Nonionic reactive surfactants. I. Synthesis and characterization

Abstract A procedure to prepare nonionic reactive surfactants with different polymerizable groups is described. The synthesis involves the initiation of living anionic ring-opening polymerization of ethylene oxide and propylene oxide (for the hydrophilic part and the hydrophobic part, respectively) by a potassium salt prepared from the stoichiometric reaction of potassium hydride and diethylene glycol monomethyl ether. The resulting anion is reacted with chloride compounds (methacryloyl, allyl, vinylacetoyl) and maleic anhydride, as well as with isobutanol chloride, leading to a nonpolymerizable compound having a similar structure. Then, it was possible to produce a range of reactive surfactants more or less reactive with the monomers. These surfactants are expected to be used further in emulsion polymerization processes (styrene and butyl acrylate). This procedure gives good control of both hydrophobic and hydrophilic parts, and the end reaction for the different functionality of surfmers is quite quantitative. All the surfactants were characterized by size-exclusion chromatography and $^1$H NMR. Physicochemical properties, such as the critical micellar concentration and the specific area, were also measured.

Keywords Living anionic ring-opening polymerization · Block copolymer poly(ethylene oxide)-b-(propylene oxide) · Nonionic reactive surfactants · Critical micellar concentration · Specific area

Introduction

The waterborne coatings industry is a huge consumer of latex from emulsion polymerization. The surfactants are essential during the latex synthesis processes to control the particle sizes and the latex stability. However, surfactants tend to migrate toward the interfaces of the film (air/film and substrate/film) or to segregate inside the film into microdomains during film formation carried out for the final applications. Then, the film loses its adhesiveness on the substrates and becomes water-sensitive. The amphiphilic species, which are nonbiodegradable, can also be rejected into the wastewater, and the resulting foam is dangerous for aquatic life.

By replacing surfactants by reactive surfactants (i.e., surfactants that are able to react during the emulsion polymerization process), the amphiphilic species will be incorporated into the macromolecular chain and will not be desorbed anymore. The subject was recently reviewed [1]. The main criterion of the success of its use is its incorporation at the surface of the latex particles by copolymerization with the main monomers. Its derivatives must not be buried inside the particles or lost in the serum surrounding the particles as either nonreacted surfactants or water-soluble species.

Theses reactive surfactants were recently studied by a network of laboratories supported by the European Community. Different reactivities of polymerizable surf-
actants were tested in emulsion polymerization. And so, an optimum behavior of reactivity was defined [2, 3, 4]. First, the “ideal” reactive surfactant should have limited reactivity versus the main monomers at the beginning of the process. This will avoid the surfactant being buried inside the particle, and also the production of water-soluble polymers. These two phenomena might be responsible for flocculation of the latex particles during the process. On the other hand, the “ideal” reactive surfactant should be very reactive at the end of the process to be well incorporated at the very surface of the particles. Then, there will be no surfactant free in the serum of the latex. The European Network got their best results with a maleic functionalized anionic reactive surfactant [4, 5], whether with a methacrylic or acrotonic reactive part, which are, respectively, too reactive and not reactive enough.

The main idea of this work is to produce nonionic reactive surfactants with different polymerizable groups which are more or less able to copolymerize with the main monomers engaged in an emulsion polymerization process. This range of reactivity of the polymerizable surfactants studied will show the influence of the surfactant double bond during the emulsion polymerization process and find out if our reactive surfactants act like an “ideal” surfmer (surfactant monomer).

In this paper, the synthesis and the characterization of nonanionic reactive surfactants with maleic, allylic, methacrylic and vinyl ether double bonds are described. A nonreactive surfactant was also synthesized in order to compare the results obtained between surfmers and an equivalent nonreactive surfactant. The macromolecular architecture of the amphiphilic species was determined from the work of Schechtman [6] and Soula and Guyot [7]. The later work showed excellent behavior in terms of stability of the latexes, provided that an adequate hydrophile–lipophile balance (HLB) balance was respected. The first author described a way to obtain surfmers by anionic polymerization block copolymers of propylene oxide (PO) and ethylene oxide (EO). The resulting alkoxide was killed with vinyl benzyl chloride, leading to a styrenic surfmer. Using other chloride species, such as methacryloyl chloride, the block copolymer can be functionalized by other reactive groups. And so, different surfmers, built from the same block copolymer, with different reactive parts can be produced. The initiator used for anionic polymerization was potassium methanol alkoxide. This alkoxide is not soluble in tetrahydrofuran (THF) at room temperature and at atmospheric pressure. So, it was decided to start the synthesis with another potassium alkoxide.

The work done by Soula and coworkers [7, 8, 9] gave us some indications about the length of each part of the block copolymer in order for the amphiphilic species to have good efficiency in emulsion polymerization processes and in colloidal stabilization. The reactive surfactant which had the best amphiphilic behavior was built from seven units of butylene oxide for the hydrophobic part and 36 units of EO for the hydrophilic part. For the replacement of butylene oxide by PO for some convenient (lower cost) reasons, a length of ten PO units for the hydrophobic part was chosen according to the HLB theory.

**Experimental**

**Materials**

All the materials involved in the anionic polymerization, in order to synthesize nonionic surfmers, need to be perfectly dry otherwise the living character is lost.

KH and NaH (both from Aldrich) were received dispersed at 40% w/w in mineral oil. The hydrides were washed with dry heptane, kept as pure powders under argon and stored in a Schlenk tube. Diethylene glycol monomethyl ether (Aldrich) and, as chloride species, methacryloyl chloride (Aldrich), isobutanyloxyl chloride (Aldrich), allyl chloride (Lancaster) and vinylacetoxy chloride (Lancaster) were stored under dry argon in a Schlenk tube over molecular sieves (3 Å). THF (Aldrich) was distilled over sodium/benzophenone and stored under dry argon. Maleic anhydride (Aldrich) was dissolved in dry THF in a Schlenk tube under dry argon and kept over molecular sieves (3 Å). EO (Fluka) is a gas in a 4 l pressure bottle. It was distilled under vacuum and collected in a trap cooled with cold ethanol. PO (Aldrich) was stirred with NaH under dry argon in a Schlenk tube, then distilled under a static vacuum and stored under dry argon in an adding funnel.

**Synthesis**

Each step of the synthesis was carried out under dry argon. The whole glassware was oven-dried, and then alternately purged under reduced pressure and dry argon several times (150-ml Schlenk tube for storage of chemicals, adding funnel for monomers and a 500-ml three-neck flask for the synthesis).

**Synthesis of the block copolymer**

Dry THF (150 g) was introduced under dry argon into a 500-ml three-neck round-bottom flask containing a magnetic stirrer. Then 1 g KH (0.025 mol), which is not soluble in THF, was carefully added under dry argon. In the same way, 3.005 ml diethylene glycol monomethyl ether (0.025 mol) was added. The reaction mixture was stirred magnetically and reacted at room temperature for 1 h under dry argon. The alkoxide formed is soluble in THF and no powder (KH) remained in the mixture.

The reactor flask was put under a static vacuum and maintained at 55 °C so that the kinetics could be monitored by a pressure sensor. The saturated vapor pressure of THF at 55 °C is noted as \( P_{\text{THF}} \). Then 43.75 ml EO (35°0.025 mol) was added several times in order to keep the pressure below 1 atm. After 6 h, the pressure reached \( P_{\text{THF}} \) again, and so the polymerization of EO was completed. Then, 17.5 ml PO (10°0.025 mol) was introduced. After 20 h, the pressure was back to \( P_{\text{THF}} \) and so all the monomer reacted. Then, the reactor was put under dry argon at atmospheric pressure and at room temperature (Fig. 1).

**Synthesis of the nonreactive surfactant**

In order to synthesize the nonreactive surfactant (Iso), the block copolymer, which was in THF at room temperature under dry argon, was functionalized with 3.9 ml isobutanyloxyl chloride