |
| 11    | PS32-b-PLDLA5 | 24   | 99    | 10.7     | 1.04 |
| 12    | PS34-b-PLDLA5 | 24   | 99    | 10.8     | 1.04 |
| 13    | PS36-b-PLDLA5 | 24   | 99    | 10.9     | 1.04 |
| 14    | PS38-b-PLDLA5 | 24   | 99    | 11.0     | 1.04 |

The PI-OH and PS-OH macrorinitiators were prepared by the anionic polymerization high-vacuum technique. The ROP of d/L-LA was performed using Sn(Oct)2, as the catalyst in toluene at 80 °C.

The anionic polymerizations of isoprene and styrene were carried out in benzene at room temperature using sec-butylithium as the initiator (Scheme 1). After the complete conversion of the monomers, the living PS and PI chains were end-capped with excess EO at room temperature. Only one EO monomeric unit reacts with the living carbanion, resulting in PS and PI with a high degree of functionalization (>99%).

PS-OH and PI-OH macrorinitiators with three different targeted molecular weights: 5, 10, and 20 kg mol−1 were prepared. Their molecular characteristics are presented in Table S1 of the Supporting Information. All polymers exhibit narrow polydispersity (<1.07), indicating that the polymers are well-defined. It was expected that anionic polymerization of isoprene using sec-BuLi as the initiator and benzene as the solvent would lead to the formation of PI having a high content of cis-1,4 microstructure, which will be discussed later in the NMR section.
methine proton from the main chain PLA (e) is used to
determine the \( M_n \) of the PLA blocks.

It is worth noting that the methylene protons of PI (b) and
the methine proton of PLLA (e) are observed as overlapped
peaks on the 400 MHz \(^1\)H NMR spectrometer. Hillmyer et al.
reported that \( M_n \) of PI-b-PLLA and the mass fraction of PLLA
in the diblock were calculated indirectly by combining \(^1\)H and
\(^{13}\)C NMR spectroscopy and comparing the result with
elemental analysis. However, in our work, we used a 950
MHz \(^1\)H spectrometer to resolve peaks (b) and (e) into a well-
separated peak (Figure 1). Thus, the \( M_n \) of PLLA can be
determined directly by quantitative end-group analysis from
the integral ratio of peak (g) with peak (e) of the PLA main
chain.

The molecular weight distributions (\( D \)) of the PS-OH and
PI-OH homopolymers as well as the PS-b-PDLA and PI-b-
PLLA diblock copolymers, were determined by GPC with
THF as the eluent. Figures 2 and S1 show the narrow
molecular weight distribution of the homo- and diblock
copolymers (\( D\) is usually <1.10), verifying the absolute control
of the anionic polymerization and ROP systems used in this
work. The GPC traces of the diblock copolymers in Figure 2
appeared in the lower elution time, indicate the increase of
molecular weight compared to the macroinitiators and thus

Figure 1. Representative \(^1\)H NMR spectra of homopolymers precursors (PS5.5-OH and PI6-OH), block copolymers (PS5.5-b-PDLA5 and PI6-b-
PLLA5), and SC PS5.5-b-SC1-b-PI6. The spectra were recorded with a 400 MHz spectrometer except for PI6-b-PLLA5 and PS5.5-b-SC1-b-PI6 [the
spectra were recorded with a 950 MHz spectrometer (CDCl3, 25 °C)].

Figure 2. GPC traces of the precursors (PS and PI) and the corresponding diblock copolymers with PLAs (THF, 35 °C, PS standards).
support the formation of a diblock copolymer. All GPC traces of the diblock copolymers are monomodal, and no indication of residue from their precursors was detected. The small shoulder between 18 and 20 min (outside of the calibration range) on the GPC trace of PI12-b-PLLA7 is attributed to 3,5-di-tert-4-butylhydroxytoluene, the radical inhibitor used to stabilize THF. The purity of the diblock copolymers is also corroborated by 2D-diffusion-ordered spectroscopy (DOSY) spectra of PS11-b-PDLA7 and PI12-b-PLLA7 (as the representative samples, Figure S2) which show that only one macromolecule exists in each sample.

The formation of diblock copolymers and the corresponding SC was further investigated by FT-IR spectroscopy. Figure 3 shows the FT-IR spectra of the homopolymers (PS11-OH and PI12-OH), block copolymers (PS11-b-PDLA7 and PI12-b-PLLA7), and PS11–SC7–PI12 as the representative samples. We focused on the vibrational stretch of the carbonyl group of polylactide (ν(C=O) band) of the PS–PDLA and PI–PLLA diblock copolymers (1755 cm⁻¹). Upon the formation of SC, the ν(C=O) band shifts to a lower wavenumber (from 1755 to 1749 cm⁻¹) (Figure 3). This shift (∼5 cm⁻¹) is in good agreement with the case of SC7 samples derived from PD/L-LA7 homopolymers (from 1755 to 1750 cm⁻¹, Figure S3) and was also observed in the literature.59 Such a shift is due to the transition of the PLA chains from a disordered state to an ordered one via the SC formation by CH₃···O and CH₃···H intermolecular H-bond interaction.15,25 In addition, the SC formation is also supported by the appearance of the characteristic absorbance peak at 908 cm⁻¹ (red arrow).50–62

CD experiments were carried out to evaluate the specific rotation of PD/L-LA of the homo and block copolymers and the change after stereocomplexation. Figure 4 shows the CD and UV absorption spectra of both PS11-b-PDLA7 and PI12-b-PLLA7 in dilute ACN solution (0.1 mg mL⁻¹). A positive Cotton effect of PI12-b-PLLA7 (left-handed helicoidal conformation) and a negative Cotton effect of PS11-b-PDLA7 (right-handed helicoidal confirmation) were observed at ∼215 nm, which is attributed to the characteristic absorption band of an n → π* transition of the carboxyl group. In contrast, the PS11–SC7–PI12 solution does not exhibit the Cotton effect (flat line, CD silence), indicating that a SC has been formed. Similar characteristics are also observed on the PD/L-LA7 and SC7 solution (Figure S4), indicating that the presence of PI and PS blocks does not hinder the formation of helicoidal conformation in diblock copolymers.

DSC was used to analyze the thermal properties of PS-OH and PI-OH macroinitiators, PS-b-PDLA and PI-b-PLLA diblock copolymers, as well as the SCs. The Tₘ values were determined by finding the midpoint between the beginning and the end of transition temperatures. Figure S5 shows the thermograms of PS-OH and PI-OH macroinitiators, and the Tₘ values are summarized in Table S1. The Tₘ of PS-OH (80 °C < TₘPS-OH < 88 °C) and PI-OH (−70 °C < TₘPI-OH < −66 °C) increase with the increase of the molecular weight. Furthermore, all Tₘ values of PS-OH and PI-OH obtained in this work are in good agreement with the Tₘ values from the previous reports, indicating the well-controlled anionic polymerization procedure.63,64

We also performed a preliminary analysis of the thermal properties of the diblock copolymers. DSC traces of PI-b-PLLA block copolymers (Figure 5) show clear Tₘs of PI (−63.5 °C < TₘPI < −59 °C). Since the Tₘ of PI is much lower than the Tₘ of PLA, the mobility of the PI block is not significantly affected by the PLA crystal, although the chain is covalently linked to the PLA block. In contrast, for several PS-b-PDLA samples, the Tₘs of PS are not observed probably because of the high melting enthalpy of the PLA or covered by
the $T_{cc}$ of PDLA (for PS18-b-PDLA10 and PS5.5-b-PDLA3.6 samples).\textsuperscript{40,65}

For both homo- and diblock copolymers, the $T_m$s of PLAs are affected significantly by the molecular weight of the PLAs (Tables 2, S2, and Figure S6); the higher the molecular weights, the higher the $T_m$s of PLAs of the polymers. In addition to the block copolymers, the $T_m$ of PLAs is also influenced by the molecular weight of the amorphous block. For most diblock copolymers (PLA3.5 and PLA7), the $T_m$s of the PLA block are lower than the $T_m$s of PLA homopolymers.

Figure 5. Endothermic DSC thermograms of diblock copolymers and the corresponding SC (the heating rate is 10 °C min$^{-1}$, under N$_2$).
having a similar molecular weight. The higher the molecular weight of the amorphous block, the lower the \( T_m \) of the PLAs. This indicates that the crystalline and amorphous blocks are miscible in the melt, causing a dilution effect (the amorphous block behaves as the macromolecular solvent surrounding the PLA crystals in the melt) to the PLA crystals and therefore decrease the \( T_m \) of PLA.\(^{40,66}\)

Double melting peaks are observed on several thermograms of PS-b-PDLA. The appearance of an endothermic double peak (for the relatively low-molecular-weight PLA copolymers) is attributed to a partial melting and recrystallization process (for the relatively low-molecular-weight PLA copolymers) is attributed to a partial melting and recrystallization process during the measurement, which is a characteristic behavior of polyesters.\(^{40}\)

Upon the formation of SCs, the \( T_m \) of the PLA increases by approximately 50–60 °C higher than the \( T_m \) of the PLA in the corresponding diblock copolymers, while for the SC derived from homopolymers, the increment of the \( T_m \) is approximately 60–70 °C. Moreover, the \( \Delta H_m \) of the PLA in PS–SC–PI samples (206 J g\(^{-1}\) < \( \Delta H_m \)PS–SC–PI < 219 J g\(^{-1}\)) also increases, being significantly higher than the \( \Delta H_m \) of the PLA in PS-b-PDLA (5 J g\(^{-1}\) < \( \Delta H_m \)PS-b-PDLA < 26 J g\(^{-1}\)) and PI-b-PPLA (5 J g\(^{-1}\) < \( \Delta H_m \)PI-b-PPLA < 32 J g\(^{-1}\)). These results confirm the formation of a more rigid and denser crystal packing with a higher thermal stability. The improvement in the thermal stability is also reflected in the increase of \( T_g \)PP and \( T_g \)PB which is 2–10 °C higher than their \( T_g \)s in block copolymers. Similarly, to the case of the diblock copolymers, the \( T_m \) and \( \Delta H_m \) of SCs tend to increase with the increase of the molecular weight of PLAs and decrease with the increase of the molecular weight of the amorphous blocks (e.g., entries 18 and 12 or entries 15 and 9).

XRD analysis was performed to confirm the formation of the SC. As shown in Figure 6, the block copolymers having PLA molecular weights of \( \sim 5 \), 7, and 10 kg mol\(^{-1}\) exhibit the characteristic diffractions at \( 2 \theta \) of about 14.5, 16.8, 19.1, and 22.5°, which is in good agreement with the peaks of PLA homopolymers (Figure S7). These diffraction patterns correspond to the orthorhombic crystal lattice of the PLA \( \alpha \)-form. The \( \alpha \)-form is the most common polymorph for PLAs obtained from a melt or a dilute solution.\(^{67}\) Both homopolymers (Figure S7) and copolymers exhibit similar reflection patterns. Obviously, there are no changes in the unit cell of the PLA crystal in the block copolymers even though PS/PI amorphous blocks coexist in the system.

The PS–SC–PI samples exhibit the diffraction patterns of a triclinic crystal with 2\( \theta \) peaks of around 11.8, 20.5, and 23.9° and agreed well with the SC peaks obtained from homopolymers (Figure S7). SCs derived from PS\(_{3.6}\)-b-PDLA, PI\(_{22}\)-b-PPLA, and PI\(_{12}\)-b-PDLA did not show clear peaks on XRD, probably because their crystalline domains are trapped inside the amorphous matrix (the majority component).

The total degree of crystallinity (\( X_c \)) of crystalline polymeric materials can be calculated from their XRD diffractograms. \( X_c \) is defined as the ratio of the area of all crystalline peaks to the total area under the XRD peaks (crystalline + amorphous). Based on DSC and XRD results, both PS and PI segments are amorphous (Figure S8). Therefore, the \( X_c \) of the diblock copolymers and their SCs obtained from XRD can be attributed to the \( X_c \) of their PLA segments.

As can be seen in Figure 6, the \( X_c \)s of PS-b-PDLAs (5% < \( X_c \) < 25%), PI-b-PPLAs (4% < \( X_c \) < 31%), and SCs (7% < \( X_c \) < 46%) increase with the increase of the molecular weight of PLAs and decrease with the increase of the molecular weight of the amorphous blocks. The trend is similar to the trend of \( \Delta H_m \) of the PLA segment obtained by DSC: PS\(_{3.6}\)-SC\(_{3.6}\)-PI\(_{10}\), PS\(_{5.5}\)-SC\(_{5.5}\)-PI\(_{10}\), PS\(_{11}\)-SC\(_{11}\)-PI\(_{10}\), PS\(_{18}\)-SC\(_{18}\)-PI\(_{12}\), and their corresponding precursor diblock copolymers show sharp XRD peaks. This clearly indicates that the fraction of crystalline domains increases with the increase of the molecular weight of PLAs. In contrast, PS\(_{3.6}\)-SC\(_{3.6}\)-PI\(_{10}\), PS\(_{11}\)-SC\(_{11}\)-PI\(_{12}\), PS\(_{18}\)-

| entry | sample | \( T_g^{pp} \) (°C) | \( T_g^{pp} \) (°C) | \( -\Delta H_m^{b} \) (J g\(^{-1}\)) | \( X_c^{c} \)% |
|-------|-------|----------------|----------------|----------------|---------|
| 1 | PS\(_{15}\)-b-PDLA\(_{10}\) | 48.9 | covered by \( T_g \) | 155.1 | 25.5 | 28.4 |
| 2 | PI\(_{12}\)-b-PLLA\(_{10}\) | 48.8 | −60.1 | 156.4 | 31.5 | 30.2 |
| 3 | PS\(_{15}\)-SC\(_{15}\)-PI\(_{12}\) | 102.6 | −60.0 | 219.9 | 46.3 | 45.1 |
| 4 | PS\(_{15}\)-b-PDLA\(_{16}\) | 93.9 | −60.5 | | | |
| 5 | PI\(_{12}\)-b-PLLA\(_{16}\) | | −97.5 | | | |
| 6 | PS\(_{15}\)-SC\(_{15}\)-PI\(_{12}\) | 90.2 | −60.1 | 148.4 | 14.7 | 15.1 |
| 7 | PI\(_{12}\)-b-PLLA\(_{12}\) | | −63.5 | 154.0 | 17.9 | 18.4 |
| 8 | PS\(_{15}\)-SC\(_{15}\)-PI\(_{12}\) | 98.5 | −60.1 | 203.9 | 31.6 | 20.7 |
| 9 | PI\(_{12}\)-b-PLLA\(_{12}\) | | −61.5 | 128.0 | 5.8 | |
| 10 | PS\(_{15}\)-b-PDLA\(_{8}\) | 56.1 | 79.3 | 129.2 | 9.7 | |
| 11 | PI\(_{12}\)-b-PLLA\(_{8}\) | 57.5 | −60.6 | 202.1 | 14.5 | 7.2 |
| 12 | PS\(_{15}\)-SC\(_{15}\)-PI\(_{12}\) | 91.4 | −60.6 | 154.7 | 21.6 | 24.1 |
| 13 | PS\(_{15}\)-b-PDLA\(_{8}\) | 48 | −61.7 | 152.3 | 468 | 30.6 |
| 14 | PI\(_{12}\)-b-PLLA\(_{8}\) | | −60.9 | 215.3 | 46.7 | 45.5 |
| 15 | PS\(_{15}\)-SC\(_{15}\)-PI\(_{4}\) | 70.7 | −60.9 | 141.3 | 17.9 | 20.7 |
| 16 | PS\(_{15}\)-b-PDLA\(_{4}\) | 65 | −62.0 | 143.4 | 23.6 | 21.1 |
| 17 | PI\(_{12}\)-b-PLLA\(_{4}\) | | −61.8 | 206.0 | 25.9 | 33.2 |
| 18 | PS\(_{15}\)-SC\(_{15}\)-PI\(_{4}\) | 65.0 | −62.0 | 143.3 | 12.1 | 4.9 |
| 19 | PS\(_{15}\)-b-PDLA\(_{4}\) | | −61.3 | 149.4 | 10.1 | 5.3 |
| 20 | PI\(_{12}\)-b-PLLA\(_{4}\) | | −61.3 | 143.3 | 10.1 | 5.3 |
| 21 | PS\(_{15}\)-SC\(_{15}\)-PI\(_{6}\) | 88 | −62.6 | 206.9 | 14.7 | 23.3 |

\(^{a}\)Measured by DSC under a \( N_2 \) atmosphere with heating rates of 10 °C min\(^{-1}\). \(^{b}\)The melting enthalpy of PLA is normalized by its mass fraction.

\(^{c}\)Determined by XRD with formula \( X_c = \text{area}_{\text{crystalline}} / \text{area}_{\text{total}} \) on XRD spectra.
SC_{3.6}−PI_{22}, and their corresponding precursors exhibit weak/no peak on XRD due to the lower PLA molecular weight (higher amorphous fractions). The overall \( X_{c0} \) of PLA copolymers (Table 2) are lower than those in homopolymers (Table S2). As Michell et al. described, “generally, the copolymers require larger supercooling for crystallization than the homopolymers.” Therefore, the presence of PS and PI (amorphous) blocks delay the crystallization process of PLA blocks in this type of melt miscible diblock copolymers.

Morphological Study of the SCs and Their Respective Precursors. All the films shown in Figure 7 were annealed at 180 °C for 5 min under vacuum before cooling to room temperature. The purpose of these preliminary AFM studies was to observe the adopted morphology under a short annealing time, similar to the sample preparation conditions prior to DSC and XRD measurements. In the case of the PS\(_{11}\)-b-PDLA\(_{7}\) precursor (Figure 7a), the image depicts islands due to the dewetting of the film to the substrate, indicating a disordered structure. Here, bright islands correspond to the PDLa\(_{7}\) block stands as islands on the free surface due to the commensurability effect between the initial film thickness and the bulk domain space, as mentioned in the previous study. Although PS and PDLA blocks have relatively similar surface energies and are expected to form the perpendicularly oriented cylindrical morphology, the island and hole formation is attributed to the fact that the polymer/substrate interface dominates the structure evolution. For the respective thin film of PI\(_{22}\)-b-PLLA\(_{10}\) (Figure 7b), the image is consistent with a weakly microphase-separated film with a combination of lines and dots as cylindrical microdomains oriented perpendicular to the surface. Similar to the above precursor, the bright segment
corresponds to the higher modulus block of crystalline PLLA, compared to that of the dark region of elastomeric PI. The same film deposition and thermal treatment were applied to PS−SC−PI. The surface area that is covered by bright spots and corresponds to the PLA domain is relatively smaller than that of the precursor’s images due to the increased amorphous region of PS and PI. Here, stereocomplexed PLA chains are clearly deployed as a bright upper layer of PLA crystals on top of the sublayer, which mainly consists of the glassy PS and soft rubbery PI confinement. Here, PLA crystallization dominates the formation of a parallel-oriented cylindrical morphology. The cross-sectional profile indicates the relative height distance between the relief crystal domain and the amorphous underlayer domain. However, further study is needed to reveal the phase behavior of this complex non-covalent PS−SC−PI triblock terpolymer system, and the results will be presented in a forthcoming paper.

### CONCLUSIONS

Well-defined PS-b-PDLA and PI-b-PLLA diblock copolymers were synthesized by combining an anionic polymerization high-vacuum technique with ROP; the molecular structure was confirmed by 1H NMR and GPC analyses. The diblock copolymers were used to prepare non-covalent triblock terpolymers, PS−SC−PIs, via the stereocomplexation of PDLA and PLLA having an equivalent PLA molecular weight. FTIR, CD, UV, DSC, and XRD spectroscopies confirmed the formation of linear non-covalent triblock terpolymers. Similar to PLA homopolymers, the thermal stability (reflected in T_g, T_m, ΔH_m, and X_c) of diblock and triblock terpolymers increases with the increase of the molecular weight of the PLA segment in the copolymers. On the contrary, the thermal stability decreases with the increase of the molecular weight of PS and PI amorphous segments.

This study opens many routes for the synthesis of various well-defined complex macromolecular architectures of PLA-based SCs.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.1c02294.

Molecular characteristics of homopolymers; GPC, FTIR, CD, UV, DSC, and XRD of homopolymers; and 2D-DOSY NMR spectra of diblock copolymers (PDF)

### AUTHOR INFORMATION

**Corresponding Author**

Nikos Hadjichristidis − Physical Sciences and Engineering Division, KAUST Catalysis Center, Polymer Synthesis Laboratory, King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia; orcid.org/0000-0003-1442-1714; Phone: +966-(0)12-8080789; Email: nikolaos.hadjichristidis@kaust.edu.sa

**Authors**

Viko Ladelta − Physical Sciences and Engineering Division, KAUST Catalysis Center, Polymer Synthesis Laboratory, King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia; orcid.org/0000-0003-0596-7571

Konstantinos Ntetsikas − Physical Sciences and Engineering Division, KAUST Catalysis Center, Polymer Synthesis Laboratory, King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia; orcid.org/0000-0002-9236-931X

George Zapsas − Physical Sciences and Engineering Division, KAUST Catalysis Center, Polymer Synthesis Laboratory, King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia; orcid.org/0000-0003-3802-3550

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.macromol.1c02294

**Notes**

The authors declare no competing financial interest.
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