

Letters

Self-Assembled Magnetic Nanowires Made Irreversible by Polymer Bridging

Cécile Goubault,^{†,‡} Fernando Leal-Calderon,[§] Jean-Louis Viovy,^{*,‡} and
Jérôme Bibette^{*,†}

Laboratoire Colloïdes et Matériaux Divisés, ESPCI/CNRS UMR 7612, 10 rue Vauquelin,
75005 Paris, France, Equipe Macromolécules et Microsystèmes en Biologie et en Médecine,
UMR 168 CNRS/Institut Curie, 26 Rue d'Ulm, 75005 Paris, France, and Laboratoire des
milieux dispersés alimentaires, Institut des Sciences et techniques des aliments de Bordeaux,
Av. des facultés, 33405 Talence Cedex, France

Received November 20, 2004. In Final Form: February 25, 2005

In this letter, we investigate the mechanism of formation of a recently discovered new type of colloid, irreversible flexible chains of magnetic particles. The chain formation mechanism is based on magnetically induced bridging by adsorbed polymers, and we investigate here the associated phase diagrams, considering both thermodynamic and kinetic aspects. This phase diagram is the consequence of a balance between entropic repulsion between polymer layers at the particles surfaces, depletion forces pushing the particles together, and a short-range attractive force developing when polymers can bridge two particles. We end up with a very simple protocol allowing the formation of long, extremely regular chains, which can find numerous applications in chemistry and biology. The perspectives for the development of a new field of "macrocolloidal chemistry" are discussed.

Introduction

Colloids can be assembled into complex materials, driven by the action of collisions and interactions between the particles. Collisions due to Brownian motion between attractive colloids lead to disordered structures such as fractal aggregates,^{1,2} gels, or solids. Previous investigations using specific interactions (such as molecular recognition) have been exploited to control aggregation rate and cluster size by tailoring the concentration and stoichiometry of ligands and receptors.^{3,4} Affinity colloidal

aggregation has been widely used for 40 years in well-known "agglutination tests" to detect and quantify proteins.⁵

Super-paramagnetic colloids allow controlling the assembly of colloidal structures by a magnetic field.^{6–9} Under a magnetic field, such particles self-organize into chains along the direction of the field: the magnetic field induces in each particle a magnetic moment collinear to the field, and these moments create a force depending on the

* To whom correspondence should be addressed. E-mail: jean-louis.viovy@curie.fr (J.-L.V.); jerome.bibette@espci.fr (J.B.).

[†] ESPCI/CNRS UMR 7612.

[‡] UMR 168 CNRS/Institut Curie.

[§] Laboratoire des milieux dispersés alimentaires, Institut des sciences et techniques des aliments de Bordeaux.

(1) Weitz, D. A.; Oliveria, M. *Phys. Rev. Lett.* **1984**, *52*, 1433–1436.

(2) Bibette, J.; Mason, T. G.; Hu, G.; Weitz, D. A.; Poulin, P. *Langmuir* **1993**, *9*, 3352–3356.

(3) Nam, J.-M.; Park, S.-J.; Mirkin, C. *J. Am. Chem. Soc.* **2002**, *124*, 3820–3821.

(4) Hiddessen, A. L.; Rodgers, S. D.; Weitz, D. A.; Hammer, D. A. *Langmuir* **2000**, *16*, 9744–9753.

(5) Plotz, C. M.; Singer, J. M. *J. Med.* **1956**, *21*, 888–892.

(6) Furst, E.; Suzuki, C.; Fermigier, M.; Gast, A. *Langmuir* **1998**, *14*, 7334–7336.

(7) Philip, J.; Mondain-Monval, O.; Leal-Calderon, F.; Bibette, J. *Bull. Mater. Sci.* **1999**, *22*, 313.

(8) Promislov, H.; Gast, A.; Fermigier, M. *J. Chem. Phys.* **1995**, *102*, 5492.

(9) Biswal, S. L.; Gast, A. P. *Phys. Rev. E* **2003**, *68*, 021402.

direction of the interparticle vector. This force is attractive when the interparticle vector lies in the field direction and repulsive when it is perpendicular to the field, leading to dynamic chainlike aggregates parallel to the field. These systems have been thoroughly investigated, thanks to their appealing physical properties and to potential applications as magnetorheological fluids. The thickness of these aggregates depends on the particles concentration, but at a low enough concentration, regular one-particle-thick chains involving hundreds of particles can be created.^{6,10} In short, to obtain perfectly linear chains, the particles must be spherical, monodisperse, strongly magnetic (attractive energy between two particles should exceed thermal energy), and Brownian (diameter inferior to about 1 μm , to avoid fast sedimentation), and they must possess a strong initial colloidal stability.

If the particles are well-stabilized and not adhering, they redisperse when the field is switched off. A contrario, if an adhesive process occurs, chains remain permanent.^{9,10,12} Such magnetic filaments, made of magnetic colloids and linkers, have interesting dynamic magneto-responsive structures. For instance, they may adopt a hairpin configuration under magnetic field. This phenomenon has given rise to a new micromechanical approach to probe linkers bending rigidity at the molecular scale.¹⁰ Self-organized in a microchip, they provide a new promising sieving matrix that can be exploited for rare cells sorting.¹¹

In this letter, we investigate a mechanism based on magnetically induced bridging by adsorbed polymers that can be used for preparing one-particle-thick irreversible magnetic filaments (first observed by Philip et al.).¹²

The principle is the following: magnetic colloids are covered with adsorbed polymers, which contribute to their colloidal stability by inducing entropic repulsive forces. When a strong enough magnetic field is applied, the colloids organize into chains and are pushed together, leading to interpenetration of their adsorbed polymer layers. For suitable conditions, the dynamics of the layers in such confined conditions can lead to bridging, which makes the filament irreversible after magnetic field removal. However, as we shall see in the following, this appealing principle involves numerous aspects of the thermodynamics of colloids and requires a rather subtle balance of the forces at play to yield filaments with the best quality. We investigate here these different aspects, studying first the phase diagram of the colloid-polymer system and then the behavior of this system in the presence of a magnetic field.

Materials and Methods

Materials. *Magnetic Particles.* The super-paramagnetic particles we used are supplied by Ademtech S. A. (www.ademtech.com). They consist of organic ferrofluid calibrated droplets dispersed in water. The ferrofluid is a suspension of $\gamma\text{-Fe}_2\text{O}_3$ ferrimagnetic nanoparticles stabilized by oleic acid in octane. The particles are obtained through a controlled emulsification technique followed by an enrichment of the magnetic content by octane extraction. The droplets are stabilized by Triton X-405 (a nonionic surfactant) and are monodisperse, with a mean diameter of 800 nm. Some of the oleic acid ($\text{p}K_a = 5.0$) initially present in the ferrofluid covers the surface of the beads, and, therefore, the beads are negatively charged at neutral pH.

(10) Goubault, C.; Jop, P.; Baudry, J.; Bertrand, E.; Fermigier, M.; Bibette, J. *Phys. Rev. Lett.* **2003**, *91*, 260802.

(11) Goubault, C.; Viovy, J.-L.; Bibette, J. In *Proceeding of MicroTAS 2003*; Northrup, M. A., Jensen, K. F., Harrison, D. J., Eds.; Transducers Research Foundation, PMMI: San Diego, CA, 2003; pp 159–163.

(12) Philip, J.; Mondain-Monval, O.; Leal-Calderon, F.; Bibette, J. *J. Phys. D: Appl. Phys.* **1997**, *30*, 2798.

(13) Klein, J.; Luckham, P. F. *Nature* **1984**, *308*, 836.

Chemical Products. The polymer used to bridge the particles is a poly(acrylic acid) (PAA) of average molecular weight 250 000 ($M_w/M_n = 1.1$; Aldrich [41,600-2]). The theta temperature for PAA in water is about 20 $^\circ\text{C}$.

Nonyl phenol ethoxylate (NP10) is a nonionic surfactant (Sigma-Aldrich, [NP 10]). Its critical micellar concentration is 7×10^{-5} M.

Methods. *Phase Diagrams.* The particles are washed and resuspended five times in an aqueous solution containing 0.1 wt % of NP10, to remove Triton X-405. A total of 20 μL of this dispersion are placed into an Eppendorf tube (0.5 mL) at a given particle volume fraction ϕ and submitted to an external field. The field gradient concentrates the particles at the bottom of the sample. The upper continuous phase is replaced by a PAA solution of concentration C_p (wt %) containing 0.1 wt % NP10. C_p ranges from 0.01 to 0.5 wt %, and ϕ varies from 0.1 to 5%. The mixture is directly observed using an optical inverse microscope (Zeiss, Axiovert 100) with a 20 \times objective and a Cohu CCD camera. Snapshot images are acquired using Scion Image software on a personal computer.

Preparation of Magnetic Filaments. Magnetic particles suspended in an aqueous solution containing PAA at concentration C_p , 0.1 wt % NP10, are introduced into an Eppendorf tube (0.5 mL), at a given volume fraction ϕ . The tube is directly placed under a homogeneous magnetic field of 25 mT for 5 min. Subsequently, 2 μL of this mixture are carefully pipetted and placed between a glass coverslip and a glass microscope slide. We checked that these manipulations did not affect filaments by performing similar experiments directly under the microscope.

Results and Discussion

Polymers can influence colloidal stability in several ways:^{13–15} (i) In good solvent, at high surface coverage, polymers grafted or adsorbed on the surface of colloids may stabilize them by entropic repulsion, a method extensively used in the colloid industry for inducing colloidal stability. (ii) At low surface coverage, adsorbed polymers may destabilize colloids and induce irreversible aggregation, by formation of bridges. (iii) The presence of polymers in the solution may, above a threshold concentration, induce reversible colloid flocculation owing to depletion effects: if two large magnetic particles approach one another, polymer coils are excluded from the region in between, leading to an uncompensated osmotic pressure within the depleted region.¹⁶ In systems dealing with adsorbed polymers, in which a thermodynamic equilibrium between adsorbed and free polymers exists, some of these different effects can coexist.

PAA is a water-soluble polyelectrolyte with $\text{p}K_a = 5.8$. In our experimental conditions, at pH 3.5 fixed by the PAA concentration, the polymer may be considered essentially neutral, and its radius of gyration is around 35 nm in a good solvent.¹⁷ We already reported¹⁸ that, at this pH, PAA adsorbs onto the particles. In the present paper, we first investigate the stability of our magnetic particles in the presence of PAA, screening PAA concentration (C_p), and particles volume fraction (ϕ) and look for the formation of aggregates (with no magnetic field applied). The behavior of the particle-polymer mixtures can be summarized by the phase diagram shown in Figure 1.

(14) Pelssers, E. G. M.; Cohen Stuart, M. A.; Fleer, G. J. *Colloids Surf.* **1989**, *38*, 15.

(15) Mondain-Monval, O.; Espert, A.; Omarjee-Rivière, P.; Bibette, J.; Leal-Calderon, F.; Philip, J.; Joanny, J.-F. *Phys. Rev. Lett.* **1998**, *80*, 1778.

(16) Vrij, A. *Pure Appl. Chem.* **1976**, *48*, 471.

(17) Bandrupp, J.; Immergut, E. G. *Polymer Handbook*, 2nd ed.; Wiley-Interscience: New York, 1975.

(18) Cohen-Tannoudji, L.; Bertrand, E.; Bressy, L.; Goubault, C.; Baudry, J.; Klein, J.; Joanny, J.-F.; Bibette, J. *Phys. Rev. Lett.* **2005**, *94*, 038301

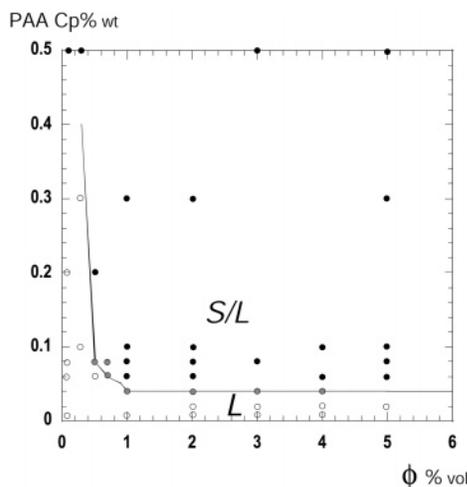


Figure 1. Phase diagram as a function of polymer concentration C_p and particle volume fraction. The different states of our samples are liquid (empty circles) and solid/liquid (full circles). The solid line denotes the onset of phase separation.

The diagram is divided into two zones by a transition line. In a first domain, the particles are Brownian and remain perfectly dispersed (L domain; Figure 2A); in a second one, the particles form aggregates coexisting with single Brownian particles (S/L domain). These aggregates (Figure 2B) seem dense and rigid (solidlike). If a solution above the transition line, for example, $C_p = 0.06$ wt %, is rapidly exchanged with water, aggregates disappear and a totally dispersed state is recovered, suggesting a reversible depletion-based aggregation. The transition line is independent of the particles volume fraction (ϕ) for $\phi > 1\%$. However, it is strongly ϕ -dependent for $\phi < 1\%$. This shape of the phase diagram suggests that aggregation is a consequence of depletion forces.¹⁹ One can evaluate the depletion energy at particle contact from¹⁶

$$U_c \cong -3/2k_B T \phi_{\text{poly}} \alpha / R_g \quad (\text{ref } 20)$$

where ϕ_{poly} is the PAA volume fraction, R_g is the radius of gyration (35 nm), and α is the particle radius ($\alpha \gg R_g$). This expression leads, for $\phi > 1\%$, to an energy $U_c \cong -3k_B T$ at the transition line, consistent with the expectation that the transition occurs when the droplet pair energy exceeds $k_B T$. For $\phi < 1\%$, entropy becomes important and aggregation occurs at higher interparticle interactions.

However, if starting from a high PAA concentration, for example, $C_p = 0.4\%$, the surrounding solution is exchanged back to a solution without polymer, numerous aggregates remain, and the reversibility of the aggregation, typical for depletion, is lost (Figure 2C,D). Aggregation probably involves a two-step mechanism: (1) aggregates are induced by depletion flocculation and (2) irreversible polymer bridging leads to the irreversible aggregation. A new phase diagram (Figure 3) can be drawn up taking into account the thermodynamical aspect (1) and the kinetic aspect (2) of the irreversible aggregates formation. Above the upper transition line, particles form irreversible aggregates that coexist with single Brownian particles (Sirr/L domain). Under the lower transition line, there are only single Brownian particles (L domain). Between these two lines, we find a region where aggregates are reversible (Srev/L domain). Interestingly, the position of the upper transition line depends on the particles/PAA incubation time: the longer the incubation time, the lower

the PAA concentration. The fact that the onset of irreversibility depends on both polymer concentration and incubation time is consistent with a mechanism involving bridging. To avoid any effect of this time-dependence in our data, all aggregation measurements are performed after a similar incubation time of 5 min.

Knowing the diagram of stability of particles in the presence of PAA, we now focus on the generation of magnetic filaments when this polymer is used to bridge them in the presence of a magnetic field. We operate as described above (Methods section).

Interestingly, in our conditions (no PAA/particles preliminary incubation time, magnetic field intensity ranging from 5 to 50 mT), it is impossible to generate filaments for a composition (C_p, ϕ) in the L domain. We also observe that the higher the polymer concentration (and as a matter of consequence the bigger the average size of the aggregates), the easier the filaments are formed. However, the presence of preexisting aggregates is detrimental to the production of filaments of uniform thickness so that a compromise must be made. We found the more appropriate PAA concentration to be 0.1 wt %.

At this concentration, a few aggregates are formed prior to applying a magnetic field, but they do not prevent the generation of uniform one-particle-thick filaments.

The fraction of particles involved in the magnetic filaments and the average length of the filaments depend on the strength and duration of application of the magnetic field, as illustrated in Figure 4.

A more detailed study of the kinetics of field-induced aggregation is beyond the scope of this communication and will be presented elsewhere.¹⁸ In short, the kinetics depends on the adsorbed PAA concentration: the kinetics is much more rapid if the PAA has been incubated only 10 min prior to applying the field than if the adsorption equilibrium is reached (after 20 h). This property has to be related with the repulsive barrier opposed by already adsorbed polymer chains to bridging.

We, thus, have independent means to control the morphology and the length of the filaments: the thickness is essentially defined by the chemical and physical properties of the solution (data not shown), whereas the duration and strength of the magnetic field control its length. When a suspension of magnetic particles ($\phi = 0.1$ vol %) is mixed with 0.1 wt % PAA and is immediately submitted to a 25-mT magnetic field during 5 min, magnetic filaments with an extremely uniform diameter of one particle and lengths of several hundreds of micrometers can be obtained (Figure 5).

Conclusion and Perspectives

This letter describes how to prepare irreversible magnetic filaments with molecules adsorbed at the surface of magnetic particles. The protocol is quite simple: all elements (i.e., magnetic particles, linkers) being initially present, the bridging is simply actuated by an external field.

We first established the phase diagram of particle/polymer mixtures in the absence of magnetic field. This phase diagram is the consequence of a balance between entropic repulsion between polymer layers at the particles surfaces, depletion forces pushing the particles together, and a short-range attractive force developing when polymers can bridge two particles. It involves three domains, a totally dispersed suspension of individual particles, a reversible aggregation domain, in which aggregates redisperse into individual particles upon dilution, and an irreversible aggregation domain, in which

(19) Meller, A.; Stavans, J. *Langmuir* **1996**, *12*, 301.

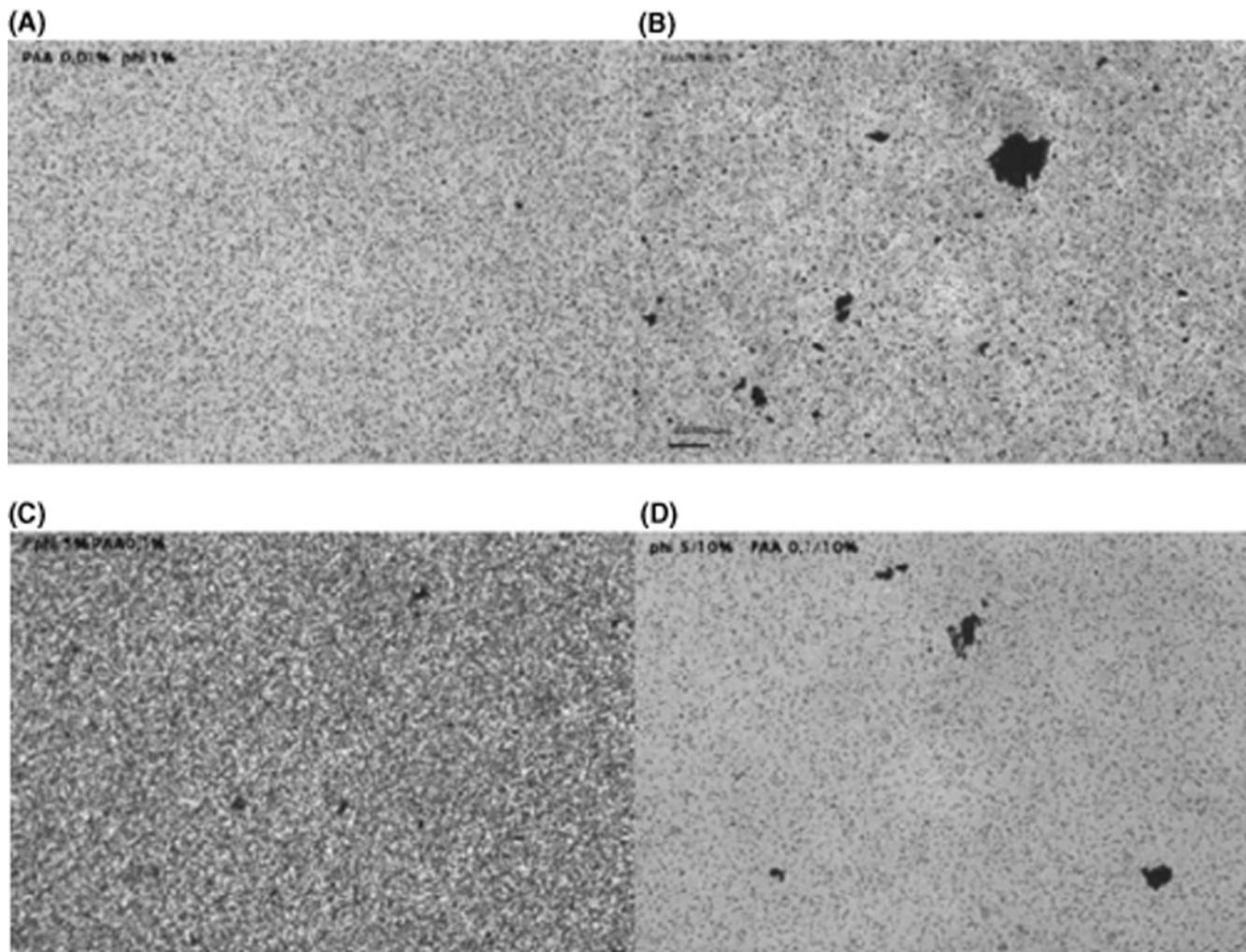


Figure 2. Stability of the particles versus polymer concentration. No magnetic field is applied. A: L domain, single Brownian particles ($\phi = 1$ vol %, $C_p = 0.01$ wt %). B: S/L domain, aggregates which coexist with single Brownian particles ($\phi = 1$ vol %, $C_p = 0.8$ wt %). C: Sirr/L domain aggregates which coexist with single Brownian particles ($\phi = 5$ vol %, $C_p = 0.1$ wt %). After dilution 10 times with pure water ($\phi = 0.5$ vol %, $C_p = 0.01$ wt %), aggregates remain (D).

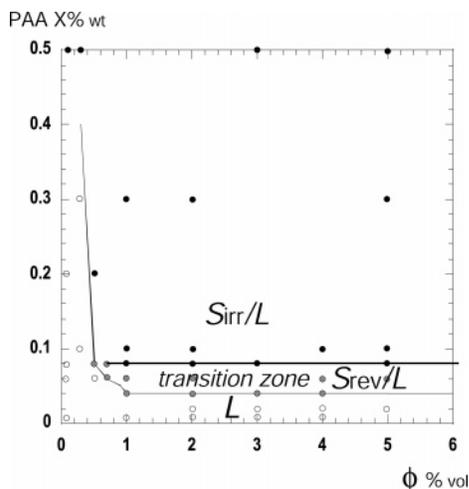


Figure 3. “Dynamic” phase diagram as a function of polymer concentration C_p and particle volume fraction. The different states of our samples are liquid (empty circles), irreversible aggregates/liquid (full circles), reversible aggregates/liquid (gray full circles). Solids lines denote the onsets of phase separation.

depletion forces push particles together strongly enough to promote bridging of neighboring particles by polymers. The phase diagram also exhibits a dependence on incuba-

tion times, related with the finite time that is necessary for overcoming the activation barrier for particle bridging.

Another interesting feature of this phase diagram is that the Sirr/Srev transition line, which marks the convenient domain for obtaining nice magnetic wires under moderate magnetic fields, is essentially independent of the magnetic particles concentration in a relatively large range of concentrations. Uniform polymer concentration is easy to achieve, but the concentration of magnetic particles is difficult to monitor and maintain precisely for long times. It is, thus, practically fortunate that only the polymer concentration has to be fixed to optimize magnetic aggregation.

Of course, different types of “stickers” will lead to different values, but we believe that the trends of the phase diagram measured here are quite general and that the qualitative conclusions drawn here will be applicable to a number of other situations. Recently, magnetic filaments were obtained by Bressy²³ using sodium caseinates, and we believe that the mechanism involved presents

(20) The expression has been established for a nonadsorbing polymer. Rigorously we should consider the adsorbed polymer quantity.

(21) Van Blaaderen, A. V. *Science* **2003**, *301*, 470.

(22) Goubault, C. Ph.D. Thesis, Université Pierre et Marie Curie, Paris, 2004.

(23) Bressy, L. Ph.D. Thesis, Université Pierre et Marie Curie, Paris, 2003.

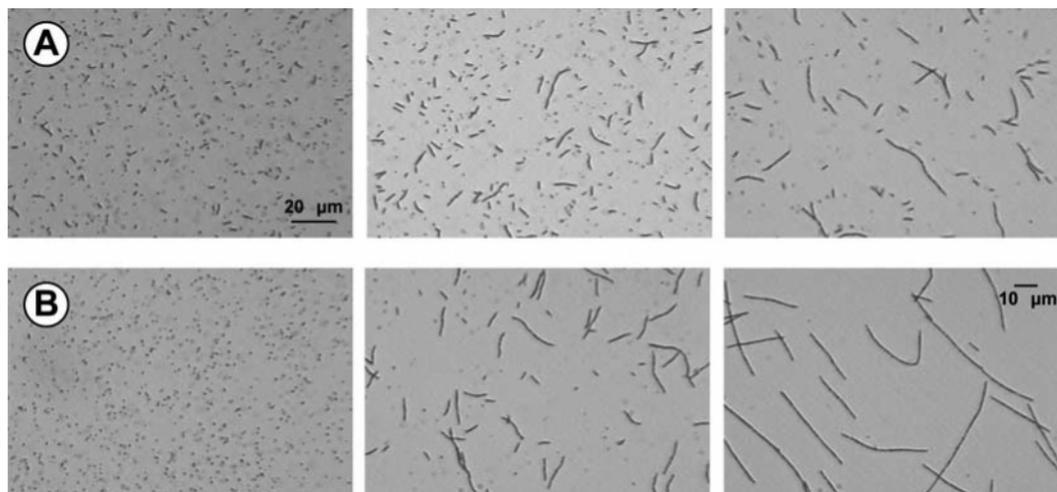


Figure 4. A: Filament length as a function of incubation time under a 10-mT magnetic field (respectively 30 s, 1 min, 2 min). B: Filament length as a function of magnetic field intensity (respectively 5 mT, 10 mT, 15 mT). The magnetic field is applied during 5 min. $\phi = 0.1$ vol %, and $X = 0.1$ wt %.

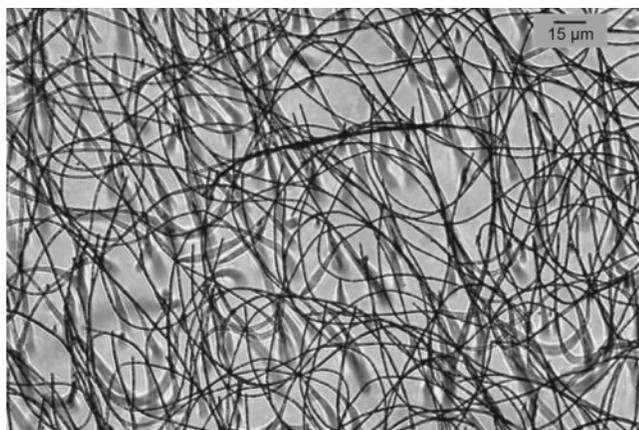


Figure 5. Long magnetic nanowires made by submitting a mixture of magnetic particles ($\phi = 0.1$ vol %) and PAA (0.1 wt %) to a 25-mT magnetic field during 5 min. The chains are bent by gravity after field removal.

some similarities with the one observed here, although caseinates present a more complex self-associating behavior than PAA.

Attempting to project to a further, although not so distant, future, we suggest that the linear magnetic wires described here and in a few earlier works^{9,12,18} extend the concept of “colloidal molecules”²¹ toward a new family of “colloidal macromolecules”. Taking inspiration from the formidable development of macromolecular chemistry in the last century, one may hope that “macrocolloids” with a rich variety of architectures, chemical compositions, and

properties are awaiting the imagination of researchers. The mechanical properties of some linear systems have been studied in earlier works^{9,18} and interesting biological application were proposed, but we believe this is only the beginning of a long story. Turning more to the materials science, for instance, one can also envision the possibility of preparing, by the development of suitable synthesis protocols, systems with more complex architectures, equivalent of the rich zoology of cross-linked polymers or copolymers. We found the bridging protocol proposed here particularly convenient, and also the one that provides so far the best quality of chains, in terms of regularity and aspect ratio. This particular bonding method is presently restricted to rather specific types of colloids. However, permanent chains made of beads with a polystyrene core^{9,22} and involving linkers made of biotin-streptavidin⁹ or caseinate²³ bonds were already demonstrated. Considering the present power of chemistry, it is reasonable to expect that chemists will be able to elaborate further innovative grafting protocols and extend both the range of colloids amenable to bead cross-linking and the physical and chemical properties of macrocolloidal objects.

Acknowledgment. C.G. thanks Pierre-Henri Puech for experimental advice and Emanuel Bertrand for fruitful discussion and careful reading of this manuscript. We are indebted to one of the reviewers for enlightening comments on the potential of colloidal polymers. This work was supported in part by the Ministry of Research “Genhomme” network, by CNRS “Microfluidics” programme, and by European RTD project NABIS (NMP4-CT-2003-505311).

LA0471442