

# Structural Control of Porous Polymeric Materials through Magnetic Gelation

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## ABSTRACT

In this work, we introduce a novel procedure to create porous polymeric materials using a process that we named magnetic gelation. The method starts with the preparation of magnetic polymer nanoparticles, composed of magnetite nanocrystals dispersed into a polymer matrix via miniemulsion polymerization. Due to the superparamagnetic behavior of the nanocrystals embedded in the polymer matrix, the nanoparticles prepared in this manner develop strong and reversible dipolar interactions only in the presence of an external magnetic field. Both the size of the nanoparticles and the amount of magnetite nanocrystals encapsulated inside them has been varied, so as to tune the strength of the magnetic interactions. Dispersions containing a few volume percentages of these magnetic nanoparticles, which are stabilized by means of electrostatic interactions, have been partially destabilized through the addition of controlled amounts of electrolytes and their self-assembly and gelation behavior in the presence and in the absence of an external magnetic field have been investigated. In the absence of magnetic fields, the particles self-assemble into random fractal clusters, which eventually percolate to form a colloidal gel. Instead, when an external magnetic field is applied, the particles align themselves in columnar structures in the direction of the field. By tuning the strength of magnetic interactions, different extent of anisotropy in the final material are obtained. The materials obtained through this magnetic gelation process have been hardened though partial fusion of the nanoparticles and characterized by means of electron microscopy.

**Keywords:** Magnetic Nanoparticles, Self-Assembly, Porous Materials, Gelation, Anisotropic Materials, Structure Control.

## 1 Introduction

Self-assembly is one the most used bottom-up approach for the preparation of materials with advanced functionalities [1]–[3]. Many efforts have been dedicated in the last ten years to design nanoparticles that can spontaneously arrange into desired structures. Spherical nanoparticles are probably the most commonly in-

vestigated type of building block, because an enormous variety of materials can be easily prepared in nanoparticulate form, with good control over size and surface functionality [2], [4]–[6]. Among the different types of particles, magnetic nanoparticles are especially interesting since they display anisotropic interactions and superparamagnetism [4], [7]. Thanks to the strong dipolar interactions that they can develop, magnetic nanoparticles have the tendency to align into strong-like structures in the presence of an applied magnetic field [8].

In this work, we introduce a novel approach, from now on referred to as magnetic gelation, which allows us to produce polymer porous monoliths with controlled anisotropic structures. Our strategy consists in extending the conventional colloidal gelation process, which generates a highly porous network of particles, to the case of magnetic nanoparticles assembled in the presence of a magnetic field. First of all, magnetic composite nanoparticles have been prepared by encapsulating magnetite nanocrystals through miniemulsion polymerization inside a polymer matrix. In this way, a suspension of electrostatically stabilized magnetic polymer colloids is produced, which are then swollen with additional monomers and initiator. Subsequently, monoliths were generated by destabilization of the magnetic nanoparticles suspension through an ionic strength increase in the presence of a magnetic field. The combination of isotropic attractive Van der Waals interactions, repulsive electrostatic interactions and magnetic dipolar interactions lead to the formation of a percolated network with controlled anisotropic structure. Mechanical stability was brought to these gels by a post-polymerization step, forming covalent bonds between the nanoparticles and leading to a rigid monolithic structure, according to a procedure developed by Butté et al. [9]. The effect of the strength of dipolar interaction on the anisotropy of the material has been investigated. Scanning electron microscopy have been used to assess the degree of anisotropy achieved.

## 2 Experimental Procedures

The synthesis of  $\text{Fe}_3\text{O}_4$  follows the coprecipitation method developed by Massart [10], with the only difference that ricinoleic acid was used as ligand to stabilize

the nanocrystals. The synthesis of monolaurylmaleate surfactant follows the method developed by Kozuka et al. [11].

100nm magnetic polymer colloids with 50 w% of magnetite were prepared by dissolving 0.5 g sodium monolaurylmaleate surfactant in 48 ml of water and by mixing 7.98 g styrene, 2.9 g diethyl ether 0.42 g divinylbenzene, 0.25 g hexadecane and 8.4 g magnetite. The two solutions were then mixed using a magnetic stirrer and ultrasonicated in an ice bath to obtain a miniemulsion. Then, 0.12 g KPS in 2 ml water were added before conducting the polymerization at 70°C for four hours. After that, the reaction mixture was cooled down to room temperature and filtered through a filter paper. The final dry fraction of the latex was 19.02%.

The preparation of 150nm magnetic polymer colloids with 20 w% of magnetite followed a similar recipe, but using 36 ml of water and 21.2 g styrene, 2.35 g divinylbenzene, 0.49 g hexadecane and 6 g magnetite. Directly after sonification, the emulsion was diluted so that the organic content decreased from 40% to 20% by adding a proper amount of a solution containing 0.023 g sodium monolaurylmaleate surfactant in 60 ml of water.

The gelation process follows the method developed by Gauckler et al. [12]. A stock swelling solution was prepared by mixing 9 g styrene, 1 g divinylbenzene and 0.1 g AIBN. The swelling of the latex was carried out as follows: an amount of the above solution equal to the 20% or 40% in weight of the dry fraction of the latex was added dropwise and mixed for 4 hours. Afterwards, 1 ml of the swollen latex was put inside the magnetic field and it was mixed with 0.5 ml urea solution(4 M) and 0.5 ml urease solution (960 units/ml), while the gel samples for magnetic torque measurements were prepared by mixing 0.5 ml swollen latex, 0.25 ml urea solution (4 M) and 0.25 ml urease solution (960 units/ml). The final weight percentage of the gel were 11.7% for the gel obtained from Latex 1, 9.5% for the gel obtained from Latex 2 and 12% for the gel obtained from latex 3. After the gelation the temperature was risen to 70°C and the postpolymerization was carried out for 24 hours in the presence of the magnetic field by means of a heating jacket.

### 3 Results and Discussion

The aim of this work is to develop a new method for the production of porous polymeric materials with anisotropic structures. In order to achieve this goal, and take advantage of the existing technology in the preparation of magnetic nanoparticles, we have chosen to exploit the natural tendency of colloidal particles to form percolating networks, called gels, when their colloidal stability is compromised in the presence of strong attractive interactions and their particle volume fraction is in the range of 1-30% volume percentage [13]. Among the different types of mechanisms that can be used to

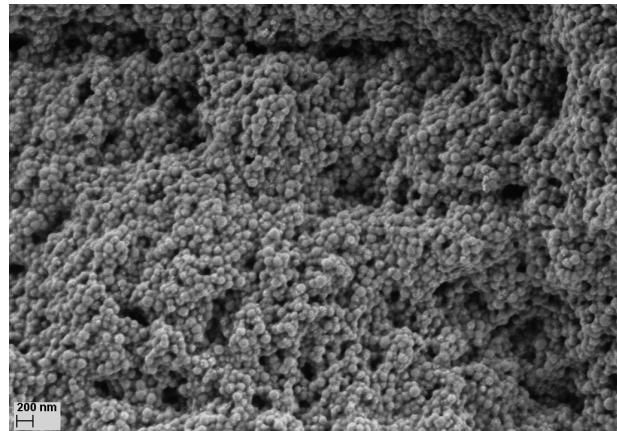


Figure 1: (a) SEM picture of a gel from latex 1 obtained in the absence of a magnetic field, showing no particles alignment.

induce the formation of colloidal gels, we have used the screening of electrostatic interactions on charged-stabilized colloidal nanoparticles, achieved by means of an ionic strength increase. By tuning the amount of charge stabilizing the nanoparticles, and the amount of electrolytes added, the kinetics of the gelation process can be regulated. The traditional colloidal gelation that has been utilized in this work has however been modified in two manners. First of all, we have used superparamagnetic nanoparticles, which can respond to the application of an external magnetic field by developing strong dipolar interactions. The second modification of conventional gelation process is the use of the reactive gelation process, developed by Butté et al. [9]. Since colloidal gels are usually very soft materials, the polymer latex nanoparticles are swollen with additional monomer and oil-soluble initiator prior to gelation. Once the gel is formed, the additional monomers are converted to polymer in order to link the nanoparticles with strong covalent bonds.

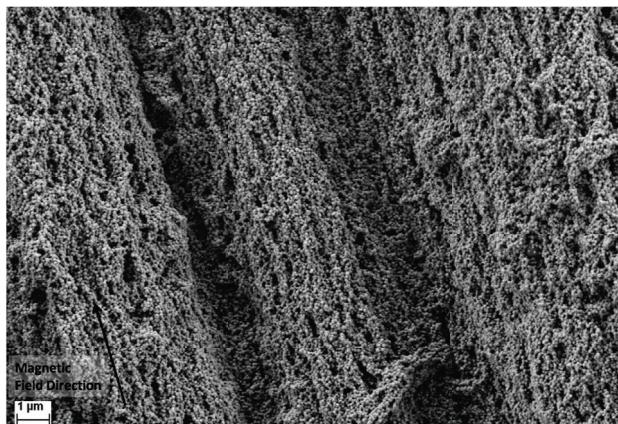
In order to avoid irreproducibility in the time required to reach the gel point and to improve the control of the gelation process a destabilization method developed by Gauckler's group [12] was used. This method uses the enzyme-catalyzed decomposition of urea, yielding one  $\text{Ca}^{2+}$  ion and two  $\text{NH}_4^+$  ions per molecule of urea, i.e. producing one double charged ion and two single charged ions from one neutral molecule, leading to an increase of the ionic strength and therefore to the electric double layer compression.

For the experiments carried out in this work two latexes were prepared that differ in magnetite content and particle size. All latexes were prepared via miniemulsion polymerization as explained in the Experimental section. The particle size and magnetite content (*i.e.* weight fraction of magnetite inside a particle) of the two latexes are different. The first latex (latex 1) has

an average diameter of 100 nm with a magnetite content of 50%. This latex has been produced with the aid of a volatile solvent. The solvent facilitates the dispersion of the high amounts of magnetite in the monomer phase and evaporates during polymerization. The second latex (latex 2) has an average diameter of 150 nm with a magnetite content of 20%, and was produced by a first creating a monomer-magnetite miniemulsion in water with a disperse phase weight fraction of 40%, followed by a dilution as described in the experimental section.



(a) low magnification

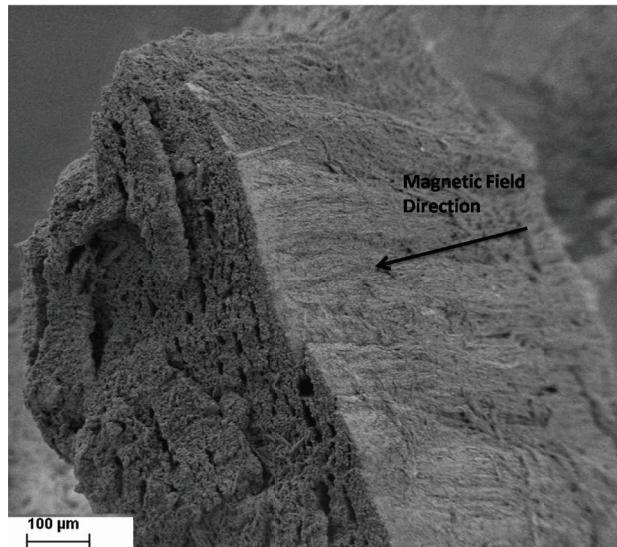


(b) high magnification

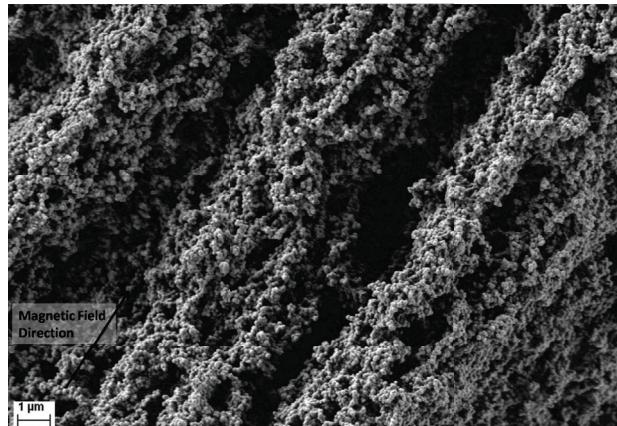
Figure 2: (a) and (b): SEM pictures of gel 2 at low and high magnification, respectively. Particles alignment is clearly visible in the SEM pictures. The direction of the applied magnetic field is indicated by the arrow.

Both latexes 1 and 2 were gelled in the presence of a magnetic field with a magnetic flux density of 1 T, yielding gels 1 and 2, respectively. For comparison purposes, Figure 1 shows the SEM picture of a typical gel obtained using latex 1 in the absence of a magnetic field. The structure of such a gel shows the expected disordered porous network of particles, without any anisotropy or specific particles alignment.

On the other hand, Figures 2(a) and 2(b) show two



(a) low magnification



(b) high magnification

Figure 3: (a) and (b): SEM pictures of gel 3 at low and high magnification, respectively. Particles alignment is clearly visible in the SEM pictures. The direction of the applied magnetic field is indicated by the arrow.

SEM pictures of gel 1, obtained from nanoparticles containing a high amount of magnetite (50w%). The SEM figures clearly reveal the presence of particles aligned into parallel fiber-like structures in the direction of the applied magnetic field. The strings are anyway not made of perfectly aligned particles, because of both the scrambling effect caused by diffusion and because particles are all of exactly the same size with the same amount of magnetite. The anisotropy of this material is anyway especially apparent in the low magnification picture, where the broken portion of the material shows an aligned side surface and a random front surface. The front surface was perpendicular to the magnetic field during gelation and has a random structure similar to that of the gel obtained in the absence of a magnetic field (see Figure 1).

Figures 3(a) and 3(b) show two SEM pictures of gel 2. Once again, clear anisotropic structures of particles aligned in strings are observed. 3(a) obtained at low magnification clearly indicates how the structure of the magnetic gels resembles qualitatively the structure of wood fibers. The structure of gel 2 can be qualitatively be compared to that of gel 1, shown in Figure 2. Gel 1 nanoparticles contain 50% magnetite and have a diameter of about 100 nm while gel 2 nanoparticles contain 20% magnetite with a diameter of 150 nm, giving comparable amounts of magnetite per particle. Both gels present qualitatively similar anisotropic structures with aligned strings in the direction of the applied magnetic field, despite the different characteristics of the latexes they are made of.

## 4 Conclusions

In this work we have introduced a novel and reliable method, which we named magnetic gelation, to produce porous polymeric monoliths with controllable anisotropic structure. This method is based on a bottom up approach composed of four steps. The first step is the production of magnetite nanocrystals stabilized with ricinoleic acid via salts coprecipitation in alkali solution. These nanocrystals are then dispersed, in a second step, in styrene so that after miniemulsion polymerization a stable magnetic latex is obtained. The suspension of magnetic nanoparticles is then swollen with additional monomer and initiator. The third step is the most important of the process, because it is the step where the monolith is obtained and its structure, in particular its anisotropy, is controlled. The latex is gelled in a magnetic field by increasing the electrolyte concentration via an enzyme catalyzed reaction. When the gelation process is carried out in the presence of a magnetic field, the alignment of the magnetic nanoparticles in the direction of the applied magnetic field can be controlled by tuning the intensity of the field. In this manner, the structure of the final porous monolith can be tuned by from fully isotropic and random, when diffusion becomes the dominating mechanism, to strongly anisotropic in one direction, with particles mostly aligned in bundles of strings. In addition to the intensity of the applied magnetic field, the anisotropy of the structure can also be controlled by varying the size of the particles and the amount of magnetite dispersed into them. All these factors affect the strength of the dipole-dipole interactions experienced by the nanoparticles. In the final fourth step, after gelation occurred, the structure is glued together by converting the remaining monomer and thus chemically crosslinking the bonds among the particles. The structure of the monoliths has been qualitatively characterized by SEM analysis. It has been shown that the produced monoliths have anisotropic structure in the direction of the applied magnetic field, whereas in the perpendicular di-

rection no alignment is observed and a random structure similar to that of a gel prepared outside a magnetic field is obtained.

## 5 Acknowledgments

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