Synthesis and Characterization of Model Polyisoprene−Polylactide Diblock Copolymers

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ABSTRACT: Model polyisoprene−polylactide (PI−PLA) diblock copolymers were synthesized by a combination of living anionic polymerization and controlled coordination-insertion polymerization. Living anionic polymerization of isoprene followed by end-capping with ethylene oxide yielded hydroxyl-terminated polyisoprenes (PI−OH) with narrow molecular weight distributions. In a second step, an aluminum alkoxide macroinitiator was formed from the equimolar reaction of triethylaluminum with the PI−OH prepolymer and subsequently utilized for the ring-opening polymerization of lactide to produce the desired PI−PLA diblock copolymer. The final molecular weight of each block was controlled through manipulation of the monomer-to-initiator ratio in both polymerizations. Well-defined blocks were obtained as evidenced by the narrow molecular weight distributions and the absence of homopolymer as characterized by GPC analysis. Molecular characterization of the block copolymers by spectroscopy (^{1}H NMR, ^{13}C NMR, and IR) and elemental analysis confirmed the relative compositions of the component blocks. We characterized the morphology of a representative PI−PLA diblock copolymer using DSC and SAXS. Both analyses indicated a microphase-separated structure characteristic of an ordered diblock copolymer. These model diblock copolymers are ideal materials for fundamental phase behavior and mechanical property studies.

Introduction

Polylactide (PLA) is a polyester produced from the ring-opening polymerization of lactide and has received much attention over the past few decades largely due to its biodegradable and biocompatible properties. Both PLA homo- and copolymers have been extensively studied for their potential uses in the biomedical field[1] and have also been investigated as potential engineering materials.[2,3] Depending upon tacticity, high-molecular-weight PLA can range from completely amorphous ($T_g \approx 60$ °C) to semicrystalline ($T_m \approx 175$ °C).[4] However, under impact and tensile testing these polymers are considered brittle.[5,6] This undesirable feature has thwarted the use of PLA as a commercial thermoplastic.

A well-known method employed to toughen brittle polymers is to incorporate a discrete phase of rubber particles into a rigid polymer matrix.[7] High impact polystyrene (HIPS) is an example of a toughened polymeric material that is prepared using this technique. There has been extensive research regarding the rubber modification of PLA via copolymerization and blending.[8] For example, Pennings and co-workers showed that tough PLA composites could be prepared through either blending or formation of block copolymers with polytrimethylene carbonate or polycaprolactone.[9] Although these types of hybrid materials have been shown to be tougher than PLA homopolymers, little attention has focused on the morphological control of these multicomponent systems. A well-established factor responsible for final mechanical properties in rubber toughened plastics, aside from the intrinsic properties of the composite materials themselves, is the morphology of the material.[10] This is not only the case for simple two-component polymer blends,[11] but the effect of morphology on the mechanical properties of various block copolymer systems has also been demonstrated.[12,13] Control of morphology in multicomponent polymer blends is critical for the formation of tough materials with superior properties. A simple two-component system we are interested in for the formation of tough PLA composites is blends of PLA with rubber−PLA diblock copolymers (A/A−B). Extensions of this system to three-component A/B/A−B blends will also be important for the formation of tough PLA materials.

As neat materials, most block copolymers phase separate into ordered nanoscopic domains due to the immiscibility of the component blocks and the covalent linkage between segments.[14−16] Theoretically predicted phase diagrams of these systems can be constructed and compare favorably with experimental results. Through control of the segment volume fraction, the morphology can easily be tailored in these unicomponent hybrid materials. The morphology of block copolymer/homopolymer blends can also be controlled through judicious choice of the component materials.[17] In addition to disordered micelles of the immiscible block in the matrix material, all of the classical and complex morphologies observed in neat block copolymers can potentially be prepared in block copolymer/homopolymer blends.[18] In model A/A−B/B ternary blends, complex morphologies such as macrophase coexisting with microphase and microphase alone have been observed, and preliminary theoretical phase diagrams have been calculated in the symmetric diblock case with general experimental agreement.[19]

The synthesis of well-defined or model block copolymers is critical for the preparation of model composite materials with controlled morphologies. Model block copolymers are defined as materials with controlled segment lengths, narrow molecular weight distributions, and no homopolymer contamination. The ability to synthesize model block copolymers will ultimately allow control over the morphology of both the neat materials and the blends.

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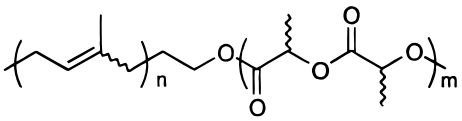
We have set out to toughen PLA through the controlled incorporation of a hydrocarbon rubber. Although there have been varied examples of rubber-modified PLA copolymers in the literature,[8] there has been relatively little work on the preparation of PLA diblock copolymers that contain hydrocarbon segments typically used for the toughening of brittle materials (e.g., polybutadiene, polyisoprene, polyisobutylene, poly(dimethylsiloxane)).[20−22] We have focused our initial research effort on a set of model polyisoprene (PI)−PLA diblock copolymers. The incorporation of PI as the rubber component will undoubtedly increase the flexibility/toughness of the brittle PLA. Precise control over the molecular parameters of the block copolymers will be necessary for the related morphological control.

The most common method for the synthesis of model diblock copolymers is by sequential monomer addition in a living polymerization, with anionic polymerization being the ubiquitous technique.[23] Although PI and PLA can be synthesized by anionic polymerization, lactide polymerization is not living due to the occurrence of side reactions such as deprotonation of the lactide monomer and transesterification.[24,25] The preferred route of polymerization is through a metal-catalyzed coordination-insertion mechanism with tin(II) 2-ethylhexanoate being the most commonly utilized intiator/catalyst.[1a] Many of these metal-catalyzed systems unfortunately are also plagued by side reactions that ultimately lead to polydisperse samples.[26] However, simple aluminum alkoxides have proven to be effective initiators for the controlled ring-opening polymerization of lactide.[27] For example, Teyssie and co-workers have synthesized polycaprolactone (PCL)−PLA diblock copolymers by sequential polymerization of caprolactone followed by lactide using aluminum isopropoxide.[28]

We have prepared and characterized a set of model diblock copolymers containing poly-4,1-isoprene and polylactide (D,L and L) using a combination of living anionic polymerization (PI) and aluminum alkoxide initiated coordination-insertion polymerization (PLA). The combination of two mechanistically distinct polymerizations for the formation of novel block copolymers has been demonstrated.[29,30] We refer to this type of diblock copolymer synthesis as a change of mechanism polymerization (CHOMP). CHOMP allows for "mechanistically incompatible" blocks to be combined into one macromolecule, leading to composite materials that cannot be prepared using the standard sequential addition of monomers technique. The model PLA diblock copolymers we have prepared using CHOMP will be ideal for fundamental structure/property relationships and phase behavior studies.



PI-PLA

Experimental Section

General Methods. All polymerization solutions were prepared and sealed in a glovebox under a dry argon atmosphere. Initial reactions were setup in pre-silanized round-bottom flasks fitted with a rubber septum and a nitrogen balloon. To avoid solvent loss, later reactions were prepared in presilanized high-pressure vessels equipped with an internal thread and a Teflon bushing fitted with a Viton O-ring (Chemglass). Infrared spectra were recorded using a Perkin-Elmer 1600. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian 300 VXR. NMR samples of the polymer and initiator were dissolved in deuterated chloroform (Cambridge) and deuterated toluene (Aldrich), respectively, at concentrations of about 1.0 wt %. Gel permeation chromatography analyses were performed on a Hewlett-Packard 1100 series liquid chromatograph equipped with a Hewlett-Packard 1047A refractive index detector and three Jordi polydivinylbenzene columns of 10^4,10^3, and 500 Å pore sizes. THF was used as the mobile phase (35 °C and 1 mL/min). Column calibration was performed with polystyrene standards (Polymer laboratories). Galbraith Laboratories Inc., Knoxville, TN, performed all elemental analyses.

Materials. Commercial solvents and reagents were used as received with the following exceptions: Isoprene (Aldrich) was twice distilled from *n*-butyllithium (Aldrich), ethylene oxide (Aldrich) was purified by sequential distillations from calcium hydride and dibutylmagnesium (Aldrich), respectively, and D,L-lactide (Aldrich) was recrystallized from ethyl acetate and dried at room temperature for approximately 16 h under reduced pressure (stored under a dry argon atmosphere and purity confirmed by ^{1}H NMR spectroscopy). The concentration of *sec*-butyllithium (Aldrich) was determined by the Gillman double titration method.[31] Degassed cyclohexane for anionic polymerizations was rigorously purified by passage through an activated alumina column for the removal of protic impurities and through a supported copper catalyst to remove trace oxygen using a home-built solvent purification line.[32] The solvent system was interfaced with a Schlenk manifold connection to allow for anhydrous/anaerobic collection. Toluene was refluxed over calcium hydride and collected in a previously flame-dried air-free flask fitted with a Teflon Chemcap valve (Chemglass).

Synthesis of PI−OH. A general polymerization procedure for the synthesis of hydroxyl-terminated polyisoprene is described below. A detailed description of the anionic polymerization apparatus and procedure has been previously reported.[33,34] Polymerization was performed in a 1 L glass reactor equipped with five internal ACE-THREDS threaded glass connectors and a Teflon-coated magnetic stir bar. Using Ace Glass bushings (nylon or Teflon) and FETFE O-rings, the reactor was fitted with three glass plugs, a glass thermowell, and a glass Y-connector. The Y-connector was equipped with three ports: two with Teflon-capped valves interfaced to a vacuum/argon manifold and a manometer. The third port was fitted with a Teflon-coated septum. The reactor was evacuated to ≈10^{-3} Torr and heated overnight to ≈ 250 °C. After cooling the glass plugs were replaced (under a positive pressure of argon) with two pretared burets of purified isoprene (56.0 g, 0.824 mol) and purified ethylene oxide (22.0 g, 0.50 mol) and an air-free flask containing dry cyclohexane (≈0.5 L). The cyclohexane flask and isoprene buret were connected directly to the reactor using the Ace Glass bushings and O-rings. A flexible metal glass end tube and a Cajon Ultratorr fitting were used to connect the ethylene oxide and allowed for the immersion in a dry ice/2-propanol bath. The reactor was evacuated and backfilled with argon five times after which the pressure was set to two PSI, and the reactor was isolated from the manifold. The pressure was monitored to ensure the absence of leaks. The cyclohexane (≈0.5 L) was added to the reactor, followed by the addition of *sec*-butyllithium (9.96 mL, 1.124 M in cyclohexane, 11.2 mmol) through the Teflon-coated septum using a syringe. The reaction temperature and pressure increased slightly upon *sec*-butyllithium addition. The isoprene was added at room temperature to the reaction flask at a steady rate, after which the reactor was placed into a water bath set at 40 °C. Upon isoprene addition the reaction pressure increased slowly up to 5.2 psi, and the temperature increased to 48 °C. The reaction solution cooled to 40 °C and was allowed to stir for 4.5 h. Next, the water bath was removed, and ethylene oxide was added at a steady rate. Upon addition, the reaction solution warmed slightly and the pressure increased significantly.[35] The reaction was allowed to stir overnight at room temperature. The reaction vessel was then

Table 1. Polymerization of D,L-Lactide (1 M) in Toluene at 70 °C and [PI−OH]/[$AlEt_3$] ≈ 1

entry	$10^{-3}\bar{M}_n$ PI−OH (NMR)	[M]/[I]	t (h)	lactide conv (%)	$10^{-3}\bar{M}_n$ (PLA) conv	$10^{-3}\bar{M}_n$ (PLA) NMR	$10^{-3}\bar{M}_n$ (total) NMR	PDI (GPC)	f_{PLA}[a]
1[b]	5.2	34	93	40	2.0	2.0	7.2	1.05	0.22
2	5.2	34	94	94	4.4	4.8	10.0	1.06	0.40
3	5.2	49	96	90	6.4	6.1	11.3	1.10	0.46
4	5.2	69	96	87	8.6	8.3	13.5	1.09	0.53
5	5.2	200	141	91	26.2	24.5	29.7	1.11	0.77
6	5.2	269	141	74	28.7	22.9	27.9	1.08	0.74
7	5.2	500	96	72	51.8	48.6	53.8	1.12	0.87
8	5.2	535	141			9.3	14.5	1.23	0.56
9	0.96	7	96	89	0.89	0.73	1.7	1.20	0.35
10	0.96	10	100	91	1.31	1.34	2.3	1.20	0.50
11	0.96	20	101	86	2.48	2.64	3.6	1.26	0.66
12	0.96	200	104			17.2	18.2	1.09	0.93
13[c]	5.2	110	100	58	9.2	9.8	15.0	1.09	0.58
14[c]	5.2	34	94	78	3.8	4.7	9.9	1.06	0.39

[a] Volume fractions were calculated using literature values for the densities of high molecular weight PI and PLA at 140 °C (see refs 48, 49, and 50). [b] [PI−OH]/[$AlEt_3$] = 0.5. [c] L-Lactide was used in this polymerization.

opened to air and quenched with acidic methanol/2-propanol (3 mL of concentrated HCl in 50 mL of methanol/50 mL of 2-propanol mixture) through one of the reactor ports. The mixture was then precipitated in a 50/50 mixture (by volume) of stirring methanol/2-propanol (3 L). The solution immediately became cloudy and was left to settle for 2 h. The top layer was then decanted off, and the cloudy viscous solution was concentrated on a rotary evaporator and subsequently dried under vacuum at 40 °C overnight. The yield was 54.54 g (95.5%), and the $\bar{M}_n$ = 5200 g/mol (by NMR spectroscopy end group analysis) was in close agreement with the targeted molecular weight ($\bar{M}_n$ = 5100 g/mol) predicted from the reaction stoichiometry. GPC analysis (in chloroform vs PS standards) gave $\bar{M}_n$ = 6300 g/mol and $\bar{M}_w/\bar{M}_n$ = 1.04.

Synthesis of PI−PLA. Lactide polymerizations were performed in toluene (1 M with respect to lactide) with the macroinitiator formed from the equimolar reaction product of $AlEt_3$ and the PI−OH prepolymer. High-molecular-weight diblock copolymers were precipitated in cold methanol, and toluene solutions of the low-molecular-weight diblock copolymers were washed with water. A sample procedure for entry 11 from Table 1 follows. A 48 mL Chemglass high-pressure vessel equipped with an internal thread was treated with a 90/10 solution (by volume) of methylene chloride/dichlorodimethylsilane and allowed to dry at ≈70 °C overnight. In a glovebox, a Teflon-coated stir bar, previously prepared 960 g/mol PI−OH (0.49 g, 0.51 mmol), and toluene (10.5 mL) were added to the pre-silanized vessel. A 1.9 M solution of $AlEt_3$ in toluene (270 μL, 0.51 mmol) was slowly added to the flask using a syringe, and the mixture was allowed to stir for 4 h at room temperature to allow for the evolution of ethane. D,L-Lactide (1.5 g, 10.41 mmol) was then added to the flask which was sealed with a Teflon bushing fitted with a Viton O-ring and removed from the glovebox. The reaction flask was then immersed into a 70 °C oil bath. After 101 h the reaction was quenched with 2 N HCl (5-fold molar excess with respect to $AlEt_3$), and the solution was washed three times with water. The polymer solution was then concentrated on a rotary evaporator and subsequently dried under vacuum at 80 °C for about 24 h. The dried block copolymer, 1.78 g (86.3% conversion of lactide), was characterized by GPC ($\bar{M}_w/\bar{M}_n$ = 1.26) and ^{1}H NMR spectroscopy ($\bar{M}_n$ = 3600 g/mol).

PI−PLA Characterization. The following sets of ^{1}H NMR and ^{13}C NMR spectroscopy resonances are representative of the polymers described in this paper. All resonances are reported in ppm (δ) downfield from tetramethylsilane (0.0 ppm). All of the resonances observed were either broad (b) or contained multiple overlapping peaks (m). PI−OH: 5.1 (b, $-CH_2-C\mathbf{H}=C(CH_3)-CH_2-$), 4.75 (m, $-CH_2-C(H)-C(CH_3)=C\mathbf{H}_2$), 3.6 (m, $C\mathbf{H}_2-OH$), 2.0 (b, $-C\mathbf{H}_2-CH=C(CH_3)-C\mathbf{H}_2-$ and $-CH_2-C(\mathbf{H})-C(CH_3)=CH_2$), 1.65 (m, $-CH_2-CH=C(C\mathbf{H}_3)-CH_2-$ and $-CH_2-C(H)-C(C\mathbf{H}_3)=CH_2$), 1.3 (m, $-C\mathbf{H}_2-C(H)-C(CH_3)=CH_2$), 1.2 (m, $-C\mathbf{H}_2-$ resonances from initiator), 0.9 (m, $-C\mathbf{H}_3$ resonances from initiator). PI−PLA: The PI resonances are the same as above, and the diblocks have a (b, $-C\mathbf{H}_2-O-$) resonance at ≈4.0 ppm. PLA resonances are as follows: 5.1 (m, $-C(O)-C(\mathbf{H})(CH_3)-O-$), 1.6 (m, $-C(O)-C(H)-(C\mathbf{H}_3)-O-$). The ^{13}C NMR spectroscopy resonances reported below are for the majority *cis*-4,1 microstructure of PI and D,L-polylactide only. The regio- and stereoisomers of PI not listed were present in low amounts and agreed with literature values.[36] PI−PLA: 169 ($-\mathbf{C}(O)-C(H)(CH_3)-O-$), 135 ($-CH_2-CH=\mathbf{C}(CH_3)-CH_2-$), 125 ($-CH_2-\mathbf{C}H=C(CH_3)-CH_2-$), 69 ($-C(O)-\mathbf{C}(H)(CH_3)-O-$), 32 ($-CH_2-CH=C(CH_3)-\mathbf{C}H_2-$), 26 ($-\mathbf{C}H_2-CH=C(CH_3)-CH_2-$), 23 ($-CH_2-CH=C(\mathbf{C}H_3)-CH_2-$), 17 ($-C(O)-C(H)(\mathbf{C}H_3)-O-$).

Infrared spectra were characteristic for general polyesters and polyisoprenes.[37] The spectra showed C−H stretches near 2900 cm^{-1} characteristic of both PI and PLA. A weak band near 1660 cm^{-1} due to the C=C stretch and the deformation bands at 1380 and 1450 cm^{-1} were indicative of the PI. Also present was the medium-intensity bands near 840 cm^{-1} from the C−H wag of the trisubstituted olefin. PLA incorporation was evident from the C=O stretch at 1750 cm^{-1} and the C−O−C stretch in the 1050−1250 cm^{-1} region.

Differential Scanning Calorimetry. Measurements were taken using a Perkin-Elmer Pyris1 DSC. An indium standard was used for calibration, and helium was the purge gas. Samples were initially heated to 80 °C and held for 10 min after which they were quenched to −100 °C and subsequently held for 5 min to allow for instrument equilibration. The scan rate used for all samples was 20 °C/min.

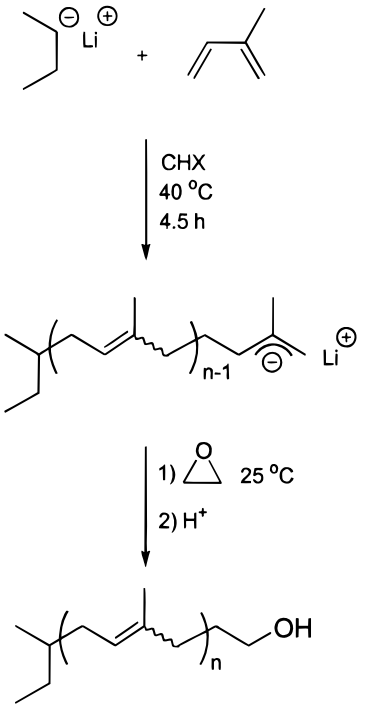
Small-Angle X-ray Scattering. SAXS measurements were taken at the University of Minnesota on a custom-built beamline. Cu Kα X-rays were generated through the use of a Rigaku RU-200BVH rotating anode X-ray machine fitted with a 0.2 × 2 mm^2 microfocus cathode and Franks mirror optics. Unsheared samples were annealed at 100 °C under reduced pressure for 12 h, and the scattering was performed at room temperature for 5−10 min. Two-dimensional diffraction patterns were collected using a multiwire area detector and subsequently corrected for detector response characteristics. Azimuthally isotropic two-dimensional scattering patterns were averaged to the one-dimensional form of intensity versus scattering wavevector $|\vec{q}| = q = 4\pi\lambda^{-1}(\sin\theta/2)$, where λ and θ are the radiation wavelength and scattering angle, respectively.

Rheology. The samples were thermostated in a controlled nitrogen atmosphere. Dynamical mechanical data were recorded on a Rheometrics solid analyzer RSA 2 equipped with a shear sandwich geometry.

Results and Discussion

Hydroxyl-Terminated Polyisoprene. Monohydroxyl-terminated polyisoprene was synthesized using living anionic polymerization techniques. To ensure the living nature of the reaction, the solvent and the monomers

Scheme 1

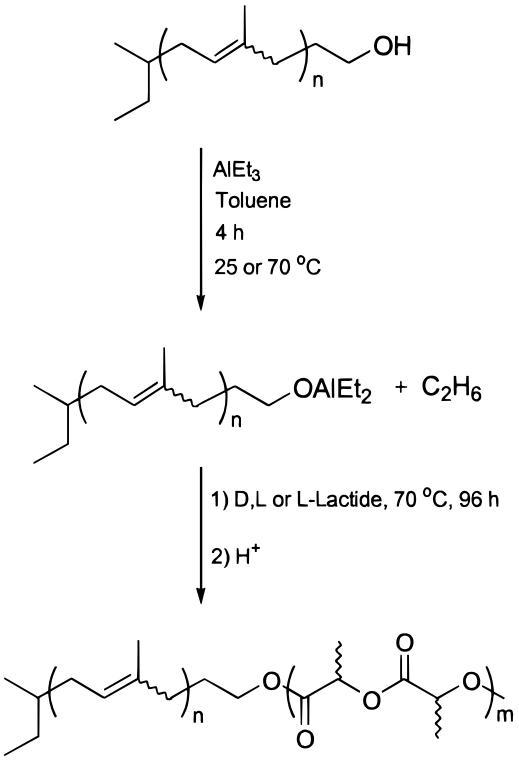


were rigorously purified prior to polymerization. The sequence of steps utilized in the synthesis of PI−OH is outlined in Scheme 1. The polymerization of isoprene was carried out in cyclohexane at 40 °C using *sec*-butyllithium as the initiator. End-capping was accomplished through the addition of excess ethylene oxide (EO) at room temperature after complete conversion of the isoprene monomer.[38] The monofunctional polymer was then liberated through the termination of the lithium alkoxide with acidic methanol/2-propanol (HCl). The resulting polymer was isolated from the residual inorganic salts through precipitation in methanol/2-propanol followed by the subsequent removal of solvent. These salts may also be eliminated through extraction of the cyclohexane/polymer solution with distilled water.

The choice of conditions given in Scheme 1 allowed for the synthesis of polyisoprene containing a high content of *cis*-4,1 microstructure, similar to natural rubber (100% *cis*-4,1), and the incorporation of a single, terminal $-CH_2-CH_2-OH$ unit. A combination of lithium initiator with a nonpolar solvent yields polymers containing the 4,1 regioisomer in excess of 90% over the 4,3 regioisomer.[39,40] The regioisomer content (92% 4,1 to 8% 4,3) was confirmed by ^{1}H NMR spectroscopy, and the large ratio of *cis*-4,1 to *trans*-4,1 (≈90% *cis*) stereoisomers was confirmed using ^{13}C NMR spectroscopy. An excess of EO could be added to the living carbanion with only one unit incorporated by the virtue of lithium alkoxide's inability to propagate EO.[41]

The high yields obtained in typical polymerizations (>98%) indicate nearly complete conversion of isoprene. These high conversions along with the living nature of the polymerization allow the prediction of the degree of polymerization from the reaction stoichiometry ($\bar{X}_n$ = [M]/[I]). The low molecular weight of the polymer enables the precise determination of molecular weight and end-capping efficiency by ^{1}H NMR spectroscopy. The mole ratio of the hydroxyl end group to the initiator end group was approximately one, establishing the

Scheme 2



presence of exactly one hydroxyl group per chain. This indicates the absence of side reactions or unwanted termination reactions during the polymerization. Since one hydroxyl group per polymer chain was confirmed, the ^{1}H NMR end group analysis was used to calculate the experimental $\bar{X}_n$. Close agreement with the monomer-to-initiator ratio derived from the reaction stoichiometry ($\bar{X}_{n_{exp}}$ = 75 and $\bar{X}_{n_{stoich}}$ = 73.5) was established. The overall average molecular weight ($\bar{M}_n$) of the polymer was calculated through addition of the initiator and end group molecular weights to the product of the repeat unit molecular weight and the calculated $\bar{X}_n$ value (NMR). The living nature of the polymerization was also supported by a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.04) obtained from GPC analysis. Using this type of procedure, PI−OH samples with molecular weights ranging from 1 to 80 kg/mol can be routinely prepared.[33,42] This versatile and controlled synthesis is critical for the preparation of well-defined PI−PLA diblock copolymers.

Polyisoprene−Polylactide Diblock Copolymers. The synthesis of PLA containing block copolymers has been demonstrated through the controlled ring-opening polymerization of lactide using aluminum alkoxide macroinitiators.[27,43] Using a similar procedure, a well-defined PI−aluminum alkoxide macroinitiator has been utilized for the preparation of a set of model PI−PLA diblock copolymers. Starting with the reaction product from Scheme 1, the sequence of reactions used in the synthesis of these model PI−PLA diblocks is depicted in Scheme 2.

Formation of the macroinitiator was accomplished through conversion of the hydroxyl end groups of polyisoprene into aluminum alkoxide end groups. The PI−OH prepolymer was dissolved in toluene followed by the equimolar addition of $AlEt_3$ under an argon atmosphere. Although the reaction was allowed to stir for 4 h at room temperature, ^{1}H NMR spectroscopic

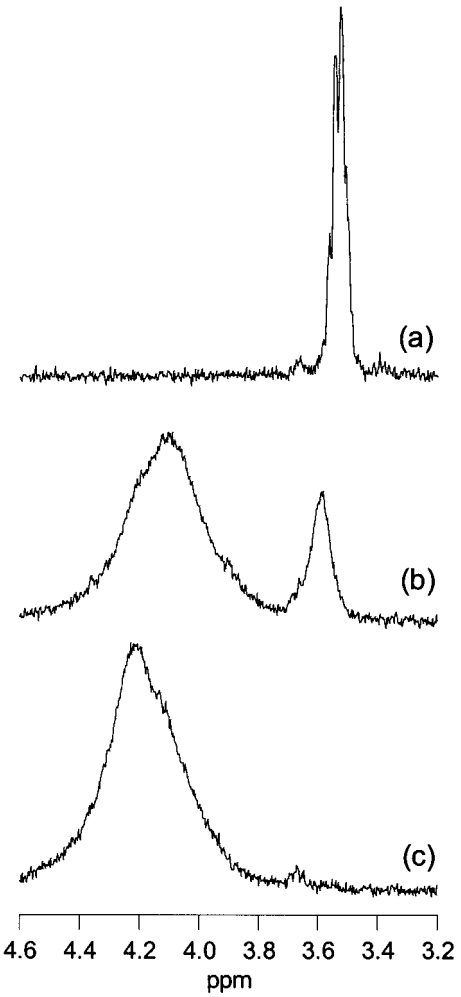


Figure 1. The 300 MHz ^{1}H NMR spectra of (a) PI−OH, (b) PI−OH and $AlEt_3$ at 25 °C, and (c) PI−OH and $AlEt_3$ at 70 °C.

analysis showed incomplete conversion of the hydroxy end group (Figure 1). The solution was heated to 70 °C for 30 min, and complete conversion was noted as the (−C**H**$_2$−OH) end group of the PI−OH prepolymer was absent in favor of a (−C**H**$_2$−O−Al−R$_2$) linkage. We have tentatively assigned three species in Figure 1 as (a) PI−OH, (b) PI−OH coordinated to an aluminum species and (b) and (c) the aluminum alkoxide macroinitiator. Teyssie and co-workers found that α-hydroxymethylene protons shifted downfield due to the interaction between the PCL−OH end groups and the aluminum alkoxide chain ends.[44] This is in agreement with the slight downfield shift we observed for PI−OH from (a) to (b). However, it is unclear as to whether the PI−OH is coordinating with the existing aluminum macroinitiator, the unreacted $AlEt_3$, or a combination of the two. Although it has been shown that aluminum alkoxides form aggregates, the coordinative nature of the above PI−aluminum macroinitiator has not been determined.[44,45] The nature of the coordination may account for the slight downfield shift seen in the macroinitator from (b) to (c). The relative intensities of the PI initiator fragment (CH(C**H**$_3$)(CH$_2$)−CH$_2$−C**H**$_3$) and the aluminum alkoxide end group (−Al−(C**H**$_2$−CH$_3$)$_2$ were approximately 6 to 4, indicating close to one chain per aluminum end group in agreement with the reaction stoichiometry.

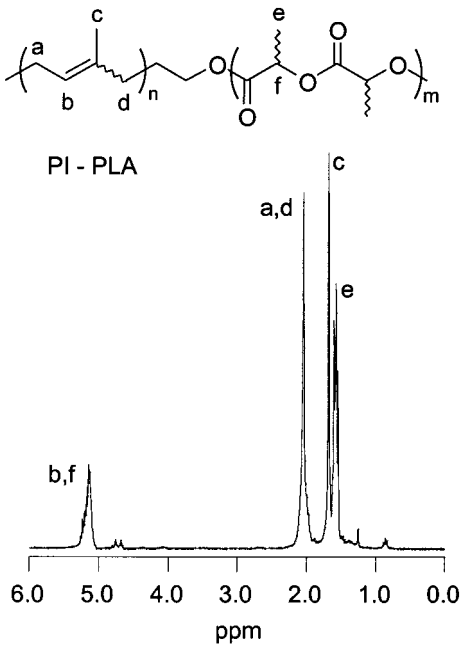


Figure 2. The 300 MHz ^{1}H NMR spectrum of a PI−PLA block copolymer (entry 14, Table 1) in $CDCl_3$.

Purified D,L-lactide was added to the macroinitiator solution, and the reaction vessel was sealed and immersed into a 70 °C oil bath. This temperature was chosen to give a moderate polymerization rate with minimal transesterification.[46] The ring-opening polymerization of lactide proceeded to relatively high conversions after ≈96 h (Table 1). The reactions were terminated with 2 N HCl (5-fold molar excess with respect to the initiator). High-molecular-weight polymers were precipitated with cold methanol and filtered, while toluene solutions of the low-molecular-weight diblocks were washed with water.[47]

Representative results for a series of model PI−PLA diblock copolymers containing varying PLA volume fractions are shown in Table 1. The molecular weight of the corresponding PI segment was fixed at either 5200 or 960 g/mol, while the PLA segment was varied through careful manipulation of the initial monomer-to-initiator ratio. Although we have not investigated the detailed kinetics of this polymerization, assuming 90% conversion of the initial D,L-lactide, the targeted molecular weight of the PLA segment could be reasonably predicted (Table 1). Under the assumption of complete isoprene recovery, conversion of the D,L-lactide was calculated from the polymerization yield after the sample had been dried under vacuum at elevated temperature, ensuring the removal of both solvent and trace lactide. The monomer conversion was then used to determine the molecular weight of the PLA segment ($\bar{M}_n$(PLA) conv, Table 1).

The PI−PLA diblock copolymer compositions were determined from ^{1}H NMR and ^{13}C NMR spectroscopy. The ^{1}H NMR signals characteristic of PI (protons a−d) and PLA (protons e and f) are shown in Figure 2. The methine proton resonance in both PI and PLA overlap ($\delta = 5.1$ ppm) so the PI−PLA was further characterized by FTIR spectroscopy, and the diblock composition was confirmed by ^{13}C NMR spectroscopy (see Experimental Section). The molecular weight of the PLA segment was then easily calculated from the ^{1}H NMR spectra since the overall molecular weight of the PI block was

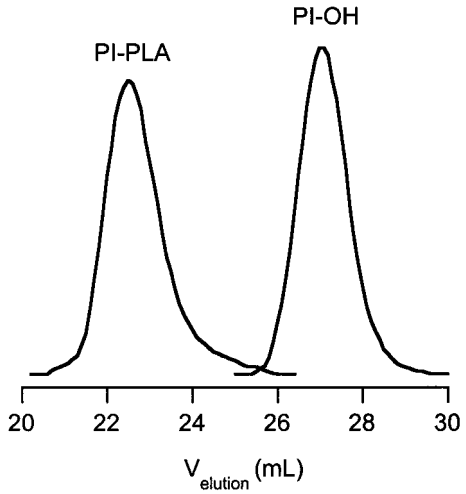


Figure 3. Gel permeation chromatograms for the PI−OH prepolymer (5.2K) and a PI−PLA (27.9K) diblock copolymer (entry 6, Table 1).

previously ascertained (by ^{1}H NMR end group analysis). The PLA molecular weight values from NMR analysis ($\bar{M}_n$(PLA) NMR, Table 1) compare satisfactorily to the values obtained through D,L-lactide conversion. Elemental analysis was performed (entry 9 Table 1) to verify the accuracy of the calculated molecular weight values. The predicted values of 68.88% C and 9.20% H in the sample were in close agreement with the values of 68.45% C and 9.20% H that were obtained from the elemental analysis. Using the calculated molecular weights of the PI and PLA segments, the respective volume fractions were calculated from the densities of the respective homopolymers at 140 °C (amorphous PLA = 1.154 g/cm^3 and 4,1-PI = 0.830 g/cm^3).[48−50]

The molecular weight distribution of the PI−PLA diblock copolymers was determined from GPC in the same manner as was described for the PI−OH homopolymer. Table 1 indicates the narrow molecular weight distribution of the diblocks ($\bar{M}_w/\bar{M}_n$ typically below 1.15), confirming the controlled nature of the ring-opening polymerization of lactide. The GPC analysis of a representative PI−PLA diblock copolymer (entry 6, Table 1) and the corresponding PI−OH prepolymer is shown in Figure 3. The diblock copolymer has a narrow molecular weight distribution and a lack of homopolymer. The GPC trace of the diblock copolymer in Figure 3 also exhibits an increase in molecular weight from the starting PI−OH, indicating the formation of a diblock copolymer.

Morphological Analysis. All of the diblock copolymers we prepared were optically homogeneous in both the melt and vitrified states. In addition, the diblock copolymers were more flexible than PLA homopolymers at equivalent molecular weights. On the basis of a simple solubility parameter analysis,[51] we estimate a segment−segment interaction parameter (χ) for PI−PLA that is approximately 5 times that of PI−PS diblock copolymers.[52] Therefore, we expect these PI−PLA diblocks to be strongly segregated in the melt state at low molecular weights. To verify this, we have performed the preliminary morphological analysis of a representative PI−PLA diblock copolymer using DSC and SAXS (entry 8, Table 1).

Differential scanning calorimetry was used to analyze the glass transition(s) of the PI−PLA diblock copolymer. Thermograms of the PI−OH prepolymer used for the synthesis and a representative PLA homopolymer (≈11000 g/mol) are given in Figure 4. The DSC traces for the PI and PLA homopolymers show a clear glass transition at −64 and 35 °C, respectively. (T_g's were estimated by taking the midpoint between the origin and termination temperatures of the overall thermal transition.) Single-phase polymer blends are characterized by a broad glass transition midway between the temperatures of the corresponding homopolymer components, where as phase-separated blends exhibit two transitions relative to the individual components.[53] The DSC scan for the representative PI−PLA diblock copolymer shown in Figure 4 has two clear glass transition temperatures that are close to the values of component homopolymers. Although this DSC data is not conclusive evidence of a ordered block copolymer with nanoscopic domains of PI and PLA, the existence of two T_g's supports a phase-separated morphology.

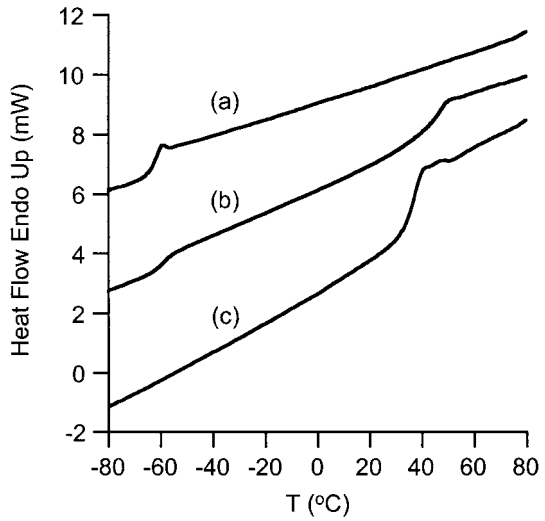


Figure 4. DSC traces of (a) PI−OH (5.2K), (b) PI−PLA diblock copolymer (entry 8, Table 1), and (c) (D,L) PLA homopolymer (≈11.0 kg/mol) taken at 20 °C/min.

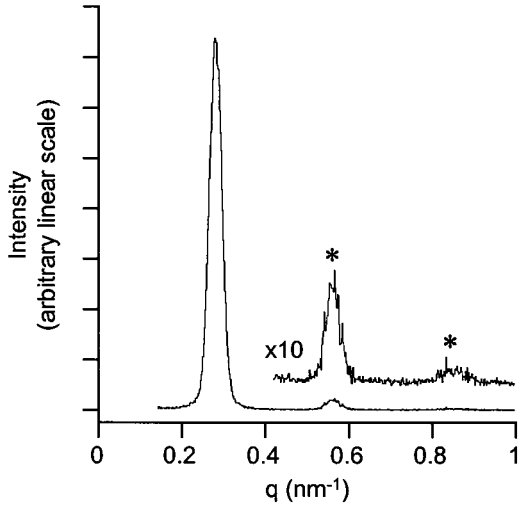


Figure 5. One-dimensional SAXS data for a PI−PLA diblock copolymer (entry 8, Table 1). The asterisks are at 2q* and 3q*.

In an effort to further characterize the morphology of this block copolymer, we performed small-angle X-ray scattering. Figure 5 shows the one-dimensional SAXS data for the representative PI−PLA diblock copolymer. The principal reflection (q*) corresponds to a fundamental spacing of 22.4 nm, and the higher-order reflec-

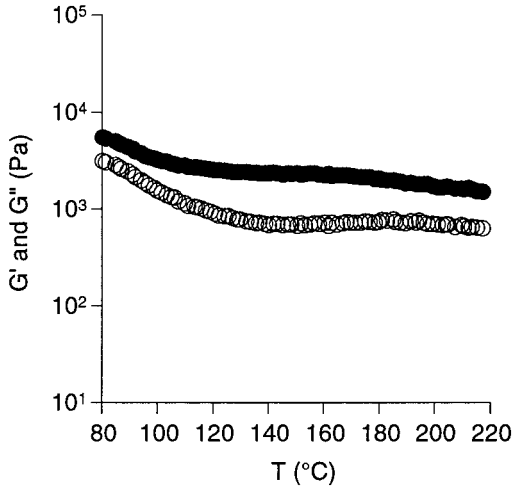


Figure 6. Temperature dependence of the low-frequency (1 rad/s) linear viscoelastic properties for a PI−PLA block copolymer (entry 3, Table 1). The dynamic elastic modulus (G', filled circles) and dynamic loss modulus (G'', open circles) are shown, and the ramp rate was 5 °C/min.

tions at $2q^*$ and $3q^*$ are indicative of a lamellar (L) morphology. A lamellar morphology was expected due to the near symmetric volume fractions of the PI and PLA segments ($f_{PLA} \approx 0.56$). From the DSC and SAXS analysis we conclude that this symmetric PI−PLA block copolymer is microphase-separated with a lamellar morphology.

In addition to the DSC and SAXS characterization, we have also studied the rheological behavior of these block copolymers. The linear viscoelastic response of a representative block copolymer (entry 3, Table 1) is shown in Figure 6. By small-angle neutron scattering, we determined that this material has a fundamental spacing of approximately 18 nm. Although no higher-order reflections were observed, the morphology of this material is presumably lamellar on the basis of the PLA volume fraction (0.46). The rheological data are essentially featureless over the experimentally accessible temperature range (greater than the T_g of PLA and less than the decomposition temperature of the block copolymer). The level of the dynamic elastic modulus (G') is indicative of a lamellar morphology based on rheological data obtained on relatively low-molecular-weight block copolymers.[54] In addition, the frequency dependence of both the dynamic elastic modulus (G') and dynamic loss modulus (G'') at 80 °C (not shown) is indicative of an ordered lamellar morphology.[55,56] This block copolymer is clearly ordered over the entire temperature window. We have not observed a definitive order−disorder transition in any of the block copolymers we have studied to date. A complete phase behavior study on this general class of PLA-based block copolymers is currently underway.

Summary

We have described a method for the synthesis of a novel set of PI−PLA diblock copolymers with PLA volume fractions ranging from 0.22 to 0.93 and total molecular weights ranging from 1.7 to 53.8 kg/mol. The combination of the living anionic polymerization of isoprene and the controlled coordination-insertion ring-opening polymerization of lactide provides an efficient and straightforward route to the synthesis of model PI−PLA diblock copolymers. The controlled nature of these polymerization mechanisms allows the ability to tailor the molecular parameters and subsequently the morphological properties. The well-defined nature of these diblocks has been determined through NMR and GPC analysis. In addition, DSC and SAXS suggest the blocks were microphase-separated. This general methodology can be easily extended to other hydrocarbon diblocks and can be utilized for the synthesis of ABC and ABA triblock copolymers as well.

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