Experimental report

09/08/2022

Proposal:	**9-11-2079**	**Council:**	4/2021
Title:	Kinetics of dye-dendrimer electrostatic self-assembly		
Research area:	Chemistry		

This proposal is a new proposal

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Samples: PAMAM dendrimer
acid yellow 38

Instrument	Requested days	Allocated days	From	To
D11	2	1	27/09/2021	28/09/2021

Abstract:

In this experiment, we will investigate the formation kinetics of supramolecular nanostructures by electrostatic self-assembly, specifically the association of cationic dendrimers with an anionic light-responsive azo-dye. Over the last years, we have established electrostatic self-assembly as a powerful route to build defined nano-objects with a variety of sizes, shapes, and functionalities, including light-switchability. Yet, to fully exploit this strategy, not only knowledge of resulting structures but also a fundamental insight into assembly and structure-reformation mechanisms is needed. For this purpose, we will use time-dependent SANS to follow particle growth and shape development in the assembly process. We have optimized an assembly process so that it can be followed in the accessible time scale of SANS and will consider results in conjunction with DLS and SLS as well as ¿-potential measurements and UV-Vis spectroscopy to reveal charge status and dye-dye interactions on the molecular scale. This experiment is part of the ILL PhD project ¿Light-Tunable Structures by Self-Assembly: In-situ SANS Under Irradiation¿.

Experimental Report

Kinetics of dye-dendrimer electrostatic self-assembly

Experiment 9-11-2079

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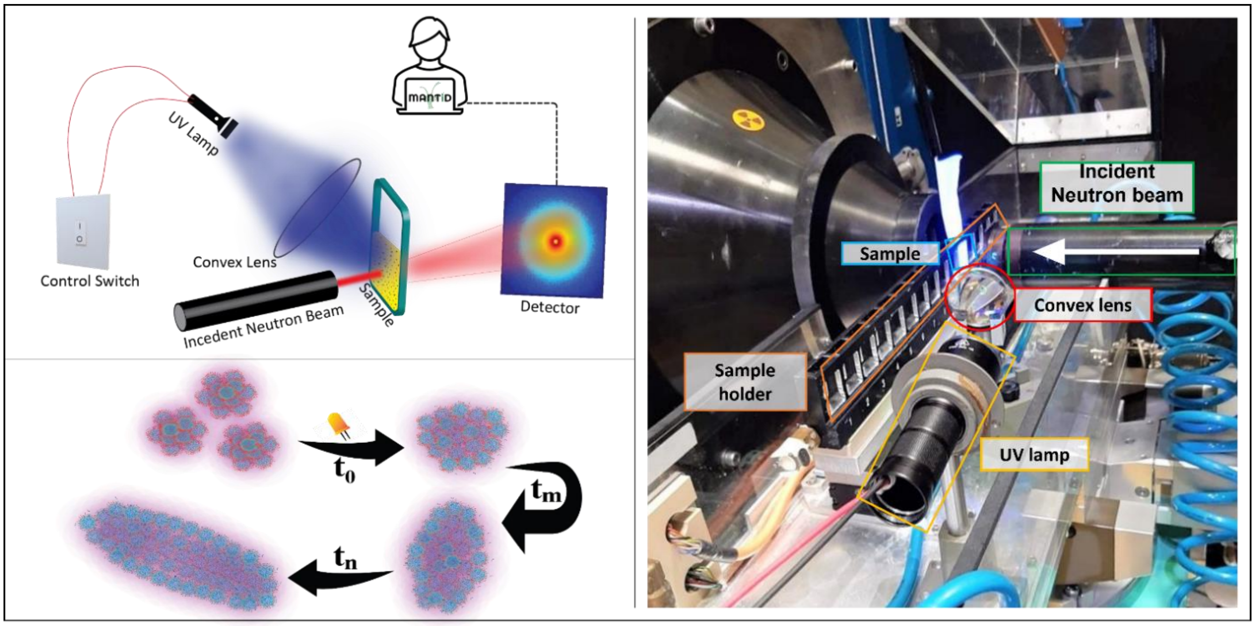
Background:

Electrostatic self-assembly is based on the interaction of opposite charges in the aqueous phase. The mixing of these positive and negative charges makes it a very facile process to generate nanoparticles in microseconds. Recently, we have developed a new method to slow down this process, which helps to characterize these self-assemblies dynamically and assists the intermediate structures until the end product. To analyze the effect of UV irradiation on structural changes with time, a home-built device is designed using in-situ UV irradiation on the SANS instrument. To fully exploit this strategy, not only knowledge of resulting structures, a fundamental insight into assembly and structure-reformation mechanisms is needed. For this purpose, we used time-dependent SANS to follow particle growth and shape development in the assembly process.

Measurements and Results:

In experiment 9-11-2079, a divalent azo dye (AY38, Acid Yellow 38) and cationic polyamidoamine (PAMAM) dendrimers were used as the key components to construct self-assembled structures in an aqueous solution. The isomerization capability of AY38 and pH-responsiveness of the dendrimers make them suitable candidates to alter the size and the shape of self-assembled particles through light irradiation and degree of protonation. In particular, the preparation method has been modified to gain insight into the formation mechanism. Slow assemblies' growth was observed time-dependently whilst the dye-molecules reconverted to the trans-isomer. As a model system, Acid Yellow 38 azo dye is mixed with generation 5 PAMAM dendrimer at a charge ratio (the ratio of the number of anionic dye sulfonate groups to the number of cationic amine groups) of 2.0 in acidic medium. For slow kinetics, the azo dye was irradiated



Scheme-1. Simplified sketch and original setup of the in-situ UV irradiation at D11 instrument in ILL. Formation of different size and shape nanoparticles are shown on the bottom left.

first and mixed with dendrimer and acid to initiate the self-assembly. Subsequently, the SANS measurement started without wasting any time.

SANS measurements were performed at the D11 instrument at different sample-detector distances (16 m and 28 m) for fast and slow kinetics, respectively at a wavelength of λ = 6Å. Fast kinetics setup is shown in Scheme-1, where a UV lamp of 365 nm wavelength is connected with a wire and can be controlled from outside of the sample area. A convex lens is used to focus the scattered UV light on the sample cuvette. The entire chamber was covered with a black cloth to protect the sample from outside light. The scattering data were collected while irradiating the sample. All samples were measured using quartz cuvettes with a path length of 2 mm. Data were corrected and put on an absolute scale, also, the solvent (D_2O) scattering was subtracted. All measurements and data are processed according to standard procedures.

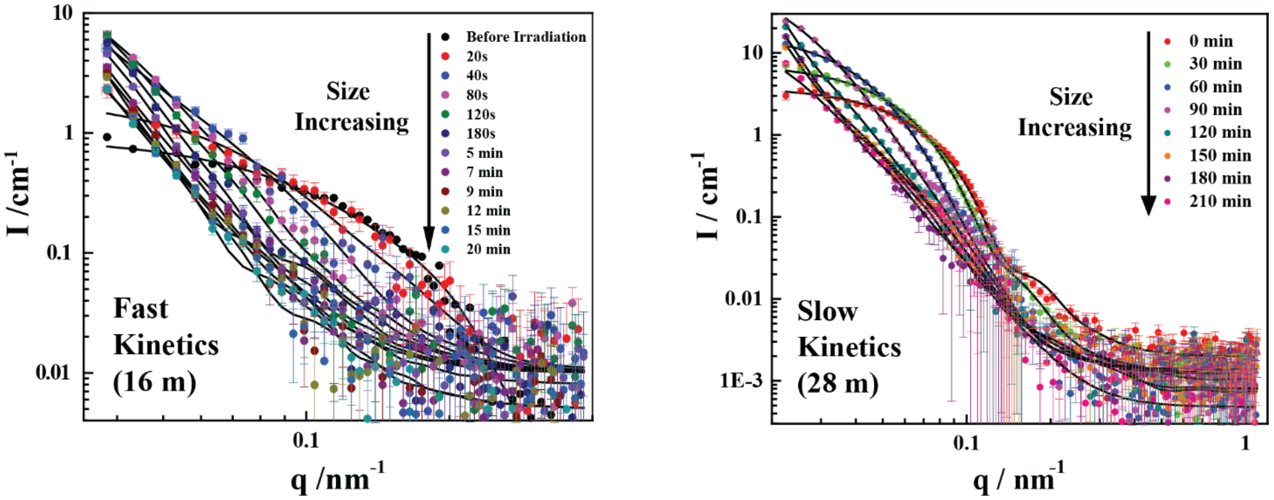


Figure-1. Both plots show the similar particle growth at different time scale in AY38/G5 self-assemblies at l_c =2.0.

In one day of beamtime, various kinetics (long and short) using the mixture of AY38 and G5 dendrimer at different charge ratios, l_c = 0.5, 2.0, and 3.0 were measured. Some of the highlights of the results are shown here in Fig-1. For slow kinetics, the sample was measured over 4 hours timespan with 30 min time slices. The nanoparticles grew from a small sphere (R = 25 nm) to elongated ellipsoidal structures of R = 30 nm with an axis ratio of 4.5. Whereas the fast kinetics results in a similar end product in 3 minutes and gets stabilized. This way we can investigate the intermediate forms in the process using the SANS technique.