Supplementary Information

Controlled Grafted Brushes of Polystyrene on Magnetic γ-Fe₂0₃ Nanoparticles via Nitroxide-Mediated Polymerization

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1 Optimization of the physico-chemical conditions for solvent transfer and silanization step

An efficient way to achieve the solvent exchange and the ions removal at the same time is the use of the dialysis technique which is a procedure that enables a control of the colloidal stability of the suspension. It was indeed demonstrated in[1] that electrostatic interactions enable the γ-Fe₂0₃ nanoparticles to stay stable during the progressive exchange of solvent molecules from acidic solution to DMAc by dialysis, thanks to the high polarity of both solvents (ε_r = 37.8 in DMAc and ε_r = 78.5 in water). Nevertheless, a single dialysis of the TBA basic solution in DMAc is not possible, as performed in[1], because of the two following reasons. First, the dialysis bag does not resist when the dialysis is performed in a solution containing a huge quantity of TBA against a bath of DMAc. We believe that this comes from the highly hygroscopic TBA ions that pump all the remaining traces of water located in the cellulose membrane of the dialysis bag, which induce some cracks within the bag. A test has shown that some leaking appear during the experiment, easily detectable from the red color of the nanoparticles. The amount of TBA in solution must thus be noticeably decreased prior to the dialysis with DMAc. Second, a minimal concentration of TBA ions in solution is required to preserve the colloidal stability of the suspension during the silanization procedure. The addition of the APTES solution will indeed induce a decrease of the pH of the solution by dilution. If the pH of the solution is lowered down to the pH range where destabilization occurs (typically below pH=12), the bounding of larger clusters by APTES molecules may induce irreversible aggregation. We checked that we obtained negatively charged γ-Fe203 nanoparticles in DMAc with such a protocol by a simple but robust test described in part 3.

2 Decrease of the quantity of free PS chains in solution as a function of the centrifugation step

The free PS chains were progressively removed from the solution of grafted PS-grafted γ-Fe₂0₃ nanoparticles by successive centifugations/redispersions (see materials and methods of main text). The free PS chains remained in the supernatant in the upper part of the centrifugation tube.

Figure S.1 presents the mass fraction of free PS after each centrifugation step during the purification process, tested three times. The mass fraction is measured by gravimetry. The procedure is very reproducible, whether the chains are hydrogenated or deuterated. After 7 centrifugations, the process is over.
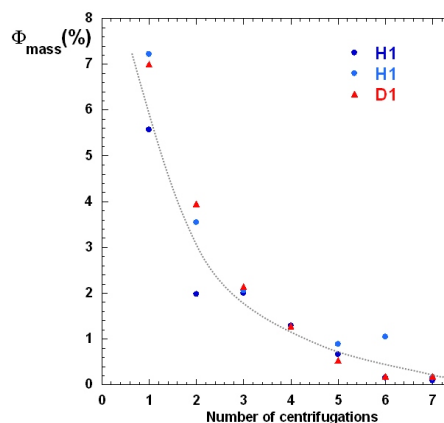

Fig SI.1 Mass fraction of free PS chains in solution in the upper part of the centrigugation tube as a funcction of the centrifugation step. Dark blue circles and light blue circles: hydrogenated chains, for two different centrifugation procedures; red triangles: deuterated chains. The dotted line is a guide for the eye.

3 Verification of the negative charge of -Fe₂0₃ nanoparticles in DMAc

In order to check that we obtained negatively charged γ-Fe₂0₃ nanoparticles in DMAc with the protocol described in main text, we performed the following simple but robust test. We added sodium polystyrenesulfonate (PSSNa), a negatively charged polyelectrolyte soluble in DMAc, into a part of the suspension at the end of the second step. No change of the macroscopic aspect of the sample occured. On the reverse, when PSSNa was added on a solution of positively charged γ-Fe203 nanoparticles in DMAc (prepared as in reference[1]) with the same [nanoparticles]/[PSSNa] ratio, an instantaneous macroscopic destabilization of the suspension occurred

driven by the electrostatic complexation between the two oppositely charged species.

4 Determination of the optimal $pH_{reservoir\_bath}$ of the first dialysis for the silanization process

The optimal $pH_{reservoir\_bath}$ has been determined as follows. We have performed the protocol described in the main text 6 times on the same alkaline aqueous solution of γ-Fe_2O_3 nanoparticles. The amount of TBA ions in the first aqueous reservoir was varied to change $pH_{reservoir\_bath}$ from 11.8 to 13 (below pH 11.8, suspensions were not stable macroscopically). The efficiency of the silanization process was valued by the effective surface density of the grafted silane molecules on the nanoparticles surface n_{graft_silane} (in mol/nm^2), measured by TGA. Figure SI.2 shows n_{graft_silane} as a function of $pH_{reservoir\_bath}$. Between pH=12 to pH=12.5, an optimum of $n_{graft\_silane} \sim 1$molecule/nm^2 was obtained. In this range of pH, the solutions appear macroscopically stable. At pH=11.8, n_{graft_silane} was decreased down to 0.6 molecules/nm^2. The decrease of the pH is too important to keep the colloidal stability of the nanoparticles. Some microscopic aggregates of nanoparticles were indeed formed and were observable by naked eye. This reduced the efficiency of the reaction. From pH=12.8 to pH=13, n_{graft_silane} was also reduced to 0.6 molecules/nm2. It is here likely that the TBA ions present in large quantity partially react here with the APTES which lower the efficiency of the silanization grafting.
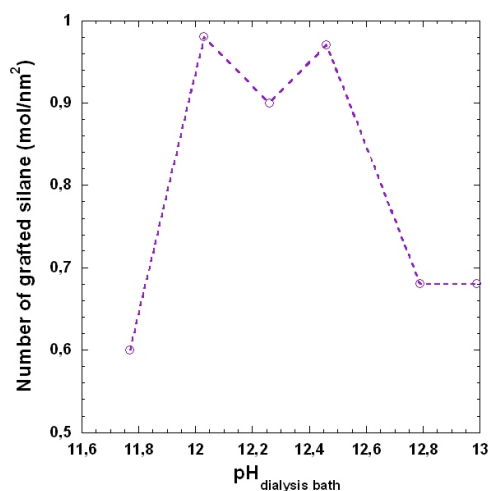

Figure SI.2 n_{graft_silane} *versus* $pH_{reservoir\_bath}$.

Reference

[1] A.-S. Robbes, J. Jestin, F. Meneau, F. Dalmas, O. Sandre, J. Perez, F. Boué, F. Cousin, *Macromolecules*, 2010, **43** (13), 5785-5796.