



	Experiment title: <u>Self-assembly of macroions and organic counterions in solution</u>	Experiment number: SC-879
Beamline: ID2	Date of experiment: from: 26.9.2001 to: 28.9.2001	Date of report: 30.8.2002
Shifts: 6	Local contact(s): Volker Urban	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): <u>Franziska Gröhn*</u> , Max Planck Institute for Polymer Research, Mainz, Germany <u>Volker Urban*</u> , ESRF, Grenoble, France <u>Agnieszka Tercjak*</u> , Max Planck Institute for Polymer Research, Mainz, Germany		

Introduction

The synthetic design of nanostructures has recently come into focus due to the potential for new “smart” materials. Natural materials have excellent properties due to their hierarchical structure down to the nanometer length scale. To be able to take advantage of such nanostructures, it is necessary to create them in a controlled manner, understand formation mechanisms and properties. We study the formation of nanostructures based on an approach that we call “electrostatic self-assembly”: the self-assembly of macroions and organic counterions in solution due to electrostatic interactions. We use organic counterions of a certain geometry, both monovalent and multivalent ones, in order to direct the structure of the assembly. Small angle x-ray scattering (SAXS) represents the crucial tool for a careful characterization that allows to relate structure and properties. Long-term goal of the project is a fundamental understanding of the interaction forces influencing the self-assembly (electrostatic, hydrophobic, stacking of aromatic compounds as well as geometric factors).

Measurements and Results

In the experiment SC-879, we have studied the formation of supramolecular architectures in solution using form-stable macroions as model system: We have used polyamidoamine (PAMAM) dendrimers of different generation, macroions with fixed star like or spherical shape and varying charge (from 4 to 1024 from G0 to G8). The 6 shifts of beamtime were used as follows:

1. Setup and alignment: sample-detector distances of 1.2 m and 10 m were chosen.
For all measurements, a wavelength of 1 Å was chosen.
2. Test measurements regarding stability of the structures upon exposure: It was found that at a sample-detector distance of 1.2 m 30 runs of 2s exposures with 1s deadtime in between runs can be made continuously without movement of the sample. Upon longer exposure, strong changes in the scattering pattern due to beam damage are observed. We found an optimum for our experiments being 35 runs of 2 s exposures with the deadtime starting with 1 s and being increased by a factor of 1.1 after each run. This way the accessible time range is sufficient to monitor the reachment of the equilibrium structure.

3. Measurement of different counterion types: a) dodecanoic acid and didoecanoic acid b) citric acid, c) naphthalene-dicarboxylic acids d) ATP: Results are a) Both, dodecanoic and didoecanoic acid connect macroions, while didoecanoic acid tends to form larger structures, b) see 5., c), see 4., d) ATP induced a phase separation and large droplets were formed so that NDC and citric acid were selected as the more promising structure forming counterions and ATP was not further considered.
4. The complexation of PAMAM dendrimers of different generations with two isomeric naphthalene dicarboxylic acids (NDC) in methanol was investigated: It turns out that the dendrimer generation, the ratio of charges of dendrimer to NDC and the geometry of the charges of the NDC influence the structure formed: Higher dendrimers tend to aggregate into larger structures. Interestingly, 1,4-NDC forms larger structures than 2,3-NDC as seems intuitively expectable due to the position of charges at the molecule. In particular for the middle generation dendrimers well-defined structures can be formed in solution: The figure gives an example for a result obtained with 1,4-NDC: The scattering curve shows expressed minima indicating aggregation into defined structures. Further, data are analyzed via indirect Fourier transformation (program ITP, developed by O. Glatter) into the pair distance distribution function. In the example given, anisotropic multi-dendrimer aggregates of about 180 nm length and 35 nanometer diameter are formed. The structure observed depends in a delicate way on the parameters given above. It is however not yet obvious, how the interplay of electrostatic, hydrophobic, stacking interaction and

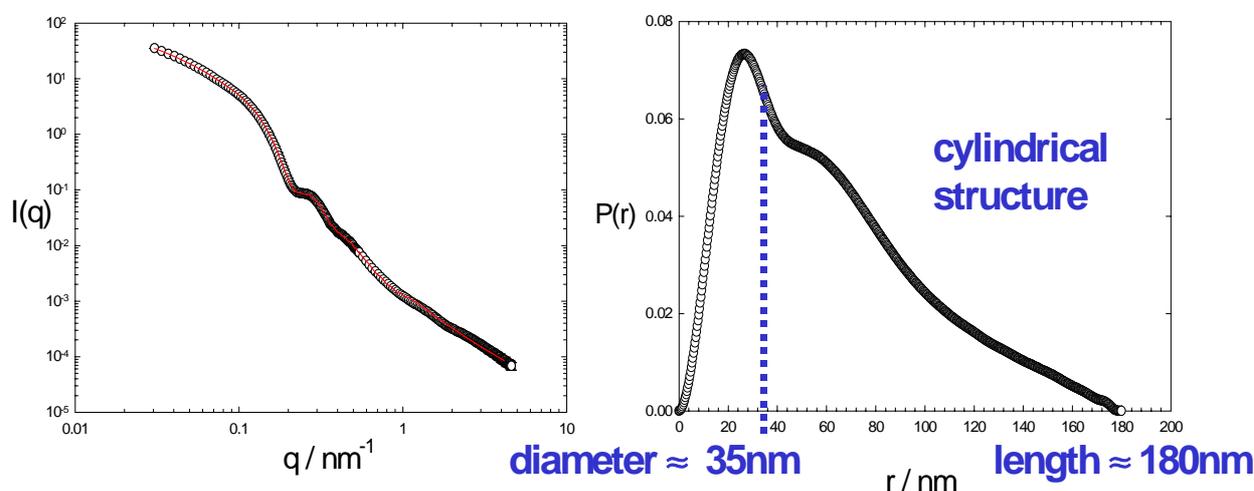


Fig.1: SAXS results for a sample of G5 PAMAM dendrimer complexed with 1,4-naphthalene dicarboxylic acid, charge:charge ratio 1:2 a) scattering curve $I(q)$ and fit b) pair distance distribution function $P(r)$ obtained by Fourier transformation of $I(q)$.

geometric factors directs the structure. Further "fine tuning" experiments within the range of the most interesting structures are planned to reveal further information.

5. Stopped flow measurements were performed on the G8 PAMAM dendrimer-citric acid system to monitor the influence of macroion/counterion ratio as well as the time-dependent structure evolution: For the dendrimer-citric acid system, spherical aggregates are formed. After mixing of the two aqueous solutions, spherical aggregates are formed that grow with time. The growth seems to be continuous, no indication of Ostwald ripening is observed.

Conclusions

The feasibility of the concept "electrostatic self-assembly" was demonstrated: Association of charged dendrimers and oppositely charged multivalent counterions can yield defined supramolecular structures in solution. However, in order to gain fundamental understanding of the underlying physical-chemistry and understand the structure formation, the concept will have to be extended and SAXS experiments will have to be continued. This experiment has shown that the high brilliance beamline ID2 is suitable for this type of stopped-flow experiments.