Multidimensional characterization of polyelectrolytes and interpolyelectrolyte complexes in aqueous solutions

Abstract:

This PhD thesis is dedicated to the study of polyelectrolytes and their self-assembly in aqueous solutions. The morphology and ionization state of individual polymer chains were investigated as well as their co-assembly with oppositely charged species. First, the charge regulation of short and long weak polyelectrolytes in aqueous solution was investigated to deeper understand their pH-responsive properties. The changes of ionization degree and charge of oligopeptides composed of 5 amino acids with acid side-chains and 5 with basic side chains were followed upon varying the pH in order to reveal the effect of interactions between the like-charged and oppositely charged groups. It was shown that intra-molecular electrostatic interactions and conformational flexibility caused the suppression of the total charge and enhancement of ionization of the peptides.

To get an insight into the distribution of local H^+ concentration in the proximity of a polyelectrolyte chain, a modified polyelectrolyte structure was used with a fluorescent pH-indicator, covalently attached at the end of the chain. Ionization of the pH-responsive fluorophore revealed its effective pK which was compared with the local H^+ concentration near the polyelectrolyte chain. It was shown that while these two values are very similar, they are not exactly equal. The difference between them is a result of the fluctuations in the small-ion distribution, chain conformation, and fluorophore ionization.

Moreover, the assembly of polyelectrolytes with oppositely charged low-molar mass compounds, proteins, homopolymers and block polyelectrolytes was studied. The ability of multivalent anionic coordination compounds of iron to bind to polyelectrolyte chains was shown for a series of polythiophene-based polycations. Quenching of polyelectrolyte fluorescence even for low concentrations revealed strong binding of the solute, thus making polythiophene-based polycations appealing for their application as luminescence sensors.

Further, the assembly of di- and triblock polyelectrolytes in aqueous solutions was investigated. The complex formation between a polyanion and a double hydrophilic block copolymer composed of a polycationic block and a neutral hydrophilic block was followed by quenching of a fluorescent label attached to the end of the polyanion chain. As a result, core/shell micelles were formed with a dynamical core composed of interpolyelectrolyte complex (IPEC), the charge of which can be tuned by varying the ratio of polymer concentrations. As an alternative approach for designing dynamical micelles with a charged shell, self-assembly of amphiphilic di- and triblock polyelectrolytes containing a hydrophobic block with low glass transition temperature were investigated. The investigation revealed that these micelles were able to encapsulate and release hydrophobic solutes as well as to form complexes with oppositely charged species, namely proteins and double hydrophilic block polyelectrolytes. It was shown that the morphology, the stability and the charge of the polyelectrolyte shell of the formed complexes strongly depends on the ionic strength and the molar ratio of oppositely charged groups.

Key words:

polyelectrolyte, block copolymer, encapsulation, release, interpolyelectrolyte complex, ampholyte, peptide, protein, pH, micelle, vesicle, scattering, microscopy, calorimetry, NMR, titration