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**“Synthesis, characterization and biomedical
applications of microbial polymalic
and polyglutamic acids derivatives.”**

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Trabajo realizado bajo la dirección de los Drs.
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Thermal Decomposition of Fungal Poly(β ,L-malic acid) and Poly(β ,L-malate)s

Summary

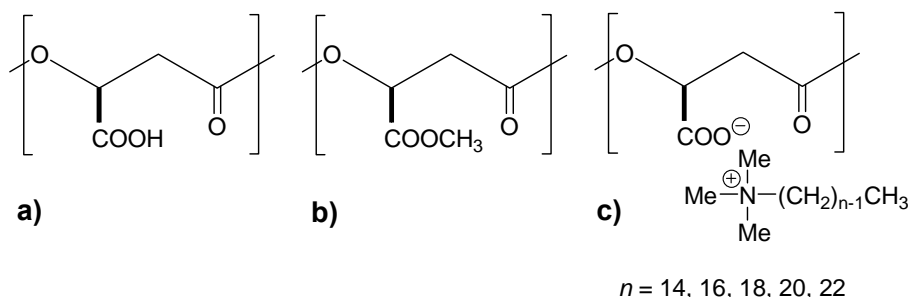
The thermal decomposition of poly(β ,L-malic acid), poly(α -methyl β ,L-malate), and ionic complexes of the polyacid with alkyltrimethylammonium salts was studied by TGA, GPC, and FTIR and NMR spectroscopy. It was found that poly(β ,L-malic acid) depolymerized above 200 °C by an unzipping mechanism with generation of fumaric acid which is then partially converted in a mixture of maleic acid and anhydride. On the contrary, random scission of the main chain was found to happen in the thermal decomposition of poly(α -methyl β ,L-malate). On the other hand, ionic poly(β ,L-malate)s degraded through a well defined three-stage process, the first one being depolymerization of the poly(malate) main chain along with decomposition of the ionic complex. Decomposition of the previously generated alkyltrimethylammonium salts followed by unspecific cracking of the resulting nitrogenated compounds happened at higher temperatures. Mechanisms partially explaining the decomposition processes of the three studied systems were proposed according to collected data.

6.1. Introduction

Poly(malic acid) (PMLA) is a carboxylic-functionalized polyester that may be produced by chemical synthesis or by biological fermentation by myxomycetes and certain filamentous fungi. Both α - and β -structures, either racemic or optically pure, may be obtained by chemical methods whereas microorganisms exclusively produce poly(β ,L-malic acid) of extremely high optical purity.¹ Since production costs by both methods are fairly high, PMLA is hardly accessible and its properties and applications have not been extensively investigated so far. Nevertheless, PMLA is a perfectly biodegradable and biocompatible polymer with exceptionally good features to function as a drug carrier to which tissue-specific tags can be covalently attached. Thus, a PMLA-based nanoconjugate consisting of several functional modules and being able to cross the blood-brain barrier (BBB) has been recently reported for brain cancer chemotherapy.² PMLA is readily water-soluble and is hydrolyzed very fast in aqueous environment, unless special precautions are taken.

The hydrolysis of synthetic PMLA has been extensively studied by Braud and Vert.³ Blocking the carboxylic side groups of PMLA has been a strategy conveniently used to modify its properties and simultaneously to slow hydrolysis. Methylation of PMLA with diazomethane renders poly(α -methyl β ,L-malate) (PAALM-1) neutral, which is a non-water-soluble crystalline product that melts around 150 °C without significant decomposition.⁴ PAALM-1 is an interesting derivative of PMLA that displays a completely different pattern of properties, assumed to retain the good biological behavior of the parent polyacid.

Coupling of PMLA with cationic surfactants of the ammonium salt type bearing long alkyl chains has been applied to produce stoichiometric ionic complexes (n ATMA·PMLA), which are soluble in organic solvents, but not in water.



Scheme 1. Chemical structures of species studied in this work. a) PMLA; b) PAALM-1; c) n ATMA·PMLA complexes.

These comblike ionic poly(malate)s adopt a biphasic amphiphilic nanostructure that melts reversibly at 30-80 °C and that may lodge hydrophobic drugs within the paraffinic subphase.⁵ The development of new derivatives of PMLA capable of being processed by thermal methods has created the need for knowledge on their thermal behavior.

However, the information that is available at present on thermal stability and the nature of degradation products of PMLA and its derivatives is extremely scarce. Holler reported in 1997 that PMLA produced by *Physarum polycephalum* decomposed above 200 °C,⁶ and more recently, a brief study based exclusively on FTIR analysis stated that fumaric acid was the main product that originated when PMLA was heated at 240 °C under an inert atmosphere.⁷

Somewhat different data were given for PMLA produced by *Aureobasidium* strains.⁸ Regarding poly(malate)s, both covalent and ionic, data are restricted to TGA parameters recorded by routine essays. This situation is in high contrast to that given for poly(β -hydroxy alkanoate)s, a related class of aliphatic polyesters, whose thermal degradation behavior has been extensively examined.⁹⁻¹² In this work, a detailed study on the thermal degradation of PMLA, PAALM-1, and *n*ATMA·PMLA complexes is carried out using a combination of analytical techniques. The purpose is to characterize the thermal behaviour of these compounds and to elucidate as deep as possible the reaction mechanisms underlying the degradation processes.

6.2. Experimental

6.2.1. Materials. PMLA used in this work was obtained spectroscopically pure by cultivation of *Physarum polycephalum* and subsequent purification as described in detail elsewhere.⁶ Methylation of PMLA was accomplished according to a previously reported method based on the reaction with diazomethane.⁴ Stoichiometric complexes *n*ATMA·PMLA were prepared by mixing PMLA and the corresponding alkyltrimethyl ammonium bromides *n*ATMA·Br, with *n* = 14, 16, 18, 20, and 22, according to previously described procedure.⁵

The main features of all these compounds in relation to the present study are given in Table 1. Infrared spectra were recorded using a Perkin-Elmer FT2000 instrument provided with a heating device. Typically, 80-100 mg of dried KBr and the appropriate amount of sample were ground extensively, and the disk was prepared in the usual way.

Gel permeation chromatography (GPC) was performed using a Waters equipment provided with a multimode Wyatt light-scattering detector. NMR spectra were recorded on a Bruker AMX-300 NMR instrument with samples dissolved in CDCl₃, either pure or after addition of trifluoroacetic acid, and using TMS as internal reference. Sample concentrations of about 1% (w/v) were used for these analyses. Both PMLA and PAALM-1 were chromatographed using 0.005 M sodium trifluoroacetatehexafluoro-2-propanol (NaTFA-HFPI), and molecular weights were absolutely estimated using a refractive index increment dn/dc of 0.160 mL·g⁻¹, which was previously determined for the PAALM-1-HFIPsystem.

All thermogravimetry (TGA) experiments were carried out in a thermobalance Perkin-Elmer TGA6 under a circulating nitrogen flow. Sample weights of about 15 mg were used in dynamical experiments. Samples were heated from ambient temperature to 500 °C at heating rates of between 2 and 40 °C·min⁻¹ were used, and sample temperature and weight were continuously recorded. Conversely, isothermal essays were carried out with sample weights of 40 mg in order to provide sufficient amounts of residual product for subsequent spectroscopy and chromatography analyses.

For the analysis of volatile emanating from decomposition, pyrolysis was performed using larger amounts of samples in a flask provided with a coldfinger to collect the condensed gases.

Table 1. Data of compounds subjected to study.

Compound	M_w^a	PD ^a	T_m^b (°C)
PMLA	36 200	1.25	216
PAALM-1	33,000	1.40	151
<i>n</i> ATMA·PMLA			
14ATMA·PMLA	106,000	1.25	n.o.
16ATMA·PMLA	115,100	1.25	30
18ATMA·PMLA	123,800	1.25	48
20ATMA·PMLA	132,400	1.25	60
22ATMA·PMLA	141,100	1.25	71
18ATMA·Br	404	-	107

^aWeight-average molecular weight and polydispersity determined by GPC. Values for complexes calculated from PMLA data taking into account corresponding repeating unit. ^bMelting temperature. For ammonium salts, refers to melting of the paraffinic phase.

6.3. Results and discussion

6.3.1. Thermal Degradation of PMLA. The TGA trace for PMLA recorded at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ under circulating nitrogen is shown in Figure 1a. The weight loss concomitant to degradation is seen to occur between 200 and 300 $^{\circ}\text{C}$, the residual material left at the end of the treatment being approximately 3% of the initial mass.

The $\sim 10\%$ of weight loss that is observed at temperatures below 150 $^{\circ}\text{C}$ corresponded to the release of water absorbed in the PMLA sample. The derivative curve consists of a main peak at 245 $^{\circ}\text{C}$ with two minor shoulders at 220 $^{\circ}\text{C}$ and 270 $^{\circ}\text{C}$, indicating that the decomposition process apparently involves three differentiated steps with weight losses of 20, 80, and 97% of the initial value, respectively.

The effect of the heating rate β within the $2\text{-}30\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ range is depicted in Figure 1b. As expected, the traces are moved to higher temperatures for increasing heating rates, whereas the three-stage decomposition pattern remains practically unmodified.

The volatile and residual products generated in every step of the thermal degradation of PMLA were analyzed by FTIR and NMR spectroscopy and by size exclusion chromatography. The onset of decomposition was characterized by following the changes that were seen in the FTIR spectra recorded at increasing heating from room temperature up to 270 $^{\circ}\text{C}$ at intervals of 5 $^{\circ}\text{C}$. Selected spectra are compared in Figure 2 demonstrating the occurrence of significant changes within the 200-220 $^{\circ}\text{C}$ range.

Around 210 $^{\circ}\text{C}$, absorption bands at 1270, 1010, and 645 cm^{-1} characteristic of fumaric acid started to appear whereas the absorbance at 1045 cm^{-1} arising from the stretching of the C-O-C main chain group decreased. Such changes were accentuated upon further heating to the point that the spectrum of fumaric acid was only observable at the end of experiment.

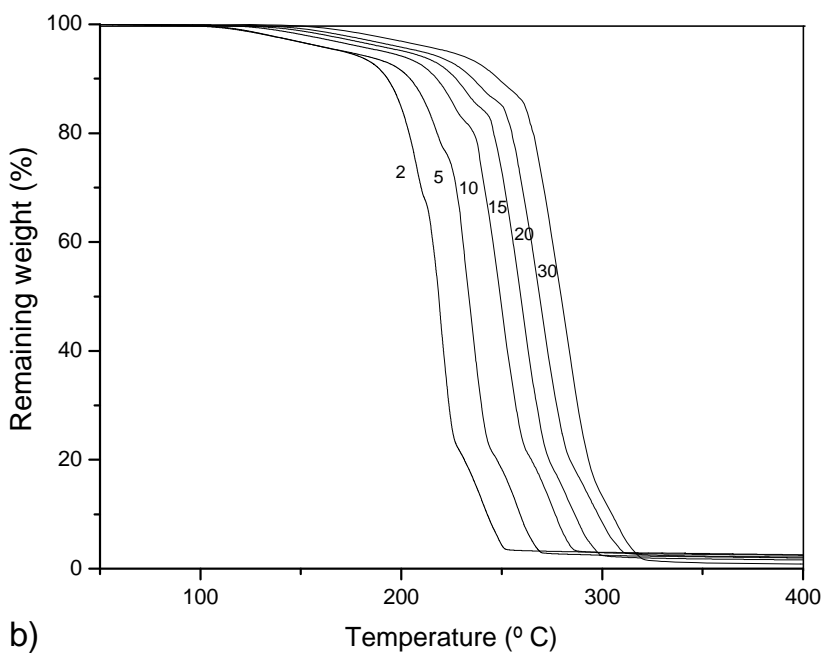
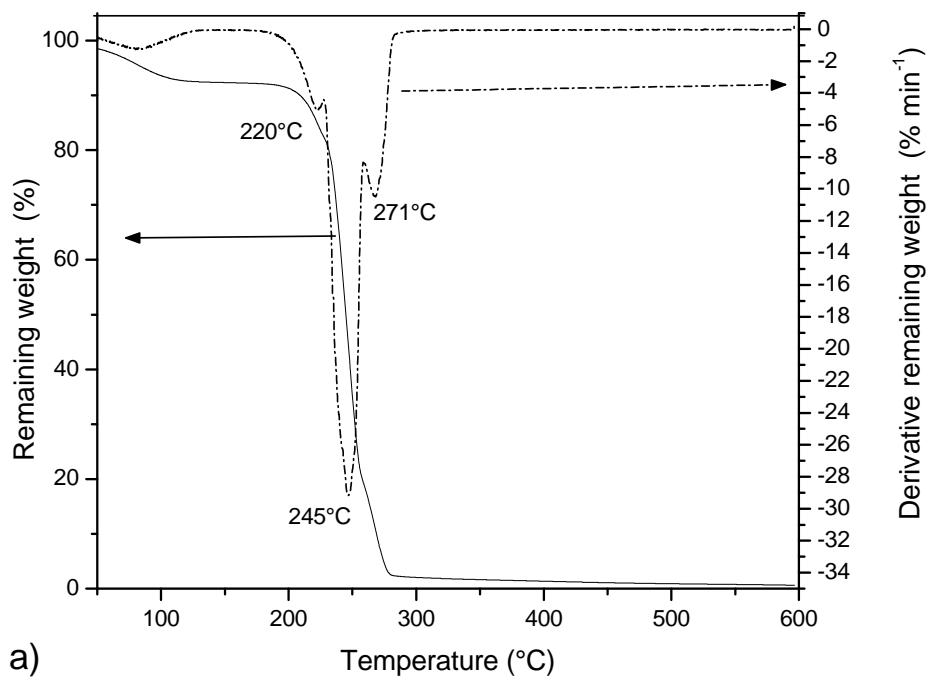


Figure 1. TGA traces of PMLA. a) TGA trace recorded at the heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ and its corresponding derivative curve. b) TGA traces recorded at the indicated heating rates.

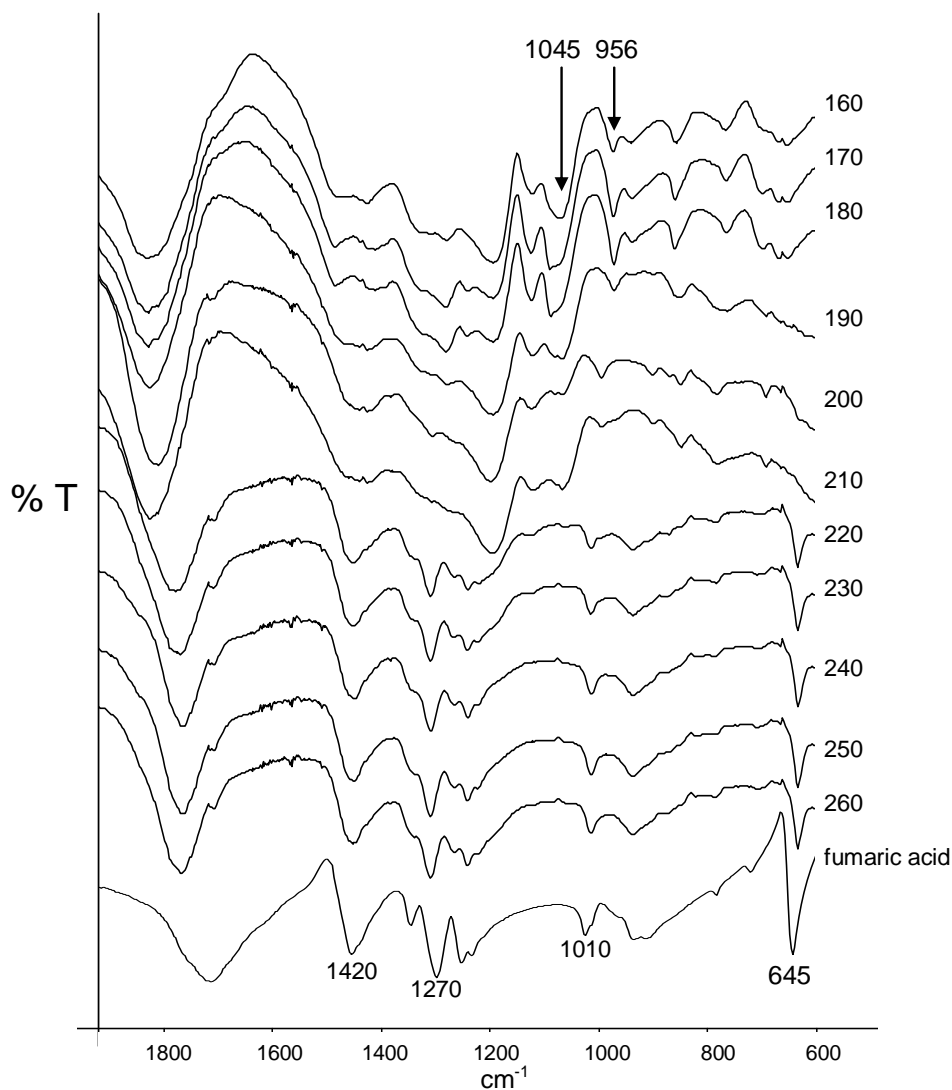


Figure 2. Infrared spectra of PMLA vs temperature. The spectrum of fumaric acid inserted at the bottom for comparison.

To analyze the degradation products that were generated at each stage, PMLA was subjected to isothermal heating at 200, 220, and 240 °C, and volatiles produced at each stage were collected for weight losses of 20, 80, and 97%, respectively.

The ^1H NMR spectra of these volatiles and the residual material generated in each stage are compared in Figure 3. Results show that PMLA decomposed in the first stage, giving fumaric acid and leaving a residue that is spectroscopically undistinguishable from the original PMLA sample. A mixture of fumaric and maleic acids was released in the second stage, the residual material being a mixture of fumaric acid and PMLA.

No residual material was left after heating at 240 °C, and the volatile material generated at this stage consisted of maleic acid accompanied by minor amounts of fumaric acid and maleic anhydride.

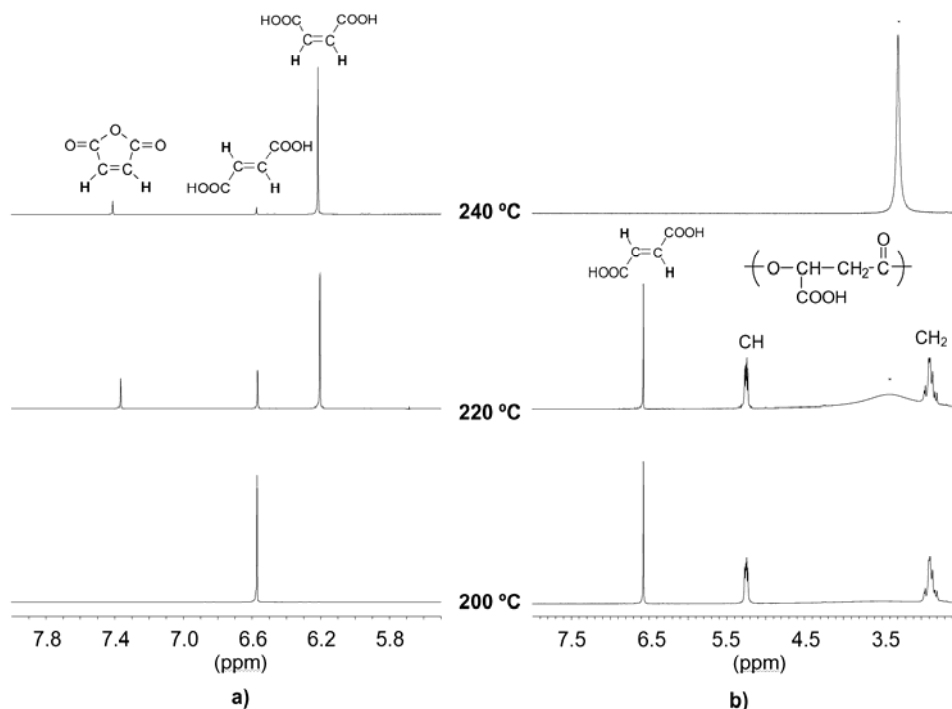


Figure 3. ¹H RMN spectra of products resulting from the thermal degradation of PMLA. at the indicated temperatures. a) Released gases. b) Residual products.

The interconversion of maleic acid to fumaric acid is a well-known isomerization process that takes place above 200 °C, and dehydration of maleic acid to anhydride is reported to occur at temperatures close to 220 °C.¹³ In a separate experiment, pure fumaric acid was subjected to the same thermal treatment applied to PMLA. It was found that the gas released upon decomposition of fumaric acid consisted of a mixture of the same three components in approximately the same proportions as in the thermal decomposition of PMLA. These results strongly suggest that maleic acid present in the volatiles released by PMLA resulted from the isomerization of fumaric acid rather than being directly produced in the decomposition of PMLA.

Since maleic acid is more volatile than fumaric acid, the slope increase of the TGA trace observed at the second stage can be simply due to the faster evaporation of maleic acid.

The decrease in the decomposition rate observed by TGA in the third stage could be due to the slower evaporation of the mixture caused by the presence of anhydride maleic, whose formation from maleic acid is favored at higher temperatures.

The GPC analysis of the residue remaining after heating PMLA afforded extremely valuable information about the degradation mechanism. In Figure 4, the M_n of the residual material left after heating at 220 °C is plotted for remaining weights of 75, 50, and 25% of the initial sample. The decay in molecular size with conversion is approximately linear with a slope close to one. This fact, together with the evidence provided by NMR that the constitution of the residual polymer remained unaltered throughout the whole degradation process, allows us to offer a mechanism for the thermal degradation of PMLA consisting of an end-of-chain unzipping reaction.

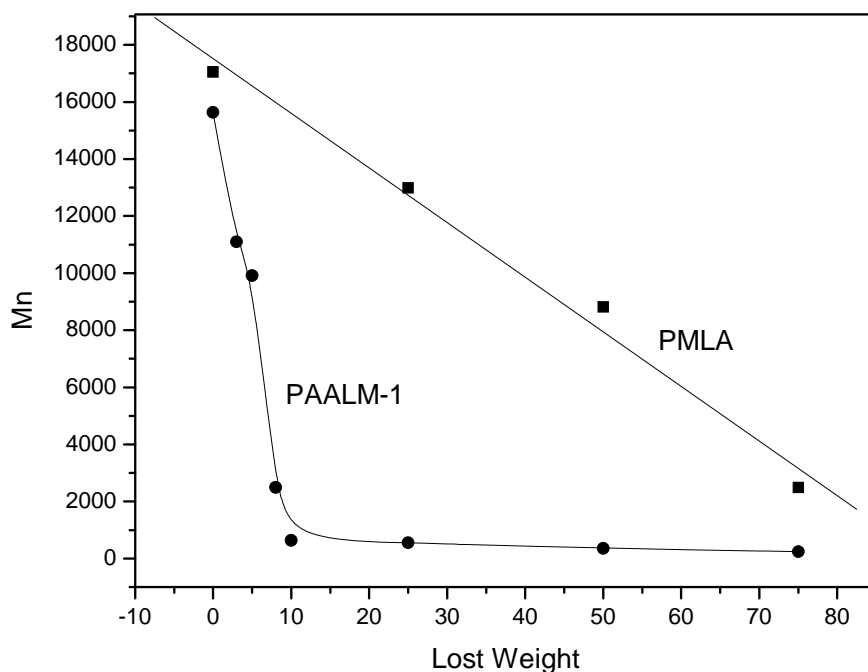
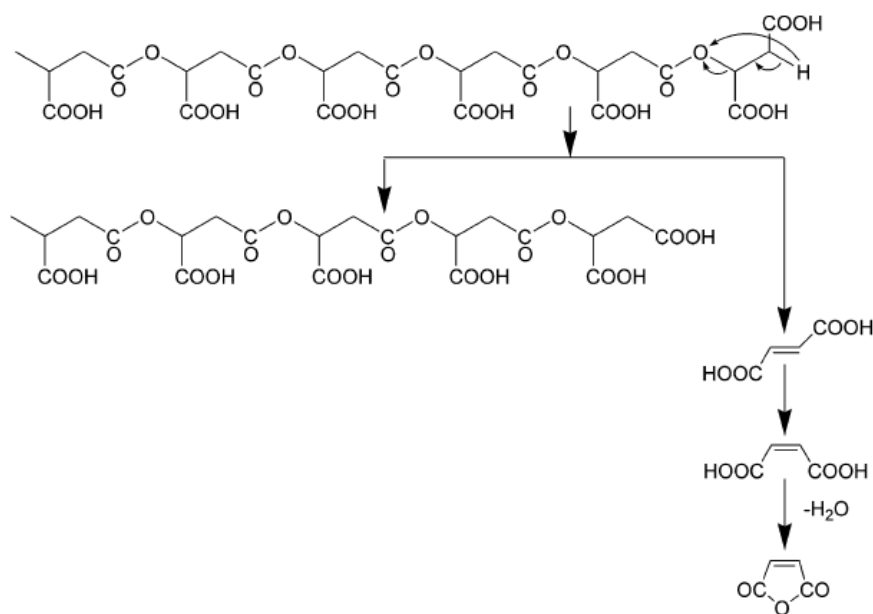


Figure 4. Evolution of the weight-average molecular weight of the residual product left in the thermal degradation of PMLA and PAALM-1.

Depolymerization would take place with the release of fumaric acid and gradually decrease of the polymer chain length, as depicted in Scheme 2. Certain polyesters such as poly(caprolactone) are known to degrade by such a type of mechanism with generation of caprolactone.¹⁴

The same degradation model has been reported for the thermal decomposition of poly(lactic acid), a polyester bearing a methyl side group on the β -carbon.¹⁵ The fact that fumaric acid instead of malic acid is produced in the thermal decomposition of PMLA is consistent with the occurrence of an α,β -elimination taking place exclusively at the chain end-unit.

This is not the case however of poly(3-hydroxybutyrate), a linear polyester with the same backbone as PMLA but bearing a methyl side group instead of the carboxylic group, which is reported to degrade by a random main chain scission mechanism based on *cis*- α,β elimination yielding short hydroxyacid oligomers.⁹⁻¹²



Scheme 2. Unzipping Mechanism Operating in the Thermal Degradation of Poly(malic acid) by Successive α,β Elimination Reaction (α -Hydrogen atoms inserted only when necessary for clarity).

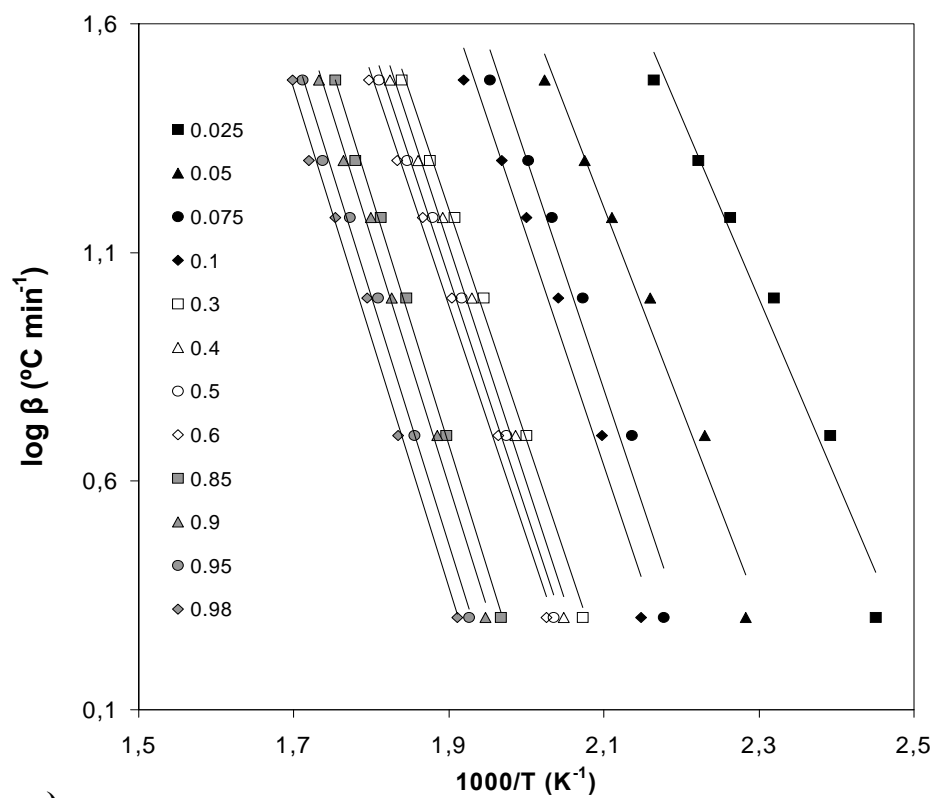
To analyze the kinetics of the degradation mechanism occurring in PMLA, the activation energy was evaluated for the three stages outlined in the TGA traces shown in Figure 1. First, the isoconversional method of Ozawa, Flynn, and Wall (OFW) was used.¹⁶ This method assumes that the conversion function $f(\alpha)$ does not change with the heating rate. Temperatures corresponding to fixed values of R in experiments carried out at different heating rates β are measured.

Plotting $\ln(\beta)$ against $1/T$ according to eq 1 (A is a preexponential factor independent of T and R is the gas constant) should give a straight line, the slope of which are directly proportional to the activation energy E . If the activation energy is the same for the various values of R , the occurrence of a single-step reaction can be ascertained. On the contrary, a change in E with the conversion degree is indicative of the occurrence of a complex reaction mechanism.

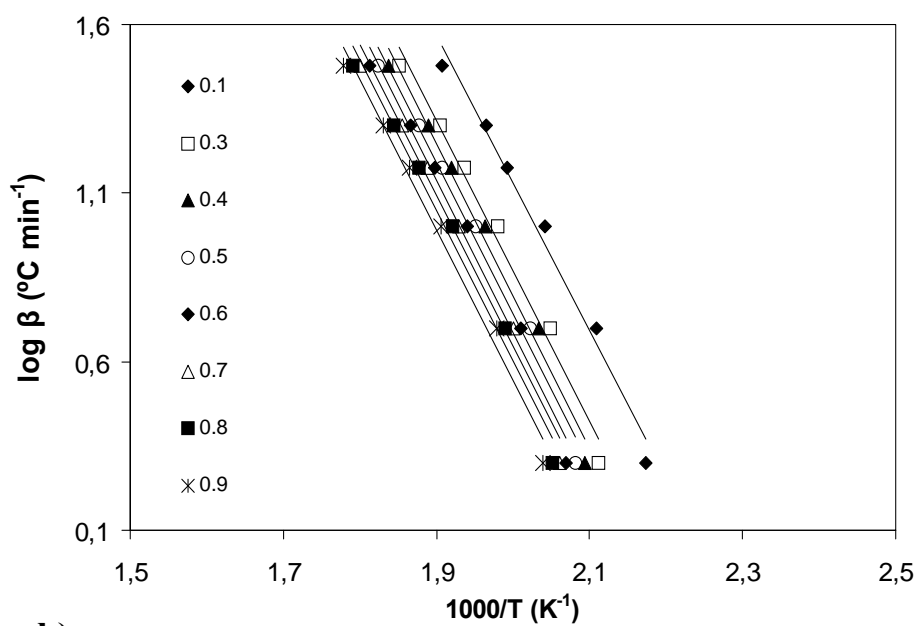
The Ozawa plots obtained for three degrees of conversion within each of the three degradation stages are shown in Figure 5a. Isoconversional lines are nearly parallel assessing the applicability of the method to the system under study. The Kissinger method,¹⁷ which calculates the activation energy from plots of the logarithm of the heating rate versus the inverse of the absolute temperature at which the decomposition rate is maximum for each stage, was also applied.

Kinetic parameters are summarized in Table 2 showing that similar E values showing similar trends were obtained by both methods. It should be stressed that very close values of the activation energy resulted for the three decomposition stages. This is consistent with the occurrence of a unique thermally decomposition mechanism for the whole degradation process. The fact that a three-stage process appears reflected in the TGA traces could be simply the result of differences in the evaporation rate of the gases released in each of the three decomposition stages. It should be noted that the E values resulting in this study are of the same order as those reported for poly(hydroxy alkanate)s when determined using the same thermogravimetric methods¹⁴ but significantly lower than those obtained by applying the Arrhenius equation.¹⁰

6.3.2. Thermal Degradation of PAALM-1. The thermal degradation of the methyl ester of PAALM-1, poly(α -methyl β ,L-malate), was studied by applying the same methodology used in the study of PMLA. At contrast to the results obtained for the polyacid, the TGA trace of PAALM-1 (Figure 6) shows a sigmoidal progression of the weight loss from the onset to the almost total disappearance of the polymer. The maximum decomposition rate appears at 250 °C, a temperature just a few degrees above that observed for PMLA when heated at the same rate. The effect of heating rate on decomposition was similar for the two polymers, i.e. TGA traces moved to higher temperatures with increased heating rates without significant modification of the shape. Ozawa plots built from these data (Figure 5b) display similar features to those displayed by PMLA plots.



a)



b)

Figure 5. Ozawa plots for TGA traces of PMLA (a) and PAALM-1 (b) for the indicated conversion degrees.

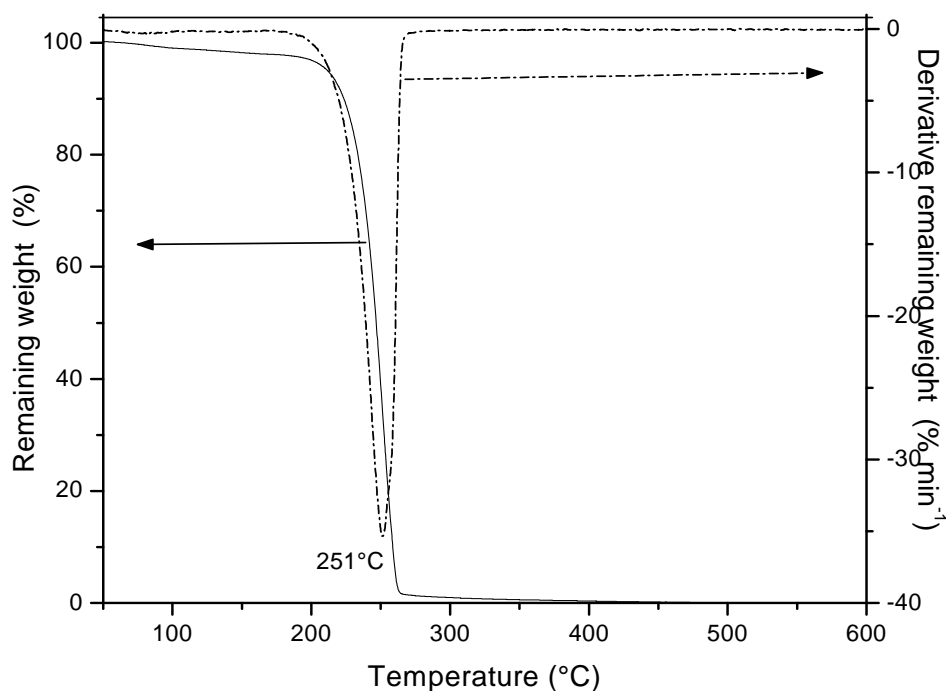


Figure 6. TGA trace of PAALM-1 recorded at the heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ and its corresponding derivative curve.

The activation energy afforded by this analysis was approximately $80\text{ kJ}\cdot\text{mol}^{-1}$, and essentially the same value resulted when the Kissinger method was applied.

As it can be seen in Table 2, such a value of E is very close to that determined for the first decomposition stage of PMLA. It can be concluded therefore that, as in the case of PMLA, it is the volatility of the released compound that determines the degradation kinetics of PAALM-1.

Table 2. Kinetic parameters of thermal degradation of PMLA and PAALM.

Compound	Step	$\Delta\alpha^a$	T_i^b ($^{\circ}\text{C}$)	T_f^b ($^{\circ}\text{C}$)	W^c (%)	E^d (kJ mol^{-1})	E^e (kJ mol^{-1})
PMLA	1	0-0.14	191	232	13.7	82.8	81.9
	2	0.14-0.86	232	268	67.9	92.5	86.3
	3	0.86-1	268	310	15.5	98.7	92.6
PAALM-1		0-1	220	260	98	81.2	80.1

^a Interval of conversion. Conversion calculated in term of mass loss as $\alpha = (W_0 - W)/(W_0 - W_{\infty})$, where W_0 , W and W_{∞} are, respectively, the initial weight, the actual weight and the final weight at the end of the degradation process. ^bInitial and final temperature of the step determined at $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. ^cStep weight lost (%) at $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. Char yield=2.9%. ^dAverage activation energy determined with the Ozawa method. ^eActivation energy determined with the Kissinger method.

The infrared spectra obtained for progressively increasing temperatures revealed changes in PAALM-1 comparable again to those observed for PMLA, the onset of decomposition appearing at a temperature only a few degrees below that for the polyacid. On the contrary, results obtained by NMR and GPC analysis concerning both composition of degraded products and molecular weight of the degraded polymer were clearly different for polymalic acid and the polymalate.

The ^1H NMR spectra of the volatile products, residual polymer, and original PAALM-1 are compared in Figure 7.

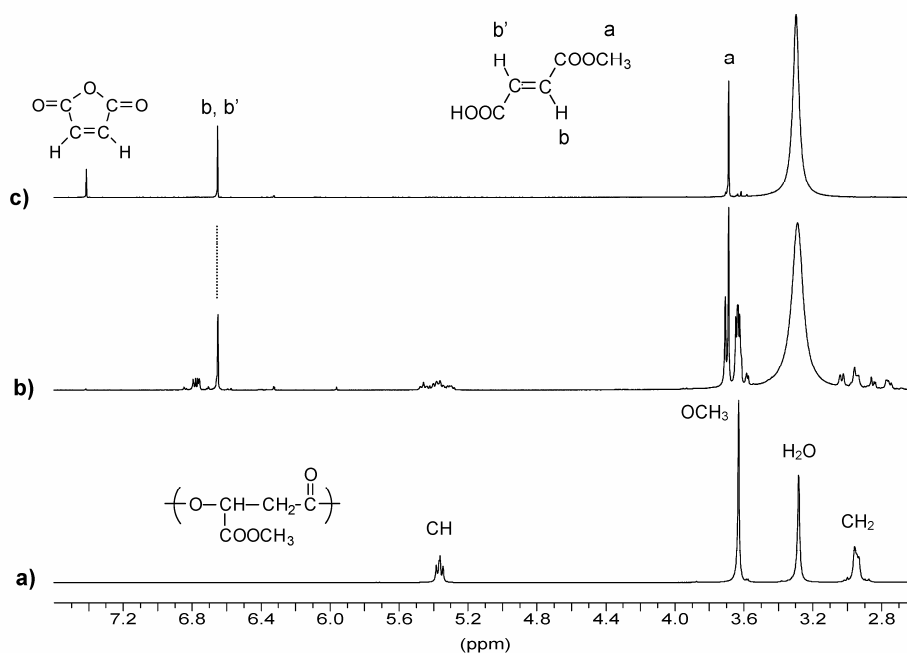


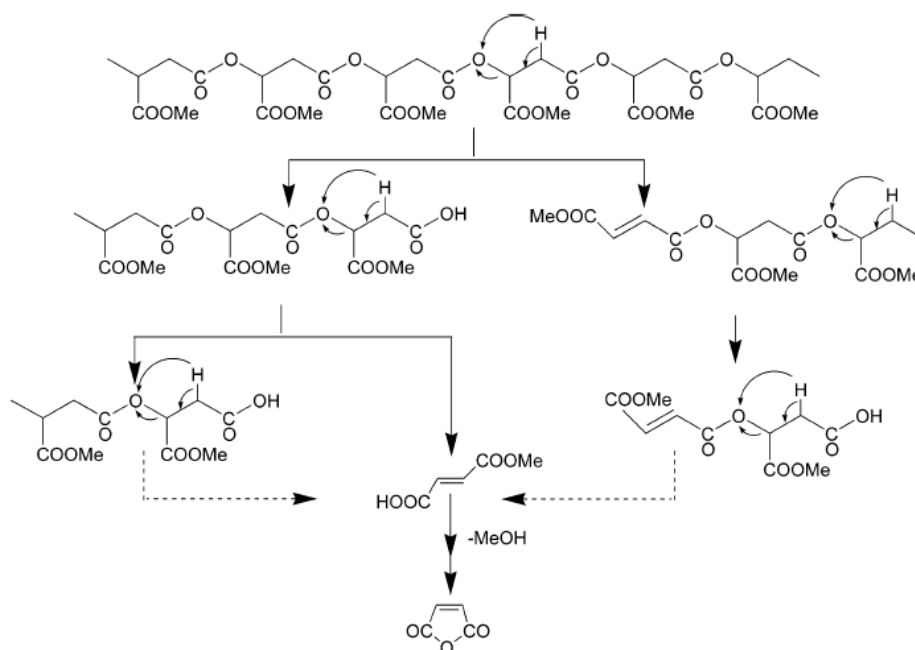
Figure 7. ^1H RMN spectra of products resulting from the thermal degradation of PAALM-1. a) Original polymer. b) Residual polymer. c) Released gases. The intensity of the peak at 3.3 ppm arising from the water present in the solvent which is more apparent for lower sample concentrations.

As it could be expected from the chemical structure of the polymer, the released gas was composed of methyl fumarate accompanied of a minor amount of maleic anhydride. The ^1H NMR spectrum of the residual material reveals the presence of chemically altered PAALM-1 containing the double bonds of crotonic acid together with a considerable amount of retained methyl fumarate.

The GPC analysis of the residual material for different conversion degrees showed a rapid decrease of the polymer size since the earliest stages of decomposition, the number-average molecular weight falling to approximately 1000 for a sample weight loss of 10% (Figure 4).

Combined NMR and GPC results indicated that thermal degradation of PAALM-1 must be explained by a random main chain scission mechanism based on the α,β -elimination reaction of the type described for poly-(hydroxy alkanate)s.^{9,10}

The occurrence of secondary cyclization reactions due to intramolecular transesterifications cannot be discarded despite the lack of evidence for the presence of cyclic products. A plausible mechanism for the thermal decomposition of PAALM-1 according to the experimental data described above is depicted in Scheme 3.



Scheme 3. Mechanism of Thermal Decomposition of Poly(R-methyl, β ,L-malate) Based on Random α,β Elimination Reaction. (α -Hydrogen atoms inserted only when necessary for clarity).

6.3.3. Thermal Degradation of *n*ATMA·PMLA Complexes. The TGA traces for the whole series of *n*ATMA·PMLA showing the mass loss as a function of temperature recorded at a rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ are compared in Figure 8a. In all cases, the traces show three decomposition stages, which become clearly differentiated in their respective derivative curves, as it is illustrated in Figure 8b for the case of 18ATMA·PMLA. Maximum rate temperature values for the three steps as well as the weights of residual material are collected in Table 3 for the whole set of complexes.

The onset temperature increases steadily with the length of the surfactant alkyl chain. Whereas first and third stages occur at temperatures essentially constant along the series, the temperature of the intermediate stage increases steadily with the length of the alkyl group.

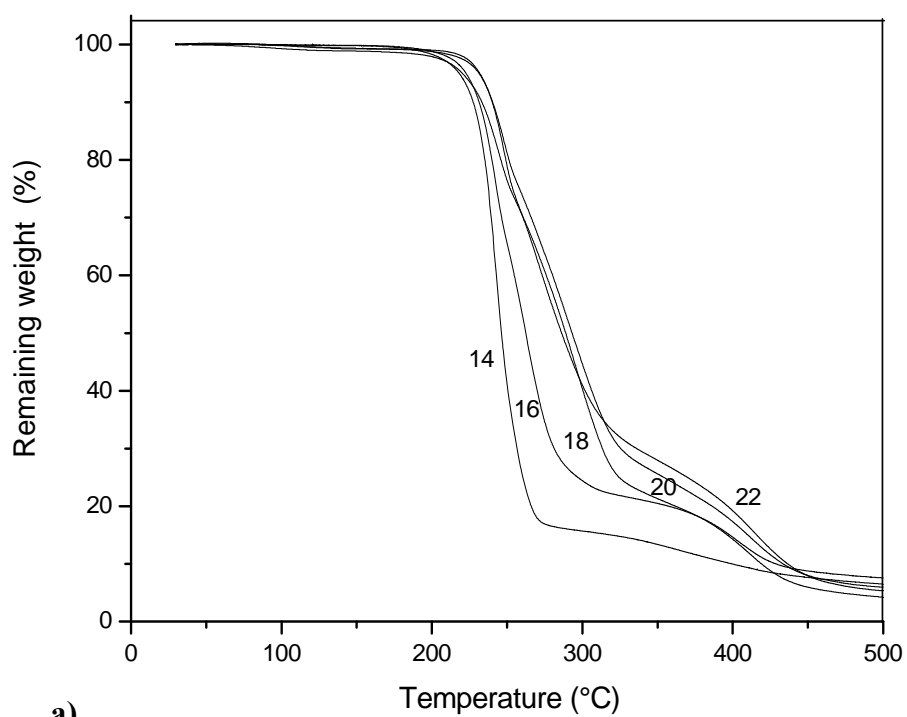
Mass losses taking place in the first stage are between 30 and 25% with values decreasing as the length of the alkyl chain increases. Mass losses between 45 and 55% occur in the second stage with a trend opposite to that observed in the first stage. The mass losses in the third stage are within the 15-20% range, showing a slight decrease with the size of the alkyl chain. The residual material remaining at the end of the process amounts to 5-6% of the original mass for all the complexes.

In support of the results obtained for the thermal degradation of *n*ATMA·PMLA complexes, the pyrolysis of the surfactant salt 18ATMA·Br was carried out, and the resulting products were examined by NMR spectroscopy. The TGA traces for this salt (results not shown) revealed a decomposition process consisting of two well differentiated stages with maximum decomposition rates at 278 °C and 370 °C, respectively. The first stage appeared to be a complex process that accounted for approximately 85% of mass loss.

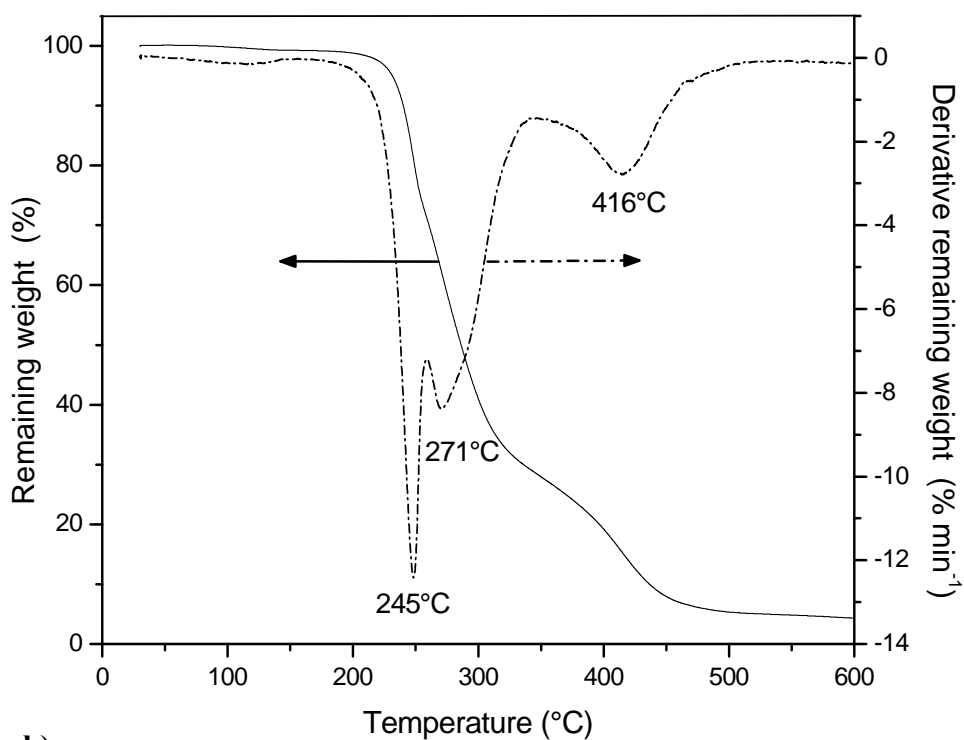
The residual material left at this stage was composed mainly of a mixture of dimethyl- and octadecylmethylamines, indicating that decomposition of the salt takes place through multiple molecular scissions and rearrangements.

Partial volatilization of the formed amines aided by the carrier effect of the nitrogen circulating gas may account for the large weight loss at this stage. The residual material left after heating at 350 °C contained almost exclusively the less volatile octadecylmethylamine. These results are in agreement with those obtained by Xie et al.¹⁸ in the study of the pyrolysis of 18ATMA·Cl by GC-MS analysis, who also reported the presence of alkyldimethylamines in the volatile products.

By analogy with the TGA trace obtained for PMLA, the sharp decomposition step of *n*ATMA·PMLA showing the maximum rate between 242 and 245 °C should correspond to the decomposition of the polyester main chain. In fact, the ¹H NMR analysis of the gases released upon heating 18ATMA·PMLA at 230 °C were found to consist of a mixture of fumaric acid (15%), maleic (65%) acid, and maleic anhydride (20%), which is very similar to that found for the decomposition of PMLA.



a)



b)

Figure 8. a) TGA traces of n ATMA·PMLA complexes recorded at the heating rate of $10\text{ °C}\cdot\text{min}^{-1}$ (n values indicated at labels). b) TGA trace of 18ATMA·PMLA and its corresponding derivative curve.

The ^1H NMR spectra of the residual material resulting from this decomposition indicated that it consisted mainly of alkyltrimethylammonium salt, most likely in the hydroxide form (Figure 9). It is known that $n\text{ATMA}\cdot\text{PMLA}$ complexes bind firmly up to about 2 mol of water per repeating unit.⁵ This absorbed water cannot be removed by standard methods, and its presence is accounted by elemental analyses and also in the ^1H NMR spectra as a broad signal at 2.8 ppm.

Decomposition of $n\text{ATMA}\cdot\text{PMLA}$ showed concomitance with the first decomposition stage observed for octadecyltrimethylammonium bromide. In fact, a minor amount of octadecyldimethylamine is observed together with the ammonium salt in the spectra shown in Figure 9b.

Experimental weight losses observed for the first decomposition step and weight losses calculated for the disappearance of the main chain by depolymerization are compared in Figure 10 for the whole set of complexes. An excellent correspondence between the two series of data is observed with differences between them being within the range of experimental error.

Thermal decomposition of the trimethyloctadecylammonium hydroxide is expected to proceed by a reaction mechanism based on the Hofmann elimination reaction with generation of trimethylamine and 1-octadecene.

The presence of this alkene was in fact detected in the volatiles released upon heating the complex at 260 °C, which demonstrated the occurrence of the Hofmann reaction during the second decomposition stage (Figure 9c).

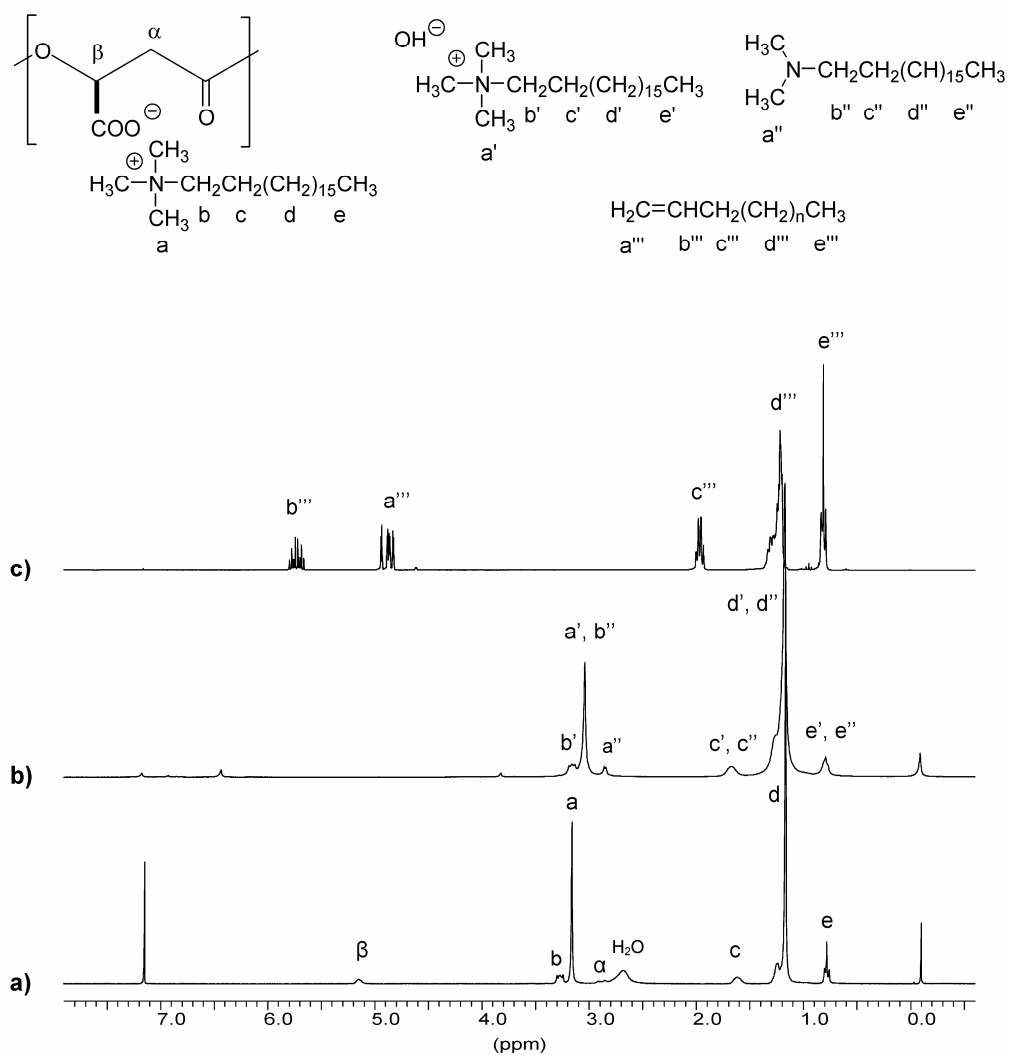


Figure 9. ^1H NMR spectra of 18ATMA·PMLA. a) Original polymer. b) Residual products left after heating at 240 °C. c) Gases released upon heating at 280 °C.

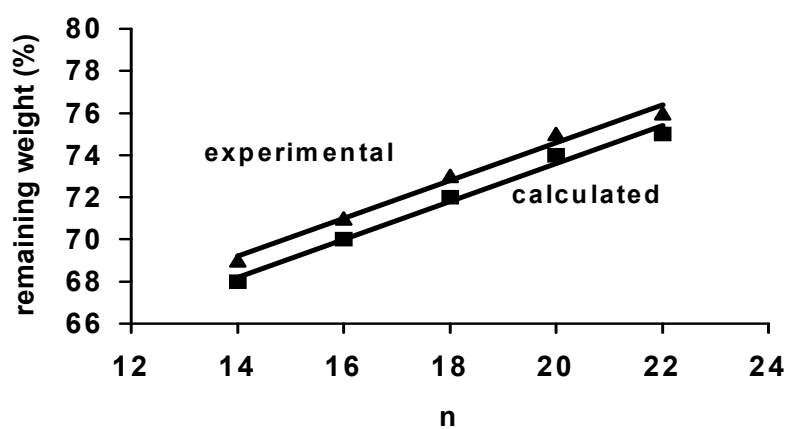
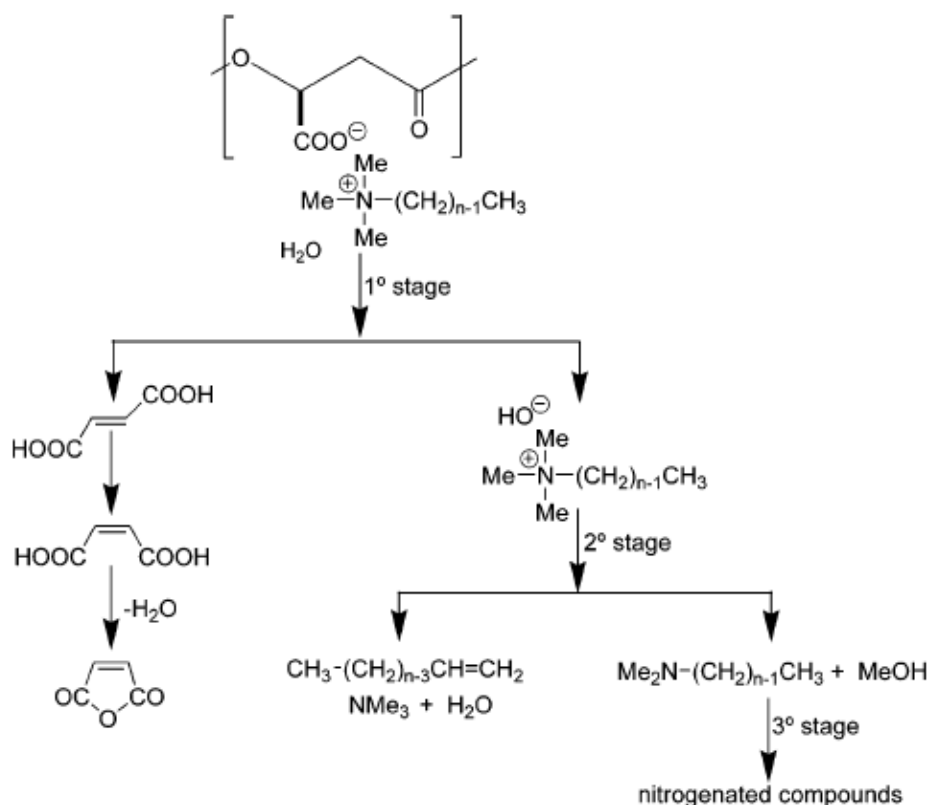


Figure 10. Calculated and experimental weight losses for the first decomposition step of $n\text{ATMA}\cdot\text{PMLA}$ complexes as a function of n .

The residual material left after this treatment consisted of a complex mixture of nitrogenated compounds of difficult spectroscopic assignment. The third decomposition step that occurred above 300 °C is thought to correspond to the cracking of the nitrogenated products left after the second stage. A partial mechanism can be reasonably proposed for the decomposition of *n*ATMA·PMLA complexes (Scheme 4) in agreement with all data recorded in this study.



Scheme 4. Main Indications of the Thermal Decomposition Mechanism from Ionic Complexes *n*ATMA·PMLA.

6.4. Conclusions

The degradation processes that occur upon heating poly(malic acid) and polymalates have been characterized by combining experimental data obtained by TGA, GPC, and FTIR and NMR spectroscopy. The underlying molecular mechanisms have been partially outlined. The main conclusions are the following:

(a) Decomposition of poly(β ,L-malic acid) (PMLA) by heating under inert atmosphere starts at temperatures near 200 °C and evolves by an unzipping depolymerization mechanism with generation of fumaric acid. Maleic acid and maleic anhydride found in the released gases are produced by isomerization and anhydridization of the initially formed fumaric acid.

(b) Thermal decomposition of poly(α -methyl β ,L-malate) (PAALM-1) proceeds mainly by random scission of the main chain with the release of methyl fumarate and production of low molecular weight oligomers.

(c) Thermal decomposition of n ATMA·PMLA complexes proceeds along three well differentiated steps. First, a quantitative decomposition of the polymalate involving unzipping depolymerization of the main chain together with decomposition of the ionic complex takes place. Hoffman elimination of the quaternary alkyltrimethylammonium hydroxide formed in the first stage and pyrolysis of unspecified nitrogenated compounds account for the other two stages observed in the thermal decomposition of these complexes.

6.5. References

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