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Synthesis and characterization of hydroxy-terminated [RS]-poly(3-hydroxybutyrate) and its utilization to block copolymerization with L-lactide to obtain a biodegradable thermoplastic elastomer

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Abstract

A telechelic poly([RS]-3-hydroxybutyrate) ([RS]-PHB) was synthesized by the ring-opening polymerization of [RS]-β-butyrolactone (βBL) in the presence of 1,4-butanediol (BD) with distannoxane as the catalyst. This polymer was found to be terminated by secondary hydroxyl groups, having an (oxytetramethylen)oxy group in the main chain. It was subjected to block copolymerization with L-lactide by the catalysis of tin (II) octoate to obtain an A–B–A type triblock copolyester comprising poly(L-lactide) (A) and [RS]-PHB (B). In this block copolymerization, the molecular weight and the unit composition of the produced copolymer were successfully controlled by changing the L-lactide/[RS]-PHB ratio in feed. Its characterization revealed that this block copolymer has high potential for use as biodegradable thermoplastic elastomer. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(3-hydroxybutyrate); Ring-opening polymerization; Telechelic polymer

1. Introduction

Bacterially produced poly(3-hydroxyalkanoates) (PHA) have been convinced to be the promising biodegradable polymers that can be utilized as bioplastics. They are produced not only by bacterial fermentation [1], but also by transgenic microorganisms [2] and plants [3]. Functional PHA have also been prepared by these biosynthetic procedures by incorporating various functional monomers or other metabolites in the polymer sequence. For example, fermentation of *Alcaligenes eutrophus* in a culture containing polyethylene glycol or polysaccharide has given a hydroxy-terminated block copolymer consisting of PHA [4,5].

On the other hand, chemical synthesis of PHA and their derivatives has also been an important subject of polymer science. Hori et al. have succeeded in preparing a high polymer of poly(3-[R]-hydroxybutyrate) ([R]-PHB) by ring-opening polymerization of four-membered [R]-β-butyrolactone ([R]-βBL) with distannoxanes as the initiators where the ring-opening of [R]-βBL proceeded with retention of the configuration or with little or no racemization [6,7]. Polymerization of racemic monomer [RS]-βBL with the same catalysts has given an atactic or syndiotactic-rich poly(3-[RS]-hydroxybutyrate) ([RS]-PHB) [8]. Unlike the optically active [R]-PHB, [RS]-PHB is elastomeric. Even the syndiotactic-rich [RS]-PHB (ordinarily 70% syndiotactic diads) shows elastomeric properties because of its low crystallinity. For their application as biodegradable elastomer, vulcanization or crosslinking is necessary for decreasing their creep behavior. However, the crosslinking of aliphatic polyesters cannot be established by the ordinary chemical or radiational method because they likely induce decomposition rather than crosslinking. The alternative vulcanization method is to introduce hard segment and to rely on the physical crosslinking by micro phase separation of the hard and soft segments. In the case of [RS]-PHB, introduction of a biodegradable hard segment can give a wholly biodegradable creep resistive elastomer, for which the mechanical properties can be controlled by the hard/soft segment ratio. The latter method has been tried by several investigators [9–11]. For example, Kricheldorf et al. recently proposed a facile method for obtaining such block copolymers based on the successive ring-opening polymerization of [RS]-βBL and L-lactide or ϵ-caprolactone with a tin (IV) catalyst [12]. The resultant A–B–A block copolymers, consisting of [RS]-PHB as the soft (B) segment and poly(L-lactide) (PLLA) or polycaprolactone as the hard

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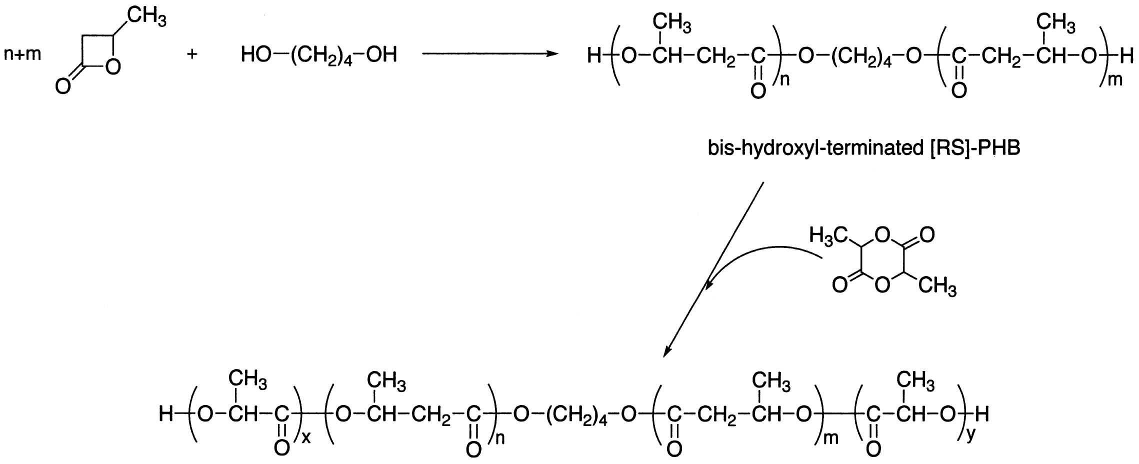


Scheme 1. Ring-opening polymerization of [RS]-βBL in the presence of BD and copolymerization with L-lactide.

(A) segment can possibly be the elastomeric biodegradable polymers, although their characterization was not fully accomplished. Since this copolymerization system is catalyzed by tin (IV) compound that is an active transesterification catalyst, unit scrambling may likely happen during the copolymerization by the transesterification mechanism, and the unit sequence of the resultant copolymers is disturbed and sometimes randomized. Particularly, during the copolymerization of L-lactide such unit scrambling is frequently induced because of its relatively high polymerization temperature. As far as we know, the ring-opening polymerization of βBL is induced by the action of such highly effective transesterification catalysts as the tin (IV) compound, while the polymerization of L-lactide is allowed in the presence of such weak Lewis acids as tin (II) octoate with little chain transfer occurring. These differences in catalyst activity and the monomer polymerizability suggest that the A–B–A block copolymer of PLLA (A) and [RS]-PHB (B) should be prepared in two-stage for escaping the unit scrambling; i.e. oligomerization of [RS]-βBL by the catalysis of tin (IV) compound and copolymerization of the resultant [RS]-PHB with L-lactide by the catalysis of tin (II) octoate.

In this study, the synthesis of the telechelic [RS]-PHB was done by the ring-opening polymerization of [RS]-βBL in the presence of 1,4-butanediol by catalysis of a distannoxane compound. Then, the resultant bishydroxy-terminated [RS]-PHB was reacted with L-lactide to obtain an A–B–A block copolymer, poly(L-lactide)–poly(3-[RS]-hydroxybutyrate)–poly(L-lactide) (PLLA–PHB–PLLA) (Scheme 1), which was evaluated as a potential thermoplastic biodegradable elastomer. The intermediate telechelic oligomer of [RS]-PHB may also be useful as the hardener of epoxy and urethane resins.

2. Experimental

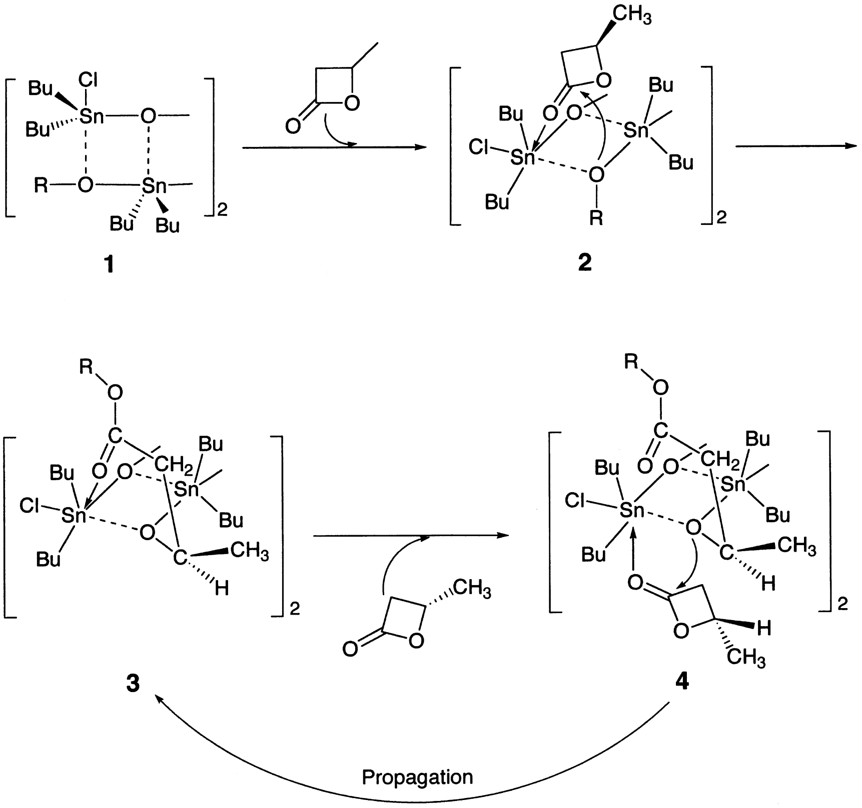
2.1. Materials

[RS]-βBL was purchased from Tokyo Kasei Kogyo (Tokyo) and purified by repeated distillation over calcium hydride at reduced pressure before use. Dibutyltin dichloride and 1,4-butanediol (BD) were used after distillation at reduced pressure. L-Lactide was supplied by Boeheringer Ingelheim (Germany) and used without purification. Toluene was distilled under a nitrogen atmosphere. Tin octoate ($SnOct_2$) was purchased from Nacalai Tesque Co. (Kyoto) and purified by distillation under high vacuum. It was dissolved in a distilled toluene to have a concentration of 0.1 g/ml.

1, 3-Dichlorotetrabutyldistannoxane (DTD) was prepared by the literature method [13,14] and purified by recrystallization from *n*-hexane before use (mp = 113–116°C).

2.2. Measurements

^{1}H NMR spectra were measured on a 500 MHz Bruker ARX500 NMR spectrometer. ^{13}C NMR spectra were measured on the latter spectrometer at 125 MHz in magnetic field. Deuterated chloroform containing 1 vol% tetramethylsilane (TMS) was used as the solvent in these NMR measurements. The number-average molecular weight (M_n) and molecular weight distribution index (M_w/M_n) were determined by gel permeation chromatography (GPC). The analyzer was composed of a Shimadzu LC-10A pump, a Shodex RI SE-31 RI detector, a Shimadzu C-R7A Chromatopac data processor, and a Shodex DEGAS KT-16 degassor. A combination of two polystyrene gel columns of Toso TSK gel G4000H_8 and G2500H_8 (7.5 mm I.D. × 300 mm, each) was used with chloroform as the eluent at 35°C. The molecular weight was calibrated according to polystyrene standards. Differential scanning calorimetry (DSC) of polymeric products was carried out on a MAC Science 3100 thermal analyzer under a nitrogen flow of 20 ml/min at a heating rate of 10°C/min using 2.0–5.0 mg of samples. Tensile properties were measured on a Tensilon UTM-4L tensile tester (Toyo Measuring Instruments CO., Ltd) with a cross-head speed of 50 mm/min



Scheme 2. Mechanism of ring-opening polymerization of [RS]-βBL in the presence of BD using DTD as the catalyst. (R: Residues of the hydroxy compounds).

for film specimen of 20 mm in length and 5 mm in width. Five data were collected and averaged.

2.3. Polymerization of [RS]-βBL

A typical procedure for the preparation of bis-hydroxy [RS]-PHB is as follows. The initiator DTD (50.9 mg, 46.0×10^{-3} mol) was dried in vacuo at 90°C for 10 h in the Schlenk-like glassware equipped with a mechanical stirrer. Subsequently, BD (57.9 mg, 0.64 mmol) and [RS]-βBL (5.31 g, 61.7 mmol) were added to it, and the reaction system was heated in an oil bath at 100°C with stirring under a nitrogen atmosphere for 8 h. The system gradually turned viscous and finally solidified. The resultant polymeric product was dissolved in chloroform (7 ml) and precipitated into an excess amount of a diethyl ether/*n*-hexane (1:3 in volume) mixture. The precipitated products were separated by decantation of the supernatant and thoroughly dried at 50°C in vacuo.

2.4. Block copolymerization

1.0 g amount of a telechelic [RS]-PHB obtained above was charged into a round-bottomed flask equipped with a mechanical stirrer and thoroughly dried in vacuo at 85°C for several hours. Then, a prescribed amount of L-lactide was added to it under a nitrogen atmosphere. Subsequently, 61 μl (0.045 mol%) of the solution of tin octoate was added. The resultant mixture was heated at 160°C with stirring for 40 min. After the reaction had finished, the product was dissolved in chloroform, and the solution was poured into an excess amount of methanol to precipitate out the polymeric product. The precipitated product was filtered, washed with methanol several times, and thoroughly dried in vacuo. By a similar method, a series of block copolymers with different compositions were prepared by changing the [RS]-PHB to L-lactide ratio in feed.

2.5. Preparation of polymer films

A polymer sample was dissolved in chloroform, cast on a glass Petri dish, solidified in air, and dried thoroughly in vacuo. Then, the transparent film formed on the dish was pealed off. The film thickness was adjusted to about 60–80 μm.

3. Results and discussion

3.1. Preparation of bis-hydroxyl-terminated [RS]-PHB

In the ordinary ring-opening polymerization of [RS]-βBL, the propagating proceeds through acyl-oxygen cleavage of the monomer that is induced by the attack of the alkoxide chain end around the catalyst site. With this transesterification mechanism, the resultant polymer should have both carboxyl and hydroxyl ends, if water is the initiating

Table 1
Results of DTD-catalyzed polymerization of [RS]-βBL in the presence of BD (polymerized in bulk)

Run No.	Feed ratio		Yield (%)[a]	Unit ratio 3HB/BD[b]	M_n (10^3 Da)			M_w/M_n[c]
	[β–BL]/[BD]	[BD]/[DTD]			Calcd.[d]	^{1}H NMR[b]	GPC[c]	
1	58/1	20/1	91	60/1	5.2	5.0	5.4	1.4
2	55/1	18/1	95	72/1	6.3	6.7	6.1	1.4
3	96/1	14/1	86	110/1	9.6	7.8	10.1	1.2
4	109/1	12/1	99	110/1	9.6	9.0	12.1	1.3

[a] After reprecipitation into *n*-haxane/diethyl ether (3:1).
[b] Determined by ^{1}H NMR.
[c] Determined by GPC (chloroform eluent), calibrated with a polystyrene standard.
[d] Calculated by 3HB/BD unit ratio.

species and an appropriate work-up is done. For introducing hydroxyl group to both ends of [RS]-PHB, chain growth to a dihydroxy compound should be directed. Since the ligant exchange between the distannoxane catalyst and the hydroxy compound is very fast, such chain growth may be possible if the polymerization is conducted under the co-existence of an active tin (IV) catalyst DTD and a dihydroxy compound. Here, BD was selected as the dihydroxy compound (Scheme 2).

Table 1 shows the results of the polymerization of [RS]-βBL in the presence of BD with DTD as the catalyst. The initiator to catalyst ratio (BD/DTD) was decreased with increasing βBL/BD ratio. The isolated yield of the polymer after the reprecipitation ranged from 86 to 99% regardless of the βBL/BD ratio. The number-average molecular weight (M_n) determined by GPC increased from 5400 to 12,100 Da with increasing the βBL/BD ratio, having a relatively narrow molecular weight distribution ($M_w/M_n = 1.2$–1.4). Figs. 1 and 2 show the typical ^{1}H and ^{13}C NMR spectra of the produced polymer (sample No. 3), respectively. In the ^{1}H NMR spectrum, the signals of the methyl, methylene, and methyne protons of the 3-hydroxybutyrate (3HB) units are detected at δ 1.28 ppm (a), 2.47–2.61 ppm (c), and 5.26 ppm (b), respectively. In addition to these signals, two methylene signals attributed to the internal (oxytetramethylen)oxy unit are shown at δ 4.11 ppm (d) and 1.72 ppm (e), and the signals of the methyne and methyl protons of the 3HB end groups are detected at δ 4.19 ppm (b′) and 1.21–1.23 ppm (a′), respectively. Furthermore, the integral ratio of the methyne signal (b′) relative to the

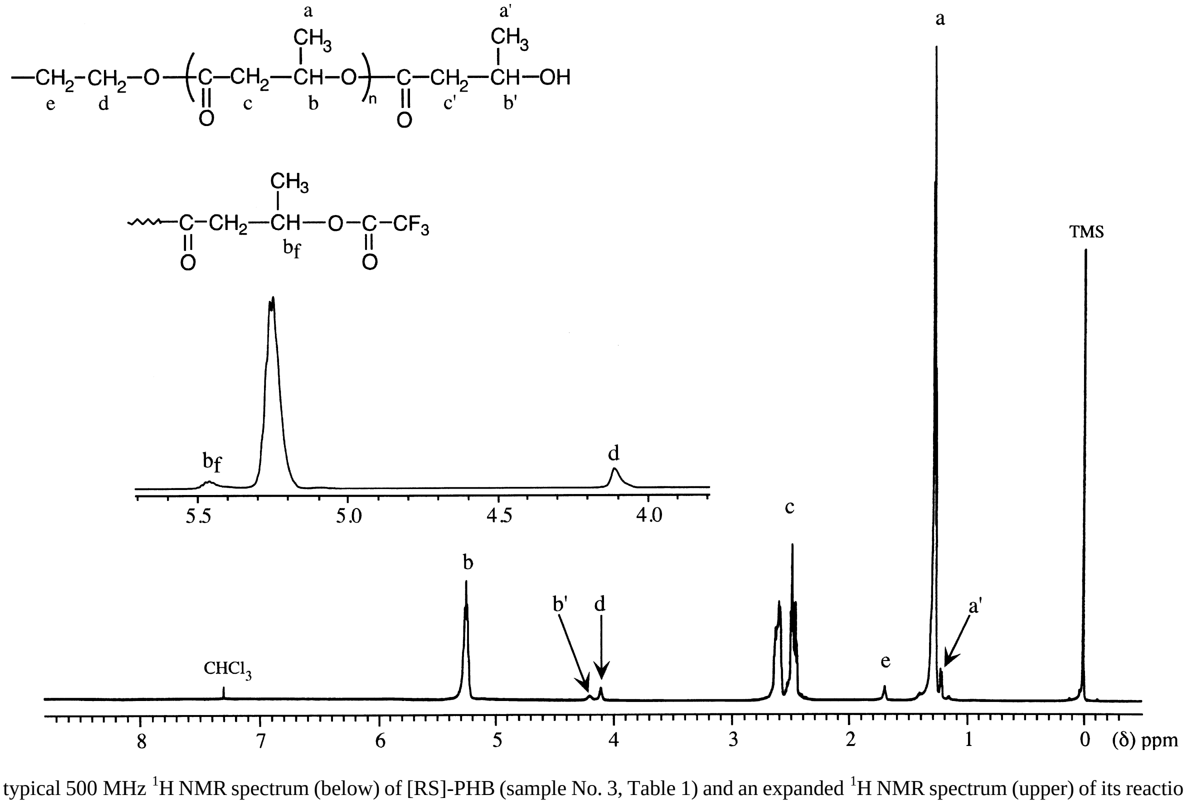


Fig. 1. A typical 500 MHz ^{1}H NMR spectrum (below) of [RS]-PHB (sample No. 3, Table 1) and an expanded ^{1}H NMR spectrum (upper) of its reaction product with an excess of trifluoroacetic anhydride.

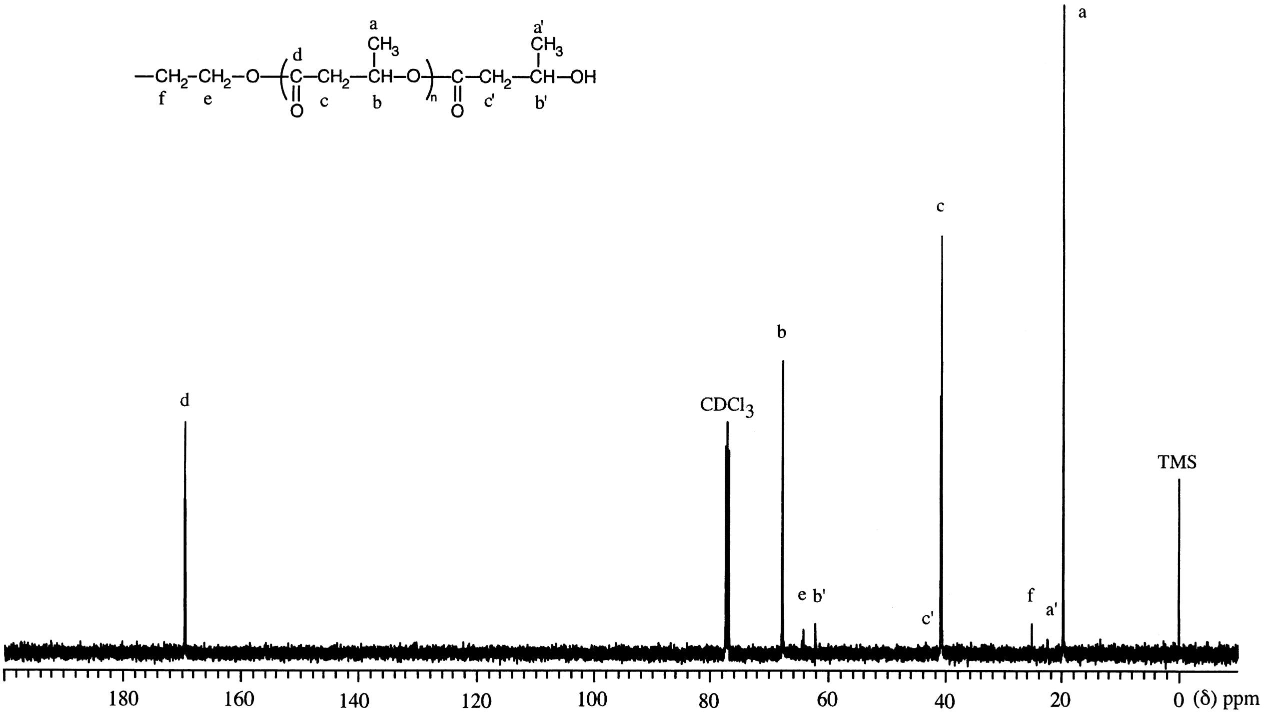


Fig. 2. A typical 125 MHz ^{13}C NMR spectrum of [RS]-PHB (sample No. 1, Table 1).

oxymethylene signal (d) is about 1/2, supporting that BD was incorporated in the polymer backbone with two hydroxy groups formed in the polymer tails. When trifluoroacetic anhydride (TFA) was added to this sample, the methyne signal at δ 4.19 ppm (b$'$) was completely replaced by the signal appearing at δ 5.47 ppm (b$_f$) as shown in the expanded ^{1}H NMR spectrum (Fig. 1 upper left). This downfield shift of the methyne signal after trifluoroacetylation also supports the presence of hydroxyl terminal groups. In the ^{13}C NMR spectrum the carbon signals due to the methyl, methylene, methyne and carbonyl carbons of the 3HB units are detected around δ 19.7 (a), 40.8 (c), 67.6 (b), and 169 ppm (d), respectively. The small signals detected around δ 62.6 (b$'$), 43.2 (c$'$), and 22.4 ppm (a$'$) can be assigned to the methyne, methylene, and methyl carbons of the 3HB end groups, respectively. Furthermore, no signal is shown around δ 173 ppm because of the absence of the carboxyl end groups. These results strongly support that the [RS]-PHB prepared in the presence of BD should have two secondary hydroxy terminals with the BD units incorporated in the polymer backbone.

The M_n values of [RS]-PHB were estimated from the integral ratio of the terminal methyne signal (b$'$) relative to the main chain methyne signal (b). The results are given in Table 1. It is known that the M_n values determined by the ^{1}H NMR spectrum agreed with the theoretical values that were calculated from the βBL/BD ratio in feed. In the samples having relatively high molecular weight (Nos. 3 and 4, Table 1), the M_n values estimated by GPC were slightly higher than those determined by the ^{1}H NMR spectrum, probably because of the increased difference in hydrodynamic volume of the polymers having higher molecular weight.

A possible polymerization mechanism is shown in Scheme 2. The initiation step is the formation of the alkoxydistannoxane **1** upon mixing DTD and BD. Then, the carbonyl group of [RS]-βBL coordinates with the Sn (IV) atom center to form the alkoxide of 3-hydroxybutyrate (**2**). Formation of such alkoxides as **1** and **3** with Sn (IV) was also supported in other catalyst system [15]. The ligand exchange does not only aid the monomer's coordination, but also stimulates the nucleophilic attack of the alkoxide toward the carbonyl group. The propagation proceeds through the repetition of the reaction involving **3** and **4**. Owing to the fast exchange of the alkoxide-Sn (IV) bond with other hydroxy groups, the chain propagation should proceed equally among the polymer tails grown from the BD hydroxy groups to form the polymer chains with similar length. Although the transesterification may possibly occur between the hydroxyl terminals and the main-chain ester groups during this propagation, it should not have happened frequently at the present reaction conditions, judging from the molecular weight distribution of the resultant polymers. This plausible mechanism can well explain the growth of [RS]-PHB from the hydroxy groups of BD.

The distribution of repeat unit stereosequences of the [RS]-PHB samples prepared above were also analyzed by 125 MHz ^{13}C NMR. The carbonyl signal at δ 169.1–169.3 ppm was split into two peaks due to the meso (m) and racemic (r) diad sequences of (R)- and (S)-3HB units. The methylene resonance at δ 40.2–40.5 ppm was also resolved into four peaks due to isotactic (mm), syndiotactic

Table 2
Stereosequence and thermal properties of telechelic [RS]-PHB

Run No.	Stereosequence		T_g (°C)[a]	T_m (°C)[b]
	m/r[c]	Syndiotactic diads (%)		
1	0.60/1	63	−5.0	40–80
2	0.63/1	61	−2.6	45–65
3	0.67/1	60	−2.0	50/80
4	0.62/1	62	−1.0	41/83

[a] Glass-transition temperature; measured by DSC (second scan), from −40 to 160°C at a rate of 10°C/min.

[b] Melting temperature; measured by DSC (first scan), from r.t. to 160°C at a rate of 10°C/min.

[c] Determined by the ^{13}C NMR spectra.

(rr), and heterotactic (mr and rm) triad sequences. The analysis of these signals revealed that the syndiotactic diad fraction was found to range from 0.60 to 0.62 (Table 2). Therefore, the telechelic [RS]-PHB samples should have only slightly syndiotactic-rich sequence, compared with the ordinary syndiotactic-rich [RS]-PHB prepared without BD added.

The thermal behavior of the telechelic [RS]-PHB samples was studied by DSC. The representative DSC thermograms (samples No. 1 and 3) are shown in Fig. 3. While an endothermic peak is exhibited around 40–80°C in the first heating scan of the low molecular weight sample, two endothermic peaks are shown in the first scan of the high molecular weight sample. The low temperature peak in the latter should be attributed to the fusion of incomplete crystals, and the high temperature peak to that of crystals with higher order [16]. The melting (T_m) and glass transition (T_g) temperatures of all the samples are given in Table 2. It is known that T_g was shown around -2 ± 3°C, being independent of molecular weight of the samples. The T_m value varied significantly with the molecular weight and appeared in wide range. Kemnitzer et al. [16] prepared the similar polymers with different catalysts and reported a close relationship between the crystallization behavior and syndiotacticity. They explained that the observation of the two distinct melting points over a wide range of temperature may be due to the distribution of tacticity of the samples. Namely, the [RS]-PHB segments with higher syndiotacticity should form the more stable crystal regions with higher thermodynamic stability and vice versa. The present telechelic [RS]-PHB samples showing such melting behaviors are considered to contain multi-modal syndiotacticity distributions in the polymer chain.

3.2. Synthesis of PLLA–[RS]-PHB–PLLA triblock copolymer

The telechelic [RS]-PHB obtained above was subjected to block copolymerization with L-lactide. The polymerization was carried out in bulk state at 160°C by using tin (II) octoate as the catalyst. The polymeric product finally obtained was isolated by reprecipitation. The results are given in Table 3. The yield of the block copolymers was very high at various molar ratios of L-lactide to [RS]-PHB prepolymer. Their molecular weight was in the range of 11,900–30,000 Da depending on the feed ratio of L-lactide, and the molecular weight distribution ($M_w/M_n = 1.2$–1.3) was narrow in every case. Fig. 4 shows the typical GPC curves of the block copolymers as compared with those of [RS]-PHB prepolymers. It is shown that in each block copolymer the peak is shifted toward a high molecular weight region compared with that of its original [RS]-PHB prepolymer with little change in molecular weight distribution.

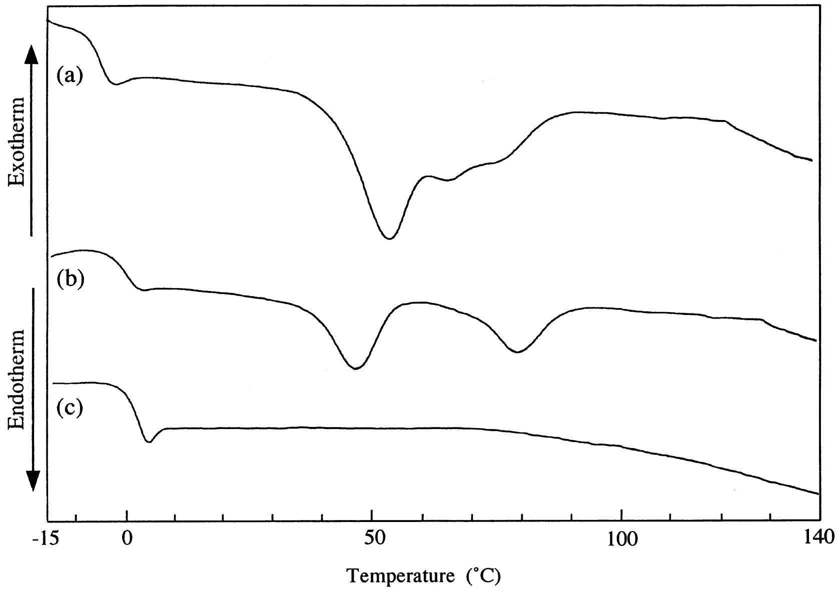


Fig. 3. DSC thermograms of [RS]-PHB: (a) sample No. 1 ($M_n = 5.4 \times 10^3$) in the first heating scan; (b) sample No. 3 ($M_n = 10.1 \times 10^3$) in the first heating scan; and (c) sample No. 3 ($M_n = 10.1 \times 10^3$) in the second heating scan.

Table 3
Results of block copolymerization of the telechelic [RS]-PHB and L-lactide (polymerized with $SnOct_2$ as catalyst for 40 min at 160°C in bulk)

Run No.	Telechelic [RS]-PHB M_n[b] (10^3 Da)	[M]/[I][a]	Unit ratio 3HB/LA[c]	Yield (%)	M_n (10^4 Da)		M_w/M_n[b]
					GPC[b]	Calcd.[d]	
1	5.4	28.1	42/58	87	1.2	1.25	1.3
2	5.4	42.0	32/68	79	1.5	1.49	1.2
3	5.4	64.5	22/78	87	2.1	2.16	1.3
4	10.1	31.8	56/44	83	1.6	1.77	1.2
5	10.1	51.6	47/53	82	2.0	2.23	1.2
6	10.1	83.6	31/69	90	3.0	3.22	1.2

[a] The monomer (M) ratio in feed relative to the total end group (I) of the prepolymer.
[b] Determined by GPC calibrated with polystyrene standard (chloroform eluent).
[c] Determined by ^1H NMR spectra.
[d] Calculated from the yield.

The M_n value estimated from GPC was almost comparable with the molecular weight calculated from the yield and composition, as summarized in Table 3.

Fig. 5 shows a typical ^1H NMR spectrum of the block copolymer obtained (sample No. 1, Table 3). Both methyl and methylene signals due to the PLLA segments (δ 1.59 ppm: CH_3 (f) and 5.16 ppm: CH (g)) can be detected in addition to the peaks due to the [RS]-PHB segments (δ 1.28 ppm: CH_3 (a), 2.47–2.61 ppm: CH_2 (c), and 5.26 ppm: CH (b)). Furthermore, the signal at δ 1.22 ppm (a′ in Fig. 1) due to the methyl group of the terminal 3HB units of [RS]-PHB was not observed for the block copolymer and completely replaced by the signal at δ 1.48–1.50 ppm (f′) which is assigned to the methyl protons of the 2-hydroxypropionate terminal of the PLLA segments. The signals (d,e) of the (oxytetramethylen)oxy groups in the [RS]-PHB segments are retained in the spectrum. Fig. 6 shows the expanded spectra of the methyne region from the ^1H NMR spectra of the block copolymer and the corresponding [RS]-PHB prepolymer. The peak at δ 4.19 ppm (b′) due to the methyne proton of the 3HB terminal was not observed in the block copolymer, either, and replaced with the signal at δ 4.36 ppm (g′) which is assigned to the methyne proton of the hydroxy terminal of the PLLA segment. These results support the triblock structure of PLLA–[RS]-PHB–PLLA which was formed by the chain growth from the hydroxy tails of the telechelic [RS]-PHB as described in Scheme 1.

The PLLA–[RS]-PHB–PLLA samples were also analyzed by 125 MHz ^{13}C NMR spectroscopy to confirm the triblock structure. Since the expanded spectrum of the carbonyl carbons (Fig. 7) showed no signal due to the alternating 3HB-LA sequences, the detrimental chain transfer reaction by ester exchange did not take place during the block copolymerization.

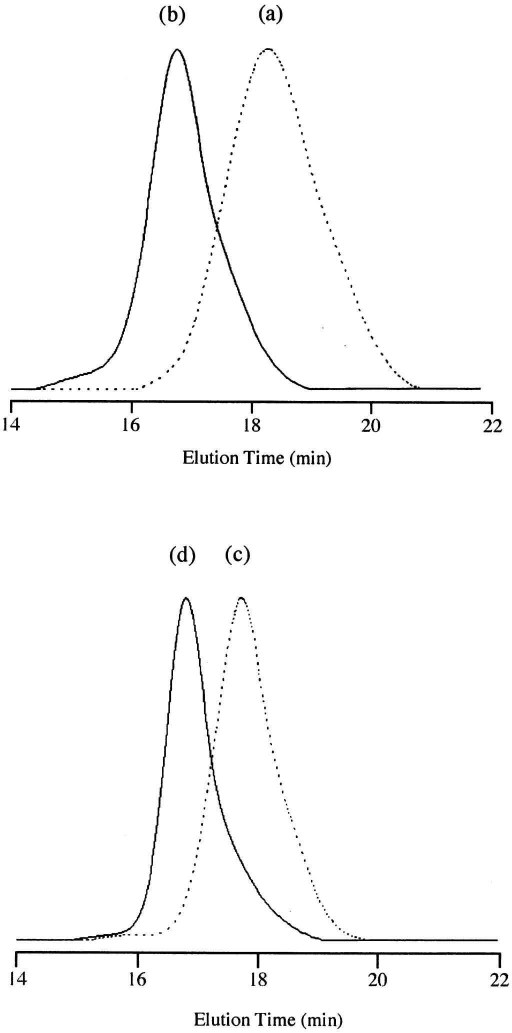


Fig. 4. Typical GPC chromatograms of: (a) the original [RS]-PHB (sample No. 1, Table 1); (b) PLLA-[RS]–PHB–PLLA (sample No. 3, Table 4); (c) the original [RS]-PHB (sample No. 3, Table 1); and (d) PLLA-[RS]–PHB–PLLA (sample No. 5, Table 4).

3.3. Thermal properties of PLLA–[RS]-PHB–PLLA triblock copolymers

Fig. 8 shows the typical DSC curves of the PLLA-[RS]–PHB–PLLA triblock copolymers having different PLLA

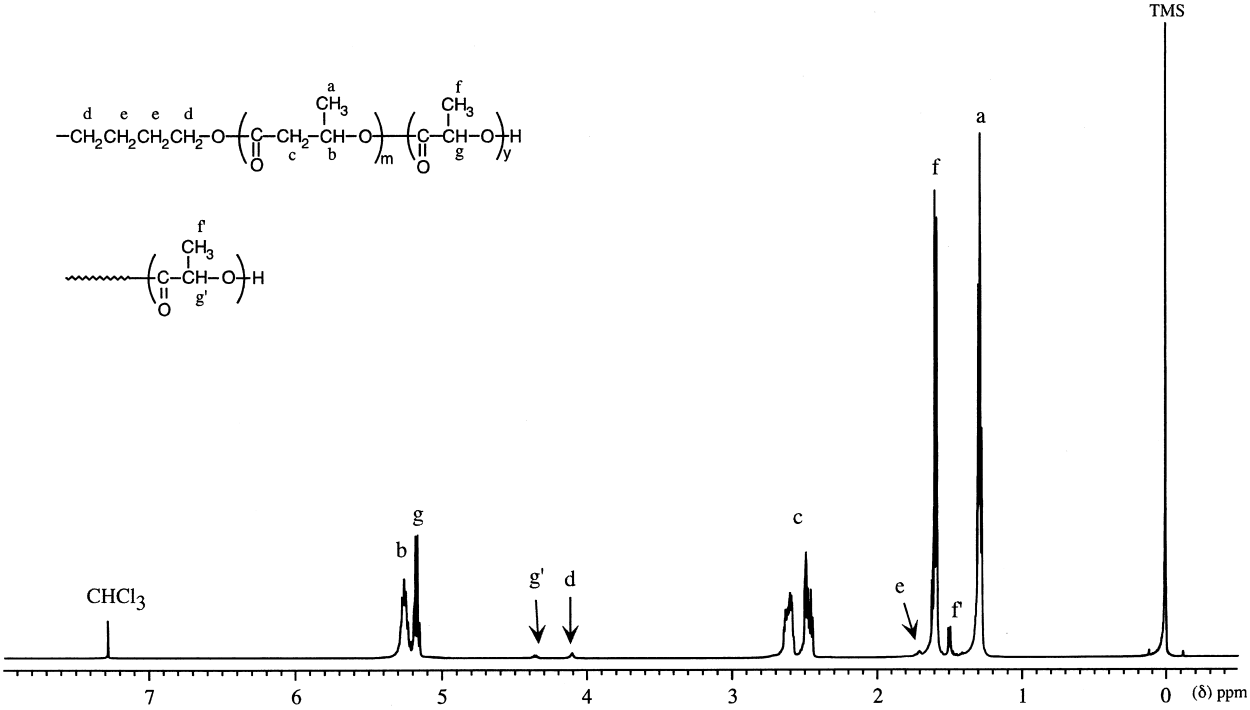


Fig. 5. A typical 500 MHz ^{1}H NMR spectrum of PLLA-[RS]–PHB–PLLA (sample No. 1, 3HB/LA = 42/58, Table 3).

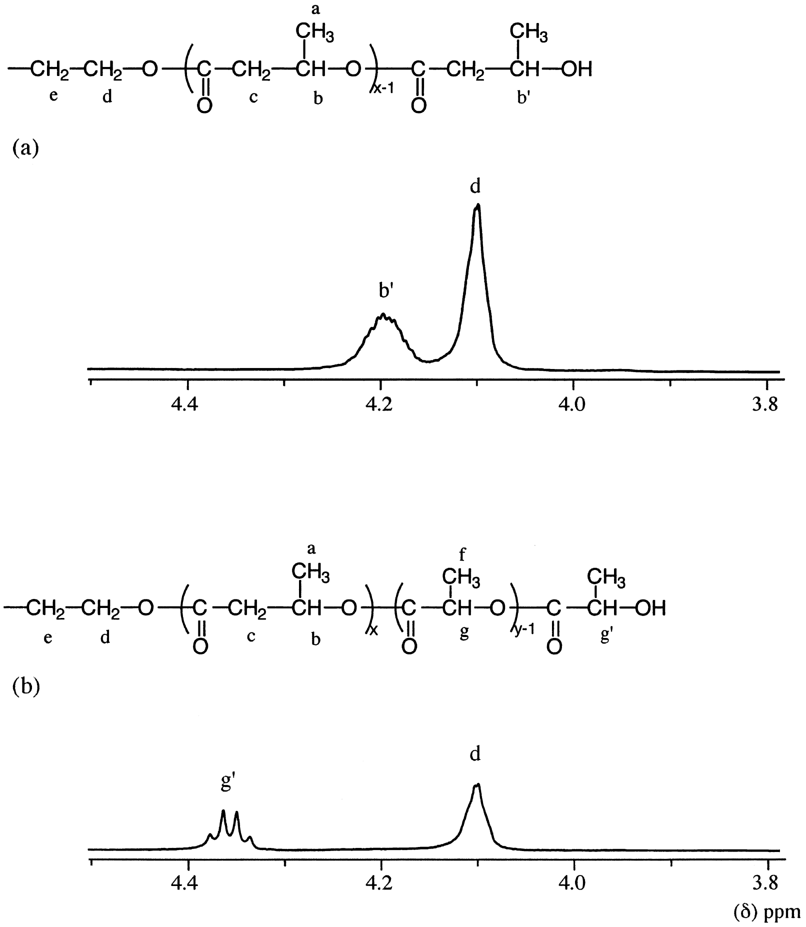


Fig. 6. Expanded terminal methyne regions in the ^{1}H NMR spectra of: (a) [RS]-PHB (sample No. 3, Table 1); and (b) PLLA-[RS]–PHB–PLLA (sample No. 4, Table 3).

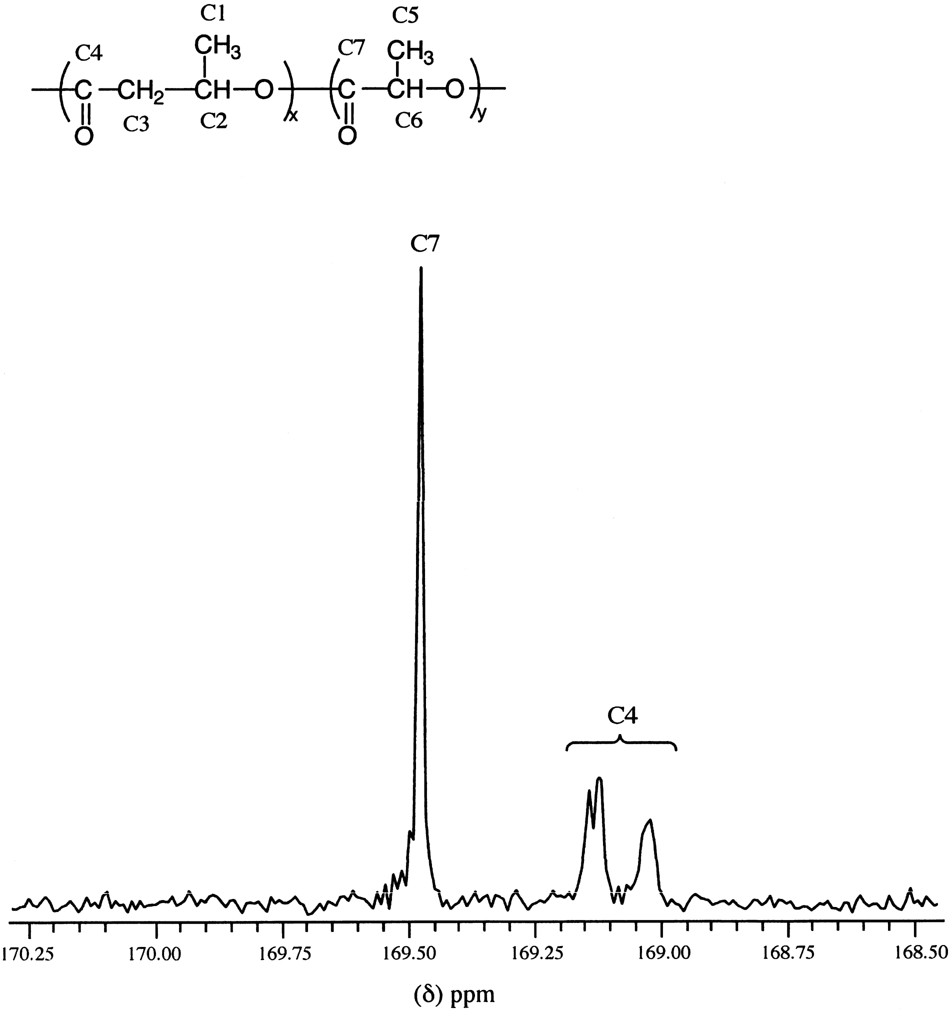


Fig. 7. Expanded carbonyl resonance region in the ^{13}C NMR spectrum of the PLLA-[RS]–PHB–PLLA (sample No. 1, Table 4).

block length on the identical [RS]-PHB block (DP = 117). The first heating curves (Fig. 8(a)–(c)) of the three samples commonly show an inflection point around 0–5°C and a large endothermic peak around 120–155°C due to the glass transition behavior of [RS]-PHB blocks and the crystal fusion of the PLLA blocks, respectively. These peaks shift to the higher temperature as the PLLA composition increases. The sample No. 4 having shorter PLLA blocks shows the two melting endotherms of [RS]-PHB, while the others having longer ones show a crystallization exotherm

Table 4
Thermal properties of the PLLA–PHB–PLLA triblock copolymers

Run No.	[RS]-PHB			PLLA			Quenched sample T_g[a] (°C)
	DP[b]	T_g[c] (°C)	T_m[c] (°C)	DP[b]	T_m[c] (°C)	χ[d] (%)	
1	63	−6.0	48	46	135	30	15
2	63	2.9	–	67	150	30	26
3	63	3.2	–	108	152	34	31
4	117	0.7	50, 71	41	124	27	14
5	117	4.1	–	69	138	21	20
6	117	4.8	–	138	152	35	47

[a] The second heating scan of the quenched sample.
[b] The average degree of polymerization of each blocks estimated by GPC.
[c] Measured by DSC analysis in the first heating scan (heating rate 10°C/min).
[d] The degree of crystallinity of PLLA was calculated by DSC.

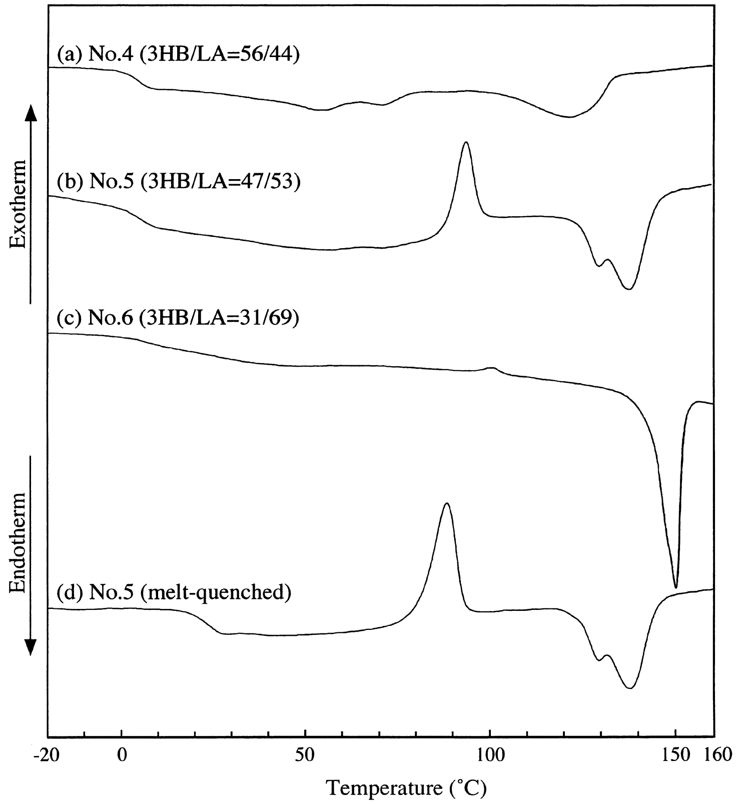


Fig. 8. DSC thermograms of PLLA-[RS]–PHB–PLLA as prepared samples: (a) No. 4 (3HB/LA = 56/44); (b) No. 5 (3HB/LA = 47/53); and (c) No. 6 (3HB/LA = 31/69) melt-quenched sample (d) No. 5.

of PLLA around 80–90°C instead of the melting endotherm of [RS]-PHB. The copolymers prepared from the shorter [RS]-PHB telechelics (DP = 63) also showed similar behaviors, although sample No. 1 showed only one melting endotherm of [RS]-PHB. The T_g and T_m values of each sample are summarized in Table 4. The crystallinity (χ) of the PLLA blocks was calculated from the DSC results according to the equation of $(\Delta H_f - \Delta H_c)/\Delta H_f{}^\circ$ where ΔH_f and ΔH_c are the heats of fusion and crystallization of the sample and $\Delta H_f{}^\circ$ is the melting enthalpy of the 100%-crystalline PLLA (93.0 J/g) [17]. The values are given in Table 4.

Since the glass transition behavior of [RS]-PHB is shown around the original T_g value of pure [RS]-PHB, both the [RS]-PHB and PLLA blocks are considered to be phase-separated. In samples No. 1 and 4 the [RS]-PHB blocks fell into crystallization, although their crystallinity was not estimated because of the lack in crystal data on the syndiotactic [RS]-PHB. On the other hand, samples No. 2, 3, and 6, having the relatively long PLLA blocks, are known to contain highly crystalline PLLA phases. In sample No. 5 showing the crystallization exotherm of PLLA, the crystallinity of the PLLA blocks was slightly lower probably because of the hindered crystallization of the PLLA segment. These results suggest that the crystallization of the syndiotactic [RS]-PHB blocks can be hindered by the PLLA segment having a degree of polymerization higher

Table 5
Mechanical properties of the polymer films of PLLA-[RS]–PHB–PLLA ([RS]-PHB: $M_n = 10,100$, $M_w/M_n = 1.18$ (Sample No. 3, Table 1))

Run No.	Composition (3HB/LA)[a]	Modulus (MPa)	Strength (MPa)	Elongation (%)	χ^b (%)
1	100/0[c]	24	15	610	–
2	56/44	30	10	200	9
3	47/53	130	14	150	10
4	31/69	160	15	86	23
5	0/100[d]	800	39	7.2	37

[a] Determined by ^{1}H NMR spectra.

[b] The degree of crystallinity of PLLA was calculated by DSC.

[c] For a preferentially syndiotactic [RS]-PHB homopolymer ($M_n = 95,000$, $M_w/M_n = 1.70$).

[d] For PLLA homopolymer ($M_n = 99,000$, $M_w/M_n = 1.86$, $T_m = 173$°C).

than 67 while the crystallization of PLLA is little interfered by the presence of the [RS]-PHB blocks.

After those samples had been heated to 160°C and quenched in liquid nitrogen, they were subjected to second heating. Fig. 8(d) shows a typical DSC curve observed in the second heating of sample No. 5. Here, the glass transition behavior is shown at 20°C that is an intermediate region between the T_g of PLLA and [RS]-PHB. The other samples also showed similar behavior in the second heating. The T_g value observed in the second heating for each of the samples is shown in the last column of Table 4. The results suggest that the syndiotactic [RS]-PHB block is miscible with the PLLA block in the amorphous state that was formed by melt-quenching. It has recently been reported that atactic [RS]-PHB ($M_n = 31,000$) is miscible with PLLA ($M_n = 140,000$) in the amorphous state of their polymer blend [18]. The present results also support the miscibility of the two polymers in amorphous state and their phase-separation behavior at crystallization, even if they are linked in a block copolymer.

3.4. Mechanical properties of the PLLA–[RS]-PHB–PLLA films

Polymer films were made from the PLLA-[RS]–PHB–PLLA samples by solution casting, and their mechanical properties were measured. Table 5 gives the tensile properties of the films of samples No. 4, 5, and 6 prepared from [RS]-PHB ($M_n = 10,100$), as compared with those of the cast films of ordinary syndiotactic [RS]-PHB ($M_n = 95,000$) and PLLA ($M_n = 99,000$) homopolymers. The Young's modulus of the copolymer films increased from 30 to 160 MPa with increasing PLLA composition from 44 to 69% or increasing crystallinity from 9 to 23%. In contrast, the elongation at break decreased from 200 to 86%. Furthermore, the Young's modulus of the copolymer films was much higher than that of the syndiotactic [RS]-PHB and much lower than that of the PLLA, while their tensile strength was almost identical with that of [RS]-PHB. These results suggest that the physical properties of the elastomeric [RS]-PHB could be improved by introducing PLLA as the crystalline hard segment.

4. Conclusions

The telechelic [RS]-PHB having hydroxyl groups on both chain ends was successfully prepared by ring-opening polymerization of [RS]-βBL in the presence of BD by using DTD as the catalyst. The produced polymer was found to have a syndiotactic-rich sequence with highly elastomeric properties. This telechelic [RS]-PHB was subjected to block copolymerization with L-lactide to synthesize the block copolymers having elastomeric [RS]-PHB as soft segment and PLLA as hard segment. The DSC thermograms of the produced PLLA-[RS]–PHB–PLLA triblock copolymers suggested a microphase separation structure if the segment crystallization was induced. The mechanical properties of the elastomeric [RS]-PHB triblock copolymers were found to be improved by the introduction of PLLA as the hard segment. From these results PLLA-[RS]–PHB–PLLA can be used as a biodegradable thermoplastic elastomer.

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References

[1] Anderson AJ, Dawes EA. Microbiol Rev 1990;54:450.
[2] Steinbuchel A, Valentin HE, Schonebaum AJ. J Environ Polym Degrad 1994;2:67.
[3] Poirier Y, Somerville C, Schechtman LA, Satkowski MM, Noda I. Int J Biol Macromol 1995;17(1):7–12.
[4] Shi FY, Gross RA, Rutherford DR. Macromolecules 1996;29:10.
[5] Shi FY, Ashby R, Gross RA. Macromolecules 1996;29:7753.
[6] Hori Y, Takahashi Y, Yamaguchi A, Nishishita T. Macromolecules 1993;26:4388.
[7] Hori Y, Suzuki M, Yamaguchi A, Nishishita T. Macromolecules 1993;26:5533.
[8] Abe H, Matsubara I, Doi Y, Hori Y, Yamaguchi A. Macromolecules 1994;27:6018.
[9] Mitomo H, Watanabe Y, Ishigaki I, Saito T. Polym Degrad Stab 1994;45:11.
[10] Mitomo H, Sasaoka T, Yoshii F, Makuuchi K, Saito T. Sen'i Gakkaishi 1996;52:623.
[11] Bahari K, Mitomo H, Enjoji T, Yoshii F, Makuuchi K. Polym Degrad Stab 1998;61:245.
[12] Kricheldorf HR, Lee SR. Macromolecules 1995;28:6718.
[13] Okawara R, Wada M. J Organomet Chem 1963;1:81.
[14] Otera J, Dan-oh N, Nozaki H. J Org Chem 1991;56:5307.
[15] Kemnitzer JE, McCarthy SP, Gross RA. Macromolecules 1993;26:6143.
[16] Kemnitzer JE, McCarthy SP, Gross RA. Macromolecules 1993;26:1221.
[17] Fischer EW, Keller A, Otun EL, Holmes PA. J Mater Sci 1984;19:2781.
[18] Focarete ML, Ceccorulli G, Scandola M, Kowalczuk M. Macromolecules 1998;31:8485.