Ionic Complexes of Polyacids and Cationic Surfactants

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

Summary: Comb-like ionic complexes were prepared from polyuronic acids (pectinic and alginic acids) and alkyltrimethylammonium surfactants bearing linear alkyl chains with 18, 20 and 22 carbon atoms. In the condensed state, these complexes were able to self-assemble in ordered structures which were thermally stable up to ~200 °C. The complexes were analysed by DSC and WAXS/SAXS and compared to their analogous made from poly(γ-glutamic acid). They all adopt a biphasic layered structure in which the main chain and the alkyl side chain alternate with a nanometric periodicity. Alkyl side chains were partially crystallized in these complexes and they show reversible melting at temperatures within the 60-80 °C range depending on the length of the polymethylene segment.

Keywords: alginic acid; comb-like ionic complexes; pectinic acid; Poly(gamma glutamic acid); polyelectrolyte surfactant complexes; polygalacturonic acid; polyuronic acid

Introduction

It is known that comb-like polymers made of a rigid main chain and a flexible side chain are able to self-assemble in biphasic layered structures sensitive to temperature changes.[1] As early as 1985, Watanabe described comb-like polymer structures made of long alkyl esters of polyglutamates.[2] In these systems the alkyl side chain is linked to the main chain by an ester bond. It is well established that in these comb-like polypeptides the main chain is in helical conformation with hydrogen bonds intramolecularly formed and the side chains coming out from the helix to fill up the interlayer space.[3] Upon heating, 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 although the interlayer spacing decreases due to the slightly contraction undergone by the polymethylene chain. Such thermal behaviour has interesting phenomenological consequences with potential technological applications such as responsive temperature membranes and thermochromic sensors.[4–6]

Recently it has been shown that comb-like systems with structure and properties similar to those described above can be generated by ionic coupling between ionic alkyl surfactants and charged polyelectrolytes (Figure 2). First work published on this type of systems was reported by Antonietti in 1994.[7] The clear advantage afforded by the systems based on ionic coupling respect to the covalent ones is simplicity of preparation; ionic complexes can be readily obtained by direct mixing of the corresponding components in aqueous medium avoiding laborious synthetic work.

In this contribution a comparative study of the complexes produced by ionic coupling of alkyltrimethyl ammonium surfactants (*n*ATMA) with either poly(γ-glutamic acid) (PGGA) or polyuronic acids (pectinic and alginic acids) is reported. PGGA is a biotechnological polypeptide obtained by aerobic fermentation of organic substrates with bacteria

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Departament d'Enginyeria Química, Universitat Politècnica de Catalunya ETSEIB, Diagonal 647, 08028 Barcelona, Spain
E-mail: sebastian.munoz@upc.edu

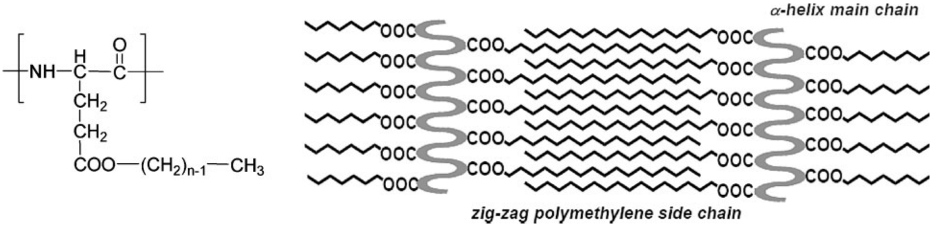

Figure 1.
Chemical structure of comb-like poly(γ-alkyl α-glutamate)s and scheme of the layered structure adopted in the solid state.

B. licheniformis. [8] The ionic complexes of this polyacid with *n*ATMA for even *n* values from 12 to 22 have been extensively studied by us and we have recently reported on their structure and properties in several papers.[9,10] On the other hand, to our knowledge no antecedents exist on ionic complexes formed from polyuronic acids so that the results presented here may be envisaged as pioneering in this field. Pectinic acid [poly(1,4-α,D-galacturonic acid), (PGaA)] was enzymatically produced and alginic acid [poly(1,4-α,L-guluronic-*co*-1,4-β,D-mannuronic acid), (PGuMnA)] was obtained by extraction from brown algae. The more relevant features of the polyacids used in this study in connection to the carried out work are listed in Table 1, and their chemical formula are given in Figure 3.

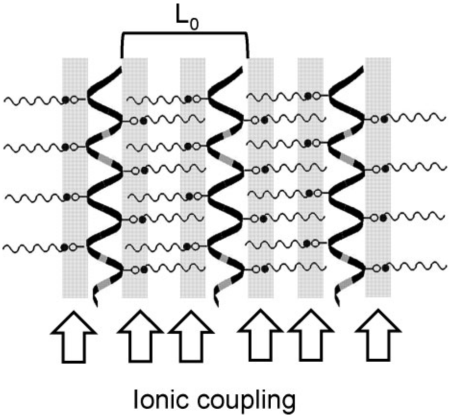

Figure 2.
Scheme of the biphasic layered structure adopted by ionic complexes made of a polyelectrolyte and an ionic alkyl surfactant.

Our efforts are currently addressed to explore the possibilities of polyuronic acids to form ionic comb-like complexes of the type described above for polyglutamic acid,[9,10] and to evaluate the influence of the polysaccharide chain on the structure and properties of these complexes compared to those made from polypeptides. A wider spectrum of behaviours may be expected for polyuronic-based complex systems given the conformational variability inherent to the polysaccharide chain and to the constitutional diversity in which polyuronic acids occur.

Experimental Part

Biosynthetic sodium poly (γ,DL-glutamate) was kindly supplied by Dr. Kubota of Meiji Co. (Japan). Naturally occurring enzymatic polygalacturonic acid and brown algae alginic sodium salt with were purchased to Sigma-Aldrich. The alkyltrimethylammonium cationic surfactant salts of general formula $RMe_3N{\bullet}Br$ with R= $-C_{18}H_{37}$ (octadecyl) were purchased from Aldrich and those with R= $-C_{20}H_{41}$ (eicosyl) and $-C_{22}H_{45}$ (docosyl) were synthesized by us according to the procedure described in the literature.[11]

Complexes were prepared following the methodology described by Ponomarenko et al. for the synthesis of same type complexes of surfactants with poly (α,L-glutamic acid).[12] 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

Table 1.
Polyacids used in this work.

Polyacid	Mw (g/mol)	Composition	Origin	% COOH
PGGA	300,000	GluA 100%, D/L = 59/41	Meiji Co (Japan)	100
PGaA	25,000-50,000	L-GaA 100%	Sigma-Aldrich	100
PGuMnA	80,000-120,000	L-Gu/D-Mn = 39/61	Sigma-Aldrich	100

maintained under stirring at temperatures between 40-60 °C for 4 hours. The formed precipitate was isolated by centrifugation and dried under vacuum.

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 20-200 °C temperature range. Time resolved X-ray 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 out within the 10-120 °C range. Small and wide angle X-ray scattering patterns (SAXS and WAXS) were acquired every minute. Semicrystalline standard PET and Ag-behenate were used for calibrations. 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.

Results and Discussion

All the *n*ATMA·PGGA complexes were readily formed as a white fine powder when equal volumes of aqueous solutions of the sodium salt of the polyacid and the *n*ATMA·Br salt at the same molar concentration were mixed and the mixture was left to stay at room temperature for a few hours.

Complexes for values of $n = 18$, 20 and 22, were prepared in yields that oscillated between 50 and 90%. Whereas all the *n*ATMA·PGGA complexes were readily soluble in chloroform, none of the complexes formed from polyuronic acid could be solubilized in common organic solvents. The strong intermolecular hydrogen-bonding occurring between the hydroxyl

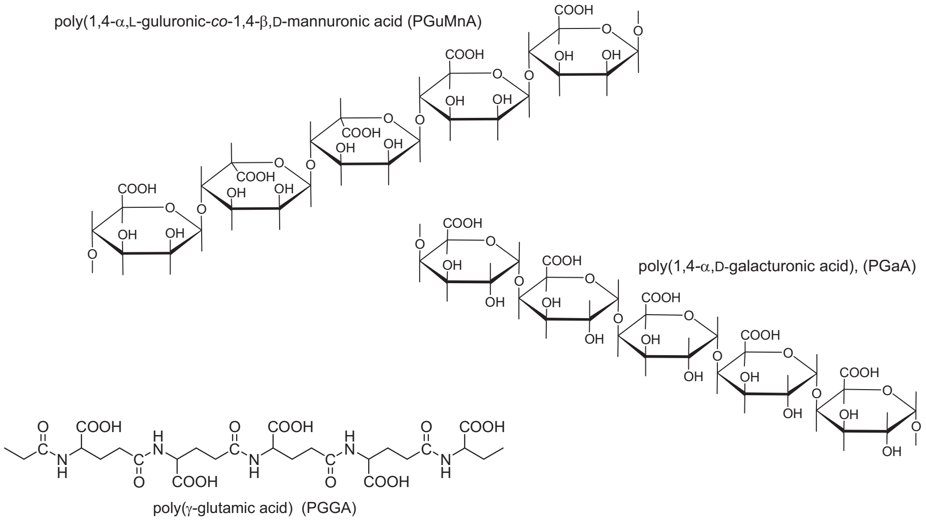

Figure 3.
Chemical formulae of the polyacids used in this work.

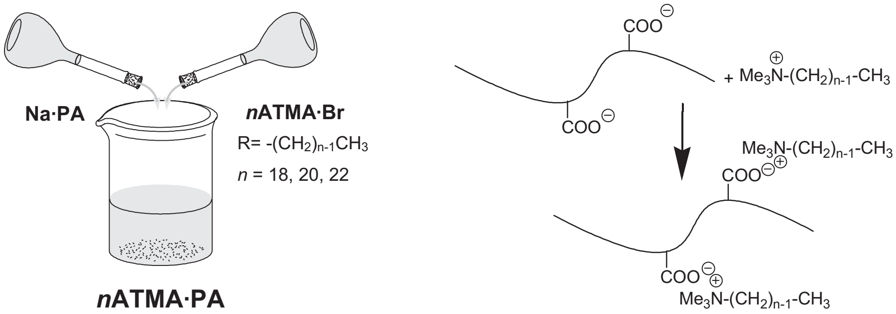

Figure 4.
Preparation of ionic complexes from polyacids and cationic surfactants.

groups of the polysaccharide chain is interpreted to be the probable cause for the remarkable insolubility displayed by these compounds.

The NMR analysis in solution of *n*ATMA·PGGA complexes revealed that they were nearly stoichiometric compounds with just a small excess of surfactant that slightly increased with the length of the alkyl chain. The low solubility of the polyuronic acid-complexes prevented us to carry out such analysis for these complexes and unfortunately the composition of these compounds is not known at this moment.

The TGA analysis showed that all complexes are fairly stable up to temperatures near 200 °C. The thermal decomposition mechanism of *n*ATMA·PGGA complexes was previously investigated in detail[13] and showed to occur through a two-stage process, the first stage being cyclodepolymerisation of the poly(γ-glutamate) main chain along with decomposition of the ionic complex promoted by the adsorbed water. The preliminary analysis of *n*ATMA·PGaA and *n*ATMA·PGuMnA indicated that they also decompose by a multi-stage mechanism with dissociation of the complex taking place in the first step but no signs of depolymerisation were detected.

The DSC analysis of the complexes evidenced that in all cases the alkyl side chain is long enough as to crystallize in a separated phase. The heating DSC traces of *n*ATMA·PGGA and *n*ATMA·PGaA complexes registered from samples coming directly from synthesis are compared in Figure 5. The endothermal peak located in the 40-80 °C range arises from the melting of the polymethylene segments, which as

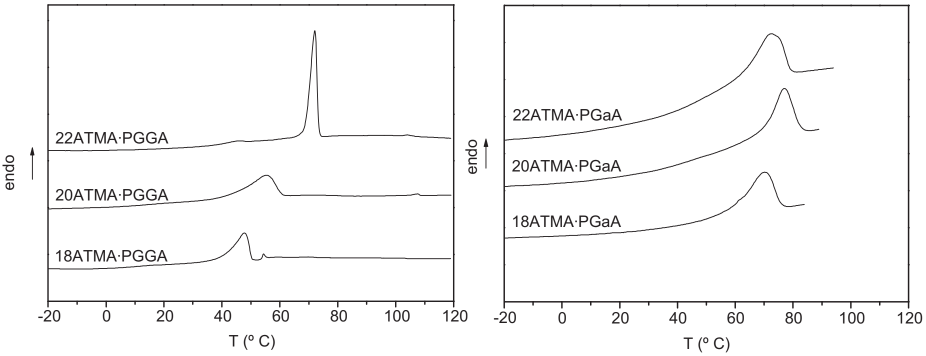

Figure 5.
DSC traces recorded at heating from the indicated complexes.

Table 2.
DSC and X-ray diffraction data of the complexes studied in this work.

Complex	DSC				XRD		
	1st Heating		2nd Heating		SAXS		WAXS
	T_m (°C)	ΔH_m (kcal·mol^{-1})	T_m (°C)	ΔH_m (kcal·mol^{-1})	d^1 (nm)	d^2 (nm)	d (nm)
***n*ATMA·PGGA**							
18	48	3.6	50	3.8	3.8	1.9	0.42
20	55	5.6	58	5.4	3.9	1.9	0.42
22	72	6.9	68	5.7	4.1	2.1	0.42
***n*ATMA·PGaA**							
18	70	4.2	52	2.5	3.4	1.7	0.42
20	77	5.3	61	1.9	3.6	1.8	0.42
22	73	7.0	66	3.8	4.0	2.0	0.42
***n*ATMA·PGuMnA**							
18	59	1.9	33	0.6	4.2;3.7	1.8	0.45; 0.42
20	65	5.0	41	2.8	3.6	1.8	0.42
22	76	7.1	60	4.1	3.8	1.9	0.42

expected, is observed to increase in temperature and enthalpy with the value of *n*. It is worth noting that the surfactants display melting peaks above 100 °C clearly distinguishable from the melting of the alkyl side chain. The absence of such peaks is taken as indicative that the excess of surfactant in these compounds, if any, should be small. In overall the melting peaks of complexes made of polyuronic acids appear broader than those of PGGA complexes. Furthermore, *n*ATMA·PGGA complexes recrystallized readily upon cooling from the melt with recovery of most of the original crystallinity whereas recrystallization of polyuronic complexes after melting was not so reliable and only could take place at moderated overheating. It seems that the presence of the polysaccharide chain hinders the crystalline packing of the alkyl side chains and makes the system less efficient for being arranged in ordered structures. Thermal data afforded by DSC analysis of melting and crystallization for the three series of complexes are compared in Table 2.

According to the DSC results described above, the powder X-ray diffraction of the complexes revealed the existence of a considerable order, as it is illustrated in Figure 6a for the case of 18ATMA·PGaA complex. The diffraction peak observed in

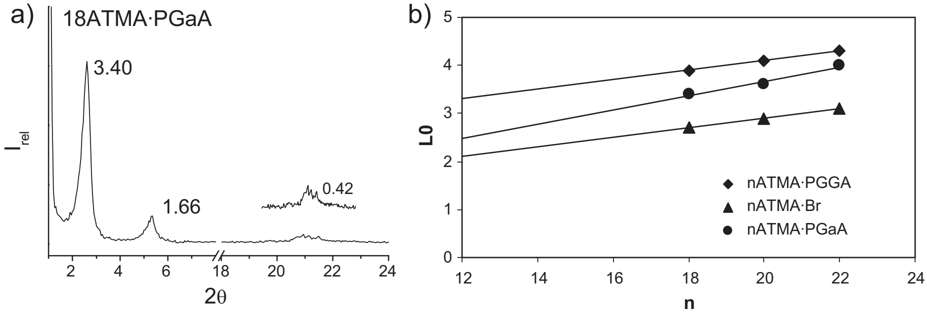

Figure 6.
a) X-Ray diffraction profile (interplanar spacing indicated in nm) of the indicated complex in the medium-low angle region. Inset: 19-23° region of WAXS displaying the 0.42 nm reflection characteristic of the crystallized paraffinic phase. b) Variation of the interlayer spacing with *n* for the PGGA and polyuronic complexes and for the *n*ATMA·Br surfactant series as well.

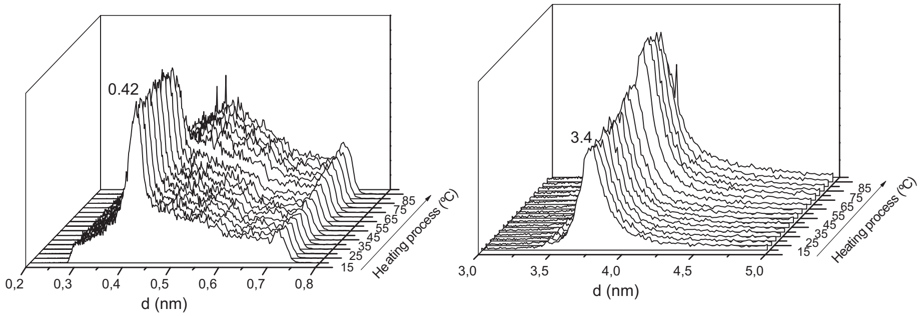

Figure 7.
Evolution of the X-ray scattering produced by 18ATMA·PGaA complex in the WAXS (left) and SAXS regions with heating from room temperature to 85 °C.

the wide-angle region with a spacing of 0.42 nm is associated to the 100 reflection produced by a crystallized paraffinic phase with the alkyl chains packed in a pseudo-hexagonal phase with $a \approx 0.48$ nm. In the small angle region, all the complexes showed definite diffraction scattering corresponding to the first and second order of a main spacing L_0 with values ranging between 3.4 and 4.2 nm and increasing almost linearly with the length of the alkyl side chain (Figure 6b). According to what is known for comb-like systems, the L_0 spacing is associated to the periodicity of the biphasic layered array in which the paraffinic phase made of alkyl side chains alternates to the phase made of polycarboxylate chains.

The structural changes concomitant to the melting of the alkyl side chain were followed by powder X-ray diffraction recorded in real time with synchrotron radiation. The evolution of the scattering profile of 18ATMA·PGaA complex with temperature in both WAXS and SAXS regions is shown in Figure 7. Upon melting, *i.e.* at temperatures about 70 °C, the 0.42 peak vanished and displaced to around 0.45 nm; it is well known that this change is consequence of the disappearance of the hexagonal crystallites leading to a disordered phase in which the polymethylene chains keep laterally packed with an average chain-to-chain distance of 0.45 nm.

The changes observed in the SAXS region reflect the dimensional variations of the interlayer spacing upon melting. The 3.4 nm peak moves slightly toward lower values indicating the occurrence of a contraction in the structure. This behaviour is similar not only to that displayed by the *n*ATMA·PGGA complexes but also to that observed for the complexes of polymalic acid previously studied by us.[14] It should be noticed that the evolution of this scattering with temperature in the covalent systems based on polyglutamates and polyaspartates takes place with an extent and sign depending on the length of the alkyl side chain and the nature of the main polypeptide chain. What is also striking is the increasing in intensity and sharpness displayed by such peak which should be associated to an improvement of the layered arrangement upon melting of the alkyl side chains. 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.

Conclusions

Ionic complexes from polyuronic acids, pectinic and alginic acids, and alkyltrimethyl ammonium surfactants with the alkyl chain been linear and containing 18, 20 and 22 carbon atoms could be prepared by mixing aqueous solutions of the corresponding salts. The resulting complexes were neither soluble in water nor in the common organic solvents. Similarly to complexes formed from poly(γ-glutamic acid), these compounds are thermally stable up to near 200 °C and decompose at higher temperatures in several steps. The thermal behaviour and diffraction properties of these complexes were also comparable to those reported for poly(γ-glutamic acid) complexes. Analogously, they seem to self-assembled in a biphasic structure in which the alkyl side chains are segregated from the main chain phase and crystallized in a pseudohexagonal or *quasi*-hexagonal lattice that melts within the ~70-80 °C range. These complexes also underwent reversible thermal transition connected to the melting-recrystallization of the paraffinic phase without significant alteration of the layered assembly.

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