Synthesis, characterization and crystallization behaviour of stereoregular poly-β-hydroxyoctanoate

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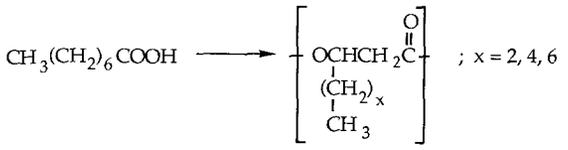
(*S*)-β-Pentyl-β-propiolactone ((*S*)-PPL) was prepared in five steps with an optical purity in excess of 97% starting from the optically pure copolymer produced by *Pseudomonas oleovorans* when grown with n-octanoic acid. The copolymer contained approximately 85 mol% of β-hydroxyoctanoate units; $x=4$, in the structure shown below.



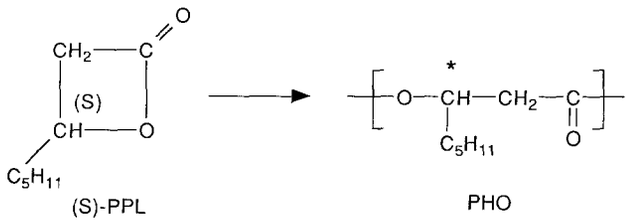
The remainder of the copolymer was hexanoate, $x=2$, and decanoate, $x=6$, units. (*S*)-PPL was polymerized to the opticaly active homopolymer, poly-β-hydroxyoctanoate (PHO) by the ring-opening polymerization of this lactone with aluminoxane and zinc alkyl catalysts. The stereochemical configurations and isomeric purities of the repeating units of the polymers obtained were determined by degrading the polymers to methyl β-hydroxyoctanoate and analysis by 250 MHz ^{1}H n.m.r. spectroscopy of the complexes of these methyl esters with a chiral europium shift reagent. The diad stereochemical sequence distributions of the polymers were determined by 50.3 MHz ^{13}C n.m.r. spectroscopy. The isothermal rates of crystallization were determined by differential scanning calorimetry (d.s.c.) for the bacterial copolymer and for two synthetic PHOs: a racemic P[(*R*,*S*)-HO], and an optically active P[(*R*)-HO]. The synthetic P[(*R*)-HO] had a higher enthalpy of fusion and a faster crystallization rate than the racemic PHO, which had a higher enthalpy of fusion and a faster crystallization rate than the bacterial PHO. These differences were explained in terms of the stereoregularities and compositions of the different polymers.

(Keywords: poly-β-hydroxyoctanoate; characterization; crystallization)

INTRODUCTION

Poly-β-substituted-β-hydroxyalkanoates (PHAs) can be obtained either from bacteria, as high molecular weight, isotactic, optically pure polymers having an (*R*)-configuration at the chiral β-carbon[1–7], or as highly isotactic, medium molecular weight polymers by the stereoregular polymerization of β-substituted-β-propiolactones with aluminoxane catalysts[8–15]. In the latter type of polymerization reaction, the ring opening of the lactone can proceed by bond breaking either between the carbonyl carbon and the oxygen atom of the lactone ring (acyl cleavage) or between the β-carbon and the oxygen atom (alkyl cleavage). In a recent study[16] in this laboratory, (*S*)-butyrolactone ((*S*)-BL), was used as a stereochemical probe to determine the mode of ring opening with three different coordination catalysts that have been used to prepare poly-β-butyrolactone (PBL) from this monomer.

In this report, a synthetic route is described for the preparation of (*S*)-β-pentyl-β-propiolactone ((*S*)-β-octanolactone) ((*S*)-PPL), in high optical purity by starting with a bacterial copolyester that contains in its structure a high proportion of (*R*)-β-hydroxyoctanoate ((*R*)-HO) repeating units. (*S*)-PPL was polymerized by using different coordination catalysts to yield optically active poly-β-pentyl-β-propiolactone, which is referred to as poly-β-hydroxyoctanoate (PHO) in this report because of its close similarity to the inclusion body polyester produced by the bacterium *Pseudomonas oleovorans* when it is grown with octanoic acid under limiting conditions[5,6].



(S)-PPL PHO

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Three different catalysts were evaluated: (1) a catalyst prepared by the reaction of triisobutylaluminium ($Al(iBu)_3$) with water in a 1:1 molar ratio (IBAO); (2) a catalyst prepared by the reaction of diethylzinc ($ZnEt_2$) with water (EZO); and (3) a commercial trimethylaluminoxane catalyst (MAO). The stereoregularities of the polymers and the configurations and isomeric purities of the repeating units were evaluated in order to determine the mode of ring opening of the lactone. It was also of interest to evaluate the crystallization behaviour of these synthetic polymers because it has been shown that bacterial PHO crystallizes very slowly[17]. Bacterial PHO is perfectly isotactic, with units having 100%(*R*)-configuration at the chiral β-carbon, but it is a copolymer containing from 5 to 15% of other units, while synthetic PHO prepared in this study is less than perfectly isotactic; both factors strongly affect crystallization behaviour.

An example of the effect of tacticity on crystalline properties is the behaviour of poly(α-methyl-α-ethyl-β-propiolactone) (PMEPL). The optically active, isotactic PMEPL always has higher equilibrium melting points, enthalpies of fusion and crystallization rates than the racemic (presumably atactic) PMEPL[18]. Similarly for polypropylene[19], the classic case, it is well known that the degree of isotacticity strongly influences crystalline morphology, including the crystallite size and lamellar crystal thickness, degree of crystallinity and the equilibrium melting temperature, T_m, and heat of fusion, ΔH_m. Another parameter that can have a significant effect on the crystallization of polymers is the molecular weight. One polymer that has been thoroughly studied for this effect is poly(ethylene terephthalate) (PET). The molecular weight of PET is well known to be important in controlling several crystallization parameters[20,21].

It was also of interest to the present study to consider that polymer–polymer complexes can form between two polymers with identical chemical compositions but opposite configurations. The formation of such stereocomplexes presumably arises from specific interactions between the two different polymers. Polymer pairs that form such complexes include: (1) either isotactic and syndiotactic poly(methyl methacrylate) (PMMA)[22] or isotactic PMMA and syndiotactic poly(methyl acrylate) (PMA)[23]; (2) optically active poly(benzyl-L-glutamate) and poly(benzyl-D-glutamate)[24–26]; (3) optically active polymers of (*R*)- and (*S*)-α-methyl-α-ethyl-β-propiolactone[18]; (4) isotactic polymers of (*R*)- and (*S*)-tert-butylthiiranes[27]; (5) isotactic polymers of (*R*)-(+)-and (*S*)-(−)-α-methylbenzyl acrylates[28]; and (6) (*R*)- and (*S*)-polylactide[29,30].

EXPERIMENTAL

Monomer and polymer characterization

^{1}H n.m.r. spectra were recorded on a Varian XL-300 spectrometer using $CDCl_3$ as solvent. ^{13}C n.m.r. spectra were recorded at 50.3 MHz on a Varian XL-200 spectrometer using $CDCl_3$ as solvent. Infra-red (i.r.) spectra were recorded on a Perkin–Elmer model 283 spectrometer. Gas chromatography (g.c.) analyses were carried out on a Perkin–Elmer 8500 with a Durobond Carbowax Megabore capillary column (15 m × 0.54 mm); carrier gas He, 17 ml min^{-1}; temperature programme, 80°C for 4 min then increased at 8°C min^{-1}. All molecular weights reported were determined by gel permeation chromatography (g.p.c.) using a Waters Model 6000A THF delivery system, model 401 refractive index detector, and model 703 data module with three Ultrastyragel 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^{-1}. The data reported are for the first heating cycle.

Monomer preparation

The monomers were synthesized as described below and characterized by ^{1}H n.m.r., g.c. (with the exception of the hydroxyacid) and i.r. The procedure used for the synthesis of the optically pure β-pentyl-β-propiolactone (PPL) was similar to that described previously[31] for (*S*)-BL and to that previously applied for the synthesis of the racemic β-pentyl-β-propiolactone ((*R*,*S*)-PPL)[32].

Methyl (R)*-3-hydroxyoctanoate.* Bacterial PHO, prepared as previously described[33] (120 g, 91 wt% of C8 units) was dissolved in 2500 ml of chloroform at room temperature, then 1500 ml of acidified methanol (5 wt%) was added within 10 min. The mixture was refluxed for 72 h. After cooling the solution to room temperature, 1500 ml of a half-saturated NaCl solution was added and the product was extracted three times with 1000 ml chloroform. The organic extracts were dried over $MgSO_4$ for 48 h and concentrated at room temperature under vacuum. The remaining residue was distilled with a Vigreux column under high vacuum to yield 70 g of pure methyl (*R*)-3-hydroxyoctanoate.

Polymerization reactions

The catalysts IBAO and EZO were synthesized by procedures similar to those described previously[15]. The catalyst MAO was purchased from Aldrich Co. The polymerization of (*S*)-PPL was carried out as described previously 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. Residual catalyst was removed from the polymer product by using acetylacetone (AcAc) as previously described[15], so that the amount of catalyst in the final polymer product was less than 0.1%.

Isothermal crystallization

The bacterial (*R*)-PHO, which was 100% isotactic, was produced in our laboratory by an improved procedure[33]. *Pseudomonas oleovorans* was grown with n-octanoic acid as the carbon source, and the content of (*R*)-β-hydroxyoctanoate units in the PHO obtained was determined by methanolysis to the hydroxyesters and g.c. analysis using the internal standardization method with decyl alcohol. The content of the C_8 units ranged from 85 to 95 wt% with the other 5–15% being (*R*)-β-hydroxyhexanoate and (*R*)-β-hydroxydecanoate units. The racemic (*R*,*S*)-PHO, which was 82% isotactic, was prepared as described previously[32]. The optically active (*R*)-PHO was prepared in the present study. The crystallization rates of these PHOs were determined using a DuPont 2000 DSC instrument on samples of 10 mg.

Table 1 Polymerization conditions and polymer yields

Polymer	Monomer configuration	Catalyst	Metal/monomer mole ratio	Polymerization temperature (°C)	Polymerization time (days)	Polymer yield[a] Crude (%)	Polymer yield[a] After AcAc treatment[a] (%)
P1	(*R,S*)	IBAO	7	80	7	81	42
P2	(*S*)	IBAO	8	80	10	100	>95
P3	(*S*)	EZO	1	80	12	68	20
P4	(*S*)	MAO	7	80	10	75	5

[a] Based on amount of monomer

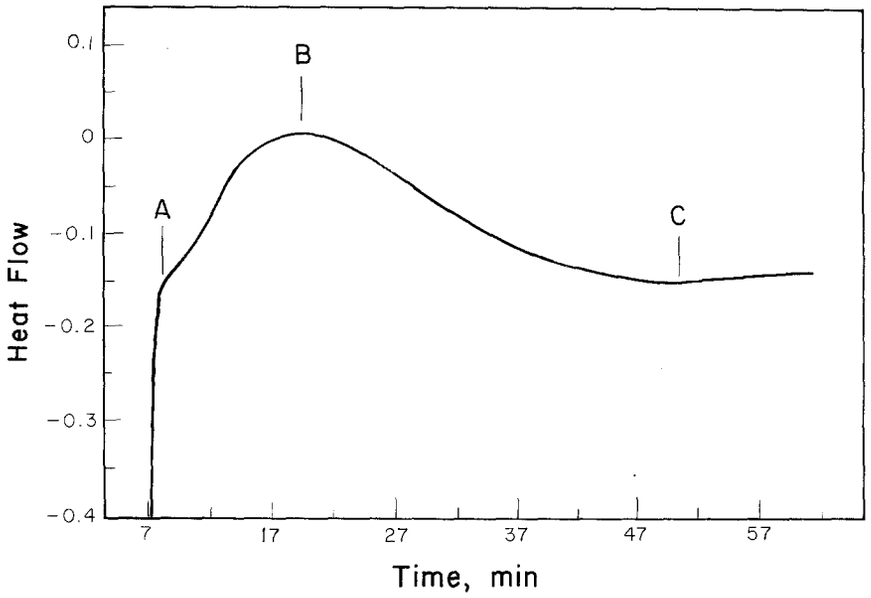


Figure 1 Heat flow *versus* time during isothermal crystallization of the optically active (*R*)-PHO at 28°C

The thermogram temperatures were calibrated using the transition temperature of indium (156°C) as the standard with dry nitrogen as the sweep gas.

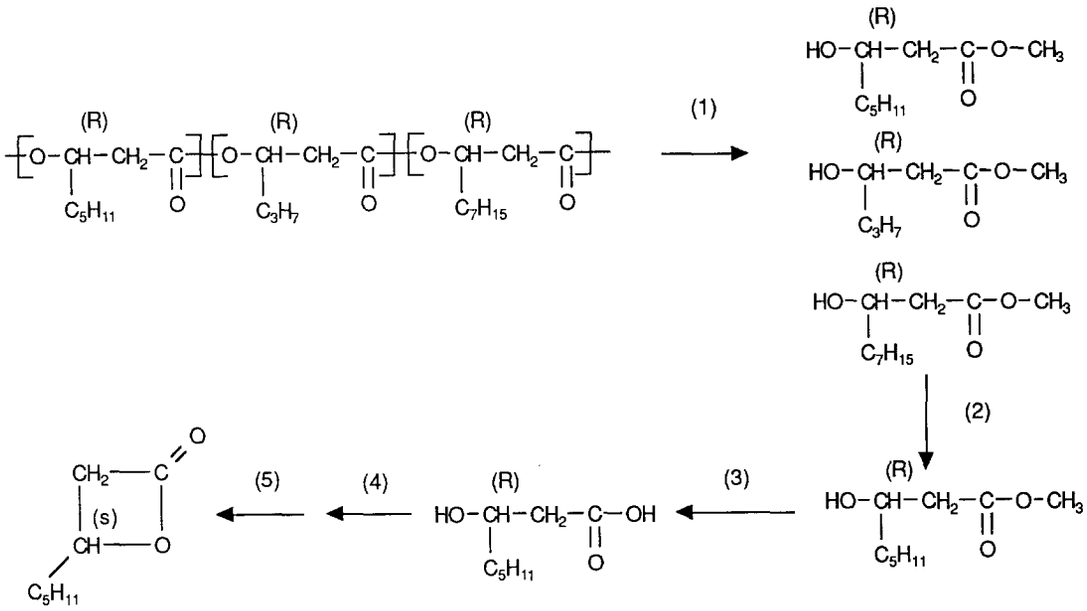
For all of the PHOs studied, the samples were first heated to 20°C above the d.s.c. melting transition peak and kept at that temperature for 5 min to ensure that complete melting had occurred. For the racemic and the bacterial PHOs, the samples were then cooled to the crystallization temperature and kept at that temperature for a given time, after which the samples were cooled quickly to −100°C, then heated to 125°C at 20°C min^{-1}. The thermogram was recorded for the last steps. For the optically active (*R*)-PHO, P2 in *Table 1*, the DuPont 2000 DSC instrument was used to monitor the heat flow from the sample during crystallization. Isothermal crystallization was carried out either by cooling the polymer melt or by heating the amorphous polymer film above the glass temperature. The high temperature crystallization was carried out by cooling the polymer melt quickly to the crystallization temperature. For crystallization at low temperature, the polymer melt was quenched, and the sample was inserted into the calorimeter cell, which was preheated to the crystallization temperature. The corresponding crystallization exotherm was recorded as a function of time until no change was observed. An example of the heat flow during the isothermal crystallization of the (*R*)-PHO is shown in the d.s.c. thermogram in *Figure 1*. Non-isothermal crystallization studies were also made on polymer blends, which were prepared by dissolving given amounts of the polymers (5 wt%) in chloroform, stirring the solution for 48 h at room temperature, slowly evaporating the solvent at room temperature and pressure, and drying at room temperature under low pressure.

RESULTS AND DISCUSSION

Monomer synthesis

The preparation of the optically pure (*S*)-PPL was carried out in five steps, as shown in *Scheme 1*.

This procedure for the synthesis of the (*S*)-PPL was similar to that described previously[31] for the synthesis of (*S*)-BL, but steps 3–5 were studied in considerable detail in our earlier study on the synthesis of (*R,S*)-PPL[33]. The optical purities of the optically active, intermediate hydroxyesters and of the final lactone were determined by comparison of their ^1H n.m.r. spectra with those of their racemic compounds when both were complexed with the chiral shift reagent tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]-europium. *Figure 2* shows the ^1H n.m.r. spectra of (*S*)-PPL with expansions of the methylene regions of both (*S*)-PPL



Scheme 1

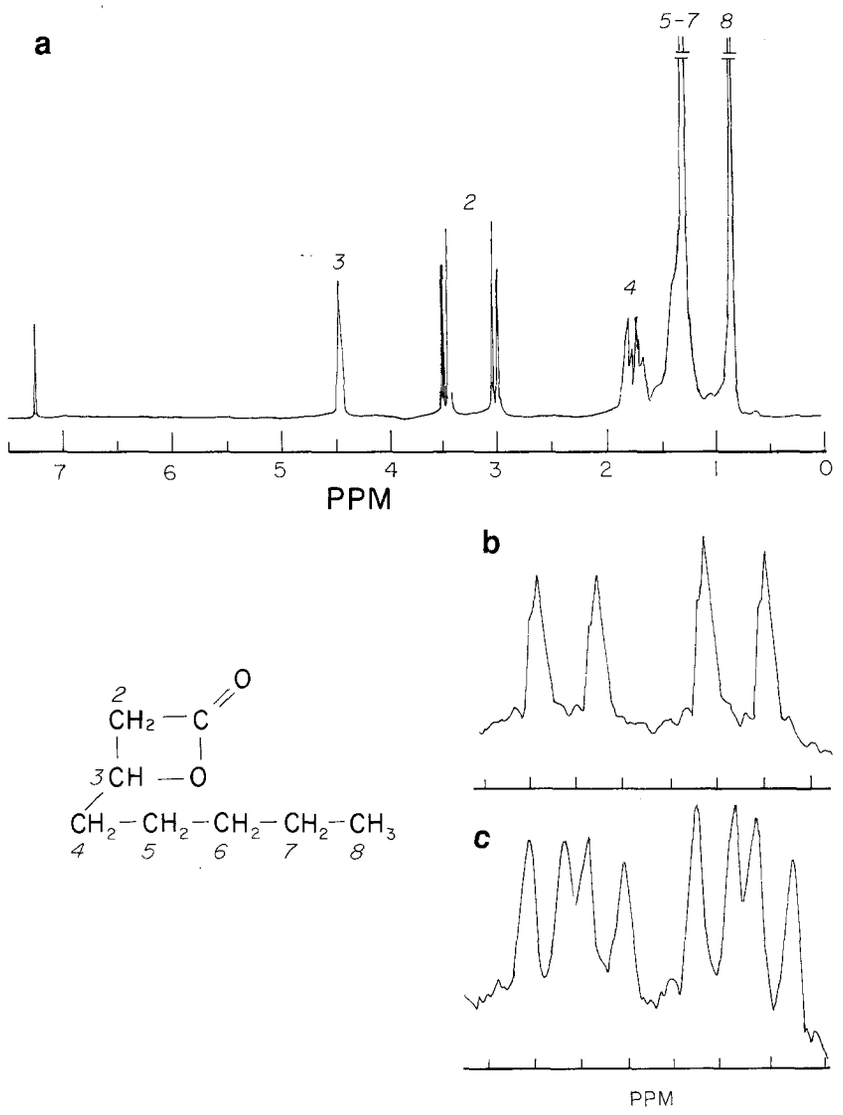


Figure 2 The ^1H n.m.r. spectrum (250 MHz) recorded at 19°C in $CDCl_3$ for (*S*)-PPL (a), and expansions of the methylene region, 2, of (*S*)-PPL (b) and of (*R,S*)-PPL (c), each of which was complexed with 20 mol% $Eu(hfc)_3$

Table 2 Physical properties of the fractions obtained from the polymerization of β-pentyl-β-propiolactone (PPL)

Polymer	Catalyst	T_g[a] (°C)	T_m[a] (°C)	ΔH_m[a] (J g^{-1})	Isotactic diads[b] (%)	Isomeric purity[c]	M_n[d] (M_w/M_n)
Bacterial (*R*)-PHO	–	−32	55	19	100	100%(*R*)	60000 (2.2)
P1	IBAO	−33	75	28	28	Racemic	82000 (8.3)
P2	IBAO	−32	72	37	~100	75%(*R*)	48000 (5.8)
P3	EZO	−35	63	36	~100	~100%(*S*)	8500
P4	MAO	−34	46	0.8	>90	>95%(*S*)	3500 (13.2)

[a] Determined by d.s.c. in the first heating cycle
[b] From integrated area of isotactic and syndiotactic peaks of the carbonyl carbon by ^{13}C n.m.r.
[c] Determined by methanolysis of the polymer samples to their corresponding methyl β-hydroxyoctanoate followed by ^{1}H n.m.r. analysis in the presence of Eu(hfc)$_3$
[d] Determined by g.p.c. analysis with polystyrene standards

and (*R,S*)-PPL in the presence of 20 mol% of the shift reagent. The expanded spectrum for (*R,S*)-PPL in *Figure 2c* contains two quadruplets. The higher field quadruplet was assigned to the methylene hydrogen atoms, 2, of the (*R*) enantiomer, by analysing a mixture of PPL stereoisomers. The expanded spectrum for (*S*)-PPL (*Figure 2b*) is predominantly a single quadruplet. From this analysis, it was determined that the sample of (*S*)-PPL analysed in *Figure 2* had an optical purity in excess of 97%.

Polymer characterization

The polymerization conditions for (*S*)-PPL and the polymer yields before and after extraction of the crude polymer with a solution of AcAc, which was used to remove the aluminium residue from the product, are summarized in *Table 1*. For comparison, the data for the polymerization of the racemic PPL are also reported in this table. The results from the characterization of the physical properties of the polymers obtained are given in *Table 2*. The stereochemical diad sequence distributions for all of the polymers of *Table 2* were determined by ^{13}C n.m.r. spectroscopy based on the carbonyl carbon atom, the chemical shift of which was sensitive to tacticity. The expansion of the carbonyl regions of the ^{13}C n.m.r. spectra of both the polymer obtained from the polymerization of (*S*)-β-PPL and the bacterial (*R*)-PHO are shown in *Figures 3a–d*. The stereoregularity of the racemic (*R,S*)-PHO was characterized previously, and the isotactic (i) and syndiotactic (s) diads were assigned as described previously[33]. Only one peak is oberved in the expansions of the bacterial polymer spectrum and in the spectra of polymers P2 and P3, indicating that all three polymers were highly isotactic. The expansion of the spectrum of polymer P4 is much broader and suggests a lower stereoregularity.

The stereoisomeric purities of the repeating units of each of the polymers were determined by the acid-catalysed methanolysis of the polymers to the constituent methyl β-hydroxyoctanoates, which were complexed with the shift reagent Eu(hfc)$_3$. The expansions of the peaks for the methyl protons, 11, in the ^{1}H n.m.r. spectra of all of the polymers of *Table 2*, as shown in *Figures 4b–f*, were used to determine tacticities. The upfield signal in these spectra was assigned to the (*R*)-stereoisomer and the downfield signal to the (*S*)-stereoisomer with the results shown in *Table 2*.

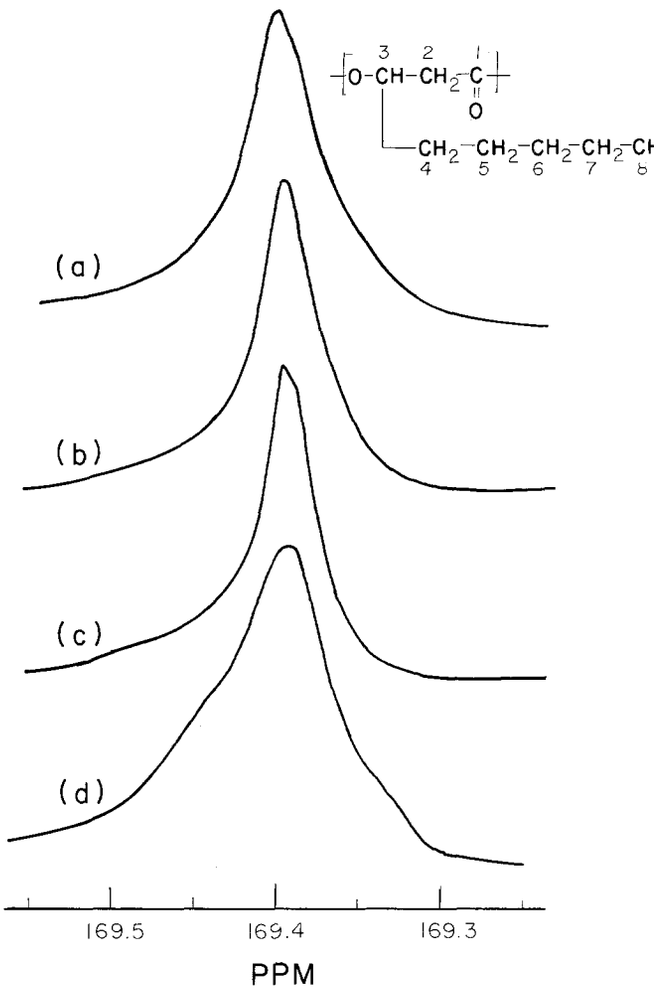


Figure 3 Expansion of the carbonyl region of the ^{13}C n.m.r. spectrum (50.3 MHz) recorded at 19°C in $CDCl_3$ for: (a) bacterial PHO; (b) polymer P2; (c) polymer P3; (d) polymer P4

From the results collected in *Tables 1* and *2*, the following conclusions can be made.

(1) The catalyst IBAO, in the polymerization reaction of both the racemic and the optically pure PPL monomers

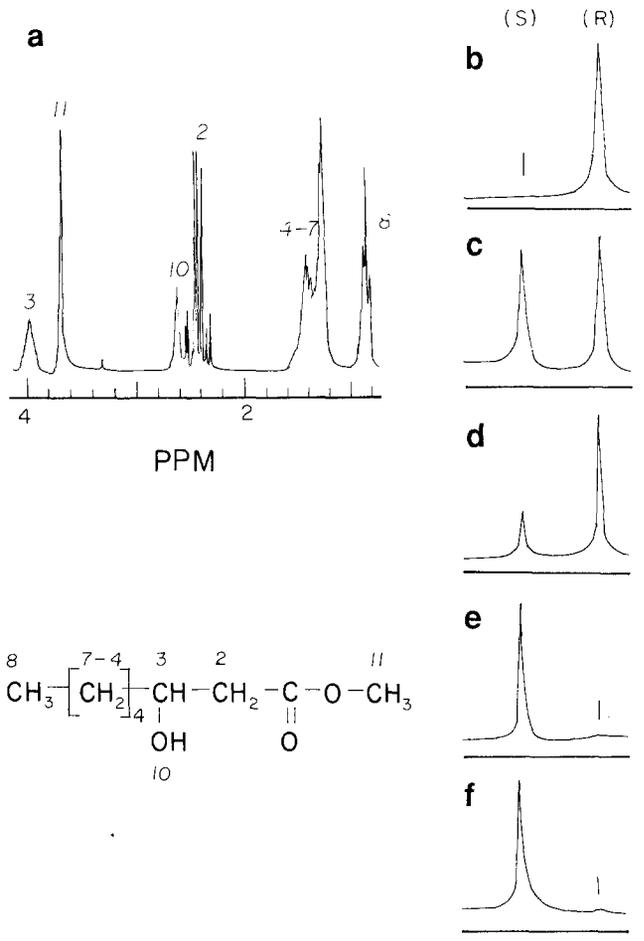


Figure 4 Expansion of the methyl ester hydrogen region, 11, from: (a) the ^{1}H n.m.r. spectra (250 MHz), recorded at 19°C in $CDCl_3$ in the presence of 20 mol% $Eu(hfc)_3$, of the methyl β-hydroxyoctanoate stereoisomers obtained from the methanolysis of: (b) bacterial PHO; (c) polymer P1; (d) polymer P2; (e) polymer P3; (f) polymer P4

(polymers P1 and P2, respectively), gave high molecular weight polymers with yields greater than 80% after AcAc treatment. These results are consistent with previous reports from this laboratory on the polymerization of racemic BL using IBAO as catalyst[33]. For the polymerization of the (*S*)-PPL, the mode of ring opening proceeded primarily by bond breaking between the β-carbon and oxygen of the lactone ring (alkyl cleavage) with 75% inversion of configuration (*Table 2*), but because syndiotactic diads were not detectable by ^{13}C n.m.r., it can be concluded that the polymeric product was highly stereoregular and close to 100% isotactic (*Table 2*). Therefore, P2 must be either a mixture of (*R*) and (*S*) homopolymers or a stereoblock copolymer with very long (*R*) and (*S*) blocks.

(2) With the zinc catalyst, EZO, the ring opening occurred by acyl cleavage with retention of configuration in excess of 97%, as was previously observed for the polymerization of (*S*)-BL[16]. The polymer obtained was highly stereoregular and isotactic but had a number-average molecular weight much lower ($M_n = 8500$) than that of the polymer obtained with the IBAO catalyst ($M_n = 48\,000$).

(3) The mode of ring opening with the catalyst MAO involved cleavage of the bond between the β-carbon and oxygen of the lactone with retention of configuration equal to 95%, but the M_n of the polymer obtained was very low (3500) and, as a result, the degree of crystallinity was also very low.

(4) The optically active polymers P2 and P3, which were obtained with both the IBAO and the EZO catalysts, had heats of fusion of 37.4 and 36.2 J g^{-1}, respectively, which were much higher than that of the racemic polymer (27.6 J g^{-1}), which in turn had a higher value than that of the bacterial polymer.

Crystallization rates

Isothermal crystallization of 75%-(R)-PHO, polymer P2. The thermogram in *Figure 1* shows the heat flow from polymer P2 during crystallization, as monitored by d.s.c. It is seen in this figure that crystallization began at A, reached an apparent maximum rate at B and was concluded by C, so for the analysis below the origin of the crystallization time, $t = 0$ min, was taken at point A. From analysis of the peak area, the relative degree of crystallinity, $x(t)$, of the polymer at any time t can be calculated according to the equation:

$$x(t) = \int_0^t (dH/dt)dt \Big/ \int_0^\infty (dH/dt)dt$$

for which $t = 0$ at point A and $t = \infty$ at the end of the crystallization (point C). Point C is the time at which 100% of attainable crystallinity is achieved for those conditions. Hence, the function $x(t)$ is the reduced crystallinity because it relates the instant crystallinity to the total that can be attained under the experimental conditions, so by equating the integrals to areas, the reduced crystallinity is obtained from the equation:

$$x(t) = A_t/A_\infty$$

in which A_t is the area under the d.s.c. curve from $t = 0$ to $t = t$, and A_∞ is the total area under the crystallization curve.

The plots of $x(t)$ *versus* t for each temperature of crystallization, T_c, are shown in *Figure 5*. The isotherms obtained were reproducible if the experiments were conducted in such a manner that the polymer sample was completely molten and degradation processes were avoided before crystallization. From *Figure 5* it was possible to evaluate either the rate of crystallization, V_c, which corresponds to the straight line section of the plot, or the time of half-crystallization, $t_{1/2}$, which is the time when the reduced crystallinity reached a value of 0.5, and is also a measure of the rate. The dependence of these values on T_c is given in *Figure 6*.

The minimum in the plot in *Figure 6* corresponds to a $t_{1/2}$ of less than 5 min for a temperature of maximum crystallization rate, T_{cmax}, of 10°C. This $t_{1/2}$ is not an absolute value because the origin, which is taken when the thermal equilibrium is reached, depends on the sensitivity of the experimental instrument used to measure crystallinity. However, this parameter provides a good estimate of the relative rates of crystallization of a family of polymers.

Isothermal crystallization of bacterial PHO and racemic PHO, polymer P1. It was not possible to follow the process of crystallization in real time by d.s.c. for these two polymers because the sensitivity of the method and the rates of crystallization were too low for both. A study of the crystallization behaviour of the bacterial PHO was recently carried out in this laboratory[33], and it was shown

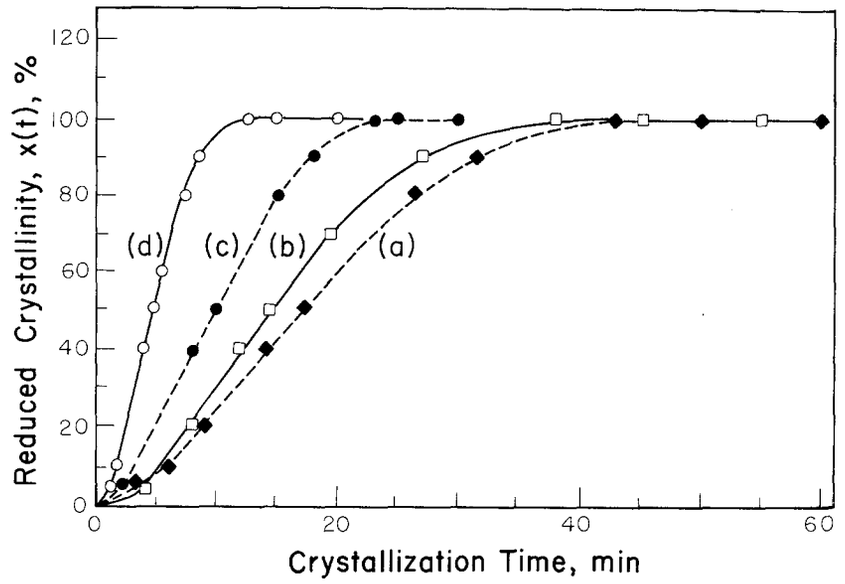


Figure 5 Increase in reduced crystallinity with time for the isothermal crystallization of polymer P2 crystallized from the melt at (a) 28.4°C, (b) 27.8°C, (c) 20.2°C, (d) 9.7°C

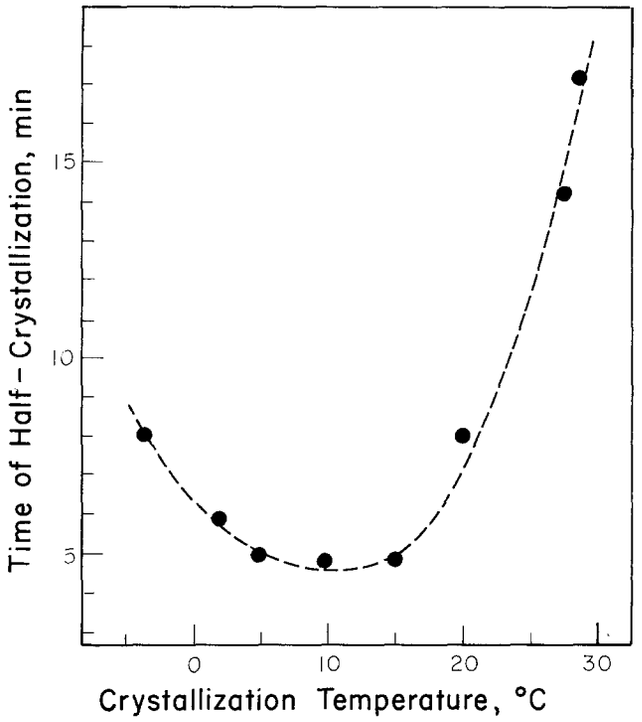


Figure 6 Crystallization half-time, $t_{1/2}$, of polymer P2 as a function of the temperature of crystallization

that the maximum value of ΔH_m after 24 h of isothermal crystallization was obtained at $T_c = 4$–5°C. It can be assumed that this maximum also corresponds to the highest rate of crystallization, so this temperature was used to evaluate crystallization kinetics in the present study. The corresponding isotherm so obtained is shown in *Figure 7a*. From this plot it was possible to determine the $t_{1/2}$, which was found to be approximately 85 min.

The crystallization rate of (*R,S*)-PHO was assumed to have a maximum at approximately 10°C, as was the case for (*R*)-PHO (*Figure 6*). A recent study[32] established the following relation between T_m and T_{cmax}: $T_{cmax}/T_m = C/(C+1)$ and $C = (1 + \Delta E/K)^{1/2}$, in which ΔE is an activation energy on the nucleation process and K is a nucleation parameter. This relation is believed to be true for many polymers[34], and because the T_m values are similar for the racemic and the optically active polymers, T_{cmax} values should also be similar. In this regard, it was found that at between 8 and 12°C there was no increase in crystallization rate for (*R*)-PHO. The isothermal rate at 10°C for (*R,S*)-PHO is shown in *Figure 7b*, from which the $t_{1/2}$ was found to be 25 min.

The minimum times of half-crystallization for the three polymers studied are compared in *Figure 8*. It is apparent that the crystallization behaviour in this family of polymers, especially the rate of crystallization, is strongly dependent on both the stereochemical structure and composition of the polymer. The difference between the value for $t_{1/2}$ of the bacterial PHO and of the synthetic PHO was due primarily to the fact that the co-units (the C_6 and C_{10} units) in the bacterial PHO were defects in the chains, which inhibited crystallization.

Polymer blends

To further elucidate the effect of the stereoregularity of the polymer on its crystallization kinetics, two mixtures of two PHOs, PB1 and PB2, were prepared by blending the polymers in different proportions. The two PHOs in both blends were P2, (the 75% (*R*)-PHO, 100% isotactic) and P3 (the 100% (*S*)-PHO, 100% isotactic). The first blend, PB1, containing 66 wt% of P2 and 33 wt% of P3, corresponded in composition to a highly stereoregular racemic polymer (either a mixture of (*R*) and (*S*) homopolymers or an (*R,S*) stereoblock copolymer), and its crystallization behaviour may be comparable to that of the synthetic racemic polymer P1, which was 83% isotactic (probably a stereoblock copolymer). The second blend, PB2, containing 33 wt% of P2 and 66 wt% of P3, corresponded in composition to a highly stereoregular polymer containing 75% (*S*)-units. This latter blend represented a stereochemical homologue of the polymer P2 but of opposite isomeric purity. A comparison of the crystallization behaviour of these blends with the other polymers studied was made for the rate of crystallization

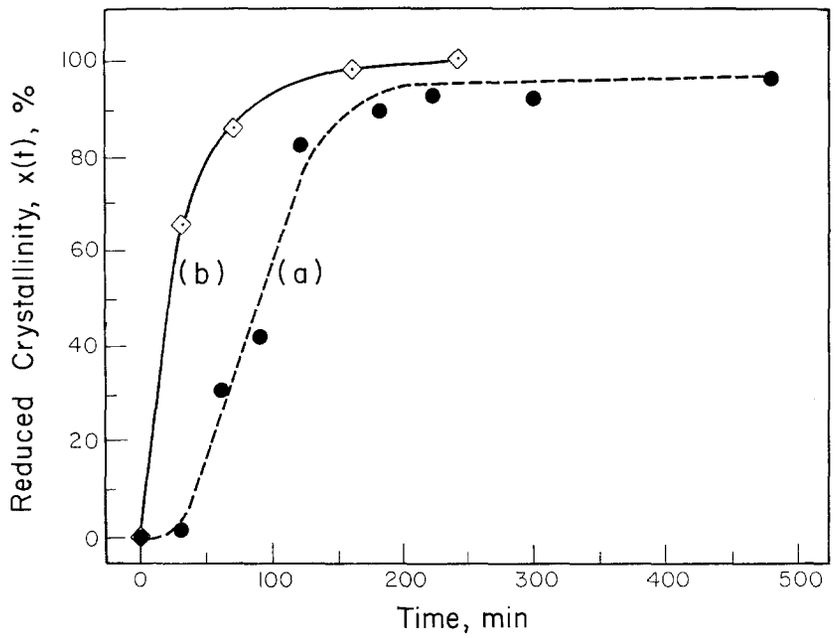


Figure 7 Reduced crystallinity as a function of crystallization time for: (a) bacterial PHO, $T_c = 4.5°C$; (b) racemic PHO (P1), $T_c = 10°C$

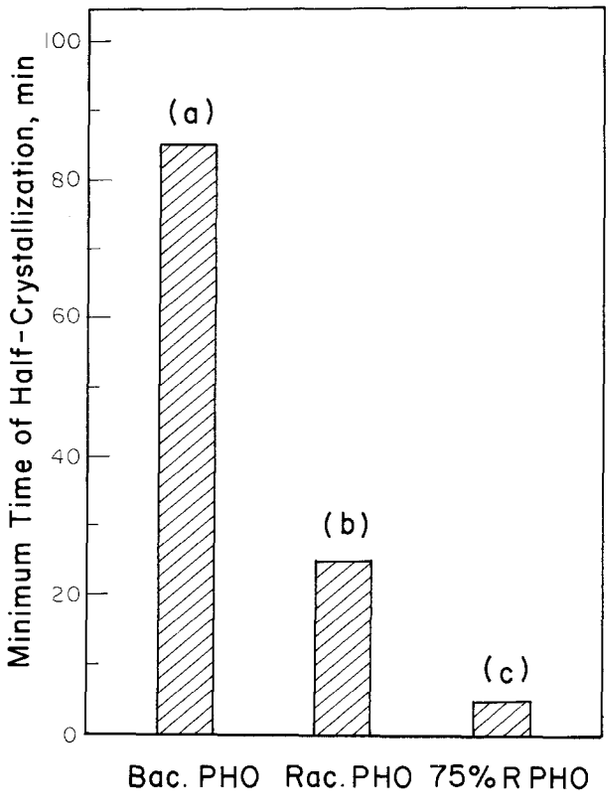


Figure 8 Comparison of the minimum time of half-crystallization of (a) bacterial PHO, $T_c = 4.5°C$; (b) racemic PHO (P1), $T_c = 10°C$; and (c) 75%(*R*)-PHO (P2), $T_c = 10°C$

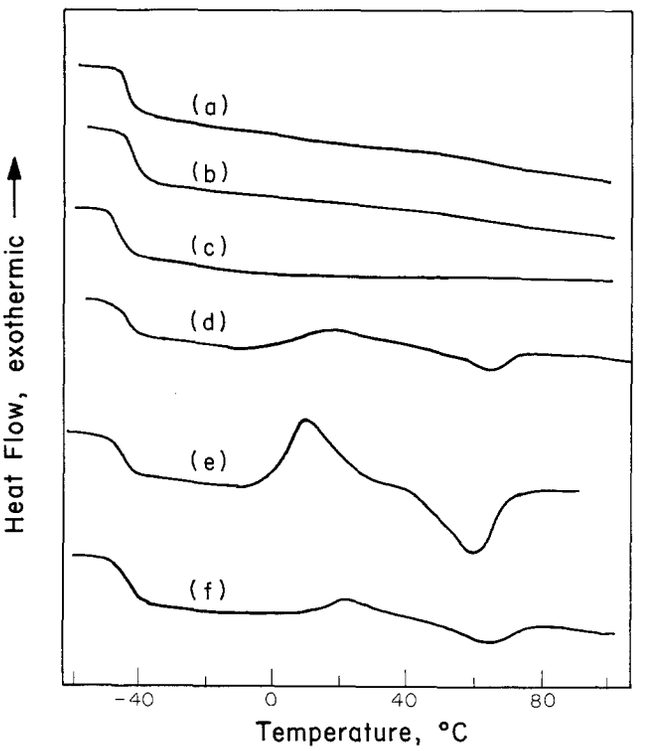


Figure 9 Heat flow as a function of temperature during the non-isothermal crystallization at 20°C min^{-1} of: (a) bacterial PHO; (b) polymer P1; (c) polymer P3; (d) polymer P2; (e) blend PB1; (f) blend PB2

of quenched amorphous samples, which were prepared by heating the samples to 20°C above T_m and quenching in liquid nitrogen.

The d.s.c. thermograms, obtained at a heating rate of 20°C min^{-1} for these blends, are presented in *Figure 9*. The non-isothermal crystallization of these samples is shown by the exothermic peaks which appear in thermograms (d)–(f) between 0 and 40°C. The crystallization peak and the ΔH_c obtained from the area under that peak were used to compare the crystallization behaviour of the blends with that of the pure polymers. Within the limits of error in determining the areas, it can be concluded that the melt-quenched samples were essentially amorphous at the start of the heating cycle at −100°C because the areas under the crystallization peaks were similar to the areas under the melting peaks. In

Table 3 Rate of crystallization of polymers at 20°C min^{-1}

Polymer or blend	Isotactic diads[a] (%)	Isomeric purity[a]	T_g[b] (°C)	T_c[b] (°C)	ΔH_c[b] (J g^{-1})	T_m[b] (°C)	ΔH_m[b] (J g^{-1})
Bacterial PHO	100	100%(*R*)	−34	–	0	–	0
P1	83	Racemic	−34.5	–	0	–	0
P2	100	75%(*R*)	−34	28	2.7	74	2.6
P3	100	100%(*S*)	−35	–	0	–	0
PB1	100	Racemic	−35	19	10	69	10.3
PB2	100	75%(*S*)	−34.7	30	2.4	73	2.5

[a] See *Table 2*, footnote *c*
b Determined by d.s.c. in the second heating cycle

Table 3, the characteristics of these crystallization rates at 20°C min^{-1} are reported.

No crystallization or melting peak was observed in the d.s.c. thermograms for either the bacterial PHO or the racemic or the (*S*)-PHO, which indicates that these polymers have very slow crystallization rates. For the natural and the racemic PHO, this result is in agreement with those from the isothermal crystallization study, in which it was impossible to monitor the crystallization directly by d.s.c. For polymers P2, PB1 and PB2, the presence of a crystallization peak in the d.s.c. thermogram demonstrated their ability to crystallize more easily under these conditions.

If the heat and the temperature of crystallization are correlated with the rate of crystallization, it is seen that the racemic blend, PB1, (T_c=19°C, ΔH_c=10 J g^{-1}) crystallized much more quickly than the optically active polymer, P2, and the optically active blend, PB2, (T_c=30°C, ΔH_c~2.4 J g^{-1}), which had similar rates. Because these latter samples were highly stereoregular, this large difference in rate is presumably related to the differences in the configurational compositions and isomeric purities of the repeating units. That is, the racemic polymer blend may have crystallized faster because there were specific interactions between the (*R*)- and (*S*)-stereoblocks in the two PHOs. Such interactions, which promote crystallization, are well known. Typical examples are the stereocomplexes formed between poly(D-lactic acid) and poly(L-lactic acid)[35] and between the two isotactic poly(α-methyl-α-ethyl-β-propiolactone)s of opposite configurations[36]. However, the racemic polymer, P1, did not show this behaviour because of its much lower stereoregularity of 83% isotactic diads compared to 100% isotactic diads for P2. An isotacticity of 83% corresponds statistically to an interruption by an opposite configuration at approximately every six isotactic repeating units, on average. These interruptions could act as point defects which could not only inhibit crystallization but also prevent the formation of interchain complexes. Further studies must be undertaken to verify stereocomplex formation, especially the effect of annealing and possibly the occurrence of gel formation of the stereocomplex in solution[34]. The effect of the molecular weight differences between the two polymers is probably of little significance because the low molecular weight polymer, P3, did not crystallize rapidly, but its blends with the high molecular weight polymer, P2, crystallize faster than P2 alone.

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