Experimental report

25/03/2017

Proposal:	**9-12-396**	**Council:**	10/2014
Title:	Structure of Silica/Polymer HybridNanoparticles - Control by pH and Length of the Attached Polymer		
Research area:	Soft condensed matter		

This proposal is a new proposal

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Samples: Silica
2-dimethylamino ethyl methacrylate
tert-butyl methacrylate

Instrument	**Requested days**	**Allocated days**	**From**	**To**
D11	2	2	04/06/2016	06/06/2016

Abstract:

In this project we want to study the structure of polymeric shells covalently bound to the surface of silica nanoparticles (SiNPs). Here we employ well defined SiNPs in the size range of 10-100 nm with polymer shells of cationic PDMAEMA or anionic PAA, with polymer chains of different length (DP = 10-150). Both polymers are pH sensitive and we are interested in how the length of the polymer chain and pH affect the structure of these hybrid nanoparticles, i. e., the denseness of the polymer layer and how softness and range of the interaction potential of these nanoparticles change. Particularly interesting is the detailed structure of the polymer shell which shall be studied by contrast variation (matching the silica core). This is a central point for subsequent studies of the interaction of these particles with membranes and also to use them as building blocks in colloidal assembly.

Experimental Report ILL
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Introduction

Research on nanostructured materials has seen prominent development in recent years. For instance, silica based functional nanoparticles have been studied for a large variety of different applications because of their easy preparation and surface modifications. An interesting modification are polymer shells around the SiO_2-NPs that allow to tune the interaction with other particles or in a biological environment. This can be achieved by a surface initiated atom-transfer radical polymerization (ATRP), that allows good control over the molecular weight of the grafted polymers. By the polymer shell one can modify the chemical and physical properties of the nanoparticles and their response to external stimuli, for instance by changing pH.[1,2] While the overall size of the polymer modified SiO_2-NPs can easily be studied by different techniques (light scattering, ζ-potential, TEM and cryo-TEM), details about the polymer structure in aqueous solutions are only available using SANS contrast variation as the polymer shell is very different in scattering length density than the silica core.

Measurements

We covered a q-range of 0.03–1 nm^{-1} with 3 S-D distances of 1.2, 6 and 20 m and a wavelength of 0.6 nm with a total measuring time of 120 min per sample. Our samples were measured at $V_{D2O}/V_{H2O} = 0.8/0.2$ (to measure the core shell structure of our NPs, $\eta_{SiO2} < \eta_{solvent}$) and at $V_{D2O}/V_{H2O} = 0.58/0.42$ to contrast match the silica core ($\eta_{SiO2} < \eta_{solvent}$). Full D_2O contrast couldn´t be achieved due sample preparation issues which would leave to undispersible aggregates.

First we checked the count rate vs the D_2O content for pure SiO_2-NPS at a S-D distance of 20 m and a wavelength of 0.6 nm with a measuring time of 10 min per sample. From the count rate measurements, we saw that the adjusted contrast almost matched the SiO_2-NP core so further sample preparation was not necessary anymore. The measurement time was adapted to have sufficiently good statistics for a meaningful analysis.

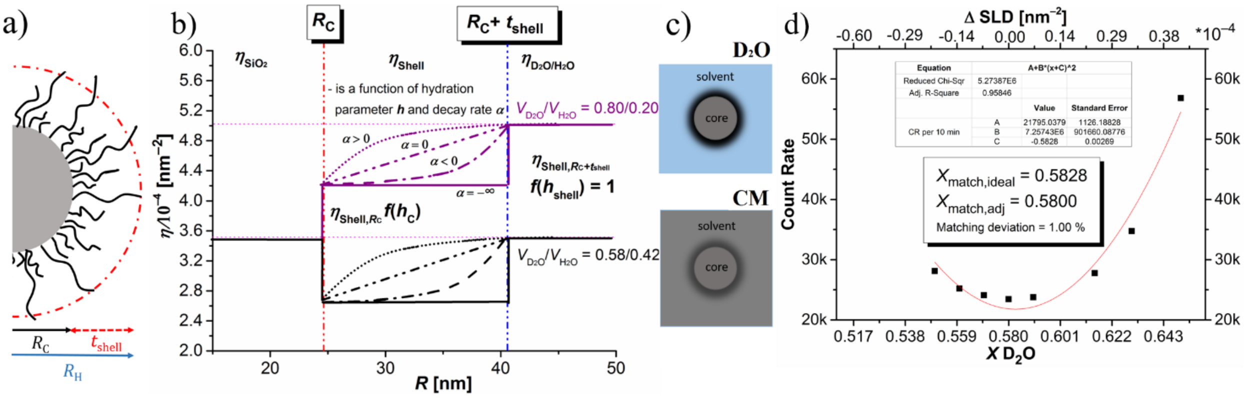

Fig. 1: **a)** Cartoon of a polymer brush grafted SiO_2-NP, **b)** different SLD profiles for core-shell particles where the SLD η is a function of the solvent reported in the reference[3]; hydration parameter at the core surface h_C and the exponential parameter α are the variable parameters, the thickness $t_{shell} = R_H - R_C$, η_{shell} was set to 1 (full decay to the SLD of the solvent); **c)** contrast cartoons for different solvent conditions, top $\eta_{SiO2} < \eta_{solvent}$, bottom $\eta_{SiO2} = \eta_{solvent}$; **d)** count rate measurement for pure SiO_2-NP

Fitting model and example data

The pH values of those solution were adjusted to 4 for SiO_2@PDMAEMA-NPs. PDMAEMA is fully charged (pKa = 7.4) so water is a good solvent for the polymer. Thus an exponential SLD profile for a core-shell form factor is the most precise model for fitting the data. To describe the scattering intensity we used a core-shell form factor with spherical symmetry to approximate the data for both contrast. The SiO_2 core was described by a homogeneous spherical form factor (R = 32.6, 70.3 nm) and those values were used for further approximation. The SLD profile of the shell varies with volume fraction of the solvent (Fig. 1). α describes the parameter for the exponential diffuse of the shell. h_C and h_{shell} are the volume fraction of solvent at the core surface (variable) and at the shell thickness whereby h_{shell} is set to 1 which describes a full SLD decay of the shell η_{shell} to $\eta_{solvent}$ of the solvent. The shell thickness t_{shell} was obtained by subtracting the hydrodynamic radius R_H of SiO_2@Polymer-NPs from the R_C.

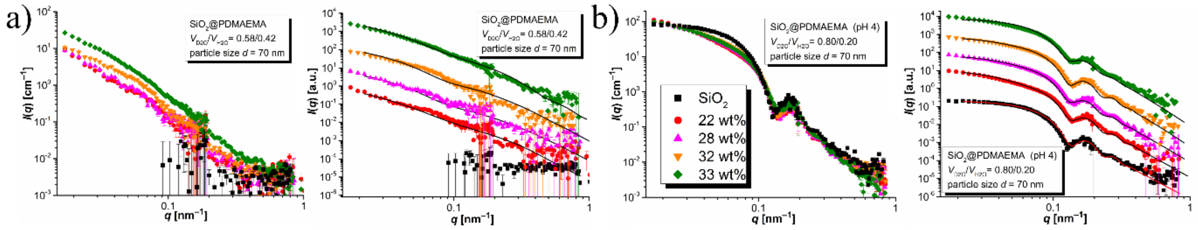

Fig 2: Data for SiO_2@PDMAEMA-NPs (R_C = 32.58 nm) **a)** $\eta_{SiO_2} = \eta_{solvent}$ left: data in absolute scale, right: data for a better view shifted; **b)** $\eta_{SiO2} < \eta_{solvent}$ left: data in absolute scale, right: data for a better view shifted with included fit; SiO_2-NPs are fitted with a spherical form factor with included fit, SiO_2-NPs fitted with spherical form factor, SiO_2@PDMAEMA-NPs fitted with the core-shell form factor from ref [3]

We measured samples with two different core sizes R_C = 32.6 and 70.3 nm by varying the amount of grafted polymer as parameter. Additionally we studied the influence of the pH for highest polymer graft on those sample. Both particle sizes show similar trends and we present data for the core radius R_C = 32.58 nm. For all polymer grafted samples α has positive values and describes an exponential SLD profile decay as described in Fig 1. The shell thickness is almost constant thus we estimated the grafting density of NPs which increases with amount of grafted polymer. The fitting results of SANS data are in good agreement of previously observed results. The volume fraction of the solvent at the core surface h_C decreases with increasing amounts of grafted polymer and thus it can be interpreted as a grafting density increase. Comparing the fitting results from both contrast absolute values differs but show the same trend towards increasing polymer grafting. All important values are summarized in table 1.

In summary, these experiments successfully allowed to characterize the structure of polymer modified SiO_2-NPs with different degrees of polymer modification and at different pH. This information is essential in the context of the further use of these NPs as functional hybrid NPs in the context of interactions with phospholipid membranes and also for designing well defined surface structured materials.

Table 1: fitting results for the spherical core-shell-form factor with exponential SLD profile decay for the shell for NP core radius R_C = 32.6 nm.

Δ*m* loss [wt]	R_H [nm]*	t_{shell} [nm]	α	h_C	PDI	t_{shell} [nm]	α	h_C	PDI
				$\eta_{SiO_2} < \eta_{solvent}$				$\eta_{SiO_2} = \eta_{solvent}$	
0 (SiO_2)	38	–	–	–	–	–	–	–	–
22	45	8.1	10.5	0.60	0.10	12.1	2.3	0.48	0.55
28	47	14.2	13.0	0.55	0.13	14.4	3.7	0.44	0.41
32	47	14.9	13.0	0.42	0.09	14.9	2.7	0.38	0.41
33	50	15.5	13.0	0.38	0.11	16.0	1.3	0.29	0.53

$\eta_{SiO_2} = 3.475*10^{-4}\ nm^2$

$\eta_{PDMAEMA} = 1.583*10^{-4}\ nm^2$ (protonated)

$\eta_{X\_D_2O = 0.80} = 5.003*10^{-4}\ nm^2$

$\eta_{X\_D_2O = 0.58} = 3.478*10^{-4}\ nm^2$

*DLS data measured at Technichal University of Berlin

References

[1] J. C. Chen, W. Q. Luo, H. D. Wang, J. M. Xiang, H. F. Jin, F. Chen *Appl. Surf. Sci.* **2010**, *256*, 2490

[2] T. Wu, Y. Zhang, X. Wang, S. Liu, *Chem. Mater.* **2010**, *20*, 101

[3] SasFit-Software →SasFit manual: https://kur.web.psi.ch/sans1/sasfit/sasfit.pdf, last accessed 03/17/2017