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Thermal Properties and Stereoregularity of Poly(3-hydroxybutyrate) Prepared from Optically Active β-Butyrolactone with a Zinc-Based Catalyst

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Introduction

An optically active poly[(*R*)-3-hydroxybutyrate], P[(*R*)-HB], is synthesized by a variety of bacteria and functions as an intracellular storage material of carbon and energy.[1,2] This P[(*R*)-HB] is a thermoplastic degradable in the environment, by either hydrolytic or enzymatic degradation processes.[3,4] Recently, industrial-scale fermentation production of P[(*R*)-HB] has begun.[5,6] An undesirable property of P[(*R*)-HB] is a thermal unstability at temperatures above the melting point (around 180 °C), and its thermal degradation during processing is significant.[7,8]

The synthesis of PHB has also been achieved by ring-opening polymerization of β-butyrolactone (β-BL) in the presence of aluminum- or zinc-based catalysts.[9-20] The polymerization of racemic β-BL with the $AlEt_3/H_2O$ catalyst leads to a mixture of crystalline isotactic PHB (with a melting temperature of 160-170 °C) and amorphous atactic PHB.[10-14,17,18] On the other hand, the $ZnEt_2/H_2O$ catalyst produces only amorphous atactic PHB.[14] An attempt to prepare optically active P[(*R*)-HB] has been made by the stereoselective polymerization of racemic β-BL with the $ZnEt_2$/(*R*)-(−)-3,3-dimethyl-1,2-butanediol catalyst, which gave PHB of only moderate enantiomeric enrichments.[19] The other attempts have been made by the polymerization of optically active (*R*)- or (*S*)-β-BL with the $AlEt_3/H_2O$[12,20] or $ZnEt_2/H_2O$[20] catalyst. The polymerization of (*S*)-β-BL with the $ZnEt_2/H_2O$ catalyst proceeded by bond breaking between the carbonyl carbon and oxygen of the lactone (acyl cleavage) with retention of the configuration to give P[(*S*)-HB].[20] In contrast, the $AlEt_3/H_2O$ catalyst led to either inversion of the *S* configuration of the lactone or racemization during the polymerization of (*S*)-β-BL.[20]

In the present paper we prepare optically active PHB samples of different stereoregularities from optically active β-BL of different enantiomeric excesses with the $ZnEt_2/H_2O$ catalyst. The effect of stereoregularity on the thermal properties of PHB is reported.

Results and Discussion

(*S*)- and (*R*)-β-BL were synthesized from (*R*)- and (*S*)-methyl-3-hydroxybutyrate, respectively. The optical purity of (*S*)-β-BL was 84%, while the optical purity of (*R*)-β-BL was 59%. The composition of (*R*)- and (*S*)-β-BL in monomer feed was varied, and the polymerization of β-BL with the $ZnEt_2/H_2O$ (1/0.7) catalyst was carried out for 5 days at 60 °C in toluene. Table I shows the molecular weights and stereoregularities of produced PHB samples 1-6. The retention of the *S* and *R* configurations of the β-BL monomer during the polymerization was confirmed by the specific optical rotation of the methyl-3-hydroxybutyrate obtained by the methanolysis of polymer samples.

The stereoregularities of PHB samples were determined from the carbonyl carbon resonance in the 125-MHz ^{13}C NMR spectra. The carbonyl resonance at 169.1-169.3 ppm (from Me_4Si) was resolved into two peaks due to isotactic (*RR,SS*) and syndiotactic (*RS,SR*) diad sequences of (*R*)- and (*S*)-HB units.[17,18] The observed isotactic diad fraction of PHB was dependent upon the *R*/*S* ratio of β-BL in the monomer feed.

Assuming the acyl cleavage of β-BL with retention of the configuration during the polymerization and a statistical sequence distribution of (*R*)- and (*S*)-HB units in PHB, one can express isotactic (i) and syndiotactic (s) diad fractions as

$$\mathrm{i} = RR + SS \qquad \mathrm{s} = RS + SR \qquad (1)$$

where *R* and *S* are the mole fractions of (*R*)- and (*S*)-β-BL in the monomer feed, respectively. The i and s diad fractions calculated with the values of *R* and *S* are in good agreement with the observed diad fractions, as shown in Table I. This result indicates that an ideal random copolymerization of (*R*)- and (*S*)-β-BL takes place in the presence of $ZnEt_2/H_2O$ catalyst.

The glass transition temperature (T_g), melting temperature (T_m), and enthalpy of fusion (ΔH_m) of PHB samples were determined from the DSC thermograms. The result is given in Table II, together with the values of bacterial P[(*R*)-HB] sample 7 ($\bar{M}_n$ = 13 000, $\bar{M}_w$ = 27 000). The T_g values were in the range −1.0 to +5.1 °C, being almost independent of the stereoregularity of PHB. In contrast, the T_m values of samples decreased from 168.7 to 88.5 °C as the isotactic diad fraction decreased from 1.00 to 0.59, as shown in Figure 1. The value of ΔH_m decreased also with a decrease in the isotactic diad fraction of PHB. This result demonstrates that the melting temperature and crystallinity of PHB polymers can be regulated by the stereoregularity of the polymer sequence.

Experimental Section

The (*S*)-β-BL monomer was prepared in four steps from (*R*)-methyl-3-hydroxybutyrate (optical purity 96%, supplied from Takasago Corp.) by the method reported by Zhang et al.[20] The optical purity of (*S*)-β-BL was 84% ($[\alpha]^{25}_{589}$ = −21.8° in $CHCl_3$, *c* = 5 g/dL). The reference value[20] for 100% pure (*S*)-β-BL was

Table I
Polymerization Results of (*R*)- and (*S*)-β-Butyrolactone with the $ZnEt_2/H_2O$ Catalyst in Toluene at 60 °C for 5 days[a]

			mol wt[c]		isotactic diad fraction	
sample no.	monomer feed ratio, *R*/*S*[b]	polym yield, %	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	obsd[d]	calcd[e]
1	8/92	84	34 000	1.5	0.85	0.86
2	21/79	68	50 000	1.2	0.71	0.67
3	29/71	57	19 000	1.3	0.59	0.59
4	50/50	80	23 000	1.5	0.53	0.50
5	65/35	71	16 000	1.2	0.59	0.55
6	79/21	75	15 000	1.2	0.68	0.67

[a] Polymerization conditions: $ZnEt_2/H_2O$ (1/0.7) = 0.03 g, β-butyrolactone = 1.0 g and toluene = 1.0 mL. [b] Calculated from optical rotation data. [c] Determined by GPC analysis, calibrated to a polystyrene standard. [d] Determined by ^{13}C NMR analysis. [e] Calculated by eq 1 with the values of *R* and *S*.

Table II
Thermal Properties of Poly(3-hydroxybutyrate) Samples

sample no.	isotactic diad fraction	T_m,[a] °C	ΔH_m,[a] J/g	T_g,[c] °C
1	0.85	135.6	64.3	4.1
2	0.71	99.5	29.0	2.2
3	0.59	*b*	0.0	4.1
4	0.53	*b*	0.0	−1.0
5	0.59	88.5	12.5	5.1
6	0.68	91.5	15.8	2.2
7[d]	1.00	168.7	105.6	4.9

[a] Melting temperature (T_m) and enthalpy of fusion (ΔH_m) were measured by DSC (first run) at 10 °C/min from 20 to 200 °C. [b] Melting temperature was detected. [c] Glass transition temperature (T_g) was measured by DSC (second run) at 20 °C/min from −100 to +200 °C. [d] Bacterial P[(*R*)-HB] of $\bar{M}_n$ = 13 000 and $\bar{M}_w$ = 27 000.

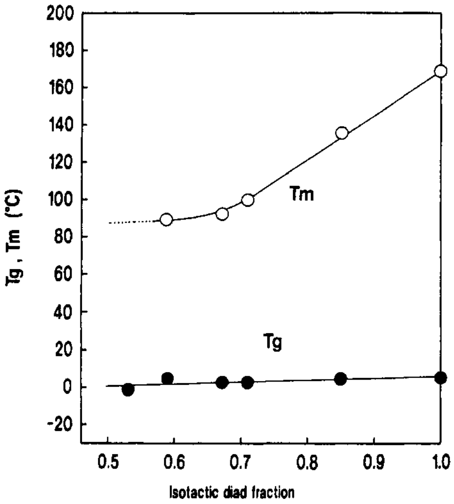

Figure 1. Effect of stereoregularity on melting temperature (T_m) and glass transition temperature (T_g) of poly(3-hydroxybutyrate).

$[\alpha]^{25}_{589}$ = −26.1° in $CHCl_3$ (c = 5 g/dL). The (*R*)-β-BL monomer was prepared from (*S*)-methyl-3-hydroxybutyrate (optical purity 96%, supplied from Takasago Corp.), and its optical purity was 59% ($[\alpha]^{25}_{589}$ = +15.4° in $CHCl_3$ (c = 5 g/dL). The composition of (*R*)- and (*S*)-β-BL in the monomer feed was varied and determined from the optical rotation data.

The $ZnEt_2/H_2O$ (1/0.7) catalyst was prepared by a reported method.[14] The polymerization of β-BL (1.0 g) with the $ZnEt_2/H_2O$ catalyst (0.03 g) was carried out in toluene (1.0 mL) for 5 days at 60 °C. The produced polymers were precipitated by adding 20 mL of methanol. The crude product was dissolved in hot chloroform and purified by reprecipitation with ether.

The 125-MHz ^{13}C NMR spectra of polymers were recorded at 27 °C on a JEOL GX-500 spectrometer in a $CDCl_3$ solution of polymer (50 mg/mL) with a 10-μs pulse width (45° pulse angle), 5-s pulse repetition, 25 000-Hz spectrral width, and 64K data points.

Calorimetric measurements (DSC) of polymers were carried out on a Shimadzu DSC-50 thermal analysis system in the temperature range −100 to +200 °C, with heating rates of 10 and 20 °C/min. The melting temperature (T_m) was taken as the peak temperature of the melting endotherm. The glass transition temperature (T_g) was taken as the inflection point of the specific heat increment at the glass transition.

Molecular weight data were obtained at 40 °C by using a Shimadzu 6A GPC system. Chloroform was used as the eluent at a flow rate of 0.5 mL/min, and a sample concentration of 1.0 mg/mL was used. Polystyrene standards with a low polydispersity were used to make a calibration curve.

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