Polymerization of surface-active monomers: 4. Copolymerization of long-chain alkyl salts of 2-dimethylaminoethyl methacrylate with methyl methacrylate or styrene

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(Received 27 March 1991; revised 24 May 1991; accepted 5 June 1991)

Radical copolymerizations of cationic, surface-active monomers, such as lauryl ($C_{12}Br$), octyl (C_8Br) and cetyl ($C_{16}Br$) bromide salts of 2-dimethylaminoethyl methacrylate with methyl methacrylate (MMA) or styrene (ST) have been studied in water and N,N-dimethylformamide (DMF) as solvent, giving an anisotropic and an isotropic solution, respectively. For both comonomer systems, the copolymerizations of $C_{12}Br$ in water were faster and exhibited a higher tendency toward alternation compared to those in DMF. It was deduced that the copolymerization in water mainly takes place at palisade layers of micelles of the cationic monomer, being responsible for increased rate and alternation of the copolymerization. The Q and e values of $C_{12}Br$ were determined on the results of the copolymerization in DMF and both were found to be higher than those of 2-dimethylaminoethyl methacrylate (DMAEMA). Such higher Q and e values for the cationic monomer could be due to an intramolecular interaction of the oxygen atom of carbonyl group with the positively charged ammonium group.

The copolymers of $C_{12}Br$ prepared here were characterized by solubility in water, solution viscosity and solubilization of azobenzene in the aqueous solution. Other micelle-forming monomers, C_8Br and $C_{16}Br$, were also used to study the effect of alkyl chain length on the copolymerization.

(Keywords: copolymerization; surface-active monomer; long-chain alkyl salt; 2-dimethylaminoethyl methacrylate; styrene; methyl methacrylate)

INTRODUCTION

Surface-active monomers are molecules having both a hydrophobic and a hydrophilic component in their structure in addition to a polymerizable group. These monomers associate in water above a certain concentration, the so-called critical micelle concentration (*cmc*), to form micellar aggregates. Many studies have been devoted to the micellar effect of monomers on polymerization[1–9]. It has been found in various systems that monomer micellization accelerates polymerization. For example, even allyl monomers such as sodium 10-undecenoate[1] and allyldimethyldodecylammonium bromide[2] have been shown to exhibit considerable polymerizability at a concentration above their *cmc*. Moreover, the current authors have found that the polymerization of lauryl bromide salt of DMAEMA, a cationic surface-active monomer, in both an aqueous and inverse micellar solution affords polymers having exceptionally high molecular weight[3,4]. Thus, monomer micellization definitely appears to facilitate polymerization. On the other hand, little has been known about the effect of monomer micellization on the copolymerization of micelle-forming monomers with vinyl monomers. Although Salamone *et al.*[10] reported a change of copolymerization parameters by a monomer micellization for the copolymerization of a surface-active monomer, 3-n-dodecyl-1-vinylimidazolium iodide, with *N*-vinylpyrrolidone, such a fact has not been confirmed in other copolymerization systems.

Surface-active monomers have also received considerable attention because of their application as polymerizable emulsifiers[11–17]. However, they have often been used without taking into account their copolymerization characteristics. Therefore, studies on the copolymerization of surface-active monomers with vinyl monomers will provide useful information about emulsion polymerization by using a polymerizable emulsifier.

The present paper deals with the copolymerizations of cationic surface-active monomers C_8Br, $C_{12}Br$ and $C_{16}Br$ with MMA or ST in isotropic and anisotropic solutions to obtain an insight into the effect of micelle formation of monomers on the rate of copolymerization and the composition of the resulting copolymers. The resulting copolymers of $C_{12}Br$ were characterized from data on solubility in water, solution viscosity and solubilization of a dye into the aqueous solutions.

EXPERIMENTAL

Reagents

Preparation and purification of cationic, surface-active monomers used here were described in our previous papers[3,4]. Methyl methacrylate (MMA) and styrene (ST), both from Wako Pure Chemicals Ind. Ltd, were employed after purification by conventional procedures. Initiators, potassium persulphate (KPS) and 2,2′-azobisisobutyramidine dihydrochloride (AIBA), reagent grade,

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were used as received from Wako Pure Chemicals Ind. Ltd. 2,2'-Azobisisobutyronitrile (AIBN, from Tokyo Kasei Ind. Co. Ltd) was recrystallized from methanol, followed by reprecipitation by using a benzene–cyclohexane system to obtain a fine powder. Preparation and purification of phenylazonaphthylthioether (ATE) were described elsewhere[4].

Water was deionized until it had a specific conductivity of 1×10^{-6} S cm^{-1} or lower and was then distilled in a nitrogen atmosphere. Dimethylformamide (DMF) was purified by distillation after dehydration over calcium hydride.

Copolymerization

For copolymerization in water, initiator, surface-active monomer and comonomer were charged in a polymerization tube (*ca.* 10 ml). Water was added to the mixture, which was then agitated at room temperature for about 30 min to obtain a homogeneous solution. The tube was degassed by a freeze–thaw technique, sealed in nitrogen atmosphere, and then placed in a constant-temperature bath thermostatically controlled at 50°C. After a definite period of time, the polymerization was terminated by the addition of water-soluble inhibitor (cupferron, nitrosophenylhydroxylamine ammonium salt). After freeze-drying the solution, the content was transferred to a large volume of hot ethyl acetate and the precipitated copolymer was filtered, washed with hot ethyl acetate, then dried in vacuum.

When DMF was used as the copolymerization solvent, the monomer solution was placed in a constant-temperature bath for a definite period of time. The polymerization mixture was poured into a large volume of ethyl acetate containing a small amount of *p*-methoxyphenol. The isolation of the copolymer was effected according to the procedures shown for the copolymerization in water.

The copolymer composition was estimated from Br content determined by a combustion flask method and elemental analysis of C, H and N.

Solubilization

Aqueous solution of the copolymer was shaken with an excess of azobenzene at 25°C for more than 4 d. Excess azobenzene was filtered off and then the resulting coloured solution was subjected to u.v. measurements by using a Shimadzu UV-180 spectrometer to determine the amount of azobenzene solubilized.

Characterization of the copolymers

I.r. and n.m.r. spectra were recorded by a Nihon Bunko S1 and a Hitachi R-24B spectrometer, respectively. Elemental analysis was made by using a Yanaco CHN analyser.

The viscosity of the resulting copolymers was measured by using a Ubbelohde viscometer at 25°C.

RESULTS AND DISCUSSION

Copolymerization of $C_{12}Br$ with MMA

The results of the copolymerization of $C_{12}Br$ with MMA in water and DMF at an equimolar monomer composition in the feed are presented in *Figures 1* and *2*, respectively. The monomer concentration of $C_{12}Br$ in water is well above the *cmc* (6.02×10^{-3} mol l^{-1} at 25°C) and MMA is completely solubilized in the micellar solution to form an apparently homogeneous solution. DMF gives an isotropic monomer solution and also dissolves the resulting copolymers. The copolymerization proceeds homogeneously even in water over a whole range of conversion because the resulting copolymers were water-soluble in contrast with the respective homopolymers. Four kinds of initiators were used here: water-soluble KPS and AIBA, and oil-soluble AIBN and ATE. The last two initiators were solubilized into micelles in water. For all initiators used here, copolymerization in water is definitely faster than that in DMF. In particular, the copolymerization with AIBA exhibits a marked increase in the rate with a change in solvent from DMF to water, although the reason remains unclear at present.

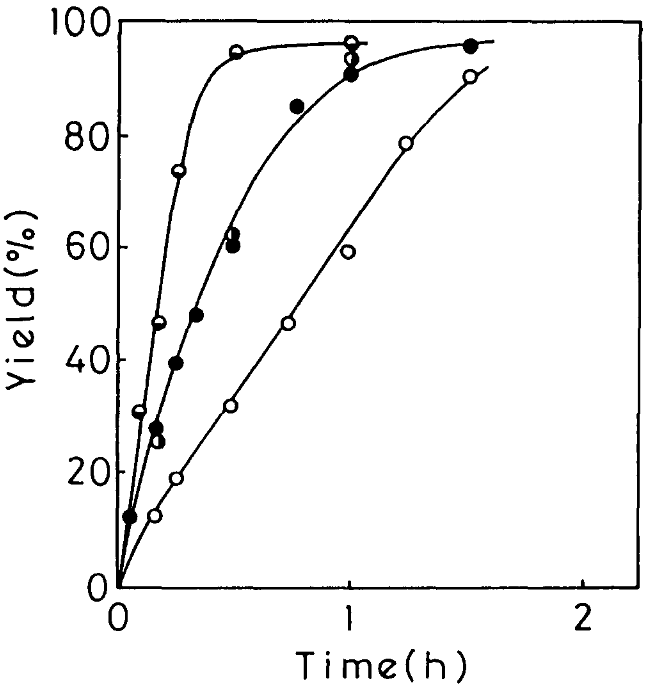

Figure 1 Copolymerization of $C_{12}Br$ with MMA in water at 50°C. Initiator: (○) AIBN; (●) KPS; (◑) ATE; (◒) AIBA; $[C_{12}Br]$ = [MMA] = 0.40 mol l^{-1}; [initiator] = 8.0×10^{-3} mol l^{-1}

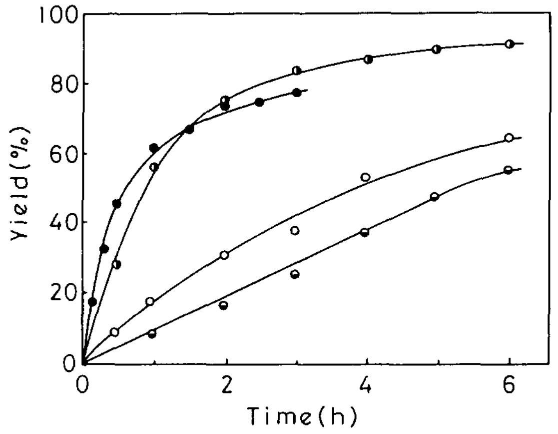

Figure 2 Copolymerization of $C_{12}Br$ with MMA in dimethylformamide at 50°C. Initiator: (○) AIBN; (●) KPS; (◑) ATE; (◒) AIBA; $[C_{12}Br]$ = [MMA] = 0.40 mol l^{-1}; [initiator] = 8.0×10^{-3} mol l^{-1}

As mentioned above, MMA is completely solubilized in the micellar solution of $C_{12}Br$ and hence the copolymerization in water appears mainly to proceed in micelles.

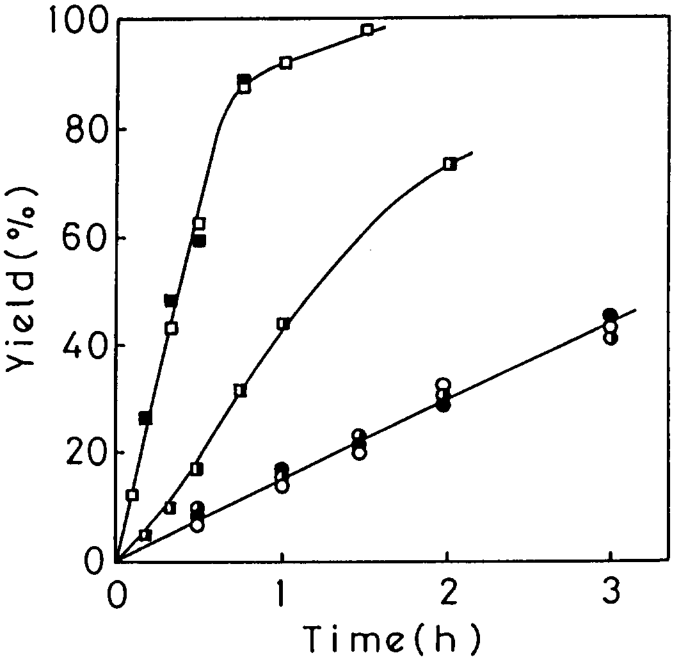

Figure 3 Copolymerizations of C_8Br, $C_{12}Br$ and $C_{16}Br$ with MMA in water and dimethylformamide at 50°C. Copolymerization system (monomer/initiator/solvent): (◑) C_8Br/DMF/AIBN; (○) $C_{12}Br$/DMF/AIBN; (●) $C_{16}Br$/DMF/AIBN; (◨) C_8Br/water/KPS; (□) $C_{12}Br$/water/KPS; (■) $C_{16}Br$/water/KPS; $[C_NBr] = [MMA] = 0.40\ mol\ l^{-1}$, where N is 8, 12 and 16; $[initiator] = 8.0 \times 10^{-3}\ mol\ l^{-1}$

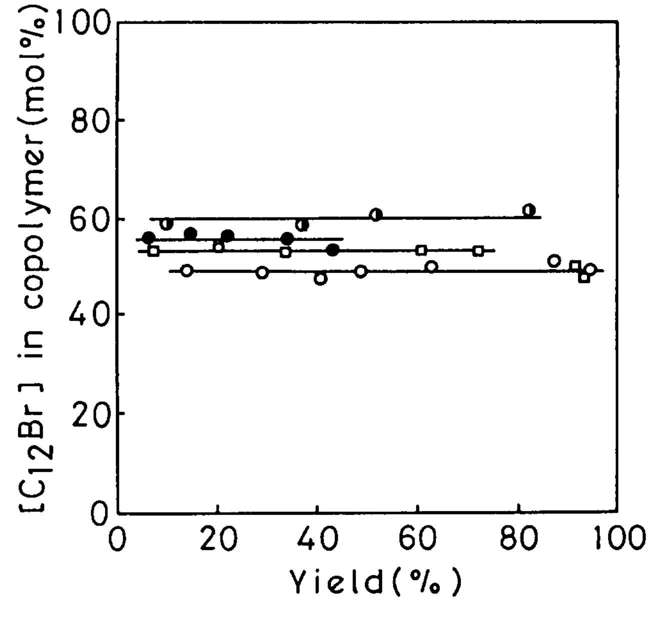

Figure 4 Dependence of the copolymer composition on the yield for the copolymerizations of $C_{12}Br$ with MMA and ST at 50°C. Comonomer/initiator/solvent/$C_{12}Br$ in monomers: (○) MMA/KPS/water/50 mol%; (◑) MMA/KPS/water/70 mol%; (●) MMA/AIBN/DMF/50 mol%; (□) ST/KPS/water/50 mol%; $[C_{12}Br] + [MMA] = 0.80\ mol\ l^{-1}$; $[initiator] = 8.0 \times 10^{-3}\ mol\ l^{-1}$

Therefore, such increased rate of copolymerization in water can be attributed to the micellization of the cationic monomer.

Figure 3 shows the results of the copolymerizations of MMA with cationic monomers having a different alkyl chain length. The rate of copolymerization in DMF is hardly dependent on the alkyl chain length. However, a change of C_8Br to $C_{12}Br$ in the cationic monomer causes a large increase in the rate of copolymerization, whereas the rate of copolymerization with $C_{16}Br$ is approximately the same as that with $C_{12}Br$. Similarly, little difference in the rates was observed for the polymerizations of $C_{12}Br$ and $C_{16}Br$[4]. Although all of the cationic monomers used here have a micelle-forming property in water, the value of *cmc* is dependent on the alkyl chain length[3,4]. The initial proportion of the monomer in micellar state can be expressed as $(c_0 - cmc)/c_0$, where c_0 is an initial monomer concentration ($0.40\ mol\ l^{-1}$). The calculated proportion is 0.66, 0.98 and 1.00 for C_8Br, $C_{12}Br$ and $C_{16}Br$, respectively. Thus, a variation in this value is in fairly good agreement with dependence of the rate of copolymerization on the alkyl chain length. This result also supports the view that micelles provide the main loci of the copolymerization.

Figure 4 represents the dependence of the copolymer composition on the copolymer yield for the copolymerization of $C_{12}Br$ with MMA, together with that with ST. The copolymer composition is little dependent on the copolymer yield up to a considerable value, especially for the copolymerization at a feed composition of $C_{12}Br$ of 70 mol% in water. *Figure 5* represents the copolymer composition as a function of monomer composition. The copolymer composition was determined for the copolymers obtained at a low copolymer yield. The copolymerization in DMF proceeded homogeneously over the whole range of the monomer composition examined. As shown by the composition curve for copolymerization in DMF, $C_{12}Br$ is slightly more reactive than MMA, though they have the same polymerizable group. The monomer reactivity ratios of MMA (M_1) and $C_{12}Br$ (M_2) estimated by the Kelen–Tüdös method[18] were $r_1 = 0.64$ and $r_2 = 0.89$, respectively. The monomer solution in water was faintly opaque at a feed composition of $C_{12}Br$ below about 30 mol%. However, there appears to be no definite discontinuity in the copolymer composition curve, as can be seen in *Figure 5*. The monomer

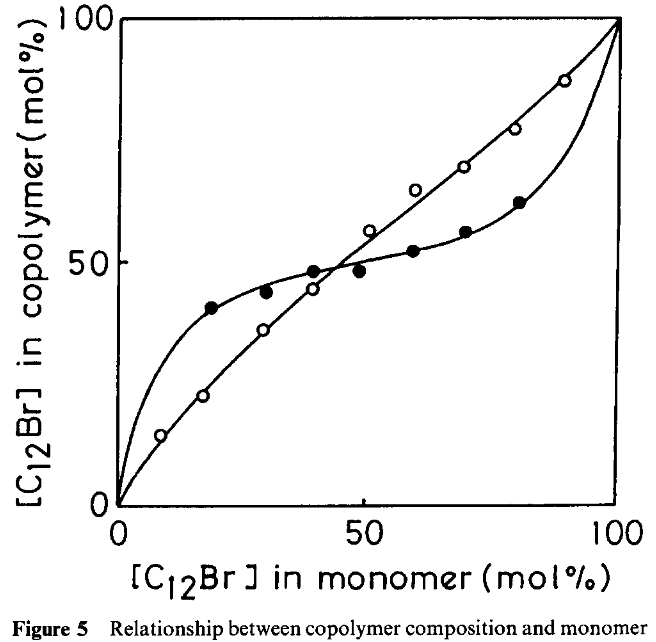

Figure 5 Relationship between copolymer composition and monomer composition for the copolymerization of $C_{12}Br$ with MMA in dimethylformamide and water at 50°C. Initiator/solvent: (○) DMF/AIBN; (●) water/KPS; $[C_{12}Br] + [MMA] = 0.80\ mol\ l^{-1}$; $[initiator] = 8.0 \times 10^{-3}\ mol\ l^{-1}$. Solid lines represent curves calculated on the monomer reactivity ratios shown in *Table 1*

reactivity ratios for copolymerization in water were 0.13 and 0.16 for MMA and $C_{12}Br$, respectively, indicating that copolymerization in water becomes more alternating.

Copolymerization of $C_{12}Br$ with ST

The copolymerization system of $C_{12}Br$ with ST at an equimolar feed composition remained homogeneous in both water and DMF over a whole range of conversion, similarly to the copolymerization system involving MMA as a comonomer. As shown in *Figure 6*, copolymerization in water was also faster than that in DMF for two initiators. Little variation in the copolymer composition with conversion was also observed, as shown in *Figure 4*.

Figure 7 shows dependences of the copolymer composition on the monomer composition for copolymerization in both solvents. The copolymerization systems exhibited appearances similar to those involving MMA as a comonomer for both solvents and the monomer solution in water became slightly turbid at a feed composition of $C_{12}Br$ below 30 mol%. The monomer reactivity ratios for $C_{12}Br$ and ST were determined by the Kelen–Tüdös method[18] to be 0.22 and 0.40 in DMF and 0.02 and 0.16 in water. These values also indicate that a change of solvent from DMF to water leads to the copolymerization having a higher alternating tendency.

Copolymerization data obtained here are summarized in *Table 1*, together with those for C_8Br and $C_{16}Br$ as a cationic monomer determined from composition curves shown in *Figure 8*. Higher alternating tendency of the copolymerizations in water could be related to loci of the copolymerization in the micelles. The polymerizable group of the cationic monomer is relatively near to a head group, and hence the groups in the micelles should be also located near the surfaces of the micelles. Both MMA and ST used here as a comonomer are polarizable molecules, and hence they will be solubilized into palisade layers of the micelles rather than the cores[19]. Since the palisade layers near the surfaces of micelles have a limited capacity to solubilize, a local monomer composition in the layers will be different from the overall monomer composition, probably being close to an equimolar composition.

In *Table 1* Q and e values of $C_{12}Br$ calculated by using the reactivity ratios for the copolymerizations in DMF, together with those of DMAEMA, are included. The calculation of Q and e values was not made with the copolymerization data in water because it seems incorrect to relate the reactivity ratios obtained for microheterogeneous systems to Q and e values. As shown in *Table 1*, both Q and e values of $C_{12}Br$ are relatively larger than those of non-ionic DMAEMA, although they

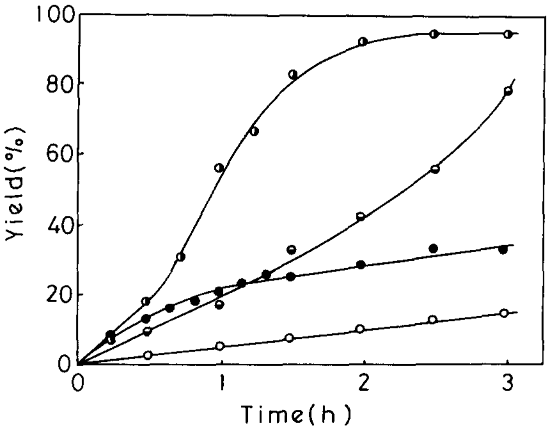

Figure 6 Copolymerization of $C_{12}Br$ with ST in water and dimethylformamide at 50°C. Initiator/solvent: (○) AIBN/DMF; (●) KPS/DMF; (○) AIBN/water; (◑) KPS/water; $[C_{12}Br] = [ST] = 0.40\ mol\ l^{-1}$; $[initiator] = 8.0 \times 10^{-3}\ mol\ l^{-1}$

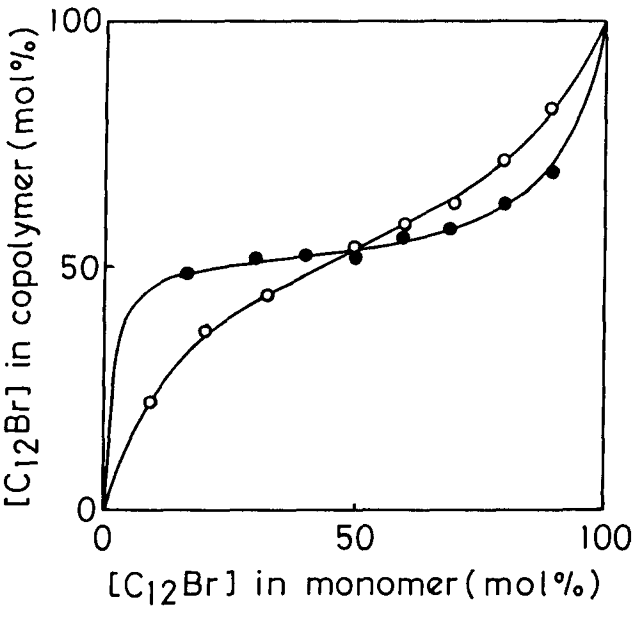

Figure 7 Relationship between copolymer composition and monomer composition for the copolymerization of $C_{12}Br$ with ST in water and dimethylformamide (DMF) at 50°C. Initiator/solvent; (○) AIBN/DMF; (●) KPS/water; $[C_{12}Br] + [ST] = 0.80\ mol\ l^{-1}$; $[initiator] = 8.0 \times 10^{-3}\ mol\ l^{-1}$. Solid lines represent curves calculated on the monomer reactivity ratios shown in *Table 1*

Table 1 Copolymerization parameters[a]

M_1	M_2	System[b]	r_1	r_2	r_1r_2	Q_2	e_2
MMA	C_8Br	KPS/water	0.26	0.06	0.016		
MMA	$C_{12}Br$	KPS/water	0.13	0.16	0.021		
MMA	$C_{12}Br$	AIBN/DMF	0.64	0.89	0.570	1.6	1.2
MMA	$C_{16}Br$	KPS/water	0.16	0.08	0.013		
ST	$C_{12}Br$	KPS/water	0.02	0.16	0.003		
ST	$C_{12}Br$	AIBN/DMF	0.22	0.40	0.088	1.3	0.81
ST	DMAEMA[c]	Bulk[d]	0.53	0.37	0.195	0.68	0.48

[a] At 50°C

[b] KPS, potassium persulphate; AIBN, azobisisobutyronitrile; DMF, dimethylformamide

[c] 2-Dimethylaminoethyl methacrylate. Copolymerization parameters are cited from 'Functional Monomers' (ed. R. H. Yocum and E. B. Nyquist), Marcell Dekker, Inc., New York, 1974, p. 690

[d] At 60°C

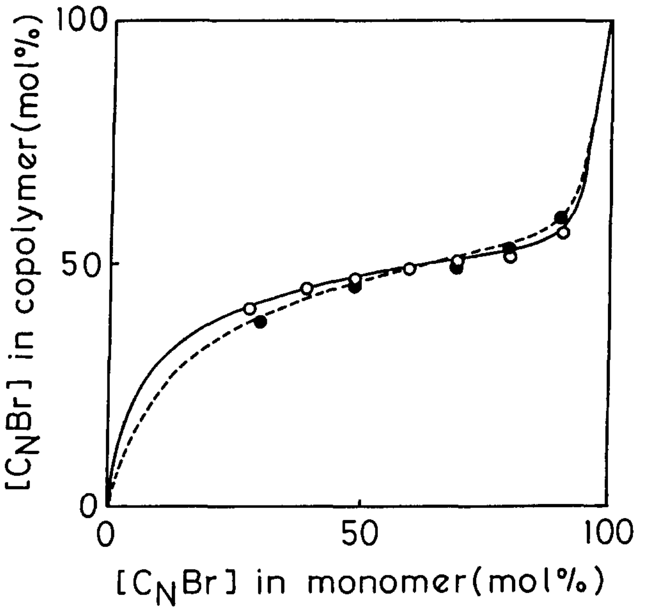

Figure 8 Relationship between copolymer composition and monomer composition for the copolymerizations of C_8Br and $C_{16}Br$ with MMA in water at 50°C: (●) C_8Br; (○) $C_{16}Br$; $[C_NBr] + [MMA] = 0.80 \text{ mol } l^{-1}$, where N is 8 and 16; $[KPS] = 8.0 \times 10^{-3} \text{ mol } l^{-1}$. Solid and broken lines represent curves calculated on the monomer reactivity ratios shown in *Table 1*

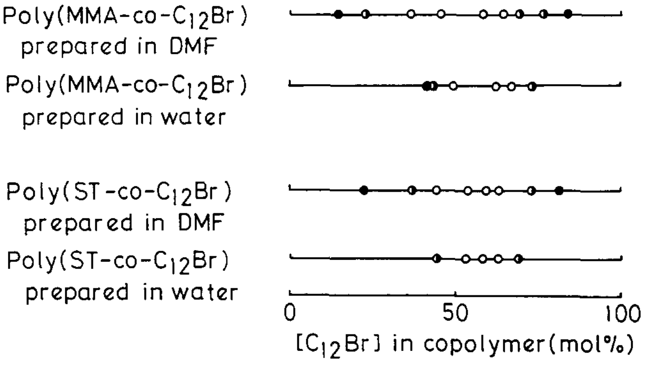

Figure 9 Solubility of the resulting copolymers in water: (○) soluble; (◑) swollen; (●) insoluble

slightly vary with the comonomers used for the copolymerizations.

Hamid and Sherrington[5] interpreted a facile hydrolysis of the cationic monomers used here in a high pH medium in terms of an intramolecular interaction of the oxygen atom of the carbonyl group with the quaternary nitrogen centre[5]. Such an interaction will lead to a longer conjugated system between a vinyl and carbonyl group in the monomer and a lower electron density of the vinyl group, resulting in increased Q and e values.

Properties of the resulting copolymers

The copolymers prepared here exhibited characteristic solubilities, especially in water. As mentioned earlier, the resulting copolymers having an approximately equimolar composition are soluble in water, although the respective homopolymers are water-insoluble.

As shown in *Figure 9*, the solubilities of the copolymers containing $C_{12}Br$ units are dependent on the copolymer composition. The composition range where the copolymer is soluble in water changes with the copolymerization system. The copolymers prepared in DMF appear to exhibit a wider composition range. This difference probably results from differences in the microstructures of the copolymers such as a sequence distribution of the monomer units and a tacticity.

Figure 10 shows concentration dependences of reduced viscosity for the copolymers of $C_{12}Br$ having an approximately equimolar composition in water and methanol. The copolymers behave as polyelectrolytes in both solvents. Moreover, it can be seen that the copolymer prepared in water exhibits a higher viscosity and that the viscosity in water becomes lower. Therefore, the copolymerizations under micellar conditions may give copolymers having a higher molecular weight, as observed in the polymerization of the cationic monomers[3,4]. Furthermore, such lower viscosity in aqueous solution will be related to the formation of 'polysoap' structures[20,21], which makes conformations of the copolymers more compact.

Figure 11 shows the results on the solubilization of azobenzene in aqueous solutions of the copolymers of $C_{12}Br$ with an approximately equimolar composition. A higher ability to solubilize is observed for the copolymers in comparison with the monomer. In general, the solubilization in a surfactant solution takes place above the *cmc*[19]. The solubilization behaviour of the copolymers shown here reflects 'polysoap' structures – intramolecular micelles – in water. As shown in *Figure 11*, the copolymers prepared in water have a higher ability to solubilize, compared with those synthesized in DMF. This may result from a difference in molecular weight of the copolymers.

Thus, the copolymerizations of cationic, surface-active monomers with hydrophobic vinyl monomers such as MMA and ST were also found to be accelerated under micellar conditions, as observed in the polymerizations

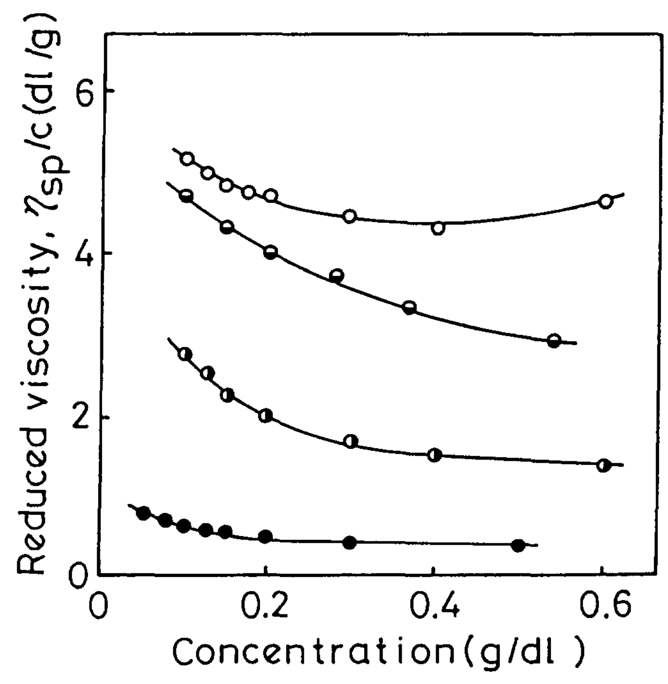

Figure 10 Concentration dependences of reduced viscosity of the resulting copolymers of $C_{12}Br$ having an approximately equimolar composition at 25°C. Comonomer/solvent for the copolymerization/solvent for the viscosity measurement: (○) MMA/water/water; (⊖) MMA/DMF/methanol; (◑) MMA/DMF/water; (●) ST/DMF/water

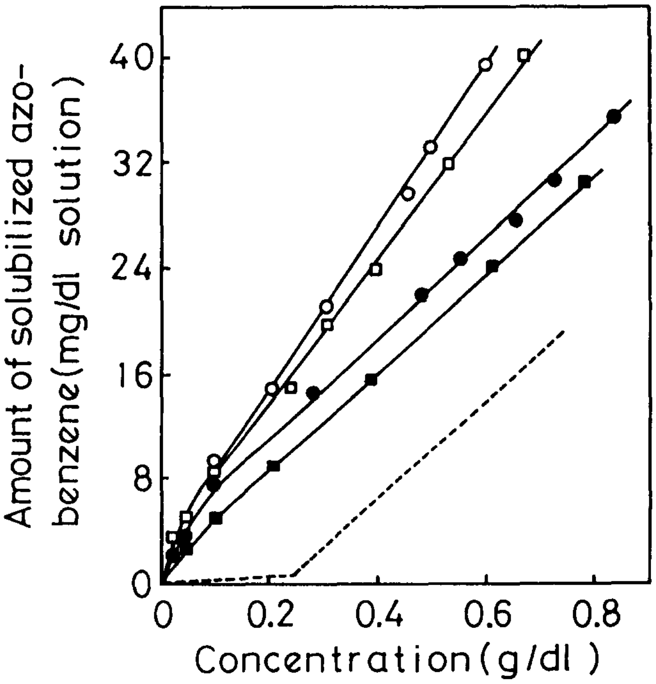

Figure 11 Solubilization of azobenzene in aqueous solutions of the resulting copolymers of $C_{12}Br$ having an approximately equimolar composition at 25°C. Comonomer/solvent for the copolymerization: (○) MMA/water;(●) MMA/DMF; (□) ST/water; (■) ST/DMF. Broken line represents the concentration dependence of the amount of azobenzene solubilized in aqueous solution of $C_{12}Br$

of the cationic monomers. Furthermore, the results obtained here indicated that the copolymerizations in anisotropic solution become more alternating than those in isotropic solution. However, it will be necessary to ascertain if such a tendency is further found in many other systems.

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