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Synthesis of iron oxide-armored latex particles by Pickering emulsion polymerization using 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) as auxiliary comonomer

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TOC graphic



ABSTRACT

Iron oxide (IO)-armored poly(methyl methacrylate) (PMMA) and polystyrene (PS) latex particles have been synthesized by surfactant-free emulsion polymerization using 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) as auxiliary comonomer. The use of pure water as dispersion medium led to unstable latexes both in the presence and absence of IO nanoparticles. In stark contrast, successful syntheses were achieved with the addition of ethanol (15 vol% based on water) to the suspension medium. Transmission electron microscopy showed well-defined "armored" structures with the IO nanoparticles located at the latex surface forming the so-called raspberry-like morphology. The reported strategy allowed the preparation of polymer/IO composite particles with up to 96 % IO incorporation efficiency and 60 % IO coverage of the latex surface. The effect of the nature of the core monomer, as well as the AMPS and IO contents on the polymerization kinetics, particle size and morphology, was studied in detail. The final nanocomposite particles possess superparamagnetic properties with high magnetic response, enabling their rapid and efficient separation under an external magnetic field. A mechanism for the formation of the IO-armored latexes is proposed.

INTRODUCTION

Superparamagnetic iron oxide (IO) nanoparticles can be employed in many biological applications such as magnetic resonance imaging (MRI),¹⁻⁴ targeted drug delivery,^{2, 5-7} hyperthermia,⁸⁻¹⁰ tissue repair,^{2, 10} cellular labeling and cell separation.^{10, 11} In most cases, it is necessary to modify the surface of the particles to achieve stability, biocompatibility and/or impart additional functionality. While many efficient methods have been developed to coat magnetic nanoparticles with natural or synthetic polymers,¹²⁻¹⁸ only few studies have reported the opposite architecture, i.e., the formation of polymer particles surrounded by magnetic nanoparticles.¹⁹ Such particles could find however interest in the removal of toxic elements from wastewater,^{20, 21} in enhanced oil recovery,²² as supports for catalysis,^{23, 24} and for biomedical applications.²⁵

The formation of polymer latex particles coated with a layer of inorganic solids can be obtained by two distinct methods.²⁶⁻²⁸ The first and most reported strategy involves the formation of socalled Pickering emulsions that are subsequently polymerized. There are numerous studies in the literature reporting the synthesis of IO-coated polymer particles using this solid-stabilized Pickering emulsion technique. However, the obtained composite particles are generally very large²⁹⁻³⁴ unless the monomer mixture is emulsified using high-shear devices to form miniemulsion droplets and submicronic latexes.³⁵⁻³⁷ Furthermore, these processes are difficult to scale-up, hampering potential industrial applications. As an alternative approach to the polymerization of Pickering (mini)emulsions, inorganic solids can also be directly employed as "Pickering" stabilizers of conventional emulsion polymerization reactions, replacing molecular surfactants. Numerous studies involving various inorganic particles and synthetic strategies have now been conducted in this area, opening the door to composite particles and coatings with a wide range of potential applications.³⁸⁻⁵⁶ The corresponding process, called "Pickering emulsion polymerization", has indeed many advantages. The size, composition and functionality of the polymer particles can be tuned easily by varying experimental conditions. In addition, the synthesis requires only a minimum number of ingredients, and in particular no molecular surfactant is left in the suspension (at the inorganic surface or in solution), making this method a valuable approach for the design of new and highly performant materials. Despite the surge of interest in the use of inorganic particles as solid stabilizers of surfactant-free emulsion polymerization processes, only little attention has been paid to IO particles.⁵⁷⁻⁵⁹ Xu et al.⁵⁷ reported the successful formation of magnetic polystyrene microspheres using 2,2'azobis(2-methylpropionamide) dihydrochloride (V50) cationic as initiator and poly(methacrylic acid) (PMAA)-functionalized IO nanoparticles as Pickering stabilizer. Electrostatic interaction between the amidine group of V50 and the carboxylate anions of PMAA under basic conditions was key in obtaining stable composite particles with the targeted raspberry-like morphology. Li et al.⁵⁸ reported the synthesis of acrylic and styrenic composite latex particles with a patchy IO overlayer through surfactant-free emulsion polymerization, using (meth)acrylic acid (MAA or AA) as auxiliary comonomer. The role of the latter was to favor in situ interactions of the inorganic particles with the latex surface. The particle morphology and the success of these syntheses were highly dependent on the composition of the monomer mixture and their reactivity ratios. The suspension pH was also shown to be a key parameter, influencing the interaction of the auxiliary comonomer with the IO surface, and hence the incorporation efficiency. More recently, the approach was extended to citric acid functionalized IO particles, combined with the use of a cationic initiator, thereby eliminating the need for auxiliary comonomers.⁵⁹ In both cases, a detailed mechanistic investigation of particle formation revealed complex interplay between IO and latex colloidal stability resulting in small composite latex particles with in the best case 90% IO incorporation efficiency, with however an irregular and relatively low surface coverage of less than 35%. With the aim of improving both the IO surface coverage and the particle morphology, while at the same time being able to maintain a high IO incorporation efficiency, we decided to investigate the use of another comonomer capable of promoting IO adsorption on the polymer particles via electrostatic interaction, independently of the pH, namely 2-acrylamido-2-methyl-1propanesulfonic acid (AMPS). Following our previous works, two different monomers were investigated: methyl methacrylate (MMA) and styrene using maghemite (γ -Fe₂O₃) nanoparticles as the sole stabilizer under batch conditions. The effect of AMPS content, IO content, ethanol addition in water and the nature of the monomer on polymerization kinetics, particle size and morphology, was thoroughly investigated in order to unravel the underlying mechanism of hybrid particles formation.

EXPERIMENTAL SECTION

Materials. Iron (II) chloride tetrahydrate (FeCl₂.4H₂O, 99 %, Aldrich), iron (III) chloride hexahydrate (FeCl₃.6H₂O, 97 %, Aldrich), iron (III) nitrate nonahydrate (Fe(NO₃)₃.6H₂O, 98 %, Acros Organics), diethyl ether (99.5%, Aldrich), hydrochloric acid (HCl, 37 %, VWR International), nitric acid (HNO₃, 65 %–70 %, VWR International) and ammonia (NH₄OH, 20 wt% aqueous solution, VWR International) were all used as received. The monomers: methyl methacrylate (MMA, 99%, Aldrich), styrene (S, 99%, Aldrich), 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS, 99%, Aldrich) and the initiator: 2,2'-azobis [2-(2-imidazolin-2-yl) propane] dihydrochloride (ADIBA, Wako Pure Chemical Industries, Ltd) were used without purification. Water was deionized before use (Purelab Classic UV, Elga LabWater).

Synthesis of ultrasmall superparamagnetic iron oxide particles. The IO particles were prepared using the Massart approach which involves the aqueous coprecipitation of iron chlorides under alkaline conditions.^{61, 62} The detailed preparation method has been reported in our previous work.⁵⁸

Preparation of magnetic composite microspheres via Pickering emulsion polymerization. Emulsion (co)polymerizations were performed in a glass-jacketed reactor equipped with a condenser and a nitrogen inlet. As a representative example (Run 5, Table 1), the IO suspension (16.13 g, *i.e.* 2.0 g of dry IO) was diluted with water (75.87 g) and ethanol (11.84 g, 15 vol% based on total water). The mixture was placed in a reactor, followed by the addition of AMPS (0.133 g) dissolved in water (5 g). This suspension was deoxygenated by purging with nitrogen for 30 min. Then, MMA (20 g) was deoxygenated, and added to the IO suspension under vigorous stirring while the temperature was raised to 70 °C. The ADIBA initiator (0.2 g, 1.0 wt% based on monomer) was dissolved in 5.0 g of degassed water and added to the reactor (considered the zero time of the polymerization). The polymerization was conducted for 2 h under mechanical stirring at 350 rpm. The experimental conditions of the polymerizations performed in this study are presented in Table 1.

Characterization techniques.

Dynamic light scattering (DLS). The particle size (average hydrodynamic diameter, Z_{av}) and the width of the particle size distribution (PdI, the higher this value, the broader the size distribution) were measured by dynamic light scattering (DLS) using the NanoZS instrument from Malvern. The data were collected using the fully automatic mode of the Zetasizer system, and depending on the size distribution, either the monomodal cumulant analysis or the CONTIN analysis was performed. The number of particles per liter of latex emulsion (N_p (L⁻¹)) was calculated using the hydrodynamic diameter determined by DLS according to the following equation:

$$N_{p} (L^{-1}) = 6 \times C \times 10^{21} / \rho \pi Z_{av.}^{3}$$
(1)

where C (g L^{-1}_{aq}) is the polymer concentration taking into account the conversion and ρ (g cm⁻³) is the density of the polymer.

The *Brunauer-Emmet-Teller (BET) specific surface area* was determined by nitrogen adsorption-desorption isotherms using a Micromeritics ASAP 200 device. Prior to analysis, the sample was purged under vacuum at 120 °C overnight to remove physisorbed water. The surface area was calculated from the linear part of the adsorption isotherm (P/P_0 =0.05-0.3) using the BET equation.

Zeta potential measurements. Zeta potential measurements were carried out using the Zeta sizer Nano ZS from Malvern Instrument. A stock suspension of the polymer or composite latex particles in deionized water was first homogenized by ultrasonication for 15 min. A few drops of this stock suspension were then added to an aqueous solution of 10^{-3} mol L⁻¹ KNO₃ and for each sample, the average value of three independent measurements was recorded.

Transmission electron microscopy. For conventional transmission electron microscopy (TEM) observations, a drop of the diluted IO or latex suspension was deposited on a carbon/Fornwarcoated copper grid, and the solvent was allowed to evaporate. The analysis was carried out at room temperature with a Philips CM120 microscope operating at an accelerating voltage of 80 kV (Centre Technologique des Microstructures (CTµ), Université Claude Bernard Lyon 1, Villeurbanne, France). The number-average (D_n) and the weight-average (D_w) particle diameters and the polydispersity index (PDI = D_w/D_n) of IO or latex particles were calculated using $D_n = \Sigma n_i D_i / \Sigma n_i$ and $D_w = \Sigma n_i D_i^4 / \Sigma n_i D_i^3$, where n_i is the number of particles with diameter D_i . Cryo-transmission electron microscopy (cryo-TEM) observations were also carried out to prevent deformation and/or degradation of the soft latex particles due to drying and/or radiation damage at room temperature. According to the method described elsewhere,⁴⁷ thin liquid films of the suspensions were formed on lacy carbon films and quench frozen in liquid ethane. The specimens were observed at low temperature (-180 °C) with a Philips CM200 'Cryo' microscope operating at 80 kV, under low dose conditions. In the particular case of Run 16 (Table 2), the armored-latex particles were washed by centrifugation at 7500 rpm for 15 minutes (AllegraTM 64R centrifuge) to remove free IO and dried in an oven. The dry particles were then embedded in an epoxy resin and ultrathin sections (< 100 nm) of the sample were prepared using a diamond knife on a ultramicrotome equipment.

Thermogravimetric analyses (TGA). TGA was used to determine the efficiency of iron oxide incorporation in the composite latex particles (*IE*), which then allows calculation of the surface coverage of the latex particles by IO (*Cov*).

IE (%) was determined by comparing the IO content of the IO-armored particles after removal of the free IO by centrifugation at 7500 rpm (AllegraTM 64R centrifuge) for 15 min (IO_{composite}), with the IO content expected to be in the composite particles taking into account the initial amount of IO and the monomer conversion (IO_{theo}). The 7500 rpm rotational speed was carefully selected to enable selective sedimentation of the latex particles while retaining the free IO in solution. If some of the iron oxide sol would also be inadvertently sedimented under these conditions, then the calculated IO incorporation efficiency would represent an upper limit value. The estimated error in the final iron oxide incorporation efficiencies is +/- 2 wt%. IO_{composite} (%) was determined by TGA on a TA instruments Q5000 IR. Typically, 10 mg of the dried sample was accurately weighed and heated from 25 to 800 °C at a rate of 10 °C min⁻¹ under an oxygen atmosphere. The remaining incombustible residue of both pure IO and pure polymer was used to correct unburned hybrid latex residues. The incorporation efficiency was then calculated as follows:

$$IE (\%) = \frac{IO_{\text{composite}} \times (100 - IO_{\text{theo}})}{IO_{\text{theo}} \times (100 - IO_{\text{composite}})} \times 100$$
(2)

where IO_{theo} (%) is the theoretical IO content before centrifugation determined from the amount of IO initially introduced and the monomer conversion determined by gravimetric analysis (after subtracting the mass of IO and initiator).

$$IO_{theo}(\%) = \frac{m_{IO}}{\left(m_{IO} + m_{\text{monomer}} \times \frac{Conversion}{100}\right)} \times 100$$
(3)

with m_{IO} the initial mass of IO introduced and $m_{monomer}$ is the total mass of monomer. Combining equations (2) and (3), it turns:

$$IE (\%) = \frac{m_{\text{monomer}} \times Conversion \times IO_{composite}}{m_{\text{IO}} (100 - IO_{composite})}$$
(4)

The surface coverage of the latex particles by IO (*Cov* %) was calculated based on IE assuming that the surface area occupied by one IO nanoparticle at the polymer particle surface is equal to the cross-sectional area of a plane bisecting that nanoparticle. The surface coverage can then be expressed as:

$$Cov (\%) = \frac{1}{4} \left(\frac{m_{\rm IO} \times IE}{m_{\rm monomer} \times Conversion} \right) \left(\frac{\rho_{\rm polymer}}{\rho_{\rm IO}} \right) \left(\frac{D_{\rm n}}{D_{\rm IO}} \right) \times 100$$
(5)

where ρ_{IO} is the apparent density of the IO nanoparticles (5.24 g cm⁻³) and D_{IO} their diameter determined by TEM (5.6 nm), $\rho_{polymer}$ is the polymer density and D_n the polymer diameter determined by TEM.

Superconducting quantum interference device (SQUID) analysis. Magnetic measurements were carried out at 300 K using a SQUID MPMS- XL5 magnetometer (Quantum Design) equipped with an integrated helium liquefier. The latexes were centrifuged at 7500 rpm for 15 minutes to remove free IO and dried before analysis.

RESULTS AND DISCUSSION

1. Preliminary emulsion polymerization experiments

Superparamagnetic IO maghemite nanoparticles were synthesized by coprecipitation of ferrous and ferric iron salts in an alkaline environment, followed by oxidation and peptization using HNO₃ according to the process of Massart et al.⁶² The resulting IO nanoparticles spontaneously redispersed in water to produce a stable colloidal suspension with a pH value of around 2.2. At this pH, the surface of the nanoparticles was positively charged (isoelectric point of 7.4).⁵⁸ The particles displayed a hydrodynamic diameter of 25 nm (PdI = 0.25) and a BET specific surface area of 166 m² g⁻¹. The IO diameter determined by TEM was 5.6 nm.

AMPS is a reactive, hydrophilic, sulfonic acid acrylic monomer with a pKa of about 2.63 AMPS is therefore negatively charged over a large range of pH values and is expected to favorably interact with the positively charged IO particles through electrostatic interactions at pH = 2. This should promote IO adhesion to the growing latex particles. To study the influence of AMPS on the emulsion polymerization of MMA in the absence of surfactant, a series of experiments with different AMPS concentrations was first carried out in the absence and presence of IO (Table 1). The experiment performed in the absence of both IO and AMPS gave stable PMMA latex particles with a diameter of around 420 nm (Run 1). When a small amount of AMPS was introduced in the recipe (0.06 g L⁻¹, Run 2), the particle size increased to 524 nm, while a further increase in AMPS concentration led to unstable latexes (Runs 3 to 5). These preliminary experiments show that the latex stability is affected by the presence of AMPS. This is likely due to the formation of hydrosoluble chains. Indeed, although in conventional emulsion polymerization the reaction primarily takes place into the monomer swollen polymer particles, the oligometric radicals formed in the aqueous phase play a major role not only in particle nucleation and stabilization, but also in the characteristics of the final latex products. Many studies on emulsion polymerization of styrene with ionic monomers such as sodium styrene sulfonate,⁶⁴ sodium 2-sulfoethyl methacrylate,⁶⁴ 1,2-dimethyl-5-vinylpyridinium methyl sulfate,⁶⁵ potassium 3-sulfopropyl methacrylate (SPM)⁶⁶ or AMPS⁶⁷⁻⁷¹ showed that these functional monomers are highly soluble in water, resulting (in a batch process) in the formation of a large amount of hydrosoluble chains. As a consequence, the surface yield of the functional group is often low, varying with the nature of the monomer and the reaction conditions. In addition to representing a waste of functional monomer, the hydrosoluble chains may also act as flocculating agents depending on their composition, molar mass and concentration.^{66, 72} The present results thus suggest the formation of hydrosoluble polymer chains in water, whose proportion increases with increasing AMPS concentration, phenomenon which would favor the formation of unstable latexes through bridging flocculation. In addition, the concomitant presence of positive and negative charges from the initiator and the monomer, respectively, could decrease the net surface charge of the latex particles and have a further negative impact on their stability.

Run	IO (g L ⁻¹)	AMPS (g L ⁻¹)	pH ^b latex	Conv. (%)	Z _{av.} ^c (nm)	PdI ^c	N_{p} (10 ¹⁵ L ⁻¹) ^d			
1	/	/	5.9	100	420	0.01	4.5			
2	/	0.06	2.2	99	524	0.11	2.2			
3	/	0.30	2.2							
4	/	0.66	2.1	Unstable after 30 min						
5	/	1.33	2.1							
6	20	/	2.2	100	451	0.07	3.6			
7	20	0.06	2.1	100	293	0.14	13			
8	20	0.33	2.1							
9	20	0.66	2.1		Unstable	after 30 m	in			
10	20	1.33	2.1							

Table 1. Experimental conditions and results of surfactant-free emulsion polymerizations of

 MMA in the presence of various IO and AMPS contents.^a

^{*a*} All experiments were carried out for 2 h with 20 wt% of MMA with respect to water, ADIBA: 1 wt%/MMA and T = 70 °C. ^{*b*} pH of the latex suspension after polymerization. ^{*c*} Determined by DLS. ^{*d*} Calculated using equation (1). All concentrations refer to the volume of water.

Despite the formation of unstable latexes in the absence of IO, a series of experiments were performed in the presence of 20 g L⁻¹ of IO (i.e., 10 wt% with respect to MMA) to investigate the potential of AMPS in the formation of IO-armored PMMA latexes. The sole presence of IO (without AMPS) led to a stable latex with a diameter of around 450 nm (Run 6 in Table 1), a

size very close to that of the latex particles synthesized in the absence of IO (Run 1) suggesting that colloidal stability is mainly provided in this case by charged initiator residues incorporated into the particles. Indeed, cryo-TEM showed the formation of spherical PMMA latex particles with almost no IO attached to their surface (Figure S1, Supporting Information). When a small amount of AMPS (0.3 wt% based on IO, i.e., 0.06 g L⁻¹) was added together with IO, significantly smaller particles with a diameter of about 290 nm were successfully obtained (Run 7, Table 1). TEM analysis indicated however that only a minor fraction of IO was attached on the particles surface, with a lot of magnetic nanoparticles remaining free in the continuous phase (Figure 1A). This experiment thus suggests that AMPS was effective in decreasing the size of the nucleated PMMA particles in the presence of IO. However, the AMPS concentration was too low to ensure efficient formation of IO-armored particles. Very similar results were reported in our previous work on the synthesis of IO-armored PS latexes using (meth)acrylic acid as auxiliary comonomer.⁵⁸ As we presumed that there were not enough AMPS units in the watersoluble oligomers to favor IO adhesion on the latex particles surface, the AMPS concentration was progressively increased from 0.33 to 1.33 g L^{-1} (i.e., from 1.6 to 6.6 wt% based on IO) while keeping a constant IO concentration of 20 g L⁻¹ (Runs 8-10 in Table 1). As in the experiments run in the absence of IO, the latexes became unstable after 30 minutes whatever the AMPS concentration. The samples were nevertheless characterized by TEM. As seen in Figure 1, the amount of free (not adsorbed) IO decreased with increasing the AMPS concentration and almost no free IO could be visualized in the surrounding environment of the composite particles for the highest AMPS concentration (1.33 g L⁻¹, Figure 1C) indicating high IO incorporation efficiency, which was obviously not quantified due to the stability issue of this sample.



Figure 1. TEM images of latex particles synthesized by surfactant-free emulsion polymerization of MMA in the presence of 10 wt% of IO based on monomer (corresponding to a concentration of 20 g L⁻¹) and increasing AMPS concentrations. A) [AMPS] = 0.06 g L⁻¹, Run 7; B) [AMPS] = 0.66 g L⁻¹, Run 9 and C) [AMPS] = 1.33 g L⁻¹, Run 10. All experiments were carried out at 70 °C with MMA: 20 wt%/water and ADIBA: 1 wt%/MMA.

2. Emulsion polymerizations performed in the presence of ethanol

2.1 Preliminary experiments

In the purely aqueous systems described above, the PMMA latexes became unstable when the AMPS concentration was higher than 0.3 g L⁻¹, both in the absence and in the presence of IO, indicating that AMPS induced latex destabilization. Although emulsion polymerization is usually conducted in pure water, interesting results have been reported when alcohol is added to water.⁷³⁻⁷⁵ In these studies, the concentration of alcohol was limited to that necessary to maintain the heterogeneous state of the medium. For example, in a soap-free emulsion polymerization of styrene with sodium vinylbenzyl sulfonate, the presence of methanol significantly reduced the size dispersity of the latex particles. According to Chonde and Krieger,⁷³ the cosolvent has several effects. It decreases the dielectric constant of the medium and increases the solubility of the monomer and growing oligomeric radicals. The resulting water-soluble oligomers are thus richer in styrene, which partially prevents polyelectrolyte formation and improves stability. Therefore, with the aim of reducing the amount of AMPS-rich hydrosoluble chains and thus improving the stability of the latex suspensions in the present

system, ethanol (15 vol%/water) was introduced in the recipe. The results are shown in Table 2 (Runs 11-14).

Run	IO (g L ⁻¹)	AMPS (g L ⁻¹)	Conv. (%)	Zav. ^b (nm)	PdI ^b	$\frac{N_p{}^c}{(10^{15}\mathrm{L}^{-1})}$	Dn ^d (TEM) (nm)	IE ^e (%)	Cov ^f (%)	
11	0	0.33	99	537	0.08	2.1	/	/	/	
12	0	0.66	99	572	0.10	1.7	/	/	/	
13	0	1.33	98	609	0.08	1.4	/	/	/	
14	20	1.33	98	404	0.09	2.6	260	93	24.8	
15	10	0.66	96	415	0.07	4.3	250	10	1.3	
16	30	1.99	99	1015	0.21	2.7	400	96	58.5	
17	40	2.65	Unstable after 30 min							

Table 2. Experimental conditions and results of surfactant-free emulsion polymerizations of MMA in the presence of AMPS and 15 vol% of ethanol (based on water) with and without IO.^{*a*}

^{*a*} All experiments were carried out for 2 h with 15 vol% EtOH/water, MMA: 20 wt%/water, ADIBA: 1 wt%/MMA and T = 70 °C. ^{*b*} Determined by DLS. ^{*c*} Calculated using equation (1). ^{*d*} Determined by TEM. ^{*e*} Determined using equation (4). ^{*f*} Determined using equation (5).

All latexes were stable and exhibited complete monomer to polymer conversions. For polymerizations performed in the absence of IO, the particle size slightly increased from 537 to 609 nm with increasing the AMPS concentration from 0.33 to 1.33 g L⁻¹ (Runs 11-13), suggesting that a too high amount of AMPS may still favor limited particle aggregation. When the latter experiment was performed in the presence of 20 g L⁻¹ of IO (Run 14), stable PMMA latex particles with a hydrodynamic diameter close to 400 nm (PdI = 0.09) were successfully produced. TEM showed the formation of spherical particles with a rough surface clearly indicating the presence of IO nanoparticles (Figure 2). Only a minor amount of IO could be identified in the continuous phase, which was also reflected in the high IO incorporation efficiency (IE = 93%). The latex surface coverage by IO (24.8 wt%) is in qualitative agreement with the visual observation and two times higher than the best results obtained in our previous work involving (meth)acrylic acids as auxiliary comonomers.⁵⁸ According to equation 5, such

increase of surface coverage is a direct consequence of the higher IE and larger particles size obtained in the present work.



Figure 2. Typical low (A) and high (B) magnification TEM images of PMMA/IO latex particles synthesized in the presence of 20 g L^{-1} of IO, 1.33 g L^{-1} of AMPS and 15 vol% EtOH/water (Run 14, see Table 2 for experimental details).

2.2 Influence of IO content in MMA emulsion polymerization

Having identified reaction conditions that gave colloidally stable PMMA/IO particles, the initial IO concentration was then systematically varied to improve the IO incorporation efficiency and increase the latex surface coverage by IO. For this purpose, a series of suspensions were prepared with IO concentrations ranging from 10 to 40 g L⁻¹ keeping a fixed AMPS content of 6.6 wt% based on IO, leading consequently to increasing amounts of AMPS in water (Runs 14 to 17 in Table 2). For the highest IO concentration, the system was unstable (Run 17), therefore the following discussion will focus on comparing only the 10, 20 and 30 g L⁻¹ experiments (Runs 15, 14 and 16, respectively). Figure 3 shows the evolution of conversion with time and of the particle diameter with conversion for these three experiments. Firstly, the conversion *versus* time plot shows similar profiles, and in all cases the conversion was complete after 45 min. The reaction rate was however slightly lower for the higher IO content, which is likely due to the concomitant increase in particle size. Indeed, as shown in Table 2 and Figure

3B, the final DLS particle diameter increased from around 400 nm for 10 or 20 g L⁻¹ of IO (Runs 15 and 14) to more than 1 μ m for 30 g L⁻¹ (Run 16, Z_{av.} = 1015 nm), while the size dispersity broadened indicating limited colloidal stability. The particle number concomitantly decreased (Figure 3C).



Figure 3. Evolution of A) conversion *versus* time, and B, C) particle diameter and particle number *versus* conversion for Pickering emulsion polymerizations of MMA performed in the presence of increasing amounts of IO (Runs 15, 14 and 16 in Table 2) and a fixed AMPS content of 6.6 wt% based on IO. The experiments were carried out with MMA: 20 wt%/water, ADIBA: 1 wt%/MMA and T = 70 °C.

The TEM images of Figure 4 show spherical particles of uniform diameter. When the IO concentration was low (10 g L^{-1}), most of IO particles remained in the aqueous phase and did not adhere to the PMMA particles surface. This observation agrees well with the calculated 17

surface coverage (Table 2, Cov = 1.3%). The contrast in the TEM images at the particle periphery tends to increase with increasing IO content, showing that the surface coverage also increases. Indeed, the increase in IO content is accompanied by an increase in AMPS concentration (Table 2) and thus by an increased number of sulfonic acid groups in the copolymer chains, thereby promoting IO/polymer interactions.



Figure 4. TEM images of IO-armored PMMA latex particles synthesized in the presence of increasing IO contents. A) 10 g L⁻¹, Run 15, B) 20 g L⁻¹, Run 14 and C) 30 g L⁻¹, Run 16. D) TEM image of an ultrathin section of the particles from Run 16 embedded in an epoxy resin (see the text for experimental details). All experiments were carried out for 2 h at 70 °C with AMPS: 6.6 wt%/IO, MMA: 20 wt%/water and ADIBA: 1 wt%/MMA (Table 2).

Comparison between the $Z_{av.}$ values determined by DLS (Table 2) and the TEM images of Figure 4 clearly shows significant differences in the particle diameters. For the lowest IO concentrations (10 and 20 g L⁻¹, Runs 15 and 14 in Table 2), the particle diameter determined 18

by TEM (around 250 nm) was smaller than the DLS particle size (400 nm, PdI = 0.09). When the IO concentration increased to 30 g L⁻¹, the discrepancy increases: the TEM diameter was about 400 nm while the Z_{av} value was close to 1 μ m (PdI = 0.21). This is likely due to the formation of AMPS-rich polymer chains that could act as flocculating agent promoting aggregation between latex particles, resulting in a high DLS diameter.

TGA was used to determine the amount of IO attached to the particle surface. In agreement with the TEM images, the quantity of IO on the polymer surface increased with increasing IO content. The nanocomposite particles synthesized using 10 g L⁻¹ of IO incorporated only 10% of the initial amount of IO (Run 15, Table 2), whereas the incorporation efficiency raised to 93% and 96% for the latex prepared with 20 g L⁻¹ and 30 g L⁻¹ of IO (Runs 14 and 16, respectively). The surface coverage (as determined from equation 5) consequently increased from 1.3 to 58.5% with increasing IO and AMPS contents.

To check whether the IO nanoparticles were located on the surface of the polymer particles or rather distributed inside, the latex was embedded in an epoxy resin after drying, then analyzed by TEM. A typical TEM image of an ultrathin section of this sample washed by centrifugation to remove any free IO is shown in Figure 4D. The general features in terms of size and shape are very similar to those observed by conventional TEM in Figure 4C. In addition, a dark and thin outline means that the particles have been cut through their center whereas a thick peripheral layer suggests that the IO particles are located on the polymer surface. As the central regions, corresponding to the polymer, are uniformly white, we can conclude that no IO is present inside the particles. These observations indicate that IO nanoparticles are located on the surface of the polymer particles instead of being distributed inside, confirming the expected armored morphology.

In the previous experiments, MMA was used to demonstrate that IO was able to play the role of solid stabilizer in the presence of AMPS. However, previous literature studies on Pickering emulsion polymerization have shown that the nature of the monomer is an important parameter that can influence particle morphology and latex stability, and thus requires attention.^{46,58} Therefore, in order to establish whether the approach could be extended to more hydrophobic monomers, MMA was replaced by styrene (Table 3).

Run	IO (g L ⁻¹)	AMPS (g L ⁻¹)	Conv. (%)	Z _{av.} ^b (nm)	PdI ^b	N_p (10 ¹⁵ L ⁻¹) ^c	Dn ^d (TEM) (nm)	IE ^e (%)	Cov (%) ^f
18	/	1.2	17	325	0.17	1.6	/	/	/
19	/	1.8	17	328	0.11	1.6	/	/	/
20	/	2.1	17	333	0.12	1.5	/	/	/
21	/	2.4	18	340	0.19	1.5	/	/	/
22	20	1.2	26	340	0.22	2.6	176	33	20.0
23	20	1.8	39	273	0.06	5.9	188	71	30.6
24	20	2.1	42	250	0.07	7.2	195	93	38.6
25	20	2.4	45	359	0.20	2.8	300	95	56.7
26	20	2.7			U	nstable after 2	20 min		

Table 3. Effect of AMPS concentration on the surfactant-free emulsion polymerizations of styrene in the absence and in the presence of IO in ethanol/water (15/100 v/v).^{*a*}

^{*a*} All experiments were carried out for 6 h with styrene: 20 wt%/water, ADIBA: 1 wt%/styrene and T = 70 °C. The pH of the final latex suspension was 2.2. ^{*b*} Determined by DLS. ^{*c*} Calculated using equation (1). ^{*d*} Determined by TEM. ^{*e*} IO incorporation efficiency determined using equation (4). ^{*f*} Latex surface coverage by IO determined using equation (5).

Blank experiments performed in pure water in the presence of AMPS again resulted in unstable latexes (data not shown) while stable latexes were obtained after the addition of 15 vol% of ethanol (Runs 18-21 in Table 3). The conversion was however lower than 20% in all cases (after 6 h of polymerization), while the particle size was little influenced by the amount of AMPS. Limiting conversions have previously been observed in the literature for surfactant-free emulsion polymerization of styrene and is due to the lower water solubility (0.45 g L⁻¹ at 50 °C)⁷⁶ and propagation rate constant ($k_p = 467$ L mol⁻¹ s⁻¹ at 70 °C)⁷⁷ of this monomer compared to MMA (solubility = 15 g L⁻¹ at 50 °C⁷⁸ and $k_p = 1070$ L mol⁻¹ s⁻¹ at 70 °C⁷⁷), leading to less efficient nucleation and relatively large particles size. In the presence of 20 g L⁻¹ of IO and 6 wt% of AMPS based on IO (1.2 g L⁻¹, Run 22 in Table 3), the monomer conversion was still limited with a plateau being reached after around 6 h, as





Figure 5. Evolutions of: A) conversion *versus* time, and B, C) particle number and particle diameter *versus* conversion for surfactant-free emulsion polymerization of styrene performed with 2.1 g L⁻¹ of AMPS in the absence of IO (Run 20, Table 3) and with increasing AMPS concentrations in the presence of 20 g L⁻¹ IO (Runs 22-25 in Table 3). All experiments were carried out at 70 °C with styrene: 20 wt%/water, ADIBA: 1 wt%/styrene and ethanol: 15 vol%/water.

Comparison of the two experiments performed under similar conditions in terms of AMPS and IO contents, but with either MMA (Run 14, Table 2) or styrene (Run 22, Table 3) highlights

the effect of the monomer nature on the outcomes of the polymerization. Replacing MMA by styrene induces a strong decrease of the polymerization rate, and hence of the final conversion, which as could be expected leads to smaller particles (176 nm for polystyrene *vs.* 260 nm for PMMA, as determined by TEM, while the particle number is very similar) and consequently also impacts the IE (33% *vs.* 93%) and the surface coverage (20% *vs.* 24%). As mentioned above, the discrepancies between the two systems probably lie in the different monomer solubilities and k_p values, which are both in favor of MMA. In addition, one should also consider the difference in AMPS reactivity between MMA and styrene. This will obviously impact the composition of the water-soluble chains and their ability to efficiently interact with the IO surface. However, to the best of our knowledge there is no study available in the literature on the determination of the reactivity ratios for the AMPS/MMA system. And the only values available for AMPS/styrene can be found in a technical notice from an AMPS provider,⁷⁹ in which the reactivity ratios are reported to be $r_{AMPS} = 0.31$ and $r_{styrene} = 1.13$ (in DMF at 60 °C). It would thus be risky to further discuss on these grounds the different behavior of the two systems.

The amount of auxiliary comonomer AMPS was next increased for a fixed IO concentration of 20 g L⁻¹ (Runs 22-25 in Table 3 and Figure 5) to evaluate its impact on the polymerization. The reaction rate increased with increasing the AMPS concentration from 1.2 to 2.4 g L⁻¹ while the final conversion increased from 26 to 45%. The concentration of AMPS also had a strong impact on the particle size and stability of the final latex. The hydrodynamic diameter was slightly bigger for the lowest AMPS concentration ($Z_{av.} = 340$ nm for 1.2 g L⁻¹, Run 22), and the latex appeared less stable as supported by the high PdI. A low fraction of IO was located on the polymer particle surface, a lot of IO remaining free in the continuous phase (Figure 6A). In contrast, with increasing AMPS concentration, more IO was adsorbed on the particle surface

leading to stable latex of smaller particles. Indeed, the hydrodynamic diameter was 273 nm for 1.8 g L⁻¹ AMPS (Run 23), and 250 nm for 2.1 g L⁻¹ (Run 24). Almost all polymer particles are covered with IO nanoparticles in the latter case (Figure 6C). The surface coverage steadily increased with increasing the amount of AMPS for these three latexes (up to 39 % for Run 24, IE reaching 93% in that case). When the AMPS concentration was further increased to 2.4 g L⁻ ¹, TEM image again showed particles homogeneously covered with IO nanoparticles, with a surface coverage close to 57 % and an IE of 95% (Figure 6D). According to DLS, the particles were however substantially bigger with a larger dispersity in size ($Z_{av} = 350 \text{ nm}$, PdI = 0.2), which may be the sign of a lower stability. This is corroborated by a significant increase of the particle diameter at ca. 30% conversion (and consequently a decrease of Np) (Figure 5B and C). Increasing further the AMPS concentration to 2.7 g L⁻¹ (Run 26) led to a complete loss of stability after 20 min of polymerization. As the amount of AMPS increases, the first P(S-co-AMPS) oligomers formed in water likely incorporated more and more AMPS units favoring a faster and more efficient capture by IO nanoparticles. This would lead to a (too) high number of polymer/IO nuclei whose stability could not be accommodated by the system inducing a limited aggregation of these nuclei in order to reduce the total surface area (Run 25). At one point, the AMPS concentration is such that the extent of this aggregation led to the complete destabilization of the system (Run 26). It is also possible that the formation of a higher amount of hydrosoluble polymers accumulating in the water phase after all IO has been captured by the latex particles promotes destabilization.



Figure 6. TEM images of IO-armored PS latex particles synthesized in the presence of 20 g L⁻¹ IO and increasing AMPS concentrations. A) 1.2 g L⁻¹, Run 22; B) 1.8 g L⁻¹, Run 23; C) 2.1 g L⁻¹, Run 24, and D) 2.4 g L⁻¹, Run 25. The experiments were carried out for 2 h at 70 °C with styrene: 20 wt%/water, ethanol: 15 vol %/water and ADIBA: 1 wt%/styrene.

With the aim of increasing the conversion, different amounts of MMA were next introduced in the recipe keeping a constant monomer content of 20 wt% based on water (Runs 27-29 in Table 4). Figure 7 shows the evolution of conversion with time and of particle diameter with conversion for these three experiments.

Run	S/MMA (wt/wt)	AMPS (g L ⁻¹)	Conv. (%)	Z _{av} ^b (nm)	PdI ^b	$\frac{N_p{}^c}{(10^{15}{ m L}^{-1})}$	D_n (TEM) (nm) d	IE ^e (%)	Cov ^f (%)
22	100/0	1.2	26	340	0.22	2.6	176	33	20.0
27	95/5	1.2	44	207	0.06	14	160	85	27.8
28	80/20	1.2	73	205	0.03	23	150	87	16.4
29	70/30	1.2	89	195	0.08	34	120	89	11.1
14	0/100	1.33	98	494	0.09	2.6	260	93	24.8

Table 4. Experimental conditions and results of surfactant-free emulsion (co)polymerization of MMA and styrene in the presence of 20 g L^{-1} of IO and 15 vol% EtOH/water.^{*a*}

^{*a*} All experiments were carried out for 6 h with monomer(s): 20 wt%/water, ADIBA: 1 wt%/monomers and T = 70 °C. The pH of the final latex suspension was 2.2. ^{*b*} Determined by DLS. ^{*c*} Calculated using equation (1). ^{*d*} Determined by TEM. ^{*e*} IO incorporation efficiency determined using equation (4). ^{*f*} Latex surface coverage by IO determined using equation (5).



Figure 7. Evolution of A) monomer conversion *versus* time and B) particle diameter *versus* conversion during surfactant-free emulsion polymerization of styrene/MMA mixtures in the presence of 20 g L⁻¹ of IO and 1.2 g L⁻¹ of AMPS. All experiments were carried out at 70 °C with styrene/MMA: 20 wt%/water, ADIBA: 1 wt%/monomers and ethanol: 15 vol%/water (see Table 4 for more details).

As expected, increasing MMA content led to an increase of the particle number, and hence to higher polymerization rates and final conversions. These improvements clearly illustrate the positive impact of higher MMA solubility and k_p on particle nucleation. For the highest initial MMA content (30 wt%, Run 29), the particle number actually increased by more than a factor

of two (from $14x10^{15}$ L⁻¹ to $34x10^{15}$ L⁻¹) although the final DLS particle size (Z_{av.} = 195 nm) was only slightly smaller than for the two other experiments (around 200 nm for 10 and 5 wt% of MMA), which is due to the higher conversion. TEM images show that a high fraction of IO was attached to the polymer surface while a few IO remained in the aqueous phase (Figure S2 in ESI). Even if the IE values were in all cases very high and similar (close to 87 %), the surface coverage gradually decreased from 28 to 11 % when the MMA content increased from 5 to 30 wt%, which is due to the increase of the particle number and total surface area.

3. Mechanism of nanocomposite particles formation

The previous series of experiments suggests favorable interaction between the oligoradicals and the IO surface induced by the presence of AMPS units. In an effort to clarify the mechanism of particle formation, some experiments were analyzed in more depth by monitoring the evolution of particle morphology during the polymerization. Figure 8 shows the development of particle morphology with time for the IO-armored PMMA latex particles synthesized in the presence of 20 g L⁻¹ of IO and 1.33 g L⁻¹ of AMPS (Run 14 in Table 2). For reaction times lower than 30 min (*i.e.*, conversions lower than *ca.* 30%), the latex particle size increased gradually with conversion (see also Figure 3B) while the particle number slightly decreased. However, most of the IO nanoparticles were present in the aqueous phase and not attached to the latex particles during this period. From 30 min to 120 min (*ca.* from 30% up to full conversion), there was a significant change in the TEM images. The IO gradually shifted from the aqueous phase to the PMMA particles surface, and polymer particles homogeneously covered with IO nanoparticles were finally obtained at the end of the reaction. A similar result was observed for styrene although the armored morphology was developed earlier, after around 30% conversion, for which there were almost no remaining free IO (see Figure S3 in the Supporting Information).



Figure 8. TEM images of PMMA/IO latex particles synthesized in the presence of 20 g L⁻¹ of IO and 1.33 g L⁻¹ of AMPS (Run 14, Table 2) for increasing conversions. The experiment was carried out at 70 °C with MMA: 20 wt%/water, ADIBA: 1 wt%/MMA and ethanol: 15 vol%/water.

Based on previous works in the literature^{42, 52, 56} and the experimental results obtained in this study, the mechanism of formation of the IO-armored composite particles can be explained as follows, using the case of MMA to illustrate the point. At the very beginning of the reaction no particles exist. Thus, the polymerization exclusively takes place in the aqueous phase, where polymer chains containing AMPS and MMA units are formed. The composition of these copolymer species depends on the relative concentration and reactivity ratios of the two monomers. The oligomeric radicals formed in the aqueous phase are initially hydrophilic and can either grow until they collapse to give primary particles according to the mechanism proposed by Fitch *et al.*⁸⁰ for surfactant-free emulsion polymerization or adsorb on the IO particles through their sulfonic acid groups. In the latter case, the adsorbed oligoradicals can

further grow and heterocoagulate with primary particles until a mature particle is formed. Once particles are generated and swollen by the monomer, the subsequent polymerization of MMA in these new loci causes their surface to increase leading to a decrease of the surface charge density. To counterbalance this effect, the growing particles have to gain new stabilizing charges by adsorbing oligoradicals from solution. During this growth period, the particle surface is thus covered by an increasing number of hydrophilic groups originating from the initiator fragments and the AMPS comonomer. With the progress of polymerization, the particles thus incorporate a greater proportion of sulfonic acid groups on their surface can also adsorb on the latex surface and increase their coverage. During the final stage of polymerization, the oligoradicals become richer in functional monomer since the monomer droplets have disappeared causing MMA concentration in water to progressively decrease. Consequently, the oligomers are enriched in AMPS and the remaining free IO nanoparticles are gradually adsorbed on the polymer surface units until there is no more IO in water.

To verify the above assumptions, we have followed the evolution of the surface charge by zeta potential measurements for MMA polymerization carried out with 1.33 g L⁻¹ of AMPS in the absence and in the presence of 20 g L⁻¹ IO (Runs 13 and 14, Table 2) (Figure 9). All analyses were performed in water, which may influence the net surface charges, but comparison of these two experiments can still provide valuable information as the reaction medium is mainly composed of water. For the latex without IO, the zeta potential first increased to a maximum (76 mV) and then decreased gradually to around 10 mV. The first part of the curve would thus correspond to the nucleation period mentioned above during which small primary particles coagulate until enough charged groups have been formed at their surface to give the particle an adequate electrostatic surface potential (i.e., the zeta potential increases). The fact that the surface charge is positive at the beginning of the reaction would indicate that the negative

charges brought by the AMPS units in the oligomers would not be enough to counterbalance or even exceed those brought by the initiator, and that these oligomers initially contain few AMPS units. The decrease in zeta potential at higher conversions suggests progressive incorporation of sulfonic acid groups at the particles surface in agreement with the above assumptions. The evolution of the zeta potential of the latex particles synthesized under the same conditions in the presence of IO shows an overall similar trend. The zeta potential increased from 65 mV to 90 mV with increasing conversion to 18 %, and then decreased to 72 mV at full conversion. The zeta potential at high conversions is however higher than for the blank latex as more and more positively charged IO particles are adsorbed on the latex surface, which again supports the above scenario.



Figure 9. Evolution of zeta potential with conversion during the surfactant-free emulsion polymerization of MMA in the presence of AMPS only (Run 13 in Table 2) and with both AMPS and IO (Run 14 in Table 2). The experiments were carried out at 70 °C with MMA: 20 wt%/water, ADIBA: 1 wt%/MMA, AMPS: 1.33 g L⁻¹, and IO: 20 g L⁻¹ (if added), with 15 vol% of ethanol/water.

4. Magnetic properties

The magnetic properties of IO-armored PMMA and PS microspheres were measured by SQUID at room temperature and the results are shown in Figure 10 (left). The magnetic hysteresis curves exhibit a S-like shape. The saturation magnetization values of IO-armored

PMMA (Run 14, Table 2) and PS latexes (Run 24, Table 3) are 6.0 and 11.5 emu g⁻¹, respectively. As expected from its higher IO content, Run 24 displays a higher magnetization value. Figure 10 (right) shows the magnetic response of this latex. The IO-armored composite particles are attracted to the magnet and spontaneously redisperse in water after removal of the magnetic field, indicating that such magnetic PS microspheres possess good superparamagnetic properties.



Figure 10. Left: saturation magnetizations of IO-armored latex particles synthesized by surfactant-free emulsion polymerization in the presence of 20 g L^{-1} IO (PMMA, Run 14 in Table 2 and PS, Run 24 in Table 3). Right: digital images of the IO-armored PS latex suspension (Run 24) before and after applying an external magnetic field showing efficient magnetic separation.

CONCLUSIONS

Well-defined "core-shell" polymer-IO hybrid particles revealing superparamagnetic properties were successfully prepared in the absence of any molecular surfactant. The use of AMPS as auxiliary comonomer in the polymerization of MMA and styrene proved to be crucial to enhance the interaction between the stabilizing IO nanoparticles and the polymer latexes. In pure water, the obtained particles showed however limited stability both in the presence and absence of IO, likely due to the formation of AMPS-rich hydrosoluble chains. This issue could be circumvented by performing the experiments in an ethanol/water mixture, which reduced the amount of water-soluble oligomers, preventing destabilization. A minimum amount of AMPS was nonetheless required to form stable IO-armored PMMA particles with minimal proportion of free (non-adsorbed IO nanoparticles) and high incorporation efficiency. In contrast, a too high AMPS concentration promoted the formation of a large amount of hydrosoluble polymer chains that could act as flocculating agent. Using the more hydrophobic styrene monomer, stable latexes with high incorporation efficiency were also obtained under similar conditions. The final conversions were however limited but could be improved by copolymerizing styrene with MMA. In both cases, monitoring of the particle morphology with the progress of polymerization showed that the formation of AMPS-containing oligomers gradually promoted adsorption of the IO nanoparticles on the polymer surface. AMPS thus proved to be an efficient auxiliary comonomer for the formation of IO-armored latex particles. These are characterized by a high density of IO nanoparticles homogeneously distributed on the particle surface, providing latexes with strong response to an external magnetic field.

SUPPORTING INFORMATION

Cryo-TEM image of PMMA/IO latex particles synthesized in the absence of AMPS. TEM images of P(S-*co*-MMA)/IO composite particles for different styrene/MMA ratios. Evolution of the morphology of the PS/IO composite latex particles with time.

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REFERENCES

Na, H. B.; H., L. J.; An, K.; Park, Y. I.; Park, M.; Lee, I. S.; Nam, D.-H.; Kim, S. T.; Kim, S.-H.; Kim, S.-W.; Lim, K.-H.; Kim, K.-S.; Kim, S.-O.; Hyeon, T., Development of a T1 contrast agent for magnetic resonance imaging using MnO nanoparticles. *Angew. Chem. Int. Ed.* 2007, *119*, 5493-5497.

2. Thomas, L. A.; Dekker, L.; Kallumadil, M.; Southern, P.; Wilson, M.; Nair, S. P.; Pankhurst, Q. A.; Parkin, I. P., Carboxylic acid-stabilised iron oxide nanoparticles for use in magnetic hyperthermia. *J. Mater. Chem.* **2009**, *19*, 6529-6535.

3. Na, H. B.; Lee, I. S.; Seo, H.; Park, Y. I.; Lee, J. H.; Kim, S.-W.; Hyeon, T., Versatile PEG-derivatized phosphine oxide ligands for water-dispersible metal oxide nanocrystals. *Chem. Commun.* **2007**, 5167-5169.

4. Gijs, M. A. M.; Lacharme, F.; Lehmann, U., Microfluidic Applications of Magnetic Particles for Biological Analysis and Catalysis. *Chem. Rev.* **2010**, *110*, 1518-1563.

5. Pankhurst, Q. A.; Connolly, J.; Jones, S. K.; Dobson, J., Applications of magnetic nanoparticles in biomedicine. *J. Phys. D: Appl. Phys.* **2003**, *36*, 167-181.

6. Arruebo, M.; Fernández-Pacheco, R.; Ibarra, M. R.; Santamaría, J., Magnetic nanoparticles for drug delivery. *Nano Today* **2007**, *2*, 22-32.

7. Ankareddi, I.; Brazel, C. S., Synthesis and characterization of grafted thermosensitive hydrogels for heating activated controlled release. *Int. J. Pharm.* **2007**, *336*, 241-247.

8. Catherine, C. B., Progress in functionalization of magnetic nanoparticles for applications in biomedicine. *J. Phys. D: Appl. Phys.* **2009**, *42*, 224003.

 Moroz, P.; Jones, S. K.; Gray, B. N., Tumor response to arterial embolization hyperthermia and direct injection hyperthermia in a rabbit liver tumor model. *J. Surg. Oncol.* 2002, 80, 149-156.

10. Gupta, A. K.; Gupta, M., Synthesis and surface engineering of iron oxide nanoparticles for biomedical applications. *Biomaterials* **2005**, *26*, 3995-4021.

 O'Connor, C. J.; Seip, C. T.; Carpenter, E. E.; Li, S.; John, V. T., Synthesis and reactivity of nanophase ferrites in reverse micellar solutions. *Nanostruct. Mater.* 1999, *12*, 65-70.

12. Sugibayashi, K.; Okumura, M.; Morimoto, Y., Biomedical applications of magnetic fluids III. Antitumour effect of magnetic albumin microsphere-entrapped adriamycin on lung metastasis of AH 7974 in rats. *Biomaterials* **1982**, *3*, 181-186.

13. Povey, A. C.; Nixon, J. R.; O'Neill, I. K., Trapping of chemical carcinogens with magnetic polyethyleneimine microcapsules: II. Effect of membrane and reactant structures. *J. Pharm. Sci.* **1987**, *76*, 194-200.

14. Kharkevich, D. A.; Alyautdin, R. N.; Filippov, V. I., Employment of magnetsusceptible microparticles for the targeting of drugs. *J. Pharm. Pharmacol.* **1989**, *41*, 286-288.

15. Flesch, C.; Delaite, C.; Dumas, P.; Bourgeat-Lami, E.; Duguet, E., Grafting of poly(epsilon-caprolactone) onto maghemite nanoparticles. *J. Polym. Sci. Part A. Polym. Chem.* **2004**, *42*, 6011-6020.

16. Flesch, C.; Bourgeat-Lami, E.; Mornet, S.; Duguet, E.; Delaite, C.; Dumas, P., Synthesis of colloidal superparamagnetic nanocomposites by grafting poly(epsilon-caprolactone) from the surface of organosilane-modified maghemite nanoparticles. *J. Polym. Sci. A. Polym. Chem.* **2005**, *43*, 3221-3231.

17. Flesch, C.; Joubert, M.; Bourgeat-Lami, E.; Mornet, S.; Duguet, E.; Delaite, C.; Dumas, P., Organosilane-modified maghemite nanoparticles and their use as co-initiator in the ring-opening polymerization of epsilon-caprolactone. *Colloid Surf. A. Physicochem. Eng. Asp.* **2005**, *262*, 150-157.

 Flesch, C.; Unterfinger, Y.; Bourgeat-Lami, E.; Duguet, E.; Delaite, C.; Dumas, P., Poly(ethylene glycol) surface coated magnetic particles. *Macromol. Rapid Commun.* 2005, 26, 1494-1498.

19. Wu, W.; Wu, Z.; Yu, T.; Jiang, C.; Kim, W. S., Recent progress on magnetic iron oxide nanoparticles: synthesis, surface functional strategies and biomedical applications. *Sci. Technol. Adv. Mater.* **2015**, *16*, 023501.

20. Bolto, B. A., Magnetic particle technology for wastewater treatment. *Waste Manag.***1990**, *10*, 11-21.

Moosavi, S.; Lai, C. W.; Gan, S.; Zamiri, G.; Akbarzadeh Pivehzhani, O.; Johan, M.
 R., Application of Efficient Magnetic Particles and Activated Carbon for Dye Removal from Wastewater. *ACS Omega* 2020, *5*, 20684-20697.

22. Yakasai, F.; Jaafar, M. Z.; Bandyopadhyay, S.; Agi, A.; Sidek, M. A., Application of iron oxide nanoparticles in oil recovery – A critical review of the properties, formulation, recent advances and prospects. *J. Petrol. Sci. Eng.* **2022**, *208*, 109438.

23. Rossi, L. M.; Costa, N. J. S.; Silva, F. P.; Wojcieszak, R., Magnetic nanomaterials in catalysis: advanced catalysts for magnetic separation and beyond. *Green Chem.* **2014**, *16*, 2906-2933.

24. Abu-Dief, A. M.; Abdel-Fatah, S. M., Development and functionalization of magnetic nanoparticles as powerful and green catalysts for organic synthesis. *J. Basic Appl. Sci.* **2018**, *7*, 55-67.

25. Zhu, X.; Zhang, S.; Zhang, L.; Liu, H.; Hu, J., Interfacial synthesis of magnetic PMMA@Fe₃O₄/Cu₃(BTC)₂ hollow microspheres through one-pot Pickering emulsion and their application as drug delivery. *RSC Adv.* **2016**, *6*, 58511-58515.

26. Bourgeat-Lami, E.; Sheibat-Othman, N.; Dos Santos, A. M., Polymer-Clay Nanocomposite Particles and Soap-free Latexes Stabilized by Clay Platelets: State of the Art and Recent Advances. In *Polymer Nanocomposites by Emulsion and Suspension Polymerization*, The Royal Society of Chemistry: 2011; pp 269-311.

27. Schrade, A.; Landfester, K.; Ziener, U., Pickering-type stabilized nanoparticles by heterophase polymerization. *Chem. Soc. Rev.* **2013**, *42*, 6823-39.

28. Bon, S. A. F., Pickering Emulsion Polymerization. In *Encyclopedia of Polymeric Nanomaterials*, 2015; pp 1-6.

29. Hasell, T.; Yang, J.; Wang, W.; Li, J.; Brown, P. D.; Poliakoff, M.; Lester, E.; Howdle, S. M., Preparation of polymer-nanoparticle composite beads by a nanoparticle-stabilised suspension polymerisation. *J. Mater. Chem.* **2007**, *17*, 4382-4386.

30. Xiao, Q.; Tan, X.; Ji, L.; Xue, J., Preparation and characterization of polyaniline/nano-Fe3O4 composites via a novel Pickering emulsion route. *Synth. Met.* **2007**, *157*, 784-791.

31. Wang, C.; Zhang, C.; Li, Y.; Chen, Y.; Tong, Z., Facile fabrication of nanocomposite microspheres with polymer cores and magnetic shells by Pickering suspension polymerization. *React. Funct. Polym.* **2009**, *69*, 750-754.

32. Yin, D.; Du, X.; Liu, H.; Zhang, Q.; Ma, L., Facile one-step fabrication of polymer microspheres with high magnetism and armored inorganic particles by Pickering emulsion polymerization. *Colloids Surf. A Physicochem. Eng. Asp.* **2012**, *414*, 289-295.

33. Kim, Y. J.; Liu, Y. D.; Seo, Y.; Choi, H. J., Pickering-Emulsion-Polymerized Polystyrene/Fe2O3 Composite Particles and Their Magnetoresponsive Characteristics. *Langmuir* **2013**, *29*, 4959-4965.

34. Abd El - Mageed, A. I. A.; Shalan, A. E.; Mohamed, L. A.; Essawy, H. A.; Taha,
F.; Dyab, A. K. F., Effect of pH and zeta potential of Pickering stabilizing magnetite
nanoparticles on the features of magnetized polystyrene microspheres. *Polym. Eng. Sci.* 2021, 61, 234-244.

35. Chae, H. S.; Piao, S. H.; Han, W. J.; Choi, H. J., Core/Shell Polystyrene/Magnetite Hybrid Nanoparticles Fabricated by Pickering Emulsion Polymerization and Their Magnetorheological Response. *Macromol. Chem. Phys.* **2018**, *219*.

36. Han, S.; Choi, J.; Seo, Y. P.; Park, I. J.; Choi, H. J.; Seo, Y., High-Performance Magnetorheological Suspensions of Pickering-Emulsion-Polymerized Polystyrene/Fe3O4 Particles with Enhanced Stability. *Langmuir* **2018**, *34*, 2807-2814.

37. Zhou, M. J.; Zhou, S. Z.; Pang, X. C.; Li, K. R.; Qiao, X. G., Preparation of superparamagnetic γ-Fe2O3@LS@PS composite latex particles through pickering miniemulsion polymerization. *Colloids Surf. A: Physicochem. Eng. Asp.* **2020**, *585*.

38. Barthet, C.; Hickey, A. J.; Cairns, D. B.; Armes, S. P., Synthesis of Novel Polymer±Silica Colloidal Nanocomposites via Free-Radical Polymerization of Vinyl Monomers. *Adv. Mater.* **1999**, *11*, 408-410.

Percy, M. J.; Barthet, C.; Lobb, J. C.; Khan, M. A.; Lascelles, S. F.; Vamvakaki,
 M.; Armes, S. P., Synthesis and Characterization of Vinyl Polymer-Silica Colloidal
 Nanocomposites. *Langmuir* 2000, *16*, 6913-6920.

40. Amalvy, J. I.; Percy, M. J.; Armes, S. P.; Wiese, H., Synthesis and Characterization of Novel Film-Forming Vinyl Polymer/Silica Colloidal Nanocomposites. *Langmuir* **2001**, *17*, 4770-4778.

41. Colver, P. J.; Colard, C. A. L.; Bon, S. A. P., Multilayered Nanocomposite Polymer
Colloids Using Emulsion Polymerization Stabilized by Solid Particles. *J. Am. Chem. Soc.* **2008**, *130*, 16850-16851.

42. Sheibat-Othman, N.; Bourgeat-Lami, E., Use of silica particles for the formation of organic-inorganic particles by surfactant-free emulsion polymerization. *Langmuir* **2009**, *25*, 10121-10133.

43. Bourgeat-Lami, E.; Guimaraes, T. R.; Pereira, A. M.; Alves, G. M.; Moreira, J. C.; Putaux, J. L.; Dos Santos, A. M., High solids content, soap-free, film-forming latexes stabilized by laponite clay platelets. *Macromol. Rapid Commun.* **2010**, *31*, 1874-1880.

44. Fielding, L. A.; Tonnar, J.; Armes, S. P., All-acrylic film-forming colloidal polymer/silica nanocomposite particles prepared by aqueous emulsion polymerization. *Langmuir* **2011**, *27*, 11129-11144.

45. Sheibat-Othman, N.; Cenacchi-Pereira, A.-M.; Santos, A. M. D.; Bourgeat-Lami, E., A kinetic investigation of surfactant-free emulsion polymerization of styrene using laponite clay platelets as stabilizers. *J. Polym. Sci. A. Polym. Chem.* **2011**, *49*, 4771-4784.

46. Teixeira, R. F. A.; McKenzie, H. S.; Boyd, A. A.; Bon, S. A. F., Pickering Emulsion Polymerization Using Laponite Clay as Stabilizer To Prepare Armored "Soft" Polymer Latexes. *Macromolecules* **2011**, *44*, 7415-7422.

47. Zgheib, N.; Putaux, J. L.; Thill, A.; D'Agosto, F.; Lansalot, M.; Bourgeat-Lami, E., Stabilization of miniemulsion droplets by cerium oxide nanoparticles: a step toward the elaboration of armored composite latexes. *Langmuir* **2012**, *28*, 6163-6174.

48. Brunier, B.; Sheibat-Othman, N.; Chevalier, Y.; Bourgeat-Lami, E., Partitioning of Laponite Clay Platelets in Pickering Emulsion Polymerization. *Langmuir* **2016**, *32*, 112-124.

49. Brunier, B.; Sheibat-Othman, N.; Chniguir, M.; Chevalier, Y.; Bourgeat-Lami, E.,
Investigation of Four Different Laponite Clays as Stabilizers in Pickering Emulsion
Polymerization. *Langmuir* 2016, *32*, 6046-6057.

50. Mirzataheri, M.; Khamisabadi, S.; Salimi, A., Characterization of styrene-co-butyl acrylate/Cloisite Na+ nanocomposite film synthesized via soap free emulsion polymerization. *Prog. Org. Coat.* **2016**, *99*, 274-281.

51. Delafresnaye, L.; Dugas, P.-Y.; Dufils, P.-E.; Chaduc, I.; Vinas, J.; Lansalot, M.; Bourgeat-Lami, E., Synthesis of clay-armored poly(vinylidene chloride-co-methyl acrylate) latexes by Pickering emulsion polymerization and their film-forming properties. *Polym. Chem.* **2017**, *8*, 6217-6232.

52. Lotierzo, A.; Bon, S. A. F., A mechanistic investigation of Pickering emulsion polymerization. *Polym. Chem.* **2017**, *8*, 5100-5111.

53. Martín-Fabiani, I.; Koh, M. L.; Dalmas, F.; Elidottir, K. L.; Hinder, S. J.; Jurewicz,
I.; Lansalot, M.; Bourgeat-Lami, E.; Keddie, J. L., Design of Waterborne Nanoceria/Polymer
Nanocomposite UV-Absorbing Coatings: Pickering versus Blended Particles. *ACS Appl. Nano Mater.* 2018, *1*, 3956-3968.

54. Morgen, T. O.; Krumova, M.; Luttikhedde, H.; Mecking, S., Free-Radical Dispersion Polymerization of Ethylene with Laponite to Polyethylene–Clay Nanocomposite Particles. *Macromolecules* **2018**, *51*, 4118-4128.

55. Qiao, X. G.; Dugas, P. Y.; Prevot, V.; Bourgeat-Lami, E., Surfactant-free synthesis of layered double hydroxide-armored latex particles. *Polym. Chem.* **2020**, *11*, 3195-3208.

56. Czajka, A.; Liao, G.; Mykhaylyk, O. O.; Armes, S. P., In situ small-angle X-ray scattering studies during the formation of polymer/silica nanocomposite particles in aqueous solution. *Chem. Sci.* **2021**, *12*, 14288-14300.

57. Xu, Z.; Xia, A.; Wang, C.; Yang, W.; Fu, S., Synthesis of raspberry-like magnetic polystyrene microspheres. *Mater. Chem. Phys.* **2007**, *103*, 494-499.

58. Li, K.; Dugas, P. Y.; Lansalot, M.; Bourgeat-Lami, E., Surfactant-Free Emulsion Polymerization Stabilized by Ultrasmall Superparamagnetic Iron Oxide Particles Using Acrylic Acid or Methacrylic Acid as Auxiliary Comonomers. *Macromolecules* **2016**, *49*, 7609-7624.

59. Li, K.; Xie, L.; Wang, B.; Yan, J.; Tang, H.; Zhou, D., Mechanistic Investigation of Surfactant-Free Emulsion Polymerization Using Magnetite Nanoparticles Modified by Citric Acid as Stabilizers. *Langmuir* **2020**, *36*, 8290-8300.

60. Corner, T., Polyelectrolyte stabilised latices part 1, preparation. *Colloids Surf.* **1981**, *3*, 119-129.

61. Massart, R., Preparation of Aqueous Magnetic Liquids in Alkaline and Acidic Media. *Mag. IEEE Trans.* **1981**, *17*, 1247-1248.

62. Massart, R.; Dubois, E.; Cabuil, V.; Hasmonay, E., Preparation and properties of monodisperse magnetic fluids. *J. Magn. Magn. Mater.* **1995**, *149*, 1-5.

63. Kortuem, G.; Vogel, W.; Andrussow, K., *Dissociation Constants of Organic Acids in Aqueous Solution*. Butterworths & Co.: 1961.

64. Juang, M. S.; Krieger, I. M., Emulsifier-Free Emulsion Polymerization with Ionic Comonomer. *J. Polym. Sci.* **1976**, *14*, 2089-2107.

65. Liu, L. J.; Krieger, I. M., Emulsifier-Free Emulsion Polymerization with Cationic Comonomer. *J. Polym. Sci. A. Polym. Chem.* **1981**, *19*, 3013-3026.

66. Guillaume, J. L.; Pichot, C.; Guillot, J., Emulsifier-Free Emulsion Copolymerization of Styrene and Butyl Acrylate. 11. Kinetic Studies in the Presence of Ionogenic Comonomers. *J. Polym. Sci. A. Polym. Chem.* **1988**, *26*, 1937-1959.

67. Marks, G. P.; Clark, A. C., Emulsion Polymerizations with 2-Acrylamido-2methylpropanesulfonic Acid. In *Specialty Monomers and Polymers*, American Chemical Society: 2000; Vol. 755, pp 46-53. 68. Chang, W.; Liu, L.; Zhang, J.; Pan, Q.; Pei, M., Preparation and Characterization of Styrene/Butyl Acrylate Emulsifier-Free Latex with 2-Acrylamido-2-Methyl Propane Sulfonic Acid as a Reactive Emulsifier. *J. Disper. Sci. Technol.* **2009**, *30*, 639-642.

69. Dai, M.; Zhang, Y.; He, P., Preparation and characterization of stable and high solid content St/BA emulsifier-free latexes in the presence of AMPS. *Polym. Bull.* **2011**, *67*, 91-100.

70. Zhang, Y.; Wang, B.; Dai, M.; Pan, S.; Zhang, F.; He, P., Studies on the Preparation of Stable and High Solid Content Emulsifier-Free Poly(MMA/BA/HEA) Latex with the Addition of AMPS and Characterization of the Obtained Copolymers. *J. Macromol. Sci. A.* **2011**, *48*, 409-415.

71. Zhang, Y.; Pan, S.; Ai, S.; Liu, H.; Wang, H.; He, P., Semi-continuous emulsion copolymerization of vinyl acetate and butyl acrylate in presence of AMPS. *Iran. Polym. J.* **2014**, *23*, 103-109.

72. Yuan, X.-y.; Dimonie, V. L.; Sudol, E. D.; Roberts, J. E.; El-Aasser, M. S., Toward an Understanding of the Role of Water-Soluble Oligomers in the Emulsion Polymerization of Styrene–Butadiene–Acrylic Acid. Mechanisms of Water-Soluble Oligomer Formation. *Macromolecules* **2002**, *35*, 8356-8370.

73. Chonde, Y.; Krieger, I. M., Emulsion Polymerization of Styrene with Ionic Comonomer in the Presence of Methanol. *J. Appl. Polym. Sci.* **1981**, *26*, 1819-1827.

74. Twigt, F.; Piet, P.; German, A. L., Preparation and co-catalytic properties of functionalized latices. *Eur. Polym. J.* **1991**, *27*, 939-945.

75. Bon, S. A. F.; van Beek, H.; Piet, P.; German, A. L., Emulsifier-Free Synthesis of Monodisperse Core-Shell Polymer Colloids Containing Chloromethyl Groups. *J. Appl. Polym. Sci.* **1995**, *58*, 19-29.

76. Lane, W. H., Determination of Solubility of Styrene in Water and of Water in Styrene. *Ind. Eng. Chem. Anal.* **1946**, *18*, 295-296.

77. Beuermann, S.; Harrisson, S.; Hutchinson, R. A.; Junkers, T.; Russell, G. T., Update and critical reanalysis of IUPAC benchmark propagation rate coefficient data. *Polym. Chem.*2022.

78. Ballard, M. J.; Napper, D. H.; Gilbert, R. G., Kinetics of emulsion polymerization of methyl methacrylate. *J. Polym. Sci. A. Polym. Chem.* **1984**, *22*, 3225-3253.

79. Ref. 12 in: <u>https://en.wikipedia.org/wiki/2-Acrylamido-2-</u> methylpropane_sulfonic_acid 80. Fitch, R. M., The homogeneous nucleation of polymer colloids. *Br. Polym. J.* **1973**, *5*, 467-483.