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Abstract. We study iron oxide nanoparticles stabilized by citrate ligands interacting with long linear poly(acrylamide) chains in the regime where the diluted chains are decorated by many smaller magnetic nanoparticles. The strength of adsorption of the particles onto polymer increases when the unbound citrate concentration decreases, as evidenced by the faster translational dynamics of the particle–polymer complexes and the slower rotational dynamics of the nanoparticles.

INTRODUCTION

A novel class of nanocomposite materials called "ferrogels" with possible applications as magnetic actuators can be obtained by embedding magnetic nanoparticles in a soft polymer matrix highly swollen by water [1]. In a previous work, we have studied such magnetic hydrogels made of the combination of a poly(acryamide) hydrogel cross-linked by N,N'-methylene-bis-acrylamide and an aqueous "citrated ferrofluid" [2]. The latter is a suspension of iron oxide nanoparticles in water at pH≈7 stabilized by surface charges provided by citrate ligands in equilibrium with unbound tri-sodium citrate electrolyte. We found that the swelling degree Q of these ferrogels (defined as the amount of absorbed water per dry polymer weight) is lower for ferrogels compared to undoped hydrogels. In addition, Q presents a minimum value as a function of salinity at low citrate salt concentration. To understand this specific role of the citrate ligands on the polymer–particle interactions, we study here a somehow simpler system consisting of linear poly(acrylamide) chains having a calculated radius of gyration in water around 100nm mixed with the same magnetic nanoparticles in different citrate buffers. The resulting mixtures are fluid and can be studied by different dynamical methods: macroscopic viscosimetry, dynamic light scattering and oscillatory magneto-birefringence in cross-fields, the latter probing the micro-rhelogy in the local environment of the nanoparticles [3].

MATERALS

We used a commercial poly(acrylamide) (PAM) homopolymer (Polysciences) known as to strongly interact with metal oxide colloids. This very long linear PAM (5–6×10^6g/mol) is commonly used as a flocculent. As for the magnetic nanoparticles, they came from ionic ferrofluids prepared by alkaline co-precipitation of $FeCl_2$ and $FeCl_3$ followed by complete oxidation using $Fe(NO_3)_3$ leading to positively charged γ-Fe_2O_3 (maghemite) nanoparticles in HNO_3 (pH=1.2). A size-sorting process yielded a fraction of narrower distribution of diameters, described by a Log-normal law of parameters d_0=6.6nm and σ=0.21. Finally the iron oxide surface was coated by tri-sodium citrate ligands leading to a stable dispersion of negatively charged nanoparticles at pH=7.2.

After complete dissolution in tri-sodium citrate of the polymer at a concentration 0.6 g/L lower than c* (which is estimated about 2.4 g/L), the citrated ferrofluid was introduced in the solutions and allowed to equilibrate overnight. Two values of the final salt concentration [Na_3Cit] were examined, respectively a low concentration (8mM) and a larger one (50mM). The volume ratio of the nanoparticles relatively to the polymer was kept at a constant value (=2) all along the dilutions required for the viscosimetry experiment.

TABLE 1. Intrinsic viscosity [η] (g⁻¹.mL) measured by capillary viscosimetry for PAM (5–6x10⁶) solutions mixed with 2 volume equivalents of citrated ferrofluid.

| [sodium citrate] =	50mM	8mM
Polymer only	535	595
Polymer + particles	495	435

RESULTS

Capillary viscosimetry shows that the conformation of chains with and without nanoparticles does not vary a lot at high citrate concentration (8% decrease at 50mM citrate), whereas the presence of nanoparticles decreases the chain swelling significantly when the citrate concentration is lower (27% decrease at 8mM). The same effect of lowering the citrate concentration on the shrinking of the polymer chains by the nanoparticles is also observed by dynamical light scattering, the hydrodynamic diameter of the polymer-ferrofluid complexes varying from d_H=107nm at 50mM of unbound citrate down to d_H=78nm at 8mM.
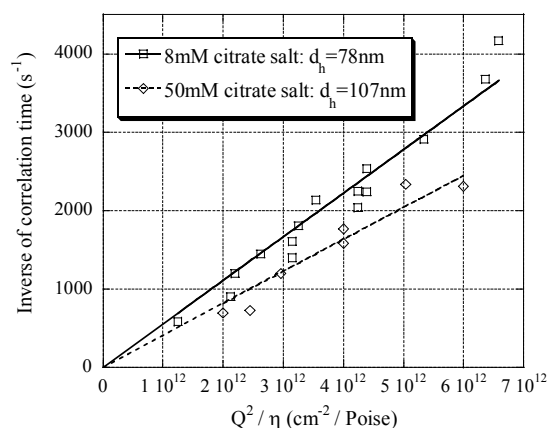

FIGURE 1. Dynamic light scattering: the hydrodynamic diameters of the polymer–particles complexes at the two citrate salt concentrations are measured from the slope of the main relaxation rate (from CONTIN fit of the correlogram) *vs.* the square of wave vector divided by viscosity.

With cross-fields magneto-birefrengence we get the frequency response of nanoparticles rotation in their local environment. In the presence of polymer, the visco-elastic behavior is evidenced by the phase shift at low frequency, increasing when [Na₃Cit] decreases. Therefore we can conclude that the nanoparticles strongly interact with the long linear poly(acrylamide) chains and that this coupling becomes stronger at lower unbound citrate salt concentration in equlibrium with the citrate ligands. An adsorption of the particles onto the chains is thus very probable, for it explains the specific effect of the citrate concentration by a competition between the citrate ligands and the polar

amide groups of the polymer to access the surface of iron oxide. In the case of complete adsorption, we calculate that on average 10^2 particles can adsorb on a single chain. Having proved that the polymer–particles complexes behave as microgels swelling and shrinking in a similar way as cross-linked ferrogels, we showed by AFM that they also exhibit a necklace morphology.
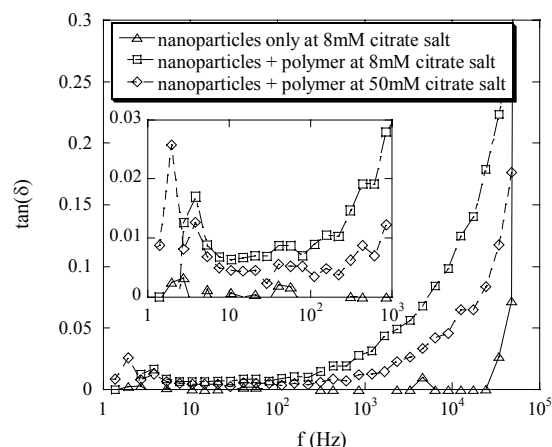
FIGURE 2. Cross-fields dynamical birefringence: the non zero phase shift angle between the magnetically induced birefringence and the ac H field is a sign of visco-elasticity.
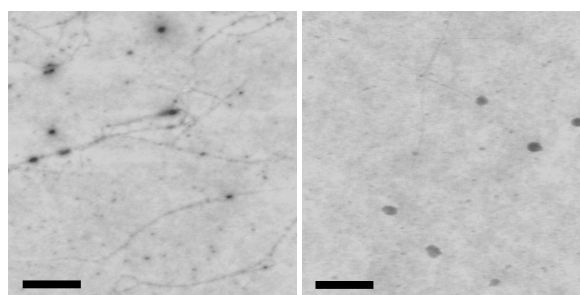
FIGURE 3. AFM pictures of PAM solutions mixed with 2 vol. of citrated ferrofluid deposited on mica at 8mM (left) and 50mM citrate (right, scale bars=500nm). Necklaces of spheres about 80nm in diameter linked to rigid segments up to 1μm long are thought to be particles-shielded polymers.

REFERENCES

1. Zrínyi, M., Barsi, L., and Büki, A., *J. Chem. Phys.* **104**, 8750-8756 (1996).

2. Galicia, A. Sandre, O. Cousin, F. Guemghar, D. Ménager, C., and Cabuil, V., *J. Phys. Cond. Mat.* **15**, S1379-S1402 (2003).

3. Hasmonay, E. Dubois, E. Neveu, S. Bacri, J.-C., and Perzynski, R., *Eur. Phys. J.* B **21**, 19-29 (2001).