Experimental report

13/09/2024

Proposal: 9-12-680 **Council:** 10/2022

Title: Thermo-stimulable hydrogels based on PEG chains cross-linked by fattyacids self-assemblies of tunable structure

Research area: Soft condensed matter

This proposal is a continuation of 9-11-2041

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Local contacts: Sylvain PREVOST

Samples: Hydroxy stearic acid (CHNO)
Polyethylene glycol (CHO)

Instrument	Requested days	Allocated days	From	To
D33	2	2	01/04/2023	03/04/2023
D22	2	0		

Abstract:

We aim here at characterizing hydrogels made of Poly(ethylene-glycol) (PEG) chains cross-linked by physical nodes made of self-assemblies of 12-hydroxystearic acid, that have a temperature tuneable structure. HSA molecules self-assemble into micrometric multilamellar tubes at low temperature and nanometric micelles above a given threshold temperature. The PEG chains are grafted by HSA moieties at each end, so that their hydrophobized extremities insert within the self-assembled HSA aggregates.
We have already studied the system with short 5k PEG chains and showed that the HSA self-assemblies transit from multilamellar tubes to decorated vesicles in presence of PEG grafted chains. We plan now at studying the system in presence of larger grafted PEG chains with contrast variations experiments to solve the respective structure of HSA aggregates and polymer chains in the mixtures. We have already successfully synthetized the deuterated chains that are necessary for such experiments.

Proposal number: 9-12-680 on **D33** (01-03/04/2023) Local Contact: PREVOST Sylvain

Participants: LE COEUR Clémence, ALMEIDA Maëva, DUDZINSKI Daniel, GRZELKA Marion, ROUSSEAU Bastien, COUSIN Fabrice

Context and objectives: 2 days were granted on D33 for the **determination of the structure of thermo-sensitive hydrogels obtained by the mixing of PEG polymers chains that are terminally grafted at both ends by 12-Hydroxystearic acid (HSA) or stearic acid (SA) with self-assemblies of HSA, a small bio based fatty acid.** HSA and SA forms multi-lamellar tubes and planar lamellae respectively at low temperature and nanometric ellipsoidal micelles above a given threshold temperature. We expected that the side hydrophobic chain of PEG will insert in fatty acid aggregates that will play the role of thermos-sensitive nodes for the resulting hydrogels. The objective of the experiment was to determine the structure of the modified PEG chains / HSA mixture for various concentrations and PEG mass chains (5k, 20k, 35k).

Materials and Methods: *Samples.* The pure fatty acids, HSA molecules, were coupled via ion pairing with the counter ion ethanolamine in order to make them soluble in water. Samples Mixtures were obtained by mixing of mother stock solutions of pure HSA molecules with modified PEG modified. The concentration of PEG varied from 5 g/L to 75 g/L. The concentration of pure HSA molecules was fixed to 20 g/L for every sample. *Measurements and data reduction.* We used one configurations reaching a q-range of 3.4 10^{-3} Å^{-1} to 0.44 Å^{-1}. All samples were measured at 20 °C and 45 °C. Transmissions, scattering of empty cell, AgBe (neutron absorber to value ambient background of experiment), scattering of hydrogenated water and differential scattering cross section of water were measured independently. Subtraction of parasitic contributions and normalization by water to take into account detectors heterogeneities were applied to raw data by the GRASP software to obtain corrected data in absolute units (cm^{-1}). Contributions from solvent and incoherent scattering were then subtracted.

Results. 1. Structure of pure solutions of terminally grafted PEG polymers. First, it was important to characterize modified PEG 5k in aqueous solution at different initial concentrations (10, 37 and 50 g/L) for mono functionalized polymer (Figure 1).

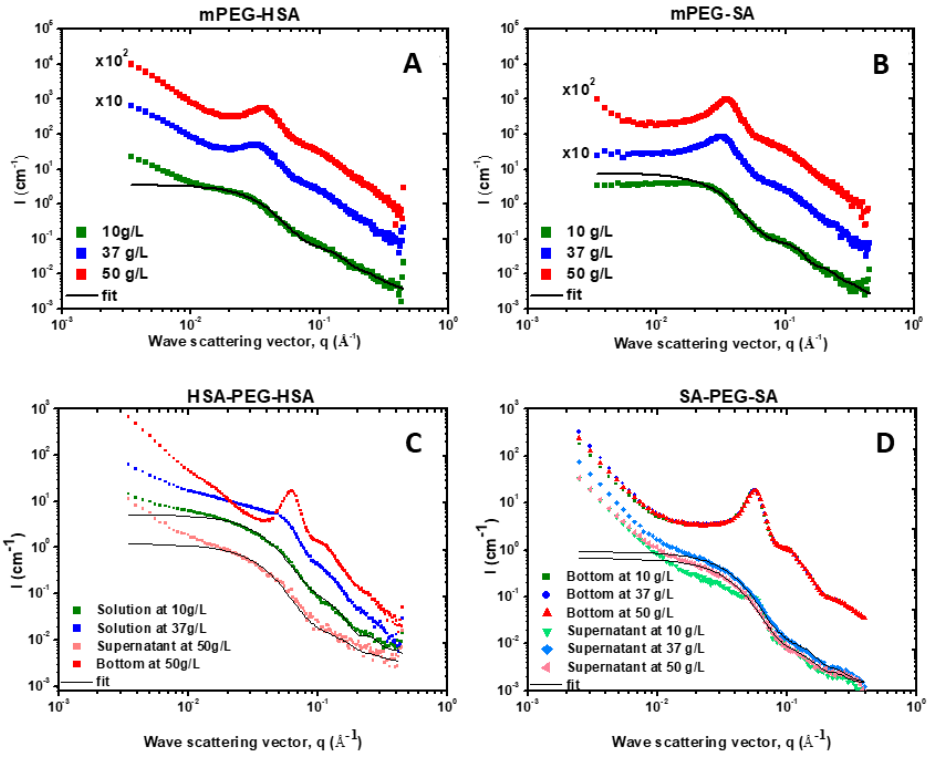

Figure 1. SANS intensity profiles for: (A) mono methyl PEG 5k grafted with HSA at 10 g L-1, 37 g L-1 and 50 g L-1 in D2O; (B) mPEG 5k grafted with SA at 10 g L-1, 37 g L-1 and 50 g L-1 in D2O. The black continuous lines correspond to the best fit by a form factor of hairy micelles; (C) methyl PEG 5k grafted with HSA at initial concentration of 10 g L-1, 37 g L-1 and 50 g L-1; (D) methyl PEG 5k grafted with SA at initial concentration of 10 g L-1, 37 g L-1 and 50 g L-1. For diphasic samples, SANS intensity of the supernatant and of the bottom phases are represented. The black continuous lines correspond to the best fit by a form factor of hairy micelles.

For di-functionalized one some samples had a phase separation between gel and liquid that were measured separately. Mono functionalized samples showed to form hairy micelles with stronger interactions with increasing concentrations. Phase separated samples shown to have a compact network of flower micelles on the gel phase and free micelles on the liquid one. The less concentrated samples were fitted by the model of hairy micelles with chains of corona in theta solvent proprosed by Pedersen et al[1]. *This work have already been published in 2024 on Journal of Molecular Liquids[2].*

2. Structure of mixtures. Then, we mixed HSA 2wt% with modified PEG at different concentrations and temperatures for 5k chains. Above the threshold temperature transition from tubes to micelles (around 37°) hairy micelles made of a fatty acid core with a PEG shell were obtained in every case (data not shown here). Below the threshold emperature we obtained pegylated multilamellar tubes at all polymer concentrations for mono modified PEG and SA-PEG-SA (Figure 3 A, B and C). Data were fitted at intermediate and high q with the Nallet model[3]. The interlamellar distances decreased with increasing concentration of polymer. For HSA-PEG-HSA we obtained pegylated vesicles that were fitted with a vesicle model. *This study will be submitted soon to a peer reviewed journal.*

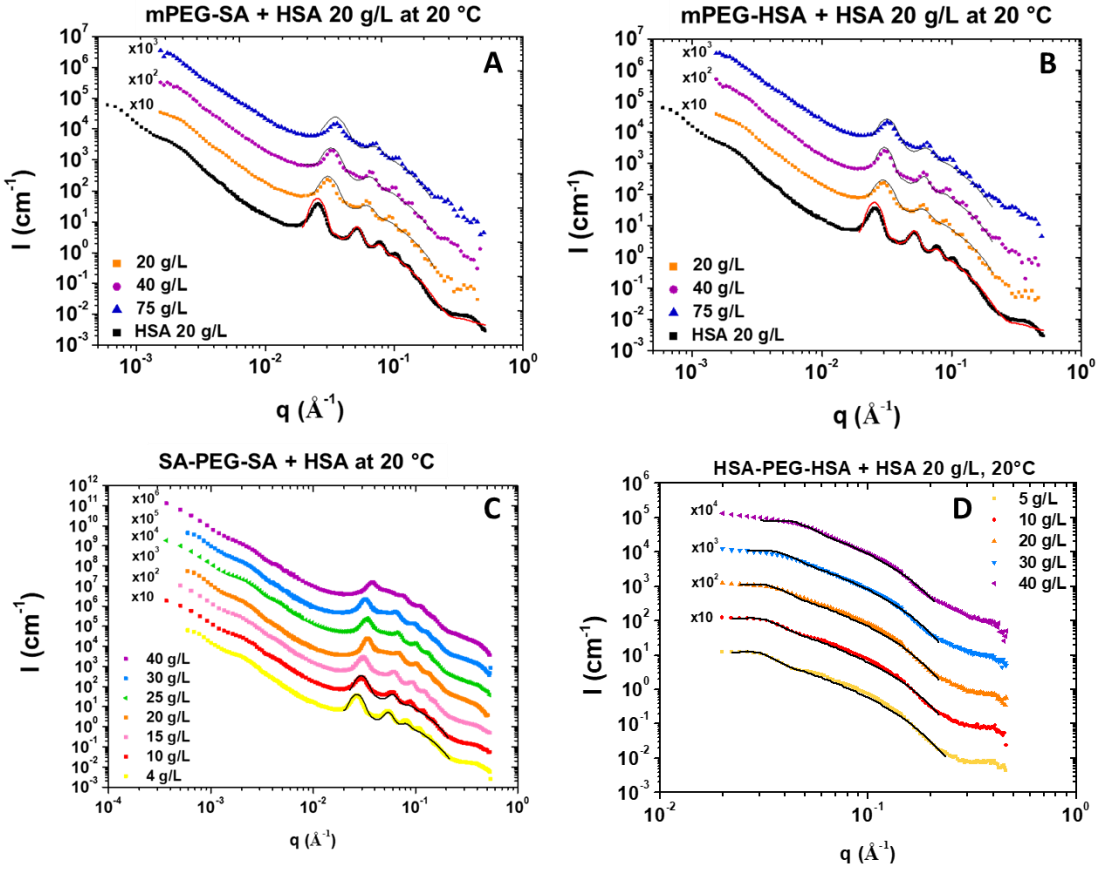

Figure 2. SANS intensity profile of mixtures with 5k chains at 20°C. A) mPEG5k-SA (B) mPEG5k-HSA; (C) SA-PEG5k-SA (D) HSA-PEG5k-HSA .

We probed then the influence of the length of the grafted polymer chain (20k and 35k) in the case of di-functionalized PEG with HSA or SA with 2wt% of HSA (Figure 3). The behavior was similar for both

chain lengths. For all the samples with a concentration of lower than 20 g/L, we recover the features of a lamellar phase (Bragg peaks periodically spaced in the intermediate region). Above this threshold concentration, the scattering features are more complex than pure lamellar systems. Analysis and interpretation are still under way.

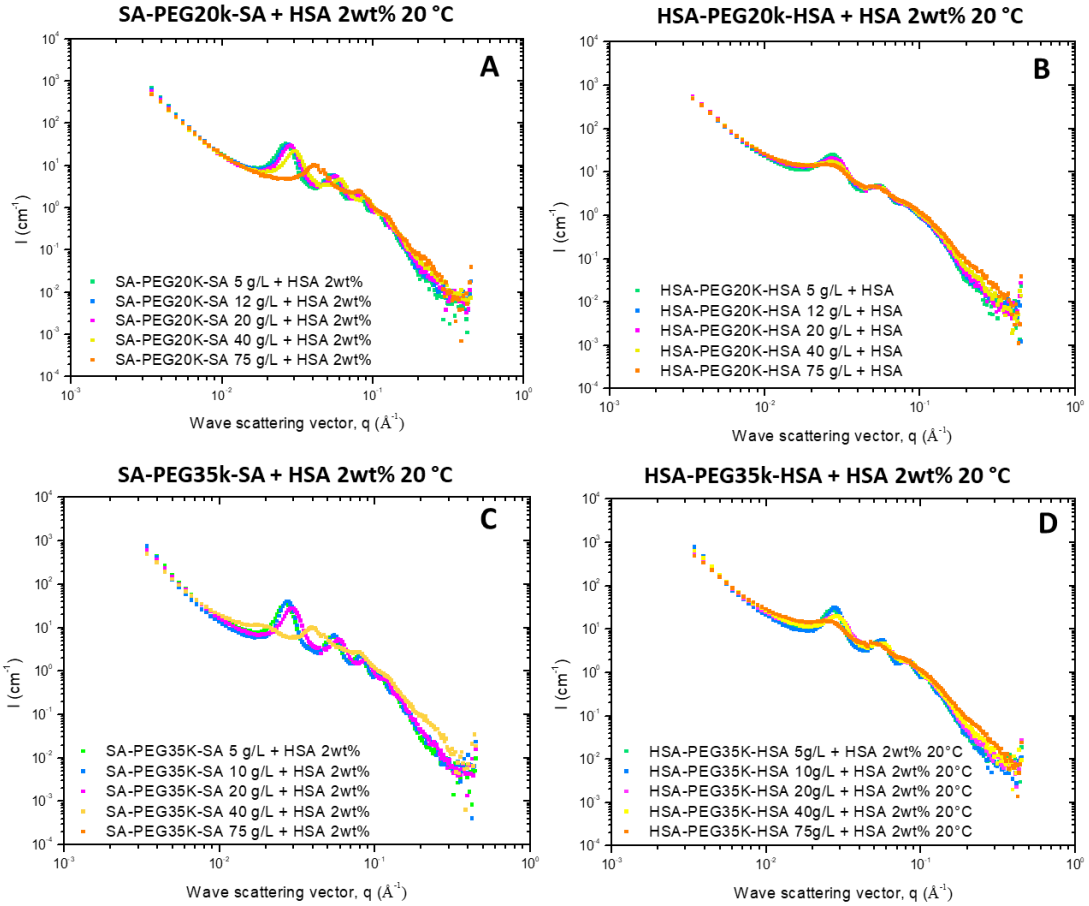

Figure 3. SANS intensity profile of mixtures with 20k and 35k chains at 20°C (A) SA-PEG20k-SA (B) HSA-PEG20k-HSA (C) SA-PEG35k-SA (D) HSA-PEG35k-HSA.

References

(1) Pedersen, J. S. Form Factors of Block Copolymer Micelles with Spherical, Ellipsoidal and Cylindrical Cores. *J Appl Crystallogr* **2000**, *33* (3), 637–640. https://doi.org/10.1107/S0021889899012248.

(2) Almeida, M.; Couturaud, B.; Rousseau, B.; Dudzinski, D.; Prévost, S.; Amiel, C.; Cousin, F.; Le Coeur, C. Pegylated Surfactants Based on Fatty Acids: 12-Hydroxystearic Acid versus Stearic Acid. *Journal of Molecular Liquids* **2024**, *411*, 125723. https://doi.org/10.1016/j.molliq.2024.125723.

(3) Nallet, F.; Laversanne, R.; Roux, D. Modelling X-Ray or Neutron Scattering Spectra of Lyotropic Lamellar Phases : Interplay between Form and Structure Factors. *J. Phys. II France* **1993**, *3* (4), 487–502. https://doi.org/10.1051/jp2:1993146.