Experiment title:
USAXS/SAXS investigations on the preparation of porous silicas mediated by PEO-based polymers
SC 790

ID02A

Date of experiment:
from: 15-06-2001 to: 18-06-2001
06-07-2001

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Report:

In previous USAXS/SAXS studies we have shown that the biogenic silica of living diatoms[1] matches in many aspects man-made mesoporous silica with amorphous structure. In nature silica polymerization in diatoms involves biopolymers e.g. proteins and proceeds under ambient conditions. It will be of great economic interest to be able to mimick the natural processes of biomineralization and to create new silica structures based on the way nature proceeds.
Polymers as polyethylene glycol (PEG) and polyethylene oxide (PEO), with their remarkable ability to produce different supramolecular structures[3], have been selected as a simple model template instead of the complicated and very expensive diatomic proteins. During the reaction in the dedicated rotating and thermostrated cell, the polymer-silica interaction was studied continously with SAXS/USAXS. To investigate typical templating properties of proteins, also selected polyamino acids were applied. Both previous USAXS and SAXS experiments[2,4] and the physical adsorption data of gases (BET) indicate that the sizes of the pores in both diatoms and as-prepared silicas are in a wide range of 10 micron to a few nanometers, and therefore the combination of USAXS and SAXS is necessary to investigate the growth of precursors and the pore formation in the reaction mixture.

Results:

a. PolyEthylene Glycol (PEG).

According to recent reports[3], the hydrophobicity-hydrophilicity ratio of templates is very important (PEG = HO-(CH_2-CH_2-O)$_n$-H). Therefore PEG600, PEG2000 and PEG20000 were chosen as templates. Moreover, the [C-C-O]/[SiO_2] ratio was set at both 0.5 and 2. Although in all log(I)-log(q) plots linear parts are present, these curves show big differences. Applying the small and hydrophilic PEG600 as template, these linear parts represent fractals with fractal dimensions between 1.9 and 2.6 and depending on both the temperature (25 ¡ª C and 90 ¡ ªC) and the PEG600/silica ratio. Because also "bumps" are present representing silica/PEG600 particles (with sizes dependent on the PEG600/silica ratio), probably these particles are the building blocks of the large fractal aggregates. With the more hydrophobic PEG2000 (although still easy soluble in water) the slope of the linear part of the scattering curve decreases to -4.0, an indication that the fractal aggregates are now replaced by homogeneous systems. The "elementary" silica-PEG2000 particles building these systems are much smaller compared to the PEG600 system, and again vary with the silica/PEG ratio. Finally, PEG20,000 shows both a fractal range, build from relatively small particles (5.2 nm), but these 65 nm aggregates combine into very big non-fractal systems. Again the silica/PEG ratio shows that more PEG results in bigger primary particles.
Because in all PEG-systems the silica-PEG particles are too big to be formed by encapsulation of one polymer strand by silica, vesicles of PEG have to be formed, and probably these vesicles are the structure-directing species during the polymerization of silica, resulting in encapsulation of the vesicles by silica. In accordance with literature[3] these vesicles are due to phase separation in the PEG/water system, and are strongly influenced by the presence of silica, especially the silica/PEG ratio.
After drying and removal of the PEG the SAXS/USAXS spectra of the obtained porous silicas show the presence of both small and very big pores, a similar (bot not the same!) pattern compared to diatoms[4]. However, the drying and removal processes also changed the silica structures, so the porous structures of the wet and dried silicas were very different.

b. PEO-based (PolyEthylene Oxide) Block Copolymer

In diatoms multi-component systems made of species-specific proteins and other organics e.g. polysaccharides may be used as templates. As model systems we therefore applied as template a complex block copolymer interacting with PEG. PEG-PPG-PEG8400 is a non-ionic block copolymer whose self-assembly characteristics lead to kinetically quenched structures.
When the PEG-PPG-PEG8400 polymer is added to silica system, a bump at 4 nm can be observed in the beginning of the reaction. After the temperature is increased to 90dC, at small length scales (< 40 nm) a fractal structure is present (D = 2.56) whereas at larger length scales (40 - 1990 nm) the silica system appears to be more dense. Addition of PEG2000 results in bigger primary particles (8.6nm). When now the temperature is increased, a few peaks appear and show no shift till the reaction finishes. According to

the slope of the (very long) linear part (-3.88), fractal systems have disappeared and only homogeneous systems are present. This phenomena indicates a strong interaction between block copolymer and PEG2000, triggered by heating.

c. PolyAmino acids.

Experiments with tri-L-serine, polyglutamate (10, 70 and 100 kDalton), polyaspartate (10 and 30 kDalton) and polyglycine (30 and 60 kDalton) were performed. It is tentatively concluded that every polyamino acid used as template will produce a different species of porous silica, both concerning the primary particles and the fractality of the aggregates or composed systems. As expected from the experiments with polymers, the size of the polyamino acid is probably more important than the size. With polyglutamate we observed that, with the same quantity of template, the 10 and 70 kDalton polyglutame formed precipates, and only the 100 kDalton species gelled with the silica solution. This is a strong indication that small polyamino acids are only encapsuled by the silica, but that, similar to the polymers, only the large polyamino acids form silica-surrounded vesicles and are able to form microsize pores in (diatomic-like) silica. Details concerning primary particles, (fractal) aggregates and pore formation will be reported as soon possible.

d. Diatoms.

At Groningen University several new species of diatoms were cultivated and processed to isolate the porous silica skeleton (frustules). In accordance with earlier experiments[4] we could confirm that every diatom has its own characteristic USAXS/SAXS pattern of slopes and peaks, with the structure factors of related pores as a significant "signature". To interpretate these data, BET-measurements of the frustules are in progress.

References:

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