Water-Soluble Interpolyelectrolyte Complexes (IPECs) - Effect of Hydrophobic Modification on Structure and Solubilisation

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Oppositely charged polyelectrolytes have a strong tendency to co-assemble in aqueous solution, thereby forming interpolyelectrolyte complexes (IPECs). Their structure depends strongly on the type of polyelectrolytes, where chemistry of the monomeric unit, degree of polymerisation, and the architecture play major roles. The typical problem of insolubility encountered upon approaching charge neutralisation may be addressed by employing polyelectrolytes with a second, neutral hydrophilic block, i.e. using a double-hydrophilic block copolymer (DHBC).
In our work, we studied a larger range of such IPECs, including DHBCs, to control the phase behaviour. Most interestingly we introduced hydrophobic modifications into the polyanion, based on poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA). By introducing different percentages of C4 to C16 alkyl chains we not only modify the assembly behaviour of their IPECs but the presence of the hydrocarbon chains also changes the solubilisation properties of the IPEC core, which normally is rather polar due to the high concentration of oppositely charged units.
The structure of the complexes formed in aqueous solution was characterised by means of static and dynamic light scattering, small-angle x-ray and neutron scattering (SAXS, SANS), and complementary cryo-TEM measurements. The focus was on how the aggregate structure depends on the mixing ratio of the two polyelectrolytes and the extend of hydrophobic modification. In parallel to this mesoscopic characterisation, we studied in detail how the solubilisation capacity of the IPECs for different drug molecules like curcumin, fenofibrate, carbamazepine, etc. depends on the choice of the IPEC components and in particular on the presence of hydrophobic modifications. These studies showed that a very marked (by factors of 50-100) enhancement of drug solubilisation can be achieved by appropriate choice of the IPEC components and in particular by the presence of the hydrophobic modification.
In summary, we find that hydrophobic modification is an interesting way to tune the structure and properties of IPECs and the solubilisation properties can be directly related to the mesoscopic IPEC structure. By combining the concepts of HM-PEs and DHBC one can control phase behaviour and structures over a large range, thereby offering the option to tune soluble IPECs for desired properties and potential applications.

Keywords:
interpolyelectrolyte complexes, solubilisation, small angle scattering