Eurasian ChemTech Journal 9 (2007) 231-242

Biodegradable Poly(ester-urethane)s Based on Poly[(R)-3-hydroxybutyrate] and Poly(ε-caprolactone) Blocks: Thermal, Mechanical and Biodegradation Behaviour

Gamal R. Saad*, Tamer M. Khalil and Magdy W. Sabaa

Department of Chemistry, Faculty of Science, University of Cairo, Giza, P.O. 12613, Egypt

Abstract

α-ω-Dihydroxy-terminated poly[(R)-3-hydroxybutyrate] (PHB-diol) ($M_n \sim 4800$) was synthesized by transesterification of the corresponding PHB homopolymer with 1,4-butanediol in presence of *p*-toluenesulfonic acid. It was subsequently combined with poly(ε-caprolactone)-diols (PCL-diols) ($M_n \sim 1260$ and 2200) acting as soft segment via 1,6-hexamethylene diisocyanate to high molecular weight poly(ester-urethane)s. The content of PHB acting as hard segments systematically varied from ~20 to 60 wt.%. The synthesized materials were characterized by FTIR, ^{1}H-NMR, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and tensile properties. In the case of segmented poly(ester-urethane)s, those samples obtained from PCL ($M_n \sim 1260$) showed an increase in T_g's with increasing PHB content, indicating some extent of PCL/PHB segment phase mixing. All of the investigated copolymers were semicrystalline with T_m of PCL phase varying from 39-47°C and PHB phase varying from 141-150°C. The TGA analysis of the investigated copolymers showed three distinct weight loss steps assigned to the thermal degradation of PHB, PCL and urethane linkage with increasing temperature, respectively. As for mechanical tensile, it was found that the ultimate strength and elongation at the breakpoint decrease with increasing PHB content. The biodegradability was studied in active soil. The results showed that the biodegradation rate of the investigated copolymers increases with increasing PHB content.

Introduction

Research in biodegradable polymers has gained considerable interest in recent years due to the increasingly attractive environmental, biomedical, and agriculture applications. Aliphatic polyesters are one of the most promising materials to be used as, *e.g.* packing materials and mulch films to solve the problems related to plastic waste accumulation. Poly[(R)-3-hydroxybutyrate], PHB, is one the most optimal polymer that appears to meet nearly all criteria. It is produced biologically from renewable resources [1-4]. It is stable under normal usage conditions, and undergoes biodegradation under different environmental conditions. Unfortunately, PHB, due to its high crystallinity, has several inherent deficiencies that limit its application as technical material. It is brittle, lacks transparency, and has a high melting temperature and a small temperature window for thermoplastic processing. Several methods have been applied to overcome these difficulties and to obtain useful materials based on bacterial PHB. One approach is to biosynthesize series of copolymers containing other hydroxyalkanoate units in the backbone of PHB. Example for this type are the copolymers of poly[(R)-3-hydroxybutyrate-co-(R)-3-hydroxyhexanoate] [5] and poly[(R)-3-hydroxybutyrate-co-4-hydroxybutyrate] [6,7] that show high elongation at break, but low tensile strength. The second approach is to attempt to control the crystallization through physical methods, blending or additives [8-15]. One of the promising approaches to modify the physical properties, to improve the processability, and to adjust the degradation rate of PHB is incorporating hydrolysable, biodegradable, and flexible polyester-segment blocks, such as pol(ε-caprolactone) (PCL), poly(butylene adiapate) (PBA) or poly(diethylene glycol adipate) (PDEGA), *etc.* [16-23] in PHB brittle

---

*corresponding author. E-mail: grsaad@yahoo.com

Printed in Kazakhstan

matrix via copolymerization. These studies have shown that the preparation of such copolymers allows overcoming the drawbacks inherent to PHB homopolymer. In this work, we report the synthesis, thermal and mechanical tensile properties of the family of high molecular weight biodegradable poly(esterurethane)s based on poly[(R)-3-hydroxybutyrate]-diol and poly(ε-caprolactone)-diol using 1,6-hexamethylene, as non-toxic connecting agent. The biodegradability of the prepared copolymers was studied in comparison with PHB.

Experimental

Materials

Bacterial poly[(R)-3-hydroxybutyrate)], PHB, was supplied from copersucar/PHB Inc., Piracicaba, Brazil. PHB was purified, prior to use, by dissolution in chloroform, filtered to remove any insoluble matter, and then reprecipitated in methanol. α,ω-Dihydroxy poly(ε-caprolactone), PCL-diols, with number-average molecular weights 1260 and 2200 were obtained from Aldrich and were degassed under vacuum at 50°C overnight. Dibutyltin dilaurate, *p*-toluenesulfonic acid (TSA) and 1,6-hexamethylene diisocyanate were supplied by Fluka and used without purification. 1,4-Butanediol was distilled under vacuum and then stored over activated 4 Å type molecular sieves. 1,2-Dichloroethane (Merck) and chloroform (Aldrich) were distilled under vacuum over 4 Å type molecular sieves, petroleum ether and 1,4-dioxane (Aldrich) were used as received. Poly(ε-caprolactone) (M_w = 80,000, polydispersity index 1.4) was purchased from Adrich.

Synthesis of Prepolymer

α,ω-Dihydroxy-poly(R-3-hydroxybutyrate), PHB-diol, (M_n ~ 4800) was prepared by the method described previously [19,24]. PHB (60 gram) was heated in 300 ml dry chloroform at 60°C under nitrogen, to which 90 ml of 1,4-butanediol and 15 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 ethanol. The solid formed was filtered and washed several times with cold methanol, acetone and diethyl ether, and then dried under vacuum at 60°C for 48 hours.

Synthesis of Poly(ester-urethane)s

Two series of poly(ester-urethane) samples were synthesized by one-step condensation reaction in solution from PHB-diol (M_n ~ 4800) as a hard segment, and PCL-diols (M_n ~ 1260 or 2200), as a soft segment, using equivalent amounts of 1,6-hexamethylene diisocyanate as connecting agent [17,19]. The selected telechelic and desired amount of hydroxylated polyesters were dissolved in dry 1,2-dichloroethane to give a concentrated 25% w/v solution, dibutyltin dilaurate 0.5% w/w, as a catalyst, and equivalent amount of 1,6-hexamethylene diisocyanate were added. The reaction mixtures were allowed to react for 3-4 days at 75°C, where the progress of the reaction was periodically checked by GPC. The copolymer obtained was precipitated in low boiling petroleum ether, redissolved in 1,4-dioxane and filtered, then precipitated in water and dried to constant weight under vacuum at 60°C, the yield was ≥ 95%.

In this work, each copolymer is designated by a code related to the structure of the soft and hard segments followed by a number indicating the approximate content of PHB in wt.% in the copolymer. For example, poly(ester-urethane) sample derived from PCL-diol with M_n ~ 1260 & M_n ~ 2200), as soft segment, and PHB-diol, as hard segment, and contains ~40% PHB is designated as UPCLI–HB–40 and UPCLII–HB–40 (where I signify M_n ~ 1260 and II signify M_n ~ 2200).

Preparation of Polymer Films

The films of PHB and poly(ester-urethane) samples (0.10-0.12 mm thickness) were prepared by solvent-casting technique from 4 wt.% chloroform solution in glass Petri dishes of known constant diameters as a casting surface. The films were dried under vacuum to constant weight and then left to stand for at least two weeks at room temperature to attain equilibrium crystallinity prior any measurements.

Characterization

Copolymers Compositions

The compositions of the investigated copolymers were determined by the analysis of ^{1}H NMR spectra recorded at 20°C in $CDCl_3$ solution on a Bruker AC-300.

FTIR-spectra were recorded using a Perkin-Elmer 398 FTIR spectrophotometer between 400-4000 cm^{-1}.

Molecular Weight Measurements

All molecular weights data were determined by gel-permeation chromatography (GPC) at 30°C using a water model 510 GPC system and a model 410 refractive index detector with 10^3-10^5 ultrastyragel column connected in series. Chloroform was used as eluent with a flow rate of 1.5 cm^3/min, and sample concentrations of 20 mg/cm^3. The number-average (M_n) and weight-average molecular weights (M_w) were calculated by using a calibration curve which was obtained by using polystyrene standards with low dispersity (polystandard series, Mainz, Germany).

DSC and TGA Measurements

Differential Scanning calorimetry (DSC), was performed on a PL-DSC (Polymer Laboratories England). The calorimeter was calibrated with ultra-pure indium. Samples (2-5 mg) were first heated from –10 to 180°C with a heating rate of 20 °C/min (Run I). The melting temperature (T_m) and the apparent melting enthalpy (ΔH_f) were determined from endothermic peaks. After keeping them at 180°C for 1 min, samples were rapidly cooled to –100°C at a rate of 80 °C/min to obtain specimen with very low crystallinity or totally amorphous, and then heated again with a heating rate of 20 °C/min to 180°C (Run II). The cold crystallization temperature (T_{cc}) and enthalpy of cold crystallization (ΔH_{cc}) were determined from exothermic peaks in Run (II). The cooling curve run (III) was scanned over the temperature range from 180°C to 40°C at a constant rate of 20 °C/min. The melt crystallization temperature (T_{mc}) and enthalpy of melt crystallization (ΔH_{mc}) were determined from the exothermic peaks in this run. Run (IV) was recorded for annealed samples from melt, using the same condition 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 measurement, and all measurements were carried out under flow of nitrogen gas (20 ml/min). The melting temperatures, (T_m) were taken at the maximum peak of the melting endotherms, while the glass transition temperature (T_g) was taken as the midpoint of the specific heat capacity in Run (II).

Thermal degradation studies were conducted in air under dynamic heating rate of 10 °C/min using a Shimadzu TGA-50H Thermal analyzer. All experiments were conducted from room temperature to 600°C and the reference material was α-alumina. The sample weights for all the experiments were taken in the range of 7-10 mg.

Tensile Strength

The doumbell-shaped samples of copolymer films (thickness 0.1±0.02 mm, base width 5±0.2 mm, base length 10±0.2 mm) were used for mechanical tests. The elongation at break and tensile strength were determined at room temperature at extension rate of 10 mm/min, using the Zwick 1445 testing machine (Zwick Gmbh, Germany). Three runs of each material were carried out.

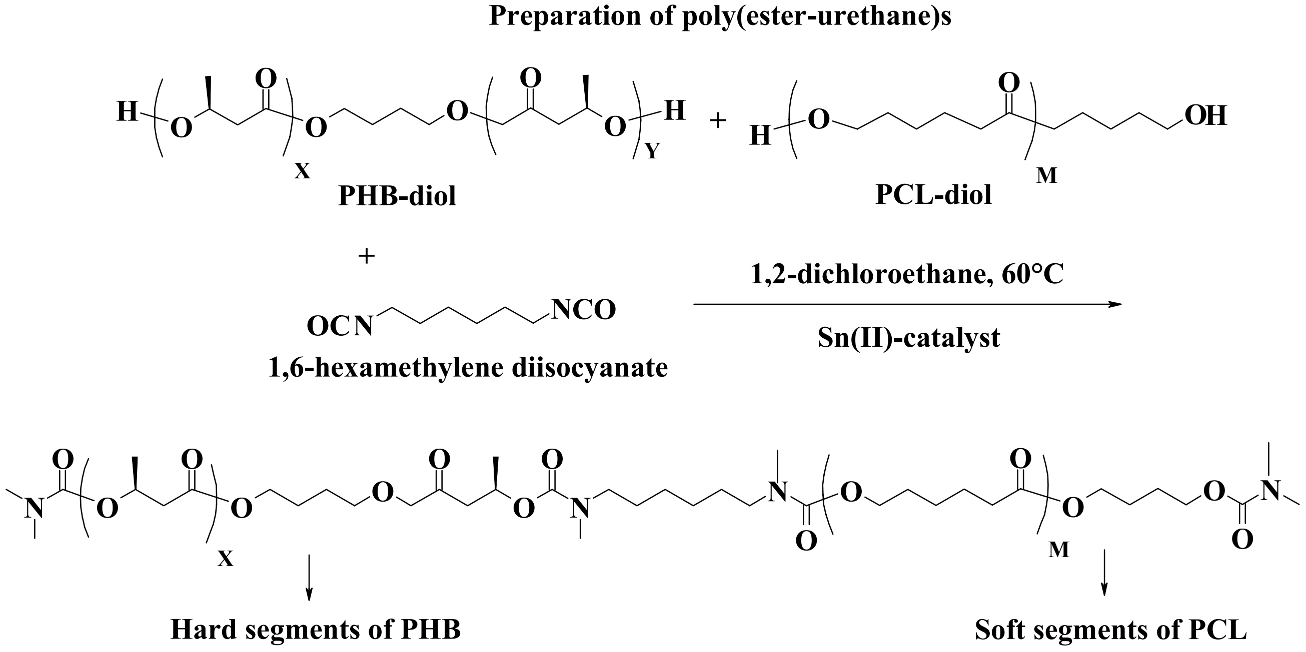
Biodegradation

Degradation studies of polymer films were conducted in active soil. Film samples (20×20 mm; 80 + 5 mg total weight) were buried in covered trays containing a standard soil mixture (1:1:1 w/w/w mix of top-soil, sand and composted mature) maintained at a moisture content of 22 to 26%, pH range of 7.5 to 8.5 and temperature range 25-30°C (10 cm depth). Film samples were recovered at different time intervals, brushed soft, washed several times with distilled water and then dried to constant weight under vacuum. The degradation of the film was conventionally evaluated in terms of weight loss by gravimetric measurements. Each treatment was set in triplicate.

Results and Discussion

Synthesis and Characterization of the Block Copoly(ester-urethane)s

In order to test the properties of the poly(ester-urethane)s in relation to chain length and the input ratio of the PHB and PCL components, we prepared two series A and B of the copolymers from PHB-diol and PCL-diols blocks (the properties of the diols used are shown in Table 1). The polymerization of the diol-terminated telechelic blocks was performed using stoichiometric amounts of 1,6-hexamethylene diisocyanate (HDI) in one step solution polymerization process in the presence of dibutyltin dilaurate as a catalyst according to Scheme 1. The content of PHB hard segments systematically varied from ~20 to ~60 wt.%. A representative ^{1}H-NMR spectrum with the assignment peaks of the copoly(ester-urethane) is shown in Fig. 1. The composition of the copolymers was determined from the integration intensity of proton chemical shifts of methine –OCH– proton of PHB units (at $\delta = 5.25$ ppm), methylene groups next to ester of PCL units (at $\delta = 4.15$ ppm) and that of –NH of urethane linkage (at



Scheme 1

δ = 4.80 ppm). The results as summarized in Table 2 demonstrate that the calculated compositional data are equivalent, within the limits of experimental error, to molar feed ratio. This seems reasonable on the basis of the near quantitative yields obtained (yield > 95%). Moreover, FTIR spectroscopy was also used to investigate the copolymers (Fig. 2). The absorption bands at 3387 cm^{-1} and 3433 cm^{-1} correspond to hydrogen-bonded –NH groups. The amide II absorption appears at 1530 cm^{-1} corresponds to non-bonded –NH groups. The IR of carbonyl groups (=CO) of PHB, PCL polyesters and connecting units are indicated at 1728, and 1686 cm^{-1} (appears as a shoulder), respectively. The absorption bands at 3939 and 2866 cm^{-1} are associated with asymmetric and symmetric –CH_2 groups, while other modes of –CH_2 vibrations are manifested by the bands at 1462, 1373 and 1238 cm^{-1}. The bands at 1180, 1053 cm^{-1} are due to the stretching of the –C–O– groups.

Table 1

The molecular weights and thermal properties of the prepolymers

Prepolymer	$M_n$$^{a)}$, g/mol	$M_w/M_n$$^{a)}$	$T_g$$^{b)}$, °C	$T_m$$^{c)}$, °C	ΔH_f, J/g	X_c%$^{d)}$, J/g
PHB-diol	4800	1.72	-13.5	152.0	82.5	56.5
PCL I-diol	1260	2.21	-61.0	45.5	70.2	51.6
PCL II-diol	2200	1.86	-63.0	54.0	79.1	58.2

a)Determined from GPC analysis in $CHCl_3$.

b)Determined from quenched samples.

c)Determined from melt crystallized samples.

d)Crystallinity percent calculated from the following equation: $X_c\% = \Delta H_f/\Delta H_f^o$, where ΔH_f^o is the thermodynamic melting point enthalpy of 100% crystalline 100% PHB and PCL. The values are 146 and 136 J/g, respectively.

Thermal Properties

Differential Scanning Calorimetry (DSC)

Figure 3 shows the DSC traces (Run I) of poly(ester-urethane) samples derived from PHB-diol and PCL-diol (M_n = 1260), series A is taken as a representative example. The main thermal transitions of all the investigated samples are summarized in Table 3. The results show that all the copolymers based on PHB and PCL prepolymers except for UPCLI-HB-60, regardless of PCL block length, exhibit two distinct melting temperatures. The lower melting endotherm corresponds to PCL soft segments as crystalline phase, decreased from 45.5 (T_m of pure PCLI prepolymer) to 40.0°C with increasing amount of PHB up to 40 wt.% in series A and from 54.0 (T_m of pure PCLII prepolymer) to 39°C with increasing PHB content up to 60 wt.% to in series B. The higher one corresponds to PHB hard segments as a crystalline phase, decreased from 152 (T_m of pure PHB prepolymer) to 150°C and 147°C in the copolymers for series A and B, respectively, as the amount of PCL.

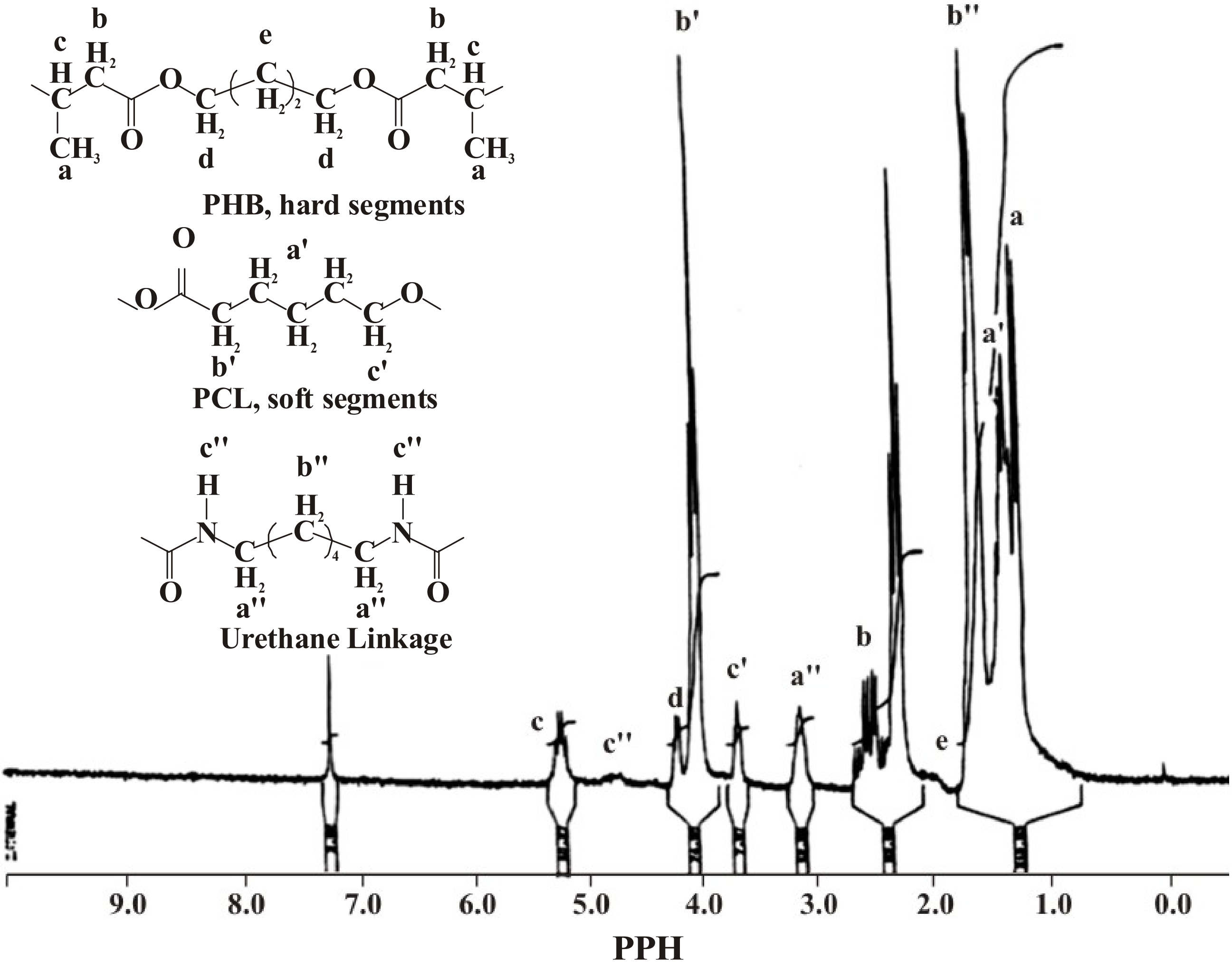


Fig. 1. ^{1}H-NMR spectrum of UPCLI-HB-20.

Table 2

Chemical composition and molecular weights of the prepared poly(ester- urethane)s

Series	Sample code	Composition[a)]			M_w[b)], g/mol	M_w/M_n[b)]
		PHB, wt.%	PCL, wt.%	Connect. Unit, wt.%		
A	UPCLI	-	87.9	12.1	73800	2.4
	UPCLI-HB-20	21.2	68.2	10.6	64000	2.0
	UPCLI-HB-40	39.7	51.5	8.8	56900	2.2
	UPCLI-HB-60	61.5	33.4	6.1	41100	2.5
B	UPCLII	-	90.9	9.1	85600	2.7
	UPCLII-HB-20	19.0	73.6	8.4	79300	3.0
	UPCLII-HB-40	39.2	54.3	6.5	61550	1.9
	UPCLII-HB-60	60.1	34.3	5.6	43000	2.7

[a)] Determined from ^{1}H-NMR spectra, expected error ~3%.

[b)] Determined from GPC analysis in $CHCl_3$ at 25°C.

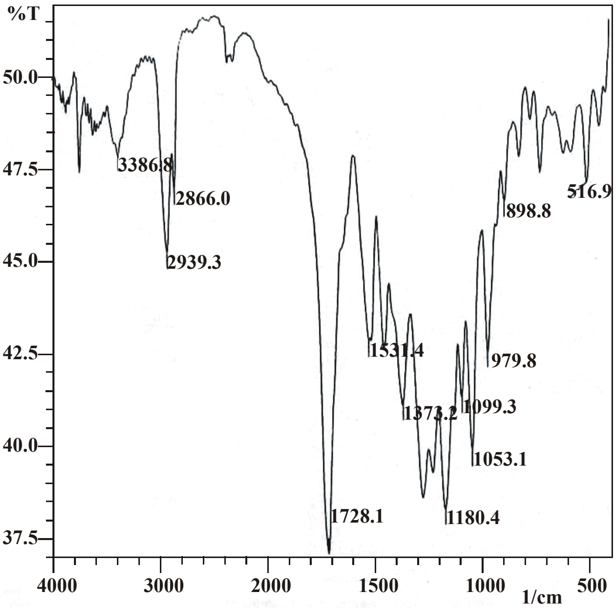


Fig. 2. IR spectrum of UPCLI-HB-20.

The ΔH_f, of both PCL and PHB is shown to decrease with the increase of its own content. Generally, the degree of crystalline perfection and the thickness of crystalline lamellae determine the melting of crystalline phase. For poly(ester-urethane) copolymers, the PCL soft and PHB hard segments are bonded chemically, so they impede each other during crystallization. The higher the PHB hard segment content, which acts as physical cross-links, the larger are the amount and the size of physical constrains imposed on the crystallization of PCL soft segments, and consequently, the decrease in the melting and enthalpy of the PCL soft segments. The thermal transitions of the DSC scans recorded after melt quenching (Run II) of copolymers, as shown in Fig. 4, are included in Table 3. Only one glass transition temperature, T_g, corresponding to PCL soft segments is detected. In the case of copolymers, those samples obtained from PCL having $M_n \sim 1260$ show an increase in T_g with increasing PHB content, indicating some extent of PCL-soft/PHB-hard segment phase mixing. This increase can be explained on the basis of a decreased mobility of the soft segments because of their attachment to stiffer urethane groups and /or the penetration of rigid PHB hard segment units into the soft segments. However, the copolymers based on PCL ($M_n \sim 2200$) show a different calorimetric behavior in the sense that T_g is nearly the same, suggesting a higher phase separation as a soft segment molecular weight increases. This result is consistent with the studies conducted by Reeve *et al.* [16], Suter *et al.* [17] and Saad *et al.* [19]. It was found that the degree of phase separation between PHB and PCL components increases with increasing the block length of PCL component. Low exothermic crystallization temperatures (T_{cc}'s), resulted from the cold crystallization of PCL and PHB components, were detected for all investigated copolymers, except UPCLI-HB-60 sample, PHB components could hardly crystallize during the cooling process. The transition at lower temperature relates to PCL phase, while the higher one corresponds to PHB phase. It can be clearly seen from the data presented in Table 3 that the characteristic T_{cc} of PHB decreases with increase of PHB content, whereas the characteristic T_{cc} of PCL blocks increases as the content of PHB block in the copolymer increases. These results can be interpreted as the mutual retardation effect of PHB and PCL segments on their own crystallization in the copolymers. Quenching from the melt provides the amorphous PCL and PHB components. Upon heating at the temperature range for the PCL segments to crystallize, the PHB segments are still in the amorphous phase because of its relatively high T_g compared to PCL, and could hardly move to crystallize. Accordingly, these frozen hard segments domains played a role of physical cross-links, which would hinder, to some extent, the ability of PCL to crystallize. Therefore, the higher the content of PHB in the copolymer, the stronger the influence of the restriction on the crystallization of PCL blocks. The thermal transitions obtained from DSC traces recorded from melt (Run III) (Fig. 5) are included in Table 3. Two melt-crystallization temperatures (T_{mc}'s) were observed in all copolymers investigated, except for UPCLI-HB-60 samples. The higher temperature peak is attributed to the crystallization of PHB hard segments, while the lower one corresponds to the crystallization of PCL soft segments. The T_{mc} and ΔH_{mc} of PCL decrease with increasing PHB content, reflecting a decrease in the rate of melt crystallization of PCL. So, for UPCLI-HB-60 copolymer based on a low molecular weight PCL blocks ($M_n \sim 1260$), the crystallization of PCL is unable to crystallize from melt during cooling. This result is ascribed to the fact that the higher the PHB content, the easier is the crystallization of the PHB hard segments, which crystallize first upon cooling and act as physical cross-links, and consequently the higher is the restriction imposed on the crystallization of the PCL soft segments.

In the DSC thermograms of the copolymers recorded after slow cooling from melt and annealed

Table 3

The chemical composition and DSC properties of the prepared poly(ester-urethane)s

Series	Sample code	T_g[a], °C	PCL-Soft Segments							PHB-Hard Segments						
			T_m[b], °C	ΔH_f[b], J/g	T_{cc}[a], °C	ΔH_{cc}[a], J/g	T_{mc}[c], °C	ΔH_{mc}[c], J/g	X_c[d], %	T_m[b], °C	ΔH_f[b], J/g	T_{cc}[a], °C	ΔH_{cc}[a], J/g	T_{mc}[c], °C	ΔH_{mc}[c], J/g	X_c[d], %
A	UPCLI-0	-46	47.3	36.9	-20.5	4.1	-13.5	33.0	30.9	-	-	-	-	-	-	-
	UPCLI-HB-20	-43	41.5	20.9	-1.5	10.3	-15.5	22.5	31.3	117, 141.5	9.4	63.5	8.5	-	-	30.4
	UPCLI-HB-40	-39	40.0	9.5	19.8	7.6	-16.4	8.6	12.6	129, 146	20.8	62.0	12.4	73.0	18.4	38.8
	UPCLI-HB-60	-37	-	-	-	-	-	-	8.7	136, 150	22.5	49.0	16.3	78.5	19.8	38.8
B	UPCLII-0	-49	48.0	39.0	-	-	1.1	25.1	31.5	-	-	-	-	-	-	-
	UPCLII-HB-20	-47	47.0	29.8	-8.8	8.7	-9.4	25.1	29.2	143	11.8	64.8	7.9	66.2	9.9	40.6
	UPCLII-HB-40	-45	43.5	21.4	-1.0	13.0	-13.0	18.9	27.0	133, 147	23.0	50.4	13.5	68.4	18.6	43.8
	UPCLII-HB-60	-43	39.0	9.7	15.5	3.2	-8.8	7.6	19.4	131, 147	39.4	46.0	19.0	74.3	35.8	44.9

[a] Determined from quenched samples.

[b] Determined from annealed samples.

[c] Determined from melt-crystallized samples.

[d] Crystallinity percent calculated from the following equation; $X_c\% = 100\Delta H_f/\Delta H_f^\circ \cdot W$, where ΔH_f° is the thermodynamic melting enthalpy of 100% crystalline PCL or PHB and W is the weight fraction of PCL or PHB component in the copolymer. The values of ΔH_f° of PCL and PHB are 136, 146 J/g, respectively.

(-) Not detected.

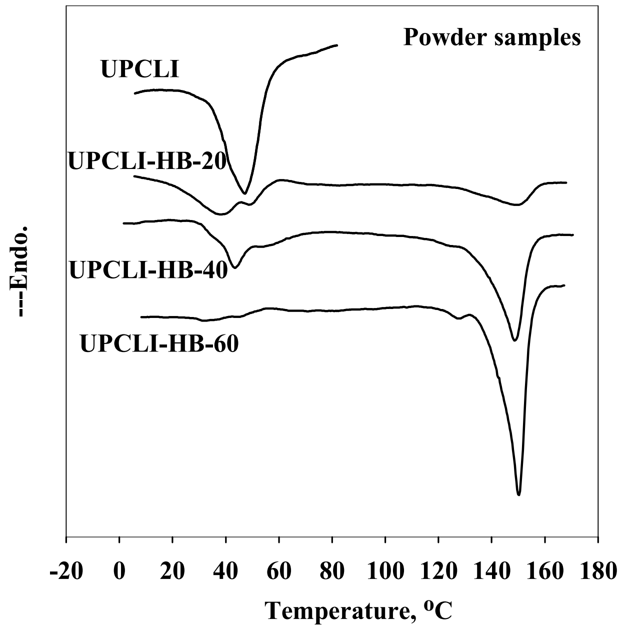


Fig. 3. DSC scans of poly(ester-urethane) samples, series A, recorded on powder samples (Run I).

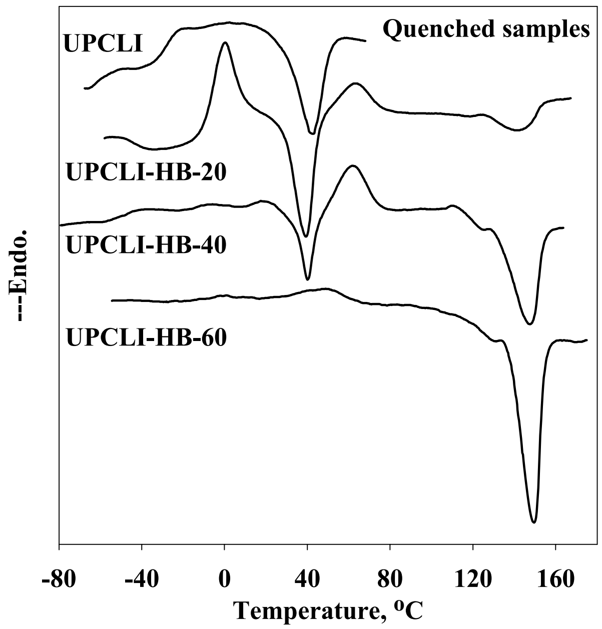


Fig. 4. DSC scans of poly(ester-urethane) samples, series A, recorded after quenching (Run II).

for one week at room temperature (Fig. 6), no obvious glass transition was detected. This may be attributed to the high crystallinity of PCL and PHB components. All the copolymers based on PHB and PCL diols, except for UPCLI-HB-60, exhibited two distinct melting temperatures, which are related to

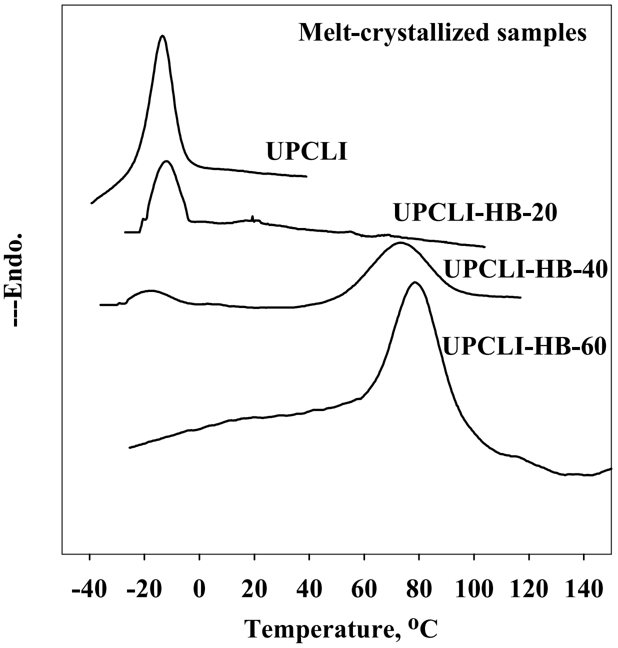


Fig. 5. DSC scans of poly(ester-urethane) samples, series A, recorded from cooling (Run III).

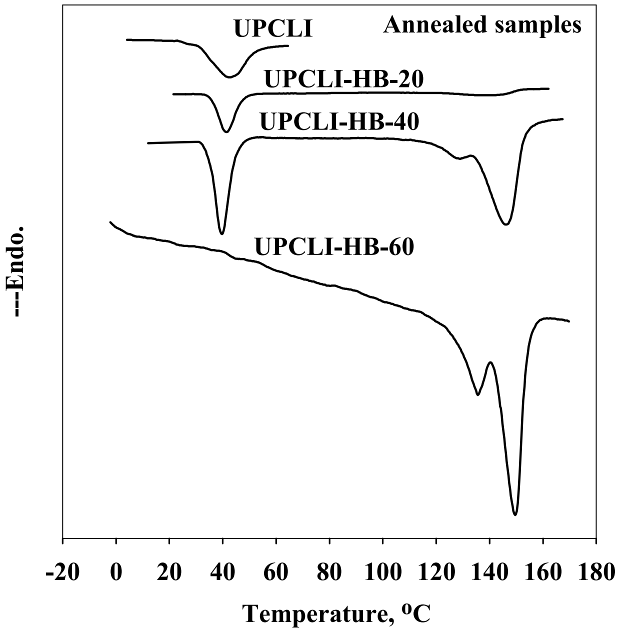


Fig. 6. DSC scans of poly(ester-urethane) samples, series A, recorded after annealing (Run IV).

the melting of crystallites of PCL soft and PHB hard segments. No exothermic crystallization peaks are detected indicating that slow cooling and annealing would allow complete crystallization. The normalized heat of fusion, *i.e.*, the value calculated for 1 g of the PCL or PHB, instead of 1 g of copolymer, is used to estimate the relative crystallinity percent (X_c%) of both PCL and PHB components:

$$X_c\% = 100\Delta H_f / \Delta H_f^{\circ} \cdot W$$

where ΔH_f^o is the heat of fusion corresponding to PCL or PHB crystalline phases, ΔH_f° is the heat of fusion of 100% crystalline PCL and PHB; the literature values being 136 J/g [25] and 146 J/g [26], respectively. *W* is the weight fraction of PCL or PHB in the copolymer. Computed results are included in Table 3, which reveals that the degree of crystallinity of either PCL or PHB increases with increasing its own contents.

Thermogravimetric Analysis

With regard to the assessment of polymer stability, thermogravimetric analysis (TGA) is usually employed to determine the temperature of initial weight loss, which can be viewed as the onset of degradation. TGA is also used to identify components in a sample. The effect of PHB content in the copolymers series A, as representative example, on the thermal stability is illustrated in Fig. 7. The thermogram of PHB homopolymer is included in the figure for the sake of comparison. In contrast to PHB homopolymer whose thermal degradation takes place as a single weight loss step [27], the temperature of maximum weight loss rate was centered at 260°C, the decomposition of copolymers is more complex. The degradation of copolymer sample based only on the PCL soft segments, namely UPCLI, showed two distinct weight loss steps. The temperature of the first step is related to PCL polyester, and the second to the urethane linkage. The investigated copolymers, based on PHB hard segments and PCL soft segments, showed three distinct decomposition steps which were assigned to the thermal decomposition of PHB, PCL and urethane linkage components in order of increasing temperature, respectively. From the TGA curves, it was found that the magnitude of each weight loss was closely correlated with the content of the corresponding components in the copolymer, according to the composition determined by ^{1}H-NMR spectroscopy (see Table 2). In comparison with the curves, the thermal stability of the copolymers is increased with increasing PCL and urethane content. Therefore, the presence of PCL and urethane components can increase the thermal stability of PHB-segments. The TGA curves of copolymers series B (data not shown here), based on longer PCL-soft segments, show a similar trend with a lower onset temperature. This result is probably attributed to the higher content of urethane linkage in copolymers based on low molecular block length of PCL soft segment, series A. Thus, it seems that the longer PCL soft segments favor the phase separation and reduce the extent of inter-urethane hydrogen bonding. Knowing that the melting point of PHB blocks in these copolymers is around 150°C, which is less than that of the T_m of the PHB homopolymer by approximately 30°C (T_m of PHB ~180°C) and at the same time is less than the thermal degradation of PHB, which occurs exclusively via random chain-scission reaction at temperature above 160°C [27], one may conclude that the investigated samples are more safe to process from their melts as compared to PHB homopolymer.

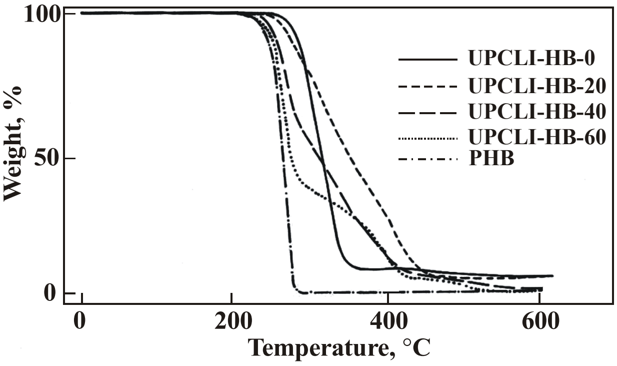


Fig. 7. TGA of PHB and poly(ester-urethane) samples, series A.

Mechanical Tensile Properties

The effect of PHB content on the tensile strength and elongation at break of the investigated copolymers cast films is given in Table 4. The data obtained indicated that both the tensile strength and elongation at break, regardless the PCL block length, had decreased with increasing PHB content. This decrease is more pronounced in copolymers based on high PCL block length (series B). This result may be mainly related to the degree of phase separation and the extent of secondary intermolecular forces. Shortening of the PCL 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 PCL block length results in more phase mixing between PHB and PCL and consequently more interfacial adhesion. Both factors have an effect on improving the mechanical properties of the end products. The decrease in the ultimate strength and elongation at break with increasing PHB content can be partially attributed to the decrease in molecular weight and the relatively rigid structure of PHB that can not be extended to the same degree as the soft PCL segments.

Table 4

Tensile properties of poly(ester-urethane) series A and B

Series	Sample code	Tensile strength*, MPa	Elongation* at break, %
A	UPCLI	24.3±0.4	910±25
	UPCLI-HB-20	21.6±0.7	810±36
	UPCLI-HB-40	17.4±0.8	610±41
	UPCLI-HB-60	13.1±0.4	180±24
B	UPCLII	25.1±0.6	890±40
	UPCLII-HB-20	19.0±0.3	760±18
	UPCLII-HB-40	15.6±0.9	505±20
	UPCLII-HB-60	11.8±0.5	136±16

*Average of three measurements

Biodegradability

Figures 8 and 9 show the weight loss of the prepared copolymers, pure PHB and PCL films after burial in soil compost. It was observed that the pure PHB film degraded faster than the copolymer during the whole degradation period. After 28 days its weight reached ~65% of the initial weight. The degraded samples appeared heterogeneously eroded and presented several holes of different sizes and deepness such that specimens degraded to about 35% of weight loss could be hardly handled because of the greater disintegration. For this, the weight loss determination after 28 days of incubation in soil was not performed. In contrast, pure PCL and poly(ester-urethane) samples based only on PCL-diols namely, UPCLI and UPCLII showed no significant variations in the biodegradation, the weight losses around 3.5% after 28 days. This indicates that PCL, UPCLI and UPCLII were more biodegradation resistant than PHB. Within the group of the investigated copolymers, the rate of biodegradation, at a given interval time, increases with increasing the content of PHB. In addition, it was found that the biodegradability of poly(ester-urethane) samples synthesized using high molecular weight PCL-diol (M_n = 2200) is a relatively faster than that synthesized using low molecular weight PCL-diol (M_n = 1260). It was reported that PHB polyester biodegradation proceeds via surface attack by intact bacteria with both the weight and thickness of film decreasing with time [28]. These bacteria can excrete extra-cellular enzymes which hydrolyze the polymer matrix into the water soluble oligomers and monomers. The soluble degradation products are then adsorbed through the cell wall of microorganisms and metabolized. Thus, the obtained results reflect that the investigated copolymers are less susceptible to biodegradation in soil compared to the pure PHB films and that, the susceptibility to biodegradation in soil increases with increasing the PHB content in the copolymers. This indicates that the biodegradation of the copolymers is mainly due to the hydrolysis of PHB component. In order to support this hypothesis, the relative composition of the copolymer before and after degradation was analyzed by thermogravimetric analysis. As previously shown (see Fig. 7), the TGA of the prepared poly(ester-urethane)s based on PHB and PCL display three distinct weight losses, whose relative magnitude changed with composition. This peculiarity was utilized to monitor and quantify the composition changes occurring in the copolymer during biodegradation in active soil. As an example, Figure 10 reports the percentage of PHB, PCL and urethane linkages of UPCLI-HB-40 remaining after different time of exposure in active soil. By comparing undegraded sample with those biodegraded samples, it is observed that PHB content decreases from ~40 wt.% to ~28 wt.% and diurethane content increases from ~11 wt.% to ~24 wt.%; meanwhile PCL content was almost constant at least during the time of experiment. This result reflects that PHB is more bio-susceptible towards biodegradation compared with PCL, which is in accordance with the data reported in the literature [29,30], while, the diurethane linkage is resistant to biodegradation [31]. The biodegradation of the copolymer is also influenced by the amount of urethane linkages. Copolymers with low content of PHB exhibit high extent of diurethane linkages (Table 2) that facilitates the formation of intermolecular hydrogen bonding, which act as physical crosslinks, which reduces the degradation. Another possible reason for the slow degradation of investigated copolymers compared with the PHB homopolymer is related to the differences in surface morphology. SEM examination of the undegraded surfaces of the PHB and the copolymers investigated showed that the surface of the control PHB had some roughness and possessed some cracks compared with the surface of the copolymers. Thus the increase of the surface area, due to the roughness and cracks, is expected to increase the biodegradability of the film in soil by inducing the attachments of the environmental microbes. This finding is consistent with the studies conducted by Molitoris *et al.* [32] and Tsuji and Suzuyoshi [33] who reported that the rate of hydrolysis of polyester was dependent on the surface area of the polymer exposed to hydrolysis.

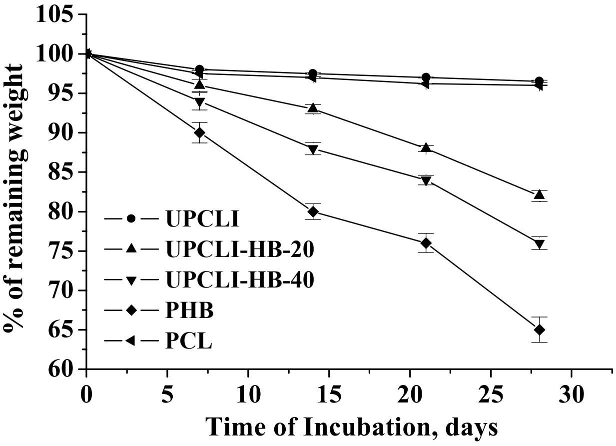


Fig. 8 . Progressive weight loss of poly(ester-urethane) samples, series A, PHB and PCL.

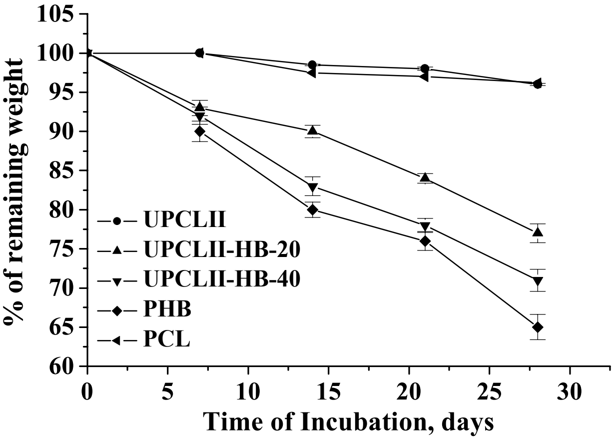


Fig. 9. Progressive weight loss of poly(ester-urethane) samples, series B, PHB and PCL.

Conclusions

The preparation of segmented poly(ester-urethane)s (PEUs) from telechelic dihydroxy-poly[(R)-3-hydroxybutyrate] obtained from bacterial PHB and a flexible block of poly(ε-caprolactone)-diols, using 1,6-hexamethylene disisocyanate, as a non toxic connecting agent, allows to overcome the difficulties connected with the use of PHB.

The relevant properties of PEUs prepared can be summarized as follows:

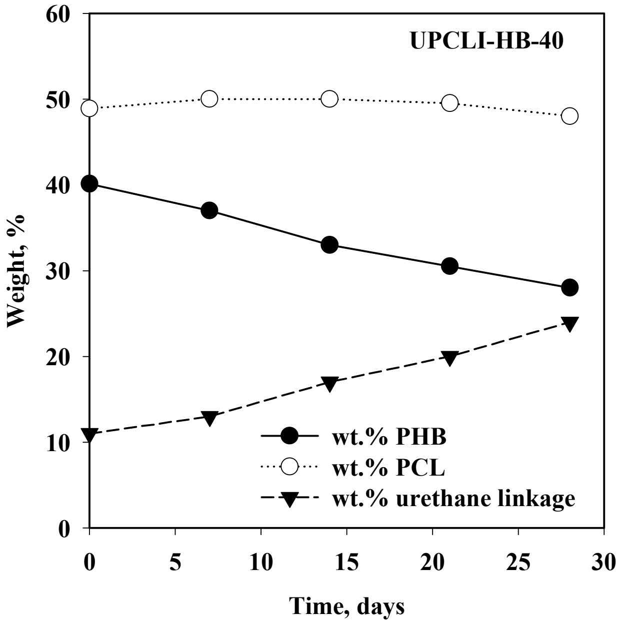


Fig. 10. Composition (by TGA) of UPCLI-HB-40 samples as a function of time exposure time in active soil.

1. They are semicrystalline thermoplastics whose crystalline domains stem from PHB and PCL components. The T_m of PHB component in such copolymer is decreased to ~147°C, around 30°C than PHB-hompolymer, while T_{onset} of the degradation is ~240°C. One may conclude that the prepared PEUs significantly broaden the window for safe thermoplastic processing compared with PHB homopolymer. All the investigated samples exhibited one T_g corresponding to PCL components. In the case of copolymers obtained from low molecular weight PCL, T_g shifted to higher temperature with increasing PHB content, indicating some extent of PCL/PHB segments phase mixing.
2. They exhibit typical plastomeric behaviour and the elongation at the breakpoint is much higher than that in the PHB homopolymer. The tensile strength and the elongation at the breakpoint of copolymer cast films decreased with increasing PHB content.
3. The biodegradation rate in burial active soil increased with increasing PHB content.

References

1. Doi, Y. Microbial Polyester; VCH Publishers. New York 1990.
2. Anderson, A.J., and Dawes, E.A. Microbial rev. 54:247 (1990).
3. Steinbüchel, A. Polyhydroxyalkanoic acids. In: Byrom D, editor.Biomaterials: novel materials from biological sources. New York, Stocktom, 1991, p.124-213.
4. Lenz, W., and Marchessault, R.H., Biomacromolecules 6:1 (2005).
5. Doi, Y., Kitamura, S., and Abe, H., Macromolecules 16:99 (1995).
6. Saito, Y., and Doi, Y., Int. J. Biol. Macromol. 16:99 (1994).
7. Su, F., Iwata, T., Tanaka, F., and Doi, Y., Macromolecules 36:6401 (2003).
8. Abe, H., Matsubara, I., and Doi, Y., Macromolecules 28:844 (1995).
9. Kumagi, Y., and Doi, Y., J. Environ. Polym. Degrad. 1:181 (1993).
10. Yoon, S.J., Chang, M.C., Kim, M.N., Kang, E.J., Kim, C., and Chin, I.J., J. Polym. Phys. 34:2543 (1996).
11. Gassner, F., and Owen, A.J., Polym. Int.39:215 (1996).
12. Dufresne, A., and Vincedon, M., Macromoecules 33:2998 (2000).
13. An, Y., Dang, L., Xmg, P., Mo, Z., Zhoang, Y., and Feng, Z., Eur. Polym. J. 33:1449 (1997).
14. Xmg, P., Ai, X., Dang, L., and Feng, Z., Macromolecules 31:6598 (1998).
15. Savenkova, L., Gercberga, Z., Nikolaeva, Dzene A, Bibers, I., and Kalnin, M., Process. Biochem. 35:573 (2000).
16. Reeve, M.S., McCarthy, S.P., and Gross, R.A., Macromolecules 26:288 (1993).
17. Hirt, T.D., Neuenschwander, P., and Suter, U.W., Macromol. Chem. Phys. 197:4253 (1996).
18. Lendleim, A., Neuenschwander, P., and Suter, U. W., Macromol. Chem. Phys 199:2785 (1998).
19. Saad, G.R., Lee, Y.J., and Seliger, H., J. Appl. Polym. Sci. 83:703 (2002).
20. Andrade, A.P., Neuenschwader, P., Hany, R., Egli, T., and Witholt, B., Macomolecules 35:4946 (2002).
21. Impallomeni, G., Giuffrida, M., Barbuzzi, T., Musumaru, G., Ballistren, A., Biomacromolecules 3:835 (2002).
22. Saad, G.R., Macromol. Biosci. 1:387 (2001).
23. Saad, G.R., and Seliger, H., Polym, Degrad. Stab. 83:101 (2004).
24. Reeve, M.S., McCarthyl, S.P., and Gross, R.A., Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 31:437 (1990).
25. Crescenzi, V., Manzini, G., Calzolari, G., and Borri, C., J. Eur. Polym. 8:449 (1972).

26. Barham, P., Keller, A. J., Otun, E. L., and Holmes, P. A., J. Mater. Sci. 19:2781 (1984).
27. Grassie, N., Murray, E. J., and Holmes, P. A., Polym. Degrad. Stab. 6:48 (1984).
28. Grassie, N., Murray, E. J., and Holmes, P. A., Polym. Degrad. Stab. 6:95 (1984).
29. Nishida, H., and Tokiwa, Y., J. Environ. Polym. Degrd. 1:65 (1993).
30. Rosa, D.S., Filbo, R. P., Chui, Q.S.H., Calli, M.R, Guedes, C.G.F., Europ. Polym. J. 39:233 (2003).
31. Rosa, D.S., Calil, M.R., Guedes, C.G.F., and Rodrigues, T.C., J. Polym. and Environ. 12:239 (2004).
32. Duprer, I., David, C., Colpaert, Loutz, J-M, and Wauven, C.V., Macromol. Chem. Phys. 200: 2508 (1999).
33. Molitoris, H.P., Moss, S.T., de-Koning, G.J.M., and Jendrossek, D., Appl. Microbiol. Biol. 46:570 (1996).Tsuji, H., and Suzuyoshi, K., Polym. Degrad. Stab. 75:347 (2002).

Received 13 February 2007.