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Novel copolyamides based on adipic acid, 1,6-hexanediamine and α-amino acids: 2. Study of properties and their biodegradability for food-packaging applications

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A novel series of biodegradable copolyamides based on the salt of 1,6-hexanediamine/adipic acid/α-amino acids were synthesized by melt polymerization at 250°C. Differential thermal analysis (d.t.a.) and wide-angle X-ray diffraction patterns were employed in order to investigate the semicrystalline/amorphous nature of the synthesized copolyamides. Several methods such as alkali hydrolysis (10% NaOH w/v, 80°C), burial in soil and enzymatic hydrolysis were employed for assessing the susceptibility of these novel copolyamides to degradation. The degradation rates of these copolyamides were evaluated with gel permeation chromatography and d.t.a. measurements and correlated with the α-amino acid structure and content as well. The fields of food packaging and agriculture (disposable plastics) could be envisaged as potential applications of these novel copolyamides.

(Keywords: biodegradability; copolyamides; adipic acid/hexanediamine)

INTRODUCTION

The continuously increasing extent of pollution of the environment has recently given rise to demands for novel biodegradable polymers mainly for applications related to food packaging and agriculture[1-3]. Initially, the main emphasis was focused on the synthesis of novel aliphatic polyesters[3-5] owing to their higher susceptibility to biodegradation with regard to other polymers such as polyamides and polyanhydrides[6,7]. Among the aliphatic polyesters, poly(ϵ-caprolactone)[8-16], poly(β-methyl-δ-valerolactone)[17,18], polylactide[5,7,19-21] and their copolymers[22-30] have been suggested as the most promising polymers from the point of view of potential applications. The usually low glass transition and melting points of most polyesters, which have been occasionally quoted as their potential disadvantages[1,2], have instigated several researchers towards direct polymerization of α-amino acids[31-37] or copolymerization of lactams with lactones[38-44] in an attempt to synthesize novel polymers endowed with desirable properties (i.e. $T_g > 30$°C and biodegradable). The biodegradability tests carried out on the copoly(ester amide)s proved to be rather promising and suggested several potential applications[1,14,15,41]. However, the extent of applications of copolyamides has been considered limited[45] for a long time because of the difficulties encountered in producing high-molecular-weight and environmentally degradable copolyamides[46,47]. In the current paper, which is the second in this series, several previously reported[48] copolyamides are further characterized and a more thorough evaluation of their biodegradability by alkali and enzymatic hydrolysis and soil burial tests is presented. Furthermore, the degradation of copolyamides at various stages was determined with g.p.c., d.t.a. and WAXD in order to correlate the effect of different degradation modes upon the structural and thermal properties of copolyamides.

EXPERIMENTAL

Materials

Adipic acid (AA) was purchased from Aldrich (UK) and was recrystallized twice from distilled water and then from acetone/petroleum ether and ethyl acetate. 1,6-Hexanediamine (1,6-HD) was purchased from Aldrich (UK) and distilled under reduced pressure twice before use. L-Tyrosine, L-proline, L-alanine and L-glycine were purchased from Sigma (UK), were analytically pure and were used without further purification.

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Polymerization apparatus

The copolyamides were synthesized with melt polycondensation at 250°C by using a fluidized bed (sand bath) equipped with a thermostat (Edwards, UK). Mixtures of the 1,6-HD and AA salt (1 : 1 mol/mol) synthesized as previously reported[48–51] 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 250°C for 2 h. Then, vacuum (0.5 mmHg) was applied 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 a fine powder. The low-molecular-weight polymers were Soxhlet extracted with methanol and chloroform for 16 h.

Elemental analysis

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

Density measurements

Densities were determined at 23°C pycnometrically[52] with toluene and by means of a density gradient column (Davenport, UK) using polymer samples previously degassed at 0.1 mmHg for 24 h[53].

Wide-angle X-ray diffraction patterns

WAXD ($2\theta = 5–40°C$) patterns were recorded using a Philips PW 1050 diffractometer (Netherlands). Five measurements were recorded per sample in order to ensure the reproducibility of our results.

Fourier-transform infra-red analysis

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

Differential thermal analysis

The glass transitions (T_g) were determined with the use of a DuPont Differential Thermal Analyzer (DTA 2000) connected with 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°C to +300°C. The calibrations of temperature and enthalpy ($J\,g^{-1}$) of the d.t.a. were made with 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 endothermic curves.

Dynamic mechanical thermal analysis

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

$\tan\delta\,(= E''/E')$ 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. 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 from 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 losses of all the samples after their alkali treatment were calculated and correlated to their 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 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 to 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).

Gel permeation chromatography 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, supplied with a Styragel column, was used and *m*-cresol as an eluent at a rate $0.6\,ml\,min^{-1}$. The calibration of the g.p.c. was conducted with a series of polystyrene samples of determined molecular weight.

Mechanical properties

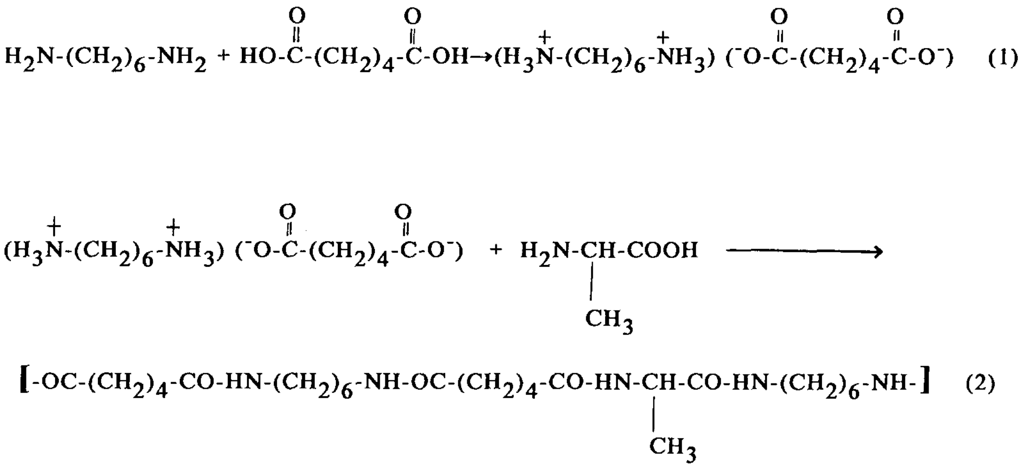
The tensile tests were conducted before and after the biodegradability experiments on a 5 ton Instron Universal Testing machine (TM-SM 1102, UK). The extension rate was maintained at $1\,mm\,s^{-1}$. The load–elongation curves were plotted and tensile modulus, tensile strength, tensile stress and percentage strain were calculated from the curves. The tensile specimens were of the following geometry: 6 mm width, 30 mm length and 5 mm thickness. A minimum of five measurements were recorded per sample.

RESULTS AND DISCUSSION

The two reactions in *Figure 1* show the general scheme of the polymerization process, first, formation of the 1,6-hexanediamine/adipic acid salt and, secondly, reaction of

Table 1 Results of elemental analyses (C, H, N) of copolyamides of nylon salt 1,6-HD/AA (1/1 mol/mol)/α-amino acids

1,6-HD (mol)	AA (mol)	α-Amino acid (mol)	Theoretically calculated (%) C	H	N	Experimentally found (%) C	H	N
50.0	50.0	–	63.9	9.8	12.4	63.9	9.8	12.4
		L-Tyrosine						
47.5	47.5	5.0	64.0	9.6	12.9	63.9	9.6	12.9
45.0	45.0	10.0	64.0	9.4	13.4	64.0	9.4	13.4
42.5	42.5	15.0	64.1	9.2	13.9	64.1	9.2	13.9
40.0	40.0	20.0	64.3	9.0	14.5	64.2	9.0	14.5
37.5	37.5	25.0	64.4	9.8	15.0	64.3	8.9	15.0
		L-Proline						
47.5	47.5	5.0	63.2	9.7	12.5	63.2	9.7	12.5
45.0	45.0	10.0	62.5	9.5	12.6	62.5	9.5	12.5
42.5	42.5	15.0	61.8	9.4	12.7	61.9	9.4	12.7
40.0	40.0	20.0	61.2	9.3	12.7	61.2	9.3	12.8
37.5	37.5	25.0	60.5	9.2	12.8	60.5	9.1	12.8
		L-Alanine						
47.5	47.5	5.0	63.5	9.7	12.7	63.4	9.7	12.6
45.0	45.0	10.0	63.0	9.6	12.9	63.0	9.6	12.9
42.5	42.5	15.0	62.5	9.5	13.1	62.4	9.5	13.2
40.0	40.0	20.0	62.0	9.4	13.4	61.9	9.4	13.4
37.5	37.5	25.0	61.5	9.3	13.7	61.5	9.3	13.7
		L-Glycine						
47.5	47.5	5.0	63.4	9.7	12.5	63.3	9.7	12.5
45.0	45.0	10.0	62.7	9.5	13.0	62.7	9.5	13.0
42.5	42.5	15.0	62.0	9.4	13.4	62.0	9.4	13.4
40.0	40.0	20.0	61.4	9.3	13.8	61.4	9.2	13.7
37.5	37.5	25.0	60.7	9.1	14.2	60.8	9.0	14.1



$$\mathrm{H_2N\text{-}(CH_2)_6\text{-}NH_2 + HO\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH \rightarrow (H_3\overset{+}{N}\text{-}(CH_2)_6\text{-}\overset{+}{N}H_3)\ ({}^{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}\text{-}O^{-})} \quad (1)$$

$$\mathrm{(H_3\overset{+}{N}\text{-}(CH_2)_6\text{-}\overset{+}{N}H_3)\ ({}^{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}\text{-}O^{-}) + H_2N\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}COOH} \longrightarrow$$

$$\mathrm{[\text{-}OC\text{-}(CH_2)_4\text{-}CO\text{-}HN\text{-}(CH_2)_6\text{-}NH\text{-}OC\text{-}(CH_2)_4\text{-}CO\text{-}HN\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}CO\text{-}HN\text{-}(CH_2)_6\text{-}NH\text{-}]} \quad (2)$$

Figure 1 General schemes of copolymerization of 1,6-HD, AA and α-amino acids (i.e. L-alanine)

this salt with α-amino acid (i.e. L-alanine) and further polymerization.

Table 1 gives the results of elemental analyses (C, H and N) for the synthesized copolymers for both theoretically calculated and experimentally determined values, which were found to be in satisfactory agreement.

The density values of the copolyamides are given in *Table 2*. They were found to depend, as reported elsewhere[48–51], on the molecular weights of the introduced α-amino acids. Thus, the higher the *MW* and the contribution of the α-amino acid, the higher the densities. The densities of the copolyamides were found to fall in the following order:

$$1,6\text{-HD/AA/L-tyrosine} > 1,6\text{-HD/AA/L-proline}$$
$$> 1,6\text{-HD/AA/L-alanine} > 1,6\text{-HD/AA/L-glycine}$$

L-Tyrosine has three reactive groups ($-NH_2$, $-COOH$, $-OH$) that could in theory react, thus resulting in a crosslinked network. However, *FT*i.r. spectra excluded the formation of such a network because no ester ($-O-C{=}O$) bond was detected at 1750 cm^{-1}. Furthermore,

Table 2 Density measurements and percentage crystallinity (X_c)[a] against time of alkali hydrolysis (h) of copolyamides of nylon salt 1,6-HD/AA (1/1 mol/mol)/α-amino acids

1,6-HD	AA	α-Amino acid	Density	X_c (%)		
(mol)	(mol)	(mol)	(g cm^{-3})	0 h	20 h	50 h
50.0	50.0	-	1.135	33.4 ± 2.1	33.5 ± 1.9	33.7 ± 2.2
		L-Tyrosine				
47.5	47.5	5.0	1.195	21.2 ± 2.1	30.0 ± 2.8	55.4 ± 4.6
45.0	45.0	10.0	1.226	13.7 ± 1.5	25.4 ± 2.3	47.9 ± 3.8
42.5	42.5	15.0	1.245	8.0 ± 0.6	16.2 ± 1.2	33.0 ± 2.9
40.0	40.0	20.0	1.268	3.1 ± 0.2	7.1 ± 0.6	16.8 ± 1.7
37.5	37.5	25.0	1.282	–	–	–
		L-Proline				
47.5	47.5	5.0	1.169	23.4 ± 2.2	29.5 ± 2.2	58.7 ± 4.2
45.0	45.0	10.0	1.198	15.7 ± 1.6	27.8 ± 1.9	49.2 ± 3.8
42.5	42.5	15.0	1.208	9.8 ± 0.8	18.9 ± 2.1	36.5 ± 3.6
40.0	40.0	20.0	1.215	4.4 ± 0.3	9.5 ± 0.8	20.4 ± 2.2
37.5	37.5	25.0	1.226	–	–	–
		L-Alanine				
47.5	47.5	5.0	1.165	26.5 ± 2.2	33.7 ± 2.8	59.7 ± 3.4
45.0	45.0	10.0	1.189	20.0 ± 1.8	30.4 ± 2.9	53.2 ± 2.9
42.5	42.5	15.0	1.197	11.3 ± 1.0	21.2 ± 3.1	39.4 ± 3.4
40.0	40.0	20.0	1.209	5.4 ± 0.4	11.3 ± 1.2	25.6 ± 2.6
37.5	37.5	25.0	1.219	–	–	–
		L-Glycine				
47.5	47.5	5.0	1.141	28.9 ± 1.8	37.2 ± 4.1	65.0 ± 3.6
45.0	45.0	10.0	1.157	22.6 ± 2.0	33.5 ± 2.1	58.6 ± 2.5
42.5	42.5	15.0	1.163	13.8 ± 3.1	24.3 ± 2.3	44.8 ± 3.6
40.0	40.0	20.0	1.175	6.9 ± 1.0	13.9 ± 1.5	30.4 ± 2.8
37.5	37.5	25.0	1.187	–	–	–

[a] Five measurements were taken per sample and the resuts are given as average ± standard deviation. Percentage crystallinity (X_c) is determined from WAXD on the insoluble fraction in 10% NaOH w/v (80°C)

solubility experiments showed that these copolymers are soluble in several solvents such as *m*-cresol, hexafluoroisopropanol and dimethylsulfoxide (DMSO), thus rejecting the formation of crosslinked networks.

The semicrystalline and, occasionally, amorphous nature of copolyamides based on the salt of 1,6-HD/AA(1 : 1 mol/mol)/α-amino acids were shown with WAXD and d.t.a. *Figure 2* shows representative traces of the copolyamide series based on the salt of 1,6-HD/AA (1 : 1 mol/mol) and different α-amino acid contents. The effect of α-amino acid content on the crystallinity (X_c) of the copolymer was found to be very crucial and as a concluding remark it could be said that when the α-amino acid content exceeds 15–20% mol/mol the copolyamide undergoes a severe change in its structural properties by becoming amorphous.

Some representative *FT*i.r. spectra of the copolyamide series of salts of 1,6-HD/AA/α-amino acids are shown in Figure 3. The most important absorptions could be summarized as follows:

1720 cm^{-1}	amino acid moiety[35–37]
1636–1645 cm^{-1}	amide band I[39–43]
1550 cm^{-1}	amide band II[39–43]

Figure 4 shows some typical d.t.a. curves where it is obvious that the incorporation of an α-amino acid depresses both the T_g and T_m of the copolyamide and also results in a substantial broadening of its endothermic peak (T_m) for the α-amino acid-rich (> 10% mol/mol) copolymers. The occasionally recorded bimodal distribution of copolyamides (i.e. nylon-6,6 or 1,6-HD/AA/L-alanine 47.5/47.5/5 mol/mol/mol) could be explained in terms of differences in size and extent of crystallized regions, which might have also been accentuated by differences in molecular-weight distribution[5].

Thermogravimetric analysis (t.g.a.) was employed for studying the thermal 'resistance' of these novel polymers. *Table 3* summarizes the t.g.a. results in terms of 'initial' and 'half' decomposition temperature ($T_{d,0}$, $T_{d,1/2}$)[54]. The predominant decomposition mechanism for condensation polymers was proved to proceed via random chain rupture[54]. The heat resistance of the copolymers with regard to their initial decomposition temperature ($T_{d,0}$) lies in the following order:

$$\text{1,6-HD/AA/L-glycine} < \text{1,6-HD/AA/L-alanine}$$
$$< \text{1,6-HD/AA/L-proline} < \text{1,6-HD/AA/L-tyrosine}$$

However, it is noteworthy that the results of half decomposition temperature show that the copolymers based on L-tyrosine (*Figure 5*) decompose in two steps, thus resulting in the highest $T_{d,1/2}$ values among the other copolymers. This two-step degradation has already been observed in previous publications[55–57] and mainly

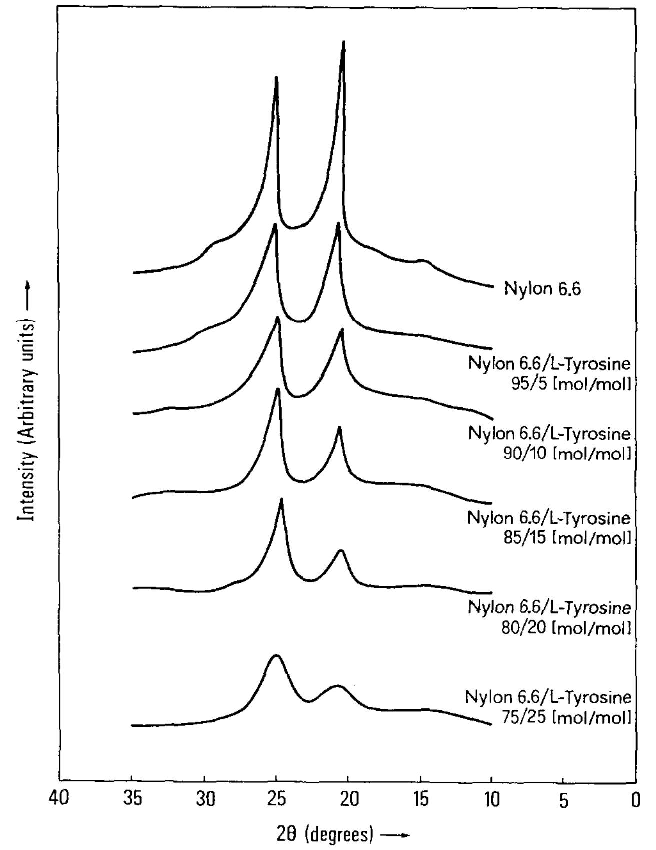


Figure 2 Wide-angle X-ray diffraction (WAXD) patterns of a series of copolyamides based on the salt of 1,6-HD/AA (1/1 mol/mol)/L-tyrosine

attributed to crosslinking/post-condensation reactions due to the availability of unreacted hydroxyl end-group (-OH).

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

In vitro degradation of copolyamides in aqueous media proceeds via a random bulk hydrolysis of amide bonds in the polymer chain. The products of degradation and in particular the carboxylic acids catalyse the degradation process. The weight losses that occurred in copolymers during the tests of alkali hydrolysis (10% w/v NaOH, 80°C) and burial in soil are presented synoptically in *Table 4*. The aqueous alkali solution is thought to initiate a 'homogeneous' degradation mechanism, whereas the burial in soil causes, at least in the beginning, a 'heterogeneous' one mainly due to inaccessibility of potential sites throughout the polymeric mass[6]. At this stage d.t.a. was employed in order to study the effect of alkali hydrolysis upon the percentage crystallinity (X_c) of the NaOH-insoluble polymeric fraction (*Figure 6*).

Table 2 shows a gradual increase in X_c of the NaOH-insoluble fraction of the copolyamides proportionally to their exposure to alkali hydrolysis, which can be explained in terms of gradual dissolution of the amorphous parts, thus resulting in higher crystallinity (X_c) values. Similar increases in percentage crystallinity (X_c) values during the early stages of both *in vitro* and *in vivo* degradation have previously been reported for several polymers such as poly(L-lactide)[21,58], polyglycolide[59] and poly(ε-caprolactone)[60]. It is generally accepted that the degradation process of biodegradable polymers occurs in two stages. In the first stage the chain scission occurs preferentially in the amorphous regions of the semicrystalline polymer. The initially random chain scissions result in a decrease of the degree of entanglement, thus facilitating and even promoting considerably the mobility of non-degradable chain segments in these regions, which initiates their recrystallization and eventually our high X_c values (d.t.a. results, *Table 2*).

However, X_c values could eventually decrease, at a later stage, when hydrolysis, after having exhausted the potential of amorphous sites, moves to degradation of chains in the remaining crystalline regions. It should be stressed that since the beginning of the latter stage is not exactly clear, occasionally an overlapping of the two stages (at least to some extent) has been suggested[59].

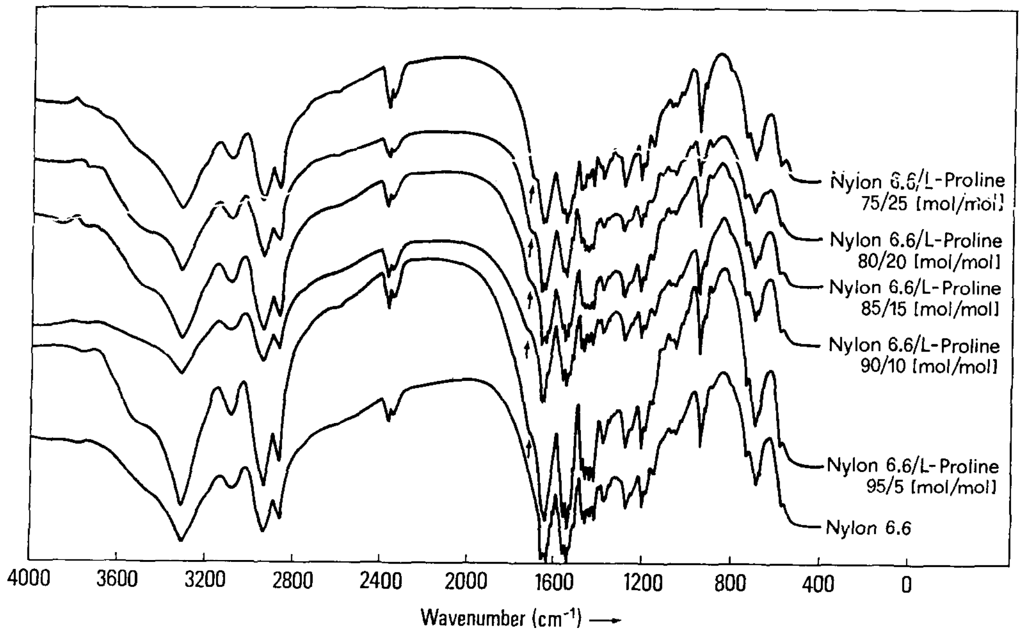


Figure 3 *FT*i.r. spectra of a series of copolyamides based on the salt of 1,6-HD/AA (1/1 mol/mol)/L-proline. The arrows indicate the absorption due to the presence of the amino acid moiety

Table 3 Initial decomposition temperatures $(T_{d,0})^a$ and half decomposition temperatures $(T_{d,1/2})^a$ of the copolyamides of nylon salt 1,6-HD/AA (1/1 mol/mol)/α-amino acids

1,6-HD (mol)	AA (mol)	α-Amino acid (mol)	$T_{d,0}$ (°C)	$T_{d,1/2}$ (°C)
50.0	50.0	–	385	431
		L-Tyrosine		
47.5	47.5	5.0	365	424
45.0	45.0	10.0	357	426
42.5	42.5	15.0	352	429
40.0	40.0	20.0	346	431
37.5	37.5	25.0	331	431
		L-Proline		
47.5	47.5	5.0	370	409
45.0	45.0	10.0	361	400
42.5	42.5	15.0	357	392
40.0	40.0	20.0	352	382
37.5	37.5	25.0	340	372
		L-Alanine		
47.5	47.5	5.0	373	417
45.0	45.0	10.0	365	408
42.5	42.5	15.0	360	400
40.0	40.0	20.0	353	391
37.5	37.5	25.0	345	380
		L-Glycine		
47.5	47.5	5.0	378	423
45.0	45.0	10.0	371	417
42.5	42.5	15.0	365	410
40.0	40.0	20.0	358	405
37.5	37.5	25.0	351	397

[a] Five measurements were taken per sample and the results are given as the average and are accurate to ±5°C

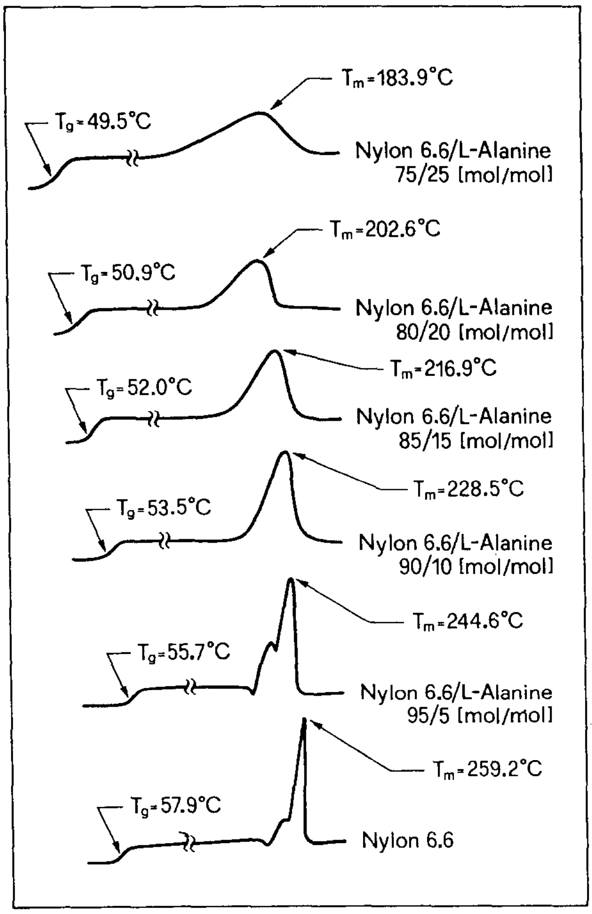


Figure 4 Normalized d.t.a. traces (to same sample weight) of a series of copolyamides based on the salt of 1,6-HD/AA (1/1 mol/mol)/L-alanine

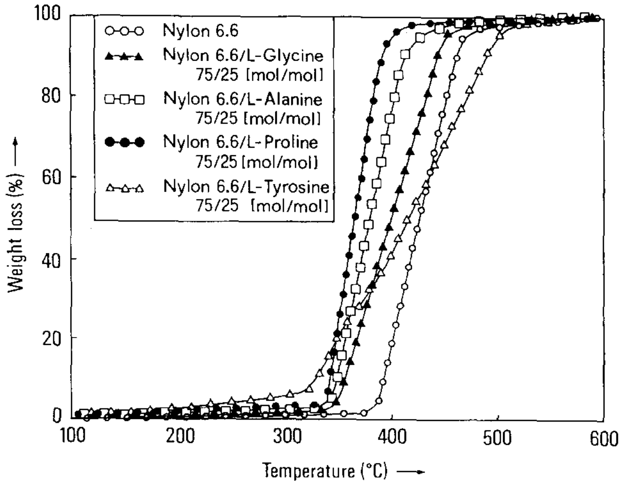


Figure 5 Thermogravimetric traces (t.g.a.) of a series of copolyamides based on the salt of 1,6-HD/AA (1/1 mol/mol)/L-tyrosine

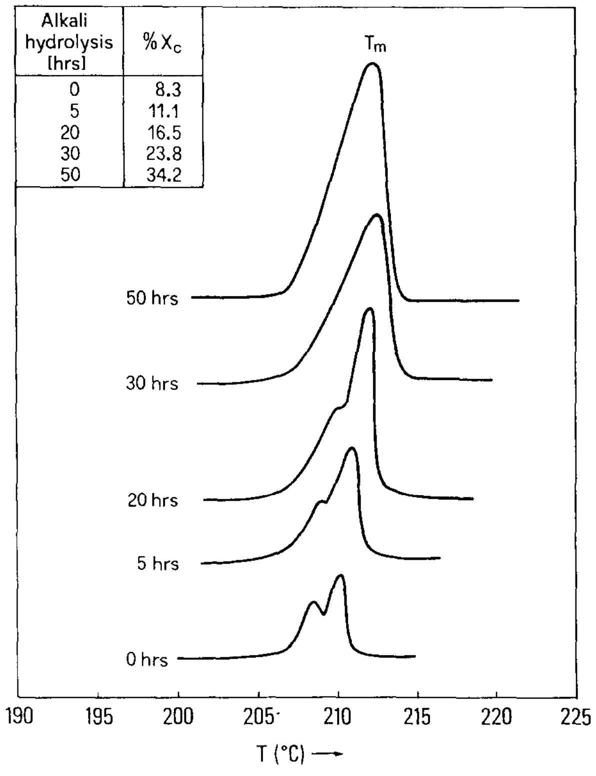


Figure 6 Effect of time of alkali hydrolysis on the percentage crystallinity (X_c) determined with d.t.a. (normalized traces to the same sample weight) of the insoluble fraction (in NaOH 10% w/v, 80°C) of a copolyamide based on the salt of 1,6-HD/AA/L-Tyrosine (42.5/42.5/15 mol/mol/mol)

The changes in molecular-weight distribution of the copolymers *versus* their exposure time to NaOH (10% w/v NaOH, 80°C) were recorded with the aid of g.p.c. and are given in *Table 5*. A substantial decrease in the molecular weights of copolymers is observed because of cleavage of covalent bonds along the polymer chain. The effect of alkali hydrolysis was stronger for the copolymers rich in α-amino acids, which underwent a significant reduction in their polymer chain, thus resulting in number-average molecular weights (M_n) as low as 2100.

Table 4 Percentage weight losses[a] of copolyamides of nylon salt 1,6-HD/AA (1/1 mol/mol)/α-amino acids against time of alkali hydrolysis (h) and soil burial (days)

			Percentage weight loss (wt %)						
			Alkali hydrolysis		Burial in soil				
1,6-HD (mol)	AA (mol)	α-Amino acid (mol)	50 h	100 h	2 days	14 days	30 days	60 days	90 days
50.0	50.0	–	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		L-Tyrosine							
47.5	47.5	5.0	19.5	36.0	0.0	2.4	3.8	5.2	7.8
45.0	45.0	10.0	21.9	41.5	0.0	3.0	4.8	6.0	8.6
42.5	42.5	15.0	25.2	47.4	0.0	3.3	6.2	8.5	10.7
40.0	40.0	20.0	31.0	55.2	0.0	4.1	7.5	9.7	12.9
37.5	37.5	25.0	36.4	68.9	0.0	4.3	8.9	13.2	16.8
		L-Proline							
47.5	47.5	5.0	17.0	32.1	0.0	2.1	3.4	4.3	6.9
45.0	45.0	10.0	19.5	36.5	0.0	2.8	4.5	5.5	7.8
42.5	42.5	15.0	22.3	41.2	0.0	3.0	5.3	7.2	9.9
40.0	40.0	20.0	27.5	48.8	0.0	3.6	6.4	8.4	11.2
37.5	37.5	25.0	31.6	62.0	0.0	4.0	7.6	11.5	14.5
		L-Alanine							
47.5	47.5	5.0	16.7	28.4	0.0	1.9	3.0	3.7	5.7
45.0	45.0	10.0	18.8	32.8	0.0	2.4	3.9	4.9	6.6
42.5	42.5	15.0	20.6	37.1	0.0	2.6	4.8	5.7	8.3
40.0	40.0	20.0	24.0	43.4	0.0	3.3	5.8	7.2	10.0
37.5	37.5	25.0	28.3	51.8	0.0	3.8	6.7	9.1	12.1
		L-Glycine							
47.5	47.5	5.0	13.4	23.0	0.0	1.5	2.4	3.2	4.9
45.0	45.0	10.0	15.6	27.5	0.0	2.0	3.3	4.0	5.4
42.5	42.5	15.0	18.9	32.3	0.0	2.4	4.5	5.2	7.6
40.0	40.0	20.0	21.0	37.5	0.0	2.9	5.1	6.7	8.7
37.5	37.5	25.0	25.2	43.8	0.0	3.4	5.8	8.5	10.9

[a] Five measurements were taken per sample and the results are given as the average and are accurate to 6%

Table 5 Changes in molecular-weight distribution (determined with g.p.c. measurements[a]) before and after the alkali hydrolysis (10% NaOH w/v, 80°C) of copolyamides of nylon salt 1,6-HD/AA (1/1 mol/mol)/α-amino acids *versus* time (h)

1,6-HD (mol)	AA (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
50.0	50.0	–	23 820	41 540	23 800	41 650	24 050	41 620	23 780	41 600
		L-Tyrosine								
47.5	47.5	5.0	17 100	33 200	15 840	32 400	9 890	24 250	4560	11 920
45.0	45.0	10.0	14 160	28 820	12 480	27 950	8 560	18 960	3980	9 300
42.5	42.5	15.0	12 280	25 410	11 000	23 640	7 390	17 200	3340	8 470
40.0	40.0	20.0	10 400	22 150	9 350	21 200	6 680	14 840	2800	7 540
37.5	37.5	25.0	8 730	17 890	7 840	18 100	5 700	13 260	2350	6 450
		L-Proline								
47.5	47.5	5.0	18 810	38 980	17 400	35 749	11 320	26 590	5320	14 000
45.0	45.0	10.0	15 340	32 600	14 220	31 450	9 500	23 450	4290	10 950
42.5	42.5	15.0	13 890	29 550	12 580	26 490	8 620	20 200	3770	9 870
40.0	40.0	20.0	11 600	24 900	10 510	22 950	7 940	18 240	3340	8 960
37.5	37.5	25.0	9 320	21 380	8 140	17 880	6 430	15 550	2950	7 780
		L-Alanine								
47.5	47.5	5.0	20 200	41 500	19 000	40 500	13 100	28 750	6 320	16 890
45.0	45.0	10.0	16 950	35 960	15 360	33 800	11 000	26 200	5100	14 270
42.5	42.5	15.0	15 100	31 890	13 940	29 850	9 500	21 890	4340	12 330
40.0	40.0	20.0	12 840	28 200	11 620	26 300	8 440	19 780	3850	10 150
37.5	37.5	25.0	10 450	24 150	9 150	22 560	6 970	18 890	3430	9 020

Table 5 continued

1,6-HD (mol)	AA (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
		L-Glycine								
47.5	47.5	5.0	21 290	43 720	20 050	43 260	14 120	31 280	7250	18 250
45.0	45.0	10.0	19 100	41 590	17 830	38 750	12 030	28 770	6210	16 500
42.5	42.5	15.0	16 720	37 280	15 160	33 650	10 360	23 850	5050	13 940
40.0	40.0	20.0	14 150	32 650	12 490	28 990	9 590	22 660	4460	12 250
37.5	37.5	25.0	11 280	27 560	9 920	24 540	7 480	21 500	3970	10 780

[a] Five measurements were taken per sample and the results are given as the average and are accurate to ±600 and ±800 for M_n and M_w, respectively

Table 6 Changes in molecular weight (determined with g.p.c. measurements[a]) of copolyamides of nylon salt 1,6-HD/AA (1/1 mol/mol)/α-amino acids *versus* time (days) of their burial in soil

1,6-HD (mol)	AA (mol)	α-Amino acid (mol)	30 days		60 days	
			M_n	M_w	M_n	M_w
50.0	50.0	–	23690	41840	23840	41810
		L-Tyrosine				
47.5	47.5	5.0	15200	36340	12350	35940
45.0	45.0	10.0	12340	32920	9870	30630
42.5	42.5	15.0	10580	31000	7620	27280
40.0	40.0	20.0	9040	28250	6830	25780
37.5	37.5	25.0	7890	26340	5750	23000
		L-Proline				
47.5	47.5	5.0	17070	39750	14340	37600
45.0	45.0	10.0	13780	37140	11260	33250
42.5	42.5	15.0	12360	33280	9980	31640
40.0	40.0	20.0	10290	31450	7840	28060
37.5	37.5	25.0	8010	28200	6360	27250
		L-Alanine				
47.5	47.5	5.0	18150	44800	15810	42740
45.0	45.0	10.0	15230	42980	13020	40670
42.5	42.5	15.0	13780	40500	11450	37550
40.0	40.0	20.0	11500	36290	9200	33880
37.5	37.5	25.0	9190	31340	7270	30310
		L-Glycine				
47.5	47.5	5.0	19740	49980	17410	47250
45.0	45.0	10.0	17620	47870	15200	46300
42.5	42.5	15.0	14960	45070	12540	43850
40.0	40.0	20.0	12800	39250	10420	38000
37.5	37.5	25.0	10110	34330	8010	32970

[a] Five measurements were recorded per sample and the results are given as the average and are accurate to ±600 and ±1000 for M_n and M_w, respectively

However, the effect of burial in soil upon the copolyamides did not prove to be so pronounced as in the case of alkali hydrolysis. A gradual decrease mainly in M_n was recorded whereas the M_w showed rather slight changes, so that the polydispersity indices were found to increase considerably, thus mirroring the broadening of the molecular-weight distribution (*Table 6*). *Figure 7* gives some representative g.p.c. traces for copolymer based on the salt of 1,6-HD/AA/L-alanine (40/40/20 mol/mol/mol). In the beginning (0 days, before burial in soil) there is only a single peak, but within 15 days a bimodal distribution appears, which persists even after 100 days. This bimodal distribution shows the broadening of the molecular-weight distribution and, in particular, the existence of regions of higher (H) and lower (L) molecular weights, respectively.

Table 7 gives the results of enzymatic hydrolysis of the copolyamides expressed in total organic carbon (*TOC*) for the water-soluble products and the changes in molecular-weight distribution as well. Both α-trypsin and α-chymotrypsin show the same tendency with regard to the *TOC* results, that is, higher *TOC* values for the copolymers richer in α-amino acids, which is the expected behaviour since these copolymers exhibit a higher susceptibility to hydrolysis. Both M_n and M_w (determined with g.p.c.) decrease (approximately by 20–30%) after the exposure of the copolymers to enzymatic hydrolysis.

Finally the effect of alkali hydrolysis upon the tensile strength of these novel copolyamides was also investigated and the results obtained are summarized in *Table 8*. Both tensile strength and tensile modulus show a dramatic decrease after the polymer samples were treated for 50 h with alkali solution (10% w/v NaOH, 80°C). In order to make more evident the relationship of number-average molecular weight (M_n) to tensile strength, *Figure 8* is given, where it is clear that there is a linear dependence of tensile strength upon the M_n with regard to the time of alkali hydrolysis.

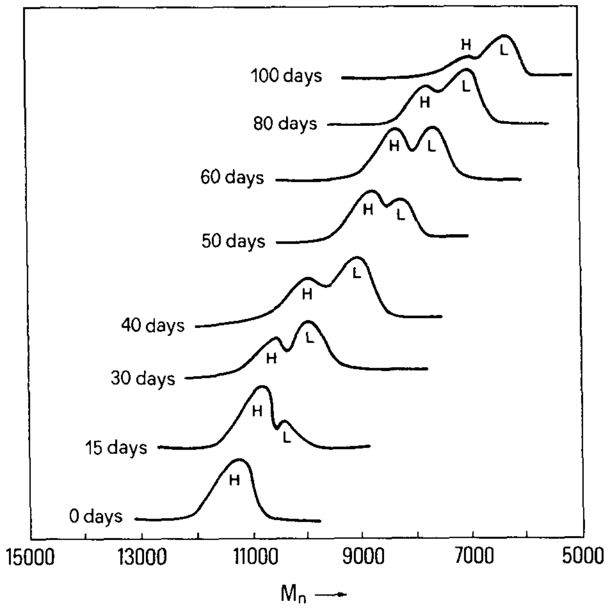


Figure 7 Effect of soil burial on the number-average molecular weight (M_n, determined with g.p.c.) of the copolyamide 1,6-HD/AA/L-alanine (40/40/20 mol/mol/mol)

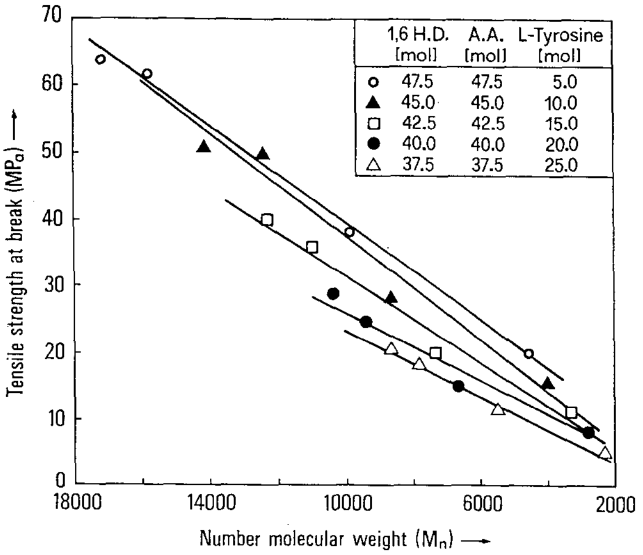


Figure 8 Schematic correlation of tensile strength (MPa) with number-average molecular-weight distribution (M_n) of a series of copolyamides based on the salt of 1,6-HD/AA (1/1 mol/mol)/L-tyrosine

Table 7 Results of enzymatic hydrolysis with 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 nylon salt 1,6-HD/AA (1/1 mol/mol)/α-amino acids expressed in *TOC* (ppm)[a] and molecular-weight distribution from g.p.c. measurements[a]

			α-Chymotrypsin			α-Trypsin		
1,6-HD (mol)	AA (mol)	α-Amino acid (mol)	*TOC* (ppm)	M_n	M_w	*TOC* (ppm)	M_n	M_w
50.0	50.0	–	0	23890	41600	0	23780	41850
		L-Trypsin						
47.5	47.5	5.0	43	16200	35760	67	15800	36020
45.0	45.0	10.0	105	12850	32420	172	12230	32670
42.5	42.5	15.0	418	10610	27840	610	9950	28180
40.0	40.0	20.0	555	8850	25990	826	8290	26450
37.5	37.5	25.0	743	7420	23020	1195	7030	23560
		L-Proline						
47.5	47.5	5.0	32	17300	40230	48	16890	40420
45.0	45.0	10.0	67	13480	34820	89	12750	35380
42.5	42.5	15.0	300	11640	31480	423	11300	31730
40.0	40.0	20.0	468	9670	27250	627	8880	28020
37.5	37.5	25.0	597	7890	24390	745	7510	24280
		L-Alanine						
47.5	47.5	5.0	20	18650	42790	37	17890	42540
45.0	45.0	10.0	48	14720	38050	63	14140	38420
42.5	42.5	15.0	210	13230	34530	285	12720	35090
40.0	40.0	20.0	340	10710	31200	412	10180	31670
37.5	37.5	25.0	465	8540	26500	598	8140	26930
		L-Glycine						
47.5	47.5	5.0	13	20560	44280	22	19990	44800
45.0	45.0	10.0	36	18000	42700	47	17670	43370
42.5	42.5	15.0	125	15830	38740	162	15280	38630
40.0	40.0	20.0	212	12000	34380	263	11610	34850
37.5	37.5	25.0	355	9220	28920	414	8840	28100

[a] Five measurements were taken per sample and the results are given as the average and are accurate to ±10, ±400 and ±800 for *TOC* (ppm), M_n and M_w, respectively

Table 8 Effect of alkali hydrolysis (10% w/v NaOH, 80°C) on the tensile strength (MPa)[a] at break and tensile modulus (GPa)[a] of copolyamides of nylon salt 1,6-HD/AA (1/1/mol/mol)/α-amino acids *versus* time (h)

			0 h		2 h		20 h		50 h	
1,6-HD (mol)	AA (mol)	α-Amino acid (mol)	*TS* (MPa)	*TM* (GPa)	*TS* (MPa)	*TM* (GPa)	*TS*(MPa)	*TM* (GPa)	*TS* (MPa)	*TM* (GPa)
50.0	50.0	–	83	2.40	82	2.37	84	2.29	82	2.36
		L-Tyrosine								
47.5	47.5	5.0	64	1.87	62	1.82	38	1.25	20	0.64
45.0	45.0	10.0	51	1.72	50	1.65	28	1.01	16	0.58
42.5	42.5	15.0	40	1.53	36	1.44	20	0.89	11	0.41
40.0	40.0	20.0	29	1.35	25	1.28	15	0.70	8	0.29
37.5	37.5	25.0	21	1.08	19	1.00	12	0.59	5	0.22
		L-Proline								
47.5	47.5	5.0	68	2.06	66	1.99	45	1.39	23	0.72
45.0	45.0	10.0	57	1.95	54	1.88	32	1.21	17	0.67
42.5	42.5	15.0	44	1.76	40	1.60	24	1.02	13	0.50
40.0	40.0	20.0	35	1.57	33	1.49	17	0.78	10	0.36
37.5	37.5	25.0	27	1.26	25	1.18	14	0.65	8	0.30
		L-Alanine								
47.5	47.5	5.0	74	2.13	71	2.08	52	1.58	25	0.82
45.0	45.0	10.0	65	2.07	63	2.01	43	1.44	22	0.65
42.5	42.5	15.0	52	1.80	49	1.68	30	1.18	16	0.53
40.0	40.0	20.0	46	1.63	45	1.57	24	0.92	14	0.42
37.5	37.5	25.0	33	1.38	30	1.34	18	0.80	9	0.38
		L-Glycine								
47.5	47.5	5.0	78	2.25	75	2.21	57	1.80	33	0.97
45.0	45.0	10.0	70	2.16	64	2.08	49	1.57	27	0.73
42.5	42.5	15.0	61	1.91	57	1.77	41	1.31	21	0.67
40.0	40.0	20.0	50	1.75	45	1.63	33	1.12	17	0.58
37.5	37.5	25.0	38	1.53	36	1.47	24	1.00	12	0.54

[a] Five measurements were taken per sample and the results are given as the average and are accurate to ±5 and ±0.2 for *TS* (MPa) and *TM* (GPa), respectively

CONCLUSIONS

Four novel series of copolyamides using commercially available precursors such as nylon-6,6 prepolymer salt and various α-amino acids (L-alanine, L-tyrosine, L-proline, L-glycine) were synthesized and characterized. When the α-amino acid content was higher than 15%, the copolyamides turned from semicrystalline to amorphous (d.t.a. and WAXD measurements). The high susceptibility of these copolyamides to degradation was confirmed with several biodegradability experiments such as alkali hydrolysis, microbial–bacterial attack (burial in soil) and enzymatic hydrolysis. Considerable percentage weight losses were recorded for the α-amino acid-rich copolyamides, which in conjunction with the recorded significant decreases in M_n, M_w and tensile properties support their eventual use for a wide range of applications.

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