Hydrolytic Degradation of Polyamides Based on L-Tartaric Acid and Diamines

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SYNOPSIS

This article describes the hydrolytic degradation of a series of nylons based on methylated L-tartaric acid and diamines. These polytartaramides were prepared by a solution polycondensation process using bis(pentachlorophenyl)-2,3-*O*-dimethyl-L-tartrate and *N,N'*-bis(trimethylsilyl)alkanediamines with 6, 8, or 12 methylene groups. The stereoregular optically active polyamides obtained were soluble in chloroform and showed intrinsic viscosities between 1.0 and 2.7 dL g^{-1}. The degradation of these polytartaramides in the form of discs has been investigated in buffered salt solutions of pH 2.3, 7.4, and 10.6, and at temperatures of 37, 55, and 70°C. The degradation was monitored by following the changes in molecular weight, mass loss, chemical constitution, and thermal properties. Our results show that these polytartaramides degrade slowly at 37°C, with a degradation rate highly depending upon the number of methylenes in the diamine unit of the polyamide. The pH of the medium has also a great influence on degradation, as well as the temperature, with an important hydrolysis rate enhancement at 70°C. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Considerable attention has been devoted during the last 25 years to the synthesis and properties of polymers containing unstable linkages in the main chain. The interest in polymers with this property is mainly due to their expanding utilization as degradable materials in medical and pharmaceutical applications and to the increasing concern about the solid waste problem and other ecological considerations.

The most important family of biodegradable polymers are the polyesters. Poly(glycolic acid), which was the first synthetic polymer used as a biodegradable suture, now has a wide field of therapeutic applications. Other synthetic polyesters also used in the same field are poly(lactic acid), poly(caprolactone), and poly(malic acid). Poly(β-hydroxybutyrate) and its copolymers are synthesized by microorganisms, and some bacteria can promote the environmental biodegradation of these polyesters. Other new families of biodegradable polymers lately developed are polyanhydrides and polyorthoesters.[1]

In some biomedical applications, for example, in the fixation of long-bone fractures, it is necessary to employ absorbable polymers with good strength properties capable of maintaining their mechanical performances over long periods of time. For these purposes, synthetic biodegradable polyesters with limited mechanical properties must be reinforced by using methods such as the preparation of block copolymers or composites.

In general, nylons have better mechanical properties than polyesters, but their rates of degradation are too slow for them to be considered as commercial biodegradable synthetic polymers. The low susceptibility to biodegradation shown by nylon 6 and nylon 66 has been increased by introducing some chemical modification in the chain structure of the polyamide. Huang et al.[2] have reported that some benzylated or hydroxylated nylons can be degraded by enzymes such as papain and protease K. Nylons 6 containing α-aminoacids such as glycine or serine are also more susceptible to degradation than commercial nylons, as has been pointed out by Bailey[3] and Gonsalves.[4] In spite of these structural modi-

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fications, the nylons obtained by these means are not degradable enough to be used in practice.

In this context, tartaric acid (2,3-dihydroxybutanedioic acid) is a diacid of interest. It is a natural compound with two asymmetric carbons that can be easily obtained in its three stereochemical forms. Furthermore, it contains a hydroxyl group attached to each α-position of the carboxylic groups. From this point of view, it can be considered close to α-hydroxy acids such as glycolic or malic acids currently used to obtain biodegradable polyesters.

Although tartaric acid and malic acid (2-hydroxybutanedioic acid) are derivatives of succinic acid, their uses as monomers for polymerization are quite different. Malic acid is mainly utilized as a α-hydroxy acid which, after cyclization, is used to prepare polyesters by a ring-opening polymerization process. These polyesters have a structure close to poly(glycolic acid) and poly(lactic acid). Derivatives of poly(malic acid)s are now being developed as biodegradable polymers for controlled release of pharmaceutical drugs.[5] On the other hand, tartaric acid has not been used as a hydroxy acid. It has only been used as a diacid that can be polycondensed with diols or diamines. The polyesters or polyamides obtained by this means bear the two free or substituted hydroxyls as lateral groups in the main chain.

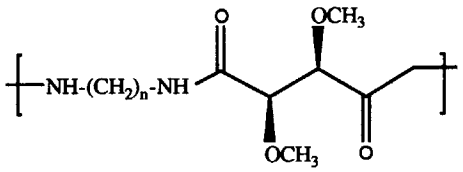
The first polyamides based on tartaric acid were described in 1967 by Minoura.[6] Ogata et al.[7,8] have published a series of articles on the polycondensation in solution of dimethyl-L-tartrate and hexamethylenediamine since 1975. Although these polyamides showed low viscosities, their size and properties could be increased by polymerization in the presence of various polymer matrices or by post-condensation at solid phase. Very recently, our group has published the synthesis of polytartaramides by polycondensation in solution of active esters of 2,3-*O*-subtituted tartaric acid and bis(trimethylsilyl)derivatives of 1,*n*-alkanediamines.[9-11] This method gave, in high yield, polytartaramides that present high viscosities, stereoregularity, and good mechanical properties. The excellent characteristics showed by the polyamides obtained by using this method have prompted us to study some possible applications for these modified nylons.

Several articles have been published about degradation of polymers based on tartaric acid. Polytartrates have been widely studied by Huang,[12] Bitritto[13] and others.[14,15] Only a few articles deal with polyamides. In 1977, Schacht[16] prepared a polymeric pesticide from hexamethylenediamine and dimethyl-L-tartrate bearing 2,6-dichlorobenzaldehyde attached to the adjacent hydroxyl groups. During the hydrolytic studies of the above polytartaramide in acidic medium, a slow release of aldehyde was detected. In this article, there is no data reported on the rate or the degradation mechanism of the polymeric support.

Aikawa[17] studied the microbial degradation of nylons. He compares the degradation by a Coryneform bacterium of some commercial nylons and a polytartaramide obtained from unsubstituted tartaric acid and hexamethylenediamine. A relationship between biodegradability and hygroscopicity is mentioned.

Recently, Akelah et al.[18] have reported the synthesis and the release rates of a pesticide or fertilizer polymeric system based on tartaric acid. 2,4-Dichlorophenoxy and 2-methyl-4-chlorophenoxy acetates of diethyl tartrate were prepared and polycondensated with various diamines. The release rate of chlorophenoxy derivatives from these polytartaramides was monitored and found to depend on the microstructure of the polymer, the temperature, and the pH of the medium. The influence of the microstructure was associated with the hydrophilic character of polymers. The more hydrophilic the polymer backbone, the faster the rate of release. When the experiments were performed at different temperatures, faster release rates were found at 80°, than 50° and 30°C. Finally, the pH effect of the medium was found to vary from one polymer to another.

To our knowledge, no articles have discussed the degradation of polytartaramides in terms of monitoring the action of the medium upon the polymer. The objective of this work has been to fill the gap existing in this type of studies by following the effects produced by buffers of different pH upon the structure of polytartaramides with n = 6, 8, and 12 methylene groups in the diamine unit (PnDMLT).



PnDMLT n = 6, 8 and 12

EXPERIMENTAL

Polymerizations

Polytartaramides were synthesized by polycondensation in solution as previously described.[11]

Spectroscopy

Infrared spectra were registered on a Perkin–Elmer 2000FT-IR spectrometer. Transmission spectra of degraded samples were obtained from small portions of polymer discs dissolved in $CHCl_3$ and cast directly on KBr plates. ATR spectra were recorded using a PE Multiple Internal Reflection Accessory with KRS-5 (thallium bromoiodide) crystal having 45° face angles. The discs were pressed against one side of the crystal, and angles of incidence of 30, 45, and 60° were used. The NMR spectra were recorded on a Bruker AMX300 spectrometer operating at 300.13 and 70.48 MHz for ^1H and ^{13}C, respectively. Sample concentrations in deuterated chloroform were typically 10 mg mL^{-1} and 50 mg mL^{-1} for the ^1H and ^{13}C spectra.

Gel Permeation Chromatography

Determinations were carried out on a system including the following components: pump (Model 510, Water Assoc.); two columns (μ-Styragel, Polymer Lab.) with exclusion limits 10^4 and 10^3 Å, respectively; detector (RI 410, Water Assoc.). Two operating conditions were used: (1) the polyamides were trifluoroacetylated with trifluoroacetic anhydride, and chloroform was used as eluent following the method of Schulz.[19] (2) The unmodified polyamide was dissolved and eluted in a mixture of chloroform and *o*-chlorophenol 95 : 5. For all the experiments, the injected volume was 50 μL; sample concentration 0.25% w/v; flow rate 0.5 mL/min. Molecular weights of polymers were determined relative to polystyrene standards (Polysciences) using a Maxima 820 computer program.

Viscosimetric Methods

Measurements were performed on a No. 150 semimicroviscometer Cannon-Ubbelohde type at 25 ± 0.1°C with dichloroacetic acid as solvent. Efflux times of four concentrations (concentration range 0–1.1 g/dL) were measured and the intrinsic viscosities were determined by the usual extrapolation to zero concentration. $\bar{M}_v$ values were obtained by applying the viscosimetric equation reported for nylon 66:[20]

$$[\eta]_{DCA} = 0.5 + 0.352\bar{M}_v^{0.551}$$

Differential Scanning Calorimetry

These were measured with a Metler TA4000 apparatus calibrated with indium. Thermal transitions (T_g and T_m) of the polymers were determined by heating polymer samples (5–10 mg) from 20 to 260°C at a heating rate of 10°C/min. Second heating thermograms were recorded after a rapid cooling to room temperature.

Polymer Degradation Studies

Films of the polymers were prepared by casting solutions in chloroform onto Petri dishes. The solvent was allowed to evaporate slowly in air at room temperature. Subsequently, the films were cut into discs with a diameter of 14 mm and dried in vacuum. Discs with a thickness of 225–275 μm and a weight of 40–50 mg were selected. For the hydrolysis experiments, each disc was kept in bottles filled to 30 mL with one of the following buffers: (a) 0.1*M* aqueous Na_2HPO_4/KH_2PO_4 with 0.03 wt % of sodium azide (pH 7.4); (b) 0.1*M* aqueous citrate/HCl with 0.03 wt % of sodium azide (pH 2.3); (c) 0.1*M* aqueous $Na_2CO_3/NaHCO_3$ with 0.03 wt % of sodium azide (pH 10.6).

Three temperatures were selected for hydrolysis, so the vials were kept in ovens maintained at 37, 55, or 70°C. After the immersion time, the retrieved samples were thoroughly rinsed with water, dried to constant weight in vacuum, and stored over $CaCl_2$ before analysis.

The following parameters were evaluated: (1) water uptake, (2) mass loss, (3) intrinsic viscosity, (4) loss of molecular weight (MW) and change in molecular weight distribution (MWD), (5) chemical structure, and (6) thermal properties.

RESULTS AND DISCUSSION

In this work we have used three polytartaramide samples with structures composed of *O*-methylated L-tartaric acid and diamines containing 6, 8, and 12 methylene groups. The initial characteristics shown by these samples are displayed in Table I.

Hydrolytic Degradation

In Figure 1 the intrinsic viscosities for the three polytartaramides are plotted against time of immersion at 37°C in buffer at pH 7.4. From this figure the important differences in hydrolytic behavior in these conditions can be observed for the three polyamides studied. For P8DMLT and P12DMLT, the intrinsic viscosity changes during the 240 days of immersion are insignificant. These data suggest that these two polyamides do not degrade in this buffer,

Table I Compared Characteristics of the Three Polytartaramides Used in This Work

Polyamide	m.p. °C	[η] dL/g	M_v[a]	M_n[b]	M_w[b]	M_w/M_n
P6DMLT	228	2.76	178500	29700	84800	2.85
P8DMLT	210	1.56	57400	14500	42000	2.89
P12DMLT	180	1.07	31800	13800	37500	2.72

[a] Calculated by applying the viscosimetric equation reported for nylon 66.
[b] Determinated by GPC with $CHCl_3$ after trifloroacetylation of the polyamide.

or the process seems to occur with extremely slow rates of degradation. For P6DMLT, the figure shows a constant slow decrease of viscosity with time, and therefore, after 240 days of treatment, there is a decrease in viscosity from the initial 2.7 value until the final 1.60 dL g^{-1}.

Figure 2 displays the data for the hydrolysis of P6DMLT and P8DMLT at pH 2.3 and 70°C. In these conditions, P6DMLT degrades quickly. In 11 days of treatment the intrinsic viscosity decreases from 2.7 to 1.18 dL g^{-1}, and 20 days later its value is 0.56 dL/g. P8DMLT clearly degrades at these conditions but at a slower rate than P6DMLT.

The results of experiments performed in different conditions showed that the sensitivity to hydrolysis of the three polytartaramides decreases in the order P6DMLT > P8DMLT > P12DMLT. It can be concluded that the degradation rates are dependent on the length of the alkanoic residue in the diamine units, i.e., slower degradation rates were observed for polytartaramides with longer alkanoic residues.

These differences in degradation are not related to the molecular weights of the samples used in this work because the faster degradation rate is found for the polyamide with a higher MW. More probably, this behavior must be related to properties resulting from the structure of these three polyamides, in particular, to the crystallinity and to the different degrees of hydrophilicity. In fact, the influence of hydrophilicity of polytartaramides has already been reported by Aikawa[17] and Akelah et al.,[18] as has already been mentioned.

In order to get insight into the hydrophilicity of these polytartaramides, we have measured this property in two different conditions. The moisture absorption from powdered polyamides samples was determinated under 100% relative humidity. We found that, after 48 h, P6DMLT had absorbed 10% of moisture, whereas P8DMLT and P12DMLT had gained only 6.4 and 3.2% of moisture, respectively.[11] More significant differences are found when the water uptake by discs of polytartaramides immersed

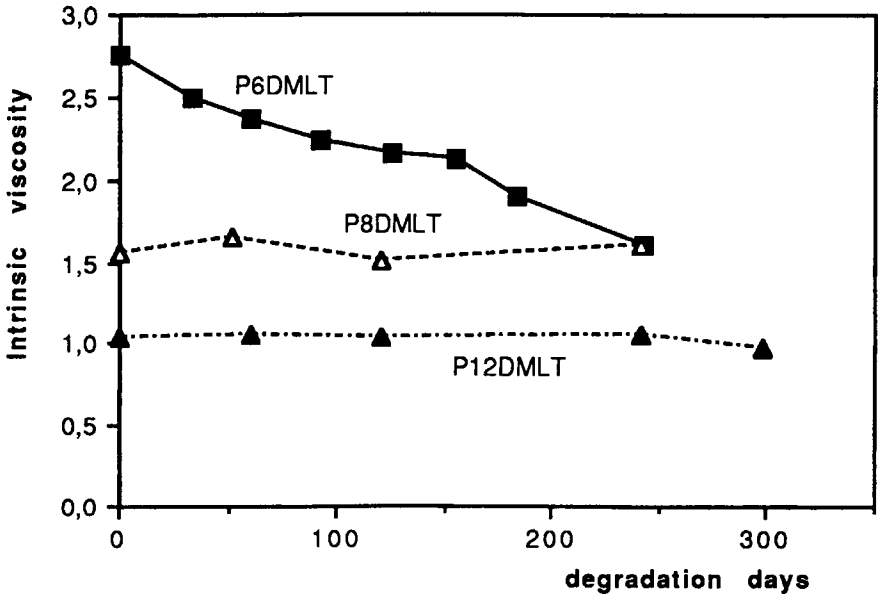


Figure 1 The relation between the intrinsic viscosity and the time of incubation during the degradation of P6DMLT, P8DMLT, and P12DMLT at pH 7.4 and 37°C.

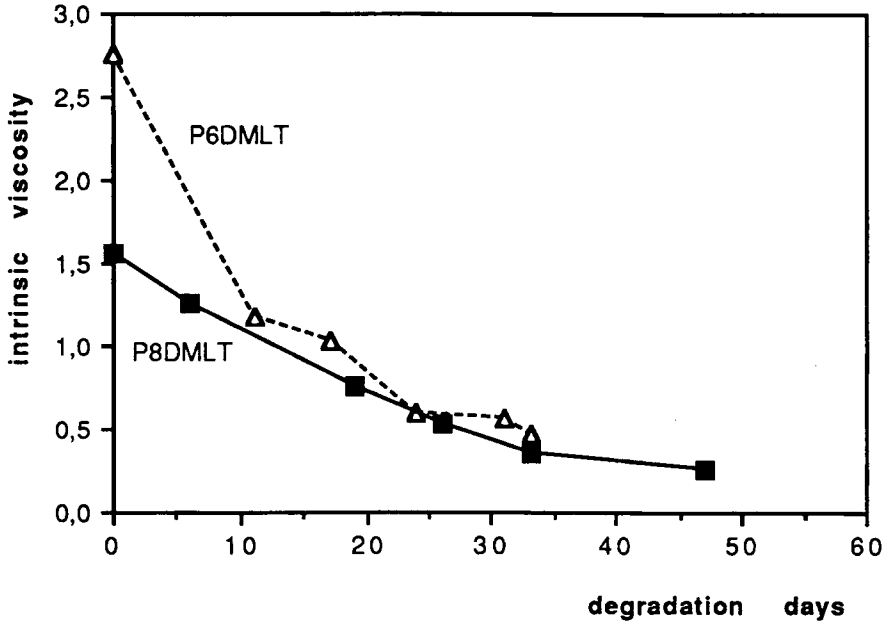


Figure 2 Variation of the intrinsic viscosity of P6DMLT and P8DMLT with the degradation time at pH 2.3 and 70°C.

in distilled water at 37°C is monitored. The data, shown in Figure 3, indicate that P6DMLT absorbs in this conditions, up to 21–26% of water, and this uptake is completed in 3 h. Furthermore, it was necessary to carefully dry the discs between filter papers to reduce the content of water from 26 to 21%. This suggests that the discs of P6DMLT could have a porous structure. On the other hand, P8DMLT and P12DMLT take up water at a slower rate. They increased their wet weight by 11 and 5%, respectively, and the discs easily reached constant wet weight when they were dried with filter paper. The results obtained confirm that the hydrophilicity in the three polytartaramides varies in the order P6DMLT > P8DMLT > P12DMLT. Indeed, it seems that P6DMLT is far more hydrophilic than P8DMLT

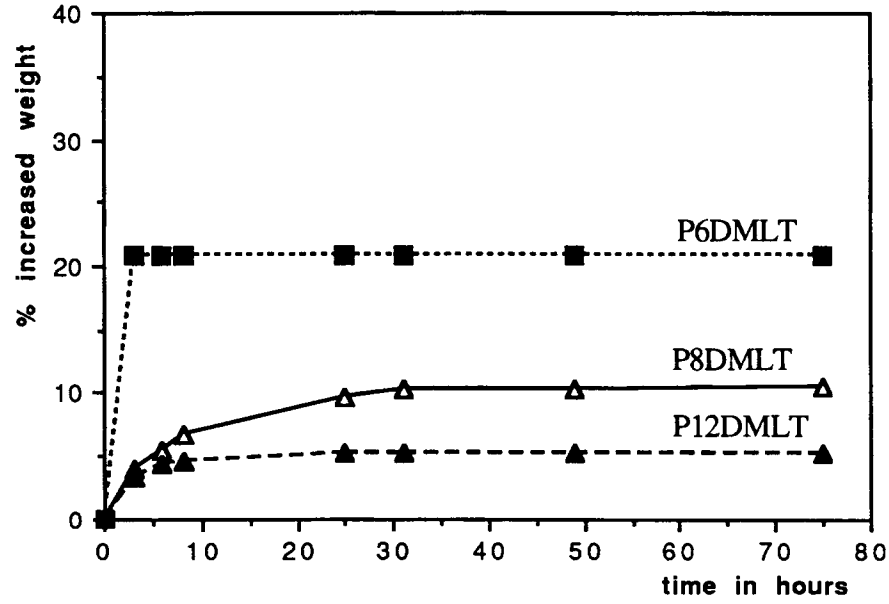


Figure 3 Water uptake of polytartaramide discs immersed in water at 37°C as a function of time.

and P12DMLT. This difference could explain the differences in degradation existing between P6DMLT and the other two polytartaramides.

Some characteristics of the P6DMLT hydrolysis in buffer pH 7.4 at 37°C are displayed in Figure 4. It shows that the molecular weight decrease starts from the onset of the experiment. Because an induction period for molecular weight loss usually reflects the time required for water to permeate the polymer mass completely, the lack of induction period found for P6DMLT confirms that water can penetrate rapidly into the polymer structure in accordance with our results shown in Figure 3.

Figure 4 also shows the water uptake data. The results show a gradual increase in water content with time that reached 40% after 1 year in the buffer. These values are best analyzed when compared with changes in $\bar{M}_n$ shown in the same figure. The increase in wet weight is simultaneous with the decrease in $\bar{M}_n$. Therefore, the increase in hydrophilicity must be associated with cleavage of amide bonds. As, in this period of degradation, the chain scission is assumed to take place preferably out of the crystalline region, the increase of weight is due to swelling in the amorphous phase of the polyamide.

Mass loss profile is also shown in Figure 4. The data show that a mass loss of 13% took place immediately at the beginning of the experiment and, after this initial decrease, mass remained unchanged during the year of incubation. This initial mass loss is present in all our degradation experiments with these polytartaramides. It is attributed by us to the exit to the medium of small molecules formed during the polymer preparation by polycondensation.

When the evolution of $\bar{M}_n$ and residual weight for P6DMLT are compared in Figure 4, it can be seen that the initial weight loss is followed by a long period of constant residual weight, during which the molecular weight decreases. This is known to be a common indication that the degradation of a polymer occurs simultaneously throughout the sample. These data suggest that the hydrolysis of this polyamide is a bulk degradation process.

Effect of pH

Three buffers were selected to evaluate the effect of the pH on degradation. For this, the hydrolysis experiments were carried out using 0.1M, pH 7.4 phosphate; 0.1M, carbonate pH 10.6; and 0.1M, citrate pH 2.3 buffers. Results obtained for polytartaramides under study are very similar. These results showed a special sensitivity of the amide bond in polytartaramides to basic medium compared with neutral and acidic media. Furthermore, when data obtained at neutral and acidic media are compared it must be pointed out that these polyamides were degraded at a slightly slower rate in acidic than in neutral buffer.

Table II summarizes the data corresponding $\bar{M}_v$, $\bar{M}_n$ and intrinsic viscosities of P6DMLT degraded at 37°C. The changes in $\bar{M}_n$ obtained from GPC for

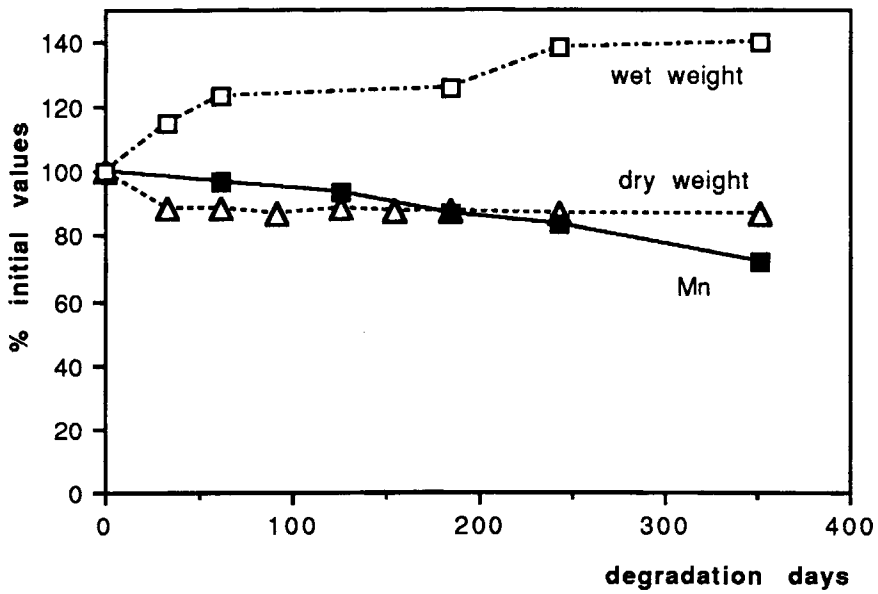


Figure 4 Change of water uptake (wet weight), mass remaining (dry weight), and molecular weight ($\bar{M}_n$) vs. the degradation time for P6DMLT at 37°C in buffer pH 7.4. $\bar{M}_n$ values were obtained by GPC in $CHCl_3$-*o*-chlorophenol.

Table II Viscosities and Molecular Weight of P6DMLT Discs after Degradation at 37°C

Time Days	pH = 2.3			pH = 7.4			pH = 10.6		
	[η] dL/g	M_v[a]	M_n[b]	[η] dL/g	M_v[a]	M_n[b]	[η] dL/g	M_v[a]	M_n[b]
0	2.76	178500	42600	2.76	178500	42600	2.76	178500	42600
13	—	—	—	—	—	—	1.41	52200	32100
21	—	—	—	—	—	—	1.19	38600	—
33	2.77	179500	—	2.50	149100	—	0.99	27600	21700
55	—	—	—	—	—	—	0.82	19600	—
61	—	—	43100	2.36	134700	40700	—	—	18000
92	—	—	—	2.24	122100	—	—	—	—
126	2.21	119600	42000	2.15	113300	39500	0.65	11900	11000
155	—	—	—	2.12	110400	—	—	—	—
184	1.91	91800	38300	1.90	90800	36400	0.46	6900	8800
243	—	—	—	1.60	66000	35200	—	—	—
292	—	—	34900	—	—	—	—	—	—
351	—	—	—	—	—	30500	—	—	—

[a] Calculated by applying the viscosimetric equation reported for nylon 66.
[b] Obtained by GPC of P6DMLT in $CHCl_3$-*o*-chlorophenol 95 : 5.

P6DMLT at 37°C are plotted in Figure 5. The data confirm the fast hydrolysis rate at pH 10.6 and the slower one at pH 7.4 and 2.3 shown by this polyamide. In fact, in neutral and acidic buffers the degradation is a linear type, characterized by a slow and constant decrease of $\bar{M}_n$ values throughout the experiment. After a year of treatment, the final $\bar{M}_n$ was about 75% of the initial value. In basic medium, the pattern of degradation is different. It is parabolic type, characterized by a fast decrease of $\bar{M}_n$ in the first 50 days of hydrolysis, where the $\bar{M}_n$ changed to one-half of the initial value. Then, the variation of $\bar{M}_n$ steadily fell with time, and after 200 days in the buffer the final $\bar{M}_n$ value was about 20% of the initial.

In Figure 6 is plotted the erosion profile of P6DMLT at 37°C and various pHs. Weight loss figures are given in Table III. From these data, it is

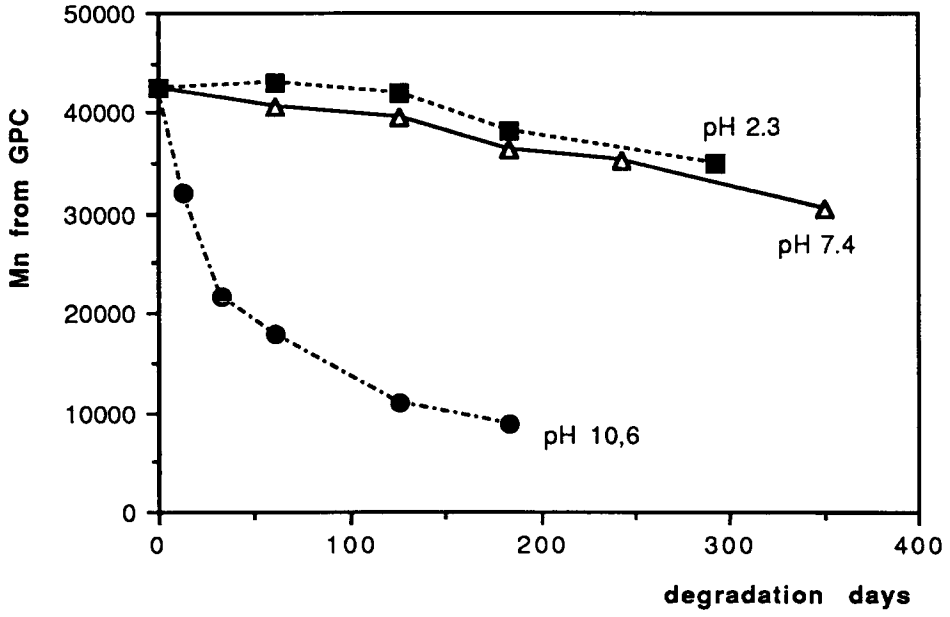


Figure 5 Effect of pH on degradation of P6DMLT at 37°C. Molecular weight decrease vs. time. $\bar{M}_n$ values were obtained by GPC in $CHCl_3$-*o*-chlorophenol.

seen that the weight loss of the discs is also influenced by the pH of the medium. In acid and neutral media, the erosion profile is the same. It is characterized by the fast loss of 12–13% of the initial weight at the start of the experiment, after which the weight remained unchanged throughout the whole period of study. On the contrary, in basic medium, after the initial loss, a continuous weight loss was observed reaching a final weight of 68% of initial value after 243 days of treatment.

Effect of Temperature

The influence of temperature on PnDMLT incubated in buffers was studied at 37, 55, and 70°C. The effect, for example, on P8DMLT at pH 7.4 in Figure 7 shows that degradation at 37°C takes place at an extremely slow rate. At 55°C the rate is slightly faster, whereas at 70°C the rate is increased several times compared to that at 55°C.

This sensitivity to temperature is too high to be attributed only to a normal Arrhenius effect. The drastic increase of the hydrolysis rate at 70°C can be explained in terms of T_g and the plastic effect caused by the molecules of water absorbed by the polyamides immersed in the buffer. The normal values of T_g for these dried polytartaramides are about 110°C, but this value must decrease when the samples are immersed in the buffer. Thus, in the process of degradation at 70°C, the polymer would be above its T_g, which facilitates the diffusion of salts contained in the buffer into the amorfous areas.

Table III Erosion of P6DMLT Discs after Degradation at 37°C

Time Days	Initial Weight Remaining %		
	pH = 2.3	pH = 7.4	pH = 10.6
0	100.0	100.0	100.0
13	—	—	91.1
21	—	—	90.8
33	87.0	88.8	86.8
55	—	—	84.8
61	87.2	88.3	—
92	86.8	87.3	83.0
126	87.1	88.7	82.0
155	87.9	88.0	—
184	88.0	87.9	—
243	—	87.3	67.7
292	86.2	—	—
351	—	86.8	—

GPC Analysis

GPC was used to monitor the changes in molecular weight and molecular weight distributions of polytartaramides during this study. In general, the choice of an appropriate eluent for the GPC analysis of polyamides is a problem that has not yet been sat-

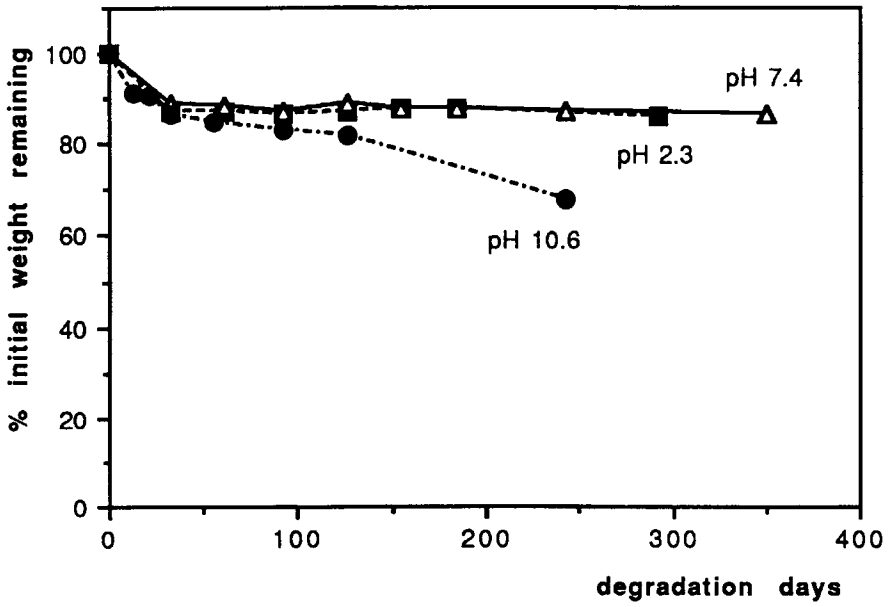


Figure 6 Effect of pH on degradation of P6DMLT at 37°C. Initial weight remaining change vs. time. (△) pH 7.4; (■) pH 2.3; (●) pH 10.6.

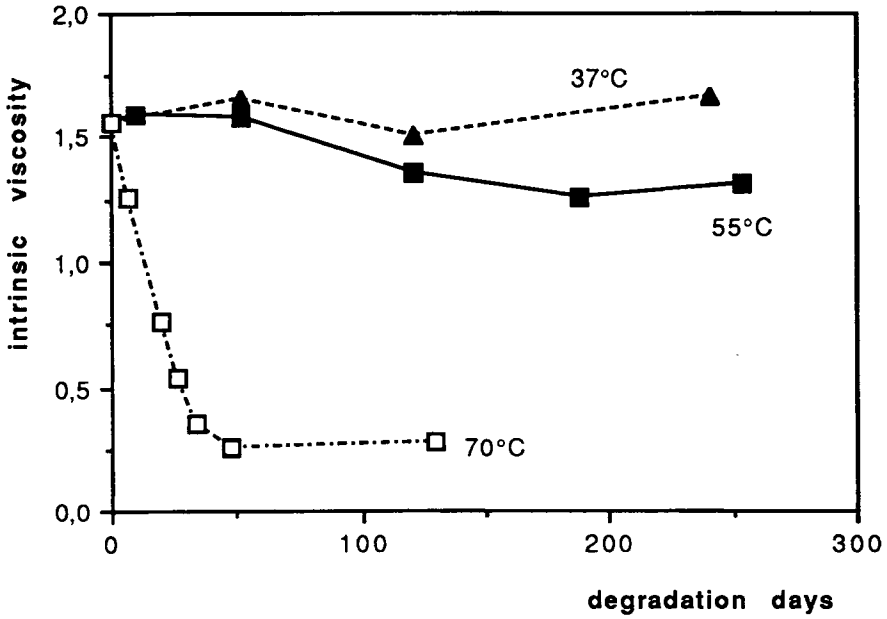


Figure 7 Effect of temperature on hydrolytic degradation of P8DMLT at pH 7.4. Decrease of intrinsic viscosity with time of degradation.

isfactorily resolved. Polyamides are not soluble in chloroform, THF, or toluene, the solvents commonly used for GPC. For this reason, the GPC of these polymers has to be developed under drastic conditions by using either highly polar solvents such as phenols, or at high temperatures with benzyl alcohol as eluent. Recently, mild methods have been used. These involve either the use of expensive fluorinated alcohols where the polyamides are soluble or the reaction with trifluoroacetic anhydride. This second reaction accomplishes a trifluoroacetylation of the NH groups of aliphatic polyamides, making them soluble in common organic solvents.

Although our polytartaramides are readily soluble in chloroform, we have already pointed out that GPC curves obtained in this eluent are complexes, probably due to the occurrence of aggregations.[9,11] In order to break these aggregations, a low proportion of a highly polar solvent such as *o*-chlorophenol was added to chloroform. When the mixture chloroform-*o*-chlorophenol 95 : 5 is used as eluent at room temperature, well-shaped chromatograms are obtained. We have used this system as a routine method to monitor the variation of molecular weight during the treatment with buffers.

Furthermore, we have completed our GPC analysis by using a second system. Because GPC analysis by trifluoroacetylation was the method used in our previous studies with these polytartaramides, we have also used this well-known method to contrast the results obtained with those of the mixture chloroform-*o*-chlorophenol 95 : 5.

As an example, GPC was used to follow the degradation of P6DMLT at pH 2.3 and 70°C. Table IV summarizes some parameters of this process, and Figure 8 displays the molecular weight evolution during hydrolysis in the above conditions. It is shown that $\bar{M}_n$ curves obtained by both GPC methods have the same shape and are very close to each other. In general, $\bar{M}_n$ values obtained with TFA–P6DMLT in $CHCl_3$ are lower than those obtained with P6DMLT except with samples of very low MW where the values are almost coincident.

On the contrary, the two chromatographic methods differ clearly in their $\bar{M}_w$ values. Those obtained with the TFA–P6DMLTA method are much lower. Another difference between the methods are the polydispersity values. The curves corresponding to $\bar{M}_n$ and $\bar{M}_w$ for the trifluoroacetylated polymer are almost parallel. Thus, the polydispersity index is maintained constant during the entire degradation period, as is shown in Table IV. The chromatograms obtained in $CHCl_3$-*o*-chlorophenol yield values of $\bar{M}_w$ too high to be considered. With this eluent, the obtained ratio $\bar{M}_w/\bar{M}_n$ is not constant throughout the experiment, but it decreases steadily, reaching a value near 2 at the end of the experiment.

The two GPC methods showed that the degradation of P6DMLT at pH 2.3 and 70°C follows a parabolic pattern. Our results indicate that the hy-

Table IV Molecular Weight Distributions and Weight Loss of P6DMLT Discs after Degradation in Buffer at pH 2.3 and 70°C

Time Days	Initial wt Remaining %	$[\eta]$ dL/g	M_v[a]	M_n[b]	M_n[c]	M_w[c]	M_w/M_n
0	100.0	2.76	178500	40700	29700	84800	2.85
11	87.8	1.18	38000	26700	17500	35700	2.04
17	87.1	1.04	30200	22700	—	—	—
24	84.4	0.60	11100	13700	10800	19300	1.78
31	80.7	0.56	9700	—	—	—	—
35	80.6	—	—	10600	—	—	—
59	—	—	—	5600	6000	12300	2.05
137	56.0	—	—	3100	5000	10100	2.01

[a] Calculated by applying the viscosimetric equation reported for nylon 66.
[b] Obtained by GPC of P6DMLT with $CHCl_3$-*o*-chlorophenol 95 : 5 as eluent.
[c] Data from GPC of trifluoroacetylated P6DMLT with $CHCl_3$ as eluent.

drolysis is characterized by a rapid decrease in $\bar{M}_n$ during the first period of degradation and a slower decrease taking place with low MW samples obtained in the final stages.

The GPC chromatograms of P6DMLT in $CHCl_3$-*o*-chlorophenol 95:5 as a function of incubation time are presented in Figure 9. The MWD curve corresponding to undegraded polymer showed a long tail due to the low MW molecules initially present in the sample. This long tail causes the wide MW distribution found for these samples in this eluent. After 17 and 24 days of hydrolysis, the curves are shifted toward lower values due to the splitting of the high MW molecules producing mainly medium MW molecules. At these stages of the degradation process the curves still showed the tail due to small molecules. Finally, after 137 days, only low MW molecules are present in the degraded disc and the tail is faintly shown in the curve. In this degraded disc, the final MW distribution approached a value near 2.

DSC Measurements

Figure 10 shows the DSC thermograms of P6DMLTA as a function of degradation time at pH 2.3 and 70°C. Figure 10(B) shows the traces corresponding to first heating, which are all characterized by two clear endothermic peaks corresponding to two melting points. This is a common feature in polyamides, related to the fusion of populations of crystallites differing in size or lamelar thickness. The existence of two melting peaks in the chromatograms is a serious obstacle to compare the melting enthalpy of these samples. This feature also prevents the use of DSC measurements to follow the quantitative change of crystallinity during degradation.

The curve of the undegraded P6DMLT shows two melting peaks with different areas. The peak corresponding to the low melting point is clearly smaller than that corresponding to the higher melting temperature. It is seen in the figure that the relative intensity of the two peaks varies with the time of degradation. Indeed, the area of the first peak increases or the area of the second peak decreases.This indicates that the tendency to hydrolysis is not the same in both crystallites.

Moreover, there is a gradual shift of the peaks toward lower temperatures with degradation. This is a consequence of a decrease of melting points with the molecular weight diminution. Table V summarizes the melting points, the glass transition temperatures, and the heats of fusion corresponding to P6DMLT degraded in the above-mentioned conditions.

Figure 10(A) displays the traces corresponding to second heating. Now, in all the cases the T_g is clearly shown, and a single melting peak appears on each curve. For samples with low molecular weight, an exothemic peak appearing near 140°C is interpreted as the result of a crystallization phenomenon. As in the first heating, the melting peaks and T_g shift to lower temperatures with time of incubation. These shifts are not important when the macromolecules maintain high molecular weight, but they become significant for $\bar{M}_n$ below 10,000.

X-Ray diffraction methods were used with the purpose of measuring the qualitative and quantitative changes in crystallinity that may occur during the hydrolysis. For example, the degradation of P6DMLT at pH 2.3 and 70°C was followed by taking x-ray diagrams from small parts of the discs after the incubation. The results obtained were not encouraging because the x-ray patterns for the whole

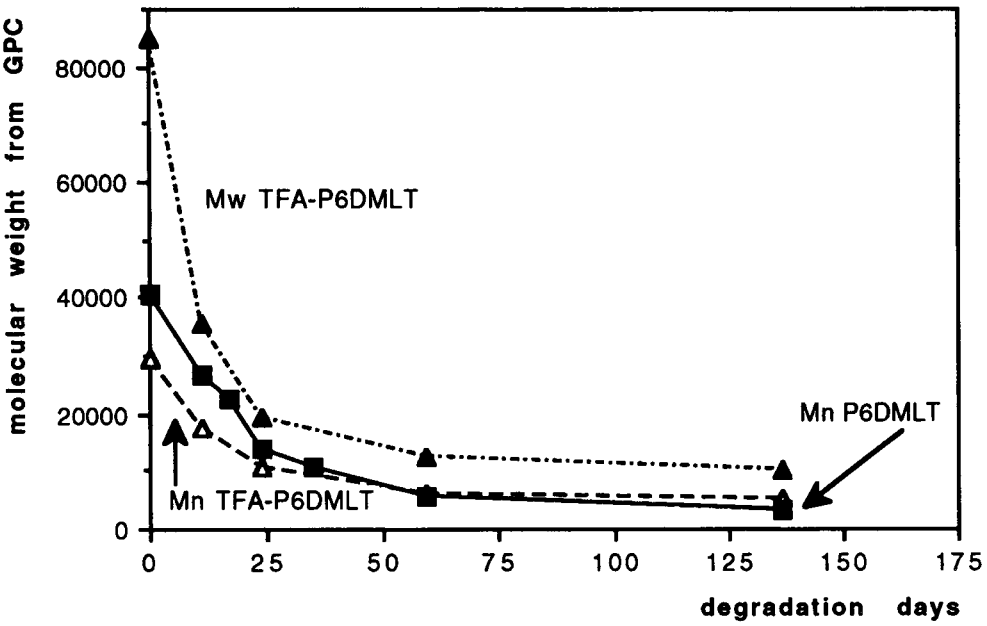


Figure 8 Changes in molecular weight of P6DMLT during the hydrolytic degradation at pH 2.3 and 70°C. (▲) $\bar{M}_w$ of triflouroacetylated P6DMLT by GPC in $CHCl_3$; (△) $\bar{M}_n$ of triflouroacetylated P6DMLT by GPC in $CHCl_3$; (■) $\bar{M}_n$ of P6DMLT by GPC in $CHCl_3$-*o*-chlorophenol 95:5.

series were identical, even for samples with important intrinsic viscosity differences, i.e., 2.76 and 0.5 dL/g. When the densitometric readings of the diagrams were outlined, the figures so obtained showed no peak intensity differences.

In a study of the hydrolysis of substituted polytartaramides it is important to verify which bond was being cleaved during the degradation, i.e., the amide bond of the main chain, the ether bond of the methoxy protecting groups, or the C—C bond be-

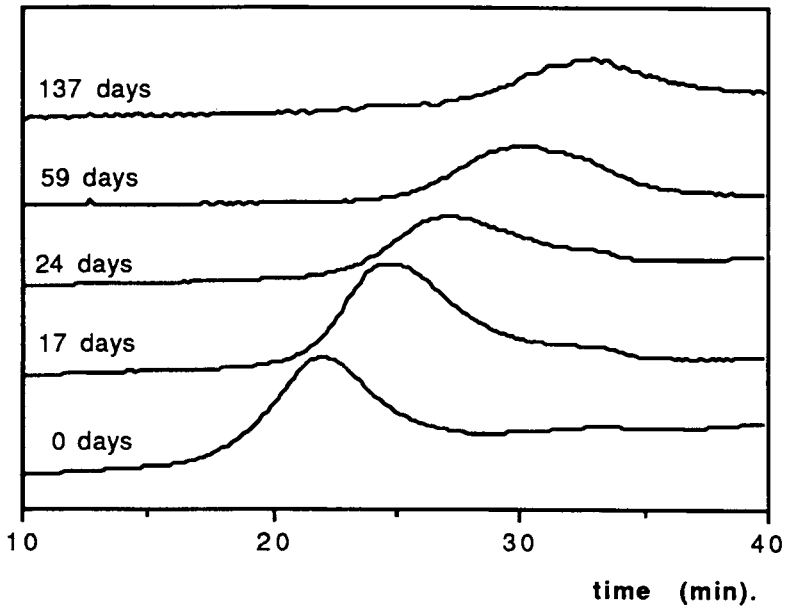


Figure 9 GPC chromatograms of P6DMLT degraded at pH 2.3 and 70°C as a function of immersion time. Chromatograms were obtained with $CHCl_3$-*o*-chlorophenol 95 : 5 as solvent.

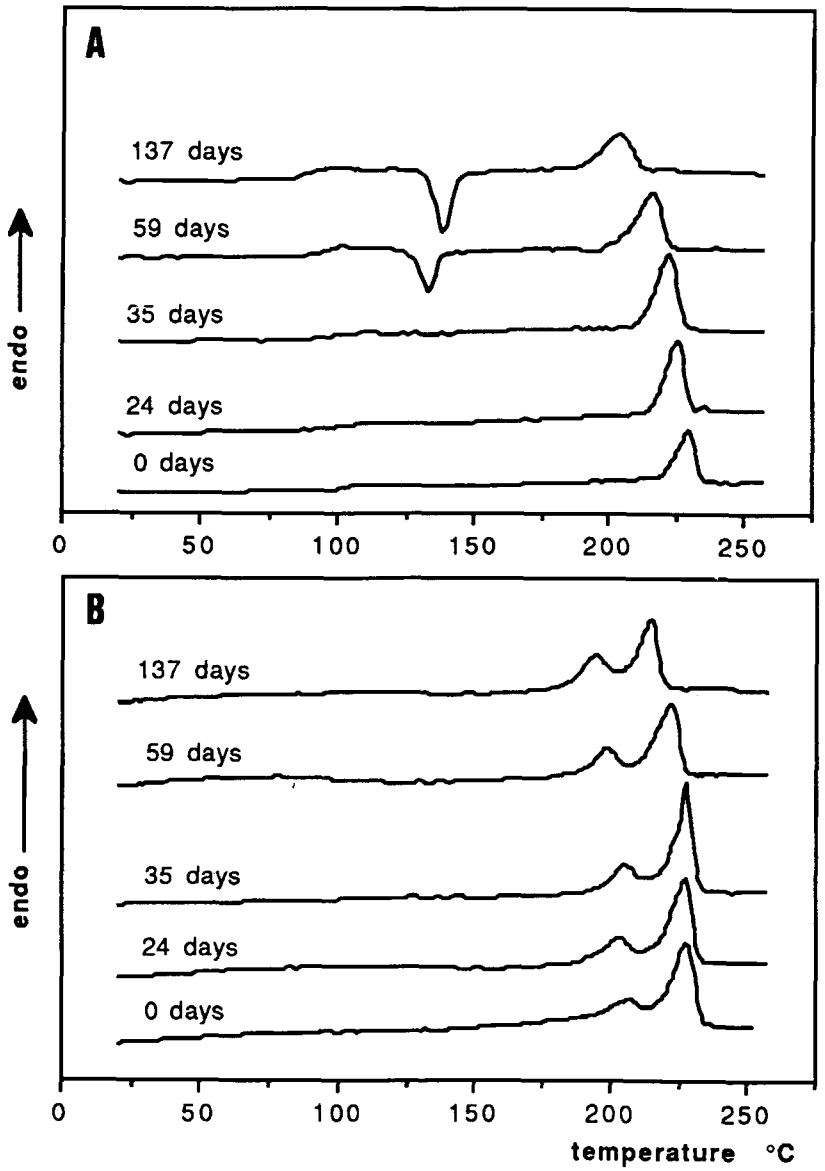


Figure 10 DSC curves of P6DMLT degraded at pH 2.3 and 70°C as a function of immersion time. (A) Thermograms corresponding to second heating. (B) Thermograms corresponding to first heating.

tween the two substituted alpha-carbons in the tartaric unit. In order to identify which bond is preferentially split during hydrolysis, samples of P6DMLTA and P8DMLTA with different degrees of degradation were analyzed by FT-IR (either with or without ATR), ^{1}H-NMR, and ^{13}C-NMR. The results for all the degraded samples analyzed were identical to the corresponding undegraded polymers.

In the final stages of degradation in buffer pH 2.3 at 70°C, samples of P8DMLTA showed limited solubility in chloroform. A sample with these characteristics was extracted with $CHCl_3$, and then the solution and the residue were compared spectroscopically. The two fractions displayed identical IR and ^{1}H-NMR, and only minor differences appeared on ^{13}C-NMR. Therefore, the similarity between the depolymerization products and the original polymers as determined by IR and NMR seems to support the hypothesis that the decrease in molecular weight in polytartaramides was mainly a depolymerization process so that chain cleavage by a simple hydrolytic mechanism seems to be the only change taking place in these polytartaramides during the process of degradation studied.

Table V Changes in Physical Properties of P6DMLT Discs after Degradation in Buffer at pH 2.3 and 70°C

Time Days	M_n[a]	T_{m_1}°C[b]	ΔH Fusion[c] J/g	T_g°c	T_{m_2}°C[d]	ΔH Fusion[d] J/g
0	40700	228.4	56.7	103.0	229.5	31.1
11	26700	—	—	—	—	—
17	22700	—	—	—	—	—
24	13700	228.2	70.8	99.2	225.8	36.1
31	—	—	—	—	—	—
35	10600	228.1	71.6	96.0	222.4	42.5
59	5600	222.4	73.5	94.8	216.6	44.1
137	3100	215.4	73.3	88.9	203.9	29.1

[a] Data of GPC are included for comparison.
[b] Corresponding to the higher of the two melting peaks found during the first heating.
[c] Obtained from the area of the two melting peaks.
[d] Corresponding to the second heating.

CONCLUSION

Results of this work demonstrate that high molecular weight polyamides containing *O*-substituted L-tartaric acid as the diacid unit undergo degradation in an aqueous medium by a simple hydrolytic mechanism.

The degradation of polytartaramides is characterized by slow rates that have been proved to be highly dependent on the length of the diamine unit. Our data show that the rate of degradation increases with the decrease of the number of methylenes in the diamine units. Hydrophilicity also increases in the same order, and it is believed that this has an important influence on degradation rate in agreement with data published by other authors either for polytartaramides or polypeptides.

During the treatment with buffers at different pHs and temperatures, it was found that the hydrolysis is strongly base catalyzed. The process is also influenced by temperature with an important hydrolysis rate increase at 70°C. The splitting of the molecules takes place owing to random chain scission of the amide group, as is suggested by the molecular weight changes. With samples in the form of disc, data of profile erosion showed that the process occurs throughout the whole polymer matrix.

We find that viscometric, GPC, and DSC methods are useful for monitoring structural processes accompanying polytartaramide hydrolysis. On the other hand, due to the scarce chemical and crystallographic changes occurring during hydrolytic degradation of these polymers, IR and NMR spectroscopy or x-ray wide-angle analysis were not useful tools.

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