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The Use of Selected Acrylate and Acrylamide-Based Surfmers and Polysoaps in the Emulsion Polymerization of Styrene

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SUMMARY: Polymerizable surfactants (surfmers) 12-acryloyloxy-dodecanoic acid and 11-acrylamidoundecanoic acid and their respective sodium salts were prepared and then polymerized to form their corresponding oligomers using reversible addition-fragmentation chain transfer (RAFT). Different concentrations of both the surfmers, their sodium salts, and their RAFT oligomers were used as polysoaps in the emulsion polymerization of styrene. Stabilities of the pre-emulsions before polymerization were determined and compared. After polymerization, particle sizes and polydispersities of the resulting polystyrene latices were determined. Sodium dodecyl sulfate (SDS) was used as a reference surfactant to compare the particle sizes and stabilities of the pre-emulsions prepared using surfmers and polymeric surfactants (polysoaps) as particle stabilizers.

Emulsion polymerization of styrene using these surfmers and polysoaps all led to latices which were stable for a period of more than six months, as indicated by constant particle sizes, whereas latices prepared using the conventional surfactant, SDS, were not as stable.

Introduction

The use of surfmers rather than conventional surfactants such as sodium dodecyl sulfate (SDS) is intended to reduce surfactant mobility in latices formed by emulsion polymerization. Conventional surfactants mainly associate with other compounds through adsorption. Latices stabilized with conventional low molar mass surfactants such as SDS

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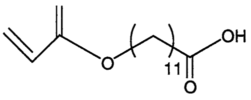
have sometimes been unable to withstand harsh service conditions, such as high shear speeds,[1] partly due to the possibility of desorption. Conventional surfactants may also migrate through a film or to the film-air surface during the film formation process.[2]

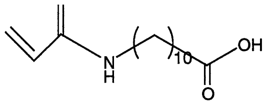
It is expected that copolymerization between a surfmer and monomer may result in a well-stabilized latex through chemically bonding the surfactant to the latex particles. Polymeric surfactants stabilize polymer latices through adsorption of the surfactants to the polymer latex particles, resulting in repulsion between latex particles. Coagulation is prevented by steric and/or electrostatic stabilization[3] (repulsion) that is provided by the highly charged regions near the surface of the particles.

In this study, the surfmers 12-acryloyloxydodecanoic acid[4] (12-ADA) and 11-acrylamidoundecanoic acid[5] (11-AAUA), their sodium salts, and their corresponding oligomers (prepared by reversible addition-fragmentation chain transfer (RAFT) polymerization) were used to prepare polystyrene (PS) latices by emulsion polymerization using these soaps as surfactants that may be chemically bound to the latex particles. The relative stabilities of the pre-emulsions and latices formed after polymerization were determined and compared with each other and with those of comparable SDS-stabilized systems. The particle sizes and polydispersities of the resulting polystyrene latices were determined and compared.

The surfmers, 12-ADA and 11-AAUA, and their sodium salts were synthesized according to reported methods.[4,5]

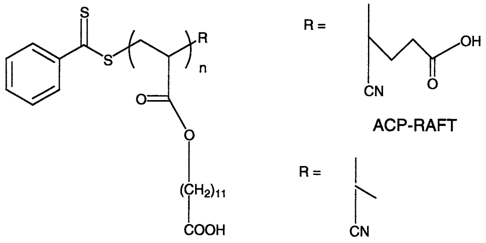


12-ADA



11-AAUA

Their polysoaps, poly(12-ADA)-ACP, poly(12-ADA)-AIBN and poly(11-AAUA)-AIBN were prepared by a RAFT[6] polymerization method using RAFT reagents (see synthesis of RAFT agents and polysoaps).



Poly(12-ADA)

ACP-RAFT

AIBN-RAFT

Experimental and Results

Surfmer synthesis

The surfmer 12-ADA was prepared by reaction of 12-hydroxydodecanoic acid and triethylamine with acryloyl chloride in dry THF. Purification was carried out using a silica gel chromatographic column. The surfmer was analyzed by ^1H NMR spectroscopy, and found to be 92% pure. The surfmer 11-AAUA was prepared from 11-aminoundecanoic acid and acryloyl chloride in water and ethanol. The product was recrystallized from aqueous ethanol, analyzed by ^1H NMR spectroscopy, and found to be 95% pure. The sodium salts were prepared by reacting the respective surfmers with NaOH in dry ethanol, followed by drying.

Synthesis of RAFT agent and polysoaps

The RAFT agents 4-cyano-4-(thiobenzoyl) sulfanyl) pentanoic acid (ACP-RAFT) and 2-cyanoprop-2-yl dithiobenzoate (AIBN-RAFT) were prepared using 2,2-azobiscyanopentanoic acid (ACP) and azobis(isobutyronitrile) (AIBN) free radical initiators respectively, using methods reported in the literature.[7] In both cases, the RAFT compounds were prepared by first preparing Grignard reagents which were then converted to dithioacids, before being reacted with dimethyl sulfoxide to give bis(thiobenzoyl) disulfide compounds. The disulfide compounds were then reacted with the corresponding azo-initiator to give the corresponding RAFT reagents. The resulting compounds were each purified by column chromatography (using a silica gel column) using a 3:2 solvent mixture of heptane/ethyl acetate as eluent. Solvent was removed and the products were dried under vacuum before ^{1}H NMR analysis. The purity of the AIBN-RAFT reagent was found to be 97%, and that of the ACP-RAFT was 95%.

For the preparation of the poly (12-ADA)-ACP oligomer, a mixture of 12-ADA and ACP-RAFT agent dissolved in acetic acid was polymerized using AIBN as initiator at 75 °C. The products were purified by column chromatography with a 1:2 mixture of ethyl acetate/dichloromethane as eluent. The polymeric product was analyzed by NMR and electrospray mass spectroscopy (ESMS); it was estimated to have a molar mass of 1400 g mol^{-1}.

Synthesis of PS latex by emulsion polymerization

Both the pre-emulsion tests and emulsion polymerization of styrene used styrene monomer, sodium borate buffer solution (pH 9), the appropriate surfactant, and $K_2S_2O_8$ initiator. Styrene was washed with 0.1 M KOH, and inhibitor removed by vacuum distillation immediately prior to use. The buffer solution was prepared from double-deionized water and sodium borate, and was used for two reasons: to ensure an approximately constant pH during the emulsion polymerization process, and because it was found that although the acid surfmers did not dissolve in deionized water, they were soluble in this buffer solution. Recrystallized potassium persulfate was used as initiator and SDS, a surfmer or polysoap as surfactant.

Stabilities of pre-emulsions

The extent to which a surfactant emulsified a starting emulsion was estimated by examining the stability of the mixed emulsion before polymerization.[8]

Surfactant (2 wt %) was first dissolved in buffer (76 wt %), after which styrene (22 wt %), and initiator (1 wt %) were added. The mixture was purged with nitrogen, and vigorously stirred for 1 hour at room temperature. After stirring ceased, the time taken for demixing was noted. The results of the pre-emulsion tests are summarized in Table 1. The longer stability times seen for the pre-emulsions with polysoaps, compared with those with some surfmers, suggest that significant surfactant adsorption occurred prior to polymerization which may imply different particle sizes/stabilization between surfactants. The surfmer 12-ADA did provided more stability to the pre-emulsions than its salt or the other surfmers. The higher stability of poly(ADA) prepared with ACP-RAFT compared with poly (ADA) prepared with AIBN-RAFT may be due to an extra stabilizing influence caused by the many carboxyl end-groups from the ACP moiety, in addition to those from the tails of the 12-ADA.

Table 1 Stability of styrene-in-water emulsions at room temperature.

Surfmer	wt % surfactant	Separation time (minutes)
AAUA	2	16
AAUA Na salt	2	9
ADA	2	190
ADA Na salt	2	24
SDS	2	160
Poly(ADA)-AIBN	0.5	150
Poly(ADA)-ACP	0.5	860
Poly(AAUA)-AIBN	0.5	130

Emulsion polymerization

Four different amounts of each surfactant, varying between 0.01 mol L^{-1} (1 wt % with respect to styrene monomer) and 0.04 mol L^{-1}, were used for emulsion polymerizations. The surfactant was dissolved in 13 mL of the sodium borate buffer solution (76 wt %). Styrene monomer (22 wt %) was then added, and the mixture stirred and degassed. The temperature was raised to 80°C, and 1 mL of a degassed buffer solution containing 1 wt % $K_2S_2O_8$ initiator (with respect to the entire emulsion) was added. The mixture was initially stirred at about 500 rpm for 20 minutes, followed by stirring for 160 minutes at about 300 rpm. The resulting latex was filtered through glass wool. Particle sizes and polydispersities of the filtered emulsions were determined by dynamic light scattering (Malvern Zetasizer 1000HS). The dependences of particle size and polydispersity on surfmer concentrations are illustrated in Figures 1 and 2. It was found that SDS, both surfmers, and their salts, stabilized PS emulsions and formed stable PS latices. In general, particle sizes and polydispersities decreased with increasing surfactant concentration. Reasonably low polydispersities of below 0.17 were obtained with all of the surfactants, although the SDS-stabilized latices had much smaller particle sizes and lower polydispersities. This suggests a short, intense period of particle formation early in the reaction in the case of SDS, which is consistent with earlier studies of emulsions stabilized using SDS.[9] The polymerizations with surfmers may have involved additional particle nucleation mechanisms, such as monomer droplet entry, as suggested by the larger particle sizes and polydispersities.

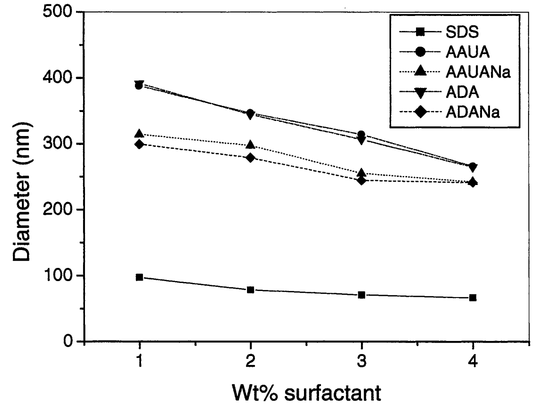


Fig. 1 Average particle size as measured by dynamic light scattering of polystyrene latices as a function of surfactant concentration for latices stabilized with SDS and surfmers.

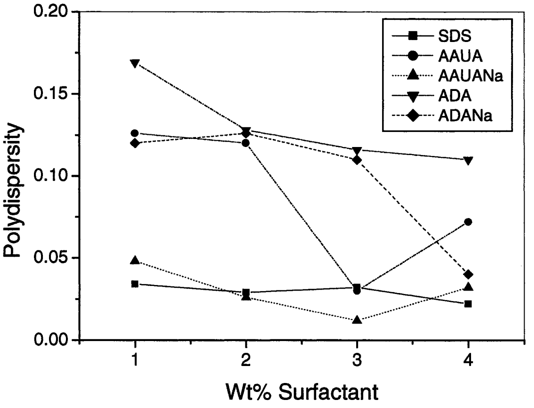


Fig. 2 Particle size distribution as measured by dynamic light scattering of polystyrene latices as a function of surfactant concentration for latices stabilized with SDS and surfmers.

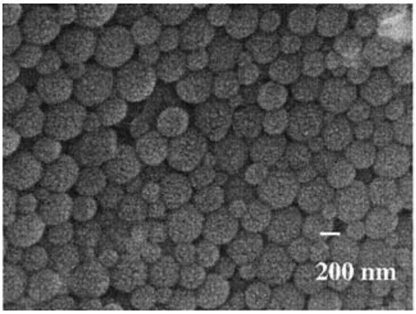


Fig. 3 SEM micrograph of dry 11-AAUA-stabilized PS latex (surfactant concentration = 4 wt %).

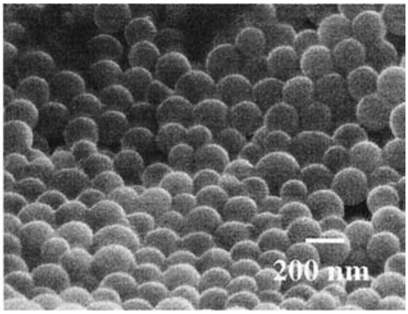
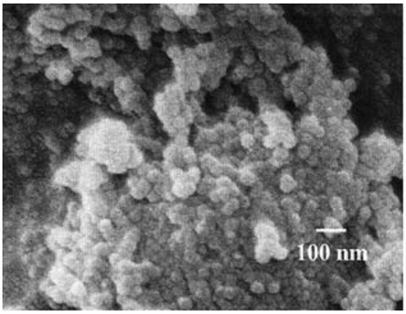


Fig. 4 SEM micrograph of dry 12-ADA-stabilized PS latex (surfactant concentration = 4 wt %).



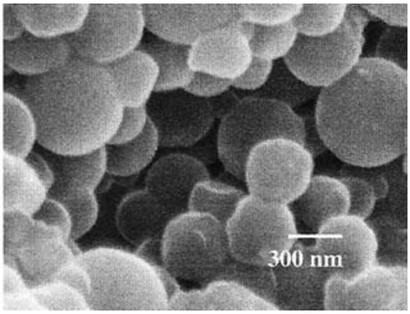


Fig. 5 SEM micrograph of dry SDS-stabilized PS latex (surfactant concentration = 4

Fig. 6 SEM micrograph of dry poly(12-ADA-ACP)-stabilized PS latex (surfactant concentration = 1 wt %).

The three PS latices shown in Figures 3 – 5 were stabilized with 4 wt % surfactant during emulsion polymerization and were purified by running through a mixed-bed ion exchange resin, followed by washing with deionized water.[10] They were then dried and examined by SEM for particle size and distribution. Latices were examined for coagulation after 6 months storage at room temperature. Surfmer-stabilized latices were more stable than the SDS-stabilized ones; the latter which showed a significant (visible) amount of coagulation, as confirmed by SEM. No visible coagulation was observed in the surfmer-stabilized latices.

Figures 3 and 4 show that stable latex particles were obtained with both surfmers, and that the product using 12-ADA as surfactant resulted in more monodisperse particles than that with 11-AAUA. The strong stabilizing effects of the surfmers were confirmed as all SEM measurements were made 6 months after the polymerization. The SDS particles in Figure 5 shows a significant amount of coagulation, which may indicate weaker stabilization than with the other surfactants, which may additionally include some steric stabilization. Polysoaps that had an AIBN-RAFT moiety from the RAFT polymerization of 12-ADA and 11-AAUA gave larger PS latex particle sizes than those of surfmer-stabilized latices, as shown in Table 2. This is supported by the SEM results in Figure 6, which show some large particles of about 600 nm for the poly(12-ADA-ACP)-stabilized latex. Although the PS latices were effectively stabilized by the polysoaps, more coagulation was noted during emulsion polymerization. Two distinct size-populations were evident in the polysoap-stabilized latices, suggesting that droplet entry occurred in addition to the normal mechanisms of particle formation.

Table 2 Particle sizes and polydispersities of 1 Wt % polysoap-stabilized PS latices.

Polysoap	Particle size (nm)	Polydispersity
Poly(12-ADA Na)	609	0.4
Poly(12-ADA)	656	0.2
Poly(AAUA)	338	0.6

Conclusions

The surfmers and polysoaps based on 12-ADA and 11-AAUA all acted as efficient surfactants in the emulsion polymerization of styrene. Larger latex particle sizes were produced with surfmers and polysoaps, compared with those of SDS-stabilized latices. The polydispersities of 12-ADA and 11-AAUA-stabilized latices were also relatively low. All of the studied surfmers and polysoaps studied acted as efficient stabilizers, regardless of whether they were used in their acid or salt forms, implying that a significant role is played by the surface carboxylate groups in the stabilization of latex particles and/or steric stabilization may impart additional stabilization. This will be further investigated in future work. As expected of true surfactants, particle size and polydispersity decreased with increasing surfactant concentration. With the polysoaps acting as surfactants, the particle sizes were large and the resulting latices were stable for at least 6 months, similarly to the surfmer-stabilized ones.

The RAFT moiety in the polysoaps was expected to facilitate control over molecular weight and polydispersity through living polymerization mechanisms,[11] although further analysis to confirm this will be necessary.

The efficiency of the selected acrylate and acrylamide-based surfmers, 12-ADA and 11-AAUA, and their polysoaps, as surfactants will be verified by further analysis, such as subjecting the latices to harsh stability tests, including electrolyte addition, freezing and thawing. Further characterization of the resulting latices is necessary in order to determine whether the surfactants stabilize the emulsion polymerization through copolymerization or adsorption, and to what extent particle formation mechanisms are influenced. The effects of RAFT moieties in controlling radical polymerisation in emulsions,[12] and their influence on particle growth also need to be studied further.

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