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Acylated and hydroxylated polyamides derived from L-tartaric acid

Abdelilah Alla, Joachim Oxelbark, Alfonso Rodríguez-Galán, Sebastián Muñoz-Guerra*

Departament d'Enginyeria Química, Universitat Politècnica de Catalunya, ETSEIB, Diagonal 647, 08028 Barcelona, Spain

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Abstract

A series of polyamides 6,4 were prepared from 1,6-hexanediamine and active esters of 2,3-di-O-acylated L-tartaric acid by polycondensation in solution. Both *O*-alkoyl and *O*-benzoyl esters were used as hydroxyl protecting groups. The resulting acylated polytartaramides were found to be semicrystalline polymers with T_m between 100 and 200 °C and T_g slightly above 100 °C. Controlled hydrolysis of the ester side group led to the preparation of poly(hexamethylene L-tartaramide)s with different content in free hydroxyl groups. These polyamides continue being crystalline but their properties largely differ from those displayed by their parent acylated polymers.
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Keywords: Polyamides; Carbohydrated-based polyamides; Hydroxylated polyamides

1. Introduction

Polyamides made from carbohydrate-based monomers have received great attention these last years [1–5]. The interest for these polyamides arises not only from the fact that they are obtained from renewable feedstock but also because novel properties can be attained upon the incorporation of carbohydrate units in the polymer main chain. Since these polyamides are much more hydrophilic and susceptible to hydrolysis than conventional nylons, they are potentially valuable for applications requiring biodegradability or hydrodegradability under mild conditions.

Most of reported carbohydrate-based polyamides were synthesised by polycondensation of aldaric acids and alkanediamines. Pioneering work in the hydroxylated polyamide field was made by Ogata et al. in the seventy's [6], who explored a variety of structures applying different reaction procedures. A crucial point of this synthesis is to avoid undesirable chain branching, for which the hydroxyl side group should be conveniently protected prior to polymerisation. Regeneration of the hydroxyl function will be achieved provided that readily removable groups are chosen for protection [7]. Nevertheless, some authors have recently succeeded in obtaining linear polyhydroxylated polyamides from unprotected aldaric acids [8,9]. Although these direct methods are highly promising, the molecular weights of the resulting polyamides are rather low, i.e. 2,000–4,000. These polyhydroxylated polyamides were reported to be water-soluble and crystalline with melting points ranging between 115 and 215 °C depending on both the size of the diamine and the configuration of the aldaric acid.

Polytartaramides, i.e. polyamides derived from tartaric acid, have been extensively studied by our group along the last decade [10,11]. Most of these polyamides were prepared from linear α,ω-alkanediamines and L-tartaric acid with the hydroxyl side groups blocked as methyl ether. These poly(alkylene di-*O*-methyl L-tartaramide)s, abbreviated P*n*DMLT, are hydrophilic polymers with satisfactory thermal and mechanical properties, and displaying enhanced solubility in organic solvents. However, P*n*DMLT persist to be reluctant to undergo hydrolytic degradation [12]. Furthermore, the methoxy group is practically unremovable preventing these compounds to be used as functionally active polymers.

In this work we want to report on polytartaramides bearing free hydroxyl groups, specifically on poly(hexamethylene L-tartaramide)s, henceforth called P6LT. It is much expected that hydroxyl-unprotected polytartaramides are more hydrophilic and, therefore, more prone to undergo both hydrolytic and enzymatic degradation than the protected polytartaramides. Such polyamides will be

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* Corresponding author.
E-mail address: sebastian.munoz@upc.edu (S. Muñoz-Guerra).

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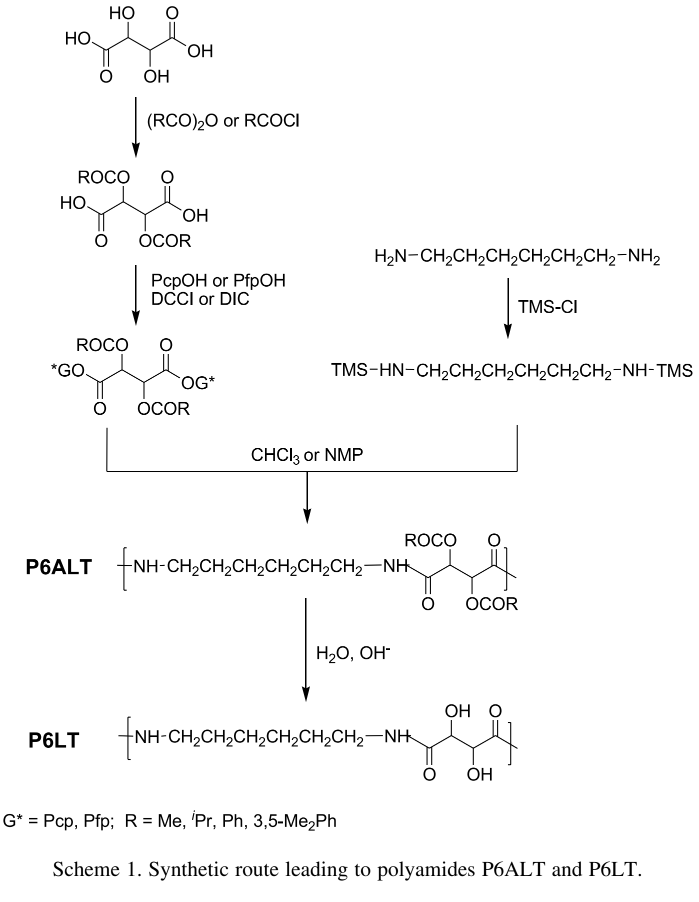
obtained by controlled hydrolysis of precursor polytartaramides (P6ALT) having the hydroxyl side groups esterified with different acyl groups. The synthesis, and characterisation of both P6ALT and P6LT are described in this paper, and some of their properties preliminary examined with reference to P6DMLT. Our interest in this study is twofold: a) To establish a procedure to prepare linear hydroxylated polytartaramides, and b) To evaluate the effect of hydroxyl protection on the pattern of behaviour of polyamides made from tartaric acid.

2. Materials and methods

All chemicals were obtained commercially from either Aldrich or Merck. They were analytical grade or higher, and used without further purification. Solvents to be used under anhydrous conditions were dried by standard methods.

The synthesis of intermediate compounds and polyamide precursors involved standard synthesis work. The detailed procedure used for the preparation of each product and their characterisation data are provided as electronic supporting material of this paper. For the synthesis of the acylated polytartaramides the following general procedure was adopted: A solution of the active ester (0.4 mmol) in the appropriate solvent (0.6 ml) was added dropwise at 0 °C to a solution of *N*,*N*′-bis(trimethylsily) hexamethylenediamine (0.4 mmol) in 0.1 ml of the solvent under a nitrogen atmosphere. The solution was further stirred for 2 h at this temperature and then left at room temperature for 72 h. The polymer was precipitated from the reaction solution by adding methanol and ether. Hydrolysis of acylated polytartaramides was performed as follows: 5 ml 25% aqueous NH_3 or NaOH (w/w) was added to a solution of 0.5 g of the polymer (P6AcT or P6BzT, respectively) in 10 ml of *N*-methyl pyrrolidone (NMP). The mixture was stirred at room temperature for a predetermined period of time. The hydrolysed polymer was precipitated by pouring into acetone, centrifuged and washed twice with acetone, and finally dried under vacuum. The spectroscopic data used for characterisation of polytartaramides are described in full detail as electronic supporting material.

Viscosities were measured in dichloroacetic acid (DCA) at 25.0 ± 0.1 °C using an Ubbelohde microviscometer. Infrared spectra were recorded on a FT-IR Perkin–Elmer 2000 instrument from KBr disks. ^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker AMX-300 spectrometer. Spectra of intermediate compounds, monomers and polymers were taken in $CDCl_3$ or DMSO, either pure or containing 10% of trifluoroacetic acid (TFA). Sample concentrations about 1 and 5% (w/v) were used for ^{1}H and ^{13}C analysis, respectively, and tetramethylsilane (TMS) was used as internal reference. ^{13}C NMR measurements were made under proton decoupling conditions at



Scheme 1. Synthetic route leading to polyamides P6ALT and P6LT.

74.48 MHz. For typical ^{1}H NMR and ^{13}C NMR spectra, the number of accumulated scans were 64 and 300–1500, respectively.

Solubility essays were made following the method reported by Braun [13]. The thermal behaviour of the polyamides was examined by DSC using a Perkin–Elmer Pyris 1 calibrated with indium. DSC data were obtained from 4 to 6 mg samples at heating/cooling rates of 10 °C min^{-1} under a nitrogen flow of 20 ml min^{-1}. Glass-transition temperatures were determined at a heating rate of 20 °C min^{-1} from rapidly melt-quenched polymer samples. Thermogravimetric analysis was performed under a nitrogen atmosphere with a Perkin–Elmer TGA-6 thermobalance at a heating rate of 10 °C min^{-1}. X-ray diffraction patterns were obtained from powdered samples in a modified Statton camera using a nickel-filtered Cu Kα radiation with a wavelength of 0.1542 nm and calibrated with molybdenum sulphide ($d_{002}=0.6147$ nm). Optical rotations of polymers were measured on a KRÜSS Automatic Digital Polarimeter P 3001 using Sodium D-line (589 nm) at room temperature in solutions at polymer concentrations within the 0.1–0.5 gdl^{-1} range.

3. Results and discussion

3.1. Acylated polytartaramides (P6ALT)

The preparation of the poly(hexamethylene di-*O*-acyl L-tartaramide)s was carried out following essentially the same procedure used previously by us for the synthesis of poly(hexamethylene di-*O*-methyl tartaramide)s [1]. The route of synthesis is depicted in Scheme 1.

Major modifications introduced in the synthesis are those required for the esterification of the hydroxyl side group of L-tartaric acid. This reaction was accomplished by treatment of L-tartaric acid with either the anhydride (R = Me) or the chloride (R = ^{i}Pr, R = Ph, 3,5-Me$_2$Ph) of the chosen acylating acid. The active esters (pentachlorophenyl (Pcp) for R = Me and ^{i}Pr, and pentafluorophenyl (Pfp) for R = Ph and 3,5-Me$_2$Ph) used as monomers were readily obtained by reaction of the acylated tartaric acid with the corresponding perhalogenated phenol. On the other side, the nucleophilicity of hexamethylenediamine was enhanced by activating it as *N*-trimethylsilyl derivative, as previously reported [1].

Polymerisation was conducted in either chloroform or NMP solution at room temperature. The resulting polyamides were obtained in 70–90% yield and they have intrinsic viscosities between 0.86 and 0.35 dl g^{-1} in DCA, which according to reported data for other poly(tartaramide)s, correspond approximately to weight-average molecular weights between 20,000 and 5000. At difference with poly(di-*O*-methyl L-tartaramide)s, the solubility of these hydroxylated polyamides is not notably enhanced with respect to that of unsubstituted polyamides, i.e. nylon 6,4. All these data are compared in detail in Table 1.

Table 1
Synthesis and properties of polyamides

Polyamide P6ALT	R	Yield (%)	[η] (dl g^{-1})	Elemental analysis			Solubility						
				C	H	N	H_2O	$CHCl_3$	ClPh	DMSO	NMP	TFE	TFA
P6AcLT	Me	69	0.86	51.96 (53.49)	7.33 (7.05)	8.69 (8.91)	–	–	–/±	+	+	+	+
P6^{i}BLT	^{i}Pr	92	0.40	57.13 (56.98)	8.15 (8.23)	7.48 (7.38)	–	–	±/+	+	+	+	+
P6BzLT	Ph	80	0.35	64.21 (63.76)	6.01 (6.32)	7.07 (6.76)	–	–	–	+	+	+	+
P6MBzLT	3,5-Me$_2$Ph	80	0.35	65.99 (66.36)	6.88 (7.28)	6.04 (5.95)	–	–	–	+	+	+	+

ClPh: chlorobenzene; DMSO: dimethyl sulfoxide; NMP: *N*-methyl pyrrolidone; TFE: trifluoroethanol; TFA: trifluoroacetic acid.

The thermal stability of P6ALT was evaluated by TGA. An illustrative thermal decomposition profile is shown in Fig. 1as for the case of P6^{i}BLT and decomposition data for the four acylated polytartaramides are compared in Table 2. The onset of decomposition appeared near above 200 °C indicating that acylated polytartaramides are much less stable than those having the hydroxyl groups protected as methyl ether. In all cases, two well resolved maximum rate decomposition peaks were observed at the proximity of 300 and 450 °C, respectively. The lower temperature decomposition peak probably corresponds to the release of the acyloxy side group whereas main chain scission with generation of carbonaceous residues is thought to take place in the second decomposition step.

Thermal transition parameters were measured by DSC and they are collected in Table 2. The glass transitions of P6ALT were found to happen above 100 °C, at T_g values comparable to that of P6DMLT, which is reported to be 106 °C. The four polytartaramides appeared to be semicrystalline with melting temperatures varying within the 150–230 °C range according to the chemical constitution of the side ester group. The heating DSC traces registered from samples coming from synthesis are compared in Fig. 1b. No crystallisation peak was usually detected upon cooling from the melt, which can be due to the inherent difficulty of the substituted polyamide chain to attain order at the used time scale, as it is known to happen in other polyamides. The X-ray diffraction analysis of powdered samples corroborated the crystalline nature of P6ALT by displaying discrete rings whose degree of sharpness correlated with the enthalpy estimated by DSC for each respective compound. The Bragg spacings appearing with medium or strong intensity in these powder diffraction patterns are listed in Table 2, where similar data reported for polytartaramide P6DMLT are included for comparison. At this preliminary stage of analysis, the only conclusion that could be drawn from these data is that acylated polytartaramides are less crystalline than P6DMLT and that their

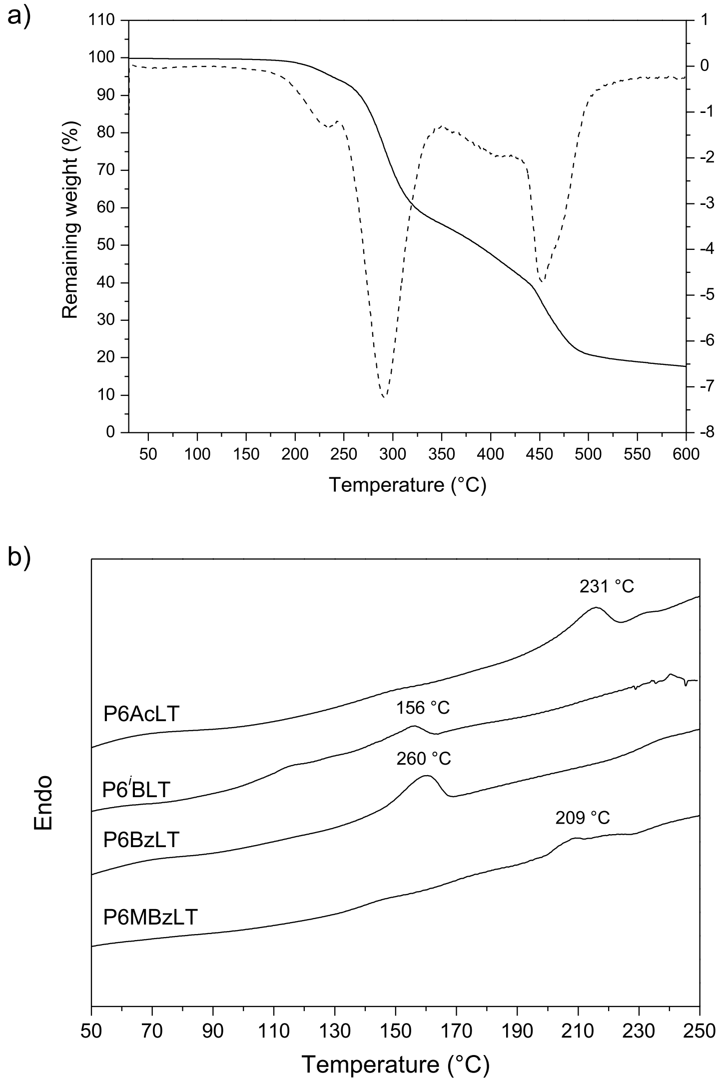


Fig. 1. a) TGA traces (weight loss: solid line, decomposition rate: dashed line) of P6^{i}BLT. b) Heating DSC traces of polyamides P6ALT.

Table 2
Thermal properties and X-ray diffraction spacing of polyamides

Polyamide	$[\alpha]_D$[a] (deg)	DSC			TGA		d (nm)
		T_g (°C)	T_m (°C)	ΔH_m (J/g)	T_d	W (%)	
P6AcLT	−32	112	231	33	**270**/461	−/64/26	1.35; 0.47; 0.42
P6^{i}BLT	−19	106	156	20	236/**291**/451	95/55/18	1.0; 0.47
P6BzLT	−84	107	160	30	228/283/**457**	84/61/17	0.97; 0.52; 0.46;0.43
P6MBzLT	−112	105	209	17	187/**309**/465	94/55/12	1.1; 0.47; 0.38
P6DMLT[b]	+90	106	230	42	250/360/**538**	90/73/23	1.08; 0.68; 0.57; 0.45; 0.42

[a] Specific optical rotation measured at room temperature.
[b] Data from Ref. [14].

crystalline structure does not seem to be very different. The specific optical activity of these polyamides varied widely with values ranking from 19° y 112° and all them show minus sign contrary to what is observed for P6DMLT. These data are shown in Table 2.

3.2. Hydroxy-free polytartaramides (P6LT)

Controlled hydrolysis of P6AcLT and P6MBzLT polyamides was performed in basic medium using either NH_3 or NaOH aqueous solution. Treatment times of 1, 5 and 30 h were used in order to obtain both partially and completely hydroxyl unprotected polyamides. The evolution of the hydrolysis was unequivocally followed by both FTIR and ^{1}H NMR.

As it is depicted in Fig. 2 for the case of polyamide P6AcLT, the infrared spectra showed the progressive disappearance of the ester band at ~1700 cm^{-1} simultaneous to the broadening and strengthening of the peak at 3500–3200 cm^{-1}, as expected from the generation of free hydroxyl groups. The corresponding ^{1}H NMR analysis of hydrolysed P6AcLT is shown in Fig. 3. The signal characteristic of the acetyl side group at ~5.7 ppm disappeared and at the same time, a new signal at ~8.3 ppm arising from the hydroxyl group emerged and

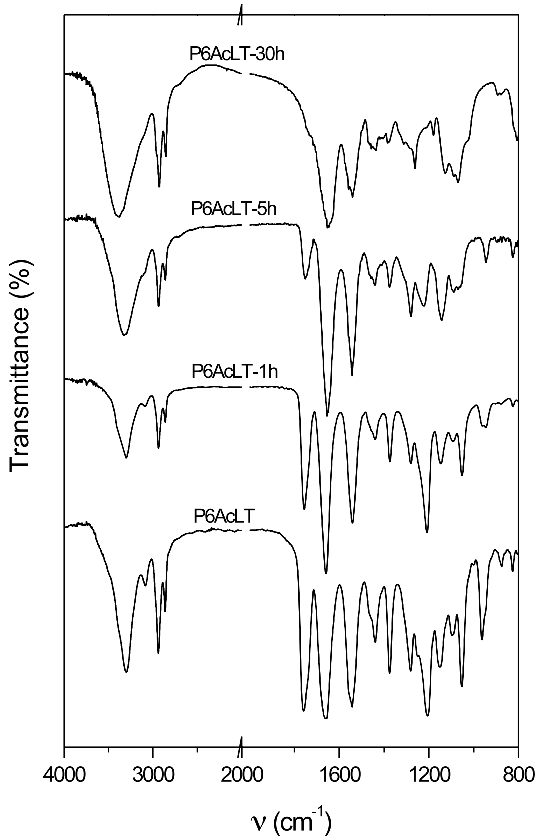


Fig. 2. FT-IR spectra of polyamides resulting from the controlled hydrolysis of P6AcLT.

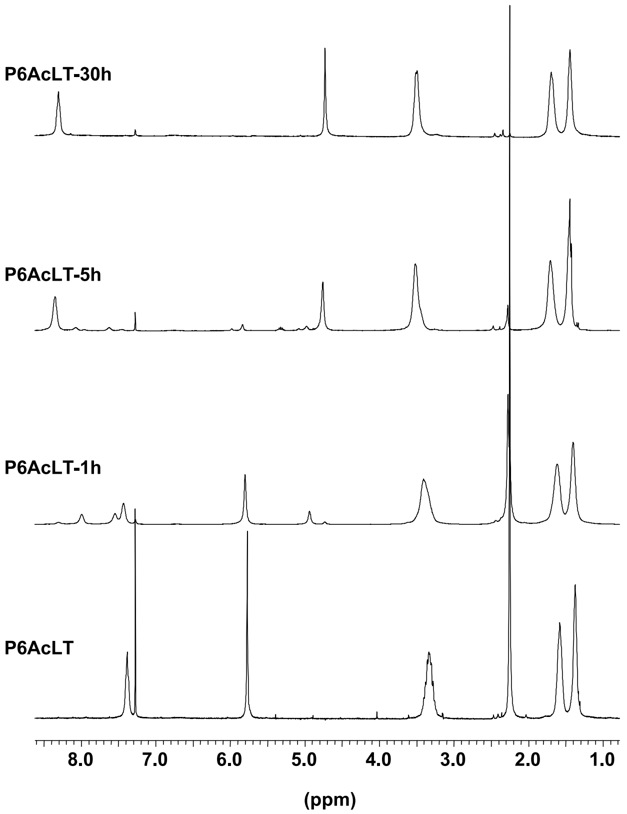
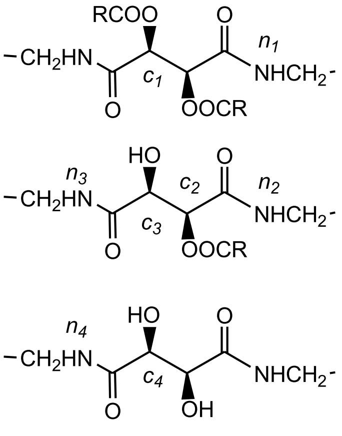


Fig. 3. Evolution of the hydrolysis of polyamide P6AcLT followed by ^{1}H NMR.

increased with the severity of the treatment. Simultaneously, changes in the chemical shift of CH and NH main chain protons signals subsequent to the chemical changes happening in the side groups were observed as expected. These data were used for quantification of the content of the hydrolysed polyamide in tartrate moieties differing in esterification degree. These units are indicated in Scheme 2 and NMR spectra of the affected signal regions with their assignments are shown in Fig. 4. The compositions of P6LT estimated by this method were corroborated by elemental analysis and the results are compared in Table 3.

Results indicated that both polyamides P6AcLT and P6MBzLT became fully deprotected after 30 h of treatment, the P6AcLT-30 h showing a decrease in viscosity (0.5 dl g^{-1}) which means that some breaking of the main chain took place along the deprotection reaction. A very rough estimation based on viscosity-molecular weight correlations established for nylons would indicate that one amide group is split when two hundreds ester side groups become hydrolised. After 5 h of hydrolysis of P6AcLT, the amount of hydroxyl groups arrived to be 78% whereas it was only 52% in the case of polyamide P6MBzLT. The lower susceptibility of the benzoylated polyamide to hydrolysis is consistent with the stronger steric impediment to water attack predictably caused by the bulky hydrophobic 3,5-dimethyl benzyl group present in this polyamide. No *meso* unit could be detected by NMR which is demonstrative that no racemisation happened along the hydrolysis process. Accordingly, the deprotected polyamides continue to be optically active.

Properties of polyamides P6LT are compared in Table 4. The solubility of polyamides P6LT was not significantly affected by the degree of hydrolysis. This behaviour is contrary to that displayed by polyhydroxylated polyamides derived from pentaric or hexaric acids, which are reported to be readily soluble in water [8]. It seems that the density of OH groups in the repeating unit of P6LT is not high enough as to counterbalance the hydrophobic nature of the hexamethylene unit. Conversely, important modifications in the thermal parameters were found. T_g diminished steadily as the content in OH increased, and exactly the opposite trend was observed for T_m. Crystallinity, as it is reflected in the melting enthalpy, appeared to increase also with the degree of hydrolysis.



Scheme 2. Possible units of polyamides P6LT differing in hydrolysis degree with indication of labelling used for NMR assignment.

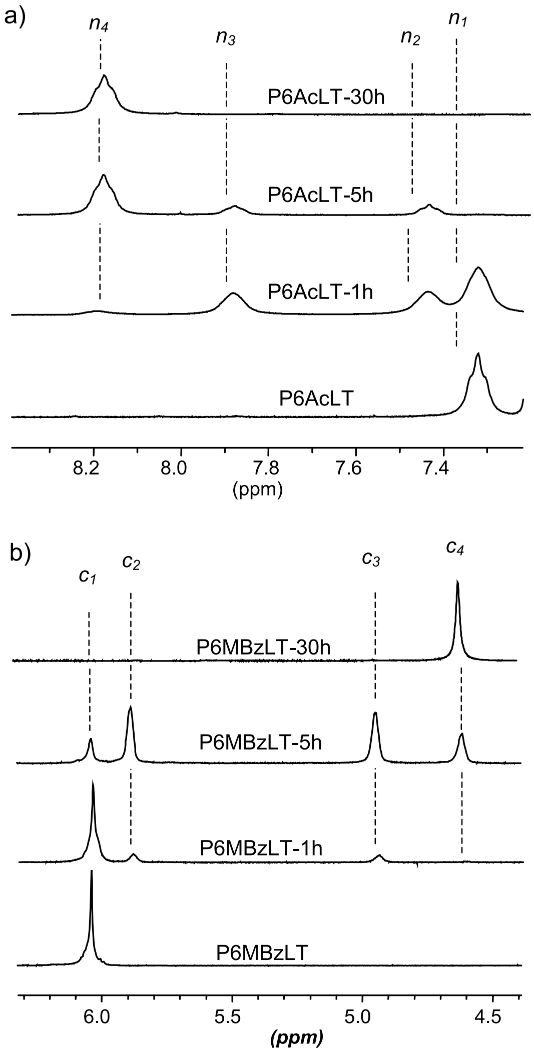


Fig. 4. ^1H NMR spectra: a) N**H** group signals of the P6AcLT, b) C**H** group signals of the P6MBzLT at different time of the hydrolysis.

4. Conclusions

Acylated poly(hexamethylene L-tartaramide)s could be prepared by applying the same methodology previously used for the synthesis of methyl protected polytartaramides. Such polyamides were obtained with molecular weights between 5000 and 20,000 and their basic properties are not significantly different from those displayed by poly(hexamethylene di-*O*-methyl L-tartaramide). The acyl group could be readily removed by controlled hydrolysis to produce the polyamide with free hydroxyl side groups.

Table 3
Side group hydrolysis of polyamides

P6LT-%	Reaction	$[\alpha]_D$[a] (deg)	Elemental analysis[b]			Composition found by NMR[c] (%)				
			C (%)	H (%)	N (%)	X	Y	Z	A	OH
P6LT-27	P6AcLT-1 h	−	51.85 (53.21)	7.27 (7.23)	9.48 (9.60)	50.3	45.9	3.8	73.2	26. 8
P6LT-78	P6AcLT-5 h	−	51.64 (52.53)	7.84 (7.65)	10.38 (11.27)	1.7	40.0	58.3	21.7	78.3
P6LT-11	P6MBzLT-1 h	−94	64.39 (67.10)	6.91 (6.98)	6.27 (6.03)	78.39	20.37	1.23	88.5	11.5
P6LT-52	P6MBzLT-5 h	−35	61.12 (62.63)	7.78 (7.25)	8.28 (7.87)	14.50	66.22	19.28	47.6	52.4
P6LT-100	P6AcLT-30 h	+24	50.00 (52.16)	8.04 (7.88)	11.42 (12.17)	0	0	100	0	100

[a] Specific optical rotation measured at room temperature.
[b] In brackets elemental analysis calculated for the composition determined by NMR.
[c] X: Completely esterified units; Y: partially esterified units; Z: completely hydrolysed units. A: Esterified groups; OH: Hydrolysed groups.

Table 4
Thermal properties and solubility of hydroxy-free poly(hexamethylene L-tartaramide)s

Polyamide	DSC			Solubility						
	T_g (°C)	T_m (°C)	ΔHm (J/g)	H_2O	$CHCl_3$	PhCl	DMSO	NMP	TFE	TFA
P6LT-11	110	143/185	5.2/10.0	−	−	−	+	+	+	+
P6LT-27	–	148/265	21.5/63.7	−	−	−	+	+	+	+
P6LT-52	99	159/193	17.8/5.1	−	−	−	+	+	+	+
P6LT-78	89	243	48.3	−	−	−	+	+	+	+
P6LT-100	89	276	60.1	−	−	−	±	−	−	+

The rate of hydrolysis was found to be depending on the chemical constitution of the acyl group. The thermal properties of polytartaramides were largely modified after complete removal of the ester group but their solubility is not significantly affected.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2005.02.046

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