Experimental report

14/02/2021

Proposal: **9-12-557** **Council:** 10/2018

Title: Polymer Adsorption onto Double Walled Imogolite Nanotubes

Research area: Chemistry

This proposal is a new proposal

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Samples: PEG
(OH)3Al2O3Ge(OH), Imogolite nanotubes

Instrument	Requested days	Allocated days	From	To
D11	2	1	21/06/2019	22/06/2019

Abstract:

We intend to study the selective adsorption of polymers onto Imogolite nanotubes (INT). Recently, the use of nanotubular clays received an outburst in literature due to the improvement of the properties of the materials and the possibility to load and release molecules for specific application. We recently succeeded in forming stable INT dispersions in water and the polymer adsorption was strongly dependent on the polymer molecular weight. The structure of these dispersions is of essential interest for the understanding of the hybrid nanocomposites obtained and their anisotropic orientation induced by excluded volume or depletion effects. These aspects are strategic for potential applications of the dispersions themselves.

PEG Adsorption onto Aluminogermanate Imogolite Nanotubes

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Imogolite nanotube (INT) is an aluminosilicate clay mineral, naturally occurring and widespread in well-drained volcanic ash soils.[1] Unlike halloysite, another tubular clay mineral,[2] INTs can be readily synthesized through hydrothermal methods.[3] The structure of these nanotubes is rather unique. The external walls consist of gibbsite-like sheet $Al(OH)_3$ while the cavity interface is formed by isolated $(SiO_3)OH$ tetrahedron units connected upright to the octahedral vacancies by covalent bonding.[4] Silicon can be replaced by germanium allowing to increase the diameter of the inner cavity from 1.5 to 3 nm for single-walled INTs.[5,6] Furthermore, modifications of the synthesis conditions offer a convenient way for designing innovative INTs with well-defined morphologies (single or double-walled structures),[7] modular interfaces (e.g. hydrophilic or hydrophobic cavities)[8–10] and high colloidal stability in aqueous media.[11–13] All these properties have led in recent years to a renewed interest in synthetic imogolite-type nanotubes as promising nanoreactors notably for molecular confinement[14–17] or photocatalytic applications.[18–22]

The thermodynamics of the polymer adsorption onto aqueous dispersions of Ge-DWINTs was investigated by ITC. The maximum amount of PEG molecules adsorbed onto the imogolite surface decreases sharply with the polymer molecular weight. The dependence of the affinity toward the Ge-DWINTs surface from the PEG molecular weight was further investigated by SANS for PEG2k and PEG20k. It should be noted that the scattering from dilute Ge-DWINTs dispersions (1 g.L^{-1}) in the same solvent has a negligible flat scattering intensity in the investigated scattering vector regime As a general feature (Figure 4), the addition of Ge-DWINTs to PEG solutions does not influence the shape of the curves. For PEG2k, only a minor increase in the overall scattering intensity is observed, indicating that Ge-DWINTs induce a clustering of the polymer chains due to the adsorption on the nanotube surface but it makes no difference on the polymer conformation. (Figure S1 in Supporting Information). This result confirms the prediction from ITC data that more than 60% of the polymer is not adsorbed onto the Ge-DWINT surface under these conditions (Figure 4b). Conversely, for PEG20k/Ge-DWINTs complexes, an increase in the scattering intensity is observed related to the adsorption of the polymer on the nanotube surface. Furthermore, the decay of the scattering intensity is shifted towards smaller q-values, which comes from a more extended configuration of the polymer coil induced by the adsorption process (Figure 4a). Going further, total scattering intensity was well fitted by the Debye equation for a non-interacting random coil,[23] providing a radius of gyration of 2.5 nm for PEG20k that increases to 2.7 nm and 3.1 nm in the presence of INTs at $R_{P/INTs}$ =18 and 4, respectively. The stretching of the polymer chain is an indication of a relatively compact organization at the solid/liquid interface. This is confirmed by the grafting density of ca. 1.6 chains nm^{-2}, estimated from ITC results. It should be noted that the fits of the scattering curves for PEG2k provided a radius of gyration of 1.5 nm with and without Ge-DWINTs in agreement with the thermodynamic prediction of negligible interactions in this case.

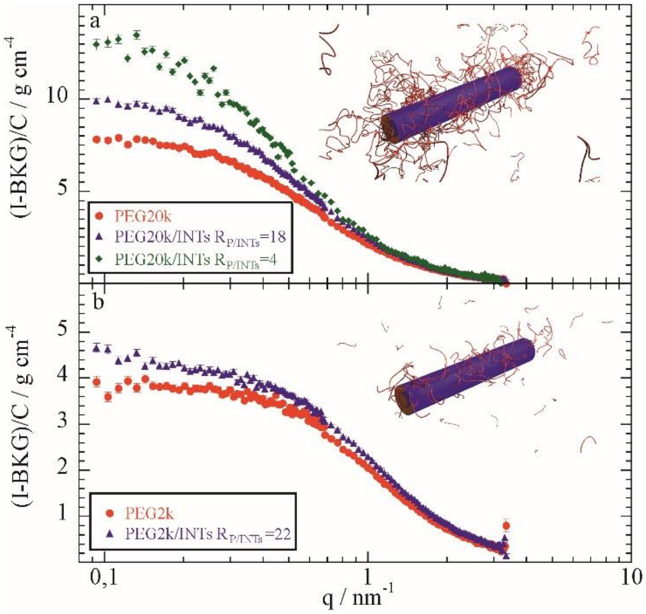

Figure 4. Neutron Scattering Intensity function after background (BKG) subtraction and polymer concentration normalization (C_P) of PEGs in the presence and absence of Ge-DWINTs (1 g.L^{-1}) at 25 °C. Solvent was H_2O/D_2O with a mass ratio of 1/10.

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