Polymerization of surface-active monomers: 7. Radical copolymerizations of anionic surface-active monomer, sodium di(10-undecenyl)sulfosuccinate, with electron-accepting monomers and vinyl monomers in micellar and isotropic solutions

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Radical copolymerizations of anionic surface-active monomer, sodium di(10-undecenyl)sulfosuccinate (DUSS), with electron-accepting monomers and vinyl monomers were studied in water, n-hexane and dioxane, giving aqueous micellar solution, reverse micellar solution and isotropic solution, respectively. The copolymerizations of DUSS with hydrophobic diethyl fumarate (EF) in aqueous micellar solution afforded the copolymer in relatively high yields as compared to those for the copolymerizations in reverse micellar and isotropic solutions. On the other hand, the copolymerization with hydrophilic fumaronitrile (FN) in isotropic solution proceeded at a higher rate than those in aqueous and reverse micellar solutions. The copolymerization with EF in the reverse micellar system was greatly accelerated by solubilization of water. The copolymers with EF prepared in aqueous micellar solution were soluble in some solvents, in contrast to those formed in reverse micellar and isotropic solutions. The copolymerization with styrene (ST) also revealed a higher rate in aqueous micellar solution as compared to those for the copolymerizations in reverse and isotropic solutions. For the emulsion polymerizations of ST and methyl methacrylate using DUSS as a polymerizable emulsifier, DUSS appeared to exhibit a retardation effect on their polymerizations.

(Keywords: radical copolymerization; surface-active monomer; micelles)

INTRODUCTION

Surface-active monomers are characteristic of micelle formation above a certain concentration, the so-called critical micelle concentration. A number of studies have been devoted to gaining insight into the effect of monomer micellization on polymerization, mainly for aqueous systems, and the micelle formation of the monomers has been found to accelerate the polymerization[1-10]. On the other hand, there have been only a few studies on the polymerization of such monomers in reverse micellar solutions[4,11-13] and the copolymerization of systems involving a surface-active monomer[14].

Sodium di(2-ethylhexyl)sulfosuccinate (AOT) is well known as a surfactant which forms reverse micelles in apolar solvents in addition to aqueous micelles in water[15]. In a previous paper[16], we reported syntheses of sodium di(10-undecenyl)sulfosuccinate (DUSS) and the analogue with a polymerizable group, n-undecyl 10-undecenylsulfosuccinate (MUSS), which exhibit solubilities similar to that of AOT; their polymerizations in isotropic and anisotropic solutions were also reported. The monomers underwent radical polymerizations only under u.v. irradiation. The effect of monomer micellization on the rate of polymerization was little observed owing to a low polymerizability resulting from their allyl group as a polymerizable group. On the other hand, allylic monomers are known to copolymerize with various electron-accepting monomers at a considerable rate to give alternating copolymers[17]. Therefore, the effect of monomer aggregation may be profoundly observed for the copolymerizations with electron-accepting monomers. Thus, the present paper deals first with the copolymerizations of DUSS with electron-accepting monomers, namely diethyl fumarate (EF), fumaronitrile (FN) and maleic anhydride (MA). The effect of monomer aggregation was studied using three different solvents, water, n-hexane and dioxane, giving aqueous micellar (or vesicular) solution, reverse micellar solution and isotropic solution, respectively.

Surface-active monomers have also been used as polymerizable emulsifiers for emulsion polymerizations in oil-in-water and water-in-oil systems[18-23]. In such applications, an important factor affecting the properties of the resulting latex solutions is the copolymerizability of the polymerizable emulsifier with vinyl monomers used as a main component. Therefore, copolymerizations of DUSS with vinyl monomers such as styrene (ST) and methyl methacrylate (MMA) were also studied.

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EXPERIMENTAL

Materials

The preparation and purification of DUSS and MUSS were carried out according to the procedures described in a previous paper[16]. Potassium persulfate (KPS; Wako Pure Chemicals Industries) was used as received. 2,2′-Azobisisobutyronitrile (AIBN; Tokyo Kasei Kogyo Co.) was recrystallized from methanol, followed by reprecipitation using benzene–petroleum ether system to obtain a finely powdered form. EF (Tokyo Kasei Kogyo Co.) was distilled under reduced pressure after dehydration. FN (Tokyo Kasei Kogyo Co.) and MA (Wako Pure Chemicals Industries) were recrystallized from diethyl ether. ST, MMA, n-hexane and dioxane (Wako Pure Chemicals Industries) were purified by distillation after dehydration according to conventional procedures. Water was deionized until the specific conductivity was 1 μS cm^{-1} or lower, and then distilled under nitrogen atmosphere before use.

Copolymerization

Copolymerizations with electron-accepting comonomers were conducted in glass tubes ($\sim$15 ml) under nitrogen atmosphere. The monomer solution was subjected to freeze–thaw cycles and sonicated before the copolymerizations. When the copolymerizations were carried out in n-hexane and dioxane, the solutions were evaporated to dryness after the addition of inhibitor. Hot ethyl acetate was added to the residues, and the copolymers were filtered and washed repeatedly with hot ethyl acetate. When the copolymerizations were conducted in water, the solutions were freeze-dried and then copolymers were isolated by the procedures described above.

Copolymerizations of DUSS with vinyl monomers at an equimolar composition in monomer mixture were conducted without stirring; the emulsion copolymerizations in excess of vinyl monomers in the feed were carried out with stirring. Methanol and diethyl ether were used to isolate the copolymers with ST and MMA, respectively, as non-solvents for the copolymers.

Characterization of the copolymers

I.r. spectra were obtained using a Jasco IR-S1 spectrophotometer. The molecular weight of the copolymers was determined by g.p.c. measurements using a Toyo Soda HLC-802A with standard polystyrene gel columns in dimethylformamide (DMF) as solvent.

The composition of the copolymers of DUSS and EF, which are soluble in water, was estimated using the colloid titration method[24], in which cationic polyelectrolyte solution (N/200 methyl glycol chitosan from Wako Pure Chemicals Industries) was added in excess to aqueous solution of the copolymer, then the amount of residual cationic polyelectrolyte was determined by back-titration with anionic polyelectrolyte solution (N/400 potassium poly(vinyl sulfate) from Wako Pure Chemicals Industries) using toluidine blue as an indicator. The number of anionic charges per unit weight of the copolymer was calculated from the reacted amount of cationic polyelectrolyte.

The composition of the copolymers of DUSS and vinyl monomers, which are soluble in chloroform and insoluble in water, was determined by elemental analysis and dye partition method[25]. In the latter method, the aqueous solution of a dye, methylene blue, was mixed with the chloroform solution of copolymer and the unreacted amounts of the dye were estimated from the amount in aqueous solution determined using a u.v. spectrophotometer (Shimadzu UV-180). The copolymer composition was calculated from the number of anionic charges per unit weight of the copolymers estimated from the reacted amounts of the dye.

RESULTS AND DISCUSSION

Copolymerizations of DUSS with electron-accepting monomers

The results of the copolymerizations of DUSS with three electron-accepting monomers, EF, FN and MA, are presented in *Table 1*. In dioxane, giving an isotropic solution, MA gives the highest yield of copolymer and FN exhibits a copolymerizability slightly higher than that of EF. There is a tendency for the copolymer yield to

Table 1 Copolymerizations of DUSS with diethyl fumarate (EF), fumaronitrile (FN), and maleic anhydride (MA)[a]

Run no.	DUSS conc. (mmol)	Comonomer	Comonomer conc. (mmol)	Initiator	Solvent	Time (h)	Yield (%)
1	1.0	EF	1.0	AIBN	Hexane	24	4.1
2	1.0	EF	1.0	AIBN	Dioxane	24	7.3
3	0.5	EF	0.5	AIBN	Water	24	67.8[b]
4	0.5	EF	0.5	AIBN	Water[c]	24	68.4
5	0.5	EF	1.0	AIBN	Water	24	80.4
6	0.5	EF	0.5	KPS	Water	24	76.7
7	0.5	FN	0.5	AIBN	Hexane	48	Trace
8	1.0	FN	1.0	AIBN	Dioxane	48	18.2
9	0.5	FN	0.5	KPS	Water	24	4.5
10	1.0	MA	1.0	AIBN	Benzene	24	56.3
11	1.0	MA	1.0	AIBN	Dioxane	24	35.4

[a] Initiator, 5 mol%; solvent, 5 ml; temp., 50°C
[b] $M_w = 2.3 \times 10^6$; $M_w/M_n = 1.5$
[c] 10 ml

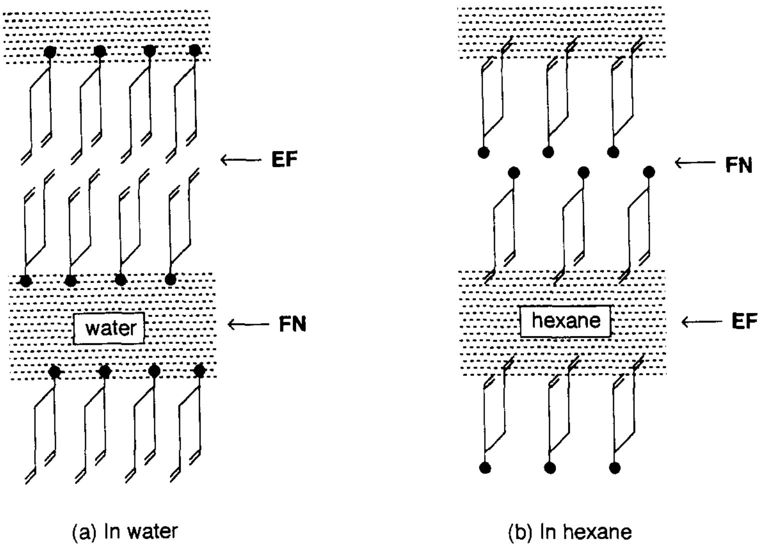

Figure 1 Schematic representations of copolymerization systems in (a) water and (b) n-hexane

increase with increase in the electron-accepting property of the comonomers[26]. The copolymerization with EF in the aqueous system affords the copolymer in relatively high yields as compared to those in the n-hexane and dioxane systems. On the other hand, the copolymer yield for the copolymerization with FN in water is lower than that for the copolymerization in dioxane. As shown in a previous paper[16], DUSS at the concentration shown in *Table 1* forms aqueous micelles (or vesicles) and reverse micelles in water and n-hexane, respectively.

In the aqueous system, polymerizable groups of DUSS are present in the hydrophobic, central cores of the micelles in which EF is solubilized, owing to the low solubility in water. Thus, both EF and polymerizable groups of DUSS exist in the cores of micelles at high local concentrations. Water-insoluble AIBN can induce copolymerization in the micelle cores and copolymerization with water-soluble KPS will also be initiated in a similar manner to conventional emulsion polymerization[27]. Thus, the higher rate of copolymerization with EF in water can be attributed to the locally high concentrations of both EF and polymerizable group of DUSS, as illustrated schematically in *Figure 1a*. On the other hand, FN is soluble in water and hence it exists outside the micelles, being remote from polymerizable groups of DUSS; this is unfavourable for copolymerization.

In n-hexane, polymerizable groups of DUSS are distributed over the outer surface of reverse micelles and the polar heads are buried in their central cores, as opposed to aqueous micelles. Therefore, the polymerizable groups are exposed to the solvent and diluted. EF molecules should be distributed outside the reverse micelles. Thus, the copolymerization components (EF and polymerizable groups of DUSS) for the reverse micellar system are probably located in an environment similar to that for an isotropic solution (see *Figure 1b*). However, the copolymer yield in n-hexane is lower than that in dioxane, particularly for the system involving FN as a comonomer. This could be because FN molecules are attracted to polar cores of reverse micelles by polar interaction and separate from polymerizable groups of DUSS, as shown in *Figure 1b*.

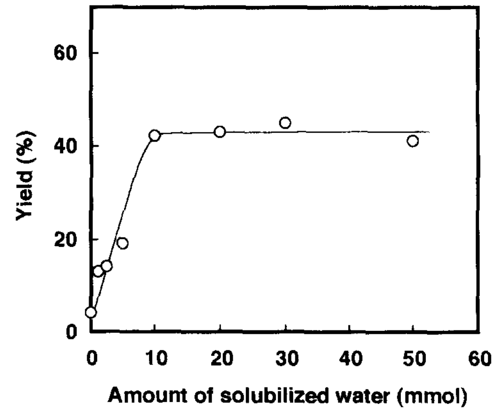

Figure 2 Copolymerization of DUSS with EF in n-hexane in the presence of water at 50°C. [DUSS] = [EF] = 1.0 mmol; AIBN, 5 mol%; n-hexane, 5 ml; time, 24 h

In the reverse micellar system, the aggregation number is not so high in the absence of water; it has been reported to be about 14 (ref. 28) and 19 (ref. 15) in n-hexane and iso-octane, respectively, for AOT. Such low aggregation numbers may be partly responsible for a small micellization effect on the copolymerization for the reverse micellar system. The aggregation number is known to increase on solubilizing water into reverse micelles[29]. *Figure 2* shows the effect of solubilization of water on the copolymerization of DUSS with EF for the reverse micellar system in n-hexane. The monomer solution is apparently homogeneous over the entire range of water content under the present conditions. The copolymer yield greatly increases with increasing the amount of solubilized water up to about $[H_2O]/[DUSS] = w_0 = 10$, and then levels off on further addition of water. The polymerization proceeds homogeneously up to $w_0 = 20$ and some water is observed to separate out from the solution during polymerization above $w_0 = 30$. The aggregation number of AOT in iso-octane has been reported to increase with the amount of solubilized water, linearly up to $w'_0 = [H_2O]/[AOT] = 10$ and then steeply[30]. At $w'_0 = 10$, it increases up to about 10 times that in the absence of water. The steep increase above $w'_0 = 10$ is due to coalescence of swollen micelles, which causes a change of the aggregated structures. Thus, the increased copolymer yield in the presence of the solubilized water for the copolymerization in n-hexane can be ascribed to an increase in the aggregation number of reverse micelles for DUSS. Little variation in the copolymer yield above $w_0 = 10$ may result from a disorder of monomer array in the aggregates caused by a coalescence of swollen micelles, as suggested for AOT[29].

Figure 3 shows the copolymer yield as a function of polymerization time for the copolymerizations of DUSS and MUSS with EF in water. DUSS copolymerizes much faster than MUSS, as can be predicted from the difference in the number of polymerizable groups for the surface-active monomers. Strangely, the tendency for the copolymer yield to saturate is observed for both copolymerization systems, though the reason remains unclear at present.

The copolymers of DUSS with EF obtained in n-hexane and dioxane are insoluble or swollen in solvents such as DMF, methanol and water, whereas the copolymers formed in water are soluble in these solvents. DUSS has two polymerizable groups in the molecule which are susceptible to crosslinking to afford the insoluble or swollen copolymer, as observed for the copolymerizations in n-hexane and dioxane. On the other hand, the formation of the soluble copolymers in aqueous systems can be ascribed to the copolymerization confined within the micellar (or vesicular) aggregates. The weight-average molecular weight M_w of the copolymer obtained in run no. 3 was 2.3×10^6 with $M_w/M_n = 1.5$. The composition of the water-soluble copolymers was determined using colloid titration, which is often employed for the quantitative determination of polyelectrolytes[24]. The molecular weight per unit charge for the copolymer prepared at an equimolar composition in the feed (run no. 3 in *Table 1*) was estimated to be 786 and it was 448 for AOT, which is in good agreement with the molecular weight (445). When the molar ratio of DUSS:EF units in the copolymer is 1:1 or 1:2, the molecular weight per unit charge is calculated to be 697 or 869, respectively. Consequently, the value for the copolymer corresponds to that for the copolymer with a composition of 2:3. Moreover, the molecular weight per unit charge was 833 for the copolymer prepared at a molar ratio of DUSS:EF = 1:2 (run no. 5 in *Table 1*), which is indicative of a composition close to 1:2. The results indicate that some amounts of residual double bond are involved in the copolymers, which was confirmed in their i.r. spectra.

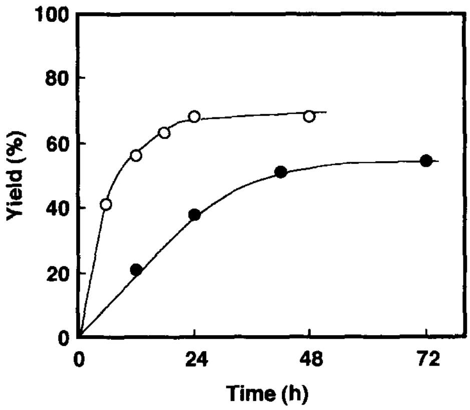

Figure 3 Copolymerizations of DUSS (○) and MUSS (●) with EF in water at 50°C. [DUSS] = [MUSS] = [EF] = 0.50 mmol; AIBN, 5 mol%; water, 5 ml

Copolymerizations of DUSS with vinyl monomers

The results of the copolymerizations of DUSS with vinyl monomers, namely ST and MMA, are presented in *Table 2*. Only a trace of copolymers is formed for the copolymerizations in n-hexane and dioxane at an equimolar composition of DUSS and ST in the feed, whereas copolymerization in water affords a higher yield of copolymer, though considerably lower compared to the copolymerization with EF. This can be attributed to a large difference in the Q values between DUSS and ST because most allyl compounds are an unconjugated monomer having a low Q value[31]. Moreoever, the content of DUSS units in the copolymers is considerably lower than that in the monomer mixture. This is also compatible with the low Q value of DUSS.

Some emulsion copolymerizations were conducted at a molar ratio of vinyl monomer to DUSS of

Table 2 Copolymerizations of DUSS with styrene (ST) and methyl methacrylate (MMA) at 50°C[a]

Run no.	DUSS (mmol)	Comonomer	Comonomer conc. (mmol)	Solvent	Appearance of solution	Time (h)	Yield (%)	DUSS (mol%) EA[b]	DUSS (mol%) DPM[c]
12	1.0	ST	1.0	Hexane	Clear solution	24	Trace	–	–
13	0.65	ST	6.5	Hexane	Clear solution	24	12.6	3.4	3.0
14	1.0	ST	1.0	Dioxane	Clear solution	24	Trace	–	–
15	0.65	ST	6.5	Dioxane	Clear solution	24	17.2	0.8	0.5
16	1.0	ST	1.0	Water	Emulsion	48	15.8	3.9	4.2
17[d]	0.65	ST	6.5	Water	Emulsion	48	61.0	1.9	1.8
18[d]	0.15	ST	5.0	Water	Emulsion	48	66.3	0.5	0.3
19[d]	AOT[e]	ST	6.5	Water	Emulsion	48	100	–	–
20[d]	0.65	MMA	6.5	Water	Emulsion	24	67.1	–	3.7

[a] AIBN, 5 mol%; solvent, 10 ml
[b] Determined by elemental analysis
[c] Determined by dye partition method
[d] KPS (5 mol%) was used in place of AIBN, with stirring
[e] Sodium di(2-ethylhexyl)sulfosuccinate (AOT; 0.65 mmol) was used in place of DUSS

10 or higher in water to examine the function of DUSS as a polymerizable emulsifier. Stable latexes were obtained for the emulsion copolymerizations. However, the copolymers with ST and MMA exhibit a relatively lower DUSS content than that in the monomer mixtures. Moreoever, the copolymer yields for the emulsion copolymerizations are also low compared with the polymer yield for the emulsion polymerization using AOT in place of DUSS as an emulsifier. Thus, DUSS appears to exert a retardation effect on the emulsion polymerizations, which is probably related to a degradative chain transfer[32] of allyl groups of DUSS in addition to a character of the unconjugated monomer.

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