Molecular Dynamics and Macroscopic Properties of Magnetic Microgels

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Abstract. Thermo-sensitive microgels based on poly(N-isopropyl acrylamide) (PNIPAM) were covered with nanoparticles of $\gamma$-Fe$_2$O$_3$ with size around 6 nm. When the inorganic cover was 18\% (w/w) respect the polymer part, the microgels presented magnetic properties in addition to their inherent thermo-sensitivity. The interactions existing between the magnetic nanoparticles and the polymer matrix provoke the shifting of the microgel volume transition to higher temperatures when the amount of $\gamma$ -Fe$_2$O$_3$ increases. The study performed using incoherent quasielastic neutron scattering (IQNS) confirms that the presence of inorganic nanoparticles affects the PNIPAM chain motions. Thus, in the swollen state both, the mean square displacement of the polymer segments and the diffusive motion of the polymer chains, decrease as the iron oxide content increases. The reduction of vibrational and diffusional motions of the polymer chains is attributed to the formation of hydrogen bonds between the amide groups of the polymer matrix and the OH groups of the magnetic nanoparticles that explains the reduction of the swelling capacity of the microgels and the shift of the polymer volume transition to higher temperatures with increasing the iron content.

1. Introduction
Materials in nature are often assembled from nanoscale building blocks and a lot of them belong to the group of organic/inorganic hybrid materials (e.g. bone, teeth, shells, proteins, etc.). The recent advances in the synthesis of nano-materials permit to prepare new smart organic/inorganic hybrid materials using nanoparticles and mesoscale structures. Furthermore, hybrid nanoparticles have attracted a huge scientific interest due to the possibility of combining different properties in individual particles, based on different compositions. These particles are commonly defined by a core-shell structure; the core often responds to an external field whereas the shell stabilizes, provides additional responsive properties, and makes compatible core and environment. Many technological applications can be foreseen for this kind of materials, including analytical chemistry (surface enhancements raman spectroscopy), separation technology (ion exchange), catalysis (nanoreactors), biochemistry (conjugates of quantum dots and antibody), and medicine (drug targeted delivery).

Materials based on PNIPAM have been extensively studied due to their special ability to respond to external stimuli. They swell at low temperature and keep collapsed for higher temperatures. We have developed an intense research activity investigating microscopic and macroscopic features along this volume transition [1-5]. On the other hand, the fabrication of magnetic micro and nanoparticles is of interest because they are good candidates for drug targeting, or contrast agents for NMR [6]. Particle size is a very important parameter since it determines if the magnetic behavior will be superparamagnetic or ferromagnetic. The fabrication of monodisperse superparamagnetic particles of $\gamma$-Fe$_2$O$_3$ is performed by chemical coprecipitation of ferric and ferrous ions in alkali solution [7]. The combination of the thermal response of the microgels with the magnetic response of the $\gamma$-Fe$_2$O$_3$ nanoparticles in a new hybrid material could be of technological interest for separation of pollutants or magnetic guiding of drugs.
2. Experimental

2.1. Materials and methods

The synthesis of the PNIPAM microgels, and of PNIPAM microgels covered with an outer shell of acrylic acid (P(NIPAM-AAS)) is described elsewhere [8-9]. In order to cover microgels with a shell of iron oxide nanoparticles, 0.1 g of P(NIPAM–AAS) microgels were dispersed in 50 mL of NaOH (0.1 M) aqueous solution. Subsequently, 50 mL of a HCl solution (0.1 M) in which we had previously dissolved 32.5 mg (0.18 mmol) of FeCl$_3$·6H$_2$O and 12 mg (0.09 mmol) of FeCl$_2$·4H$_2$O (Fe$^{II}$/Fe$^{III}$ molar ratio = 0.5) was slowly added drop wise to the microgel dispersion under continuous stirring at 25 °C. At the end of this process the milky microgel dispersion turned to red-orange, indicating iron oxide formation. Changing the ratio microgels/iron is possible to modify the inorganic content of the hybrid material. Table 1 shows the concentration of each component used in the production of microgels with different concentration of iron oxide.

The microgel particles were studied using transmission electron microscopy (TEM) in a JEOL-2000FX microscope operating at 200 kV. Dynamic light scattering experiments (DLS) were carried out on dilute microgel dispersions (0.02% w/w) to examine the particle size at the volume phase transition using a Malvern Nano-ZS system with a He–Ne laser working at 632.8 nm. TGA measurements were performed on a TGA/Start System (Mettler Toledo) to determine the iron content of the hybrid microparticles. The charge of the microgels was determined using a Particle Charge Detector model PCD 03 μMütek. The molecular dynamics of the polymer network was studied using incoherent elastic (IES) and quasi-elastic (IQNS) neutron scattering at the Institut Laue Langevin in Grenoble. The IES and IQNS measurements were performed using the high energy resolution (1 μeV) neutron backscattering spectrometer IN10. The IQNS spectra were recorded at 290 and 330 K.

| Sample name          | P(NIPA-AAS) microgels (mg) | FeCl$_2$·4H$_2$O (mmol) | FeCl$_3$·6H$_2$O (mmol) | γ-Fe$_2$O$_3$ (%) obtained from TGA |
|----------------------|---------------------------|--------------------------|--------------------------|------------------------------------|
| Fe10-P(NIPAM-AAS)    | 100                       | 0.09                     | 0.18                     | 10                                 |
| Fe18-P(NIPAM-AAS)    | 100                       | 0.18                     | 0.36                     | 18                                 |
| Fe28-P(NIPAM-AAS)    | 100                       | 0.24                     | 0.54                     | 28                                 |
| Fe38-P(NIPAM-AAS)    | 100                       | 0.36                     | 0.72                     | 38                                 |

2.2. The incoherent scattering function

The analysis of the IQNS data was carried out considering the molecular motion formed by the combination of a faster vibrational component with a mean square displacement $<u^2>^{1/2}$ and a translational diffusion motion with diffusion constant $D$ [10-11]. For Fickian diffusion the dynamic structure factor is a Lorentzian function, with a half-width at half-maximum $DQ^2$. Thus, the scattering function can be written as,

$$S(Q,\omega) = \exp(-\frac{1}{3}<u^2>Q^2)\delta(\omega) \otimes \frac{1}{\pi} \frac{DQ^2}{(DQ^2)^2 + \omega^2}$$

where $\delta(\omega)$ is a delta function, and $\otimes$ is the convolution product in $\omega$. The mean square displacement $<u^2>^{1/2}$ can be derived from the $Q^2$ dependence of $S(Q,0)$ at fixed temperature, and $D$ is obtained from the fitting of the quasielastic component with a Lorentzian function [12].
3. Results
The magnetic response of the Fe28-P(NIPAM-AAS) microgels is illustrated in Fig. 1. The hybrid microgels are dispersed in water (Fig. 1) but form a film on the flash wall following the magnetic field lines when a magnet of 0.24 T is approached (Fig. 2).

Fig. 2 shows a TEM image of the Fe28-P(NIPAM-AAc) microgels. The particles are spherical and nearly monodisperse. Fig. 3 shows the weight loss of the different PNIPAM microgels as a function of temperature. The temperature for the maximum weight-loss rate, Tp, is 294 °C for P(NIPAM-AAS) microgels. As can be seen in Fig. 3, Tp increases with the content of γ-Fe2O3 nanoparticles in the microgel. A small amount of nanoparticles is effective to shift the Tp towards higher values which means that they enhance the thermal stability of the microgels. The reduction of PNIPAM degradation temperature could be related with the reduction of molecular mobility induced by the presence of nanoparticles that could suppress chain transfer reactions.

The hydrodynamic diameter (obtained from DLS) of the microgels as a function of the temperature is presented in Fig. 4. In the swollen state, the hydrodynamic diameter decreases with increasing γ-Fe2O3 content, probably due to the interactions between the iron nanoparticles and the polymer matrix that reduces the swelling capacity of the microgels. On the other hand, in the collapsed state the size of the Fe28P(NIPAM-AAS) is larger than for the other microgels.

Diffusional motions of polymer chain segments can be investigated using inelastic neutron scattering since they are prominent in the quasielastic scattering region. Furthermore, by dispersing the microgels in D2O is possible to obtain enough contrast between the polymer network and the solvent.

The elastic neutron-scattering function \( S(Q, \omega=0) \) normalized to its value at 5 K, \( S(Q, 0)_{5K} \) was measured as a function of the temperature with IN10 using the so-called “fixed elastic window” method. The apparent mean square displacement \( <u^2>^{1/2} \) of the polymer chains can be obtained analyzing the \( Q \) dependence of \( S(Q,0) \) at fixed temperature

\[
\ln \frac{S(Q,0)}{S(Q,0)_{5K}} = -\frac{1}{3} \left( <u^2(T)> - <u^2(5K)> \right) \cdot Q^2
\]
Assuming that at 5 K there are no motions \(<u^2(5K)> = 0\) we can derive \(<u^2(T)\>\) from the dependence of the intensity with \(Q^2\) and the results are presented in Fig.5. In this figure, we can see that below 280, when D\(_2\)O is frozen, \(<u^2(T)\> = 0.7 \text{ A}^2\), independently of the microgel composition. However, when D\(_2\)O melts, \(<u^2(T)\>\) increases abruptly until reaching an approximately constant value that depends on the composition of the microgels. Thus the highest \(\gamma\)-Fe\(_2\)O\(_3\) content corresponds with the smallest \(<u^2(T)\>\) value. We attribute this effect to the iron nanoparticles that hinder the vibrational motions of the polymer chains in the swollen microgels.

Above the volume transition temperature the behavior is different. At 307 K begins the collapse of the microgels and the process involve the approaching of neighbor polymer chains and the release of the swollen water. The result of this process is a compact polymer structure whose vibrational motions are restricted and the value of \(<u^2(T)\>\) resembles that of the polymer matrix in the frozen state. However, the value of the mean square displacement varies depending on the composition of the polymer matrix. Thus, for the P(NIPAM-AAS) the steep decrease is not so remarkable as in the neat PNIPAM microgels, probably due to the presence of COO\(^-\) groups that hinder the collapse by electrostatic repulsions (the charge of these microgels is 23.6 C/g much higher than 4.7 C/g for pure PNIPAM ). In the case of the microgels with \(\gamma\)-Fe\(_2\)O\(_3\), the COO\(^-\) groups are partially neutralized (the charge...
is only 0.23 C/g) and the variation in the vibrational amplitude is not as large as for pure PNIPAM. It appears that the magnetic nanoparticles introduce a physical barrier that hinders the approximation of the polymer chains, impeding the complete collapse of the microgel.

The diffusive motions of the polymer network were investigated at 290 K and 330 K measuring the IQNS at IN10. In Fig.6 we show the quasielastic component, for Q=0.5 Å⁻¹, at the two selected temperatures for samples with different content of iron nanoparticles. Fig.6 shows that depending on the state of the microgels (swollen or collapsed) the polymer chains present different dynamics. In the swollen state (290 K) the S(Q,ω) function is wider than in the collapsed state, which indicates that at low temperatures the system behaves like soft matter becoming harder in the collapsed state (330 K). Additionally, we can observe that when the amount of iron increases the difference between S(Q,ω) in the swollen and collapsed states is reduced indicating a hardening of these microgels at low temperature. The fitting of the quasielastic data (points) was made using equation (1) and the result of the fitting is shown as a continuous line in Fig.6. From the fitting of S(Q,ω) we obtained the half-width at the half-maximum $\Gamma(Q) \approx DQ^2$, and from the slope we calculated the average diffusion coefficient $D$ (see Fig.7) of the polymer chain segments in the environment of $\gamma$-Fe₂O₃ nanoparticles.

![Figure 6. The $S(Q,\omega)$ function shows the different dynamics of P(NIPAM-AAS) networks in the swollen (290 K) and collapsed (330 K) state for microgels with different amount of iron nanoparticles.](image)

![Figure 7. Diffusion coefficient derived from IQNS measurements as a function of Fe content.](image)

The variation of $D$ follows an opposite tendency to most solids and liquids for which D increases when temperature is raised whereas in the hybrid microgels $D$ decreases with increasing temperature. The incorporation of $\gamma$-Fe₂O₃ nanoparticles considerably reduces the $D$ value at the swollen and slightly changes $D$ at the collapsed state. Furthermore, as the iron content increases the value of $D$ in the swollen and collapsed states approached.

### 4. Conclusions

The interaction that exists between $\gamma$-Fe₂O₃ nanoparticles and PNIPAM polymer chains, mainly hydrogen bonds, could reduce the mean square displacement of the polymer segments from an average value of 5.6 Å² in pure PNIPAM microgels down to a value of 3.6 Å² in the Fe₂O₃P(NIPAM-AAS) microgels. In addition, the apparent diffusion coefficient of the polymer segments became smaller
when the iron oxide content is increased and this result is associated with the increment of the volume transition temperature of the microgel and the polymer degradation temperature.

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