

The Distribution of Soap in the Polymerization System for Preparation of Carboxylated Polystyrene Latexes

KAZUYUKI SAKOTA and TAKUJI OKAYA, *Central Research Laboratories, Kuraray Co., Ltd., Kurashiki, Okayama, Japan*

Synopsis

The distribution of soap in the polymerization system for preparation of carboxylated polystyrene latexes has been investigated. The critical micelle concentration (*CMC*) for sodium dodecyl sulfate (SDS) in the polymerization system was determined by surface tension measurement to be 0.173 mmole/l. The solubility of styrene (St) in the aqueous phase of the polymerization system was determined by NMR measurement to be 4.52 mmole/l. It was confirmed by NMR measurement that at the concentration of SDS higher than the *CMC*, St is solubilized in the interior of the SDS micelles, and the concentration of solubilized St is almost proportional to the concentration of micellar SDS. From this relationship, the number and radius of SDS micelles containing solubilized St can be determined.

INTRODUCTION

Recently, some workers^{1,2} have investigated the polymerization of styrene or methyl methacrylate in the aqueous phase and clarified that a slight amount of soap strongly affects the formation of particles by adsorbing on the surface of growing radicals formed in the aqueous phase or primary particles formed by the precipitation of growing radicals.

In a previous paper,³ the authors have demonstrated that stable, soap-free carboxylated polystyrene latexes can be obtained by copolymerizing carboxylic monomers at the appropriate degree of neutralization and that the number of particles is much enhanced by the presence of a slight amount of soap. This indicates that, although the formation of particles can predominantly be attributed to the precipitation of growing radicals formed in the aqueous phase, the slight amount of soap plays an important role in the formation of particles.

In the present paper, the distribution of soap in the above-described polymerization system was determined to elucidate the role of soap in the formation of particles.

EXPERIMENTAL

Materials

Deionized water was used. Deuterium oxide for spectroscopy (D₂O; purity 99.75%) was used. Extrapure-grade potassium sulfate (K₂SO₄), sodium dodecyl

sulfate (SDS; Tokyo Chemical Industry Co., Ltd.), sodium hydrogen carbonate (NaHCO_3), and heptane were used without further purification. Extrapure-grade styrene (St) and acrylic acid (AA) were used after distillation under reduced pressure.

Procedures

The surface tension was measured at 70°C by means of a De Noüy tensiometer as reported by Powney et al.⁴ The critical micelle concentration (CMC) was determined from the break in the surface tension-concentration curve.

The NMR measurement was made at 30°C with a 60 Mc spectrometer or at 70°C with a 100 Mc spectrometer using the time-averaging technique, if necessary, to enhance the signal-to-noise ratio. The chemical shift was determined based on the external reference of the mixture of tetramethylsilane (TMS) and methylene chloride (CH_2Cl_2).

The NMR sample of the polymerization system was prepared as follows. The prescribed amounts of AA, sodium hydrogen carbonate, SDS, and potassium sulfate dissolved in deuterium oxide were placed in a sample tube and heated to, and kept at, 70°C. Then, the prescribed amount of St was introduced as a separate phase on the aqueous phase, and the sample tube was shaken slowly to avoid the emulsification of St in the aqueous phase at 70°C. After the completion of equilibration, the separate phase of St was removed.

RESULTS AND DISCUSSION

Critical Micelle Concentration in the Polymerization System

In the previous paper,³ it was demonstrated that stable soap-free carboxylated polystyrene latexes can be obtained by copolymerizing AA and fumaric acid at a degree of neutralization of about 0.85. However, stable soap-free carboxylated polystyrene latexes can be obtained also by copolymerizing only AA at a degree of neutralization of about 0.80, as will be described in a subsequent paper.⁵ Consequently, in the present paper, the formulation for the polymerization system was established as shown in Table I for convenience. In this polymerization system, the degree of neutralization of AA defined as the ratio of the equivalent of sodium hydrogen carbonate to AA was maintained at 0.80, and equimolar potassium sulfate was substituted for the initiator potassium persulfate to avoid the initiation of polymerization during the measurement without

TABLE I
Formulation for the Polymerization System

Ingredient	Weight parts
Water	100
St	variable
AA	5
NaHCO_3	4.66
SDS	variable
K_2SO_4	0.85

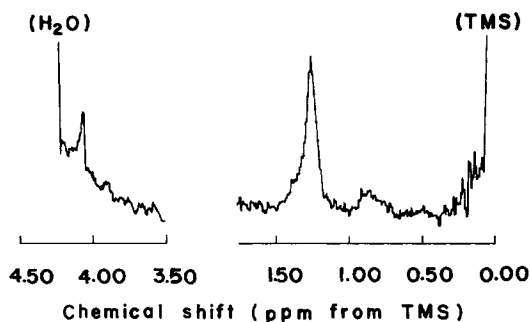


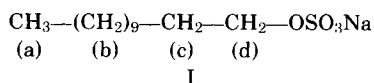
Fig. 1. NMR spectrum of SDS in the polymerization system P-7 observed at 70°C (100 Mc; 32 scans).

affecting the ionic strength. In the following discussion the density of the aqueous phase was assumed to be 1 g/cm³.

In the measurement of surface tension, St was excluded from the formulation in Table I to avoid the contamination on the surface of the aqueous phase. The *CMC* for SDS thus determined was 0.173 mmole/l., which corresponds to about 0.0054 weight parts in the formulation in Table I. In the actual polymerization system, the distribution of soap seems to be affected by the partition of AA between St and the aqueous phase. This effect, however, may almost be neglected because of the small partition coefficient of AA between St and water.⁶ Consequently, the above-described *CMC* for SDS may not differ so much from that in the actual polymerization system. Naturally, the above-described *CMC* for SDS is much lower than the *CMC* of about 8 mmole/l. reported for SDS in pure water at 60°C because of the fairly high ionic strength in the polymerization system.⁴

NMR Spectra of the Polymerization System

The NMR spectra of polymerization systems established based on the formulation in Table I were observed. For the NMR measurement, deuterium oxide was substituted for water, and a minimum amount of St for the completion of equilibration was used to avoid a change in concentration of AA in the aqueous phase. The typical NMR spectra of the polymerization system are shown in Figures 1 and 2. In Figure 1 are observed resonances at 0.85, 1.27, and 4.07 ppm from TMS, which are assigned to the (a), (b), and (d) protons of SDS, respectively, as shown in the following formula:



In Figure 2 are observed the resonances of methylene and methine protons of AA and St in the range of 5.00–7.00 ppm from TMS and the resonances of phenyl protons of St in the range of 7.00–7.50 ppm from TMS.

Based on the above assignment, chemical shifts of SDS and St in the polymerization systems were determined, and the results are shown in Table II. In the polymerization system P-6, the resonance of phenyl protons of St may be attributed to the slightly dissolved St in the aqueous phase.⁷ In the polymerization system P-17, since the concentration of SDS is much higher than the *CMC*

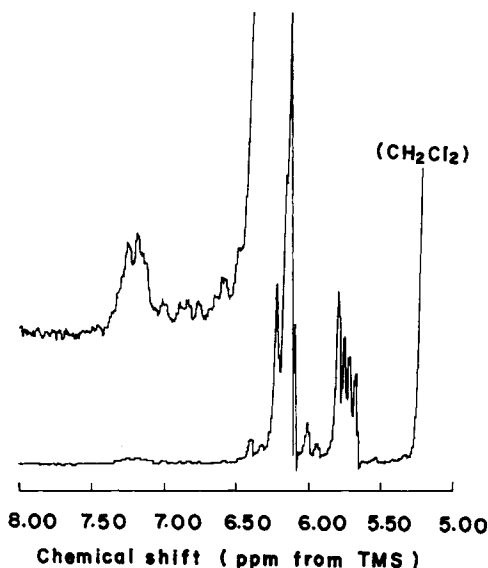


Fig. 2. NMR spectrum of AA and St in the polymerization system P-7 observed at 70°C (100 Mc; 32 scans).

described above, most part of SDS will be micellar and only a small portion of SDS will be monomolecular. In the polymerization system P-7, it is apparent, in comparison with P-17, that the resonances of the (a) and (b) protons of SDS shift to a higher field in the presence of St. This indicates that in the polymerization system P-7, SDS micelles contain solubilized St,⁸ which may bring about a change of magnetic environment for the (a) and (b) protons of SDS. To confirm this, the NMR spectra of heptane and the mixture of heptane and St were observed, and the chemical shifts of methyl and methylene protons of heptane were determined. The results are shown in Table III. It is apparent from Table III that the resonances of the methyl and methylene protons of heptane shift to a higher field in the presence of St, which suggests that the above-described consideration is appropriate. In the polymerization system P-7, it is apparent, in comparison with P-6, that the resonance of phenyl protons of St also shifts to a higher field in the presence of SDS, which may also be attributed to the

TABLE II
Chemical Shifts of SDS and St in the Polymerization System

Run no.	Polymerization system ^a		Chemical shifts, ppm from TMS ^b			
	Concentration of SDS, mmole/l.	Amount of St	(a)	(b)	(d)	(e)
			P-6	0.00	minimum ^c	—
P-17	1.60	none	0.99	1.40	4.07	—
P-7	1.60	minimum ^c	0.85	1.27	4.07	7.21

^a See Table I. D₂O was substituted for water.

^b Observed at 70°C (100 Mc); (a), (b), and (d) represent protons of SDS in formula I and (e) represents phenyl protons of St.

^c The minimum amount of St for the completion of equilibration.

TABLE III
Change in Chemical Shifts of Heptane in the Presence of St

Composition, mole fraction		Chemical shifts, ppm from TMS ^a	
Heptane	St	Methyl	Methylene
1.00	0.00	0.60	1.00
0.50	0.50	0.45	0.80

^a Observed at 30°C (60 Mc).

TABLE IV
Change in Concentration of St with Concentration of SDS
in the Polymerization System^a

Run no.	Concentration of SDS, mmole/l.	Concentration of St, mmole/l.
P-6 ^b	0.00	4.52
P-7 ^b	1.60	7.94
P-24	3.21	6.48
P-25	6.41	17.5
P-28	63.0	97.4

^a See Table I. D₂O was substituted for water.

solubilization of St in the interior of SDS micelles. Furthermore, Table II shows that the resonance of the (d) protons of SDS does not shift in the presence of St, which may indicate that sulfate endgroups of micellar SDS are located on the surface of the micelle and the (d) protons adjacent to sulfate endgroups are surrounded by water rather than by hydrocarbon.

Solubilization of Styrene in the Polymerization System

As described above, two types of St may exist in the polymerization system; that is, St dissolved in the aqueous phase and St solubilized in the interior of SDS micelles. The concentration of St in the polymerization system can be determined from the NMR spectrum of the polymerization system, that is, from the ratio of the phenyl protons of St to the methylene and methine protons of AA and St.

In Table IV, the change of the concentration of St with concentration of SDS in the polymerization system is shown. The concentration of St in the polymerization system P-6 in Table IV, which corresponds to the solubility of St in the aqueous phase of the polymerization system, is somewhat higher than the solubility of St in pure water.⁷ This may be attributed to the presence of AA which enhances the solubility of St. It is apparent from Table IV that the concentration of St increases with the increase in the concentration of SDS.

The concentrations of micellar SDS and solubilized St in the polymerization system were calculated to clarify the relationship between them. The results are shown in Table V. The concentration of micellar SDS was calculated by subtracting the *CMC* for SDS in the polymerization system from the concentration of total SDS in Table IV on the assumption that the *CMC* does not change in the presence of St. The concentration of solubilized St was calculated by

TABLE V
Calculation Results of the Concentrations of Micellar SDS and Solubilized St
in the Polymerization System^a

Concentration of micellar SDS, mmole/l.	Concentration of solubilized St, mmole/l.
1.43	3.42
3.03	1.96
6.23	13.0
62.8	92.9

^a Calculated from data in Table IV.

subtracting the above-described solubility of St in the aqueous phase of the polymerization system from the concentration of total St in Table IV.

The relationship between the concentration of micellar SDS and the concentration of solubilized St in Table V can be described as in Figure 3. The approximately linear relationship in Figure 3 can be represented by the following equation:

$$[\text{St}] = 1.45[\text{SDS}] \quad (1)$$

where $[\text{St}]$ and $[\text{SDS}]$ are the molar concentration of solubilized St and the molar concentration of micellar SDS, respectively.

Distribution of Soap and Styrene in the Polymerization System

Based on the above considerations, the distribution of SDS and St in the polymerization system was investigated. From eq. (1), the concentration of solubilized St can be calculated from the concentration of micellar SDS. Consequently, the number and radius of SDS micelles containing solubilized St can also be calculated based on the following assumption: all micelles are uniform and spherical; sulfate endgroups of SDS are located on the surface of micelles and occupy the constant molecular area; and the interior of micelles is filled with St and hydrocarbon chains of SDS. From some geometric relationships, the

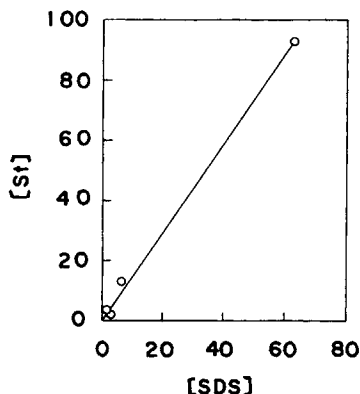


Fig. 3. Relationship between the concentration of micellar SDS and concentration of solubilized St in the polymerization system: $[\text{SDS}]$ = concentration of micellar SDS, mmole/l.; $[\text{St}]$ = concentration of solubilized St, mmole/l.

TABLE VI
Calculation Results of the Distribution of SDS and St in the Polymerization System

Concentration of SDS, mmole/l.		Concentration of solubilized St, mmole/l. ^a	Number of micelles, × 10 ¹⁷ /l. ^b	Radius of micelle, Å ^c
Total	Micellar			
0.000	0.000	0.000	0.00	—
0.160	0.000	0.000	0.00	—
0.321	0.148	0.215	1.28	47.0
0.642	0.469	0.680	4.07	47.0
1.60	1.43	2.07	12.4	47.0
3.21	3.03	4.39	26.5	46.9
6.41	6.23	9.03	53.8	47.1
16.0	15.8	22.9	137	47.0
31.8	31.6	45.8	274	47.0
63.0	62.8	91.1	547	46.9

^a Calculated from eq. (1).

^b Calculated from eq. (2).

^c Calculated from eq. (3).

number and radius of micelles in the polymerization system can be described by the following equations:

$$M = (nA)^3/[36\pi(nB + C)^2] \quad (2)$$

$$r = 3(nB + C)/(nA) \quad (3)$$

where M is the number of micelles per unit volume, r is the radius of the hydrocarbon portion of micelle, n is the number of micellar SDS molecules per unit volume, A is the molecular area of SDS, B is the molecular volume of the hydrocarbon chain of SDS, and C is the volume of solubilized St per unit volume. In the polymerization system, n can be obtained by subtracting the CMC for SDS in the polymerization system from the concentration of total SDS on the assumption that the CMC does not change in the presence of St and C can be obtained from eq. (1). B can be calculated to be $3.50 \times 10^2 \text{ \AA}^3$ by the method of Tartar.⁹ A seems to be about 40 \AA^2 .^{9,10}

Thus, the number and radius of SDS micelles containing solubilized St were calculated in a wide range of SDS concentration. The results are shown in Table VI. Naturally, it is apparent from Table VI that at the concentration of SDS higher than the CMC a large number of micelles are formed. As can be predicted from eqs. (1), (2), and (3), the number of micelles is proportional to the concentration of micellar SDS, whereas the radius of micelle is constant irrespective of the concentration of micellar SDS. In the above-described consideration, the adsorption of SDS on the surface of emulsified St which may affect the distribution of SDS has not been taken into account. In practice, however, the soap adsorbed on the surface of emulsified monomer may be neglected because ordinarily this soap will represent only a small fraction of the total present.^{11,12} It has been demonstrated³ that in this polymerization system, although the formation of particles may predominantly be attributed to the precipitation of growing radicals formed in aqueous phase, the number and uniformity of particles is strongly dependent on the concentration of SDS. This may be explained by the above-described distribution of SDS and St in the polymerization system, and detailed discussions from this point of view will be described elsewhere.

References

1. I. D. Robb, *J. Polym. Sci. A-1*, **7**, 417 (1969).
2. R. M. Fitch and C. H. Tsai, *Polymer Colloids*, Plenum Press, New York, 1971, pp. 73-102.
3. K. Sakota and T. Okaya, *J. Appl. Polym. Sci.*, **20**, 1745 (1976).
4. J. Powney and C. C. Addison, *Trans. Faraday Soc.*, **33**, 1243 (1937).
5. K. Sakota and T. Okaya, *J. Appl. Polym. Sci.*, **21**, 1035 (1977).
6. K. Sakota and T. Okaya, *J. Appl. Polym. Sci.*, **20**, 2583 (1976).
7. E. C. Leonard, *Vinyl and Diene Monomers*, Wiley-Interscience, New York, 1970, pp. 498-503.
8. P. H. Elworthy, A. T. Florence, and C. B. Macfarlane, *Solubilization by Surface-Active Agents*, Chapman and Hall, London, 1968.
9. H. V. Tartar, *J. Phys. Chem.*, **59**, 1195 (1955).
10. J. W. Vanderhoff and H. J. van den Hul, *J. Macromol. Sci., Chem.*, **7**, 677 (1973).
11. W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948).
12. W. D. Harkins, *J. Amer. Chem. Soc.*, **69**, 1428 (1947).

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