The Regulation of Emulsion Polymerization with Fluorocarbon-Hydrocarbon Emulsifiers Mixture

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The emulsion polymerization of styrene using a mixture of sodium dodecyl sulfate (SDS) and lithium fluorooctane sulfonate (LiFOS) has been studied. The polymerization rate decreased upon increasing the mole fraction of LiFOS, and was dependent on the solubilized amount of styrene in mixed surfactant solutions of SDS and LiFOS. The particle size increased upon increasing the mole fraction of LiFOS on the whole, and the molecular weight of the polymer formed in latices decreased upon increasing the mole fraction of LiFOS. Furthermore, the molecular-weight distribution of the latex polymer formed in mixed emulsifier solutions was considerably wider than that of the latex polymer formed in a single-emulsifier solution. It was confirmed from the above results that LiFOS had a repressive effect on the polymerization rate, and that it affected the number of particles and the molecular weight in the emulsion-polymerization process.

In the process of emulsion polymerization, the emulsifier plays an important role for the following two reasons: 1) It offers sites for polymerization, as does the micelle being acted upon for the solubilization of a monomer, and 2) It produces a stability of the synthetic latex, which has been influenced by the nature of the emulsifiers being used in the synthesis.[1–3] During emulsion polymerization, mixtures of emulsifiers have been generally used. However, a systematic study regarding the effect of emulsifier mixtures on emulsion polymerization was limited to nonion-nonion or nonion-anion hydrocarbon type surfactant systems.[4–6]

Recently, fluorocarbon surfactants have been given attention due to their peculiar natures: A low affinity for both water and oil and a good resistance against acidic, alkaline, oxidative, and reductive reagents. The surface tension of fluorocarbon surfactants is lower than that of hydrocarbon surfactants at an air–water interface, and fluorocarbon surfactants have higher surface activities.[7–11]

Suzuki et al. investigated the effect of the addition of a fluorocarbon surfactant on the micellization of hydrocarbon surfactants using the solubilization of the keto–enol tautomerism of *p*-benzoylacetanilide. They observed that the addition of a fluorocarbon surfactant was effective to expulse any materials solubilized in the micelles of a hydrocarbon surfactant by forming a mixed micelle.[12] This expulsive effect of a fluorocarbon surfactant would be interesting for the study of emulsion polymerization and, in particular the process of nucleation for a latex particle.

In this work, the emulsion polymerization of styrene in the presence of mixtures of fluorocarbon and hydrocarbon surfactants was studied by measuring the polymerization rates, particle sizes and molecular-weight distributions. The emulsifiers employed were sodium dodecyl sulfate (SDS) and lithium fluorooctanesulfonate (LiFOS).

Experimental

Materials. Potassium fluorooctane sulfonate ($C_8F_{17}SO_3K$) was repeatedly washed with water to remove water-soluble impurities, then dried at 80 °C. To prepare a lithium salt of fluorooctane sulfonate, fluorooctanesulfonic acid ($C_8F_{17}SO_3H$) was obtained by the distillation of the potassium salt in the presence of sulfuric acid (95%, guaranteed grade sample) at 180 °C, 10 mmHg. Then, it was neutralized by lithium hydroxide. Thus obtained lithium fluorooctane sulfonate ($C_8F_{17}SO_3Li$; LiFOS) was purified by repeated crystallization from dioxane after an extraction with ethanol. The purity of this sample was confirmed by an elemental analysis and by a surface tension measurement.

Sodium dodecyl sulfate (SDS) for biochemical use (Wako Pure Chemical Industries Ltd.) was purified by crystallization twice from ethanol, and was carefully dried in vacuo for 60 h before use. The purity of the sample was confirmed by the same method mentioned above.

Styrene was distilled twice under a dried nitrogen atmosphere, and was stored in a refrigerator under nitrogen before use.

For an initiator, potassium peroxodisulfate ($K_2S_2O_8$) was an analytical grade supplied by Wako Pure Chemical Industries Ltd.

Water was purified by a Milli-Q Water-Purification System.

Procedure. Each emulsion polymerization run was made using a batch process in a one-liter glass reactor fitted with a metal screw, thermometer and facilities for charging and sampling. A typical polymerization recipe is shown in Table 1. Emulsifiers (SDS and LiFOS) were mixed by two

Table 1. Emulsion Polymerization Recipe

Ingredients	Grams	Moles
Styrene	50	0.48
Water	250	13.9
Potassium peroxodisulfate	0.2	0.00755
Emulsifiers (SDS, LiFOS)	—	0.02

procedures. In the first procedure, while maintaining the same total moles of the emulsifiers, the mixed ratios of SDS and LiFOS were varied shown in Table 1.

In the second procedure, surfactant mixtures were prepared by adding various quantities of LiFOS to a definite quantity of SDS, whereas the total concentration of the mixed emulsifiers changed in each reaction system. Before the polymerization, water and emulsifiers were added to the reactor at room temperature, then a styrene monomer was added. After that, the reaction flask was immersed in a constant temperature bath which was adjusted to 60±1 °C under a nitrogen atmosphere. The mixture was stirred at 250 min^{-1}. After rising up the temperature to 60 °C, an initiator was added to the contents in the reactor.

The samples for determinations of conversion, particle size, and molecular-weight distribution were collected with pipettes at fixed intervals. The procedure for the determination of the conversion was as follows. To terminate the polymerization reaction, 5 cm^3 of a p-benzoquinone methanol solution (1.5 g dm^{-3}) as an inhibitor was added to 5 cm^3 samples in glass bottles. Then, the unreacted styrene monomer, methanol, and water were evaporated at 70 °C and the conversion percentages of styrene to polystyrene were estimated by measuring the dried samples on the assumption that the (monomer+polymer)/water was constant throughout the reaction.

In order to determine the particle sizes and the molecular-weight distributions after a reaction time of 90 min, the samples were rapidly cooled in cold water (0 °C). Particle sizes and size distributions were determined by transmission electron microscopy (TEM) and by submicron particle sizer (MARVERN AUTOSIZER MODEL-700). Measurements were carried out under the following conditions: The temperature was 25.0 °C, the refractive index was 1.33, and the viscosity was 0.8909cP.

The weight-average molecular-weights and the molecular weight distributions of each polystyrene latex sample were determined using gel permeation chromatography.

The solubilized amounts of ethylbenzene as a substitute for styrene in the mixed surfactant solutions were measured by means of a spectrophotometer at a wavelength of 262.6 nm at 25 °C.

Results and Discussion

Before the emulsion polymerization of styrene in the presence of SDS and LiFOS, it was necessary to confirm the stability of the emulsion particles being prepared with an aqueous mixture of LiFOS and SDS in the polymerization process. In order to evaluate the stability of the emulsion particles in each surfactant component, a percentage of coagulum was used which was estimated by the ratio of coagulum to the total amount of residue in a defined volume for each emulsion after a 90 min reaction time during the polymerization process. From the above experiments, only a few visible coagulums were observed and the coagulation ratios were below 1% for every mixed ratio of the emulsifiers. This result suggests that mixtures of SDS and LiFOS at every ratio were suitable for the stabilization of the emulsion polymerization of styrene.

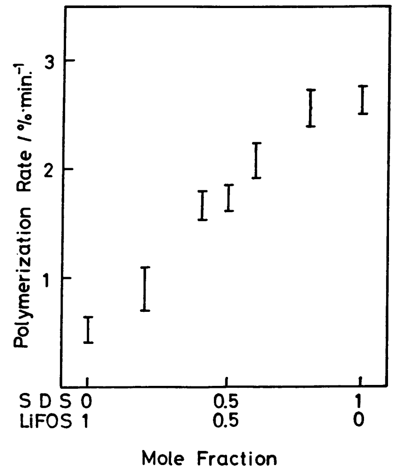

Fig. 1. The polymerization rate with mole fraction of emulsifiers; Lithium fluorooctane sulfonate (LiFOS) and sodium dodecyl sulfate (SDS), Temperature; 60 °C.

Polymerization Rate. In the first procedure, in the presence of mixtures of various mole fractions of SDS and LiFOS, the time-conversion curves in the emulsion polymerization of styrene were obtained. The polymerization rates (% min^{-1}) were calculated from the time-conversion curves in the initial period, and the results are shown in Fig. 1. The polymerization rate with SDS alone was 2.8% min^{-1} and that with LiFOS alone was 0.5% min.$^{-1}$ The polymerization rate decreased upon increasing the mole fraction of LiFOS. This result suggests that LiFOS has a depressive effect on the polymerization rates.

In the polymerization of styrene in the presence of a water-soluble initiator, the polymerization sites are considered to be in the water phase. However, a styrene monomer is only slightly soluble in water. Thus, the solubilization phenomenon of styrene in surfactant micelles became important for providing an initiation site for polymerization. Indeed, an emulsion polymerization using a styrene nearly occurred above the critical micelle concentration (cmc) in an aqueous surfactant solution.

The solubilizing power of the surfactant and the solubilized amount of monomer affect the polymerization rate in the emulsion polymerization, and it has been supported that the polymerization rate is proportional to the solubilizing power of various surfactant solutions.[13] In this work, it was assumed that the solubilized amount of ethylbenzene was similar to that of styrene in several aqueous solutions of SDS or LiFOS. The solubilized amounts of ethylbenzene were increased in proportion to the concentration of the aqueous surfactant solutions

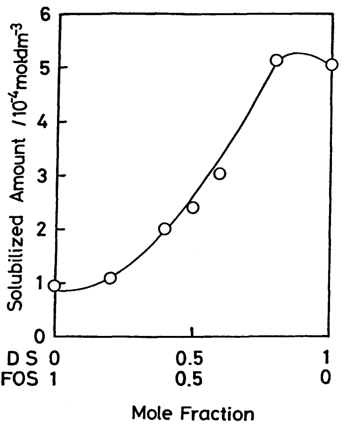

Fig. 2. Solubilized amount of ethylbenzene in mixed surfactant aqueous solution; 20 mmol dm^{-3}, Surfactants; SDS and LiFOS, Temperature; 25 °C.

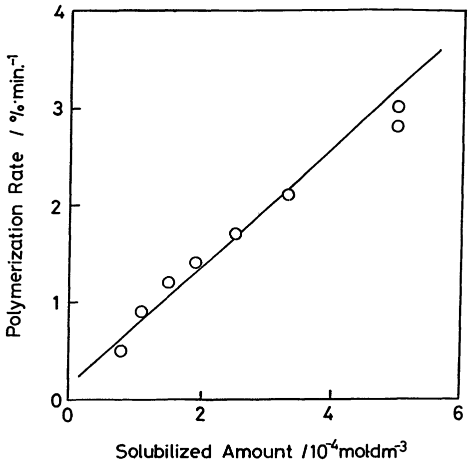

Fig. 3. Polymerization rate as a function of solubilized amount of ethylbenzene at various molar ratios of SDS and LiFOS.

above their cmc. Here, the cmc of an aqueous solution of SDS was 7.9 mmol dm^{-3} and that of an aqueous solution of LiFOS was 6.5 mmol dm^{-3}.

The solubilized amounts of ethylbenzene at total concentrations of 20 mmol dm^{-3} are shown in Fig. 2 as a function of the mole fraction. The solubilized amount in a SDS aqueous solution was about 52 mmol dm^{-3} and that in a LiFOS solution was 8 mmol dm^{-3}, whereas the solubilizing power of SDS was seven times as large as that of LiFOS. The solubilized amount of ethylbenzene decreased upon increasing the mole fraction of LiFOS, but had a maximum value at 0.8 of the mole fraction of LiFOS.

Figure 3 shows the relationship between the polymerization rates and the solubilized amounts at various mole fractions of SDS and LiFOS. As the polymerization rate is proportional to the solubilized amount, it is clear that the polymerization rate in the emulsion polymerization of styrene was influenced by the solubilized amount of styrene in the mixed-surfactant solution.

As a second procedure, an emulsion polymerization of styrene was carried out using mixed emulsifiers prepared by adding various quantities of LiFOS to a definite quantity of SDS. The obtained results are shown in Fig. 4. In this procedure, every condition in the emulsion polymerization pathway was the same as that in the first procedure except for the concentration of the emulsifiers.

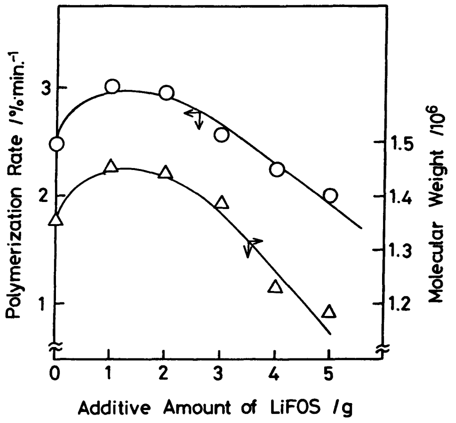

Fig. 4. The effect of additive amount of LiFOS to SDS (6.0 g) on polymerization rate and molecular weight.

These results indicate that by adding a small amount of LiFOS to SDS, the polymerization rate increases, however, a further addition of LiFOS causes the polymerization rate to decrease, compared with that for SDS alone. During the first stage, an acceleration of the polymerization rate by adding LiFOS can be correlated with an increase in the total amount of emulsifiers in the reaction system. On the other hand, a deacceleration of polymerization rate occurred upon a further addition of LiFOS, in spite of an increase in the total amount of the emulsifiers. This result was almost similar to one shown in Fig. 2; the polymerization rate decreased upon increasing the mole fraction of LiFOS. This fact seems to be attributed to the expulsive effect, that added LiFOS expelles styrene radicals from the micelles in aqueous surfactants solutions, resulting in a depression of the polymerization rate.[12]

Particle Size and Particle Number Concentration. By electron micrography, the number-average particle diameter (D_n) and the polydispersity (D_w/D_n) were determined, respectively. By light scattering, the z-average particle diameter (D_z) and the polydispersity index (Pusey's Q factor) which gave an indication of the breadth of the size distribution, were determined.[14,15] These results are shown in Table 2.

The particle size of latex formed with various mixed ratios of SDS and LiFOS, which was

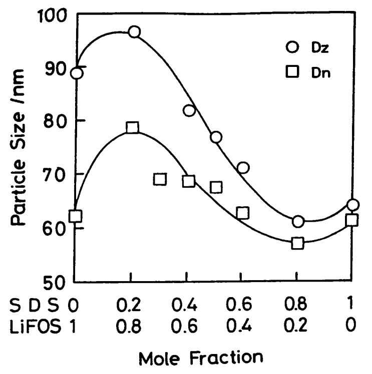

Fig. 5. The change of latex particle size with molar ratio of SDS and LiFOS; Total emulsifiers mole (0.02 mol), (○): z-average diameter, (□): number-average diameter.

Table 2. Particle Size and Size Distribution as a Function of Molar Ratio of SDS and LiFOS

Mole fraction		Light scattering method		Electron micrography method	
SDS	LiFOS	D_z/nm	Q.f	D_n/nm	D_w/D_n
1.0	0	64.0	0.074	61.2	1.15
0.8	0.2	61.0	0.092	56.9	1.11
0.6	0.4	71.1	0.06	62.5	1.13
0.5	0.5	76.8	0.04	67.3	1.11
0.4	0.6	81.9	0.082	67.9	1.06
0.3	0.7	79.4	0.076	67.9	1.04
0.2	0.8	97.0	0.076	78.9	1.07
0	1.0	88.3	0.12	61.2	1.09

determined by both methods, has a relatively narrow distribution. From this result, the latices were determined to be exceedingly monodispersed spheres. The change in the latex particle size with the mole fraction of the emulsifiers is shown in Fig. 5.

There are many methods for measuring the particle size, and each determined average diameter provides a difference in size. The difference between the number-average diameter and the z-average diameter is caused by measurement method.[16] According to Wesslaw's experiment, the light scattering method has an upper limit in its application for a determination of the particle size; for instance, 400 nm to the size of polystyrene particles.[17]

It can be seen from Fig. 5 that all sizes are less than 400 nm. The z-average particle diameter vs. the mole fraction curve indicates, on the whole, that the particle size becomes large upon increasing the mole fraction of LiFOS. This is because the polymerization rates decrease upon increasing the mole fraction of LiFOS. Namely, when the polymerization rate is slow, the period during which the emulsion droplets and polymer particles coexist is prolonged. As a result, latex particle sizes continuously increase up to the depletion of droplets of the monomer.

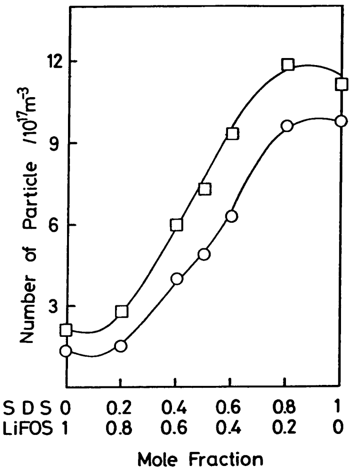

Fig. 6. Number of particles vs. mole fraction of SDS and LiFOS at total moles (0.02 mol), (○): Number of particles from z-average diameter, (□): Number of particles from number-average diameter.

Although the tendency described above regarding the z-average diameter was also observed for the number average diameters, it became much smaller. Especially, the higher the mole fraction of LiFOS was, the greater the gap between the number-average diameter and the z-average diameter became. This difference resulted from an apparent increase in the average diameter, determined by the light scattering which is capable of detecting the particle being coalesced in a suspended state.

There was a minimum value for both the average diameters at 8:2 of molar ratio of SDS and LiFOS. The z-average diameter was 56.9 nm and the number-average diameter was 61.0 nm at this mole fraction. At the same molar ratio of surfactant solutions of two emulsifiers, the solubilized amount and the polymerization rate were maximum. Thus, it was proven that the particle size increased if the mixed emulsifiers contained a small amount of LiFOS. At a high mole fraction of LiFOS, the average diameters of the latices became smaller since the polymerization rate was so slow that particle nucleation could not sufficiently progress.

The number of particles formed per cubic meter of the aqueous phase (N) was calculated from the z-average diameter or the number-average diameter, and the conversion rates. A diagram of the particle numbers plotted against the mixed emulsifiers is shown in Fig. 6. It was found that the number of particles calculated from the z-average diameter and the number-average diameter behaved similarly to each other upon a change in the mole fractions of the emulsifiers. Since latex particles are dispersed in a suspended state, the z-average diameter determined by

Table 3. The Change of Weight-average Molecular Weight (M_w) and Molecular Weight Distribution (M_w/M_n) with Mole Fraction of SDS and LiFOS

SDS	: LiFOS	M_w (X10^{+6})	M_w/M_n
0	1.0	0.812	2.69
0.2	0.8	1.090	9.33
0.4	0.6	1.266	7.84
0.5	0.5	1.347	6.71
0.6	0.4	1.223	6.20
0.8	0.2	1.458	6.44
1.0	0	1.475	3.56

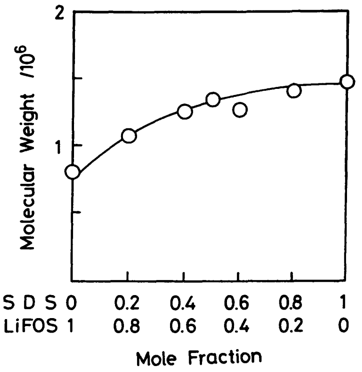

Fig. 7. The change of weight-average molecular weight with mole fraction of SDS and LiFOS.

light scattering should be used to determine the number of particles. From these results, it can be seen that the number of particles increases all over upon increasing the mole fraction of SDS. Also, it has a maximum at a molar ratio of 8:2 for SDS to LiFOS. These results can be explained by the same reasoning as mentioned above regarding particle size changes.

Molecular Weight and Its Distribution. The molecular weight of a formed latex polymer was measured after being dissolved in tetrahydrofuran by gel permeation chromatography (GPC). The same samples that were used for the particle-size measurement were used again. The weight-average molecular weights (M_w) and molecular weight distributions (M_w/M_n) of several polymer latices were calculated using Shimadzu Chromatopac C-R2AX.

Table 3 shows the weight-average molecular weights (M_w) and the molecular weight distributions (M_w/M_n), and Fig. 7 shows the change in the weight-average molecular weight with the mole fraction of mixed surfactant solutions of SDS and LiFOS. From M_w/M_n for the molecular weight distribution of the formed latices shown in Table 3, it was found that the breadth of the molecular weight distribution of the latices formed with mixed emulsifiers of SDS and LiFOS were rather broadened, compared with that of latices formed with single emulsifiers of SDS or LiFOS. These results demonstrate that the composition of emulsion and micelle in the mixed surfactant solution of SDS and LiFOS has a much wider distribution than that in a single emulsifier.

The change in the weight-average molecular weight of latex polymer against the mole fraction of a mixed surfactant solution of SDS and LiFOS is shown in Fig. 7. The molecular weight decreases upon increasing the mole fraction of LiFOS, in agreement with changes in the polymerization rate. As shown in Fig. 4, the molecular weight of the polymer latices formed with the mixed emulsifiers prepared by adding various quantities of LiFOS to a definite quantity of SDS, decreased upon adding LiFOS. The result agreed with the behavior of the polymerization rates. These results indicate that the addition of LiFOS to SDS in a mixed surfactant solution decreases the molecular weight of the latices. Accordingly, the addition of LiFOS has a repressive effect on the growth of the molecular weight of the latex polymer.

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