



Grafting in polymeric dispersions stabilized with Alkali-Soluble Resins: Towards the production of leaching-free waterborne coatings

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ABSTRACT

Alkali-soluble resins (ASRs) are a type of polymeric surfactants that can beneficially improve the properties of waterborne dispersed polymers, thus attracting great attention from the industrial point of view. When used as protective colloids in emulsion polymerization systems, grafting reactions between the surfactants molecules and the particles may occur. These grafting reactions can prevent the release to the environment of the surfactant when the dispersion is employed in formulations for coating. Two different mechanisms lie behind grafting reactions, i.e. hydrogen abstraction by reactive radicals from acrylic moieties, followed by propagation of the newly-formed active center, and the incorporation through polymerizable double bonds present on the backbone of the ASR. In this work, quantification of grafting using three different model ASRs revealed appreciable amounts of linking in different experimental conditions. Moreover, the discrimination of the two different contributions to grafting indicated that incorporation of reactive double bonds is the predominant pathway leading to extended linking. These findings may help the design of the new generation of leaching-free waterborne coatings with reduced environmental impact.

1. Introduction

The pressure towards greener and solvent-free alternatives in the field of polymeric coatings is constantly increasing the demand of waterborne film-forming dispersions. Emulsion polymerization is the principal technique to produce such materials; in this respect, surfactants are essential to provide kinetic stability to lyophobic colloids. Beyond the stabilization of the final latex, emulsifiers molecules play a central role in the nucleation process, controlling the evolution of particles size distribution [1]. While the importance of the surfactants for the synthesis and the shelf-life of emulsion polymers is clear, many studies revealed that the presence of emulsifiers in the application stage, especially in film-forming products, is unfavourable. Surfactants may migrate to the air-film and film-substrate interfaces, together with the assembly in hydrophilic domains inside the film. As a consequence, the films can suffer of poor adhesion, reduced barrier properties and enhanced water sensitivity [2–6]. It is worthy to underline that after migration, surfactants molecules may be leached out by water and released into the environment. The chemical nature of most commercial emulsifiers implies a limited degradability, and relevant amounts of surfactants can be accumulated in water and soil [7].

Many ways to reduce the amount of migratory surfactants have

been developed, such as emulsifier-free synthesis [8] and the use of polymerizable surfactants (surfmers), emulsifiers that can be incorporated through reactive double bonds in the polymers backbones [9]. However, despite the promising appeal of these techniques, they have found limited application in large scale productions. For the surfmers, in particular, the reactivity of the emulsifier needs to be finely tuned with the characteristics of the other monomers. Fast incorporation causes the burial of the surfactant inside the growing particles, thus becoming useless for colloidal stabilization. On the other hand, lower reactivity may provoke limited incorporation and, at the end, a migratory behaviour. Although strategies for optimal incorporation have been proposed, this lack of “robustness” limits the industrial diffusion of surfmers [10–12].

Polymeric surfactants revealed as an efficient alternative to migratory surfactants, since they strongly adsorb on the surface of the polymeric particles [13]. Moreover, higher molecular weights decrease the kinetics of migration in the stage of film formation. In this context, well defined amphiphilic block copolymers with acrylic moieties have been proven as suitable stabilizers on emulsion polymerization [14,15]. Alkali-soluble resins (ASRs) combine the benefits of polymeric surfactants with a series of improved properties of the resulting latexes, such as Newtonian-like flow, improved capability of pigments dispersion,

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very good mechanical responses and resistance to freeze–thaw cycles [16,17]. From the chemical point of view, they are random copolymers of hydrophobic monomers (typically acrylate esters, methacrylate esters and vinyl aromatic monomers) and hydrophilic monomers, mostly acrylic and methacrylic acid. The molecular weight of the polymer normally ranges between 5000 and 20,000 Da. When working at a pH above the pK_a of the carboxylic groups (around 4.5), they become soluble and they can be used as protective colloids, providing electrosteric stability to the dispersion.

Despite the great importance from the industrial point of view, emulsion polymerization systems stabilized with ASRs have not been largely studied. The main feature observed when polymerizing in batch common monomers, such as styrene (S), methyl methacrylate, ethyl methacrylate, *n*-butyl methacrylate (BMA) and *n*-butyl acrylate (BA) is a clear reduction of the rate of reaction, if compared to a common electrostatic surfactant [18–22]. The results are generally explained assuming the formation of a hairy layer of protective colloid around the particles, hindering the entry of radicals [23]. Peck and Asua identified in detail the particular mechanisms decreasing the radical entry [24], while Caballero and co-workers quantified the contributions of three phenomena responsible for the reduction of radical entry in mini-emulsion systems; the resistance to diffusion, charge repulsion and hydrogen abstraction. The relevance of these phenomena depends on the type of ASR, the hydrophilicity of radicals produced by the initiator and the nature of the monomers [25]. The formation of a “midchain radical” after hydrogen abstraction in the hairy layer was also proposed by Thickett et al. to explain the limited number of radicals per particles found in electrosterically stabilized systems [26–28]. The hydrogen abstraction process may also explain the experimental findings that part of the resin chemically grafts to the particles during the process [20,22,29]. Similar grafting reactions between protective colloids and particles have been described also for other types of polymeric surfactants, like poly(vinyl alcohol) [30,31]. However, some ways of ASRs synthesis described in the literature employ high-temperature bulk processes [32]; under such conditions, and in the presence of appreciable amounts of S, hydrogen abstraction on benzylic positions, followed by β -scission, leads to the formation of terminal double bonds on the backbone of the resin [33]. In this respect, the resulting ASR can be seen as a macromonomer, providing another possible mechanism for grafting (Fig. 1).

In this work, three macromonomer-type ASRs have been studied on semi-batch emulsion polymerization systems. Their stabilization capability and the effect on nucleation and kinetics have been analysed; furthermore an estimation of the contribution to grafting of hydrogen abstraction and incorporation through terminal double bonds in ASRs stabilized emulsion polymerization has been studied for the first time, providing an insight on mechanism behind grafting.

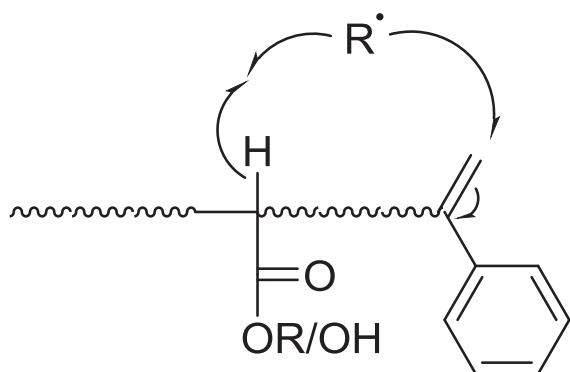


Fig. 1. Possible mechanisms of grafting in ASRs stabilized latexes, through hydrogen abstraction or polymerizable double bonds.

2. Experimental

2.1. Materials

Three different ASRs, indicated as C1, C2 and C3, were provided as flakes by BASF SE and used as received; the chemical compositions of the resins, as well as the acid values (AV) and the molecular weights (Mw), are reported in Table 1. Technical grade monomers BA (Quimirogra) and BMA (Sigma Aldrich) were used as received without any further purification, as well as sodium persulfate (NaPS, Sigma Aldrich) as initiator. Aqueous ammonia 28–30% was purchased from Sigma Aldrich. Deionised water was used throughout the work.

2.2. Methods

The conversion of monomers was determined gravimetrically. Approximately 3 mL of samples were withdrawn from the reactor and transferred into aluminium cups having 2–3 drops of an aqueous solution of hydroquinone (1 wt% in water, Panreac). The samples in the cups were dried in an oven at 60 °C until constant weight.

Z-Average particle diameters were determined by dynamic light scattering (DLS) performed on a Malvern Zetasizer Nano-S instrument using a scattering angle of 173° at a standard temperature of 25 °C. Before the analysis, the samples taken from the reactor were diluted with deionised water to prevent multiple scattering. The numbers of particles (N_p) were calculated from measurements of particles size with the described technique and the polymer mass in the reactor determined with conversion analyses, using the following equation:

$$N_p = \frac{6w_p}{\pi\rho_p d_v^3} \quad (1)$$

where w_p is the mass of the polymer in grams, ρ_p is the density of the polymer particles (g/cm^3) and d_v is the average particles size expressed in cm.

The volume average particles size distributions were measured with a Matec CHDF3000 equipped with a UV detector operating at 254 nm using a flux of 1 mL/min. The column was a PL-PSDA Type 2 (Agilent). Each sample was firstly diluted to 1% solids content, filtered through a 1.2 μm filter and injected with an autosampler (25 μL). The eluent was an aqueous solution of sodium dihydrogenphosphate (0.24 g/L), sodium laurylsulfate (0.5 g/L), Brij35 (poly alkylenglycoether, 2 g/L) and sodium azide (0.2 g/L).

The iodine value of the resins was determined using the Kaufmann method [34]. The resins were dissolved in chloroform/acetic acid, then an excess solution of bromine in methanol was added. After stirring for 30 min in dark, the samples were diluted with water and treated with a solution of potassium iodide. The excess of iodine was potentiometric backtitrated with sodium thiosulfate.

The acid value of the ASRs was determined dissolving the resin in *N,N*-dimethylformamide (Sigma Aldrich) and performing a potentiometric titration with tetrabutylammonium hydroxide (1.0 M in methanol, Sigma Aldrich).

Molecular weight distributions of polymers were measured by GPC. Samples were dried and diluted in THF (HPLC grade, Scharlau) to a concentration of 2 mg/mL. To 5 mL of the mixture, 35 μL of (trimethylsilyl)diazomethane (solution approximately 2 M in diethylether, Acros Organics) were added in order to methylate the carboxylic acid groups. The samples were let reacting for at least 24 h, then the yellowish solutions were filtered through a 0.45 μm nylon filter before injection. The GPC set up consisted of a pump (LC-20A, Shimadzu), an autosampler (Waters 717), a refractive index detector (Waters 2410) and three columns in series (Styragel HR2, HR4 and HR6 with pore sizes ranging from 10^2 to 10^6 Å). Chromatograms were obtained at 35 °C using a THF flow rate of 1 mL/min. The equipment was calibrated using narrow polystyrene (PS) standards ranging from 595 Da to

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