

Standard Experimental Report
(All fields are mandatory)

Proposal title: Photo-responsive supramolecular polymer bottlebrushes in solution

Proposal number: A02-1-916

Beamline: D2AM

Shifts: 6

Date(s) of experiment: from: May 22nd

to: May 24th

Date of report: 12/09/2023

- Objective & expected results (less than 10 lines): -

The aim of this SAXS run on D2AM (which took place from May 22nd to the 24th) was to investigate the self-assembling properties of various polymers into 1D supramolecular nano-cylinders. This experimental report is divided into two main sections. First, the self-assembly and light-responsiveness of photo-responsive nano-cylinders formed through cooperative H-bonding were studied in an organic solvent (namely toluene). Next, the self-assembly of Janus nano-cylinders through complementary H-bonding stickers was studied in aqueous media, and we aimed to understand the mechanism of self-assembly during the solution preparation.

- Results and the conclusions of the study (main part): -

1) Photo-responsive polymer bottlebrushes in organic media: self-assembly and light responsiveness

Azo-(U-PEO)₂ (see **Figure 1**) consists of an azobenzene-bisurea self-assembling core, decorated with poly-(ethylene oxide) (PEO) polymer arms, providing solubility in both water and some organic solvents. This compound can self-assemble into 1D nano-structures through cooperative and directional H-bonding of the urea units, as long as the azobenzene is in its *trans* configuration (which is planar). Azobenzene can photo-isomerize to *cis*-Azo upon UV irradiation, which is no longer planar, and should lead to the disruption of the nano-cylinders. Note that this isomerization is reversible and can be achieved either by thermal relaxation in the dark, or re-irradiating the solution with blue light, meaning that reversible disassembly could potentially be achieved. While this system was previously studied in water using light scattering techniques, SAXS analysis was required to study it in toluene, due to insufficient contrast of PEO in toluene using light scattering. Furthermore, **synchrotron SAXS** was a particularly adapted technique for monitoring disassembly/re-assembly kinetics, due to the very fast scan rate. The main results from this study are presented in this first section of the experimental report. Note that all solutions were prepared in deuterated solvent, since we had a SANS run a few days after the SAXS run.

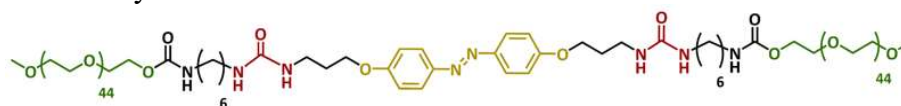


Figure 1. Chemical structure of Azo-(U-PEO)₂

The polymer was directly dissolved in toluene at 10 g/L and probed by SAXS. It was first verified that no degradation of the polymer occurred upon SAXS beam exposure (data not shown). As can be seen in **Figure 2**, a q^{-1} angular dependence is present, which is typical of anisotropic 1D nano-particles. Due to the absence of a Guinier plateau, the exact length of the nano-cylinders could not be determined.

The solution was then irradiated with UV light, and SAXS revealed a decrease in scattered intensity, but the q^{-1} dependence remained, suggesting a portion of cylinders were disrupted, but not all. Re-irradiating with blue light (450 nm) led to complete recovery of the *trans* isomer, and therefore re-assembly. These results strongly suggest that the system is in thermodynamic equilibrium. The data are currently being fit in order to determine the radius of the assemblies.

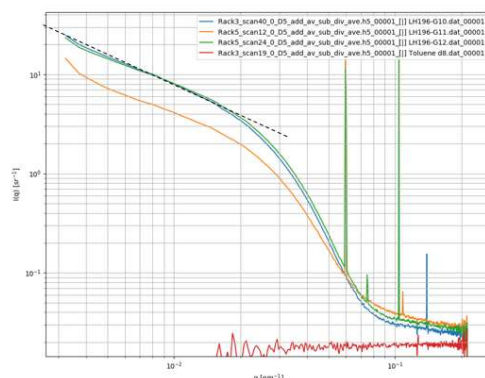


Figure 2. SAXS data of the polymer in toluene at 10 g/L. **Blue** curve: no irradiation. **Orange**: after 365 nm irradiation. **Green** curve: after a second irradiation at 450 nm. Black dotted line is a q^{-1} visual guide.

Next, light induced disassembly/re-assembly kinetics were probed, by directly irradiating the solution during SAXS analysis. The solution was first irradiated with UV light (**Figure 3A**) over the course of 6 minutes, leading to a strong decrease in scattered intensity. Then, the UV LED was turned off, and SAXS analysis continued during 4 minutes, leading to a slight increase in scattered intensity. We hypothesize that this is due to rapid re-organization of the remaining *trans* isomer into new nano-cylinders. The solution was then irradiated with blue light, leading to a rapid increase in scattered intensity, reaching the initial state within approx. 35 seconds (**Figure 3B**). Finally, irradiation cycles were performed, which demonstrated that no degradation occurred during photo-isomerization, and that the isomerizations were reproducible and reversible.

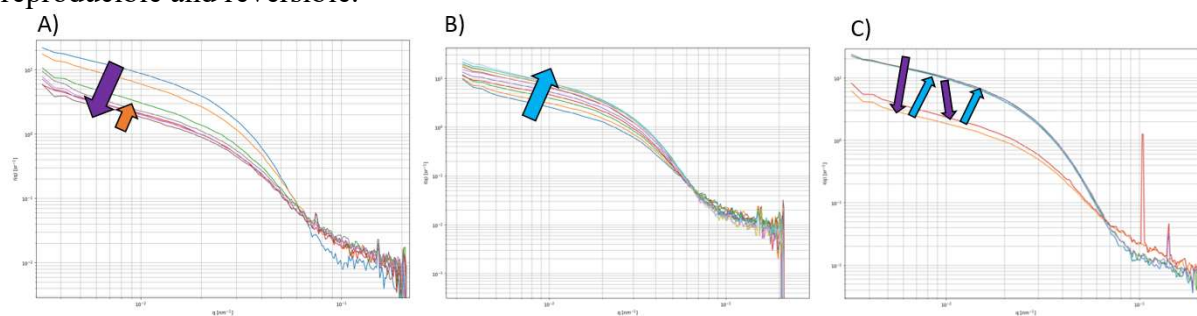


Figure 3. **A)** First irradiation using UV light (365 nm). **B)** Second irradiation with blue light (450 nm). **C)** Irradiation cycles.

2) Supramolecular Janus nanocylinders: influence of the process in aqueous medium

Janus particles are asymmetric nanoparticles with two faces of different compositions and features. It was shown that the equimolar co-assembly in solution of two polymers end-functionalized with non-symmetrical and complementary hydrogen bonding stickers led to the formation of Janus nanorods (JNR) but the mechanism of their formation was unknown (**Figure 5**). It was however shown that this strategy led to frozen JNR in aqueous medium;

which was achieved by first dissolving the polymers in a strong H-bond competing solvent such as DMSO (in which unimers are present), followed by the addition of water (the process was therefore coined the “water/DMSO” route). The aim of this work was to study the influence of different parameters during the self-assembly process on the final characteristics of the assemblies.

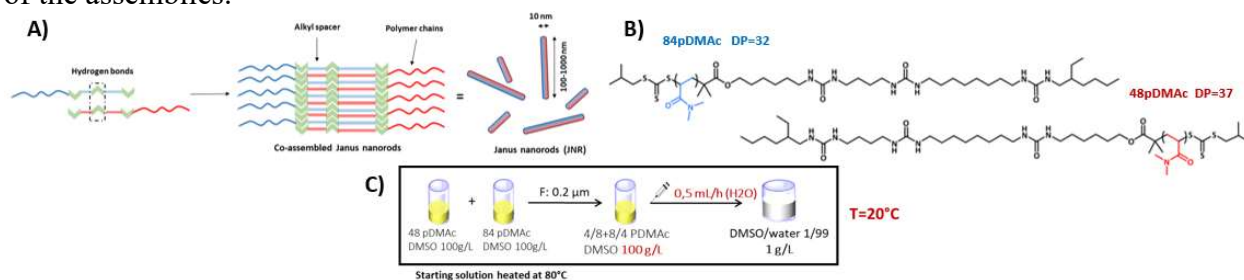


Figure 5. A) Scheme of supramolecular Janus nanorods co-assembly. B) Chemical structure of the studied polymers. C) Schematic representation of the self-assembly process.

Two different H-bond competing solvents were studied: DMSO- d_6 (“water/DMSO” route), which is the usual solvent used to prepare the nanorods, and MeOD- d_4 (“water/MeOD” route). Three other parameters were explored to see the effect on the assembly: the water addition flow rate and the preparation temperature. As can be seen in **Figure 6**, the parameters studied appear to have little influence over the local structure (radius, morphology) of the assemblies, regardless of the choice of initial solvent. Due to the absence of a Guinier plateau, the influence of the process on the final length of the assemblies could not be assessed by SAXS (cryoTEM and light-scattering experiments have been done).

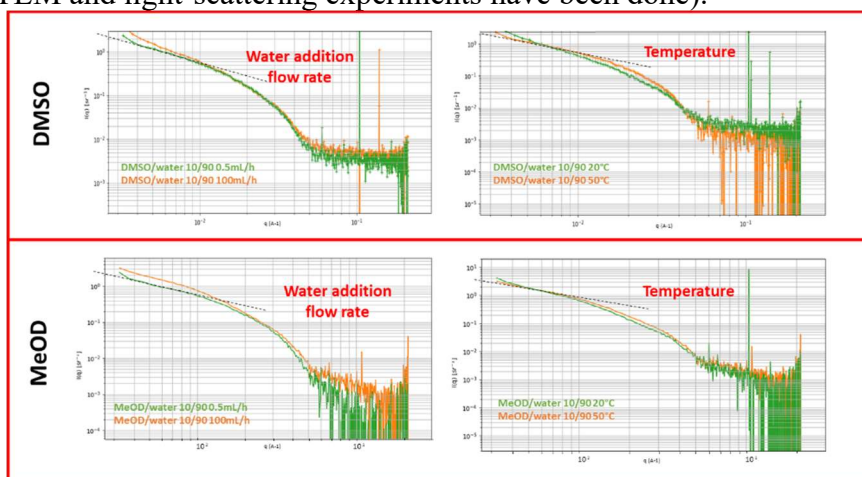


Figure 6. SAXS data of the co-assembly using the “Water/DMSO” (top) and “Water/MeOD” (bottom) processes, studying the influence of water addition rate (0.5 vs. 100 mL/H, left) and temperature during water addition (20 vs. 50°C, right). Black dotted line is a q^{-1} visual aid.

- Justification and comments about the use of beam time (5 lines max.): -

We required SAXS beamtime due to other techniques such as light scattering providing insufficient contrast, and also required the fast acquisition times for kinetic experiments.

- Publication(s): -

An article regarding the photo-responsive assemblies is currently being written (authored by Harvey, Morfin, Schweins, Brotons, Bouteiller, Nicol and Colombani), and a second article regarding the Janus nano-cylinders is also being written (authored by Kalem, Morfin, Schweins, Brotons, Bouteiller, Nicol and Colombani).