Supporting information

Homogeneous Dispersion of Magnetic Nanoparticles Aggregates in a PS Nanocomposite: Highly Reproducible Hierarchical Structure tuned by the Nanoparticles' Size.

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1 SAXS spectra of suspensions of γFe_2O_3 magnetic nanoparticles in H_2O and DMAc

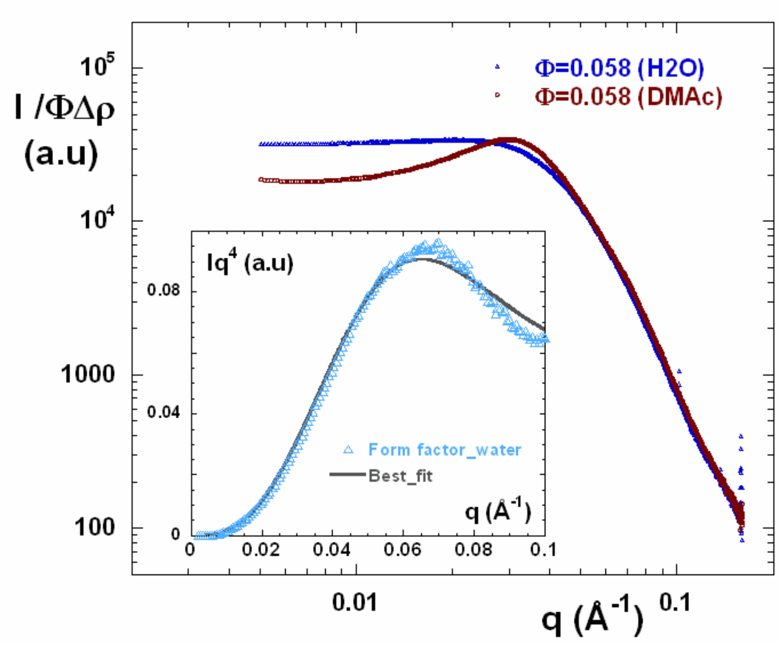

Figure SI 1.a: SAXS scattering curves for the suspensions of nanoparticles A either in water or in DMAc presented in a $I(q)/\Phi\Delta\rho = f(q)$ representation. $\Delta\rho$ stands either for $(\rho_{mag} - \rho_{DMAc})^2$ or $(\rho_{mag} - \rho_{water})^2$ depending on the solvent used. Inset: $q^4I(q)$ versus q for $\Phi_{mag} = 0.001$ in water. The full line corresponds to the best fit of the form factor.

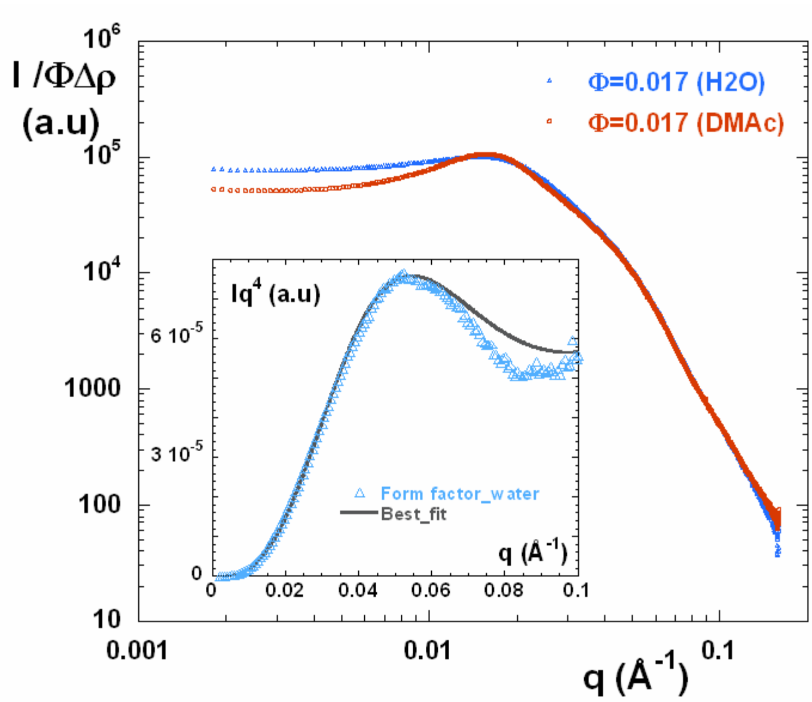

Figure SI 1.b: SAXS scattering curves for the suspensions of nanoparticles B either in water or in DMAc presented in a I(q)/ΦΔρ = f(q) representation. Δρ stands either for $(\rho_{mag} - \rho_{DMAc})^2$ or $(\rho_{mag} - \rho_{water})^2$ depending on the solvent used. Inset: $q^4I(q)$ versus q for $\Phi_{mag} = 0.001$ in water. The full line corresponds to the best fit of the form factor.

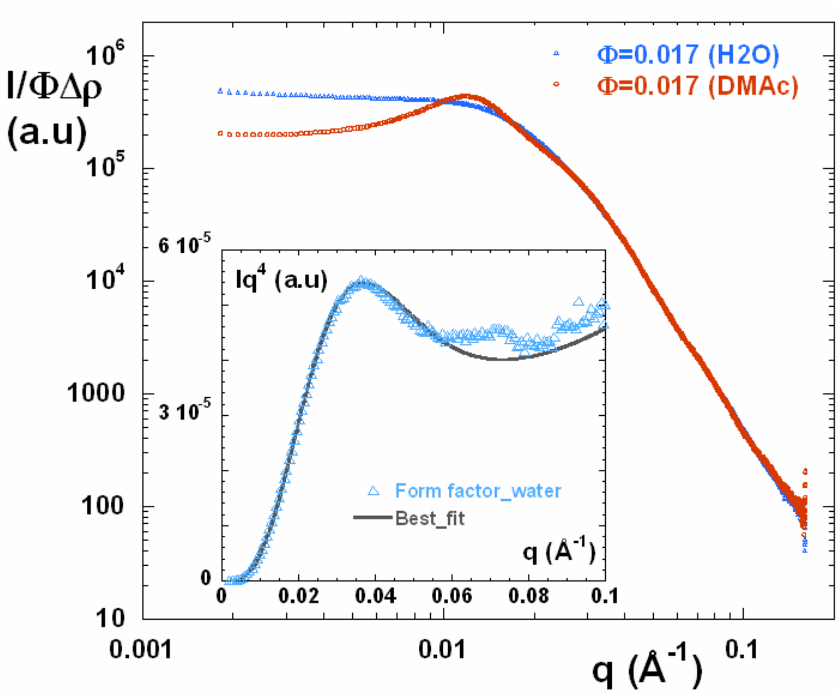

Figure SI 1.c: SAXS scattering curves for the suspensions of nanoparticles D either in water or in DMAc presented in a I(q)/ΦΔρ = f(q) representation. Δρ stands either for $(\rho_{mag} - \rho_{DMAc})^2$ or $(\rho_{mag} - \rho_{water})^2$ depending on the solvent used. Inset: $q^4I(q)$ versus q for $\Phi_{mag} = 0.001$ in water. The full line corresponds to the best fit of the form factor.

2 Magnetization curves of suspensions of γFe_2O_3 magnetic nanoparticles in H_2O

In order to determine the volume fraction of the different suspensions after synthesis and the size distribution of the nanoparticles, we have measured the magnetization curves of the suspensions in H_2O.

We briefly recall the principle here. Each nanoparticle bears a magnetic moment $\vec{\mu}$ which is of the order of 10^4 Bohr magnetons. Its modulus $|\vec{\mu}| = m_S V_{magn}$ is proportional to the magnetic volume V_{magn} of the nanoparticles and to m_S the magnetization of the maghemite. Under a large applied field $\vec{H}$, this magnetic moment $\vec{\mu}$ orientates along the field direction. In a liquid suspension of γ-Fe_2O_3 nanoparticles of radius ~ 4 nm, it also rotates mechanically the core of the nanoparticle. The alignment of $\vec{\mu}$ along $\vec{H}$ provides to the suspension a macroscopic magnetization M. At saturation, all the magnetic moments align along $\vec{H}$, then M = M_S= $m_S\Phi$. For intermediate fields, the behavior of the suspension is superparamagnetic. For a suspension of monodisperse nanoparticles of radius R, M is well described by the first Langevin law L(R) at low Φ (when dipole-dipole correlations are neglected) :

$$M(H) = M_S(\coth\frac{\mu_0\mu H}{kT} - \frac{kT}{\mu_0\mu H}) \quad \text{with } M_S=m_s\Phi \qquad (1)$$

For polydisperse suspensions, the shape of the curves M(H) is modified by the log-normal size distribution of the particles size P(R0, s) (see equation 2 of main text) :

$$\frac{M(H)}{M_S}(R_0,\sigma) = \frac{\int_0^\infty d^3P(R)L(R,H)dR}{\int_0^\infty d^3P(R)dR} \qquad (2)$$

At low H, in the linear regime, the magnetization curve is proportional to the magnetic susceptibility of the nanoparticles. The magnetization curves are presented for the different batches of nanoparticles A, B, C and D in Figure SI.1.

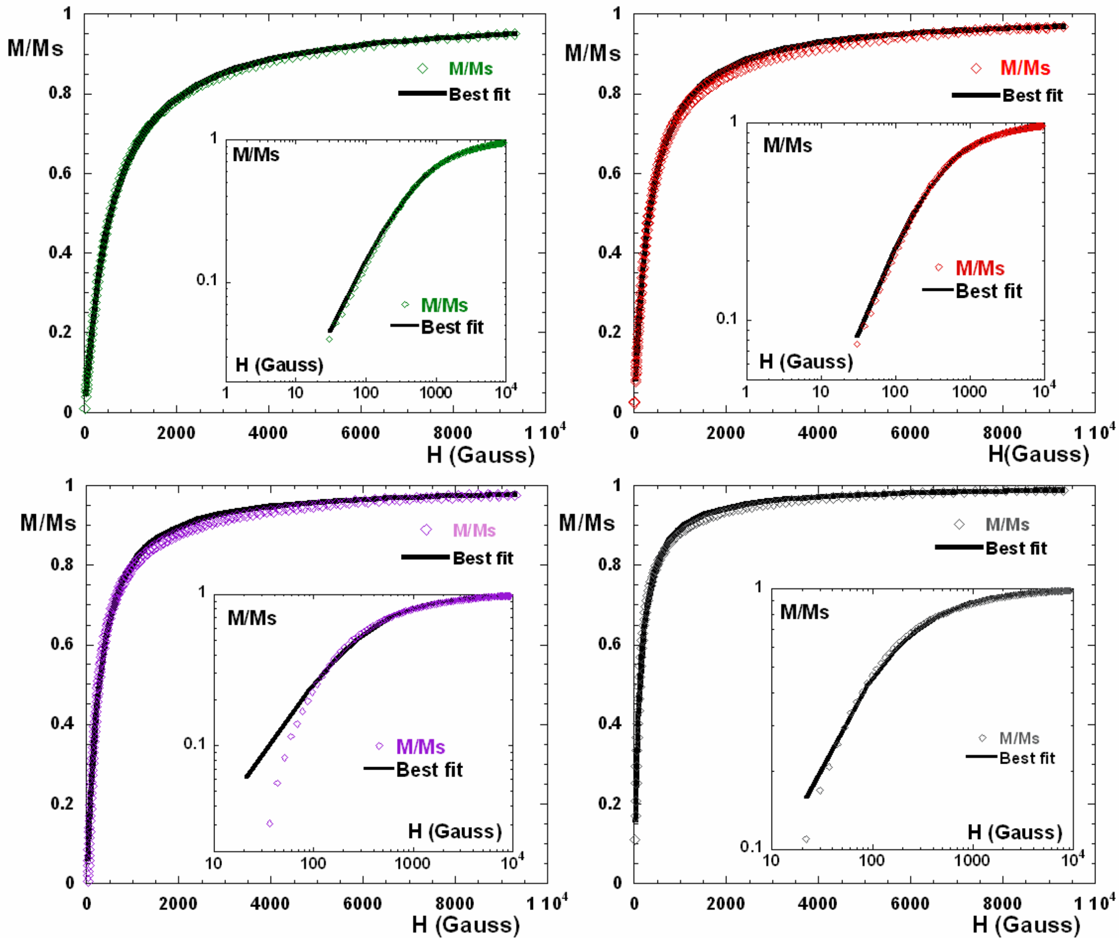

Figure SI.2: Magnetization curve of the suspensions of γFe_2O_3 nanoparticles in H_2O. The magnetization curves are modelled by the first Langevin law and take into account the polydispersity of the nanoparticles. Inset: same curves in log-log scale. (a) batch A; (b) batch B; (c) batch C; (d) batch D.

3 SAXS spectra of γFe_2O_3 nanoparticles in the nanocomposite polymeric films

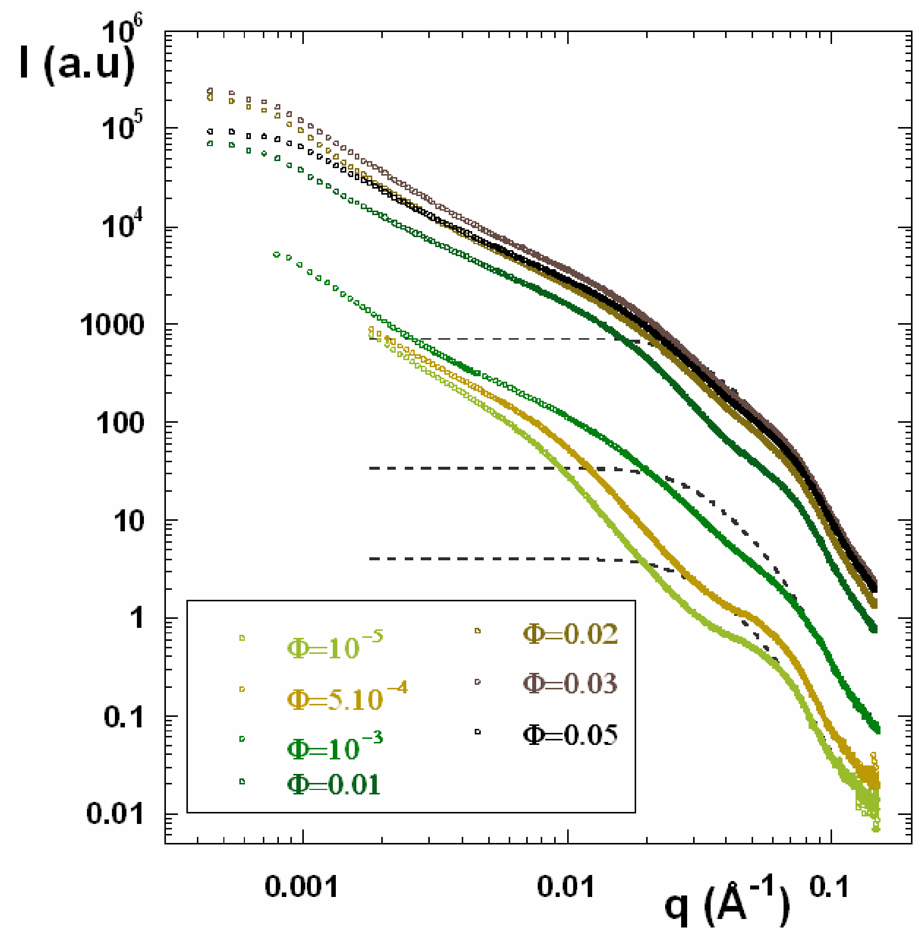

Figure SI.3.a: SAXS scattering curves of the γFe_2O_3 nanoparticles in the PS polymeric matrix obtained by SAXS for nanoparticles A. The dashed lines correspond to the form factor of the nanoparticles.

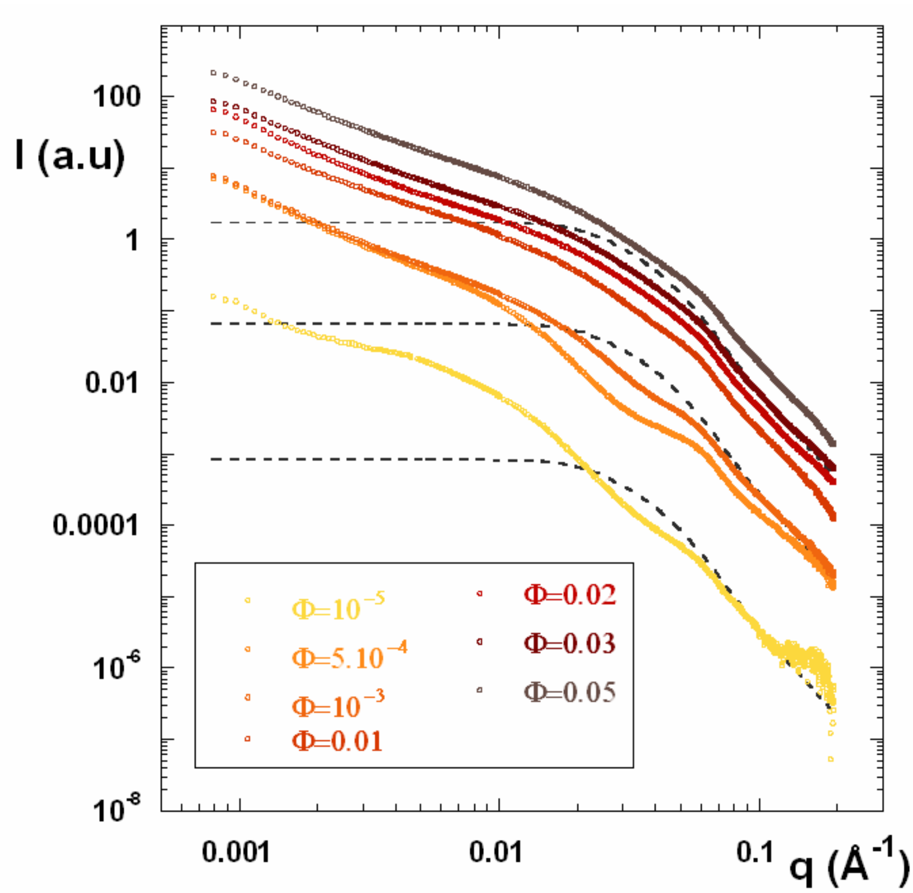

Figure SI.3.b: SAXS scattering curves of the γFe_2O_3 nanoparticles in the PS polymeric matrix obtained by SAXS for nanoparticles B. The dashed lines correspond to the form factor of the nanoparticles.

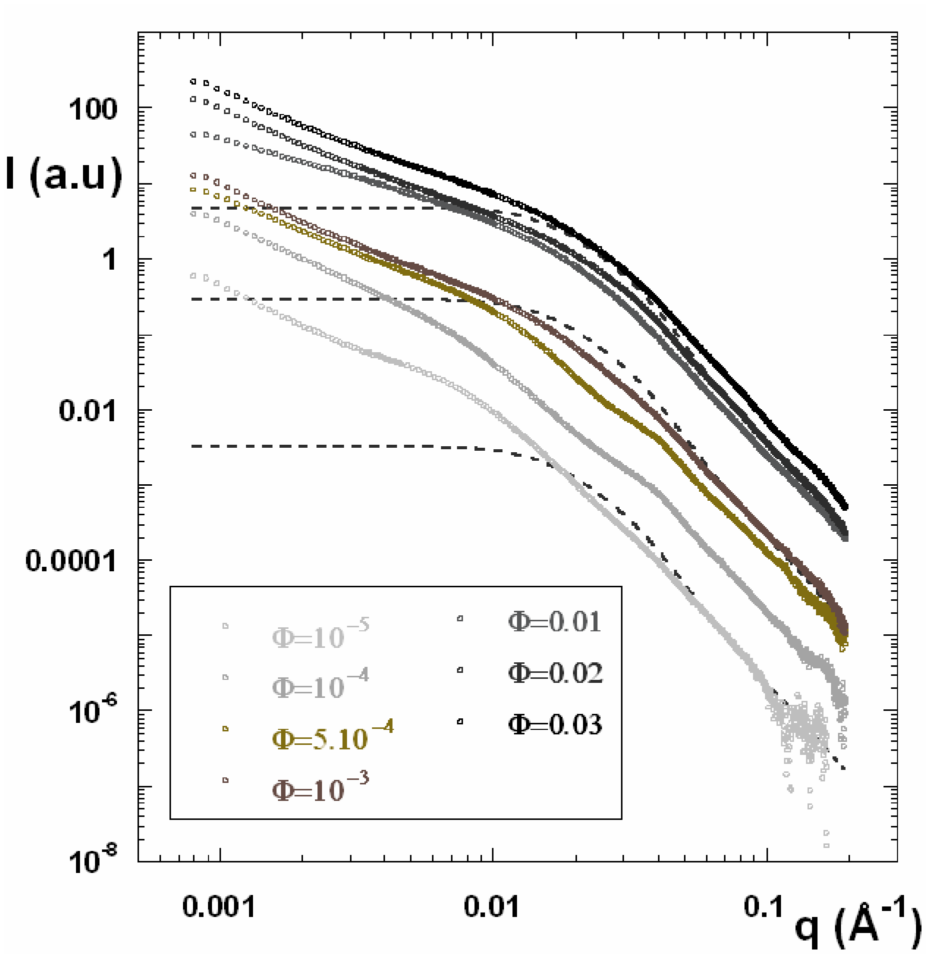

Figure SI.3.c: SAXS scattering curves of the γFe_2O_3 nanoparticles in the PS polymeric matrix obtained by SAXS for nanoparticles D. The dashed lines correspond to the form factor of the nanoparticles.