*Macromol. Symp.* ***151,*** *371–376 (2000)*

# Radical Copolymerization of Allyl Type of Polymerizable Surfactants with Acrylonitrile in Aqueous Carbon Black Dispersion

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ABSTRACT: Radical copolymerization of allyl type of polymerizable surfactants, [1-nonylphenyl-2-poly(oxyethylene) (m)]-3-allyloxypropane ammonium sulfates (SE-mN: m = 5, 10, 20), and acrylonitrile (AN) with potassium persulfate (KPS) as the initiator in aqueous carbon black (CB) dispersion was studied to prepare the CB dispersion with a high dispersion stability. The dispersion with the highest stability was obtained for the copolymerization system using SE-5N which exhibited the largest amount of adsorption onto CB particles at saturation. Anionic groups of SE-mN molecules immobilized at the surface of CB particles were found to make a major contribution to the dispersion stabilization. Some interfacial properties of SE-mNs and a peculiar solubility of the copolymers in water are also described.

## Introduction

Polymerizable surfactants are vinyl monomers having surface-active properties and characterized by the micelle formation and the adsorption at interfaces in contrast with common vinyl monomers. They have been mainly developed as the reactive emulsifier in emulsion polymerization and already employed in industry. On the other hand, they can be also applied to the surface modification of solid materials through the adsorption followed by the immobilization$^{1)}$. Although such applications have been demonstrated for inorganic solids$^{2-4)}$, only a few attempts have been made for organic solids other than polymeric microspheres. We have found that the copolymerization of an allyl type of polymerizable surfactant, SE-mN (m=10 in Figure 1), with AN in aqueous CB dispersion gives the dispersions with a relatively good stability, which can be used as the water-borne black ink for ink-jet printer, and that AN is an efficient comonomer for immobilizing SE-10N molecules adsorbed on the surface of CB particles$^{5)}$.

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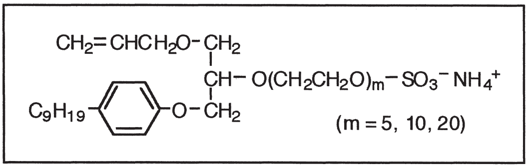

Figure 1. Molecular structure of SE-mNs.

In this work, further studies on the preparation of the CB dispersion with a higher stability have been done for the copolymerization system composed of SE-mNs having different lengths of polyoxyethylene (POE) chain (m=5, 10 or 20), AN as the comonomer and KPS as the initiator in the aqueous CB dispersion, schematically represented in Figure 2, and factors governing the stability of the resulting dispersions were discussed in terms of their interfacial properties of SE-mNs as well as the solubility of the resulting copolymers in water.

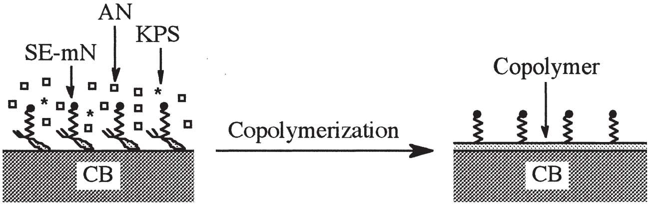

Figure 2. Schematic representation for the copolymerization system involving CB particles in aqueous system.

## Experimental

SE-mNs were received from Asahi Denka Ind. (Japan) and purified by reprecipitation using methylene dichloride/n-hexane as solvent/nonsolvent before use. CB, specific surface area 150 $m^2/g$, was used as received from Mitsubishi Chemical Co. (Japan). Surface tension and micellar aggregation number for aqueous SE-mN solutions were determined by a Wilhelmy plate method and a static fluorescence quenching method, respectively. The aqueous dispersion of CB was sonicated for 1 h and then subjected to the copolymerization with stirring under a nitrogen atmosphere. The conversion of SE-mNs was calculated from their residual amount determined using an UV spectrophotometer for the copolymerization in the presence of CB particles. The dispersion stability was estimated from the sedimentation of the dispersion in acetone under centrifugation.

## Results and discussion

### *Interfacial properties of SE-mNs*

For three kinds of anionic, polymerizable surfactants used here, SE-mNs (m=5, 10, 20), critical micelle concentrations (cmcs) and areas occupied by a SE-mN molecule at saturation at air/water interface ($a_s$s) were determined from their concentration dependence of surface tension at 25°C: $6.1 \times 10^{-5}$, $2.4 \times 10^{-4}$, and $3.1 \times 10^{-4}$ M for the cmcs and 96, 161, and 213Å$^2$ for the $a_s$s. The $a_s$ values are considerably larger, as compared with those for POE alkylphenols of the corresponding POE chain length, probably because of the allyl group in their molecules. In further, SE-mNs exhibited relatively high efficiencies of adsorption ($pC_{20}$s) at air/water interface, irrespective of their ionic character. Micellar aggregation number of SE-10N determined by a static fluorescence quenching method was around 10 at concentrations slightly above the cmc and greatly increased with increasing the concentration.

The adsorption of SE-mNs on CB particles from their aqueous solutions showed a strong affinity and gave the Langmuir type of isotherms The amount of adsorption at saturation increased with decrease in the POE chain length of SE-mN. Nonionic analog of SE-10N exhibited the saturated amount of adsorption slightly higher than that of SE-5N. The areas occupied by a SE-mN molecule at CB/water interface calculated from the saturated amounts of adsorption onto CB particles at 25°C were 120, 191, and 234Å$^2$ for SE-5N, SE-10N, and SE-20N, respectively, which are further larger than those for the adsorption at air/water interface. Consequently, SE-mN molecules would be adsorbed with their bulky hydrophobic groups lying flat at the surface of CB particles and their hydrophilic heads towards the aqueous phase.

### *Copolymerization with AN and solubility of the copolymers in water*

All of SE-mNs fail to homopolymerize but well copolymerize with AN in aqueous micellar solutions. The copolymerizations using KPS as the initiator in aqueous micellar solutions were much faster than those in dioxane and, interestingly, yielded the copolymers with compositions close to the monomer compositions over a fairly wide feed range. On the other hand, the copolymers with high AN contents were formed for the copolymerizations in dioxane, as predicted from the monomer reactivity ratios of allyl monomers and AN. The copolymers formed in aqueous micellar solutions exhibited the solubility in water dependent on the feed ratio of AN to SE-mN in the copolymerizations. All of SE-mNs yielded the copolymers soluble in water both before and after their isolation for the copolymerizations at the equimolar feed. On the other hand, the copolymers formed for the copolymerizations at higher feed ratios of AN to SE-mN remained soluble during the copolymerizations and became insoluble after the isolation. Such alteration in the water-solubility of the copolymers was dependent not only SE-mN used and the feed ratio of AN to SE-mN but also on the feed concentration of SE-mNs for the copolymerizations.

### *Copolymerizations with AN in Aqueous CB Dispersion*

SE-mNs are well adsorbed onto CB particles from their aqueous solutions to give CB dispersions with a fairly good stability. However, the dispersions are rapidly sedimented in acetone and not stable enough to use as the ink for ink-jet printer owing to the desorption of SE-mNs in use and during storage. On the other hand, the dispersions obtained through the copolymerizations of SE-mNs with AN in aqueous CB dispersion remain dispersed even in acetone for a considerably long period. Such dispersion stabilization can be ascribed to the head groups of SE-mN molecules immobilized on the CB particles by the copolymerizations. Thus, the stability of the dispersions formed by the copolymerizations can be conveniently estimated using the absorbance of the dispersions in acetone after the centrifugation at a certain rotation speed for a definite period, 460 sec in this work. Table 1 shows some results on the conversion of SE-mN for the copolymerizations at the molar ratio of AN to SE-mN of 9 in 5 wt% CB dispersion and on the stability of the resulting dispersions expressed in the relative absorbance after the centrifugation at 500 or 5000 rpm. The dispersion prepared using SE-5N remains dispersed after the centrifugation at 5000 rpm for 460 sec. Thus, the dispersion stability is the highest for the dispersion formed with SE-5N and decreases with increase in the POE chain length of SE-mN. The copolymerization using the nonionic analog of SE-10N,

Table 1. Conversion of SE-mNs amd dispersion stability of CB dispersions prepared by the copolymerization of SE-mN with AN in aqueous CB dispersion a)

| SE-mN | (wt%) | Conversion b) (%) | Relative absorbance c) At 500 rpm | At 5000 rpm |
|---|---|---|---|---|
| SE-5N | 1.0 | 83.0 | 1.00 | 1.00 |
| SE-10N | 3.0 | 87.4 | 1.00 | 0.06 |
| SE-20N | 5.0 | 73.2 | 0.01 | — |

a) Copolymerization:AN/SE-mN (molar ratio), 9; KPS, 5 mol%; CB, 5 wt%; time, 48h; temp., 60°C.
b) For SE-mN.
c) For the dispersion after centrifugation at 500 or 5000 rpm for 460 sec in acetone, relative to that for the dispersion before centrifugation.

which exhibited the highest saturated amount of adsorption onto CB particles, yielded the dispersion with the stability as low as that of the dispersion obtained with SE-20N. Therefore, the anionic group of SE-mN molecules would make a major contribution to the dispersion stabilization even in acetone rather than POE chain. In general, the dispersion stabilization is provide by electrostatic and steric repulsions between dispersed particles and, for the CB dispersions prepared here, these repulsive forces should increase with increase in the number and POE chain length, respectively, of SE-mN molecules immobilized on CB particles. In this work, SE-mN with the shorter POE chain length yielded the dispersion with the higher stability. As described above, the amount adsorption of SE-mN onto CB particles is higher for SE-mN with the shorter POE chain length. These results indicate that the number of immobilized SE-mN molecules, i.e., the number of anionic group, is a decisive factor governing the stability of the dispersions prepared by the present method. Thus, PEO chains of SE-mN molecules immobilized on CB particles seem to make little contribution to the dispersion stability evaluated in the present study, though they may play a role in the dispersion stabilization in the presence of electrolytes.

The results presented here demonstrate that SE-mN molecules adsorbed on CB particles are successfully immobilized through the copolymerization with AN as the comonomer. Such copolymerization method would be applied to the systems involving organic particles other than CB particles.

## Conclusion

Anionic, allyl type of polymerizable surfactants, SE-mNs, adsorbed onto CB particles in aqueous media were successfully immobilized by the copolymerization systems composed of AN as the comonomer and KPS as the initiator to yield the dispersions with a high stability. The stability of the resulting dispersions was mainly dependent on the number of anionic group, rather than POE chain length, of the SE-mN molecules immobilized. Great improvement of the dispersion stabilization was achieved for the copolymerization system using SE-5N as the polymerizable surfactant.

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