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Self-Stabilized Magnetic Polymeric Composite Nanoparticles by Emulsifier-Free Miniemulsion Polymerization

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Self-stabilized magnetic polymeric composite nanoparticles (SS-MPCPs) were prepared by emulsifier-free miniemulsion polymerization using styrene (St) as a monomer, sodium *p*-styrenesulfonate (NaSS) as an ionic comonomer, hexadecane (HD) as a hydrophobe, and 2,2'-azodiisobutyronitrile (AIBN) as an initiator in the presence of hydrophobic magnetite particles. The hydrophobic magnetite particles with an average size of about 10 nm were prepared by the acidification of the water-based magnetite ferrofluid, previously synthesized by a chemical coprecipitation method. Some colloidal features of the synthesized SS-MPCPs were analyzed. The morphology and the particle size distributions (PSDs) of the SS-MPCPs were observed and analyzed by transmission electron microscopy (TEM). The surface charge density was determined by conductometric titration. The surface hairy layer and the colloidal stability of SS-MPCPs against different electrolytes were determined by photon correlation spectroscopy (PCS). The average Fe₃O₄ content of SS-MPCPs was determined by thermogravimetric analysis (TGA). Vibrating sample magnetometry (VSM) was used to analyze the magnetic properties of the SS-MPCPs under dry conditions. The results show that the encapsulation of magnetite is successful and the distribution of magnetite particles inside SS-MPCPs is mainly in the core of the particles. The best SS-MPCPs prepared had a relatively narrow PSD, exhibited superparamagnetism, and possessed some magnetic response.

Introduction

One of the fastest growing and outstanding fields of materials science is the preparation of new particles that may be used for manufacturing novel materials with certain well-defined properties and functions. In this way, nanotechnology is making great steps forward in the improvement of existing materials and the creation of innovative materials in the colloidal range based on both inorganic and polymeric materials as well as nanocomposites consisting of a mixture of both of them.

Magnetic polymeric composite particles (MPCPs) have extensive applications in biomedical,^{1,2} bioengineering, and biotechnology fields, such as cell separation,³ immunossays,⁴ nucleic acid purification,⁵ DNA separation,⁶ enzyme immobilization,⁷ magnetic resonance imaging,⁸ and hyperthermia.⁹ MPCPs exhibit high magnetic susceptibility to an external

magnetic field, and in addition, they are easily further functionalized and surface-modified by the attachment of various bioactive molecules.¹⁰ In all the cases, MPCPs should fulfill certain criteria to fit further biotechnological applications,¹¹ such as no sedimentation, uniform size and size distribution, high and uniform magnetic content, superparamagnetic behavior, no toxicity, and no iron leaking. In general, however, the polymerization process for the encapsulation of magnetite may produce three possible types of particles in the resulting magnetic latex, i.e., magnetic polymeric composite particles (MPCPs; with magnetite encapsulated inside), pure polymer particles (PPPs; without magnetite inside), and bare (free) magnetite particles (BMPs; without polymer coating). The existence of PPPs is not desirable because the magnetic properties of the composite particles will be decreased, and the existence of BMPs is also not desired because they cannot be further functionalized due to their bare surfaces without polymer surrounding. In addition, particle size distribution (PSD) should be as narrow as possible so that MPCPs can respond to an external magnetic field as uniformly as possible. Hence, the challenges in almost all the strategies to prepare MPCPs are to minimize, even eliminate, the formation of PPPs and BMPs during the preparation stage with an even greater challenge in obtaining MPCPs with very narrow PSD. To date, however, these important issues have not been analyzed and studied in detail in the literature.

The preparation process of MPCPs consists of two steps: (i) the preparation of ferrofluid and (ii) the encapsulation of the resulting ferrofluid with polymer.

Ferrofluids can be classified according to the hydrophilicity–hydrophobicity of the stabilizers used as hydrophilic and

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hydrophobic ferrofluids. They are stable dispersions of ultrafine magnetic particles in an organic or aqueous carrier medium. The stabilization of these ultrafine magnetic particles can be achieved by adsorption of stabilizers to hinder particles flocculation and sedimentation. Magnetite, Fe_3O_4 , is the most common magnetic material used, and it is usually prepared by chemical coprecipitation of an aqueous of $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution ($\text{Fe}^{3+}/\text{Fe}^{2+} = 2:1$ (mol)) with a base in the presence of stabilizer, such as oleic acid, the most commonly used one.

MPCPs can also be classified into two types, i.e., hydrophobic magnetic particles and hydrophilic magnetic particles, based on the hydrophilicity–hydrophobicity of the coating polymers. A great deal of strategies for the preparation of MPCPs has been used to encapsulate magnetic particles inside polymers by various polymerization methods.^{12–19} However, for the preparation of hydrophobic MPCPs, in which a hydrophobic polymer such as polystyrene is used, miniemulsion polymerization is the most appropriate and effective technique for magnetite encapsulation.^{11,20–25} It is well-known that in miniemulsion polymerization the nucleation occurs mainly inside monomer droplets. When magnetite particles are hydrophobic and dispersed directly in monomer droplets before polymerization, they will be encapsulated directly and do not need to diffuse into micelles; thus, the mass transfer of such a huge amount (in volume) of magnetite particles can be avoided thoroughly by miniemulsion polymerization.

Miniemulsion polymerization is composed of submicrometer-sized monomer droplets stabilized with an emulsifier against coalescence and with a costabilizer to minimize Ostwald ripening.^{11,26} The main difficulty in the process of miniemulsion polymerization is to avoid micellar nucleation and reduce homogeneous nucleation in order to ensure monomer droplet nucleation. In the case of the encapsulation of inorganic particles, such as magnetite particles, micellar and homogeneous nucleation will result in the formation of PPPs decreasing encapsulation degree.

Sodium dodecyl sulfate (SDS) is the most often used emulsifier in miniemulsion polymerization.^{27–29} In our previous work,²⁰ the effect of the amount of SDS on the production of MPCPs by miniemulsion polymerization was investigated. It was found that SDS works as a high-efficiency emulsifier in the preparation of MPCPs by this polymerization technique; reducing the amount

Table 1. Recipes Used in the Emulsifier-Free Miniemulsion Polymerizations^a

latex	AIBN (%)	HD (%)	NaSS (%)
SS–MPCPs–5	4.0	15.0	5.0
SS–MPCPs–10	4.0	15.0	10.0
SS–MPCPs–15	4.0	15.0	15.0
SS–MPCPs–20	4.0	15.0	20.0
SS–MPCPs–25	4.0	15.0	25.0

reaction conditions: $T = 70\text{ }^\circ\text{C}$; rpm = 49; reaction time = 21 h; DDI water = 63.0 g; $\text{Fe}_3\text{O}_4\text{-St} = 7.0\text{ g}$

^a All the percentages are based on the total amount of Fe_3O_4 and St.

of SDS improved the magnetite encapsulation degree, narrowed the PSD, and reduced the number of BMPs and PPPs at the same time. The optimum percentage of SDS, based on the total amount of styrene and magnetite, was 2–3%, but it was impossible to avoid the formation of PPPs because of the micellar nucleation.

On the other hand, sodium *p*-styrenesulfonate (NaSS) is a kind of ionic monomer. When it is used as comonomer, the sulfonic groups are covalently anchored onto the surface of the polymer particles obtained. These particles will be more stable than those stabilized by the physically adsorbed ionic groups coming from emulsifiers such as SDS, because the migration/desorption of ionic groups is avoided.

In this work, emulsifier-free miniemulsion polymerization was used to prepare self-stabilized MPCPs using hydrophobic magnetite particles, styrene (St) as a monomer, NaSS as an ionic comonomer, hexadecane (HD) as a hydrophobe, and azodiisobutyronitrile (AIBN) as an initiator. In order to obtain self-stabilized MPCPs with narrow PSDs and a high degree of magnetite encapsulation, the effect of the amount of NaSS on mean particle diameter, PSD, surface charge density, hairy layer, colloidal stability against electrolytes, morphology and magnetite distribution, and magnetic response of the different MPCPs prepared were analyzed in detail.

Experimental Section

Materials. Styrene (St) monomer was purified by washing with a 10% (weight %) sodium hydroxide aqueous solution and stored at $-18\text{ }^\circ\text{C}$ until use. Sodium *p*-styrenesulfonate (NaSS, Aldrich), hexadecane (HD, Sigma-Aldrich), azodiisobutyronitrile (AIBN, Fluka), iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Sigma), iron(II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, Aldrich), oleic acid (OA, Aldrich), 25% ammonium hydroxide solution (NH_4OH , Fluka), 1 N hydrochloric acid (HCl, Panreac), sodium hydroxide (NaOH, Panreac), sodium chloride (NaCl, Panreac), and calcium chloride (CaCl_2 , Fluka) were used without further purification. Double deionized (DDI) water was used throughout the work.

Preparation of Magnetite Particles. Hydrophilic magnetite particles were prepared by stoichiometric chemical coprecipitation of ferrous and ferric salts, as reported previously.²⁰ In this way, a water-based magnetite ferrofluid was obtained.

On the other hand, hydrophobic magnetite particles were prepared by acidifying hydrophilic magnetite particles.²⁰ In this way, an oil-based Fe_3O_4 ferrofluid ($\text{Fe}_3\text{O}_4\text{-St}$) was obtained with a 10% in weight with respect to St.

Preparation of Magnetic Polymeric Composite Particles (MPCPs). Before the polymerization reactions were carried out, all the components of the emulsifier-free miniemulsion polymerization recipes were pre-emulsified. On the basis of the recipes given in Table 1, NaSS was dissolved in DDI water, and AIBN was dissolved in the mixture of HD and $\text{Fe}_3\text{O}_4\text{-St}$. Then, the two solutions were mixed together under stirring provided by a magnetic bar stirrer for 10 min and miniemulsified (model 450 sonifier, Branson) in an ice-cooled bath. All the miniemulsions were prepared under the same optimized conditions (output control, 8; duty cycle, 80%; sonication time, 10 min).

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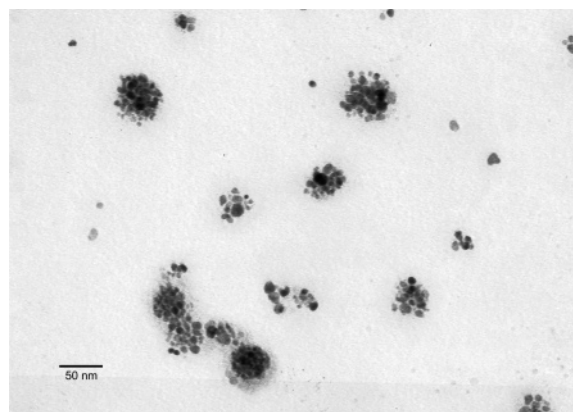


Figure 1. Water-based magnetite particles observed by TEM.

The emulsifier-free miniemulsion polymerizations were carried in 0.10 L glass bottles immersed in a thermostatic bath. The bottles were tumbled end-over-end at 49 rpm. Once all the reagents were introduced and miniemulsified into the bottles, as was described before, the bottles were purged with nitrogen for 10 min and then introduced into the thermostatic bath at 70 °C for 21 h.

Magnetite and Latex Characterizations. Transmission electron microscopy (TEM, Hitachi H-7000 FA) was used to observe and analyze the PSDs and the microscopic morphology of magnetite particles and SS-MPCPs. The particle size distributions (PSDs) were determined from TEM microphotographs on representative samples of more than 1000 particles of magnetic latexes and analyzed using the software *Bolero* (AQ Systems). Number- (\bar{d}_n), weight- (\bar{d}_w), and volume-average (\bar{d}_v) diameters as well as polydispersity indices (PDI) were calculated from the PSDs.³⁰

The final magnetic latexes were cleaned by the serum replacement method in order to determine accurately the surface charge density, and to determine the thickness of the hairy layer of the magnetic latex particles.

The surface charge density (σ , $\mu\text{C}/\text{cm}^2$) of the magnetic latexes was determined by conductometric titration, taking into account the volume and concentration of the titration agent (NaOH) used and the surface area of the latex particles.³¹

In order to find evidence of the existence of a hairy layer on the surface of the magnetic latexes, the mean hydrodynamic particle diameters (\bar{d}_{PCS} , nm) were obtained by photon correlation spectroscopy (PCS, Malvern Zetasizer Nano ZS) at different concentrations of sodium chloride (NaCl) and calcium chloride (CaCl_2).

Thermogravimetric analysis (TGA, Universal V3.5B TA instruments) was used to determine the average Fe_3O_4 content of representative MPCPs samples. The Fe_3O_4 content of MPCPs was given according to the weight percentage of the residue remaining after thermal analysis from room temperature to 1000 °C under nitrogen atmosphere.

A vibrating sample magnetometer (VSM, LDJ-9600, America LDJ Company) was used to analyze the magnetic properties of magnetite and MPCPs under dry conditions.

Results and Discussion

Preparation of Hydrophobic Magnetite Ferrofluid. The magnetic particles should be smaller than 15 nm to ensure that the magnetite particles exhibit superparamagnetic behavior. Superparamagnetic particles are of great interest because they do not retain any magnetism after removal of the magnetic field. On the other hand, to increase magnetic activity, many of the nanomagnets must be first gather into one large particulate entity.³²

In Figure 1, a microphotograph of the hydrophilic magnetite particles synthesized is shown. As can be seen, the size of a

single magnetite particle was about 6–15 nm, with the average size being about 10 nm, but the particles were found in large particulate aggregates or domains of about 25–70 nm. However, the most important and favorable point for endowing MPCPs with superparamagnetic behavior is that the single magnetite particles should be completely separated from one another.

As was mentioned before, magnetite particles must be hydrophobic in order to be dispersed in St. In this way, the miniemulsion polymerization process will take place in the St monomer droplets containing the magnetite particles previously dispersed inside them. Therefore, ammonium oleate was transferred to OA with a strong acid.²⁰ The transformation of the hydrophilic–hydrophobic character of magnetite particles is fundamental for encapsulating them successfully inside the polymer particles.

Unfortunately, the dispersion of magnetite particles in styrene could not be analyzed directly by TEM because styrene dissolved the support film of Formvar placed on the copper grids used to observe the latex samples by TEM. However, according to the measurement of the magnetite particles by PCS, the hydrodynamic diameter of the particulate aggregates dispersed in St (29.2 nm) was much smaller than that when they were dispersed in water (63.8 nm). This indicated that St could intercalate into the interspaces between single magnetite particles when magnetite particles were dispersed in it. Therefore, the resulted hydrophobic magnetite particles could endow the MPCPs with superparamagnetic behavior.

Preparation of SS-MPCPs. Effect of the Amount of NaSS. The size of the latex particles determines the total surface area of MPCPs and particle properties such as adsorption capacity, while PSD affects the response of MPCPs to an external magnetic field. Therefore, the ideal MPCPs must have a particle size smaller than 100 nm and a monodisperse PSD, so that the total surface area is as large as possible and MPCPs can respond to an external magnetic field as uniform as possible. As the amount of the ionic monomer used has a strong effect on the particle size and PSD of the resulting colloidal polymer particles, the effect of the amount of NaSS on the production of SS-MPCPs was investigated by the preparation of SS-MPCPs using different amounts of NaSS, and maintaining the rest of the experimental conditions unchanged (see Table 1).

TEM microphotographs of the SS-MPCPs synthesized with different amounts of NaSS are shown in Figure 2. As can be seen, the amount of NaSS had a notable effect on the magnetite encapsulation degree, particle size, and PSDs of the SS-MPCPs. From 5% to 15% of NaSS, the encapsulation degree was increased, and some BMPs but no PPPs were observed. At 20% NaSS, the encapsulation of magnetite was successful, and neither BMPs nor PPPs were observed. The absence of PPPs formed during the polymerization process indicated that monomer droplet nucleation was achieved entirely by using an emulsifier-free miniemulsion polymerization technique. Micellar nucleation was avoided completely in the absence of emulsifier, and homogeneous nucleation was also prevented. However, when the concentration of NaSS was 25%, a significant number of PPPs were observed. At this concentration, the amount of oligomers formed in the aqueous phase is enough to stabilize the particles generated by homogeneous nucleation, and pure polymer particles were produced.

In Table 2 and in Figure 3, average diameters and PDIs and PSDs of the different SS-MPCPs synthesized are shown, respectively. As can be seen, particle sizes and PDIs decreased, and PSDs became narrower when the amount of NaSS increased up to 20%. Furthermore, the PSD of SS-MPCPs-20 was relatively

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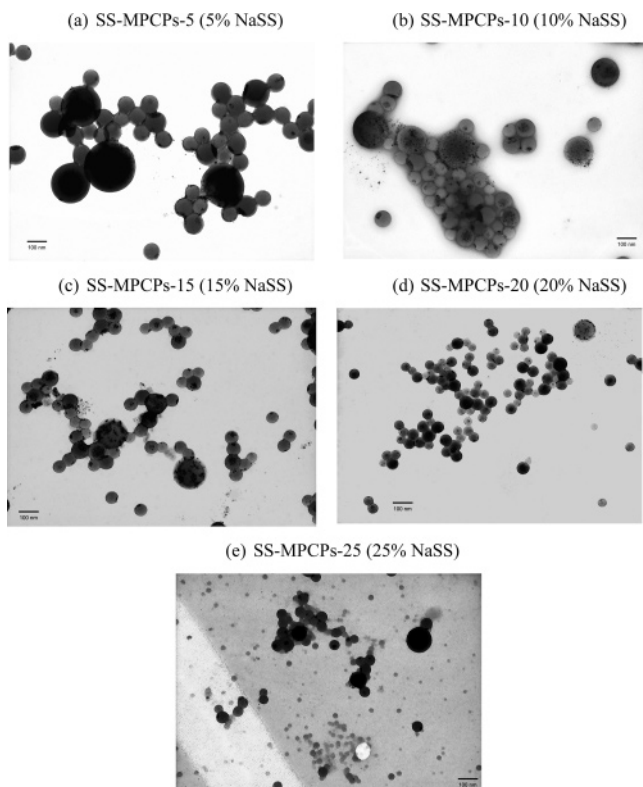


Figure 2. TEM microphotograph of SS-MPCPs prepared with different amounts of NaSS.

Table 2. Average Diameters and Polydispersity Indices (PDI) Obtained from the PSDs Analyzed by TEM of the Different SS-MPCPs Synthesized

latex	\bar{d}_n (nm)	\bar{d}_w (nm)	\bar{d}_v (nm)	PDI
SS-MPCPs-5	151.3	255.2	173.6	1.686
SS-MPCPs-10	121.8	190.9	143.0	1.567
SS-MPCPs-15	109.6	161.8	122.7	1.476
SS-MPCPs-20	76.9	83.1	78.7	1.081
SS-MPCPs-25	41.3	79.2	51.5	1.920

narrow, and its PDI (1.081) was close to monodispersity in size ($PDI < 1.05$) according to Tsaur et al.³³ However, at 25% NaSS, the particle size of the SS-MPCPs decreased, but the PSD was very broad ($PDI = 1.920$), presenting a clear bimodality. This was due to the generation of a high amount of small PPPs by the homogeneous nucleation mechanism (see Figures 2e and 3e).

In addition, in the TEM micrographs (Figure 2) and in the PSDs (Figure 3) of all the SS-MPCPs prepared, the existence of a few large composite particles can be observed in all the different latexes.

Morphology and Magnetite Distribution of the SS-MPCPs. The distribution of magnetite inside composite particles is an important factor, which can influence the magnetic characteristics of composite particles. As can be seen in the micrographs shown in Figure 2, in all the SS-MPCPs synthesized the magnetite particles are mainly in the core of the composite particles. However, in the MPCPs prepared using SDS as emulsifier,²⁰ the magnetite particles were almost all located in the outer layer of the composite particles, and the distribution of magnetite particles was nonuniform.

Due to the ionic character of NaSS, the copolymerization of St with NaSS increases the hydrophilicity of the polymer formed

and enhances the hydrophobicity of oleic acid-coated magnetite particles. Thus, magnetite particles are mainly in the core of SS-MPCPs.

On the other hand, as was commented before, there are a few large composite particles in the magnetic latexes. As can be seen in Figure 2, the distribution of magnetite particles inside the largest composite particles is completely different from that of the smallest ones. This means that the formation of this kind of particle is due to aggregation among some of the particles formed. Besides, it can be seen that the numbers of magnetite particles encapsulated inside each magnetic particle are not the same.

Stabilization Mechanism of Emulsifier-Free Miniemulsion Polymerization. As mentioned before, miniemulsion polymerization generally is composed of submicrometer-sized monomer droplets stabilized with an emulsifier against coalescence and with a costabilizer (hydrophobe) to minimize Ostwald ripening. However, in this work the ionic comonomer NaSS was used instead of an ionic emulsifier. The structural formula of NaSS is shown in Figure 4. One head is a hydrophilic group (sulfonic), and another head is a hydrophobic group. It is not really an emulsifier, although it has the ability to decrease the surface tension of water to some extent, which is a basic feature of an emulsifier.

In Figure 5, the stabilization mechanism of SS-MPCPs prepared by miniemulsion polymerization in the absence of an emulsifier using hexadecane (HD) as hydrophobe and NaSS as stabilizer is shown. As can be seen, NaSS was dissolved in DDI water, and AIBN was dissolved in the mixture of HD and Fe_3O_4 -St. Then, the two solutions were mixed together under stirring and sonicated. Once a stable miniemulsion was obtained, the temperature was raised to 70 °C and monomer droplets polymerized. The sulfonic groups of NaSS anchored covalently onto the particle surface avoid the migration occurring with conventional emulsifier molecules enhancing the stability of the particles and increasing the hydrophilicity of the copolymer with respect to the encapsulated oleic acid-coated magnetite particles. Moreover, this fact favors the concentration of magnetite particles in the core of the composite particles.

Colloidal and Surface Characterizations of SS-MPCPs. **Surface Charge Density.** Colloidal stability of electrostatically stabilized polymer particles strongly depends on surface charge density, nature of the surface ionizable groups, and salt concentration in the dispersion.³⁴ Therefore, an accurate determination of the surface charge density of the latex particles is really necessary.

The surface charge density of latex SS-MPCPs-20 is shown in Table 3. As can be seen, there are two contributions to the total surface charge density of the particles. The first one is due to the strong acid groups provided by the sulfonic groups ($-SO_3^-$) of NaSS, and the second one is due to the weak acid groups provided by the carboxylic groups anchored on particle surface.

There is no doubt about the precedence of the sulfonic groups coming from NaSS taking into account that uncharged AIBN was used as initiator. On the other hand, carboxylic groups were also detected on the surface of SS-MPCPs, and their charge density was high enough to be neglected. Considering all the possibilities, the main source of carboxylic groups was oleic acid, which was used as a stabilizer of the magnetite particles to prevent agglomeration.

Oleic acid (OA) is an unsaturated acid containing a polar carboxylic group, which trends toward the aqueous phase. Therefore, the excess of OA can diffuse from the core to the

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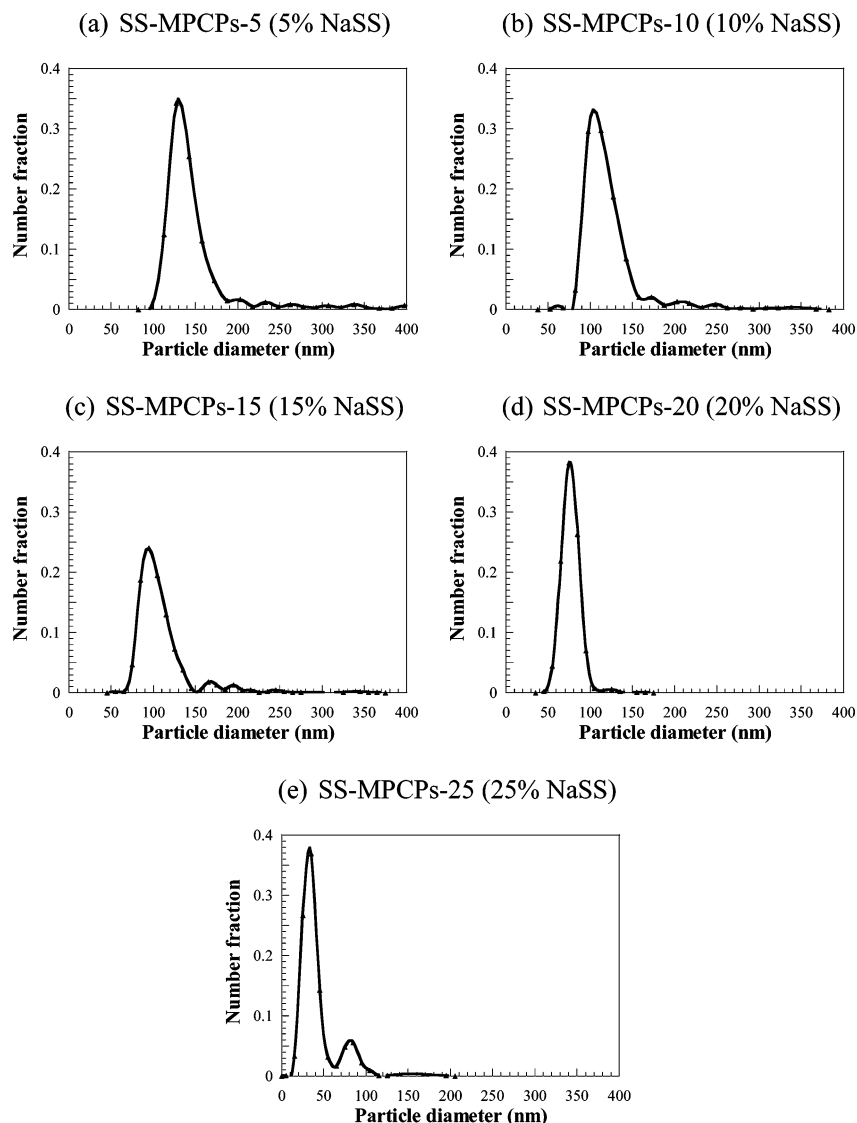


Figure 3. PSDs of SS-MPCPs prepared with different amounts of NaSS.

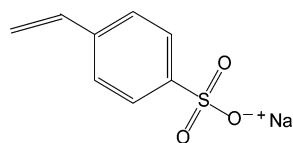


Figure 4. Structural formula of NaSS molecule.

surface of the magnetic latex, acting as an emulsifier. This fact can be justified by the pH value (4.06) of the magnetic latex dispersion. The percentage of OA distributed on the surface of SS-MPCPs can be calculated by comparing the amount of surface carboxylic groups with the total amount of OA used in the preparation of magnetite particles.

According to the recipe to synthesize the latex SS-MPCPs-20 shown in Table 1, and taking into account the Fe_3O_4 content measured by TGA (as discussed later), the composition of latex SS-MPCPs-20 is $\text{St/NaSS/Fe}_3\text{O}_4/\text{OA} = 66.01/16.67/9.29/8.03$ wt %. Assuming that overall conversion was 100% and that all the NaSS used polymerized on the surface of the composite particles, the theoretical maximum surface charge density provided by sulfonic groups should be $106.91 \mu\text{C}/\text{cm}^2$. Therefore, the percentage of sulfonic groups on the surface of the composite particles with respect to its maximum value is 31.06%. Likewise, the maximum surface charge density that can be provided by the

carboxylic groups is $37.60 \mu\text{C}/\text{cm}^2$. In this way, the percentage of OA on the surface of the SS-MPCPs is 64.06%.

Colloidal Stability Against Electrolytes and Surface Hairy Layer. The flexible polymeric chains that are on the surface of the latex particles adopt different conformations depending on the ionic strength of the medium.³⁵ These polymeric chains, if present on the surface, are extended to the aqueous phase due to the electrostatic repulsions between the ionic end-chain groups and the groups anchored on the surface, forming the “hairy layer”. With the aim of proving the existence of a hairy layer on the surface of the SS-MPCPs synthesized, the effect of different types of electrolytes (NaCl and CaCl_2) on the thickness of the hairy layer was analyzed. At the same time, the colloidal stability of the magnetic latex SS-MPCPs-20 against the two electrolytes was analyzed.

Figure 6 shows the particle hydrodynamic mean diameter (nm) of latex SS-MPCPs-20 versus NaCl concentration. The highest value of the mean diameter corresponds to the hydrodynamic diameter of the particles dispersed in the aqueous medium in the absence of electrolyte. When the dispersion medium is water or an electrolyte aqueous solution having a low ionic strength, the

(35) Santos, R. M.; Forcada, J. J. *Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 501–511.

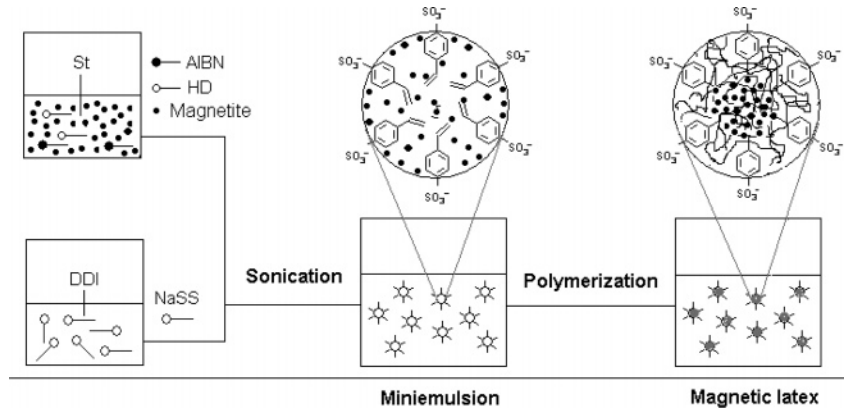


Figure 5. Schematic diagram of the stabilization mechanism for the SS-MPCPs obtained by emulsifier-free miniemulsion polymerization.

Table 3. Surface Charge Density of SS-MPCPs-20 Latex

latex	$\sigma_{\text{strong}} (\mu\text{C}/\text{cm}^2)$	$\sigma_{\text{weak}} (\mu\text{C}/\text{cm}^2)$
SS-MPCPs-20	33.21	24.08

surface polymeric chains are extended to the aqueous phase due to the electrostatic repulsions between their ionic or charged groups. This situation corresponds to the maximum hydrodynamic size of the polymeric particles. By increasing ionic strength, polymer chains are progressively collapsed onto the particle surfaces, diminishing the hydrodynamic diameter of the particles. At high ionic strengths, the chains are completely collapsed onto the surface, corresponding to the minimum particle diameter. Furthermore, no aggregation of particles was observed in the range of concentration of NaCl studied. This indicated that the magnetic latex particles synthesized were stable enough at relative high concentrations of monovalent salt due to the high surface charge and hydration, which diminish the free energy of the system and prevent the agglomeration of the particles. This behavior was also observed in the case of functionalized latexes with surface acetal^{35,36} and aldehyde³⁶ groups. The difference between the mean diameter when the dispersion medium is water and the mean diameter at the highest ionic strength without coagulation, divided by 2, was taken as the thickness of the hairy layer. For the SS-MPCPs-20 latex, the value of the thickness of the hairy layer obtained using NaCl was 21 ± 1 nm.

In Figure 7, the changes in the hydrodynamic mean diameter of SS-MPCPs-20 magnetic latex at different CaCl_2 electrolyte concentrations are shown. As can be seen, at low concentrations of CaCl_2 the change in the hydrodynamic diameters was similar to that observed when NaCl was used as electrolyte, but the concentration of CaCl_2 at which the chains collapsed completely onto the surface and the particle diameter reached a minimum value was much lower than that of when NaCl was used as electrolyte. In this case, the value of the thickness obtained was 22.5 ± 1.1 nm. However, at higher concentrations of CaCl_2 , the hydrodynamic diameter increased, due to the coagulation of the particles.

The different behavior that a monovalent (NaCl) and a divalent (CaCl_2) electrolyte provoke on the thickness of the hairy layer is due to the different conformations that flexible polymeric chains can adopt at different ionic strengths. At the same molar concentration of NaCl and CaCl_2 , the ionic strength of the CaCl_2 solution is higher than that of the NaCl solution; thus, the flexible chains extended to the aqueous phase of the SS-MPCPs-20 collapse more tightly if they are dispersed in a CaCl_2 solution.

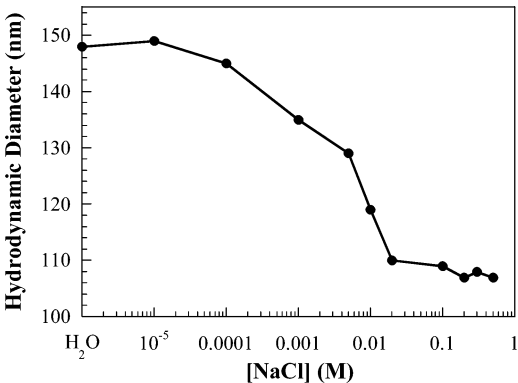


Figure 6. Hydrodynamic diameters of SS-MPCPs-20 at different concentrations of sodium chloride.

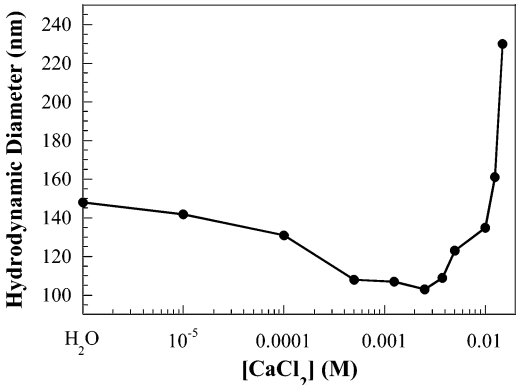


Figure 7. Hydrodynamic diameters of SS-MPCPs-20 at different concentrations of calcium chloride.

Magnetic Properties. Magnetic Component Content. The magnetic responses of composite magnetic materials increase with increasing magnetic component content. Likewise, the magnetic response of the SS-MPCPs synthesized is related to the magnetically susceptible component located inside the particles, i.e., the encapsulated Fe_3O_4 . Therefore, the Fe_3O_4 content is of singular importance for the magnetic response of the SS-MPCPs composite latexes. In order to determine the magnetite content of SS-MPCPs-20 latex, a TGA was carried out, and the curve obtained is shown in Figure 8.

By means of TGA, the polymer should be decomposed completely when the temperature is high enough, but if there are inorganic materials in the sample, they should remain. Therefore, at the end of the TGA process, the residue obtained is only due to the inorganic material.

(36) Búcsi, A.; Forcada, J.; Gibanel, S.; Heroguez, V.; Fontanille, M.; Gnanou, Y. *Macromolecules* **1998**, *31*, 2087–2097.

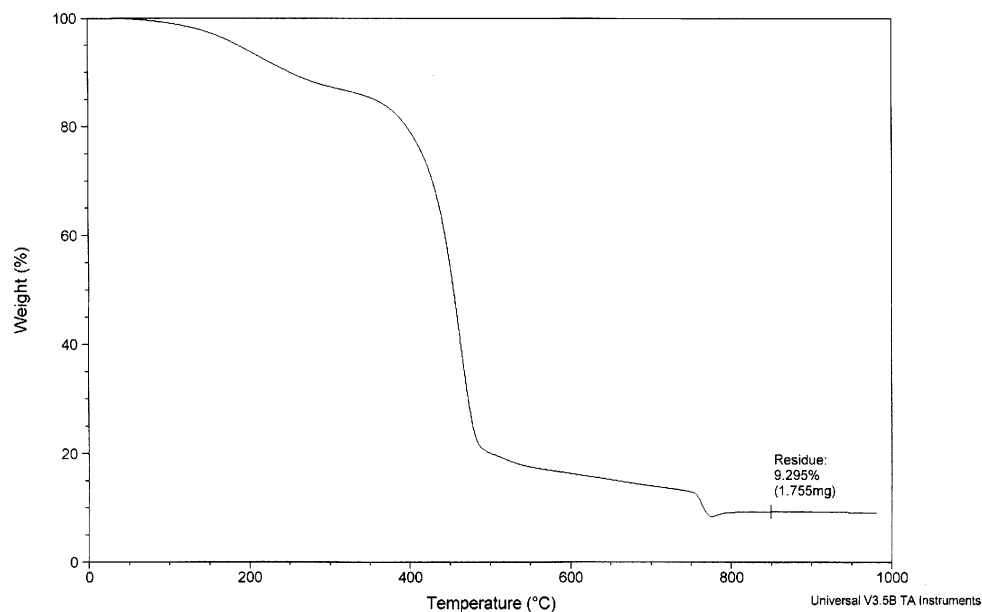


Figure 8. TGA curve of SS-MPCPs-20.

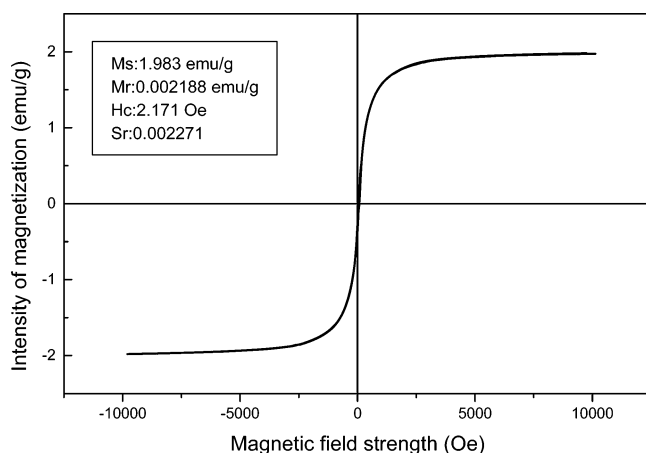


Figure 9. Magnetic hysteresis loop of SS-MPCPs-20.

As can be seen in Figure 8, when temperature reached about 800 °C the weight of the sample was constant and the residue was 9.295%. In addition, there was no increase in weight resulting from the oxidation of Fe_3O_4 to Fe_2O_3 , because TGA was carried out under nitrogen atmosphere. This fact indicated that the Fe_3O_4 content for the SS-MPCPs-20 latex was 9.295%.

Magnetic Response. Magnetic response is a vital property of magnetic materials. The magnetic hysteresis loop characterizes the response ability (magnetization, M) of magnetic materials to an external magnetic field (denoted by the magnetic field strength, H). It can provide the major magnetic parameters of magnetic materials, that is, saturation magnetization (M_s , it reflects the magnetizability of magnetic materials), coercive force (H_c , it characterizes the ability of magnetic materials to retain magnetization when the external magnetic field is removed), magnetic remanence (M_r , it reflects the remaining magnetization of magnetic materials when an external magnetic field is removed), and squareness ratio (S_r , it characterizes the magnetic hysteresis loss). In this work, the magnetic hysteresis loop of SS-MPCPs-20 latex was measured by VSM to characterize the magnetic properties of the composite latex.

In Figure 9, the magnetic hysteresis loop of SS-MPCPs-20 is shown. It looks like a single, S-like curve in shape. This point can be confirmed by the fact that the value of squareness ratio

(S_r) was nearly zero (0.002271). The magnetic remanence (M_r) was nearly zero (0.002188 emu/g), indicating that there was almost no remaining magnetization when the external magnetic field was removed. The coercive force (H_c) of SS-MPCPs-20 was 2.171 Oe (for soft magnetic materials, it is 0.063–12.6 Oe), showing that SS-MPCPs-20 latex particles were not able to retain magnetization when the external magnetic field was removed. All the data for S_r , M_r , and H_c demonstrated that SS-MPCPs-20 latex particles exhibited superparamagnetism, which favors the redispersion of SS-MPCPs-20 after the external magnetic field is removed. Because the particle size of the magnetic particles was about 10 nm, each particle corresponded to a single crystal domain, exhibiting only one orientation of the magnetic moment. This explains why SS-MPCPs-20 composite latex exhibited superparamagnetic properties. The saturation magnetization of SS-MPCPs-20 was 1.983 emu/g, indicating that SS-MPCPs-20 latex particles possessed some magnetic response.

In comparison of this magnetic latex with a commercial one,³⁷ both latexes exhibited superparamagnetic properties, but SS-MPCPs-20 has a lower amount of magnetite encapsulated inside polystyrene particles and a smaller particle diameter than that of the commercial one. Furthermore, SS-MPCPs-20 latex particles have sulfonic and carboxylic surface groups.

Conclusions

Emulsifier-free miniemulsion polymerization using an ionic monomer (NaSS) was used to prepare self-stabilized magnetic polymeric composite particles. The results showed that the encapsulation of magnetite was successful by using this technique.

NaSS works as a high-efficiency stabilizer in the preparation of SS-MPCPs by emulsifier-free miniemulsion polymerization. Increasing the amount of NaSS improves the magnetite encapsulation degree, decreases the particle size, narrows the PSD, and reduces the number of BMPs and PPPs at the same time. The optimum percentage of NaSS, based on the total amount of St and magnetite, is 20%. At higher concentrations of NaSS, high amounts of PPPs were observed.

The distribution of magnetite particles inside the SS-MPCPs was mainly in the core of the composite magnetic particles, with

(37) Martinez-Pedrero, F.; Tirado-Miranda, M.; Schmitt, A.; Callejas-Fernandez, J. *Colloid Surf., A* **2005**, 270–271, 317–322.

the number of magnetite particles encapsulated inside each magnetic particle being different.

The surface strong and weak acid groups of the more monodisperse magnetic latex (SS-MPCPs-20) were quantified. The strong acid groups were provided by the sulfonic groups ($-\text{SO}_3^-$) of NaSS, and the weak acid groups came from the carboxylic groups of the OA. In addition, the existence of a hairy layer on the surface of the particles was proven.

The magnetic hysteresis loop of the SS-MPCPs-20 composite latex was a single, S-like curve. These magnetic latex particles exhibited superparamagnetism and possessed some magnetic response.

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