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ORIGINAL CONTRIBUTION

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Polymerization of amphiphilic quaternary ammonium salts of acrylic, methacrylic, and ethacrylic acids

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Abstract The polymerization behavior of dodecyltrimethylammonium methacrylate, and hexadecyltrimethylammonium acrylate, methacrylate and ethacrylate as amphiphilic monomers bearing a polymerizable double bond outside the micelle shell was investigated in micellar solution. Although the monomers did not have spontaneous polymerizability, they polymerized in the presence of both oil-soluble and water-soluble radical initiators, in spite of the difference of the expected location solubilizing initiator molecules. The profit based on micelle-forming of the monomer on the polymerization in water disappeared by the addition of sodium chloride into the polymerizing system due to the increased dissociation between cationic micelles and the polymerizable counter ions.

Key words Polymerizable amphiphiles – cationic surfactants – micelles – (meth) acrylates – radical polymerization

Introduction

Polymerizable amphiphilic compound carries a vinyl double bond together with hydrophilic and hydrophobic moieties in a molecule. When conventional ionic surfactant pairs with a vinyl monomer ion, such as 2-methacryloyloxyethyltrimethylammonium cation and methacrylate anion as a counter ion, it becomes also a polymerizable amphiphile. The photo-polymerization of dioctadecyldimethylammonium methacrylate [1, 2], dioctadecyldimethylammonium acrylate [2], dioctadecyldimethylammonium 2-acrylamido-2-methyl-1-propanesulfonate [2] and 2-methacryloyloxyethyltrimethylammonium dihexadecylphosphate [3] as vesicle-forming monomer, and hexadecyltrimethylammonium methacrylate [4] as micelle-forming one, has been reported.

We have recently found that some amphiphilic monomers, such as sodium dodecyl 2-hydroxy-3-methacryloyloxypropyl phosphate [5] and dodecyl-2-methacryloyloxyethyldimethylammonium bromide [6], polymerize spontaneously above their critical micelle concentrations (CMC) in water. The aggregation state of the monomer or the molecular motion of the monomer in the micelles, which is alterable by its alkyl chain length and additives, closely relates to its spontaneous polymerizability, that is, the formation of initiating radical species by thermal reaction between the monomer molecules [7].

Lerebours et al. have reported that hexadecyltrimethylammonium methacrylate polymerizes only at the concentration above its CMC in water by UV or γ-ray irradiation or by heating in the presence of a radical initiator [4]. This behavior is quite similar to that observed in the polymerization of other typical amphiphilic monomers [8, 9].

The location of a polymerizable double bond in the monomer micelles is divided into three types from the geometrical aspect of the monomer structure; *a* in the hydrophobic core (the double bond is attached to the end of hydrocarbon chain; ex. ω-methacryloyloxyundecyltrimethylammonium bromide [10]), *b* in the vicinity inside shell (the double bond is attached to the head group with a short spacer; ex. dodecyl 2-methacryloyloxyethyldimethylammonium bromide [6, 10]), *c* in the vicinity outside shell (the double bond exists in the counter ion; ex. hexadecyltrimethylammonium methacrylate [4]). Furthermore, in micellar solution of ionic surfactants, a part of counter ions are intimately associated with the charged head groups of the surfactants in Stern layer as "bound" counter ions, and the remainders are present in Gouy–Chapman double layer as "unbound" counter ions [11]. Size, hydrophobicity and basicity of the counter ions would also affect the structure of the aggregates. Thus, it is particularly interesting to elucidate the effect of location of double bond toward the polymerizability.

The present paper reports on the polymerization behavior of dodecyltrimethylammonium methacrylate ($C_{12}AM$), and hexadecyltrimethylammonium acrylate ($C_{16}AA$), methacrylate ($C_{16}AM$) and ethacrylate ($C_{16}AE$) belonging to type *c* mentioned above, composed of ions with different size, hydrophobicity, and basicity.

Experimental

Materials

All reagents were obtained commercially unless otherwise noted. Dodecyltrimethylammonium chloride and hexadecyltrimethylammonium bromide were recrystallized

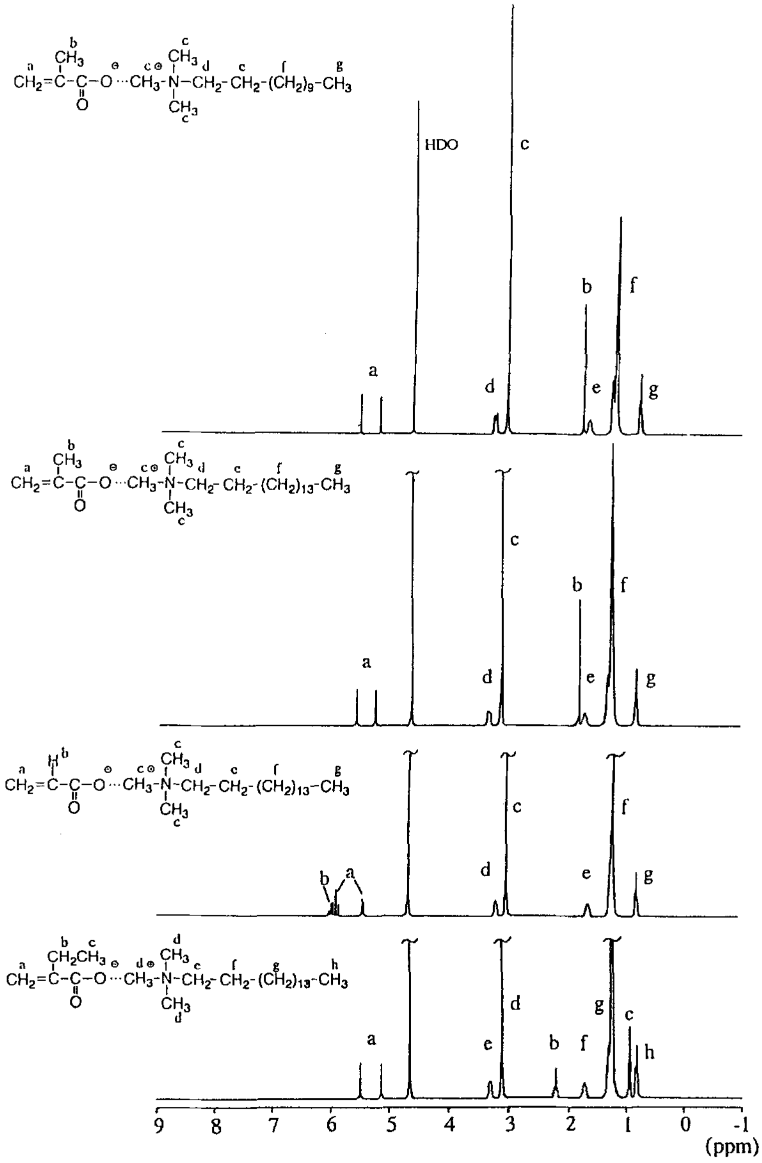


Fig. 1 ^{1}H-NMR spectra of monomers in D_2O

from acetone. Pure reagent grade acrylic and methacrylic acids were used without further purification. Ethacrylic acid was synthesized from diethyl malonate as described by Cheng et al. [12].

Oil-soluble and water-soluble free radical initiators were recrystallized from appropriate solvents; 2,2′-azobisisobutyronitrile (AIBN) from methanol, dimethyl 2,2′-azobisisobutyrate (MAIB) from hexane, 4,4′-azobis (4-cyanovaleric acid) (ACVA) from methanol/water (2/1 by volume), 2, 2′-azobis [2-methyl-N-(2-hydroxyethyl) propionamide] (AHPA) from methanol, and potassium peroxodisulfate (KPS) from water.

Heavy water (99 atom%D) purchased from Aldrich was used as a solvent for the polymerization, in order to make it possible to measure ^{1}H-NMR spectra of the polymerization mixture.

Monomers

Counter ions of the corresponding quaternary ammonium salts were exchanged to polymerizable anions by passing their methanolic solutions through an anion exchange resin Amberlyst A-27 column [2]. After confirmation of the absence of halogen ions in the effluent by aqueous silver nitrate as an indicator, methanol was removed, and the residue was recrystallized twice from acetone to obtain colorless crystalline monomer salts. Their structure and purity were confirmed by ^{1}H-NMR spectra in D_2O using JEOL JMN-A400 (Fig. 1).

CMC of the monomers was determined by surface tension measurement using a du Noüy tensiometer at room temperature (Fig. 2).

Polymerization

The polymerization was carried out in D_2O in a sealed glass tube after removing dissolved oxygen by freeze-thaw technique. After a given time, into the polymerization mixture containing the resulting polymer precipitated as a tacky material, sodium chloride was added to dissolve the polymer for ^{1}H-NMR measurement. The monomer-to-polymer conversion was monitored with the decrease of absorption peaks based on the vinyl double bond in the ^{1}H-NMR specra (Fig. 3).

Photo-polymerization was performed in a degassed Pyrex tube under UV irradiation by Toshiba high-pressure mercury lamp SHL-100 UVQ-2 at 30 °C in the absence of initiator.

Results and discussion

Properties of monomers

CMC of the monomers determined are tabulated in Table 1. These values decreased in the order of (1) C12AM > C16AM, and (2) C16AA > C16AM > C16AE, corresponding to the general rule; an increase in hydrophobicity of surfactant reduces its CMC. On the effect of size of the counter ion, Egorov et al. have reported that its increase also reduces the CMC in agreement with our results [13]. Although in principle the salt of a weaker acid and a strong base shows higher pH in water, the opposite tendency was observed in the present case (Table 1). This is interpretable based on the concentration of dissolved ions in continuous phase which is determined by the CMC; the higher CMC the higher pH.

Attempted thermal polymerization

The thermal polymerizations of C_{12}AM and C_{16}AM were attempted without added radical initiator in darkness at the concentrations (5.0×10^{-2} mol/L for C_{12}AM and 2.0×10^{-2} mol/L for C_{16}AM) above their CMC at 80 °C for 24 h. No polymerization was observed in

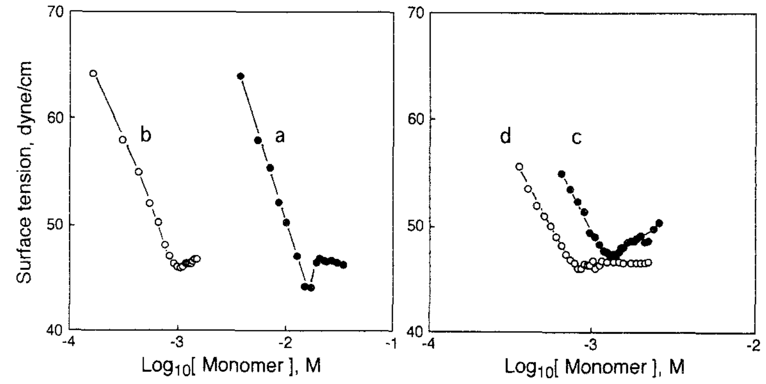


Fig. 2 Plots of surface tension vs log[monomer]. a C_{12}AM, b C_{16}AM, c C_{16}AA, d C_{16}AE

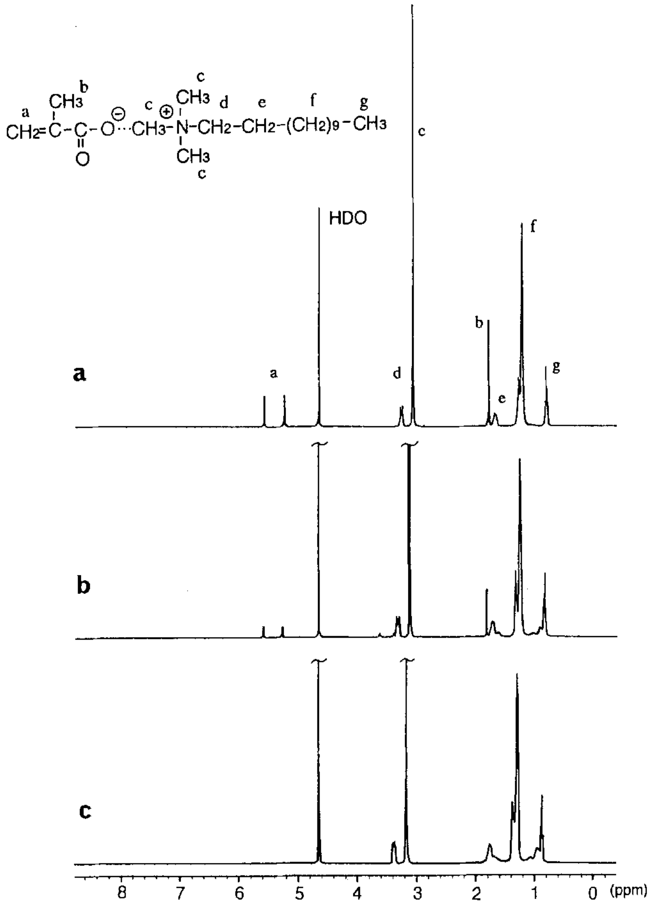


Fig. 3 ^{1}H-NMR spectra of C_{12}AM solution (0.05 mol/L) in D_2O containing sodium chloride. a before polymerization, b after polymerized until 70% conversion, c after polymerized quantitatively

Table 1 CMC of the monomers and pH of the monomer solutions, and pKa of conjugate acids [14] of the counter-ions

	C_{12}AM	C_{16}AA	C_{16}AM	C_{16}AE
CMC × 10^3 mol/L	16.0	1.3	1.0	0.82
pH of aq. solun. at 2.0 × 10^{-2} mol/L	–	9.53	8.54	7.87
pKa at 25 °C	–	4.255	4.429	–

contrast to the case of alkyl 2-methacryloyloxyethyldimethylammonium bromide having high spontaneous polymerizability [6].

The aggregation state of polymerizable moieties is a dominant factor to control a radical generation in the spontaneous polymerization of micellized monomers, and they must moderately interact each other [7]. In the present case, aggregation and organization of vinyl double bonds would be insufficient, because of the existence of "unbound" counter ions bearing the double bonds [11], leading to a decrease of the interaction between them in the counter ions.

By UV irradiation for 40 h, both monomers gave the polymer in the conversion 10.1% and 65.0%, respectively.

Polymerization with various radical initiators

Various oil-soluble and water-soluble radical initiators including azo and peroxo compounds described in the experimental section were used. AIBN and MAIB are typical non-ionizable oil-soluble initiators, and they are possibly solubilized in the hydrophobic micelle core. ACVA and AHPA are ionic and non-ionic water-soluble azo compounds, and they seem to be present at the interface of micelles and continuous phase; especially ACVA is able to form the salt with a quaternary ammonium amphiphile as described below for KPS. Although KPS is the most well-known inorganic water-soluble peroxo compound, by admixing with a surface-active quaternary ammonium compound in water it turns out to be oil-soluble quaternary ammonium peroxodisulfate [15, 16], which seems to behave like a surface active compound. The solubilized states of the initiators in the micellar solution are illustrated in Fig. 4.

The results of the polymerization of the amphiphiles in D_2O with various radical initiators are summarized in Table 2, and the typical time-conversion curves are shown in Fig. 5.

The radicals produced in the vicinity outside the micelles are possible to easily initiate the polymerization of (meth) acrylic moieties, while the radicals produced in the micelle core must diffuse to outside the micelle to initiate the polymerization. Despite a difference of the expected location solubilizing initiator molecules, all of them initiated the polymerization of the monomers in rather high activity. Especially for the oil-soluble initiators, it may be correlated to the emulsion polymerization with them [17, 18]. The detailed initiation process remains as a subject to be elucidated.

In the series of C_{16} salt, the polymerizability decreased in the order of acrylate > methacrylate ≫ ethacrylate in good agreement with that in acid form in bulk as an isotropic system [12]. In other words, the polymerizability of α-substituted acrylates was not greatly altered even by micelle formation.

As also shown in Fig. 5, after prolonged heating both MAIB and AHPA gave ca. 90% conversion for the polymerization of C_{16}AM at the initial monomer concentration of 2.0×10^{-2} mol/L which was 20 times higher than its CMC. On the other hand, when the initial monomer concentration was reduced to 0.3×10^{-2} mol/L, which

Fig. 4 Illustration of solubilized state of radical initiators in micellar solution

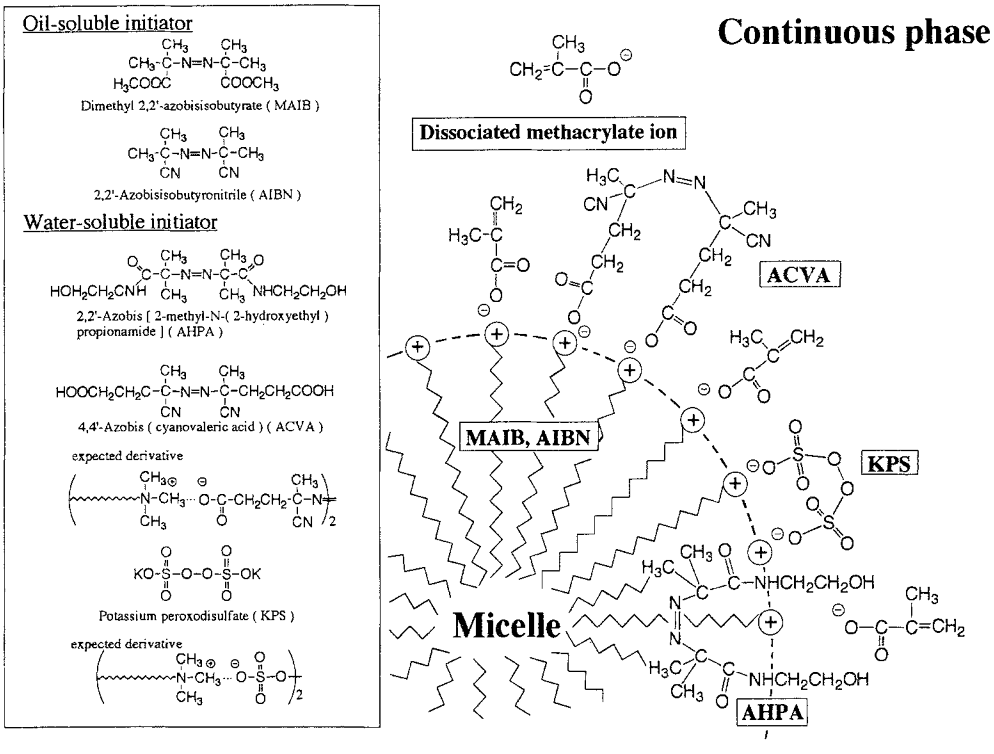


Table 2 Polymerization of amphiphilic salts with various radical initiators in D_2O at 60 °C for 40 h, $[C_{12}AM] = 5.0 \times 10^{-2}$ mol/L; $[\text{Initiator}] = 2.5 \times 10^{-3}$ mol/L, $[C_{16}\text{salt}] = 2.0 \times 10^{-2}$ mol/L; $[\text{Initiator}] = 1.0 \times 10^{-3}$ mol/L

Initiator	Conversion, %			
	$C_{12}AM$	$C_{16}AA$	$C_{16}AM$	$C_{16}AE$
AIBN	58.1	97.8	79.7	6.9
MAIB	39.6	95.0	79.8	10.1
ACVA	60.0	92.2	77.4	9.6
AHPA	35.3	97.2	88.2	7.3
KPS	43.1	52.8	41.3	13.2

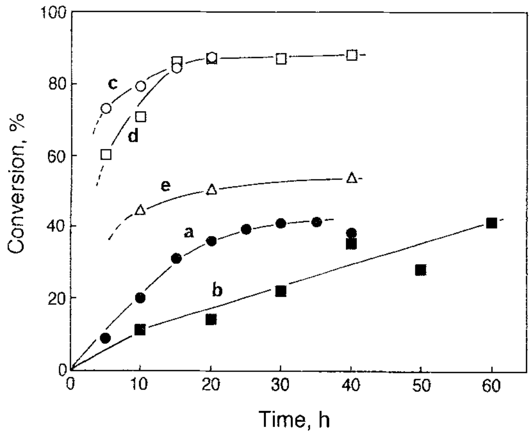


Fig. 5 Time-conversion curves in the polymerization of $C_{12}AM$ and $C_{16}AM$ at 60 °C; [Initiator] = 5 mol% based on the monomer. a$[C_{12}AM] = 5.0 \times 10^{-2}$ mol/L, MAIB; b$[C_{12}AM] = 5.0 \times 10^{-2}$ mol/L, AHPA; c$[C_{16}AM] = 2.0 \times 10^{-2}$ mol/L, MAIB; d$[C_{16}AM] = 2.0 \times 10^{-2}$ mol/L, AHPA; e$[C_{16}AM] = 0.3 \times 10^{-2}$ mol/L, AHPA

was three times higher than its CMC, the limited conversion was lowered to ca. 55%. In the case of $C_{12}AM$ at the initial concentration of 5.0×10^{-2} mol/L being ca. three times higher than its CMC, the conversion was limited at ca. 40%. If the monomers dissolved in continuous phase are not practically responsible for the polymerization and only the micellized monomers are active for the polymerization, as has been shown from the effect of micelle formation on the polymerization [4, 8, 9], the actual monomer concentration is roughly estimated by subtracting CMC from the monomer concentration in the feed as described by Cochin et al. [19]. Consequently, the limit of conversion observed is qualitatively interpretable by inactivity of the monomer dissolved in the continuous phase.

Half-life periods of decomposition of the azo initiators at 60 °C are ca. 1200 min in toluene for MAIB and ca. 9000 min in water for AHPA [20]. For MAIB the expected location of the initiator solubilized in the micelles (Fig. 4) seems to be unsuitable in the initiation efficiency of polymerization of the monomer outside micelles. The fact that faster polymerization at the initial stage with MAIB than that with AHPA in cases of both $C_{12}AM$ and $C_{16}AM$

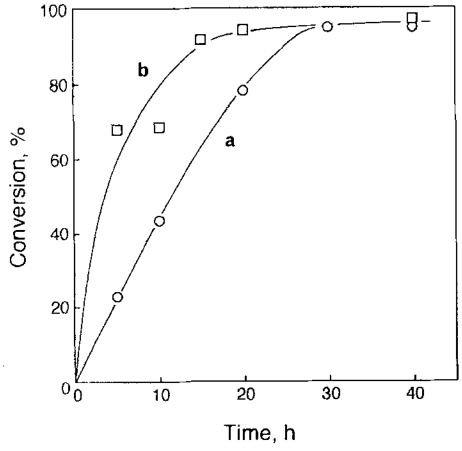
was observed, as shown in Fig. 5, suggests that faster radical generation from MAIB overcomes a disadvantage of the location solubilized. However, as shown in Fig. 6, in comparison of the polymerization of $C_{16}AA$ with MAIB and AHPA, the polymerization with AHPA proceeded at a rather higher rate in contrast with the cases of methacrylate monomers. This shows that the efficiency in the initiation of polymerization is significantly higher for AHPA in the case of acrylate monomer, probably because of the decreased hydrophobicity of the monomer anion which facilitates the reaction with hydrophilic initiator radicals outside the micelles.

In methanol giving an isotropic solution, only a small amount of the polymers was produced from $C_{12}AM$ and $C_{16}AM$, emphasizing an importance of micelle formation.

Polymerization in the presence of sodium chloride

The addition of a large amount of sodium chloride to the polymerizing mixture increases the ionic strength of the solution, and increases the dissociation between the cationic micelles and methacrylate anions or polymethacrylate anions produced. Thus, in this system, the contribution of the micelle to the polymerization will disappear. Figure 7 shows the effect of sodium chloride on the polymerization of $C_{12}AM$ and $C_{16}AM$. The polymer yield at a given time was increased with increasing [sodium chloride]/[monomer] ratio through a minimum value (curves a and b). The appearance of the minimum or the decrease of the polymer yield at lower [sodium chloride]/[monomer] ratio proves the disappearance of the contribution of the cationic micelles, where apparent polymerizability of micellar monomer is expected to be higher than that of free monomer or the monomer in the continuous phase mainly due to the concentration effect as discussed in foregoing section.

Fig. 6 Time-conversion curves in the polymerization of $C_{16}AA$ at 60 °C; $[C_{16}AA] = 2.0 \times 10^{-2}$ mol/L, [Initiator] = 5 mol% based on the monomer. a with MAIB, b with AHPA



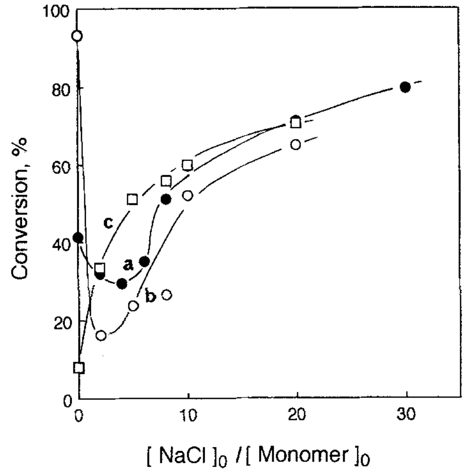


Fig. 7 Effect of sodium chloride on the polymerization of $C_{12}AM$, $C_{16}AM$ and sodium methacrylate with AHPA at 60 °C for 60 h; [Monomer] = 5.0×10^{-2} mol/L, [AHPA] = 5 mol% based on the monomer. a $C_{12}AM$, b $C_{16}AM$, c sodium methacrylate

Curve c in Fig. 7 shows the effect of sodium chloride on the polymerization of sodium methacrylate in the absence of cationic micelles, where the increased polymer yield with increasing [sodium chloride]/[monomer] ratio indicates the reduction of Coulombic repulsion between the growing polymer chain ends and the charged monomers to facilitate the propagation, as already reported for aqueous polymerization of sodium acrylate in the presence of sodium chloride [21]. Thus, the higher polymer yields at the higher [sodium chloride]/[monomer] ratio in curves a and b would be interpreted by this effect.

Conclusion

(Meth) acrylate counter ion of a cationic micelle has higher polymerizability than free (meth) acrylate ion in aqueous phase, although it is not spontaneously polymerizable. The addition of a large quantity of sodium chloride increases the dissociation between cationic micelles and (meth) acrylate counter ions, and the high polymerizability of the counter ions diminishes. On the other hand, the increase of ionic strength in the presence of sodium chloride facilitates the propagation due to the reduction of Coulombic repulsion between the growing polymer chain ends and the charged monomers. Thus, the polymerization of (meth) acrylate ions in the presence of both cationic micelles and sodium chloride gives the superposed results of the rate-increasing and -decreasing effects competing each other.

References

1. Regen SL, Shin JS, Yamaguchi K (1984) J Am Chem Soc 106:2446
2. Horiuchi T, Toda H, Tanaka M (1990) Nippon Kagaku Kaishi:1029
3. Ringsdorf H, Schlarb B, Tyminski PN, O'Brien DF (1988) Macromolecules 21: 671
4. Lerebours B, Perly B, Pileni MP (1988) Chem Phys Lett 147:503
5. Yasuda Y, Rindo K, Aoki S (1992) Makromol Chem 193:2875
6. Yasuda Y, Rindo K, Tsushima R, Aoki S (1993) Makromol Chem 194:1893
7. Yasuda Y, Rindo K, Aoki S (1993) Polym J 25:1203; Aoki S, Yasuda Y (1994) Kobunshi 43:539
8. Larrabee, Jr CE, Sprague ED (1979) J Polym Sci Polym Lett Ed 17:749
9. Hamid SM, Sherrington DC (1986) J Chem Soc Chem Commun:936
10. Hamid SM, Sherrington DC (1987) Polymer 28:325
11. Fisher LR, Oakenfull DG (1977) Chem Soc Revs 6:25
12. Cheng JS, Yamada B, Otsu T (1991) J Polym Sci Part A Polym Chem 29:1837
13. Egorov VV, Ksenofontova OB, Batrakova EV, Zubov VP (1988) Kolloidn Zh 50:821
14. Riddick JA, Bunger WB, Sakano TK (1986) In:Organic Solvents-Physical Properties and Methods of Purification-, 4th ed, Wiley, New York
15. Nagai K, Ohishi Y, Ishiyama K, Kuramoto N (1989) J Appl Polym Sci 38:2183
16. Nagai K, Kataoka H, Kuramoto N (1993) Kobunshi Ronbunshu 50:263
17. Nomura M, Fujita K (1989) Makromol Chem Rapid Commun 10:581
18. Asua JM, Rodriguetz VS, Sudol ED, El-Aasser MS (1989) J Polym Sci Part A Polym Chem 27:3569
19. Cochin D, Zana R, Candau F (1993) Macromolecules 26:5765
20. Wako Pure Chemical Ind Ltd (1993) Technical Note for Azo Polymerization Initiators
21. Ito H, Shimizu S, Suzuki S (1955) Kogyo Kagaku Zasshi 58:278