Self-assembly of polymers or copolymers and ferrofluids leading to either 1-d, 2-d or 3-d aggregates decorated with magnetic nanoparticles

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A novel type of hybrid colloids is presented, based on the association of several polymeric systems and ferrofluids. On the one hand, we use inorganic nanoparticles made of magnetic iron oxide prepared at the L12C, which response to a magnetic field of low intensity. On the other hand the organic part is made either of long linear polycrylamide chains or of mesoscopic structures (vesicles and micelles) self-assembled from amphiphile polybutadiene-b-poly(glutamic acid) di-block copolymers, which conformation is pH-sensitive. Those PB-b-PGA polybutadiene-b-poly(glutamic acid) di-block copolymers, which conformation is pH-sensitive. Those PB-b-PGA copolymers bearing a cross-linkable hydrophobic block and a hydrophilic peptidic block have been synthesized recently at the LCPO by combining anionic polymerization and ring-opening polymerization. Their polydispersity indices are small enough to obtain well defined self-assembled aggregates. For example the PB48-b-PGA100 copolymer leads in water to closed bilayers. Belonging to this new class of polymeric vesicles called polymersomes by F. Bates (see also 3 for a review on the frame of a future freezing of the structures. In this paper, we present a few cases representative of the reachable structures:

- **PB**<sub>48</sub>-b-PGA<sub>100</sub> copolymer leads in water to closed bilayers. The polydispersity indices are small enough to obtain well defined self-assembled aggregates. For example the PB<sub>48</sub>-b-PGA<sub>100</sub> copolymer leads in water to closed bilayers.
- **PB**<sub>48</sub>-b-PGA<sub>114</sub> and **PB**<sub>48</sub>-b-PGA<sub>145</sub> which self-assemble in water as micelles of hydrodynamic diameters \(d_H = 60\text{nm}\) and \(d_H = 70\text{nm}\) respectively, the internal diameter of the hydrophobic core being \(d_{int} = 14\text{nm}\) as measured by SANS in both cases 8.
- **PB**<sub>48</sub>-b-PGA<sub>64</sub> which forms closed membranes in water, i.e. vesicles characterized by an outer diameter \(d_{out} = 100\text{nm}\) and a bilayer thickness \(d_{bil} = 14\text{nm}\).

We report also results obtained with a commercial polyacrylamide homopolymer (Polysciences) known as to properly dispersed in a solvent. Therefore we examined a series of PB-b-PGA copolymers which differ by the length of their polypeptid PBA block, their hydrophobic block PB being chosen to enable an easy way to cross-linking within the frame of a future freezing of the structures. In this paper, we present a few cases representative of the reachable structures:

- **PB**<sub>48</sub>-b-PGA<sub>114</sub> and **PB**<sub>48</sub>-b-PGA<sub>145</sub> which self-assemble in water as micelles of hydrodynamic diameters \(d_H = 60\text{nm}\) and \(d_H = 70\text{nm}\) respectively, the internal diameter of the hydrophobic core being \(d_{int} = 14\text{nm}\) as measured by SANS in both cases 8.
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We report also results obtained with a commercial polyacrylamide homopolymer (Polysciences) known as to properly interact with metal oxide colloids. This very long linear PAM 5–6x10<sup>6</sup>g/mol is commonly used as flocculent. We tested the association of these two copolymers and this homopolymer with three either aqueous or organic ferrofluids, which grain size polydispersity had been reduced in a first step by the method of fractionated phase separations 8 with added excess HNO<sub>3</sub>:

- 1S1-HNO<sub>3</sub> acidic ferrofluid, which is an aqueous acidic ferrofluid (pH=1.2) with a particle size distribution characterized by a Log-normal law of parameters \(d_0 = 0.6\text{mm}\) and \(\sigma = 2.01\). Its iron oxide surface is coated simply by H<sup>+</sup> protons, thereby leaving a free access for a
future grafting by the glutamic acid moieties of the copolymers or by the amide groups of polyacryamide.

- S1S-Na₃Cit citrated ferrofluid, which comes from the previous acidic ferrofluid after coating by tri-sodium citrate ligands, thus enabling a dispersion at pH=7.
- S2-CH₂Cl₂ surfacted ferrofluid, which is grafted by a phosphoric di-ester type tensioactive (Beycostat NE) for a solubilization in dichloromethane. It also has a slightly broader distribution of particle sizes (d₀=6.8 nm, σ=0.24).

Table 1. Short summary of samples and self-assembled hybrid objects including their dimensionality:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>PB₄₈-PGA₁₁₄ and PB₄₈-PGA₁₄₅</th>
<th>PAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₂-CH₂Cl₂</td>
<td>(A) 3-d filled magnetic micelles</td>
<td>no</td>
<td>interaction</td>
</tr>
<tr>
<td>S₁S-HNO₃</td>
<td>no proper dispersion</td>
<td>3-d filled micelles and few 2-d vesicles in CH₂Cl₂</td>
<td>3-d hybrid network of fibers in water</td>
</tr>
<tr>
<td>S₁S-Na₃Cit</td>
<td>no interaction</td>
<td>(C) 3-d filled magnetic vesicles</td>
<td>(D) 1-d necklaces</td>
</tr>
</tbody>
</table>

The assembly of each copolymer mixed with either 1 or 2 equivalents of the surfacted ferrofluid S₂-CH₂Cl₂ was favored by first eliminating the dichloromethane then redispersing the objects in water, after deprotonating the acidic groups of the copolymer with NaOH to raise the pH up to 7. In the case of the bare acidic particles S₁S-HNO₃, the flocculation was induced almost instantaneously after addition of either PAM or of a PB-b-PGA copolymer. The supernatant could then be easily replaced by CH₂Cl₂. Finally with the S₁S-Na₃Cit ferrofluid, the interaction with all the polymers did not lead to any visible destabilization.

After three weeks, all suspensions were analyzed by dynamic light scattering (DLS) and small angle neutrons scattering (SANS). Thus we could show that some of the (co)polymer–particles aggregates reach an equilibrium shape and a proper dispersion state.

(A). Sample PB₄₈-PGA₁₁₄ mixed with the S₂-CH₂Cl₂ surfacted ferrofluid leads to a dispersion of magnetic micelles in water, which diameters dₐ are equal to 430nm and 225nm for 1 and 2 mass equivalents respectively. The large increase of the outer diameter compared to unloaded micelles (dₐ=70nm) suggest that their hydrophobic cores are filled with nanoparticles at a high local concentration. The short inter-particle distance given around 80 Å by the position of the structure peak (Fig.1) corresponds to a volume fraction of nanoparticles inside the micelles about 30%. This high encapsulation yield together with the global 3-d shape of the aggregates are confirmed by a look at the TEM and AFM images in the case of PB₄₈-PGA₁₁₄, which show large and thick baggies of inorganic particles. Please note that the copolymer samples combined with 2 mass equivalents of ferrofluid lead to final volume fractions Φ of nanoparticles (from titration of iron) which are 6–7 times smaller than those with 1 mass equivalent. This discrepancy originates from the fact that the objects are fully dispersed only in the former case but not in the latter case. Thus at 2 equiv., we get supernatants which are globally more dilute in copolymer–particles complexes.

(B). Vesicles of PB₄₈-PGA₅₆ still form in water when in the presence of S₂-CH₂Cl₂, their outer diameter being significantly increased (dₐ equal to 620nm and 210nm for 1 and 2 mass equivalents respectively). Due to their hydrophobicity, the surfacted nanoparticles are confined in
2-d between the two leaflets of the copolymer bilayer, as proved separately by the SANS measurements, the TEM pictures and the AFM imaging (which in addition contains a valuable topographical information). To the authors’ knowledge this is the first described case of vesicles with a fluid magnetic membrane. Several magnetic shells were already mentioned in literature\textsuperscript{11,12}, but none as hollow and floppy as ours. An appropriately designed theory describing their deformation under an applied magnetic field predicts a prolate–oblate transition in that case\textsuperscript{13}.

![Fig. 3. SANS curves for the PB\textsubscript{48}–PGA\textsubscript{56} copolymer mixed with 1 and 2 equiv. of the hydrophobic nanoparticles S\textsubscript{2}-CH\textsubscript{2}Cl\textsubscript{2}. In the small-Q region, the form factor of the aggregates follows a power law with slope approximately \(-2\), which is characteristic of a flat sample. The structure peak due to particles at contact is absent for 1 equivalent.](image1)

b) AFM pictures of the same sample (the bar measures 500nm on the left and 150nm on the right). The uniform film visible around the objects is likely the pure copolymer bilayer spreading onto the mica substrate, with a measured height \(\delta_{AFM}=4.5\)nm. The vesicles appear holey on the pictures because the strong adhesion of those soft shells on high energy surfaces (freshly cleaved mica for AFM or Formvar coated graphite for TEM) necessitates the ripping of the bilayers (a sort of like peeled orange skins!).

![Fig. 4a) TEM picture of a magnetic membrane made of PB\textsubscript{48}–PGA\textsubscript{56} and 1 equiv. of S\textsubscript{2}-CH\textsubscript{2}Cl\textsubscript{2}, showing only the nanoparticles because of the low electron density of the polymer compared to the iron oxide (bar length is 333nm); b) AFM pictures of the same sample (the bar measures 500nm on the left and 150nm on the right). The uniform film visible around the objects is likely the pure copolymer bilayer spreading onto the mica substrate, with a measured height \(\delta_{AFM}=4.5\)nm. The vesicles appear holey on the pictures because the strong adhesion of those soft shells on high energy surfaces (freshly cleaved mica for AFM or Formvar coated graphite for TEM) necessitates the ripping of the bilayers (a sort of like peeled orange skins!).](image2)

(C) Vesicles self-assembling in water from PB\textsubscript{48}–PGA\textsubscript{56} can also be filled in their inner aqueous compartment with a neutral ferrofluid just as S1S-Na\textsubscript{3}Cit, thereby obtaining magnetic polymersomes analogous to magnetoliposomes\textsuperscript{14}, which are lipid vesicles loaded with an aqueous ferrofluid at pH7. In the same way as for magnetic liposomes, after preparing the vesicles one can separate them from non-encapsulated nanoparticles by column chromatography with Sephacryl S1000 as separating medium\textsuperscript{14}. The sorting process is studied by a look at the structure factor \(S_{\text{max}}(Q)\).

![Fig. 5. SANS curves for PB\textsubscript{48}–PGA\textsubscript{56} vesicles prepared in the citrated ferrofluid S1S-Na\textsubscript{3}Cit before and after column fractionation. The low-Q region is a part of the form factor of large 3-d objects present in both samples. The structure peak in the initial unsorted dispersion gives a local concentration \(\Phi_{\text{local}}=11\%\) inside the vesicles superior to the average concentration \(\Phi=6\%\) (from iron titration). The less pronounced shoulder still visible on the curve after passage through the column corresponds to \(\Phi_{\text{local}}=0.07\%,\) which is 3–4 times higher than the average \(\Phi=0.02\%.\) The enrichment of loaded vesicles compared to free particles is thus concomitant with a global dilution of all the objects and a partial leak-out of the vesicles, maybe due to a larger size of copolymer vesicles than liposomes described in 14, compared to the porosity of the separating medium.](image3)

(D) Solutions of linear PAM with 2 vol. equivalents of S1S-Na\textsubscript{3}Cit citrated ferrofluid at low and high [Na\textsubscript{3}Cit]

We finish this article by presenting another example of polymer–ferrofluid hybrid leading this time to 1-d objects.
For this purpose, we dissolved long linear chains of PAM 5–6x10^6 g/mol having a (calculated) radius of gyration in water around 100nm. We mixed the solutions with the S1S-Na3Cit ferrofluid at two final values of the unbound tri-sodium citrate salt concentration [Na3Cit]=8mM and 50mM respectively. The volume ratio of nanoparticles relatively to polymer was kept at a constant value (=2).

Table 2. Intrinsic viscosity [η] (g⁻¹.mL) measured by capillary viscosimetry for PAM solutions mixed with 2 vol. of S1S-Na3Cit citrated ferrofluid at two values of [Na3Cit]:

<table>
<thead>
<tr>
<th></th>
<th>50mM citrate</th>
<th>8mM citrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAM only</td>
<td>535</td>
<td>595</td>
</tr>
<tr>
<td>PAM + particles</td>
<td>495</td>
<td>435</td>
</tr>
</tbody>
</table>

These data above show that the conformation of chains with and without nanoparticles does not vary a lot at high citrate concentration (8% decrease at 50mM free citrate), whereas the presence of nanoparticles decreases the chain swelling significantly when the citrate concentration is lower (27% decrease at 8mM citrate). 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 varies from dH=107nm at 50mM of unbound citrate down to dH=78nm at 8mM. Therefore we can conclude that the nanoparticles strongly interact with the long linear polyacrylamide chains and that this coupling becomes stronger at lower unbound citrate salt concentration in equilibrium with the citrate ligands. An adsorption of the particles onto the chains is thus very probable, because 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 adsorb on a single chain. Having shown that the polymer–particles complexes behave as microgels swelling and shrinking in a similar way as cross-linked ferrogels, we have a look at their morphology.

which diameter is estimated about 37nm from the cut-off.

Now that we elucidated the self-assembly of those 1-d, 2-d or 3-d hybrid objects made of magnetic nanoparticles and (co)polymers, the next steps of this study will consist in attempting to modify their shape thanks to a magnetic field. Their magnetic response could be studied by anisotropic SANS measurements. In the case of a static B field first, one easily predicts to obtain a simple ellipsoidal deformation. Then with a time varying field B (for instance a rotating field) we could generate further complex shapes like the starfish-like ones well known for concentrated ferrofluid droplets. Preparing those original shapes with samples at the mesoscopic scale represents a challenge for the physical chemistry community. The aggregates of ferrofluids with di-block rod-coil copolymers or linear homopolymers open a possible route to reach this goal, also offering the possibility to freeze the structures by cross-linking unsaturated blocks like polybutadiene.

8. F. Chécot, S. Lecommandoux, A. Brûlet, in preparation