Thermal Degradation of Polyuronic Acids and their Ionic Complexes

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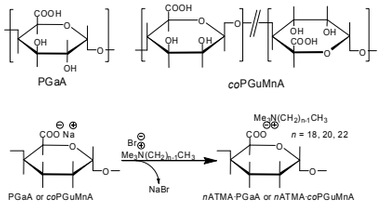
Introduction

Our research is currently addressed to comb-like systems based on ionic complexes of biotechnological polyacids and alkyltrimethyl-ammonium surfactants bearing long alkyl groups.

In this work we report on the thermal degradation under inert atmosphere of the polyuronic acids PGaA and *co*PGuMnA and their alkylammonium ionic complexes *n*ATMA·PGaA and *n*ATMA·coPGuMnA (*n* = 18, 20 and 22)



Scheme 1. Chemical structures of pectinic (PGaA) and alginic (*co*PGuMnA) acids (up). Coupling reaction leading to alkylammonium-polyuronic acid complexes (down).

Results

Ionic coupling of polyuronic acids with surfactants was conducted in water solution to prepare non-soluble comb-like complexes. These amphiphilic complexes are arranged in a biphasic layered structure with the paraffinic phase made of alkyl side chains alternating with the hydrophilic phase made of polyuronic main chains. The complexes displayed the thermal behaviour typical of comb-like systems carrying long polymethylene groups, which melt at temperatures between 40 and 80 ºC without significant disruption of the layered arrangement.

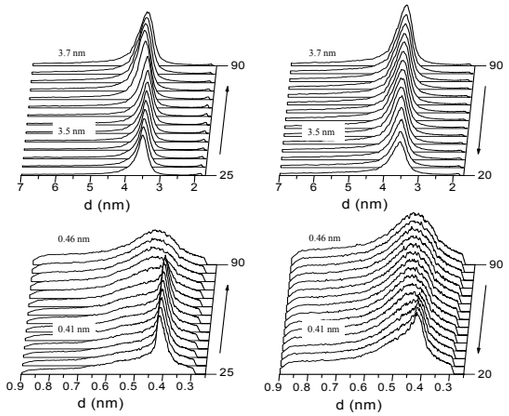


Figure 1. Real time SAXS (up) and WAXS (down) profiles of 20ATMA·PGaA at heating (left) and cooling (right).

Thermal stability of the polyuronic acids and their ionic complexes was investigated through thermogravimetric analysis. TGA analysis results of these polymers are compared in Table 1.

The TGA traces revealed that these polymers are highly hygroscopic with an initial loss of water near to 90 ºC. The polyuronic acids present a one-step degradation process that starts about 230 ºC with the maximum degradation rate around 250 ºC.

Table 1. Thermal paramethers of polyuronic acis and their ionic complexes

Compound	T_o [a] (ºC)	T_d [b] (ºC)	W [c] (%)
PGaA	232	252	16
*18*ATMA·PGaA	211	229/270/381	65/17/0
20ATMA·PGaA	212	227/281/398	66/18/0
22ATMA·PGaA	207	219/301/411	71/22/0
Na·*co*PGuMnA	227	237	23
18ATMA· *co*PGuMnA	204	210-217/266/381	58/13/0
20ATMA· *co*PGuMnA	206	211-220/289/392	58/16/0
22ATMA· *co*PGuMnA	202	209/301/400	65/20/0

[a] Onset decomposition temperature.
[b] Maximum rate decomposition temperature.
[c] Remaining weight at the end of each step.

FT-IR spectra of the solid residues resulting from isothermal treatment of the polyuronic acids at different temperatures showed a continuous decease in intensity of bands with temperature. The main changes detected were the gradual shifting of the C=O of polyuronic acids from 1720 cm^{-1} to 1700 cm^{-1} indicating the formation of a new C=O band. The formation of diene group (1580-1600 cm^{-1}) was also observed. At 400 ºC the *co*PGuMnA showed a new spectrum with two principal bands at 1438 cm^{-1} and 1135 cm^{-1} that suggest the formation of ether groups.

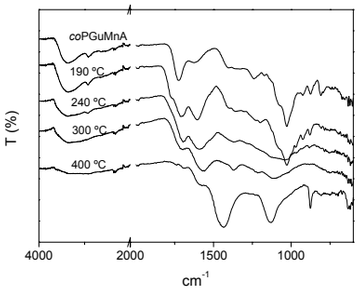


Figure 2. FTIR spectra of polyalginic acid and its chars

^{1}H-NMR analysis of the volatiles arising from isothermal degradation treatment at 210 and 250 ºC, in the case of the polyuronic acids, reveals the presence of water as main product and the occurrence of formic and acetic acids, and furfural at amounts increasing with the time of treatment.

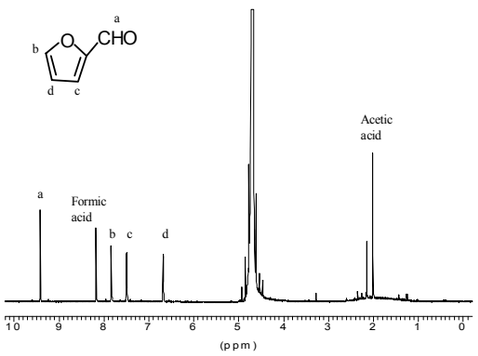


Figure 3. ^{1}H-NMR spectrum of volatiles resulting from pyrolysis.

The TGA traces of the ionic complexes showed a three-step degradation process, T_{max} of the last two steps seems to be related with the length of the side group.

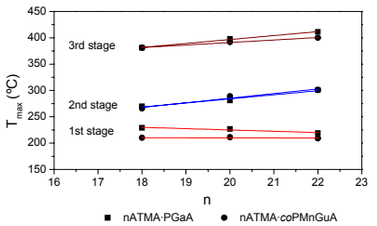


Figure 4. T_{max} vs *n* of the polyuronic ionic complexes at different stages of degradation process

The ionic complexes degraded through a much more complicated process implying several parallel and successive decomposition reactions. The ^{1}H-NMR spectra revealed in the volatiles the presence of methanol, *N,N*-dimethylalkylamine and trimethylamine. These results suggest that dissociation of the ionic complex occurred at the first stage of decomposition followed by a simultaneous degradation of the alkylammonium surfactant and the polyuronic acid.

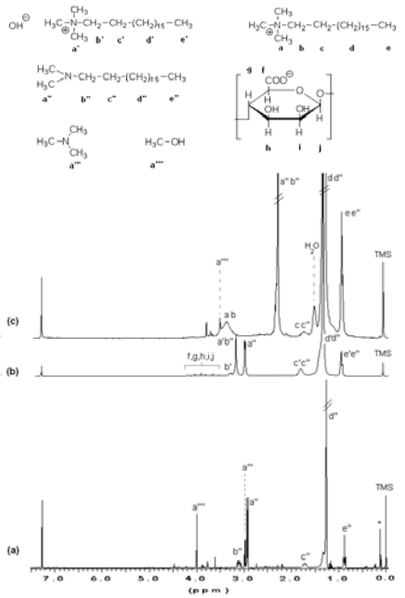


Figure 5. ^{1}H-NMR spectra of products resulting from thermal degradation. (a) Volatile products ($CDCl_3$/TFA). (b) Solid residues ($CDCl_3$/TFA). (c) Solid residues ($CDCl_3$)

Aknowledgements

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