Novel biodegradable copolyamides based on adipic acid, bis(*p*-aminocyclohexyl)methane and several α-amino acids: synthesis, characterization and study of their degradability for food packaging applications: 4

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Novel biodegradable copolyamides were synthesized using the bulk polycondensation method. The statistical copolyamides produced by the simultaneous reaction of the salt of adipic acid and bis(*p*-aminocyclohexyl)methane and several α-amino acids were characterized by elemental analyses, density and viscosity measurements and Fourier transform infra-red spectroscopy. The semicrystalline or amorphous nature of these novel copolyamides was confirmed both by differential thermal analysis measurements and wide-angle X-ray diffraction patterns. Their biodegradability was investigated by testing their resistance to alkali hydrolysis (10% w/v NaOH), to microbial/bacterial attack when buried in soil and to enzymatic hydrolysis. The biodegradation of copolyamides was followed using gel permeation chromatography and differential thermal analysis. Possible applications of these polymers could be envisaged in the fields of agriculture, packaging and medicine.

(Keywords: biodegradability; copolyamides; α-amino acids)

INTRODUCTION

In the past, the main incentive and the most important requirement for novel synthetic polymers was their lack of susceptibility to biodegradation, mainly caused by micro-organisms, enzymes and insects, and their resistance to climatic changes[1,2]. Recently the focus of research for synthesis of novel polymers has undergone significant changes because of a considerable increase in applications for biodegradable plastics[3]. Research has been aimed at the synthesis of bioerodible–biodegradable polymeric systems suited for temporary implants in animals and humans or appropriate for pharmaceutical and agrochemical devices that release active chemicals in a controlled manner[4]. Controlled drug delivery and biodegradable sutures are the most commonly mentioned applications of polymeric materials for biomedical and pharmaceutical use[3–6]. Several other applications of biodegradable polymers can be found in agriculture, for example, growing trees in bags, where the currently used non-degradable polyethylene has to be gradually replaced[3], and in waste disposal[7]. The latter has exerted a strong pressure towards the development of appropriate biodegradable polymers because of the intensity of the ecological problem caused by increased amounts of non-degradable plastic litter[3,7].

The biodegradation of the amide bonds of synthetic polyamides has attracted the interest of research workers because of their structural similarity to natural polymers (i.e. proteins)[8]. Although the biocompatibility of the amide group of synthetic polymers, such as nylon 6 and nylon 6,6, has been proved by their implantation in dogs, the changes that these polymers underwent (surface cracks and erosion for nylon 6 and 80% loss of tensile strength for nylon 6,6) were not considered adequate for classifying these polymers as biodegradable[9–11]. Therefore, several researchers tried to synthesize biodegradable polyamides by imitating as far as possible the procedures occurring in nature, in particular in collagen[3]. A large number of copolyamides were synthesized mainly using a wide range of α-amino acids as starting materials[1,2,12–18]. For most of these polymers a certain degree of biodegradability has been claimed, which could eventually render them 'appealing' despite their relatively high cost. Previous publications reported the synthesis, thermal properties, X-ray studies and density measurements of polyamides based on bis(*p*-aminocyclohexyl)methane (PACM) and several diacids which are characterized by high temperature thermal stability and are not susceptible to biodegradation[19–21].

The aim of this work is to synthesize and characterize a series of novel biodegradable copolymers based on commercially available monomers such as adipic acid

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(AA) and PACM and several α-amino acids and, finally, to compare their properties to those reported in previous publications[15-21].

EXPERIMENTAL

Materials

Adipic acid (AA) was purchased from Aldrich (UK) and recrystallized twice from distilled water and then from acetone/petroleum ether and ethyl acetate. L-Tyrosine, L-proline, L-alanine and L-glycine, purchased from Sigma (UK), were analytically pure and used without further purification. Bis(*p*-aminocyclohexyl)methane (PACM-20) was a gift from Air Products and Chemicals Inc. (USA) and was distilled twice before use. PACM-20 was treated as described elsewhere[19,20] in order to obtain the following isomer composition of diamine (%) *cis-cis/cis–trans/trans–trans*: 51.5/28.5/20.0, confirmed by gas chromatography.

Polymerization apparatus

The copolyamides were synthesized by melt polycondensation at 260°C using a fluidized bed (sand bath) equipped with a thermostat (Edwards, UK). Mixtures of the AA/PACM sale (1:1 mol/mol) synthesized as previously reported[19,20] and α-amino acids were fed into the polymerization tube at room temperature (23 ± 1°C) and heated at a rate of 5°C min^{-1} under a stream of dry N_2 and held at 260°C for 2 h. Then, vacuum was applied (0.5 mm Hg (66.6 Pa)) for 1 h in order to remove the water formed during the reaction and volatile components (low molecular weight oligomers or residual monomers). Finally, the Pyrex polymerization tube was cooled to room temperature in air. The polymers were cut into pieces and milled to fine powder. The low-molecular-weight polymers were extracted first with methanol and then with toluene in a Soxhlet apparatus for 16 h.

Elemental analysis

The elemental analyses (% C, H and N) of the novel copolyamides were carried out using a Carlo Erba 1106-EA apparatus.

Density measurements

Densities were determined at 23°C pycnometrically[22] with toluene and by means of a density gradient column (Davenport, UK) using polymer samples previously degassed at 0.1 mmHg (13.3 Pa) for 24 h[23].

Viscosity measurements

Reduced specific viscosities were determined with 0.1, 0.25, 0.5, 0.75 and 1 wt% polymer solutions in *m*-cresol (twice distilled) using an Ubbelohde-type viscometer.

Wide-angle X-ray diffraction patterns (WAXDP)

WAXDP ($2\theta = 5$–$40°$) were recorded using a Phillips PW 1050 Diffractometer (The Netherlands). Five measurements were recorded per sample in order to ensure the reproducibility of our results.

Fourier transform infra-red analysis (FT-*i.r.*)

FT-i.r. spectra were recorded on a Nicolet (DX II) (USA) spectrophotometer model using KBr (1% w/w polymer/KBr) discs. The spectra were plotted using a Hewlett Packard Color Pro plotter.

Differential thermal analysis (*d.t.a.*)

The glass transitions (T_g) were determined with the use of a DuPont Differential Thermal Analyser (DTA, 2000) connected to an IBM computer PC/2 and a Hewlett Packard Color Pro plotter. The heating rate was 5°C min^{-1} and the temperature range was from −50 to 300°C. The calibrations of temperature and heat enthalpy ($J\,g^{-1}$) of the DTA were made using indium. Five measurements were recorded per sample. The glass transitions (T_g) were defined as the midpoints of step changes in heat capacities (ΔC_p). The melting points (T_m) were defined as the peaks of the endothermic curves.

Dynamic mechanical thermal analysis (*d.m.t.a.*)

D.m.t.a. measurements were carried out using a PL-DMTA (Mark II, UK) connected to an Olivetti PC 286 and a Hewlett Packard Color Pro plotter. The heating rate was 5°C min^{-1}, frequencies 1, 5, 10, 30 and 100 Hz and the dimensions of the bars were 40 mm length, 7 mm width and 3.2 mm thickness. Five measurements were recorded per sample.

Tan δ ($= E''/E'$) and E'' (loss modulus) were defined as the peaks of the curves whereas E' (storage modulus) was defined by the intersection of the extrapolations of the two linear parts.

Thermogravimetric analysis (*t.g.a.*)

T.g.a. measurements were carried out with a Shimadzu model DT-30 TGA (Japan) at a heating rate of 5°C min^{-1} under a stream of dry N_2.

Biodegradability experiments

Alkali hydrolysis. The alkali hydrolysis of a copolymer film (cast with CF_3COOH) was carried out at 80°C in 10% NaOH (w/v) aqueous solution for up to 50 h for all the samples. The weight loss of all the samples after their alkali treatment was calculated and correlated to their α-amino acid content.

Microbial–bacterial attack. Several films of each copolymer were buried in soil which was a 50/50 mixture of potting compost bought from a garden centre and garden soil from a compost heap, which was rich in microbiological activity. The trays containing the soil were stored in an incubator at 37°C. The decrease in weight was checked by weighing the polymer films every day at the beginning and every other week towards the end of the experiments.

Enzymatic hydrolysis. The enzymatic hydrolysis of copolymers was determined by adding 15 mg of copolymer in α-chymotrypsin and α-trypsin/phosphate buffer (KH_2PO_4/Na_2HPO_4, pH 7.0) (500 units/25 μl and 2420 units/25 μl, respectively). The extent of biodegradation was estimated by measuring the TOC (total organic carbon) concentration corresponding to the amount of water-soluble hydrolysed products with a TOC analyser (Shimadzu, Japan). Blank TOC tests were also carried out on buffer solutions containing either only the enzymes or only the polymers and their results were deducted from the above-mentioned TOC values in order to determine the net TOC values, which were due exclusively to the enzymatic hydrolysis of copolymers.

Table 1 Percentage yield after Soxhlet extraction with toluene and methanol of copolyamides AA/PACM/α-amino acids

AA (mol)	PACM (mol)	α-Amino acid (mol)	Solubility in toluene (%)	Solubility in methanol (%)	Final yield (%)
50	50	–	0.58	0.13	99.29
		L-Tyrosine			
47.5	47.5	5.0	1.27	0.22	98.51
45.0	45.0	10.0	1.42	0.35	98.23
42.5	42.5	15.0	1.69	0.40	97.91
40.0	40.0	20.0	1.95	0.56	97.49
35.0	35.0	30.0	2.43	0.73	96.84
		L-Proline			
47.5	47.5	5.0	1.10	0.20	98.70
45.0	45.0	10.0	1.33	0.34	98.33
40.0	40.0	20.0	1.61	0.45	97.94
35.0	35.0	30.0	2.25	0.71	97.04
30.0	30.0	40.0	2.52	0.92	96.56
25.0	25.0	50.0	3.13	1.03	95.84
		L-Glycine			
47.5	47.5	5.0	0.98	0.15	98.87
45.0	45.0	10.0	1.19	0.27	98.54
42.5	42.5	15.0	1.45	0.39	98.16
40.0	40.0	20.0	1.59	0.53	97.88
35.0	35.0	30.0	2.25	0.65	97.10
		L-Alanine			
47.5	47.5	5.0	0.85	0.21	98.94
45.0	45.0	10.0	0.95	0.30	98.75
42.5	42.5	15.0	1.32	0.28	98.40
40.0	40.0	20.0	1.44	0.40	98.16
30.0	30.0	40.0	2.05	0.46	97.49
25.0	25.0	50.0	3.00	0.68	96.32

Table 2 Results of elemental analyses of copolyamides AA/PACM/α-amino acids

AA (mol)	PACM (mol)	α-Amino acid (mol)	Theoretically calculated (%)			Experimentally found (%)		
			C	H	N	C	H	N
50	50	–	72.06	8.85	8.85	71.99	8.88	8.87
		L-Tyrosine						
47.5	47.5	5.0	71.91	8.75	8.84	71.82	8.78	8.86
45.0	45.0	10.0	71.76	8.64	8.84	71.70	8.67	8.83
42.5	42.5	15.0	71.60	8.52	8.83	71.58	8.55	8.81
40.0	40.0	20.0	71.44	8.40	8.82	71.40	8.46	8.79
35.0	35.0	30.0	71.07	8.14	8.81	71.00	8.20	8.77
		L-Proline						
47.5	47.5	5.0	71.74	8.86	9.02	71.72	8.90	9.00
45.0	45.0	10.0	71.40	8.88	9.20	71.35	8.89	9.23
40.0	40.0	20.0	70.69	8.90	9.59	70.70	8.92	9.55
35.0	35.0	30.0	69.92	8.94	10.01	69.97	8.95	9.96
30.0	30.0	40.0	69.07	8.97	10.47	69.11	8.99	10.43
25.0	25.0	50.0	68.15	9.01	10.97	68.10	9.05	10.94
		L-Glycine						
47.5	47.5	5.0	71.50	8.78	9.14	71.46	8.83	9.12
45.0	45.0	10.0	70.91	8.71	9.45	70.85	8.76	9.43
42.5	42.5	15.0	70.27	8.63	9.79	70.30	8.61	9.77
40.0	40.0	20.0	69.58	8.55	10.15	69.52	8.53	10.11
35.0	35.0	30.0	68.05	8.37	10.95	68.00	8.41	10.90
		L-Alanine						
47.5	47.5	5.0	71.56	8.81	9.10	71.50	8.90	9.13
45.0	45.0	10.0	71.04	8.76	9.36	71.08	8.72	9.34
42.5	42.5	15.0	70.48	8.72	9.65	70.45	8.70	9.70
40.0	40.0	20.0	69.90	8.67	9.94	69.80	8.65	10.05
30.0	30.0	40.0	67.12	8.43	11.35	67.01	8.52	11.30
25.0	25.0	50.0	65.42	8.29	12.21	65.53	8.14	12.19

Gel permeation chromatography (g.p.c.) measurements

The determination of the molecular weight distribution of the copolyamides was carried out with g.p.c. measurements both before and after the biodegradability experiments. A Waters (USA) g.p.c. system was used with a Styragel column and *m*-cresol as an eluent at a rate of 0.6 ml min^{-1}. The calibration of the instrument was conducted with a series of polystyrene samples of known molecular weight.

RESULTS AND DISCUSSION

Synthesis and characterization of novel copolyamides

Table 1 shows the percentage yield before and after Soxhlet extraction of the copolyamides with methanol and toluene. The low-molecular-weight polymers/oligomers that are isolated with Soxhlet are within the range 1–4.16%, thus resulting in final yields of over 95%. This is in agreement with previous publications[1,2,16 18] where it was found that the α-amino acids are characterized by high reactivity when heated at temperatures above 200°C in the presence of a diacid and a diamine (AA and PACM, respectively). Therefore, it could be claimed that this polymeric system (salt of AA and PACM/α-amino acids) shows a reactivity almost equivalent to that of nylon salt prepolymers (i.e. nylon 6,6 or nylon 6,10) which have approximately 100% yield except for mechanical losses[24].

Table 2 gives the results of elemental analyses (C, H and N) for the synthesized copolymers both theoretically calculated and experimentally determined. The theoretically calculated values agree satisfactorily with the experimentally found ones. L-Tyrosine has three end-groups which could react and therefore the number of possible combinations is higher than in the case of the other α-amino acids. Although there are three different structures (a, b and c), shown in *Figure 1*, into which these copolyamides could be combined (by loss of water), the *FT*-i.r. spectra support the presence of structure (α) because no adsorption for O–C=O (in the region 1750–1800 cm^{-1}) was recorded.

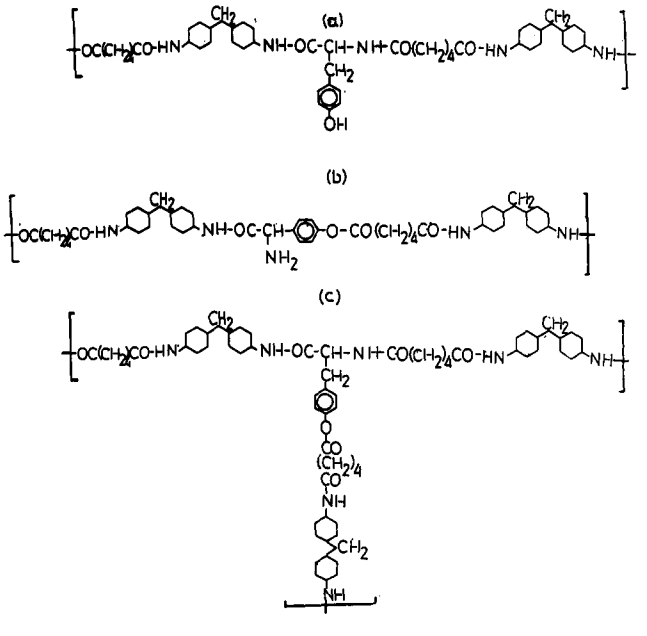

Figure 1 Several possible structures of copolyamides AA/PACM/L-tyrosine

Table 3 Densities and reduced specific viscosities of copolyamides AA/PACM/α-amino acids

AA (mol)	PACM (mol)	α-Amino acid (mol)	Density ($dl\,g^{-1}$)	Reduced specific viscosity (η_{sp}/C)[a]
50	50	–	1.064	1.42
		L-Tyrosine		
47.5	47.5	5.0	1.067	1.51
45.0	45.0	10.0	1.072	1.20
42.5	42.5	15.0	1.080	0.83
40.0	40.0	20.0	1.088	0.59
35.0	35.0	30.0	1.095	0.37
		L-Proline		
47.5	47.5	5.0	1.066	1.46
45.0	45.0	10.0	1.070	1.07
40.0	40.0	20.0	1.077	0.52
35.0	35.0	30.0	1.089	0.33
30.0	30.0	40.0	1.096	0.28
25.0	25.0	50.0	1.107	0.21
		L-Glycine		
47.5	47.5	5.0	1.065	1.33
45.0	45.0	10.0	1.067	0.92
42.5	42.5	15.0	1.068	0.69
40.0	40.0	20.0	1.072	0.44
35.0	35.0	30.0	1.078	0.27
		L-Alanine		
47.5	47.5	5.0	1.066	1.55
45.0	45.0	10.0	1.069	1.32
42.5	42.5	15.0	1.071	1.01
40.0	40.0	20.0	1.074	0.80
30.0	30.0	40.0	1.093	0.68
25.0	25.0	50.0	1.102	0.42

[a] Determined in a solution of 0.5 g polymer in 100 ml *m*-cresol at $22 \pm 1°C$

The results of density and viscosity measurements of the copolyamides are summarized in *Table 3*. The densities of the copolyamides were found to increase almost linearly with the increase in the comonomer α-amino acid contribution which was also the case in a number of previous publications[1,2,16,18]. The higher the molecular weight of the incorporated α-amino acid, the higher is the density of the copolyamide. Consequently, the densities of copolyamides fall in the following order: AA/PACM/L-glycine < AA/PACM/L-alanine < AA/PACM/L-proline < AA/PACM/L-tyrosine.

In contrast to densities, the reduced specific viscosities show exactly the opposite tendency, that is, an increase in the comonomer α-amino acid ratio considerably decreases the reduced specific viscosities. This behaviour could be explained if the molecular weights by number or by weight (M_n, M_w) determined by g.p.c. are taken into account. In fact, the M_n values of the copolymers decrease with an increase in the α-amino acid content, as it is shown in the following section. Since the viscosities are directly proportional to the M_n of the copolymers, lower M_n values would be equivalent to low viscosity values. All the AA/PACM/L-tyrosine polymers were entirely soluble in DMSO, *m*-cresol and hexafluoroisopropanol, thus showing that no crosslinked polymers were formed.

The semicrystalline nature of the copolyamides AA/PACM/α-amino acids was shown with the aid of WAXDP, where several sharp peaks were detected. Some representative WAXDP for the series AA/PACM/L-alanine are shown in *Figure 2*. However, when the α-amino acid content exceeds 20 mol% of the copolymer the semicrystalline copolymer turns into an amorphous one.

The WAXDP and thermal analysis of several other biodegradable copolyamides based on nylon 6,6 salts/α-amino acids by polycondensation[2] and polyaddition[17], respectively, confirmed their semicrystalline and amorphous character at low amino acid contents (< 20 mol%) and high amino acid contents (> 20 mol%), respectively.

The *FT*-i.r. spectra for all the series of the novel copolyamides were recorded. The *FT*-i.r. spectra of AA/PACM/L-alanine series are shown in *Figure 3*. The formation of an amide bond in all the copolyamides was confirmed by the presence of absorptions at 1636 1645 cm^{-1} and 1550 cm^{-1} (amide band I and amide band II, respectively)[1,2,18,25]. An absorption at ~1720 cm^{-1} occurring in the i.r. spectra of all the copolyamides was attributed to the presence of amino acid moiety as previously reported[1,2,18].

Table 4 gives the glass transition temperature (T_g) determined both from d.t.a. and d.m.t.a. measurements, the melting peaks (T_m) and the percentage crystallinities (x_c) of the synthesized copolyamides. The T_g values from d.m.t.a. measurements are given as determined from tan δ, log E' and log E''. By using multifrequencies the activation energies at T_g were also calculated. The absence of endotherm peaks in d.t.a. measurements for copolymers

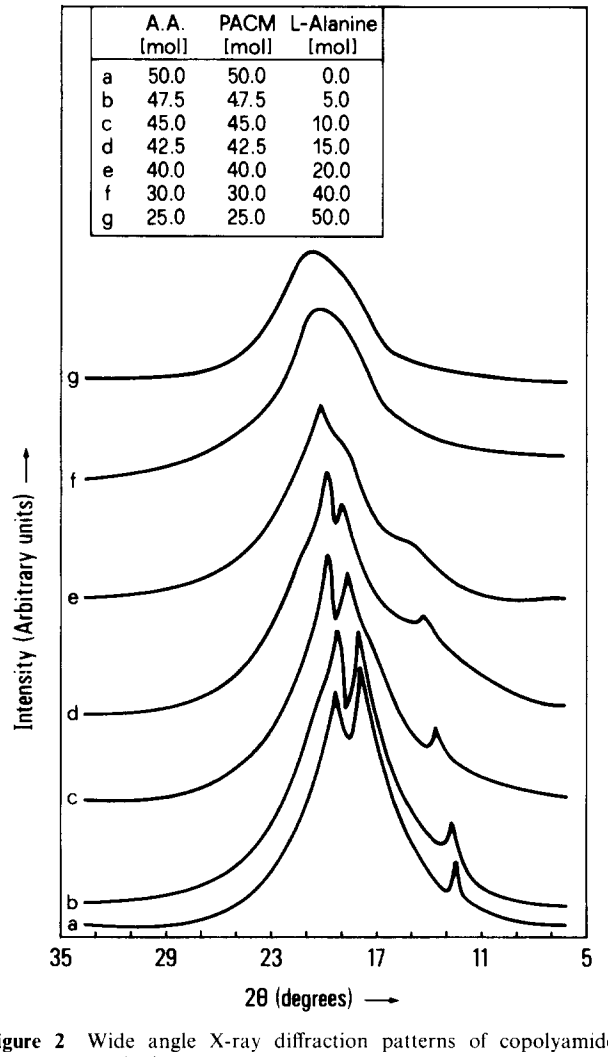

Figure 2 Wide angle X-ray diffraction patterns of copolyamides AA/PACM/L-alanine

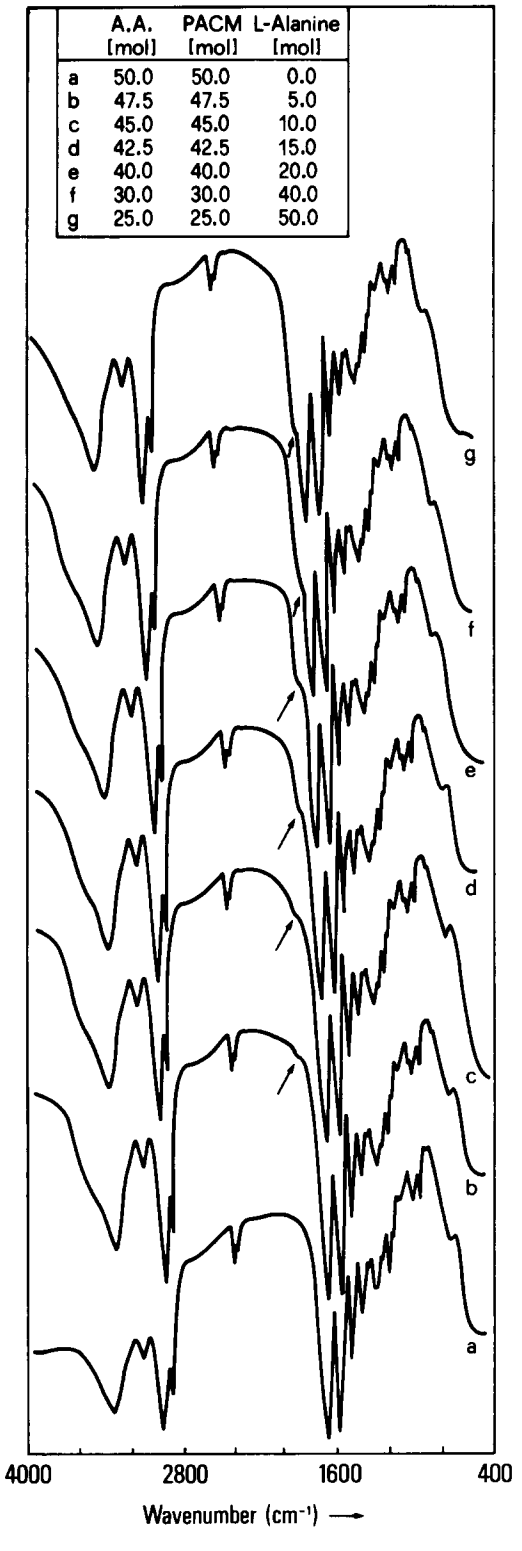

Figure 3 *FT*-i.r. spectra of copolyamides AA/PACM/L-alanine (arrows indicate the existence of α-amino acid moieties)

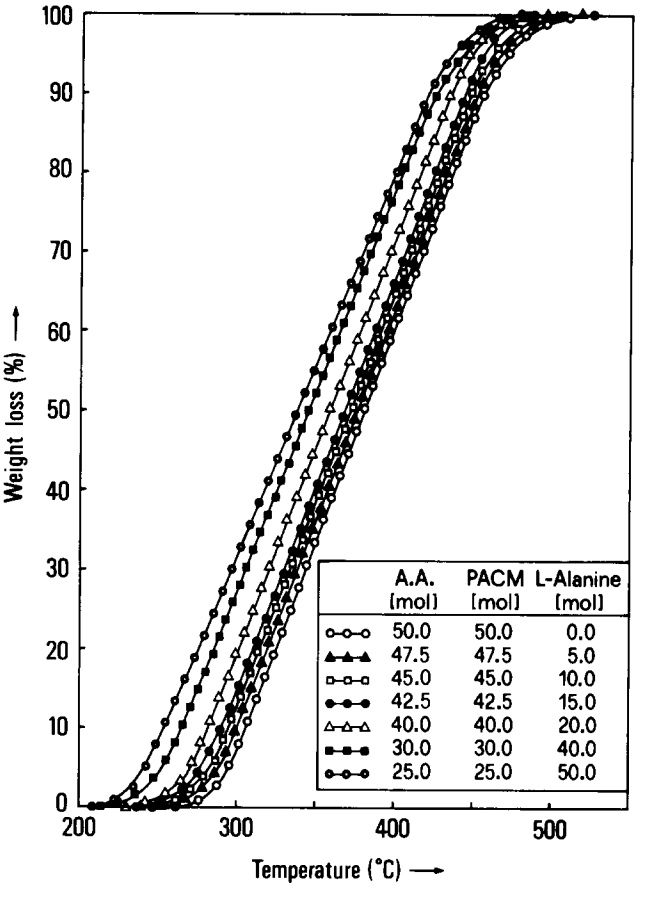

Figure 4 Thermogravimetric analysis (t.g.a.) of copolyamides AA/PACM/L-alanine

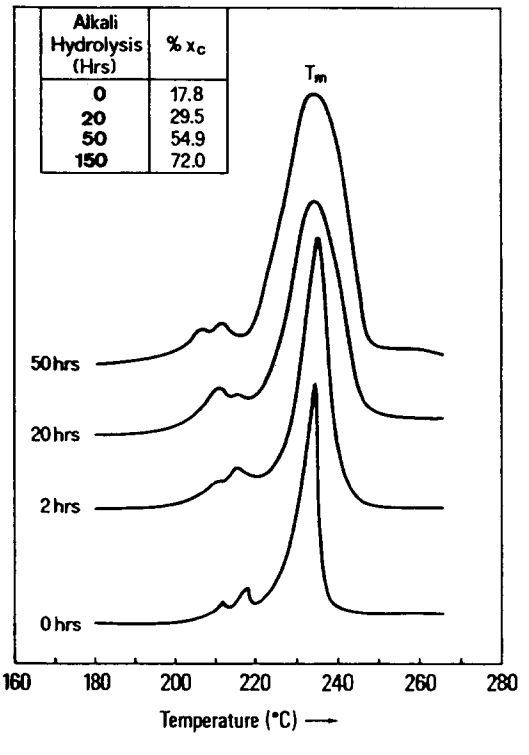

Figure 5 D.s.c. traces of the insoluble part in 10% NaOH (80°C) of copolyamide AA/PACM/L-alanine: 45/45/10(mol%) which show the increase in percentage crystallinity due to dissolution of the amorphous part

with high contents of α-amino acids (>20 mol%) is in accordance with the above-mentioned results from WAXDP. Satisfactory agreement was found between the T_g values obtained with d.t.a. and the log E'' values (from d.m.t.a. measurements) as reported in several previous publications[25–29]. The measured T_g values were considerably lower than those reported for the copolyamides of the salt of adipic acid and isophorone diamine (IPD)/α-amino acids; this could be interpreted in terms of the enhanced asymmetric (branched) structure that IPD can provide

Table 4 Effect of alkali hydrolysis (10% NaOH w/v, 80°C) on the glass transition temperatures (T_g) determined from d.s.c. and d.m.t.a. measurements[a], melting point (T_m), percentage crystallinity[b] (x_c) and activation energies ΔE at T_g of copolyamides AA/PACM/α-amino acids *versus* time (h)

AA (mol)	PACM (mol)	α-Amino acid (mol)	$T_{g(av.)}$[c]			T_m (°C)			ΔE (kJ mol^{-1} K^{-1})			x_c (%)		
			0 h	20 h	50 h	0 h	20 h	50 h	0 h	20 h	50 h	0 h	20 h	50 h
50	50	–	127.4±1.2	126.8±1.5	125.1±2.0	263.5±1.6	262.7±1.9	261.0±2.5	89±4	87±6	85±8	35±1	32±2	33±1
		L-Tyrosine												
47.5	47.5	5.0	129.7±2.2	104.3±2.5	70.2±2.9	247.8±1.8	206.7±3.1	155.8±4.0	93±6	62±5	13±2	21±3	29±2	38±3
45.0	45.0	10.0	132.4±1.9	106.5±3.4	72.5±3.1	238.0±2.0	199.0±2.5	150.4±2.3	98±8	66±6	16±3	12±1	21±2	33±2
42.5	42.5	15.0	134.8±2.4	108.0±4.1	75.9±3.0	226.9±2.3	185.2±1.9	136.2±3.7	107±10	75±8	26±3	8±1	16±1	22±2
40.0	40.0	20.0	139.9±3.1	113.1±3.5	78.6±2.4	223.1±1.9	181.3±2.4	130.5±2.6	123±12	91±9	41±4	3±1	7±1	14±2
35.0	35.0	30.0	144.8±2.1	118.4±2.9	82.3±2.1	–	–	–	135±11	102±10	56±6	–	–	–
		L-Proline												
47.5	47.5	5.0	129.2±2.0	103.6±3.7	68.0±2.5	251.3±2.0	209.8±2.3	160.4±3.2	92±8	60±7	11±1	25±3	34±3	47±3
45.0	45.0	10.0	131.7±2.5	105.2±4.4	70.1±3.2	243.0±2.3	203.4±3.2	151.8±4.1	96±9	63±6	13±2	15±2	25±3	39±4
40.0	40.0	20.0	138.6±3.2	110.9±5.2	75.4±4.5	231.5±2.5	190.0±2.5	141.0±3.4	119±11	83±9	35±4	5±1	9±1	20±2
35.0	35.0	30.0	143.2±1.8	116.2±6.0	79.8±3.4	–	–	–	131±13	100±12	50±6	–	–	–
30.0	30.0	40.0	154.7±1.9	123.5±2.4	87.2±2.9	–	–	–	140±15	111±10	59±7	–	–	–
25.0	25.0	50.0	155.6±2.3	129.0±3.3	87.9±3.2	–	–	–	146±12	114±11	65±8	–	–	–
		L-Glycine												
47.5	47.5	5.0	127.7±2.0	101.5±2.6	65.0±2.2	255.0±2.4	213.9±2.4	162.8±1.9	89±7	55±6	8±1	33±2	48±3	72±5
45.0	45.0	10.0	129.2±1.9	102.6±1.9	67.2±3.5	247.6±2.2	206.5±3.5	155.7±2.7	92±9	59±8	11±2	21±1	33±3	58±6
42.5	42.5	15.0	131.9±2.3	103.9±2.5	68.4±4.0	241.5±1.8	201.0±2.1	150.2±1.7	98±9	66±7	17±2	13±1	21±2	39±4
40.0	40.0	20.0	135.2±3.2	105.4±3.7	70.9±2.6	235.7±2.1	193.9±2.6	142.5±2.2	105±11	73±8	25±3	8±1	17±1	32±3
35.0	35.0	30.0	140.0±1.6	110.0±4.2	77.2±3.5	–	–	–	114±13	83±7	32±4	–	–	–
		L-Alanine												
47.5	47.5	5.0	128.4±1.7	102.4±2.4	67.1±2.0	253.1±1.6	211.8±2.5	161.4±2.2	91±7	58±6	10±1	30±3	44±3	68±5
45.0	45.0	10.0	130.8±2.6	103.7±3.8	68.9±2.5	245.2±1.9	204.9±3.6	153.5±3.0	94±8	61±7	12±1	18±2	30±2	55±3
42.5	42.5	15.0	133.6±2.8	105.6±4.0	70.4±2.8	238.5±1.5	197.5±4.0	147.0±2.5	103±10	70±8	23±2	12±1	25±2	43±2
40.0	40.0	20.0	136.7±3.1	107.8±3.5	72.7±3.0	233.4±2.3	191.8±3.4	140.8±2.8	114±12	81±9	32±4	6±1	17±1	33±3
30.0	30.0	40.0	151.9±4.2	120.0±3.4	84.5±3.4	–	–	–	135±13	105±11	55±6	–	–	–
25.0	25.0	50.0	152.3±2.3	127.0±3.6	84.9±4.1	–	–	–	140±15	109±12	58±7	–	–	–

[a] Five measurements were taken per sample and the results are given as mean ± standard deviation

[b] Percentage crystallinity is the average from d.s.c. and WAXDP; analyses carried out on the solid part insoluble in 10% NaOH w/v (80°C)

[c] $T_{g(av.)} = [T_{g(d.s.c.)} + T_{g(log E')}]/2$

Table 5 Initial decomposition temperatures ($T_{d,0}$) and half decomposition temperatures ($T_{d,1/2}$) of the copolyamides AA/PACM/α-amino acids determined from t.g.a. measurements[a]

AA (mol)	PACM (mol)	α-Amino acid (mol)	$T_{d,0}$ (°C)	$T_{d,1/2}$ (°C)
50	50	–	291.5±4.9	383.8±5.7
		L-Tyrosine		
47.5	47.5	5.0	273.7±4.6	384.2±5.4
45.0	45.0	10.0	265.6±6.0	381.5±6.7
42.5	42.5	15.0	256.0±5.8	375.8±4.8
40.0	40.0	20.0	250.4±3.9	367.3±6.0
35.0	35.0	30.0	244.8±5.3	359.4±5.6
		L-Proline		
47.5	47.5	5.0	277.5±3.5	372.5±6.8
45.0	45.0	10.0	267.0±4.7	367.4±6.5
40.0	40.0	20.0	255.2±3.8	352.9±4.8
35.0	35.0	30.0	247.4±4.9	341.2±5.5
30.0	30.0	40.0	238.7±5.4	335.0±6.0
25.0	25.0	50.0	232.5±6.1	326.2±5.7
		L-Glycine		
47.5	47.5	5.0	282.4±4.5	377.8±5.6
45.0	45.0	10.0	271.9±8.2	372.9±6.5
42.5	42.5	15.0	264.8±6.3	367.0±4.7
40.0	40.0	20.0	258.0±4.9	356.7±4.4
35.0	35.0	30.0	251.9±5.0	348.2±5.4
		L-Alanine		
47.5	47.5	5.0	285.9±5.7	381.4±5.5
45.0	45.0	10.0	276.5±6.8	376.0±3.8
42.5	42.5	15.0	270.3±5.0	370.4±4.3
40.0	40.0	20.0	263.8±4.5	361.5±2.9
30.0	30.0	40.0	247.0±3.9	347.9±5.7
25.0	25.0	50.0	238.8±4.7	337.4±6.0

[a] Five measurements were taken per sample and the results are given as mean ± standard deviation

(since all the other comonomers are the same) compared with PACM which has a certain degree of symmetry[30]. The glass transition temperatures of these novel copolyamides fall approximately in the following order: AA/PACM/L-glycine < AA/PACM/L-alanine < AA/PACM/L-proline/AA/PACM/L-tyrosine. This order is similar to the one previously established from the AA/IPD/α-amino acid copolymers[1], and can be explained in terms of structural differences derived from their stereochemical configurations; in particular, the presence of side or bulky pendent groups in the copolyamide can initially interfere with the hydrogen bonding, prevent regular chain packing and thus result in the enhancement of their amorphous character[30–32]. Therefore, if the comonomer unit can interfere with chain packing by distortion in one or more directions as is the case mainly with L-tyrosine and also with L-proline and L-alanine, the amorphous nature of the copolymer becomes more pronounced compared with other linear comonomer units (having no pendent groups) like L-glycine.

The activation energies (ΔE) of copolyamides (*Table 4*) at T_g show the same tendency as the T_g measurements; that is, the ΔE increases with incorporation of comonomers with pendent groups while the presence of linear comonomer units has a very limited influence upon the ΔE. Both melting points (T_m) and percentage crystallinities (x_c) of the copolyamides display a decrease with an increase in the α-amino acid content. The copolyamides whose α-amino acid content is higher than 20 mol% exhibit a totally amorphous character since there is no detectable T_m and their x_c equals 0 (*Table 4*).

Thermal decomposition of a polymer does not occur until the temperature is so high that primary chemical bonds are separated. The heat resistance of a polymer is usually characterized by its temperatures of initial ($T_{d,0}$) and half decomposition ($T_{d,1/2}$)[33]. $T_{d,0}$ is defined as the temperature at which the weight loss during heating can just be measured and is defined as the inclination point of the weight loss/temperature curve. $T_{d,1/2}$ is the temperature at which the weight loss of a polymer during pyrolysis (at a constant temperature rise) reaches 50% of its final value. Chain depolymerization and random decomposition are considered to be the two main types of thermal decomposition[34,35]. In the case of condensation polymers (such as the copolyamides of this paper) it has been found that the prevailing degradation mechanism is the random chain rupture[33]. The t.g.a. measurements of the copolyamides (*Table 5*, *Figure 4*) showed that their $T_{d,0}$ is higher than 250°C, which facilitates their possible use for a wide range of applications. Although, generally speaking, higher α-amino acid contents promoted lower $T_{d,0}$ temperatures, it was found, quite surprisingly, that the copolyamides containing L-tyrosine showed lower $T_{d,0}$ (despite their higher T_g) but higher $T_{d,1/2}$ than the copolymers with the other amino acids. This could be explained if an analysis of the overall decomposition mechanism is made. In the first stage of pyrolysis it has been confirmed that disproportionation reactions take place[36,37]. According to the currently existing mechanistic scheme[33], hydrogen atoms of the aliphatic comonomer units (i.e. adipic acid, CH_2 of PACM) are prone to move to the aromatic radicals/nuclei (i.e. L-tyrosine) for saturation purposes. However, the aromatic units could also induce postcondensation reactions/crosslinking (especially promoted in the presence of C=O or –OH) which may have a beneficial effect upon the degradation kinetics by retarding them, thus explaining the above-mentioned higher $T_{d,1/2}$ observed for the series of salts of AA and PACM/α-amino acids than the other copolyamide series.

Biodegradability experiments: analysis and correlation of the results with the contribution of comonomer structures of the copolyamides

The biodegradability of polymers has become a very debatable subject because of the publication of many controversial, and occasionally contradictory, data reporting the biodegradation of the same polymers[6,38–42]. These problems arose mainly through the lack of a unified approach towards the investigation of biodegradability of polymers and the variation both in molecular weights and in purity of the investigated polymers[7]. Although it is generally believed that recycling of polymers would be the ultimate solution to waste disposal, many efforts are still focused on the synthesis of novel, low-cost biodegradable polymers[3,6].

The cleavage of labile/hydrolysable bonds is the key to the biodegradation of polymers. The test of alkali hydrolysis, which has been previously applied to several series of novel polymers[1,2,16–18], was equally used in these copolyamides as a biodegradability test. *Table 6* gives the percentage weight losses of the novel copolyamides subjected to 10% NaOH w/v aqueous solution *versus* time.

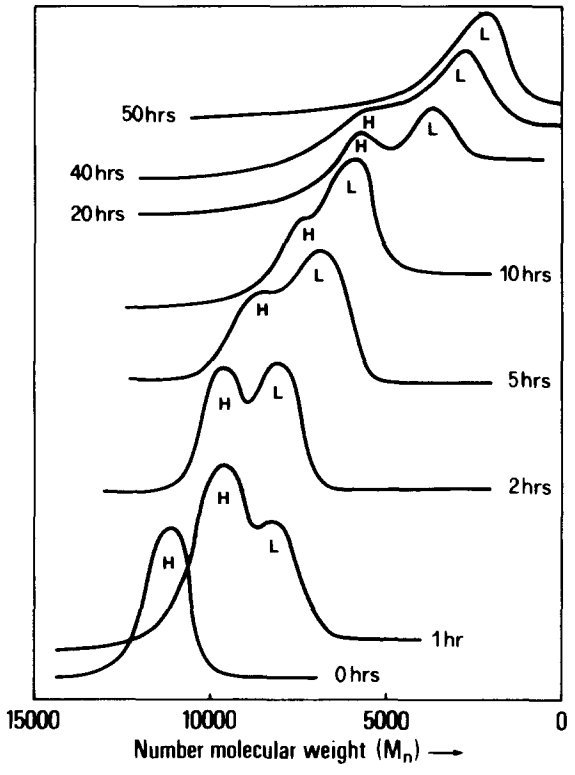

Figure 6 Effect of alkali hydrolysis (10% NaOH w/v, 80°C) on the M_n of copolyamide AA/PACM/L-tyrosine: 40/40/20(mol%)

Table 7 summarizes the percentage weight losses of our copolyamides after they have remained buried in soil for different times. It is evident that the degradation mechanism in the case of the copolyamides buried in soil is different to that governing the alkali hydrolysis. Therefore, a concise description of the main stages of polymer degradation from the mechanistic point of view would be beneficial in identifying the governing mechanism in each case.

The three[7] or four stages[3] which have been suggested for describing the polymer degradation could be concisely summarized as follows:

1. Hydration which is translated into disruption of van der Waals' forces and hydrogen bonds. Mechanism occurring mainly at the surface occasionally also described as 'heterogeneous'.
2. Strength loss linked to initial cleavage of backbone covalent bonds (biodegradation). Mechanism occurring throughout the bulk of the polymer, also described as 'homogeneous'.
3. Loss of mass integrity which is related to further cleavage of covalent bonds leading to even lower molecular weights. Mechanism also occurring through the bulk of the polymer and called 'homogeneous'.
4. Dissolution of low-molecular-weight species followed by their assimilation.

The degradation of copolyamides with alkali hydrolysis

Table 6 Percentage weight loss of copolyamides AA/PACM/α-amino acids by alkali hydrolysis (10% NaOH w/v) at 80°C against time

AA (mol)	PACM (mol)	α-Amino acid (mol)	Percentage weight loss (% wt)[a] at: 1 h	2 h	5 h	10 h	20 h	30 h	40 h	50 h
50	50	–	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		L-Tyrosine								
47.5	47.5	5.0	0.3±0.02	0.6±0.01	1.0±0.04	2.8±0.03	4.5±0.19	8.1±0.19	14.2±0.84	22.1±0.95
45.0	45.0	10.0	1.2±0.10	1.7±0.12	2.5±0.14	5.3±0.22	8.9±0.25	13.5±0.78	21.0±1.14	30.5±1.16
42.5	42.5	15.0	1.6±0.11	2.4±0.13	3.2±0.20	6.1±0.34	10.2±0.83	16.9±1.12	25.4±1.25	38.4±1.42
40.0	40.0	20.0	2.1±0.16	3.8±0.21	5.0±0.33	7.4±0.82	13.5±0.98	22.3±1.84	32.9±2.14	45.7±2.85
35.0	35.0	30.0	3.5±0.19	5.4±0.49	7.7±1.31	11.8±1.31	19.3±1.72	27.3±2.45	39.0±4.20	58.6±2.54
		L-Proline								
47.5	47.5	5.0	0.8±0.03	1.2±0.07	2.7±0.09	6.3±0.57	12.5±1.31	17.3±1.94	34.5±2.86	47.2±3.95
45.0	45.0	10.0	2.9±0.25	5.1±0.42	8.9±0.72	13.6±1.41	23.4±2.20	41.5±2.95	47.4±4.55	50.0±4.83
40.0	40.0	20.0	4.8±0.42	8.0±0.71	12.5±1.41	24.3±2.16	37.9±4.04	57.8±5.42	64.5±6.70	70.4±7.13
35.0	35.0	30.0	7.5±0.69	13.2±1.40	31.5±3.42	45.6±3.95	54.8±5.90	69.5±7.30	78.2±8.54	79.4±8.58
30.0	30.0	40.0	9.2±0.73	16.5±1.48	34.8±4.34	51.2±4.86	58.6±5.23	73.4±6.85	82.8±7.42	85.4±8.40
25.0	25.0	50.0	10.4±1.00	19.2±1.75	38.4±3.92	55.5±4.85	62.4±5.33	75.9±6.00	85.8±7.59	89.0±9.85
		L-Glycine								
47.5	47.5	5.0	0.6±0.03	1.3±0.10	2.4±0.12	5.7±0.17	9.7±0.22	14.2±0.39	23.9±1.04	44.2±1.92
45.0	45.0	10.0	2.7±0.04	4.6±0.19	7.3±0.92	11.8±0.85	20.9±1.23	38.7±2.15	47.0±3.87	51.2±4.33
42.5	42.5	15.0	3.3±0.09	6.2±0.45	8.9±0.73	16.5±1.31	25.8±2.15	46.3±3.94	54.7±4.85	57.6±5.42
40.0	40.0	20.0	4.1±0.13	7.4±0.83	10.3±0.85	21.6±2.00	31.9±3.00	52.4±5.10	61.9±5.73	66.4±6.32
35.0	35.0	30.0	6.2±0.24	10.9±0.92	26.7±1.82	41.5±3.32	49.6±4.32	65.0±5.75	73.8±6.85	77.5±7.40
		L-Alanine								
47.5	47.5	5.0	0.4±0.02	0.9±0.07	1.5±0.09	3.9±0.08	6.8±0.13	11.8±0.42	22.5±0.73	35.5±1.95
45.0	45.0	10.0	1.8±0.09	3.0±0.11	4.7±0.14	9.2±0.19	17.3±0.49	34.6±1.25	42.4±2.59	44.0±3.21
42.5	42.5	15.0	2.7±0.12	3.9±0.23	6.5±0.39	13.2±1.04	20.5±1.48	38.9±2.54	50.8±3.25	52.4±2.98
40.0	40.0	20.0	3.6±0.20	5.4±0.39	8.7±0.81	18.3±0.95	24.5±2.13	43.8±3.54	59.2±4.50	64.5±3.92
30.0	30.0	40.0	6.4±0.59	10.7±1.11	18.9±2.25	27.4±2.34	41.5±3.50	53.6±4.51	68.9±5.64	73.2±4.95
25.0	25.0	50.0	9.2±0.88	19.2±1.25	25.4±2.10	39.5±2.75	50.4±4.20	67.3±5.45	74.2±6.50	78.9±6.42

[a] Five measurements were taken per sample and the results are given as mean ± standard deviation

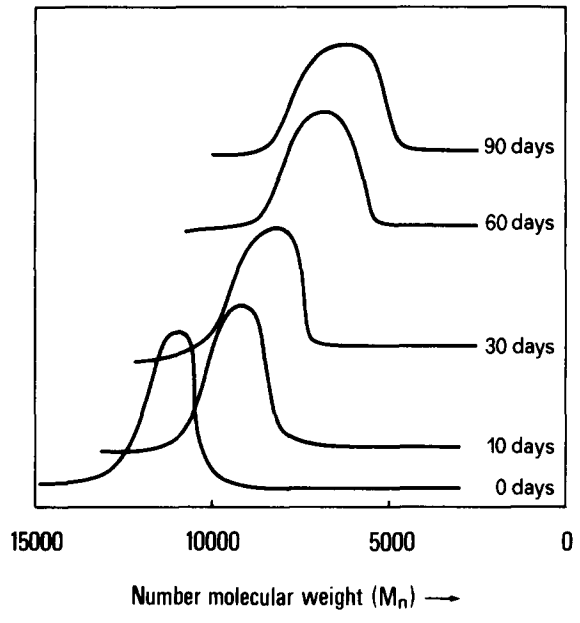

Figure 7 Effect of burial in soil enriched with micro-organisms and bacteria on the M_n of copolyamide AA/PACM/L-tyrosine: 40/40/20 (mol%)

is a homogeneous mechanism taking place throughout the polymeric mass and is described by mechanisms 2 and 3. In contrast, a superficial biodegradation is the case when the copolyamide films are buried in soil. The latter case is described by mechanism 1. Homogeneous polymer degradation (in bulk) has been previously studied for copolyamides based on AA/IPD/α-amino acids[1], nylon 6,6/α-amino acids[2] and polyesters[6,43–46] whereas heterogeneous degradation was investigated in copolyamides[1] (mainly for comparison purposes and to gain an insight of the mechanism), and in polyanhydrides[44,45].

The part insoluble in NaOH (10% w/v, 80°C) of the copolymer [mol. ratio AA/PACM/L-alanine: 40/40/20] was studied by d.s.c. for determination of percentage crystallinity. *Figure 5* shows an increase in crystallinity (x_c) which could be attributed to gradual removal of the amorphous part of the copolymer. Furthermore, the broadening of the melting (T_m) peaks is partly due to differentiation in molecular weight distribution, as confirmed by the g.p.c. results (*Table 8*).

The degradation rate of the copolyamides AA/PACM/α-amino acids was followed with the aid of g.p.c. *Figures 6* and *7* show some g.p.c. traces of copolyamide

Table 7 Percentage weight loss of copolyamides AA/PACM/α-amino acids buried in soil at 37°C *versus* time (days)

AA (mol)	PACM (mol)	α-Amino acid (mol)	Percentage weight loss[a] (% wt) at day: 2	14	30	60	90
50	50	–	0.0	0.0	0.0	0.0	0.0
		L-Tyrosine					
47.5	47.5	5.0	0.0	0.2±0.01	0.7±0.06	1.5±0.09	1.8±0.16
45.0	45.0	10.0	0.0	0.3±0.02	1.0±0.08	1.9±0.18	2.7±0.21
42.5	42.5	15.0	0.0	0.6±0.05	1.7±0.09	2.6±0.22	3.5±0.30
40.0	40.0	20.0	0.0	1.1±0.08	2.3±1.45	3.3±0.42	4.4±0.45
35.0	35.0	30.0	0.0	1.7±0.13	2.9±0.31	4.5±0.41	5.9±0.53
		L-Proline					
47.5	47.5	5.0	0.0	0.1±0.01	0.3±0.01	0.8±0.06	1.3±0.11
45.0	45.0	10.0	0.0	0.2±0.01	0.5±0.03	1.2±0.11	2.0±0.15
40.0	40.0	20.0	0.0	0.6±0.04	1.3±0.12	1.8±0.15	3.5±0.33
35.0	35.0	30.0	0.0	0.9±0.07	1.6±0.15	2.7±0.23	4.6±0.40
30.0	30.0	40.0	0.0	1.1±0.10	2.3±0.19	3.4±0.31	5.8±0.49
25.0	25.0	50.0	0.0	2.3±0.18	3.7±0.28	4.4±0.29	6.5±0.57
		L-Glycine					
47.5	47.5	5.0	0.0	0.2±0.03	0.4±0.06	1.0±0.15	1.5±0.13
45.0	45.0	10.0	0.0	0.3±0.06	0.6±0.09	1.4±0.20	2.3±0.19
42.5	42.5	15.0	0.0	0.5±0.08	0.9±0.17	2.0±0.26	3.1±0.24
40.0	40.0	20.0	0.0	0.8±0.11	1.5±0.19	2.5±0.30	3.9±0.35
35.0	35.0	30.0	0.0	1.1±0.15	1.9±0.25	3.2±0.43	5.0±0.44
		L-Alanine					
47.5	47.5	5.0	0.0	0.3±0.02	0.5±0.03	1.3±0.10	1.7±0.16
45.0	45.0	10.0	0.0	0.4±0.03	0.8±0.06	1.6±0.15	2.5±0.20
42.5	42.5	15.0	0.0	0.6±0.06	1.4±0.12	2.3±0.21	3.3±0.29
40.0	40.0	20.0	0.0	0.9±0.08	2.1±0.17	3.1±0.09	4.2±0.41
30.0	30.0	40.0	0.0	1.3±0.11	2.6±0.22	4.2±0.38	6.7±0.58
25.0	25.0	50.0	0.0	2.5±0.20	4.0±0.35	5.6±0.49	7.4±0.65

[a] Five measurements were taken per sample and the results are given as mean ± standard deviation

Table 8 Changes in molecular weight distribution (determined with g.p.c. measurements[a]) before and after the alkali hydrolysis (10% NaOH w/v) of copolyamides AA/PACM/α-amino acids *versus* time

AA (mol)	PACM (mol)	α-Amino acid (mol)	0 h		2 h		20 h		50 h	
			M_n	M_w	M_n	M_w	M_n	M_w	M_n	M_w
50	50	–	21 500 ± 430	37 860 ± 650	21 400 ± 810	38 550 ± 810	20 900 ± 540	39 250 ± 690	20 750 ± 450	40 400 ± 850
		L-Tyrosine								
47.5	47.5	5.0	15 000 ± 670	29 320 ± 980	13 840 ± 480	25 800 ± 790	8 640 ± 420	14 300 ± 640	6 650 ± 250	11 880 ± 440
45.0	45.0	10.0	14 250 ± 590	27 450 ± 620	12 350 ± 720	23 250 ± 840	7 150 ± 300	12 650 ± 750	5 720 ± 220	10 250 ± 390
42.5	42.5	15.0	12 830 ± 810	23 840 ± 650	11 100 ± 640	20 790 ± 750	6 370 ± 220	11 230 ± 660	4 270 ± 260	8 100 ± 310
40.0	40.0	20.0	10 870 ± 560	19 460 ± 850	9890 ± 570	17 850 ± 690	5 940 ± 280	9 870 ± 570	2 780 ± 210	5 260 ± 250
35.0	35.0	30.0	10 100 ± 490	18 130 ± 940	8 740 ± 380	15 710 ± 800	5 150 ± 250	8 980 ± 310	2 420 ± 190	4 170 ± 230
		L-Proline								
47.5	47.5	5.0	19 200 ± 550	35 950 ± 850	16 800 ± 450	30 200 ± 780	10 530 ± 650	18 720 ± 950	8 400 ± 750	15 600 ± 920
45.0	45.0	10.0	17 800 ± 440	33 540 ± 940	15 100 ± 560	28 960 ± 850	8 840 ± 340	15 100 ± 420	7 150 ± 550	13 250 ± 720
40.0	40.0	20.0	15 350 ± 600	29 520 ± 850	13 420 ± 520	24 500 ± 650	7 950 ± 430	13 200 ± 650	6 240 ± 310	11 400 ± 510
35.0	35.0	30.0	14 100 ± 750	27 400 ± 790	12 000 ± 530	23 100 ± 780	6 740 ± 350	11 540 ± 720	5 100 ± 250	9 980 ± 380
30.0	30.0	40.0	12 600 ± 500	23 810 ± 680	11 150 ± 450	21 430 ± 800	5 800 ± 290	10 250 ± 620	4 280 ± 240	7 860 ± 270
25.0	25.0	50.0	11 200 ± 630	20 450 ± 750	9 890 ± 500	17 520 ± 740	4 350 ± 340	8 180 ± 450	3 840 ± 310	6 930 ± 420
		L-Glycine								
47.5	47.5	5.0	17 900 ± 780	33 450 ± 950	16 100 ± 590	28 590 ± 850	9 820 ± 390	15 600 ± 730	7 700 ± 420	13 900 ± 540
45.0	45.0	10.0	16 400 ± 750	31 250 ± 870	14 300 ± 720	26 540 ± 760	8 100 ± 420	14 320 ± 770	6 800 ± 330	12 840 ± 490
42.5	42.5	15.0	15 750 ± 680	28 320 ± 590	13 650 ± 520	25 200 ± 620	7 390 ± 350	13 200 ± 580	6 100 ± 400	11 380 ± 380
40.0	40.0	20.0	14 670 ± 590	26 300 ± 750	11 780 ± 660	21 980 ± 590	6 650 ± 330	11 000 ± 650	5 650 ± 310	10 200 ± 420
35.0	35.0	30.0	12 900 ± 420	21 470 ± 550	9 870 ± 450	20 000 ± 780	5 780 ± 420	10 200 ± 450	4 750 ± 300	8 330 ± 460
		L-Alanine								
47.5	47.5	5.0	16 200 ± 710	32 100 ± 980	15 400 ± 670	27 400 ± 540	9 150 ± 280	15 500 ± 490	7 140 ± 350	13 330 ± 650
45.0	45.0	10.0	15 100 ± 640	29 720 ± 850	14 000 ± 750	25 860 ± 490	7 630 ± 320	13 870 ± 520	6 250 ± 430	12 500 ± 590
42.5	42.5	15.0	14 070 ± 590	27 300 ± 930	12 480 ± 630	24 130 ± 560	6 840 ± 250	11 700 ± 380	5 420 ± 390	10 370 ± 480
40.0	40.0	20.0	12 860 ± 480	23 250 ± 500	10 190 ± 470	19 870 ± 740	6 190 ± 270	10 240 ± 480	4 930 ± 420	8 900 ± 540
30.0	30.0	40.0	11 000 ± 620	20 140 ± 490	8 870 ± 440	15 350 ± 430	5 610 ± 260	9 630 ± 420	4 350 ± 270	7 830 ± 410
25.0	25.0	50.0	9 980 ± 380	17 850 ± 480	7 360 ± 450	12 410 ± 570	4 830 ± 220	7 890 ± 200	3 890 ± 230	6 750 ± 370

[a] Five measurements were taken per sample and the results are given as mean ± standard deviation

AA/PACM/L-tyrosine (40/40/20) hydrolytically degraded (*Figure 6*) and buried in soil (*Figure 7*) *versus* time.

The first observation is that the more asymmetric and statistical the copolyamide becomes with the increase in the comonomer unit of α-amino acid, the lower its molecular weight and the faster its degradation process. All the results from the g.p.c. measurements both before and after the alkali hydrolysis (10% NaOH solution) and the microbial/bacterial attack (burial in soil) *versus* time are summarized in *Tables 8* and *9*. A gradual shift towards lower molecular weight distributions of the copolyamide is observed *versus* time and sometimes a significant broadening of the peaks was also observed. The increase in the polydispersity indices ($n = M_w/M_n$) observed in both *Tables 8* and *9* confirms that the observed tendency in *Figures 5* and *6* (broadening of peaks, lower M_n with degradation) is the general tendency for all the series of synthesized copolyamides. It is worth mentioning, however, that the lowering of M_n in the case of copolyamides buried in soil is less extensive than in alkali hydrolysis, whereas the broadening of peaks is more accentuated since the polydispersity factor is higher for the hydrolysed copolyamides buried in soil than for those with alkali hydrolysis. The differences evident both from g.p.c. traces (*Figures 6* and *7*) and from *Tables 8* and *9* could be attributed to the extensive penetration of the polymer matrix by the alkali solution, thus resulting in more effective degradation, whereas a limited selective degradation occurs when the copolyamides are buried in soil because of lower susceptibility of the substrate due to the lower number of available active sites mainly located at the surface[3].

The results of enzymatic hydrolysis (α-chymotrypsin and α-trypsin) of copolyamides (*Table 10*) agree with the results from weight loss experiments (*Tables 6* and *7*). The TOC measurements indicated the following order in terms of susceptibility to biodegradation: AA/PACM/L-proline > AA/PACM/L-alanine > AA/PACM/L-glycine > AA/PACM/L-tyrosine. The suggested order of copolymer susceptibility to biodegradation is in satisfactory agreement with previous publications[47-49] where it was shown that the presence of bulky or pendent groups has an adverse effect upon the susceptibility of polymers to biodegradation.

Table 9 Changes in molecular weight distribution (determined by g.p.c.[a]) after the copolyamides (AA/PACM/α-amino acids) remained buried in soil at 37°C for different times (days)

AA (mol)	PACM (mol)	α-Amino acid (mol)	30 days		60 days	
			M_n	M_w	M_n	M_w
		L-Tyrosine				
47.5	47.5	5.0	13400±450	27900±830	10720±560	27420±650
45.0	45.0	10.0	12940±380	26540±900	10140±640	25980±780
42.5	42.5	15.0	11570±610	24590±960	9730±750	22380±800
40.0	40.0	20.0	9470±520	19280±870	6590±670	18000±570
35.0	35.0	30.0	8890±450	17990±880	5850±550	17260±640
		L-Proline				
47.5	47.5	5.0	18110±650	35340±580	16000±880	33800±980
45.0	45.0	10.0	16230±720	32820±930	14340±540	30250±710
40.0	40.0	20.0	13950±590	28980±850	12330±390	26770±820
35.0	35.0	30.0	12780±460	26790±760	11290±420	24780±780
30.0	30.0	40.0	11150±660	22900±650	9470±420	20740±800
25.0	25.0	50.0	9840±530	19300±720	8730±290	17870±490
		L-Glycine				
47.5	47.5	5.0	16300±480	32900±1100	14150±430	29870±740
45.0	45.0	10.0	14800±530	30120±980	12960±340	27320±880
42.5	42.5	15.0	14120±350	28200±740	12210±450	26100±950
40.0	40.0	20.0	12280±300	25900±650	10150±280	23240±770
35.0	35.0	30.0	10750±340	20980±730	8970±340	19370±650
		L-Alanine				
47.5	47.5	5.0	14400±370	29880±790	12270±510	27340±590
45.0	45.0	10.0	13350±430	28340±800	11500±440	25970±820
42.5	42.5	15.0	12000±410	25700±750	9790±310	23200±750
40.0	40.0	20.0	11050±350	22980±960	9000±280	21780±670
30.0	30.0	40.0	9320±300	19220±810	7740±300	17930±720
25.0	25.0	50.0	8250±370	16900±450	6020±250	14560±380

[a] Five measurements were taken per sample and the results are given as mean ± standard deviation

CONCLUSIONS

The copolymerization of diacid (AA) and diamine (PACM) in the presence of several α-amino acids resulted in novel copolyamides of a wide M_n range (10000–22000). The thermal properties (T_g, T_m, x_c) of these copolyamides showed a decrease with an increase in their α-amino acid content. Their susceptibility to degradation became evident only when the α-amino acid content of the polymers was higher than 10 mol%. The weight loss experiments by alkali hydrolysis and burial in soil of the polymers proceeded considerably faster in the former than in the latter case and the g.p.c. measurements gave lower M_n values (by 20–50% of the initial M_n) thus confirming the occurrence of degradation. Furthermore, tests of enzymatic hydrolysis supported our conclusions from other biodegradability experiments because TOC values began to increase substantially only in polymers whose amino acid content is higher than 15 mol%.

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Table 10 Results of enzymatic hydrolysis, α-chymotrypsin and α-trypsin in phosphate buffer (15 mg of polymer in 2 ml of buffer KH_2PO_4/Na_2HPO_4, pH 7.0) of copolyamides of AA/PACM/α-amino acids expressed in TOC

AA (mol)	PACM (mol)	α-Amino acid (mol)	TOC (ppm)	
			α-Chymotrypsin	α-Trypsin
50	50	–	0	0
		L-Tyrosine		
47.5	47.5	5.0	20	27
45.0	45.0	10.0	58	64
42.5	42.5	15.0	105	141
40.0	40.0	20.0	180	205
35.0	35.0	30.0	275	320
		L-Proline		
47.5	47.5	5.0	55	64
45.0	45.0	10.0	142	200
40.0	40.0	20.0	275	345
35.0	35.0	30.0	540	632
30.0	30.0	40.0	729	815
25.0	25.0	50.0	800	1020
		L-Glycine		
47.5	47.5	5.0	32	41
45.0	45.0	10.0	74	100
42.5	42.5	15.0	125	172
40.0	40.0	20.0	248	315
35.0	35.0	30.0	329	420
		L-Alanine		
47.5	47.5	5.0	40	43
45.0	45.0	10.0	95	106
42.5	42.5	15.0	180	191
40.0	40.0	20.0	360	355
30.0	30.0	40.0	485	497
25.0	25.0	50.0	600	655

[a] Five measurements were taken per sample and the results are given as means

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