Experimental report

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Proposal: 9-11-1938 **Council:** 4/2019

Title: Conformation of single-chain nano-particles surrounded by linear chains: reversible vs irreversible bonds

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: PMMA-based NPs in dPMMA linear

Instrument	Requested days	Allocated days	From	To
D22	2	2	05/02/2020	07/02/2020
D33	2	0		

Abstract:

We want to check the coarse-grained simulations prediction of crumpled globular-like conformations of SCNPs when they are surrounded by linear polymer chains in bulk conditions for both, reversible and irreversible SCNPs. We want to determine the dependence of the scaling exponent with the degree of cross-linking and verify the a priori unexpected result that for equal fraction of reactive monomers, the compaction degree is higher for SCNPs forming reversible bonds than for SCNPs obtained by irreversible crosslinking.

Conformation of single-chain nano-particles surrounded by linear chains: reversible vs irreversible bonds

Proposal 9-11-1938. Experimental report

D22 – 05/02/2020 to 07/02/2020 – Local contact: Dr Lionel Porcar.

The main aim of this proposal is to measure the form factor of single-chain nanoparticles formed via intramolecular cross-linking of individual linear polymeric chains with irreversible and reversible cross-links, surrounded by linear chains. We had performed extensive coarse-grained simulations of SCNPs in a melt of linear chains revealing that under crowding conditions the SCNP adopt a compact conformation with a Flory exponent $\nu \approx 1/3$ (compared to the Gaussian conformation with $\nu \approx 1/2$ of linear polymers) irrespective of the type of cross-linking. The goal of this experiment was to confirm the simulation results showed in Figure 1 and that the structure of the SCNP is only controlled by the number of bonds and not by its internal dynamics.

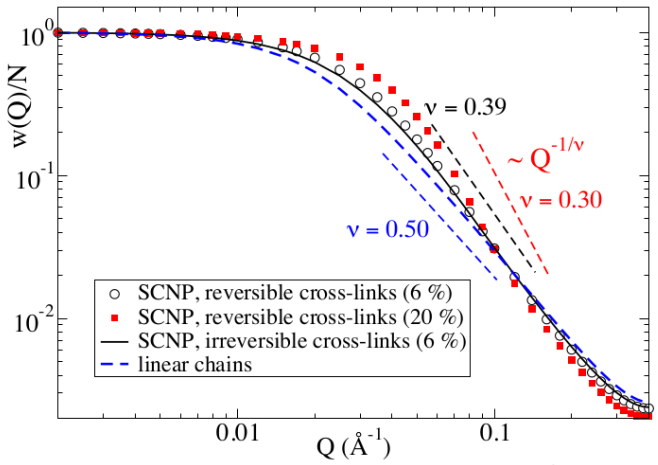

Figure 1: Form factor of a simulated SCNP with reversible cross-links surrounded by linear chains (circles (squares): 6% (20%) of the monomers form cross-links) compared with the case where the bonds are irreversible (6% of reacted monomers, solid line) and with the linear chain (Gaussian coil) (dashed line). The fractal regimes with the corresponding scaling exponents are also shown.

For that purpose, we synthesized SCNPs with varying cross-linking density between 9 and 27% and reversible and irreversible cross-links. The precursor polymer consisted of poly[(methyl methacrylate)-co-(2-Acetoacetoxy)ethyl methacrylate] (PMMA-co-AEMA: M_w = 167 kDa; PDI=1.19) and the AEMA moieties could be bifunctionally linked reversibly by addition of Cu^{2+} ions (Cu-SCNP) and irreversibly via Michael addition reaction of ethylene glycol diacrylate as a cross-linker (Mi-SCNP). The percentage MMA/AEMA in the precursor was of 72/28 and from it reversible and irreversible SCNPs, with a different degree of crosslinking (c: 33%, 66% and 100% with respect to the AEMA amount), were obtained.

SANS experiments on the instrument D22 were carried out at room temperature (295K). We used a neutron wavelength λ=6Å and 3 different configurations of sample-to-detector/collimation distances (2 m/2.8 m, 5.6 m/5.6 m and 17.6 m/17.6 m) to cover a Q interval from 0.003 to 0.45 Å^{-1}. The sample transmission was measured at the same wavelength and a distance 17.6 m. The background was measured under the same conditions and subtracted from the measurements with labeled samples.

First, we measured 5mg/ml of hydrogenated SCNPs in deuterated linear PMMA of high molecular weight (300 kDa). As reference, we also performed the same measurement on a sample with 5mg/ml of the precursor in the same linear matrix. Unfortunately, the samples could not be heated above the glass transition temperature of the PMMA (~430 K) to induce mobility. This was due to thermal instability of the SCNPs at high temperatures, as observed in our previous TGA characterization of the SCNPs. Instead, we measured concentrated crowded solutions by varying also the temperature (295K, 355K and 395K). All the solutions had a total concentration of 400mg/ml (5mg/ml of SCNPs or precursor and 395mg/ml of d-PMMA) in deuterated DMF. In particular, we measured the form factor of Cu-SCNPs (c = 100%, 66% and 33%), Mi-SCNPs (c = 100%, 66% and 33%) and precursor in solutions with d-PMMA with 2 different molecular weights: 9kDa and 200kDa.

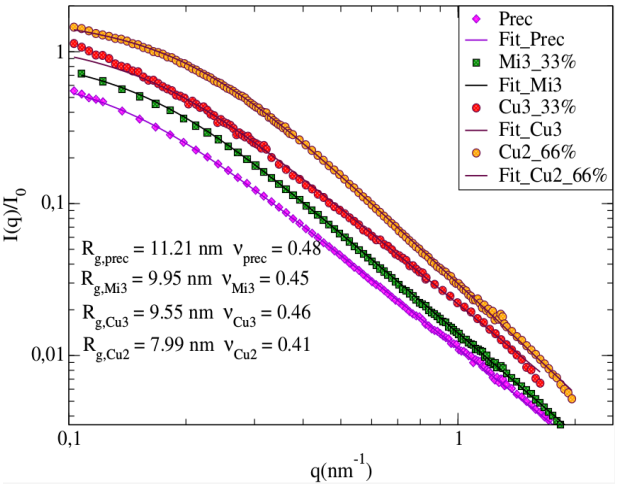

Figure 2: Comparison of the form factor of SCNPs with reversible bonds with different degree of crosslinking (circles: red 33% and orange 66%) compared with the case where the bonds are irreversible (square: green 33% of crosslinking) and with the precursor (magenta diamonds). All the NPs are surrounded by d-PMMA with M_w = 9kDa in solutions of 400mg/ml in d-DMF. Solid lines are the fits in terms of generalized Gaussian functions obtained for the different curves. The values of the fitting parameters (gyration radius R_g and scaling Flory exponent ν) are also reported in the figure. All the curves are normalized with respect to the initial intensity value obtained by the fit (I_0) and then shifted by a factor in order to make easier the visualization.

Figure 2 shows the form factor of the precursor and Cu-SCNPs with 33 and 66% and Mi-SCNP with 33% cross-linking in a crowded solution with 9k-dPMMA. The experimental curves fitted well to a generalized coil model for polymer chains. The exponent obtained from the fit for the precursor (0.48) is very close to the one expected for Gaussian chains (0.5). In addition, as the cross-linking density increases the Flory exponent of the SCNP decreases reaching ~0.4 for 66% Cu cross-links. For the same cross-linking density, the curves of SCNPs with reversible and irreversible bonds overlap quite nicely in agreement with simulations.

The exponents found for the SCNPs are higher than in the simulations. This is likely due to the weaker crowding effects in the solution at 400 mg/mL than at the melt density of the simulations. Moreover, we found no significant changes for the form factors of the reversible SCNPs in solutions by varying the temperature, which again suggests that the bond lifetime does not affect the structure of the synthesized SCNPs. In summary, this preliminary analysis seems to strongly support the hypothesis of the independence of the conformations of crowded SCNPs on the nature (static or dynamic) of its topology (given by its network of bonds).

Finally, we performed a fast feasibility test on gold nanoparticles grafted with linear and cyclic polymers.