Poly(alkyl methacrylate-b-sulfonated glycidyl methacrylate). A New Amphiphilic Polymeric Surfactant for the Preparation and Stabilization of Polymer Acrylic Latexes in Aqueous Medium

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ABSTRACT: Poly(alkyl methacrylate-b-sulfonated glycidyl methacrylate) are a new class of amphiphilic block copolymers that can be used for the preparation and stabilization of very fine and stable polymer acrylic latexes in aqueous medium. The strong anionic block poly(alkyl methacrylate) creates an electrostatic double layer for the stabilized latex particles. High critical coagulation concentrations were obtained for these polymer latex surfactant-stabilized latexes. By substitution of the poly(vinyl methacrylate) block by a poly(alkyl methacrylate) block in the radial emulsion polymerization of latexes, the polymeric surfactant becomes completely linked with the particles, and cross-linking occurs as evidenced by GPC measurements. Photon correlation spectroscopy measurements give an estimate of the average adsorbed layer thickness, closely corresponding to the extended chain length of the polyelectrolyte block.

Introduction

Polymer latexes, particularly in aqueous medium, represent nowadays a topic of prime importance for both basic science and application research. Several types of polymer surfactants are being used successfully in the preparation and stabilization of those latexes. As a few typical nonlimitative examples, suffice it to cite the following: nonionic block copolymers, such as poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) and poly(poly(ethylene oxide-b-propylene oxide-b-ethylene oxide)), used to stabilize polyurethane latexes in water;4 copolymers comprising poly(vinyl alcohol) or poly(acrylic acid), which owe their particular amphiphilic nature to some thickness of unreacted vinyl acetate or acrylate units respectively, after hydrolysis; and copolymer containing sequences of quaternized amino groups of, e.g., poly(ethylene oxide), poly(vinylpyrrolidines), and poly(aaminomethylacrylates).

Polymer surfactants offer the advantage of important steric stabilization of dispersions, while most classical low molecular weight (MW) surfactants only operate through electrostatic effects. The ideal combination of both mechanisms, which has been called "electrostatic stabilization by Napier" and is beautifully exemplified in nature, chemical reactions involving block copolymers in surfactants comprising one strong polyelectrolyte block.

Many exciting investigations and possible applications ask for such a strong anionic polyelectrolyte block: indeed nonionic poly(ethylene oxide) (PEO) becomes insoluble in water at elevated temperature, while weak polyelectrolyte blocks display pH-dependent ionization, causing variable solvation of polymer coils and consequently changing of steric barrier properties, i.e., poly(ethylene oxide) acid and quaternized poly(aminomethylacrylates). In that respect, we want to report here on the properties of polymer latexes stabilized with a new family of poly(alkyl methacrylate-b-sulfonated glycidyl methacrylate) block polymers (PAMMA-b-SGMMA). As illustrated hereafter, these block copolymers act as good polymer surfactants, as well as for the poststabilization of acrylic latexes, as for the radical emulsion polymerization of several monomers (e.g., ethyl or butyl acrylate and methacrylate).

Experimental Section

Reduction emulsion polymerizations: Latexes were prepared batchwise under magnetic stirring in a nitrogen-flushed reaction vessel equipped with a reflux condenser. For a typical emulsion polymerization, 20 g of ethyl acrylate in 80 g of water, containing 1 g of PMMA-b-SGMMA and 100 mg of K$_2$CO$_3$ was stirred at 150 rpm. After peeling off the acrylate monomer through the emulsion, it was heated at 80 °C in a water bath, whereupon the emulsion polymerization started. A white bluish latex had formed after a few minutes, but heating was continued for another 30 min. After filtration a 98% yield was obtained.

For postpolymerization purposes, a poly(ethyl acrylate) latex was prepared with similar equipment, using a very low amount (0.13%) of sodium oleyl taurode sulfonate (NaOTaS), a classical low molecular weight surfactant, in a radical initiated K$_2$CO$_3$ emulsion polymerization in water (80 °C, 30 min): it displayed a mean diameter of 78.3 ± 0.19 nm. To this latex were added (at room temperature) increasing quantities of a solution of PMMA-b-SGMMA in water, the systems being kept under stirring overnight for equilibration.

GPC measurements were carried out in THF at 45 °C using a Hewlett Packard 1090 liquid chromatograph equipped with four Polymer Laboratories PS gel columns (5, 10, 50, 100 A) and a Hewlett-Packard 1092 refractive index detector. A PS calibration curve allowed estimation of Mw. For cross-linked particles, previous filtration on a 0.45-μm mesh eliminated the peak (monitored on a Waters 200 instrument) seen in Figure 6 (trace c).

Mean particle diameters were obtained by photon correlation spectroscopy (PCS) at 25 °C. A Malvern apparatus equipped with a He-Ne Arga Laser Physics laser was used. The scattered intensity was measured under a 90° angle.

For determination of the critical coagulation concentration (CCC) of the stabilized latex, a Ubbelohde's temperature was added. Two different block copolymers were used (samples 1 and 2, Table 1), displaying the same composition but different MWs, the CCC being determined as the ratio of concentration or inversely proportional to the stability ratio. The stability ratio is defined as $d = 1/W$. The CCC is then determined as $W = 1/e, log_{10} \log_{10} = 0.5$.

Results and Discussion

PAMMA-b-SGMMA’s were synthesized as previously reported,5 and characteristic data for the three block copolymers, used, all of them water-soluble, are reported in Table 1.

Characterization of the Electrostatic Barrier in Poststabilized Systems. A block copolymer poststabilized latex is represented as in Chart 1, where the hydrophobic PMMA blocks (A) are adsorbed at the surface of the latex particle and the well-solubilized sulfonated PGMA blocks (B) constitute the electrostatic barrier. Characterization of that barrier was achieved by using photon correlation spectroscopy (PCS): for that purpose, postpolymerization experiments were carried out by adding an aqueous solution of the polymer surfactant to the classically prepared poly(ethyl acrylate) (PEA) latex having a mean particle diameter of 78.1 ± 0.19 nm (see the Experimental Section). Successive addition of block copolymer to the latex resulted in a regular increase of the PCS particle size, upon adsorption of the amphiphilic macromolecules at its surface. With PCS one measures the so-called hydrodynamic diameter of the particle. In the case of a monomeric surfactant, this diameter represents the hard particle core plus a small average thickness of the adsorbed material. When a steric barrier is present, the average adsorbed layer thickness is much higher.

Figure 1 shows the electrokinetic properties of the block copolymer PEA latex in comparison with a classical PEA latex prepared with sodium oleyl taurode sulfonate as a function of pH. The potential was measured with the help of the Smoluchowski equation is about the same for the two types of latexes and practically independent of pH. This guarantees a stable dispersion over a broad pH range. The difference between a latex prepared with NaOTaS and one prepared with PAMMA-b-SGMMA block polymer

Figure 1. Adsorbed layer thickness of the electrostatic barrier on PEA latex particles versus an added amount of PMMA-b-SGMMA block copolymer.
lies in the fact that electrostatic repulsion starts to act on an approaching particle much further away from the solid particle. On the other hand, it now polishes the stabilized PEA (Chart D). As a result of this, the attraction energy, which is high in a close approach situation, is consequently shielded and out of operation. The aforementioned data finally indicate that the so-called electrostatic barrier should be highly efficient in preventing these particles from flocculation. This was indeed demonstrated by measurement of the critical coagulation concentration (CCC) by stopped flow spectrometry. For a PEA latex stabilized with a PMMA-b-SMGMA surfactant, a CCC of 1.9 M was determined (see the Experimental Section), in sharp contrast to the CCC values of many colloidal systems stabilized with classical low MW surfactants and having CCC's lower than 0.15 M.\(^{10}\) Figure 4 shows the dependence of the stability ratio \(W\) (see the Experimental Section) as a function of added KCl. The onset of the horizontal part of the curve, where the system shifts from a slow to a fast flocculation mechanism, is the CCC representative for the stability of the latex toward flocculation.

Radical "Emulsion" Polymerization with PMMA-b-SMGMA as a Polymeric Surfactant. Latices were prepared according to the Experimental Part, using a PMMA-b-SMGMA copolymer (sample 13). A reasonably narrow particle size distribution was obtained with a Z-average mean of 90.0 nm and a standard deviation of 31.1 nm, based on a log normal fit of the data. A typical particle size distribution is shown in Figure 5.

Another important size feature is the content of microporous coagulum as defined in ref 10. This coagulum cannot be measured by using a PCS technique, due to the fact that PCS requires a very high dilution, so that the small quantity of the upper micron particles (between 10\(^{-4}\) and 10\(^{-5}\) vol%) disapper. Moreover, quite a large quantity can be achieved with a so-called Coulter threshold technique.\(^{10}\) Table II shows a comparison of a classically prepared PEA latex and the block copolymer prepared latex with respect to the number of upper micron particles present. Typically this quantity determines the filtration properties of the latices and affects its coating properties.

In addition, the same table shows the increase of the amount of microporous coagulum when the latices are mixed with a high molecular weight polyelectrolyte such as gelatin. The increase is typically due to the bridging flocculation. The block copolymer-PEA latex apparently shows a better protection against this phenomenon than a latex prepared with a classical low molecular weight emulsifier (NaOTs) for block polyelectrolyte stabilizing chains of not too high molecular weight.

While PMMA-b-SMGMA stabilizes latex particles by adsorption of the hydrophobic part of the polymer at their surfaces, a molecular modification of the polymeric surfactant can lead to another still more interesting anchoring mechanism. Polyallyl methylacrylate-b-sulfonated glyclyl methacrylate) (PMMA-b-SMGMA) proved indeed to be also a very efficient polymeric surfactant for the radical emulsion polymerization. Acrylic latices with a mean particle diameter (Z-average) of about 150 nm were readily prepared in nearly quantitative yield. Moreover, as polymerization proceeds, this surfactant will be covalently linked to the particles and will thus lead to their cross-linking by the allyl moiety. This was supported by GPC chromatograms of latices to which THF was added to dissolve the soluble polymer. Three different latices were prepared: (a) with NaOTs, (b) with PMMA-b-SMGMA, and (c) with PMMA-b-SMGMA. Latices a and b give GPC chromatograms (Figure 6a,b) showing the existence of a soluble polymer with a broad molecular weight distribution, roughly going from 10\(^3\) to 10\(^4\) with a peak MW of about 2 X 10\(^3\). In contrast, the GPC chromatogram of latex c (Figure 6c) displays an entirely different elution pattern: it hardly shows soluble polymer in the 10\(^2\) range, but one important peak appears at the exclusion limit of the GPC when no filtration was done, this peak is suppressed when finer mesh (0.45-μm) preliminary filtration is applied. That should be due to cross-linked latex particles having a very large hydrodynamic volume as compared to soluble polymer coils and thus passing through the columns without separation (see the Experimental Section). It is plausible that preparation of latices in the presence of PMMA-b-SMGMA leads to the expected cross-linking with the polymeric surfactant covalently anchored on these particles. This situation promotes striking properties, as illustrated by the fact that small particles with a relatively small narrow size distribution can equally be prepared this way, the stability of which against coagulation is amazingly high; since these latices can be diluted with, e.g., 1 M or 1 M NaO\(_3\) solutions, without noticeable macroscopic precipitation. Chart 1c illustrates this latter situation, as compared to the other possible stabilization modes and morphologies (low-MW surfactant a) and adsorbed block copolymer b).

Conclusions. The use of an amphiphilic block polymer containing one strong polyelectrolyte moiety as a polymer surfactant in the radical emulsion polymerization of different monomers allows for the preparation of very fine and stable latices. By adsorbing the adsorbing PMMA block for a PAMA-b-SMGMA block, the emulsifier becomes covalently linked with the particles and cross-linking occurs as evidenced by GPC experiments. On the other hand, it was shown that the adsorption of the block polymer at a latex particle surface leads to an increase in that particle diameter, creating an electrostatic barrier and possible applications for the polymeric surfactant as a poststabilizer of preformed latexes. As shown, the PMMA-b-SMGMA stabilized latices are indicative of their considerable resistance against flocculation. These results are to be related to previous studies\(^{18}\) illustrating the high efficiency of a (poly styrene-b-allyl methacrylate) diblock copolymer in stabilizing upon adsorption of carbon black particles (ca. 300 nm) dispersions in isooctane. Such approach obviously paves the way for a powerful control of surface properties, morphologies, and dynamic behavior of particle dispersions in liquids, either organic or water.

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