Polymerization of surface-active monomers: 5. Syntheses and polymerizations of anionic surface-active monomers: sodium di(10-undecenyl)sulphosuccinate and sodium n-undecyl 10-undecenylsulphosuccinate

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Novel, anionic surface-active monomers, sodium di(10-undecenyl)sulphosuccinate (DUSS) and sodium n-undecyl 10-undecenylsulphosuccinate (MUSS) were prepared. The monomers were soluble in both water and apolar organic solvents on heating. DUSS and MUSS in water exhibited Kraft points at about 39°C and 48°C, respectively. The critical micelle concentrations for aqueous solutions of DUSS and MUSS at 50°C were determined to be 2.4×10^{-5} and 1.2×10^{-5} mol l^{-1}, respectively. Polymerization of the monomers in darkness and under u.v. irradiation at 50°C were studied using three different solvents, namely water, n-hexane and dioxane, giving aqueous micelles (or vesicles), reversed micelles and isotropic solution, respectively. Only traces of polymers were formed for the polymerizations in darkness, while the polymerizations under u.v. irradiation gave polymers, except for the polymerization of MUSS in dioxane. The solvents used for the polymerization were observed to exert an effect on the solubility of the polymers of DUSS and only the polymer obtained from the polymerization in water was soluble in solvents such as water and *N,N*-dimethylformamide. Thus, the monomer aggregation, especially for the aqueous system, was found to affect the structure of the resulting polymers.

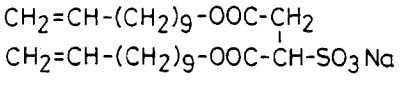
(Keywords: polymerization; surface-active monomer; sodium di(10-undecenyl)sulphosuccinate; sodium n-undecyl 10-undecenylsulphosuccinate; aqueous micelles; vesicles; reverse micelles)

INTRODUCTION

Surface-active monomers are of an amphiphilic structure, composed of one hydrophilic headgroup and one or two hydrophobic tails in addition to a polymerizable group. These molecules associate in water above a certain concentration, the so-called critical micelle concentration (CMC), to form molecular aggregates such as micelles or vesicles. The polymerization of vesicle-forming monomers, which have mostly two hydrophobic chains per headgroup, has received much attention because of the wide application of their polymerized vesicles with an increased stability[1].

On the other hand, there have also been a number of studies on the polymerization of micelle-forming monomers having a single hydrophobic chain and the micellar aggregation of the monomers has been found to accelerate their polymerization, mainly for the aqueous systems[2–9]. However, only a few studies have been undertaken on the polymerization of micelle-forming monomers in apolar solvents where they form so-called reverse micelles[10,11]. Sodium dioctylsulphosuccinate (AOT) is well known to be soluble in both water and apolar solvents and it is a typical surfactant which is most frequently used in apolar media[12]. Therefore, a surface-active monomer with a structure like AOT will be suitable for studying the effect of micelle formation of the monomer on the polymerization for both aqueous and apolar, non-aqueous systems.

The present study deals with the syntheses, characterizations and polymerizations of the anionic surface-active monomers bearing two polymerizable groups, sodium di(10-undecenyl)sulphosuccinate (DUSS) and one polymerizable group, sodium undecyl 10-undecenylsulphosuccinate (MUSS). The effect of monomer aggregation on polymerization was studied using three different solvents—water, n-hexane and dioxane—giving aqueous micellar (or vesicular) solution, reverse micellar solution and isotropic solution, respectively.



DUSS

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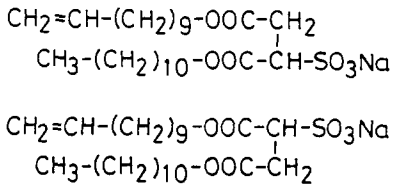


MUSS

EXPERIMENTAL

Materials

10-Undecen-1-ol and n-undecyl alcohol (Tokyo Kasei Kogyo Co., Ltd) were used without further purification. Maleic anhydride and sodium bisulphite ($NaHSO_3$) were used as received (Wako Pure Chemicals Industries, Ltd). 2,2'-Azobisisobutyronitrile (AIBN) and azobenzene (AB) (Wako Pure Chemical Industries, Ltd) were recrystallized from methanol. Sodium di(2-ethylhexyl)sulphosuccinate (AOT) (Nikko Chemical Co. Ltd) was purified according to the procedure of Muto and Meguro[13]. Sodium dodecyl sulphate (SDS) (Tokyo Kasei Kogyo Co., Ltd) was used after repeated recrystallization from water. Water was deionized until it had a specific conductivity of 1 $\mu S\,cm^{-1}$ or lower, then distilled in nitrogen atmosphere. Dioxane and n-hexane were purified by distillation after dehydration over sodium wires.

Syntheses of DUSS and MUSS

DUSS and MUSS were prepared through the reactions shown in *Scheme 1*.

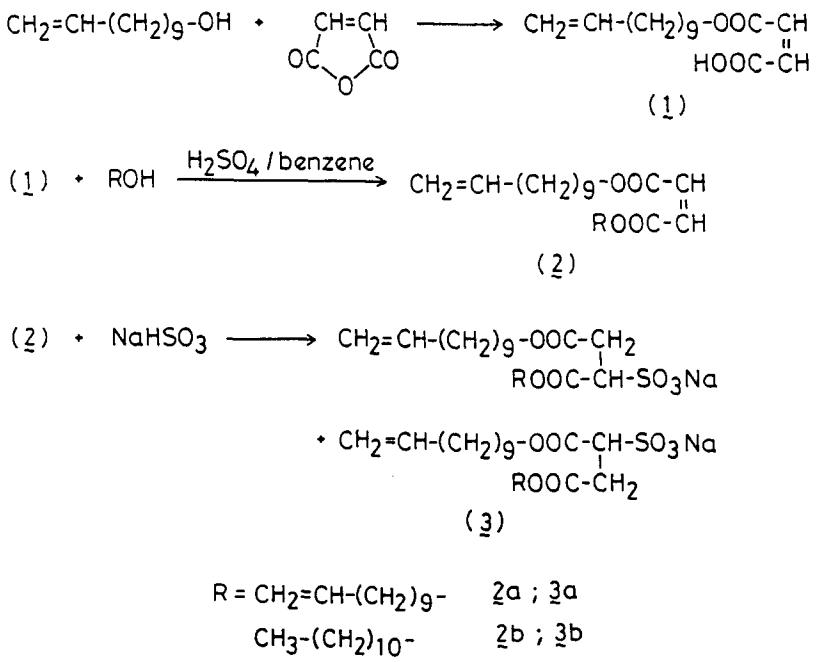
Mono(10-undecenyl) maleate (***1***). In a 200 ml flask were charged 19.6 g (0.20 mol) of maleic anhydride and 75.0 g (0.44 mol) of 10-undecen-1-ol and the mixture was heated up to about 100°C. After reaction for 3 h, the complete disappearance of maleic anhydride was confirmed by ^1H n.m.r. The solution containing the resulting monoester, denoted as solution A, was used for the subsequent preparation of the diester. The solution A was cooled to room temperature, mixed with about 200 ml of petroleum ether, then allowed to stand in a refrigerator to crystallize the monoester. The monoester was collected by filtration and recrystallized from petroleum ether: yield, 74.7%; m.p. 35.5–36.5°C.

Di(10-undecenyl) maleate (***2a***). The solution A was transferred to a 500 ml flask equipped with a Dean-Stark trap and mixed with 300 ml of benzene containing 1 ml of concentrated sulphuric acid. The mixture was heated under reflux, separating the resulting water in the trap, until the distillate was no longer turbid. The disappearance of the carboxylic group of the monoester was monitored by ^1H n.m.r. The mixture was evaporated using a rotary evaporator to remove a residual amount of benzene, mixed with about 200 ml of petroleum ether, washed with 5% $NaHCO_3$ and saturated NaCl solution, and then dried over anhydrous sodium sulphate.

10-Undecenyl undecyl maleate (***2b***) was prepared through the reaction of 38.6 g (0.14 mol) of the purified **1** with 37.0 g (0.22 mol) of n-undecyl alcohol in 200 ml of benzene containing 1 ml of concentrated sulphuric acid according to the procedure described above.

The crude esters, **2a** and **2b**, were obtained in almost quantitative yield and used for the subsequent sulphonation after distillation under reduced pressure.

DUSS (***3a***). $NaHSO_3$ (8.9 g, 85.6 mmol) was dissolved in water to prepare 40 wt% solution. The solution was mixed with 30 g (71.3 mmol) of the diester **2a** in a 100 ml flask and heated with stirring at 100°C for 24 h. The reaction mixture was then subjected to freeze drying, followed by washing with cold acetone. The residue was refluxed in methanol for 3 h and then insoluble materials (unreacted $NaHSO_3$) were separated by filtration. The filtrate was evaporated to dryness. The crude product was first recrystallized from water and then acetone. Leaflet crystals were obtained in a yield of 37%: m.p. 162–163°C.



Scheme 1

Analysis. Found: C, 57.66%; H, 8.87%. Calculated for $C_{26}H_{45}SO_7Na \cdot H_2O$: C, 57.54%; H, 8.73%.

MUSS (3b). The sulphonation of **2b** and the purification of the resulting MUSS were carried out using a similar procedure to that described for DUSS: yield, 31%; m.p. 172–173°C.

Analysis. Found: C, 57.59%; H, 9.40%. Calculated for $C_{26}H_{47}SO_7Na \cdot H_2O$: C, 57.33%; H, 9.07%.

Determination of CMC in water

The CMC of the aqueous solution was determined by an electrical conductivity method using a conductometer (Toa Model CM-2A) at 50°C. The CMC was taken as the surfactant concentration giving an inflection point in the plots of the specific conductivity as a function of the concentration. The dye solubilization method, using azobenzene as a dye, was also used to determine the CMC for DUSS. The aqueous solution of DUSS was shaken with an excess of azobenzene for more than 4 days at 50°C. Excess azobenzene was filtered off and then the absorbance of the solution was measured using a u.v. spectrophotometer to determine the amount of the solubilized azobenzene. The CMC was determined from an inflection point in the plots of the amount of the solubilized azobenzene against the surfactant concentration.

Polymerization

The polymerizations in darkness and with u.v. irradiation were carried out under nitrogen atmosphere using glass tubes (~15 ml) wrapped with aluminium foil and quartz tubes (~15 ml), respectively. The u.v. light was supplied by a high pressure mercury lamp of 400 W.

Polymerization in water was carried out using the following procedures: definite amounts of DUSS (or MUSS) and AIBN were added to 5 ml of water in the tubes and the dispersion was subjected to freeze–thaw cycles. The dispersion was sonicated with a sonicator (Bransonic Sonifier Model 52) for 20 min at 50°C to dissolve the contents and then the tube was placed in a constant temperature bath regulated at 50°C. After definite periods of time, the solution was freeze dried. The contents were transferred to a 100 ml flask, hot ethyl acetate was added, the precipitated polymer was filtered, and then washed with hot ethyl acetate.

The polymerizations in n-hexane and dioxane were also carried out after the sonication of the monomer mixture. The polymer was isolated by filtering the polymerization mixture, and then washed with hot ethyl acetate.

Measurements

I.r. spectra were recorded by a Jasco IR-S1 spectrometer using KBr pellets. ^{1}H n.m.r. spectra were obtained in CD_3OD for monomers or $(CD_3)_2SO$ for polymers by a Hitachi R-24B (60 MHz) spectrometer. U.v. and d.s.c. measurements were carried out using a spectrophotometer (Shimadzu UV-180) and differential scanning calorimeter (Daini-Seikosha DSC-100), respectively.

RESULTS AND DISCUSSION

Syntheses of DUSS and MUSS

As shown in *Scheme 1*, DUSS was prepared through the synthesis of di(10-undecenyl) maleate followed by sulphonation, and MUSS was synthesized through the esterification of mono(10-undecenyl) maleate with n-undecyl alcohol followed by the sulphonation. Both of the monomers were obtained in the form of leaflet crystals.

I.r. spectra of DUSS and MUSS are depicted in *Figures 1a* and *b*, respectively. Both spectra show characteristic peaks of vinyl groups at 3000, 1640, 1000 and 900 cm^{-1}, ester groups at 1730 and 1230 cm^{-1}, and a sulphonate group at 1160 and 1040 cm^{-1}. The absorptions due to the vinyl group for MUSS are weaker compared to those for DUSS, corresponding to the number of the vinyl group. The relatively sharp absorption at about 3600 cm^{-1} seems to be due to the formation of a hydrate, as demonstrated by the results of the elemental analysis.

^{1}H n.m.r. spectra of DUSS and MUSS are shown in *Figures 2a* and *b*, respectively. The spectra are very similar

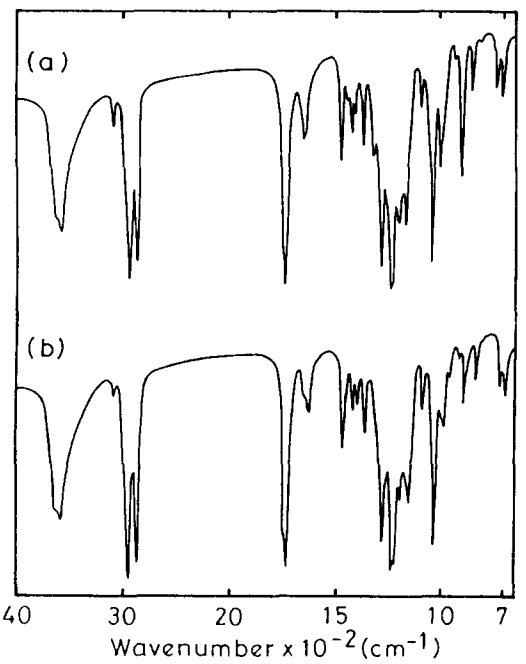


Figure 1 I.r. spectra of (a) DUSS and (b) MUSS

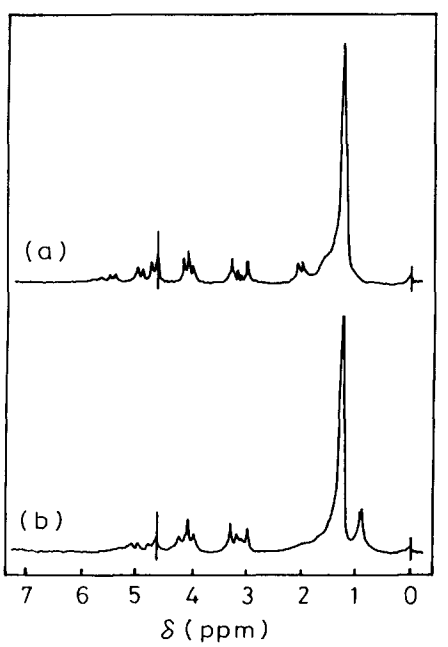


Figure 2 ^{1}H n.m.r. spectra of (a) DUSS and (b) MUSS

to that of AOT recorded in CD_3OD[14]. The peak at $\delta = 0.8$ for MUSS is due to methyl protons (3H). The spectra exhibit several peaks due to a variety of methylene groups: $-CH_2-CH_2-CH_2-$ at $\delta = 1.1$–1.8 (28H for DUSS and 32H for MUSS), $=CH-CH_2-$ at $\delta = 1.8$–2.2 (4H for DUSS and 2H for MUSS), $-CO-CH_2-$ at about $\delta = 3.1$ (2H) and $-O-CH_2-$ at $\delta = 4.0$–4.3. The peaks at $\delta = 4.0$–4.3 (5H) include those due to the methine proton on the carbon atom substituted with the sulphonate group. The multiple peaks in the range of $\delta = 4.7$–6.3 arise from vinyl protons (6H for DUSS and 3H for MUSS). The spectra also reveal the peaks resulted from CH_3OH and H_2O at about $\delta = 3.3$ and 4.7, respectively. The former is due to the water of crystallization contained in the monomers and the latter is involved in the solvent (CD_3OD) used for the measurements.

For MUSS, there are two possible structures having the sulphonate group at a different position of the succinate group. Even the ^{13}C n.m.r. spectrum gave no definite evidence for the identification, though the purified MUSS was obtained as crystals and exhibited a relatively sharp melting point like a compound. However, MUSS could be composed of two isomers.

Properties of DUSS and MUSS

The solubilities of DUSS and MUSS are shown in *Table 1*, together with that of AOT. It is well known that AOT is soluble in not only polar solvents such as water, methanol and DMF but also apolar solvents such as n-hexane and benzene, though insoluble in acetonitrile. The solubilities of these monomers on heating are quite similar to those of AOT, except that the monomers are insoluble in diethyl ether. Moreover, MUSS appears to have lower solubility in solvents compared to DUSS which is less soluble than AOT.

As shown in *Table 1*, both DUSS and MUSS are hardly soluble in water at room temperature, whereas they were observed to dissolve above a certain temperature on heating, indicating the presence of the Kraft point[15]. The temperature dependences of the specific conductivity for the aqueous dispersions of DUSS and MUSS are depicted in *Figure 3*. For both dispersions, the conductivity gradually increases with increasing temperature and then steeply rises near about 39°C and 48°C for DUSS and MUSS, respectively. Such temperature dependences of the conductivity can be mainly ascribed to the variation

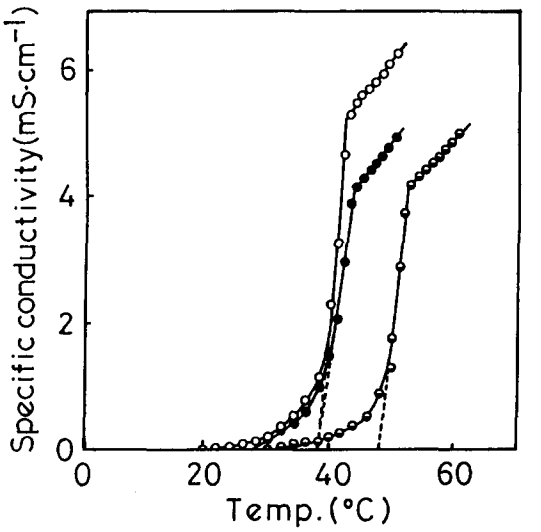


Figure 3 Temperature dependences of specific conductivity for the aqueous suspensions of DUSS and MUSS. ○, DUSS 1.0 g/water 30 ml; ●, DUSS 0.5 g/water 30 ml; ◒, MUSS 0.5 g/water 30 ml

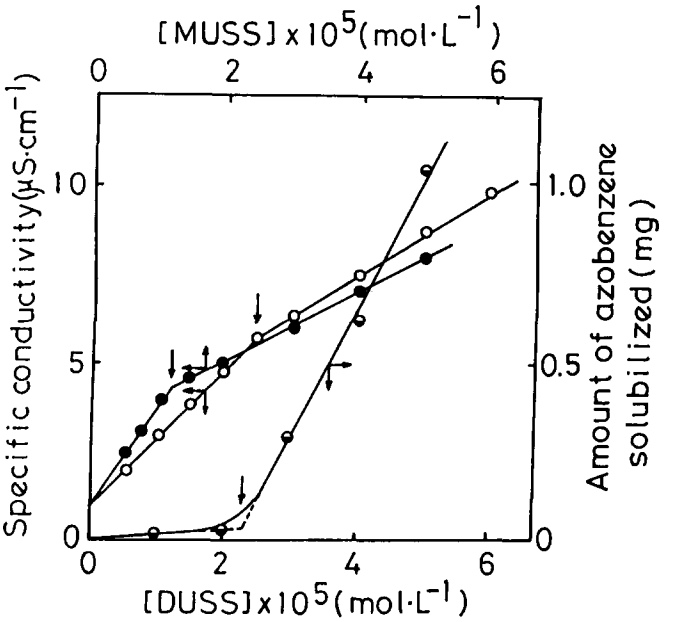


Figure 4 Concentration dependences of specific conductivity and amount of azobenzene solubilized (for 20 ml solution) for DUSS and MUSS solutions in water at 50°C. The arrows refer to the critical micelle concentrations

Table 1 Solubilities[a] of DUSS, MUSS and AOT at room temperature (R) and on heating (H)

	DUSS		MUSS		AOT	
Solvent	R	H	R	H	R	H
n-Hexane	−	+	−	+	+	+
Diethylether	−	−	−	−	+	+
Carbon tetrachloride	−	+	−	+	+	+
Benzene	−	+	−	+	+	+
Ethyl acetate	−	+	−	+	+	+
Dioxane	+	+	−	+	+	+
Chloroform	+	+	−	+	+	+
Acetone	−	+	−	+	+	+
Acetonitrile	−	−	−	−	−	−
Methanol	+	+	+	+	+	+
Dimethylformamide	+	+	+	+	+	+
Water	−	+	−	+	+	+

[a] +, Soluble; −, insoluble

in the solubility of the monomers with temperature, because the onset of dissolution at these temperatures was also observed with the naked eye. The solubility of ionic surfactants in water is known to increase dramatically at a temperature slightly above the Kraft point[15]. Moreover, a steep rise in the conductivity was also observed at about 16°C for SDS, which is in good agreement with the Kraft point, 16°C[16]. Therefore, the Kraft points for DUSS and MUSS are at about 39°C and 48°C, respectively.

The determination of CMC in water was carried out at 50°C above the Kraft points. *Figure 4* shows plots of the specific conductivity of aqueous solutions of DUSS and MUSS against their concentration, together with a dependence of the amount of azobenzene solubilized in a fixed volume of DUSS solution on the concentration. The conductivity depends linearly on the concentration

Table 2 Critical micelle concentration ($mol\,l^{-1}$)

	Conductivity	Dye solubilization	Reference
DUSS	2.5×10^{-5} (50°C)	2.3×10^{-5} (50°C)	This work
MUSS	1.2×10^{-5} (50°C)	–	This work
AOT	3.8×10^{-3} (25°C)	3.3×10^{-3} (25°C)	This work
AOT	–	4.1×10^{-3} (25°C)	25
AOT	–	3.5×10^{-3} (30°C)	26
AOT	3.7×10^{-3} (30°C)	–	26

with an inflection point referred to as the CMC. The CMC values for DUSS and MUSS are presented in *Table 2*, together with that of AOT. As predicted from the difference in the carbon number of hydrocarbon chains, the CMC values of DUSS and MUSS are considerably lower than that of AOT. In general, a linear relationship is known to exist between the logarithm of CMC and the number of carbon atoms (N) in the alkyl chain for surfactants. The following relationship has been reported for sodium n-dialkylsulphosuccinate in water at 50°C[17]: $\log CMC = 2.08 - 0.681N$, where CMC is expressed in $mol\,l^{-1}$ and N is the number of carbon atoms for one alkyl ester group. The CMC values of DUSS gave about 10 for N and hence the vinyl group appears to correspond to one methyl group. On the other hand, the CMC value of MUSS is reduced to a half of that for MUSS because of a decreased number of unsaturation in the alkyl chain.

Sodium n-dialkylsulphosuccinates having an alkyl chain with more than 10 carbon atoms have been reported to form large vesicles or lamella in water[18] and to exhibit the phase transition behaviour of bilayer membranes[19]: sodium di(n-dodecyl)sulphosuccinate shows the phase transition temperature at 28°C with the transition enthalpy of $23\,kJ\,mol^{-1}$, while these values for sodium di(n-decyl)sulphosuccinate were not assigned. The sonicated sample of DUSS in water exhibited only an endothermic peak at 40°C, which is near the Kraft point, with enthalpy of $63\,kJ\,mol^{-1}$. The enthalpy is too large compared to the transition enthalpy reported for bilayer membranes of such dialkyl amphiphiles[20]. Therefore, the endothermic peak for DUSS solution can be ascribed to the steep variation in the solubility at the temperature corresponding to the Kraft point. On the other hand, di(10-undecenyl)phosphate has been reported to form vesicles from the aqueous solution, based on electron microscopic observation[21]. Thus, the aqueous solution of DUSS seems to assume an aggregated structure like bilayer membranes, which is of lower order.

Polymerizations of DUSS and MUSS

The results of the polymerization of DUSS in darkness and under u.v. irradiation in three different solvents are presented in *Table 3*. The solvents—water, n-hexane and dioxane—were used for the polymerizations to examine the effect of monomer aggregation on the polymerization behaviour. The monomer solution in n-hexane was observed to develop a characteristic colour on addition of 7,7,8,8-tetracyanoquinodimethane and hence the monomers in n-hexane are in the aggregated state, so-called reverse micelles[22], where the polar heads of the DUSS are buried in the central core as opposed to micelles in water. The solutions in dioxane are isotropic[23].

Only a trace of the polymer is formed for the polymerizations with a radical initiator in darkness, as predicted from the allyl group as a polymerizable group. On the other hand, the polymerizations under u.v. irradiation give polymers in three systems studied here, though the yields are not so high.

In *Table 4* are shown the results of polymerization of MUSS in three solvents giving different solution systems. Similarly to the polymerizations of DUSS, the polymerizations in darkness give only a trace of polymers. Furthermore, polymers are formed for the polymerization systems in n-hexane and water under u.v. irradiation. However, polymerization in dioxane affords only a trace of polymer even under u.v. irradiation. Thus, there seems to be a more pronounced effect of solvents, which affect the structures of monomer aggregates, on the polymerization of MUSS rather than that of DUSS, though the reason remains unclear at present.

Solubilities of the resulting polymers

Table 5 shows the solubilities of the resulting polymers in solvents such as DMF, methanol and water. The polymers of DUSS yielded by polymerizations in n-hexane and dioxane are swollen or insoluble, while polymerization in water yields a polymer soluble in DMF and water. I.r. and ^1H n.m.r. spectra for the polymer formed in water are presented in *Figure 5*. These spectra reveal the existence of residual vinyl groups and the n.m.r.

Table 3 Polymerization of DUSS at 50°C[a]

Run no.	Polymerization			Yield (%)
	Method	Solvent	Time (h)	
1	Dark	Hexane	120	Trace
2	U.v. irrad.	Hexane	48	27.9
3	Dark	Dioxane	96	Trace
4	U.v. irrad.	Dioxane	24	19.9
5	Dark	Water	24	Trace
6	U.v. irrad.	Water	24	18.4

[a] DUSS, 1 mmol; AIBN, 10 mol%; solvent, 5 ml; temperature, 50°C

Table 4 Polymerization of MUSS at 50°C[a]

Run no.	Polymerization			Yield (%)
	Method	Solvent	Time (h)	
7	Dark	Hexane	72	Trace
8	U.v. irrad.	Hexane	48	12.7
9	Dark	Dioxane	96	Trace
10	U.v. irrad.	Dioxane	48	Trace
11	Dark	Water	96	Trace
12	U.v. irrad.	Water	24	26.7

[a] MUSS, 1 mmol; AIBN, 10 mol%; solvent, 5 ml; temperature, 50°C

Table 5 Solubilities of poly(DUSS) and poly(MUSS) on heating

Polymer	Run no.[a]	Solubility[b] in		
		DMF	Methanol	Water
Poly(DUSS)	2	+/−	+/−	+/−
	4	+/−	−	+/−
	6	+	+/−	+
Poly(MUSS)	8	+	+	+
	12	+/−	−	+

[a] For the polymerizations see *Tables 3* and *4*
[b] +, Soluble; +/−, swollen; −, insoluble

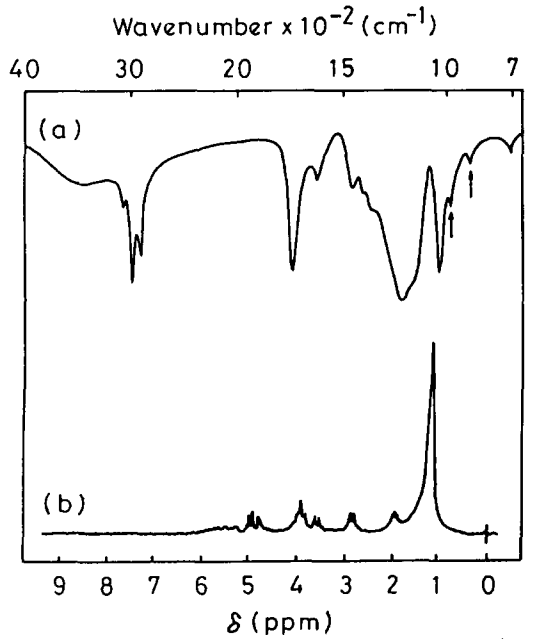


Figure 5 (a) I.r. and (b) ^1H n.m.r. spectra of poly(DUSS) prepared in water (run no. 6 in *Table 3*). The arrows refer to the absorption of vinyl groups

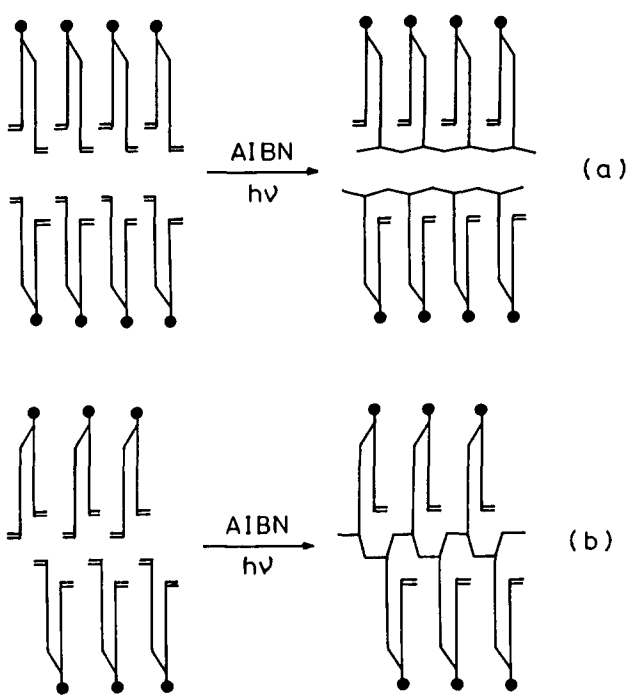


Figure 6 Schematic representations of the polymerization of DUSS in water: propagation (a) and /or (b)

spectrum showed that about one of two vinyl groups in the monomer remains unreacted. Similar results have been found for the polymerization of di(10-undecenyl) phosphate[21].

DUSS is a bifunctional monomer and hence it could be susceptible to crosslinking during polymerization. In n-hexane the vinyl groups are distributed over the outer surface of reverse micelles and in dioxane the monomer exists in the form of free monomer. Thus, polymerizations in these systems could be liable to crosslinking, resulting in the formation of insoluble polymers. On the other hand, soluble polymer is obtained for polymerization in an aqueous system. In water, the vinyl groups are directed to the inner side of probable bilayer membranes and polymerization could proceed within the aggregated structure. DUSS has two vinyl groups at different distances from the polar head. Therefore, it is likely that only one of two vinyl groups takes part in the polymerization (see *Figure 6*), as suggested for the polymerization of a phospholipid having a diacetylene group in the alkyl chains[24].

On the other hand, soluble polymers are formed for both polymerization systems of MUSS in n-hexane and water, as predicted from the monofunctional monomer.

Thus, the formation of aggregated structures such as micelles (or vesicles) and reverse micelles affects not only the polymerization rate but also the structure of the resulting polymers.

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