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ORIGINAL CONTRIBUTION

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Synthesis and polymerization of tail-type cationic polymerizable surfactants and hydrophobic counter-anion induced association of polyelectrolytes

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Abstract A series of tail-type cationic surface-active monomers with the cationic charge at the ω-end (1; ST-C$_m$-AB, $m=5$, 7, and 9, where ST is a styrenic group, C$_m$ the alkylene chain at the 4-position of styrene, and AB is alkyltrimethylammonium bromide) have been synthesized as a novel cationic polymerizable surfactant. Their fundamental physicochemical properties such as critical micelle concentration (*cmc*) and weight-average aggregation number of the micelle ($N_{\mathrm{w(agg)}}$) have been characterized in water at 25 °C by static light-scattering measurements. The *cmc* values determined for the tail-type surfactant monomers are two-orders of magnitude smaller than those of the corresponding head-type cationic surfactant monomers (2; ST-C$_1$-AC-C$_m$). The $N_{\mathrm{w(agg)}}$ of ST-C$_m$-AB is 68 for $m=5$, 156 for $m=7$, and 413 for $m=9$. Free-radical homopolymerization of ST-C$_7$-AB proceeds very rapidly in water as a result of organization in the micelle to afford the corresponding amphiphilic cationic polyelectrolyte with $M_{\mathrm{w}}=3.63\times10^6$ and 23 nm hydrodynamic radius at 25 °C. Emulsion copolymerization of styrene with ST-C$_m$-AB also proceeds rapidly to afford very stable cationic polystyrene latex particles of 30–60 nm diameter. The amphiphilic cationic polyelectrolyte of poly(ST-C$_7$-AB) is likely to assume a compact conformation with high segment density in 0.1 mol L^{-1} NaCl in water. Addition of hydrophobic aromatic counter-anions with an weak acid group, for example potassium hydrogen phthalate (PHK) and sodium salicylate, to a salt-free aqueous solution of poly(ST-C$_7$-AB) induces intermolecular aggregation and increases the solution viscosity substantially, often producing gels and precipitation at high polymer concentration.

Keywords Polymerizable cationic surfactant · Polyelectrolyte · Radical polymerization · Micelle · Hydrophobic counterion · Polysoap

Introduction

Amphiphiles bearing hydrophobic and hydrophilic segments have attracted much attention in recent years because of their resemblance to biological systems and their strong tendency for self-organization in aqueous environments due to the hydrophobic effect [1, 2, 3, 4, 5]. There is also a practical interest in micelle-forming substances based on their many attractive properties and thus their potential uses, e.g. as protective colloids, emulsifiers, surfactants, wetting agents, lubricants, viscosity modifiers, foaming agents, and pharmaceutical and cosmetic formulation ingredients.

A polymerizable, reactive surfactant molecule is a surfactant but also a monomer. It may self-organize in aqueous solution into a micellar aggregation state at a concentration greater than its critical micelle concentration (*cmc*). It may be used as a monomer or comonomer for polymerization to afford a variety of amphiphilic polymers. Recently, reactive surface-active monomers and their amphiphilic polymers have attracted considerable attention in the industrial applications as paint, coatings, cosmetics, inks, etc. [6, 7, 8, 9, 10]. Surfactants play a crucial role in the production and applications of the dispersed polymers. They are very important for nucleation of the latex particles, emulsification of monomer droplets and preformed polymers, and stabilization of the resulting polymer particles during a heterogeneous polymerization. The negative effects in conventional non-polymerizable surfactant molecules, however, are caused by desorption of the surfactant molecules from the surface of the latex particles and migration during the film-formation process. Reactive surfactants are considered to be a promising way of reducing the negative effects of the surfactant molecules in which they are covalently bound to the polymer material [11, 12, 13, 14]. Therefore, there have been a number of studies on the synthesis and (co-)polymerization of anionic, cationic, and nonionic micelle-forming monomers and solution properties of the resulting polymers, as reviewed by Laschewsky [15]. The fundamental physicochemical properties such as *cmc* and degree of aggregation number for the surface-active monomers, and structural characterization of the resulting polymers, however, have not necessarily been well documented.

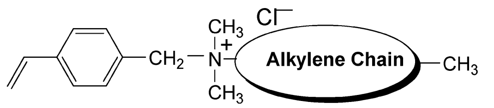
Over the past two decades we have been interested in amphiphilic poly(ethylene oxide) (PEO) macromonomers with a hydrophobic polymerizing end group, which are one type of polymerizable surfactant [16, 17]. Their radical co- and homo-polymerizabilities have been investigated in various media including homogeneous, organized, and heterogeneous (emulsion and dispersion) systems [18, 19]. Homopolymerization of the macromonomers unusually proceeded rapidly to quantitatively afford regular comb-shaped amphiphilic polymers with high degree of polymerization. The dilute aqueous solution behavior of the resulting amphiphilic polymers has been characterized by light scattering, viscometry, fluorescence spectroscopy, and small-angle X-ray scattering [20, 21]. The polymerization behavior was related to the physicochemical properties in the aggregation states and to the molecular structure.

In an extension of our PEO macromonomer studies, we discuss in this paper preparation of a series of novel tail-type cationic polymerizable surfactants with a cationic charge at the ω-end, (1) ST-C$_m$-AB with $m = 5$, 7, and 9, as shown in Scheme 1 [22]. Aggregation properties of the monomers are characterized in water by static light scattering and compared to those of the corresponding head-type monomers, (2) ST-C$_1$-AC-C$_m$. Micellar homopolymerization of ST-C$_m$-AB and emulsion copolymerization with styrene are also explored in water under various conditions. Dilute aqueous solution properties of the resulting amphiphilic polyelectrolytes are characterized by light-scattering experiments. The influences of hydrophobic counter-anions on the solution properties of amphiphilic cationic polyelectrolytes are also documented.

Tail-Type Cationic Surface-Active Monomers

(1) ST-C$_m$-AB, m=5,7,and 9

Head-Type Cationic Surface-Active Monomers



(2) ST-C$_1$-AC-C$_m$, m=8,12,and 16

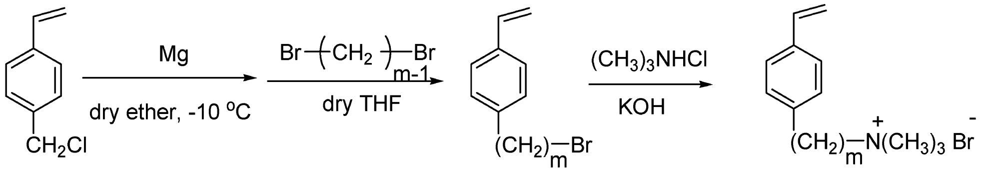
Scheme 1

Experimental

Synthesis of ST-C$_m$-AB

Novel surface-active monomers, ST-C$_m$-AB, were prepared according to Scheme 2. *p*-Vinylbenzyl chloride

Scheme 2



(1)ST-C$_m$-AB, m=5,7, and 9

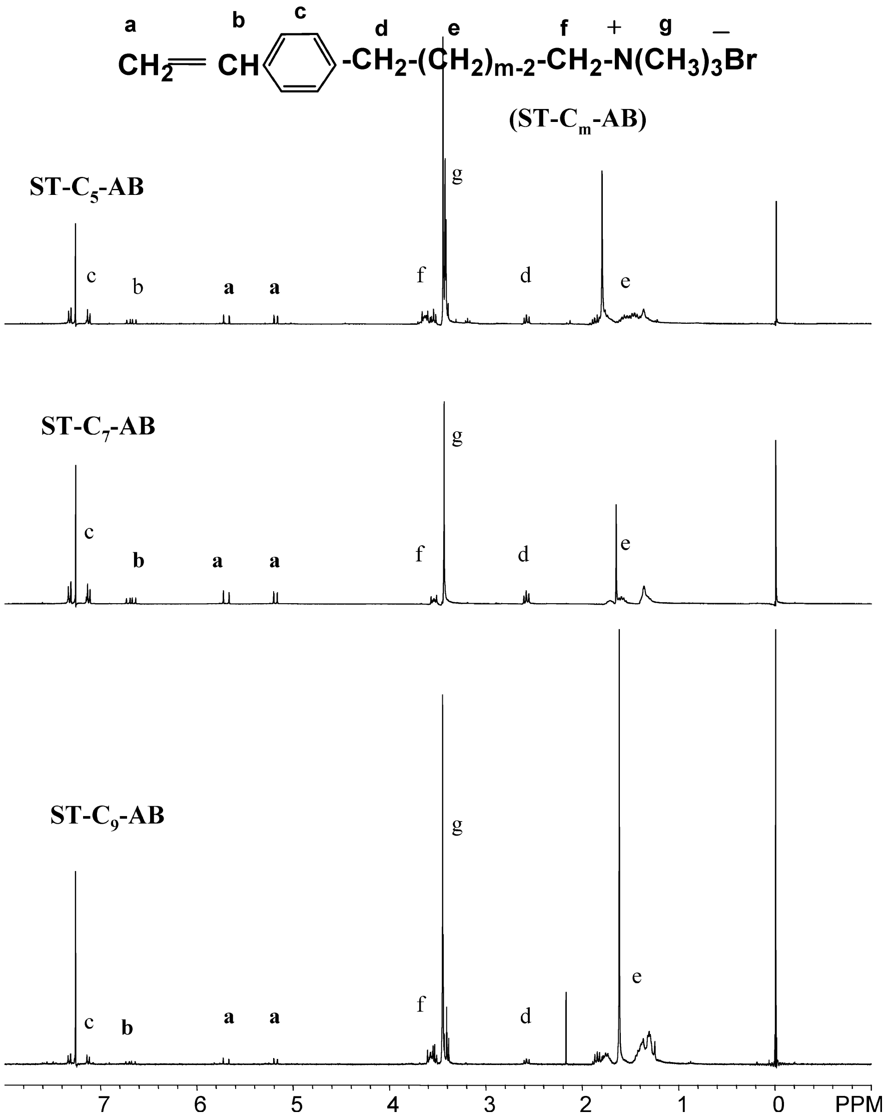


Fig. 1 ^{1}H NMR spectra of cationic surface-active monomers ST-C$_m$-AB in $CDCl_3$ at 20 °C

(VBC; Seimi Chemical, Japan) was reacted with excess magnesium turnings in dry ether at −10 °C under nitrogen atmosphere for 30 min using iodine as catalyst. The Grignard reagent obtained was added dropwise to a stirred solution of 1,4-dibromobutane, 1,6-dibromohexane, or 1,8-dibromooctane in dry tetrahydrofuran containing LiCl and $CuCl_2$ as catalyst, at 0 °C, under nitrogen atmosphere [23]. After addition was complete the mixture was stirred for one night at room temperature. The reaction was stopped by adding methanol. The reaction mixture was concentrated in vacuum, poured into water, and extracted with ether. The ether layer was dried over anhydrous $MgSO_4$ and concentrated, and the residue was distilled in vacuum in the presence of DPPH (1,1-diphenyl picrylhydrazyl). The product was dissolved in acetone and quaternized with trimethylamine, which was produced by mixing trimethylamine hydrochloride with 2 mol L^{-1} KOH, for 3 days at room temperature [24]. After evaporation, the crude product was dissolved in chloroform and filtered. The solution was precipitated in diethyl ether and dried under reduced pressure to afford the quaternized product. The overall yield of ST-C$_m$-AB was 20–36%. ^{1}H NMR spectra of ST-C$_m$-AB in $CDCl_3$, presented in Fig. 1, support the molecular structure of ST-C$_m$-AB.

Materials

Styrene was washed with aqueous sodium thiosulfate and aqueous sodium hydroxide and distilled over calcium hydride under reduced pressure just before use. The initiators, 4,4′-azobis(4-cyanovaleric acid), AVA, dimethyl-2,2′-azobis(isobutyrate), MAIB, and 2,2′-azobis(2-amidinopropane) hydrochloride, V-50, were used as supplied commercially. Water was purified with a

Millipore Milli-Q purification system and used within a few hours. Organic salts were of the highest grade available and used without further purification. The homopolymers, poly(ST-C_m-AB) for static light-scattering measurement were purified by dialysis against deionized water for 1 week and recovered by freeze drying.

Homopolymerization of ST-C_m-AB and emulsion copolymerization with styrene

Radical homopolymerization and emulsion copolymerization with styrene were performed at 60 °C in a three-necked, round-bottom flask equipped with a magnetic stirrer under nitrogen atmosphere [19]. Deionized water and monomer were introduced to a 100-mL reactor and degassed for approximately 30 min. The polymerization was started by addition of the initiator, dissolved in water, under ultrasonic vibration. The conversion of ST-C_m-AB was monitored by the decrease of the peaks (5.0–6.0 ppm) due to the vinyl group in the ^{1}H NMR spectrum in $CDCl_3$. Styrene conversion was determined by the weight method.

Measurements

^{1}H NMR spectra were recorded on a Varian Mercury 300 spectrometer in D_2O and $CDCl_3$ at 20 °C. The conditions were 16 times accumulation and 30 s pulse-delay time.

Surface tension measurement was carried out with a surface tensiometer CBVP-A3 type (Kyowa Interface Science) at room temperature in water [19].

Static light-scattering measurements for micelle solutions in water were performed with an intensity monitor of an ELS 8000 (Otsuka Electronics) equipped with 10 mW He–Ne laser (632.8 nm) as an incident beam at 25 °C. The Rayleigh ratio of the scattered light was based on the Rayleigh ratio $R(90) = 11.84\times10^{-6}\ \mathrm{cm}^{-1}$ at a scattered angle of 90° of pure benzene at 25 °C [19, 25]. Static light-scattering and dynamic light-scattering (DLS) measurements for poly(ST-C_7-AB) in 0.1 mol L^{-1} NaCl were also run with a DLS-8000 (Otsuka Electronics) with 10 mW He–Ne laser at scattered angles from 30° to 130°. The decay profiles of DLS at a scattered angle of 90° were analyzed using the CONTIN analysis method. The latex diameters were also measured using the same equipment at 25 °C.

The refractive index increment (d n/d c) measurements were performed in water and 0.1 mol L^{-1} NaCl with an RM-102 refractometer (Otsuka Electronics) at 25 °C.

Viscometry measurements were carried out using a conventional capillary viscometer of the Ubbelohde type at 25 °C.

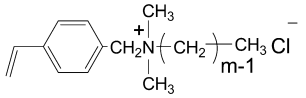
Results and discussion

First, we report physicochemical properties of the surfactant, ST-C_m-AB including *cmc* and aggregation number in water. Second, homopolymerization and emulsion copolymerization with styrene in water are studied. Third, dilute solution properties of the resulting poly(ST-C_7-AB) are presented, together with intermolecular association on addition of hydrophobic counter-anions.

Aggregation behavior of ST-C_m-AB into micelles in water

Figure 2 shows a plot of the Rayleigh ratio $R(90)$ of an aqueous solution of ST-C_m-AB surfactants at a scattered angle of 90°, against concentration, at 25 °C. The scattered intensity or $R(90)$ increased steeply at concentrations above that to be identified as the *cmc*. The values of *cmc* determined are listed in Table 1. The reference values [22, 26] for the head-type surface-active monomers, ST-C_1-AC-C_m (Structure 1) are also presented in the table for comparison. One clearly finds that the *cmc* of the ST-C_m-AB decreases reasonably with increasing hydrophobicity, i.e. alkylene chain length, *m*. An interesting point to be noted in this table is that the *cmc* values for the tail-type surfactant molecules are two orders of magnitude smaller than those of the corresponding head-type molecules, implying that molecular structure in the former surfactants may be preferable for micelle formation to that of the latter surfactants. The *cmc* values are compared directly in Fig. 3 in which semi-logarithmic plots of *cmc* against alkylene chain length, *m*, are shown. From the figure one obtains an empirical relationship between *cmc* and *m* as in the equations:

ST-C_1-AC-C_m



Structure 1

$$\ln(cmc) = 0.042 - 8.93m \quad (\mathrm{ST}\text{ - }\mathrm{C}_m\text{ - }\mathrm{AB}) \tag{1}$$

$$\ln(cmc) = 3.28 - 7.27m \quad (\mathrm{ST}\text{ - }\mathrm{C1}\text{ - }\mathrm{AC}\text{ - }\mathrm{C}_m) \tag{2}$$

When the particle size of the aggregates is sufficiently small compared with the wavelength of incident light, their molecular weight may be evaluated by means of the equation:

$$\frac{K(C - cmc)}{R(90)} = \frac{1}{M_{\mathrm{w(agg)}}} + 2A_2(C - cmc) + \cdots\cdots \tag{3}$$

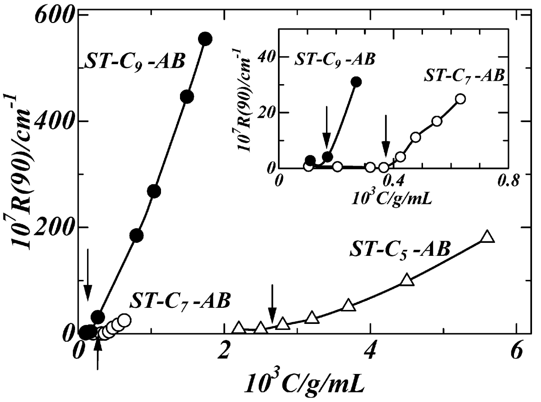


Fig. 2 Dependence of Rayleigh ratio at a scattering angle of 90°, $R(90)$, on the concentration of ST-C_5-AB (*triangles*), ST-C_7-AB(*empty circles*), and ST-C_9-AB (*filled circles*) at 25 °C. The *arrows* indicate critical micelle concentrations (*cmc*)

Table 1 Characteristics of ST-C_m-AB and ST-C_1-AB-C_m micelles in water at 25 °C

	cmc (mmol L^{-1})	$10^{-4}\times Mw_{(agg)}$	$N_{w(agg)}$	Ref.
ST-C_1-AB	600	–	–	[22]
ST-C_5-AB	8.3	2.1_3	68	This study
ST-C_7-AB[a]	1.1	5.4_4	156	This study
ST-C_9-AB	0.65	$15._2$	413	This study
ST-C_1-AC-C_8	84	–	–	[26]
ST-C_1-AC-C_{12}	3.8	–	–	[26]
ST-C_1-AC-C_{16}	0.25	–	–	[26]

[a] *cmc* value determined by surface tension measurement is 0.94 mmol L^{-1}

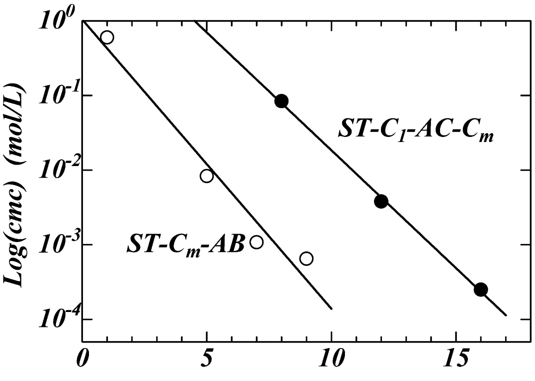


Fig. 3 Semi-logarithmic plots of *cmc* value against alkylene chain length (m) for tail-type cationic surface-active monomers ST-C_m-AB (*empty circles*) and head-type surface-active monomers ST-C_1-AC-C_m (*filled circles*)

where $M_{w(agg)}$ is the weight-averaged molecular weight of aggregates, A_2 is the second virial coefficient, and $K = 4\pi^2 n_o^2 (\mathrm{d}\,n/\mathrm{d}\,c)^2/(\lambda_o^4 N_A)$ in which n_o is the refractive index of the solvent, d n/d c is the excess refractive index

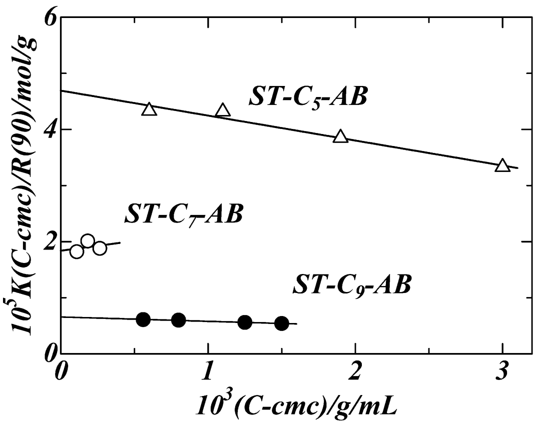


Fig. 4 Dependence of $K(C\text{-}cmc)/R(90)$ on (C-*cmc*) for ST-C_5-AB (*triangles*), ST-C_7-AB(*empty circles*), and ST-C_9-AB (*filled circles*) at 25 °C

Table 2 Micellar homopolymerization of ST-C_m-AB with different initiators in water[a]

ST-C_m-AB	[Monomer] (mmol L^{-1})	Initiator	Polym. time (min)	Conv. (%)
ST-C_5-AB	50	AVA	30	28
ST-C_7-AB	10	AVA	20	17
ST-C_7-AB	100	AVA	30	40
ST-C_7-AB[b]	100	AVA	180	>98
ST-C_7-AB	100	MAIB	20	20
ST-C_7-AB	100	MAIB	30	38
ST-C_7-AB	100	V-50	20	15
ST-C_7-AB	100	V-50	30	34
ST-C_9-AB	100	AVA	180	>98

[a] Polymerizations were carried out at 60 °C. [Initiator] = 1.0 mmol L^{-1}

[b] $Mw = 3.63\times10^6$, determined by light scattering in 0.1 mol L^{-1} NaCl at 25 °C

AVA: 4,4′-azobis(4-cyanovaleric acid)

MAIB: Dimethyl-2,2′-azobis(isobutyrate)

V-50: 2,2′-Azobis(2-amidinopropane) hydrochloride

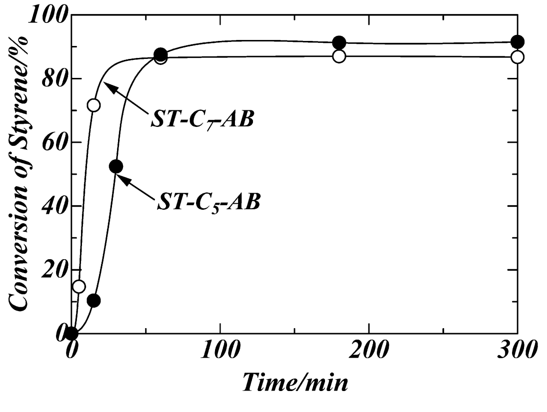


Fig. 5 Fractional conversion of styrene against time plots for emulsion copolymerization of styrene with ST-C_5-AB (*filled circles*) and ST-C_7-AB(*empty circles*) with V-50 at 60 °C; [styrene] = 0.975 mol L^{-1}, [ST-C_5-AB] = 32 mmol L^{-1}, [ST-C_7-AB] = 30 mmol L^{-1}, and [V-50] = 3.6 mmol L^{-1}

Table 3 Emulsion and micellar copolymerization of styrene with ST-C_m-AB at 60 °C[a]

ST-C_m-AB	[Styrene] (mmol L^{-1})	[ST-C_m-AB] (mmol L^{-1})	[V-50] (mmol L^{-1})	Dia. (nm)[b]
Micellar copolymerization				
ST-C_7-AB	30.0	25.1	0.13	-
ST-C_7-AB	67.8	50.3	0.50	25
Emulsion copolymerization				
ST-C_5-AB	975	32	3.6	30
ST-C_7-AB	975	30	3.6	60
ST-C_7-AB	966	59	3.8	40

[a] Copolymerization time = 24 h

[b] Diameter was determined by dynamic light-scattering measurements

increment, λ_o is the wavelength, and N_A is Avogadro's number.

Figure 4 shows the dependence on micelle concentration of Debye plots at a scattered angle of 90°. The weight-averaged molecular weight is determined from the intercept of this plot and results are summarized in Table 1. The weight-average aggregation number, $N_{w(agg)}$ of the micelle increases steeply with alkylene chain length. The surfactant molecules with a styrenic group seem to form a micelle with $N_{w(agg)}$ larger than that of the corresponding conventional linear aliphatic cationic surfactants (N_{agg} of cetyltrimethylammonium bromide (CTAB) is 61 at 25 °C) [27]. The negative second virial coefficient (A_2) in Fig. 4 indicates that the micelles tend to aggregate into a larger aggregation state with increasing concentration.

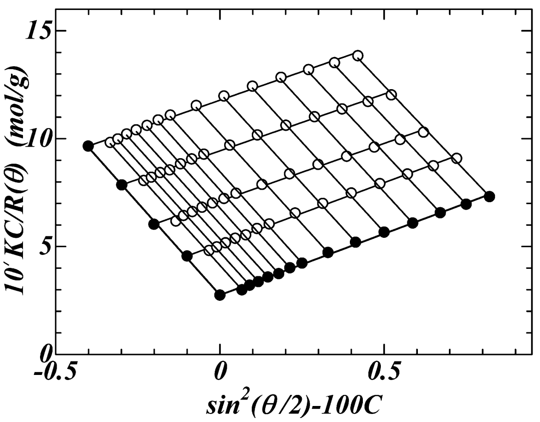


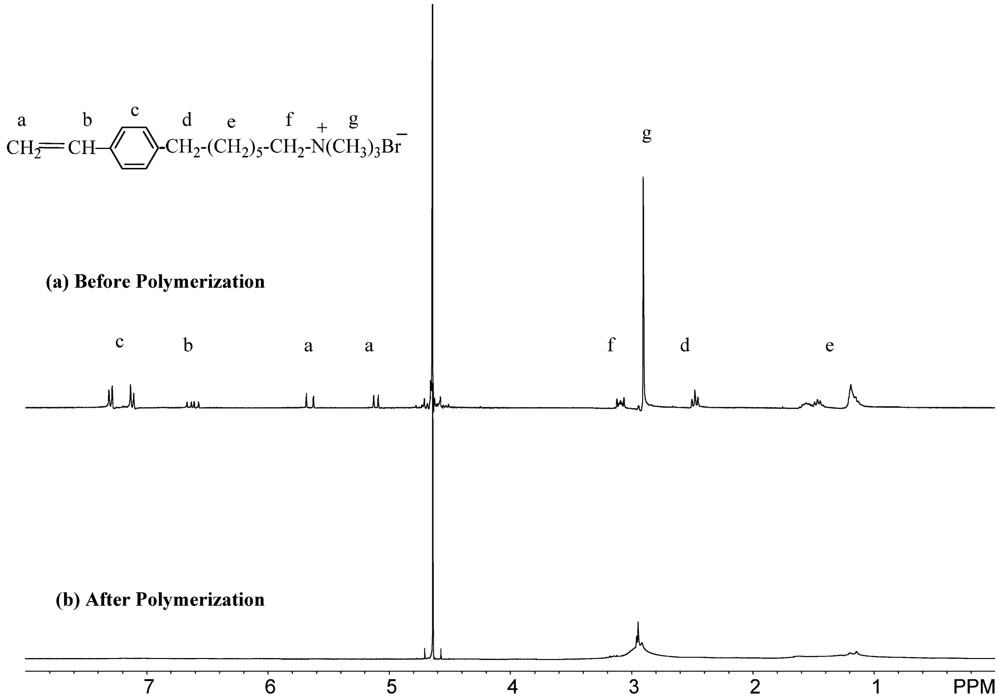
Fig. 6 Zimm plots for poly(ST-C_7-AB) in 0.1 mol L^{-1} NaCl at 25 °C. The poly(ST-C_7-AB) was prepared by the micellar homopolymerization at 60 °C for 24 h; [ST-C_7-AB] = 100 mmol L^{-1}, [AVA] = 1.0 mmol L^{-1}

Micellar homopolymerization and emulsion copolymerization

Results from micellar polymerization of the monomers in water with various radical initiators were summarized in Table 2. One sees that the polymerization proceeds very rapidly at 60 °C to afford water-soluble amphiphilic cationic polyelectrolytes. No significant effect of the species of initiators used on the polymerization is observed.

Figure 5 represents a time–evolution curve of the emulsion copolymerization of styrene with ST-C_m-AB in water with V-50 as an initiator at 60 °C. One finds that

Fig. 7 ^{1}H NMR spectra of ST-C_7-AB in D_2O at 20 °C (**a**) before and (**b**) after polymerization for 24 h with AVA as an initiator at 60 °C; [ST-C_7-AB] = 50 mmol L^{-1}. [AVA] = 0.5 mmol L^{-1}



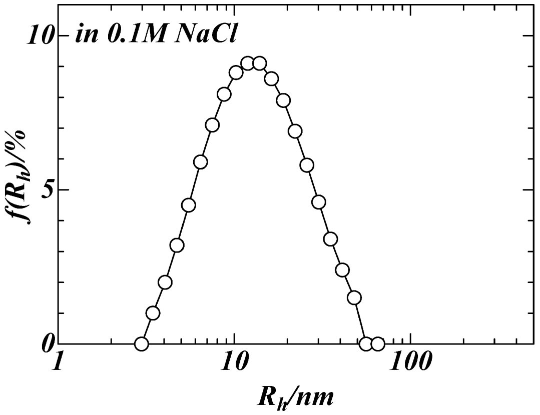


Fig. 8 Particle-size distribution of poly(ST-C_7-AB) with $M_w = 3.63 \times 10^6$ at $C_S = 0.1$ mol L^{-1} NaCl

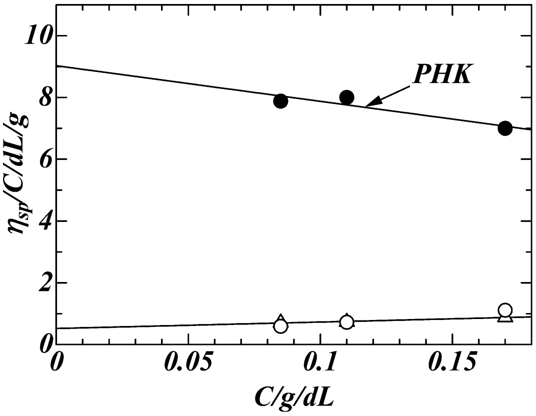


Fig. 9 Huggins plots of poly(ST-C_7-AB) with $M_w = 3.63 \times 10^6$ in salt-free aqueous solution (*empty circles*) and in the presence of an equivalent-molar amount of hydrophobic organic salts, potassium hydrogen phthalate (PHK) (*filled circles*) and sodium benzoate (SB) (*triangles*) at 25 °C

the polymerization also proceeds very rapidly to afford cationic polystyrene latex particles 30–60 nm in diameter, as listed in Table 3.

Dilute aqueous solution properties of poly(ST-C_7-AB)

The homopolymers poly(ST-C_m-AB) dissolve completely in water at room temperature. This solubility behavior is completely different from that of the head-type poly(ST-C_1-AC-C_m) with the same alkylene chain [26]. Figure 6 shows Zimm plot for the poly(ST-C_7-AB) in 0.1 mol L^{-1} NaCl at 25 °C. From this plot, one may determine M_w to be 3.63×10^6 g mol^{-1} and $A_2 = 8.5 \times 10^{-5}$ cm^3 g^{-2} mol by extrapolating to zero concentration and zero scattered angle. It may be worth to noting that M_w of the resulting cationic polyelectrolyte is much higher than that of polystyrene obtained in homogeneous polymerization of styrene at the same monomer and initiator concentrations, supporting the micellar polymerization. From comparison of $M_{w(agg)}$ in Table 1 with the M_w of poly(ST-C_7-AB) 67 micelles polymerize to afford a polymer during this micellar organized polymerization.

Figure 7 shows ^{1}H NMR spectra before and after polymerization of ST-C_7-AB in D_2O at 20 °C. The NMR peaks due to the polystyrene in poly(ST-C_7-AB) disappear whereas alkylene chain near ω-charge are

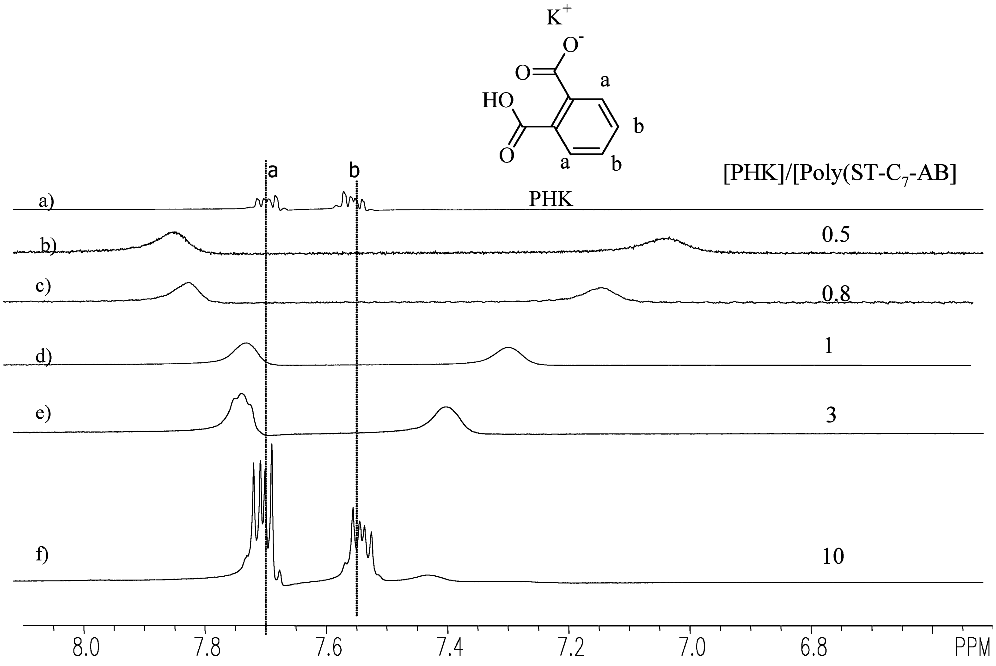


Fig. 10 Revolution of ^{1}H NMR spectra of PHK with different mole ratios of [PHK] to [poly(ST-C_7-AB)] in D_2O at 20 °C; [PHK] = 1.0×10^{-2} mol L^{-1}

detected. The restricted motion of the hydrophobic main chain due to the formation of association in water is likely to be responsible [20]. Figure 8 shows the result of dynamic light scattering of poly(ST-C_7-AB) in 0.1 mol L^{-1} NaCl at 25 °C. Average hydrodynamic radius (R_h) is 22.8 nm. When one assumes an ideal rigid sphere radius R_h, segment density ρ may be calculated by use of the equation [19]:

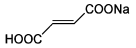
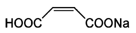
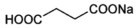
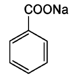
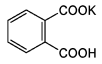
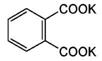
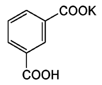
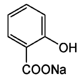
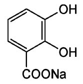
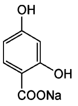
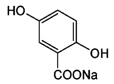
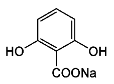
$$\rho = \frac{3M_w}{4\pi R_h^3 N_A} \tag{4}$$

The ρ value for poly(ST-C_7-AB) in 0.1 mol L^{-1} NaCl at 25 °C is calculated to be 0.12 g mL^{-1}, which is 100 times higher than that of general linear polymer molecule in a good solvent. The results may imply that the resulting poly(ST-C_7-AB) chain assumes a compact conformation with high segment density in 0.1 mol L^{-1} NaCl at 25 °C.

Hydrophobic counter-anion induced association of poly(ST-C_7-AB)

Some cationic surfactant molecules are known to form rod-like or thread-like micelles under some conditions [27, 28, 29, 30]. Ekwall et al. [27] have reported that CTAB can form rod-like micelles at a concentration greater than 9 g dL^{-1} in aqueous solution. Shikata et al. have also reported that CTAB complexes with hydrophobic counter-anion, sodium salicylate (NaSal) in aqueous solution to form very long and stable threadlike micelles with exhibit remarkable viscoelasticity [31]. Although the mechanism is not still clearly understood, these threadlike micellar solutions are similar to polymer solutions and their unique behavior can be described by "living polymer" models [32].

Table 4 Interactions between Poly(ST-C_7-AB) with different counter-anions[a]

Salts	Appearance	
	0.05mol/L	0.10mol/L
	Low Viscosity	Low Viscosity
	Low Viscosity	Low Viscosity
	Low Viscosity	Low Viscosity
	Low Viscosity	Low Viscosity
	High Viscosity	Gelation
	Low Viscosity	Low Viscosity
	Low Viscosity	Low Viscosity
	High Viscosity	Gelation
	High Viscosity	Gelation
	Precipitation[2]	Precipitation
	High Viscosity	Gelation
	Precipitation[3]	Precipitation

[1] [Counter-anion]/[Poly(ST-C_7-AB)]=1.0

[2] at 0.022mol/L, high viscosity

[3] at 0.022mol/L, precipitation, and at 0.015mol/L, H_2O phase + gel phase

The influence of hydrophobic counter-anions on the solution behavior of the amphiphilic cationic polyelectrolytes, poly(ST-C_7-AB) in salt-free water were explored. Figure 9 shows Huggins plots for poly(ST-C_7-AB) in salt-free solution and for the solution containing an equivalent amount of sodium benzoate (NaB) and potassium hydrogen phthalate (PHK) as a salt. It may be worth to be noting that PHK with both a carboxylate anion and a carboxylic acid group remarkably increases the viscosity but NaB with an only carboxylate anion does not. This experimental result might suggest that the original bromide counter-anions are partly replaced by the hydrophobic anions. The compact conformation of the poly(ST-C_7-AB) chain might have a number of hydrophobic microdomains. It also produces, in the vicinity of a polyelectrolyte chain, higher electrostatic field than random coil-like polyelectrolyte chain. According to "counterion condensation" theory in polyelectrolyte dilute solution [33], poly(ST-C_7-AB) chain should strongly condense the counterions. The hydrophobic PHK and NaB molecules are, therefore, attracted by both electrostatic interaction and hydrophobic interaction. The existence of carboxylic acid group in PHK molecule may remarkably increase intermolecular attractive interaction to result in wormy micelles. Figure 10 shows ^1H NMR spectra of the PHK molecule in D_2O at different mole ratios of the poly(ST-C_7-AB). Two interesting observations are the broadening and chemical shifting of the aromatic protons of PHK, implying strong interactions among a polyelectrolyte chain and PHK ions. The influences of the structure of counter-anion on salt-free solution behavior of poly(ST-C_7-AB) were investigated and the results are shown in Table 4. Experimental criteria for counterion-induced aggregation of the amphiphilic polyelectrolyte chain seem to be the hydrophobicity and the existence of the neighboring weak acid group (OH or COOH) in the counter-anion. Detailed studies on this subject are now in progress.

Conclusions

Novel tail-type cationic surface-active monomers have been synthesized and their fundamental physicochemical properties such as critical micelle concentration (*cmc*) and weight-average aggregation number of the micelle ($N_{w(agg)}$) have been characterized. The *cmc* values for the tail-type surfactant monomers are two-order magnitude smaller than those of the corresponding head-type cationic surfactant monomers. ST-C_m-AB forms a giant micelle with $N_{w(agg)} = 68$ for $m = 5$, 156 for $m = 7$, and 413 for $m = 9$. Free-radical homopolymerization of ST-C_7-AB and emulsion copolymerization with styrene proceed very rapidly in water, affording the corresponding cationic polyelectrolyte with $M_w = 3.63 \times 10^6$ and very stable cationic polystyrene latex particles 30–60 nm in diameter, respectively. The amphiphilic cationic polyelectrolyte poly(ST-C_7-AB) takes a unimolecular micelle-like conformation in water. Addition of hydrophobic counter-anions with an weak acid group such as potassium hydrogen phthalate (PHK) and sodium salicylate to a salt-free aqueous solution of poly(ST-C_7-AB) induces intermolecular aggregation which substantially increases solution viscosity and often causes gelling and precipitation at high polymer concentration.

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References

1. Goddard ED, Gruber JV (1999) (eds) Principles of polymer science and technology in cosmetics and personal care. Marcel Dekker, New York
2. McCormick CL, Bock J, Schulz DN (1989) Encyclopedia of polymer science and engineering, vol 17. Wiley, New York, p 730
3. Glass JE (1996) (ed) Hydrophilic polymer, performance with environmental acceptability, Advances in chemistry series 248, ACS, Washington, DC
4. Morishima Y, Nomura S, Seki M, Ikeda T, Kamachi M (1995) Macromolecules 28:2874
5. Akiyoshi K, Deguchi S, Noguchi N, Yamaguchi S, Sunamoto J (1993) Macromolecules 26:3062
6. Paleos CM, Makkiaris A (1988) J Macromol Sci Rev Macromol Chem Phys C28:403
7. Chew CH, Gan LM (1985) J Polym Sci Polym Chem Ed 22:3383
8. Nagai K, Ohishi Y, Inaba H, Kudo S (1985) J Polym Sci Polym Chem Ed 23:1221
9. Nagai K, Ohishi Y (1987) J Polym Sci Polym Chem Ed 25:1
10. Aoki A, Morimoto Y (1996) Polym Bull 37:777
11. Asua JM, Schoonbrood HAS (1998) Acta Polym 49:671
12. Guyot A, Tauer K (1994) Adv Polym Sci 111:43
13. Nagai K (1996) Trends Polym Sci 4:122
14. Guyot A (1996) Curr Opin Colloid Interface Sci 1:580
15. Laschewsky A (1995) Adv Polym Sci 124:1
16. Ito K (1998) Prog Polym Sci 23:581
17. Ito K, Kawaguchi S (1999) Adv Polym Sci 142:129
18. Ito K, Tanaka K, Tanaka H, Imai G, Kawaguchi S, Itsuno S (1991) Macromolecules 24:2348
19. Maniruzzaman M, Kawaguchi S, Ito K (2000) Macromolecules 33:1583
20. Kawaguchi S, Maniruzzaman M, Katsuragi K, Matsumoto H, Iriany Ito K, Hugenberg N, Schmidt M (2002) Polym J 34:253
21. Kawaguchi S, Akaike K, Zhang Z-M, Matsumoto H, Ito K (1998) Polym J 30:1004
22. Aoki S, Morimoto Y, Nomura A (1996) Polym J 28:1014
23. Chao D, Itsuno S, Ito K (1991) Polym J 23:1045
24. Yoshinaga K, Nakashima F, Nishi T (1999) Colloid Polym Sci 277:136
25. Kawaguchi S, Imai G, Suzuki J, Miyahara A, Kitano T, Ito K (1997) Polymer 38:2885
26. Cochin D, Zana R, Candau F (1993) Polym Int 30:491
27. Ekwall P, Mandell L, Solyom P (1971) J Colloid Interface Sci 35:519
28. Bunton CA (1973) Reaction kinetics in micelles. Plenum, New York
29. Gravsholt SJ (1976) Colloid Interface Sci 57:575
30. Rehage H, Hoffmann H (1982) Rheol Acta 21:561
31. Shikata T, Hirata H, Kotaka T (1987) Langmuir 3:1081
32. Cates ME (1987) Macromolecules 20:2289
33. Manning GS (1969) J Chem Phys 51:924