Experimental report

25/10/2019

Proposal:	**9-11-1910**	**Council:**	10/2018
Title:	Kinetic pathways in light responsive dye-polyelectrolyte complexes		
Research area:	Soft condensed matter		

This proposal is a new proposal

Main proposer:	**Nico Oliver CARL**
Experimental team:	Nico Oliver CARL
Local contacts:	Ralf SCHWEINS

Samples: D2O
C3H3NaO2

Instrument	Requested days	Allocated days	From	To
D11	2	2	15/06/2019	17/06/2019

Abstract:

Light responsive materials have gained significant attention in the last years due to their application in photothermal therapy, sensing or as molecular motors. Supramolecular particles of ionic dye molecules and oppositely charged macromolecules have recently been used to create a wide variety of different particle shapes. These assemblies can be controlled by the dye structure, pH, ionic strength but most interestingly by light. For this the trans->cis isomerization of an ionic azobenzene dye has been used. This approach is highly interesting since it can be reversibly switched with light without damaging the dye by photobleaching.

Based on these findings we used a cationic azo dye and an anionic polyelectrolyte to create well-defined supramolecular structures. These structures can be disassembled by light and consequently reassembled again by two different pathways. These two processes result in two different final structures. This proposal aims to shed light on this process.

Experimental Report 9-11-1910

Controlling self-assembly with light

Experimental team: Nico Carl, Wenke Müller,Ralf Schweins

Data of the experiment: 15.06.-17.06.2019

Introduction

The aim of the experiment was to investigate the self-assembly of a divalent azobenzene cation (diAzoEt, shown in Figure 1) and an oppositely charged polyelectrolyte. Mixing dye and polyelectrolyte results in the formation of well-defined aggregates with a spherical structure. Upon light exposure at 365 nm the *trans*-to-*cis* isomerization of the dye takes place and the structures dissolve, resulting in individual PA chains and *cis*-dye acting as screening salt (c.f. Figure 1A). Relaxation back to the *trans*-isomer initiate reformation of the structures. The aim of this proposal was to study this reassembly process *in situ* with time-resolved small-angle light scattering (SANS).

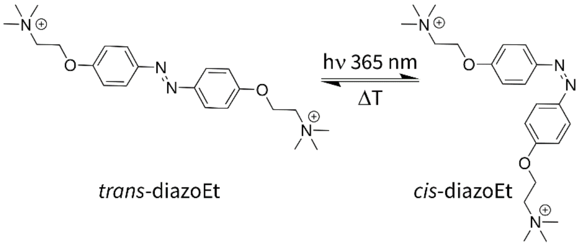

Figure 1: Chemical structure of the *trans* and *cis*-isomer of diAzoEt.

Samples and technique

Fully hydrogenated sodium polyacrylate (M_w = 300 kg/mol) was mixed with the diAzoEt at a certain charge ratio Z, with Z being defined as

$$Z = \frac{2\,[diAzoEt]}{[PA]}$$

[diAzoEt] is the concentration of dye and [PA] the concentration of acrylate monomer units.

For all experiments a sample in heavy water (D_2O) at a charge ratio of Z = 0.8 was used as the formed aggregates were found to be long term stable. Above charge ratios of 1.0 the aggregates precipitated and below 0.7 no structure formation was found. Figure 2B shows photographs of the sample before and after irradiation. The turbidity of the sample before irradiation clearly indicates the presence of larger, self-assembled structures.

A typical experiment consisted of measuring the sample at three sample-to-detector samples (39m, 8m and 1.4 m) and consequently irradiating the sample for 30 minutes at 365 nm. This results in disassembly of the aggregates. With time the structures reform as more and more dye is converted back to the *trans* isomer. This process was investigated with acquisition rates between 30 s and 1 min. In order to obtain sufficient statistics 5 mm 404 Hellma cells with a circular neutron beam of 15 mm diameter were used. In order to avoid that relaxation takes place *via* light induced *cis*-to-*trans* isomerization the sample environment was kept in complete darkness. Two irradiation-reassembly experiments were performed at a given temperature to record the kinetics at 39m and 8m sample-to-detector distance. The respective final structures were characterized by measuring the sample over the full q range. It turned out that the process is reliable and that the scattering curves from repetitive measurements perfectly overlap. In total, the self-assembly process was studied *in situ* at three temperatures: 45°C, 58°C and 66°C.

Results and discussion

Figure 2A shows the SANS profile before and after irradiation. They show that the aggregates before irradiation have a spherical structure and are composed of highly swollen polymer chains. After light irradiation, the forward scattering decreases by nearly three orders of magnitude and the form factor oscillations disappear. This indicates that the polymer chains are present as single chains in solution.

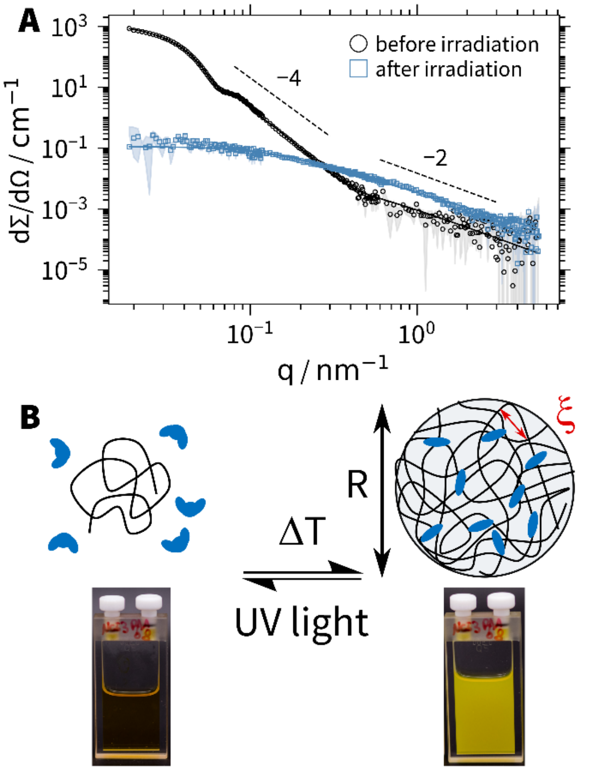

Figure 2: **A** SANS profiles of PA-diAzoEt complexes at a charge ratio Z = 0.8 after mixing (black) and after irradiation of the same sample (blue). The solid lines represent fits to the model of a homogeneous sphere composed of swollen polymer coils[1] (black) and the model of a generalized Gaussian chain[2] (blue) at 25°C. **B** Sketch of the structure before and after irradiation and photographs of the corresponding samples.

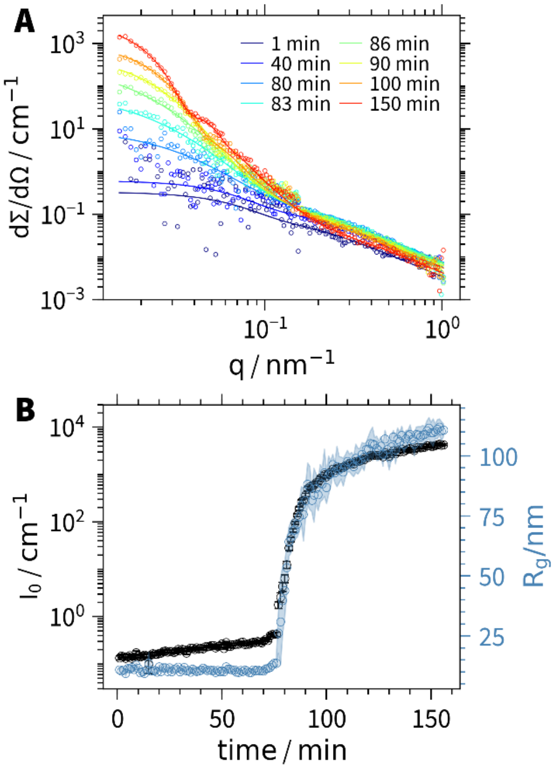

Figure 3: **A** Selected SANS profiles of reforming PA-diAzoEt complexes after irradiation and reassembly at 45°C. The solid lines represent fits to the model of a mixture of free polymer chains and complexes. **B** Forward scattering I_0 and radius of gyration R_g as a function of time for the reforming PA-diAzoEt complexes at 45°C. The acquisition time for each point was 1 min.

After irradiation the *cis*-isomer is converted back into the *trans*-isomer which results in the reformation of the comples. This reassembly process was studied with time-resolved SANS (TR-SANS), which allows monitoring the self-assembly process *in-situ* and gives an insight into the mechanism.

Figure 3A shows selected SANS curves from the TR-SANS experiments at 45°C. The data from the measurements at 39 m and 8 m sample-to-detector distance overlap perfectly. The experiments shows that up to 80 min the scattering curves barely change. From 80 min on a rapid formation of well-defined form factor oscillations and a strong increase of the forward scattering takes place. This is also visible in the results from the Guinier analysis of the scattering curves in Figure 4B. The forward scattering as well as radius of gyration stay nearly constants up to 80 min. Afterwards both quantities increase rapidly. The measurements at the two other temperatures show a similar trend as the sample at 45°C but the structure formation is faster.

A form factor model composed of a mixture of free polymer chains and spherical complexes can fit the scattering data at all temperatures. The analysis of the scattering data reveal three characteristic rate constants. The first one is associated with the cis-to-trans isomerization,which is the rate-limiting step of the process. Step II is the nucealtion of be particles, followed by growth to the final size (step III). The three characteristic rate constants are plotted in an Arrhenius plot in Figure 7B. They yield the activations energies shown in Table 1 for the three processes.

In summary, TR-SANS allowed to get an insight into the self-assembly process. The process is interpreted as a nucleation and growth mechanism. It is worth mentioning, that the weak interaction of neutrons with matter is essential to the success of the described experiment. Using light or X-rays immediately triggers the *cis*-to-*trans* isomerization. The high flux of the ILL allows monitoring the process in real time and the low momentum transfers available at D11 are crucial, as the forming structures are rather large.

Table 1: Activation energies from the form factor fits of the SANS data.

Step	Activation energy /kJ mol^{-1}
I	86.7 ± 12.3
II	43.9 ± 15.0
III	36.1 ± 10.4

References:

[1] J. S. Pedersen, I. W. Hamley, C. Y. Ryu, T. P. Lodge, *Macromolecules* **2000**, *33*, 542–550.

[2] B. Hammouda, *Polym. Charact.* **1993**, *106*, 87–133.