Comparative Degradation Data between 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 derived from 1,4-butanediol, sebacic acid and L-alanine (PABA8) or glycine (PGBG8) have been prepared and characterized. For comparative purposes the related polyesters 4,10 and 6,10 have also been studied. The calorimetric analysis shows that the inclusion of amino acids improves thermal properties such as melting temperature without reducing significantly their thermal stability. All polymers show hydrolytic and enzymatic degradability. The degradation rates of the poly(ester amide)s were higher for the alanine derivative (PABA8) due to its low crystallinity and the higher specificity of the essayed proteolitic enzymes. The polyesters were degraded faster only when enzymes with an estearase activity were employed.

Keywords: Hydrolytic degradation, enzymatic degradation, α-amino acids, poly(ester amide)s, polyesters.

INTRODUCTION

There has been a growing interest in aliphatic polyesters 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 dicarboxylics acids like succinic acid and adipic acid. 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 constitute another family of polymers which has also applications such as degradable thermoplastics and, in addition, with improved mechanical properties compared to those of polyesters as expected from their potential hydrogen bonding interactions. In this sense, Bayer has been commercializing different polymers since 1996 under the trademark BAK, which are based on adipic acid, caprolactam and hexamethylene-diamine as amide components and 1,4-butanediol and ethylene glycol as ester components. A wide range of applications has been suggested due to their performance and simple processing. They include biowaste bags, agricultural films, cemetery decoration and one-way disposable dishes[2].

Our recent efforts have focused on the study of sequential poly(ester amide)s that include different α-amino acids, since they may enhance their biodegradability due to the susceptibility to enzymatic degradation 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[3,4,5]. Thus, this acid has been chosen as a constituent of the polymers investigated in this paper. These also incorporate 1,4-butanediol, like the indicated and commercially available polyesters and poly(ester amide)s. They also contain glycine (PGBG8) or L-alanine (PABA8) as α-amino acids,

since very low melting points are obtained with amino acids that have bulkier lateral groups[5]. The new polymers are named indicating the sequence amino acid-diol-amino acid 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 polyester (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 PGHG8 polymer.

METHODS

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

Intrinsic viscosities were determined with a Cannon-Ubbelhode microviscometer in dichloroacetic solutions at 25 ± 0.1 °C. The molecular weight distribution of polyesters was measured with a GPC apparatus (Water Assoc., Model 510) equipped with a Maxima 820 computer program. Molecular weights (M_n and M_w) are only indicative because they were calculated using polystyrene standards (Polysciences). A set of two μ-Stiragel (Polymer Lab.) columns with a limited exclusion weight of 10^4 and 10^3, and a RI 410 (Water Assoc.) detector were used. Polymers were dissolved and eluted in a

chloroform / *o*-chlorophenol (90/10, v/v) mixture at a flow rate of 0.5 mL/min (injected volume 100 μl, sample concentration 2.5 mg/mL).

Infrared absorption spectra were recorded with a Perkin-Elmer 1600 FT-IR 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. NMR spectra of poly(ester amide)s were registered from chloroform/trifluoroacetic acid solutions, whereas a chloroform solution was used for polyesters. 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 ^{1}H- and ^{13}C-NMR investigations, respectively. Thermal analysis was performed by differential scanning calorimetry with a Perkin-Elmer DSC-PYRIS 1 using indium metal for calibration. Thermogravimetric analysis was carried out with a Perkin Elmer TGA-6 thermobalance.

Plates of 1.5 cm x 1.5 cm x 200 μm were cut off from films prepared by melt pressing 200 mg of powder samples. Plates of PABA8 were annealed at 70 °C for 12 hours, before degradation experiments, in order to increase their crystallinity. Hydrolytic degradation studies were carried out in different conditions: a) pH 7.4 sodium phosphate buffer at 37 °C and b) distilled water at 55 °C (all samples), and 70 °C (only for poly(ester amide)s). Enzymatic degradation studies were performed at 37 °C by using lipases from *Candida cylindracea* (943 units/mg) and *Pseudomonas cepacia* (1500 units/mg), and proteolytic enzymes such as papain (30,000 units/mg, No. 7144) and proteinase K (*Tritirachium album*, 13 units/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 mM) and ethylenediaminetetraacetic

disodium salt (30 mM) for activation. Solutions were renewed every 72 hours 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. Mass loss, intrinsic viscosity, and changes in NMR and IR spectra were evaluated in all these different degradation experiments. Surfaces of polymer films after degradation tests were also observed with a JEOL JSM-6400 scanning electron microscope.

RESULTS AND DISCUSSION

Characterization

Table 1 summarizes the intrinsic viscosities of the synthesized polymers. 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 polyesters could also be obtained from GPC analysis due to 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, showing a higher polydispersity index for polyester 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, coming directly from polymerization, were heated at 20 °C/min through fusion and left in the melt state for 2 minutes. 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 get data for the melt crystallized samples. Heats of fusion were used to evaluate the crystallinity of samples (solution- and melt-crystallized samples) taking

into account the heats of fusion for 100 % crystalline materials. These values (ΔH_f^{eq}) were estimated from the reported[8] group contributions 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 1. As expected, crystallinity is lower when samples crystallize from the melt. Melting temperatures of polyesters are in agreement with previously reported data (60[9], 62[10] or 67[11] °C for polyester 4,10, and 67[12] or 78[13] °C for polyester 6,10) and significantly lower than those found for the new poly(ester amide)s. Thus, the incorporation of α-amino acid units like L-alanine and glycine improves thermal properties. Note that melting temperatures increase approximately 100° and 50 °C for glycine and alanine derivatives. It should also be pointed out that the crystallinity of PGBG8 is comparable to the parent polyester (PE 4,10).

Table 1 also shows how the side group of the amino acid reduces both melting temperature and crystallinity. In fact, PABA8 could not crystallize from the melt, since only a glass transition temperature of 32 °C (C_p = 0.15 kJ/mol °C) indicative of an amorphous state was observed in the third calorimetric run. However, the sample could be recrystallized by a three-hours annealing at 70 °C that gives 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 get samples with a comparable crystallinity (35-45 % for polyesters and PGHG8).

The decomposition temperatures $T_{d,0}$ (inclination point in the loss of weight vs. temperature curve) and $T_{d,1/2}$ (temperature at which the loss of weight has reached 50%) were determined by thermogravimetry at a heating rate of 10 °C/min. Both poly(ester amide)s begin decomposition at 300 ± 7 °C, as summarized in Table 1. Note that this value is much higher than the melting temperature (more than 140°C). Consequently,

the applicability of these polymers is not impaired. Furthermore, their thermal stability is comparable to that of the related polyesters.

IR and RMN spectroscopic data of the polymers (Table 2) are in total agreement with their anticipated chemical constitution. The infrared spectra of the synthesized poly(ester amide)s 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 2. As expected from our molecular weight estimations and the physical properties of polymers, we could not detect any additional peak corresponding to terminal groups in ^{1}H- and ^{13}C-NMR spectra of the four tested polymers.

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 due to the low melting temperature of polyesters. However, experiments at 70 °C were also carried out with poly(ester amide)s. Both weight mass loss and changes in the intrinsic viscosity of the remaining samples were evaluated. PABA8 was the polymer with a highest weight loss (56 % after 50 days at 55 °C) and a biggest change in intrinsic viscosity (from 0,8 to 0,36 dL/g after 50 days at 55°C). The poly(ester amide) PGBG8 also degrades well, though at a slower rate probably because of its higher crystallinity. In this way, experiments at 70 °C demonstrated the high degradability of both poly(ester amide)s and confirmed that the lateral group of the amino acid affects on the susceptibility to the

hydrolytic degradation. Polyesters also degrade steadily but at a lower rate than the related poly(ester amide)s. Comparative results of samples after 50 days of treatment are summarized in Table 3. It is worth noting that minor differences between the degradation of PE 4,10 and PE 6,10 are found. Thus, polyester 4,10 shows a major change in the intrinsic viscosity and also a major weight loss than PE 6,10, though it is the sample with the highest initial molecular weight. The different hydrophylicity 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. Results of both the least (PE 6,10) and most degradable (PABA8) polymers are shown in Figure 3. The trends observed under the accelarated 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.

^{1}H-NMR spectra of the degraded poly(ester amide)s show that the signal at 4.37 ppm (CH_2-OCO-) decreases in intensity, while only one additional signal at 3.88 ppm (-CH_2-OH), indicative of terminal unesterified groups, appears and increases in intensity with degradation time (Figure 4a). This result clearly indicates that the hydrolysis of these poly(ester amide)s takes place through the ester linkages, an observation that was previously reported for similar polymers[4,5,14]. Infrared spectroscopy is also fully consistent with this conclusion, since 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, since 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 estearases.

Our previous studies[14] on similar sequential poly(ester amide)s 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 5a and Table 4 clearly indicate that poly(ester amide)s degrade faster than the selected polyesters. It should also be emphasized that the alanine derivatives are much more sensitive to the enzymes, probably due to both their lower crystallinity and the different enzyme specificity towards 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).

^{1}H-NMR spectra (Figure 4b) showed that both amide and ester linkages of poly(ester amide)s were cleaved during the enzymatic 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, indicative of terminal carboxylic groups ($-CH_2COOH$) appears. Some evidence for ester bond hydrolysis by the action of α-chymiotripsin, papain and proteinase K on related poly (ester amide)s has been 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 5b and Table 4 show the results of degradability with estearases such as lipases from *Candida cylindracea* and *Pseudomonas cepacia*. Some observations can be indicated: a) all polymers degrade faster with enzymes than under accelerated hydrolytic conditions; b) lipase from *Pseudomonas cepacia* is more effective in the degradation process of polyesters, whereas lipase from *Candida cylindracea* appears to be more effective with poly(ester amide)s; c) polyesters degrade faster in lipase from *Pseudomonas cepacia* than poly(ester amide)s, in contrast with the results obtained in accelerated hydrolytic media or in proteolytic enzymes. ^{1}H-NMR spectra (Figure 4c) indicate that degradation takes place through cleavage of ester linkages, as expected from the especifity 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 poly(ester amide)s. 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, after incubation in the degradation media, the appearance of numerous crevasses, being their extension and proportion an additional indication of the degradation process (Figure 6).

CONCLUSIONS

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

1. Two new poly(ester amide)s derived from 1,4-butanediol, sebacic acid and L-alanine or glycine have been prepared following two different procedures: 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 poly(ester amide)s are higher than that of polyesters derived from similar diols and dicarboxylic acids. Hydrogen bond interactions between amide groups play a fundamental role, increasing the range of temperatures at which the new materials belong to the solid state. Side groups of amino acids reduce both crystallinity and melting temperature of polymers.
3. In spite of the presence of α-amino acids, both poly(ester amide)s are thermally stable, since decomposition begins at 300 ± 7 °C. These polymers can be easily processed from the melt state.
4. The new poly(ester amide) degrades faster than related polyesters in both aqueous and proteolytic enzymatic media. However, polyesters show a higher degradability in an estearase medium.
5. PABA8 degrades more quickly than the glycine derivative (PGBG8). This fact may be attributed to differences on crystallinity and on the specificity of the essayed enzymes towards alanine or glycine units.
6. Polyester derived from 1,4-butanediol shows a 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 behaviour.

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FIGURE CAPTIONS

Figure 1. Sequence of three DSC scans carried out with the PGBG8 sample: a) heating run at 20 °C/min; b) cooling run at 10 °C/min after keeping the sample in the melt state for two minutes; c) reheating run at 20 °C/min.

Figure 2. Plot of the remaining weight (a) and intrinsic viscosity (b) versus degradation time under accelerated conditions for the polyesters and poly(ester amide)s studied in this work. Polymers were immersed in distilled water at 55 °C (--) or 70 °C (—).

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

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

Figure 5. Plot of the remaining weight versus degradation time in enzymatic media containing proteases (a) and estearases (b) for PE 4,10 (□), PE 6,10 (◆),PGBG8 (○) and PABA8 (Δ) samples. Continuous lines correspond to proteinase K or lipase from *Candida cylindracea*, whereas dashed lines correspond to media with papain or lipase from *Pseudomonas cepacia*. Note that polyesters degrade in *Pseudomonas cepacia* after an induction time of approximately three days.

Figure 6. Scanning electron micrographs of different PABA8 plates. (a) 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) Plate after 50 days of exposure under accelerated hydrolytic conditions (70 °C): numerous pores and crevasses appear on the surface; (c) Same as (b), but observed at a higher magnification;

(d) Small recovered fragment of a plate exposed to the proteinase K enzymatic medium for only one day: note with respect to (c) that deeper fissures appear; (e) Surface (right) and fracture side (left) of a plate after 15 of incubation in the *Candida cylindracea* enzymatic medium. Scale bars: 10 μm (a, c, d and e) and 100 μm (b).

Table 1. Intrinsic viscosities and calorimetric data of the polymers studied in this work.

Polymer	[η] (dL/g)	1st run			2nd run		3rd run			$T_{d,0}$ (°C)	$T_{d,1/2}$ (°C)
		T_f (°C)	ΔH_f (kJ/mol)	χ (%)	T_c (°C)	ΔH_c (kJ/mol)	T_f (°C)	ΔH_f (kJ/mol)	χ (%)		
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

Table 2. Main spectroscopic data of the polymers studied in this work.

a) 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

b) ^{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*C*H(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.

Table 3.Weight loss (%) and intrinsic viscosity (dL/g) of the polymers studied in this work after 50 days of exposure in distilled water at 55 °C (a) or 70 °C (b).

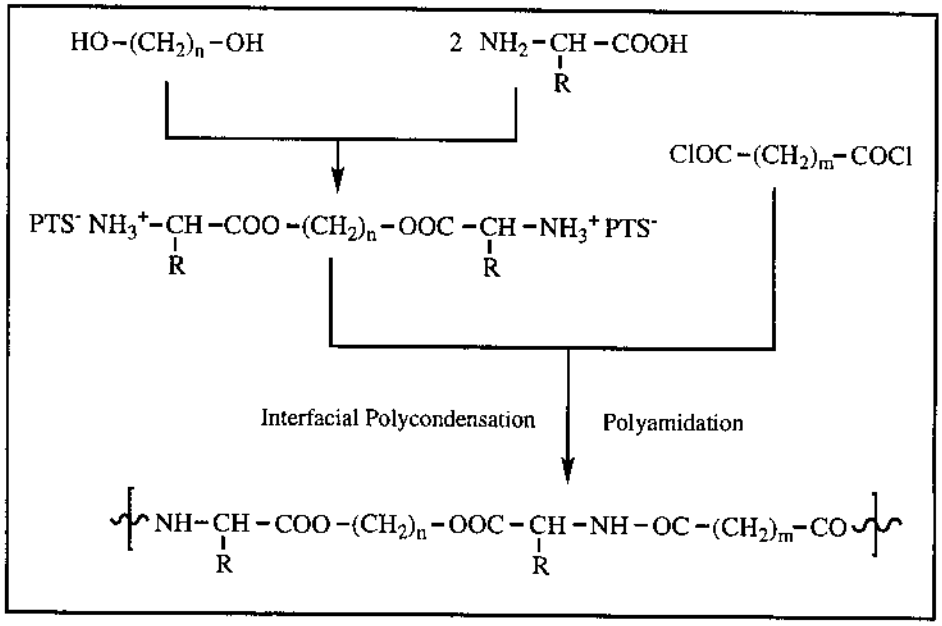
Polymer	Weight loss	$\|\eta\|$
PE 4,10[a]	6	0.84
PE 6,10[a]	3	0.79
PGBG8[a]	18	0.48
PABA8[a]	56	0.36
PGBG8[b]	62	0.29
PABA8[b]	66	0.20

Table 4. Remaining weight (%) of films of the studied polymers after 15 days of exposure in the indicated enzymatic media.

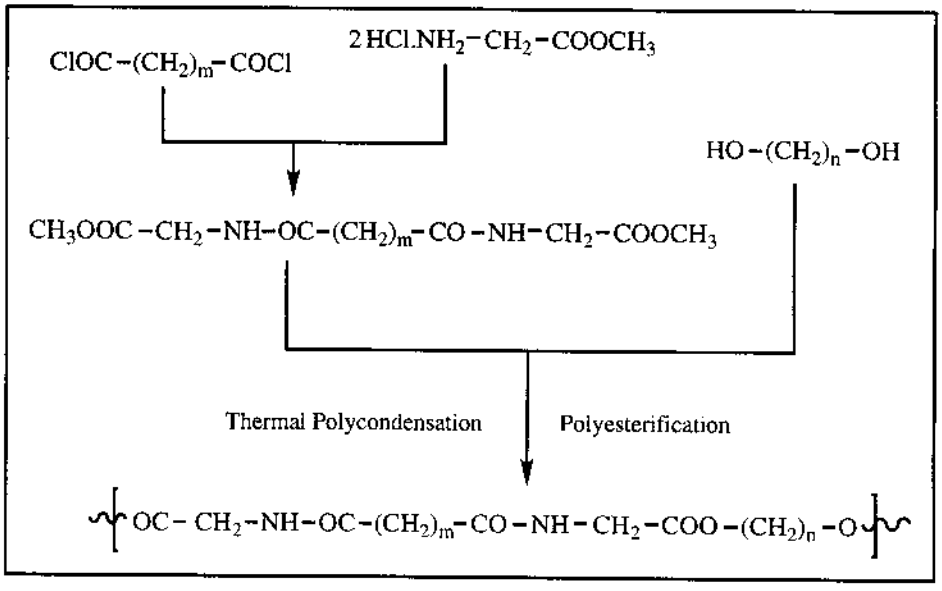
Polymer	Remaining weight			
	Proteinase K	Papain	Lipase from *Candida Cylindracea*	Lipase from *Pseudomona Cepacia*
PE 4,10	97	96	98	0[a]
PE 6,10	99	98	99	5.5
PGBG8	96	82	94.5	98.2
PABA8	0[b]	0	77.0	77.5

[a]The sample disappears after only nine days of exposure.
[b]The sample disappears after only four days of exposure.

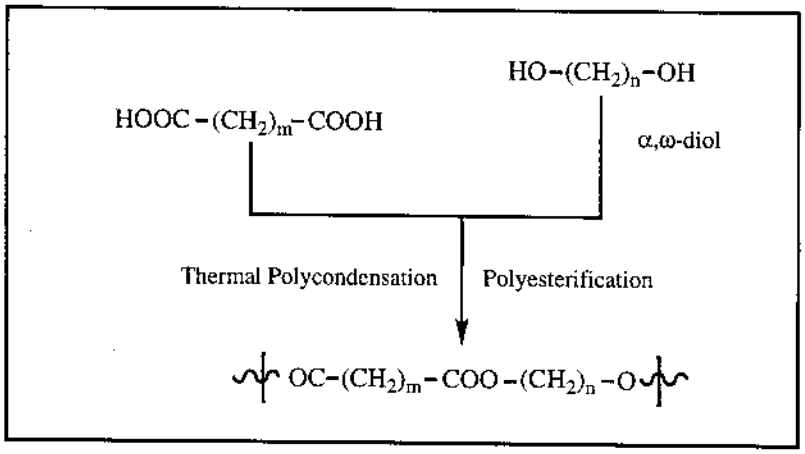
a)


HO-(CH2)n-OH
2 NH2-CH-COOH
R
ClOC-(CH2)m-COCl
PTS- NH3+-CH-COO-(CH2)n-OOC-CH-NH3+ PTS-
R
R
Interfacial Polycondensation
Polyamidation
NH-CH-COO-(CH2)n-OOC-CH-NH-OC-(CH2)m-CO
R
R

b)


ClOC-(CH2)m-COCl
2 HCl.NH2-CH2-COOCH3
HO-(CH2)n-OH
CH3OOC-CH2-NH-OC-(CH2)m-CO-NH-CH2-COOCH3
Thermal Polycondensation
Polyesterification
OC-CH2-NH-OC-(CH2)m-CO-NH-CH2-COO-(CH2)n-O

c)


HO-(CH2)n-OH
HOOC-(CH2)m-COOH
α,ω-diol
Thermal Polycondensation
Polyesterification
OC-(CH2)m-COO-(CH2)n-O

Scheme 1

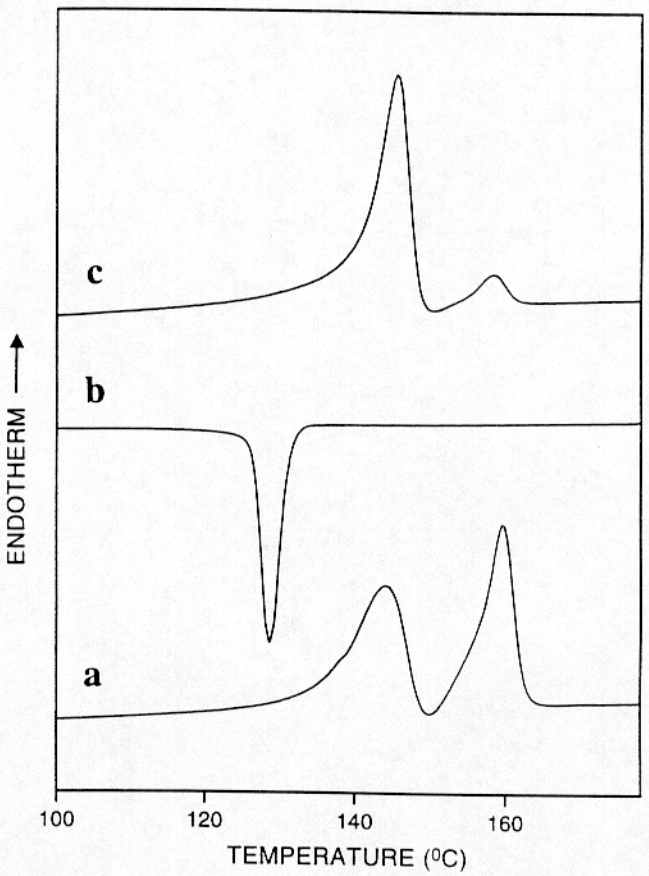


FIGURE 1
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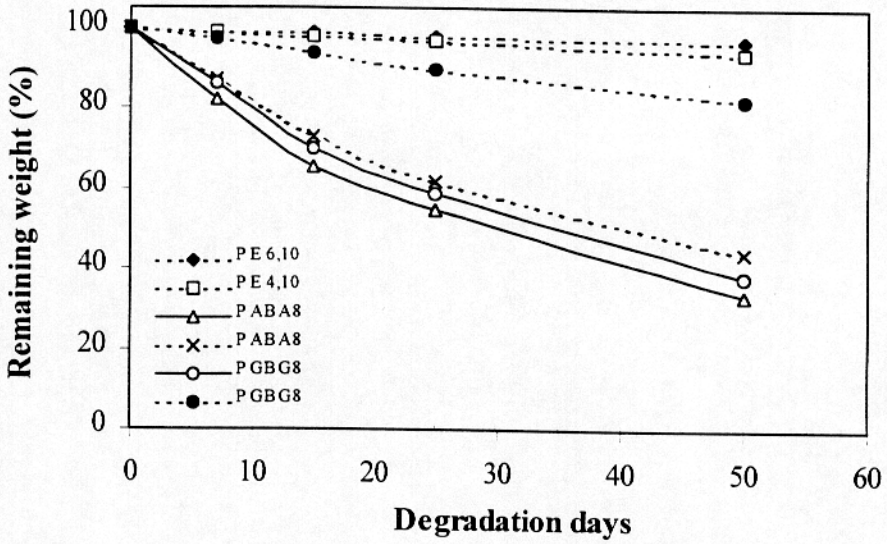
a)



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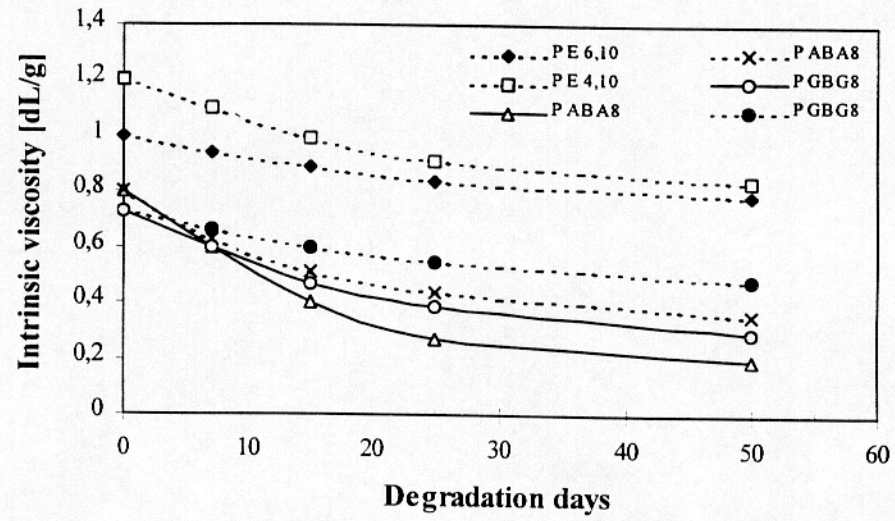

FIGURE 2
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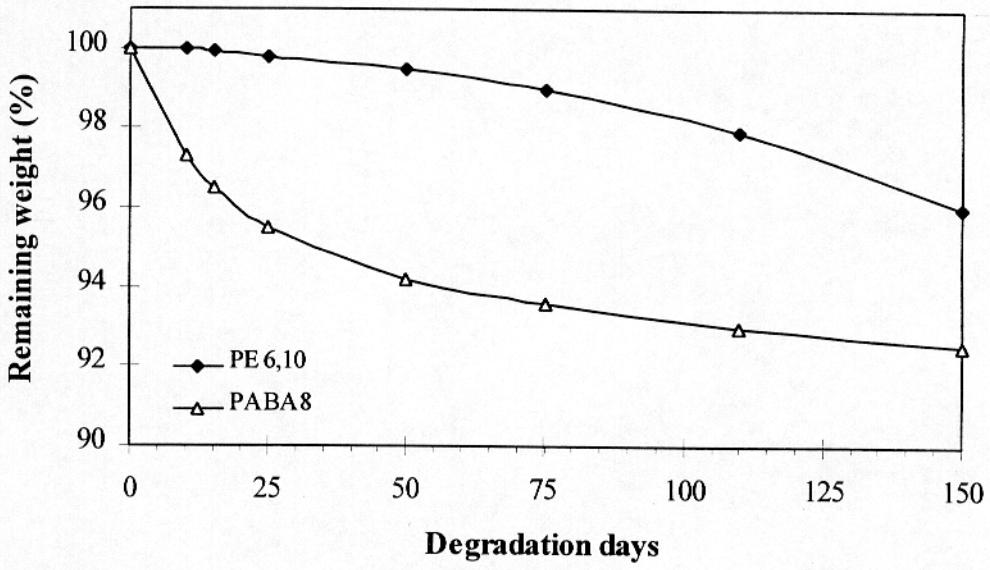
a)



b)

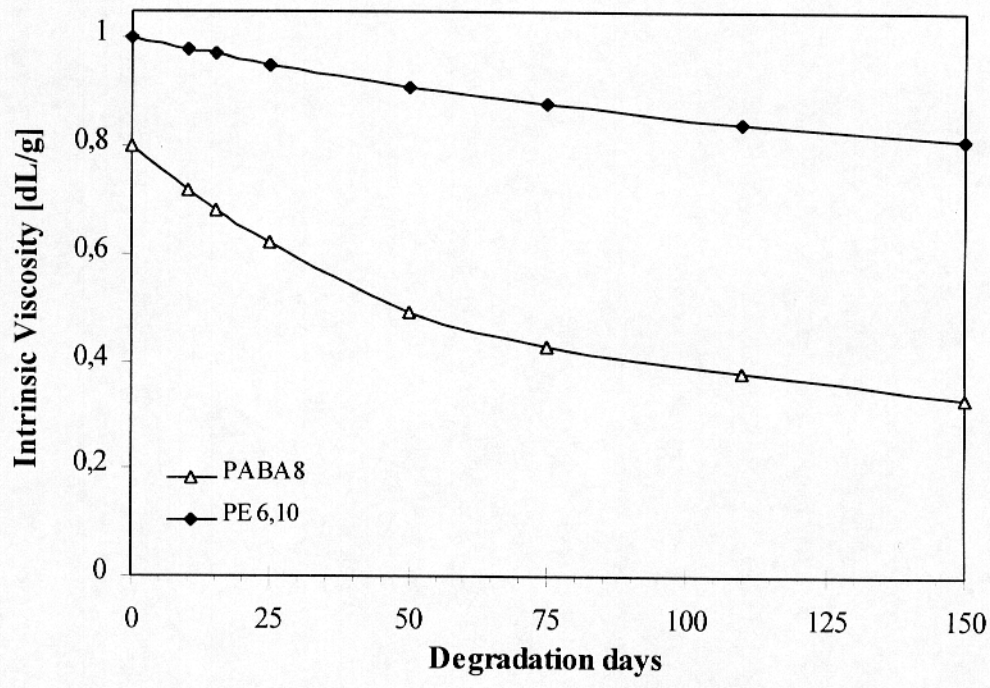


FIGURE 3
Montané *et al.*

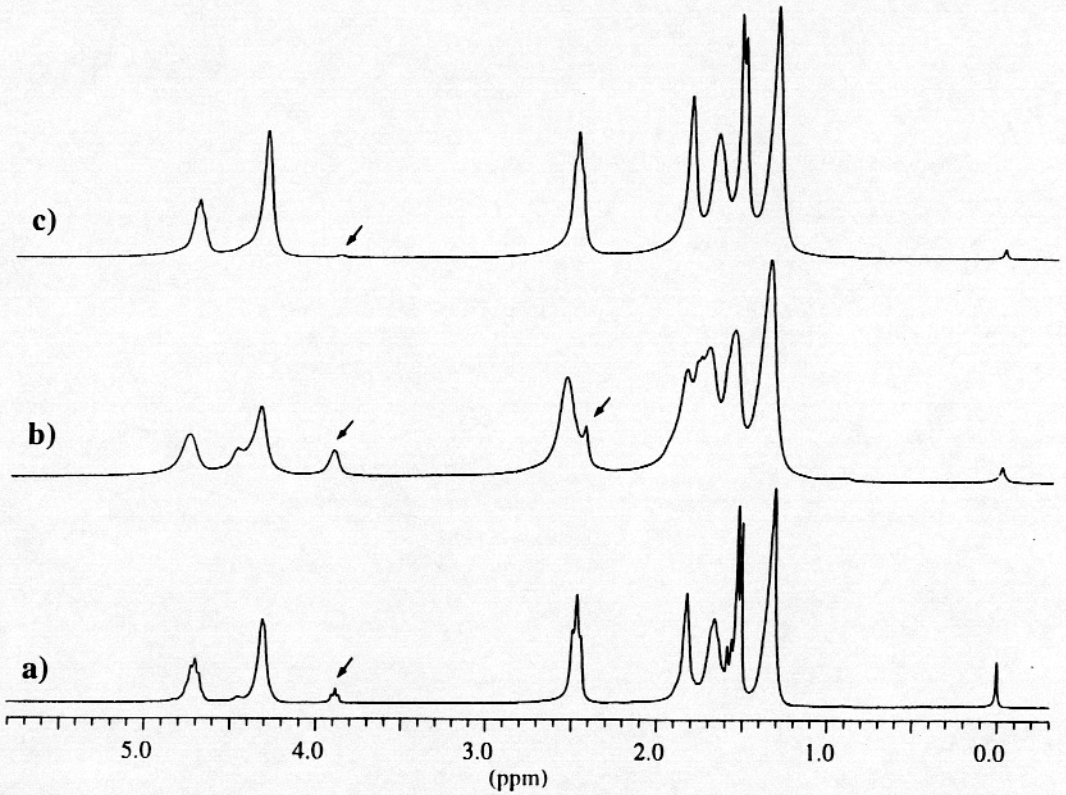
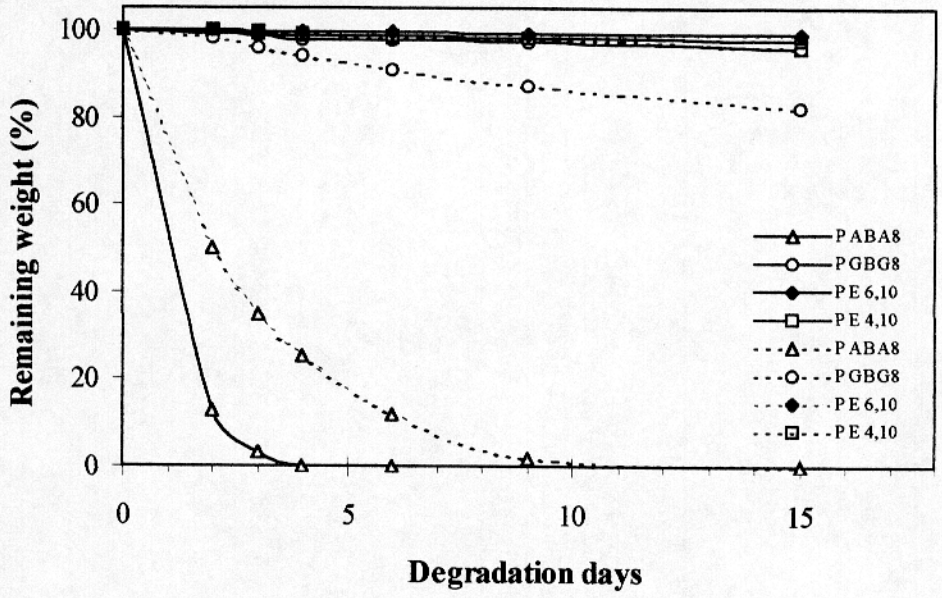


FIGURE 4
Montané *et al.*

a)



b)

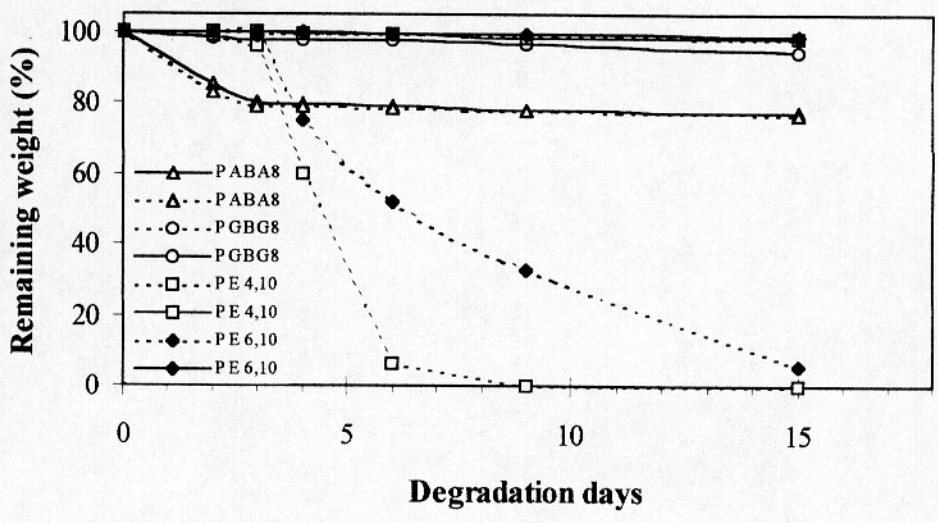


FIGURE 5
Montané *et al.*

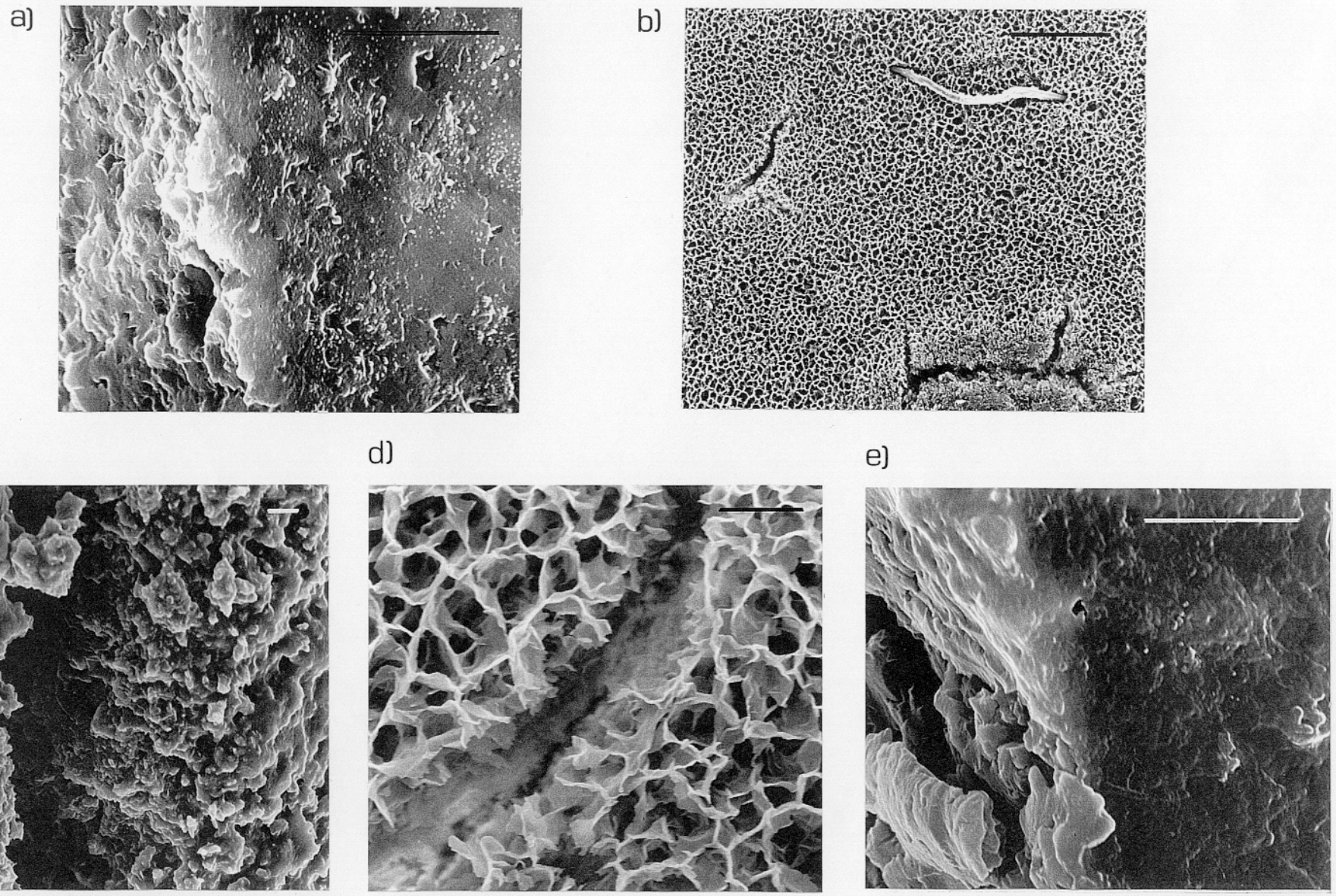


FIGURE 6
Montané *et al.*