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José Alberto Galicia, Fabrice Cousin, Emmanuelle Dubois, Valérie Cabuil, Olivier Sandre, et al..
Local structure of polymeric ferrogels. *Journal of Magnetism and Magnetic Materials*, 2010, 323 (10),
pp.1211-1215. 10.1016/j.jmmm.2010.11.008 . hal-02169248

HAL Id: hal-02169248

<https://hal.science/hal-02169248>

Submitted on 31 May 2020

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Local structure of polymeric ferrogels

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Author manuscript version of article available in its final form on the publisher's website: DOI 10.1016/j.jmmm.2010.11.008

Abstract

We synthesize hybrid gels incorporating γ -Fe₂O₃ nanoparticles (NP's), citrate coated, in a polyacrylamide (PAM) network. The local organisation and the rotational degrees of magnetic nanoparticles are probed in the conditions of gel synthesis and also at swelling equilibrium, to correlate the homogeneous/ inhomogeneous structure of the ferrogels to the synthesis parameters and to their macroscopic elasticity. NP adsorption on the PAM network at low citrate concentration is responsible for the reinforcing of the polymer structure. At higher citrate concentration, due to a competition between citrate and NP's, the nanoparticles desorb from the polymer structure weakening the system.

PACS 82.35.NP; 61.05.fg; 78.20.Ls

Keywords: Nanoparticles in polymers; Neutron scattering; Magneto-optical effect

1. Introduction

Polymeric ferrogels are organic/inorganic composites prepared for ferroelastic applications. They are based on the intimate mixing of polymeric gels and magnetic particles [1, 2]. Frequently, in order to mechanically reinforce the polymeric structure, the particles are aggregated [3, 4, 5]. The swelling of the system is then seriously hindered. Our aim in this work is to understand how to reinforce homogeneously a polymeric gel with nanoparticles (NPs), keeping as far as possible the swelling properties of the gel. We choose to use here a versatile model-system combining - the well-known poly(acrylamide) (PAM) polymeric system and - magnetic NPs as fillers, in order to also use these NPs as local probes of the system. Our objective is to point out the problems and to determine the relevant parameters for a homogeneous/inhomogeneous NP incorporation reinforcing the polymer structure. We associate two

experimental techniques, a static probing of the NP distribution in the ferrogel by Small Angle Neutron Scattering (SANS) with a dynamic probing of the NP rotational degrees of freedom by relaxation of magneto-optical birefringence.

2. Experimental

PAM networks are well known for their swelling properties and worldly used as superabsorbing microbeads or as separation media in biochemistry for electrophoresis. The gels are here obtained by polymerizing acrylamide (AM) monomers either in aqueous medium (for hydrogels) or in a colloidal suspension of citrate-coated maghemite NPs (for ferrogels) in the presence of the cross-linking agent *N,N'*-methylenebis-acrylamide (BAM). Hydrogels and ferrogels are out-of-equilibrium systems in their synthesis conditions with a mesh size ξ_{synth} , which is strongly dependent on $CL = BAM/AM$ the cross-linking ratio of the system, here $0.5\% \leq CL \leq 2\%$ in order to have homogeneous hydrogels [6]. Put in a water bath (at the same

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ionic strength as the synthesis medium) they swell by absorbing water, reaching swelling equilibrium in typically three weeks. In the case of pure PAM hydrogel at

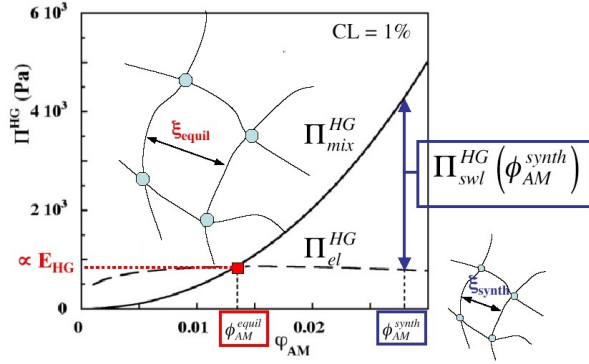


Figure 1: Mixing (full line) and elastic (dashed line) osmotic pressure of hydrogels at $CL = 1\%$ as a function of the volume fraction ϕ_{AM} of AM. The polymeric array is sketched in synthesis and swelling conditions

$CL = 1\%$, Figure 1 illustrates the behavior of its mixing Π_{mix}^{HG} and of its elastic Π_{el}^{HG} osmotic pressures as a function of the volume fraction ϕ_{AM} of AM. During the swelling process, the mesh of the polymeric array evolves from ξ_{synth} towards ξ_{equil} and at swelling equilibrium $\Pi_{mix}^{HG} = \Pi_{el}^{HG}$, their value being proportional to the Young modulus E_{HG} of the hydrogel. On the contrary in the synthesis conditions, Π_{mix}^{HG} and Π_{el}^{HG} differ by an osmotic pressure Π_{swl}^{HG} .

While synthesizing ferrogels, Π_{swl}^{HG} has to be compatible with the NP osmotic pressure Π^{ML} in the magnetic liquid (ML) used for the synthesis. Basically Π^{ML} depends on - the NP volume fraction Φ , - the NP diameter d and - the ML ionic strength [7].

Two parameters are thus important to consider in the synthesis conditions : the geometrical ratio $R_S = d^3/\xi_{synth}^3$ and the osmotic ratio $R_{\Pi} = \Pi^{ML}/\Pi_{swl}^{HG}$. We show below how they tune the homogeneity/inhomogeneity of the composite. They depend on the following synthesis parameters : - CL and ϕ_{AM}^{synth} for the polymeric solution and - d , Φ_{synth} and $[cit]_{free}$ the concentration of free citrate species for the ML.

2.1. Experimental conditions

The ferrogels are prepared as described in [9] at $CL = 0.5\%$, 1% or 2% , with ML at $pH = 7.2$, based on γ - Fe_2O_3 NPs synthesized as in [8], stabilized by a citrate coating, with d of the order of 10 nm. The osmotic compression technique allows us to precisely fix - Φ_{synth} between 1% and 9% and - $[cit]_{free}$ in synthesis conditions

and also at swelling equilibrium (here $[cit]_{free} = 8 \cdot 10^{-3} \text{ mol.L}^{-1}$ or 0.1 mol.L^{-1} in both cases) [7].

Attempts to prepare ferrogels at R_{Π} larger than 1 have led to samples macroscopically inhomogeneous.

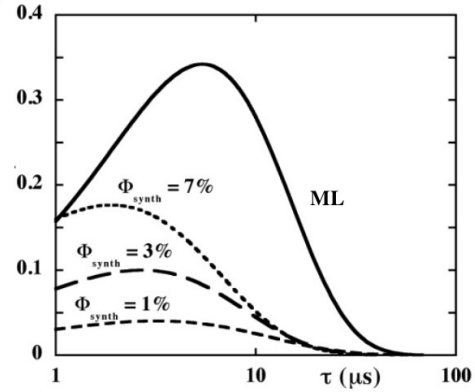


Figure 2: Normalized distributions of NP rotational times - in the initial ML and - in ferrogels in synthesis conditions at various Φ_{synth} ($[cit]_{free} = 8 \cdot 10^{-3} \text{ mol.L}^{-1}$). The proportion of rotating NPs increases as Φ_{synth} increases.

2.2. Measurements

We develop several measurements in order to answer to the following questions. How varies the local distribution of NPs in the ferrogels? Is the distribution homogeneous or are there local pockets of magnetic liquid? Are the NPs free to rotate or are they decorating the polymeric chains? What happens during the swelling process? Is there any release of NP?

We thus determine the swelling ratios G_{synth} in the synthesis conditions and G_{equil} at swelling equilibrium by weight measurements as $G_{synth,equil} = (m_{FG} - m_{dry})/(m_{dry} - m_{NP})$ and also the ratio R of NP release as $R = (m_{part}^{synth} - m_{part}^{equil})/m_{part}^{synth}$.

It is checked that $\Phi_{equil} = \Phi_{synth}(1-R)G_{synth}/G_{equil} \leq \Phi_{synth}$ by determination of the NP volume fractions Φ_{synth} and Φ_{equil} with iron titration using Atomic Emission Spectroscopy.

NP structure factors are determined by SANS in the initial magnetic liquids and in the ferrogels at swelling equilibrium, at LLB facility (CEA-Saclay, France) on PAXY spectrometer for wave-vectors $0.0065 \text{ \AA}^{-1} \leq q \leq 0.15 \text{ \AA}^{-1}$ [10]. In the ferrogels, the neutron scattering contrast of the solvent is adjusted to match that of the PAM replacing water by a 44/56% H_2O/D_2O mixture. In these conditions the nuclear contribution of the NP largely dominates their magnetic contribution [11]. Thanks to the NP magneto-optical properties,

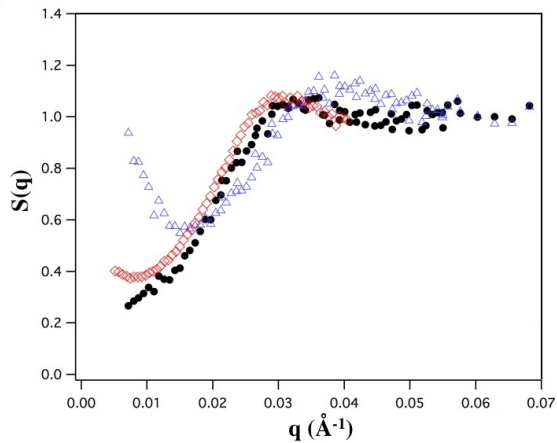


Figure 3: NP structure factor $S(q)$ in the initial ML at $\Phi = 3\%$ (black dots) and in ferrogels at swelling equilibrium : (red open circles) $\Phi_{equil} = 3\%$ synthesized at $\Phi_{synth} = 7\%$, $CL = 0.5\%$, $R_S < 1$ and $R_{II} < 1$ (homogeneous ferrogel); (blue triangles) $\Phi_{equil} = 0.76\%$, synthesized at $\Phi_{synth} = 3\%$, $CL = 2\%$, $R_S \sim 1$ and $R_{II} < 1$ (heterogeneous ferrogel - see ahead Table 1 - Series I); Here $[cit]_{free} = 8 \cdot 10^{-3} \text{ mol.L}^{-1}$.

we measure by magneto-birefringence the proportion of NPs free to rotate in the ferrogels and their distribution of characteristic rotational time, in synthesis conditions and at swelling equilibrium [10, 12].

3. Results and discussion at low $[cit]_{free}$

We first study systems at $[cit]_{free} = 8 \cdot 10^{-3} \text{ mol.L}^{-1}$ both in synthesis conditions and at swelling equilibrium.

3.1. Experimental results at $R_S < 1$ and $R_{II} < 1$

In the synthesis conditions, a large quantity of NPs are blocked in rotation as attested by the distributions of NP rotating times presented in Figure 2, deduced from the measurements of magneto-birefringence and normalized in order to directly show the proportion of rotating NPs with respect to the initial ML. The proportion of blocked NPs varies with Φ_{synth} .

At swelling equilibrium, we observe that the NP release R is important and that it is smoothly increasing with Φ_{synth} up to a saturation at R of the order of 50% for Φ_{synth} larger than 4%. The swelling ratios G_{equil}^{FG} are larger than G_{synth}^{HG} and always smaller than G_{equil}^{HG} meaning that the NPs partly hinder the swelling of the polymeric chains.

The NP volume fraction Φ_{equil} remaining in the ferrogels at swelling equilibrium roughly equals that of

blocked NPs in the synthesis conditions. Magneto-birefringence shows that almost all these NPs remaining in the ferrogel at swelling equilibrium, are also blocked in rotation, while the SANS measurements give structure factors $S(q)$ close to those of pure MLs at $\Phi \sim \Phi_{equil}$. In Figure 3, the structure factor of the ferrogel synthesized at $\Phi_{synth} = 7\%$ and $R_S < 1$ presents in swelling conditions a maximum at $q_{max} = 0.032 \text{ \AA}^{-1}$, corresponding to a most probable interparticle distance $\delta_{mp} \sim 200 \text{ \AA}$, of the same order as the mesh size $\xi_{equil} = 170 \text{ \AA}$ of the polymeric array and as the mean interparticle distance δ_{mean} deduced from the value $\Phi_{equil} = 3\%$ of the ferrogel. It demonstrates that the NP dispersions in the swollen ferrogels are rather homogeneous with roughly one NP per mesh of the polymeric array. These NPs being blocked in rotation [10], they homogeneously decorate the polymeric array and reinforce the network as can be attested by a mechanical probing of the elastic properties of these swollen ferrogels [9]. Figure 4 shows the relative variation of Young modulus E_{FG} of swollen ferrogels at $CL = 1\%$, $R_S < 1$ and $R_{II} < 1$ as a function of the ratio Φ_{equil}/ϕ_{AM} . The NPs increase here the Young modulus up to a factor 10. It can be adjusted by: $E_{FG} = E_{HG}(1 + 0.1e^{3.8\Phi_{equil}/\phi_{AM}})$.

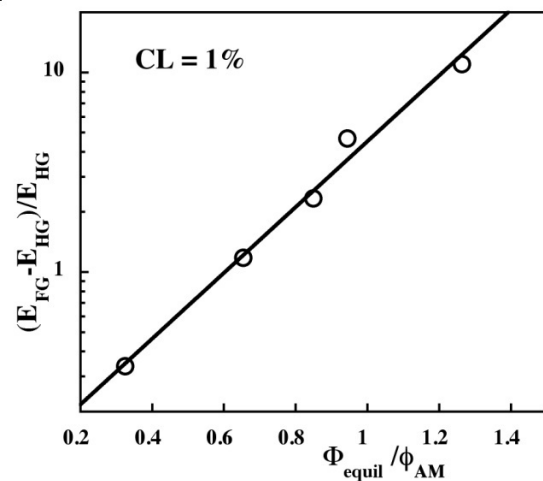


Figure 4: Semi-logarithmic representation of $(E_{FG} - E_{HG})/E_{HG}$ as a function of the ratio Φ_{equil}/ϕ_{AM} , E_{FG} is the Young modulus of swollen ferrogels at $CL = 1\%$, $R_S < 1$ and $R_{II} < 1$ and E_{HG} the Young modulus of the corresponding hydrogel, here $[cit]_{free} = 8 \cdot 10^{-3} \text{ mol.L}^{-1}$. The full line is a best fit of the data (see text).

Figure 5 compares the volume ratio of blocked nanoparticles inside the ferrogel before and after the swelling process as a function of Φ_{synth} . These blocked NPs are adsorbed on the polymeric network in the synthesis conditions and remain adsorbed at swelling equi-

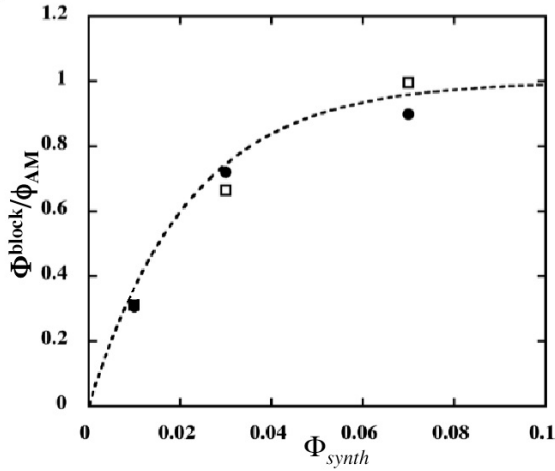


Figure 5: Nanoparticle adsorption in homogeneously decorated networks ($[cit]_{free} = 8 \cdot 10^{-3} \text{ mol.L}^{-1}$, $CL = 0.5\%$, $R_S < 1$ and $R_{II} < 1$); Volume ratio of blocked NP's with respect to polymer - in the synthesis conditions (closed circles) and - at swelling equilibrium (open squares) versus initial volume fraction of nanoparticles Φ_{synth} . Dotted line is a guide for the eye.

librium. It is indeed these NP's adsorbed on the PAM chains which are reinforcing the polymeric array.

These attractive interactions existing between iron oxide nanoparticles and the PAM chains in the ferrogels are ascribed to hydrogen bonds between the carbonyl groups of the polymer (each monomer bearing a primary amide function) and hydroxyl functions at the iron oxide surface, either Fe-OH directly at the solid surface or hydroxyl end-groups from the citrate ligands coating the nanoparticles. The hypothesis of H-bonds formation between PAM and many oxides was proposed long ago [13]. It was evidenced by different experimental techniques [14, 15]. Such H-bonds were also invoked in the kinetics of adsorption of PAM onto the haematite ($\alpha\text{-Fe}_2\text{O}_3$) surface, which has a chemical reactivity close to maghemite ($\gamma\text{-Fe}_2\text{O}_3$) [16]. This NP's - PAM adsorption is also evidenced by AFM probing as attested by Figure 6 which shows the formation of NP's necklaces along PAM chains [17].

3.2. Experimental results at $R_S \sim 1$ and $R_{II} < 1$

In these conditions, the swelling ratios of the ferrogels remain constant : $G_{equil}^{FG} = G_{synth}^{FG}$ and the release ratio R equals either 0 for $\Phi_{synth} < 4\%$ or almost 1 for $\Phi_{synth} > 4\%$ (see series I in Table 1).

The SANS probing at swelling equilibrium shows an up-turn of $S(q)$ at low q 's marking some NP inhomogeneities in the ferrogel (see Figure 3). This up-turn,

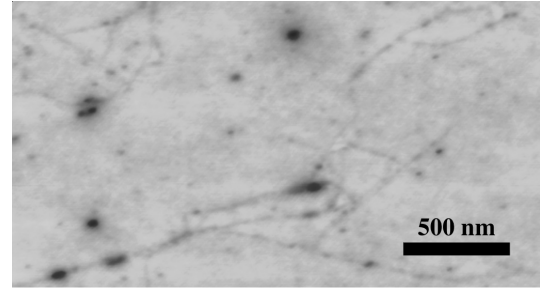


Figure 6: AFM picture of a dilute system of PAM chains and citrate-coated maghemite NP's at $[cit]_{free} = 8 \cdot 10^{-3} \text{ mol.L}^{-1}$ deposited on a mica substrate.

which is more and more marked as Φ_{synth} increases, is associated to a bump at intermediate q_{max} pointing the most-probable interparticle distance δ_{mp} in the FG. For example in the ferrogel at $CL = 2\%$ of Figure 3, q_{max} equals 0.038 \AA^{-1} meaning $\delta_{mp} \sim 165 \text{ \AA}$, which is much larger than the value ξ_{equil} that would be obtained in a homogeneous hydrogel. As well it is smaller than the mean interparticle distance deduced from Φ_{equil} (but of the same order as the one deduced from Φ_{synth}).

Both in the synthesis conditions and at swelling equilibrium, magneto-birefringence measurements show that the NPs free to rotate have a characteristic rotational time close to that of the initial MF. At swelling equilibrium, if there is no NP release, some NPs are blocked, however if the release ratio R is large the majority of the NPs are blocked in rotation. All these observations converge to the picture sketched in Figure 5 for the ferrogels synthesized at $R_S \sim 1$. In the synthesis conditions, the polymeric network has a very heterogeneous structure with areas of tight mesh size (excluding NPs) coexisting with pockets free of polymer and full of ML. At low Φ_{synth} , the ferrogels, unable to swell in the water bath, release no NP. As Φ_{synth} becomes larger than 4%, the ML-pockets becomes too large and/or too numerous, they tear up in the swelling bath, leaving behind NP-decorated walls with a NP-interspacing close to that of the previous inside-pocket ML.

4. Results and discussion at high $[cit]_{free}$

Let us now examine systems either synthesized at $[cit]_{free} = 8 \cdot 10^{-3} \text{ mol.L}^{-1}$ and then swollen at equilibrium in a bath at $[cit]_{free} = 0.1 \text{ mol.L}^{-1}$, or systems both synthesized and swollen at equilibrium with $[cit]_{free} = 0.1 \text{ mol.L}^{-1}$.

A first set of experiments is undertaken at $R_S < 1$, $R_{II} < 1$, $CL = 0.5\%$ and 1% , with ferrogels synthesized

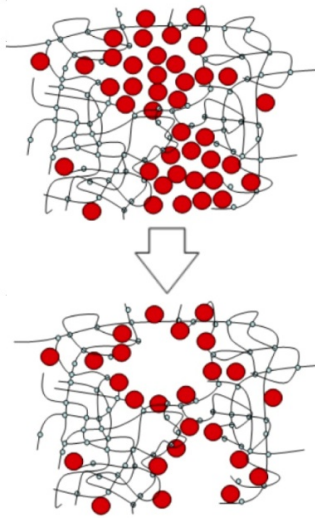


Figure 7: Picture of the heterogeneous ferrogels at $R_S \sim 1$, $R_{II} < 1$ (see series I of Table 1): (left) with pockets full of ML in the synthesis conditions, (right) with empty NP-decorated pockets.

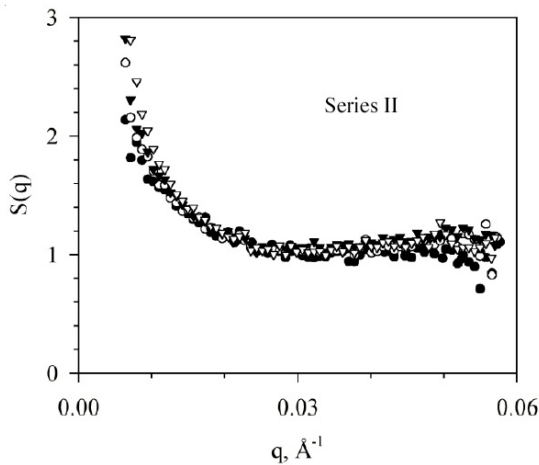


Figure 8: Structure factor $S(q)$ of samples from series II synthesized at $[cit]_{free} = 8 \cdot 10^{-3} \text{ mol.L}^{-1}$ and swollen at $[cit]_{free} = 0.1 \text{ mol.L}^{-1}$; Symbols $\Phi_{equil}^{II} = 0.14\%$ (closed circles), 0.2% (open circles), 0.54% (closed triangles) and 0.67% (open triangles).

$\Phi_{synth}(\%)$	$\Phi_{equil}^I(\%)$	$\Phi_{equil}^{II}(\%)$	$\Phi_{equil}^{III}(\%)$
1	0.97 (*)	0.14	0.08
3	2.95 (*)	0.2	0.38
5	0.76	0.54	0.54
7	0.82	0.67	0.71

Table 1: Experiments in heterogeneous ferrogels at $R_S \sim 1$, $R_{II} < 1$ and $CL = 2\%$, Φ_{synth} and Φ_{equil} for the three series I, II and III described in the text. (*) Samples without any NP's release, thus with unteared ML-pockets.

at $[cit]_{free} = 8 \cdot 10^{-3} \text{ mol.L}^{-1}$ and swollen at equilibrium at 0.1 mol.L^{-1} . Only small modifications are detected in the measurements of R , G_{equil} and Φ_{equil} . The release ratio R and the swelling ratio G_{equil} are both 30% larger, which lets suspect that the interaction between NP's and polymeric chains is slightly decreased and that free citrate enters in competition with NP's in the PAM adsorption process.

A second set of measurements is presented in Table I. These experiments are performed at $R_S \sim 1$, $R_{II} < 1$ and $CL = 2\%$, series I correspond to samples both synthesized and swollen at $[cit]_{free} = 8 \cdot 10^{-3} \text{ mol.L}^{-1}$ (as those of section 3-2), series II to samples synthesized at $[cit]_{free} = 8 \cdot 10^{-3} \text{ mol.L}^{-1}$ and swollen at $[cit]_{free} = 0.1 \text{ mol.L}^{-1}$, serie III to samples both synthesized and swollen at $[cit]_{free} = 0.1 \text{ mol.L}^{-1}$. The only visible effect of the large concentration of citrate either in synthesis conditions or in swelling conditions is to provoke a large NP release at $\Phi_{synth} = 1\%$ and 3% , tearing up any heterogeneous ML pocket in these ferrogels. As a summary of Table I, we can say that either there is no release and no swelling in the swelling bath then $\Phi_{equil} \sim \Phi_{synth}$ and some ML pockets are remaining in the ferrogel (samples marked with (*) in table 1), or the ML pockets tear up in the swelling bath, then only few NP's remain in the gel and $\Phi_{equil} \sim \Phi_{synth}/10$.

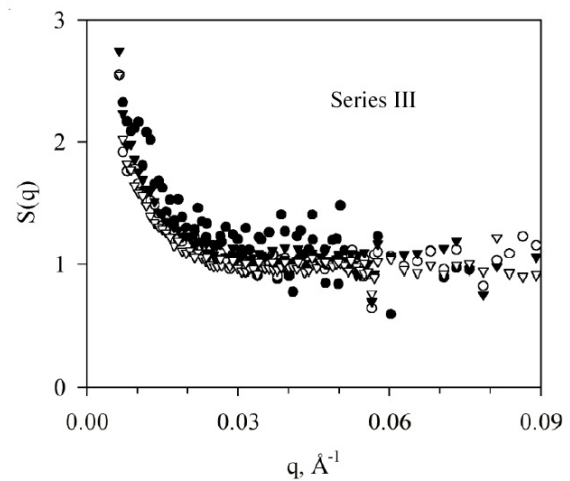


Figure 9: Structure factor $S(q)$ of samples from series III both synthesized and swollen at $[cit]_{free} = 0.1 \text{ mol.L}^{-1}$; Symbols $\Phi_{equil}^{III} = 0.08\%$ (closed circles), 0.38% (open circles), 0.54% (closed triangles) and 0.71% (open triangles).

Small Angle Neutron Scattering experiments have been performed on these samples. The NP structure factor $S(q)$ of the sample from Series I at $\Phi_{equil}^I = 0.76\%$

was presented previously in Figure 3. Those of series II and III are plotted in Figures 7 and 8. They are completely similar for both series whatever is Φ_{synth} . They reveal an inhomogeneous distribution of NP's, without any correlation peak associated to a most probable interparticle distance, contrary to what is observed in Figure 3. These $S(q)$ are on the contrary very close to the structure factor in the pure ML at $[cit]_{\text{free}} = 0.1 \text{ mol.L}^{-1}$, where the interparticle interaction is attractive. We should note that they are independent on the value of $[cit]_{\text{free}}$ in the synthesis conditions, on the contrary it is the value of $[cit]_{\text{free}}$ in the swelling bath which determines the final structure.

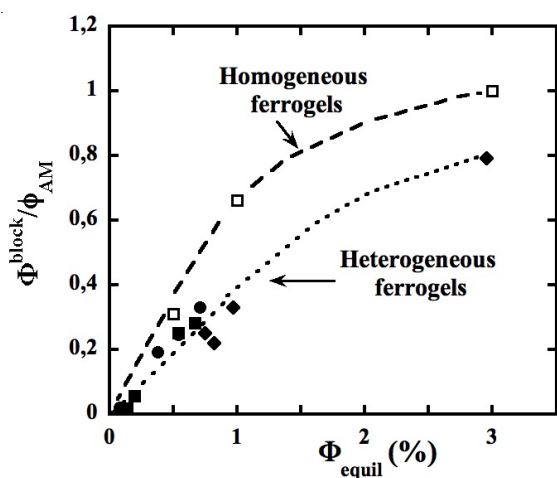


Figure 10: Volume ratio of blocked NP's with respect to polymer at swelling equilibrium versus NP's volume fraction at swelling equilibrium Φ_{equil} . Comparison between: - homogeneously decorated networks at $CL = 0.5\%$, $R_S < 1$ and $R_{\Pi} < 1$ (open squares: $[cit]_{\text{free}} = 8 \cdot 10^{-3} \text{ mol.L}^{-1}$ both in synthesis conditions and at swelling equilibrium) and - inhomogeneous networks at $CL = 2\%$, $R_S \sim 1$ and $R_{\Pi} < 1$ (closed symbols samples of Table I, diamonds: series I, squares: series II and circles: series III). Dashed and dotted lines are guides for the eye.

A probing of these samples by relaxation of magneto-optical birefringence is also performed, allowing to deduce the proportion of blocked NP's in the various ferrogels. Figure 10 compares $\Phi^{\text{block}}/\phi_{\text{AM}}$, the volume ratio of blocked NP's with respect to polymer in the swollen ferrogels as a function of Φ_{equil} for homogeneously decorated networks and for the three series of heterogeneous networks of Table 1. There is a clear shift in NP's adsorption between the homogeneously decorated networks and the heterogeneous ones. However in the heterogeneous case, there is no visible effect of the value of $[cit]_{\text{free}}$ on $\Phi^{\text{block}}/\phi_{\text{AM}}$, all the samples of Table 1 join together in the same master curve at $\Phi_{\text{equil}} < 1\%$. The

value of $[cit]_{\text{free}}$ only determines the low value of Φ_{equil} . There are here two kinds of competitions with the process of NP's adsorption on PAM chains, the adsorption of free citrate on PAM and NP's interparticle attractions.

5. Conclusion

In these ferrogels synthesized at $R_{\Pi} < 1$ and $[cit]_{\text{free}} = 8 \cdot 10^{-3} \text{ mol.L}^{-1}$, there is a coexistence of free-to-rotate NPs and of adsorbed ones on the PAM network. It is present both in the inhomogeneous gels ($R_S \sim 1$) and in the homogeneous ones ($R_S < 1$) where it explains the observed reinforcing of the polymeric network. This adsorption, presumably due to H-bonding between NP's and PAM chains enters in competition with other processes at larger $[cit]_{\text{free}}$ values, the relevant value for the final structure being that of the swelling bath.

Acknowledgments

We thank D. Talbot for the ML synthesis and for the chemical titration of iron in the ferrogels. This work was supported by CONACYT Mexico.

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