Comparative Degradation Data of Polyesters and Related Poly(ester amide)s Derived from 1,4-Butanediol, Sebacic Acid, and α-Amino Acids

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ABSTRACT: Two new sequential poly(ester amide)s (PEAs) derived from 1,4-butanediol, sebacic acid, and L-alanine (PABA8) or glycine (PGBG8) are prepared and characterized. For comparative purposes the related polyesters (PEs) 4,10 and 6,10 are also studied. The calorimetric analysis shows that the inclusion of amino acids improves the thermal properties such as the melting temperature without a significant reduction in their thermal stability. All polymers show hydrolytic and enzymatic degradability. The degradation rates of the PEAs are higher for the alanine derivative (PABA8) because of its low crystallinity and the higher specificity of the essayed proteolytic enzymes. The PEs are only degraded faster when enzymes with esterase activity are employed. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1815–1824, 2002

Key words: hydrolytic degradation; enzymatic degradation; α-amino acids; poly(ester amide)s; polyesters

INTRODUCTION

There has been a growing interest in aliphatic polyesters (PEs) derived from diols and dicarboxylic acids since the development of BIONOLLE by Showa Highpolymer Co in 1990. This polymer is produced through the polycondensation reaction of ethylene glycol and 1,4-butanediol and dicarboxylic acids like succinic and adipic acids. The good processability and properties of this material suggest different potential applications such as composting or shopping bags and shampoo, cosmetic, or beverage bottles.[1] Poly(ester amide)s (PEAs) constitute another family of polymers that also has applications such as degradable thermoplastics and has improved mechanical properties compared to those of PEs as would be expected from their potential hydrogen bonding interactions. In this sense, Bayer has been commercializing different polymers since 1996 under the trademark BAK, which is based on adipic acid, caprolactam, and hexamethylenediamine as the amide components and 1,4-butanediol and ethylene glycol as the ester components. A wide range of applications has been suggested that is due to their performance and simple processing. They include biowaste bags, agricultural films, cemetery decorations, and one-way disposable dishes[2].

Our recent efforts have focused on the study of sequential PEAs that include different α-amino acids, because they may enhance their biodegradability due to their susceptibility to enzymatic degrada-

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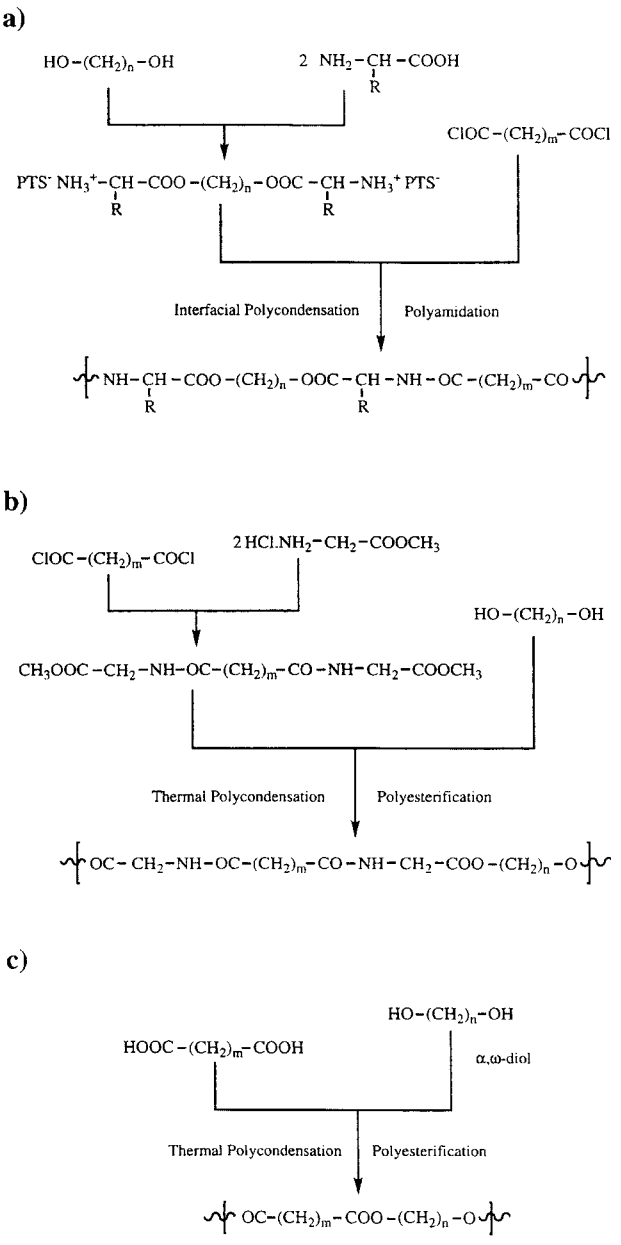
tion with proteases. Polymers with the sequence —NHCH(R)CO—O(CH_2)$_n$O—COCH(R)NH—CO(CH_2)$_m$CO— can be easily synthesized via interfacial polymerization and obtained with high yield and adequate molecular weight in the case of sebacic acid derivatives.[3–5] Thus, this acid has been chosen as a constituent of the polymers investigated in this article. These also incorporate 1,4-butanediol, like the indicated and commercially available PEs and PEAs. They also contain glycine (PGBG8) or L-alanine (PABA8) as α-amino acids, because very low melting points are obtained with amino acids that have bulkier lateral groups.[5] The new polymers are named to indicate the amino acid–diol–amino acid sequence by using the first letter of each residue (GBG or ABA) and the number of methylene groups (8) of the dicarboxylic unit. For the sake of completeness, data are compared with the parent PE (PE 4,10) derived from 1,4-butanediol and sebacic acid and that derived from a diol with a greater number of methylene groups (PE 6,10). In this case the unit repeat has a methylene content equal to the PGBG8 polymer.

EXPERIMENTAL

The PABA8 PEA was synthesized by interfacial polymerization following the procedure outlined in Scheme 1(a) and previously reported for related derivatives.[3,4,6] On the other hand, PGBG8 was prepared by thermal polyesterification (190°C) as indicated in Scheme 1(b). This new synthesis route was undertaken because of the difficulty in esterifying 1,4-butanediol with glycine.[7] The PEs were prepared from sebacic acid and an excess of the appropriate diol (2.2/1 molar ratio) by thermal polycondensation at 190°C and using titanium butoxyde as a catalyst [Scheme 1(c)]. The PE 4,10, PE 6,10, and PABA8 compounds were purified by precipitation of chloroform solutions with ether whereas PGBG8 was precipitated with acetone from a formic acid solution.

The intrinsic viscosities were determined with a Canon Ubbelohde microviscometer in dichloroacetic solutions at 25 ± 0.1°C. The molecular weight distribution of the PEs was measured with a gel permeation chromatography (GPC) apparatus (model 510, Waters) equipped with a Maxima 820 computer program. The number-average and weight-average molecular weights are only indicated because they were calculated using polystyrene standards (Polysciences). A set of two ultra-Styragel (Polymer Laboratories) columns with a limited exclusion weight of 10^4 and 10^3 and a RI 410 (Waters) detector were used. The polymers were dissolved and eluted in a chloroform/*o*-chlorophenol (90/10, v/v) mixture at a flow rate of 0.5 mL/min (100 μL injected volume, 2.5 mg/mL sample concentration).



Scheme 1 The synthesis of (a) PABA8 prepared by interfacial polymerization and (b) PGBG8 prepared by thermal polyesterification.

Table I Intrinsic Viscosities and Calorimetric Data of the Polymers Studied in This Work

		First Run			Second Run		Third Run				
Polymer	$[\eta]$ (dL/g)	T_f (°C)	ΔH_f (kJ/mol)	χ (%)	T_c (°C)	ΔH_c (kJ/mol)	T_f (°C)	ΔH_f (kJ/mol)	χ (%)	$T_{d,0}$ (°C)	$T_{d,1/2}$ (°C)
PE 4,10	1.20	66	22.6	53	47	14.7	66	15.1	35	381	447
PE 6,10	1.00	66	30.7	60	51	20.7	70	22.6	44	360	435
PGBG8	0.73	144/160	14.9/12.2	49	129	19.1	146/158	20.5/1.8	41	293	421
PABA8	0.80	99/110	14.1	25	—	—	—	—	—	306	393

The IR absorption spectra were recorded with a Perkin–Elmer 1600 FTIR spectrometer in the 4000–500 cm^{-1} range from films obtained by evaporation of chloroform (PE 4,10, PE 6,10, and PABA8) or formic acid (PGBG8) solutions. The NMR spectra of the PEAs were registered from chloroform/trifluoroacetic acid solutions, and a chloroform solution was used for the PEs. The chemical displacements were calibrated using tetramethylsilane as an internal standard. A Bruker AMX-300 spectrometer operating at 300.1 and 75.5 MHz was used for ^1H- and ^{13}C-NMR investigations, respectively. A thermal analysis was performed by differential scanning calorimetry (DSC) with a Perkin–Elmer DSC-Pyris 1 using indium for calibration. Thermogravimetric analysis was carried out with a Perkin–Elmer TGA-6 thermobalance.

Plates (1.5 cm × 1.5 cm × 200 μm) were cut from films prepared by melt pressing 200 mg of the powder samples. The plates of PABA8 were annealed at 70°C for 12 h before the degradation experiments to increase their crystallinity. Hydrolytic degradation studies were carried out in different conditions: in pH 7.4 sodium phosphate buffer at 37°C, in distilled water at 55°C for all samples, and in distilled water at 70°C only for PEAs. Enzymatic degradation studies were performed at 37°C by using lipases from *Candida cylindracea* (943 U/mg) and *Pseudomonas cepacia* (1500 U/mg) and proteolytic enzymes such as papain (30,000 U/mg, no. 7144) and proteinase K (*Tritirachium album*, 13 U/mg). The media consisted of a sodium phosphate buffer (pH 6.0 for papain and 7.2 for the other enzymes) containing sodium azide (0.03%) to prevent microbial growth and the appropriate enzyme. In the case of papain, the solution also contained L-cysteine (34 m*M*) and ethylenediaminetetraacetic disodium salt (30 m*M*) for activation. Solutions were renewed every 72 h because of enzymatic activity loss. In all cases, the plates were placed in glass vials containing the degradation media (30 mL for hydrolytic and 10 mL for enzymatic) and removed after the prescribed times. The mass loss, intrinsic viscosity, and changes in the NMR and IR spectra were evaluated in all of the degradation

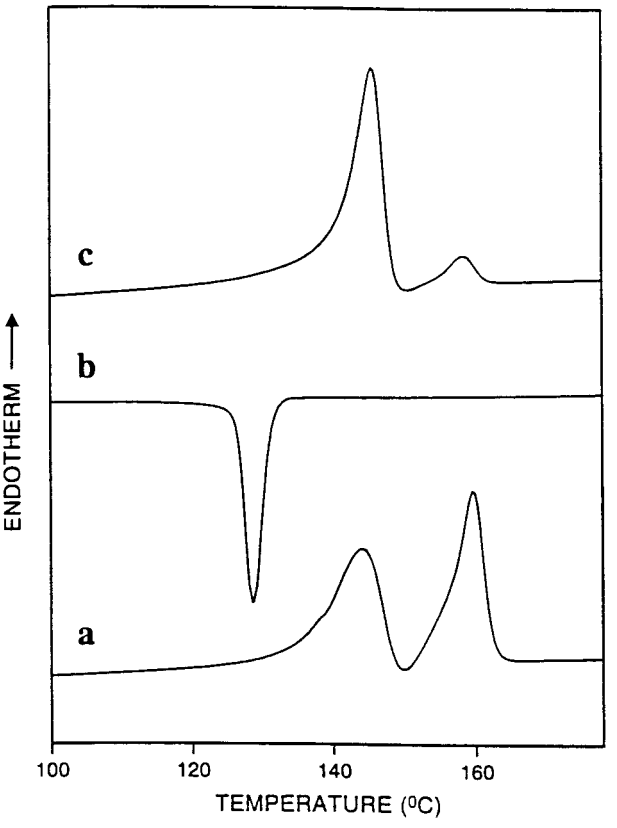


Figure 1 The sequence of three DSC scans carried out with the PGBG8 sample: a heating run at 20°C/min (trace a), a cooling run at 10°C/min after keeping the sample in the melt state for 2 min (trace b), and a reheating run at 20°C/min (trace c).

Table II Main Spectroscopic Data of the Polymers Studied in This Work

	Infrared spectroscopy[a]				
	Amide A	Amide B	C = O (ester)	Amide I	Amide II
PE 4,10	—	—	1733	—	—
PE 6,10	—	—	1731	—	—
PGBG8	3312	3070	1736	1645	1546
PABA8	3288	3059	1739	1639	1542

	^{1}H- and ^{13}C-NMR spectroscopy[b]:							
	PE 4,10		PE 6,10		PGBG8		PABA8	
	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
O—CH_2—	4.08	63.7	4.20	64.1	4.37	67.3	4.37	67.3
O—CH_2—*CH_2*—	1.69	24.9	1.74	28.6	1.87	24.8	1.88	24.9
O—CH_2—CH_2—*CH_2*—	—	—	1.44	25.0	—	—	—	—
CO—*CH_2*—	2.28	34.3	2.45	34.3	2.56	35.3	2.56	35.2
CO—CH_2—*CH_2*—	1.60	25.3	1.67	25.6	1.73	26.0	1.73	26.1
CO—CH_2—CH_2—*CH_2*—*CH_2*—	1.29	29.4	1.33	29.1	1.37	28.8, 29.0	1.37	28.8, 29.0
CH_3	—	—	—	—	—	—	1.57	16.8
NH—	—	—	—	—	7.89	—	7.89	—
NH*CH_2*CO—	—	—	—	—	4.28	42.6	—	—
NH*CH*(CH_3)CO—	—	—	—	—	—	—	4.77	50.6
CO—O—	—	173.8	—	173.8	—	171.8	—	174.8
CO—NH—	—	—	—	—	—	180.5	—	179.8

[a] Absorption bands in cm^{-1}.
[b] Chemical displacements in ppm and referred to TMS.

experiments. The surfaces of the polymer films after the degradation tests were also observed with a Jeol JSM-6400 scanning electron microscope.

RESULTS AND DISCUSSION

Characterization

Table I summarizes the intrinsic viscosities of the synthesized polymers. The values in the 0.7–1.2 dL/g range were measured in dichloroacetic acid, indicating moderately high molecular weights. In this sense, all samples showed fiber- and film-forming properties. Illustrative molecular weights of the two PEs could also be obtained from GPC analysis because of their solubility in chloroform. Thus, number-average molecular weights of 46,500 and 26,300 were estimated for PE 4,10 and PE 6,10, respectively. The corresponding weight-average molecular weights were 163,000 and 68,000, which show a higher polydispersity index for PE 4,10 (3.5 with respect to 2.6 for PE 6,10).

The calorimetric analysis of each polymer consisted of three DSC scans as shown in Figure 1 for PGBG8. In the first run the samples direct from polymerization were heated at 20°C/min through fusion and left in the melt state for 2 min. Subsequent cooling was performed at 10°C/min to observe crystallization from the melt. A second heating was performed at 20°C/min to check the reproducibility of the transitions and to obtain data for the melt crystallized samples. The heats of fusion (ΔH_f) were used to evaluate the crystallinity of the samples (solution- and melt-crystallized samples), taking into account the heats of fusion for 100% crystalline materials (ΔH_f^{eq}). These values were estimated from the reported[8] group contributions

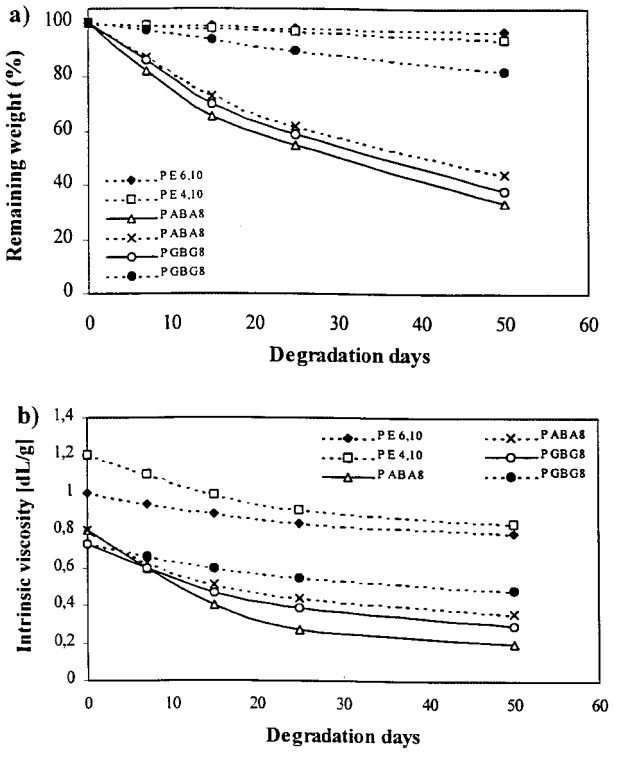


Figure 2 A plot of the (a) remaining weight and (b) intrinsic viscosity versus the degradation time under accelerated conditions for the PEs and PEAs. The polymers were immersed in distilled water at (- - -) 55 or (—) 70°C.

of ester (−2.5 kJ/mol), amide (2.0 kJ/mol), $CH(CH_3)$ (4.7 kJ/mol), and methylene (4.0 kJ/mol). The main calorimetric parameters of the studied polymers are summarized in Table I. As expected, the crystallinity is lower when samples crystallize from the melt. The melting temperatures of the PEs are in agreement with previously reported data (60, 62, or 67°C for PE 4,10,[9–11] and 67 or 78°C for PE 6,10[12,13]) and significantly lower than those found for the new PEAs. Thus, the incorporation of α-amino acid units like L-alanine and glycine improves the thermal properties. Note that the melting temperatures increase approximately 100 and 50°C for glycine and alanine derivatives, respectively. It should also be pointed out that the crystallinity of PGBG8 is comparable to the parent PE (PE 4,10).

Table I also shows how the side group of the amino acid reduces both the melting temperature and the crystallinity. In fact, PABA8 could not crystallize from the melt, because only a glass-transition temperature of 32°C (C_p = 0.15 kJ/mol °C), which is indicative of an amorphous state, was observed in the third calorimetric run. However, the sample could be recrystallized by a 3-h annealing at 70°C that gave a degree of crystallinity higher than 31%. This thermal treatment was applied to the films prepared from the melt and used for degradation studies in order to procure samples with comparable crystallinity (35–45% for PEs and PGBG8).

The decomposition temperatures ($T_{d,0}$, the inclination point in the loss of weight vs the temperature curve, and $T_{d,1/2}$, the temperature at which the weight loss reaches 50%) were determined by thermogravimetry at a heating rate of 10°C/min. Both PEAs begin decomposition at 300 ± 7°C, as summarized in Table I. Note that this value is much higher than the melting temperature (>140°C). Consequently, the applicability of these polymers is not impaired. Further, their thermal stability is comparable to that of the related PEs.

The IR and NMR spectroscopic data of the polymers (Table II) are in total agreement with their anticipated chemical constitution. The IR spectra of the synthesized PEAs show the characteristic amide absorption bands indicative of hydrogen bonding interactions. Small differences were found between the alanine and glycine derivatives. In particular, note the position of the amide A and B bands, which suggests a stronger hydrogen bond interaction for PABA8. Two-dimensional NMR was recorded to ensure the assignment of the chemical shifts given in Table II. As expected from our molecular weight estimations and the physical properties of polymers, we could not detect any additional peak

Table III Weight Loss (%) and Intrinsic Viscosity (dL/g) of the Polymers Studied in This Work After 50 Days of Exposure in Distilled Water

Polymer	Weight Loss	[η]
PE 4.10[a]	6	0.84
PE 6.10[a]	3	0.79
PGBG8[a]	18	0.48
PABA8[a]	56	0.36
PGBG8[b]	62	0.29
PABA8[b]	66	0.20

[a] Distilled at 55°C.
[b] Distilled at 70°C.

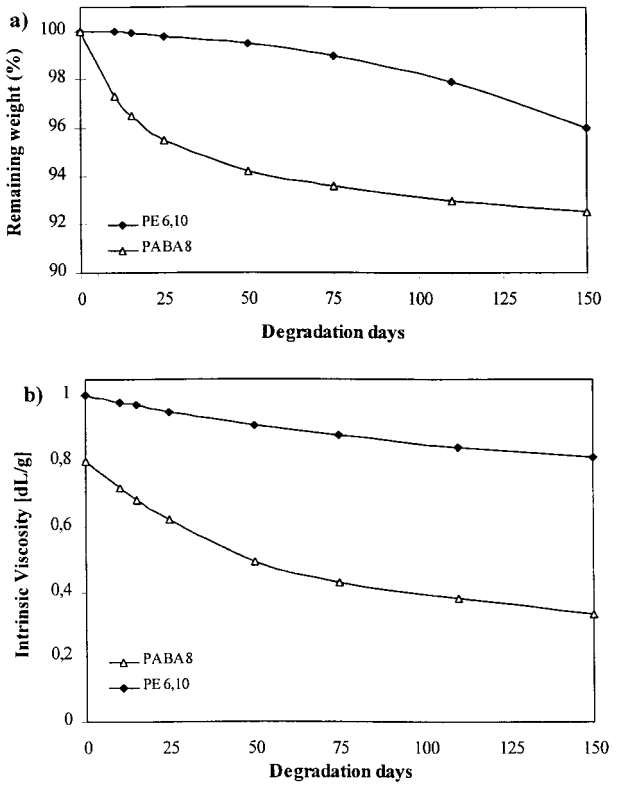


Figure 3 The plot of the (a) remaining weight and (b) intrinsic viscosity versus the degradation time in a pH 7.4 sodium phosphate buffer at 37°C for PE 6,10 and PABA8.

corresponding to terminal groups in the ^{1}H- and ^{13}C-NMR spectra of the four polymers that were tested.

Hydrolytic Degradation

Figure 2 shows the results of hydrolytic degradation under accelerated conditions. All polymers were submitted under identical conditions for comparative purposes. Thus, the temperature of the aqueous media was limited to 55°C because of the low melting temperature of the PEs. However, experiments at 70°C were also carried out with PEAs. The weight mass loss and the changes in the intrinsic viscosity of the remaining samples were evaluated. PABA8 was the polymer with the highest weight loss (56% after 50 days at 55°C) and the biggest change in the intrinsic viscosity (from 0.8 to 0.36 dL/g after 50 days at 55°C). The PGBG8 PEA also degrades well, although at a slower rate, probably because of its higher crystallinity. In this way, experiments at 70°C demonstrated the high degradability of both PEAs and confirmed that the lateral group of the amino acid affects the susceptibility to hydrolytic degradation. The PEs also degrade steadily but at a lower rate than the related PEAs. The comparative results of samples after 50 days of treatment are summarized in Table III. It is worth noting that minor differences between the degradation of PE 4,10 and PE 6,10 are found. Thus, PE 4,10 shows more of a major change in the intrinsic viscosity and a major weight loss than PE 6,10, although it is the sample with the highest initial molecular weight. The different hydrophilicities of the two samples may be responsible for the major degradability of the 1,4-butanediol derivative.

Hydrolytic degradation was also studied in a pH 7.4 sodium phosphate buffer at 37°C in order to simulate physiological conditions. The results of the least (PE 6,10) and the most (PABA8) degradable polymers are shown in Figure 3. The trends observed under the accelerated conditions can even be detected, but the experiments had to be prolonged for over 150 days. Note also that the weight loss of PABA8 reaches only 7.5% after 150 days of exposure.

The ^{1}H-NMR spectra of the degraded PEAs show that the signal at 4.37 ppm (CH_2—OCO—) decreases in intensity while only one additional

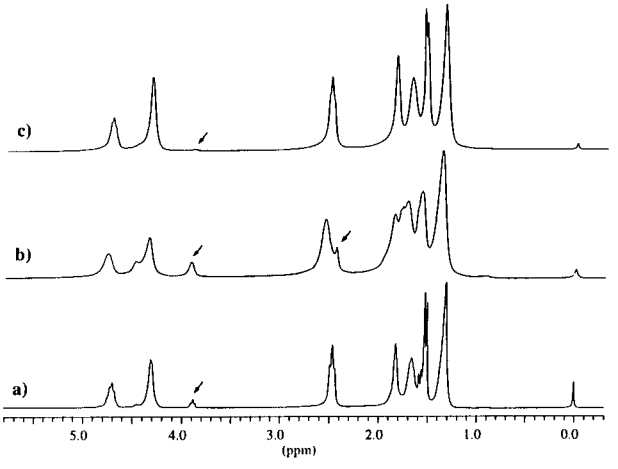


Figure 4 The ^{1}H-NMR spectra of PABA8 samples after exposure for 50 days in distilled water at 70°C (spectrum a), 1 day in a proteinase K enzymatic medium at 37°C (spectrum b), and 15 days in a lipase enzymatic (*Candida cylindracea*) medium at 37°C (spectrum c). The new signals indicative of ester and/or amide cleavages are indicated.

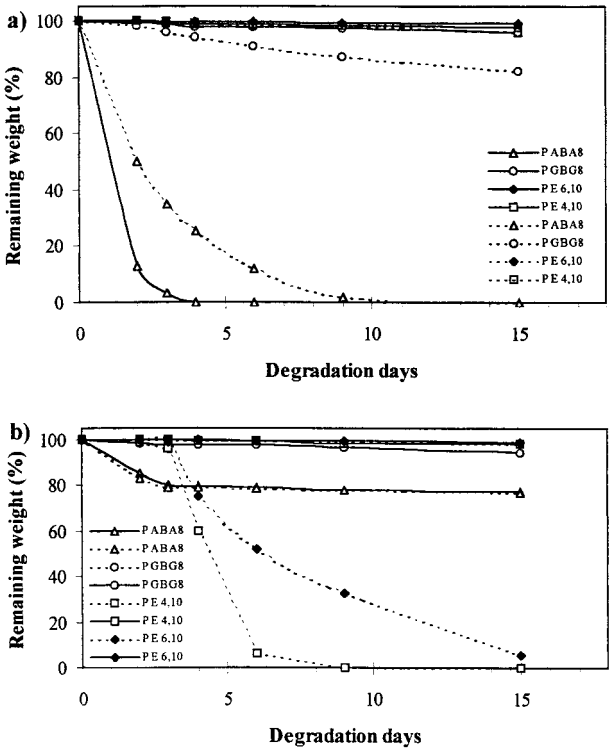


Figure 5 A plot of the remaining weight versus the degradation time in enzymatic media containing (a) proteases and (b) esterases for PE 4,10, PE 6,10, PGBG8, and PABA8 samples. (—) The proteinase K or lipase from *Candida cylindracea* and (- - -) the media with papain or lipase from *Pseudomonas cepacia*. Note that PEs degrade in *P. cepacia* after an induction time of approximately 3 days.

signal at 3.88 ppm (—CH_2—OH), which is indicative of terminal unesterified groups, appears and increases in intensity with the degradation time (Fig. 4, spectrum a). This result clearly indicates that the hydrolysis of these PEAs takes place through the ester linkages, an observation that was previously reported for similar polymers.[4,5,14] The IR spectroscopy is also fully consistent with this conclusion, because the relative intensity of the ester absorption band (1736 and 1739 cm^{-1} for PGBG8 and PABA8, respectively) decreases with the exposure time.

Enzymatic Degradation

Degradation was only monitored by measurements of the remaining weight after exposure in the degradation media, because it is well known that the enzymatic process takes place at the film surface in the initial stages. Thus, the changes in the intrinsic viscosity of the remaining samples are expected to be minimal. The study was carried out with two families of enzymes: proteases and esterases.

Our previous studies[14] on similar sequential PEAs showed that degradation was enhanced in proteolytic enzymes such as proteinase K or papain. For this reason, they were selected for this research. The results shown in Figure 5(a) and Table IV clearly indicate that PEAs degrade faster than the selected PEs. It should also be emphasized that the alanine derivatives are much more sensitive to the enzymes, probably because of their lower crystallinity and the different enzyme specificities toward glycine or alanine units. In this sense, note that PABA8 is degraded more rapidly with proteinase K whereas papain is more effective for the glycine derivative (PGBG8).

The ^{1}H-NMR spectra (Fig. 4, spectrum b) showed that the amide and ester linkages of the PEAs were both cleaved during the enzymatic

Table IV Remaining Weight (%) of Films of the Studied Polymers After 15 Days of Exposure in the Indicated Enzymatic Media

	Remaining Weight			
Polymer	Proteinase K	Papain	Lipase from *Candida cylindracea*	Lipase from *Pseudomonas cepacia*
PE 4,10	97	96	98	0[a]
PE 6,10	99	98	99	5.5
PGBG8	96	82	94.5	98
PABA8	0[b]	0	77	77.5

[a] The sample disappears after only 9 days of exposure.
[b] The sample disappears after only 4 days of exposure.

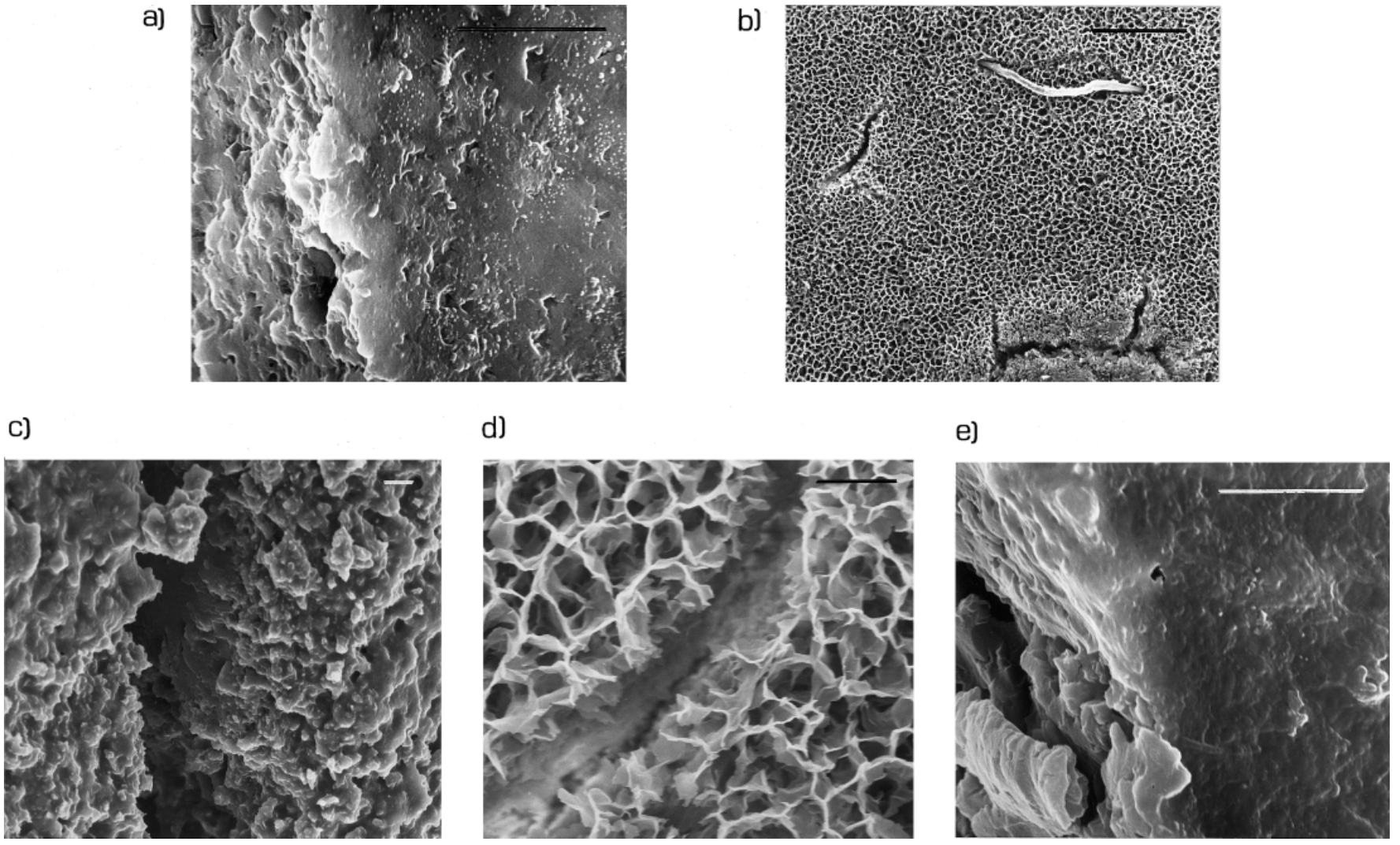


Figure 6 Scanning electron micrographs of different PABA8 plates. (a) The initial sample: the surface of the plate is practically smooth as shown on the right side of the micrograph (the left side corresponds to the lateral fracture surface); (b) the plate after 50 days of exposure under accelerated hydrolytic conditions (70°C): numerous pores and crevasses appear on the surface; (c) the plate after 50 days of exposure under accelerated hydrolytic conditions (70°C) but observed at a higher magnification; (d) a small recovered fragment of a plate exposed to the proteinase K enzymatic medium for only 1 day: note that deeper fissures appear as compared to (c); and (e) the surface (right) and fracture (left) side of a plate after a 15-day incubation in the *Candida cylindracea* enzymatic medium. Scale bars = (a,c–e) 10 and (b) 100 μm.

degradation. Thus, in addition to the 3.88 ppm signal attributed to the —CH_2OH protons produced by an ester cleavage, a new signal at 2.44 ppm appears, indicating terminal carboxylic groups (—CH_2COOH). Some evidence for ester bond hydrolysis by the action of α-chymotripsin, papain, and proteinase K on related PEAs was previously reported[15] and is in agreement with our observations. However, in our case, amide cleavages are also clearly detected, being more evident and predominant for the alanine derivative in both enzymatic media.

Figure 5(b) and Table IV show the results of the degradability with esterases such as lipases from *Candida cylindracea* and *Pseudomonas cepacia*. The following observations were made: all polymers degrade faster with enzymes than under accelerated hydrolytic conditions; lipase from *P. cepacia* is more effective in the degradation process of PEs whereas lipase from *C. cylindracea* appears to be more effective with PEAs; and PEs degrade faster in lipase from *P. cepacia* than PEAs, in contrast with the results obtained in accelerated hydrolytic media or in proteolytic enzymes. The ^{1}H-NMR spectra (Fig. 4, spectrum c) indicate that degradation takes place through cleavage of ester linkages, as expected from the specificity of the selected enzymes. In spite of its highest molecular weight, the remaining weight of PE 4,10 is always lower than the recovered one for PE 6,10 after equivalent exposure times. As mentioned before, we think that the higher hydrophilicity of the 1,4-butanediol derivative plays an important role. Slight differences are also found in the degradation rate of the two PEAs. In this case, we think that the lower crystallinity of PABA8 is an important factor to take into account.

The superficial texture of samples changes dramatically during degradation and shows the appearance of numerous crevasses after incubation in the degradation media, their extension and proportion being an additional indication of the degradation process (Fig. 6).

CONCLUSIONS

The results obtained in this work can be summarized as follows:

1. Two new PEAs derived from 1,4-butanediol, sebacic acid, and L-alanine or glycine were prepared by interfacial polyamidation and thermal polyesterification. In both cases, polymers were obtained with high yields and adequate molecular weights to give film- and fiber-forming properties.
2. Calorimetric analysis shows that the fusion temperatures of the new PEAs are higher than that of PEs derived from similar diols and dicarboxylic acids. The hydrogen bond interactions between the amide groups play a fundamental role, increasing the range of temperatures at which the new materials belong to the solid state. The side groups of the amino acids reduce the crystallinity and melting temperature of the polymers.
3. In spite of the presence of α-amino acids, both PEAs are thermally stable, because decomposition begins at 300 $\pm$ 7°C. These polymers can be easily processed from the melt state.
4. The new PEA degrades faster than related PEs in both aqueous and proteolytic enzymatic media. However, the PEs show higher degradability in an esterase medium.
5. The alanine derivative (PABA8) degrades more quickly than the glycine derivative (PGBG8). This fact may be attributed to differences in the crystallinity and the specificity of the essayed enzymes toward alanine or glycine units.
6. The PE derived from 1,4-butanediol shows faster degradability than that constituted by 1,6-hexanediol in spite of its higher molecular weight. The higher hydrophilicity of the former polymer may be the main explanation for this behavior.

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