Experimental report

18/11/2021

Proposal: 9-12-621 **Council:** 4/2020

Title: Decorating gold nanoparticles withcyclic polymer chains: effect of topology on the properties of the corona

Research area: Soft condensed matter

This proposal is a new proposal

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Experimental team: Lionel PORCAR

Local contacts: Lionel PORCAR

Samples: Au-NPs with cyclic polyethyleneoxide in D2O/H2O
Au-NPs with linear polyethyleneoxide in D2O/H2O

Instrument	Requested days	Allocated days	From	To
D22	1	1	11/02/2021	12/02/2021

Abstract:

DLS experiments on Au-nanoparticles with grafted PEO chains suggest a more extended conformation for cyclic polymers than for their linear analogues in the brushes of the corona. By means of SANS on solutions where the solvent matches the gold core, we want to determine the scattering length density profile of the corona for both topologies as a function of the molecular mass and graft density.

Decorating gold nanoparticles with cyclic polymer chains: effect of topology on the properties of the corona

Proposal 9-12-621. Experimental report

Instrument: D22 –Local contact: Dr. Lionel Porcar.

We have developed in our group a method to produce cyclic brushes of poly(ethylene oxide) (CPEO) on gold nanoparticles. DLS experiments suggested a more extended conformation for cyclic polymers than for their linear analogues in the brushes of the corona. The main aim of this proposal is to study by means of SANS the scattering length density profile of the corona for both topologies as a function of the molecular mass and graft density. To achieve this, we measured samples where the gold particle core was contrast-matched to the solvent by mixing the appropriate amounts of H_2O and D_2O.

For that purpose, we synthesized two series of samples of similar graft density (~0.5 chains/nm2) and AuNP size (13nmØ) in water (H_2O/D_2O): a) cyclic brushes of PEO on gold nanoparticles (CPEO@AuNP) of 3 molecular weights Mw (2, 6 and 11 kDa) and b) analogous linear PEO brushes (LPEO@AuNP).

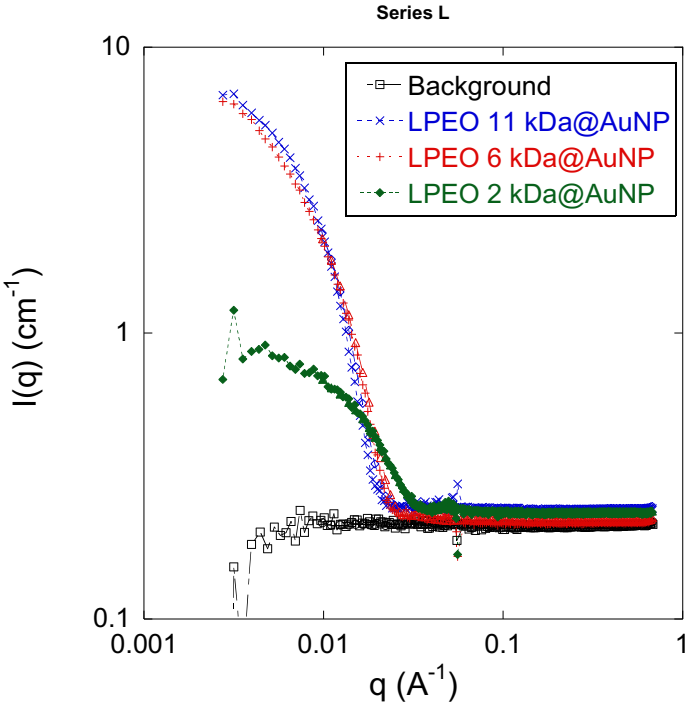

Figure 1: SANS patterns of representative gold nanoparticles grafted with linear PEGs (LPEO@AuNP) in H_2O/D_2O matching the Au-core. The backround H_2O/D_2O solvent background is also shown.

SANS experiments on the instrument D22 were carried out at room temperature. We used a neutron wavelength λ=6 Å and 2 different configurations of sample-to-detector/collimation distances (5.6 m/5.6 m and 17.6 m/17.6 m) to cover a q interval from 0.003 to 0.7 $Å^{-1}$. The sample transmission was measured at the same

wavelength and a distance of 17.6 m. The mainly incoherent background coming from the solvent was measured under the same conditions.

First, we measured the gold nanoparticles grafted with linear polymers. Figure 1 shows the SANS patterns of representative gold nanoparticles grafted with linear PEGs in H_2O/D_2O matching the gold core. The scattering curves show the typical scattering of spherical objects with a Guinier type of scattering at very low q and a subsequent sharp descent of intensity. The values of the radius of gyration deduced from the Guinier regime were significantly larger than that of the gold core. This hints to the fact that were are measuring the form factor of the grafting polymer shell. A detailed analysis including parameter free and model fitting will help elucidate the structural details as a function of the grafting chain molecular weight.

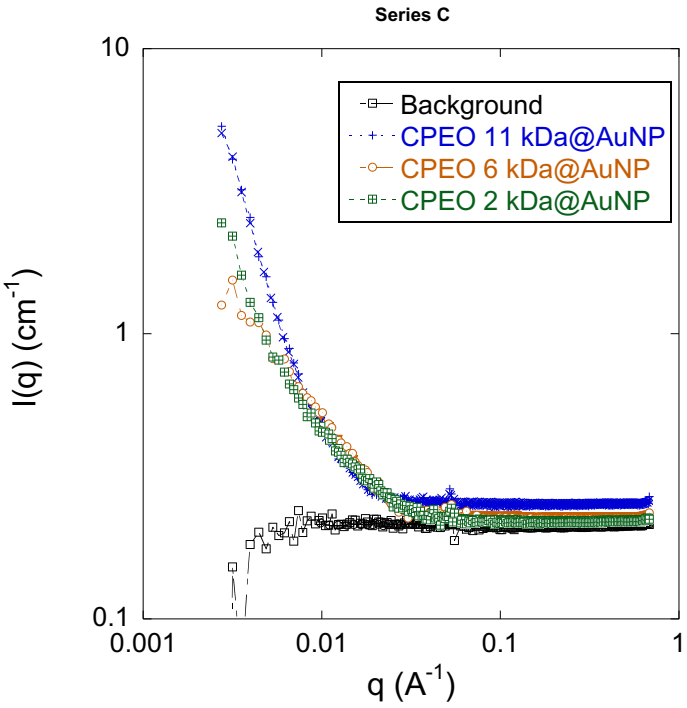

Figure 2: SANS patterns of representative gold nanoparticles grafted with cyclic PEGs (CPEO@AuNP) in H_2O/D_2O matching the Au-core. The H_2O/D_2O solvent background is also shown.

We then measured the gold nanoparticles grafted with cyclic PEGs. Figure 2 shows the scattering patterns of representative CPEG@AuNPs. Unfortunately, unlike the scattering curves shown in Figure 1 for the LPEG@AuNPs, here the scattering curves in many cases do not arrive to a low q plateau expected for spherical particles in the size range considered (of the same order of the sizes of the corresponding linear analogues or smaller, in a first approach). Thus, we conclude that these samples are aggregated and it will be difficult (if possible) to isolate the single-particle form factor.

Finally, we performed a contrast variation test on the CPEG 2 kDa@AuNPs where in addition to the matched core contrast conditions, we measured the full contrast conditions in D_2O. However, that sample also showed signs of aggregation.