Experimental report

11/09/2023

Proposal: 9-11-2108 **Council:** 10/2022

Title: Photo-responsive supramolecular polymer bottlebrushes in solution

Research area: Chemistry

This proposal is a new proposal

Main proposer: Luke HARVEY

Experimental team: Olivier COLOMBANI
Erwan NICOL
Guillaume BROTONS
Sandra KALEM
Luke HARVEY

Local contacts: Ralf SCHWEINS

Samples: CDCl3
Toluene-d8
Azo-(U-PEO)2
D2O/DMSO 99/1 vol/vol mixture

Instrument	Requested days	Allocated days	From	To
D33	1	0		
D22	1	1	27/05/2023	28/05/2023

Abstract:

The objective of the current proposal is to investigate the characteristics (diameter, mass per unit length) of isolated polymeric nanocylinders formed by self-assembly in solution of polymers bearing hydrogen bonding (urea) and azobenzene units, and to determine their response to light irradiation. The latter indeed promotes trans-cis isomerization of the azobenzene unit, thereby disrupting hydrogen bonding and promoting disassembly according to preliminary light scattering results. The self-assembly will be investigated in water, toluene-d8, CDCl3 and toluene/CDCl3 mixtures which result in different strengths of the self-assembly.

Experimental report- Run 9-11-2108 - May the 27th and 28th 2023

Hydrogen bonded photo-responsive or Janus supramolecular polymer bottlebrushes in solution

Luke Harvey[a], Sandra Kalem[a], Ralf Schweins[b], Guillaume Brotons[a], Laurent Bouteiller[c], Erwan Nicol[a*], Olivier Colombani[a*]

[a] Institut des Molécules et Matériaux du Mans (IMMM), UMR 6283 CNRS, Le Mans Université, 72085 Le Mans, Cedex 9, France

[b] Institut Max von Laue-Paul Langevin, 71 Av. des Martyrs, F-38042 Grenoble, France

[c] Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, Equipe Chimie des Polymères, 4 Place Jussieu, F-75005 Paris, France

The aim of this SANS run on D22 (which took place from May 27th to the 28th) was to investigate the self-assembling properties of various polymers into 1D supramolecular nano-cylinders. First, the study of supramolecular photo-responsive nano-cylinders formed through H-bonding in organic solvents is presented, which we aim to publish in a first article (by *Harvey, Schweins, Brotons, Morfin, Bouteiller, Nicol and Colombani*).

Next, the study of supramolecular Janus nano-cylinders formed through complementary electron donor/acceptor groups coupled with H-bonding is presented, which we intend as a second article (*with the same authors + Choisnet, Canevet and Sallé, our collaborators from Angers on this topic*).

Finally, supramolecular Janus nano-cylinders formed through H-bonding in water are studied, with a focus on the influence of the assembly process on the characteristics of the assemblies. Here, additional experiments are required to lead to a third 3rd publication (by *Kalem, Rieger, Siefker, Pensec, Schweins, Morfin, Brotons, Bouteiller, Nicol and Colombani*).

1) Study of photo-responsive supramolecular nano-cylinders in organic media

All solutions were prepared at 10 g/L unless specified otherwise.

The structure of Azo-(U-PEO)$_2$ is described in **Figure 1**. The polymer consists of a photo-responsive azobenzene core, a bis-urea to drive self-assembly through strong, cooperative H-bonding, and polymer arms (poly-(ethylene oxide), PEO) which imparts solubility in both water and some organic solvents (such as toluene and chloroform). In its thermodynamically stable state, azobenzene is in the trans configuration, which is planar and permits 1D self-assembly, but after photo-isomerization, it isomerizes to cis-azobenzene, which is not planar and should disrupt self-assembly.

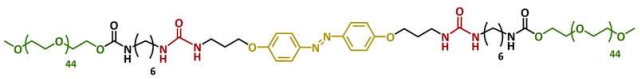

Figure 1. Chemical structure of Azo-(U-PEO)$_2$

The main aim of this SANS run was to study the self-assembling and light-responsive properties of this polymer in organic solvents, and in particular in chloroform (a solvent where only SANS provided a sufficient contrast, contrary to light and X-ray scattering). The major results of this study are plotted in **Figure 2**.

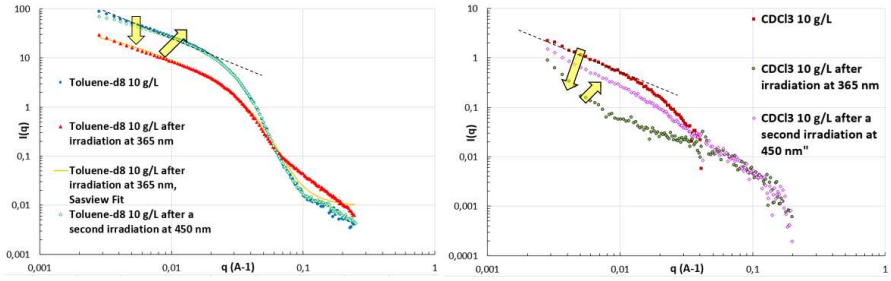

Figure 2. SANS data of toluene-d_8 solutions (left) and $CDCl_3$ solutions of Azo-(U-PEO)2 at 10 g/L, prior to irradiation, after UV irradiation (365 nm) and after a second blue light irradiation (450 nm). The black dotted line is a q^{-1} visual aid.

In both solvents, a q^{-1} angular dependency was present on the initial solutions, which is typical of 1D nano-particles, indicating that the polymer is self-assembled in these conditions. After UV irradiation, triggering photo-isomerization to *cis*-Azo, a notable decrease of scattering intensity was observed, indicating that considerable disassembly occurred. In chloroform, apart from the

presence of large spurious aggregates dominating the scattering at low q, the scattering profile indicates a strong decrease of the amount of nanocylinders. In toluene, recovery of *trans*-Azo leads to the same initial scattering, indicating that reversible re-assembly occurs, a major result provided by this run. In chloroform, the reversibility of the assembly is not total, which could be explained by the fact that only 80% of the *cis*-Azo converts back to *trans*-Azo upon blue light irradiation. We hypothesize that since chloroform is slightly more H-bond competitive than toluene, it slightly weakens the assemblies, meaning that total disassembly can be achieved (whereas disassembly was only partial in toluene). The data could be fitted (not shown here because the fits have not been optimized yet) prior to light irradiation with models of cylinders with a radius in the 5 nm range and lengths > 100 nm. After irradiation, fitting of the data requires to take into account the presence of smaller objects in addition to the remaining nanocylinders.

2) Study of Janus nano-cylinders in organic solvent

The aim of this part was to study the self-assembly of Janus nano-cylinders through the self-assembly of PEO-NDI-U_2 and DAN-U_2-PS (see **Figure 3**) in toluene. These two polymers possess complementary bis-ureas and donor/acceptor units, which lead to the formation of Janus nano-cylinders (i.e. having two faces of different chemical composition) through cooperative H-bonding and charge transfer complex.

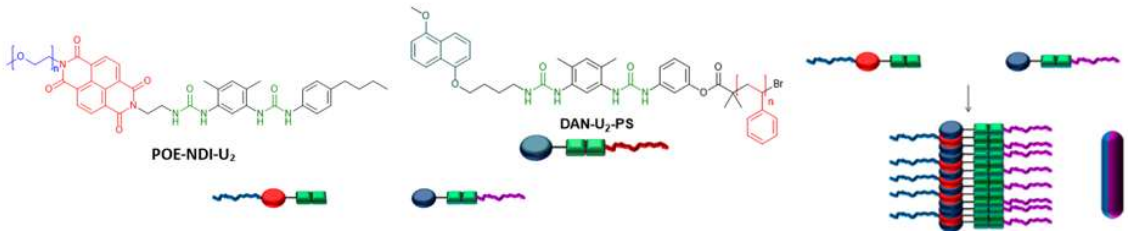

Figure 3. Chemical structure of the two polymers and schematic representation of their self-assembly into Janus nano-cylinders.

The sample was prepared by directly dissolving both polymers in toluene-d_8 (total polymer concentration of 10 g/L) in stoichiometric ratios. Then, 10% of DMSO-d_6 was added to verify that it disrupts the nano-cylinders (as DMSO is a strong H-bond competitor). As can be seen in **Figure 4**, a q^{-1} angular dependency is present in toluene-d_8, confirming the formation of nano-cylinders. After addition of DMSO, the sample barely scatters, indicating that the DMSO had effectively disrupted the assemblies, confirming that the co-assembly is strongly driven by H-bonding. Fitting of the data is currently undergoing.

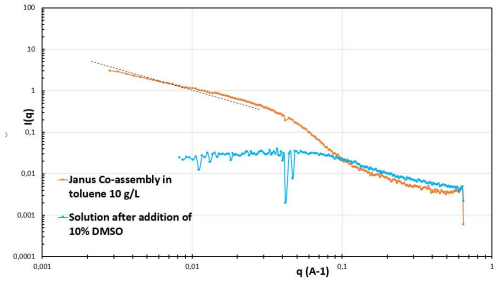

Figure 4. SANS data of the co-assembly at 10 g/L in toluene-d_8 (orange curve) and after addition of 10% of DMSO-d_6 (toluene-d_8/DMSO-d_6 90/10 v/v) (blue curve) (after subtracting solvent contribution). Black dotted line is a q^{-1} visual aid.

3) Supramolecular Janus nanocylinders: controlling their characteristics through 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.

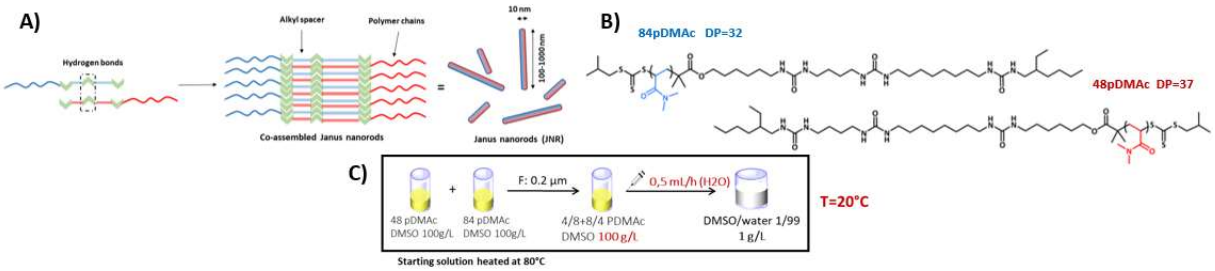

Figure 5. A) Scheme of supramolecular Janus nanorods co-assembly. B) Chemical structure of the studied polymers. C) Schematic representation of the self-assembly process.

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, the preparation temperature and the starting concentration. 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 SANS (cryoTEM and light-scattering experiments have been done).

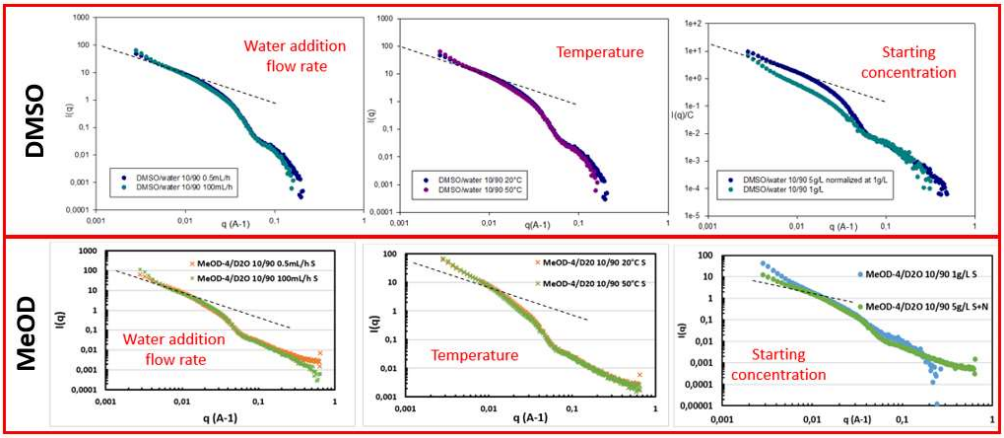

Figure 6. SANS data of the co-assembly using the "Water/DMSO" (top) and "Water/MeOD" (bottom) processes, studying the influence of water addition rate (0.5 vs. 100 mL/H, left), temperature during water addition (20 vs. 50°C, middle), and starting polymer concentration (100 vs. 50 g/L, data normalized by the concentration, right). Black dotted line is a q^{-1} visual aid.

Lastly, we aimed to better understand the self-assembly mechanism, by analysing the solutions at different solvent compositions. Note that this cannot be achieved by light scattering because the contrast of the polymer is too low in DMSO for light scattering experiments. In both cases, at 0% water, no angular dependence is observed and unimers appear to be present. At low water content, an upward trend at low q-values suggests the presence of aggregates. Finally, at higher water content (20% for DMSO and 50% for MeOD), a q^{-1} trend is observed, consistent with the formation of long nano-cylinders. Past this critical water content however, little difference was observed, indicating that the addition of D_2O leads to an on-off association of the JNR. Fitting is rendered difficult because of the presence of aggregates of cylinders scattering strongly at low q, but is under way.

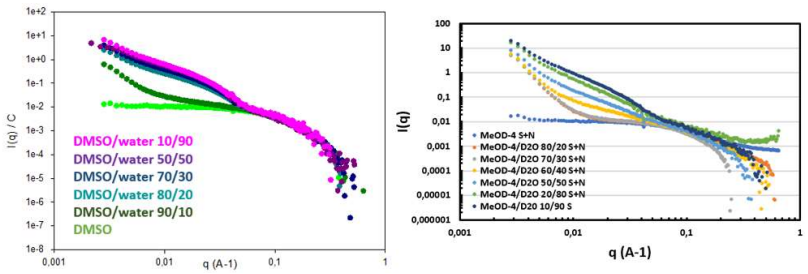

Figure 7. Studying the co-assembly at different solvent compositions starting from either pure DMSO (left) or pure MeOD (right).