Experimental report

15/09/2023

Proposal: **9-10-1760** **Council:** 10/2022

Title: Characterisation of polyoxometalate rich micelles using small angle neutron scattering

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: D2O
POM Phosphotungstic acid [PW12O40]3-
POM Silicotungstic acid [SiW12O40]4-
Poly(ethyleneoxidepolyacrylate)-b-Poly(2-aminoethyl methacrylate)
Poly(ethyleneoxidepolyacrylate)-b-Poly(acrylicacid)

Instrument	Requested days	Allocated days	From	To
D33	2	0		
D22	2	2	29/06/2023	01/07/2023

Abstract:

We are studying newly developed Polyion complex (PIC) micelles that have unparalleled significance in the construction of functionalised and ordered mesoporous materials. They are fabricated through the electrostatic complexation of a charged double hydrophilic block copolymer (DHBC) with an oppositely charged polyelectrolyte. Micellisation can be controlled by physico-chemical parameters such as a pH change, a property of predominant importance in templating agents employed for the preparation of ordered materials. Micellar formation is promoted during the condensation of silica as they act as templating agent and, once the material is fabricated, the dismantling and revealing of porosity follows. The intense study of PIC micelles has opened a new array of opportunities. Recently, our group developed a novel absorbing micelle preparation strategy; a fascinating extension of studies carried out till date.

Experimental Report

Characterisation of polyoxometalate rich micelles using small angle neutron scattering

Experiment 9-10-1760

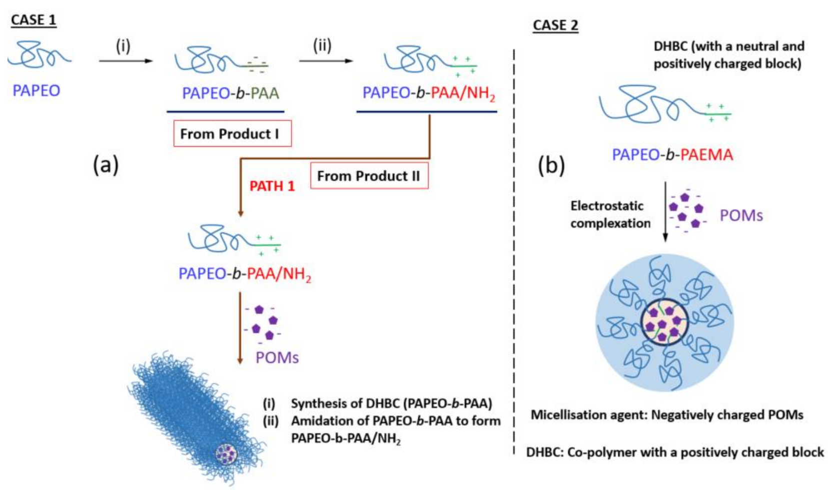
Ananthapadmanabhan UNNIKRISHNAN, Ralf SCHWEINS, Julien SCHMITT, Corine GERARDIN

Background

PolyIon complex (PIC) micelles have crucial mark in the fabrication of functionalised and ordered mesoporous materials. PIC micelles are constructed through the electrostatic complexation of a charged double hydrophilic block copolymer (DHBC) with an oppositely charged polyelectrolyte. The micellization of PIC structures is controlled by physico-chemical parameters such as pH variation. The micelle formed through the above methodology acts as a templating agent, and condensation of the silica precursor over the micelles yields a hybrid material. Once the hybrid materials are constructed, dismantling of micelles and revealing of porosity follow (typically through pH regulation). Understanding the structure and shape of the micelles would be key for their effective use in the formation of porous materials of controlled topologies, with applications in catalysis and drug delivery.

Measurements and Results

In the experiment 9-10-1760, two different DHBCs were envisaged. The first, PAPEO-*b*-PAA exhibits a poly(ethyleneoxidepolyacrylate) (PAPEO) neutral block and an ionisable poly (acrylic acid) block (PAA) that is later modified via an amidation procedure to introduce NH_2 groups, giving the polymer PAPEO-*b*-PAA/NH_2. The second, PAPEO-*b*-PAEMA, is made of the same PAPEO neutral block and a positively charged aminoethyl methacrylate block (PAEMA) block. Those DHBCs along with negatively charged polyelectrolytes such as Polyoxometalates (POMs such as $[PW_{12}O_{40}]^{3-}$ and $[SiW_{12}O_{40}]^{4-}$), Poly (Acrylic acid) (PAA) and Poly (Styrene Sulfonate) (PSS) can form PIC micelles at an ideal pH around 5.5.



Scheme-1. Schematic representation consolidating the fabrication of micelles with POMs (a) PAPEO-*b*-PAA/NH_2 based micelles (b) PAPEO-*b*-PAEMA based micelles

The D22 instrument was used for the SANS measurement. At a wavelength $\lambda = 6.0$ Å, a sufficient q-range of 0.003 Å$^{-1} \leq q \leq 0.6$ Å^{-1} was obtained. All samples were measured using quartz cuvettes with a path length of 2 mm (1 mm for the starting materials by itself). 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.

Our initial plan was to employ PAPEO-*b*-PAA/NH_2 and PAPEO-*b*-PAEMA individually along with POMs as the micellization agent, to form the PIC micelles (*Scheme 1*). However, the results were not convincing. The SANS plots (of PAPEO-*b*-PAEMA with POMs) indicated a strong aggregation with a clear Porod behaviour (**Figure 1**). Hence, we decided to focus mostly on negatively charged polyelectrolytes (such as PAA 5.1 kD, PAA 2.1 kD and PSS 1kD) as micellization agents at specific charge ratio between acid/NH_2 of copolymer and micellization agent respectively (found through DLS) for the formation of micelles. PAPEO-*b*-PAEMA was our primary focus out of the two DHBCs for the above measurements due to a much larger number of amine groups in the polymer. Various combinations of $P(APEO)_m$-*b*-$P(AEMA)_n$ having different degree of polymerisation (DP, **table 1**) along with micellization agents such as PAA 5.1 kD, PAA 2.1 kD and PSS were studied in detail (see all the DHBC/micellization agent combinations in **table 2**). We studied the effect of charge ratio (CR) between DHBC and micellization agent and pH to establish the pH-range where micelles are formed. At optimum CR and pH, the effect of concentration (1 to 5 wt%) was monitored to observe the possible emergence of interactions. All those measurements were carried in D_2O, but contrast variation studies were tried to see if we could differentiate the core and the shell of those micelles.

Serial No.	DHBC Synthesised	DP (APEO)	DP (AEMA)
1	PAPEO-*b*-PAEMA	21	21
2	PAPEO-*b*-PAEMA	21	16
3	PAPEO-*b*-PAEMA	21	12

Table 1. DHBC batches synthesised

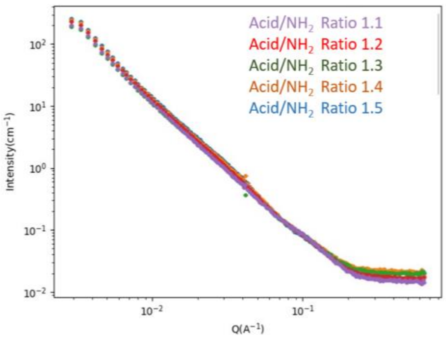


Figure 1. SANS plot corresponding to the different charge ratios employed for $P(APEO)_{25}$-b-$P(AEMA)_{17}$ micelles with POMs

Co-polymer	Micellisation agent	AA/NH_2 Ratio	R_h (nm, Angle 90°)
$PAPEO_{21}$-*b*-$PAEMA_{21}$	PAA_2.1 kD	1.5	44 (PDI- 25 %)
$PAPEO_{21}$-*b*-$PAEMA_{21}$	PSS_1 kD	1.0	33.0 (PDI- 31 %)
$PAPEO_{25}$-*b*-$PAEMA_{17}$	PAA_2.1 kD	1.5	80.0 (PDI- 13 %)
$PAPEO_{25}$-*b*-$PAEMA_{17}$	PSS_1 kD	0.9	139.0 (PDI- 19 %)
$PAPEO_{21}$-*b*-$PAEMA_{12}$	PAA_2.1 kD	1.7	108.0 (PDI- 16 %)

Table 2. Combinations of DHBCs and micellisation agents measured

The SANS result proved that well-defined stable species could be derived from the combination of the $P(APEO)_m$-*b*-$P(AEMA)_n$ with negatively charged micellization agents (*Figure* 2).

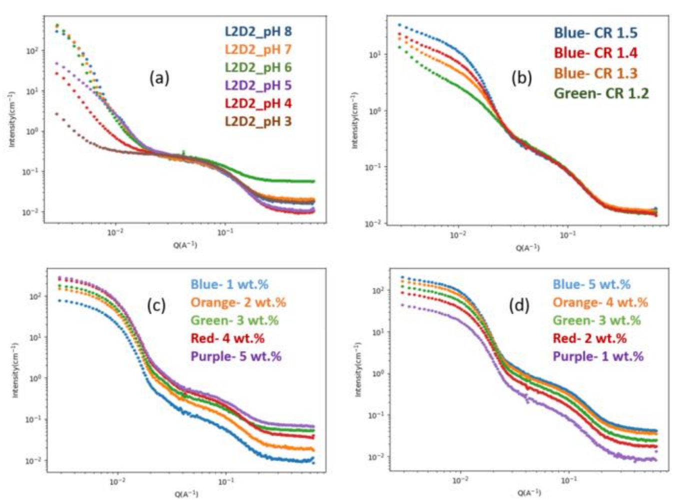


Figure 2. SANS plots (a) pH dependent study of micelles through $PAPEO_{25}$-*b*-$PAEMA_{17}$ & PAA (2.1 kD) combination (b) Charge ratio study of $PAPEO_{21}$-*b*-$PAEMA_{21}$ & PAA (5.1 kD) based micelles (c) concentrations measurement of $PAPEO_{21}$-b-$PAEMA_{21}$ & PAA (2.1 kD) micelles (d) Concentration study of $PAPEO_{21}$-b-$PAEMA_{21}$ & PSS (1.1 kD) derived structures

Using pH variation measurements (see **Figure 2.a.**), we observed an increase in intensity with a clear signal from micelles at low angles for pH ranging between 5 to 8. At lower pH, the signal of micelles disappears, in agreement with DLS studies. Let us note that the signal observed at ca. q=0.1 Å^{-1} is related to DHBC possibly remaining in suspension. **Figure 2.b.** focuses on the effect of the charge ratio (CR) onto the micelles with a clear change in the micelle signal. The type of micellization agent drastically influences the shape of the micelles, as seen in **Figure 1.b to d**, giving results for $PAPEO_{21}$-*b*-$PAEMA_{21}$ and PAA (5.1 kD), PAA (2.1 kD) and PSS (1 kD) respectively. While the former gives cylindrical micelles, the other two give patterns associated to spherical micelles. Moreover, the effect of concentration was also probed (see **Figure 2.c.** and **Figure 2 .d.**). We are currently fitting those patterns to extract the size of the micelles and evidence the possible emergence of interactions between them.

The contrast variation trials were unsuccessful with these systems, mostly as the polyelectrolyte used have a SLD which is close to the one of the DHBC, making it difficult to distinguish between the core and the shell of the micelles. Once more if stable and well-defined micelles can be obtained using POMs, as they have very different SLDs compared to the DHBC, it will make those contrast variation studies more successful.

Concluding, the beamtime at D22 (Experiment 9-10-1760), ILL was a success and major information was collected with respect to the individual PAPEO-*b*-PAEMA micelles, measured at relatively low concentrations (1 to 5 wt% were micelle-micelle interactions are weak) formed along with the micellization agents such as PAA 5.1 kD, PAA 2.1 kD and PSS 1 kD. In the experiment to follow, it would be interesting to look at higher concentrations for those micelles to study in more details the micelle structure factor and the formation of mesophases at high concentration. Further, we saw that PAPEO-b-PAA/NH_2, due to the lower amount of amine groups and the large amount of acrylic acid groups on the backbone can form micelles with Oligochitosan (OC2500) as the micellization agent. This would be an interesting alternative system to study to form mesoporous material functionalised with both amine and acrylate groups. That would require characterise in more details the micelles structure.