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Synthesis and Polymerization of (*R*,*S*)-β-Pentyl-β-propiolactone

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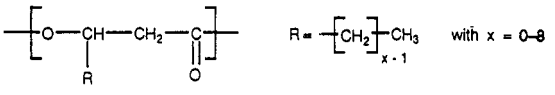
ABSTRACT: Racemic β-pentyl-β-propiolactone was synthesized in five steps and polymerized with an aluminoxane catalyst. The last step of the monomer synthesis was the pyrolysis of 2-ethoxy-2-methyl-6-pentyl-1,3-dioxan-4-one, and the side reactions which occur in this step and compete with the formation of the lactone were identified. The crude product of the polymerization of the lactone was fractionated, and the stereoregularity, crystallinity, and molecular weight of each fraction was determined. The aluminoxane catalyst gave an amorphous fraction of low molecular weight and stereoregularity and a high molecular weight fraction, which was crystalline and highly stereoregular.

Introduction

Poly[(*R*)-β-hydroxyalkanoates] (PHAs) form an interesting series of polyesters because they are potential sources of biodegradable thermoplastic materials. These polymers can be produced by a wide variety of bacteria, in which they function as intracellular carbon and energy storage products.[1-6] The best known example of this series is poly[(*R*)-β-hydroxybutyrate] (PHB) in which R = CH_3 in the following structure, but the production of this homopolymer by bacteria may be more an exception than a rule. In many cases, the PHAs, produced by microorganisms, consist of two or more different repeating units, which can have pendant groups as long as *n*-nonyl,[6] as indicated in the following structure.



PHAs with the same type of repeating units can also be obtained by the ring-opening polymerization reactions of appropriate β-monosubstituted β-propiolactones, and this reaction can also be used to prepare copolymers that are not available from the biosynthetic route. The main problem in this method is to control the stereochemistry of the ring-opening polymerization of the lactones in order to obtain a polymer with high stereoregularity because the bacterial PHAs always contain only the *R* chiral center at the β-position. That is, the bacterial polyesters are always 100% isotactic. In this report, a synthetic route is described for the preparation and the polymerization of (*R*,*S*)-β-pentyl-β-propiolactone, that is, the PHA with $x = 4$.

Several methods are known for the preparation of β-lactones, but most require intermediates that are less readily accessible than β-hydroxy acids, which can be prepared with a very high optical purity.[7-10] The cyclization of β-hydroxy acids to β-lactones has recently been carried out by a reaction of the acid with an orthoester at 50–100 °C to yield a 4-oxo-1,3-dioxane, which can be readily converted to a β-lactone by heat.[10,11] While the yield of this reaction is almost quantitative for an α-substituted β-lactone,[11] it is not very high for the preparation of β-substituted β-lactones.[10] In the present study, it was found that the preparation of (*R*,*S*)-β-pentyl-β-propiolactone by this reaction sequence was accompanied by side reactions. The products of these reactions were identified by ^1H NMR so that experimental conditions could be determined to increase the yield of the desired lactone.

The polymerization of racemic β-butyrolactone (BL) to form poly[(*R*,*S*)-β-hydroxybutyrate] (P[(*R*,*S*)-HB]) has previously been carried out by using the catalyst obtained from the reaction between either triethyl- or trimethylaluminum and water.[12-16] These aluminum-based catalysts, which are termed aluminoxanes, can yield highly stereoregular, crystalline polymers. The catalyst obtained from the reaction of diethylzinc with water, in contrast, forms only an atactic, amorphous P[(*R*,*S*)-HB]. The inability of the zinc catalyst system to give stereoregular polymers has been ascribed to the absence of coordination of the lactone monomer to the zinc atom.

This report is concerned with the polymerization of (*R*,*S*)-β-pentyl-β-propiolactone by using a catalyst ob-

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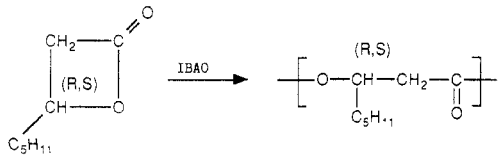
tained from the reaction of triisobutylaluminum with water, which is referred to in the discussion as the IBAO catalyst, as follows:



The polymeric products from this reaction were separated by solvent fractionation and characterized for stereoregularity, crystallinity, and molecular weight.

Experimental Section

Monomer and Polymer Characterization. ^{1}H NMR spectra were recorded on a Varian XL-300 spectrometer using $CDCl_3$ as solvent. The following abbreviations are used to present the ^{1}H NMR spectra results: s = singlet, t = triplet, m = multiplet, b = broad, vb = very broad. ^{13}C NMR spectra were recorded at 50.3 MHz on a Varian XL-200 spectrometer using $CDCl_3$ as solvent. Infrared spectra (IR) were recorded on a Perkin-Elmer Model 283 spectrometer. Gas chromatography (GC) was carried out on a Perkin-Elmer 8500 using a Durobond Carbowax megabore capillary column (15 m, 0.54 mm; He carrier gas, 17 mL/min; temperature program: 80 °C for 4 min, then temperature increased at 8 °C/min). All molecular weights reported were determined by gel permeation chromatography (GPC) using a Waters Model 6000A with a THF delivery system, a Model 401 refractive index detector, and a Model 703 data module with three Ultratyragel linear columns. Polystyrene standards with a low polydispersity were used to generate a calibration curve. The heat of fusion (ΔH_m), glass transition temperature (T_g), and melting temperature (T_m) for all polymer samples were evaluated by using a DuPont 2000 instrument on samples of 10 mg at a heating rate of 20 °C/min. The reported data are for the first heating cycle.

Monomer Preparation. The monomer was synthesized as described below and characterized by ^{1}H NMR, GC (with the exception of the hydroxy acid), and IR. Intermediate compound a in the reaction sequence shown in Scheme I was prepared as previously described in the literature[17] for the synthesis of β-ketooctanoic acid methyl esters. The procedure used for the synthesis of the lactone was similar to that previously described[10] for β-butyrolactone.

Methyl 3-Oxooctanoate (a). The dianion of methyl acetoacetate was prepared by adding 23.2 g (0.20 mol) of distilled methyl acetoacetate under an atmosphere of dry nitrogen, with continuous stirring at 0 °C, to a mixture of 500 mL of anhydrous THF and 6.60 g (0.22 mol) of sodium hydride. Stirring was continued for 30 min, and then 84 mL (0.21 mol) of a 2.5 M *n*-butyllithium solution in hexane was added while keepng the temperature at 0 °C. After 10 min of stirring, 27.4 g of butyl bromide (0.2 mol) was added dropwise at 0 °C. Stirring was continued overnight while the reaction mixture was kept in an ice bath, and then the mixture was reacted with a solution of 40 mL of concentrated hydrochloric acid in 100 mL of water while cooling again with ice. The layers were separated, the aqueous layer was extracted with ether, and the collected organic layers were washed with water, dried over magnesium sulfate, and concentrated under vacuum. The residue was distilled at 85 °C under reduced pressure to yield 18.2 g (53%) of a pure monomer: ^{1}H NMR (300 MHz, $CDCl_3$) 0.86 (t, 3 H), 1.27 (m 4 H), 1.57 (m, 2 H), 2.50 (t, 2 H), 3.43 (s, 2 H), 3.7 (s, 3 H) ppm.

Methyl 3-Hydroxyoctanoate (b). Potassium borohydride (0.72 g (13.3 mmol)) was added in small portions over a period of 30 min to a solution of 9.09 g (52.8 mmol) of methyl 3-oxooctanoate (a) in 90 mL of anhydrous ethanol while keeping the temperature at 0 °C. The mixture was stirred at 0 °C for an additional 2 h, poured into water, and extracted three times with ether. The ether extracts were washed three times with water, dried over magnesium sulfate, and concentrated under vacuum. The crude residue was distilled at 95 °C under reduced pressure to yield 7.4 g (80.5%) of methyl 3-hydroxyoctanoate: ^{1}H NMR (300 MHz, $CDCl_3$) 0.85 (t, 3 H), 1.2–1.6 (b, 6 H), 2.44 (m, 2 H), 2.62 (b, 1 H), 3.68 (s, 3 H), 3.98 (m, 1 H) ppm.

3-Hydroxyoctanoic Acid (c). A solution of 10.07 g (57.9 mmol) of the hydroxy ester b in 50 mL of ethanol was poured into a solution of 21.0 g (374 mmol) of potassium hydroxide, 400 mL of ethanol, and 20 mL of water over a period of 2 h while keeping the temperature at 0 °C. The mixture was stirred at 0 °C overnight and then concentrated to dryness under reduced pressure. The residue was dissolved in a small quantity of water, washed twice with ether, acidified with an 18% solution of hydrochloric acid in water at 0 °C, and extracted three times with chloroform. The extracts were dried over magnesium sulfate, concentrated under reduced pressure, and recrystallized in hexane to yield 7.22 g (78%) of 3-hydroxyoctanoic acid: ^{1}H NMR (300 MHz, $CDCl_3$) 0.86 (t, 3 H), 1.2–1.6 (b, 6 H), 2.51 (m, 2 H), 4.04 (b, 1 H), 6.2–7 (vb, 2 H) ppm.

2-Ethoxy-2-methyl-6-pentyl-1,3-dioxan-4-one (d). Triethyl orthoacetate (3.6 g (22 mmol)) was added dropwise over a period of 1 h at 0 °C to a solution of 3.04 g (19 mmol) of the hydroxy acid c in 30 mL of benzene. The mixture then heated to reflux during 2 h and then concentrated under reduced pressure at 20 °C to yield 4.2 of a crude product. This product could be distilled at 110 °C under low pressure to give a pure compound, but the distillate decomposed partially (50%): ^{1}H NMR (300 MHz, $CDCl_3$) 0.85 (t, 3 H), 1.17 (t, 3 H), 1.2–1.6 (b, 6 H), 1.62 (s, 3 H), 2.45 (m, 2 H), 3.6 (m, 2 H), 4.3 (m, 1 H) ppm.

β-Pentyl-β-propiolactone (e). The crude product d (10 g (43 mmol)) was heated at 85 °C with continuous stirring over a period of 11 h, after which the product was distilled under reduced pressure to yield 1.05 g (17%) of pure e. By using the pure compound of d, the same procedure gave 1.9 g (31%) of pure e: ^{1}H NMR (300 MHz, $CDCl_3$ 0.87 (t, 3 H), 1.2–1.9 (b, 6 H), 3.26 (m, 2 H), 4.49 (m, 1 H) ppm. The expanded spectrum of the 2 H region showed that the peaks at 3.26 ppm were two double doublets, as expected for an ABX system.

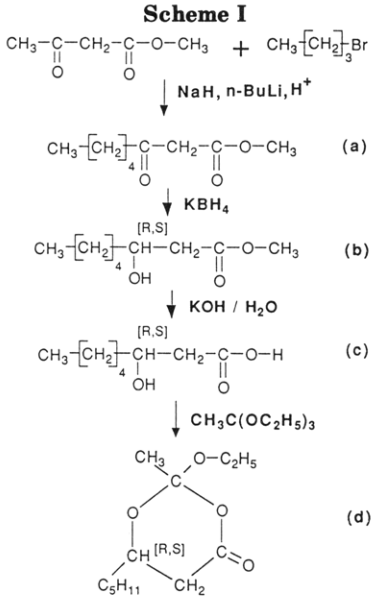
Polymerization Reaction. The aluminoxane catalyst obtained by the reaction of triisobutylaluminum with water in a 1.1:1 ratio (IBAO catalyst) was synthesized by a procedure similar to that described previously[15] for the preparation of the EAO catalyst. The polymerization of (*R,S*)-β-pentyl-β-propiolactone with the IBAO catalyst was carried out as previously described for the polymerization of (*R,S*)-BL[15] in flame-dried glassware by transferring all reactants through septum caps with a syringe under a nitrogen atmosphere. Predried β-pentyl-β-propiolactone (1 g (7 mmol)) was introduced into the polymerization ampule, and a mixture of 2.4 mL of dried hexane and 3 mL of dried toluene was added to the reactor, followed by 0.6 mL of a solution of the IBAO catalyst (0.9 mmol of Al/mL). The ampule was cooled in a liquid nitrogen bath and sealed, and the polymerization reaction was carried out at 80 °C for 10 days. Residual aluminum catalyst was removed from the polymer product by using acetylacetone (AcAc) as previously described[15] so that the amount of aluminum in the final polymer product was less than 0.1% as determined by microanalysis. The polymer fraction that was insoluble in AcAc was further fractionated by dissolution in chloroform (5 wt %) and precipitation in ethanol. The insoluble fraction so obtained was combined with hexane (0.1 wt %) and stirred at 20 °C for a period of 3 days, collected by filtration, and dried under vacuum.

Results and Discussion

Monomer Synthesis. The preparation of 2-ethoxy-2-methyl-6-pentyl-1,3-dioxan-4-one was carried out in four steps as shown in Scheme I. The crude yield for conversion of c to d was greater than 90%, but d was very difficult to isolate by distillation in a high yield because of its thermal instability. ^{1}H NMR (see Figure 1, in which all the products of decomposition of d are identified from spectra of the products obtained at each temperature used in the thermolysis) and GC analysis showed that three competing processes occurred during thermolysis of the cyclic orthoester, as shown in Scheme II.

The rate of thermolysis of d increased greatly with increasing temperature from 75 to 115 °C as shown in

Scheme I



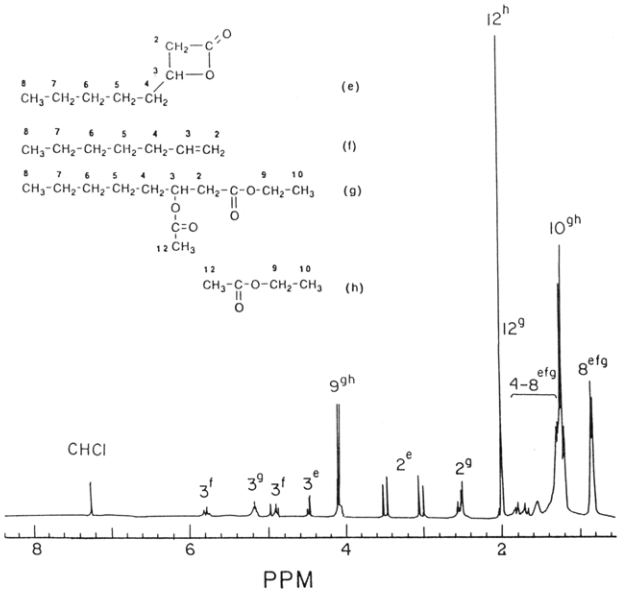


Figure 1. 300-MHz ^{1}H NMR spectrum recorded at 19 °C in $CDCl_3$ of the products of the thermolysis of d; for each of the products e–h the peak is identified by carbon number with product letter as superscript.

Scheme II

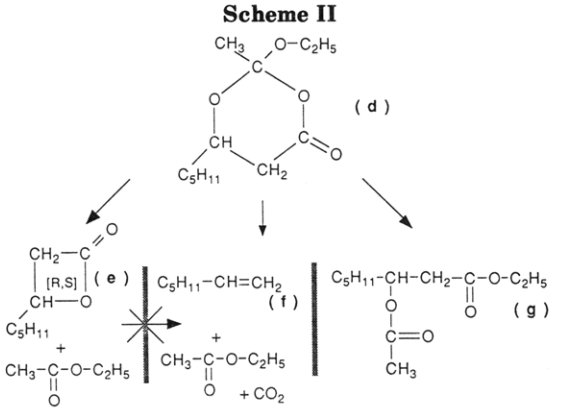


Figure 2, and the molar ratio of the three different products e–g from the decomposition of d also depended on the temperature of the thermolysis. The crude yield for formation of β-pentyl-β-propiolactone (e) went through a maximum of ca. 42% at a temperature of ca. 85 °C, as

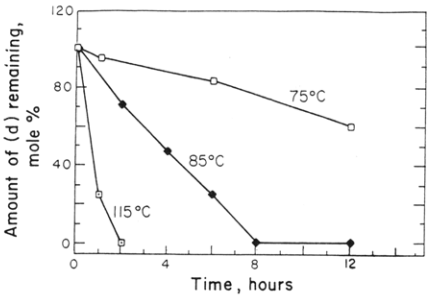


Figure 2. Decomposition of d at 115, 85, and 75 °C.

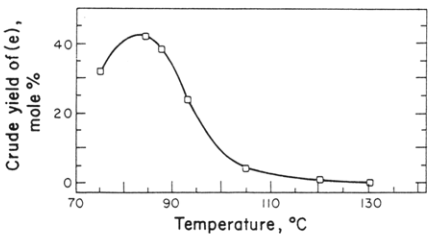


Figure 3. Formation of e as a function of temperature after complete thermolysis of d.

shown in Figure 3. At temperatures below 80 °C the formation of g was predominant, while above 90 °C a more rapid formation of 1-heptene (f) was observed, and the yield of f was almost 100% for temperatures higher than 120 °C. This compound is obtained directly from the cyclic orthoester because the β-lactone was stable at 120 °C for 2 h. That is, the orthoester can form either e, f, or g by either of three competing reactions, but above 120 °C only the reaction to form f occurred. Heating the lactone e for 2 h at 120 °C did not form f. As part of this study, it was shown that the presence of a solvent such as chloroform, pyridine, or tetramethylene sulfone or of an acid such as *p*-toluenesulfonic acid did not increase the yield of the lactone.

Polymer Characterization. The results for the characterization of the physical properties of the different fractions of polymers obtained by polymerization of e with the IBAO catalyst are given in Table I. From these results, it can be concluded that, in regard to the yields and molecular weights, the IBAO catalyst was more efficient than other aluminoxane catalysts previously used for the polymerization of BL.[14,15,18] A previous study[14] disclosed an empirical relationship between the polymerizability of β-substituted β-propiolactones by the ethylaluminoxane catalyst with respect to the effect of the substituent group in the monomer on the polymerization reaction. That is, increasing the size of the alkyl substituent was found to decrease the rate of polymerization, presumably by a cooperative effect of electronic and steric factors, so that the yield of crude polymer decreased from 78 to 26% when the methyl substituent was replaced by an ethyl group. These results suggest that the polymerizability of β-pentyl-β-propiolactone should be very low, but in the present study, the yield of the crude product was 81%. Also, in previous studies on the polymerization of (*R*,*S*)-β-butyrolactone with aluminoxane catalysts obtained from either trimethyl- or triethylaluminum, the yield of the AcAc-insoluble fractions was typically well below 50% with a value of M_n below 40 000 in all cases, but in the present study of the yield of the AcAc-insoluble fraction was 42% with an M_n value of 42 000.

The fractions obtained by solvent fractionation were characterized to determine the relationships between stereoregularity, molecular weight, and thermal behavior including glass transition (T_g), melting transition (T_m),

Table I. Physical Properties of the Fractions Obtained from the Polymerization of β-Pentyl-β-propiolactone by the IBAO Catalyst

polymer frac	yield,[a] %	M_n[b] (M_w/M_n)	isotactic diads, %[c]	T_g,[d] °C	T_m,[d] °C	ΔH_m,[d] J/g
AcAc-insoluble	42	42000 (9.8)	76	−31	78	19.5
AcAc-soluble	39	7100 (1.6)	58	−32	*e*	*e*
ethanol-insoluble[f]	35	61400 (7.9)	83	−32	78	21.5
hexane-insoluble[f]	30	82000 (6.3)	82	−33	75	27

[a] Based on amount of monomer. [b] Determined by GPC analysis with polystyrene standards. [c] From integrated areas of isotactic and syndiotactic peaks of the carbonyl carbon by ^{13}C NMR. [d] Determined by DSC in the first heating cycle. [e] No endotherm in thermogram. [f] From the AcAc-insoluble fraction.

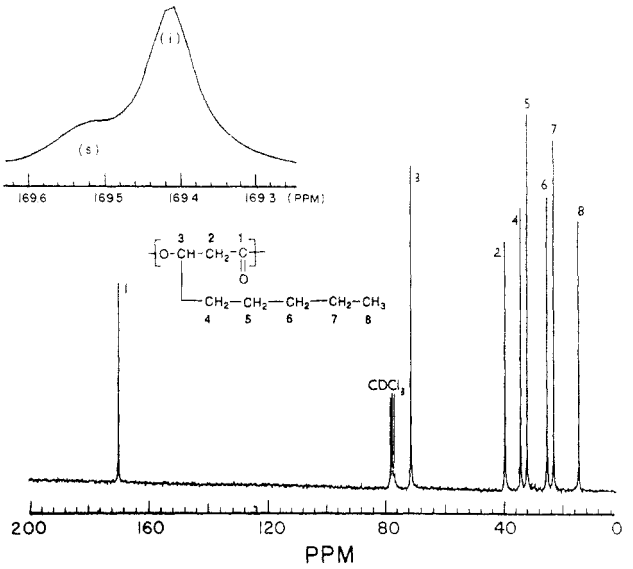


Figure 4. 50.3-MHz ^{13}C NMR spectrum recorded at 19 °C in $CDCl_3$ of the ethanol-insoluble fraction of poly[(*R,S*)-β-pentyl-β-propiolactone] with expansion of peak 1 showing syndiotactic (s) and isotactic (i) diads.

and heat of fusion (ΔH_m). The high molecular weight polymer was obtained by fractionation first with ethanol and then with hexane. The M_n value increased from 42 000 for the initial AcAc-insoluble fraction to 82 000 for the hexane-insoluble fraction. Although the GPC chromatograms of the different fractions did not show bimodal distributions, it was apparent that the product was a complex mixture of polymers because the polydispersities (M_w/M_n) remained quite high for all of the high molecular weight fractions even after fractionation. Only the low molecular weight polymer, the AcAc-soluble fraction with an M_n of 7100, had a lower polydispersity (1.6).

The stereochemical diad sequence distribution for each fraction was determined by ^{13}C NMR spectroscopy from the carbonyl carbon shift, which was sensitive to tacticity. That is, as shown in Figure 4 for the spectrum of the ethanol-insoluble fraction, diad sequences can be clearly distinguished by expansion of the carbonyl carbon region at 169 ppm so that two peaks appear. The upfield and downfield peaks correspond to isotactic (i) and syndiotactic (s) diad sequences, respectively, as previously described,[15] and the tacticity can be determined by integration of the two peaks. By this method the highest stereoregularity polymer obtained was of 83%, which is comparable to those found for the polymerization of (*R,S*)-β-butyrolactone[15] but lower than those obtained by Araki and coworkers,[19] who reported that the acetone-insoluble fraction of synthetic P[(*R,S*)-HB] had a ^{13}C NMR spectrum indistinguishable from that of the 100% isotactic, natural P[(*R*)-HB].

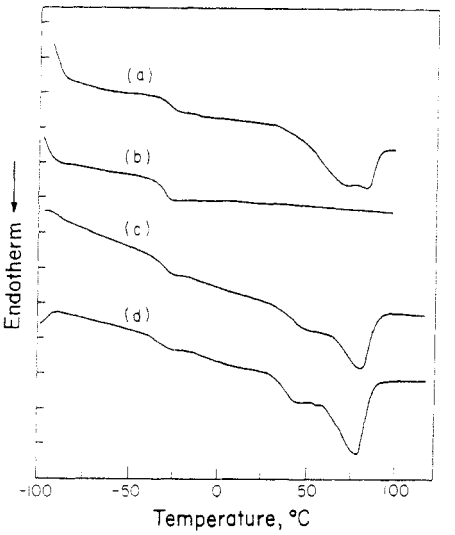


Figure 5. DSC thermograms of poly[(*R,S*)-β-pentyl β-propiolactone]: (a) AcAc-insoluble fraction: (b) AcAc-soluble fraction: (c) ethanol-insoluble; (d) hexane-insoluble fraction.

Conclusion

From the GPC and stereoregularity results shown in Table I it can be concluded that the IBAO catalyst produced fractions which had both high degrees of stereoregularity and high molecular weights (the ethanol- and hexane-insoluble fractions) and a fraction which had a much lower degree of stereoregularity and molecular weight (the AcAc-soluble fraction). This observation suggests that the IBAO catalyst had at least two different types of active centers, as previously reported[15] for the EAO catalyst. IBAO was used in the present study because our earlier studies with β-butyrolactone showed that this aluminoxane was a much better catalyst than either MAO or EAO.[20]

The DSC thermograms of the four different fractions are collected in Figure 5. Thermograms a, c, and d show glass transitions and melting endotherms, but thermogram b exhibits only a glass transition. From these results, and those of the ^{13}C NMR and GPC, the following conclusions can be made:

(1) The IBAO catalyst produced a complex polymeric product which could be separated into a high molecular weight, highly crystalline fraction, as indicated by wide-angle X-ray diffraction (AcAc-insoluble fraction; M_n = 42000, ΔH_m = 19.5 J·g^{-1}), and a low molecular weight amorphous fraction (AcAc-soluble fraction; M_n = 7100, no melting peak); this observation is consistent with the proposal that the catalyst contains two different active sites.

(2) The degree of crystallinity of the polymer increased by dissolving the low-tacticity fraction of the AcAc-insoluble fraction in ethanol and in hexane. The heat of fusion (see Table I) increased from 19.5 J·g^{-1} for the AcAc-insoluble-fraction, to 22 J·g^{-1} for the ethanol-insoluble fraction, to 27.5 J·g^{-1} for the hexane-insoluble fraction. The melting transition temperatures for the three insoluble fractions are also reported in Table I. The endothermic peaks of these transitions were quite broad, and the peak temperatures reported in Table I, although slightly different, are believed to represent essentially the same melt transition temperatures. The first fractionation caused the removal of a low molecular weight and low stereoregular polymer fraction, and the second fractionation apparently removed additional low molecular weight polymer so that the stereoregularity was essentially the

same, but the molecular weight increased and the polydispersity decreased.

(3) The shoulders observed on the low-temperature side of the DSC melting endotherms cannot be explained at present, but it is likely that they represent premelting of imperfect crystalline regions.

(4) The peak transition temperatures were almost independent of the molecular weight and stereoregularity, and only the breadth and the area of the melting peak endotherms were different in each case.

(5) Poly[(*R*,*S*)-β-pentyl-β-propiolactone] prepared in this study can be compared to a similar polymer produced by the bacterium *Pseudomonas oleovorans* grown with *n*-octanoic acid. The bacterial polymer is a copolymer containing 85–90 wt % of (*R*)-β-hydroxyoctanoate units, and the polymer with 85% octanoate units has a melting temperature and a heat of fusion of 55 °C and 18 J·g^{-1}, respectively. The higher values (T_m = 75 °C, ΔH_m = 27.5 J·g^{-1}) of the present polymer are to be expected because the bacterial PHO is a copolymer, but another explanation may be that the present stereoregular poly[(*R*,*S*)-β-pentyl-β-propiolactone] may be able to form an internal stereocomplex between the *R*- and *S*-segments of the chains, as has been observed, for example, for (*R*)- and (*S*)-polylactides[21] and for blends of isotactic and syndiotactic poly(methyl methacrylates).[22] This possibility will be considered further in a subsequent report on the synthesis and polymerization of monomer e of high optical purity.[23]

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