Unique Associative Properties of Copolymers of Sodium Acrylate and Oligo(ethylene oxide) Alkyl Ether Methacrylates in Water

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ABSTRACT: A series of random copolymers of sodium acrylate and oligo(ethylene oxide) alkyl ether methacrylates ($C_n E_m MA$) with different lengths of ethylene oxide (EO) and alkyl groups were prepared by free-radical copolymerization at varying copolymer compositions. The lengths of the EO units (the number of EO units) (m) and the numbers of carbon atoms in the alkyl groups (n) ranged from 0 to 8.7 and 1 to 6, respectively. The copolymers with n = 1 and m = 1-8.7 exhibited a marked increase in solution viscosity at polymer concentrations (C_p) higher than their overlap concentrations (C^*) when the $C_n E_m MA$ contents (x) in the copolymers were in a certain limited range. Namely, there was an optimum x value that yielded the highest viscosity as a consequence of the competition between inter- and intrapolymer associations; the maximum viscosities occurred around $x \approx 25$, 15, 10, 7, and 3 mol % for m = 1, 2, 3, 4.2, and 8.7, respectively. The maximum viscosity decreased significantly as n was increased on going from 1 to 6, and for the copolymers with n = 6, no increase in the viscosity occurred, a trend opposite to what is expected to interpolymer hydrophobic associations. When $C_p > C^*$, steady-shear viscosity depended on the nature of countercations; the viscosities were found to be higher in the order $Li^+ > Na^+ \gg NH_4^+$, whereas reduced viscosity in dilute regime ($C_p < C^*$) was independent of the species of the cations. Rheological properties were found to be typical of transient networks formed through very weak interpolymer associations. Thus, the large increase in solution viscosity was explained by simultaneous interactions of countercations with EO units via coordination and with the polyanion via counterion condensation.

Introduction

Over the past two decades, self-associative watersoluble polymers have been the subject of continued interest not only in academia but also in industrial communities because these materials are an important class of macromolecules that are used for a variety of commercial applications as associative thickeners (AT) and rheology modifiers (RM).¹⁻⁴ AT and RM polymers are particularly important for industrial processes and commercial products such as paint, coatings, printing, paper, ceramic, drug, and cosmetic and personal care goods. The associative performance of these polymers is based on a strong tendency for interpolymer associations that are driven by noncovalent forces such as electrostatic, hydrogen bonding, van der Waals, and hydrophobic interactions. Most of AT and RM polymers known to date are based on hydrophobic interactions as a major driving force for the interpolymer association in water. These polymers are designed such that interpolymer association occurs predominantly over intrapolymer association.

In our earlier work, we reported that random copolymers of sodium acrylate (NaAA) and methacrylates substituted with $C_{12}H_{25}(OCH_2CH_2)_m$ -, where m = 2, 6, and 25 form transient networks as a result of interpolymer hydrophobic associations of the $C_{12}H_{25}(OCH_2 CH_2)_m$ - side-chain groups.^{5,6} In the course of the work,

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we came across the fact that similar copolymers in which the C_{12} (dodecyl group) was replaced with C_1 (methyl group) had a strong tendency for interpolymer associations when the copolymer compositions are within a certain limited range. This rather unexpected finding prompted us to undertake a systematic study on the associative properties of the copolymers of NaAA and methacrylates substituted with $C_nH_{2n+1}(OCH_2CH_2)_m$ — of a series of the numbers of carbon atoms in the alkyl group (*n*) and ethylene oxide (EO) repeat units (*m*) (C_nE_mMA).

This paper is concerned with associative properties in water of the random copolymers of NaAA and $C_n E_m$ -MA where n = 1-6 and m = 0-8.7 (poly(NaAA/ $C_n E_m$ -MA(x) in Chart 1), focusing on the effects of n and m as well as the content of the methacrylate unit in the copolymer (x) on rheological properties. All viscosity and viscoelastic measurements were performed in 0.1 M NaCl aqueous solutions of pH 10 unless otherwise noted. On the basis of experimental results, we will discuss a mechanism for interpolymer association.

Experimental Section

Materials. Acrylic acid (AA) (Aldrich Chemical Co.), methyl methacrylate (Wako Pure Chemical Co.), and 2-hydroxyethyl methacrylate (Wako Pure Chemical Co.) were distilled under reduced pressure. Oligo(ethylene oxide) monoalkyl ethers of various lengths of the EO and alkyl chains, $C_nH_{2n+1}(OCH_2-CH_2)_mOH$, where n = 0, 1, 2, 4, and 6 and m = 1, 2, and 3 were purchased from Kanto Chemical Co. (n = 1, m = 2), Wako Pure Chemical Co. (n = 1, m = 3; n = 4, m = 2), Sigma-Aldrich Japan Co. (n = 0, m = 2; n = 1, m = 1; n = 2, m = 2), and Tokyo Kasei Kogyo Co. (n = 6, m = 2) and used as received. Methacrylates substituted with $CH_3(OCH_2CH_2)_m$ -, where

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Chart 1. Structure of Poly(NaAA/C_nE_mMA(x))



Table 1. Compositions and Molecular Weights of Copolymers of NaAA and CH₃(OCH₂CH₂)_m-Substituted Methacrylate, Poly(NaAA/C₁E_mMA(x)), with Varying EO Lengths (m) and Methacrylate Contents (x) in the Copolymer

EO length (m)	C_1E_mMA in feed (mol %)	C_1E_mMA in copolymer ^a (mol %) (x)	$M_{ m w}{}^b$ (×10 ⁵)	$M_{ m w}/M_{ m n}^{b}$
0	10	10	1.3	1.9
0	30	28	1.8	2.6
1	5	5	3.6	3.6
1	10	10	3.7	1.9
1	20	20	2.2	1.9
1	30	27	2.6	1.9
1	50	45	3.1	3.4
2	5	5	2.6	1.6
2	10	10	2.6	2.0
2	20	20	2.9	1.9
2	30	28	1.3	3.0
3	5	5	3.8	1.8
3	10	10	2.5	1.8
3	20	20	2.6	2.3
4.2	2	2	1.4	2.4
4.2	5	5	1.2	2.3
4.2	10	9	1.0	2.8
4.2	20	20	0.9	2.9
8.7	2	2	1.2	2.5
8.7	5	5	1.0	2.7
8.7	10	10	0.9	2.7

 a Determined by ¹H NMR in D₂O. b Determined with the polymers in the acidic form by GPC using DMF containing 20 mM LiBr as eluent. $M_{\rm w}$ and $M_{\rm n}$ values were calibrated with polystyrene standard samples.

m = 4.2 and 8.7 on average, were a gift from Shin-Nakamura Chemical Co. and used without further purification. Methacryloyl chloride (Wako Pure Chemical Co.) was used without further purification. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Pyrene was recrystallized twice from ethanol. Water was purified with a Millipore Milli-Q system. Other reagents were used as received.

Monomers. A representative example for the synthesis of $C_n E_m MA$, where n = 1 and m = 2 is as follows: Methacryloyl chloride (12 mL, 0.11 mol) was added to a benzene solution of diethylene glycol monomethyl ether (C_1E_2) (27 g, 0.22 mol) and triethylamine (10 mL), followed by stirring for an additional 12 h at room temperature. After removing triethylamine HCl salt by filtration, the benzene solution was washed with a 0.1 M NaCl aqueous solution. After evaporation of benzene, the crude product was purified by distillation under reduced pressure: yield 89% (19 g); bp 65–66 °C (at 0.2 mmHg). The other methacrylate monomers were synthesized in a manner similar to this procedure.

Polymers. Copolymers of AA and $C_n E_m MA$ were prepared by free radical copolymerization. A representative example for the procedure of the copolymerization is as follows: To a mixture of AA and $C_n E_m MA$, a benzene solution of AIBN was added. The mixture was degassed by purging with Ar gas for 30 min at room temperature, and then the mixture was stirred under an Ar atmosphere at 65 °C for 12 h. As the polymerization proceeded, resulting polymers precipitated from the solution. After removal of benzene, crude polymer was purified by reprecipitation from an ethanol solution into a large excess of *n*-hexane, and then the polymer was dissolved in a dilute NaOH aqueous solution. The alkaline solution was dialyzed against pure water for a week and the polymer was recovered by freeze-drying. The copolymer compositions were determined from ¹H NMR spectra in D_2O at 30 °C on the basis of the ratio of the area intensities of resonance peaks at 0.5-2.6 and 3.3-

Table 2. Compositions and Molecular Weights of Copolymers of NaAA and

 $C_nH_{2n+1}(OCH_2CH_2)_m$ -Substituted Methacrylate, Poly(NaAA/ $C_nE_mMA(x)$), with Varying Lengths of Alkyl Group (n), EO Lengths (m), and Methacrylate Contents (x) in the Copolymer

alkyl length	EO length	$C_n E_m MA$ in feed	$C_n E_m MA$ in copolymer ^{<i>a</i>}	$M_{ m w}{}^b$	
<i>(n)</i>	(m)	(mol %)	$(\mathrm{mol}\ \%)(x)$	$(\times 10^{5})$	$M_{\rm w}/M_{\rm n}{}^b$
2	2	5	5	2.5	2.7
2	2	10	10	1.3	2.2
2	2	20	16	1.3	3.5
2	2	30	25	1.3	2.9
2	2	50	35	1.9	3.3
4	2	5	4	1.7	2.9
4	2	10	7	1.0	2.2
4	2	30	17	0.9	2.3
6	2	5	4	1.6	2.5
6	2	10	7	1.1	2.8
6	2	30	12	1.2	2.9
\mathbf{H}^{c}	1	5	5	1.2	2.7
\mathbf{H}^{c}	1	10	10	3.0	3.1
\mathbf{H}^{c}	1	20	20	1.7	3.4
\mathbf{H}^{c}	2	5	4	1.7	3.4
\mathbf{H}^{c}	2	10	9	2.9	3.3
\mathbf{H}^{c}	2	20	18	1.2	3.6

^{*a*} Determined by ¹H NMR in D₂O. ^{*b*} Determined with hydrolyzed polymers by GPC using water/acetonitrile (80/20, v/v) containing 0.1 M NaNO₃ as eluent. $M_{\rm w}$ and $M_{\rm n}$ values were calibrated with sodium polystyrenesulfonate standard samples. ^{*c*} H(OCH₂CH₂)_{*m*}-substituted methacrylate.

3.8 ppm associated with the main chain and EO protons in the $C_n E_m MA$ unit, respectively. The copolymer compositions and molecular weights for all the copolymers are summarized in Tables 1 and 2.

Measurements. Gel Permeation Chromatography (GPC). GPC measurements were performed using a JASCO GPC-900 instrument equipped with a JASCO RI-930 refractive index detector. For poly(NaAA/ $C_1E_mMA(x)$) copolymers, the polymer samples were acidified into the carboxylic acid form prior to GPC measurements. GPC analysis was performed using an Asahipak GF-7M HQ column (Shodex) with use of a 20 mM LiBr DMF solution as eluent at 40 °C. Polystyrene standard samples were used for molecular weight calibration.

GPC measurements were also conducted with hydrolyzed polymer samples on the same instrument equipped with TSKgel α -M (Tosoh) columns using a mixed solvent of water and acetonitrile (80/20, v/v) containing 0.1 M NaNO₃ as eluent at 40 °C. The hydrolysis of the poly(NaAA/C_nE_mMA(x)) samples was carried out in a 2 M NaOH aqueous solution at 80 °C for 12 h to completely eliminate the C_nH_{2n+1}(OCH₂-CH₂)_m- side-chain groups. Sodium polystyrenesulfonate standard samples were employed for molecular weight calibration.

¹**H NMR.** ¹H NMR spectra were recorded on a JEOL JNM EX-270 NMR using $CDCl_3$ or D_2O as solvent.

Rheometric Analysis. Rheological measurements were performed with a REOLOGICA DynAlyser 100 stress-controlled rheometer equipped with a cone and plate at 25 °C using a circulating water bath for temperature control. The radius of the cone was 40 mm, and the angle between the cone and plate was 4°. Steady-shear measurements were conducted in the shear stress range 0.03-1 Pa.

Viscosities in a dilute regime were measured using a Ubbelohde type viscometer at 25 °C. Intrinsic viscosities ([η]) were determined from Huggins plots.

Fluorescence Measurements. Steady-state fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrometer using a 1 cm path length quartz cuvette. Emission spectra of pyrene were measured with excitation at 334 nm. The slit widths for both excitation and emission sides were maintained at 2.5 nm during measurement.



Figure 1. Comparison of steady-shear viscosities and their dependence on shear rate for poly(NaAA/C₁E₁MA(*x*)) (a) and poly(NaAA/HE₁MA(*x*)) (b) of varying contents of the meth-acrylate unit in the copolymer (*x*): $C_{\rm p} = 10$ g/L, pH = 10, [NaCl] = 0.1 M, 25 °C.

Results

Comparison of NaAA Copolymers with 2-Hydroxyethyl Methacrylate and with 2-Methoxyethyl Methacrylate. As listed in Tables 1 and 2, copolymer compositions for all poly(NaAA/ $C_nE_mMA(x)$) samples (Chart 1) prepared in the present study are practically the same as those in the monomer feed, and the values of M_w are on the order of 10⁵. Copolymers of NaAA and a methacrylate substituted with a hydroxylend-capped EO, H(OCH₂CH₂)_m, were also prepared (Table 2) and used as reference polymers for comparison.

Figure 1 compares steady-shear viscosities of 10 g/L aqueous solutions of the copolymers of NaAA and 2-methoxyethyl methacrylate (C_1E_1MA) and those of the copolymers of NaAA and 2-hydroxyethyl methacrylate (HE_1MA) of similar molecular weights. Steady-shear viscosity of poly(NaAA/C₁ E_1 MA(x)) depends strongly on the content of the methacrylate in the copolymer (x), as can be seen in Figure 1a. As the methacrylate content is increased from 5 to 10 mol %, the viscosity increases only slightly, and the solution viscosities are practically independent of the shear rate (a Newtonian fluid). When the methacrylate content is increased to 20 mol %, the viscosity increases by orders of magnitude, and the solutions exhibit considerable shear thinning even at very low shear rates on the order of 10^{-3} s⁻¹. With a further increase in the methacrylate content up to 45 mol %, the viscosity drops markedly and becomes independent of the shear rate. These observations with $poly(NaAA/C_1E_1MA(x))$ are in sharp contrast to those observed with the NaAA/HE₁MA(x) copolymers. The NaAA/HE₁MA(x) copolymers with $x = 5-20 \mod \%$ exhibit viscosities similar to those of poly(NaAA/C1E1-MA(x)) with x = 5, 10, and 45 mol % independent of the



Figure 2. Dependence of steady-shear viscosities for poly-(NaAA/ C_nE_2 MA(x)) on the methacrylate content in the copolymer (x) for different lengths of alkyl group (n) at the end of the EO unit: $C_p = 10$ g/L, pH = 10, [NaCl] = 0.1 M, shear rate = 0.1 s⁻¹, 25 °C.

shear rate (Figure 1b). It should be noted here that for sample solutions with low viscosities (poly(NaAA/C₁E₁-MA(x)) of x = 5, 10, and 45 mol % and poly(NaAA/HE₁-MA(x)) of x = 5, 10, and 20 mol %) steady-shear viscosities at shear rates lower than those shown in Figure 1 were unable to be estimated with the rheometer used in this study because the lower limit of shear stress was more or less 0.03 Pa.

In a separate experiment, we found that solution viscosities of copolymers of NaAA and 2-(2-hydroxyethoxy)ethyl methacrylate (HE₂MA) were much higher than those of the NaAA/HE₁MA copolymers of similar molecular weights and that the viscosity behavior was similar to that of $poly(NaAA/C_1E_2MA(x))$, viscosity increasing strongly showing a strong shear thinning effect (data not shown). In the case where intra- and interpolymer associations are competing depending on the polymer conformation, shear thinning is often observed arising from a transition from inter- to intrapolymer associations induced under shear conditions. A strong shear thinning effect indicates that a large fraction of the elastically active interpolymer junctions have been severed. Consequently, the above observations, taken together with the data shown in Figure 1, suggest that ether bonds in the EO side chain of the methacrylate unit are playing an important role for interpolymer association, affecting the number density of elastically active cross-linked chains.

Effect of Alkyl Length. Steady-shear viscosity of $poly(NaAA/C_nE_mMA(x))$ in semidilute and concentrated regimes depends strongly on the EO length (m) and the alkyl length (n) as well as the $C_n E_m MA$ content (x) in the copolymer, giving rise to a maximum viscosity at a certain level of *x* depending on *m* and *n*. To clarify the origin of the interpolymer association that is responsible for the viscosity increase, we first looked into the effect of the alkyl length on the viscosity. Figure 2 shows steady-shear viscosities (measured at a shear rate of 0.1 s^{-1}) for poly(NaAA/C_nE₂MA(x)) (EO length is 2) with varying alkyl lengths plotted as a function of the methacrylate content in the copolymer. Clearly seen from Figure 2 is that interpolymer association is more favorable for the copolymers with shorter alkyl lengths. This trend is completely opposite to what is expected for interpolymer hydrophobic association. Therefore, we ruled out the possibility of hydrophobic interactions playing a main role for the viscosity increase. In the case of methyl, ethyl, and *n*-butyl groups, the steady-shear viscosity first increases and then decreases with increasing methacrylate content, showing a maximum



Figure 3. I_3/I_1 ratios in pyrene fluorescence spectra plotted as a function of the methacrylate content in poly(NaAA/ C_n E₂-MA(*x*)) of varying lengths of alkyl group (*n*): $C_p = 10$ g/L, pH = 10, [NaCl] = 0.1 M, 25 °C.



Figure 4. Steady-shear viscosities for poly(NaAA/C₁ E_m MA-(*x*)) of varying lengths of the EO unit (*m*) plotted as a function of the methacrylate content in the copolymer (*x*): $C_p = 10$ g/L, pH = 10, [NaCl] = 0.1 M, shear rate = 0.1 s⁻¹, 25 °C.

viscosity value. The maximum viscosity is lower for longer alkyl chains, and there is no increase in viscosity for n = 6 (*n*-hexyl). The bell-shaped profile of the plot in Figure 2 can be explained in terms of the balance of interpolymer vs intrapolymer associations, as will be discussed later.

Fluorescence spectra of pyrene probes solubilized in aqueous solutions of the copolymers indicated that hydrophobic associations occur more favorably for longer alkyl groups, since the intensity of the third vibronic band relative to that of the symmetry forbidden first vibronic band (I_3/I_1) reflects micropolarity around the probes, I_3/I_1 increasing with decreasing micropolarity.⁷ As shown in Figure 3, I_3/I_1 increases with increasing methacrylate content in the copolymer, and higher I_3/I_1 ratios were observed for copolymers with longer alkyl chains. From these observations, it is clear that the hydrophobic association does not contribute to the increase in viscosity. Therefore, it can be concluded that the hydrophobic association of the alkyl groups occurs predominantly within the same polymer chain.

Effect of EO Length. Figure 4 shows how steadyshear viscosity (measured at a shear rate of 0.1 s^{-1}) depends on the methacrylate content in the copolymer when the EO length is varied from m = 0 to 8.7 for poly-(NaAA/C₁E_mMA(x)) (the terminal alkyl group is methyl). In the case of m = 0 (i.e., copolymer of NaAA and methyl methacrylate), the viscosity decreases slightly with increasing the methacrylate content. For all the copolymers with m = 1-8.7, a bell-shaped dependence of the steady-shear viscosity on the copolymer composition was observed. Note that the x value that yields a maximum viscosity shifts toward lower contents of the methacrylate on going from m = 1 to 8.7, although there



Figure 5. Steady-shear viscosities for poly(NaAA/C₁E_mMA-(x)) of varying lengths of the EO unit (m) plotted as a function of the unit molar ratio of [EO]/[NaAA]: $C_p = 10$ g/L, pH = 10, [NaCl] = 0.1 M, shear rate = 0.1 s⁻¹, 25 °C.



Figure 6. Intrinsic viscosity ($[\eta]$) plotted as a function of the methacrylate content in poly(NaAA/C₁E₂MA(x)): pH = 10, [NaCl] = 0.1 M, 25 °C.

is not much difference in the maximum viscosity values for m = 1-8.7.

In Figure 5, the viscosities are plotted as a function of the molar ratio of EO to NaAA units ([EO]/[NaAA]) in the copolymer. Noteworthy is that the maximum viscosities appear in the neighborhood of [EO]/[NaAA] ~ 0.3 regardless of the EO length. Furthermore, the viscosity increases with increasing [EO]/[NaAA] ratio before reaching a maximum value following nearly the same trend independent of the EO length. After reaching the maximum, however, the viscosity decreases with increasing [EO]/[NaAA] ratio more significantly for shorter EO lengths. These observations suggest the presence of an optimum number of associative units per polymer chain that results in a maximum extent of interpolymer associations. Given that the molecular weights of all the copolymers are similar (Table 1), this optimum number of associative groups should be reflected in the [EO]/[NaAA] ratio of ~ 0.3 . We will come back to this point in the Discussion section.

Effect of Polymer Concentration. Figure 6 shows intrinsic viscosity plotted as a function of the methacrylate content in $poly(NaAA/C_1E_2MA(x))$. The intrinsic viscosities were determined by extrapolating reduced viscosity in a dilute regime to the zero concentration. The reduced viscosity vs polymer concentration plots at a salt concentration of 0.1 M NaCl gave linear relationships with positive slopes for all the copolymers with different contents of the methacrylate units (data not shown). As is clearly seen in Figure 6, the intrinsic viscosity decreases monotonically with increasing methacrylate content. This trend is remarkably different from the bell-shaped dependence of the steady-shear viscosity on the methacrylate content observed in a semidilute regime (Figure 4).

Presented in Figure 7 is a dependence of steady-shear viscosity on the polymer concentration (C_p) for poly-(NaAA/C₁E₂MA(10)). The viscosity increases only gradu-



Figure 7. Dependence of steady-shear viscosity on the polymer concentration for poly(NaAA/C₁E₂MA(10)): pH = 10, [NaCl] = 0.1 M, shear rate = 10^{-1} s^{-1} , 25 °C.



Figure 8. Comparison of salt effects on reduced viscosity at $C_{\rm p} = 1$ g/L (a) and steady-shear viscosity at $C_{\rm p} = 10$ g/L measured at a shear rate = 0.1 s⁻¹ (b): pH = 10, 25 °C.

ally in the dilute regime, and it starts to increase steeply near $C_{\rm p} \approx 2$ g/L. In general, an overlap concentration (C^*) can be estimated from the intrinsic viscosity using the relationship $C^* \approx 1/[\eta]$.⁸ For poly(NaAA/C₁E₂MA-(10)), C^* was thus estimated to be 2.75 g/L. In Figure 7, a $C_{\rm p}$ at which a drastic increase in the viscosity starts to occur appears to be slightly lower than C^* . When C_p $< C^*$, each polymer chain behaves as an independent entity, and hence the solution viscosity increases only moderately with increasing C_p . When $C_p > C^*$, on the other hand, polymer chains may entangle and hence the solution viscosity increases more significantly with increasing $C_{\rm p}$. However, if polymer chains associate when they overlap at $C_p > C^*$, the solution viscosity increases drastically with increasing C_p . Therefore, the steep increase in the viscosity observed in Figure 7 is apparently due to the formation of physical cross-links between polymer chains when they overlap. The bellshaped dependence of steady-shear viscosity on the methacrylate content (Figure 4) can be observed only when $C_p > C^*$. It is indicated that the cross-links formed at $C_p > C^*$ are unable to be sustained as such under a shear flow even at a very low shear rate on the order of 10^{-3} s⁻¹, as can be seen from a marked shear thinning (Figure 1). This means that polymer networks are formed by very weak interpolymer associations.

Effects of Ionic Strength and Countercations. Figure 8 compares effects of added salt on the reduced viscosity at $C_p = 1$ g/L (<C*) and the steady-shear viscosity at $C_p = 10$ g/L (>C*) for poly(NaAA/C₁E₂MA-

Table 3. Influences of the Type of Cations on Solution Viscosity of Poly(NaAA/C₁E₂MA(20))

counterion	$\operatorname{added}_{\operatorname{salt}^a}$	reduced viscosity at 1 g/L (L/g)	steady-shear viscosity at 10 g/L (Pa•s)	
${f Li^+}\ {f Na^+}\ {f NH_4^+}$	LiCl NaCl NH4Cl	0.58 0.63 0.57	$4.5 \\ 1.7 \\ 0.082$	
a [Salt] = 0.1 M.				



Figure 9. Dependence of steady-shear viscosity on pH for poly(NaAA/C₁E₂MA(10)): $C_p = 10$ g/L, [NaCl] = 0.1 M, shear rate = 0.1 s⁻¹, 25 °C.

(10)). The reduced viscosity at $C_{\rm p} < C^*$ decreases by nearly 2 orders of magnitude upon addition of 0.1 M NaCl, and then the viscosity decreases only slightly as the salt concentration is further increased (Figure 8a). In contrast, the steady-shear viscosity at $C_{\rm p} > C^*$ is much less dependent on the salt concentration in the low salt concentration region (Figure 8b), decreasing to only about one-half of its value upon addition of 0.1 M NaCl.

An important observation is that steady-shear viscosity at $C_p = 10 \text{ g/L}(>C^*)$ depends strongly on the nature of cationic species present as counterions. Table 3 compares reduced viscosity in a dilute regime where $C_{\rm p}$ $< C^*$ and steady-shear viscosity at $C_p = 10 \text{ g/L} (>C^*)$ for three different cationic species, i.e., Li⁺, Na⁺, NH₄⁺ ions. Salts added to solutions of the polymers with Li⁺ Na⁺, and NH₄⁺ counterions are LiCl, NaCl, and NH₄-Cl, respectively. For solutions at $C_{\rm p} = 10$ g/L (> C^*), the highest steady-shear viscosity was observed with Li⁺ ions, whereas no significant increase in viscosity was observed with NH_4^+ ions. On the other hand, for solutions at $C_{\rm p} = 1$ g/L (< C^*), reduced viscosities are independent of the nature of cationic species. These observations suggest that interaction of countercations with EO is responsible for interpolymer associations, as will be discussed later. The steady-shear viscosity at $C_{\rm p}$ = 10 g/L (> C^*) for poly(NaAA/C₁E₂MA(10)) is almost independent of pH (Figure 9). This finding suggests that interactions of protons with EO can contribute in a fashion similar to the increase in steady-shear viscosity.

Viscoelastic Properties. Hereafter, viscoelastic characteristics of aqueous solutions of the copolymers will be discussed in detail focusing on a representative polymer, poly(NaAA/C₁E₂MA(10)), where the number of EO units is 2 with the methyl terminal group and the content of the methacrylate is 10 mol %. In steady-shear viscosity measurements, sample solutions are subjected to a large deformation whereas in dynamic rheological measurements, small oscillatory deformations are imposed on a sample solution. Dependences of storage (G') and loss (G'') moduli on angular frequency are usually used to characterize the viscoelastic behavior of a sample solution, where G' and G'' reflect the elastic and viscous behavior of the sample solution, respectively. It was confirmed that dilute solutions of poly(NaAA/C₁E₂-

Figure 10. Storage (G') and loss (G'') moduli as a function of angular frequency for poly(NaAA/C₁E₂MA(10)) measured with a shear stress of 0.03 Pa: $C_p = 20$ g/L, pH = 10, [NaCl] = 0.1 M, 25 °C.

Figure 11. Dependences of storage (*G'*) and loss (*G''*) moduli on shear stress applied to a solution of poly(NaAA/C₁E₂MA-(10)) at a constant angular frequency of 0.628 rad/s (0.1 Hz): $C_{\rm p} = 20$ g/L, pH = 10, [NaCl] = 0.1 M, 25 °C.

MA(10)) show a dominant viscous property whereas semidilute and concentrated solutions show a dominant elastic property. In Figure 10, G' and G'' are plotted as a function of angular frequency measured at a shear stress of 0.03 Pa applied to a solution of 20 g/L poly- $(NaAA/C_1E_2MA(10))$. As can be seen from Figure 11, viscoelastic responses seem to be within the linear regime when shear stresses used for the angular frequency sweeps are smaller than ca. 0.07 Pa, where the values of \hat{G}' and G'' remain practically constant independent of the applied stress. The solution of poly- $(NaAA/C_1E_2MA(10))$ at 20 g/L exhibits the characteristic viscoelastic behavior of gels when shear stresses applied are smaller than ca. 0.5 Pa, the values of G' vary little with angular frequency, and G' is always higher than G'' over the range of angular frequencies monitored. In general, it can be inferred that G' reflects the number density of mechanically active junctions while G'' reflects the effective volume occupied by the mechanically active polymer network. Thus, the data show in Figure 10 mean that the elastic response dominates over that of the viscous flow. Consequently, it is evidenced that the polymers form a physical gel at $C_{\rm p}=20$ g/L. However, as the shear stress is increased, apparent values of G' decrease significantly, especially in a lowfrequency region. This means that the solution becomes less elastic when a larger stress is applied to the sample. These observations indicate that the polymer cross-links are only transient and can be readily disrupted even when a weak shear stress is imposed.

Creep recovery techniques often provide useful information about viscoelastic properties of complex fluids having a long relaxation time.⁹ An example of creep and recovery curves for poly(NaAA/C₁E₂MA(10)) is presented in Figure 12a. This creep experiment was performed such that a very small shear stress of 0.05

Figure 12. (a) Creep compliance plotted as a function of time for $poly(NaAA/C_1E_2MA(10))$: $C_p = 50$ g/L, pH = 10, [NaCl] = 0.1 M, 25 °C. The compliance was recorded when a shear stress of 0.05 Pa was applied for 30 min and after the shear stress was removed. (b) A four-element mechanical model used to fit to the creep and recovery data.

Pa was applied to a polymer solution of a higher concentration (50 g/L) of poly(NaAA/C₁E₂MA(10)) for 30 min, and the strain was monitored as a function of time during the shear stress was applied and after the shear stress was removed. Creep characteristics of viscoelastic fluids are often analyzed by using a four-element mechanical model where a Maxwell body and a Voigt body are connected in series (Figure 12b).⁹ When a constant shear stress is applied instantaneously to a viscoelastic solution at time (t) zero, the creep compliance at any given time t is represented as

$$J(t) = J_0 + J_d \{1 - \exp(-t/\lambda)\} + t/\eta$$
 (1)

where J(t) is the creep compliance at time t, J_0 is the instantaneous compliance for the elastic deformation of the Maxwell body at the applied shear stress of 0.05 Pa, J_d is the compliance for the Voigt body, λ is the retardation time for the creep, and η is the steady-state viscosity at the applied shear stress of 0.05 Pa. When the shear stress is removed at $t = t_1$, the recovery follows a pattern similar to the creep compliance; an instantaneous elastic recovery is followed by a retarded elastic recovery which is represented by

$$J(t) = J_{\rm r} \exp\{-(t - t_1)/\lambda\} + t_1/\eta$$
 (2)

where J_r is the creep compliance immediately before the shear stress is removed at $t = t_1$. The data for the creep and recovery phases (Figure 12) were best-fitted to eqs 1 and 2, respectively. The steady shear viscosity at a very low shear stress of 0.05 Pa for the 50 g/L polymer solution was found to be extremely high; from the best fit, $\eta = 1.5 \times 10^5$ Pa·s was estimated. The steady-state compliance (J_e) is related to J_0 and J_d as $J_e = J_0 + J_d$. Thus, the terminal relaxation time (τ) can be estimated from the relation $\tau = J_e \eta$ as 2.1 × 10⁴ s. These results, taken together with results from oscillatory measurements, indicate that the polymer solution is characteristic of transient gels formed from extremely weak interpolymer associations.

Figure 13. Schematic illustration of a model for counterionmediated interpolymer associations.

Discussion

From the facts that the dependence of the steadyshear viscosity at $C_p > C^*$ on added salt is remarkably different from that of the reduced viscosity at $C_p < C^*$ (Figure 8a,b) such that the former is dependent on the nature of counterions, higher in the order Li⁺ > Na⁺ » NH₄⁺, while the latter is virtually independent of the type of the cations (Table 3), it is evident that the increase in the steady-shear viscosity at $C_{\rm p} > C^*$ is based on the interaction of the EO groups with countercations. According to Manning theory, ^{10,11} ca. 60% of polymer charges for poly(NaAA/ $C_n E_m MA(10)$) are electrostatically neutralized by condensed countercations that are closely bound to the polymer main chain. These condensed counterions may find a way to interact with the EO chain in the $C_n E_m MA$ unit by coordinating with the ether oxygens. Such simultaneous interactions of the condensed countercations with the polymer through electrostatic forces and coordination with the EO side chain may provide a driving force for an interpolymer interaction. In other words, condensed cations can mediate polymer-polymer associations, forming weak junctions between polymer chains, as schematically illustrated in Figure 13. In fact, the order in the strength of such coordination $(Li^+ > Na^+ \gg NH_4^+)$ agrees with the order of the increase in viscosity at $C_{\rm p}$ $> C^*$.

According to this postulated model (Figure 13), the attraction between polymer chains should be little influenced by pH changes, as can be seen in Figure 9, because protons can also coordinate with the ether oxygen in the EO unit. As the concentration of added salt is increased, the fraction of the countercations that interact simultaneously with the polyanion and the EO side chain decreases, and hence the mediating effect of the countercation should decrease (Figure 8b), following a trend completely different from that of the shielding of electrostatic repulsions by added salt (Figure 8a).

The foregoing model illustrated in Figure 13 is similar to a model proposed for interactions between micelles of anionic surfactants and poly(ethylene oxide) (PEO). Dubin and co-workers^{12,13} suggested that countercations electrostatically bound to a sodium dodecyl sulfate (SDS) micelle could simultaneously coordinate with PEO oxygens, thus the EO unit in PEO behaving like a "pseudocation". Schwuger¹⁴ also pointed out a possibility that oxygen atom of the ether linkage with its lone electron pair could possibly become slightly positively charged as a result of the coordination of cations, which could favor an interaction with the negatively charged surfactant anion.

In the case of hydrophobically modified water-soluble polymers, interpolymer association occurs competing with intrapolymer association, and the balance of the inter- and intrapolymer associations depends strongly on the number of hydrophobes attached to a polymer chain. There is a general tendency that interpolymer association is favorable when the number of polymerbound hydrophobes is very small and interpolymer association becomes unfavorable when the number of hydrophobes is increased.^{15,16} Thus, there is an optimum hydrophobe content that leads to the highest viscosity as a result of the competition between inter- and intrapolymer associations of hydrophobes. It is reasonable to think that the same tendency applies to associations driven by any other noncovalent forces than hydrophobic ones. Therefore, in the case of poly(NaAA/ $C_n E_m MA(x)$), it can be presumed that there is an optimum number of EO units per polymer chain resulting in a maximum degree of interpolymer associations. This optimum number may correspond to a ratio of $[EO]/[NaAA] \sim 0.3$ at which viscosity is maximized (Figure 5). As the number of the EO groups per chain is increased beyond this level, intrapolymer interactions will become more favorable. The larger number of intrapolymer associations will cause the polymer chain to coil into a more compact conformation, thereby making interpolymer associations more unfavorable.

When the length of hydrophobic alkyl groups in some amphiphilic water-soluble polymers is increased, the polymers tend to form a more extended network structure through interpolymer hydrophobic associations.¹⁷ In the case of poly(NaAA/ $C_n E_m MA(x)$), however, it appears that intrapolymer hydrophobic associations are more favorable for longer alkyl chains, resulting in a folded chain conformation which is an unfavorable situation for interpolymer simultaneous coordination/ electrostatic interactions to occur (Figure 2). Another effect of the length of the alkyl chain in poly(NaAA/ $C_n E_m MA(x)$) that one can think of is a possibility that the alkyl groups may hinder coordination interactions of EO units with countercations condensed on the polymer chain.

Even though the coordination energy per EO unit is very small, the total interaction energy per polymer chain can be large enough to retain polymer chains cross-linked. However, the interpolymer associations are not sufficiently strong to sustain the cross-linked structure under shear conditions even at low shear rates on the order of 10^{-3} s⁻¹. The nature of the interpolymer junctions of this copolymer is unique in that the association sites or junctions can move along on the polymer chain because Na⁺ cations that are territorially bound to the anionic polymer can move freely along the main chain while simultaneously coordinating to EO units. If shear stress is imposed, some junctions may be broken as a result of local deformation of segments but some of the severed junctions may be re-formed at a site different from its original site through the relaxation of the chain conformation. Thus, the long relaxation time observed may be a reflection of the slowest viscoelastic process for the associating polymer chains to be totally severed apart form each other.

Conclusions

Random copolymers of NaAA and $C_n E_m MA$ where n = 1 and m = 1-8.7 exhibit a large increase in solution viscosity when $C_p > C^*$. There is an optimum content

of $C_n E_m MA$ in the copolymer, resulting in the highest viscosity as a consequence of the competition between inter- and intrapolymer associations. When $C_p > C^*$, steady-shear viscosity strongly depends on the type of countercation species. The viscosity was found to be higher in the order Li⁺ > Na⁺ \gg NH₄⁺, whereas reduced viscosity in a dilute regime ($C_p < C^*$) is independent of the type of the cations. Rheological properties are typical of transient networks formed by very weak interpolymer associations. An interpolymer association model was proposed where simultaneous interactions of countercations with EO units via coordination and condensation on the polymer are the origin for the interpolymer association.

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