Magnetic Field Induced Polymerization of Molecularly Imprinted Polymers

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Abstract

In this work, we developed a novel approach to the preparation of molecularly imprinted polymer (MIP) coatings directly onto magnetic multicore nanoparticles (MMCs) by using alternating magnetic fields (AMFs) to trigger the polymerization reaction. MIPs were synthetized with rhodamine 123 (R123) as

model template molecule, methacrylic acid (MAA) as functional monomer and trimethylolpropane trimethacrylate (TRIM) as cross-linker. The amount of iron oxide nanoparticles and the composition of the polymerization mixture were optimized to enable the thermal polymerization of a thin MIP shell on each MMC by using electromagnetic heating without altering the properties of the recognition layer. The thickness of the polymerized MIP layer grafted onto the MMCs was fine-tuned by adjusting the dose of electromagnetic field (101.4 kHz, total power dissipation = 105 W). The resulting magnetic multicore MIP nanoparticles (MMC-MIPs) were characterized by FT-IR and X-ray diffraction spectroscopy, transmission electron microscopy and dynamic light scattering.

Introduction

Molecular imprinting involves the copolymerization of functionalized and cross-linkable monomers in the presence of a template molecule (usually the analyte or an analyte surrogate). The cavities formed after the template removal are tailor-made to be complementary in size, shape and functional groups to the target molecules. These engineered materials can be used as artificial recognition units capable of replacing antibodies, enzymes and other biological receptors in various applications including biomimetic sensors, chromatography, controlled drug delivery and catalysis.[1]

Nano- and micro-MIP structures have so far been prepared by using a number of techniques including electrical deposition, photolithography, microstereolithography, mechanical microspotting, soft-lithography, e-beam and electrospinning.[2-10] Nanocomposite MIPs are the result of including an inorganic material into the polymeric matrix in order to endow it with additional properties such as magnetic susceptibility or luminescence.[11-13] Incorporating superparamagnetic iron oxide cores, quantum dot microcrystals or metallic NPs, among others, has expanded the use of MIPs to several fields.[14] Magnetic MIP nanoparticles (MNP-MIPs) are especially promising in this respect because

using magnetic fields to remove nanocomposites from solution is often much faster, and more selective and efficient, than centrifugation or filtration.[15-16]

MIPs from magnetic cores can be grafted by free radical polymerization, usually with thermal or photochemical initiation, or by controlled/living radical polymerization (CRP).[13] Free-radical processes do not afford control of the size and architecture of the resulting macromolecules, or polymerization only around magnetic NPs. By contrast, CRP-based processes allow the production of more controlled polymeric network structures with effective molecular recognition properties around the magnetic cores. However, they involve several steps, use special reagents and are usually slower than classical radical polymerization.[15-17] Recently, Panagiotopoulou et al.[17] succeeded in preparing MIP-coated quantum dots (QDs) by using visible fluorescent light emitted by QDs upon excitation with UV light as an internal light source for photopolymerization. Also, they used visible-light ($NaYF_4:Yb^{3+}$, Er^{3+}) and UV-light ($Na_{0.6}K_{0.4}YF_4:Yb^{3+}$, Tm^{3+}) emitting upconverting nanoparticles as cores and excited them at 980 nm to obtain polymeric shells by photopolymerization.[18]

Inductive heating is a well-established method for raising the temperature of a conducting material locally with an alternating magnetic field (AMF). Electromagnetic heating usually results from Joule dissipation via eddy currents. This method is currently used for a variety of technological purposes ranging from aircraft applications[19] to graphene synthesis.[20] Magnetic hysteresis, which also causes energy losses – and hence heating – is an additional source of heating in magnetic materials.[21] This property has driven the use of magnetic nanoparticles (MNPs) to produce local heating in nanotechnological applications used as heat generators to induce localized tumour cell death under the action of high - frequency AMFs, a process known as *magnetic hyperthermia* and used in oncological nanotherapies.[22,23] MNPs have also been used to assist organic syntheses in flow reactors[24,25] to induce shape memory effects in thermoplastic polymers[26], in analytical separations and in curing polymeric materials[27], among other applications.[20,28-30] Recently, magnetic multicore nanoparticles (MMCs), also known as nanoflowers, have

been proven to show enhanced heating efficiencies compared to the single core nanoparticles[31,32]. These MMCs consist of densely packed MNP cores forming a larger particle. The magnetic cores of MMC are normally made of MNPs where magnetization reversal is mainly due to Neel relaxation. In the case of iron oxide, Nèel relaxation is dominant for particles smaller than 12 nm.[33] Consequently, these MMCs are much more heating efficient for applications where nanoparticles are immobilized, as in the case of magnetic field induced polymerization of MIP.

This paper reports a new approach to the production of molecularly imprinted polymers onto the surface of MMC-MIPs by using inductive heating to trigger the polymerization reaction. The process involves applying an external alternating current (AC) magnetic field to a solution containing iron oxide MMCs and the MIP pre-polymerization mixture under continuous mechanical agitation. MMCs are selectively heated by the alternating magnetic field, which causes the formation of a thin MIP layer onto their surface without altering the structure of the coated nanomaterial nor the properties of the MIP coating. The polymers were synthetized by using rhodamine 123 (R123) as model template molecule. As stated elsewhere,[4] non-covalent interactions of methacrylic acid (MAA) with the amino functional groups in R123 produce well-defined, high-affinity binding sites in the polymer network. This led us to choose MAA to prepare the MMC-MIPs. The monomer was used in combination with TRIM as cross-linker and acetonitrile as porogen. The MIP consisted of the template (T), functional monomer (FM) and cross-linker (CL) in a 1:8:8 mole proportion. Non imprinted magnetic multicores (MMC-NIPs) were prepared in the absence of the template.

Experimental

Reagents and materials

Rhodamine 123 (R123), rhodamine 6G (R6G) and fluorescein (FLU) were supplied by Acros (Geel, Belgium). Methacrylic acid (MAA) and trifluoroacetic acid (TFA) (HPLC grade, 99%) were from Fluka (Buchs, Switzerland). The initiator, 2,2-*azobis*(2,4-dimethylvaleronitrile) (ABDV), with an operating temperature of 50 °C, was purchased from Wako Specialty Chemicals (Neuss, Germany) and used without further purification.

Trimethylolpropane trimethacrylate (TRIM) was obtained from Sigma-Aldrich (St. Louis, MO, USA). Iron sulphate and boric acid were supplied by Panreac (Barcelona, Spain).

HPLC-grade acetonitrile (AcN) and methanol (MeOH) were purchased from SDS (Peypin, France), and HPLC water was obtained by purification through a Milli-Q system from Millipore (Bedford, MA). All solutions for HPLC were passed through a nylon filter of 0.45 μm pore size before use. HEPES was supplied by Aldrich (Steinheim, Germany).

Synthesis of Fe_3O_4 nanoparticles

The Fe_3O_4 MMC used were synthesized by using the solvothermal method. Briefly, an amount of 2.43 g of $FeCl_3$ $6H_2O$ was mixed with 6.48 g of sodium acetate and 1.58 mL of poliethyleneglycol in 72 mL of ethyleneglycol. The mixture was shaken at room temperature for 30 min and then transferred to two 50 mL teflon reactors that were heated at 190 °C for 24 h. The resulting black particles were washed twice with 250 mL of methanol and twice with 250 mL of water, removed from solution by using a permanent magnet and dried under vacuum at 50 °C.

MIP synthesis

The MIP composition was similar to that optimized in a previous work.[4] The template molecule (R123; 0.029 mmol), the functional monomer (MAA, 0.23

mmol), 10 mg of MMCs and 1.5 mL of acetonitrile were placed in a 250 µL insert of a 2.0 mL HPLC glass vial and shaken for 15 min. After adding TRIM (0.23 mmol) and 3 mg of the initiator (ABDV), the vial was capped with a rubber septum and the mixture purged with argon for 5 min. Then, the vial was placed inside a coil made from copper tube of 4 mm i.d. and cooled with water (Figure 2) for application of an electromagnetic field of 101.4 kHz (total power dissipation = 105 W). The high currents needed to obtain a high magnetic field and power were produced by having capacitor C1 in resonance with the combination of C2 and inductance (L) at the driving frequency ($\omega = 2\pi f$):

$$\frac{1}{C_1 \omega} = L\omega - \frac{1}{C_2 \omega}$$

With this configuration, currents exceeding 30 A could be induced in the coil and magnetic fields over 80,000 A/m (0.1 T) produced at high frequency. After polymerization, the template molecule was extracted by successive washing in ethanol (3 x 2 h). Finally, the coated NPs were dried in a vacuum oven at 50 ºC overnight. A non-imprinted polymer (NIP) was prepared in the same way except that no template molecule was used.

HPLC-UV analysis

The chromatographic system consisted of an HP-1200 series high performance liquid chromatograph (HPLC) from Agilent Technologies (Palo Alto, CA, USA) equipped with a quaternary pump, on-line degasser, autosampler, automatic injector, column thermostat and diode-array (DAD) detector. The dyes were quantified by using an Excel 2 C_{18}-PFP (2) column (100 x 2.1 mm, 2 µm size) from ACE (Aberdeen, Scotland). The mobile phase consisted of a mixture of 40% (v/v) AcN and 60% (v/v) water containing 0.1% TFA. Analyses were performed at a flow rate of 0.4 mL min^{-1} and a column temperature of 40 ºC. The injected volume was 10 µL and all dyes were eluted within 10 min. The UV-Vis absorption detector was set at 510 nm. For quantification, calibration standards were prepared by using the mobile phase to dilute an appropriate

volume of 200 mg L^{-1} dye stock solution in DMSO. All measurements were made in triplicate.

Physical characterization

The crystallographic structure of the MMC and MMC-MIP particles was examined on an X'Pert MPD X-ray diffractometer from Philips (Altmelo, The Netherlands) using CuK_{α} radiation (λ= 0.154 nm). Diffraction data were acquired over the 2θ range 5-75⁰, using room temperature, a step size of 0.015⁰ and a speed of 1 s $step^{-1}$. The morphology of MMCs was examined with a Jeol JEM 2100 TEM operating at 300 kV. Before measurement, the samples were dispersed in n-butanol and a drop of the resulting colloid was deposited over copper grids coated with holey carbon films. The hydrodynamic size (Z-average size) of the NPs was determined by (Dynamic Light Scattering) DLS with a Zetasizer Nano ZS (Malvern Instruments, Herrenberg, Germany) operating in the back-scattering mode at 173⁰ with a He-Ne laser beam (λ = 632.8 nm) at 25 ⁰C. FTIR spectra were measured in an Alpha ATR infrared spectrophotometer from Brucker (Billerica, MA, USA) equipped with a DTGS detector from Microwatt (Stuart, FL, USA). The samples were measured in ATR mode, on a single-pass Ge cristal.

A Superconducting Quantum Interference Device (SQUID) from Quantum Design (San Diego, CA, USA) was used to assess the magnetic properties of the nanoparticles before and after polymerization. Hysteresis loops were measured at room (300 K) and low (10 K) temperature. The thermal dependence of magnetization was also assessed, using field-cooled (FC) and zero-field (ZFC) conditions with a magnetic field of 100 Oe for both cooling and measuring.

Equilibrium rebinding experiments

MIP/NIP-coated MMCs (10 mg) were weighed separately into 1.5 mL HPLC glass vials for mixing with 1 mL of acetonitrile containing increasing

concentrations of R123 over the range 0.003-2.0 mM and stirred at room temperature in the dark for 24 h. The concentration of free analyte (F) remaining in the supernatant after incubation was determined by HPLC-DAD. The amount of polymer-bound analyte (B) was calculated by subtracting that of non-bound analyte (F) from the initial analyte concentration in the mixture. Thirteen experimental points per binding isotherm were recorded. Adsorption kinetic experiments were carried out by shaking a mixture of 1 mL of a 1 mg mL^{-1} R123 solution in acetonitrile and 10mg of MMC-MIP/NIPs at room temperature for 1-140 min after magnetic separation. The concentration of R123 in the supernatant was then determined by HPLC-DAD to estimate the amount of MMC-bound R123.

Results and discussion

Synthesis of the MMC-MIPs

The composition of the polymerization mixture was optimized by determining the amount of MMCs needed to induce local heating and trigger the polymerization, and the solvent-to-total monomer concentration for polymerization. The resulting magnetic MMC-MIP/NIPs were characterized by XRD, TEM and DLS, and their performance in the selective extraction of R123 was assessed from equilibrium rebinding measurements. In a preliminary experiment, the amount of Fe_3O_4 MMC in the pre-polymerization mixture was varied from 1 to 20 mg, and the volume of porogen (acetonitrile) was calculated by using a $V_{ACN}/(V_{ACN} + V_{total\ monomers})$ ratio of 0.57-0.95. No polymerization was observed with less than 10 mg of Fe_3O_4; also, amounts of 20 mg or greater led to the formation of a bulk polymer.

In a second experiment, the amount of MMCs was kept constant at 10 mg and the $V_{ACN}/(V_{ACN} + V_{total\ monomers})$ ratio varied from 0.57 to 0.95 in order to assess its influence on the textural properties of the resulting polymer.[34] These values

were selected in terms of previously reported ratios for preparing bulk polymers[29], MIP nanoparticles[35] or MMC-MIPs.[36] As can be seen from Table S.1 (Supplementary Information), $V_{ACN}/(V_{ACN} + V_{total\ monomers})$ ratios lower than 0.65 resulted in the formation of a bulk polymer, whereas values over the range 0.75 - 0.90 led to a gel-like polymer. Only a $V_{ACN}/(V_{ACN} + V_{total\ monomers})$ ratio of 0.95 allowed MMC-MIPs to be obtained.

The formation of an MIP thin layer on the surface of the MMCs requires a high enough local temperature to start the polymerization reaction by homolytic cleavage of a covalent bond in the azo initiator. Also, a large temperature gradient between the surface of the MMCs and the bulk liquid must be established. Otherwise, polymerization occurs not only on particle surfaces but also in solution, thereby favouring coalescence between particles. The effect of the polymerization time on the size and dispersity of the MMC was assessed by DLS. As can be seen in Table S.2, the diameter of the MMC-MIPs, as well as the polydispersity index, increases with the polymerization time.

Morphology and structure of the core-shell nanostructures

Figure 3, which compares the XRD patterns before and after 1h of polymerization by inductive heating, allows to confirm whether the polymerization conditions altered the structure of the MMCs. The diffraction patterns exhibited well-defined diffraction maxima indexed to 220, 311, 400, 422, 440 and 511 reflections both before and after polymerization. These reflections are typical of the cubic inverse-spinel structure of magnetite (JCPDS card no. 19-0629 for Fe_3O_4). The peaks after polymerization are less defined and wider because the presence of the polymeric layer surrounding the nanoparticles makes the signal to noise ratio worse. This is also the reason why the (422) reflection, the less intense one, cannot be resolved after polymerization.

It is thus obvious that neither magnetic inductive heating nor formation of the MIP layer on the MMCs caused any phase change in the iron oxide NPs. The average crystallite size of the uncoated MMCs and MMC-MIPs as determined from Scherrer's formula $(D = K\lambda/\beta\cos\theta)$[37] was estimated to be 10.8 and 11.7 nm, respectively. The crystal lattice parameter was not significantly altered by coating (0.839±0.002 and 0.838±0.002 nm before and after polymerization, respectively); also, it was similar to that for standard magnetite (a = 0.8396 nm).

The chemical composition of the polymer-coated iron oxide MMCs was determined by FT-IR spectroscopy. Figure 4 shows the spectra for MMCs and the MMC-MIPs. Polymer coating did not alter the position of the strong band at ca. 588 cm^{-1} – which was assigned to the characteristic absorption of Fe-O bond stretching vibration – but decreased its intensity.

The band at ca. 1620 cm^{-1} was assigned to bending vibrations of adsorbed water on the surface of the iron oxide cores. The broad band at 3432 cm^{-1} also reflects the presence of water molecules on the MMC surface[38]. The spectra for the MMC-MIPs exhibited vibrational bands at 1467 cm^{-1} (C-H and H-C-H bending) and at 2963 cm^{-1} (C-H stretching vibrations in -CH3 and -CH2 groups). On the other hand, the band at 1467 cm^{-1} can be assigned to bending vibrations in C-H and H-C-H bonds. The absorbance peak at 1732 cm^{-1} corresponds to stretching vibrations in C=O bonds and the broad peak around 3434 cm^{-1} to O-H stretching vibrations in carboxyl groups. Finally, the bands at 1261 and 1150 cm^{-1} correspond to symmetric and asymmetric stretching in C-O bonds.

Figure 5 shows the TEM images for as-prepared MMC as well as and MMC-MIPs after 15 and 60 min of magnetically induced polymerization. The micrograph of as-prepared MMCs (Figure 5.a) confirms the structure of multicore, *i.e.* cores of 10 nm in diameter densely-packed in a particle of approximately 60 nm.[39,40] The micrographs taken in MMC-MIPs (Figures 5.b and 5.c) confirms the formation of an imprinted shell on the surface of the MMC. The images reveal also an increase of particle aggregation as polymerization time increases.

As derived from the structural characterization, inductive heating allows one to produce ferromagnetic nanostructures coated with polymeric films of controlled thickness without significantly altering the structure of the nanoparticles.

Magnetic properties

The strong magnetic field applied and the high temperature achieved around the MMCs made it advisable to check whether the magnetic properties of the ferromagnetic iron oxide nanoparticles were changed by effect of the polymerization process. Figure 6 summarizes the magnetic properties of the nanoparticles before and after 120 min of polymerization.

The hysteresis loop for the initial nanoparticles (before polymerization) at room temperature is typical of a superparamagnetic material – no coercivity or remanence is observed. On the other hand, the low-temperature loop is typical of a ferromagnetic material (the coercive field was 117 Oe and the remanence ratio, M_R/M_S, 0.15) (see Figure 6.a).

The magnetic behavior after polymerization (Figure 6.b) was qualitatively identical: the core shell nanoparticles were superparamagnetic at room temperature but exhibited coercivity and remanence at a low temperature. Saturation magnetization was considerably lower (11.1 emu/g versus 70 emu/g at room temperature). This was clearly the result of polymerization: only the core contributed to the magnetic signal but both the ferromagnetic core and the polymeric shell contributed to the mass, which resulted in decreased saturation magnetization. There were also slight changes in remanence and coercivity at a low temperature. Both exhibited a small increase possibly due to a slight crystallization of the cores. A comparison of the hysteresis loops clearly reveals that, as expected from the structural analysis, the magnetic properties of the MMCs were not affected by the polymerization process.

The thermal evolution of magnetization before and after polymerization (Figure 6.c) was also very similar. In both cases, FC and ZFC converged immediately

above room temperature, which confirms that the blocking temperature did not change by effect of polymerization. A blocking temperature close to the room temperature confirms that the iron oxides cores of 10 nm inside the MMC are strongly interacting due to the dense packing in the MMCs.[41]

Adsorption kinetics

The kinetic characteristics of R123 adsorption on the MMC-MIPs and MMC-NIPs (Figure 7) were analysed by using the pseudo first-order[42] and pseudo second-order[43] kinetic models to examine the experimental data. The statistical criterion used to assess the goodness-of-fit of the models was the coefficient of determination (r^2).

In the pseudo first-order equation, diffusion is the rate-limiting step for adsorption and the reaction kinetics can be expressed as follows:

$$[A] = [A]_0 e^{-k_1 t} \qquad (2)$$

where [A] is the concentration (mg g^{-1}) of R123 adsorbed at contact time t, [A]$_0$ the initial concentration of R123 and k_1 (1/min) the equilibrium rate constant of pseudo first-order sorption. The adsorption half time, $t_{1/2}$, can be expressed as:

$$t_{1/2} = \frac{-\ln 0.5}{k_1} \qquad (3)$$

The pseudo second-order kinetic model conforms to the following equation:

$$[a] = \frac{[A]_0}{\frac{1}{[A]_0 k_2 t} + 1} \qquad (4)$$

where k_^{2} (g mg^{-1} min^{-1}) is the rate constant of pseudo second-order adsorption, from which the adsorption half time can be calculated as follows:

$$t_{1/2} = \frac{1}{k_2 [A]_0} \qquad (5)$$

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As can be seen, the adsorption half time, $t_{1/2}$, was invariably much smaller for the imprinted polymer than it was for the non-imprinted polymer.

Table 1: Pseudo first- and second-order constants

	Pseudo first-order kinetic model				Pseudo second-order kinetic model			
	$[A]_0$	$K_1 \times 10^1$	$t_{1/2}$	r^2	$[A]_0$	$K_2 \times 10^3$	$t_{1/2}$	r^2
	mg g^{-1}	min^{-1}	min		mg g^{-1}	min^{-1}	min	
MMC-MIP	95.76	1.77	3.92	0.980	107.84	3.91	2.17	0.997
MMC-NIP	93.67	0.08	43.54	0.950	98.17	0.13	88.1	0.990

Table 1 summarizes the kinetic results for R123 adsorption onto the MMC-MIPs and MMC-NIPs and Figure 7 is a plot of *[A]* versus *t*. As can be seen from the table, the corrected correlation coefficients (r^2) for the pseudo second-order kinetic model were higher than those for the pseudo first-order model. Therefore, the adsorption of R123 onto MIP/NIP is accurately described by the pseudo second-order model and the rate of the process may be governed by chemical adsorption, specific surface area and the absence of internal diffusion resistance.[38]

As can be seen from Figure 7, approximately 85% of the initial concentration of R123 was adsorbed by the polymer within 15 min. Adsorption levelled off after 50 min, however. These results suggest that the imprinted cavities with the highest affinity for R123 were those at the surface of the MNP-MIPs, which facilitated access by the template. Equilibrium was thus reached faster. Also, the rate constant for the MIP was always higher than that for the NIP irrespective of fitting model.

Determination of the binding site distribution and affinities

The binding properties and uniformity of binding sites in the MMC-MIPs were established in equilibrium binding experiments.[44] The experimental data were fitted to the Freundlich (FI) isotherm model:[45]

$$B = \alpha F^m \qquad (6)$$

where B and F are the concentrations of bound and free R123, respectively; and α is a fitting constant related to the number of binding sites in the polymer (N_T) and their average affinity for the guest (K_0). The heterogeneity index of the polymer was represented by m, which decreased from 1 to 0 as the heterogeneity of the binding sites increased. These parameters were calculated from a plot of log B versus log F.[45]

$$\overline{K}_{K1-K2} = \left(\frac{m}{m-1}\right)\left(\frac{K_1^{1-m}-K_2^{1-m}}{K_1^{-m}-K_2^{-m}}\right) \qquad (7)$$

The apparent number of binding sites per gram of material, N_{K1-K2}, and the average apparent association constant, $\overline{K}_{K1-K2}$, as derived from Rampey's equations (equations 6 and 7) are shown in Table 2.[46]

Figure 8 gathers the experimental data. The apparent number of binding sites for R123 in the MMC-MIPs (37 ± 2 μmol g^{-1}) was significantly large relative to the non-imprinted polymer (NIP) (17 ± 2 μmol g^{-1}). This was also the case with the average apparent association constant (30 ± 3 versus 13 ± 1 mM^{-1}). Therefore, the particles were indeed imprinted with the polymer.

The selectivity of the imprinted material was assessed from the equilibrium binding isotherms for rhodamine 6G, a structurally related analogue, and for fluorescein, an unrelated compound. The fitted data are shown in Table 2. In both cases, the MMC-MIPs exhibited a higher analyte binding capacity than did the corresponding NIPs which showed similar retention of all target compounds.

Table 2. Freundlich fitting parameters, weighted average affinity ($\overline{K}_{K1-K2}$) and total number of binding sites (N_{K1-K2}) for the selected analyte in the MNP-MIPs and MNP-NIPs (13 data points per binding)

Polymer / coated MMC	m	a μmol g^{-1}(mM^{-1})^m	$\overline{K}_{K1-K2}$ mM^{-1}	$\overline{K}_{range}$ mM^{-1}	N_{K1-K2} μmol g^{-1}	r^2
R123/MIP	0.69±0.06	64±4	30±3	0.85-7513	37±2	0.998
R123/NIP	0.74±0.05	27±2	13±1	0.63-2501	17±2	0.997
R6G/MIP	0.61±0.04	39±2	16±1	0.64-1051	31±2	0.998
R6G/NIP	0.70±0.05	25±3	10±1	0.59-781	18±2	0.996
fluorescein/MIP	0.60±0.04	34±3	16±1	0.67-892	27±2	0.996
fluorescein/MIP	0.68±0.04	23±3	10±1	0.61-531	17±2	0.998

However, the average apparent association constant for R123 in the MIP was almost twice those for the other dyes and the total number of binding sites was also greater for R123, which testifies to the selectivity of the imprinted material for the target template and the efficiency of the imprinting process. The heterogeneity parameter was always higher for the NIP than for the MIP, which reflects a lower heterogeneity of the material.

Conclusions

As shown here, applying a high-frequency magnetic field increases the local temperature on the surface of MMCs and allows the production of polymer-coated MMCs in a short time. In comparison with existing methods for the synthesis of MMC-MIPs the proposed methodology is simpler, as it does not require several reaction steps, faster and polymerization occurs only on particle surfaces not in solution. The characteristics of the resulting polymer layer are

considerably influenced by the size and density of magnetic cores in the pre-polymerization solution. MIP-coated MMCs exhibited good selectivity and fast binding kinetics. This novel approach could therefore be useful to prepare MIPs selective towards photolabile or thermolabile templates. We are currently testing the applicability of this this polymerization method to deposit uniform polymer coatings onto other magnetic nanostructures such as nanowires (NWs).

Supporting Information Available

Information on the ratio for polymerization of the MMC-MIPs is included as Supporting Information.

Acknowledgement

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Figure captions

Figure 1: Chemical structure and acronyms of the template molecule (rhodamine 123) and the other fluorescent molecules included in the study.

Figure 2: Experimental set-up used to synthesize magnetic nanostructures. C_1 and C_2: capacitors. L: inductance.

Figure 3: XRD pattern for the MMCs before and after MIP coating. Both spectra are corrected from background. The diffraction maxima are indexed as reflections typical of the cubic inverse-spinel structure of magnetite (JCPDS card no. 19-0629).

Figure 4: FTIR spectra measured in bare Fe_3O_4 NPs (red dashed lines) and MMC-MIPs (blue dashed lines).

Figure 5: Transmission Electron Microscopy images of a) as-prepared MMCs, b) MMC-MIPs after 15 min of polymerization and c) MMC-MIPs after 60 min. of polymerization.

Figure 6: Hysteresis loops measured at room and low temperature for MMCs (a) and MMC-MIPs (b). FC-ZFC curves measured for the same sets of nanoparticles as (a) and (b) panels.

Figure 7: Adsorption kinetics of R123 by the MNP-MIPs (blue circles) and MNP-NIPs (red triangles). Values estimated by assuming first-order kinetics (dashed line) and second-order kinetics (solid line).

Figure 8: Equilibrium binding isotherms for the uptake of R123 (blue circles), R6G (red diamonds) and fluorescein (green squares) in the MMC-MIPs (solid line) and MMC-NIPs (dashed line). Experimental data were fitted to the Freundlich (FI) isotherm model.