Supplementary Material (ESI) for Soft Matter

Magnetic Gelation: a new method for the preparation of polymeric anisotropic porous materials. Supporting Data

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Experimental

Materials

Divinylbenzene technical grade (DVB), 2,2′-azobisisobutyronitrile purum $\geq 98\%$ (AIBN), Diethyl ether puriss, n-dodecanol $> 99.5\%$ and urease from jack beans 30.0 U/mg were obtained from Fluka. Urea pro analisis was obtained from Merck. Iron(II) chloride ReagentPlus 99% ($FeCl_2$), ricinoleic acid technical grade $> 80\%$ (RA) and acetone spectrophotometric $\geq 99.5\%$ were obtained from Sigma-Aldrich. Iron(III) chloride extra pure 99+% and *n*-hexadecane 99% (HD) were obtained from Acros Organics. Styrene general purpose grade (St) was obtained from Fisher Scientific. Potassium persulfate 99.0% min was obtained from Alfa Aesar. Maleic anhydride puriss. was obtained from Brunschwig Ag. Hexane 96% multisolvent was obtained from Scharlau. Sodium hydroxide was obtained from Brenntag Schweizerhall AG. Potassium persulfate (KPS) 99.0% min was obtained from Alfa Aesar. If not specified the chemicals were used as obtained.

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Instrumentation

In this work, the following instrumentation was used. The magnet used for decanting during magnetite production was a neodymium-iron-boron alloy (NdFeB) magnet from Webcraft GmbH, $40 \times 40 \times 20$ mm with a magnetic field strength of 0.20 T at the magnet's surface and 0.05 T at 3 cm distance from the surface. Magnetite nanocrystals were filtered using a separator consisting of two parallel plates, each containing three Neodymium-iron-boron alloy (NdFeB) magnets from Webcraft GmbH, measuring $40 \times 20 \times 10$ mm. The two facing plates had opposite polarization and the distance between them could be varied using a screw mechanism. A glass tube filled with a length of 15 cm steel wool was fixed between them. Inside the tube, the magnetic field strength was 0.17 T. Ultrasonication was performed using a Digital Sonifier S-450D from Branson. Mixing or dissolving was done using a Elma Transsonic 460/H sonication bath. Evaporation of solvents was achieved using a Büchi Rotavapor R-200 in conjunction with a Büchi B-490 heating bath and Büchi V-800 vacuum controller. Thermogravimetric measurements were done using a Mettler Toledo HG53 Halogen Moisture Analyzer. Magnetic field measurements were done using a 5180 Gauss Tesla Meter from F.W. Bell. Dynamic light scattering measurements were performed with a Zeta Nano ZN (Malvern Instruments, UK). The mean hydrodynamic diameter was obtained by fitting the autocorrelation function with the cumulant method, which also yields the polydispersity index (PDI), a measure of the width of the particle size distribution, defined as:[1]

$$PDI = \frac{R_4 R_6}{(R_5)^2} - 1 \tag{1}$$

where R_i is the i^{th} moment of the particle size distribution. The closer the values of PDI are to zero, the narrower is the corresponding particle size distribution.

TEM pictures were recorded by a FEI Morgagni 268, SEM pictures were recorded by a Zeiss Gemini 1530 FEG. All gel monoliths were cut into small pieces before SEM pictures, in order to facilitate the visualization of their internal structure. Electric conductivity of the solution was measured by a Mettler Toledo SevenMulti conductometer. The electromagnet used for the magnetic gel

preparation was a GMV Magnet Systems Model 5403 powered by a Sorensen DLM40-75E amplifier. Vibrating Sample Magnetometry (VSM) measurements were performed using a Princeton Measurements Corporation MicroMag 3900 Vibrating Sample Magnetometer. Magnetic torque measurements were carried out using a custom-built device capable of applying magnetic fields up to 1.5 T.[2] In order to carry out the measurements, cubic monoliths with a volume of 1 cm^3 were prepared. Each monolith was then put in a cylindrical sample holder and the magnetic torque experienced by the monolith was measured as the sample was rotated by 360°. The measurement was repeated by changing the axis of rotation of the sample, so that three measurements could be carried along three perpendicular directions of the sample. For samples prepared in the presence of an external magnetic field, one of the directions was always chosen to be the one along which the field was applied during preparation. In order to account for the torque experienced by the sample holder, a blank measurement with an empty cell was performed and the measured torque was subtracted from the torque measured in the presence of the sample. Additionally, the torque experienced by the sample at zero applied magnetic field was also subtracted.

Synthesis of magnetic nanocrystals

The synthesis of Fe_3O_4 follows the coprecipitation method developed by Massart,[3] and modified by others.[4–6] Magnetic nanocrystals were prepared by dissolving 3.9 g $FeCl_2$ and 10.71 g $FeCl_3$ (which gives a 1:2 molar ratio) in 180 ml water. Then 8.44 g ricinoleic acid (RA) were dissolved in 4.74 g acetone and added to the aqueous salt solution while stirring vigorously. After heating to 80 °C, 27 ml of 25% aqueous ammonia solution were added and the mixture was stirred for 30 min at 80 °C. For the recovery of the nanocrystals, 2 ml RA were dissolved in 400 ml acetone to produce an Ac-ligand solution. The magnetite was then washed twice with 100 ml pure acetone. Then, it was washed once with 20 ml water and 80 ml Ac-ligand. It was then washed three times with 50 ml water and 100 ml Ac-ligand. Finally, it was washed twice with 100 ml pure acetone. The washing was done by adding the specified amount of liquid to the magnetite, mixing for a few seconds using an ultrasound bath and then collecting the magnetite at the bottom of a beaker

by holding a strong magnet directly beneath it. When the solution became clear, the liquid was removed by decantation. After the washing, the magnetite was left to dry at air for 12 hours. It was then dissolved in 100 ml of diethyl ether and magnetically filtered through a length of 15 cm ethyl ether-cleaned steel wool in a magnetic field, using a standard procedure.[7] The steel wool was flushed with an excess of ethyl ether afterwards. The solvent was then evaporated using a Rotavapor.

Production of the sodium monolaurylmaleate surfactant

The synthesis of monolaurylmaleate follows the method developed by Kozuka et al.[8] In a first step, monolaurylmaleate was produced by dissolving 98.10 g maleic anhydride in 186.11 g *n*-lauryl alcohol and stirring for two hours at 80 °C. The solution was allowed to cool and 255.5 g were recrystallized from hexane, which corresponds to a yield of 89.9%. Secondly, sodium monolaurylmaleate was produced. 63 g monolaurylmaleate was dissolved in 46.38 g of acetone at 40 °C. 18 g of 50% aqueous sodium hydroxide solution were added dropwise with agitation at 60 °C. After keeping stirring for further thirty minutes at 60 °C, the solution was cooled to 0 °C and filtered. The obtained white, crystalline powder was washed with ice-cold acetone.

Synthesis of magnetic colloids

Three different latexes were prepared via miniemulsion polymerization. Below one can find the three recipes used. For all the experiments the sonication was carried out in the same way, with a sonication amplitude of 70% of the allowed maximum at a 0.5 cycle for 15 minutes effectively while stirring the solution at 250 rpm using a magnetic stirrer.

Preparation of Latex 1

The polymerization was prepared by dissolving 0.5 g sodium monolaurylmaleate surfactant in 48 ml of water and by mixing 11.40 g styrene, 0.6 g divinylbenzene, 0.25 g hexadecane, 3 g mag-

netite and 0.12 g AIBN. 2 ml of the surfactant solution were removed and stored for later use. The two solutions were then mixed using a magnetic stirrer and ultrasonified in an ice bath to obtain a miniemulsion. The 2 ml removed earlier were added to the emulsion directly after sonication. The reaction was then conducted 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 23.57%.

Preparation of Latex 2

The polymerization was 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 ultrasonified 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%.

Preparation of Latex 3

The polymerization was prepared by dissolving 0.29 g sodium monolaurylmaleate surfactant in 36 ml of water and 21.2 g styrene, 2.35 g divinylbenzene, 0.49 g hexadecane and 6 g magnetite were mixed. These two solutions were mixed using a magnetic stirrer and ultrasonified in an ice bath to obtain a miniemulsion. 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. 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 24.02%.

Gelation

The gelation process follows the method developed by Gauckler et al.[9] 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 solid weight percentage of the gels 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, corresponding to a particle volume fraction of 9.5%, 7% and 9.5% respectively . 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.

References

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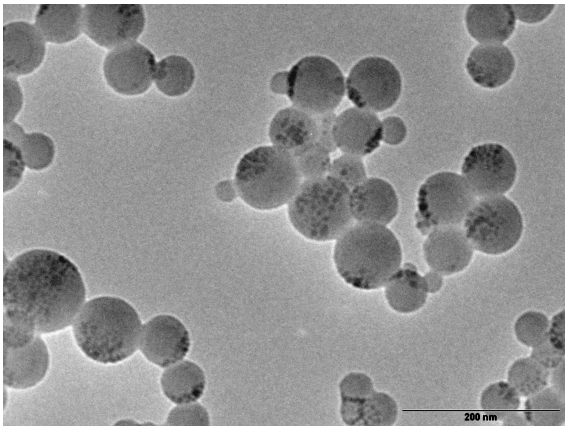
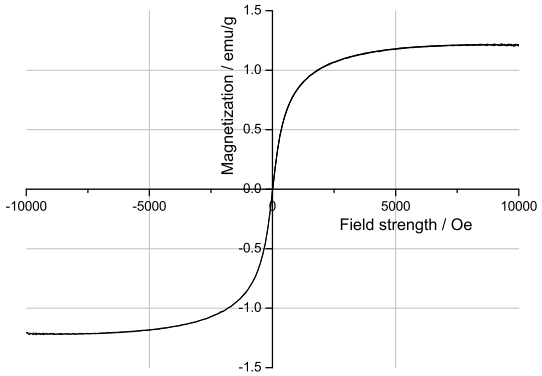
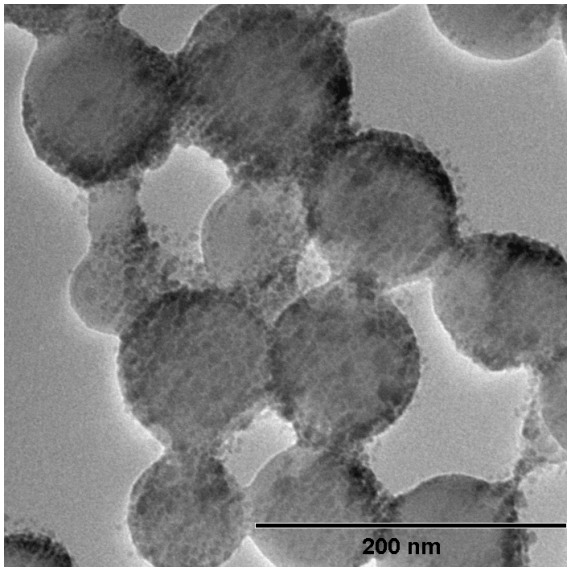


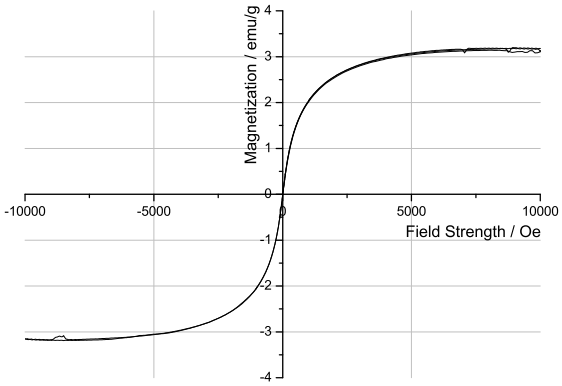
(a) TEM latex 1



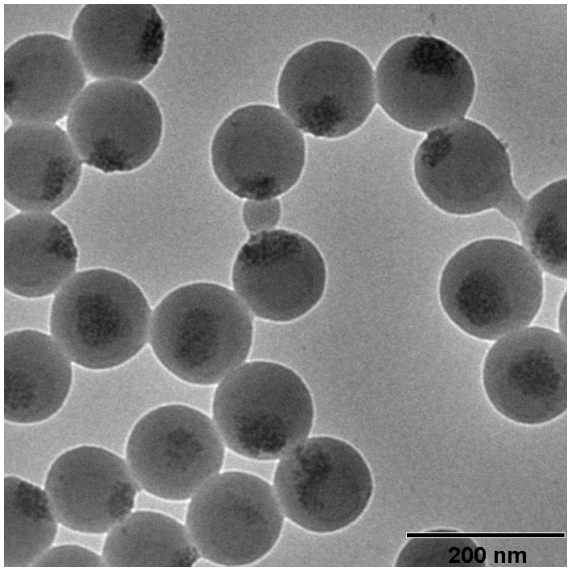
(b) VSM latex 1



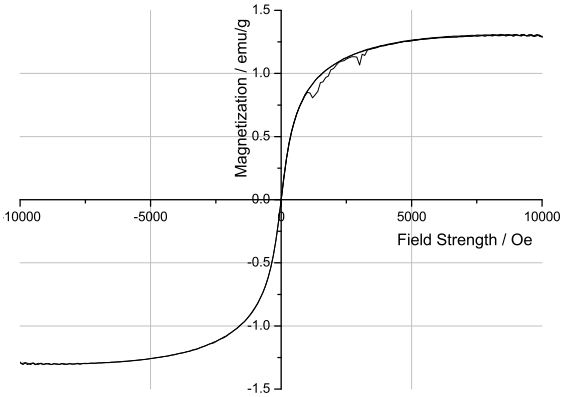
(c) TEM latex 2



(d) VSM latex 2

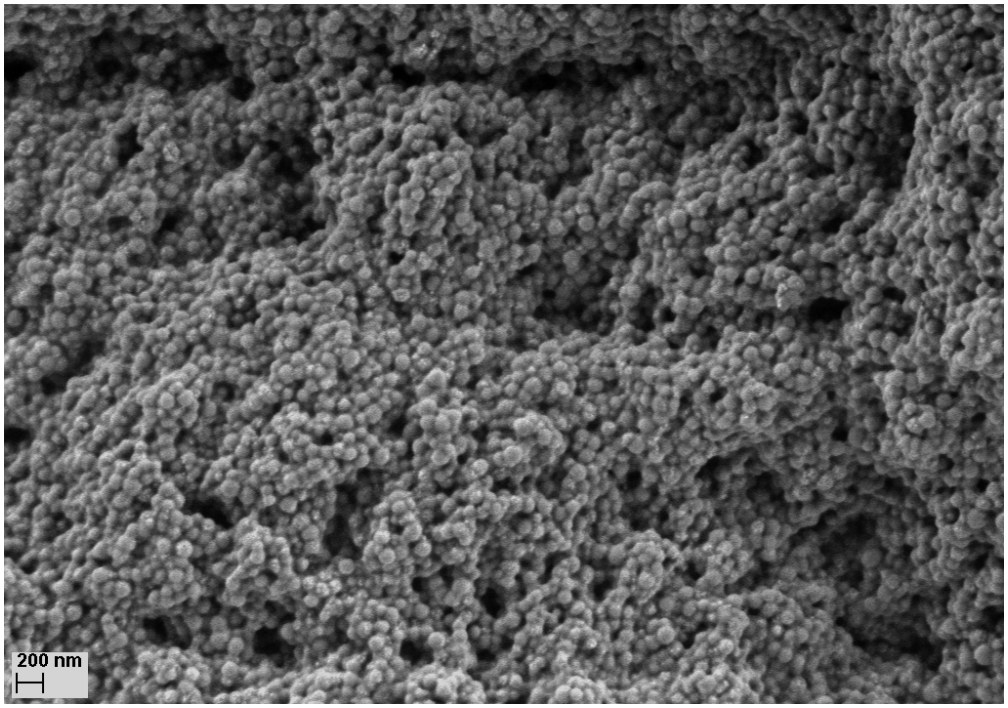


(e) TEM latex 3

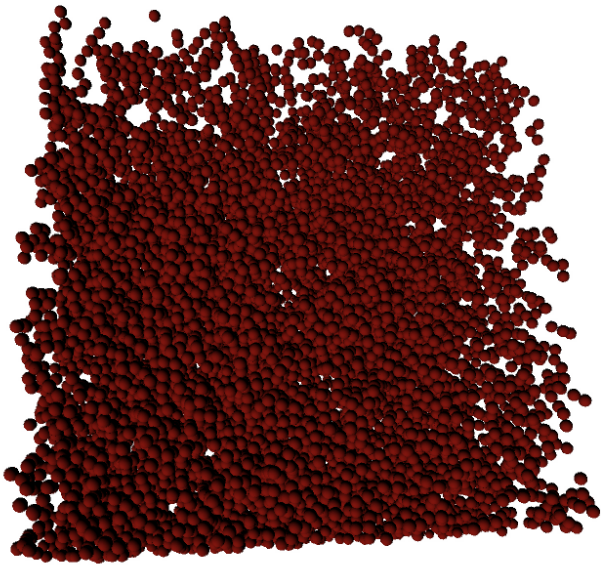


(f) VSM latex 3

Figure 1: TEM pictures and VSM measurements of latexes 1, 2, and 3.



(a) SEM picture



(b) Brownian Dynamic simulation

Figure 2: (a) SEM picture and (b) Brownian Dynamic simulation of a gel from latex 2 obtained in the absence of a magnetic field, both showing no particles alignment.