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Simple route to prepare stable liquid marbles using poly(ionic liquid)s

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ABSTRACT

Individual "liquid marbles" were prepared by encapsulation of water droplets using flocculated polymer latexes stabilized with poly(ionic liquid)s. At first, the emulsion polymerization of poly(styrene) and poly(methyl methacrylate) using different poly(ionic liquid)s as stabilizers was investigated. Stable latexes composed of spherical polymer particles with sizes ranging between 300 and 700 nm as characterized by dynamic light scattering and scanning electron microscopy were obtained. Subsequently, the polymer particles were flocculated by anion exchange precipitation of the poly(ionic liquid)s provoked by the addition of lithium bis(trifluoromethanesulfonyl)imide salt. After simple filtration and drying processes, the flocculated latexes led to hydrophobic powders with similar micrograin size compared to the original latexes. Very stable "liquid marbles" were prepared by gently shaking water droplets of different volumes onto the hydrophobic powders. The morphology and stability of the liquid marbles were characterized by optical and confocal microscopy.

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1. Introduction

"Liquid marbles" are usually defined as liquid (generally water) droplets covered with an exterior shell of a hydrophobic powder [1]. They can be easily prepared using highly hydrophobic particles such as lycopodium powder, polyvinylidene fluoride (PVDF) or silica particles and despite of the simplicity of their composition, "liquid marbles" are perfect non-wetting systems [2,3]. The liquid droplets are stabilized by self-organization of the hydrophobic particles at the air/liquid interface resulting in a low adhesion to the substrate (non-sticky droplet), which makes them suitable for numerous applications namely for gas and pH sensing, micro-reactors and micro-fluidics, biotechnology, pharmaceutical and also for cosmetics and personal care products [4–7].

The use of polymer powders obtained from polymer latexes as stabilizers of "liquid marbles" is particularly attractive. Polymer latexes are versatile precursors of microparticulate powders which composition and surface functionality can be easily tuned. For instance, the preparation of responsive "liquid marbles" or remotely controllable "liquid marbles" which can be ruptured or moved by pH, ultraviolet light or an external magnetic field have been recently reported [4–9]. In the first case, Dupin and Armes pioneered the use of poly(styrene) powders obtained by flocculation of latexes stabilized with pH responsive polymers such as poly(2-diethylamino)ethyl methacrylate or poly(2-vinylpyridine). These polymers are water soluble when protonated at low pH and insoluble at basic pH. Due to this property, they were used to stabilize polystyrene polymer latex at low pH and provoke its flocculation at high pHs. Furthermore, the pH responsive polymers modified the surface of the polymer particles, which were used to design water "liquid marbles" that break upon pH changes.

Similarly to pH responsive polymers, the hydrophobic/hydrophilic character of the poly(ionic liquid)s can be easily tailored by changing the counter-anion which classifies them as "salt" responsive polymers [10]. For instance, when a salt like $NaBF_4$, $NaPF_6$ or Li $(CF_3SO_2)_2N$ is added to an aqueous solution of a water soluble polycation, a new poly(ionic liquid) is formed by anion-exchange precipitation. The obtained poly(ionic liquid)s showed hydrophobic character and tailored wettability with water depending on the counter-anion [11]. Poly(ionic liquid)s having TFSI counter-anions can even be applied for the preparation of superhydrophobic coatings [12].

In this work, we show a simple procedure for the preparation of water "liquid marbles" taking advantage of the "salt responsive" character of the poly(ionic liquid)s. Polymer powders were obtained by emulsion polymerization and subsequent flocculation of poly(styrene) or poly(methyl methacrylate) polymer latexes stabilized by poly(ionic liquid)s. The use of a minimum amount of poly(ionic liquid)s as stabilizers and flocculation

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agents is the key to make this method simple and versatile. Here we report, for the first time, the use of poly(ionic liquid)s as liquid marble stabilizers extending the wide range of applications of poly(ionic liquid)s [13].

2. Experimental

2.1. Methods and materials

Methyl methacrylate monomer (MMA, 99%), Styrene (St, 99%), 2,2′-azobis(2-methylpropionamide) dihydrochloride (AIBA, 97%), poly(dimethyldiallylammonium chloride) [poly(DADMA$^+$Cl$^-$)] (Mw < 100,000 g/mol, 35 wt.% aqueous solution) (wt. is the weight based on the total weight), Rhodamine B and sodium hexafluorophosphate ($NaPF_6$, 98%) were purchased from Sigma–Aldrich. Lithium bis(trifluoromethanesulfonyl) imide (≥99%, TFSI Li) was supplied by Solvionic. Poly (1-vinyl-3-ethylimidazolium bromide) (Poly(ViEtIm$^+$ Br$^-$), Mw = 134.000 g/mol, Mw/Mn = 1.83) was prepared as reported before [10a].

The particle size and the particle size distribution were measured by dynamic light scattering (Nanosizer, Malvern) and scanning electron microscopy (SEM). Energy-dispersive X-ray spectroscopy (EDEX) and (SEM) were performed with a JEOL JSM-6400 instrument. The samples were placed on an adhesive coat and sputter-coated with gold before examination with the microscope using an al-Tec SCD sputtering unit-004. The SEM micrographs were analyzed with ImageJ Launcher software. The number average latex diameter was estimated by counting ~300 dry particles by SEM. ^{1}H NMR measurements were carried out using deuterated chloroform (isotopic purity 99.96 atom% D, $CDCl_3$; Aldrich) on a Brüker Avance 500 (500 MHz) spectrometer. Fourier transform infrared spectroscopy measurements (FTIR) were conducted on a Nicolet 6700 spectrometer. The characterization of the morphology of the "liquid marbles" was performed by a confocal microscope LEICA LCS SP2 AOBS after embedding a water solution of Rhodamine B in the "liquid marble".

2.2. General procedure for the preparation of polymer latexes by emulsion polymerization

Different poly(styrene) (PS) and poly(methyl methacrylate) (PMMA) latexes were prepared by aqueous emulsion polymerization (10 wt.%) varying the amount of poly(ionic liquid)s poly(DADMA$^+$Cl$^-$) or poly(ViEtIm$^+$ Br$^-$), stabilizers. In a standard reaction, the monomer methyl methacrylate or styrene was added to a solution containing the poly(ionic liquid) stabilizer in ultra pure water and the mixture was purged with N_2 for 15 min. The mixture was then heated to 70 °C and then, the initiator (AIBA, 1% wbm) (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.

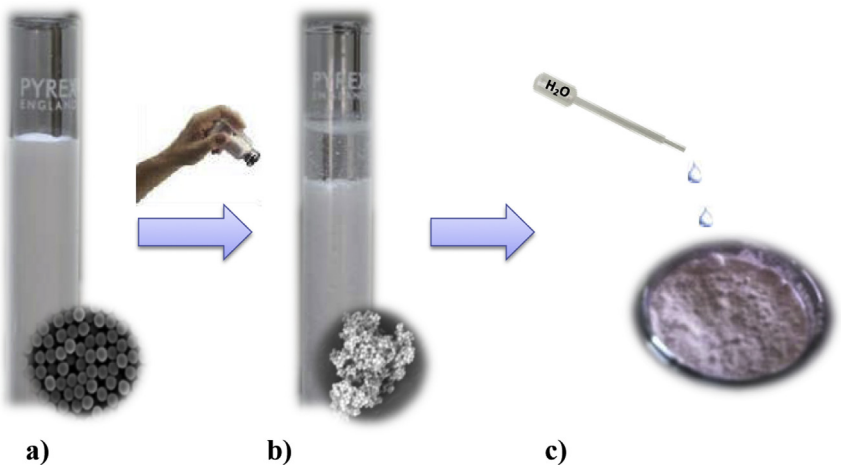
2.3. General procedure of the anion exchange reaction

The anion exchange reactions which were carried out in the polymer latexes, were based on the procedure previously reported in the literature [10]. An aqueous solution containing the hydrophobic salt [$NaPF_6$ or Li TFSI] (1.5 M excess related to the cationic groups) was drop wise added to the polymer latex obtained from the emulsion polymerization reaction, under constant stirring. The latex particles flocculated into a hydrophobic powder which was filtered and dried by lyophilization for 48 h.

3. Results and discussion

3.1. General strategy for the preparation of water "liquid marbles"

Individual "liquid marbles" were prepared by encapsulation of water droplets using flocculated polymer latexes stabilized with poly(ionic liquid)s. The schematic procedure for the preparation of "liquid marbles" that will be explained in detail during this manuscript is shown in Scheme 1. Initially, the emulsion polymerization of poly(styrene) or poly(methyl methacrylate) using different poly(ionic liquid)s stabilizers was investigated. By this method, polymer latexes composed of spherical polymer particles with sizes ranging between 300 and 700 nm were obtained. Then, the polymer particles were flocculated by anion exchange precipitation of the poly(ionic liquid) provoked by the addition of a salt such as Li TFSI or $NaPF_6$. After a simple filtration and drying process, the flocculated latexes turn into hydrophobic powders. To end up, individual "liquid marbles" were prepared by gently shaking water droplets of different volumes onto a layer of the obtained hydrophobic polymer powders.



Scheme 1. Schematic illustration of the general preparation method of "liquid marbles" a) polymer latex, b) salt induced flocculation and c) liquid marble formation by droping and shaking water onto the polymer powders.

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