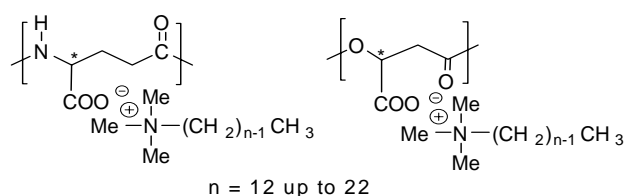


COMBINED WAXS AND SAXS REAL-TIME STUDY OF PHASE TRANSITIONS IN COMB-LIKE IONIC COMPLEXES OF BIOSYNTHETIC POLYPEPTIDES AND POLYESTERS

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Comb-like polymers made of a backbone chain with attached long flexible side groups are able to form supramolecular assemblies of both academic and technological interest. Our research is currently addressed to this type of systems when formed by stoichiometric ionic complexes of biotechnological polyacids and alkyltrimethylammonium surfactants bearing long alkyl groups. Specifically, poly(γ -glutamic) (PGGA) and poly(β ,L-malic) (PMLA) acids are the biopolymers under study.



In the solid state, these complexes adopt an amphiphilic layered structure with the alkyl side chains crystallized in a separate microphase (hexagonal or rhombic) that intercalates between the sheets constituted by the main chains. The periodicity of this structure oscillates between 2.5 and 5 nm depending on the length of the alkyl group. Such a structure has been revealed to be very sensitive to temperature showing thermal transitions that are accompanied by clearly perceivable dimensional changes in the period of the supramolecular structure.^{1,2} The detailed molecular and lattice changes taking place upon such transition are issues that still remain to be disclosed.

In this communication we describe the results obtained in the simultaneous WAXS-SAXS analysis on isotropic samples of these complexes carried out in real-time by synchrotron radiation under variable temperature in the 20-115 °C range. The changes in long spacings corresponding to contraction or expansion of the supramolecular layered structure were observed to depend on both side chain length and nature of the main chain, and in some cases, they take place involving intermediate well defined structures. On the other hand, the paraffinic phase behaved according to a common pattern consisting of a shifting of the 0.42 nm to 0.45 nm spacing, which corresponds to the melting of the polymethylene chains. All these changes were found to be almost fully reversible.

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