



Effect of ionic monomer concentration on latex and film properties for surfactant-free high solids content polymer dispersions



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ABSTRACT

Sodium styrene sulfonate (NaSS) was used to stabilize waterborne poly(methyl methacrylate/butyl acrylate) dispersions obtained by surfactant-free seeded semicontinuous emulsion polymerization at 50 wt% solids content. The effect of NaSS concentration (0.175–3.6 wbm%) on the reaction kinetics, NaSS incorporation onto particles, colloidal stability and properties of emulsifier-free latexes and films was investigated.

It was found that fraction of NaSS that was incorporated onto polymer particles increased with its concentration due to the increase of the ionic strength, which shifted the adsorption equilibrium of the NaSS containing oligoradicals towards the polymer particles. Properties of the latexes (freeze-thaw and salt stability) improved with the concentration of NaSS and its incorporation. The lack of migration and formation of aggregates of the stabilizing moieties in the polymer films was demonstrated by water contact angle measurements and AFM images. This resulted in improved properties of the films (gloss, water uptake and mechanical strength).

1. Introduction

Surfactants are necessary components in the production of waterborne dispersed polymers, owing to their role in monomer emulsification, particle nucleation and colloidal stability during synthesis and storage. However, since they are physically attached to the polymer particles, they desorb from the particles and migrate during and after film formation leading to undesired effects on the film properties, such as lower gloss, poorer adhesion to the substrate and higher water sensitivity [1]. Another aspect which is generally disregarded is the environmental impact of the leaked surfactants from the films in paint and coating applications.

These adverse effects initiated the development of new approaches to produce emulsion polymers without migratory surfactants by providing covalent attachment of the stabilizing moieties onto the polymer particles. One method is to use reactive surfactants (so called surfmers) [2]. Ideally, the surfmer should be fully incorporated into the polymer chains and be located at the surface of the polymer particles [3]. These are conflicting requirements for semicontinuous operations because full incorporation requires reactive surfmers that tend to become buried within the polymer particles as the particles grow during the process. Optimal surfmer feed policies can be developed to maximize incorporation limiting burying [4], but their use is limited to the specific monomer system for which the strategy was developed. Another approach is surfactant-free emulsion polymerization using ionic initiators or functional monomers bearing carboxylate [5–8], sulfate [8,9], sulfonate [6,10–13], or amino [14] groups. The use of initiators as the sole source

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of stabilization is not advisable because changes in the concentration of initiator considerably affect the reaction kinetics and molecular weight. On the other hand, some of the functional monomers have practical limitations. The stabilization efficiency and chemical incorporation of carboxylic acids are dependent on the pH of the reaction medium [6,8], sulfate groups are subject to hydrolysis [15] and amines produce positively charged particles, which limit the range of applications of these latexes because most of the natural surfaces are anionic and hence cationic stabilized latexes tend to stick to them. On the other hand, sulfonate functional monomers are stable over a wide range of temperature and pH values [13].

Sodium styrene sulfonate (NaSS) is commercially available and has a styrenic double bond, which makes it attractive to be used in surfactant-free emulsion polymerization formulations. The challenge of using NaSS for stabilization is that it is highly water soluble and tends to polymerize in the aqueous phase. This often leads to the formation of free polyelectrolytes that do not contribute to the particle stabilization and may even cause bridging coagulation. Therefore, the aim is to minimize the amount of water soluble polymer and maximize the chemical incorporation of NaSS onto the particles and hence to achieve not only the colloidal stability of the dispersion but also to reduce the water sensitivity of the film.

We have recently reported that NaSS incorporation increased with the water solubility of the comonomer independently on the type of functional group (acrylate, methacrylate or styrene) [16]. Moreover, the incorporation of NaSS improved significantly when a redox initiator (*tert*-butyl hydroperoxide/ascorbic acid) yielding hydrophobic radicals was used [17]. Stable surfactant-free latexes meeting the industrial requirements of high solids (≥ 50 wt%) and semicontinuous operation were prepared by using moderate amounts of NaSS for a wide range of monomers (acrylate, methacrylate and styrene). Solids contents over 60 wt% were also reached with a high incorporation of NaSS ($> 80\%$) and moderate viscosity [17].

Improvements in latex and film properties have been reported for surfmer based surfactant-free systems. These properties include salt stability [18,19], freeze-thaw stability [19], gloss [18], water sensitivity [18,20–23] mechanical stability [21] and adhesive properties [24]. On the other hand, the studies demonstrating improvements in latex and film properties for surfactant-free waterborne polymer dispersions stabilized solely by ionic monomers are limited [16,17,25–27]. Dai et al. [25] performed the synthesis of high solids content (50 wt%) poly(styrene/butyl acrylate) latexes by using 2-acrylamido-2-methyl propane sulfonic acid (AMPS) and reported better water resistance and solvent resistance compared to conventional systems. However, none of the latexes were stable towards freeze-thawing. Chang et al. [27] reported slight improvement in salt stability of 40 wt% poly(styrene/butyl acrylate) latexes prepared by AMPS. Tang et al. [26] reported an improvement in tensile strength and water resistance for the films prepared from 60 wt% solids content poly(methyl methacrylate/butyl acrylate) latexes synthesized by using 3-allyloxy-2-hydroxyl-propane sulfonate. However, none of these studies tried to explain the properties considering the extent of chemical incorporation of sulfonate monomer on polymer particles. In our previous work [17] the superior salt and freeze-thaw stability and the moderate water uptake of latexes stabilized with NaSS over the conventionally stabilized latexes was related to the high incorporation of NaSS.

In a conventional emulsion polymerization, the concentration of surfactant is one of the key variables in the formulation because it affects almost any aspect of the process (kinetics, colloidal stability), the properties of the latex (particle size distribution, molecular weight distribution) and the properties of the film (minimum film formation temperature, water sensitivity, gloss, adhesion). In a surfactant-free emulsion polymerization stabilized with NaSS, this monomer plays the role of surfactant, and hence it is expected that its concentration will strongly affect the polymerization and the properties of both latexes and films. The effect of NaSS concentration on the particle size [10], surface charge density [11] and size distribution [13] and also on the polymerization rate [13] was studied before. Surprisingly, no reports on the effect of NaSS concentration on the incorporation and subsequently on latex and film properties have been published. Therefore, in this work the effect of the concentration of NaSS on the reaction kinetics, NaSS incorporation onto polymer particles, and properties of latexes and films was investigated under industrial-like conditions (50 wt% solids content and semicontinuous operation).

2. Experimental

2.1. Materials

The monomers methyl methacrylate (MMA, purity 99.9%, 45–55 ppm monomethyl ether hydroquinone (MEHQ), Quimidroga), *n*-butyl acrylate (BA, purity 99.5%, 10–20 ppm MEHQ, Quimidroga) and sodium *p*-styrene sulfonate (NaSS, purity $\geq 90\%$, Sigma Aldrich), the components of redox initiator system (oxidant *tert*-butyl hydroperoxide, TBHP, 70 wt% aqueous solution, Luperox Sigma Aldrich, and reductant ascorbic acid, AsAc, purity $\geq 99\%$, Acros), and the conventional surfactant sodium dodecyl sulfate (SDS, Sigma-Aldrich) were used without further purification. Distilled water was utilized in all the reactions. Hydroquinone (HQ, purity 99%, Panreac) and dimethyl formamide (DMF, chromatography grade, Fisher) were used as received.

2.2. Polymerizations

The recipe used to synthesize the seed is given in Table 1. The procedure of synthesis is presented in Supporting Information. The seed had 116 nm Z-ave particle size and it was used in all of the seeded semicontinuous emulsion polymerization reactions except for the control one. 1.3 wbm% SDS was used in the synthesis of NaSS-free control seed with an aim to achieve a similar particle size (Z-ave particle size 117 nm). The molar ratio of used SDS to NaSS is 0.5, meaning double amount of NaSS was necessary to achieve similar size of the seed.

For the seeded semicontinuous emulsion polymerization reactions, a 1 L reactor equipped with a stainless steel two-stage three-bladed Ekato MIG impeller, a reflux condenser, a N₂ inlet, a temperature probe and feeding inlets, was utilized. A typical coating

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