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From Polymer Latexes to Multifunctional Liquid Marbles

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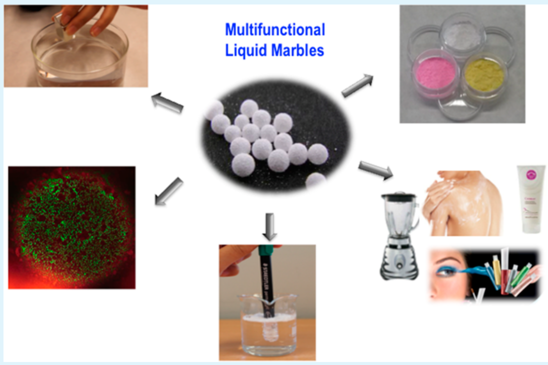
Supporting Information



ABSTRACT: A simple method to prepare multifunctional liquid marbles and dry water with magnetic, color, and fluorescent properties is presented. Multifunctional liquid marbles were prepared by encapsulation of water droplets using flocculated polymer latexes. First, the emulsion polymerization reaction of polystyrene and poly(benzyl methacrylate) was carried out using cheap and commercially available cationic surfactants. Subsequently, flocculation of the latex was provoked by an anion-exchange reaction of the cationic surfactant by the addition of lithium bis(trifluoromethanesulfonyl)imide salt. The flocculated polymer latex was filtered and dried, leading to very hydrophobic micronanoparticulated powders. These powders showed a great ability to stabilize the air/water interface. Stable liquid marbles were obtained by rolling water droplets onto the hydrophobic powders previously prepared. The use of very small polystyrene nanoparticles led us to the preparation of very stable and the biggest known liquid marbles up to 2.5 mL of water. Furthermore, the introduction of fluorescent comonomer dyes into the polymer powders allowed us to obtain new morphological images and new knowledge about the structure of liquid marbles by confocal microscopy. Furthermore, the introduction of magnetic nanoparticles into the polymer latex led to magnetic responsive liquid marbles, where the iron oxide nanoparticles are protected within a polymer. Altogether this method represents an accessible and general platform for the preparation of multifunctional liquid marbles and dry water, which may contribute to extending of their actual range of applications.

KEYWORDS: *liquid marbles, cationic surfactants, polymer latexes, emulsion polymerization, ionic liquids*

1. INTRODUCTION

Since Aussillous and Quéré reported about liquid marbles more than 20 years ago,[1] there has been continuous interest in studying and improving their functionalities and applications. Liquid marbles are usually defined as liquid (generally water) droplets coated with an exterior shell of hydrophobic powder.[2−5] However, hydrophilic particles have also been reported in the bibliography as liquid marble stabilizers.[6−9] The water droplets are stabilized by self-organization of the hydrophobic or hydrophilic particles at the air/liquid interface. Liquid marbles display nonadhesive and nonwetting behavior toward many surfaces, therefore affording unique ways of liquid droplet manipulation.[1] When liquid marbles exist in macroscale, they appear as free-flowing powder, even if they are composed mostly of liquid weight. This micronized form is also referred to as dry liquid because it appears as a dry, solid particulate material rather than a continuous fluid. Liquid marbles and dry water have been proposed for different applications such as gas and pH sensing, microreactors, microfluidics, biotechnology, and drug delivery and also for cosmetics and personal care products.[10−20]

Conventional hydrophobic powders used for the preparation of liquid marbles are commercial hydrophobic silica particles, powders of hydrophobic polymers (such as polyethylene, polystyrene, and polylactide), natural hydrophobic lycopodium powders,[1] or carbon black powders.[5] The common requirements for the powders are hydrophobic surface chemical composition and relatively small powder grain size. Although hydrophobic polymer powders can be obtained by different technologies, the use of polymer latexes as stabilizers of liquid marbles is particularly attractive. Polymer latexes are usually prepared by emulsion or miniemulsion polymerizations, which are highly developed technologies that allow good control over the particle size, shape, morphology, and functionality. Thus, Dupin and Armes pioneered the use of polymer latexes as versatile precursors of polystyrene microparticulate powders.[10−13] The critical step in going from a polymer latex to a microparticulate hydrophobic powder is the latex flocculation step. After flocculation and purification, the recovered polymer

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powders, which were initially dispersed in water, must have a hydrophobic enough surface to stabilize the water/air interface. Most of the emulsion/miniemulsion polymerization processes involve the use of small ionic surfactants to stabilize the polymer microparticles in water. Surfactants are amphiphilic compounds that remain in the polymer powders after coagulation, decreasing their hydrophobic character and limiting their use in stabilizing water liquid marbles. For this reason, all of the approaches reported so far use polymeric surfactants instead of small surfactants. Some polymeric surfactants or stabilizers can be used as coagulating agents by changing their hydrophilic/hydrophobic character using an external stimulus such as the pH, ionic strength, or temperature. Typical examples are pH-sensitive polymeric stabilizers such as poly(2-ethylamino)ethyl methacrylate or poly(2-vinylpyridine). In pioneering work, the polymeric stabilizers were water-soluble when protonated at low pH and able to stabilize a polymer latex. Upon a change of the pH in the polymer latex, the polymeric stabilizer became hydrophobic and insoluble, provoking flocculation of the latex and leading to hydrophobic polymer powders.

Recently, we reported the use of poly(ionic liquid)s as stabilizers in emulsion polymerizations, in which after metathesis anion exchange provoked flocculation of the polymer latexes.[21] The obtained polymer microparticulate powders were hydrophobic enough to effectively stabilize water liquid marbles. This anion exchange used in the case of cationic poly(ionic liquid)s is known to be effective in the case of small cationic molecules such as ionic liquids. For this reason, we came up with the idea of combining commonly used small cationic surfactants and anion-exchange metathesis. In this paper, we present this combination, which allows one to go from polymer latexes to multifunctional liquid marbles in a simple way. The method is based on the use of commercially available cheap surfactants without the need for designing fancy polymeric stabilizers. Furthermore, we show here how the method allows the synthesis of powders of different sizes and functionalities that can be used to investigate and better understand the structure of liquid marbles. The preparation of multifunctional liquid marbles with properties such as magnetism, fluorescence, or coloring is also demonstrated by incorporating dye molecules or inorganic nanoparticles into the polymer latexes.

2. EXPERIMENTAL SECTION

2.1. Methods and Materials. Styrene (99%), benzyl methacrylate (BzMA; 96%), 2,2′-azobis(2-methylpropionamide)dihydrochloride (AIBA; 97%), 2,2′-azobis(2-methylproprionitrile) (AIBN; 98%), dodecyltrymethylammonium bromide (DTAB; 97%), benzyldimethylhexadecylammonium chloride (HDBAC; 98%), hexadecane (HD; 99%), rhodamine B (95%), and fluorescein *O*-methacrylate (97%) were purchased by Sigma-Aldrich. Hexadecyltrimethylammonium bromide (HDTAB; 98%) and lithium bis(trifluoromethanesulfonyl)-imide (TFSI Li; ≥99%) were supplied by Fluka and Solvionic, respectively. Magnetite nanoparticles (Fe_3O_4-S) were prepared as reported before.[22] Rhodamine B1 acrylate dye was synthesized based on the procedure mentioned previously (details are given in the Supporting Information, SI).[23]

The particle size and particle-size distribution were measured by dynamic light scattering (DLS; Nanosizer, Malvern) and by scanning electron microscopy (SEM). Before characterization by SEM, the samples were placed on an adhesive coat and sputter-coated with gold using an al-Tec SCD sputtering unit 004. The SEM micrographs were analyzed with *ImageJ Launcher* software. The number-average particle diameter of the latex was estimated by counting ≈300 dry particles by SEM. Transmission electron microscopy (TEM) was used to characterize the morphology of magnetic polymer nanoparticles with a TECNAI G^2 20 (TWIN 200 kV LaB_6). Fourier transform infrared (FTIR) analysis was conducted for the latexes and dried powders using a Nicolet 6700 spectrometer. Characterization of the liquid marble morphology was performed by a LEICA LCS SP2 AOBS confocal microscope. ^1H and C^{13} NMR measurements were carried out using deuterated chloroform ($CDCl_3$; Euriso-top) as the solvent.

2.2. Basic Preparation of Polymer Latexes Stabilized with Cationic Surfactants by Emulsion Polymerization. Different polystyrene (PS) and poly(benzyl methacrylate) (PBzMA) latexes were prepared by aqueous emulsion polymerization by varying the solids contents (% SC) and emulsifier (DTAB, HDBAC, or HDTAB). In a standard reaction, the monomer BzMA or styrene was added to a solution containing the emulsifier in deionized water (Milli-Q quality) and the mixture was purged with nitrogen for 15 min. The mixture was heated to 70 °C, and then the initiator (AIBA, 1% wbm, where wbm is the weight based on the monomer weight) was injected in a shot. The polymerization was allowed to react for 24 h under constant stirring. The final monomer conversion was calculated by gravimetry.

2.3. Synthesis of Colored Polymer Latexes by Emulsion Polymerization. Different-colored PS latexes were prepared by aqueous emulsion polymerization (10% SC). In a standard reaction, the monomer styrene was added to the solution containing deionized water (Milli-Q quality), the emulsifier HDTAB (1% wbm), and fluorescein *O*-methacrylate or acrylate functionalized Rhodamine B1 (1 or 0.23% wbm, respectively). Then the reaction was carried out as previously described at 70 °C for 24 h with AIBA as the initiator (1% wbm).

2.4. Synthesis of Magnetic Polymer Latexes by Miniemulsion Polymerization. In a typical formulation, a PS latex was prepared by aqueous miniemulsion polymerization (10% SC). First, a coarse emulsion was formed by mixing the monomer styrene, the emulsifier HDTAB (1% wbm), HD (10% wbm), and a dispersion of magnetite nanoparticles (10% wbm) in deionized water (Milli-Q quality). The coarse emulsion was stirred for 15 min and sonified (model 450 sonifier, Branson) to produce a miniemulsion in an ice-cooled bath. The miniemulsion was prepared under optimized conditions (output control, 8; duty cycle, 80%; sonification time, 10 min). After sonication of the coarse emulsion, the dispersion was placed in a 0.10 L glass bottle and the initiator (AIBN, 1% wbm) was injected. Once all reactants were introduced, the bottle was purged with nitrogen for 10 min, then introduced into a thermostatic bath at 70 °C, and tumbled end over end at 49 rpm for 24 h. The final monomer conversion of PS with magnetic nanoparticles was almost full with negligible coagulum. Moreover, no significant change between the droplet and particle sizes was observed, supporting the droplet nucleation mechanism.

2.5. General Procedure for the Flocculation Process by an Anion-Exchange Reaction. Anion-exchange reactions were carried out on different formulations of polymer latexes synthesized. The procedure used was based on the one previously reported in the literature.[24,25] An aqueous solution containing the hydrophobic salt TFSI Li (1.5 M excess related to the cationic group present in the structure of the emulsifier) was dropwise added to the polymer latex under constant stirring. The flocculated latex particles turned into a hydrophobic powder, which was filtered and dried by lyophilization for 48 h.

2.6. Preparation of Dry Water Using Hydrophobic Polymer Powders. In a typical procedure, a hydrophobic powder (10 wt %, where wt is the weight based in the total weight) was mixed with water (90 wt %), and then the mixture was homogenized using a basic mixer at rates of 6000−10000 rpm stirring for around 15 min, until a fluffy powder was obtained.

3. RESULTS AND DISCUSSION

3.1. General Strategy for the Preparation of Hydrophobic Powders by Flocculation of Polymer Latexes Stabilized with Cationic Surfactants. Individual liquid

Scheme 1. Schematic Illustration of the General Preparation Method of PS Microparticulated Powders by Flocculation of Cationic Latexes

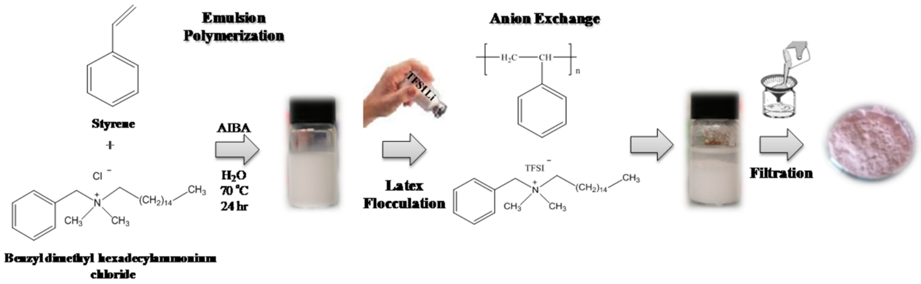


Table 1. Summary of Emulsion Polymerization Reactions Carried Out in Batch Conditions at 70 °C for 24 h

entry	monomer	emulsifier	emulsifier (% wbm^a)	SC (%)	Dv (nm)	conversion (S_0)	PDI	coagulum (%)
1	styrene	DTAB	1	10	486^b	76	0.034^d	2.2
2	styrene	DTAB	2	10	372^b	100	0.096^d	0
3	styrene	HDTAB	0.5	10	112^b	95	0.018^d	0
4	styrene	HDTAB	1	10	99^b	100	0.027^d	0
5	styrene	HDTAB	1	40	120^b	99	0.227^d	7
6	BzMA	HDTAB	1	10	71^b	98	0.024^d	0
7	styrene	HDTAB	2	10	92^b	100	0.018^d	0
8	styrene	HDBAC	0.5	10	500^c	72	0.279^e	0
9	styrene	HDBAC	1	10	375^c	82	0.154^e	0
10	styrene	HDBAC	2	10	81^b	100	0.045^d	0

[a] wbm (weight based on the monomer weight). [b] ζ-average diameter determined by DLS at 20 °C. [c] Volume-average diameter determined by SEM (n = 300). [d] Polydispersity index determined by DLS. [e] Polydispersity index determined by SEM.

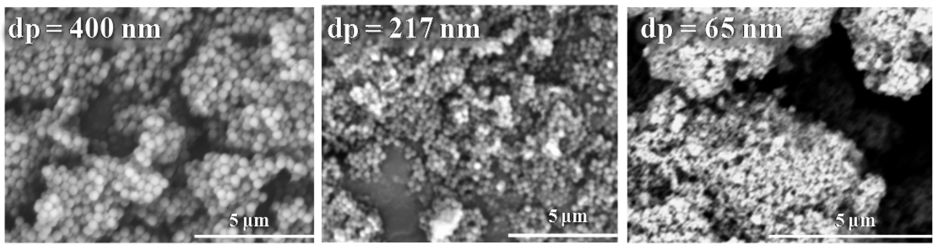


Figure 1. SEM micrographs of PS powders of different microparticle sizes obtained by flocculation of the polymer latexes.

marbles were prepared by encapsulation of water liquid droplets using flocculated polymer latexes stabilized with cationic emulsifiers. The schematic procedure used for the preparation of hydrophobic microparticulate polymer powders is shown in Scheme 1. At first, the emulsion polymerization of a hydrophobic monomer such as styrene or BzMA was carried out using AIBA as the radical initiator and with several cationic surfactants. After synthesis of the polymer latex, the stabilized polymer microparticles were flocculated by an anion-exchange reaction by the addition of a salt such as TFSI Li. In this process, the typical halide anion of the cationic surfactant was exchanged by bis(trifluoromethanesulfonyl)imide (TFSI$^-$), making the surfactant nonsoluble in water and provoking destabilization of the latex. Then hydrophobic powders were obtained by a simple filtration and drying process of the flocculated latexes.

In the first step, we investigated the preparation of different polymer latexes by emulsion polymerization of styrene or BzMA monomers at 70 °C. Three different commercial cationic emulsifiers were used such as DTAB, HDTAB, and HDBAC at different amounts (0.5–2% wbm).

The experimental results are presented in Table 1. In all cases, the monomer conversion was complete using 2% wbm of emulsifier. The final polymer latex obtained did not present any significant coagulum formation (<2%) using 10% SC, whereas when the amount of solids content was increased (entry 5), some coagulum formation was observed (7%). The average particle size was measured by DLS for monodispersed systems and by SEM for polydispersed ones. The first interesting observation is the low polydispersity (<0.1) of the particle size for the majority of runs. As expected, the higher the concentration of the emulsifier, the smaller the particle sizes achieved because the higher the number of micelles and hence the higher the number of particles nucleated. As it be seen for entries 8–10 for PS stabilized with HDBAC, the particle size increased from 80 to 375 nm and to 500 nm as the amount of emulsifier was decreased from 2 to 1 to 0.5%.

In the second step described in Scheme 1, the polymer latexes were flocculated by the addition of an excess of the fluorine-containing salt TFSI Li. Anion exchange of the halide anions (Cl^-, Br^-) of the cationic surfactant by the added fluorine-containing anion (TFSI$^-$) took place. This led to an immediate flocculation of the polymer latex due to an increase in the hydrophicity of the surfactant. Then hydrophobic PS or PBzMA powders were quantitatively obtained by filtration of the flocculated latexes before subsequent lyophilization.

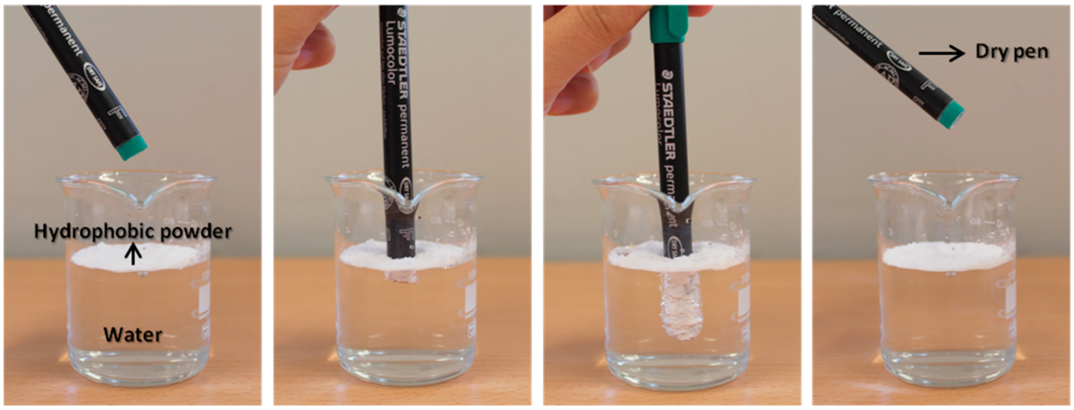


Figure 2. Pictures representing the introduction of a pen into water protected by a layer of hydrophobic PS powders.

The obtained hydrophobic powders were characterized by SEM and FTIR. Figure 1 shows the SEM images of powders obtained after flocculation of three PS latexes previously synthesized (entries 8−10 in Table 1). These images are representative of all of the latexes and micronanoparticulated polymer powders prepared in this work. It is worth mentioning that the polymer particle size and shape did not change significantly after the flocculation step. Moreover, the previous trend observed for the polymer latexes regarding the decrease of the particle size when the amount of emulsifier increased occurred as well for the correspondent hydrophobic powders because polymer microparticles formed by individual nanoparticle sizes of 400, 217, and 65 nm were observed after flocculation. Moreover, different stabilization performances were observed when the three emulsifiers used were compared. As can be seen in Table 1 (entries 1, 4, and 9), when the same polymeric conditions were used, the final particle sizes were very different. When DTAB was used (entry 1 in Table1), bigger particles were obtained (486 nm). The alkyl chain length (C-12) of this surfactant and its lower stabilization capacity (notice also that some coagulum was formed in this reaction) may be the reason for the larger particles. On the other hand, when HDTAB was used (entry 4 in Table 1), small particle sizes (99 nm) were obtained by an increase of the alkyl group (C-16) that is more hydrophobic and effective in stabilization of the system. Finally, when HDBAC was used (entry 9 in Table 1), again an increase on the particle-size diameter was observed (375 nm) compared to that of the HDTAB system. In this case, the difference can be related to the molecular weight of these two surfactants (M_w = 364.45 and 396.09 g/mol for HDTAB and HDBAC, respectively); because the amount of surfactant used was calculated on a weight basis, more moles of HDTAB were used and therefore lower particle sizes were obtained in that case.

The final polymer powders are formed by aggregates or clusters of spherical microparticles very homogeneous in size. Some differences were observed between the particle-size diameters before and after the flocculation procedure; however, these deviations were minor taking into account the errors and the different methods used.

The polymer powders were characterized by FTIR to investigate the presence of the fluorinated anion. Figure S1 in the SI shows the FTIR spectrum of the PS latex using HDBAC as the surfactant and the corresponding spectrum for the hydrophobic powder after the TFSI$^-$ anion-exchange reaction. The spectrum of the latex shows the classical bands associated with PS. Interestingly, the spectrum of the corresponding hydrophobic powder includes the bands of PS together with new small bands associated with the TFSI$^-$ anions (TFSI$^-$ ≈ 1200 and 1144 cm^{-1}). The presence of these bands confirms that the anion-exchange reaction takes place and the exchanged surfactant is present on the surface of the PS microparticles.

To show the hydrophobicity of the powders, we carried out the following experiment. A layer of powder was added to a beaker containing water. The added hydrophobic PS powder floated at the surface of the water, forming a thick layer. Then, we introduced an object into the water, which in Figure 2 is exemplified with a pen. When the pen was taken out from the water, it was completely dry without any wetting signs. Basically, the hydrophobic powder protected the water/air interface, preventing external objects from breaking it and getting into the water. The experiment corroborates that our powders are good candidates to stabilize liquid marbles because of their high ability to protect the water/air interface.

3.2. Preparation and Characterization of Water Liquid Marbles. Individual liquid marbles were then prepared by rolling water droplets of different volumes into the hydrophobic powders. Formation of liquid marbles occurs when the hydrophobic powder is coated on a water droplet. The polymer particles immediately coated the liquid droplet, with the powder bed being essential to obtaining stable liquid marbles. The polymer particles self-assembled at the air/liquid interface, promoting the nonsticky properties of this material on the glass or water surface, as was reported before.[1] In all cases, the microparticulated powders obtained from the polymer latexes reported in Table 1 spontaneously coated the small water liquid droplets (10 μL), forming liquid marbles. Liquid marbles were therefore prepared using powders of different microparticle sizes and chemical nature (either PS or PBzMA) and synthesized using different cationic surfactants.

The synthetic versatility given by emulsion polymerization allowed us to investigate the effect of the powder microparticle size on the stability of the water liquid marbles. First, the stability of the liquid marbles was investigated by placing them onto a water liquid surface. Notably enough, we observed that the micrograin size had an impact, which was not mentioned before. The liquid marbles formed using PS powders of microparticles having a size of 344 nm were only stable for less than 10 min on water and then broke up by themselves. Liquid marbles formed using powders with a grain size of 217 nm were stable for 10 min, and the marbles formed using powders with a grain size of 63 nm were stable for more than 60 min without breaking. This experiment showed that the liquid marbles were more stable when the smallest size micronanoparticles were used to form the self-assembled layer. This fact was not demonstrated before in the scientific literature.

A similar effect was observed when we investigated evaporation of the encapsulated water inside a liquid marble. This experiment was carried out by weighting over time a water liquid marble placed on a glass surface at room temperature until complete evaporation of the water inside the marble. Figure 3 shows the evaporation rate of the internal water, for the three liquid marbles reported before. The experiments were performed at room temperature, and as shown in Figure 3, evaporation of a 100 μL water droplet took place within 255 min for the liquid marbles formed with the large micrograin particles (344 and 217 nm). Interestingly, evaporation of the water inside the liquid marble encapsulated with the smallest microparticles took 60 min more than that in the previous case of bigger microparticles. These two experiments are supported by confocal images of liquid marbles coated with different micrograin particle sizes available in the SI (Figure S3). Altogether, the results demonstrate a more densely packed solid layer, and as a consequence, more stable liquid marbles are prepared by using hydrophobic powders with smaller particle size.

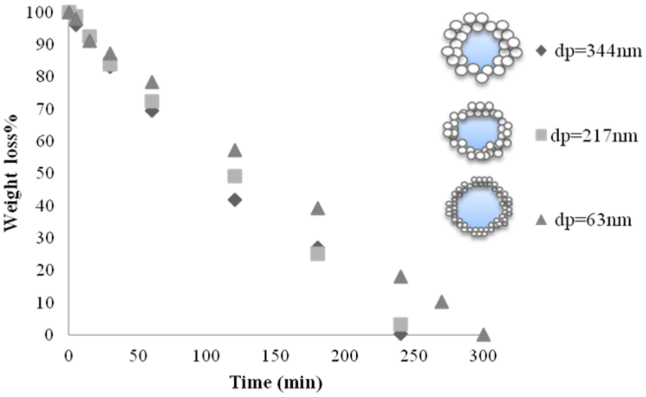


Figure 3. Weight loss percentage as a function of the elapsed time of a water droplet (100 μL) coated with different micrograin-sized particles (dp = particle diameter).

Finally, the effect of the powders in the preparation of liquid marbles of different sizes was investigated. Figure 4 shows a picture of liquid marbles with different sizes coated by two different powders with microparticle sizes of 217 and 65 nm, respectively. In both cases, liquid marbles could be prepared by encapsulating water droplets of 10, 50, and 100 μL and 1 and 2 mL. Furthermore, it is worth noting that, with 65 nm nanoparticulated powders, we were able to prepare the biggest liquid marbles reported so far by encapsulating a water droplet of 2.5 mL.

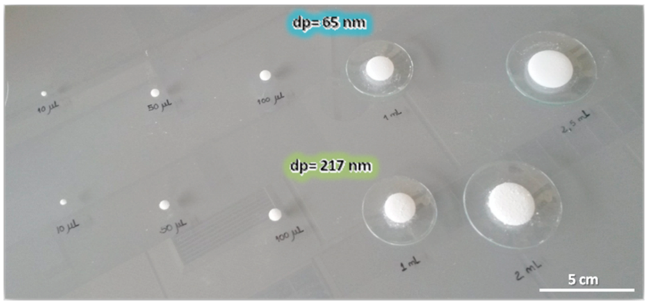


Figure 4. Picture of liquid marbles of different sizes encapsulated by powders formed by aggregates of microparticles of 65 and 217 nm, respectively.

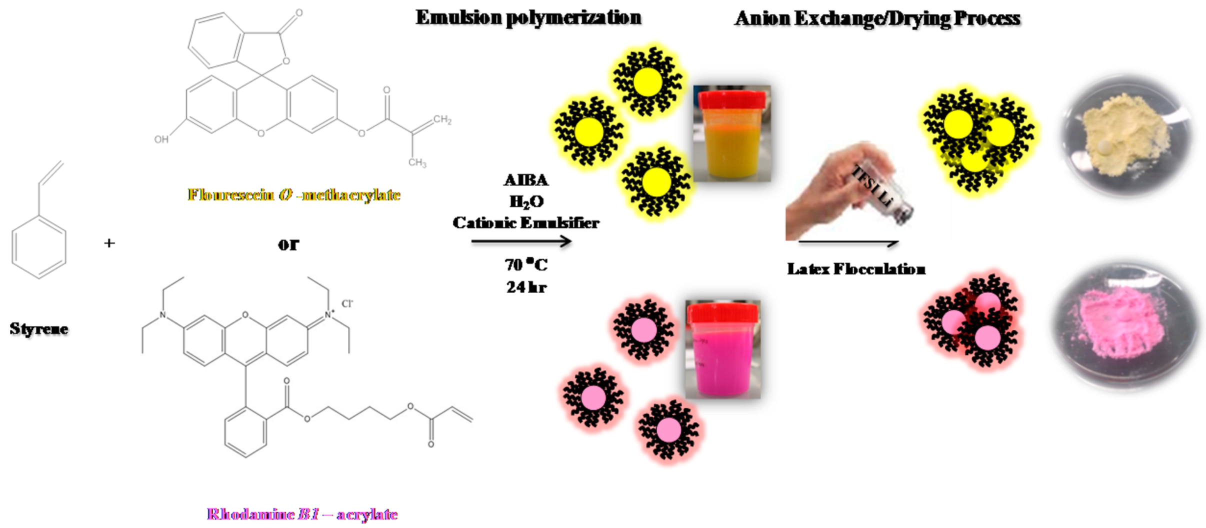
3.3. Multifunctional Liquid Marbles Prepared by Flocculation of Polymer Particles Stabilized with Cationic Emulsifiers.

3.3.1. Colored and Fluorescent Liquid Marbles. As mentioned in the Introduction, one of the potential applications of liquid marbles is in the area of cosmetics and personal care products. Hence, the incorporation of color in the liquid marbles is an interesting option.[11−19] It is well-known that emulsion polymerization allows the easy incorporation of different dyes within the polymer latex. As an example, we synthesized two different PS latexes incorporating dyes such as fluorescein *O*-methacrylate and rhodamine B1 acrylate. As shown in Scheme 2, this was carried out by copolymerization of a small amount of the corresponding (meth)acrylate monomer dye. Similar to the previous cases, latexes with particle sizes of 89 and 65 nm were quantitatively obtained without coagulum using HDTAB as the cationic surfactant. In this case, the latexes were colored (yellow and pink), as shown in Scheme 2. In a second step, the anion-exchange reaction was carried out by the addition of a slight excess of TFSI Li salt, which provoked flocculation of the polymer particles. The powders were recovered by filtration and further lyophilization. As shown in Scheme 2, poly(styrene-*co*-fluorescein *O*-methacrylate) powders were yellow and poly(styrene-*co*-Rhodamine B1 acrylate) powders pink.

These hydrophobic powders were used to prepare colored and fluorescent liquid marbles. The liquid marbles were stable, floating on the water surface even for more than 1 h. The possibility of having hydrophobic powders functionalized with a fluorescent dye allows us to obtain further information on the structure/morphology of the liquid marbles. Usually, liquid marbles can only be looked at by optical microscopy, X-ray tomography, or confocal microscopy.[26] In confocal microscopy, a fluorescent dye is added to the water droplet to obtain the contrast for the images. In a typical experiment, a liquid marble is formed by coating a droplet of an aqueous solution of the dye Rhodamine B using a shell of PS powder (Figure 5, first experiment).[26] The obtained images of those liquid marbles are shown in the top part of Figure 5. In addition, for the first time, we could prepare liquid marbles with polymer powders that incorporated a fluorescent dye (Figure 5, second experiment). The images obtained by confocal microscopy are shown in the bottom part of Figure 5. In this case, the water inside was dark, and the fluorescence that comes from the polymer shell, which includes the fluorescein *O*-methacrylate dye, was green. Both complementary liquid marbles were viewed using two lens, 5× numerical aperture (NA) 0.10 and 10× NA 0.40. The resulting pictures after analysis were obtained, taking the information referent to the fluorescence mode, by excitation emission of the dyes Rhodamine B or fluorescein *O*-methacrylate. The pictures presented in Figure 5 were captured across the plane from the equator to the north or south of the liquid marbles (Figure 5b,e) or focusing on a particular region of the interface between the liquid core and the outer powder layer (Figure 5c,f).

As can be seen in Figure 5, the confocal microscopy images of the liquid marbles coated with fluorescent polymer powder allowed an improvement of the definition of images compared to the conventional pictures in which the dye is added to the

Scheme 2. Reaction Pathway for the Preparation of Hydrophobic Powders from Fluorescent/Colored Polymer Latexes Which Include Monomeric Dyes



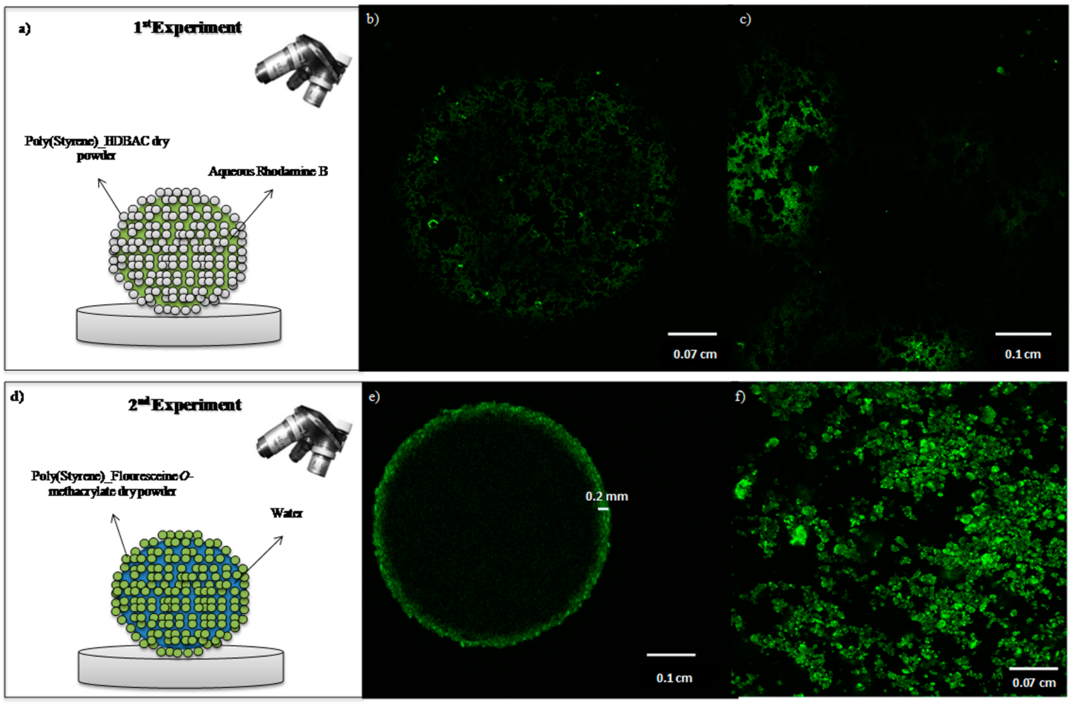
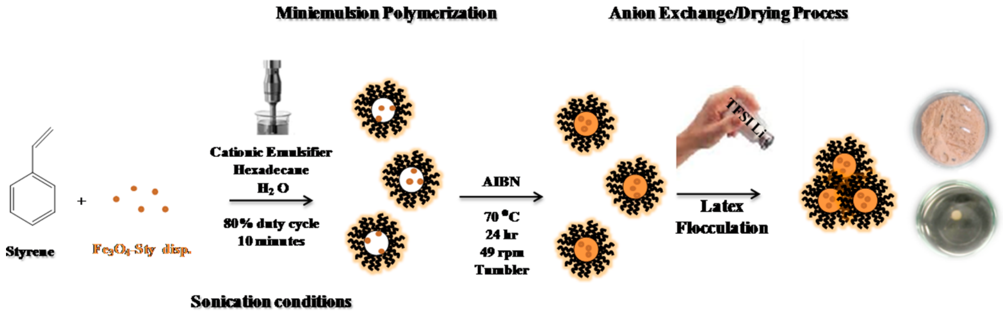


Figure 5. Confocal microscopy images of liquid marbles. (a) Classical confocal microscopy experiment where the fluorescent dye is incorporated into the water droplet. (b) Image looking into a liquid marble encapsulating aqueous Rhodamine B into the liquid core. (c) Cross-sectional view of the liquid marble surface encapsulating aqueous Rhodamine B into the liquid core. (d) New confocal microscopy experiment where the fluorescent dye is incorporated into the polymer shell. (e) Image looking into a liquid marble coated with a fluorescein *O*-methacrylate based powder. (f) Cross-sectional view of a liquid marble coated with a fluorescein *O*-methacrylate based powder.

water. From these new images, complementary information is obtained about the surface roughness of the polymer shell and its structure around the water droplet surface. For instance, from Figure 5f, it is possible to see that these liquid marbles have significant roughness in appearance and the powder shell is made up of aggregates separated by liquid region spacing, as mentioned before by Bormashenko et al.[27] Moreover, as previously reported, the thickness of the liquid marbles is not uniform because the liquid marble wall is composed of a combination of mono- and multilayers of particles. Therefore, from Figure 5e, it is possible to determine by contrast of the powder multilayer that the thickness of the powder shell for a water droplet of 5 μL is about 0.2 ±0.01 mm. The approximate calculation was performed using *ImageJ Launcher* software. The previous works regarding the use of a confocal microscope to capture images of liquid marbles cited some limitations, particularly in showing a clear image of the solid/liquid interface and loss of laser scattering when the laser hit the powder shell.[26] Our fluorescent polymer powders significantly improved the pictures, solving some of the limitations of the imaging of liquid marbles mentioned before.

Scheme 3. Reaction Pathway for the Preparation of Magnetic Polymer Powders from Polymer Latexes Including Magnetite Nanoparticles



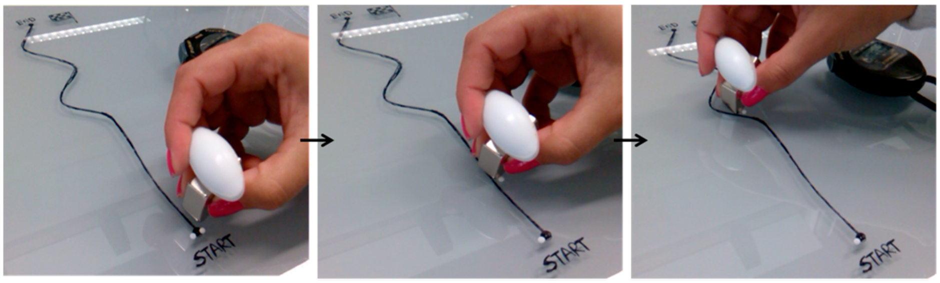


Figure 7. Images illustrating the selective movement of a magnetic liquid marble by using a magnet.

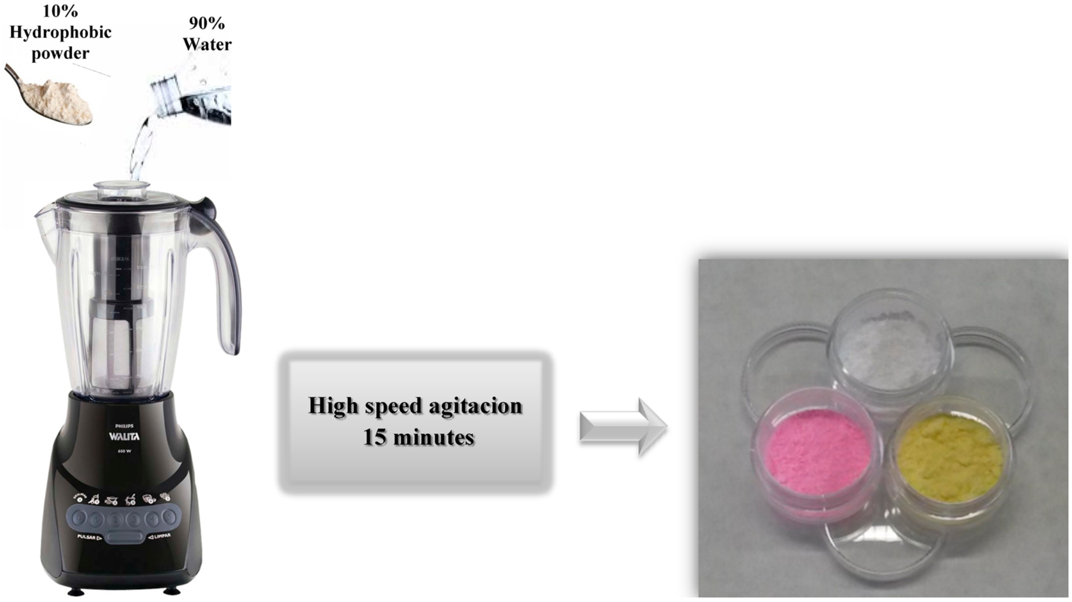
3.3.2. Magnetic Liquid Marbles. Controlled manipulation of small volumes of liquid, either flow or droplet, is very important in miniature systems for different kinds of applications such as in microfluidic systems.[28,29] Magnetic manipulation of liquid marbles offers a great opportunity for the liquid inside to be detected by external optical equipment on-demand.[30,31] Magnetic liquid marbles were first reported by Lin et al. by using highly hydrophobic Fe_3O_4 powders to cover the water droplet. Here, we report a simple procedure to develop polymer powders with magnetic properties by flocculation of the polymer latex, which includes magnetite nanoparticles, as shown in Scheme 3. The magnetic polymer latex was prepared using the method developed by Ramos and Forcada, where magnetite nanoparticles were encapsulated into PS microparticles by miniemulsion polymerization.[22] In our case, we just used a cationic emulsifier instead of an anionic one to stabilize the latex, which in a subsequent step was flocculated by anion exchange, as in the previous cases. Encapsulation of magnetite nanoparticles into the polymer particles led our magnetic liquid marbles be less prone to suffering toxic effects compared with the ones reported before, in which the modified magnetic nanoparticles were directed in contact with the air and liquid.

The hydrophobic powder presented in Scheme 3 shows a yellowish-brown color because of the presence of magnetite nanoparticles. TEM was used to corroborate the presence and morphology of magnetic nanoparticles within the polymer powders (Figure S4 in the SI). The particle size diameter of the magnetite nanoparticles is about 10 nm and the distribution of these into the polymer particles indicates that some of them were encapsulated at the interior but most of them were in the surface of PS nanoparticles. This powder was applied to develop liquid marbles encapsulating a 10 μL water droplet. The obtained liquid marbles showed magnetic response upon a magnetic field and high stability by floating in the water surface for more than 1 h. To illustrate this, the response of these liquid marbles using a magnet is shown in Figure 7. As exemplified in the picture, the liquid marble which does not include magnetic nanoparticles stays at the start, whereas the magnetic liquid marble arrives to the end. Notably, the encapsulation of a very small amount of magnetic nanoparticles (10% wbm) into the PS latexes allows the preparation of magnetic-responsive liquid marbles. A video showing the movement of a magnetic liquid marble onto a water surface is available in the SI. The fact that the Fe_3O_4 magnetic nanoparticles are protected within the polymer micropowders may bring some benefits for the stability or potential toxicity of magnetic-responsive liquid marbles.

3.3.3. Dry Water Based on Multifunctional Hydrophobic Polymer Powders. In summary, hydrophobic polymer powders were used to prepare dry water.[32] When liquid marbles exist in macroscale, they appear as free-flowing powder, even if they are composed mostly for liquid weight. This micronized form is also referred to as dry water because of its appearance as a dry, solid particulate material rather than as a fluid. Dry water has received significant interest, in particular because of their high surface area compared to bulk water and high stability over months, which makes them interesting materials for applications such as carbon dioxide capture.[33,34] However, reports focused on the preparation of dry water with different functionalities are rather limited.

The procedure used to prepare dry water using the multifunctional polymer powders is exemplified in Scheme 4.[35,36] In a typical procedure, a hydrophobic powder (10 wt %) was placed in a container with water (90 wt %). Then the mixture was homogenized using a basic mixer at high-rpm stirring for around 15 min. After this, the obtained dry water looks and behaves like standard solid powders. However, once they were slightly pressed onto a surface, i.e., the skin, they become liquid. The incorporation of dyes into the hydrophobic powders allowed us to prepare dry water that shows different functions such as color or fluorescence, which may be of interest for applications in cosmetics. Furthermore, it is possible

Scheme 4. Preparation Procedure and Final Appearance of Dry Water Obtained Using Functional Hydrophobic Polymer Powders



to combine different functional powders into the same shake, which leads to dry water with several functions such as pink color and magnetic properties. Altogether, the polymer latex technology allows for the preparation of hydrophobic powders, which open the possibility of designing multifunctional dry water.

4. CONCLUSIONS

In this paper, we report an anion-exchange flocculation method that allows one to go from polymer latexes to multifunctional liquid marbles. Thus, styrene monomer droplets stabilized by cationic surfactants in water are transformed by emulsion polymerization and subsequent flocculation in PS powders covered by hydrophobic anions. The flocculated polymers are microparticluated powders that show a good ability to stabilize the water/air interface. This method allowed easy control of the particle size and the introduction of dyes and magnetic nanoparticles into the hydrophobic powders. As a result of size control, the use of very small microparticulated polymer powders led us to the preparation of very stable huge liquid marbles. Furthermore, the introduction of fluorescent comonomer dyes allowed us to obtain new images of liquid marbles by confocal microscopy. Finally, we demonstrated a simple method to prepare dry water with magnetic, color, and fluorescent properties that may open new applications in different areas.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

FTIR spectra of the PS latex and the corresponding flocculated polymer powder, experimental procedure to synthesize the functionalized Rhodamine B1 acrylate dye, confocal images of liquid marbles coated with different micrograin sizes, TEM micrographs of the hybrid PS latex containing magnetic nanoparticles, and a video showing the movement of a magnetic liquid marble onto a water surface. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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