Experimental report

25/01/2024

Proposal:	**9-11-2137**	**Council:**	4/2023
Title:	Crowded Solutions of Single-Chain Nanoparticles with Reversible Bonds: Do Fractal Globular ConformationsSurvive?		
Research area:	Soft condensed matter		

This proposal is a resubmission of 9-11-2102

Main proposer:	**Maria Aranzazu ARBE MENDEZ**
Experimental team:	Maria Isabel ASENJO SANZ Ainara RUIZ Nisha Pawar CHAUHAN
Local contacts:	Lionel PORCAR

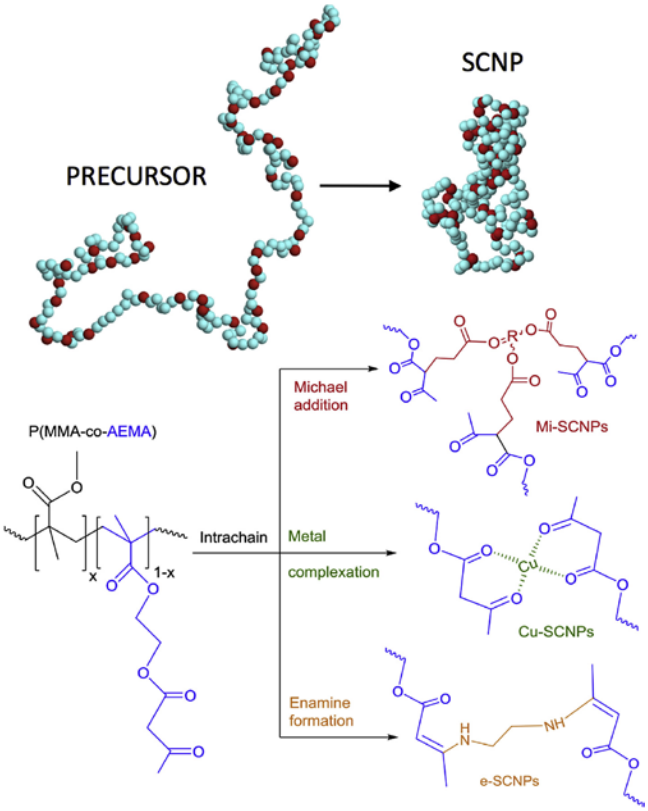
Samples: Background samples
hSCNPs and dSCNPs in bulk
hSCNPs and dSCNPs in matching solvent

Instrument	Requested days	Allocated days	From	To
D22	1	1	05/12/2023	06/12/2023

Abstract:

To broaden the functionalities and areas of applicability of Single-Chain Nano-Particles (SNCPs), the implementation of reversible bonds via noncovalent and dynamically covalent interactions is currently being explored. The single-chain character of such SCNPs in solution is lost when the concentration is high enough, leading to formation of aggregates and eventually a percolating network. The combination of potential self-healing properties associated to the reversibility of the network with the intrinsic functionality of SCNPs paves the way to the design of smart materials by using SCNPs as building blocks. Our aim here is to characterize the intramolecular conformations of SCNPs with reversible bonds in solution, exploring a broad range of concentrations from far below the overlap concentration to the concentrated regime and melt, and to establish differences with the behaviour found for crowded solutions of irreversible SCNPs with no intermolecular bonds. Preliminary simulations by some of us indeed point to important differences.

SANS experiments were carried out on solutions (in dimethyl formamide, DMF) of reversible single-chain nano-particles (SCNPs) obtained through metal complexation (see scheme below), using linear copolymers of methyl methacrylate (MMA) and (2-acetoacetoxy)ethyl methacrylate (AEMA) as precursors. Solutions were filling Hellma cuvettes of 1mm thickness. A wavelength of 6Å was used, with two collimations set up (17.6 and 5.6m). To exploit labelling, we used protonated macromolecules (M_w=237kDa, PDI=1.27) and deuterated macromolecules (M_w=249.9kDa, PDI=1.37). Obtaining perdeuterated copolymers of this material is not easy, since the deuterated AEMA monomer is not commercially available. We established a collaboration with the deuteration lab in Jülich and the perspectives of a successful synthesis were promising –in fact, it should be doable--. However, due to several unfortunate circumstances, it was not possible to produce fully deuterated stuff. Therefore, in the experiment we used macromolecules where the MMA monomer is deuterated and the AEMA monomer is protonated. Since this is the minority component (29%), the SLD is still much higher than that of the fully protonated chains. The molecular weight of protonated and deuterated chains was such that they contain a very similar number of monomers, as required in the experiments we performed.



Scheme. Upper part: MD-simulation snapshot of a linear precursor chain and a SCNP obtained through internal cross-linking processes. Red beads represent the reactive groups. The lower part shows three particular synthesis routes that can be applied to the precursor chains used in this experiment.

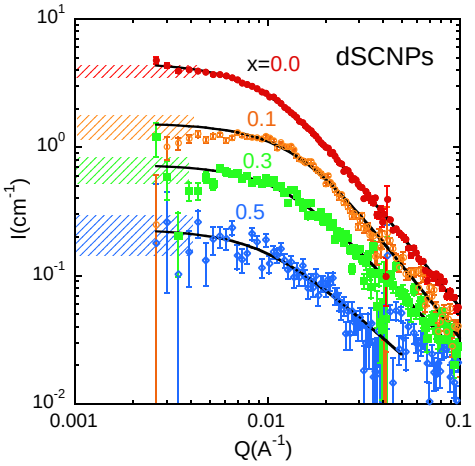
Our interest was to access the form factor of the macromolecules in solutions with increasing concentration. This requires high-concentration label methods. The experiments thus consisted of mixing protonated and deuterated polymers (with a volume fraction ϕ of deuterated stuff) with total polymer concentration c in a solvent of SLD ρ_s. We thus had to determine the ZAC condition

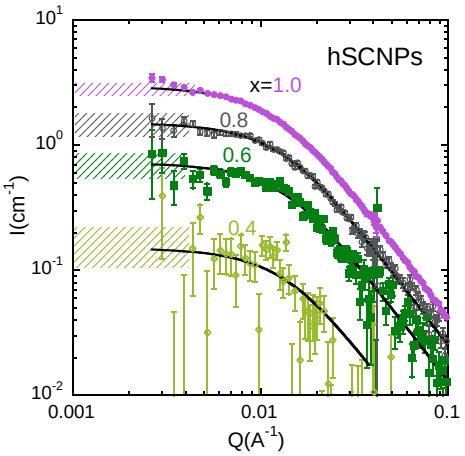
$$\phi\ \rho_d + (1-\phi)\ \rho_h - \rho_s = 0$$

where ρ_d (ρ_h) is the SLD of the deuterated (protonated) chains. We chose ϕ =0.5 to maximize the intensity of the intramolecular contribution to the scattering, weighted by $\phi\ (1-\phi)\ (\rho_h - \rho_s)^2\ nV^2$ (n: number of chains per unit volume; V: volume of the macromolecule). Then, ZAC condition requires

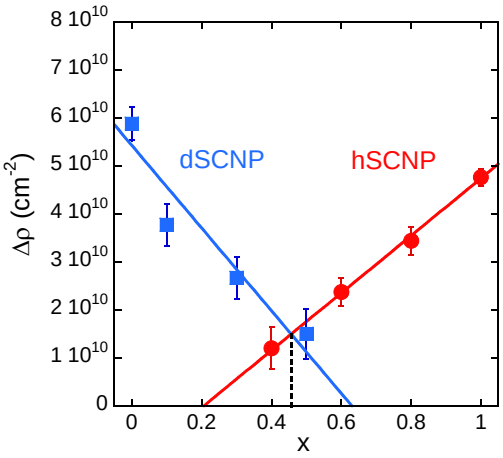
$$\rho_d - \rho_s = \rho_s - \rho_h$$

This was experimentally determined by measuring solutions of either deuterated or protonated SCNPs (at 5mg/mL) in solvents with varying SLD, i. e., with different volume fraction x of deuterated DMF. Below are the obtained results, described in terms of generalized Gaussian functions.



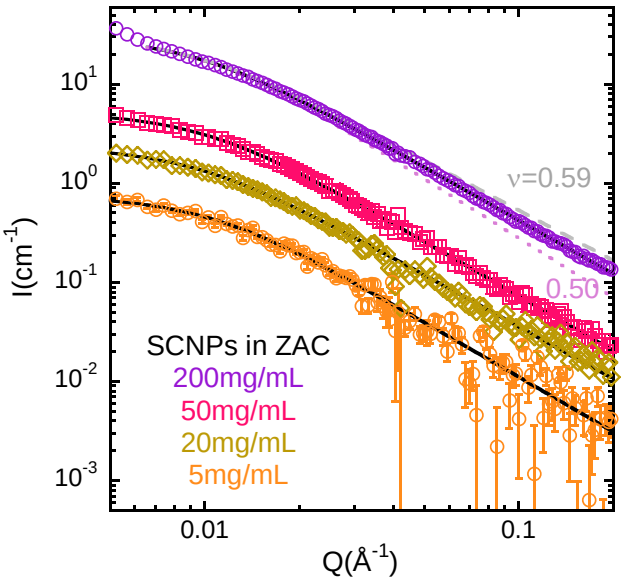


From the values of $I(Q->0)=(\rho_{d(h)} - \rho_s)^2 nV^2$ intensity, we deduced the x-dependence of $\Delta\rho=abs(\rho_{d(h)} - \rho_s)$. The ZAC condition thus corresponds to x=0.45 (see Figure below)

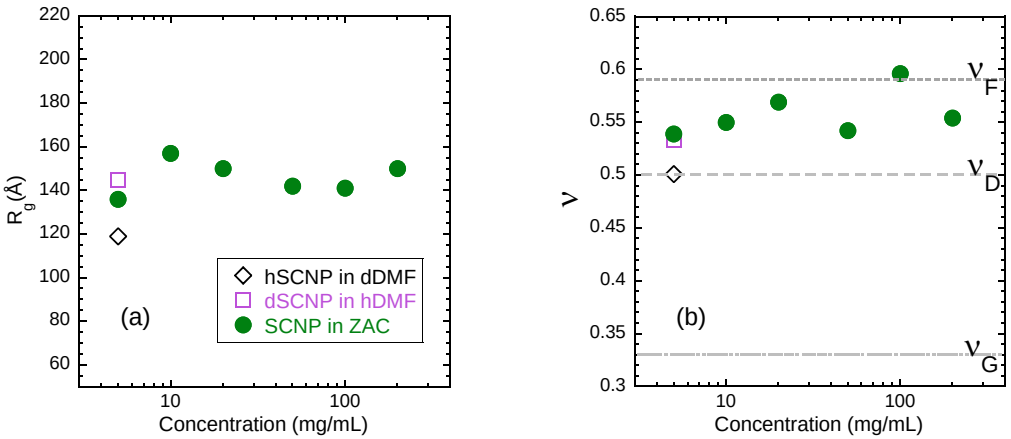


Samples in ZAC were prepared satisfying this condition. Since filling cuvettes with samples at high concentrations is very difficult (they form a gel), pre-disolved samples with a first guess estimation of the solvent compositionhad been prepared in the home laboratory, and the final composition was tuned after this determination. We note that the experiment was limited to a maximum concentration value of 200mg/mL. We tried to prepare a sample with 400mg/mL but it was impossible to obtain good results. On the other hand, unfortunately we run out of sample to be able to prepare a bulk sample.

Some representative results of the SANS experiments in ZAC are shown in the Figure below.



From the fits of generalized Gaussian coils to the results, we obtained the size (radius of gyration, R_g) and scaling exponent ν as function of concentration:



As predicted from the simulations, the chain conformation of reversible SCNPs is practically unaltered upon crowding.

With this experiment we thus demonstrate that applying high-concentration label techniques is feasible also in this kind of samples where the deuteration is not complete, and provide experimental evidence for the simulations predictions.