Thermal Decomposition in Polyol: an Efficient Process for the Synthesis of Magnetic Nanoparticles

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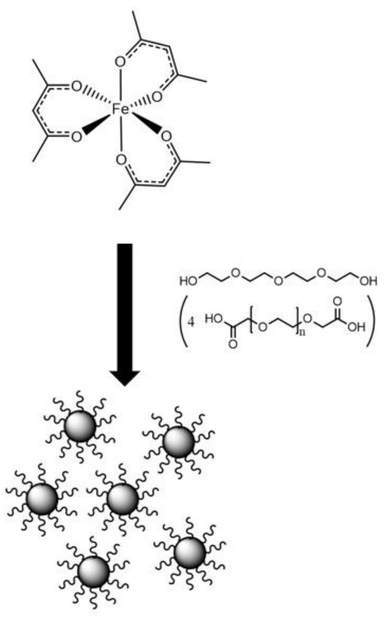


Introduction

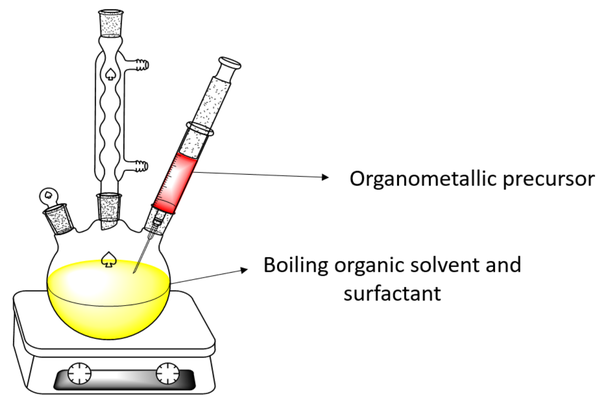
Iron oxide nanoparticles (IONP) are widely studied for their superparamagnetic properties making them suitable as MRI contrast agents. If many synthesis pathways have been described, one of the most popular is the thermal decomposition of organometallic compounds; the success of this process lying on its ability to produce IONPs with a good control over their size, shape, and crystallinity. Typically, the process takes place in high boiling solvent in the presence of hydrophobic surfactants (i.e. oleic acid and/or oleylamine). As a consequence, the resulting nano-objects need further surface modifications to allow water transfer.[a]

To avoid this pitfall, we propose to modify the original process by changing the hydrophobic materials by hydrophilic ones. Owing to its interesting properties (viscosity and high boiling point), tetraethylene glycol appears as a suitable solvent for IONP synthesis. Here we investigate two parameters: the influence of PEG-diCOOH as stabiliser and the heating duration.

Method

PEG-diCOOH influence

$Fe(acac)_3$ in tetraethylene glycol (50mM) was injected in a pre-heated solution of TEG. Reaction time and temperature were fixed at 5 minutes and 250°C respectively. Different precursor/PEG-diCOOH ratios were tested to evaluate their influence on the properties (size, magnetic properties and colloidal stability) of the resulting objects.

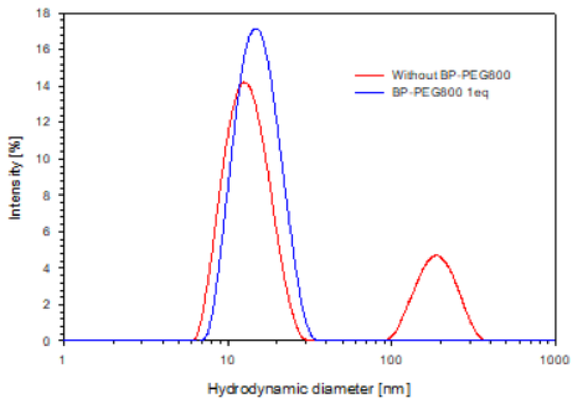


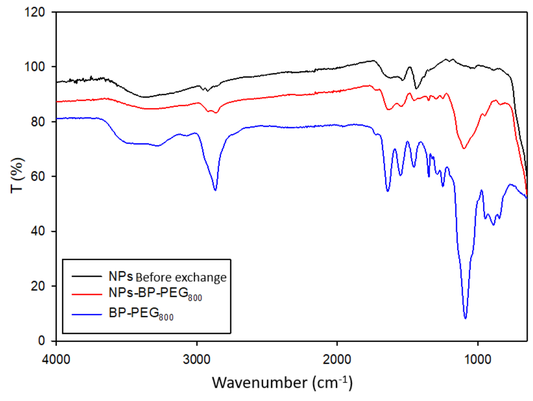
Heating duration

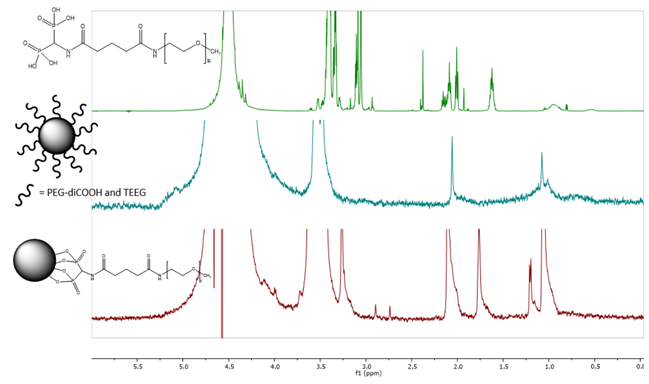
The particles were synthesised by the same method but the precursor/PEG-diCOOH ratio was set at [1:3] and different reaction times were tested, i.e. 30s, 1min, 2min, 5min, 10min. However, before two minutes, the collected solutions were too diluted to be analyzed.

Particles stabilisation

After synthesis, the particles were easily isolated and transferred in water. The as-obtained particles were stabilised by mean of ligand addition process, using a "home-made" system (i.e. BP-PEG_{800}). The efficiency of the process was assessed by FT-IR and NMR (HR-MAS) spectroscopy. By proceeding this way, stable suspensions were obtained.



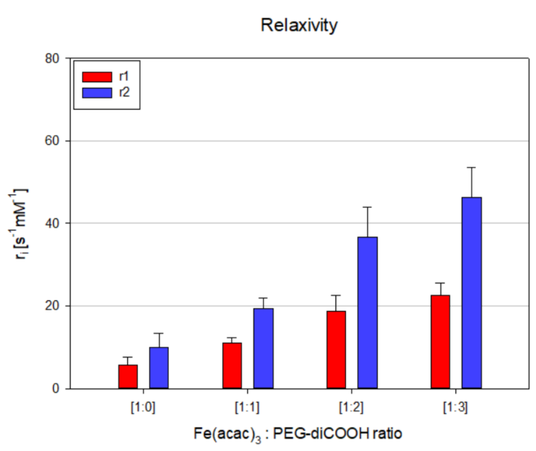


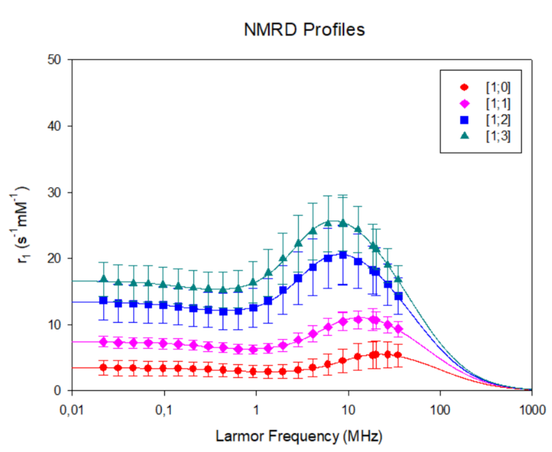


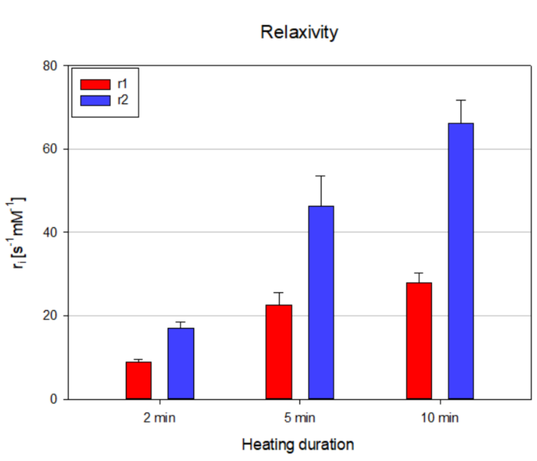
Results

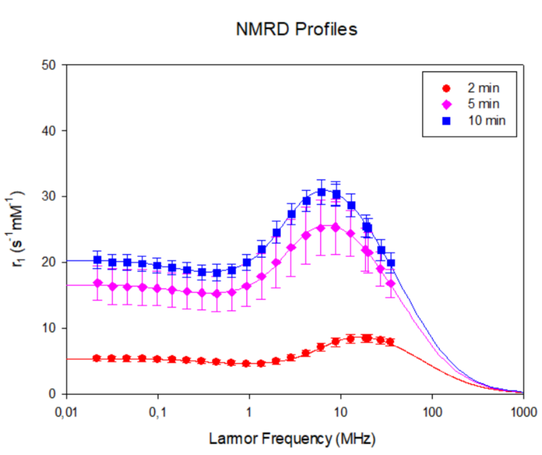
Interestingly, we observed that the presence of PEG-diCOOH in the solution has an influence on the physico-chemical properties of the resulting IONPs. This observation could be correlated to the ability of such structure to modify the decomposition kinetics, impacting thus the germination and particle's growth steps.

The results compared to those obtained with hydrophobic surfactants show an increase of the magnetic properties with similar particle sizes. This leads us to hypothesize an increase of the magnetic core growth but not of the particle global size.[b]









Samples	Precursor/PEG-diCOOH	M_{sat} ($A.m^2.k^{-1}$)	Radius (nm)
1	[1:0]	30,9	4,01
2	[1:1]	36,8	4,53
3	[1:2]	41,8	5,24
4	[1:3]	44,5	5,42

Samples	Reaction time (min)	M_{sat} ($A.m^2.k^{-1}$)	Radius (nm)
1	2	34,5	4,36
2	5	44,5	5,42
3	10	48,0	5,47

Conclusions

In conclusion, the described protocol enables to synthesize hydrophilic IONP with interesting magnetic properties. The use of PEG-diCOOH stabiliser during the process clearly impact these properties. For further studies we would like to adapt this synthesis pathway to flow chemistry to gain more control over synthesis parameters such as heating time and pressure. Furthermore, flow synthesis should allow better reproducibility and scaling-up.

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References: [a] Stanicki et al., « An update on the applications and characteristics of magnetic iron oxide nanoparticles for drug delivery ».
[b] Vangijzegem et al., « Influence of Experimental Parameters of a Continuous Flow Process on the Properties of Very Small Iron Oxide Nanoparticles (VSION) Designed for T1-Weighted Magnetic Resonance Imaging (MRI) ».

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