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Influence of the electrostatic interactions in a Pickering emulsion polymerization for the synthesis of silica–polystyrene hybrid nanoparticles

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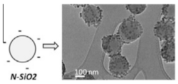
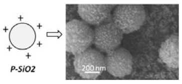
GRAPHICAL ABSTRACT





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ABSTRACT

Hypothesis: Silica–polystyrene hybrid nanoparticles were synthesized by Pickering emulsion polymerization. The coupling effect of initiator type and silica surface charge was studied to exhibit the predominant role of electrostatic interactions in the synthesis mechanisms.
Experiments: Non-ionic hydrophobic initiator (2,2′-azobis(2-methylpropionitrile), AIBN) or anionic hydrophilic initiator (sodium persulfate, NaPS), and positively or negatively charged silica were used as reactants with styrene for Pickering emulsion polymerization. Their interactions were evaluated by Zeta potential measurements. The droplet size and the stability of the Pickering emulsions, and the hybrid particle morphology, surface coverage, size and agglomeration were evaluated by laser granulometry and microscopy.
Findings: Similar surface charge between negatively charged silica particles and an anionic initiator led to strong repulsions and thus to non-covered polystyrene nanoparticles. With positively charged silica, a high decoration was obtained due to attractive interactions between the inorganic and the organic phases, but a strong agglomeration was also observed. The use of a non-ionic initiator led to a homogeneous coverage with negatively charged silica. With positively charged silica micronic sizes were formed by following two different mechanisms. These data, by enriching the existing literature, led to a more complete and robust description of the emulsion polymerization synthesis for hybrid nanostructures.

1. Introduction

Organic–inorganic hybrid structures have attracted a lot of interest from all the scientific community in recent years, and became rapidly a multidisciplinary field of research, where chemists, material scientists, physicists, and biologists converge for the development of new designed and smart structures [1,2]. The combination of organic properties (plasticity, deformability, shaping and structural properties, lightness, optical properties, and biocompatibility) and inorganic properties (mechanical properties, density, cost, structural, optical, electronic properties, and biocompatibility) make the development of hybrid nanostructures a very exciting approach in the research of new materials and new applications [3–5]. A wide variety of colloidal inorganic nanoparticles have been employed for synthesizing hybrid structures, such as natural or synthetic clays [6], metallic oxides (TiO_2 [7], CuO [8], Al_2O_3 [9]) magnetic oxide [10], and carbon black [11]. Silica is a very interesting candidate and has been studied extensively [12–14], because of its multiple properties as a model material, as a reinforcing agent or filler.

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Organic–inorganic hybrid nanostructures where the polymeric part is the core are generally obtained by sol–gel reactions at the polymer surface with a coupling agent [14–16]. More complex structures could be obtained via heterophase polymerization processes, such as dispersion or emulsion polymerization [17–19]. By introducing some inorganic colloids, the use of surfactant is not mandatory anymore [20]. The concept of Pickering emulsion polymerization can thus be introduced, where surfactants are replaced by solid particles as emulsion stabilizers during the reaction of polymerization [21–27].

Two mechanisms have been proposed to describe the principle of stabilization in Pickering emulsions. The first one considers that solid particles are adsorbed at the oil–water interface to form a particle monolayer acting as a rigid film and providing a mechanical barrier to coalescence [28,29]. The particle attachment at the oil–water interface is non-reversible, leading to a more efficient stabilization than surfactant adsorption. This mechanism was extensively supported by a theoretical approach and thermodynamic calculations, which can be found in very well-detailed publications [30,31,26]. The type of emulsion (O/W or W/O) is determined by the particle wettability at the oil–water interface: the less wetted liquid becomes the dispersed phase [32]. The contact angle (θ) of the particles with the aqueous phase will lead to O/W emulsion if $\theta < 90°$ (e.g., silica, clay), and to W/O if $\theta > 90$ °C (e.g., carbon black). However if the particles are either too hydrophilic or too hydrophobic, they may remain in either the aqueous or oil phase. Therefore several methods were investigated to modify particle hydrophilicity [33–36]. The second mechanism that governs Pickering emulsion stabilization is based on particle–particle interactions leading to the formation of a three-dimensional network of particles in the continuous phase. An enhanced stability is obtained through the increase of viscosity. This has been observed particularly in clay-based systems [37,38].

Pickering emulsion polymerization was used for the synthesis of silica–polystyrene hybrid particles [39–41], and different mechanisms were proposed by several authors. Sheibat-Othman et al. used colloidal silica and styrene in the presence of a PEG-based macromonomer capable of adsorbing at the inorganic surface [20]. The mechanism described here was a classical reaction of emulsion polymerization with a copolymerization between the styrene and the macromonomer chains. However the anionic nature of the initiator (ammonium persulfate, APS) was not considered in that case, whereas other authors have mentioned an important role of their interactions with the polymer and the silica. For example Lee et al. considered positively charged colloidal silica with styrene and potassium persulfate (KPS) as an initiator [42]. Hybrid silica–polystyrene particles were obtained by surfactant-free emulsion polymerization, which was attributed to an electrostatic attraction between the inorganic particles and the growing oligomers. They could also observe that the addition time of silica was a key parameter which controlled the final particle size of the hybrid particles. In other studies, Ma et al. compared two initiators: VA-086 (non-ionic) and KPS (anionic) [43,44] with negatively charged colloidal silica. Two distinct mechanisms were proposed: a coagulative nucleation mechanism with the non-ionic initiator, where the inorganic particles organize themselves at the growing oligomers interface by self-assembly, leading to submicronic sizes. With the anionic initiator, a droplet nucleation mechanism was followed, where radicals enter monomer droplets and polymerize into solid cores, resulting in lower silica coverage and micronic sizes. Similar mechanisms were proposed by Schmid et al. for the synthesis of hybrid silica–polystyrene particles when an alcoholic dispersion polymerization reaction was conducted, where the charge of the initiator was also determinant for the final structure [45,46].

These literature data tend to show that the interactions between the inorganic particles and the growing oligomers (through the nature of the initiator) are determinant for a better control of the structure of the hybrid particles. For this aim, nanoparticles of silica of different surface charge (positive and negative charge) and two types of initiators (hydrophilic and anionic: sodium persulfate NaPS, and hydrophobic and non-ionic: 2,2′-azobis(2-methylpropionitrile AIBN) were used. Moreover in the context of Pickering emulsions, organic molecules are generally added [33,34] to modify the nanoparticle wettability. Poly(ethylene glycol) methyl ether methacrylate (PEGMA) was chosen as a neutral macromonomer, because it can adsorb onto silica surfaces through the presence of hydrogen bondings [20,47] (Fig. 1). The double bond of the methacrylate group allows a co-polymerization with the monomer. An anionic polyelectrolyte (sodium polystyrene sulfonate, PSS) was used in combination with the positive silica because of an attractive interaction between the positive surface charge of silica and the negative sulfonate groups [48] (Fig. 1). We chose to use organic species which were not surfactants (neither anionic such as the classical surfactant sodium dodecyl sulfate (SDS) nor cationic such as hexadecyltrimethylammonium bromide (CTAB)) in order to avoid them to compete with the silica particles during the emulsion process, and prevent the formation of micelles. The motivation of this work is to give a broader view on the possible interactions between the inorganic and the organic phases, and their influence for the synthesis of silica–polystyrene hybrid nanoparticles via Pickering emulsion polymerization. These hybrid particles are dedicated to our current research in the development of new colloidal ceramic processes such as colloidal granulation [49]. They will be used as a new source of polymer to promote a higher plasticity or to give a controlled porosity with a better interaction with the inorganic phase through its hybrid feature.

2. Experimental

2.1. Materials

The monomer styrene, and the organic surface modifiers poly (ethylene glycol) methyl ether methacrylate (PEGMA, Mn = 2.080 g mol^{-1}, Aldrich) and poly (sodium 4-styrenesulfonate) (PSS, Mw = 1.000.000 g mol^{-1}, Aldrich) were provided by Aldrich and used without further purification. Two initiators were employed: a hydrophilic and anionic initiator sodium persulfate (NaPS), and a hydrophobic and non-ionic initiator 2,2′-azobis(2-me

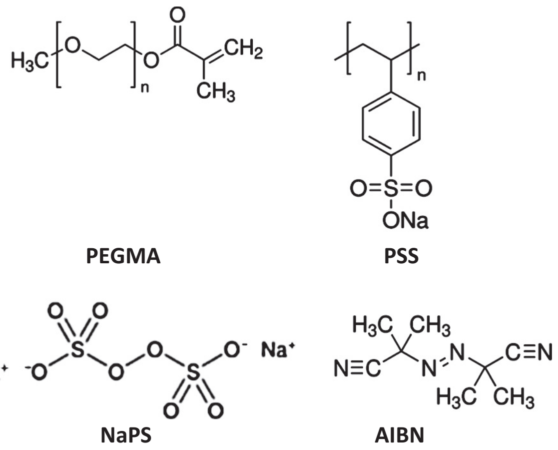

Fig. 1. Chemical structure of the organic surface modifiers and the initiators for the emulsion polymerization of styrene in presence of colloidal silica.