

Synthesis and Characterization of Biodegradable Poly(Ester-Urethanes) Based on Bacterial Poly(R-3-Hydroxybutyrate)

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ABSTRACT: A series of poly(R-3-hydroxybutyrate)/poly(ϵ -caprolactone)/1,6-hexamethylene diisocyanate-segmented poly(ester-urethanes), having different compositions and different block lengths, were synthesized by one-step solution polymerization. The molecular weight of poly(R-3-hydroxybutyrate)-diol, PHB-diol, hard segments was in the range of 2100–4400 and poly(ϵ -caprolactone)-diol, PCL-diol, soft segments in the range of 1080–5800. The materials obtained were investigated by using differential scanning calorimetry, wide angle X-ray diffraction and mechanical measurements. All poly(ester-urethanes) investigated were semicrystalline with T_m varying within 126–148°C. DSC results showed that T_g are shifted to higher temperature with increasing content of PHB hard segments and decreasing molecular weight of PCL soft segments. This indicates partial compatibility of the two phases. In poly(ester-urethanes) made from PCL soft segments of molecular weight ($M_n \geq 2200$), a PCL crystalline phase, in addition to the PHB crystalline phase, was observed. As for the mechanical tensile properties of poly(ester-urethane) cast films, it was found that the ultimate strength and the elongation at the breakpoint decrease with increasing PHB hard segment content. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 703–718, 2002

Key words: biodegradable poly(ester-urethanes); thermal behaviour; mechanical properties; morphology

INTRODUCTION

Bacterial poly[(R)-3-hydroxybutyrate] (PHB) is a well-known thermoplastic polyester that has many advantageous properties, including biodegradability, biocompatibility, and optical activity.^{1–3} However, the brittleness, narrow processability window, and high cost of production, as compared with conventional synthetic polymers,

limits its application. One approach to improve the properties of PHB is to incorporate other hydroxyalkanoate units such as 3-hydroxyvalerate into the polymer backbone.^{4–9} An alternative approach is to use blends with other kinds of polymers and/or plasticizers.^{10–25}

By contrast, the synthetic poly(ϵ -caprolactone) (PCL), which readily crystallizes, is an important member of the aliphatic polyester family, and known to be susceptible to biological degradation. Nevertheless, this material suffers from its low melting point, limiting its wide application.

Brittle thermoplastic polymers can be toughened significantly upon the introduction of a discrete rubbery phase within the brittle matrix.

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Suter et al.²⁶ used PCL as a soft segment to toughen the brittle PHB thermoplastic by chain coupling through the urethane linkages of telechelic dihydroxy-terminated poly[(R)-3-hydroxybutyrate] or poly[(R)-3-hydroxybutyrate-co-(R)-3-hydroxyvalerate] (containing 4 mol % HV) and poly(ϵ -caprolactone)-diol, PCL-diol, with diisocyanate. Recently; these investigators reported the synthesis of another poly(ester-urethane) series by substituting PCL-diol with poly[(glycolide-co- ϵ -caprolactone)]-diol, having different composition and monomer sequence distribution, aiming at the control of the rate of hydrolytic degradation.²⁷

Poly(urethanes) elastomers are generally multiblock copolymers comprising soft and hard segments. The morphology and properties of thermoplastic poly(ester-urethane) elastomers are greatly influenced by the compatibility of its individual components, the ratio of hard and soft segment blocks, the average block lengths of segments, and the thermal history of final materials.

These considerations prompted us to undertake more systematic research on 3-hydroxyalkanoate-based poly(ester-urethanes). Our objective was to find chemical methods with which to prepare PHB-based materials having improved processability and mechanical properties, without affecting the desirable biocompatible and biodegradable properties. In this article, we report the synthesis of a family of biodegradable poly(ester-urethanes). These multiblock copolymers have been synthesized from diol-terminated poly[(R)-3-hydroxybutyrate]s, PHB-diols, as hard segments and poly(ϵ -caprolactone)-diols, PCL-diols, as soft segments. As a junction, 1,6-hexamethylene diisocyanate was employed as a nontoxic connecting unit.

To correlate the morphology and thermal and mechanical properties more thoroughly with the compositions, it is advantageous to prepare a large series of poly(ester-urethanes) made from the above-mentioned biodegradable macrodiols with different compositions and different block lengths.

EXPERIMENTAL

Materials

Biological poly[(R)-3-hydroxybutyrate] (PHB) was a generous gift of Copersucar (Piracicaba, Brazil). The sample was purified by dissolution in chloro-

form, filtration to remove any insoluble fraction, and reprecipitation in diethyl ether. ϵ -Caprolactone (Aldrich) and dichloroethane (Merck) were distilled over calcium hydride under vacuum. 1,4-Butanediol was distilled under vacuum over 4-Å molecular sieves. 1,6-Hexamethylene diisocyanate, dibutyltin dilaurate, and *p*-toluene sulfonic acid (Fluka) were used as received.

Prepolymer Synthesis

PCL-diols of various molecular weights were synthesized by ring opening polymerization of ϵ -caprolactone, using 1,4-butanediol as the initiator and dibutyltin dilaurate as the catalyst. Reactions were carried out by heating at 130°C under argon atmosphere for different time intervals. The amount of ϵ -caprolactone varied from 3 to 20 mole for 1 mole of OH of the 1,4-butanediol.

PHB-diols of the desired molecular weights were prepared by the method described previously.²⁹ PHB (30 g) was heated in 300 mL dry chloroform at 60°C under argon atmosphere, to which 42 g of 1,4-butanediol and 10 g of anhydrous *p*-toluenesulfonic acid were added successively. The temperature of the reaction was kept constant at 60°C; aliquots were taken periodically from the reaction vessel to follow the progress of the reaction. The aliquots were precipitated from chloroform by cold methanol; the solid formed was separated by filtration and washed successively with cold methanol, acetone, and diethyl ether, and then dried under vacuum.

Copolymer Synthesis

Copolymerization of telechelic PCL-diol and PHB-diol, was carried out in dry 1,2-dichloroethane using an equimolar amounts of 1,6-hexamethylene diisocyanate as a coupling agent and dibutyltin dilaurate as a catalyst by the method described previously.²⁷ All the copolymers were separated in high yields ($\geq 95\%$) from the reaction mixture by precipitation in a large amount of low boiling petroleum ether. The isolated copolymers were redissolved in 1,4-dioxane, filtered, reprecipitated in water, and dried under vacuum at 70°C.

Preparation of Films

Films of the investigated poly(ester-urethane) (0.1–0.15 mm thickness) were prepared by conventional solution-casting techniques from 5 wt % solutions in chloroform using glass Petri dishes as

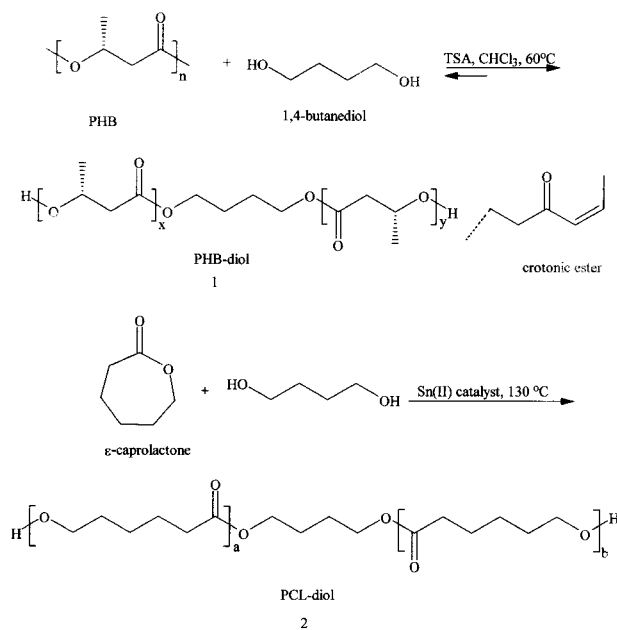
casting surfaces. The films produced were dried in a vacuum to constant weight and then left to stand for ≥ 2 weeks at room temperature to attain equilibrium crystallinity before any measurements.

Measurements

Perkin–Elmer DSC-7 differential scanning calorimeter (DSC) was employed to study the glass-transition temperature (T_g), and melting of PHB and PCL phases. The apparatus was calibrated for temperature, heat and heat flow according to the method recommended by GEFTA³⁰ (Germany). During the first scan run, the samples were heated from -100 to 180°C with a heating rate $10^\circ\text{C}/\text{min}$. For T_g , the samples were heated from 30 to 160°C with a heating rate $20^\circ\text{C}/\text{min}$ and then maintained at 160°C for 2 min before rapid cooling to -100°C (cooling rate $-80^\circ\text{C}/\text{min}$). The samples were then reheated to 180°C with a heating rate $10^\circ\text{C}/\text{min}$ (second scan). A third scan run was taken immediately after slow cooling ($-5^\circ\text{C}/\text{min}$) from melt at 160°C , using the same conditions as for the first run. To minimize the risk of degradation of the copolymers and the consequent molecular weight decrease, a new sample was used for each measurements. Most information was collected from the second and third scans. The glass T_g was taken as the midpoint of the specific heat increment and the melting point, T_m , as the maximum peak temperature of melting endotherms. The enthalpies of fusion, ΔH_f , were directly obtained from the areas under peaks.

Molecular weight and dispersity were determined by using a GPC Waters model 510 pump, model 410 refractive index detector, and model 730 data module with 10^3 – 10^5 -Å Ultrastaygel column in series. Chloroform was used as an eluent at a flow rate of $1.5\text{ cm}^3/\text{min}$. Sample concentrations of $20\text{ mg}/\text{cm}^3$ and injection volumes of $60\text{ }\mu\text{L}$ were used. Poly(styrene) standard with low polydispersity (Polystandard series, Mainz) were used to establish the calibration curve.

MALDI-TOF MS experiments were performed on a Bruker REFLEX III MALDI-TOF mass spectrometer with a nitrogen laser (337 nm). All mass spectra were obtained in the delayed extraction and reflector mode, with an accelerating voltage at 25 kV for the positive mode or at 20 kV at the negative mode. Oligomer samples were dissolved in CH_3Cl ($10\text{ mg}/\text{mL}$). 2,5-Dihydroxybenzoic acid (DHBA) matrix solution was prepared by dissolving 30 mg in 1 mL CH_3Cl ; matrix and oligomer solutions were then mixed in a $10 : 1$ ratio. The



Scheme 1

MALDI target was pre-spotted with 1 – $2\text{ }\mu\text{L}$ NaCl solution ($1\text{ mg}/\text{mL}$ in methanol) and allowed to air dry; 1 – $2\text{ }\mu\text{L}$ of matrix/oligomer was deposited onto the sample target and air dried.

^1H -nuclear magnetic resonance ($^1\text{H-NMR}$) spectra were recorded on a Bruker AC-200 and AC-400 spectrometers, CDCl_3 was used as a solvent and tetramethylsilane (TMS) as the internal reference.

The stress–strain curves for solution-cast films of poly(ester-urethanes) were obtained at 25°C at a strain rate of $10\text{ mm}/\text{min}$, using the Zwick 1445 Test machine (Zwick GmbH, Germany). Samples taken were of 50-mm length, 4-mm width, and 100 – $150\text{-}\mu\text{m}$ thickness, with 13-mm free length. At least three samples were measured, and the mechanical tensile data were determined from these curves as an average of three specimens.

The morphologies of PHB and PCL in poly(ester-urethanes) were observed with a Zeiss optical microscope equipped with crossed polarizers and a Linkham hot stage. The cast films (2 mg) were first heated from 30° to 180°C at a rate of $50^\circ\text{C}/\text{min}$. Samples were maintained at 180°C for 1 min and then cooled rapidly to the desired crystallization temperature.

Wide-angle X-ray diffraction of copolymer films were recorded at 25°C on Siemens D500 diffractometer employing nickel-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.524\text{ \AA}$; 30 kV , 180 mA) in the 2θ range 2 – 40° , using a scan speed of $2.0^\circ/\text{min}$.

Table I Reaction Conditions, Thermal and Molecular Weight Characteristics of PHB-Diols

Sample	Temp. (°C)	Time (h)	Recovery (%)	M_n (g/mol)	M_w/M_n	T_g (°C)	T_m (°C)	ΔH_f (J/g)	X_c %
PHB	—	—	—	31200	3.37		173.0	88.9	60.1 ^a
						2.0	172.5	86.8	59.5 ^b
PHBI	60	30	67	2100	1.52		131.0	96.3	66.0
						-22	129.8	84.9	58.2
PHBII	60	22	78	3000	1.61		144.0	82.8	56.7
						-15	142.0	95.1	65.2
PHBIII	60	16	89	4400	1.59		150.6	95.2	65.1
						-13	149.0	92.2	63.2

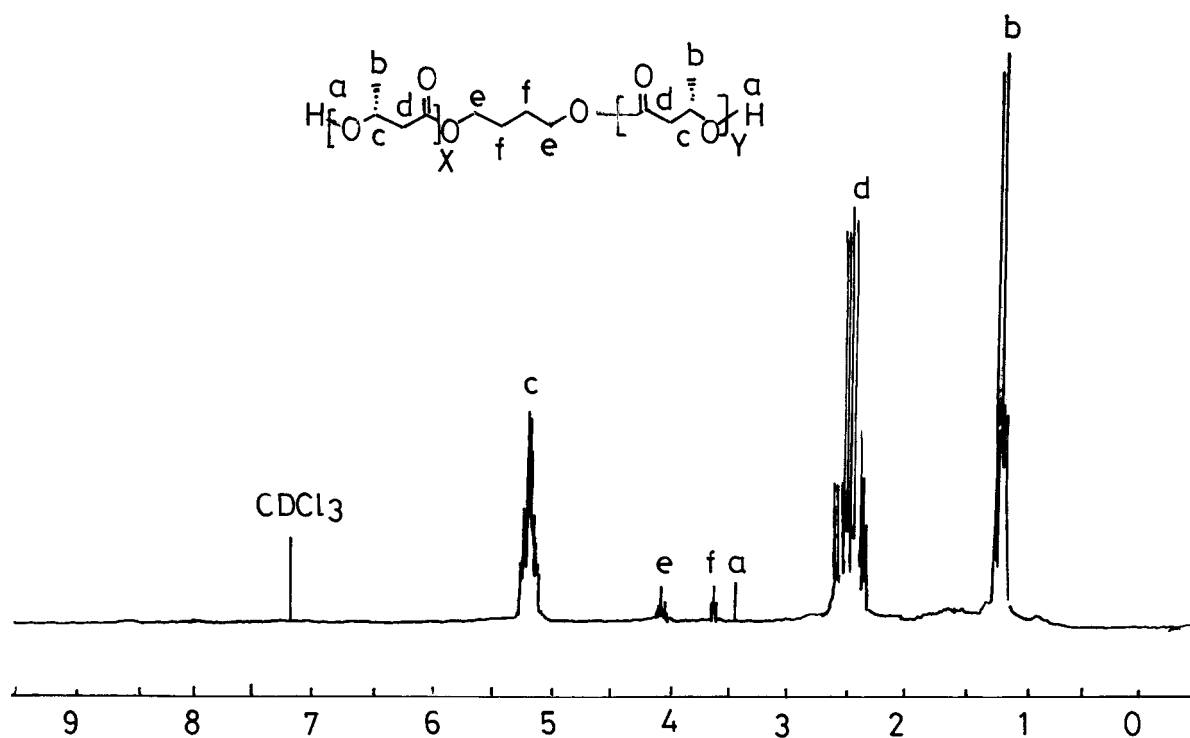
^a Values recorded from first run.^b Values recorded from second run.

RESULTS AND DISCUSSION

Synthesis and Characterization of Telechelics PHB-Diol and PCL-Diol Oligomers

The synthesis of telechelic PHB-diols, as depicted in Scheme 1, involves the transesterification of high-molecular-weight bacterial poly[(R)-3-hydroxybutyrate] with 1,4-butanediol, using *p*-toluene sulfonic acid (TSA) as a catalyst. The reaction conditions, average number molecular weight, M_n , polydispersity, M_w/M_n , and DSC data of the

obtained PHB-diols are listed in Table I. These PHB-diols are denoted as PHBI, PHBII, and PHBIII for PHB-diols having M_n 2100, 3000, and 4400, respectively. Figure 1 shows the ¹H-NMR spectrum of PHBI with the assignment peaks. Two sets of complex signals were observed at 4.28 and 3.65, consistent with the formation of ester linkages between PHB terminal carboxyl group and 1,4-butanediol. The hydroxyl protons were observed at 3.4. Beside the formation of the expected telechelic PHB-diol, another side reaction

**Figure 1** 400 MHz ¹H-NMR spectrum of PHB-diol, PHBI, in CDCl₃.

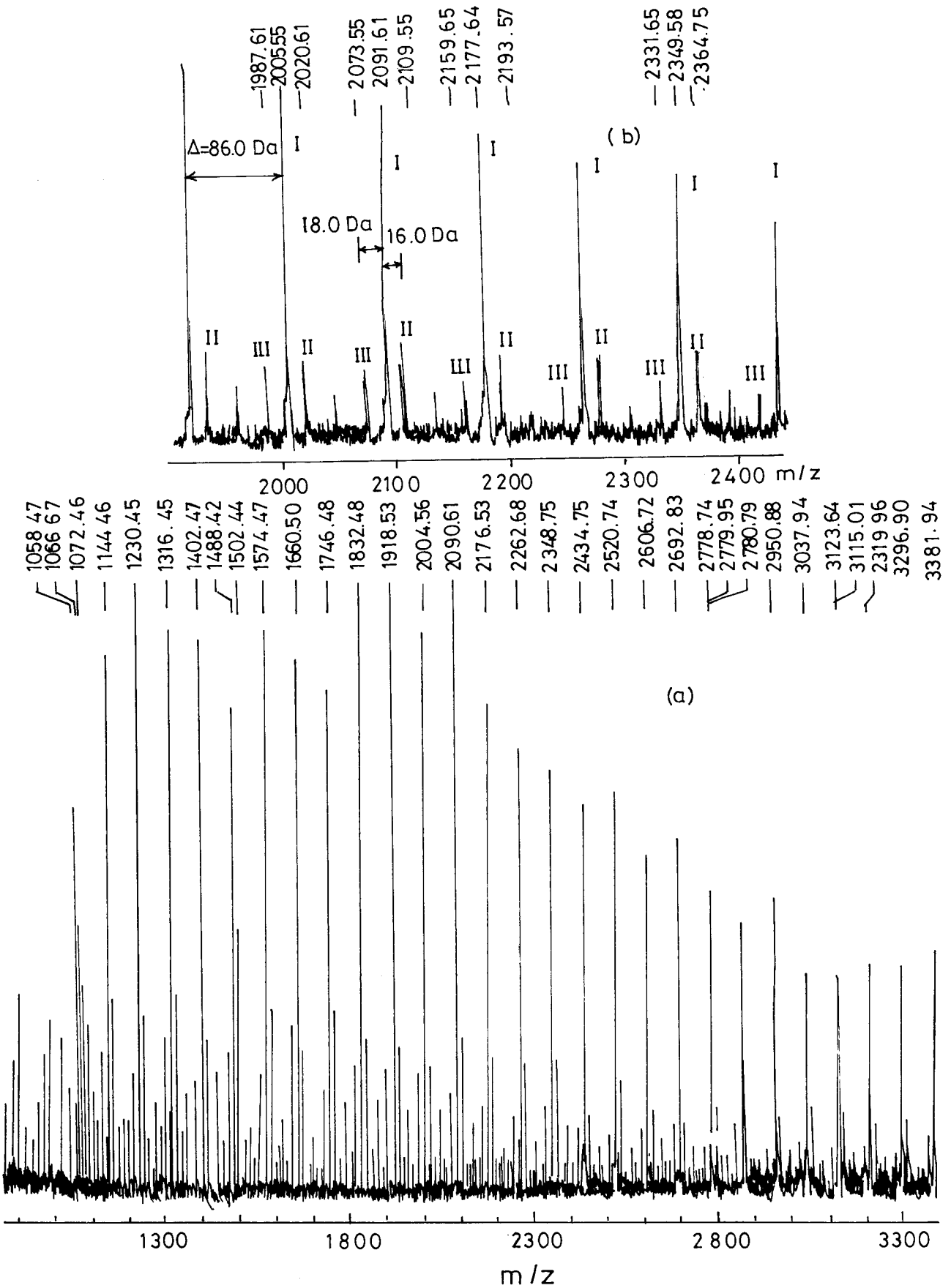


Figure 2 MALDI-TOF mass spectrum of PHB-diol, PHBI.

Table II Reaction Conditions, Thermal and Molecular Weight Characteristics of PCL-Diols

Sample	Feed Ratio [M]/[OH]	Temp. (°C)	Time (h)	Yield (%)	M_n (g/mol)	M_w/M_n	T_g (°C)	T_m (°C)	ΔH_f (J/g)	X_c % ^a
PCLI	3	130	12	85	1080	1.55	-64.0	43.0	70.2	51.6
PCLII	5	130	16	80	2200	2.21	-63.0	49.0	83.7	61.5
PCLIII	10	130	20	88	3700	1.86	-63.0	53.0	86.0	63.2
PCLIV	20	130	24	92	5800	1.90	-62.0	62.7	88.5	65.1

^a Values recorded from melt-quenched samples (second run).

may take place during transesterification (see Scheme 1). This side reaction is presumably the formation of a crotonic ester end group which is assumed to take place after the transesterification process in the presence of TSA catalyst. To investigate the extent of such a side reaction, the end groups in the reaction product were determined by MALDI-TOF mass spectra.^{31–34} The spectrum of a typical PHB-diol reaction product is shown in Figure 2, in which a series of peaks of high intensity (series I) is observed together with a number of low-intensity peaks (series II and III). Obviously, the peaks with each individual series are separated by exactly 86 Da, i.e., the molecular weight of an individual PHB repeating unit. The most intense peaks, I, correspond to the homologous series of the Na⁺-PHB-diol, $[\text{OCH}(\text{CH}_3)\text{CH}_2\text{CO}]_n[\text{O}(\text{CH}_2)_4\text{O}][2\text{H}][\text{Na}^+]$. For example, the peak appears at 1058.5 is the combined masses of 2H of two ends hydroxyl groups, 11-mers, $[-\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}-]$ connecting unit and Na⁺ ion. In addition to the Na⁺-PHB-diol peaks, another peak series, II and III, of minor intensity could be identified in expanded spectrum [Fig. 2(b)]. These peaks appear at masses 16 Da higher and 18 Da lower than the main peaks, which may be assigned to the K⁺-PHB-diol (series II) and crotonic ester end groups (series III), which may be formed by water elimination as a side reaction. The percentage of nonreactive crotonic ester endgroups in the oligomer, as calculated from the relative peak heights, is less than 4%. This value is small enough to permit the preparation of high-molecular-weight copolymers with another macrodiols through chain extension.

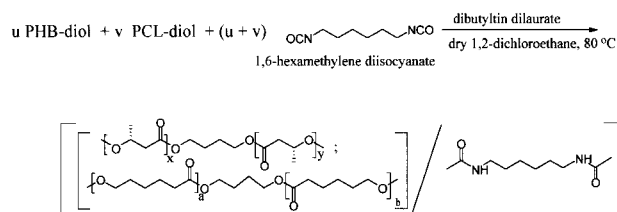
The synthesis of PCL-diols, included in Scheme 1, involves the reaction of 1,4-butanediol, as an initiator, with ϵ -caprolactone in the presence of dibutyltin dilaurate as a catalyst. In view of the reported role,³⁵ the use of a diol initiator in the ring opening polymerization results in a polymer molecule with two hydroxyl groups each at both

ends. The number average molecular weight at any time is proportional to the conversion of the polymerization and to the initial $[\epsilon\text{-CL}]/[\text{OH}]$ ratio. The reaction conditions, M_n , M_w/M_n and other characteristics of the PCL-diols are presented in Table II. The PCL-diols are denoted as PCLI, PCLII, PCLIII, and PCLIV for PCL-diols having M_n 1080, 2200, 3700, and 5800, respectively.

It can be observed from Table I that the T_m and T_g values of PHB-diols are directly related to the molecular weight; i.e., a low-molecular-weight oligomer possesses low T_m and T_g . The relatively high enthalpy of fusion (ΔH_f) of the PHB-diols oligomers indicate a high degree of crystallinity. Based on the literature value for the heat of fusion of 100% crystalline PHB (146 J/g³⁶) the degree of crystallinity for our samples was calculated to be in the range of $65 \pm 5\%$. By contrast, the T_m and ΔH_f of PCL-diols, as shown in Table II, are found to increase with increasing molecular weight. The enthalpy of fusion of 100% crystalline PCL (136 J/g³⁷) was used to calculate the crystallinity of PCL-diol samples. The values were found to be within the range of 52–63%, depending on M_n .

Synthesis and Characterization of Poly(Ester-Urethanes)

A series of poly(ester-urethanes) were synthesized from telechelic blocks of PHB-diol and PCL-diol with different input molar ratio, using stoichiometric amounts of 1,6-hexamethylene diisocyanate (HDI) in a one-step solution polymerization process according to Scheme 2. In order to clarify the effect of PHB and PCL diols block lengths on the thermal and mechanical properties, another series of poly(ester-urethanes) was synthesized keeping the PHB hard segment content constant ($\cong 50$ wt %) and the other two com-



Scheme 2

ponents—PCL and urethane linkage—constitute the ranging 50%, but with varying proportion. This could be carried out using PHB and PCL diols with different molecular lengths and HDI, which is equivalent to total [OH] groups in both macrodiols. The extent of reaction of the latter series was checked periodically at different time intervals by GPC in order to isolate copolymer samples with comparable molecular weights. Tables III and IV show the composition of the reactant mixtures, block lengths of PHB-diols and PCL-diols (M_n), compositions of poly(ester-urethanes), weight average molecular weights (M_w) and polydispersities (M_w/M_n). The calculation of the compositions of the poly(ester-urethanes) copolymers was based on the assumption that all component blocks became part of copolymers; this is reasonable on the basis of the near-quantitative yields ($\geq 95\%$). Hence, the composition of the copolymer reflects the input of the components. $^1\text{H-}$

NMR analysis confirmed that the copolymer contained both respective unit structures of PHB and PCL with a composition indistinguishable from that expected from the ratio of starting materials within the limits of precision of $^1\text{H-NMR}$. In all cases, GPC chromatograms of the synthesized multiblock poly(ester-urethanes) show peaks that were unimodal and of higher molecular weight than the starting PHB-diol and PCL-diol prepolymer. No starting material was detected in the chromatogram of the isolated polymers. As can be seen in Table III, the molecular weight of the synthetic copolymer, regardless the block lengths of PCL-diols, decreases with increasing PHB hard segment content. This may be attributed to the presence of a small fraction of PHB prepolymer with unreactive crotonic ester endgroups.

The nomenclature assigned to the poly(ester-urethanes) prepared is as follows. For poly(ester-urethanes) derived from PHB-diols and PCL-diols, the first number following PHBI, PHBII, and PHBIII refers to the wt % of PHB, while the second one refers to the approximate soft-segment molecular weight (in thousands). For poly(ester-urethanes) based on PCL-diol only, the numbers following PCLII, PCLIII and PCLIV refer to the wt % of PCL soft segment and the soft segment molecular weight (in thousands), respectively.

Table III Poly(Ester-Urethanes) Synthesized from Telechelics PHB-Diol and PCL-Diol With 1,6-Hexamethylene Diisocyanate, HDI

Sample	M_n of PHB-Diol	M_n of PCL-Diol	PHB-Diol, wt % (mol %)	PCL-Diol, wt % (mol %)	Junction Unit, wt % (mol %)	M_w of Copolymer	M_w/M_n
PCLII-93-2.2	—	2200	—	92.9 (100)	7.1 (100)	510000	2.3
PHBII-29-2.2	3000	2200	29.2 (25)	64.2 (75)	6.6 (100)	460000	2.2
PHBII-54-2.2	3000	2200	54.2 (50)	39.7 (50)	6.1 (100)	447000	1.8
PHBII-76-2.2	3000	2200	75.8 (75)	18.5 (25)	5.7 (100)	119000	1.9
PCLIII-96-3.7	—	3700	—	95.7 (100)	4.3 (100)	231000	2.9
PHBII-20-3.7	3000	3700	20.3 (25)	75.1 (75)	4.6 (100)	225000	3.4
PHBII-43-3.7	3000	3700	42.6 (50)	52.6 (50)	4.8 (100)	144000	2.9
PHBII-67-3.7	3000	3700	67.3 (75)	27.7 (25)	5.0 (100)	82000	2.4
PCLIV-97-5.8	—	5800	—	97.2 (100)	2.8 (100)	80500	2.7
PHBII-14-5.8	3000	5800	14.2 (25)	82.6 (75)	3.2 (100)	74000	2.5
PHBII-33-5.8	3000	5800	32.8 (50)	63.5 (50)	3.6 (100)	72800	2.9
PHBII-58-5.8	3000	5800	58.2 (75)	37.5 (25)	4.3 (100)	71000	2.3
PHBI-15-3.7	2100	3700	15.1 (25)	80.0 (75)	4.9 (100)	77400	2.7
PHBI-34-3.7	2100	3700	34.2 (50)	60.3 (50)	5.5 (100)	67500	3.1
PHBI-59-3.7	2100	3700	59.0 (75)	34.7 (25)	6.3 (100)	52000	2.3

Table IV Synthesized Poly(Ester-Urethanes) Containing ~50 wt % PHB-Diol as Hard Segment

Sample	M_n of PHB-Diol	M_n of PCL-Diol	PHB-Diol, wt % (mol %)	PCL-Diol, wt % (mol %)	Junction Unit, wt % (mol %)	M_w of Copolymer	M_w/M_n
PHBI-50-1.08	2100	1080	50.0 (65)	39.8 (35)	10.2 (100)	74000	2.7
PHBI-50-2.2	2100	2200	50.4 (55)	42.3 (45)	7.3 (100)	71600	2.5
PHBI-50-3.7	2100	3700	49.8 (67)	44.2 (33)	6.0 (100)	68300	2.2
PHBI-50-5.8	2100	5800	49.2 (75)	45.4 (25)	5.3 (100)	68000	3.2
PHBII-50-2.2	3000	2200	50.3 (46)	43.4 (54)	6.3 (100)	86500	2.4
PHBII-50-3.7	3000	3700	50.1 (58)	45.0 (42)	4.9 (100)	81000	2.1
PHBI-50-5.8	3000	5800	49.1 (67)	46.8 (33)	4.1 (100)	72000	2.2
PHBIII-50-1.080	4400	1080	50.3 (23)	41.3 (77)	8.4 (100)	83000	2.3
PHBIII-50-2.2	4400	2200	50.1 (36)	44.6 (64)	5.3 (100)	73000	2.1
PHBIII-50-3.7	4400	3700	50.2 (48)	45.8 (52)	4.0 (100)	86500	1.9
PHBIII-50-5.8	4400	5800	50.5 (49)	46.2 (41)	3.3 (100)	87200	2.2

Thermal Properties

The thermal transitions of the investigated poly(ester-urethanes) cast films derived from PHB and PCL diols with different molar ratios are given in Tables V and VI. Typical DSC thermograms are presented in Figures 3–5. The results show that at the first heating scan no obvious glass transition was detected. This may be attributed to high crystallinity of the PCL and/or PHB components. No endothermic melting transition of the PCL soft segments was observed for PHBII-54-2.2 and PHBII-76-2.2. Whereas the sample PHBII-29-2.2 possesses melting endotherm corresponding to the PCL-soft segment crystalline phase. However, when the PCL-molecular weight was increased to 3700 and 5800, a peak melting transition corresponding to soft domains was observed, irrespective of the PHB hard segment content, indicating the ease of formation of a PCL crystalline phase together with the PHB crystalline phase. The appearance of the soft segment crystallinity in the poly(ester-urethanes) prepared from PCL $M_n = 2200$ with low PHB content could mean that, at lower hard segment content, the hard segment domains exert less filler effects, allowing the crystallization of PCL-soft segments to occur at such soft segment molecular weight. During the second scan, the samples pass through several transitions. The low temperature inflection point is related to the glass transition of the amorphous PCL-soft segments; the next concern the exothermic crystallization of PCL and/or PHB segments, as well as the endothermic melting of the crystalline frac-

tion of the PCL-soft domain. The last endotherm is related to melting of crystalline PHB hard segments. The above mentioned transitions are listed in Tables V and VI. As can be seen from these tables, the glass transition temperature of the soft segment is always higher than that reported for PCL-diol prepolymers or that of the prepared poly(ester-urethanes) based only on PCL-diol. Their values lie between those of the PHB and PCL macrodiols employed. In addition, the T_g values shift to higher temperatures upon increasing the PHB-hard segment content or decreasing the molecular weight of the PCL soft segments. This shift in the T_g is taken as an indication for the differences encountered in phase mixing. The greater the amount of PHB hard segment dissolved in the PCL-soft domains, the more restrictive are the soft domains, and the higher the expected T_g of the PCL-soft segment in the poly(ester-urethane). Comparing the T_g values of the pure PCL-diols or poly(ester-urethanes) based on PCL only with those associated with poly(ester-urethanes) based on PHB and PCL, it appears that the difference increases with increasing the PHB-content and decreasing the PCL-prepolymer molecular weight. This finding may suggest partial miscibility of PHB hard and PCL-soft segments, which would increase as the content of hard segment increases and the length of PCL-block decreases.

Similarly, and in a parallel manner, the exothermic peak due to the PCL soft segment crystallization and endothermic one due to its melting, appear in poly(ester-urethane) samples pre-

Table V Effect of Soft Segment Molecular Weight and Compositions on the Thermal Properties of Poly(Ester-Urethanes)

Sample	Scan ^a	T_m (°C)	PCL-Segment			P(3HB)-Segment		
			ΔH_f (J/g) ^b	X_c % ^c	T_m (°C)	ΔH_f (J/g) ^b	X_c % ^c	T_g (°C)
PCLII-93-2.2	1	55.5	59.7	46.7	—	—	—	—
	2	46.0	60.7	44.9	—	—	—	-62.0
	3	46.0	62.2	45.9	—	—	—	—
PHBII-29-2.2	1	49.5	5.7	4.2	134.0	53.5	36.6	—
	2	38.5	6.4	4.6	133.5	55.6	38.1	-43.0
	3	38.0	6.1	4.5	133.0	57.2	39.2	—
PHBII-54-2.2	1	—	—	—	138.5	60.2	41.2	—
	2	—	—	—	137.0	63.4	43.3	-26.5
	3	—	—	—	137.0	65.0	44.5	—
PHBII-76-2.2	1	—	—	—	141.0	64.5	44.2	—
	2	—	—	—	138.5	67.0	45.9	-18.3
	3	—	—	—	137.5	63.9	43.7	—
PCLIV-97-5.8	1	62.7	80.8	59.4	—	—	—	—
	2	55.5	62.3	54.5	—	—	—	-59.0
	3	56.0	76.0	55.9	—	—	—	—
PHBII-14-5.8	1	60.3	66.6	49.9	141.0	69.5	47.9	—
	2	51.0	62.0	54.6	138.5	73.0	50.0	-50.1
	3	51.5	68.4	50.3	138.0	77.4	53.1	—
PHBII-33-5.8	1	52.0	51.7	38.1	139.5	68.5	46.9	—
	2	49.5	49.6	36.4	138.0	75.0	51.3	-45.2
	3	50.3	50.9	34.8	138.4	72.8	49.9	—
PHBII-58-5.8	1	48.5	32.8	24.1	140.0	63.0	43.2	—
	2	43.6	29.3	21.6	138.4	78.6	53.8	-42.3
	3	44.5	26.1	19.2	138.8	75.9	52.0	—

^a Number indicates the heating scan recorded. (1) DSC scans of samples prepared by solution casting, (2) DSC scans recorded after rapid quenching and (3) DSC scans after slow cooling.

^b Enthalpy of fusion calculated per gram soft or hard segments, rather than per gram polymer.

^c Crystallinity percent calculated from the following equation: $X_c\% = \Delta H_f / 100 \Delta H_f^\circ$, where ΔH_f° is the thermodynamic melting point enthalpy of 100% crystalline P(3HB) or 100% crystalline PCL. ΔH_f is the enthalpy of fusion per gram HB or PCL in the copolymer.

pared from long PCL segments ($M_n \geq 2200$), except for PHBII-54-2.2 and PHBII-76-2.2. This finding is consistent with previous study by Suter et al.²⁷ These workers found that a PCL crystalline was not detected for poly(ester-urethanes) made from PCL-diol with $M_n \cong 1200$ and 2000. Reeve et al.³⁸ pointed out that PHB-PCL diblock copolymers with short PCL ($M_n \cong 1000$) showed only the PHB crystalline phase. With increasing chain length of PCL ($M_n \cong 3300$) the PCL crystalline phase, in addition to the PHB crystalline phase, were detected. In some cases, soft segment melting is observed only during the third scan, as shown in samples PHBI-50-2.2 and PHBII-50-2.2, which indicates that the slow cooling promotes

crystallization of PCL and consequently enhances the phase separation of PHB and PCL components. The normalized heat of fusion, i.e., the value calculated for 1 g of the PCL soft segments content, instead of 1 g of copolymer, is used to estimate the crystallinity of the soft segments. Taking the literature value for the heat of fusion of 100% crystalline PCL,³⁷ the crystallinity, X_c , of the investigated samples was calculated (see Tables V and VI). The heat of fusion (or crystallinity) clearly decreases with increasing the PHB content and/or decreasing the PCL block length. A reasonable explanation for this finding can be obtained, taking into consideration the chain structure characteristic of this kind of segmented

Table VI Effect of Soft and Hard Segment Molecular Weights on the Thermal Properties of Poly(Ester-Urethanes) Containing ≈ 50 wt % Content of PHB

Sample	Scan ^a	PCL-Segment			PHB-Segment			
		T_m (°C)	ΔH_f (J/g) ^b	X_c % ^c	T_m (°C)	ΔH_f (J/g) ^b	X_c % ^c	T_g (°C)
PHBI-50-1.08	1	—	—	—	126.0	72.5	49.64	—
	2	—	—	—	—	—	—	-25.5
	3	—	—	—	128	15.5	10.6	—
PHBI-50-2.2	1	—	—	—	131.6	61.4	42.1	—
	2	—	—	—	132.0	54.6	37.4	-31.6
	3	32.5	10.7	7.9	128.5	53.7	36.8	—
PHBI-50-3.7	1	46.8	11.1	8.1	129.0	57.2	39.2	—
	2	47.1	18.0	13.3	128.8	45.0	30.9	-33.8
	3	46.5	19.7	14.5	129.4	59.0	40.4	—
PHBI-50-5.8	1	47.6	28.9	21.2	132.8	62.9	43.1	—
	2	49.5	55.0	40.4	131.6	64.3	44.0	-42.4
	3	48.8	59.0	43.4	132.1	62.9	43.1	—
PHBII-50-2.2	1	—	—	—	140.5	62.0	42.3	—
	2	—	—	—	137.0	68.0	46.6	-37.4
	3	38.3	12.5	24.4	136.8	66.5	45.5	—
PHBII-50-3.7	1	48.8	6.1	11.8	141.0	64.6	44.2	—
	2	47.7	18.6	33.9	140.0	66.0	45.2	-41.8
	3	43.5	21.3	38.9	140.0	70.6	48.4	—
PHBII-50-5.8	1	48.6	5.1	8.9	140.7	63.5	43.5	—
	2	47.3	20.1	35.4	138.5	65.8	45.1	-49.0
	3	42.5	21.8	38.4	137.0	73.9	50.1	—
PHBIII-50-1.08	1	—	—	—	148.0	62.1	42.5	—
	2	—	—	—	146.0	68.0	46.6	-30.7
	3	—	—	—	147.2	69.3	47.4	—
PHBIII-50-2.2	1	—	—	—	150.0	69.3	55.3	—
	2	33.5	19.2	14.2	148.8	81.1	54.9	-37.6
	3	34.5	23.6	17.9	147.2	73.2	50.1	—
PHBIII-50-3.7	1	50.0	33.5	24.6	149.0	76.0	52.0	—
	2	46.5	41.4	30.4	147.5	76.8	52.6	-46.8
	3	35.4	41.3	30.3	147.2	78.3	53.6	—
PHBIII-50-5.8	1	46.4	25.3	18.8	149.0	71.2	48.8	—
	2	49.0	48.6	34.3	148.5	75.4	51.6	-48.4
	3	44.0	57.9	42.6	149.0	80.3	55.0	—

poly(ester-urethanes). Quenching from the melt provides an amorphous PCL and PHB components. Upon heating, at the temperature range for the PCL soft segments to crystallize the PHB hard segments, because of its relatively high T_g compared with PCL, would be frozen in a glassy state and could hardly move and crystallize. Accordingly, these frozen hard segment domains played a role just like physical crosslinks, which would hinder, to some extent, the ability of PCL to

crystallize. The increase of the hard segment content, the larger the number and size of physical crosslinks in the copolymers and, therefore, the stronger the influence of the hard segments imposed on the crystallization of the PCL-soft segment. By contrast, upon slow cooling the copolymer from the melt, PHB is able to crystallize according to a spherulitic morphology, while the PCL component is still in liquid state. Thus, some fraction of PCL components might be easily incor-

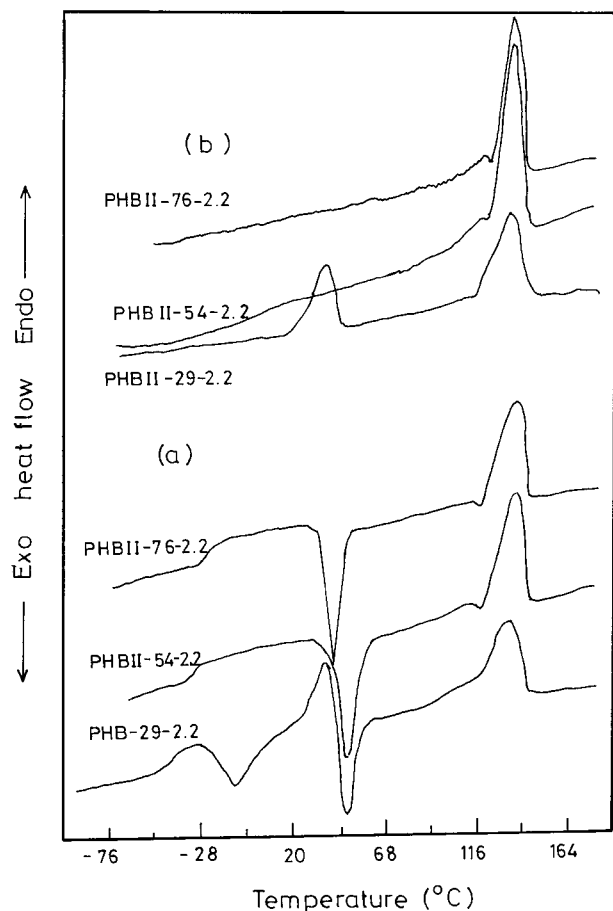


Figure 3 DSC thermograms of poly(ester-urethane) series made from PHB-diol ($M_n = 3000$) and PCL-diol ($M_n = 2200$) of different compositions: (a) during the second heating scan ($10^\circ\text{C}/\text{min}$) recorded after quenching, and (b) during the third heating scan ($10^\circ\text{C}/\text{min}$) recorded after slow cooling ($-5^\circ\text{C}/\text{min}$) from melt.

porated into interlamellar regions of PHB, giving rise, with uncrystallized PHB, to the formation of homogeneous mixed phase. This fraction of PCL involved in the formation of the amorphous interlamellar mixture increases by increasing the content of PHB and decreasing PCL molecular weights. As consequence, the crystallinity of PCL component decreases with increasing PHB content and decreasing PCL molecular weight. Although such hypothesis requires further systematic study on the crystallization behavior of both components isothermally, it seems reasonable.

The endothermic peak, that appears at ~ 130 – 150°C , is related to the melting of the PHB hard segments. The T_m values are dependent, to some extent, on the length and the relative ratio of PCL and PHB segments. In the poly(ester-urethane) series prepared from PCL ($M_n = 2200$), the T_m

decreases with increasing PCL content, while remains almost constant in (polyester-urethanes) prepared from PCL ($M_n = 5800$), as shown in Figure 6. This might be explained on the basis of partial miscibility of PHB and PCL components in poly(ester-urethanes) made from short PCL block lengths ($M_n \leq 2200$), which is well consistent with the conclusion derived from the T_g measurements. Although the melting endotherm, corresponding to the PHB crystalline phase, was not observed in the PHBI-50-1.08 sample in the second run, it appeared after slow cooling from melt in the third scan. This behavior is explained by the fact that the crystallization process is time dependent. Since the crystallinity is mainly affected by the heat treatment, the PHB is still

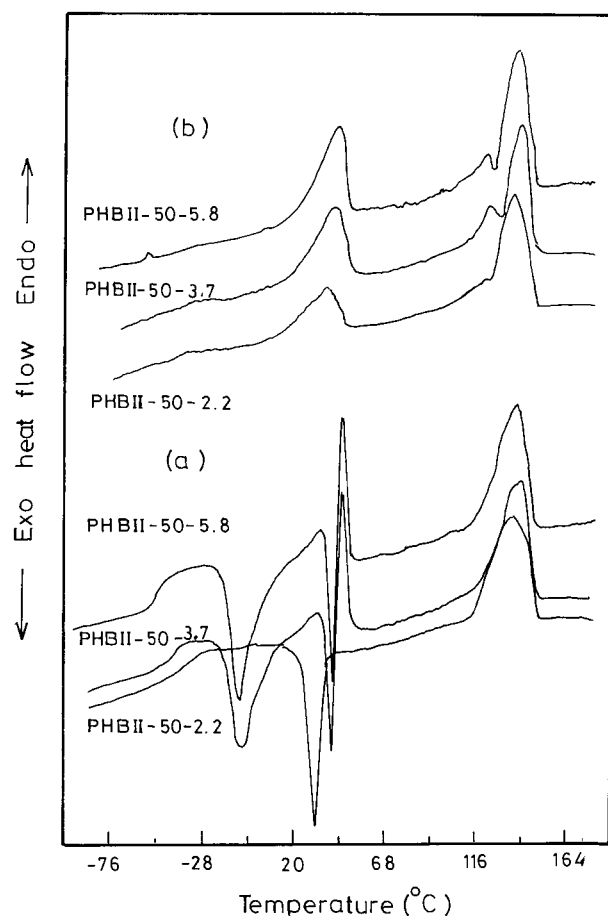


Figure 4 DSC thermograms of poly(ester-urethane) series made from PHB-diol ($M_n = 3000$) and PCL-diol with different M_n at fixed hard segment content (50 wt %): (a) during the second heating scan ($10^\circ\text{C}/\text{min}$) recorded after quenching, and (b) during the third heating scan ($10^\circ\text{C}/\text{min}$) recorded after slow cooling ($-5^\circ\text{C}/\text{min}$) from melt.

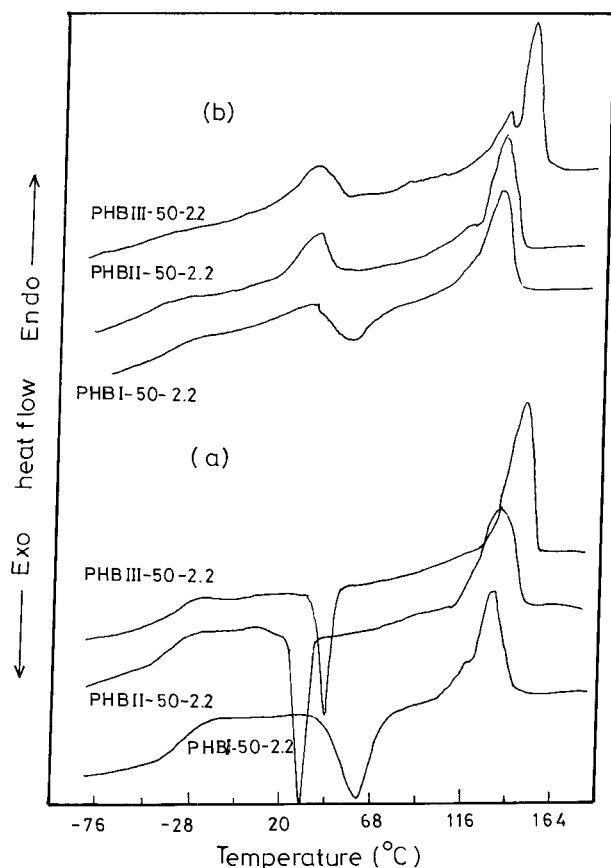


Figure 5 DSC thermograms of poly(ester-urethane) series made from PCL-diol ($M_n = 2200$) and PHB-diol with different M_n of fixed hard segment content (50 wt %): (a) during the second heating scan ($10^\circ\text{C}/\text{min}$) recorded after rapid quenching, and (b) during the third heating scan ($10^\circ\text{C}/\text{min}$) recorded after slow cooling ($-5^\circ\text{C}/\text{min}$) from melt.

amorphous at the start of the third run. Therefore, it is not surprising to see a crystallization exotherm in the DSC thermogram recorded after slow cooling above the T_g , followed by melting [see Fig. 5(b)]. In such cases, time is insufficient for the nucleation to take place and thus crystallization is delayed for samples with such a PHB block length ($M_n = 2100$).

Another phenomenon worth mentioning is the double peak melting of PHB hard segments in poly(ester-urethanes), which is similar to the melting behavior of PHB homopolymer. The lower temperature peak, which appears as a shoulder, is attributable to the fusion of the crystallites formed on cooling from the melt, while the higher one is attributed to the fusion of spherulites recrystallized and perfected during the subsequent DSC heating scans.

It is interesting to note from Tables V and VI that the relative crystallinity, X_c , of PHB hard segments, as calculated from the ratio of the normalized heat of fusion to the heat of fusion of 100% crystalline PHB, is slightly dependent on the chemical composition and block length of the concerned macrodiols.

Regarding the cold exothermic crystallization peaks of PHB hard segments, as shown in Figures 3(a)–5(a), they are shifted to higher temperature with increasing the PCL content and PCL block length of the copolymer. This indicates that the crystallization of PHB in the copolymer is restricted by the presence of PCL; the rate of the nonisothermal crystallization of PHB in the copolymer is slower than either of PHB-diols or PHB homopolymer.

The crystallization of PHB from melt was traced using a polarizing optical microscope under isothermal conditions. Figure 7 shows the optical micrographs of some poly(ester-urethane) samples isothermally crystallized at 80°C . It was found that the PHB phase is able to crystallize with a spherulitic morphology, even in the poly(ester-urethane) sample with 14.2 wt % PHB (sample PHBII-14-5.8), but the texture and growth of spherulites are affected by the PCL content. Preliminary results show the existence of a wide variety of morphologies. Compared with the PHB homopolymer, the radii of PHB spherulites in the poly(ester-urethane) samples are smaller, and their growth is slower.

The DSC thermograms of some poly(ester-urethanes) recorded after slow cooling (third scan) are given in Figures 3(b)–5(b). Transitions, normalized heat of fusion, and crystallinity are in-

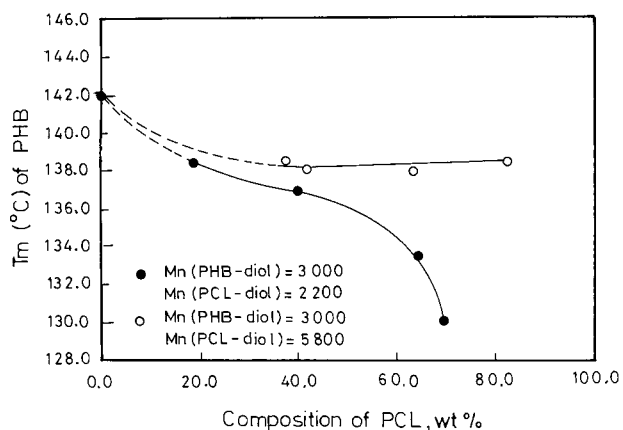


Figure 6 Effect of PCL content on the melting point of PHB crystalline phase of some poly(ester-urethanes).

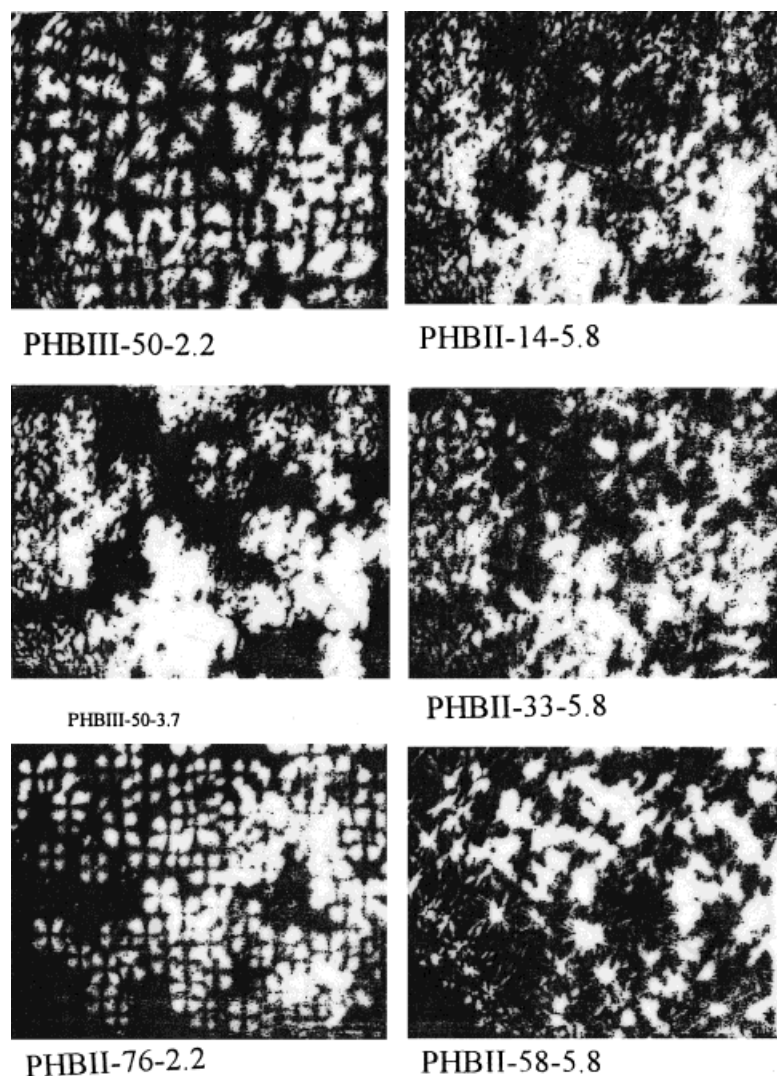


Figure 7 Optical micrographs of PHB spherulites in poly(ester-urethane) crystallized at 80°C.

cluded in Tables V and VI. As mentioned before, the poly(ester-urethane) samples made from PCL $M_n \geq 2200$, except for samples PHBII-54-2.2 and PHBII-76-2.2, exhibited two distinct endothermic melting peaks, which are related to the melting of crystallites, due to PCL soft and PHB hard segments. Thus, slow cooling would allow complete crystallization, as evidenced by the absence of the exothermic peaks of PCL and PHB components in the subsequent heating runs.

Wide-Angle X-Ray Analysis

Wide-angle X-ray scans for some poly(ester-urethane) samples are presented in Figure 8. Comparing the diffraction patterns of PCLII-93-2.2 sample with the other poly(ester-urethane) sam-

ples based on PCL and PHB components, no PCL diffraction patterns characteristic of PCL crystalline phase were observed for PHBII-76-2.2, PHBII-54-2.2, PHBII-50-1.080, and PHBII-50-2.2 samples. In contrast, PHBII-29-2.2, PHBII-50-3.7, and PHBII-50-5.8 possess a sharp diffraction patterns corresponding to PHB and PCL crystalline phases. This finding is consistent with the DSC measurements presented above and suggests that there is a lower limit of PCL molecular weight below which the PCL-soft domains were unable to crystallize in the presence of PHB hard domains.

Mechanical Tensile Properties

The results of the tensile properties for some poly(ester-urethane) cast films (stored at room tem-

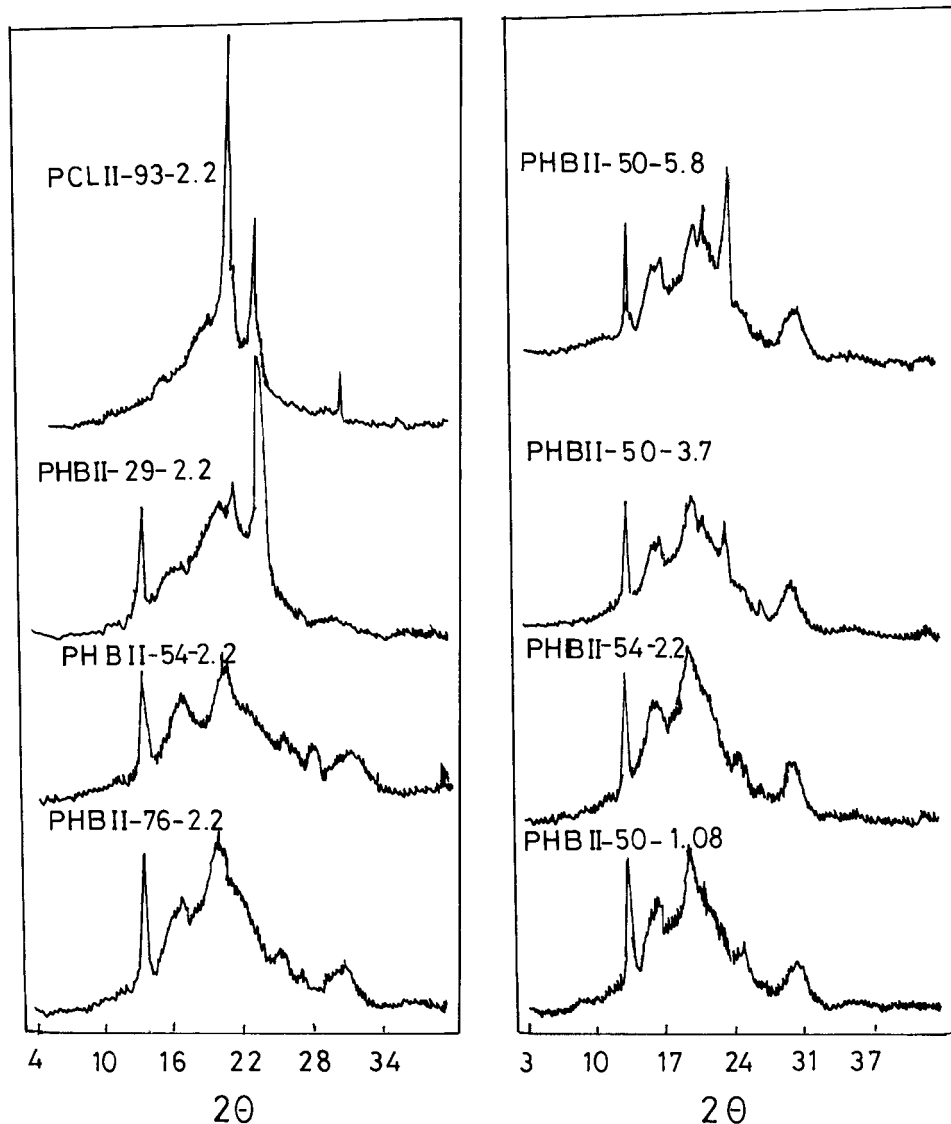


Figure 8 Wide-angle X-ray diffraction patterns of poly(ester-urethanes) cast films.

perature for several weeks) are given in Table VII, and typical engineering stress-strain diagram, as representative example, is shown in Figure 9. The results show that poly(ester-urethane) based only on PCL soft segments and those containing both PCL and PHB with low PHB content were ductile plastics, exhibiting yield point, increased flexibility, and much higher percentage strain at the break point. Poly(ester-urethane) samples of moderate and high PHB content were tough, moderately extensible elastomers. Generally, an increase of PHB content decreases the tensile strength and elongation at the break point. This decrease is more dramatic in copolymers with longer PHB segments. The lower mo-

lecular weights of poly(ester-urethane) samples with moderate and high PHB content could be responsible for some of the decrease in the ultimate tensile strength and elongation. In addition to this factor, there are many intrinsic properties, such as the degree of phase separation, the percent crystallinity, crystallite sizes, and distribution of crystallites, that control the mechanical properties of the endproduct.

By comparing some poly(ester-urethane) samples with comparable molecular weight and containing the same amount of PHB hard segment content (≈ 50 wt % PHB), but differing in the length of their PCL soft segment (Table VII), we find that the tensile strength and elongation de-

crease as PCL block length increases; however, the lowering of the tensile strength, appears to be small compared with elongation. This result may be mainly correlated to the degree of phase separation and the extent of secondary intermolecular forces. Shortening of the PCL soft blocks results in a higher concentration of urethane linkages, which in turn enhances secondary bonding to take place during the stress crystallization process. Also, the decrease in length of PCL soft blocks results in more miscibility between PHB and PCL and consequently more interfacial adhesion. Both factors have an effect on improving the mechanical properties of the products.

CONCLUSIONS

Segmented biodegradable poly(ester-urethanes) of high molecular weight can be easily synthesized through the chain extension of poly(3-R-hydroxybutyrate)-diol and poly(ϵ -caprolactone)-diol prepolymers with 1,6-hexamethylene diisocyanate. All the materials prepared were semicrystalline with melting points ranging within 126–148°C. DSC and wide-angle X-ray results were consistent and showed that poly(ester-urethanes) made from high-molecular-weight soft segments have a greater phase separation than their low-molecular-weight analogues, attributed to the thermodynamic immiscibility of PHB and

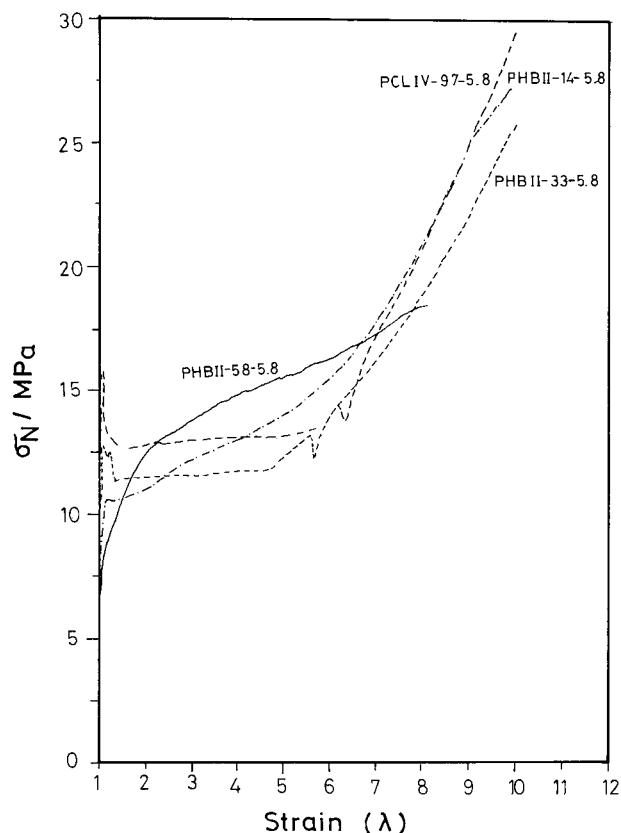


Figure 9 Stress–strain diagrams of poly(ester-urethane) series with different compositions of PHB and PCL, M_n (PHB-diol) = 3000 and M_n (PCL-diol) = 3700.

Table VII Tensile Properties of Some Poly(Ester-Urethanes)

Sample	Tensile Strength (σ_N), MPa	Elongation to Break (%)
PCIII-96-3.7	27.2 ± 0.3	990 ± 55
PCLIV-97-5.8	30.5 ± 1.4	923 ± 39
PHBI-15-3.7	19.4 ± 0.7	935 ± 48
PHBI-34-3.7	16.7 ± 0.3	684 ± 34
PHBI-50-3.7	11.0 ± 0.5	413 ± 19
PHBII-20-3.7	22.6 ± 0.9	892 ± 36
PHBII-43-3.7	16.9 ± 0.5	638 ± 33
PHBII-67-3.7	11.2 ± 0.6	105 ± 18
PHBII-14-5.8	25.9 ± 1.2	902 ± 81
PHBII-33-5.8	26.7 ± 0.8	840 ± 5
PHBII-58-5.8	20.5 ± 1.0	706 ± 40
PHBII-50-2.2	12.4 ± 0.5	278 ± 8
PHBII-50-3.7	11.9 ± 0.2	198 ± 24
PHBII-50-5.8	11.6 ± 0.3	117 ± 12

PCL segments in the high-molecular-weight species. The tensile strength and elongation at the breakpoint of cast films are found to be mainly dependent on the weight fraction of the PHB hard segments. Thus, the results obtained in this work suggest that the thermal and mechanical properties can be controlled by changing the compositions as well as the block lengths of both hard PHB and soft PCL prepolymers. From previous work,³⁹ it can be expected that all these copolymers will be stable materials for most applications, but will readily biodegrade upon composting or soil deposition.

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