Light scattering applied to self-assembling systems

1. Uncharged Systems

Static and dynamic light scattering provide a unique tool to study the shape and size of systems on a length scale ranging from 1 nm to several µm. Light scattering techniques are non-evasive and can be used to learn about the in situ structure of a system as it forms in solvent, contrary to for example electron microscopy or atomic force microscopy. We applied light scattering to two newly developed molecular systems that were designed to spontaneously self-organize into a one-dimensional structure: Ring-coil triblock copolymers [1] and dendron rodcoil molecules [2].

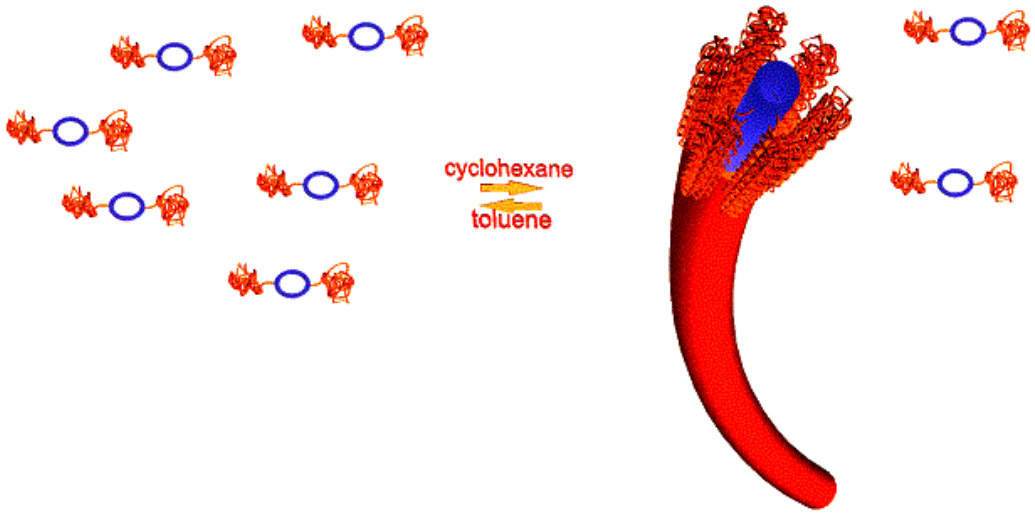

Fig.1: Schematic view of the Ring coil triblock copolymer which are in equilibrium with formed aggregates

Ring-coil triblock copolymers consist of a rigid ring with two polymer coils attached. When dissolved in a solvent that is a poor solvent for the ring but a good solvent for the coils rodlike aggregates are supposed to form, as shown in Figure 1. Static light scattering on solutions of ring-coil triblock copolymers in cyclohexane indeed shows the presence of rigid rods whose length increases with time and decreases with increasing molecular weight of the coils. Dynamic light scattering gives a hydrodynamic size of the aggregates and shows the presence of unaggregated ring-coil triblock copolymers.

Dendron rodcoil molecules, on the other hand, comprise a dendritic unit capable of forming hydrogen bonds, attached to a rodcoil molecule. It is supposed that four dendron rodcoils self-assemble into a tetramer via hydrogen bonds. The tetramers then form a columnar structure with the tetramers stitched along the column axis via additional hydrogen bonds. In this case, static light scattering shows the presence of wormlike chains, with a persistence length of 45 nm [2].

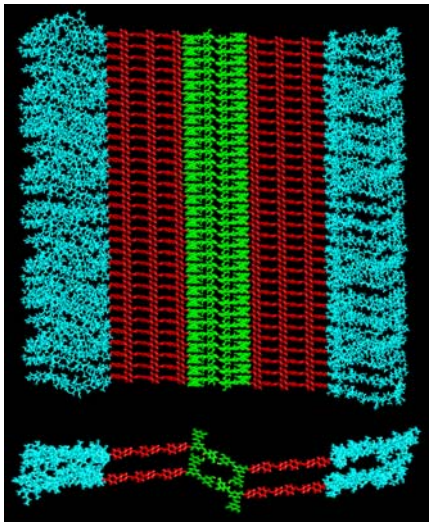

Fig. 2: Schematic view of the aggregates formed by the dendron-rod-coil tirblocks.

For both systems an unexpected discrepancy appears: Dynamic light scattering indicates an aggregate size which is a factor two larger than found with static light scattering. This problem is the subject of ongoing research.

1. Polyelectrolytes

Recent numerical modelling and analytical theory support earlier claims that attractive interactions between rodlike macroions of the same charge give rise to complex superstructures in aqueous solutions of polyelectrolytes. The structures arise from mutual attractions mediated by counterions which remain nonuniformly condensed near the rod surface. Double-helical DNA is a system frequently addressed in this context. The implications of attractive forces between negatively charged DNA strands themselves and other charged biosystems such as proteins or phospholipid membranes have been amply discussed (e. g. superfolding, creation of DNA vectors).

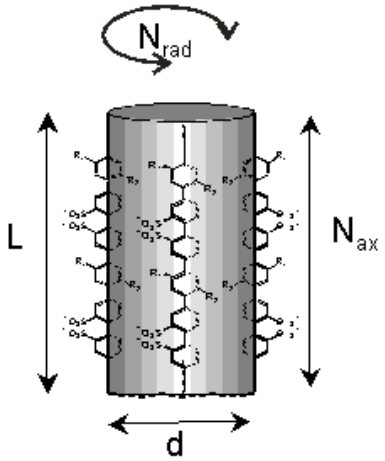

Fig. 3: Schematic view of the cylindrical micelle formed by the poly(p-phenylene)s

The goal is to use a simple synthetic model system based on poly(p-phenylene)s which mimics some of the principle phenomena governing interactions between biopolymeric

systems. The primary structure consists of a rigid poly(p-phenylene) backbone with sulfonate and n-alkyl side-groups which together render the polyelectrolyte amphiphilic. In water it forms cylindrical micelles of defined radial aggregation number with a negatively charged surface on account of the sulfonate groups. These micelles undergo further association to form lyotropic objects of internal nematic order on the 500 nm length scale. The actual length depends on the chain length and also on the counterion.

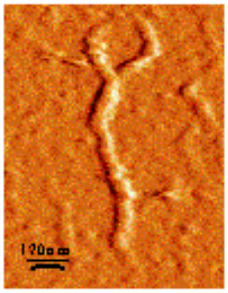

Fig. 4: AFM image of poly(p-phenylene) micelle.

Future research includes the investigation of the influence of parameters as concentration, main chain length and counterion valency as well as the length of the aliphatic side chains on the structure formation. By comparison with simulation results a better physical understanding of aggregation behavior should be achieved.

References:

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[2] E.R. Zubarev, S.I. Stupp, Journal of Physical Chemistry B, A light scattering study of the self-assembly of dendron rodcoil molecules, B.J. de Gans, S. Wiegand, 106 (2002), p.9730-9736.

[3] J. Belack, S. Wiegand, D. Vlassopoulos, G. Fytas, G. Wegner, Structure and Dynamics of a shape persistent polyelectrolyte of the poly(para-phenylene) type, manuscript prepared for submission to Macromolecules.

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