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Polymer 42 (2001) 9243–9252

polymer

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Side-chain micellization in random copolymers of sodium acrylate and methacrylates substituted with nonionic surfactant moieties: a comparison with sodium 2-(acrylamido)-2-methylpropanesulfonate copolymers

Tetsuya Noda, Akihito Hashidzume, Yotaro Morishima*

Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

Received 23 April 2001; received in revised form 14 June 2001; accepted 19 June 2001

Abstract

The micelle formation of random copolymers of sodium acrylate (NaAA) and a methacrylate substituted with $HO(CH_2CH_2O)_mC_{12}H_{25}$ ($C_{12}E_m$) where $m = 2$, 6 or 25 (DE*m*MA) in 0.1 M NaCl aqueous solutions at pH = 10 was investigated in comparison with that of random copolymers of sodium 2-(acrylamido)-2-methylpropanesulfonate (NaAMPS) and DE*m*MA. Apparent critical micelle concentrations and aggregation numbers of the polymer-bound $C_{12}E_m$ moieties in micelles formed from the NaAA-based copolymers of $m = 2$, 6 and 25 were nearly the same as those found for the NaAMPS-based copolymers of $m = 2$, 6 and 25 comparing at the same m. Zero-shear viscosity (η_0) increased gradually with increasing polymer concentration (C_p) in a dilute regime, followed by a drastic increase at higher C_p, which is a common feature for both the copolymers. However, the dependence of η_0 on m for the NaAA copolymers is completely opposite to that for the NaAMPS copolymers. In a semidilute regime, η_0 for the NaAA copolymer of $m = 2$ was ca. 3 and 6 orders of magnitude higher than those of the NaAA copolymers with $m = 6$ and 25, respectively, whereas η_0 for the NaAMPS copolymer of $m = 2$ was ca. 1 and 3 orders of magnitude lower than those of the NaAMPS copolymers with $m = 6$ and 25, respectively. At $m = 2$, η_0 for the NaAA copolymer is ca. 8 orders of magnitude higher than that for the NaAMPS copolymer. This large difference in the viscosity behavior of the NaAA- and NaAMPS-based copolymers was attributed to a much stronger tendency of the NaAA-based copolymer to undergo inter-polymer association when m is small. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Side-chain micellization; Sodium acrylate; Nonionic surfactant moieties

1. Introduction

In recent years, self-assembling ionic and nonionic water-soluble polymers covalently modified with hydrophobes have attracted considerable interest of researchers in industry and academia because of their potential in various applications, and also because of their similarity to some biological macromolecules [1–5]. In hydrophobically modified ionic polymers, self-assembly is mainly driven by the balance of hydrophobic association and electrostatic repulsion depending markedly on their macromolecular architectures. It has been well established that, in random copolymers of ionic and hydrophobic monomers, the types of ion-containing [6–12] and hydrophobe-containing [13–20] monomers, copolymer composition [13,14,20–25], and sequence distribution of hydrophobic and ionic monomer units along the polymer chain [22] are important factors that determine the self-associative properties of the polymers.

We have reported on the self-association behavior of random copolymers of sodium 2-(acrylamido)-2-methylpropanesulfonate (NaAMPS) with various hydrophobe-containing comonomers focusing mainly on the effects of the type of hydrophobes and spacer bond between the hydrophobe and polymer backbone [19,26,27]. The nature of the spacer bond, such as the length and flexibility of the spacer, is an important factor to control the self-association of polymer-bound hydrophobes, because the motion and conformational freedom of the hydrophobe are restrained by polymer chains [19,26–31]. A series of our earlier papers have dealt with self-assembling phenomena of random copolymers (Chart 1) of NaAMPS and a methacrylate substituted with $HO(CH_2CH_2O)_mC_{12}H_{25}$ ($C_{12}E_m$) (abbreviated as DE*m*MA), where $m = 2$, 6 or 25, with an emphasis put upon the effect of the length of the ethylene oxide (EO) spacer between the C_{12} chain and polymer backbone [30–32]. In these copolymers, $C_{12}E_m$ surfactant moieties are held

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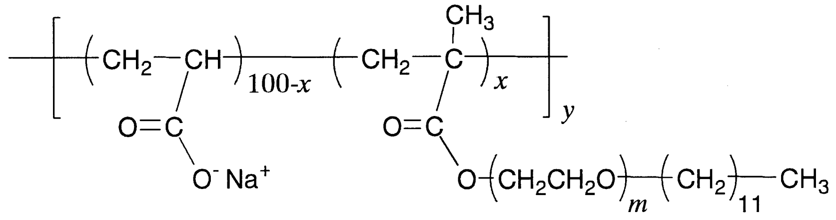
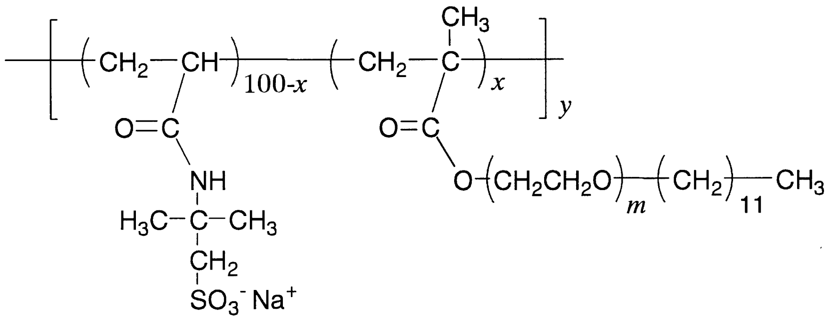
* Corresponding author. Tel./fax: +81-6-6850-5461.
E-mail address: morisima@chem.sci.osaka-u.ac.jp (Y. Morishima).

PII: S0032-3861(01)00466-9



$m = 2$, $x = 3$, 7, and 12	NaAA/DE2MA
6, $x = 3$, 7, and 12	NaAA/DE6MA
25, $x = 5$, 9, and 12	NaAA/DE25MA



$m = 2$, $x = 1$, 10, and 15	NaAMPS/DE2MA
6, $x = 1$, 5, 10, and 20	NaAMPS/DE6MA
25, $x = 1$, 3, 5, 7, 10, 15, 20, and 30	NaAMPS/DE25MA

Chart 1. NaAA/DE*m*MA and NaAMPS/DE*m*MA copolymers.

sufficiently close together on the same polymer chain allowing them to associate into a micelle-like assembly within the same polymer molecule, but some surfactant groups on different polymer chains participate in the self-assembling event to the extent that a stable aggregation number of the surfactant units in a micelle is attained [30,31]. Thus, polymer chains are crosslinked through the interpolymer side-chain micellization, forming a network structure of polymer chains. An important conclusion from our previous work is that the NaAMPS copolymer with a longer EO spacer undergoes side-chain micellization more favorably among different polymer chains to form a network structure. This conclusion is mainly based on the observation that solution viscosities for the NaAMPS copolymers with $m = 25$ were roughly two and three orders of magnitude higher than those of the copolymers with $m = 6$ and 2, respectively when compared at the same polymer concentration [31].

McCormick and co-workers [6–12] have reported on the influence of the chemical structure of anionic repeat units in polyelectrolytes on various solution properties such as rheological properties, phase separation in the presence of divalent cations, and responsiveness to changes in pH and ionic strength. One of their interesting studies is concerned with the self-association properties of hydrophobically modified polyanions [6]. They have revealed that interpolymer hydrophobic associations occur more favorably in polymers with charged groups located closer to the polymer backbone, and the tendency for interpolymer association is stronger for polymers having carboxylate anions than those having sulfonate anions [6].

We were motivated by these important results by McCormick and co-workers [6–12] to investigate self-assembling properties of copolymers of sodium acrylate (NaAA) and DE*m*MA with varying *m* in comparison with those of NaAMPS/DE*m*MA copolymers. Thus, in the present work, we synthesized copolymers of NaAA and DE*m*MA (where $m = 2$, 6 or 25) with varying compositions (Chart 1) and studied side-chain micellization and hence, network formation of the NaAA/DE*m*MA copolymers in 0.1 M NaCl aqueous solutions at a constant pH of 10.

Sodium (meth)acrylate copolymers with EO-based surfactant comonomers structurally similar to those synthesized in the present work are known as an associative thickener (AT polymer) [33–38]. The contents of the associative comonomers in the AT copolymers are usually less than 2 mol% which is normally enough to act as 'stickers'. A structural feature of the NaAA/DE*m*MA copolymers in the present study, as compared with the AT copolymers, is that a much larger number of surfactant moieties are loaded on a polymer chain allowing the polymer-bound surfactant moieties to undergo side-chain micellization rather than to act simply as stickers.

In this paper, we report on the effects of the EO spacer length (m) on the apparent critical micelle concentration (cmc), aggregation number (N_{agg}) of the side-chain hydrophobes in the polymer-bound micelle and steady-shear viscosity of the NaAA/DE*m*MA copolymers. Results are compared with those of the NaAMPS/DE*m*MA copolymers.

2. Experimental

2.1. Materials

Acrylic acid (AA) was purchased from Wako Pure Chemical Co. and purified by distillation under reduced pressure. Methacrylates substituted with $HO(CH_2CH_2O)_mC_{12}H_{25}$, DE*m*MA, where $m = 2$, 6 and 25, (abbreviated as DE2MA, DE6MA, and DE25MA, respectively) were synthesized as reported previously [30,31]. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Pyrene was recrystallized twice from ethanol. Water was purified with a Millipore Milli-Q system. *N*,*N*-Dimethylformamide (DMF) was distilled under reduced pressure over calcium hydride. Other reagents were used as received.

2.2. Polymers

Copolymers of AA and DE*m*MA were prepared by free radical copolymerization in the presence of AIBN in DMF at 60°C. A representative copolymerization procedure is as follows: Predetermined amounts of AA, DE*m*MA, and AIBN were dissolved in DMF. The solution was outgassed in a glass ampule on a high vacuum line by six freeze-pump-thaw cycles. The ampule was then sealed under high vacuum. Copolymerization was carried out at 60°C for 24 h. The reaction mixture was poured into a large excess of diethyl ether to precipitate resulting polymers. The polymer was purified by reprecipitation from a methanol solution into a large excess of diethyl ether three times, and then the polymer was dissolved in water by adding a small amount of a 5.0 M NaOH aqueous solution to neutralize the polymer. The solution pH was finally adjusted to 10 and dialyzed against pure water for a week using a cellulose tube (Viskase Sales Co., pore size: 36/32, corresponding to a cutoff molecular weight of 12,000–14,000). The polymer was recovered by a freeze-drying technique. The compositions of the copolymers were determined from ^1H NMR spectra.

Copolymers of sodium 2-(acrylamido)-2-methylpropanesulfonate and DE*m*MA (where $m = 2$, 6 and 25) are those synthesized in our earlier work [31].

2.3. Measurements

2.3.1. NMR

^1H-NMR spectra of the copolymers were measured on a JEOL GSX-400 NMR spectrometer at 60°C using D_2O as a solvent. Two-dimensional nuclear Overhauser effect (NOE) spectroscopy (NOESY) data were obtained for the NaAMPS/DE*m*MA copolymers ($m = 2$, 6 and 25) with a DE*m*MA content of 10 mol% with a Varian UNITY-600 spectrometer in D_2O at 30°C. Experiments were performed using a standard pulse sequence [39]. Mixing time before the acquisition of free induction decay was carefully varied and fixed to 50 ms to obtain a genuine NOE and to avoid the effect of spin diffusion. Chemical shifts in all data were determined using tetramethylsilane as an internal standard.

2.3.2. Gel permeation chromatography (GPC)

GPC measurements were performed at 40°C with a JASCO GPC-900 system equipped with an Asahipak GF-7M HQ column (Shodex) in combination with JASCO UV-975 (290 nm) and RI-930 detectors. Methanol containing 0.1 M $LiClO_4$ was used as eluent with an elution rate of 1.0 ml/min. Sample solutions were prepared as follows: solid samples of NaAA/DE*m*MA copolymers were dissolved in methanol, followed by addition of a 5.0 M HCl aqueous solution to completely protonate the copolymers. The methanol solution was dialyzed against methanol for a week. The protonated polymer samples were recovered by evaporating methanol and then dissolved in methanol containing 0.1 M $LiClO_4$ for GPC measurements. Molecular weights of the polymers were calibrated with standard poly(ethylene oxide) samples (Scientific Polymer Products, Inc.).

2.3.4. Absorption spectra

Absorption spectra were recorded on a JASCO V-550 spectrophotometer using a 1.0 cm path length quartz cuvette. The concentration of pyrene solubilized in the presence of polymer was calculated from the absorbance at 338 nm using the molar extinction coefficient $\epsilon_{338} = 37{,}000\ M^{-1}\ cm^{-1}$ [40].

2.3.5. Fluorescence

Sample solutions of the NaAA/DE*m*MA copolymers for fluorescence measurements were prepared as follows: a stock solution of polymer (12.5 g/l) was prepared by dissolving the polymer in a 0.1 M NaCl aqueous solution containing pyrene at a known concentration, and the pH was adjusted to 10 by adding a small amount of a 10 M NaOH aqueous solution using a micro-syringe with stirring. The solution was allowed to stand for 1 day for equilibration. The stock solution thus prepared was diluted with a 0.1 M NaCl aqueous solution containing pyrene at a known concentration, and the pH was re-adjusted to 10 by adding a smallest possible amount of an aqueous NaOH solution of a proper concentration (1–10 M). Aqueous pyrene solutions of known concentrations were prepared by diluting pyrene-saturated water as reported previously [26,30].

2.3.5.1. Steady-state fluorescence spectra. Steady-state fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Emission spectra of pyrene probes were measured with excitation at 337 nm at room temperature. Excitation spectra were monitored at 372 nm. The slit widths for both the excitation and emission sides were maintained at 2.5 nm during the measurement. For the determination of the apparent cmc of the polymer, excitation spectra of pyrene were measured at varying concentrations of the polymer following the method reported by Wilhelm et al. [41]. All measurements were performed with a pyrene concentration of 1×10^{-7} M. Experimental details were reported elsewhere [27,30,31].

2.3.5.2. Fluorescence decays. Fluorescence decay data were collected on a HORIBA NAES 550 system equipped with a flash lamp filled with H_2. Sample solutions containing pyrene as a fluorescence probe were excited at 337 nm, and pyrene fluorescence was monitored at 400 nm with a band pass filter (Toshiba KL-40) and a cutoff filter (Toshiba L-38) placed between the sample and detector. Sample solutions were purged with Ar for 30 min prior to measurement. The observed decay is a convolution of the sample decay function and the instrumental response function [27,30,31].

The aggregation number (N_{agg}) of the polymer hydrophobes was determined by a time-resolved fluorescence technique using pyrene as a fluorescence probe. A kinetic model proposed by Infelta [42,43] and Tachiya [44,45] for fluorescence quenching in monodisperse surfactant micellar systems was used for analysis of fluorescence decay data. Quenching of pyrene monomer fluorescence due to excimer formation was used to determine N_{agg}. Experimental details were reported elsewhere [27,30,31].

2.3.6. Steady-shear viscosity

The steady-shear viscosities of polymer solutions were measured at 25°C on a RheoLogica DynAlyser 100 stress-control rheometer equipped with a cone and plate. The radius of the cone is 40 mm, and the angle between the cone and plate is 4.0°.

3. Results

3.1. Characterization of NaAA/DEmMA copolymers

For copolymerization of water-soluble monomers and surfactant-substituted associative comonomers in water, a ‘micelle’ or ‘emulsion’ polymerization technique is often employed in the presence or absence of non-polymerizable surfactants [29,46–50]. This technique normally results in a copolymer with a blocky sequence distribution [22,47,48]. To obtain random copolymers, in the present work, we employed a homogeneous solution polymerization technique using DMF, a common solvent for acrylic acid (AA), DE*m*MA, and the resulting copolymer.

Fig. 1 shows an example of ^{1}H NMR spectra for an NaAA/DE6MA copolymer measured in D_2O. The mol% content of the DE*m*MA unit in the copolymer (f_{DEm}) was determined from the ratio of the area intensities of the resonance band associated with methylene protons in the EO group (3.8–4.1 ppm) and the bands associated with α-methyl, methylene, and methine protons in the main chain (1.2–2.5 ppm) by taking into account the band due to methylene protons in the dodecyl group overlapping near 1.5 ppm. Values of f_{DEm} thus estimated for all the NaAA/DE*m*MA copolymers synthesized in this work are listed in Table 1.

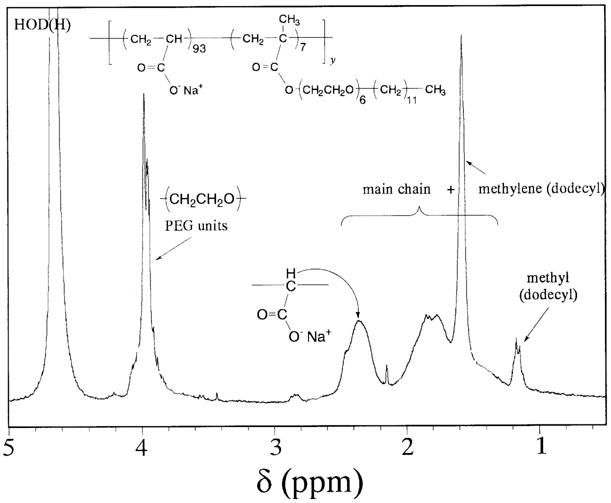


Fig. 1. 400 MHz ^{1}H NMR spectrum for the NaAA/DE6MA copolymer with $f_{DE6} = 7$ mol% in D_2O at 60°C.

For the calculation of the number of side-chain $C_{12}E_m$ surfactant units per polymer chain, we estimated the number-average molecular weight (M_n) of the NaAA/DE*m*MA copolymer by GPC using methanol containing 0.10 M $LiClO_4$ as an eluent and standard poly(ethylene

Table 1
Characteristics of NaAA/DE*m*MA copolymers

Comonomer	f_{DEm} (mol%)[a]	M_w[b] (10^4)	M_w/M_n[b]	Number of $C_{12}E_m$ (per polymer chain)	cmc[c] (g/l)
DE2MA	3	3.5	2.3	4	3.0×10^{-1}
	7	4.2	2.5	11	2.6×10^{-2}
	12	4.3	2.1	20	3.5×10^{-2}
DE6MA	3	3.8	2.4	4	6.4×10^{-2}
	7	4.2	2.6	9	8.4×10^{-3}
	12	4.4	2.3	18	3.8×10^{-3}
DE25MA	5	3.7	2.2	5	3.5×10^{-2}
	9	5.4	2.8	8	7.0×10^{-3}
	12	7.6	2.3	16	5.8×10^{-3}

[a] Determined by ^{1}H NMR in D_2O.

[b] Determined by GPC using a 0.1 M $LiClO_4$ methanol solution as eluent. Standard poly(ethylene oxide) samples were used for the calibration of the molecular weight.

[c] Determined from steady-state fluorescence excitation spectra of pyrene probes.

oxide) samples for calibration of M_n and weight-average molecular weight (M_w). In a separate experiment, we confirmed that M_w estimated by GPC is reasonably close to M_w determined by static light scattering in methanol containing 0.10 M $LiClO_4$. Therefore, we believe that M_w and M_n values estimated by GPC are reasonably good estimates of real molecular weights. These values are listed in Table 1. Values of M_w are on the order of 10^4 for all the copolymers, increasing slightly with increasing f_{DEm}, and molecular weight distributions (M_w/M_n) range of 2.1–2.8. From f_{DEm} and M_n values, the number of DE*m*MA units per polymer chain was roughly calculated for each copolymer, as listed in Table 1.

3.2. Apparent critical micelle concentration

In aqueous solutions of NaAA/DE*m*MA copolymers, dodecyl groups can associate within the same polymer chain (intrapolymer association) and also between different polymer chains (interpolymer association). In a dilute regime, the polymer showed a tendency for intrapolymer association, but as the polymer concentration (C_p) was increased to a certain level, the polymer exhibited a reasonably sharp onset for interpolymer association. In this paper, we define an apparent cmc as a polymer concentration at which interpolymer association starts to occur.

We previously reported that NaAMPS/DE*m*MA ($m = 2$, 6 or 25) copolymers showed an apparent cmc that was determined by fluorescence excitation spectra using pyrene as a probe [30,31]. This method is based on the fact that the 0–0 absorption maximum for pyrene in water at 334 nm shifts to 337 nm when pyrene is solubilized in a micellar phase [40,51,52]. We used the same method to determine an apparent cmc for NaAA/DE*m*MA copolymers. Fig. 2 shows an example of excitation spectra for pyrene probes solubilized in aqueous solutions of the NaAA/DE6MA copolymer with $f_{DE6} = 12$ mol% at different C_p. The ratio of the intensity at 337 nm relative to that at 334 nm (I_{337}/I_{334}), estimated from excitation spectra, increased with C_p. Fig. 3 shows an example of the I_{337}/I_{334} ratios for pyrene probes solubilized in aqueous solutions of the NaAA/DE*m*MA copolymers with $f_{DEm} = 12$ mol% at different C_p. The I_{337}/I_{334} ratio increases with increasing C_p, showing a sigmoidal curve.

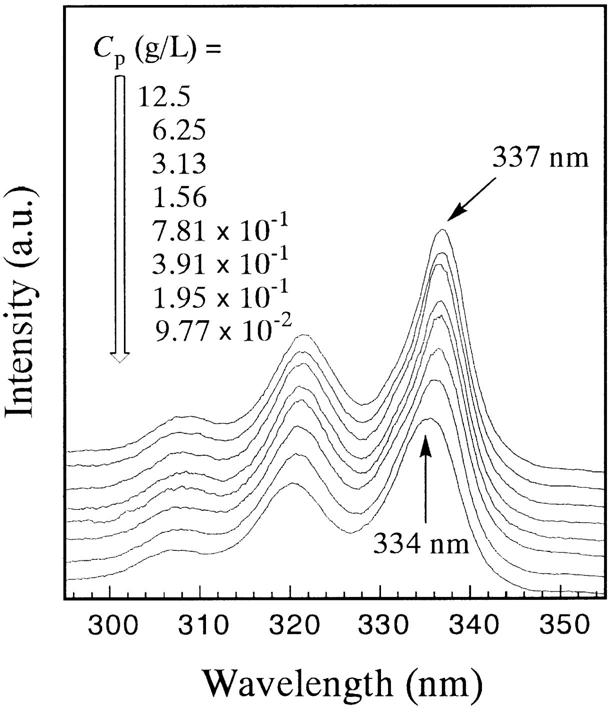


Fig. 2. Steady-state fluorescence excitation spectra monitored at 372 nm for pyrene probes in 0.1 M NaCl aqueous solutions in the presence of varying concentrations of the NaAA/DE6MA copolymer with $f_{DE6} = 12$ mol% : [pyrene] = 1.0×10^{-7} M.

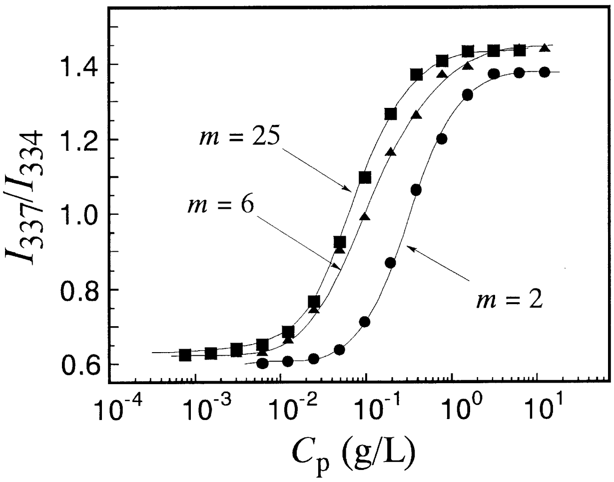


Fig. 3. Plots of the I_{337}/I_{334} ratio against the polymer concentration for the NaAA/DE*m*MA copolymers ($f_{DEm} = 12$ mol%) with varying m in 0.1 M NaCl aqueous solutions at pH 10: [pyrene] = 1.0×10^{-7} M.

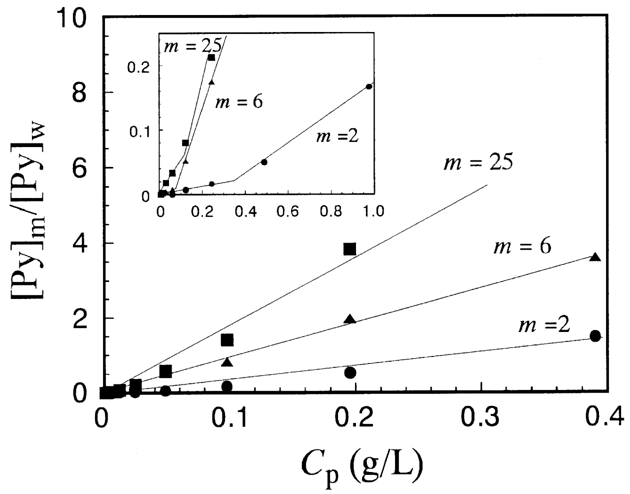


Fig. 4. Plots of $[Py]_m/[Py]_w$ estimated from the I_{337}/I_{334} ratio against the polymer concentration for the NaAA/DE*m*MA copolymers ($f_{DEm} = 12$ mol%) with varying m in 0.1 M NaCl aqueous solutions. The inset shows plots for a low C_p region on an expanded scale.

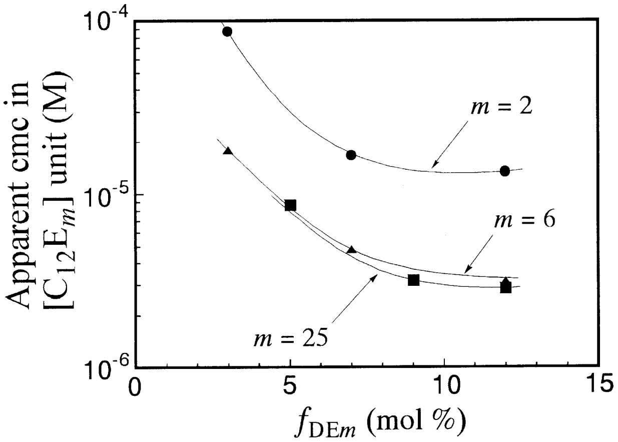


Fig. 5. Apparent cmc in terms of the molar concentration of the surfactant unit for the NaAA/DE*m*MA copolymers of varying *m* plotted as a function of f_{DEm}.

From I_{337}/I_{334} at a given C_p, along with the minimum and maximum I_{337}/I_{334} ratios observed in regimes of very low and high C_p, respectively, one can calculate a ratio of pyrene concentrations in the micellar and aqueous phases ($[Py]_m/[Py]_w$) at a given C_p according to a method reported in the literature [41]. Fig. 4 shows plots of $[Py]_m/[Py]_w$ as a function of C_p for the NaAA/DE*m*MA copolymers with $f_{DEm} =$ 12 mol%. We estimated apparent cmc values from a break observed in the $[Py]_m/[Py]_w$ vs. C_p plot (inset in Fig. 4). Apparent cmc values thus estimated for all the NaAA/DE*m*MA copolymers are listed in Table 1.

Fig. 5 shows the apparent cmc represented as the unit molar concentration of polymer-bound $C_{12}E_m$ groups plotted as a function of f_{DEm}. The apparent cmc decreases with increasing f_{DEm} for all the NaAA/DE*m*MA copolymers. As the length of EO spacer increases from $m = 2$ to 6, the apparent cmc decreases significantly, but as *m* further increases to 25, there is no further decrease in the apparent cmc. A similar tendency was observed for the corresponding NaAMPS copolymers in our prior work [31]. It should be noted here that as in the case of the NaAMPS/DE*m*MA copolymers, the apparent cmcs for the NaAA/DE*m*MA copolymers with varying f_{DEm} are much lower than those for the corresponding free $C_{12}E_m$ surfactants, i.e. 8.5×10^{-5} M for free $C_{12}E_6$ surfactants [53] and 2.8×10^{-4} M for $C_{12}E_{25}$ which we determined previously [31].

3.3. Aggregation number of polymer-bound $C_{12}E_m$ surfactants

We determined N_{agg} of the polymer-bound $C_{12}E_m$ surfactant units in a micelle formed from NaAA/DE*m*MA copolymers using a fluorescence technique based on the excimer formation of pyrene probes solubilized in the polymer-bound micelle [30,31]. This method uses a simple kinetic model proposed independently by Infelta [42,43] and Tachiya [44,45] to which fluorescence decay data are fitted. This analysis allows one to determine the ratio of the pyrene concentration to the micelle concentration from which one can calculate N_{agg} [27,30,31]. Fluorescence decays were measured for the NaAA/DE*m*MA copolymers with varying *m* at several different concentrations of the polymer and pyrene. It was confirmed that pyrene fluorescence decays for polymer solutions (≥0.781 g/l) with a very small amount of solubilized pyrene (1.0×10^{-7} M) were best-fitted to a single-exponential function with an unperturbed fluorescence lifetime (τ_0) of ca. 391 ns for all the copolymers independent of *m* (data not shown).

Fig. 6 shows plots of mean N_{agg} values thus estimated as a function of the molar concentrations of $C_{12}E_m$ residues in the NaAA/DE*m*MA ($f_{DEm} = 12$ mol%) copolymers converted from C_p. Values of N_{agg} for all the NaAA/DE*m*MA copolymers are independent of C_p within experimental errors. There is a large effect of the EO spacer length on N_{agg}. The N_{agg} values are on the order of 700 for $m = 2$, but the values decrease down to ca. 100 for $m = 6$ and 40 for $m =$ 25. This tendency is similar to that observed for NaAMPS/DE*m*MA copolymers of $m = 2$, 6 or 25 in our earlier work [31]. In the case of free $C_{12}E_m$ surfactant molecules, N_{agg} values are 220 ± 50 for $m = 6$ and 40 ± 2 for $m = 25$ [31]. These values are quite close to those observed for the polymer-bound $C_{12}E_m$ micelles, suggesting that the polymer-bound $C_{12}E_m$ surfactants can behave as if they were free entities when the EO length is $m \geq 6$. In the case of $m = 2$, we cannot compare polymer-bound $C_{12}E_2$ and free $C_{12}E_2$ molecules, because the free surfactant is not soluble in water [53].

In the case of the NaAA/DE*m*MA copolymers with $f_{DEm} = 12$ mol%, the numbers of polymer chains that participate in the formation of one micelle unit are calculated from N_{agg}, and the average numbers of $C_{12}E_m$ units per polymer chain (Table 1) to be at least 34, 7, and 3 for the NaAA copolymers of $m = 2$, 6 and 25, respectively. Thus, it

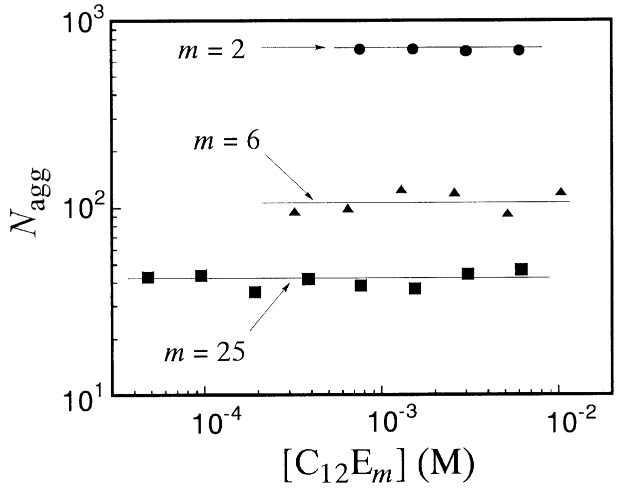


Fig. 6. Dependence of N_{agg} on the polymer concentration for the NaAA/DE*m*MA copolymers ($f_{DEm} = 12$ mol%) with varying *m* in 0.1 M NaCl aqueous solutions. The polymer concentration is represented as the molar concentration of the polymer-bound surfactant unit.

is obvious that each micelle is formed from interpolymer associations as well as intrapolymer associations, yielding a polymer network structure in which the micelle acts a crosslinking junction.

3.4. Steady-shear viscosity of polymer solutions

The formation of crosslinking through interpolymer side-chain micellization of the $C_{12}E_m$ surfactant moieties results in a large increase in solution viscosity depending on C_p. Zero-shear viscosities (η_0) for the NaAA/DE*m*MA copolymers with $f_{DEm} = 12$ mol% in 0.1 M NaCl aqueous solutions are plotted in Fig. 7 as a function of C_p over the C_p range of ca. 1–55 g/l. In fact, viscosity values in Fig. 7 are steady-shear viscosities measured at a shear rate of 10^{-3} s^{-1} at which the solutions were confirmed to behave as a Newtonian fluid. Therefore, these viscosities can be regarded as η_0. Since the viscosity in a higher C_p regime (>55 g/l) strongly depends on the shear rate even at lower shear rates ($<10^{-3}$ s^{-1}), exhibiting non-Newtonian behavior, we could not determine η_0 values at $C_p > 55$ g/l. The viscosity increases gradually with increasing C_p in a low C_p region, but it increases more significantly at C_p higher than ca. 8, 13, and 30 g/l for the copolymers with $m = 2$, 6 and 25, respectively. At C_p higher than these values, the extent of crosslinking increases greatly with increasing C_p, yielding a macroscopic network. The viscosities for the NaAA/DE*m*MA copolymer with $m = 2$ are roughly six and three orders of magnitude higher than those for the copolymers with $m = 25$ and 6, respectively at $C_p > 30$ g/l, indicating that the size of the network structure is much larger for the copolymer with shorter EO spacer.

The dependence of η_0 on the EO spacer length observed for the NaAA/DE*m*MA copolymers is completely opposite to that observed for NaAMPS/DE*m*MA copolymers reported in an earlier paper [31]. Namely, in the case of the NaAMPS/DE*m*MA copolymers ($f_{DEm} = 10$ mol%), a C_p at which the viscosity started to increase was lower for the copolymer with longer EO spacer length, and beyond this C_p, η_0 values were larger for the copolymers with longer EO spacer length [31]. As compared in Fig. 8, the viscosity decreases with increasing m for the NaAA/DE*m*MA copolymers, whereas it increases with m in the case of NaAMPS/DE*m*MA copolymers [31]. Furthermore, there is a huge difference in the magnitude of the viscosity between the NaAA/DE*m*MA and NaAMPS/DE*m*MA copolymers when the EO spacer is short. When compared at $m = 2$, η_0 for the NaAA copolymer is nearly eight orders of magnitude higher than that for the NaAMPS copolymer. The difference in the viscosity becomes smaller as m increases, and at $m = 25$, η_0 for the NaAA/DE*m*MA copolymer becomes smaller than that for the NaAMPS/DE*m*MA copolymer although they are nearly on the same order of magnitude. This trend indicates that the influence of the polymer backbone on the network formation is attenuated with an increase in the EO spacer length.

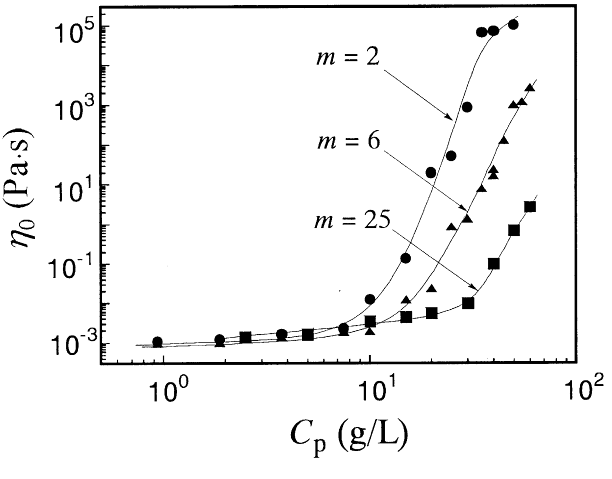


Fig. 7. Zero shear viscosity (η_0) at 25°C for the NaAA/DE*m*MA copolymers ($f_{DEm} = 12$ mol%) with varying m in 0.1 M NaCl aqueous solutions plotted as a function of the polymer concentration.

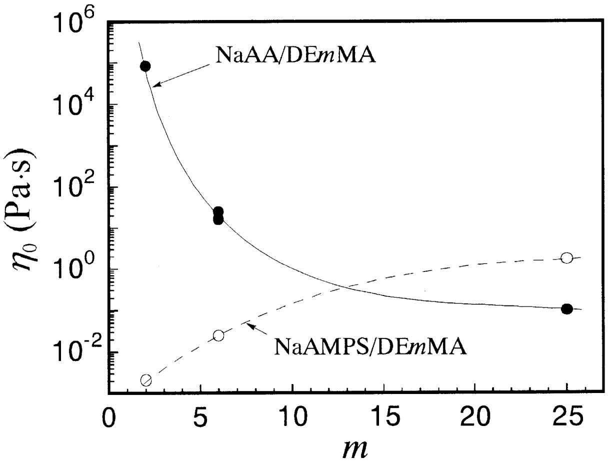
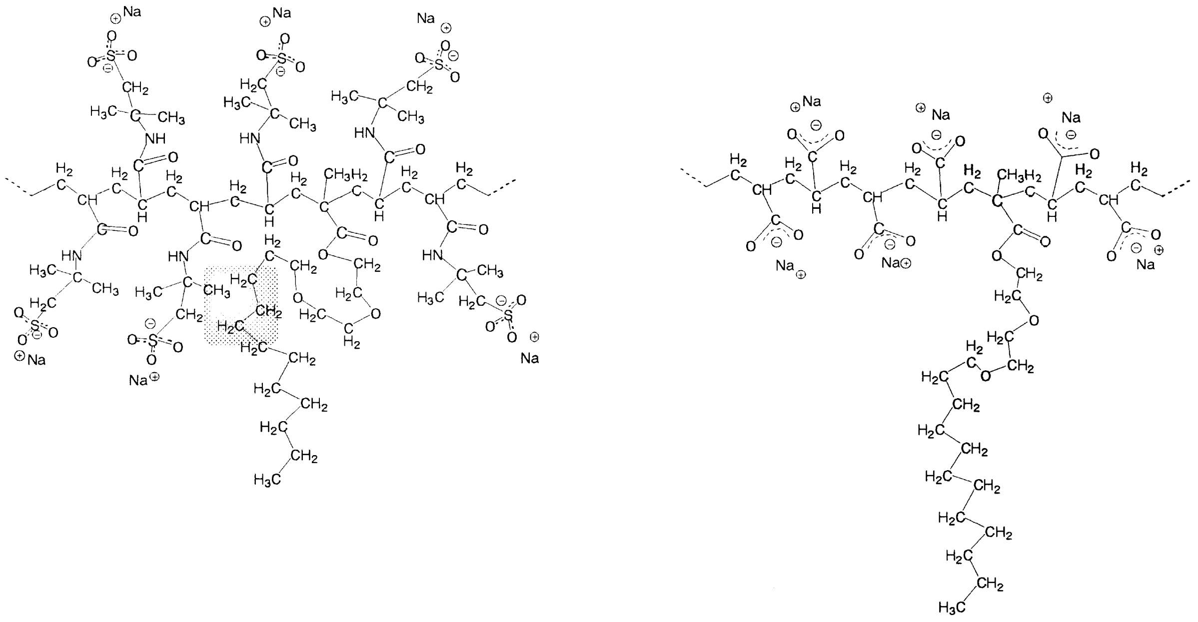


Fig. 8. Comparison of the dependencies of η_0 on m for the NaAA/DE*m*MA ($f_{DEm} = 12$ mol%) copolymers at $C_p = 40.0$ g/l and NaAMPS/DE*m*MA ($f_{DEm} = 10$ mol%) copolymers at $C_p = 50.0$ g/l in 0.1 M NaCl aqueous solution.

4. Discussion

Copolymers of NaAA/DE*m*MA and NaAMPS/DE*m*MA are similar in that $C_{12}E_m$ surfactant moieties in the copolymers undergo side-chain micellization, exhibiting apparent cmcs and aggregation numbers similar to those observed for free $C_{12}E_m$ surfactant molecules when $m = 6$ and 25 [30,31]. However, the NaAA- and NaAMPS-based copolymers are strikingly different in the influence of the EO spacer length on the solution viscosity.

Given the micelle acts as a crosslinking junction, the number of micelles in which $C_{12}E_m$ surfactant units on one polymer chain participate can be regarded as the number of crosslinking junctions per chain [54–58]. If all the surfactant units on one polymer chain were to undergo



AMPS/DE2MA copolymer

NaAA/DE2MA copolymer

Fig. 9. Schematic representations of NaAA/DE*m*MA and NaAMPS/DE*m*MA copolymers of $m = 2$.

completely intrapolymer association to assemble into the same micelle, the polymer chain would be regarded as having only one junction. Hence, the stronger is the tendency for intrapolymer surfactant association, the less number of junctions are formed per chain. The sharp decrease in η_0 with increasing m for the NaAA/DE*m*MA copolymer (Fig. 8) corresponds to a sharp decrease in the number of crosslinking junctions per chain, i.e. a tendency for intrapolymer surfactant association increases considerably with increasing EO spacer length. In contrast, for the NaAMPS/DE*m*MA copolymer, the number of junctions per chain increases with increasing m, i.e. a tendency for intrapolymer surfactant association decreases with increasing EO spacer length. The tendency for intrapolymer association for the NaAMPS/DE*m*MA with $m = 2$ and 6 are much stronger than that for the corresponding NaAA copolymers. When $m = 25$, however, the two copolymers exhibit a similar extent of intrapolymer association although the tendency is slightly weaker for the NaAMPS/DE*m*MA copolymer than for the NaAA copolymer.

McCormick and co-workers [6] have reported that terpolymers of acrylamide (AM), *n*-decylacrylamide (C10AM), and NaAA exhibit much stronger tendency for interpolymer hydrophobic associations than do terpolymers of AM, C10AM, and NaAMPS. The striking difference between the NaAA/DE*m*MA and NaAMPS/DE*m*MA copolymers of $m = 2$ and 6 in the present study may be compared with the difference between the NaAA/AM/C10AM and NaAMPS/AM/C10AM terpolymers. A characteristic feature of the NaAMPS repeat unit, as compared to the NaAA repeat unit, is that in the NaAMPS unit, charged groups are separated via several bonds from the backbone, allowing the charged groups to extend out farther from the backbone. Furthermore, as pointed out by McCormick and co-workers [6], the geminal dimethyl groups in the NaAMPS units may be hydrophobic enough to associate with neighboring hydrophobes on the same polymer chain, and hence interfere with interpolymer associations of the hydrophobes. These considerations are also relevant to the NaAA/DE*m*MA and NaAMPS/DE*m*MA copolymers in the present study. As conceptually illustrated in Fig. 9, when the EO spacer length is short, the geminal dimethyl group in the NaAMPS repeat unit may associate with dodecyl groups in the $C_{12}E_m$ surfactant unit on the same polymer chain. If such intrapolymer associations between the NaAMPS unit and the pendent $C_{12}E_m$ group occur, the C_{12} chains would be folded into a polymer coil rather than sticking out from the backbone, resulting in further intrapolymer associations with other C_{12} chains within the same polymer molecule. Hence, the polymer chain would be folded into a closed conformation, a situation where interpolymer hydrophobic association is unfavorable. As the EO spacer length increases, the interaction between the geminal dimethyl groups in NaAMPS and dodecyl groups becomes less favorable, and hence the polymer chain tends to adopt an open conformation with the $C_{12}E_m$ surfactant units extending out from the polymer chain, a situation where interpolymer hydrophobic association is favorable.

We attempted to see if there is an interaction between the NaAMPS geminal dimethyl and dodecyl groups in the NaAMPS-based copolymer by nuclear Overhauser effect (NOE) spectroscopy (NOESY) [59]. We measured NOESY spectra for a series of the NaAMPS/DE*m*MA copolymers with varying m (data not shown). Cross peaks between protons in the geminal dimethyl and dodecyl methylene groups, arising from the incoherent transfer of magnetization between the protons through dipole–dipole interactions, were observed only as a shoulder on a tail of a large diagonal peak. Therefore, unfortunately, we could not quantify the NOE intensity. However, from a subtle decrease in the relative intensity of the shoulder with increasing m, the presence of an interaction between the geminal methyl and dodecyl methylene groups was suggested for the NaAMPS copolymers particularly in the case of $m = 2$.

5. Conclusions

Micelle formation of random copolymers of NaAA and DEmMA ($m = 2$, 6 or 25) in 0.1 M NaCl aqueous solutions at pH = 10 was investigated, and experimental results were discussed in comparison with our previous results on the micelle formation of random copolymers of NaAMPS and DEmMA ($m = 2$, 6 or 25). The polymer-bound $C_{12}E_m$ surfactant moieties undergo association to form micelles within the same polymer chain and between different polymer chains, and hence the polymer chains are crosslinked, forming a network structure. Viscosity behavior of the NaAA-based copolymers was found to be strikingly different from that of the NaAMPS copolymer, although apparent cmcs and aggregation numbers of the polymer-bound $C_{12}E_m$ moieties in micelles formed from the NaAA-based copolymers were nearly the same as those found for the NaAMPS copolymers when the EO spacer length is the same. It was found that η_0 increased gradually with increasing C_p for both the copolymers in a dilute regime, followed by a drastic increase at higher C_p for both the copolymers. However, when compared at $m = 2$, η_0 for the NaAA copolymer is nearly eight orders of magnitude higher than that for the NaAMPS copolymer. This difference in the viscosity became smaller as m increased, and at $m = 25$, η_0 for the NaAA copolymer became smaller than that for the NaAMPS copolymer, suggesting that the influence of the polymer backbone on the network formation is minimized if the EO spacer length (m) is increased to 25. In a semidilute regime, η_0 for the NaAA copolymer of $m = 2$ was ca. 3 and 6 orders of magnitude higher than those of the NaAA copolymers of $m = 6$ and 25, respectively, indicating that the size of the network formed through side-chain micellization of the NaAA copolymer is larger for the copolymer with shorter EO spacer. This dependence of η_0 on the EO spacer length observed for the NaAA copolymers is completely opposite to that observed for the NaAMPS copolymer, i.e. η_0 for the NaAMPS copolymer of $m = 2$ was ca. 1 and 3 orders of magnitude lower than those of the NaAMPS copolymers of $m = 6$ and 25, respectively. These remarkable differences in the viscosity behavior between the NaAA- and NaAMPS-based copolymers were attributed to a much stronger tendency of the NaAA-based copolymer to undergo interpolymer association when the EO spacer length is short.

Acknowledgements

This work was supported in part by Shorai Foundation for Science and Technology and in part by a Grant-in-Aid for Scientific Research No. 10450354 from the Ministry of Education, Science, Sports and Culture, Japan.

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