December, 1986] © *1986 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 59, 3741—3746 (1986)* 3741

The Regulation of Emulsion Polymerization of Styrene with Anionic-Nonionic Emulsifier Mixtures

Kazufumi Kato,* Harumi Kondo, Kunio Esumi, and Kenjiro Meguro
Department of Applied Chemistry and Institute of Colloid and Interface Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

(Received April 24, 1986)

The emulsion polymerization of styrene was carried out in the presence of mixtures of a nonionic surfactant (poly(oxyethylene) hexadecyl ether; BC-20) and an anionic surfactant (sodium dodecyl sulfate; SDS or lithium perfluorooctanesulfonate; LiFOS). The polymerization rate changed with the hydrophile-lypophile balance (HLB) of the BC-*n* series. The polymerization rate considerably increased on the addition of SDS or LiFOS. However, the further addition of LiFOS caused a gradual depression of the polymerization rate. The polymerization rate was not dependent on the amount of styrene solubilized in the mixed emulsifier solution. The particle sizes decreased remarkably on adding SDS. The molecular weights of polystyrene in latex synthesized in mixed emulsifier solutions were larger than those in a single emulsifier solution. The molecular-weight distributions of polystyrene formed in mixed emulsifier solutions were wider than those of polystyrene formed in a single emulsifier solution. These results may be attributed to properties such as the composition and the charge density of the mixed micelles, and to the solubilized amount of styrene monomer in the mixed nonionic-anionic emulsifier solutions.

There are many reports concerning the physical properties of mixed surfactant solutions, such as, size, form, aggregation number, composition of components and surface charge of the mixed micelles.[1-3] Mixtures of emulsifiers have been also used for emulsion polymerization. There are also some reports about the effect of mixtures of emulsifiers on the emulsion polymerization process, compared with that of a single emulsifier.[4-6] The emulsifiers play important roles: for example, their micelles offer sites for polymerization and they stabilize the synthesized latex in the process of emulsion polymerization.[7-9]

In our previous paper, the emulsion polymerization of styrene in the presence of a mixture of anionic fluorocarbon-anionic hydrocarbon emulsifiers was studied.[10] And it has been confirmed that the fluorocarbon surfactant has the effect of slowing down the polymerization rate. The addition of a fluorocarbon emulsifier reduced the particle number concentration of the latex and the molecular weight of the polystyrene latex formed. It also caused an increase in the size of the latex particles.

In this work, the emulsion polymerization of styrene was carried out using a mixture of a nonionic emulsifier and an anionic emulsifier (sodium dodecyl sulfate; SDS, or lithium perfluorooctanesulfonate; LiFOS). The effect of the mixture of nonionic-anionic emulsifiers on the emulsion polymerization process was investigated by measuring the polymerization rate, the particle size, the molecular weight and their distribution.

Experimental

Materials. Poly(oxyethylene) hexadecyl ethers (RO-$(C_2H_4O)_nH$; BC-*n*) were used as nonionic emulsifiers. As anionic emulsifiers, sodium dodecyl sulfate ($C_{12}H_{25}OSO_3Na$; SDS) and lithium perfluorooctanesulfonate($C_8F_{17}SO_3Li$; LiFOS) were used. LiFOS was prepared by the same synthesis described in the previous paper.[10] SDS was marketed for biochemical use (Wako Pure Chem. Ind. Ltd.) and was purified by recrystallization twice from ethanol. The purities of the SDS and LiFOS were confirmed by elemental analysis and the absence of a minimum in the surface tension measurement. BC-*n* (Nikko Chemical Co.) were used without further purification.

The styrene monomer was distilled under a nitrogen atmosphere, and was stored in a refrigerator under nitrogen before use. For an initiator potassium peroxodisulfate ($K_2S_2O_8$) of analytical grade supplied by Wako Pure Chemical Ind. Ltd. was used. Water was purified by Milli-Q Reagent Grade Water System (Millipor Ltd.) until its specific conductivity fell below 0.1 $\mu S\,cm^{-1}$.

Procedure. Each run of emulsion polymerization was done 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. The main conditions of the emulsifiers using in the polymerization process were as follows.

a) HLB in BC-*n* series are varied. Each hydrophile-lypophile balance (HLB) of BC-*n* series is summarized in Table 2.

b) The amounts of BC-20 (HLB; 17) are varied.

c) Mixing ratios of anionic-nonionic emulsifiers are varied. The changes in the mixing conditions were done in two ways; one of them was made up by adding various quantities of SDS or LiFOS to a definite quantity of BC-20 (5.0 g), and the other was made up by varing the mixed ratios of each emulsifier (SDS-BC-20, LiFOS-BC-20).

At first, the water and emulsifier were added to the reactor at room temperature. The styrene monomer was then added. The reactor was immersed in a constant temperature bath adjusted to 60±1 °C under a nitrogen atmosphere, and the mixture was stirred at 250 rpm. When the temperature reached 60 °C, the aqueous solution of potassium peroxodisulfate (0.2 g/50 cm^3) was added to the contents in the reactor to initiate the polymerization.

The 5 cm^3 of emulsion samples for determination of the conversion ratio in the polymerization process was withdrawn with pipettes at fixed intervals. The samples were poured into 5 cm^3 of *p*-benzoquinone methanol solution (1.5

Table 1. Emulsion Polymerization Recipe

Ingredients	Grams
Styrene	50
Water	250
Potassium peroxodisulfate	0.2
Emulsifier	Poly(oxyethylene) hexadecyl ether (BC) BC-20 (H.L.B.:17) Sodium dodecyl sulfate (SDS) Lithium perfluorooctane sulfonate (LiFOS)

Table 2. Hydrophile-Lypophile Balance (HLB) of Poly(oxyethylene) Hexadecyl Ether (BC-*n*) Series

BC-*n*	H.L.B.
n:10	13.5
n:15	15.5
n:20	17.0
n:23	18.0
n:25	18.5
n:30	19.5
n:40	20.0

g dm^{-3}) as an inhibitor to terminate the polymerization reaction. Then, the unreacted styrene monomer, methanol and water were evaporated at 70°C. The percent conversions of styrene to polystyrene were estimated by measuring the ratios: (polymer/total monomer) 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 of the latex particles after 90 min of reaction time, the samples were cooled rapidly in cold water (0 °C). The particle sizes and the size distributions were determined by a submicron particle sizer (AUTOSIZER MODEL-700; Malvern Instruments Ltd.). This was carried out at 25.0 °C by assuming that the refractive index of the latex-suspended solution was 1.33 and its viscosity 8.909*10^{-4} Pas.[11,12] Their polydispersity indexes (Pusey'Q factor) which gave an indication of the breadth of the size distribution were determined.

The molecular-weight distributions of polystyrene latex samples were measured by using a gel permeation chromatograph (GPC) fitted with a packed column (Showa Denko Co. A-80M). The weight-average molecular weights (M_w) and their molecular-weight distributions (M_w/M_n) were calculated with a Shimadzu Chromatopac C-R2AX.

The amounts of ethylbenzene solubilized in the mixed emulsifier solutions were determined spectrophotemetrically by measuring the absorbance of ethylbenzene at a wavelength of 262.6 nm at 25 °C. It was assumed that the solubilized amount of ethylbenzene was similar to that of styrene in several emulsifier solutions.

Results and Discussion

In general, emulsifiers play important roles in the good running of emulsion polymerization. Especially, nonionic emulsifiers have a high selectivity toward the emulsification of the monomer and the stabilization of emulsion droplets and polymer particles. Greth has systematically studied the suitabilities of nonionic emulsifiers for several monomers, such as, styrene and vinyl acetate. He has also reported that the solubility of a monomer for water is correlated with the HLB of nonionic emulsifiers, which give good stability to the latex.[4]

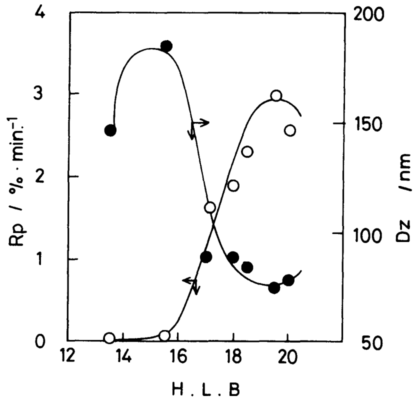

Fig. 1. The effect of hydrophile-lypophile balance (HLB) of poly(oxyethylene) hexadecyl ethers (BC-*n*) on polymerization rate (Rp) and particle size (Dz). Amount of BC-*n*; 10.0g.

In our report, the emulsion polymerization of styrene was carried out by using BC-*n* series as nonionic emulsifiers which have various different HLB. The time-conversion curves were first obtained and the polymerization rates (%min^{-1}) were calculated from their initial slopes. The effects of HLB of BC-*n* on the polymerization rate and on the particle size are shown in Fig. 1. It can be seen that the polymerization rate has a maximum value in the range of 17—20 of the HLB. The polymerization rate is dependent on the HLB of the BC-*n*. The particle size was also changed with the HLB. The change of particle size will be caused by the change of the number of latex particles accompanying the change of the polymerization rate with HLB.

It was confirmed in the first stage that the latex formed by using the nonionic emulsifiers (BC-*n*) of its HLB ranged at 17—20 was stable. In the next stage, the effect of the concentration of BC-20 (HLB; 17) on the polymerization rate and on the size of latex particle was examined. The changes of the polymerization rate (Rp) and the particle size of the latex formed with the change of the concentration of BC-20 are shown in Fig. 2. From this figure, it is evident that an exponential increase in polymerization rate accompanies an arith-

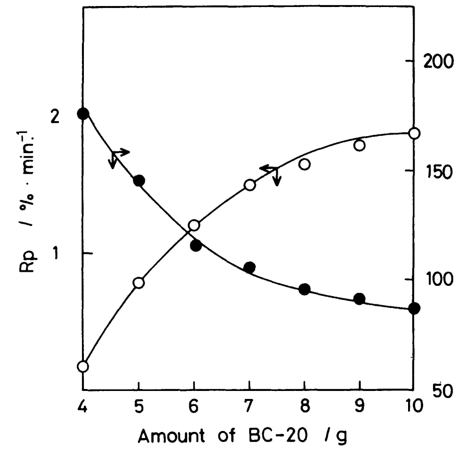

Fig. 2. The change of polymerization rate (Rp) and particle size (Dz) with amount of BC-20 (g).

metic increase in the concentration of BC-20 [BC-20]. Indeed, this relationship can be mathematically expressed as;

$$Rp \propto [\text{BC-20}]^{0.17}$$

The mechanism of particle formation in emulsion polymerization has been studied by many workers. According to the micellar nucleation theory of Smith-Ewart,[7] the number concentration (N) and the polymerization rate can be expressed as follows; when a homogeneous nucleation occurred in the emulsion polymerization of a water-insoluble monomer such as a styrene;

$$N \propto [\mathrm{I}]^{2/5}[\mathrm{S}]^{3/5}$$
$$Rp \propto (N/2)[\mathrm{M}]$$

where [I] is the initiator concentration, [S] the emulsifier concentration and [M] the monomer concentration. These expressions have been proven to be valid only for the emulsion polymerization of a water-insoluble monomer in an aqueous solution of an anionic emulsifier above its cmc. However, when the nonionic emulsifiers were used in emulsion polymerization, the Smith-Ewart theory does not often coincide with the polymerization process, owing to the change of several factors; HLB, solubilized amount and their affinity for the monomer.[4,6]

In this study, the polymerization rate increased in proportion to the BC-20 concentration of 0.17 power. This power value is further changeable with temperature, mixing process, mixed ratio of water to monomer and conversion. Therefore, it was confirmed that the Smith-Ewart theory was inapplicable to this emulsion polymerization system of styrene in the presence of BC-20.

Figure 3 shows the change of the polymerization rate when various quantities of SDS or LiFOS are added to a definite quantity of BC-20, whereas the total amount of the mixed emulsifiers is different in each reaction system. Figure 4 shows the change of the polymerization rate with various mixed ratios in the emulsifier mixtures, by keeping the total amount of emulsifiers constant. It can be seen from Fig. 3 that the polymerization rate increases with increase of the additive amount of SDS or LiFOS. Especially, only a small addition of anionic emulsifier to the system caused a steep increase of the polymerization rate. Figure 4 indicates that the polymerization rate in the mixture of (SDS-BC-20) or (LiFOS-BC-20) is much larger than that using each single emulsifier (BC-20, SDS or LiFOS).

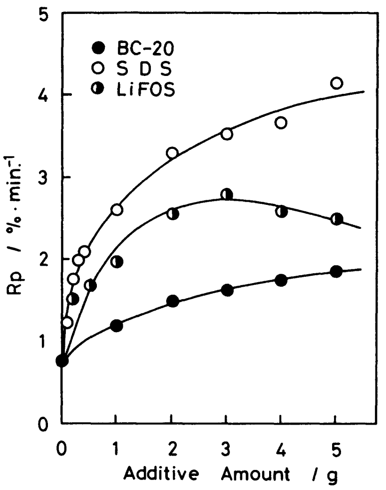

Fig. 3. Polymerization rate (Rp) as a function of additive amount of SDS(○), LiFOS(◑), BC-20(●) to BC-20 (5.0g).

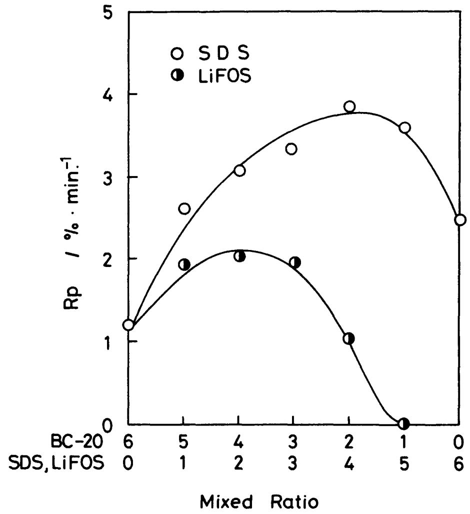

Fig. 4. The change of polymerization rate (Rp) with mixed ratio of (BC-20–SDS) or (BC-20–LiFOS) at the total concentration of 6.0g 250cm^{-3}.

In this work, it was assumed that the solubilized amount of ethylbenzene was equal to that of styrene in the emulsifier solutions. The solubilized amount of ethylbenzene is shown in Fig. 5 as a function of the additive amount of each emulsifier being adjusted by

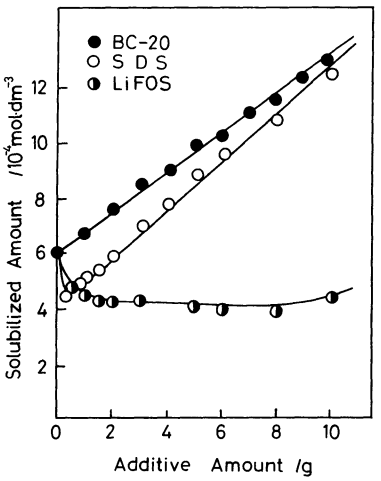

Fig. 5. Solubilized amount of ethylbenzene in mixed emulsifier aqueous solution as a function of additive amount of emulsifiers; SDS(○), LiFOS(◑), BC-20(●) to BC-20, at temperature 25°C.

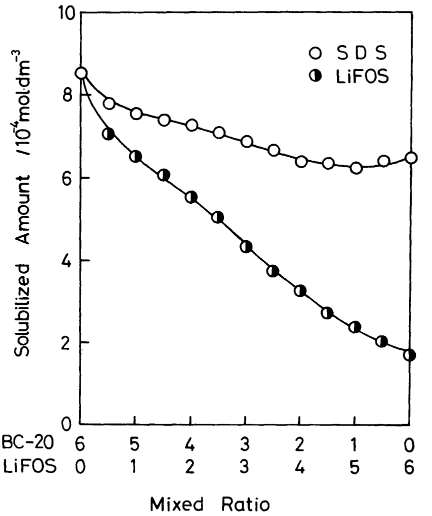

Fig. 6. Solubilized amount of ethylbenzene in mixed emulsifier aqueous solution as a function of mixed ratio of (BC-20–SDS) or (BC-20–LiFOS) at temperature 25°C.

the same amounts of emulsifiers as used in Fig. 3. The solubilized amount of ethylbenzene is also shown in Fig. 6 as a function of the mixed ratio of (SDS–BC-20) or (LiFOS–BC-20) being adjusted as indicated in Fig. 4. By the addition of the emulsifier, the solubilized amount of ethylbenzene increased in proportion to the concentration of BC-20 and this increase of the solubilized amount was higher than that in the case of a nonionic-anionic emulsifier mixture. The solubilized amount of ethylbenzene in the mixed solutions by adding a little amount of SDS to BC-20 became smaller than that in the case of single nonionic emulsifier. However, on the further addition of SDS, the solubilized amount of ethylbenzene increased. This amount was always smaller than that of the solubilized amount in the same concentration of BC-20.

It is known that the polymerization rate is proportional to the solubilizing power of various emulsifiers.[13] By a comparison between Figs. 3 and 5, while the solubilized amount of ethylbenzene in the mixed emulsifier solution, (BC-20–SDS) or (BC-20–LiFOS), was smaller than that in the single BC-20 solution, the polymerization rate in the former solution was larger than in the latter. In Fig. 4, the polymerization rate is seemed to increase with mixing the emulsifiers more than in the case of a single emulsifier, while the solubilized amount of styrene is reduced in the mixed emulsifier solutions. This would be expected from the same effect in the solubilized amount of ethylbenzene as shown in Fig. 6. These results confirmed that the polymerization rate was not much associated with the solubilized amount in nonionic-anionic emulsifier mixtures.

In general, it is difficult to predict the properties of mixed nonionic-anionic surfactant solutions theoretically,[2,3] such as the micelle size, the aggregation number and the composition in their mixed micelles. This is because of the specific difference in the interaction among hydrophilic polar groups of their molecules in the mixed micelles, compared with that in single micelles. Therefore, emulsion polymerization with nonionic-anionic emulsifier mixture cannot be directly attributed to the solubilized amount in mixed emulsifier solutions.

In the mixture of BC-20–LiFOS, the polymerization rate increased with increase of the addition of LiFOS. But the further addition of LiFOS caused the polymerization rate to decrease in spite of an increase in the total amount of the emulsifiers. In a previous paper,[10] it was confirmed that LiFOS has a repressive effect on the polymerization rate. According to Suzuki et al.[14] it was also reported that the addition of a fluorocarbon surfactant is effective to expel any materials solubilized in the micelles of a hydrocarbon surfactant by forming mixed micelles. From the above consideration, it is also supported that the deacceleration of the polymerization rate occurs due to the expulsive effect of LiFOS. The added LiFOS expels styryl radicals from the micelles in aqueous emulsifier solutions, resulting in a depression of the polymerization rate. However, this effect was slight in this nonionic-anionic emulsifier mixture.

The particle number concentration in synthesized latex per cubic meter of the aqueous phase (N) was calculated from the z-average diameter and the conversion ratio, and the diagram of the particle number concentration plotted against the addition of emulsifiers is shown in Fig. 7. The increase of the number of latex particle is seemed to be caused by the increase of the number of micelles and the increase in the number of emulsion particle with the total amount of emulsifier in the reaction solution. The increase of the particle number concentration caused by the addition of SDS or LiFOS is much larger than that with BC-20, while further addition of LiFOS causes a gradual

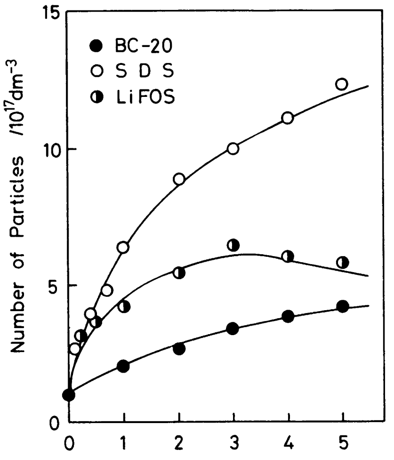

Fig. 7. Particle number concentration as a function of additive amount of SDS(○), LiFOS(◑), BC-20(●).

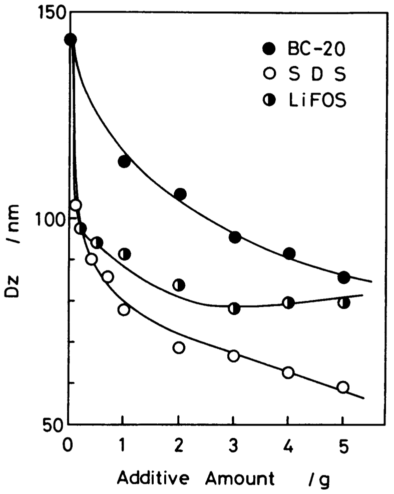

Fig. 8. Particle size (Dz) as a function of additive amount of emulsifiers; SDS(○), LiFOS(◑), BC-20(●).

Table 3. Weight-Average Molecular Weight (M_w) and Molecular-Weight Distribution (M_w/M_n) of Formed Polystyrene Latex

Mixed Ratio	Molecular Weight	
BC-20 : SDS	M_w ($\times 10^6$)	M_w/M_n
6 : 0	1.29	3.85
5 : 1	1.63	4.15
4 : 2	1.65	4.55
3 : 3	1.64	4.40
2 : 4	1.67	4.60
1 : 5	1.43	4.93
0 : 6	0.77	3.19
BC-20 : LiFOS	M_w ($\times 10^6$)	M_w/M_n
6 : 0	1.29	3.85
5 : 1	1.39	4.55
4 : 2	1.29	4.57
3 : 3	1.37	5.05
2 : 4	0.99	4.50
1 : 5	0.55	1.75
0 : 6	—	—

decrease in the particle number concentration. These results can be explained by the same reason as mentioned about the change of the polymerization rate, for example, the variation of the composition in nonionic-anionic emulsifier micelles and the change of the solubilized amount of monomer in mixed emulsifier solutions.

The change in the latex particle size with the addition of BC-20, SDS, LiFOS to BC-20 (5.0 g) is shown in Fig. 8. Each particle size became smaller with increasing the addition of emulsifiers. The explanation for this result is based on the number of latex particles with the addition of the emulsifier, resulting in the increase of the polymerization rate. That is to say, as the particle number increases, the amount of monomer which is supplied for one latex particle decreases. In other words, since the polymerization of water-insoluble monomer proceeds in micelles containing monomer, the slower the polymerization rate is, the longer is the time in which the polymer particles and emulsion droplets coexist. As a result, the latex particle sizes are continuously increasing up to the depletion of monomer droplets. Furthermore, the particle size decreases with only a small addition of the anionic emulsifier, compared with the corresponding addition of BC-20. The remarkable decrease of particle sizes may occur because of the considerable increase in the number of latex particles. As an anionic is added to a nonionic emulsifier, the composition of the mixed micelles changes and the charge density of the anionic head group in the mixed micelles' surface increases. This increase of surface charge may bring about the increase in the repulsion between styryl oligomeric radical and the micelles. Actually, it has been established that the surface properties of a mixed micelle are remarkably changed upon a small addition of an anionic to a nonionic surfactant. This has been shown by measuring the surface potential,[1] and self-diffusion coefficients and line width at half height by NMR.[3]

The molecular-weight of the polystyrene latex formed was measured by GPC after being dissolved in tetrahydrofuran. These samples were the same ones used for the particle size measurement. The weight-average molecular weights (M_w) and their molecular weight distributions (M_w/M_n) are shown in Table 3 as a function of mixed ratio of (BC-20-SDS) or (BC-20-LiFOS). It was found that the breadth of the molecular-weight distribution of the polystyrene formed in a latex by using the mixed emulsifiers was rather broadened compared with that by using each single emulsifier. These results demonstrate that the compositions of emulsions and micelles in the mixed emulsifier solutions have a much wider distribution than that in a single emulsifier solution. The M_w of polystyrene latex formed with mixed emulsifiers increased more than that of polystyrene latex formed with each single emulsifier. The increase of M_w on adding SDS was higher than that on adding LiFOS. These results depend on the change of the polymerization rate and the particle number concentration with the mixed ratio of emulsifiers.

References

1) M. Nakagaki, S. Yokoyama and I. Yamamoto, *Nippon Kagaku Kaishi,* **1982**, 1865.

2) N. Nishikido, *J. Colloid Interface Sci.,* **60**, 242 (1977).

3) P. G. Nilsson and B. Lindman, *J. Phys. Chem,* **88**, 5391 (1984).

4) G. G. Greth and J. E. Wilson, *J. Appl. Polym. Sci.,* **5**, 135 (1961).

5) S. Muroi, *Kogyo Kagaku Zasshi,* **68**, 1785 (1965).

6) S. S. Medvedev, I. A. Gritskova, A. V. Zuikov, L. I. Sedakova and G. D. Berejnol, *J. Macromol. Sci. Chem.,* **A7**, 715 (1973).

7) W. V. Smith and R. H. Ewart, *J. Chem. Phys.,* **16**, 592 (1948).

8) R. N. Haward, *J. Polym. Sci,* **4**, 273 (1949).

9) F. K. Hansen and J. Ugelstad, *J. Polym. Sci. Polym. Chem. Ed,* **16**, 1953 (1978).

10) K. Kato, K. Esumi, and K. Meguro, *Bull. Chem. Soc. Jpn.,* **59**, 249 (1986).

11) P. N. Pussey, "Indusrial Polymer; Characterization by Molecular Weights," ed by Green and Dietz, Transcripta Books, London (1973).

12) S. W. Provencher, J. Hendrix, L. D. Maeyer, and N. Paulussen, *J.Chem.Phys.,* **69**, 4273 (1978).

13) I. M. Kolthoff, E. J. Meehan and C. W. Car, *J. Polym. Sci.,* **6**, 73 (1951).

14) T. Suzuki, K. Esumi, and K. Meguro, *J. Colloid Interface Sci.,* **93**, 205 (1983).