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Reactive Surfactant in the Emulsion Copolymerization of Methyl Methacrylate and Octyl Acrylate

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The emulsion copolymerization of methyl methacrylate and octyl acrylate was studied using a reactive surfactant ammonium sulfate allyloxy nonylphenoxy poly(ethyleneoxy) (10) ether (DNS-86), and a conventional surfactant sodium dodecylbenzene sulfonate (DBS) with a similar structure as a comparison sample. A series of latex samples have been prepared with two kinds of surfactants, and their properties have been characterized and compared. ^{1}H-NMR proves that the reactive surfactant has been incorporated into the resulting copolymers. The atomic force microscopy (AFM) proves that the reactive surfactant DNS-86 migrate to the surface of the latex film to a much less degree than the conventional surfactant DBS. Transmission electron microscopy (TEM) demonstrates that there are some differences in the particle morphologies. The stability and water-resistance of the latex films prepared by reactive surfactant DNS-86 are better than those prepared by the conventional surfactant DBS.

Keywords: reactive surfactant; emulsion copolymerization; latex; acrylate

1 Introduction

Surfactants play an important role in the latex preparation and application. They strongly influence the nucleation of the latex particles, emulsification of monomer droplets, stabilization of the polymer particles during the polymerization, and the shelf-life stability of the products (1–4). However, the use of conventional surfactant such as sodium lauryl sulfate (SLS) can have negative effects on product properties due to its physical adsorption on the polymer particles. First, they can cause foaming during application and processing of latexes; second, once the latexes have been applied as films, the surfactant can migrate to the film-air surface, which affects the film gloss, and can also migrate to the film-substrate interface, thus lowering film adhesion. Third, a low-molecular weight surfactant brings about poor water resistance. Besides, there can be further problems during processing of latexes. For example, they may migrate to other phases or react with other ingredients when mixed with other ingredients, and they can desorb under the high shear, which causes destabilization (5–6). Several methods can be used to eliminate such disadvantages. In surfactant-free emulsion polymerization, the latex particle is stabilized by the sulfate end groups derived from the persulfate initiator. However, because of the relatively low particle surface charge density, a significant amount of coagulum can form during the reaction by this method, particularly during the preparation of high solid content latex. Functional monomers can copolymerize with the monomer and contribute to the hydrophilic-lipophilic balance on the latex particles (7), thus replacing the surfactant and avoiding the defects caused by the conventional surfactant. However, because of the high solubility of functional monomers in water, large amounts of undesirable water-soluble oligomers can often be formed. A more promising method is to use reactive surfactants, which ensures the chemical incorporation of the surfactant into the latex particles during the course of the polymerization (8–10). Therefore, the desorption of the surfactant from the latex particle surface or migration in the polymer film is eliminated.

Much work has been done with the use of reactive surfactants in emulsion polymerization. For example, Zhao et al. (11) have prepared different fluorescent organic nanoparticles (FONS) from microemulsion with semi-continuous emulsion copolymerization of methyl methacrylate (MMA) and a reactive anionic surfactant. Chen and Chang (12) reported that the surfactant migration was reduced when a reactive

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surfactant was used. Improvements in water resistance and adhesions, as well as better resistance against electrolyte solutions (13) have also been reported. Kim et al. (14) have produced stable rod-like nano-particles by using reactive surfactant with a varying aspect ratio. Soula et al. (15) have reported the synthesis of stable core-shell latexes with low levels of coagulum and controlled particle size. The latexes display excellent stability to electrolytes, freeze-thaw cycles, and shear flocculation. Additionally, the reactive surfactants lead to films with superior performance as a result of reduced migration of surfactant to the surface (contact-angle measurements) and dimensional stability as well as less water uptake when the films are dipped in water. Aramendia et al. (16) have discovered that both vapor and water permeability were lower for a film cast from a latex stabilized with a nonionic reactive surfactant than for a film obtained from a latex containing a nonionic conventional surfactant. Sindt et al. (17) have also reported the use of a maleate reactive surfactant, and found an improvement in stability against freeze-thawing cycles and latex stability against divalent electrolyte solutions. Hartmann et al. (18) reported the polymerization of divinyl benzene in a liquid crystal template by reactive surfactant dodecylammonium methacrylate, A 20 wt% surfactant can form cubic bicontinuous phases, even upon addition of divinyl benzene.

The reactive surfactant DNS-86 has an excellent emulsifying ability and high reactivity on latex. During the pre-emulsion stage, pre-emulsion having the DNS-86 will not separate into a monomer layer and water layer, so the reactive surfactant DNS-86 has excellent emulsifying ability. When using this surfactant in emulsion copolymerization, it can have high conversion, and improve the latex performance and appearance of films. Furthermore, it can improve the water-resistance of latex films. However, no study has been carried out to date on the effect of this surfactant on emulsion copolymerization.

In this article, we have studied the reactive surfactant DNS-86 in the acrylate emulsion copolymerization by semi-continuous technique. The reactive surfactant DNS-86 incorporation into the polymer was proved by ^{1}H-NMR. The migration of surfactants to the particles surface was characterized by AFM. The latex particle morphology was characterized by TEM. We also discussed the stability of latex (including polymerization stability, storage stability and freeze-thaw stability) and water-absorption of films. Comparison has been made with the conventional surfactant DBS with the similar structure.

2 Experimental

2.1 Materials

Methyl methacrylate (MMA, technical grade), Octyl acrylate (OcA, technical grade) were used as received; other components, ammonium persulfate (APS) initiator and sodium hydrogen carbonate ($NaHCO_3$), were also used as received.

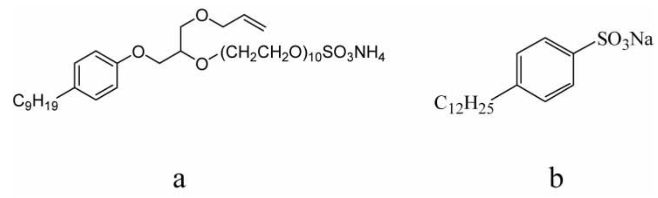


Fig. 1. The structures of surfactants: a. DNS-86 and b. DBS.

The reactive surfactant used in the study was: the ammonium sulfate allyloxy nonylphenoxy poly(ethyleneoxy) (10) ether, abbreviated “DNS-86,” was provided by Guangzhou Shuangjian Trading Co., Ltd. Sodium dodecylbenzene sulfonate (DBS) was used as a conventional surfactant. All experiments were performed with deionized water. The structures of the surfactants referred to above are shown in Figure 1.

2.2 Preparation of Acrylic Copolymer Latex

Copolymerization was carried out in a four-neck round-bottom flask equipped with a magnetic stirrer, thermometer, addition funnel, and reflux condenser. A basic recipe can be found in Table 1. At first, 25 g of water was added into the reactor. When the temperature reached to 82°C, 30% of the initiator solution was injected into the reaction kettle, and 3% of pre-emulsion was injected into the reaction kettle. The pre-emulsion was prepared by adding all of the surfactants and part of the water, stirred for half an hour, then MMA, OcA, and $NaHCO_3$ was added. The droplet size of the pre-emulsion is 4.0 mm. The stability of pre-emulsion is very good, since it is not laminated when stored for 24 h. The remaining pre-emulsion and the rest of the initiator solution were fed continuously over a period of 2.5–3 h. Upon completion of the pre-emulsion and the initiator fee, polymerization was allowed to continue for an additional 1 h at 85°C. The pre-emulsion was continuously stirred during the feeding stage the entire time. At last, the emulsion was cooled down to room temperature. The theoretical solid content of the emulsion product is about 55%.

2.3 Characterization

The solid content and conversion were measured by gravimetric analysis. 1–2 g of latex was cast onto a Petri dish

Table 1. The basic recipe of emulsion copolymerization

Compound	Total charge
MMA	50 g
OcA	50 g
Surfactant	1.5–4%[a]
Initiator	0.4%[a]
$NaHCO_3$	0.3 g
Deionized water	80 g

[a] Indicates the percent of total monomer weight.

and dried at 105°C until a constant weight was attained. The solid content and the final conversion were calculated by the following equations, respectively:

$$\text{Solid content (wt\%)} = \frac{W_2 - W_0}{W_1 - W_0} \times 100\%$$

W_0 is the weight of the Petri dish and W_1 and W_2 are the weight of latex before and after drying to the constant weight, respectively.

$$\text{Conversion (wt\%)} = \frac{\text{Solid content (wt\%)} \times W_3}{W_4} \times 100\%$$

W_3 is the total weight of all the materials put in the flask before polymerization, and W_4 is the total weight of monomers.

The amount of coagulum was measured by collecting the solid deposited on the reactor walls and stirrer, and the residual of filtered latex. It is expressed as the weight of coagulum per total weight of monomer added.

^{1}H-NMR spectra were obtained on a Varian Unity Inova 600 NMR spectrometer using d-chloroform ($CDCl_3$) as the solvent, if not otherwise specified.

AFM measurements were performed by imaging samples with a Digital Instruments Nanoscope IIIa with a Multimode Head. The height images were obtained while the instrument was operated in the tapping mode under ambient conditions. The data was taken at the fundamental resonance frequency of the cantilevers which was around 300 kHz. For AFM measurements, 1–2 drops of the corresponding latex were casted onto freshly cleaved glass plates and then dried at room temperature.

TEM photographs of the composites were obtained at 60 kV using a JEM-100SX. The latexes were negatively stained with an aqueous solution of 2% uranium acetate (UAc). In order to prepare the samples, the latex was diluted to about 0.1% solids content and a drop of UAc was added to a 5 ml portion of the diluted solution. A drop of the resulting mixture was then placed on a formvar-coated grid and the water was removed by adsorbing it with a filter paper. Micrographs were recorded on negative films, which were subsequently scanned.

For the freeze-thaw stability test, about 10 g latex was kept at −5°C for 18h, then at 20°C for 6 h, and repeated five times, we can then observe the state of latex.

Storage stability measurements were performed by adding 10 g latex in a sealed glass bottle, keptat 50°C for 20 h, then 3 h at room temperature, observed and the state of latex was recorded.

Water absorption ratio was determined according to ASTMD570-8. The copolymer films for the analysis were prepared by casting copolymers onto a Petri dish and letting the solvent evaporate slowly at room temperature. The sample size was 2.0 cm in length, 1.5 cm in width, and 0.60 ± 0.10 mm in thickness. The latex films were soaked in deionized water for a certain time, then the sample was taken out from the deionized water, excess water at film surfaces was gently removed via using weighed Kimwipes.

$$\text{Water absorption\% (wt\%)} = \frac{W_1 - W_0}{W_0} \times 100\%$$

W_0 and W_1 are the weight of the films before and after the films absorb water, respectively.

3 Results and Discussion

3.1 *Reactive Surfactant Incorporation*

In order to find proofs of reactive surfactant incorporation into the polymer, the latex prepared by the reactive surfactant DNS-86 was extracted by hot acetone for 24 h to extract the oligomers with small molecular weight or non-reacted surfactant. Then the extracted products were analyzed by ^{1}H-NMR.

Figure 2 is the ^{1}H-NMR spectra of the acrylate copolymer. From Figure 2, we can see that there is a surfactant peak around 7.4 ppm. Since the acetone extraction has the small molecular weight or non-reacted surfactant to solve into the acetone solvent, the 7.4 ppm peak should be assigned to the reactive surfactant DNS-86. That is, the reactive surfactant DNS-86 has already been incorporated into the acrylate copolymer.

3.2 *Migration of Surfactant*

During drying of a latex film, the physically adsorbed surfactant may either remain adsorbed at the particle surface or phase separation with the latex. If the surfactant undergoes phase separation, the water flux may carry it onto the film surface. Otherwise, it may accumulate in the interstices between the particles. From there, it will migrate to the film-air or film-substrate interface through a long-term exudation process.

In this investigation, AFM was used to observe the surface morphology of the films directly and to monitor possible

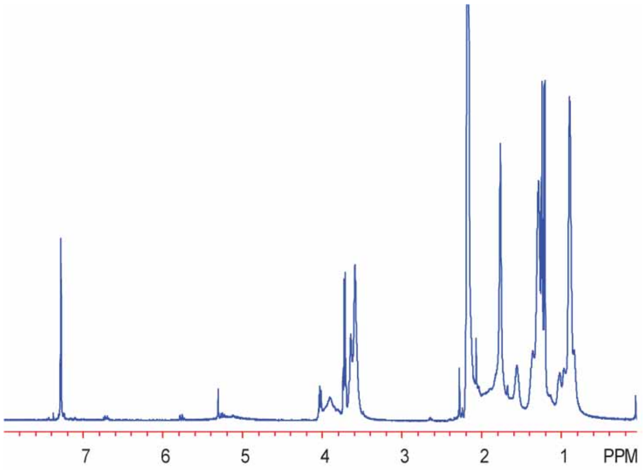
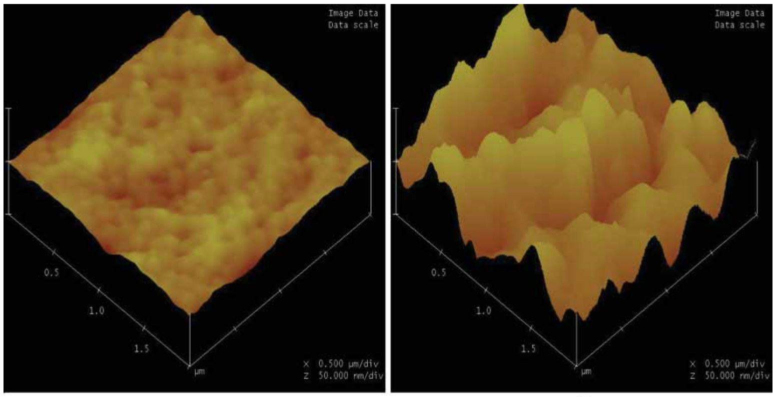


Fig. 2. ^{1}H-NMR spectrum of latex prepared by DNS-86.



a b

Fig. 3. AFM image of a film cast from DBS stabilized latex before (a) and after (b) rinsed with water.

migration of unanchored reactive surfactant. Films made from DBS stabilized latex were used as a reference sample. The latex had a particle diameter of about 160–270 nm. The topology of films made from latex stabilized by DBS, and the DNS-86 are shown in Figures 3–4. Figure 3(a) shows a film formed from DBS stabilized latex. The film has a smooth surface, and contours of the particles as would be expected. After rinsing with water, large pits were created (Figure 3b). This change in the film morphology resulted by the migrating surfactant DBS. During the drying stage, DBS moves with the evaporating water toward the film surface where it crystallizes to form a continuous separate phase, covering the total surface area. Upon rinsing with water, the highly water-soluble DBS is washed away. The roughness of the remaining film surface is caused by a disruption of particle packing by the migrating surfactant phase. This phenomenon was previously described by Juhue′ et al. (19).

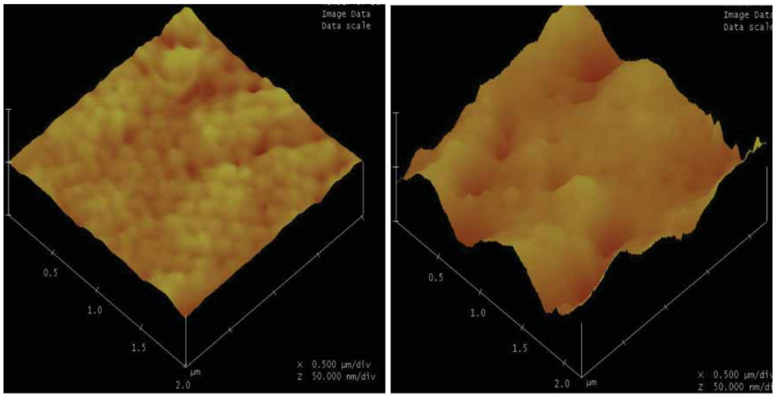
Figure 4 shows the films formed from DNS-86 stabilized latex before and after it was rinsed with water. It can be seen that when using the reactive surfactant DNS-86, the appearance of the films have fewer and shallower holes than prepared with conventional surfactant DBS after being rinsed with water. This clearly indicates that the reactive surfactant DNS-86, having a substantial portion, is chemically incorporated into the latex particles. This further indicates that there is nearly no surfactant migration onto the film-substrate and film-air interfaces.

3.3 Latex Morphology

Figures 5–6 are the TEM photographs with the use of different surfactants in different dosages. As seen in Figure 5, when using the reactive surfactants DNS-86, the particles exhibit regular spherical structure. However, when using the conventional surfactant DBS, the surface of some particles have adsorbed some small particles (Figure 6c). Furthermore, the particles have cemented each other. The reason is that the reactive surfactant DNS-86, which has a carbon-carbon double bond, can be chemically incorporated into the latex particles during polymerization, as proved in our front ^{1}H-NMR analysis.

3.4 Stability Test

Table 2 shows the effect of the reactive surfactant on the conversion and stability of latex. From Table 2, it can be seen that when using the reactive surfactant DNS-86, the latex conversion is high, polymerization stability and storage stability are



c d

Fig. 4. AFM image of a film cast from DNS-86 stabilized latex before (c) and after (d) rinsed with water.

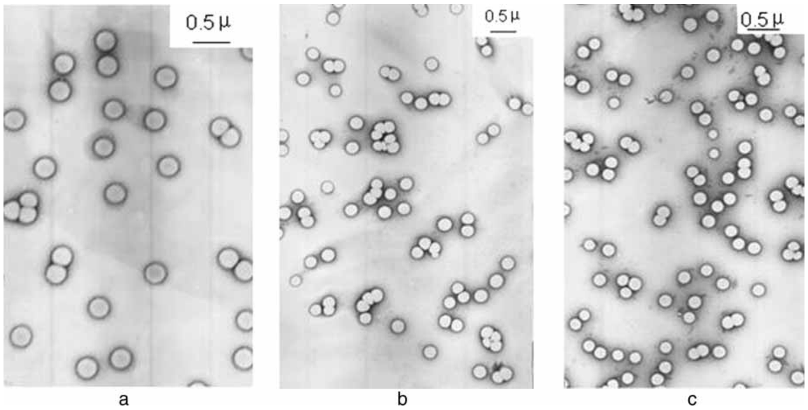


Fig. 5. TEM photograghs of latex particles from different DNS-86 dosages. a: 2%, b: 3%, c: 4%.

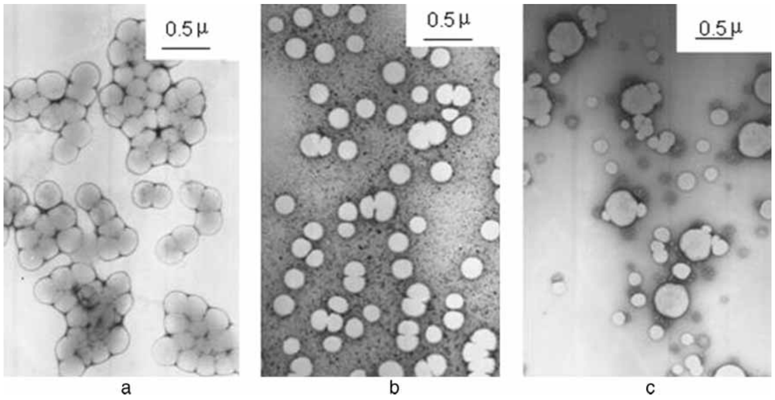


Fig. 6. TEM photograghs of latex particles from different DBS dosages. a: 1%, b: 2%, c: 3%.

Table 2. The influence of reactive surfactant on the conversion and stability of latex

Latex sample	Conversion (%)	Coagulation (%)[a]	Storage stability	Freeze-thaw
DNS-86 (%)[a] 1.5	95.06	2.90	No laminate[b] and no insoluble matter[c]	Flocculation
2	99.56	0	No laminate and no insoluble matter	No flocculation
2.5	98.99	0	No laminate and no insoluble matter	Flocculation
3	99.28	0	No laminate and no insoluble matter	Flocculation
3.5	99.24	0	No laminate and no insoluble matter	Flocculation
DBS (%)[a] 1.5	94.48	5.21	No laminate and no insoluble matter	Flocculation
2	99.23	0	No laminate and no insoluble matter	Flocculation
2.5	98.41	8.09	No laminate and no insoluble matter	Flocculation
3	96.93	0	No laminate and no insoluble matter	Flocculation
3.5	95.69	0	No laminate and no insoluble matter	Flocculation

[a] Indicates the percent of total monomer weight.
[b] Laminate here means that the emulsion separate into monomer layer and water layer.
[c] No insoluble matter means that there are not precipitates in the emulsion.

very good. But in the freeze-thaw test, most of the latexes flocculated. Furthermore, the stability prepared by the reactive surfactant DNS-86 is better than that prepared by the conventional surfactant DBS. This can be explained by the fact that the reactive surfactant DNS-86 is mainly connected with the latex particles by covalent bond, while the conventional surfactant DBS is only physically adsorbed onto the particle surface.

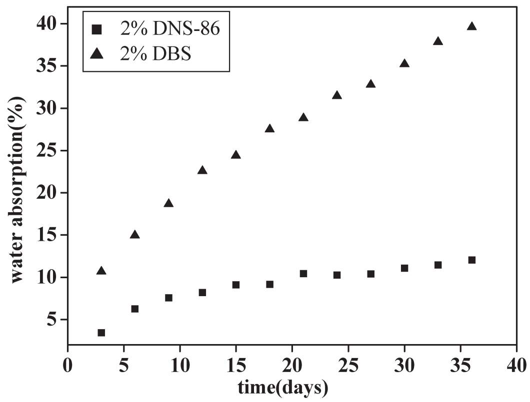


Fig. 7. Water absorption of the latex films prepared with different surfactants.

3.5 *Water Absorption*

Figure 7 shows the water absorption of the latex films prepared with different surfactants at different times. In Figure 7, we can see that the water absorption increased with increasing the time for all latex samples. However, the water absorption of the latex film prepared by the conventional surfactant DBS is 3–3.5 times larger than that prepared by the reactive surfactant DNS-86. The reason can be explained as, the conventional surfactant DBS is physically adsorbed onto the particle surface, which is unstable and is easy to migrate to the surface of the latex film, so the water resistance of the film is poor. For the film prepared with the reactive surfactant DNS-86, since the reactive surfactant can copolymerize with the main monomer and become covalently bound to form an integral polymeric material, there is nearly no surfactant to migrate to the film surface, so it adsorbs less water and the water resistance is good. The water absorption difference is another indirect proof that the reactive surfactant DNS-86 has been copolymerized into the acrylate copolymer.

4 Conclusions

The acrylate latex was successfully synthesized with a semi-continuous technique by using the reactive surfactant DNS-86 and the conventional surfactant DBS. ^{1}H-NMR proved that the reactive surfactant DNS-86 has successful chemical incorporation into the copolymers. AFM proves that the reactive surfactant DNS-86 migrates to the surface of the latex film to a much less degree than the conventional surfactant DBS. TEM demonstrates that the particles exhibit a regular spherical structure, while using the reactive surfactant DNS-86. The stability of the latex prepared by the reactive surfactant DNS-86 is better than that prepared by the conventional surfactant DBS. The water absorption of latex films prepared by the reactive surfactant DNS-86 is less than that prepared by the conventional surfactant DBS. Overall, compared with the latex prepared by the conventional surfactant DBS, the reactive surfactant DNS-86 can obviously improve the latex properties.

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