

## ATOM TRANSFER RADICAL POLYMERIZATION FROM SILICA NANOPARTICLES : FOLLOWING CHEMICAL SYNTHESIS USING S.A.N.S.

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At LLB, we develop a chemistry group to synthesize new materials for which neutron techniques are particularly useful (this includes labeling using deuteration). The present work is an intricate combination of chemistry synthesis and neutron scattering. The aim is to produce grafted nanoparticles, and consecutive nanomaterials, which are studied by SANS at the different steps of the procedure. We wish to keep the nanoparticles in a state of individual dispersion. Connection is systematically done between the information provided by SANS and our effort in improvement of the synthetic process.

The effort in synthesis was to use and develop the rather new “grafting from” method, combined with controlled polymerizations -in our case atom transfer radical polymerization (ATRP)- It consists in grafting first an initiator molecule, making polymerization start from the particle surface, under controlled conditions (“living polymerisation”) [1]. Moreover, grafting the initiator is done in two steps to avoid steric hinderances encountered for large molecules, These three key features yield a high degree of grafting and good control in the chain growth. Another new feature of the work is avoiding aggregation for each reaction step: we kept the nanoparticles in the same solvent to avoid drying of the particles or changes in the solvent quality. For each step, aggregation has been followed using SANS. First, SANS showed that the silica particles staid well-dispersed after the two grafting steps (functionalization and over-grafting). The polymerization (here we take the example of styrene) was done after adding so-called “sacrificial initiator”, free in solution, because of the small concentration of grafted initiator The backdraw is that we generate free chains in the solution but they can be separated by centrifugation or filtration.

During and at the end of polymerisation, the chemical tests were carefully performed, most of them at the lab. The fact that the semi logarithmic plot of monomer conversion with time

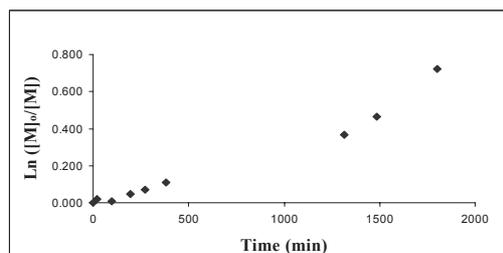


Figure. 1. Logarithm of monomer conversion versus time.

is linear (see Fig. 1) attest a good control of the polymerisation rate. Size Exclusion Chromatography (SEC) was performed on the free chains which showed masses (100 000) of the same order as the grafted chains (130000): the latter were separated from the silica surface by etching with Fluorhydric acid. The slight difference suggests steric congestion of initiators at the surface of the particles, which remains a point to improve. But the rather narrow chain mass distribution ( $M_w/M_n \sim 1.3$ ) confirms the control and leads to well characterized particles.

We also used off-lab techniques: e.g. thermogravimetry (burning the polymer at high T) to check the amount of grafted polystyrene (after removing the “free chains”) The grafted / free chains ratio is of the order of grafted/free initiator ratio, but lower.

Now that advanced chemical characterisation is satisfactory, we can use SANS to follow the polymerization. A first new information is the level of aggregation of silica beads(Fig.2). To measure it, we matched the scattering length density of the solvent to the one of the polymer, using a mixture of hydrogenated /deuterated solvent.

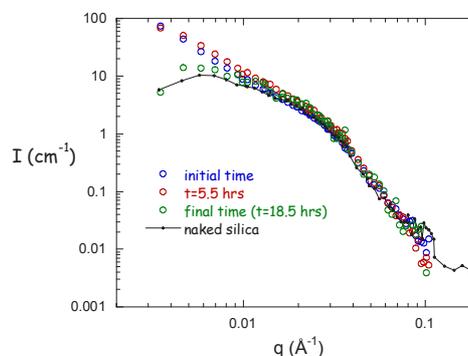


Figure 2: Scattered signal from silica only (polymer matching) at 3 times of polymerisation.

The full line is the scattering curve for silica before the reaction. At the initial step, when no polymer has yet been formed, the low- $q$  scattering, indicates the presence of large aggregates, probably because the presence of styrene has reduced the polarity of the solvent (at this stage particles are stabilised by electrostatic repulsion). At the end of polymerization, the low- $q$  signal decreases (i.e. the aggregates size decreases) and becomes very close to the signal of the naked silica. In summary, grafting polymer on silica spheres has reduced aggregation and stabilized the colloidal dispersion. (probably because of repulsion between the polymer grafted brushes).

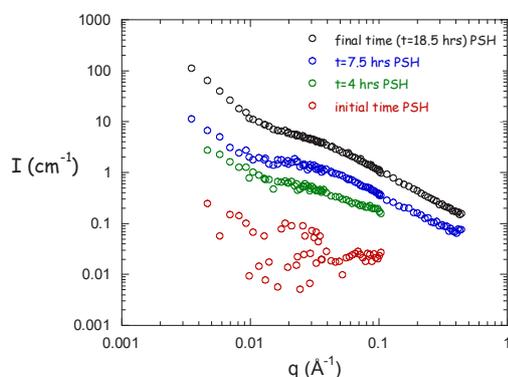


Figure 3. Scattered intensity by hydrogenated styrene grafted on nanoparticles in silica matching conditions at different stages of the polymerization.

We can also follow the structure and conformation of the grafted polymer layer. We used here the possibility of matching the solvent to silica beads. The figure 3 presents the scattering curves for grafted particles with hydrogenated polymer, from initial to final stage. The first curve (initial time) verifies the correct matching conditions (flat signal without polymer). When the polymerization process starts, the low- $q$  intensity increases. This is a qualitative indication of the presence of polymer. At large  $q$ , the signal slowly decreases, with a slope (around 1.65) characteristic of polymer scattering in this  $q$ -range. We also observe a shoulder at lower  $q \sim 0.02 \text{ \AA}^{-1}$ . If the grafted particles scatter like hollow spheres, this shoulder could be the signature of the grafted polymer. A shift of the shoulder position towards the low- $q$  values should then indicate the growth of the polymer layer

## References

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around the particle. And this shift is actually observed in experimental data. Nevertheless, this shoulder could also be due to the scattering of the free polymer chains present in the sample. Simple subtraction of the signal of a solution of such free chains is unaccurate for sure, because it ignores all kind of interactions between free and grafted chains. Therefore, to progress in this way, we used centrifugation to remove free chains (for the same sample presented, before centrifugation, in Fig. 3). The shoulder is still present (lower curve of Fig.4), and even more clear cut, a proof that it was not due to free chains. Fig.4 also shows a sample synthesized with deuterated monomer, for which contrast with solvent is larger. The shoulder is still observed in that case, at the same  $q$  value. Such joint information for two contrasts yields an unambiguous SANS signature of hollow spheres of polymer-grafted-silica particles. However, refined analysis using fitting models requires to account for aggregation which occurs during reaction. The corresponding calculation are on the way. The next important step is to define new physical and chemical routes to maintain colloidal stability through the different steps of the grafting procedure, a task which will combine both types of knowledge in our team.

Another extension of this work is to produce, and characterize films of polymer where those nanoparticles are embedded in the same polymer than the grafted one.

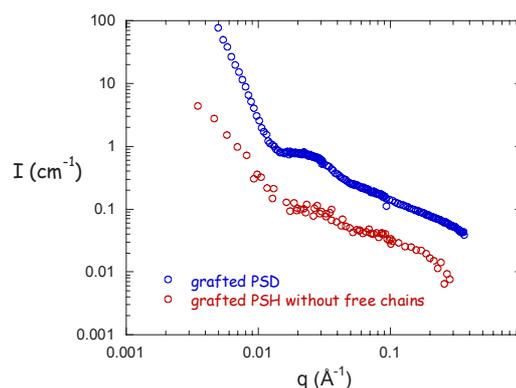


Figure 4.  $I(q)$  in silica matching conditions at final polymerisation stage, for normal polystyrene after removing free chains (PSH, red) and deuterated polystyrene (PSD, blue).