

Synthesis and Characterization of Fluorocarbon-Containing, Hydrophobically Associative Poly(Acrylic Acid-co-R_F-Poly(ethylene glycol) Macromonomer)

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ABSTRACT: Fluorocarbon- or hydrocarbon-end-capped poly(ethylene glycol) (PEG) macromonomers were prepared with coupling methods. Several factors affecting the synthesis were studied, and the optimal condition was ascertained. The critical micelle concentrations of these macromonomers were determined with the fluorescence method. Novel fluorocarbon-containing, hydrophobically modified, alkali-soluble copolymers were made by the copolymerization of fluorocarbon- or hydrocarbon-alkyl-end-capped PEG macromonomers with acrylic acid in an organic solvent. The effects of the macromonomer contents, polymerization conditions, spacer, temperature, shear rate, pH, and addition of salt and various surfactants on the solution viscosity were preliminarily investigated. A very strong hydrophobic association was found for these copolymer solutions. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1035–1047, 2002; DOI 10.1002/app.10393

Key words: macromonomers; poly(ethylene glycol); fluorocarbon-containing; hydrophobically associative; poly(acrylic acid); viscosity; fluorescence

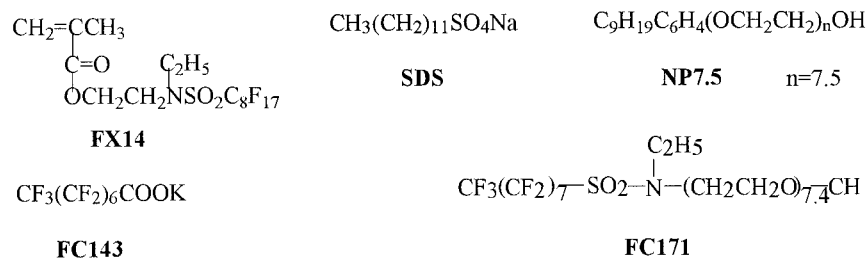
INTRODUCTION

The copolymerization of macromonomers over the past 2 decades has made it possible to prepare a variety of structurally well-defined graft copolymers.^{1–4} In particular, poly(ethylene glycol)

(PEG) macromonomers² can be conveniently synthesized by the living anionic polymerization of ethylene oxide followed by appropriate end-functionalization/coupling reactions with monomer groups. PEG is one of the structurally simplest macromolecules but exhibits complicated solution properties. It is unique among those polymers in being soluble in many organic solvents and water. Its macromonomers are used as building blocks in the synthesis of amphiphilic graft copolymers capable of forming stable aggregates in solution. For instance, a wide spectrum of hydrophilic–

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Scheme 1 Structures of comonomer FX14 and anionic and nonionic surfactants.

hydrophobic properties can be displayed with changes in the R and n values of macromonomers.⁵ Also, the synthesis of high molecular weight, amphiphilic, comblike or starlike graft polymers is made possible by the copolymerization of PEG macromonomers.²

The copolymerization of hydrophilic monomers and hydrophobic comonomers typically requires the presence of high surfactant/monomer ratios to disperse or dissolve the comonomer and/or copolymer product in the aqueous medium.⁶ This may be avoided by the use of PEG macromonomers with inborn surfactant character. For instance, the synthesis of hydrophobically associated acrylate copolymers has been reported through the copolymerization of hydrocarbon-end-capped PEG acrylate macromonomers ($n = 20-40$).⁷ Recently, Jenkins⁸ et al. synthesized a high-performance associative thickener (AT) by the copolymerization of methacrylic acid and ethyl acrylate along with an acrylate macromonomer; their dilute and semidilute solution properties with and without the presence of sodium dodecylsulfate and C_{12}EO_5 were investigated.⁹⁻¹³ A detailed mechanism was proposed with regard to the microstructure under a variety of conditions.

In our previous work, a series of fluorocarbon-containing, hydrophobically associating polymers (FHAPs) were synthesized, and strong aggregation in FHAP solutions was found.¹⁴⁻¹⁶ Contrary to the large number of studies dealing with hydrophobically associated, water-soluble polymers (HAWSPs) containing long hydrocarbon chains, little research has been documented so far on the synthesis and solution properties of HAWSP-containing, fluorocarbon-end-capped macromonomers, such as fluorocarbon-end-capped PEG monoacrylate.¹⁷ Additionally, a blocky hydrophobic group was found not to be indispensable for strong association in the solution copolymerization system.¹⁸ Whether similar results can be obtained for these special hydrophobic monomers

with a PEG spacer inserted between the hydrophobe and backbone is worthy of study. Therefore, in this article, we report on the synthesis of fluorocarbon-end-capped PEG macromonomers, the copolymerization of these macromonomers with acrylic acid (AA), and the characterization of the polymer solution properties.

EXPERIMENTAL

Materials

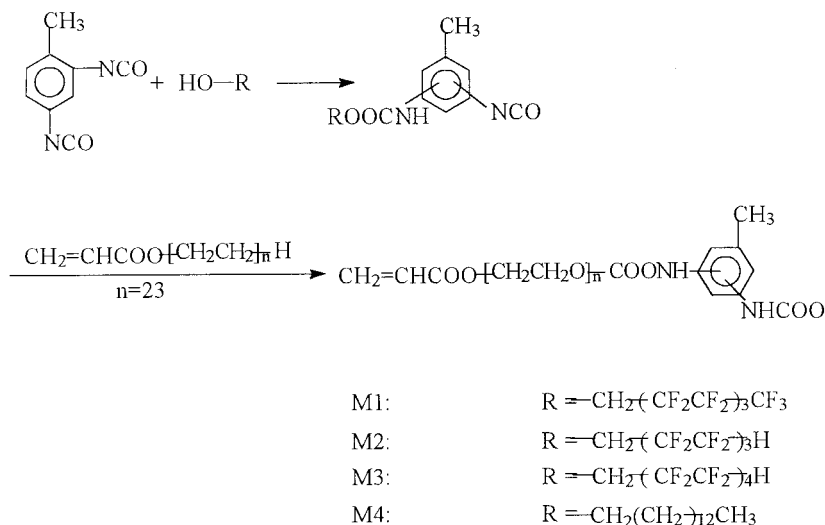
AA (analytical reagent), 2,4- and 2,6-toluene diisocyanate (TDI; analytical reagent), n -tetradecanol (analytical reagent), 1,1,7-trihydroperfluoroheptanol (THFH), 1,1,9-trihydroperfluorononanol (purchased from a pilot plant of SIOC, Shanghai, China, technical grade), pentadecafluorooctanoic acid (technical grade, Shanghai 3F Co., Shanghai, China), and dibutyltin laureate (analytical reagent) were used as received. α -Monoacrylate- ω -monohydroxyl-PEG (ethylene oxide = 23) was purchased from Monomer-Polymer Labs, Inc. (Feasterville, PA). Azobisisobutyronitrile (AIBN) was recrystallized from methanol. 1,4-Dioxane (analytical reagent) was redistilled before use. The structures of 2-(N -ethylperfluorooctanesulfonamido)ethyl methacrylate (FX14) and the surfactants (SDS, NP7.5, FC143, and FC171) are shown in Scheme 1.

Synthesis and Characterization

The synthesis route of M2 and the structures of the macromonomers (M1-M4) are shown in Scheme 2. The syntheses of the four macromonomers are similar. The synthesis process is detailed in the following subsections.

Mono(1,1,7-trihydroperfluoroheptanol)-Substituted 2,4- and 2,6-TDI

Into a 250-mL, three-necked, round-bottom flask, 33.05 g (189.7 mmol) of freshly distilled 2,4- or



Scheme 2 Synthesis of M2 and structures of M1, M2, M3, and M4.

2,6-TDI and 100 mL of dry tetrahydrofuran (THF) were added, and the resulting solution was purged with nitrogen. Then, 10 g (30.1 mmol) of THFH in 50 mL of dry THF was slowly added, and the mixture was stirred overnight at 60°C. After 24 h, excessive TDI was removed by evacuation under reduced pressure (1 mmHg) at 130–140°C. The remaining TDI was successively removed by refluxing with 80 mL of dry *n*-hexane, followed by dry-ice cooling for 2 h and quick decanting of the supernatant from the waxy residue. Refluxing with *n*-hexane and decanting were repeated several times for complete removal of excess TDI from the mono(1,1,7-trihydroperfluoroheptanol)-substituted 2,4- or 2,6-TDI product. This intermediate was dried *in vacuo* for several hours, giving 2.0 g of a yellow solid (13% yield).

¹H-NMR (300 MHz, CDCl₃, δ, ppm): 7.3–7.7, 6.6–7.2 (3H, m, aromatic ring), 5.9–6.0 (1H, t, CF₂H), 4.4–4.8 (2H, t, O—CH₂—CF₂), 3.7 (1H, s, NH), 2.1 (3H, s, CH₃). ¹⁹F-NMR (300 MHz, CDCl₃, δ, ppm): 43 (2F), 45–47 (6F), 52–53 (2F), 59–61 (2F).

***α*-Monoacrylate-*ω*-mono(1,1,7-trihydrododecafluoroheptanol)-Substituted-2,4- and 2,6-TDI-End-Capped PEG macromonomer (M2)**

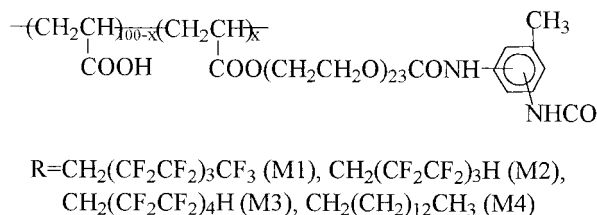
α-Monoacrylate-*ω*-monohydroxyl-PEG (2.0 g, 1.9 mmol) and 1.0 g (1.9 mmol) of mono(1,1,7-trihydroperfluoroheptanol)-substituted 2,4- and 2,6-TDI were placed in a 100-mL, three-necked, round-bottom flask and dissolved in 50 mL of dry ethylene glycol diethyl ether; then, several drops of

dibutyltin laureate were added to the mixture. The reaction mixture was stirred for 10 h at 90–100°C under nitrogen. The resulting homogeneous solution was poured into 300 mL of hexane, and the liquid was decanted from the precipitate and extracted twice with 200 mL of hexane and 200 mL of diethyl ether. The solid was refluxed in 35 mL of ethyl acrylate and precipitated by the addition of 100 mL of hexane. The resultant product was vacuum-dried, affording 1.42 g of a yellow-brown, waxy solid (47% yield).

¹H-NMR (300 MHz, CDCl₃, δ, ppm): 6.9–7.2, 7.6–7.8 (3H, m, aromatic ring), 5.7–6.4 (4H, m, CH₂=CH—C=O, CF₂H), 4.7–4.8 (2H, t, CH₂CF₂), 4.2 (2H, t, —CH₂—O—C=O), 3.6 [90H, m, —CH₂—O—(CH₂CH₂O)_{n-2}—CH₂—], 2.1 (3H, s, CH₃), 8.0–8.1, 9.2 (2H, —CO—NH—). ¹⁹F-NMR (300 MHz, CDCl₃, δ, ppm): 43 (2F), 45–49 (6F), 52–53 (2F), 60–61 (2F).

Copolymerization of AA and Fluorocarbon-PEG Macromonomers

A typical synthesis involved the reaction of AA (2 g) and a certain amount of macromonomer dissolved in 20 mL of 1,4-dioxane in a 50-mL, round-bottom flask capped with a rubber stopper. AIBN (4.8 mg) dissolved in dioxane was injected into the flask. The solution was purged with dry pure nitrogen in an ice–water bath for 30 min and then immersed in a 50 ± 0.5°C oil bath with magnetic stirring for 15 h. After the addition of 20–30 mL of dioxane for dissolution of the gel-like product, the copolymer was obtained by precipitation into



Scheme 3 Structure of macromonomer-modified PAA.

diethyl ether. The product was vacuum-dried at 50°C for at least 20 h. The AA copolymers were dissolved in deionized water. Then, after the pH was adjusted to 11 by the addition of 1M NaOH, the polymer was precipitated in a large excess of anhydrous diethyl ether and dried as described previously.

The acidic copolymer structure is shown in Scheme 3. Here the nomenclature of these polymer samples is explained. Samples are represented as poly(acrylic acid) (PAA)-M_n-X where M_n is M1, M2, M3, or M4 (the macromonomer copolymerized with AA) and X is the molar percentage of the macromonomer (the feed amount). For example, PAA-M2-1.0 indicates that M2 is used as a comonomer in polymerization with AA and accounts for 1 mol % of the total feed. The others are analogous.

Characterization and Measurements

¹H-NMR spectra and ¹⁹F-NMR spectra were obtained with a Bruker 300AM instrument with tetramethylsilane and trifluoroacetic acid as external standards, respectively. Fluorescence was recorded on a static FZ-I fluorescent spectrometer with a 7.5-nm excitation slit (333 nm) and a 5-nm emission slit. Fluorine contents of the copolymers (as weight percentages) were determined by anionic chromatography on a Dionex2010I instrument. Viscosities were measured at 25 ± 0.5°C on a Wells Brookfield viscometer equipped with two different spindle sizes (18 and 34). Polymer solutions were prepared in deionized water, and the pH values of solutions were adjusted to about 9, except for the research on the pH effect on the solution viscosity.

RESULTS AND DISCUSSION

Synthesis of the Fluorocarbon-Containing PEG Macromonomers

Three fluorocarbon-end-capped PEG macromonomers and one hydrocarbon-end-capped PEG macromonomer were successfully synthesized, and the structures were confirmed with IR, ¹H-NMR, and ¹⁹F-NMR.

Because of the difficulty of removing excess TDI, the first step of the synthesis needed to be performed very carefully. Many factors affected the yield and purity of this step, the reaction temperature and catalyst amount being the most important. As shown in Table I, a large amount of catalyst increased conversion but also accelerated side reactions affecting product purity. Therefore, the success of the reaction was highly dependent on the amount of catalyst, and this, in turn, correlated with the reaction time, temperature, and concentration of reactants in the system. As side reactions were enhanced at higher temperatures, reaction temperature needed to be kept as low as possible. For the second step, the molar ratio of TDI-mTHFH to α-monoacrylate-ω-monohydroxyl-PEG was the most important factor.

The intensity ratios I_1/I_3 and I_{338}/I_{333} , plotted against the concentration of the macromonomer surfactant M4, are illustrated in Figure 1. At low

Critical Micelle Concentration (cmc) of the Surfactant Macromonomers

The aforementioned hydrophobically modified macromonomers could be characterized as surfactants because of the coexistence of long hydrophilic PEG units in the molecular chains and hydrophobic fluorocarbon or hydrocarbon units at the end. It is well known^{15,16} that pyrene dissolves preferentially in the hydrophobic microdomains of micelles, and this leads to decreased I_1/I_3 intensity ratios, that is, the ratio of the first band to the third band in the pyrene emission spectra, and increased I_{338}/I_{333} ratios, that is, the ratio obtained from (0,0) bands of pyrene excitation spectra.

The intensity ratios I_1/I_3 and I_{338}/I_{333} , plotted against the concentration of the macromonomer surfactant M4, are illustrated in Figure 1. At low

Table I Relationship Between M2 Yield and Reaction Temperature and Added Catalyst

Temperature (°C)	Catalyst (g) ^a	Yield (%)
60	—	79
80	—	85
100	—	50
60	0.0443	105
60	0.0176	88.5
40	0.0499	72

^aDibutyltin laureate in our work.

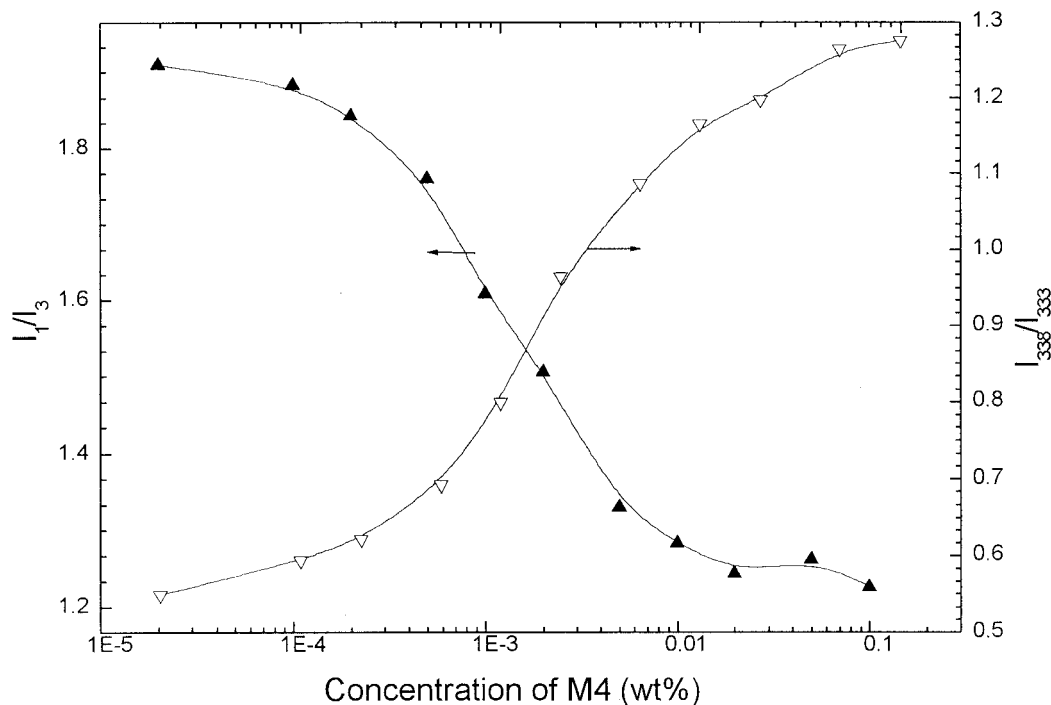


Figure 1 M4 cmc characterized by (▲) I_1/I_3 and (▽) I_{338}/I_{333} .

M4 concentrations, the probe experienced an aqueous environment: I_1/I_3 was about 1.9 and I_{338}/I_{333} was about 0.5. With increasing M4 concentration, I_1/I_3 and I_{338}/I_{333} decreased and increased simultaneously; this indicated the partitioning of pyrene in a hydrophobic environment. However, the variation of I_1/I_3 and I_{338}/I_{333} , which covered almost 2 decades of M4 concentrations, was more progressive than for conventional surfactants. This agreed with the three other macromonomers and was attributed to a less cooperative association of the hydrophobic moieties. Above about $10^{-2}M$, the I_1/I_3 and I_{338}/I_{333} ratios remained relatively constant, indicating an unchanging microenvironment that was sufficiently hydrophobic for pyrene. According to the results reported by Racey and Stebe¹⁹ concerning the association ability of CF_2 being equal to $1.7 CH_2$, M1 and M3 should pose the same apparent cmc as M4. As shown in Table II, however, the apparent cmc of M4 was 1 decade lower than cmc of the two fluorocarbon-modified macromonomers. This may be ascribed to the poor compatibility of pyrene with the fluorocarbon micelles. Even for the three fluorocarbon-modified surfactants, the cmc values were very close despite the different lengths and end units of the fluorocarbon groups.

Copolymerization of the Macromonomers with AA

The conversions of the fluorocarbon macromonomers M1, M2, and M3 in copolymerizations with AA, as determined by anionic chromatography, are listed in Table III and did not exceed 30%. A similar result was reported by Piculell and co-workers^{20,21}; macromonomer conversions in the copolymerizations of PEG monoacrylate (molecular weight = 5000–7000) with AA were between 22 and 26%. The low reactivity ratios of the macromonomers were assumed to correlate with the high molecular weight, giving rise to diffusion-controlled effects in this system.^{1,2,22}

The effects of water, cyclohexane, and ethyl acetate as cosolvents (1/1 v/v) in the 1,4-dioxane copolymerizations were explored briefly. As

Table II PEG macromonomer cmc

Sample	End-Capped Group	cmc ^a (wt %)
M1	$CF_3(CF_2)_6CH_2-$	3×10^{-3}
M2	$H(CF_2CF_2)_3CH_2-$	1.6×10^{-3}
M3	$H(CF_2CF_2)_4CH_2-$	2.6×10^{-3}
M4	$CH_3(CH_2)_{13}-$	3×10^{-4}

^aDetermined by fluorescence method.

Table III Characterization of Three Series of Fluorocarbon-Containing PAA-co-Macromer^a

Feed Ratio	1.0% Macromer		1.5% Macromer		2.0% Macromer	
	F(%) ^b	Conversion (%)	F(%)	Conversion (%)	F(%)	Conversion (%)
M1	0.58	22.2	1.05	28.5	1.26	27.3
M2	0.28	16.9	0.39	16.3	0.46	15.3
M3	—	—	0.98	37.8	1.52	47.0

^aPolymerization was carried out in 1,4-dioxane at 50°C, and all samples were in their sodium form.

^bDetermined by anionic chromatography.

shown in Table IV, the 1/1 dioxane/cyclohexane mixture favored increased conversion of M2, whereas in the presence of ethyl acetate the conversion decreased. Temperature changes did not seem to affect macromonomer incorporation significantly. Apparently, the presence of cyclohexane affected the reactivity ratios of the two monomers. This is not yet well understood.

It can be concluded that the distribution of the macromonomer along the PAA backbone was random for this system when solvent copolymerization was adopted and the feed ratio of the macromonomer to AA was not greater than 2 mol %.²³ The architectures of the polymer samples, therefore, differed from those obtained by micelle polymerization, by which microblock or multisticker structures can be obtained.^{24,25} Solution properties, induced by the association of statistically distributed fluorocarbon groups, are discussed next.

Viscometric Study of Macromonomer-Modified PAA

Effect of the Macromonomer Feed Ratio and Polymerization Media

The critical aggregation concentration (cac) is an important empirical parameter for characterizing

the association ability of hydrophobically modified polymers. Above the cac, a dramatic increase in polymer solution viscosity is observed that can be ascribed to the formation of physical crosslinks via intermolecular hydrophobic association. Therefore, the cac is a measure of the tendency of a particular copolymer toward hydrophobic association, and its value decreases with increasingly efficient interpolymer association.

Given the dependence of viscosity on the shear rate in typical HAWSPs, the Brookfield viscosity transition concentration (BVTC), above which the solution viscosity increases far more dramatically than below, does not directly correspond to the so-called cac. However, they are quantitatively consistent, and a lower BVTC value corresponds to a stronger transient network.

As shown in Figure 2, the BVTC of a solution of an AA/M2 copolymer was strongly dependent on the M2 content. Therefore, no enhancement in solution viscosity was observed at an M2/AA feed ratio of 0.5 mol %, whereas at a higher M2 content (PAA-M2-1.0) the BVTC decreased dramatically. However, when the M2 feed ratio increased from 1.5 to 2.0 mol %, the BVTC decreased slightly. Apparently, above this M2 content, the associative ability of the modified polymer decreased. This effect was noted by Zhang et al.¹⁴ several

Table IV Effect of Polymerization Condition on the Conversion of M2

	Polymerization Condition				
	Dioxane	Dioxane (80°C) ^a	Dioxane/Water (1/1, v/v)	Dioxane/Cyclohexane (1/1, v/v)	Dioxane/Ethyl Acetate (1/1, v/v)
F (%) ^b	0.46	0.57	0.46	1.55	0.38
Conversion (%)	15.3	19.1	15.3	52.1	12.8

^aOther samples were prepared at 50°C.

^bSamples were in their sodium form and fluorine percentage was determined by anionic chromatography.

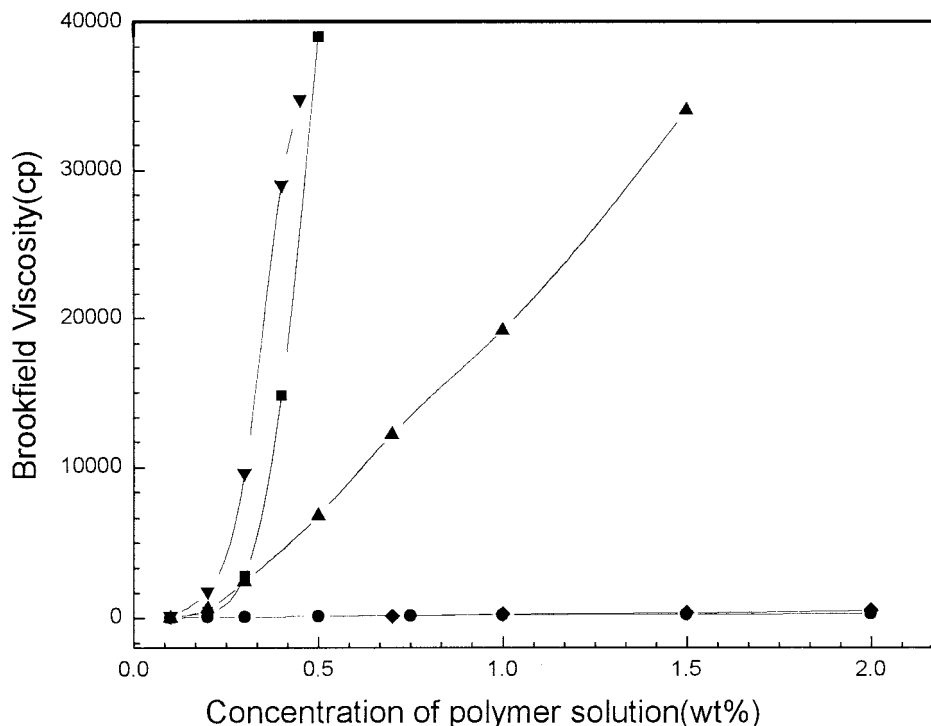


Figure 2 Effect of the macromonomer content on the viscosity of a polymer solution at a shear rate of 0.42 s^{-1} : (●) PAA, (◆) PAA-M2-0.5, (▲) PAA-M2-1.0, (▼) PAA-M2-1.5, and (■) PAA-M2-2.0.

years ago for 2-(*N*-ethylperfluorooctanesulfoamido)ethyl (meth)acrylate-acrylamide copolymers. In that case, at a constant copolymer concentration, the apparent viscosity plotted as a function of the comonomer content was bell-shaped. This has been attributed to competing intramolecular association and has been well documented for similar hydrocarbon-modified, water-soluble polymers.^{6,8,10}

As indicated previously, the presence of cosolvents during copolymerization affected the conversion of M2. Furthermore, the solution properties of copolymers prepared in different solvents also differed. For instance, as shown in Table IV and Figure 3, PAA-M2-2.0 obtained from 1,4-dioxane at 50°C possessed a greater thickening ability in comparison with that of the corresponding copolymer with the same comonomer content but prepared in a dioxane/water mixture. The same appears to be the case for copolymer PAA-M2-1.5 (M2 content = 0.244 mol %) compared with copolymer PAA-M2-2.0 prepared in dioxane/ethyl acetate and having almost the same overall comonomer content (M2 content = 0.256 mol %). Therefore, the synthesis conditions were apparently important (as discussed later) on the

basis of the relatively lower hydrophobic content. An increase in the temperature or the addition of a second solvent, either polar or nonpolar, during polymerization reduced the solution viscosity of the corresponding product without exception. Although a sample prepared in a mixture of 1,4-dioxane and cyclohexane had the highest content of hydrophobic groups, it presented the worst viscosifying ability. Copolymerizations carried out in 1,4-dioxane/water, 1,4-dioxane/ethyl acetate, or 1,4-dioxane at 80°C , seemed to decrease the molecular weight and, therefore, the thickening ability. For copolymers made in 1,4-dioxane/cyclohexane, however, low molecular weight should not be considered the key factor. The very high hydrophobic content, compared with the contents of the others, seemed to reduce the effective intermolecular association because of excessive depletion of hydrophobic groups by intramolecular association.

Effect of the Spacer

As shown in Figure 4, the thickening abilities of the PAA copolymers of macromonomers M1-M4 were similar and far greater than those of the

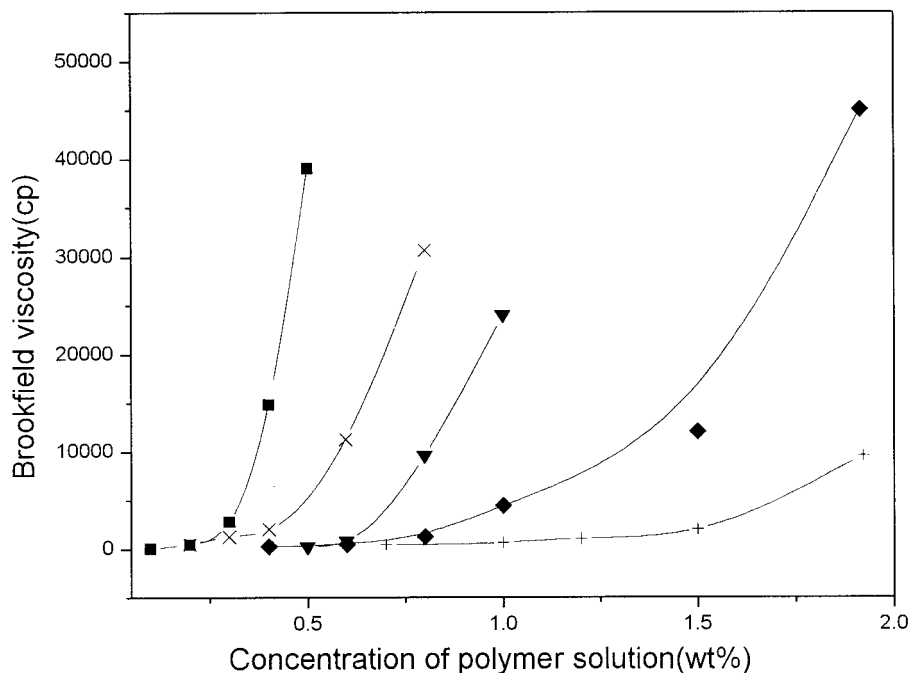


Figure 3 Effect of the polymerization conditions on the solution properties of PAA-M2-2.0: (■) 1,4-dioxane, (×) 1,4-dioxane/water (1/1), (▼) 1,4-dioxane (80°C), (◆) 1,4-dioxane/ethyl acetate (1/1), and (+) 1,4-dioxane/cyclohexane (1/1).

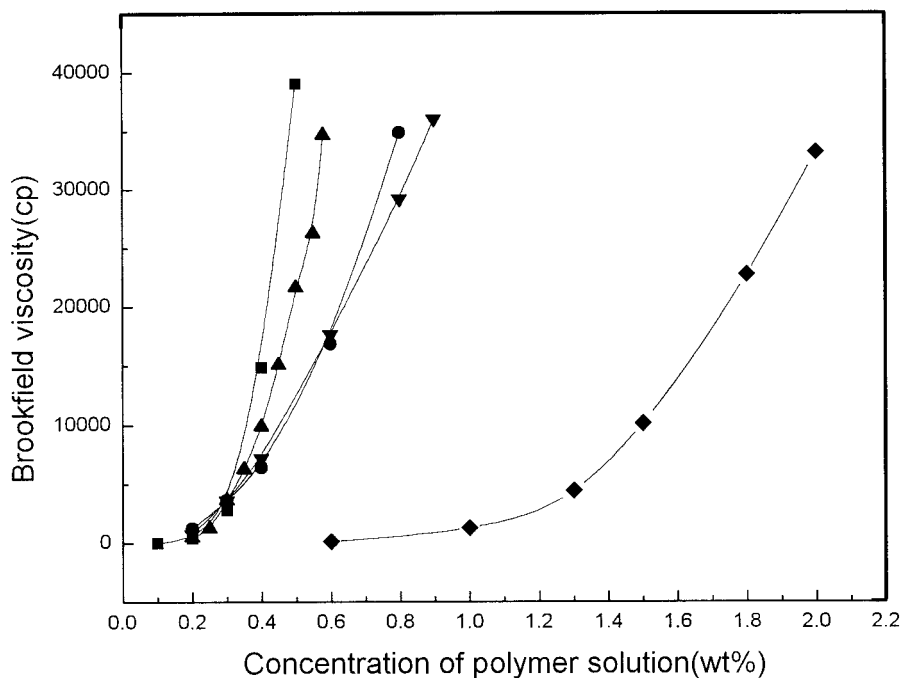


Figure 4 Effect of the PEG spacer on the solution properties of the copolymers: (▲) PAA-M1-2.0, (■) PAA-M2-2.0, (▼) PAA-M3-2.0, (●) PAA-M4-2.0, and (◆) PAA-FX14-2.0.

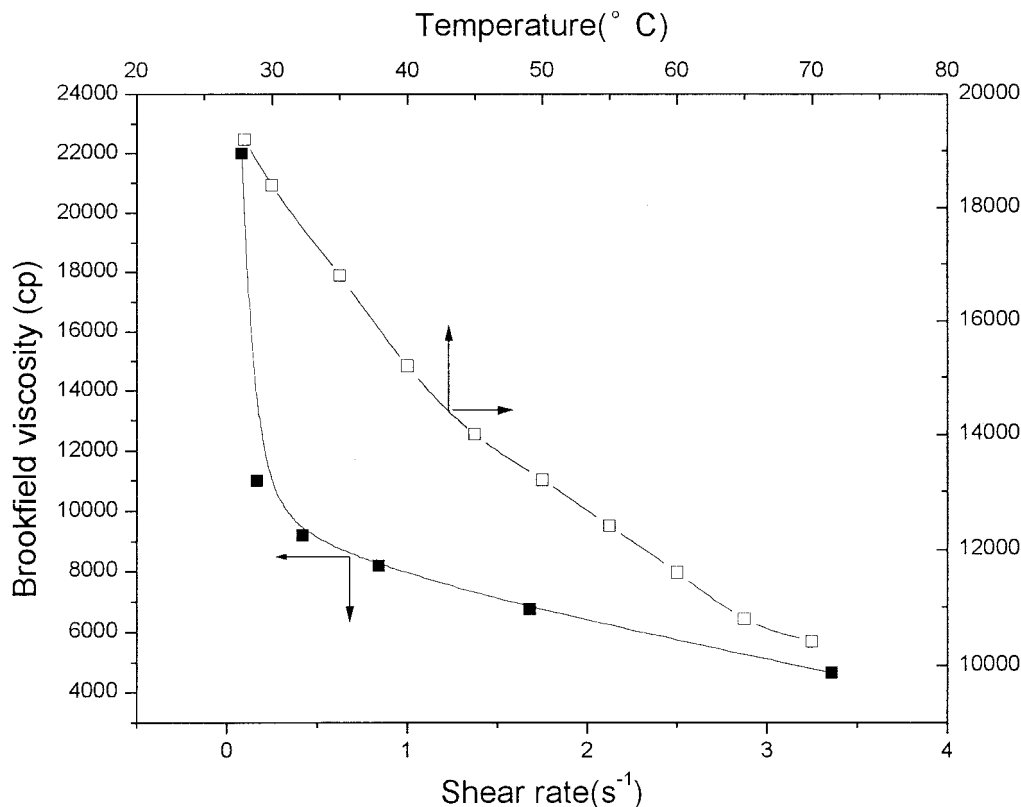


Figure 5 Effect of the shear rate and temperature on the solution properties: (□) PAA-M1-2.0 (0.3 wt %) and (■) PAA-M2-1.5 (0.3 wt %).

copolymers of AA with FX14 (the structure is shown in Scheme 1). The BTVC values of the macromonomer copolymers were about 5 times lower. This agrees with earlier studies by Hwang and Hogen-Esch,²⁶ demonstrating that increasing the hydrophilic spacer lengths led to stronger hydrophobic association in copolymers of acrylamide and acrylates containing PEG spacer groups with one, two, or three ethylene oxide units. This was explained by a decoupling of the motions of the hydrophobic groups from those of the hydrophobes in the hydrophobic microdomains, which led to a more favorable entropy of association.

In this system, the spacer consisted of about 23 oxyethylene groups (weight-average molecular weight/number-average molecular weight < 1.1 for PEG monoacrylate), and the solution viscosities of the copolymers modified by these macromonomers were far higher than those with FX14. Because of the much lower conversions of these four macromonomers with respect to FX14 (for which the conversion usually reached 90 mol %) at an equal molar feed ratio, the more distinguished associative ability of the hydrophobically

modified macromonomer was evident. This confirmed the promoting effect of the flexible spacer on hydrophobic association. Also shown in Figure 4, the viscosity profiles of the PAA-M4-2.0 copolymers were similar to those of the perfluorocarbon macromonomer copolymers of M1, M2, and M3, indicating that the hydrophobicities of the C₁₄H₂₉ and C₈F₁₇ groups were similar. However, the different chain lengths and end units of fluorocarbon groups seemed to have no evident effect on the solution viscosity, and PAA-M2-2.0 seemed to be most effective in increasing viscosity.

Effect of the Temperature and Shear Rate

As shown in Figure 5, the viscosity of PAA-M2-1.5 at low shear (0.42 s⁻¹) decreased progressively with increasing temperature. It was postulated that there existed physical associative junctions in the polymer solution. Transient physical crosslinks via intermolecular association became more unstable and were ready to be dissociated and destroyed by shear with increased tempera-

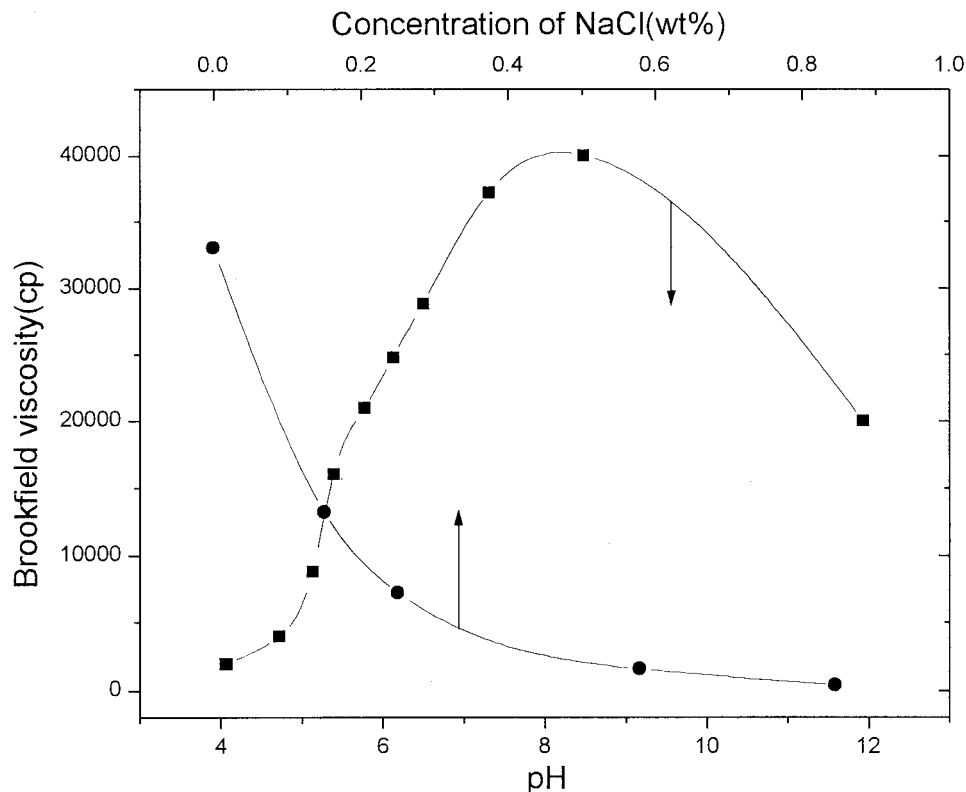


Figure 6 Effect of the pH and NaCl on the polymer solution properties: (■) PAA-M2-2.0 (1.0 wt %) and (●) PAA-M3-1.5 (0.5 wt %).

ture. A similar thickening phenomenon could also be displayed with an increasing shear rate at a fixed temperature. A catastrophic viscosity decrease of a PAA-M1-2.0 solution was evident when the shear rate was increased from 0.084 to 0.42 s^{-1} . The relaxation speed of most of the physical junctions that maintained the associative network obviously could not keep up with the shear-induced breakup of the junctions when the shear rate was greater than 0.42 s^{-1} . The physically crosslinked network, therefore, was mainly destroyed during the experimental timescale, and an abrupt decrease in the Brookfield viscosity occurred. However, the viscosity decrease induced by heating was more progressive within the temperature range investigated in comparison with the decrease by shear, which was attributed to the different means by which heating and shear destroyed the associative network. Despite the discrepancy of thinning behaviors, an increase in temperature had the same thinning effect as an increase in shear rate, which was presumably characteristic of a physically crosslinked, pseudo-plastic fluid.

Effects of the pH and Salt Addition

As shown in Figure 6, the apparent viscosity of 0.5 wt % PAA-M2-2.0 first increased to a maximum around pH 8 and then decreased as the pH was raised further. The increase in the solution viscosity with pH was likely due to electrostatic repulsion along the PAA backbone, which was expected to reduce the intramolecular hydrophobic association and thereby release the associative groups and increase the chance to form intermolecular associations. More ionization of the PAA backbone would also cause repulsion between PAA and thereby inhibit the intermolecular association of hydrophobic groups. Obviously, the decrease in intramolecular association and the increase in intermolecular association were preferentially favored by the pH increasing from 4 to 8. However, above pH 9, a decrease in viscosity was observed that was ascribed to greater electrostatic screening by the increasing counterion concentration. The latter flexibilized the backbone once again, inhibiting intermolecular association. Meanwhile, the augmentation of the

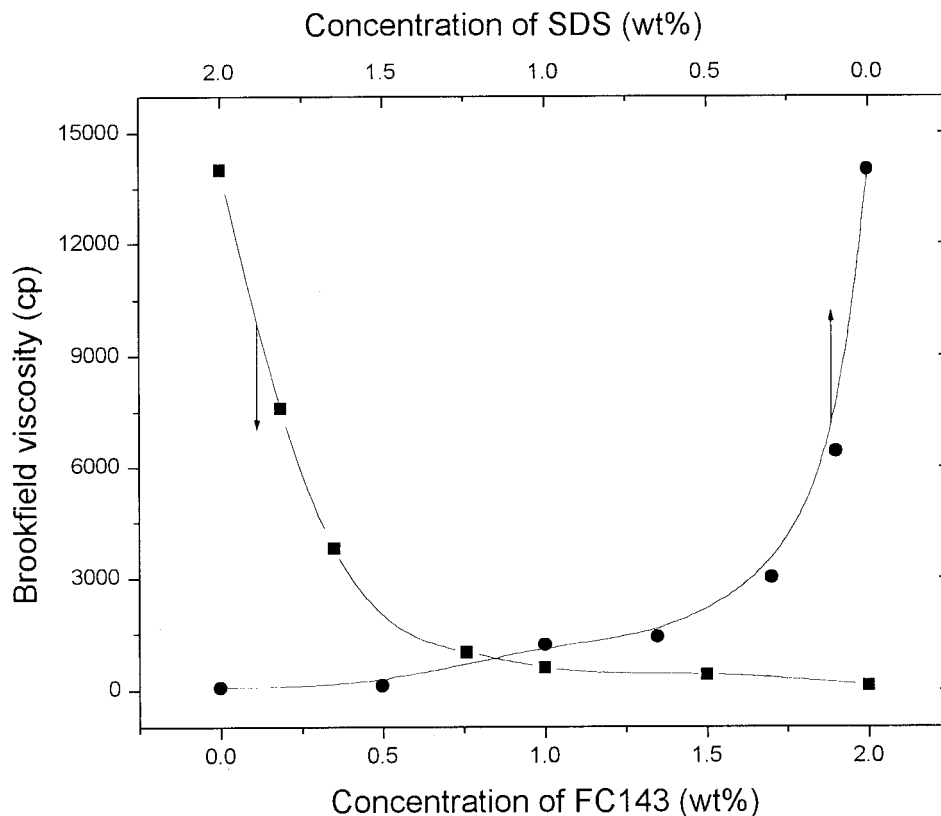


Figure 7 Effect of FC143 and SDS on the polymer solution viscosity of PAA-M1-1.0 (0.45 wt %): (■) FC143 and (●) SDS.

backbone charge, with the pH increasing from 8 to 12, was far less and negligible in comparison with that from 4 to 8. Therefore, electrostatic screening predominated over electrostatic repulsion when the pH was adjusted from 8 to 12. This was also consistent with a large decrease in viscosity with increasing NaCl concentration (Fig. 6). Therefore, at higher salt concentrations, the increased screening led to coil collapse and a shift toward greater intramolecular association.

Effect of the Surfactants

The addition of surfactants to hydrocarbon-modified hydrophilic polymers^{12,13} is well known to lead to the formation of mixed micelles containing two or more polymer-bound hydrophobic groups (micellar bridging), which results in a thickening effect on the polymer solution. At even higher concentrations, a decrease in viscosity is observed, indicating interpolymer dissociation caused by the breakup of the micellar bridging (micellar saturation). For the ATs of Jenkins, it was reported that the zero-shear viscosity of the poly-

mer solution first increased and then decreased with the progressive introduction of SDS;¹² this was interpreted as being a reflection of the process of the formation of micellelike network junctions succeeded by their breakup. For the nonionic surfactant $C_{12}EO_4$,¹³ however, a continuous increase in viscosity is observed, and a transition from micellar junction to vesicle junction upon the successive addition of $C_{12}EO_5$ is assumed. However, no reports have appeared for fluorocarbon-end-capped PEG macromonomer grafted polymers. We report here on the effects of both anionic surfactants, FC143 and SDS, and nonionic surfactants, FC171 and Np7.5 (the structures are shown in Scheme 1). The effects of anionic and nonionic surfactants on the properties of polymer solutions were investigated.

As shown in Figure 7, upon the addition of both FC143 and SDS, the viscosity of 0.45 wt % solutions of PAA-M1-1.0 decreased. In both cases, the decreases in viscosity were most dramatic at very low surfactant concentrations and well below the cmc of the surfactants. This indicated that

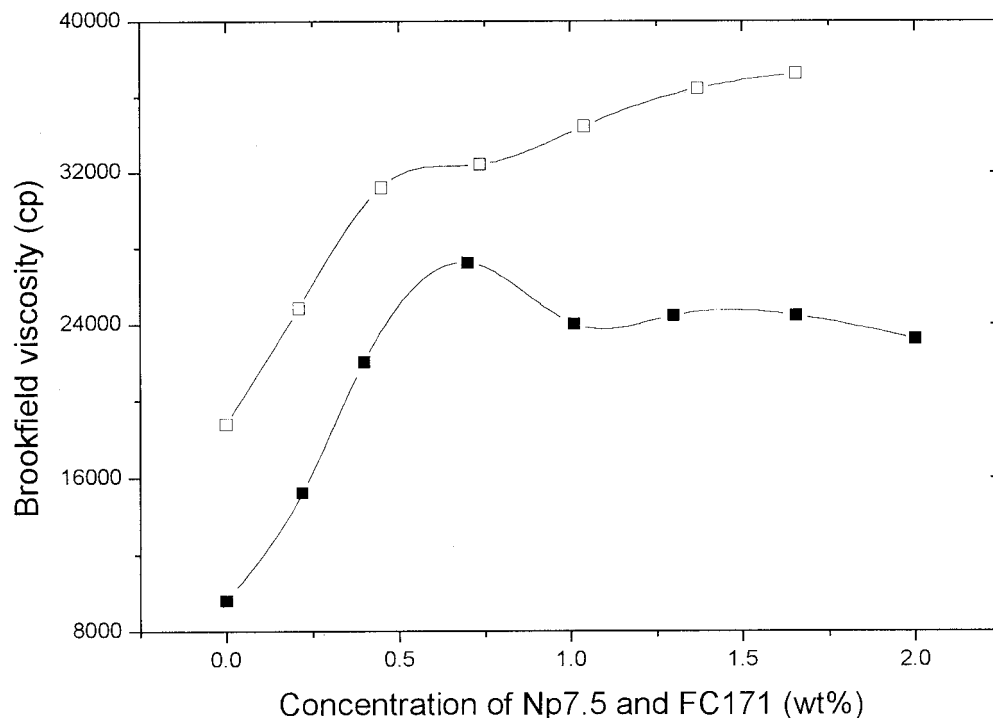


Figure 8 Effect of Np7.5 and FC171 on the polymer solution viscosity: (■) PAA-M3-2.0 (0.5 wt %) and Np7.5 and (□) PAA-M3-2.0 (1.0 wt %) and FC171.

well-associated aggregates preexisted in the solution and, upon the addition of FC143 or SDS, micellar saturation rather than micellar bridging took effect whether the surfactant was FC143 or SDS. This was contrary to the observed effects of SDS and FC143 for fluorocarbon-modified poly(*N,N*-dimethylacrylamide), for which the addition of FC143 was shown to lead to stronger micellar bridging in comparison with the addition of SDS. It was assumed that the spacer-separated hydrophobic groups had more freedom to associate with one another than those without the poly(ethylene oxide) spacer. Therefore, intramolecular and intermolecular associations were more complete. The addition of an anionic surfactant, whether fluorocarbon or hydrocarbon, seemed to induce two effects: the disassociation of hydrophobic microdomains for the participation of surfactant tails and the screening of backbone charges for the addition of surfactant counterions. Both decreased the solution viscosity. The detailed mechanism is still under research.

For nonionic surfactants, two distinct effects were seen. As shown in Figure 8, the addition of the hydrocarbon surfactant Np7.5 to a solution of 0.5 wt % PAA-M3-2 increased the solution viscosity, whereas almost no effect was observed for

FC171. The Np7.5-induced increase in solution viscosity was different from that of the system of Jenkins, in which a 2-decade increase in viscosity was observed. In our system, before the addition of Np7.5, aggregates composed of fluorocarbon groups preexisted. Because of the poor miscibility, Np7.5 was assumed not to participate in the aggregation or create new aggregates by bridging with other unassociated fluorocarbon groups. The slight increase in viscosity upon the addition of Np7.5 was principally due to the hydrogen bonds between ethylene oxide units of PEG and Np7.5. As for FC171, the fluorocarbon tail could theoretically be inserted into preexisting microdomains. However, the PEG shell around the fluorocarbon core perhaps made the insertion difficult. Also, the junction-forming effect and the junction-breaking effect, induced concomitantly with the addition of Np7.5, seemed to offset each other, as illustrated by the constant viscosity.

CONCLUSION

Fluorocarbon- or hydrocarbon-containing PEG macromonomers were synthesized with a coupling method, and the synthesis conditions were

systematically studied. The appropriate control of the reaction time, amount of catalyst, molar ratio of the reactants, and other factors brought about satisfactory results. The cmc values of the macromonomers showed that they were at the same level despite the different lengths of fluorocarbon groups and end units (CF_3 or CF_2H). Copolymers of macromonomers with AA were synthesized by solution copolymerization. The conversion of the macromonomers was low because of their low reactivity in the system; changing the copolymerization medium improved their conversion. These polymers could be used as thickeners because of the strong hydrophobic association between the fluorocarbon groups. The solution viscosity was adjusted by changes in the macromonomer contents in the copolymers, the shear rate, the pH value, and the temperature or by the addition of salt and various surfactants.

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