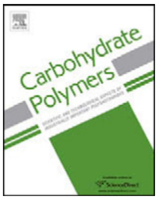
Carbohydrate Polymers 86 (2011) 484–490

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol



# Comb-like ionic complexes of pectinic and alginic acids with alkyltrimethylammonium surfactants

Ainhoa Tolentino, Abdelilah Alla, Antxon Martínez de Ilarduya, Sebastián Muñoz-Guerra*

*Department dïEnginyeria Química, Universitat Politècnica de Catalunya, ETSEIB, Diagonal 647, Barcelona 08028, Spain*

ARTICLE INFO

*Article history:*
Received 2 February 2011
Received in revised form 26 April 2011
Accepted 27 April 2011
Available online 7 May 2011

*Keywords:*
Ionic polymer complex
Comb-like polymer
Polyuronic acid
Alginic acid
Surfactant polyuronic complex

## ABSTRACT

Ionic coupling of both polygalacturonic and alginic acids with alkyltrimethyl ammonium surfactants containing 18, 20 and 22 carbon atoms in the alkyl side chain 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 chains. The complexes displayed the thermal behaviour typical of comb-like systems carrying long polymethylene groups, which melt at temperatures between 40 and 80 °C without significant disruption of the layered arrangement. Melting temperature, crystallinity and thermal stability were slightly higher for the polygalacturonic complexes and all they increased almost steadily with the length of the alkyl chain within each series. The melting-crystallization process was followed by combined WAXS/SAXS and $^{13}$C CP-MAS NMR, which revealed that the transition involves an expansion-contraction of the structure that may attain up to 20% of the original dimension. The transition takes place without large conformational changes and is not fully reversible.

## 1. Introduction

As it is widely known, a comb-like polymer is a highly branched polymer in which the main chain and the side chain have constitutions different enough as to form two separates phases. The structure adopted in the solid state by these systems varies between two limiting cases: (a) A fully disordered globular arrangement typical of systems in which, both main and side chains are non-crystallizable, and (b) a well-ordered layered structure with the two phases alternating periodically with a spacing that depends on the length of the side chain; this is the usual arrangement adopted by comb-like polymers in which the two phases are able to crystallize (Loos & Muñoz-Guerra, 2005; Plate & Shibaev, 1974).

Different authors have reported extensively on the biphasic structure of poly(alkyl glutamate)s (Morillo, Martínez de Ilarduya, & Muñoz-Guerra, 2001; Morillo, Alla, Martínez de Ilarduya, & Muñoz-Guerra, 2003) and poly(alkyl aspartate)s (López-Carrasquero, Montserrat, Martínez de Ilarduya, & Muñoz-Guerra, 1995; Martínez de Ilarduya, Alemán, García-Alvarez, López-Carrasquero, & Muñoz-Guerra, 1999) with long alkyl groups containing from 12 to 22 carbon atoms, in which the polypeptide chains in the alpha-helix conformation are arranged side-by-side in sheets with the alkyl side chain in fully extended conformation and crystallized with an orientation more or less normal to the sheet plane. When these systems are heated, the alkyl side chains melt but the conformation of the main chain remains essentially unaltered retaining the helical arrangement and keeping its position in the lattice. The layered structure is therefore preserved but the interlayer spacing slightly varies due to the conformational change undergone by the polymethylene chain (Loos & Muñoz-Guerra, 2005). Such thermal behaviour has interesting phenomenological consequences with potential technological applications such as thermoresponsive-permeoselective membranes and thermochromic sensors (Compañ et al., 2002; Muñoz-Guerra et al., 2002).

Recently it has been shown that comb-like systems with structures and properties similar to those described above can be generated by coupling between ionic alkyl surfactants and charged polyelectrolytes (Fig. 1). Alkyltrimethylammonium-poly($\alpha$-glutamate)s complexes were the systems firstly reported with such characteristics (Ponomarenko, Waddon, Tirrell, & MacKnight, 1996). Similar complexes of poly($\gamma$-glutamate)s (García-Alvarez, Alvarez, Alla, Martínez de Ilarduya, & Muñoz-Guerra, 2005; Pérez-Camero et al., 2004) and poly($\beta$,L-malate)s (Portilla-Arias, García-Alvarez, Martínez de Ilarduya, Holler, & Muñoz-Guerra, 2006) have been later studied in great detail in our group with special attention paid to their structure and thermal properties. The clear advantage afforded by the systems based on ionic coupling respect to the covalent systems is their greater simplicity of preparation. Ionic complexes can be readily obtained by

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* Corresponding author. Tel.: +34 934016680; fax: +34 934017150.
*E-mail address:* sebastian.munoz@upc.edu (S. Muñoz-Guerra).

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doi:10.1016/j.carbpol.2011.04.072

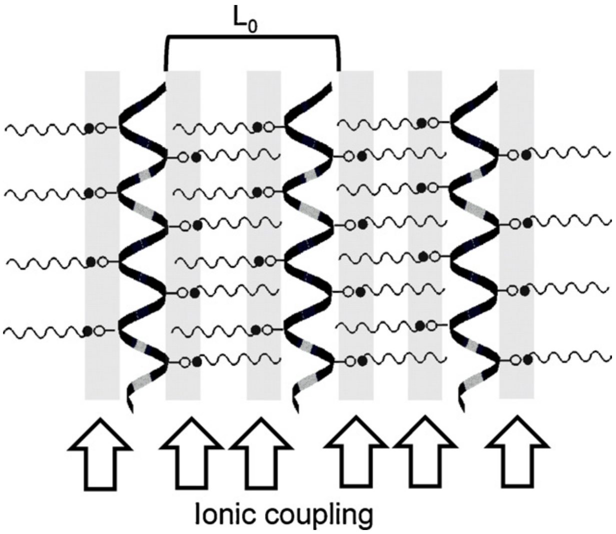

**Fig. 1.** Side view of the layered structure adopted by comb-like ionic polymer complexes.

direct mixing of the corresponding components dissolved in aqueous medium and avoiding thus laborious synthetic work.

In this paper a structure-property study of the complexes produced by ionic coupling of alkyltrimethylammonium surfactants (*n*ATMA, *n* is the number of carbon atoms contained in the alkyl chain with even values from 18 to 22) with polyuronic acids, specifically, pectinic and alginic acids (Fig. 2), is reported. Pectinic acid is the homopolysaccharide poly(1,4-α-D-galacturonic acid), abbreviated PGaA, whereas alginic acid is the copolymer poly(1,4-α-L-guluronic-*co*-1,4-β-D-mannuronic acid), abbreviated *co*PGuMnA, with the two comonomeric uronate units distributed in a blocky microstructure (Dumitriu, 1998). The interaction of both pectinic and alginic acids with different types of cationic surfactants has been object of several studies in these last years (Ropers, Meister, Blume, & Ralet, 2008) and also the formation of nanoparticles with antimicrobial properties made of alginate complexes has been described (Asker, Weiss, & McClements, 2009). Nevertheless, the comb-like complexes formed from polyuronic acids and quaternary ammonium surfactants have not been studied so far. Worthy to notice that a rather close approach to these systems based on coupling of cationic surfactants and starch partially functionalized with carboxylic groups has been very recently reported (Balsamo et al., 2011). A preliminary account of the present work was presented in the EPF2009 congress and made available in the corresponding published symposium account (Tolentino, Martínez de Ilarduya, Alla, & Muñoz-Guerra, 2010).

## 2. Experimental

### 2.1. Materials

The alkyltrimethylammonium surfactant bromide salts of general formula $RMe_3N{\cdot}Br$ were either purchased from Aldrich ($R = –C_{18}H_{37}$ (stearyl)) or synthesized by us according to the procedure described in the literature ($R = –C_{20}H_{41}$ (eicosyl) and $–C_{22}H_{45}$ (docosyl)) (Hendrix & Von Rosenberg, 1976). The polyuronic acids were purchased to Sigma–Aldrich. The pectinic acid sample with a $M_w$ = 25,000–50,000 g mol$^{-1}$ was enzymatically produced, and the alginic acid sodium salt was obtained by extraction from brown algae with a $M_w$ = 80,000–120,000 g mol$^{-1}$ and has a L-Gu/D-Mn ratio of 39/61.

### 2.2. Complexes preparation

Complexes were prepared following the methodology described by us for the synthesis of complexes of *n*ATMA surfactants with poly(γ-glutamic acid) (García-Alvarez et al., 2005; Pérez-Camero et al., 2004) and poly(β-L-malic acid) (Portilla-Arias et al., 2006). In summary, an aqueous solution of the surfactant was added to an equimolecular solution of the sodium salt of the polyacid. The aqueous mixture was maintained under stirring at temperatures between 40 and 60 °C for 4 h. The formed precipitate was isolated from the sodium bromide solution by centrifugation, washed with water, and dried under vacuum.

### 2.3. Structure and thermal characterization methods

Thermal analysis was performed with a Perkin-Elmer Pyris 1 DSC instrument and calibrated with indium. 2–4 mg samples were subjected to heating and cooling rates of 10 °C min$^{-1}$ under a nitrogen atmosphere in the −30 to 120 °C temperature range. Time-resolved X-ray diffraction experiments were carried out at the A2 beamline of DORIS at HASYLAB in Hamburg. Non-isothermal treatments at heating and cooling rates of 5 °C min$^{-1}$ were carried

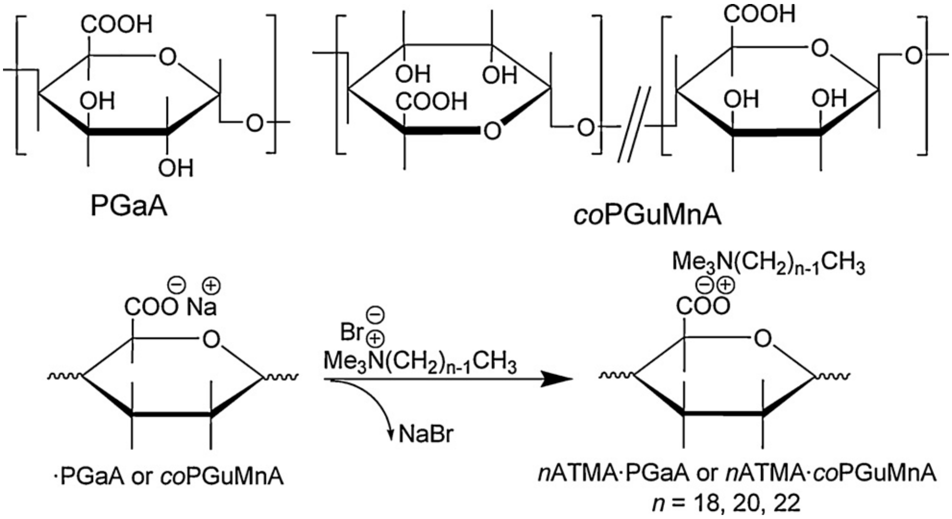

**Fig. 2.** *Top*: Chemical structures of pectinic (PGaA) and alginic (*co*PGuMnA) acids. *Bottom*: Coupling reaction leading to alkyltrimethylammonium-polyuronic acid complexes (hydroxyl and glycosyl groups are not indicated).

**Table 1**
Thermal data of polyuronic complexes measured by TGA and DSC.

| Complex | TGA | | | DSC | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $^\circ T_d$[a] (°C) | $T_d$[b] (°C) | $W$[c] (%) | 1st heating | | | | | 2nd heating | | Cooling | |
| | | | | $T_{m1}$ (°C) | $\Delta H_{m1}$ | $n_c^H$ | $\Delta S_{m1}$[d] (cal $K^{-1}$ $mol^{-1}$) | $n_c^s$ | $T_{m2}$ (°C) | $\Delta H_{m2}$ (kcal $mol^{-1}$) | $T_c$ (°C) | $\Delta H_C$ (kcal $mol^{-1}$) |
| nATMAPGaA | | | | | | | | | | | | |
| 18 | 211 | 229/270/381 | 70/18/0 | 70 | 4.2 | 6.0 | 12.2 | 6.1 | 52 | 2.5 | 50 | −2.7 |
| 20 | 212 | 227/281/398 | 68/19/0 | 77 | 5.3 | 7.6 | 15.1 | 7.6 | 61 | 1.9 | 55 | −3.5 |
| 22 | 207 | 219/301/411 | 73/23/0 | 73 | 7.0 | 10 | 20.2 | 10.1 | 66 | 3.8 | 59 | −5.1 |
| nATMAcoPGuMnA | | | | | | | | | | | | |
| 18 | 204 | 210–217/266/381 | 66/15/0 | 58 | 2.2 | 2.6 | 6.6 | 2.8 | 47 | 0.8 | 41 | −0.8 |
| 20 | 206 | 211–220/289/392 | 66/18/0 | 68 | 3.7 | 4.4 | 10.9 | 4.6 | 53 | 0.7 | 47 | −0.7 |
| 22 | 202 | 209/301/400 | 73/22/0 | 76 | 5.6 | 6.6 | 16.0 | 6.8 | 64 | 2.8 | 57 | −2.9 |

[a] Onset decomposition temperature calculated by the tangent method.
[b] Maximum rate decomposition temperature for each decomposition step.
[c] Remaining weights at the end of the respective decomposition stages.
[d] Values calculated from experimental enthalpy and temperature data; $\Delta H_m/T_m$.

out within the 10–120 °C temperature range. Small and wide angle X-ray scattering patterns (SAXS and WAXS) were acquired simultaneously every minute. Semicrystalline standard PET and Ag-behenate were used for calibrations. Other X-ray diffraction experiments were also recorded in a Siemens D5000 instrument from samples in powder form using a radiation of 0.154 nm wavelength. Solid state $^{13}C$ CP/MAS NMR spectra were recorded at 75.5 MHz in a Bruker AMX-300 instrument equipped with a CP/MAS accessory and an Eurotherm variable temperature controller. Samples of 100–200 mg weight were spun at 3.9–4.0 kHz in a cylindrical ceramic rotor. All spectra were acquired with contact and repetition times of 2 ms and 5 s, respectively, and 512–1024 scans were accumulated. The spectral width was 31.2 kHz, and the number of data points was 4 K. Chemical shifts were externally calibrated against the methylene peak of glycine appearing at 43.3 ppm.

## 3. Results and discussion

### 3.1. Synthesis of complexes

As it is depicted in Fig. 2, the procedure leading to the complexes is extremely simple. The complexes were readily formed and precipitated when equimolecular aqueous solutions of the sodium polyuronate and *n*ATMA·Br salt were mixed, and the mixture was left to stand at room temperature for a few hours. Yields approximated to 75 and 85% for pectinic and alginic complexes, respectively. The complexes were recovered as white hygroscopic powders that rapidly take up water in contact with the atmosphere. After an exhaustive exploratory testing, it was concluded that, at difference with complexes based on polypeptides, the polyuronic complexes are non-soluble in most of common organic solvents, although they become swollen in some chlorinated hydrocarbons and were soluble in warm *m*-cresol. The exceptional insolubility displayed by these complexes should be attributed to the occurrence of frequent intermolecular hydrogen-bonding tightly interlocking the polysaccharide chains. The NMR analysis of ionic complexes made of long alkyl surfactants that have been previously reported has shown all them to have a nearly stoichiomeric composition in the two counterparts. In the present case, a similar analysis is unfortunately not feasible because the non-solubility of these polyuronic complexes; in the absence of any opposite evidence, it will be reasonable to assume that the composition of these complexes must be no far from stoichiometric composition.

### 3.2. Thermal properties

The thermal behaviour of *n*ATMA·PUrA complexes was examined by both TGA and DSC, and results are compared in Table 1. The TGA analysis showed that complexes start to decompose at temperatures above 200 °C.

Decomposition took place along a multi-stage mechanism involving at least three successive stages which are defined by three maximum rate decomposition temperatures in the 210–230 °C, 260–300 °C and 380–410 °C ranges, respectively, with no residual material left at the end of the last stage. According to $^\circ T_d$ and the first step decomposition temperature values, complexes of pectinic acid appear to be slightly resistant to heating than the alginic ones, and comparison of the temperatures for the second and third decomposition steps reveals that the thermal stability increases steadily with *n* in both series. The DSC analysis revealed that all complexes have a melting peak in the 50–80 °C range showing a trend of increasing temperature and enthalpy with the increase in length of the alkyl side chain. An exothermic peak indicative of crystallization is observed upon cooling after melting although the crystallinity attained is much lower than originally attained, and crystallization could take place only if the overheating above melting is restricted to a few tens of degrees. The heating and cooling DSC traces registered from the 18ATMA complexes of both pectinic and alginic acids are depicted in Fig. 3. Thermal data of melting and crystallization for the three series of complexes afforded by DSC analysis are compared in Table 1. According to which is well known for polyglutamates and polymalates complexes (García-Alvarez et al., 2005; Pérez-Camero et al., 2004; Portilla-Arias et al., 2006), the endothermic peak located in the 40–80 °C range is interpreted to arise from the melting of the polymethylene segments. It can be inferred from the broaden shape displayed by the melting peaks that, compared to polypeptide and polyester chains, the polysaccharide chain hinders the crystalline packing of the alkyl side chains and reduces the efficiency of the system for being arranged in ordered structures. This effect is even more pronounced for the complexes made of alginic acid, where melting enthalpies of the recrystallized material only are able to reach tenths of a kcal $mol^{-1}$. It does make sense to interpret that after melting, a fraction of hydrogen bonds is disrupted and their rebuilding must require appropriate time and temperature conditions. It is worth noting that surfactants display melting peaks above 100 °C clearly distinguishable from the melting of the alkyl side chain; the absence of such peaks in the DSC traces of complexes indicates that the excess of surfactant in these compounds, if any, must be small.

The plot of the melting enthalpy against the number of carbons contained in the alkyl surfactant group for pectinic and alginic acid complexes (Fig. 4a) consists of two almost parallel straight lines with a slope of 0.7–0.8 kcal $mol^{-1}\cdot CH_2^{-1}$ indicating that the paraffinic crystal lattice must be similar in both cases. Conversely, a difference of nearly 5 kcal $mol^{-1}$ is observed between the two

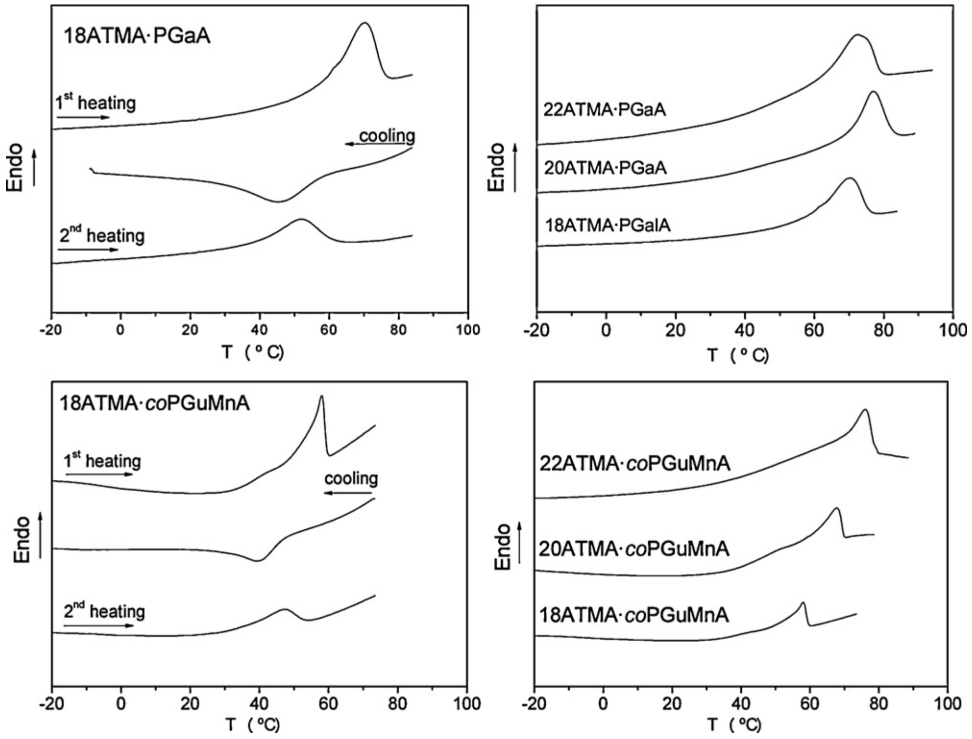

**Fig. 3.** DSC traces of *n*ATMA·PGaA and *n*ATMA·*co*PGuMnA.

series as the *y*-intercept is concerned. The higher enthalpy values observed for *n*ATMA·PGaA complexes reveal a higher crystallinity of the paraffinic phase in this series. The number of crystallized methylenes $n_c$, inferred from enthalpy data, is plotted against *n* in Fig. 4b, which shows an almost exact linear dependence with the same slope for the two series. Specifically, $n_c$ takes values between 6 and 10 for the *n*ATMA·PGaA complexes and between 2 and 6 for the *n*ATMA·*co*PGuMnA complexes. It is noteworthy that only a minor fraction of the methylenes contained in the paraffinic phase is able to crystallize and that such fraction is significantly greater in the case of pectinic complexes. The lower crystallizability displayed by *n*ATMA·*co*PGuMnA complexes can be attributed to the chain microstructure heterogeneity of the poly(guluronic-*co*-mannuronic) chain.

### 3.3. The biphasic structure of the complexes

According to the DSC results described above, the X-ray diffraction analysis of the *n*ATMA·PUrA complexes revealed the existence of a considerable order, at both short and medium range. The powder X-ray diffraction diagram recorded from the 20ATMA·PGaA complex is depicted in Fig. 5a for illustration. This X-ray scattering pattern, which is characterized by the presence of the two peaks at ~0.42 nm and ~3.5 nm is shared by all the complexes examined in this work; the precise spacing values appearing for all the complexes are listed in Table 2.

In all the complexes but in 18ATMA·*co*PGuMnA, the 0.42 nm reflection is the only one appearing in the wide-angle region. According to what is known for polyglutamates and polymalates complexes (García-Alvarez et al., 2005; Pérez-Camero et al., 2004; Portilla-Arias et al., 2006), such reflection should be associated with the 100 interplanar spacing of a crystallized paraffinic phase with the alkyl chains packed in a pseudohexagonal phase with $a \approx 0.48$ nm. The strong sharp peak appearing in the medium angle region, which is invariably accompanied by a second order peak, arises from a ~3–4 nm periodical spacing ($L_0$), which tends to increase with the value of *n* in both series. The $L_0$ values of the complexes together with the values reported for the

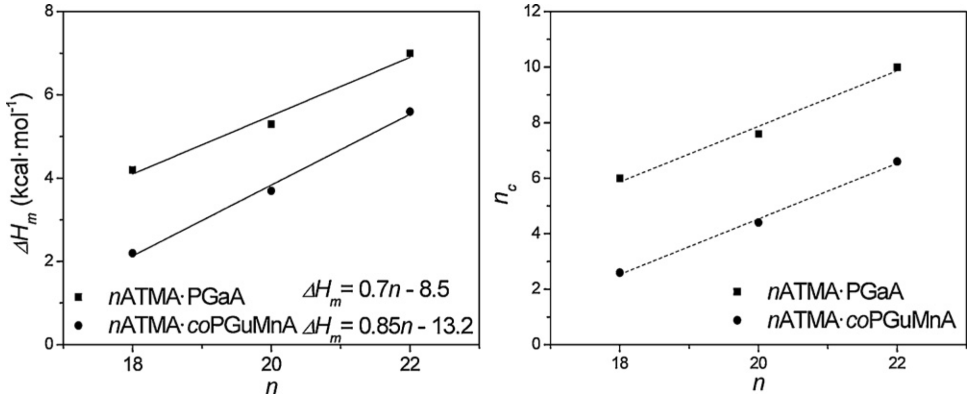

**Fig. 4.** Methylene melting enthalpy, $\Delta H_m$ (a), and number of crystallized methylene units, $n_c$ (b), as a function of the number of methylenes, *n*, contained in the alkyl side chain.

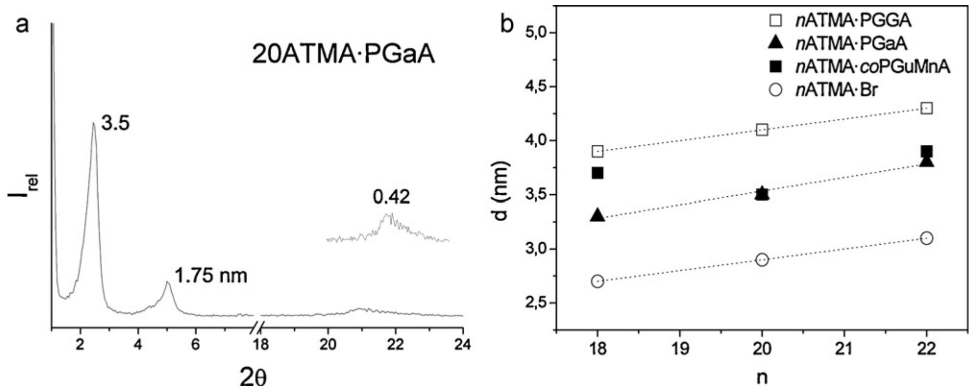

**Fig. 5.** (a) X-Ray diffraction profile of the indicated complex in the SAXS region. *Inset*: 19–23° region of WAXS displaying the 0.42 nm reflection characteristic of the crystallized paraffinic phase. (b) Variation of the interlayer spacing with *n* for the indicated series of complexes and for the *n*ATMA·Br surfactant series.

polyglutamate complexes (*n*ATMA·PGGA) are plotted against *n* in Fig. 5b. A straight line is obtained for the *n*ATMA·PGaA series with a slope of 0.125 nm·$CH_2^{-1}$ comparable to the 0.10 value observed for the *n*ATMA·PGGA. A 0.10–0.125 nm value is acceptable with the rise of the methylene unit of a chain in full-extended conformation. In the case of the *n*ATMA·*co*PGuMnA, the $L_0$ spacing changes unevenly with *n* although the overall trends seem to follow the other series. According to what is well known for comb-like systems, the $L_0$ spacing is associated with the periodicity of a biphasic layered structure in which the paraffinic phase made of alkyl side chains alternates to the hydrophilic phase made of polysaccharide chains.

### 3.4. Thermal transitions

The structural changes accompanying the melting of the alkyl side chain were followed by powder X-ray diffraction recorded at real time with synchrotron radiation. The evolution of the scattering profile of 20ATMA·PGaA complex with temperature in both WAXS and SAXS regions is shown in Fig. 6. Upon melting, *i.e.* at temperatures about 70 °C, the 0.42 peak vanished and displaced to around 0.45 nm; the changes observed in the SAXS region reflect the dimensional variations of the interlayer spacing upon melting. The 3.5 nm peak moves slightly toward higher values indicating the occurrence of an expansion in the structure of 0.2 nm. This pattern of behaviour can be taken as representative of the *n*ATMA·PUrA complexes and it reflects the structural changes that take place in the layered arrangement. The disruption of the pseudohexagonal paraffinic crystal lattice leads to a liquid phase in which the polymethylene chains are packed with an average chain-to-chain distance of 0.45 nm. Simultaneously, a slight rearrangement occurs involving a spacing out around 5% and 10% of the original value for the pectinic and alginic acid, respectively. The SAXS and WAXS values measured for the complexes below and above melting are compared in Table 2.

**Table 2**
X-ray data of polyuronic complexes subjected to heating.[a]

| | SAXS | | WAXS | |
|---|---|---|---|---|
| nATMA PUrA | $L_0^{20\,°C}$ | $L_0^{T_m}$ | $d_{0\,0\,1}^{20\,°C}$ | $d_{0\,0\,1}^{T_m}$ |
| PGaA | | | | |
| 18 | 3.3 | 3.4 | 0.41 | 0.46 |
| 20 | 3.5 | 3.7 | 0.41 | 0.46 |
| 22 | 3.8 | 4.1 | 0.41 | 0.46 |
| coPGuMnA | | | | |
| 18[b] | 3.7 | 4.2 | 0.42 | 0.46 |
| | 4.2 | | 0.45 | |
| 20 | 3.5 | 4.3 | 0.42 | 0.46 |
| 22 | 3.9 | 4.3 | 0.42 | 0.46 |

[a] Lamellar spacings ($L_0$) and interplanar distances ($d_{0\,0\,1}$) at 20 °C and at the melting temperature.

[b] Two spacings seen at 20 °C due to partial melting of this complex at this temperature.

The heating effect on the structure is similar to that displayed by polyglutamates and polymalates, both esters and complexes, previously studied by us (García-Alvarez et al., 2005; Morillo et al., 2001, 2003; Pérez-Camero et al., 2004; Portilla-Arias et al., 2006). It should be noticed however that the changes taking place in $L_0$ with temperature, in both magnitude and sign, are depending on the chemical nature of the polymer chain as well as on the nature of the bond linking the alkyl side chain to the main chain. The evolution of the SAXS profiles at heating and cooling deserves special attention. The increasing intensity and sharpness displayed by the 3–4 nm peak with temperature is really striking; such changes denote an improvement in the layered arrangement with temperature, which even continues above melting. Although it could be explained assuming that the main chain sheets can be accommodated better when the interlayer structure become more fluid, this is a complex point that required further attention. Furthermore, the full reversibility of the process suggests that the structural modification must be essentially dimensional without implying severe molecular rearrangements.

The conformational changes involved in the melting of the alkyl side chain of *n*ATMA·PUrA were investigated by $^{13}C$ CP-MAS NMR since the application of this technique in the transitions happening in comblike polymers induced by heating effects is wealthy documented (Yamanobe et al., 1988). It is well known that melting of a paraffinic lattice implies a *anti*-to-*gauche* transition in the dihedrals of the polymethylene segments, which is reflected in changes in the shifts of the implicated carbon resonance peaks. The changes taking place in the $^{13}C$ NMR spectrum of 18ATMA·PGaA and 18ATMA·*co*PGuMnA upon successive heating and cooling are shown in Fig. 7. In 18ATMA·PGaA at 25 °C, the peak arising from the inner methylenes of the alkyl side chain in *anti* conformation appeared near to 33 ppm, whereas at 80 °C, the peak is upfield displaced to 30 ppm which is the shift expected for a polymethylene chain undergoing a fast transition between the *anti* and *gauche* conformers. At intermediate temperatures, both peaks are present since the melting proceeds along a broad temperature range and upon cooling to 25 °C, the initial spectrum is fully recovered. In the case of 18ATMA·*co*PGuMnA, the changes are similar although the spectrum at 25 °C shows the double peak indicating that the octadecyl chain is partially melted at this temperature in this complex. This observation is unique in the whole set of complexes here studied and accounts for the second spacing observed at 4.2 nm in the SAXS profile of 18ATMA·*co*PGuMnA (Table 2). The pattern of

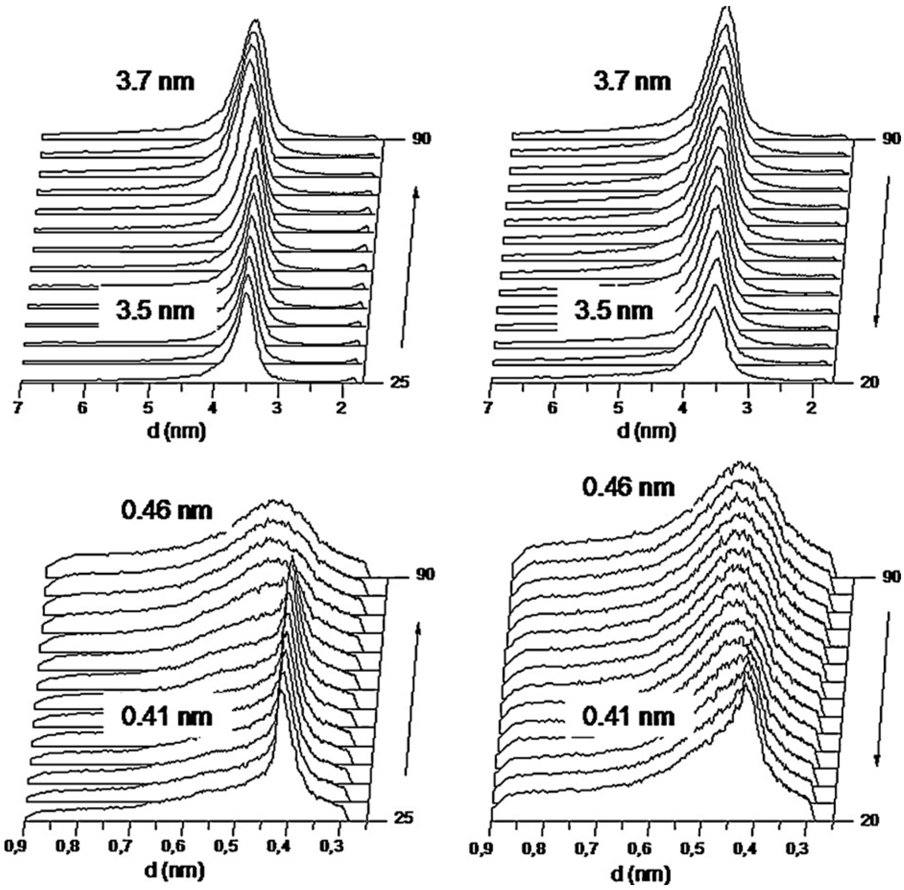

**Fig. 6.** Real time SAXS (top) and WAXS (bottom) profiles of 20ATMA·PGaA at heating (left) and cooling (right).

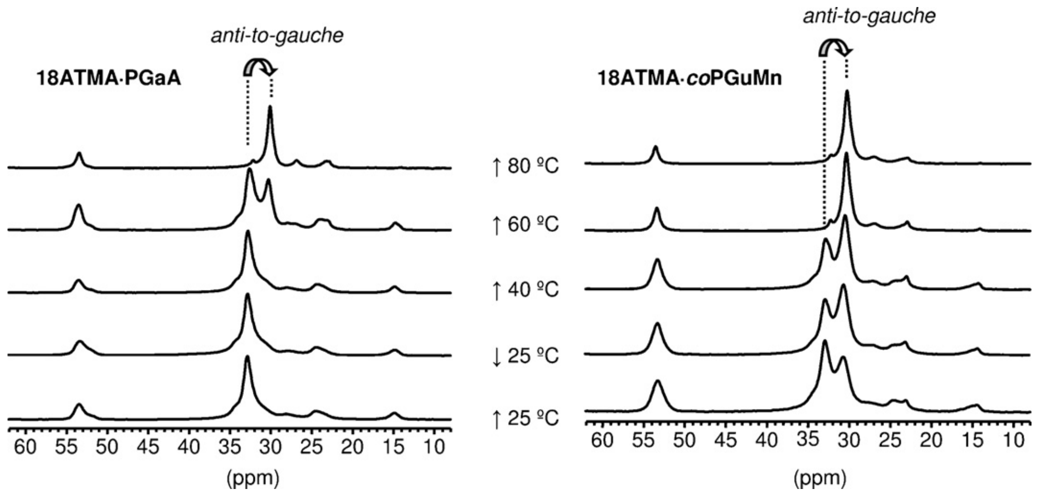

**Fig. 7.** $^{13}$C CP-MAS NMR spectra of polyuronic complexes revealing the *anti*-to-*gauche* transition of inner paraffinic methylenes that takes place upon heating and cooling.

changes described for 18ATMA·PGaA is shared by all the complexes studied in this work and it is similar to that described for the A–B transition happening in comblike polyaspartates and polyglutamates, both covalent and ionic, by effect of heating (García-Alvarez et al., 2005; López-Carrasquero et al., 1995; Martínez de Ilarduya et al., 1999; Morillo et al., 2001, 2003; Pérez-Camero et al., 2004). The NMR results not only give strong support to DSC and X-ray diffraction interpretations given above, but also provided helpful information to understand the melting process at the molecular level. The fact that a good amount of methylenes remain at *anti* conformation after melting indicates that the polymethylene chain looses the crystalline order without abandoning the stretched conformation. This should be the reason for the small dimensional change involved in the transition and for the outstanding willingness of the system to recover the original structure.

## 4. Conclusions

Comb-like ionic complexes of polypectinic acid (polygalacturonic acid) and polyalginic acid were prepared by coupling with alkyltrimethylammonium surfactants bearing long alkyl chains of 18, 20 and 22 carbon atoms. The resulting complexes are not soluble in water neither in most of common organic solvents and are stable up to temperatures above 200 °C. These complexes crystallize in a biphasic layered structure which displays melting and recrystallization of the alkyl side chain at temperatures between 40 and 80 °C. The transition temperatures and crystallinity increase with the length of the alkyl side chain and are higher for the pectinic acid complexes suggesting that a better molecular arrangement is reached in this case. The melting-recrystallization process is reversible, happens instantaneously and involves a significant dimensional change in the structure. This interesting behaviour confers to these complexes high interest as potential membranes with thermoresponsive properties.

## Acknowledgements

We thank the MCINN of Spain for Grant MAT2009-14053-C02-01 and the Basque Government for the Ph.D. grant awarded to Ainhoa Tolentino.

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