Ionic complexes of naturally occurring polyacids and cationic surfactants

A. Tolentino, A. Alla, and S. Muñoz-Guerra

Departament d’Enginyeria Química, Universitat Politécnica de Catalunya, ETSEIB, Diagonal 647, 08028 Barcelona, Spain

Stoichiometric comb-like complexes of bacterial poly(γ-glutamic) (PGGA) and poly(β,L-malic) (PMLA) acids with \textit{n}-alkyltrimethyl ammonium surfactants (\textit{n}ATMA) bearing long linear alkyl side chains have been recently reported.\textsuperscript{1,3} These complexes adopt biphasic layered structures with a periodicity between 3.5 and 4.5 nm according to the length of the alkyl chain. In these structures the side chains are separated in a hexagonal paraffinic phase that melts at temperatures between 45 and 70 °C whereas the main chain phase retains the ordered arrangement up to temperatures above 250 °C.

In this communication we describe the results obtained in the simultaneous WAXS-SAXS real-time analysis on isotropic samples obtained from ion complexes prepared from naturally occurring polyuronic acids, specifically, poly(α,D-galacturonic acid), (PGal) and poly(α,L-guluronic-co-β,D-mannuronic acid), (AlgA), and \textit{n}ATMA with \textit{n} = 18, 20 and 22 as surfactants, and those obtained on hybrid nanocomposites generated from mixtures of \textit{18}ATMA·PGGA and Cloisite 30B containing 3, 10, 20 and 30% of inorganic material.

All the experiments were carried out by synchrotron radiation at the A2 beamline of DORIS, DESY under variable temperature in the 10-120 °C range at a heating/cooling rate of 5 °C/min.

As was seen in previous experiments with \textit{n}ATMA·PGGA, the ionic complexes of polyuronic acids seem to be 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 \textit{quasi}-hexagonal lattice that melts within the ~70-80 °C range.\textsuperscript{4} Upon heating from 20°C (Figure 1), an expansion of the interlayer spacing associated to the melt of the side chain was observed in the SAXS patterns followed by appreciable increase in the area of the peak after the melt. The SAXS and WAXS patterns show a reversible process with some difficulties to crystallize.
Both SAXS and WAXS scattering patterns of the ionic nanocomposites showed reversible changes at corresponding to the melt/crystallization of the paraffinic phase (WAXS) or involving rearrangements at the supramolecular layered structure (SAXS). These preliminary experiments revealed significant changes in SAXS profiles (Figure 2). A new weak and broad peak at around 4.5 nm was observed in the scattering patterns of the ionic complex nanocomposites nATMA·PGGA-MMT 3% which increased with the content the amount of the clay in the ionic complexes. These results provide evidences supporting the occurrence of intercalated structures with an arrangement similar to that adopted by the nATMA·PGGA complexes.

Acknowledgements

Authors acknowledge the help given by CICYT with project MAT2006-13209-C02-02, the Basque Government for the Ph.D. grant awarded to Ainhoa Tolentino and DESY with project I-20051075EC which made possible the utilization of the A2 Beamline HASYLAB synchrotron facility in Hamburg.

References