

## Degradable poly(ester amide)s based on L-tartaric acid

A. Alla, A. Rodríguez-Galán\*, A. Martínez de Ilarduya and S. Muñoz-Guerra

*Departamento de Ingeniería Química, Universidad Politécnica de Cataluña ETSIIB, Diagonal 647, E-08028 Barcelona, Spain*

*(Received 17 June 1996; revised 10 December 1996)*

A series of poly(ester amide)s with ester/amide group ratios ranging from 1/99 to 1/4 were obtained using 1,6-hexanediamine, 1,6-hexanediol and 2,3-di-*O*-methoxy-L-tartaric and succinic acids as building blocks. The ester linkages were introduced in pairs using as comonomer the diacid resulting from the esterification of 1,6-hexanediol with 2 mol of succinic anhydride. Polycondensation reactions were carried out in solution at room temperature with the diamine activated as the *N,N'*-bis(trimethylsilyl) derivative and the two diacids as bis(pentachlorophenyl) esters. The prepared poly(ester amide)s have number average molecular weights in the range 10 000–40 000, display optical activity and are soluble in chloroform. These copolymers were found to be highly crystalline with melting points above 200°C and mechanical moduli comparable to those reported for the parent polyamide poly(hexamethylene-di-*O*-methyl-L-tartaramide). They were degraded by aqueous buffer of pH 7.4 at a rate that increased with the content of the copolymer in succinic acid units. <sup>1</sup>H n.m.r. evidenced that no reactions other than those entailing the hydrolysis of the main chain ester bonds appear to take place at polymer degradation. © 1997 Elsevier Science Ltd.

**(Keywords: poly(ester amide)s; polytartar(ester amide)s; hydrolytic degradation)**

### INTRODUCTION

As a part of our studies addressed to the development of new degradable polyamides based on carbohydrates<sup>1–3</sup>, we have recently reported on polytartaramides, i.e. polyamides prepared from tartaric acid<sup>4–7</sup>. Among the different types of polytartaramides that have been explored, those prepared from 2,3-di-*O*-methyl-L-tartaric acid and 1,*n*-alkanediamines, which are abbreviated as P*n*DMLT in previous publications, deserve special attention because they are easily accessible and display a desirable pattern of thermal and mechanical properties. These polyamides can be distinguished from conventional nylons in undergoing appreciable hydrolysis under mild conditions<sup>8</sup>. Such susceptibility towards degradation has been related to the presence of the methoxyl side groups attached to the diacid unit, which favour the nucleophilic attack on the carbonyl group and increase the hydrophilicity of the polymer.

The interesting properties of L-tartaric acid as a building block for the construction of biodegradable condensation polymers have been long appreciated. Highly biodegradable polytartrates were investigated in the 1970s<sup>9–11</sup> and their potential applications as controlled releasing agents have been explored in the last few years<sup>12</sup>. With a similar purpose, certain hydroxyl-free polytartaramides have been examined recently<sup>13</sup>, although the first investigations into this family of polymers were reported at the end of the 1960s<sup>14</sup>. On the other hand, no study has been made so far of

copolymers of L-tartaric acid with diamines and diols in spite of the fact that poly(ester amide)s are widely recognized as polymers displaying a good combination of properties not achievable by other methods<sup>15</sup>. Thus, incorporation of small amounts of ester groups into nylons has proven to be an efficient approach to design polyamides with enhanced degradability without losing many of their genuine physical properties<sup>16</sup>.

In this paper we report on a series of poly(ester amide)s containing varying amounts of ester linkages (*Figure 1*), which are prepared from di-*O*-methyl-L-tartaric acid, succinic acid, 1,6-hexanediamine and 1,6-hexanediol. They will be abbreviated as P6STE<sub>*x*</sub>A<sub>*y*</sub>, where *x* and *y* stand for the content of ester and amide linkages, respectively. These poly(ester amide)s may be considered as deriving from poly(hexamethylene di-*O*-methyl-L-tartaramide) (P6DMLT), a member of the P*n*DMLT polytartaramide family whose structure and properties have been extensively studied by our group<sup>4,17</sup>. P6DMLT is a highly crystalline polyamide which melts at 230°C and is slowly hydrolysed at pH 7.4. The object of the present work is to enhance the degradability of P6DMLT by introducing controlled amounts of ester groups into the backbone of the polyamide and to evaluate the extent to which the physical properties become affected by such modifications. The new poly(ester amide)s have been fully characterized by chemical and spectroscopic methods and their thermal and mechanical properties preliminarily estimated and compared with those reported for the parent polyamide P6DMLT. Finally, a systematic study of the hydrolytic degradation in aqueous buffer at pH 7.4

\* To whom correspondence should be addressed

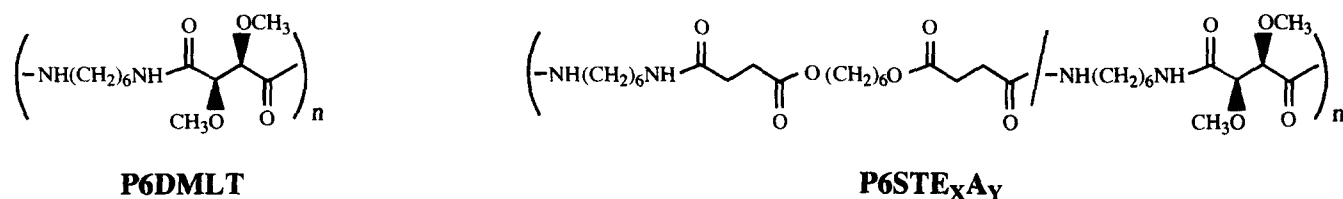


Figure 1 Chemical structure of P6DMLT and P6STExAy

and 37°C of some representative members of the series has been carried out.

## EXPERIMENTAL

### Materials and methods

Diethyl-L-tartrate, succinic anhydride and 1,6-hexanediol were supplied by Merck whereas, 1,6-hexanediamine was purchased from Fluka. All these reagents were used as received. Solvents to be used under anhydrous conditions were dried by appropriate standard methods.

Viscosimetric measurements were performed with a semi-microviscometer Cannon-Ubbelohde at  $25 \pm 0.1^\circ\text{C}$  using dichloroacetic acid as solvent. Gel permeation chromatography (g.p.c.) was carried out on a Water Associates instrument equipped with two columns having exclusion limits of  $10^4$  and  $10^3$  Å, respectively, and provided with a refractive index detector. Samples were run in a 19/1 chloroform/2-chlorophenol mixture. Molecular weights of the polymers were estimated against polystyrene standards.

Infrared (i.r.) spectra were registered on a Perkin-Elmer 2000 Fourier transform i.r. (FTi.r.) apparatus. The spectra of monomers were registered from KBr discs whereas films cast from chloroform were used in the analysis of polymers.  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (n.m.r.) were recorded on a Bruker AMX-300 instrument operating at 300.13 and 75.48 MHz, respectively, using tetramethylsilane as internal standard.  $^1\text{H}$ - $^{13}\text{C}$  heteronuclear shift correlation 2D spectra were recorded with the pulse sequences HXCO and COLOC for short- and long-range coupling respectively.

Differential scanning calorimetry (d.s.c.) measurements were performed on a Perkin-Elmer DSC-4 instrument equipped with a cooling accessory.  $T_m$  values were measured at heating rates  $20^\circ\text{C min}^{-1}$  from films prepared by casting from chloroform solutions and subjected to annealing treatment.  $T_g$  values were determined at heating rates of  $40^\circ\text{C min}^{-1}$  from samples which had been rapidly cooled from the melt. Mechanical properties were determined on a Minimat instrument from Polymer Laboratories. Dumb-bell shaped samples 11 mm in length, 3 mm in width and 0.22–0.30 mm thick were used in stress-strain experiments which were carried out at a deformation rate of  $0.8 \text{ mm min}^{-1}$ . The parameter values were averaged from a minimum of 10 measurements for each polymeric sample.

Hydrolysis experiments were carried out according to the following methodology: an 8% (w/v) solution of polymer in chloroform was evaporated on a Petri dish in  $37^\circ\text{C}$  to form films which were detached by the addition of isopropanol and then dried *in vacuo*. Discs of 14 mm diameter and 0.20–0.22 mm thick were cut from selected areas of the film, displaying an homogeneous appearance. Incubation was performed at  $37^\circ\text{C}$  with the discs

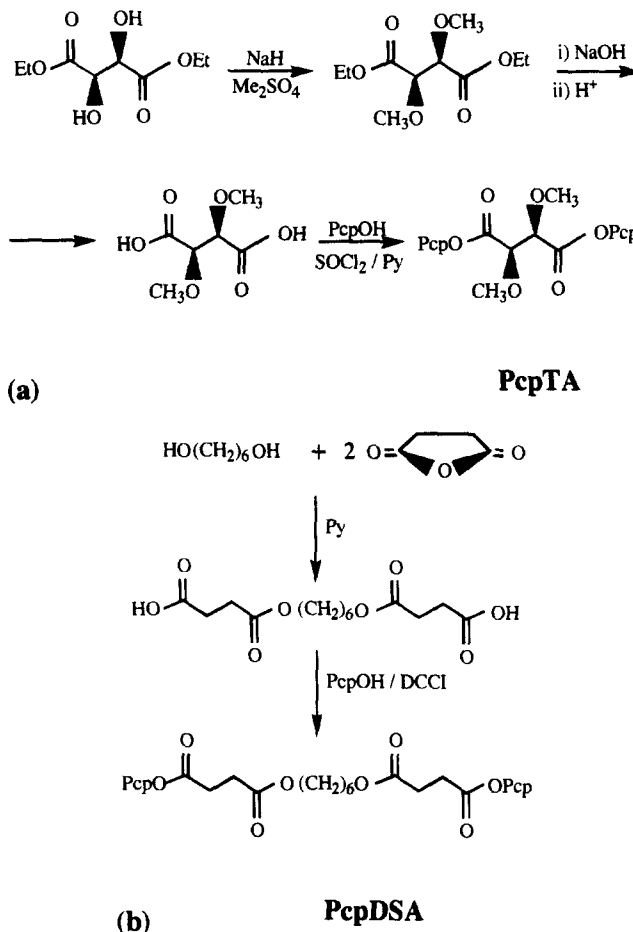


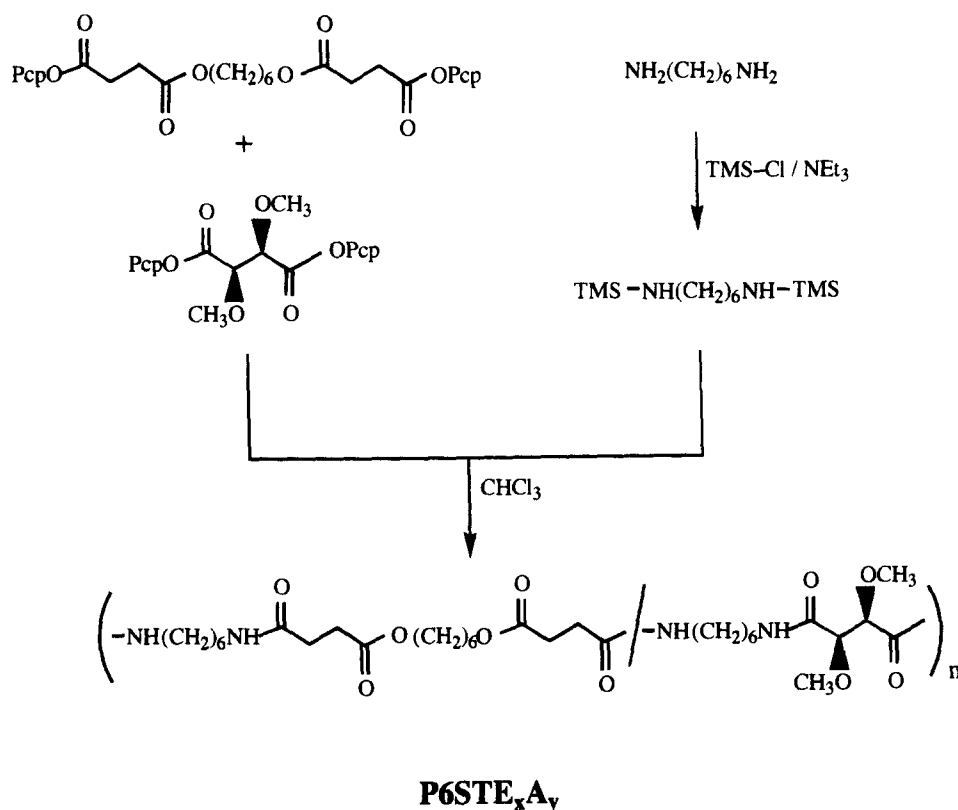
Figure 2 Scheme for the synthesis of activated diacidic monomers

placed in glass vials containing 30 ml of pH 7.4 sodium phosphate buffer. After the prescribed times, the discs were removed from the vials, rinsed thoroughly with distilled water and dried *in vacuo* for several days to constant weight.

### Synthesis of monomers and polymers

The reaction strategy to obtain P6STExAy is outlined in Figures 2 and 3 where the following abbreviations have been used. Pcp: pentachlorophenyl; TMS: trimethylsilyl; PcpTA: bis(pentachlorophenyl)-di-O-methyl-L-tartrate; PcpDSA: bis(pentachlorophenyl)-5,12-dioxa-4,13-dioxohexadecanedioate.

**Monomers.** The synthesis of PcpTA was carried out according to the reaction scheme shown in Figure 2a. The procedure has been recently described by us in full detail<sup>5</sup>. *N,N'*-Bis(trimethylsilyl)-1,6-hexanediamine was prepared according to Pierce<sup>18</sup> and purified by distillation *in vacuo*. PcpDSA was synthesized following the



**Figure 3** Scheme for polymerization reaction leading to poly(ester amide)s P6STE<sub>x</sub>A<sub>y</sub>.

scheme depicted in *Figure 2b*. The experimental details of the synthesis procedure as well as the data used for the characterization of this product are as follows.

*Bis(pentachlorophenyl)-5,12-dioxo-4,13-dioxo-hexadecanedioate (PcpDSA)*. To a stirred solution of 5,12-dioxo-4,13-dioxohexadecanedioic acid<sup>19</sup> (6.3 mmol) and pentachlorophenol (14.5 mmol) in chloroform (25 ml) at 0°C, a solution of dicyclohexylcarbodiimide (14.5 mmol) in the same solvent (5 ml) was added dropwise. The mixture was allowed to reach room temperature and left to react under these conditions for four days. All the dicyclohexylurea formed was filtered off and the resulting clear solution was concentrated to a solid residue which was rinsed thoroughly with ether and recrystallized twice from tetrahydrofuran/heptane (2/3). Yield: 57%; mp: 141–143°C. Anal. calcd for C<sub>26</sub>H<sub>20</sub>Cl<sub>10</sub>O<sub>8</sub>: C, 38.32; H, 2.47; Cl, 43.50. Found: C, 38.35; H, 2.44; Cl, 43.52. I.r. (cm<sup>-1</sup>, film from CDCl<sub>3</sub>): 1789 (Pcp ester C=O) and 1746 (alkyl ester C=O). <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>): δ 4.12 (*t*, 4H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 3.03 (*t*, 4H, PcpOOCCH<sub>2</sub>), 2.78 (*t*, 4H, CH<sub>2</sub>OOCCH<sub>2</sub>), 1.65 (*m*, 4H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.39 (*m*, 4H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C n.m.r. (CDCl<sub>3</sub>): δ 171.48 (COOCH<sub>2</sub>), 168.32 (COOPcp), 144.19, 132.03, 131.63, 127.67 (C<sub>6</sub>Cl<sub>5</sub>), 64.97 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 28.81 (CH<sub>2</sub>OOCCH<sub>2</sub>), 28.70 (PcpOOCCH<sub>2</sub>), 28.47 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 25.54 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>).

*Polymerization reactions.* The copolymers were obtained by polycondensation of mixtures of PcpTA, PcpDSA and the activated 1,6-hexanediamine as shown in the scheme in *Figure 3*. The ester/amide content of the copolymer was chosen by fixing the composition of the feed in PcpTA and PcpDSA. In this work, two procedures, differing in both the reaction temperature and the manner in which monomers were mixed with each

other, have been used to carry out the polymerization reactions.

*Procedure A.* A mixture of PcpTA and PcpDSA (8.7 mmol) in the chosen ratio was added in small portions to a stirred solution of *N,N'*-bis(trimethylsilyl)-1,6-hexanediamine (8.7 mmol) in dried chloroform (20 ml) at 0°C under a nitrogen atmosphere. The reaction mixture was stirred for 1 h, then for 48 h at room temperature and finally refluxed for a further 2 h. After cooling, the mixture was poured into boiling isopropanol, and the precipitated polymer was separated by filtration and washed thoroughly with ethanol and ether. Final purification was accomplished by repeated precipitation in the chloroform–isopropanol system.

*Procedure B.* To a solution of a mixture of PcpTA and PcpDSA (11.2 mmol) in dried chloroform (30 ml) maintained at 35°C, *N,N'*-bis(trimethylsilyl)-1,6-hexanediamine (11.2 mmol) was added dropwise with a syringe for 30 min. The reaction mixture was stirred for 24 h at 35°C, then for other 24 h at room temperature and finally refluxed for 2 h. The working out of the polymer was similar to that described for procedure A.

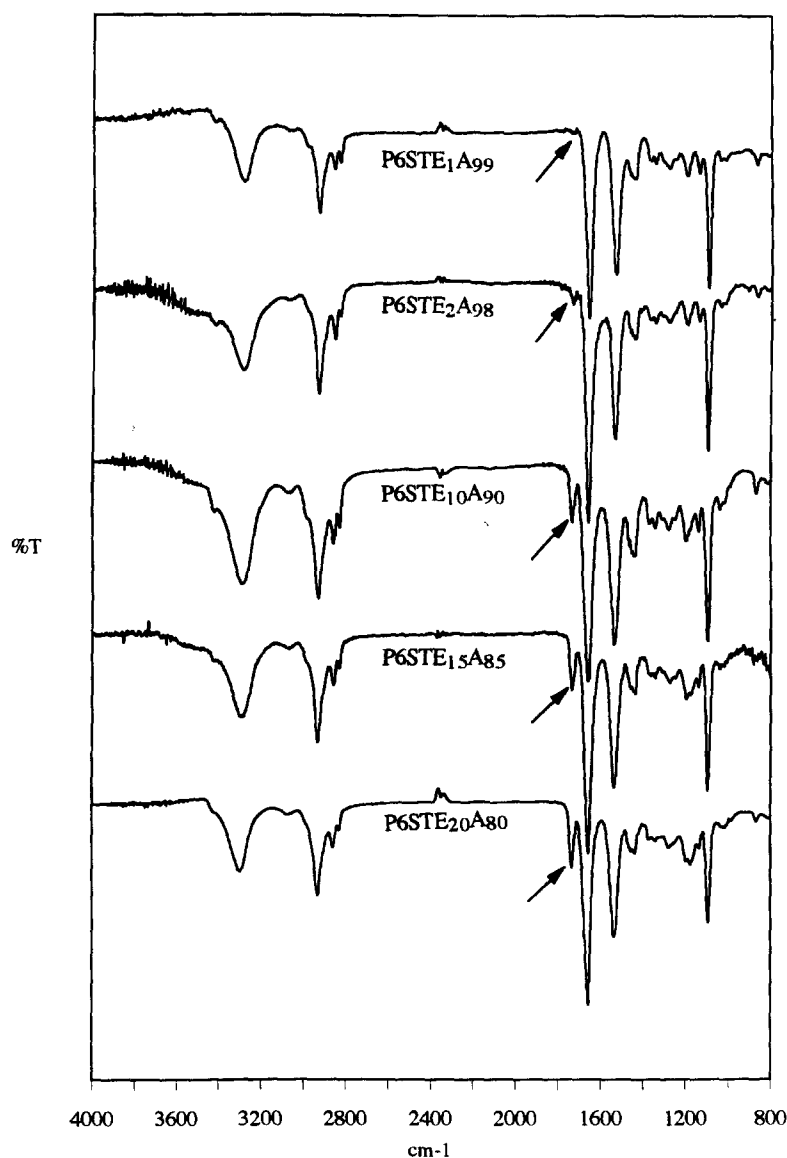
## RESULTS AND DISCUSSION

### *Synthesis of polymers*

The polycondensation method that we have used for the preparation of P6STE<sub>x</sub>A<sub>y</sub> was developed by Katsarava *et al.*<sup>20</sup> and has later been used by us in the synthesis of a variety of polytartaramides<sup>4–7</sup>. The efficiency of this method in rendering high molecular weight polymers in good yields relies on the activation of all the monomers intervening in the reaction as well as in the use of a solvent effective for both monomers and polymers. A

**Table 1** Polymerization and characterization data for poly(ester amide)s

Copolymer	DSA/TA <sup>a</sup>	Procedure <sup>b</sup>	Yield (%)	$[\eta]^c$ (dl g <sup>-1</sup> )	$M_n^d$	$M_w^d$
P6STE <sub>1</sub> A <sub>99</sub>	3/97	B	94.6	1.27	34 000	136 400
P6STE <sub>2</sub> A <sub>98</sub>	3/97	A	93.5	0.30	4050	9500
P6STE <sub>2</sub> A <sub>98</sub>	3/47	B	87.9	0.95	26 600	83 400
P6STE <sub>3</sub> A <sub>97</sub>	1/49	A	81.6	0.76	17 400	106 900
P6STE <sub>5</sub> A <sub>95</sub>	1/19	A	87.9	0.66	9600	46 100
P6STE <sub>10</sub> A <sub>90</sub>	1/9	A	92.5	0.75	12 600	58 800
P6STE <sub>15</sub> A <sub>85</sub>	1/4	A	89.1	1.72	30 700	146 300
P6STE <sub>20</sub> A <sub>80</sub>	3/7	A	88.3	0.73	11 900	52 500

<sup>a</sup> Monomer ratio in the feed<sup>b</sup> Procedure followed for mixing the monomers<sup>c</sup> Intrinsic viscosity measured in dichloroacetic acid at 25°C<sup>d</sup> Average number and weight molecular weights measured by g.p.c.**Figure 4** I.r. spectra of poly(ester amide)s. The arrows indicate the absorption due to the ester bonds

series of poly(ester amide)s whose content in ester groups ranges approximately from 1.5 to 20% was prepared and the results obtained thereby are presented in *Table 1*. Polymerizations were conducted in chloroform since this was the solvent used previously by us in the preparation of polytartaramides<sup>4,5</sup>. Procedure A, based on the addition of the diacids mixture on to the activated diamine at 0°C,

has been mostly used. This led to polymers with intrinsic viscosities as high as 2 dl g<sup>-1</sup> in high yields. However, occasionally, the reaction mixture became jellified during the addition of the monomers, and low molecular weight polymers then resulted. The problem could be avoided by using procedure B, which consists of adding the activated diamine on to the diacids mixture at 35°C.

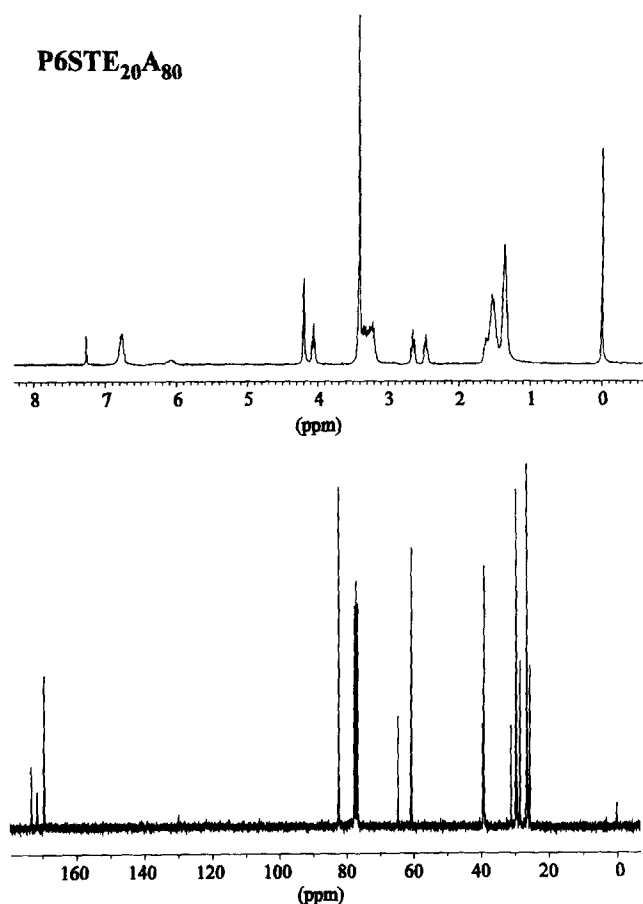


Figure 5  $^1\text{H}$  n.m.r. (300.13 MHz) and  $^{13}\text{C}$  n.m.r. (75.48 MHz) spectra of P6STE<sub>20</sub>A<sub>80</sub>

Using this procedure, the viscosity of the mixture increases steadily and high molecular weight polymers are invariably produced.

The chemical constitution of the resulting polymers was ascertained by elemental analysis as well as by FT i.r. and  $^1\text{H}/^{13}\text{C}$  n.m.r. spectroscopies. The contents of C, H and N experimentally found were in agreement with the values predicted for the corresponding compositions provided that 0.5 mol of water per repeating unit, which represents about 3–5% on a weight basis, was assumed to be present in the polymer. This makes sense since all these compounds display a high hygroscopicity. Moreover, P6DMLT was reported to contain a similar amount of absorbed water<sup>5</sup>. The i.r. spectra show the characteristic absorption bands anticipated for the constitution of these poly(ester amide)s: 3290–3310  $\text{cm}^{-1}$  (amide A), 3070–3090  $\text{cm}^{-1}$  (amide B), 1738–1746  $\text{cm}^{-1}$  (ester C=O), 1659–1669  $\text{cm}^{-1}$  (amide C=O, amide I), 1515–1545  $\text{cm}^{-1}$  (amide II) and 1090–1110  $\text{cm}^{-1}$  (ether C–O). The spectra of five P6STE<sub>x</sub>A<sub>y</sub>s with increasing contents of ester groups are compared in Figure 4, showing that the amide I/C=O ester intensity ratio varies according to the composition. On the other hand,  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectra are fully consistent with the chemical constitution expected for these poly(ester amide)s provided that disuccinate units (DSA) and the tartaramide units (TA) are randomly distributed along the copolymer chain. In Figure 5, the  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectra of P6STE<sub>20</sub>A<sub>80</sub> are shown for illustration. A complete assignment of the peaks appearing in both types of spectra was feasible on the basis of n.m.r. data

previously reported on polytartaramide P6DMLT<sup>5</sup> and with the help of two-dimensional n.m.r. experiments. A detailed account of these assignments is schematically given in Figure 6. In this figure, chemical shift values are specifically denoted for P6STE<sub>20</sub>A<sub>80</sub>, but the assignment pattern is applicable to the whole series of poly(ester amide)s, the only difference worth mentioning being the position of the NH peak in the  $^1\text{H}$  n.m.r. spectra.

#### Copolymer composition

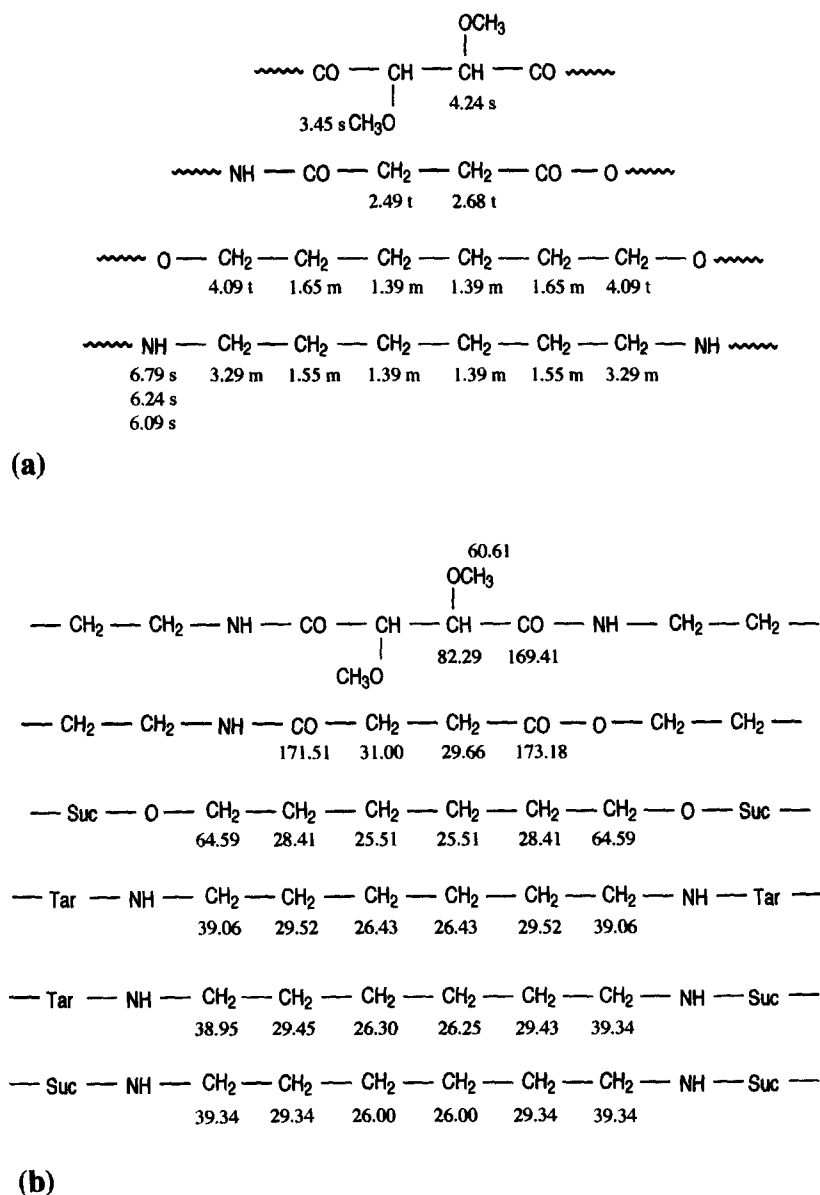
Variations in the ester/amide ratio of the copolymers were reflected in their elemental analyses and in both i.r. and n.m.r. spectra in the way expected because of the feed compositions used for each case. As can be clearly seen in Figure 4, the absorbance of the ester C=O band relative to the amide C=O band increases with the ester/amide ratio used in the polymerization feed. On the other hand, the elemental analysis turn out to be sensitive to composition variations only for contents of ester units higher than 10%. Nevertheless, the quantitative evaluation of the copolymer composition could be accurately accomplished for the whole series by  $^1\text{H}$  n.m.r. The singlet at 4.24 ppm arising from the methine protons of tartaric acid and the three triplets at 2.68, 2.49 and 4.09 ppm, corresponding to the two methylenes of succinic acid and the first methylene of the hexanediol unit, were used for this purpose. The percentage of TA units relative to DSA units in a P6STE<sub>x</sub>A<sub>y</sub> is given by

$$\% \text{TA} = 100 \frac{2A_{\text{CH(TA)}}}{2A_{\text{CH(TA)}} + A_{\text{CH}_2(\text{DSA})}}$$

In the above expression,  $A_{\text{CH(TA)}}$  is the area of the methine singlet and  $A_{\text{CH}_2(\text{DSA})}$  is the average area of the three methylene triplets. The calculated compositions are given in Table 2 together with the monomer feed ratios used for each polymer. In general, the ester content found in copolymers prepared by procedure A is close to that selected for their respective feeds, indicating that the diamine has no preference for either of the two diacids. Conversely, copolymers obtained by procedure B contain slightly fewer ester groups than expected, considering the composition of the feed. These results suggest that the diamine prefers tartaric acid over succinic acid when the condensation reaction takes place at 35°C.

#### Solubility and moisture sorption

All the poly(ester amide)s P6STE<sub>x</sub>A<sub>y</sub> display the same solubility pattern irrespective of their molecular weight and composition. They are readily soluble in dichloroacetic acid and formic acid as well as in chloroform, but they are not soluble in 1,2,4-trichlorobenzene, acetone or ethanol at any temperature. Although these polymers are markedly hydrophilic, they are not visibly affected by water, as will be shown below. On the other hand, they swell in dimethyl sulfoxide at room temperature and become solubilized in this solvent under moderate heating. The solubility of these polymers in chloroform is consistent with the behaviour observed for polytartaramides in general<sup>3–7</sup> and represents a departure from the usual trend shown by conventional polyamides whose solubility is usually restricted to strong hydrogen bond-breaking solvents. The exceptional affinity of polytartaramides for chloroform has been related to the tendency of these polymers to adopt regular conformations in helicogenic solvents<sup>5</sup>.



**Figure 6** Assignments of n.m.r. signals for poly(ester amide) P6STE<sub>20</sub>A<sub>80</sub>. Chemical shifts are denoted in ppm. (a) <sup>1</sup>H n.m.r.; (b) <sup>13</sup>C n.m.r.

Polytartaramides P<sub>n</sub>DMLT have been reported to be more hydrophilic than conventional nylons, a property which is thought to be due to the presence of the two highly polar methoxyl groups attached to the diacid unit. Thus, P6DMLT absorbs 12% of water in 48 h when left standing in 100% relative humidity at room temperature. Hydroscopicity of polytartaramides was shown to run parallel to the value of *n*, i.e. to the length of the polymethylene segment in the diamine unit.

The hygroscopicity of P6STE<sub>x</sub>A<sub>y</sub> has been evaluated by measuring the moisture sorption in disc samples exposed to 100% of relative humidity at room temperature (Figure 7). The total water uptake under such conditions ranges between 8.3% for P6STE<sub>20</sub>A<sub>80</sub> and 14.5% for P6STE<sub>1</sub>A<sub>99</sub> with more than 75% of the absorption taking place during the first 10 h of exposure. As expected, both the absorption rate and the amount of absorbed water increase with the density of methoxy groups in the poly(ester amide) chain, i.e. with the abundance of tartaric units in the copolymer.

Moisture sorption in room humidity, which usually oscillates between 65 and 85%, has also been measured

for some poly(ester amide)s, and results are compared with those obtained at 100% relative humidity in Figure 7. In this case, the total water uptake reached a maximum of 3% after about 12 h of exposure with most of the sorption occurring in the first few hours. As an example, P6STE<sub>10</sub>A<sub>90</sub> absorbs about 1.6% of moisture in less than 1 h. These results are of practical interest for a convenient handling of these polymer samples during both thermal and mechanical determinations.

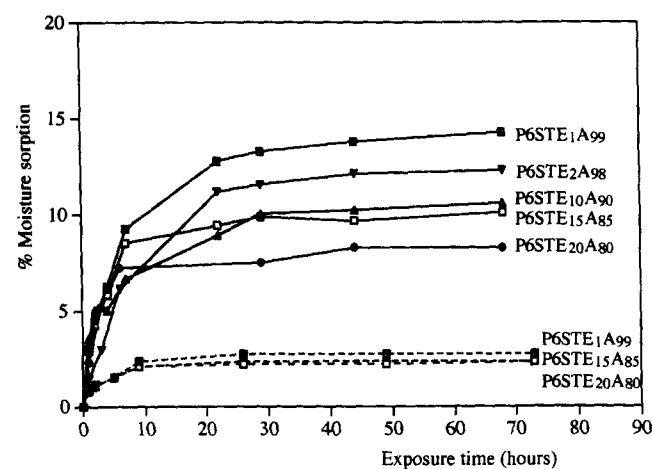
#### Thermal and mechanical properties

The *T<sub>m</sub>* and  $\Delta H_m$  values of P6STE<sub>x</sub>A<sub>y</sub> measured by d.s.c. are listed in Table 3 where data obtained for P6DMLT under similar conditions have been included for comparison. All poly(ester amide)s appear to be crystalline, showing well-defined melting peaks with associated melting enthalpies comparable to homopolytartaramides. Furthermore, both the position and intensity of the peaks become reproduced in the second heating traces, revealing the ability of these polymers to crystallize from the melt.

In Figure 8, the heating and cooling traces obtained for

**Table 2** Composition of poly(ester amide)s

Copolymer	DSA/TA <sup>a</sup>	Composition <sup>b</sup>			Elemental analysis <sup>c</sup>		
		DSA/TA	Ester/amide	SA/TA	C	H	N
P6STE <sub>1</sub> A <sub>99</sub> <sup>d</sup>	3/97	1.6/98.4	1.5/98.5	3.2/96.8	53.55 (54.07)	8.55 (8.67)	10.13 (10.40)
P6STE <sub>2</sub> A <sub>98</sub>	3/97	2.6/97.4	2.3/97.7	5.1/94.9			
P6STE <sub>2</sub> A <sub>98</sub> <sup>d</sup>	3/47	2.2/97.8	2.2/97.8	4.4/95.6	53.79 (54.13)	8.64 (8.67)	9.98 (10.37)
P6STE <sub>3</sub> A <sub>97</sub>	1/49	3.2/96.8	3.1/96.9	6.2/93.8	53.33 (54.22)	8.31 (8.67)	9.97 (10.32)
P6STE <sub>5</sub> A <sub>95</sub>	1/19	1.0/19.0	4.8/95.2	9.9/90.1	53.91 (54.38)	8.46 (8.67)	10.05 (10.23)
P6STE <sub>10</sub> A <sub>90</sub>	1/9	10.7/89.3	9.6/90.4	19.3/80.7	54.36 (54.88)	8.36 (8.66)	9.99 (9.96)
P6STE <sub>15</sub> A <sub>95</sub>	1/4	9.0/41.0	15.2/84.8	30.5/69.5	55.05 (55.49)	8.66 (8.65)	9.42 (9.63)
P6STE <sub>20</sub> A <sub>80</sub>	3/7	24.7/75.3	19.9/80.1	40.6/60.4	56.08 (56.01)	8.58 (8.65)	9.10 (9.34)

<sup>a</sup> Ratio of the two diacid comonomers in the polymerization feed<sup>b</sup> Copolymer composition determined by <sup>1</sup>H n.m.r. and expressed as: comonomer ratio (DSA/TA), ester/amide ratio and succinic acid/tartaric acid ratio (SA/TA)<sup>c</sup> In parentheses, elemental composition calculated for the copolymers with the indicated compositions<sup>d</sup> Polymers obtained by procedure B**Figure 7** Moisture sorption of P6STE<sub>x</sub>A<sub>y</sub> as a function of time at 100% relative humidity (solid lines) and under room conditions (dashed lines)

P6STE<sub>10</sub>A<sub>90</sub> are shown for illustration. In the first heating thermogram, the  $T_m$  is observed as a prominent, well-defined endotherm above 200°C and the  $T_g$  is detected as a slight variation in the slope of the trace. As depicted in the insets in *Figure 8*, the two transition temperatures of P6STE<sub>x</sub>A<sub>y</sub>,  $T_g$  and  $T_m$ , were observed to vary with composition according to expectation although the depressing effect appears to be much more pronounced in the glass transition. Whereas  $T_m$  decreases slightly from 232 to 204°C when the content of ester groups increases from 0 to 20%,  $T_g$  was observed to fall by more than 50°C in the same interval of compositions. A plot of  $T_m$  and  $T_g$  of P6STE<sub>x</sub>A<sub>y</sub> against the percentage of tartaric units with respect to the total diacid content, showing the steady variation found for both cases, is represented in *Figure 9*. On the other hand, melting enthalpies do not significantly vary for contents of ester groups below 10%, indicating that crystallinity of P6DMLT is not severely affected by the presence of the succinate moieties in the range of compositions that is being studied.

**Table 3** Thermal, mechanical and optical properties of P6STE<sub>x</sub>A<sub>y</sub>

Polyamide	Thermal data <sup>a</sup>			Mechanical parameters <sup>b</sup> (MPa)		Specific rotation <sup>c</sup> [ $\alpha$ ] <sub>D</sub> , (deg.)
	$T_g$ (°C)	$T_m$ (°C)	$\Delta H_m$ (J g <sup>-1</sup> )	Young modulus	Tensile strength	
P6STE <sub>0</sub> A <sub>100</sub> <sup>d</sup>	116	232	41.9	1600	53	96.0
P6STE <sub>1</sub> A <sub>99</sub>	96	229	36.9	1200	39	92.7
P6STE <sub>2</sub> A <sub>98</sub>	94	231	34.0	1120	38	80.8
P6STE <sub>3</sub> A <sub>97</sub>	94	231	36.7	1230	41	82.6
P6STE <sub>5</sub> A <sub>95</sub>	90	230	36.7			86.7
P6STE <sub>10</sub> A <sub>90</sub>	84	224	39.6	990	37	83.6
P6STE <sub>15</sub> A <sub>85</sub>	75	210	20.7	500	23	73.2
P6STE <sub>20</sub> A <sub>80</sub>	59	204	20.3	700	31	63.8

<sup>a</sup> Measured by d.s.c.<sup>b</sup> Measured in stress-strain experiments<sup>c</sup> Measured in chloroform at 25°C<sup>d</sup> Poly(hexamethylene-di-O-L-tartaramide) referred in the text as P6DMLT

Poly(ester amide) samples from synthesis are white or slightly yellow powders. Consistent films with a uniform milky appearance may be prepared by casting from chloroform at slow rates of evaporation whereas transparent films are obtained if the solvent is rapidly removed. The ability of P6STE<sub>x</sub>A<sub>y</sub> to render these films

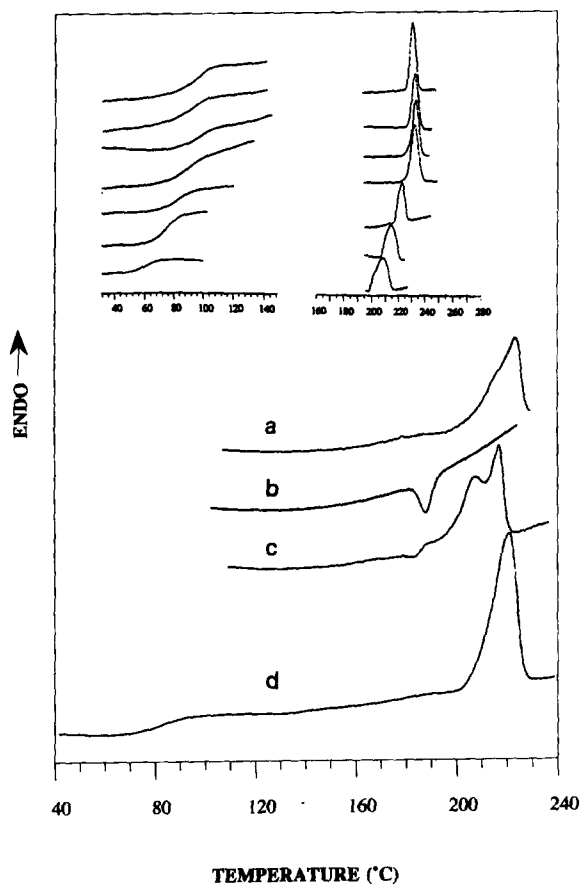
is seriously limited by the molecular weight of the polymer. In practical terms, it was observed that intrinsic viscosities above 0.7 dl g<sup>-1</sup> were required to obtain homogeneous films with the minimum quality needed for carrying out reliable mechanical testing.

Mechanical parameters of P6STE<sub>x</sub>A<sub>y</sub> measured in stress-strain experiments are listed in Table 3 where they are compared with those recorded for P6DMLT. The effect of composition on the Young moduli and tensile strengths of the poly(ester amide)s is reflected overall as a decrease in the magnitude of both parameters with the increase in ester content. As a consequence, the relatively hard and rigid nature of P6DMLT changes, being rather soft and flexible in the case of P6STE<sub>20</sub>A<sub>80</sub> where 20% of the amide groups have been replaced by ester groups. Since the ultimate elongation increases in the same way no appreciable decay in the tenacity of the plastic seems to be apparent.

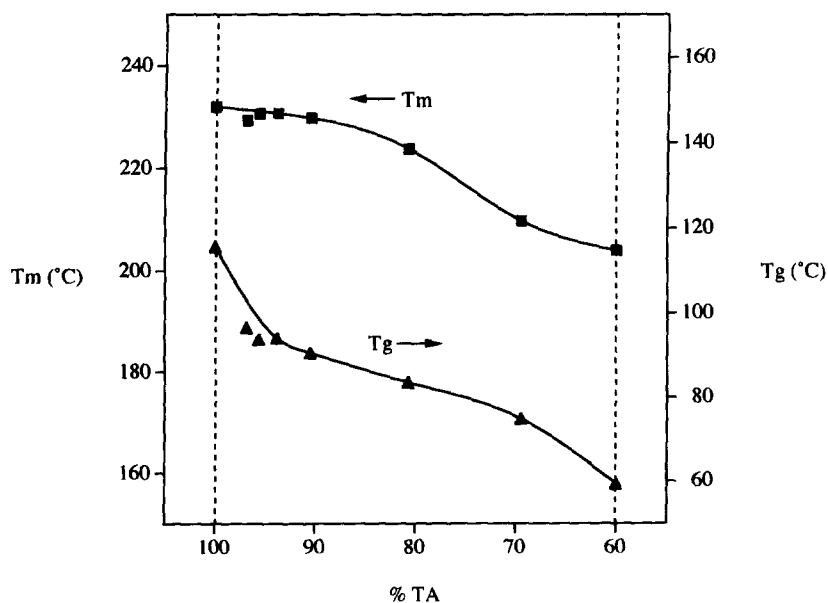
*Hydrolytic degradation*

The susceptibility of the three poly(ester amide)s P6STE<sub>10</sub>A<sub>90</sub>, P6STE<sub>15</sub>A<sub>85</sub> and P6STE<sub>20</sub>A<sub>80</sub> to hydrolytic degradation in pH 7.4 buffer at 37°C was evaluated and compared with that exhibited by the polytartaramide P6DMLT previously studied by us<sup>8</sup>. Mass losses and changes in both intrinsic viscosities and molecular weights of polymers degraded for different periods of time are presented in Table 4, revealing that apparent changes take place in all cases from the early stages of incubation. These results are plotted in Figures 10a and 10b, which show graphically the evolution of degradation with time. Some significant features of these plots are the following: (a) the molecular weight is observed to decrease rapidly during the first two months of incubation, after which a limiting value of about 5000 is reached; (b) weight losses in poly(ester amide)s take place continuously without any apparent ceasing of the process and ending in the complete erosion of the polymer sample; and (c) the weight loss rate in the three poly(ester amide)s is higher than in P6DMLT and increases with the content of ester groups in the polymer.

The fact that sample erosion continued while no



**Figure 8** D.s.c. traces of P6STE<sub>10</sub>A<sub>90</sub>: (a) first heating trace from a film cast from chloroform; (b) cooling trace; (c) second heating trace; (d) heating trace from a rapidly cooled sample. Insets: *T<sub>g</sub>* (left) and *T<sub>m</sub>* (right) variations with composition of the polymer (top: P6STE<sub>1</sub>A<sub>99</sub>; bottom: P6STE<sub>20</sub>A<sub>80</sub>)



**Figure 9** Plot of *T<sub>g</sub>* and *T<sub>m</sub>* against composition of P6STE<sub>x</sub>A<sub>y</sub>



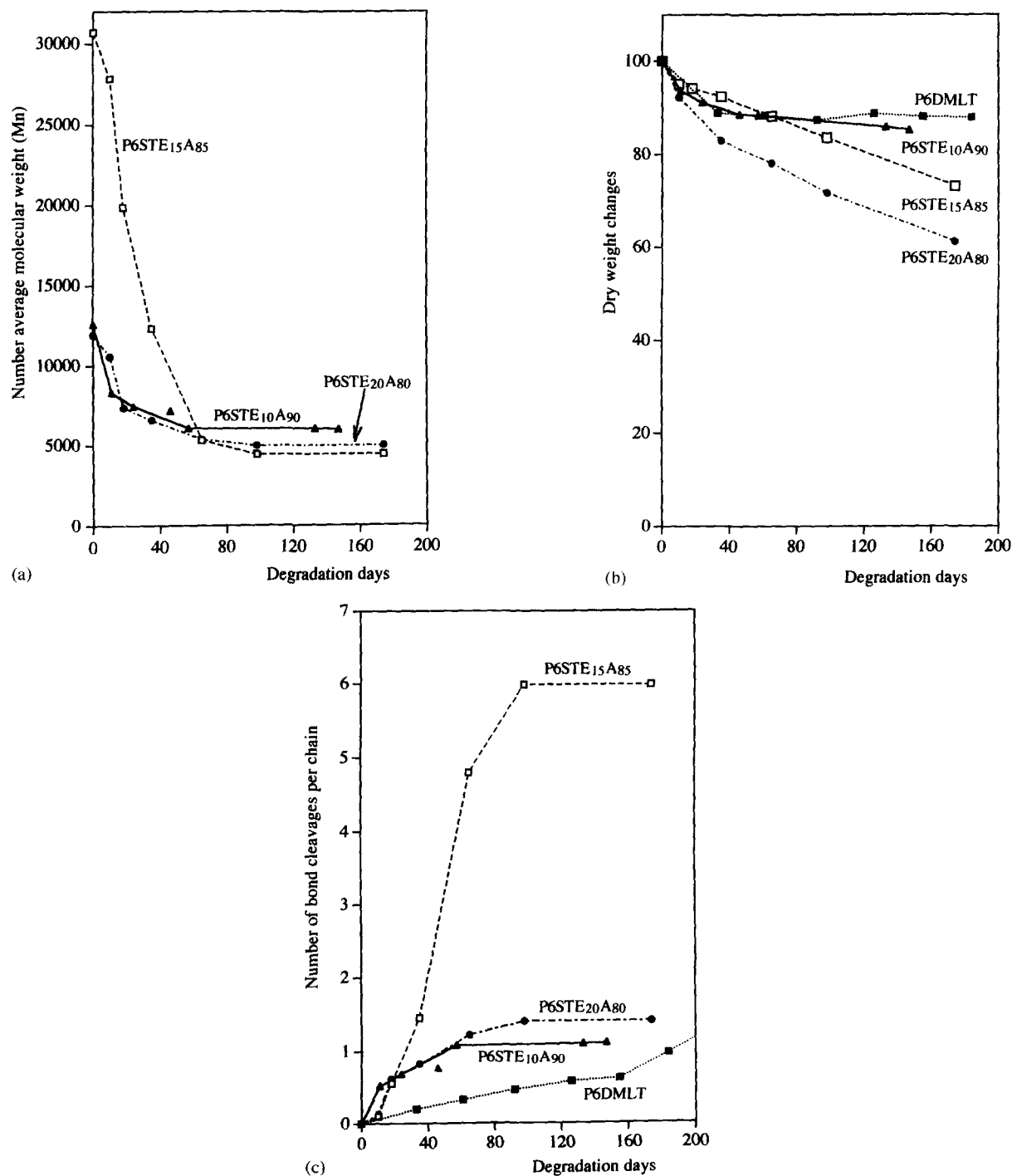
**Table 4** Erosion and molecular weight decrease in poly(ester amide)s degraded in pH 7.4 buffer at 37°C

Time (weeks)	P6STE <sub>10</sub> A <sub>90</sub>			P6STE <sub>15</sub> A <sub>85</sub>			P6STE <sub>20</sub> A <sub>80</sub>		
	W <sup>a</sup> (%)	[η] <sup>b</sup> (dl g <sup>-1</sup> )	M <sub>n</sub> /M <sub>w</sub> <sup>c</sup> (10 <sup>-3</sup> )	W <sup>a</sup> (%)	[η] <sup>b</sup> (dl g <sup>-1</sup> )	M <sub>n</sub> /M <sub>w</sub> <sup>c</sup> (10 <sup>-3</sup> )	W <sup>a</sup> (%)	[η] <sup>b</sup> (dl g <sup>-1</sup> )	M <sub>n</sub> /M <sub>w</sub> <sup>c</sup> (10 <sup>-3</sup> )
0	100	0.75	12.6/58.8	100	1.72	30.7/146.3	100	0.73	11.9/52.3
1-2	93.7	0.53	8.3/24.2	95.1	1.23	27.8/72.1	92.2	0.46	10.5/21.2
3-4	91.0	0.41	7.5/19.3	94.1	0.93	19.8/51.3		0.41	7.4/17.4
5-6	88.5	0.40	7.1/17.4	92.4	0.61	12.3/28.7	82.6	0.31	6.5/13.6
8-9	88.3	0.40	6.0/14.7	88.2	0.49	5.3/16.2	78.1	0.31	5.3/11.6
14-15	85.9	0.32	6.0/13.2	83.5	0.36	4.4/10.1	71.7	0.29	5.9/9.9
20	85.2	0.33	5.9/12.7						
25				73.2	0.30	4.4/7.7	61.2	0.26	4.9/8.0

<sup>a</sup> % of remaining weight

<sup>b</sup> Intrinsic viscosity measured in dichloroacetic acid at 25°C

<sup>c</sup> Average molecular weights measured by g.p.c.



**Figure 10** Hydrolytic degradation plots of the indicated poly(ester amide)s in pH 7.4 buffer at 37°C: (a) changes in M<sub>n</sub>; (b) weight losses; (c) average number of broken bonds per chain

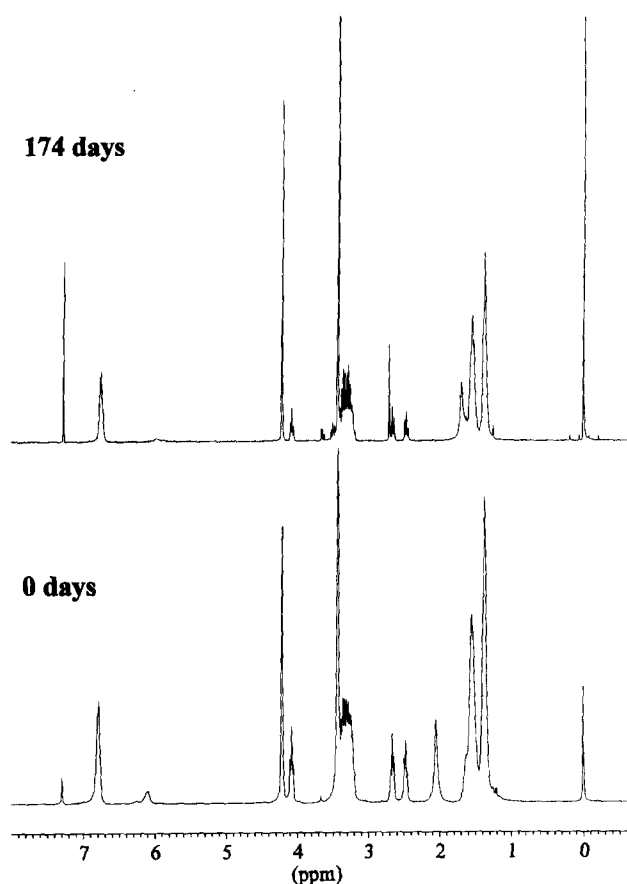


Figure 11  $^1\text{H}$  n.m.r. spectra of P6STE<sub>15</sub>A<sub>85</sub> before and after degradation for 174 days

changes in the molecular weight were detected simultaneously may be rationalized if solubilization of the polymer fragments with a size below the limiting molecular weight is assumed to occur. Since small fragments are removed from the disc, both viscosity and elution volume in g.p.c. of the remaining polymer are not affected by the degradation process occurring at this stage.

The dissimilar and broad molecular weight distributions of the polyamides used in this study are drawbacks that should not be ignored. The contribution of the low molecular weight fraction originally present in the sample to the apparent overall rates of both molecular weight decay and weight loss is difficult to evaluate since they would be extracted by the incubation medium. On the other hand, the relatively sudden fall of  $M_n$  observed for P6STE<sub>15</sub>A<sub>85</sub> when compared to the other polyamides studied may be attributed to its higher initial molecular weight. This may be corroborated if the number of chain bonds split per polymer chain, estimated as  $N = [M_{n(0)}/M_{n(t)}] - 1$ , is represented as a function of time. The plot is shown in Figure 10c, revealing that about six bonds are hydrolysed in P6STE<sub>15</sub>A<sub>85</sub> whereas only one is cloven in the other two poly(ester amide)s, achieving a similar limiting chain in every case. Moreover, cleavage of the first bond takes approximately the same time in all the three polymers. The plot provides further evidence that the number of broken bonds in P6DMLT under similar conditions is comparatively negligible.

A preliminary analysis of the degraded polymers has been carried out by  $^1\text{H}$  n.m.r. in order to get a first insight into the molecular mechanism responsible for the degradation of P6STE<sub>x</sub>A<sub>y</sub>. In Figure 11, the proton

spectra of poly(ester amide) P6STE<sub>15</sub>A<sub>85</sub>, before and after incubation for approximately six months, are compared. No changes concerning the signals arising from the protons contained in the tartaric moieties are detected, revealing that neither the methoxyl side groups nor the backbone amide bonds are involved in the degradation process. On the other hand, signals corresponding to succinic moieties appear much more complicated in the spectrum of the degraded sample as expected, due to the variety of chemical structures that may arise from the hydrolysis of the succinate groups. It can be concluded, therefore, that degradation of these poly(ester amide)s takes place essentially through cleavage of ester bonds as could be logically anticipated from the relatively higher susceptibility of such groups to hydrolysis.

#### ACKNOWLEDGEMENT

Financial support given by CICYT (Comisión Interministerial de Ciencia y Tecnología), Grant No. MAT93-0555-CO2-02, is gratefully acknowledged.

#### REFERENCES

- Bou, J. J., Iribarren, I., Rodríguez-Galán, A. and Muñoz-Guerra, S., in *Biodegradable Polymers and Plastics*, ed. M. Vert. Royal Society of Chemistry, Cambridge, UK, 1992, pp. 271–274.
- Bueno, M., Galbis, J. A., García, M. G., DePaz, M. V., Zamora, F., Bou, J. J. and Muñoz-Guerra, S., in *Biodegradable Polymers and Plastics*, ed. M. Vert. Royal Society of Chemistry, Cambridge, UK, 1992, pp. 237–240.
- Bou, J. J., Rodríguez-Galán, A. and Muñoz-Guerra, S., in *The Polymeric Materials Encyclopedia*, ed. J. C. Salamone. CRC Press, Boca Raton, F. L., 1996, pp. 561–569.
- Rodríguez-Galán, A., Bou, J. J. and Muñoz-Guerra, S., *J. Polym. Sci., Polym. Chem. Ed.*, 1992, **30**, 713.
- Bou, J. J., Rodríguez-Galán, A. and Muñoz-Guerra, S., *Macromolecules*, 1993, **26**, 5664.
- Bou, J. J., Iribarren, I. and Muñoz-Guerra, S., *Macromolecules*, 1994, **27**, 5263.
- Bou, J. J. and Muñoz-Guerra, S., *Polymer*, 1995, **36**, 181.
- Ruiz-Donaire, P., Muñoz-Guerra, S. and Rodríguez-Galán, A., *J. Appl. Polym. Sci.*, 1995, **58**, 41.
- Huang, S. J., Bell, J. P., Knox, J. R., Atwood, H., Leong, K. W., Natarajan, K., Pavlisko, J., Roby, M. and Shoemaker, N., *ACS Symposium Ser., Textile and Paper Chem. Technol.*, 1977, **49**, 73.
- Bitritto, M. M., Bell, J. P., Brenckle, G. M., Huang, S. J. and Knox, J. R., *J. Appl. Polym. Sci., Appl. Polym. Symp.*, 1979, **35**, 405.
- Huang, S. J., Bitritto, M. M., Leong, K. W., Paulisco, J., Roby, M. and Knox, J. R., *Adv. Chem. Ser.*, 1978, **169**, 205.
- Dibenedetto, L. J. and Huang, S. J., *Polym. Degrad. and Stab.*, 1994, **45**, 249.
- Akelah, A., Kenawy, E. R. and Sherrington, D. C., *Eur. Polym. J.*, 1995, **31**, 903.
- Ogata, N. and Hosoda, Y., *J. Polym. Sci., Polym. Chem. Ed.*, 1975, **13**, 1793.
- Williams, J. L. R., Laakso, T. M. and Contois, L. E., *J. Polym. Sci.*, 1962, **61**, 353.
- Gonsalves, K. E., Chen, X. and Cameron, J. A., *Macromolecules*, 1992, **25**, 3309.
- Iribarren, I., Alemán, C., Bou, J. J. and Muñoz-Guerra, S., *Macromolecules*, 1996, **29**, 4397–4405.
- Pierce, A. E., *Silylation of Organic Compounds*, Pierce Chemical Co., Rockford, IL, 1968, pp. 7–26.
- Tsamantakis, A. and Carriere, F., *Angew. Makromol. Chem.*, 1982, **104**, 19.
- Katsarava, R. M., Kharadze, D. P., Avalishvili, L. M. and Zaalishvili, M. M., *Makromol. Chem., Rapid Commun.*, 1984, **5**, 585.