Experimental report

02/04/2016

Proposal: 9-10-1295 **Council:** 10/2012

Title: In situ analysis of structural changes in ionic nanoassemblies upon irradiation

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: Giacomo MARIANI

Experimental team: Giacomo MARIANI

Local contacts: Ralf SCHWEINS

Samples: C,H,N, S,O, Cl, Na: PAMAM dendrimers and dye molecules dissolved in D2O

Instrument	Requested days	Allocated days	From	To
D11	3	3	16/07/2013	19/07/2013

Abstract:

Complex macromolecular structures that can respond to external triggers can be obtained by self-assembly through non-covalent interactions. Recently we have introduced electrostatic self-assembly as a new concept for the formation of well-defined light-triggerable supramolecular nano-objects in aqueous solutions. So far, only start and end structure have been characterized in detail. Goal of this experiment is to fundamentally understand the structural rearrangement processes. Focus will be to study the light-induced structural changes after an initial irradiation and during a 20 min irradiation in a time-resolved manner. Results will allow detecting particle coagulation, growth and shape changes in a dynamic manner.

Experimental report

Unfortunately, due to a technical problem, it was not possible to measure what was originally proposed. Instead of measuring the structural changes induced by UV-light irradiation over time on self-assemblies of PAMAM dendrimers and oppositely charged dyes, we characterized the structure of a new light sensitive system. Linear polyelectrolytes such as poly(diallyldimethyl-ammonium chloride) (PDADMAC) and Poly(*N*-methyl-4-vinylpyridinium nitrate) (QPVP) have been used in combination with three different dyes: one trivalent (Ar27), one divalent (Ar26) and one that trans-cis isomerize upon irradiation (Ay38). The experimental curves have been fitted according to structural models. Interestingly, each dye/polyelectrolyte system results in different nanoparticles: Ar27 and PDADMAC, for example, form core-shell cylinder with a total length of 700 n, inner radius R_c = 6 nm and total radius R_t = 16 nm, while Ar26/PDADMAC results in core-shell ellipsoids with a major axis R_{maj} = 130 nm and minor axis R_{min} = 15 nm (Figure 1). The same shapes are formed when these dyes are used in combination with QPVP (Figure 2), however dimensions differ. For example, the cylinder formed by Ar27 and QPVP is almost half of the one formed by Ar27 and PDADMAC. Hence, the nanoparticle structure is defined by the molecular structure of the dye.

SANS before and after irradiation for Ay38 and PDADMAC is shown in Figure 3. It reveals a shape transition: before irradiation, Ay38-PDADMAC forms flexible cylinders with elliptical cross-sections; after irradiation, the system exhibits core-shell ellipsoids. The flexible cylinder is longer than 1 μm, and the cross-section has a major axis R_{maj} = 14 nm and a minor axis R_{min} = 5 nm. The ellipsoid formed upon irradiation has a major axis R_{maj} = 200 nm and a minor axis R_{min} = 20 nm; the inner core has r_{maj} = 60 nm and r_{min} = 10 nm. Interestingly, when Ay38 is combined with QPVP, irradiation does not induce a shape transition, and the nanoparticle size remains almost unchanged. This may be due to the additional π-interaction that can occur between the aromatic rings of the polymer and the dye, likely preventing shape changes.

In conclusion, stable and well-defined nanoparticles with a strongly light-switchable structure form with an ionic azo dye and an oppositely charged polyelectrolyte through ionic and π-π interaction in aqueous solution. Versatile self-assembly is possible with a simple linear flexible polyelectrolyte. The light-induced shape in the case of Ay38 and PDADMAC is of special interest since it is the first time that shape transition is observed for this kind of systems. The SANS results are part of a recently submitted communication.

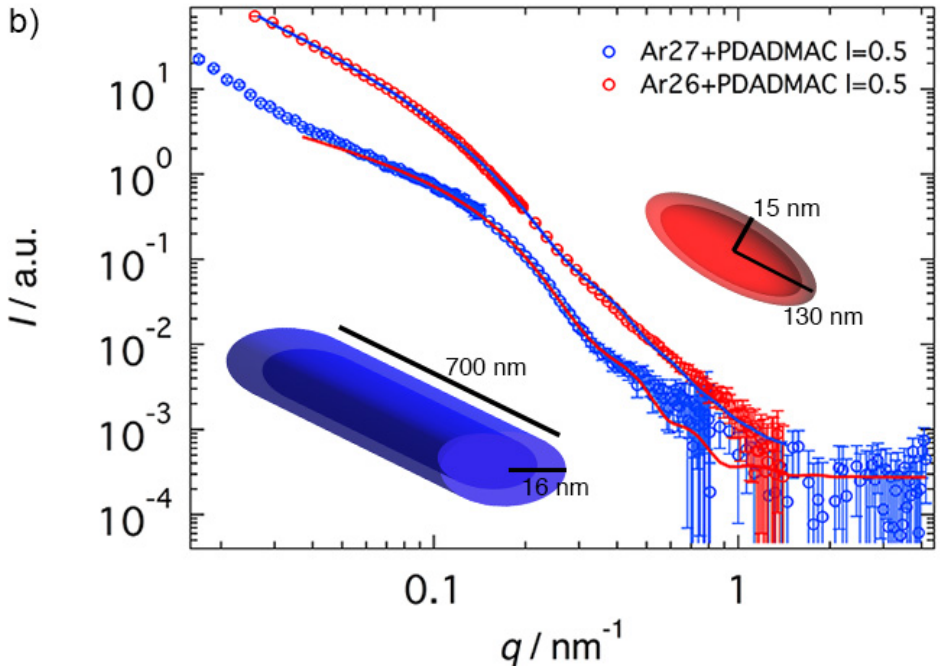

Figure 1. SANS curves for Ar26-PDADMAC and Ar27-PDADMAC at l_c = 0.5: Different dyes cause different supramolecular nanoparticle shapes.

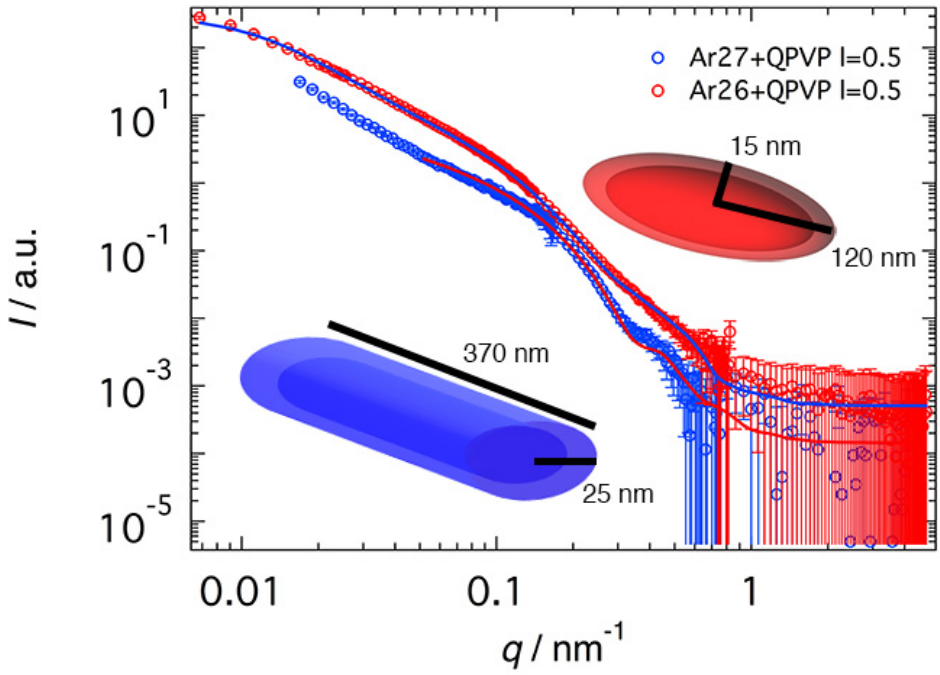

Figure 2. SANS results for A26-QPVP and Ar27-QPVP at l_c = 0.5.

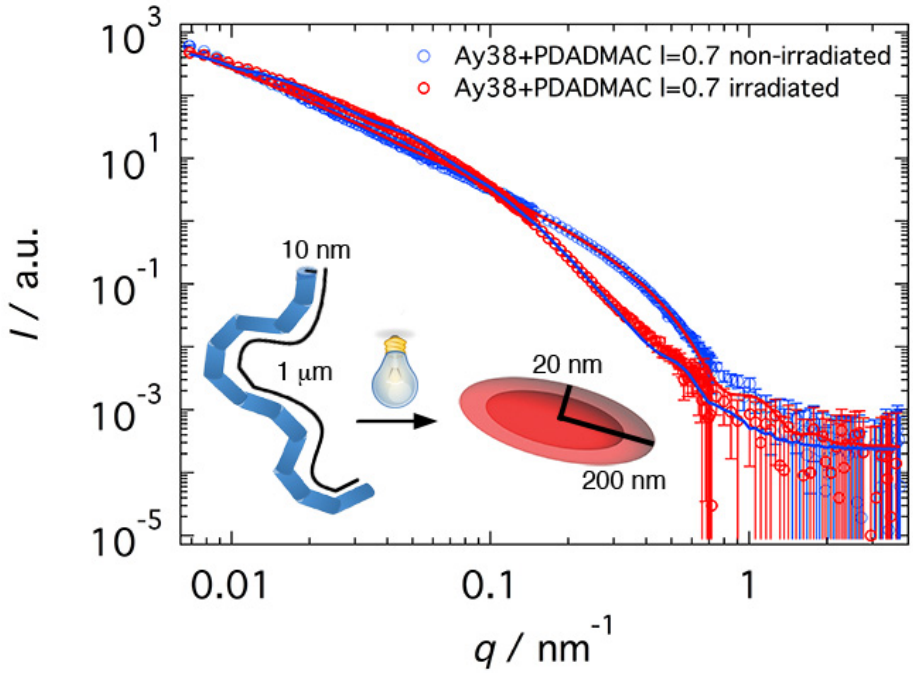

Figure 2. Light-switchable nanoparticle shape: SANS for Ay38-PDADMAC assemblies before and after irradiation (l_c = 0.7). Light induces a shape transition from flexible cylinders with elliptical cross-section to core-shell ellipsoids.