Experimental report

05/04/2016

Proposal: 9-10-1366 **Council:** 4/2014

Title: Dendrimer-dye electrostatic self-assembly: a time-resolved SANS study.

Research area: Soft condensed matter

This proposal is a continuation of 9-10-1296

Main proposer: Giacomo MARIANI

Experimental team: Giacomo MARIANI
Juan Pablo FUENZALIDA WERNER
Anne KUTZ
Franziska GROEHN
Federica CARDUCCI
Flavia BASSANI
Diego Romano PERINELLI
Simona RANERI
Sofia DALL ORSO

Local contacts: Ralf SCHWEINS

Samples: Organic dyes mixed with PAMAM dendrimers

Instrument	Requested days	Allocated days	From	To
D11	3	2	19/09/2014	21/09/2014

Abstract:

Self-assembly is an effective method to produce complex macromolecular structures of interest for example in nanotechnology or as carrier systems. Recently we have introduced a new concept of electrostatic self-assembly for the formation of well-defined supramolecular nanoscale assemblies of various shapes in solution. As part of the ILL PhD project, the goal of this experiment is to provide insight into the structure formation mechanisms. The model system under investigation will consist of a cationic poly(amidoamine) generation four dendrimer and a divalent anionic sulfonate dye (Ar26) and a trivalent one (SuAVAc). The system will be studied by SANS using a new, improved, mixing cell. This will be crucial for studying the process time resolved and in detail. These experiments will be part of the project of the ILL-PhD student Giacomo Mariani, the long-term objective of which is to gain fundamental insight into dynamic structure directing effects in the self-assembly.

Experimental Report

During the experiment 9-10-1366 we wanted to measure the self-assembly of positively charged generation 4 PAMAM dendrimer and oppositely charged divalent dye acid red 26 (Ar26) following the nanoparticle formation directly on the beam. A new measurement cell was developed in collaboration with ILL. The cell is connected to a titration instrument, which can be controlled by NOMAD. First, the dendrimer is at a pH where it is uncharged (i.e. pH 10.5) and no aggregation occurs. Upon acid addition (for example *HCl*), the dendrimer gets charged and the self-assembly is initiated under stirring. The process ends at pH 3.5 where all the primary and tertiary amines of the dendrimer are protonated. The titration instrument, at the same time, starts the self-assembly injecting *HCl* and records the pH changes. When the pH is 3.5 it sends a signal to NOMAD who starts the SANS measurement. The first day of experiment the special pH probe of the titration instrument breaks down. No replacement was available on such a short notice; hence, the experiment has been redesigned.

We decided to investigate nanoparticle structure as a function of solution pH. This may give insights on nanoparticle stabilization, a key and so far not fully understood topic in electrostatic self-assembly. We investigated the self-assembly of G4 PAMAM dendrimers and oppositely charged dyes. Three dyes with different valency were investigates: Ar26 and ABnOHARAc, divalent, and the trivalent APhAcOHRAc. In the case of Ar26/PAMAM, two different loading ratios have been investigated to understand the role of this parameter in nanoparticle stabilization. The SANS curves for Ar26/PAMAM are reported in Figure 1. The data have been fitted according to structural models; the results are depicted in Figure 2. The dimensions of the supramolecular nanoparticles can be tuned over a wide range by regulating the pH, with a higher pH yielding larger nanoparticles. For example in the case of the dendrimer-APhAcOHRAc assemblies, spheres with radius from R = 46 nm (pH 3.5) to R = 165 nm (pH 6.7) are formed. Moreover, pH can be use to tune nanoparticle shape. For example, for Ar26, the pH can be used as a trigger to switch between nanoscale cylinders with elliptical cross section and spherical nanoparticles; for ABnOHRAc between long flexible cylinders up to 2 μm length and shorter (100-500 nm) stiff cylinders. These structural characterization together with light scattering and ζ-potential measurements have been recently published: G. Mariani, R. Schweins, F. Gröhn Structure Tuning of Electrostatically Self-Assembled Nanoparticles through pH *J. Phys Chem B* **2016**, *120*, 1380-1389.

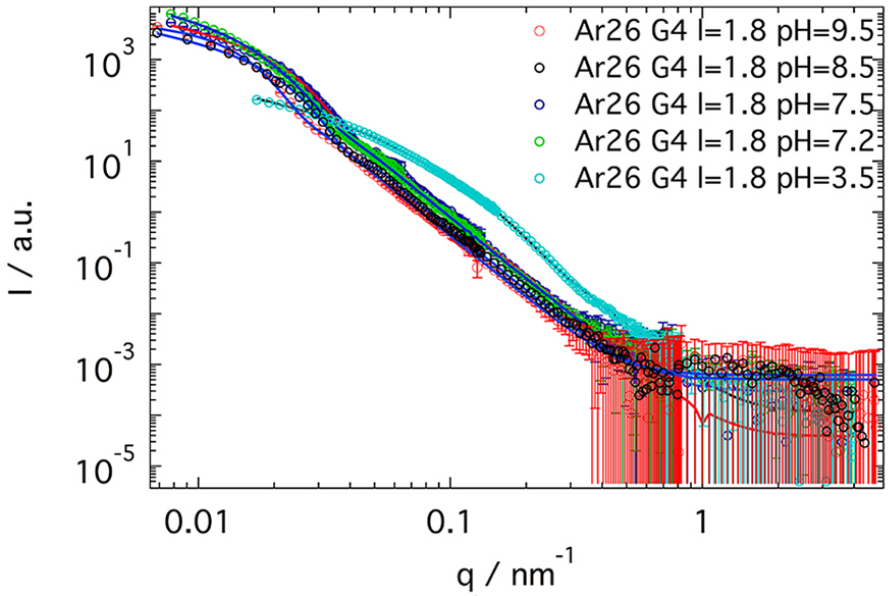

Figure 1. SANS scattering curves for Ar26-dendrimer, loading ratio *I* = 1.8 at different pH.

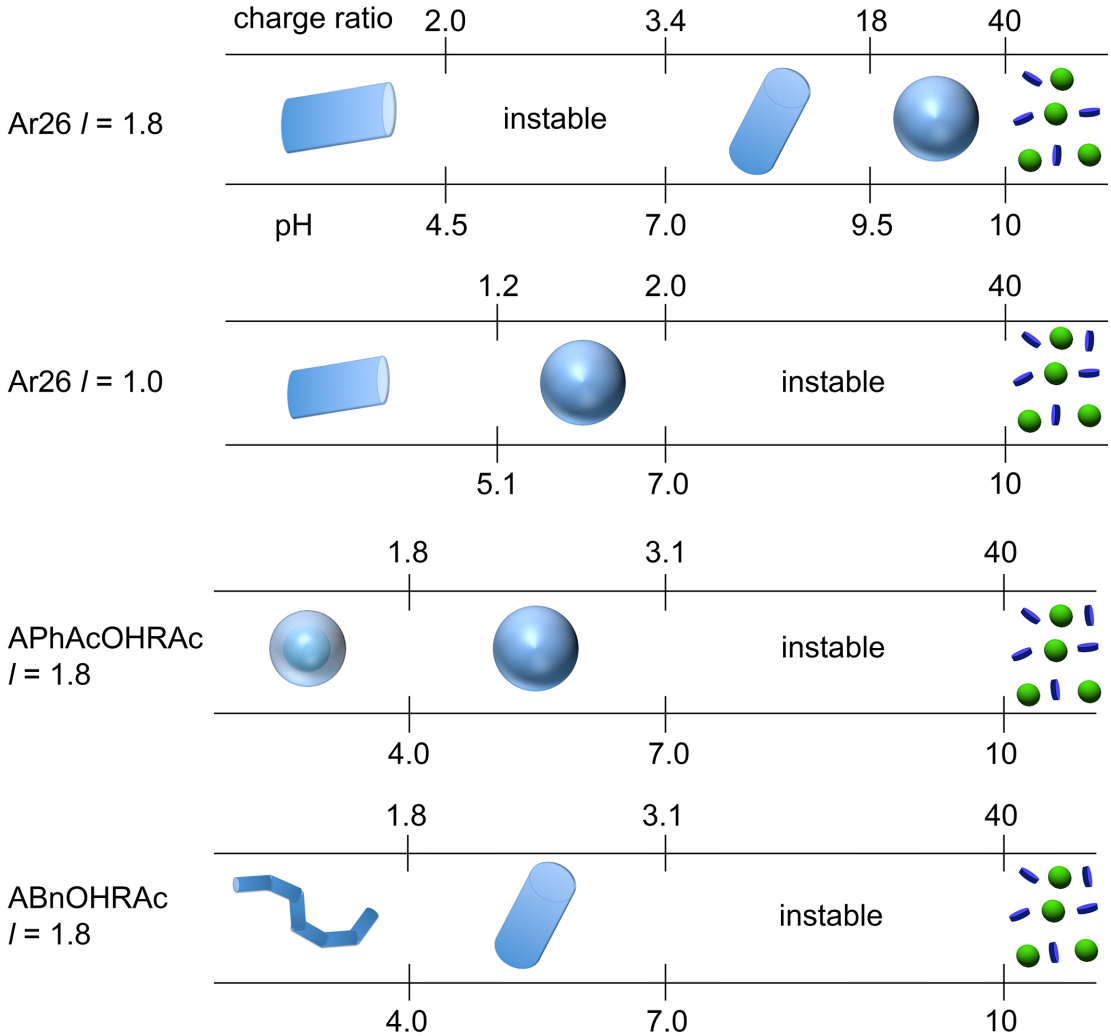

Figure 2. Stability plots for Ar26 and dendrimer G4 at *I* = 1.8 and 1.0, for APhAcOHRAc and ABnOHRAc at *I* = 1.8.