Preparation and Characterization of 
(R)-Poly(β-hydroxybutyrate)-Poly(ε-caprolactone) and 
(R)-Poly(β-hydroxybutyrate)-Poly(lactide) Degradable Diblock Copolymers

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ABSTRACT: Natural-origin (R)-poly(β-hydroxybutyrate) (PHB) was degraded by acid-catalyzed methanolysis to form low molecular weight (average DP = 26) stereoisomerically pure PHB chains. The hydroxyl terminus of these polymers was then reacted with AlEt₃ to form a PHB-O-AlEt₃ macroinitiator species. These macroinitiators were then used to carry out the ring-opening polymerizations of ε-caprolactone and lactide monomers to prepare PHB-PCL, PHB-ε-l-PLA, and PHB-ε-l-PLA A-B diblock copolymers of variable chain segment lengths. Various A-B diblocks were characterized by VPO to determine the $M_\text{n}$ values, and therefore the respective chain segment lengths. Analysis by GPC showed that, in all cases, the diblocks gave unimodal peaks. The identification of the 1H NMR methyl doublet which corresponds to the hydroxyl end group repeat unit for the PHB prepolymer, its subsequent disappearance after the formation of the PHB-ε-l-PLA diblock, and the identification of the resultant 1H NMR methyl doublet due to the new hydroxyl terminal ε-lactide repeat unit were used in combination with the VPO and GPC results to confirm that we did indeed form these new PHB diblock copolymers. The diblock copolymers were analyzed by DSC and X-ray diffraction to determine their thermal and crystalline properties, respectively. It was shown that for diblocks (PHB DP = 26 in all cases) with short PCL (DP = 12) and ε-l-PLA (DP = 13) chain segments, PCL and PLA crystalline phases did not form. With increased chain lengths of the B chain segment (PCL DP = 38 and 51, ε-l-PLA DP = 23) the crystallization of both components of the diblock was observed as a superposition of the respective X-ray diffraction patterns. The PHB-ε-l-PLA diblock (PHB DP = 26, ε-l-PLA DP = 23) when melted and then rapidly quenched from the melt was kinetically frozen into a solid-state morphology such that miscibility of the two component chain segments resulted (a new $T_g$ at approximately 20 °C was observed). Phase separation occurred when the diblock copolymer was annealed at 55 °C for 24 h prior to DSC analysis.

Introduction

Poly(β-hydroxyalkanoates) (PHAs) are a class of β-monoalkyl-substituted poly(β-esters) which are naturally occurring in a wide variety of bacterial microorganisms. The biosynthesis of this family of materials with methyl (β-hydroxybutyrate), ethyl (β-hydroxyvalerate, HV), vinyl, long n-alkyl, branched alkyl, phenyl, and a variety of other functional side chains as well as repeat units containing 4-hydroxybutyrate provides a wide range of physical and biological properties. The most well-known of the PHA family is the homopolymer PHB and copolymers P(HB-co-HV), which have been shown to be biodegradable and useful physical properties, slow hydrolytic degradation, and favorable preliminary studies on in-vivo properties. PHB and P(HB-co-HV) are expected to be disposable biodegradable plastics as well as specialty medical products.

Poly(ε-caprolactone) (PCL) and polylactide (PLA) are polyesters that have displayed much promise as materials for controlled release of drugs, due to their biocompatibility and degradability. In addition, the biological degradability of PCL upon environmental exposures is well established. Lactide and ε-caprolactone polymerizations have been studied using a variety of catalysts and reaction conditions. In some cases, the living character of the catalyst–polymerization system has provided a route to the synthesis of a number of A-B diblock copolymers containing PCL and PLA chain segments with control over the block molecular weights.

Preliminary studies which used PHA chain segments obtained by the degradation of natural-origin PHB for the synthesis of PHB-containing block copolymers have been reported by our laboratory. Work by Yalpani and Marchessault has demonstrated the use of degraded natural-origin PHB for the synthesis of PHB-poly saccharide conjugates.

PHB and P(HB-co-HV) blends which are designed to be completely biodegradably as well as blends with specific synthetic polymers (known to be biologically inert) have been investigated in our laboratory. Information on the effects of crystallinity and blend morphology on the biodegradability of PHB- and P(HB-co-HV)-containing materials has been reported. The blending of PHAs (as well as other environmentally degradable materials) with both natural and synthetic polymers is an area of great potential for the purpose of tailoring the physico-mechanical properties as well as modulation of the kinetics of material biodegradation.

Biodegradable diblock copolymers may serve as emulsifiers for the respective blends of biodegradable homopolymers. Therefore, the synthesis and study of such copolymers is of extreme importance. The diblock copolymers can be used to decrease the size of the blend component domains, decrease the interfacial tension, and improve the mechanical properties of immiscible polymer blends. Since the impact of blend morphological parameters on polymer degradability is at present not understood, correlating the effect of diblock copolymers on blend morphology and degradability will be an area of
extreme interest for future research work.

In this paper, important new diblock copolymers containing (R)-PHB as a block segment were obtained. Natural-origin (R)-PHB of high molecular weight was degraded by controlled acid-catalyzed methanolation to provide low molecular weight (R)-PHB polymers with an active hydroxyl functionality in addition to a methyl ester at the two respective chain end groups. This strategy for the synthesis of reactive low molecular weight (R)-PHB was adopted in favor of the more lengthy synthesis by ring-opening methods.\(^4\) The hydroxy-terminated low molecular weight (R)-PHB was then reacted with triethylaluminum to form macroinitiators for the ring-opening polymerization of \(\varepsilon\)-caprolactone, DL-lactide, and L,L-lactide. The structure and molecular weight of these diblock copolymers were studied by \(^1\)H nuclear magnetic resonance (NMR), vapor pressure osmometry (VPO), and gel permeation chromatography (GPC). In addition, the thermal and crystalline characteristics of these diblock copolymers were investigated by differential scanning calorimetry (DSC) and X-ray diffraction techniques.

**Experimental Section**

**Instrumental Methods.** Nuclear Magnetic Resonance (NMR). Proton (\(^1\)H) NMR spectra were recorded on a Bruker WP-270 MHz spectrometer at 270 MHz. \(^1\)H NMR chemical shifts (ppm) are reported downfield from 0.00 ppm using tetramethylsilane (TMS) as an internal reference. The parameters for the polymer spectra are as follows: 3.5\% (w/w) polymer in CDCl\(_3\), temperature 308 K, pulse width 4.9 \(\mu\)s, 32K data points, relaxation delay 0.5 s, 100-200 transients. Peak areas were determined by spectrometer integration.

**Infrared Spectra (IR).** Spectra were recorded on polymer films cast from chloroform solution onto NaCl plates using a Bruker IFS 113v FT-IR at 25 \(^\circ\)C.

**Molecular Weight Measurements.** Molecular weights and dispersities were determined by GPC and VPO. Studies by GPC were conducted using a Waters Model 150 pump, Model 410 refractive index detector, and Model 730 data module with 500-10\(^5\)-A Ultrastrayragel columns in series. Chloroform was used as the eluent at a flow rate of 1.0 mL/min. Sample concentrations of 0.5\% (w/v) and injection volumes of 100 \(\mu\)L were used. Polystyrene standards with a low polydispersity (Aldrich) were used to generate a calibration curve. The VPO (UIC, Inc., Model 070) was calibrated with biphenyl in dichloromethane at 33 \(^\circ\)C, and the polymers were run in dichloromethane at 33 \(^\circ\)C to obtain \(M_n\) values.

**Thermal Analysis.** DSC was conducted on a Du Pont DSC 2010 equipped with a TA 2000 data station, using between 7.0 and 12.0 mg of sample, a heating rate of 10 \(^\circ\)C/min, and a nitrogen purge.

**X-ray Diffraction.** X-ray diffraction measurements were made by using a Rigaku Geigerflex operating at a voltage of 40 kV and a current of 25 mA. The X-ray beam was pinhole collimated. Nickel-filtered Cu K\(_{\alpha}\) radiation (\(\lambda = 1.542\) \(\AA\)) was used. The sample exposure times varied from 12 to 17 h. The sample-to-film distance used was 9.96 cm.

**Synthetic Procedures.** PHB Methanolysis. The controlled methanolysis of PHB (natural origin, obtained from ICI) was carried out by a modification of a literature method\(^4\) to obtain a monohydroxy-terminated PHB methyl ester prepolymer. The high molecular weight natural-origin PHB was purified by dissolution in chloroform, removal of the chloroform-insoluble material by filtration through Celite 521 (Aldrich), precipitation of the filtered chloroform solution into methanol, and washing of the precipitate with methanol. The molecular weight of this starting material was measured as \(M_n = 371,000\) and \(M_w = 121,000\) by GPC (see above).

Pure PHB (8 g) was dissolved in chloroform (600 mL, distilled twice from anhydrous phosphorus pentoxide under argon) in a 1000-mL two-neck round-bottomed flask. The flask was placed in a waterbath at 35 \(^\circ\)C and fit with an overhead stirrer and argon inlet. A 5\% sulfuric acid in methanol (v/v) (distilled over sodium under argon) solution was added, and 200 mL of this solution was added to the PHB solution to initiate polymer methanolysis. Aliquots were removed periodically from the degradation to follow the progress of the reaction. The aliquots were extracted with a 5\% (v/v) aqueous solution and distilled water until neutrality; the organic layer was dried over anhydrous magnesium sulfate, precipitated into a 10 times excess of methanol, centrifuged, and dried. The molecular weight of the resulting PHB prepolymer was then measured by GPC. When the PHB was degraded to the desired molecular weight, the remaining reaction solution was extracted with sodium bicarbonate and distilled water and the polymer isolated as described above for the withdrawn aliquots. The prepolymer was further purified by dissolution in chloroform, precipitation into cold methanol, separation of the white solid prepolymer by filtration, and drying of the product in vacuo at 35 \(^\circ\)C. The results of \(^1\)H NMR, GPC, VPO, and DSC analyses of the prepolymer are presented in the Results and Discussion Section, below, whereas the IR spectrum obtained was almost identical to that of the starting natural-origin polymer.

**Synthesis of PHB-PCL and PHB-PLA Diblocks.** Considerable precautions were taken during the formation of the diethylaluminum PHB-alkoxide macroinitiator and subsequent ring-opening polymerizations to avoid reactions which would give other oxoaluminum species. The glassware used for macroinitiator formation and polymerizations was silanized with chlorotrimethylsilane, washed with methanol, oven-dried, and subsequently flame-dried under vacuum and purged with argon. All chemical transfers were conducted either by gas-tight syringes or cannulation under argon which was passed through columns of anhydrous phosphorus pentoxide coated silica (obtained from Fluka, column dimensions 50 x 4.5 cm) and silica (obtained from VWR, column dimensions 80 x 6 cm).\(^3\) Triethylaluminum (1.9 M) in toluene and 2,4-pentanediol (AcAc) were obtained from Aldrich and used as received. Dichloromethane was further purified by distillation (Burdick & Jackson) over sodium under argon. Dichloromethane (10 mL) was dried for 24 h over calcium hydride and distilled under reduced pressure. All lactides (Boehringer Ingelheim and Polysciences) were recrystallized from dry toluene and dried under vacuum at room temperature using anhydrous phosphorus pentoxide as desiccant. \(N,N\)-Dimethyl-\(N\)-ethylhexylenediamine (DMEDA) obtained from Aldrich was dried and distilled over calcium hydride. Triethylaluminum (1.9 M) in toluene and 2,4-pentanediol (AcAc) were obtained from Aldrich and used as received. Dichloromethane was further distilled (Burdick & Jackson) over calcium hydride, and anhydrous phosphorus pentoxide was added to dry under argon (see above).

Triethylaluminum solution (0.24 M, 4.55 x 10\(^4\) mol), dichloromethane (2 mL), and DMEDA (0.14 M, 9.1 x 10\(^4\) mol) were transferred into a 25-mL internal volume ampule capped with a rubber septum. In a separate ampule, 1.0 g of the PHB prepolymer (\(M_n = 2200, \text{DP} = 26\)) was dried for 16 h using a drying pistol (40 \(^\circ\)C, 50 \(\mu\)Hg). To this ampule was transferred dichloromethane (16 mL), and the PHB prepolymer was dissolved. The PHB prepolymer solution was then transferred into the ampule containing the triethylaluminum, dichloromethane solution, and the resulting solution was stirred at room temperature for 3 h to form the macroinitiator solution. For the synthesis of PHB-PCL diblocks, \(\varepsilon\)-CL (1.0 g for DP = 12, 2.23 g for DP = 38, 3.26 g for DP = 51) was transferred into the ampule containing the macroinitiator solution. The ampule was cooled, sealed under vacuum, and placed into an oil bath at 40 \(^\circ\)C for between 18 and 48 h (see Table 1).

The synthesis of PHB-PCL diblocks (the procedure followed was identical for L,L- and DL-lactide monomer stereoisomerizations) involved first adding the triethylaluminum, dichloromethane solution to the ampule containing the lactide monomer. L,L-lactide (3.20 g for DP = 231) was added to the ampule containing the lactide monomer (described above), sealed, and placed into an oil bath at 60 \(^\circ\)C for 2 days prior to the polymerization. Dichloromethane (10 mL) was transferred into the ampule, and the lactide was dissolved. The lactide solution was then transferred into the ampule containing the macroinitiator solution (described above), sealed, and placed into an oil bath at either 50 or 70 \(^\circ\)C for time periods ranging from 3 to 16 days (see Table 1).

All PHB-b-polymers were isolated in an identical manner. The ampule contents were poured directly into a 10 volume excess of cold methanol; the resultant precipitate was separated by centrifugation and then stirred overnight in AcAc to remove residual organoaluminum molecules (7.5 mL of AcAc/g of precipitate). The AcAc product solution/slurry was then poured
Table I

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<th>Polymerization Condition, Yields, and Molecular Weight Analysis of Diblock Copolymers Containing a PHB Chain Segment</th>
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a Methanol-insoluble product after purification. (See the Experimental Section.) b Obtained via VPO. Samples were analyzed in dichloroethane with biphenyl as the standard. c Obtained via GPC. Chloroform was used as the eluent, and a calibration curve was constructed from polystyrene standards. d The numbers in brackets correspond to the block DP's of the corresponding segments in the diblock copolymer.

Figure 1. Scheme for the preparation of PHB-b-polyesters by the formation of a PHB-O-AlE2 macroinitiator species and subsequent ring-opening polymerizations of ε-caprolactone or lactide monomers.

into a 10 volume excess of cold methanol; the resulting precipitate was separated by centrifugation and dissolved in chloroform; the chloroform product solution was then precipitated into cold methanol.

Spectra of the diblock copolymer products above obtained by 1H NMR and IR spectroscopy were consistent with that expected. Additional characterization by GPC, VPO, DSC, X-ray diffraction, and NMR structural analysis as well as yields for the products formed is provided in the Results and Discussion section.

Results and Discussion

The synthesis of low molecular weight PHB was carried out by performing an acid-catalyzed methanolysis on natural-origin PHB. This provided a free secondary hydroxyl functionality as well as a methyl ester protected carboxylic acid for the two respective chain ends of the polymer chains. The methanolysis reaction was allowed to proceed for 6 h to produce PHB chains with an $M_n$ value of 2200 (DP = 26, abbreviated as PHB [26]) as determined by VPO (see the Experimental Section) and a polydispersity ($M_w/M_n$) value of 1.76 as determined by GPC (see the Experimental Section). This hydroxyl-functionalized low molecular weight PHB sample was used for the formation of a PHB-O-AlE2 macroinitiator species (see the Experimental Section) following methodology previously developed for a hydroxyl-functionalized PCL prepolymers (see the Experimental Section). The PHB-O-AlE2 macroinitiator species was then used for the preparation of PHB-PCL, PHB-D,L-PLA, and PHB-L-PLA diblocks by catalyzing the ring-opening polymerization of ε-caprolactone, D,L-lactide, and L-lactide, respectively (see Figure 1). Table I shows the polymerization conditions, yields, block lengths (determined by VPO), and polydispersities (determined by GPC), for the respective product copolymers.

GPC chromatographs of the synthesized diblock copolymers showed, in all cases, peaks which were unimodal and higher in molecular weight than the PHB prepolymer. VPO data also showed increases in molecular weight for the diblocks relative to the PHB prepolymer (see Table I). In addition, the samples were analyzed by 1H NMR
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Figure 3. $^1$H NMR spectrum (270 MHz) in CDCl$_3$ of the PHB prepolymer PHB [26]. (b) An expansion of the PHB methyl region from the $^1$H NMR spectrum in a. (c) An expansion of the methyl region from the $^1$H NMR spectrum (270 MHz) in CDCl$_3$ of PHB [26] reacted with trifluoroacetic anhydride, which confirmed that all of the copolymer diblocks contained both respective repeat unit structures (see Figure 2a as a representative example).

Figure 2a shows the $^1$H NMR spectrum of PHB–L-PLA [26–23], and parts b–d of Figure 2 display expansions of the PLA methyl region (hydrogens e', e'', and e''') from $^1$H NMR spectra of this diblock copolymer recorded under the conditions specified below. In Figure 2b, the expansion of the methyl region from Figure 2a is displayed, whereas in parts c and d of Figure 2, the expanded methyl regions are from spectra of this copolymer mixed with 20% by weight d,L-PLA and reacted with trifluoroacetic anhydride, respectively. The upfield shoulders at 1.589 and 1.564 ppm and the peak at 1.536 ppm in Figure 2c are due to stereochemical sequences present in the d,L-PLA component. These three peaks were, of course, observed in the $^1$H NMR spectrum of d,L-PLA in the absence of the diblock (spectra not shown). Therefore, comparison of the expansions shown in parts b and c of Figure 2 clearly shows that the upfield and downfield doublets at 1.496/1.470 (assigned to hydrogens e', $J_{e'e'} = 7.0$ Hz) and 1.603/1.576 ppm (assigned to hydrogens e'', $J_{e'e''} = 7.0$ Hz), respectively, are not due to stereochemical effects, while the doublet at 1.586/1.560 ppm (assigned to hydrogens e) is due to long isotactic stereosequences. It can therefore be concluded that the polymerization of L-lactide by the PHB–Q–AIE$_2$ macroinitiator species did not result in any noticeable loss in the enantiomeric purity of the lactide stereocenters. The decrease in intensity of the upfield doublet (1.494/1.468 ppm, labeled as e', $J_{e'e'} = 7.0$ Hz) and the appearance of a new doublet downfield at 1.699/1.673 ppm ($J_{e'e''} = 7.0$ Hz) upon reaction of the diblock with trifluoroacetic anhydride (see Figure 2d) suggest that the peaks at 1.494/1.468 ppm are due to the L-PLA segment repeat unit which is at the hydroxy terminus. It is also suggested from the above analysis that the methyl doublet resonances at 1.160/1.153 ppm (more clearly resolved in Figure 2b) are due to the e'' protons of the lactate repeat units linked to an adjacent PHB segment.

The PHB prepolymer, PHB [26], was similarly reacted with trifluoroacetic anhydride, and the $^1$H NMR spectra before and after the reaction were compared (see expansions of the methyl regions displayed in parts b and c of Figure 3, respectively). A decrease in the intensity of the upfield doublet (1.236/1.213 ppm, assigned to hydrogens a', $J_{a'a''} = 6.2$ Hz) in Figure 3b and the appearance of a downfield doublet (1.429/1.406 ppm, $J_{a'a''} = 6.2$ Hz) in Figure 3c upon reaction of the PHB prepolymer with trifluoroacetic anhydride suggest that the upfield methyl resonance doublet is due to the (R)-PHB prepolymer repeat unit that is at the hydroxyl terminus (labeled as a'). Since the doublet at 1.236/1.213 ppm due to hydrogens a' was not observed for PHB–PCL or PHB–PLA diblock copolymers and the resonance due to the hydroxyl terminal methyl resonance of the PLA segment was observed (for PHB–PLA diblocks), this then provides additional evidence that the diblock copolymers synthesized herein were indeed formed as described in Figure 1.

DSC thermograms for the PHB–PCL diblock copolymers synthesized with different PCL chain segment lengths are shown in Figure 4. In addition, a compilation of the numerical values corresponding to the thermal transitions...
observed is presented in Table II. The first heating scans on samples, prepared by solution precipitation, showed that for the PHB–PCL [26–12] sample no melting endotherm corresponding to that of a PCL crystalline phase was observed. However, when the PCL chain segment DP was increased to 38 and 51, peak melting transitions ($T_m$) at 57 and 53 °C were observed, indicating that PCL crystalline phases were now formed. Interestingly, the weak endotherm observed for the solution-precipitated PHB–PCL [26–38] diblock sample increased from 1.58 to 8.1 cal/g while the $T_m$ decreased from 57 to 47 °C for a third heating scan which was recorded after melt-annealing the sample at 25 °C for 3 weeks (see Figure 4, sample designated with an asterisk, and Table II). This suggests that the melting and subsequent crystallization at room temperature of the PHB–PCL [26–38] sample increased the degree of crystallinity and lowers the degree of order as compared to the initial solvent-precipitated sample. In addition, the PHB crystalline phase of the PHB–PCL diblock copolymers shows a slight depression of its $T_m$ (from 147 to 139 °C) as the DP of the PCL chain segment increases from 38 to 51. The $T_m$ value of the PHB prepolymer sample (DP = 26) prepared by solution precipitation was 148 °C which agrees rather well with the $T_m$ values of the PHB crystalline phases formed by the PHB–PCL diblock copolymers with PCL chain segment DP values of 12 and 38. X-ray analysis of the PHB–PCL diblocks and corresponding homopolymers was performed (see the Experimental Section), and the d-spacings measured were recorded in Table III. The existence of d-spacings for the diblock copolymer samples which result from a superposition of those expected for the respective homopolymers were used herein as evidence that both components of the diblock formed distinct crystalline phases. From observation of Table III, it appears that a PCL crystalline phase was not formed for the PHB–PCL [26–12] diblock but was present for the longer PCL chain segment diblocks. This is in agreement with the DSC measurements presented above.

DSC analyses were also performed on the PHB–PLA diblocks (see Table II and Figures 5 and 6). Interestingly, a comparison of the second heating scans for the PHB–PCL diblocks with PHB and PLA homopolymers are presented in Table II. The thermal analysis of these samples showed that the melting and crystallization temperatures of PHB–PLA diblock copolymers are significantly lower than those of the respective homopolymers. This is consistent with the results obtained by X-ray diffraction analysis which showed that the PHB–PLA diblock copolymers have a lower degree of crystallinity compared to the homopolymers. The melting and crystallization temperatures of the PHB–PLA diblock copolymers are presented in Table III. The thermal analysis of these samples showed that the melting and crystallization temperatures of PHB–PLA diblock copolymers are significantly lower than those of the respective homopolymers. This is consistent with the results obtained by X-ray diffraction analysis which showed that the PHB–PLA diblock copolymers have a lower degree of crystallinity compared to the homopolymers. The thermal analysis of these samples showed that the melting and crystallization temperatures of PHB–PLA diblock copolymers are significantly lower than those of the respective homopolymers. This is consistent with the results obtained by X-ray diffraction analysis which showed that the PHB–PLA diblock copolymers have a lower degree of crystallinity compared to the homopolymers. The thermal analysis of these samples showed that the melting and crystallization temperatures of PHB–PLA diblock copolymers are significantly lower than those of the respective homopolymers. This is consistent with the results obtained by X-ray diffraction analysis which showed that the PHB–PLA diblock copolymers have a lower degree of crystallinity compared to the homopolymers. The thermal analysis of these samples showed that the melting and crystallization temperatures of PHB–PLA diblock copolymers are significantly lower than those of the respective homopolymers. This is consistent with the results obtained by X-ray diffraction analysis which showed that the PHB–PLA diblock copolymers have a lower degree of crystallinity compared to the homopolymers. The thermal analysis of these samples showed that the melting and crystallization temperatures of PHB–PLA diblock copolymers are significantly lower than those of the respective homopolymers. This is consistent with the results obtained by X-ray diffraction analysis which showed that the PHB–PLA diblock copolymers have a lower degree of crystallinity compared to the homopolymers. The thermal analysis of these samples showed that the melting and crystallization temperatures of PHB–PLA diblock copolymers are significantly lower than those of the respective homopolymers. This is consistent with the results obtained by X-ray diffraction analysis which showed that the PHB–PLA diblock copolymers have a lower degree of crystallinity compared to the homopolymers. The thermal analysis of these samples showed that the melting and crystallization temperatures of PHB–PLA diblock copolymers are significantly lower than those of the respective homopolymers. This is consistent with the results obtained by X-ray diffraction analysis which showed that the PHB–PLA diblock copolymers have a lower degree of crystallinity compared to the homopolymers. The thermal analysis of these samples showed that the melting and crystallization temperatures of PHB–PLA diblock copolymers are significantly lower than those of the respective homopolymers. This is consistent with the results obtained by X-ray diffraction analysis which showed that the PHB–PLA diblock copolymers have a lower degree of crystallinity compared to the homopolymers. The thermal analysis of these samples showed that the melting and crystallization temperatures of PHB–PLA diblock copolymers are significantly lower than those of the respective homopolymers. This is consistent with the results obtained by X-ray diffraction analysis which showed that the PHB–PLA diblock copolymers have a lower degree of crystallinity compared to the homopolymers. The thermal analysis of these samples showed that the melting and crystallization temperatures of PHB–PLA diblock copolymers are significantly lower than those of the respective homopolymers. This is consistent with the results obtained by X-ray diffraction analysis which showed that the PHB–PLA diblock copolymers have a lower degree of crystallinity compared to the homopolymers. The thermal analysis of these samples showed that the melting and crystallization temperatures of PHB–PLA diblock copolymers are significantly lower than those of the respective homopolymers. This is consistent with the results obtained by X-ray diffraction analysis which showed that the PHB–PLA diblock copolymers have a lower degree of crystallinity compared to the homopolymers.
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Conclusions
Methodology was developed for the preparation of PHB-PCL and PHB-PLA diblock copolymers. Characterization of these copolymers by VPO was used to determine the respective chain segment lengths. GPC analysis of the products showed, in all cases, unimodal peaks which were higher in molecular weight than the starting pre-

L-PLA [26–13] sample containing a relatively shorter PLA chain segment length, is forming both PHB and PLA crystalline phases. Once again, X-ray diffraction patterns were recorded for the PHB-PLA diblock copolymers and confirmed that both a PHB and a PLA crystalline phase were formed for the PHB-L-PLA [26–23] diblock (see Table III). This was apparent since the X-ray diffraction of the PHB-L-PLA [26–23] diblock was a superposition of the diffraction patterns for both (R)-PHB and L-PLA. In contrast, the PHB-L-PLA [26–13] diblock showed an X-ray diffraction pattern which corresponded to that for only (R)-PHB. Also of interest is the observation that a T_g intermediate to that expected for PHB and PLA (at approximately 20 °C) was observed for PHB-L-PLA [26–23] during the second heating scan (see Figure 5b). For the PHB-L-PLA [26–13] first and second heating scans (see parts a and b of Figure 5, respectively), the PHB-L-PLA [26–23] first heating scan, T_g values were observed which correspond to the respective component polymers (approximately 0 °C for PHB [26] and approximately 55 °C for PLA [46]). It appears, therefore, that the PHB and PLA phases of the diblock sample when quickly quenched from the melt are kinetically frozen into a solid-state morphology such that the PHB and PLA remain as one phase. Indeed, this shows the miscibility of the PHB and PLA chain segments in the melt. When this same sample is slowly cooled from the melt and melt annealed at 55 °C, phase separation occurs and two T_g values corresponding to the PHB and PLA phases are once again observed.

To further investigate these results, a blend of (R)-PHB [26] and L-PLA [23] homopolymers in a 40/60 (w/w) ratio (simulating the w/w ratio present in the [26–23] diblock) was formed by solvent precipitation. Both the diblock, PHB-L-PLA [26–23], and the blend were melted in a first heating DSC scan and then slowly cooled (equilibrating with room temperature) to room temperature. The samples were then further cooled to −50 °C with liquid nitrogen, after which the second heating scans were performed (see Figure 6). The second heating scan for PHB-L-PLA [26–23] (thermogram a, Figure 6) showed three T_g transitions at −16, +18, and +40 °C and a heat of fusion of 6 cal/g (11 cal/g total enthalpy at 136 °C minus 5 cal/g crystallization enthalpy at 83 °C). Observation of thermogram b in Figure 6 for the second heating scan of the blend showed no observable T_g transitions and a heat of fusion of 15 cal/g for the melting enthalpy at 147 °C. This suggests a relatively higher degree of sample crystallinity of the PHB [26]/L-PLA [23] blend as compared to the PHB-PLA [26–23] diblock after melting and slow cooling. In addition, these results suggest that when a covalent bond exists between the respective chain segments, the rates of crystallization and phase separation of the respective components from the melt decrease. However, it is interesting to note that when the blend is subjected to a first heating scan and immediately quenched and a second heating scan performed, the intermediate T_g at approximately 20 °C is once again observed. Thus, both the diblock and the blend may form this miscible solid-state morphology under the appropriate conditions, but the relative rates of phase separation are significantly different when a covalent bond is introduced between the respective component polymers.

Conclusions
Methodology was developed for the preparation of PHB-PCL and PHB-PLA diblock copolymers. Characterization of these copolymers by VPO was used to determine the respective chain segment lengths. GPC analysis of the products showed, in all cases, unimodal peaks which were higher in molecular weight than the starting pre-
polymer. 1H NMR analysis was used to confirm that the L-lactide monomer was polymerized by the PHB-O-AlEt₂ macroinitiator species without significant loss of enantiomeric purity. In addition, the identification of polymer end-group 1H NMR resonances was used to confirm the proposed structure for the polymer products.

From analysis of the diblocks by DSC and X-ray diffraction it was shown for diblocks with short PCL (DP = 12) and L-PLA (DP = 13) chain segments that PCL and PLA crystalline phases were not formed. For the PHB-L-PLA [26-23] diblock copolymer, the PHB and PLA can be kinetically frozen into a solid-state morphology such that the PHB and L-PLA component chain segments are miscible. Study of a blend of (R)-PHP and L-PLA which simulated the chain lengths and weight fractions of the PHB-L-PLA [26-23] diblock components clearly showed the effects of the covalent linkage between the respective chain segments of the diblock in decreasing the rates of crystallization and phase separation.

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References and Notes

(35) (a) See: Reference 31, above, which describes the synthesis of a PCL-O-AlEt₂ macroinitiator species.
(36) (a) See ref 24, above, which describes the synthesis of a PCL-O-AlEt₂ macroinitiator species.
(37) (a) See ref 24 for a 1H NMR spectrum of PCL-O-PLA. (b) For a 2H NMR spectrum of natural-origin (R)-PHB, see: Dui, Y.; Kunioka, M.; Nakamura, Y.; Soga, K. Macromolecules 1986, 19, 1274. (c) See ref 23 for a 1H NMR spectrum of oligopoly(L-lactide).