Experimental Report

15/01/2014

Proposal:	**9-10-1296**	**Council:**	10/2012
Title:	Time resolved study of dye-dendrimer assembly formation		

This proposal is a new proposal

Research Area: Soft condensed matter

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Samples: C,H,N, S,O, Cl, Na: PAMAM dendrimers and dye molecules dissolved in D_2O

Instrument	Req. Days	All. Days	From	To
D11	3	2	27/07/2013	29/07/2013

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. The system will be studied by SANS and, for the first time, a new measurement cell will be used. 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

In the experiment 9-10-1296 we focussed on the electrostatic self assembly process between PAMAM dendrimers and trivalent dyes,followed directly in situ on the neutron beam. As discussed in the proposal, the two building blocks don't interact at pH 10, while they create nano particle when the pH it's switched to pH 3.5. At this pH the PAMAM dendrimer is fully charged and it can interact with the dye. In particular the sizes and/or the different shapes were followed as a function of time to understand if the growth is controlled by an Ostwald-ripening process or happens continuously.

Unfortunately we experienced problems with our particular experimental set-up (reported in figure 1). We wanted to change the pH directly on the instrument, following the different stages of the process. During the experiment an unpredictable problem of dead time due to the particular software/hardware configuration arises. A lose of time between the moment the solution reach the right pH at which starting the measurement and the real measurement start makes impossible to follow the first, more interesting, steps of the reaction.

Despite this problem, we were able to make some test with the stop-flow set-up. This set-up is not perfect for our system because it doesn't provide control on the reaction. With this system it's possible only to control the quantity of acid inserted into the solution, without further pH measurements. It's therefore impossible to know exactly the final pH of the solution, making difficult to make comparison between different measurements. The mixing of acid and the basic solution of PAMAM and the dye is also not uniform allowing a gradient of pH that can lead to precipitation. Nevertheless, the usage of the stop-flow cell allowed us to understand the time window in which the process is over. From our results the process can be considered over after 4 s. In the next months we will develop a new set-up, solving the problem of dead time.

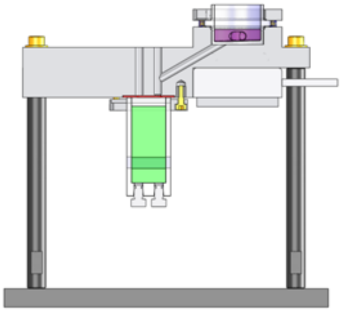

Figure 1: Time dependent cell. In purple the mixing place, in green the measurement cell. Mixing and measuring are decoupled, when pH 3.5 is reached the solution goes in the green part and the measurement starts.