Effects of Water-Soluble Spacers on the Hydrophobic Association of Fluorocarbon-Modified Poly(acrylamide)

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ABSTRACT: A number of acrylamide–acrylate copolymers were synthesized in which the acrylate (CH_2=$CHCOO(CH_2CH_2O)_nR$) is hydrophobic on account of the presence of a 1,1-dihydroperfluorooctyl group or a dodecyl group connected to the acrylate via a $-(CH_2CH_2O)_n$ hydrophilic spacer (n = 0–3). Copolymerization of these monomers was initiated by sodium metabisulfite and ammonium persulfate at 60 °C in aqueous media in the presence of surfactants and acetone. The low shear viscosities of 0.5 wt % solutions of these copolymers as a function of comonomer molar content gave bell-shaped curves having maxima at 0.10–0.60 mol % comonomer, consistent with competitive inter- and intramolecular hydrophobic association. The copolymers having perfluorocarbon pendent groups gave higher viscosities at lower comonomer content. Furthermore, for both the hydrocarbon- and perfluorocarbon-containing copolymers the viscosities increased, and the comonomer content at the viscosity maximum decreased, with increasing spacer length. The increased effectiveness of the longer spacers is attributed to entropy effects in the formation of polymer assemblies.

Introduction

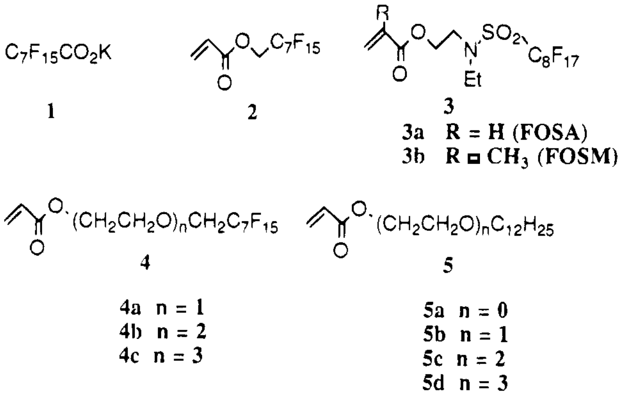
Hydrophobically associating polymers are synthetically derived, water-soluble polymers that contain a small fraction of hydrophobic groups. They have recently become an important class of viscosifying polymers because of their unique rheological properties.[1–16] When dissolved in aqueous solutions, hydrophobically associating water-soluble polymers exhibit enhanced solution shear-dependent viscosity resulting from formation of a transient network via intermolecular association of the hydrophobic groups.[17–25] In this way, very large supermolecular polymer clusters are formed that greatly contribute to viscosity. The resulting polymer clusters are readily disrupted upon application of shear, giving typical pseudoplastic behavior. Upon removal of the shear, the solution viscosities are completely recovered. Applications of polymers of this type include mobility control agents,[1–13] enhanced oil recovery,[26,27] drag reduction polymers,[27] formulation thickeners for coatings,[28–31] cosmetics, etc.

Hydrophobically modified water-soluble polymers may be synthesized by several methods including (1) the grafting of a small amount of long-chain hydrophobes onto water-soluble polymers, such as polysaccharides,[4,17,32–34], poly(vinyl alcohol), etc., (2) copolymerization of a hydrophilic monomer, such as acrylamide, with a small amount of a comonomer containing a hydrophobic group,[5,6,8,9,11–13] and 3) end-capping of a water-soluble polymer, such as poly(ethylene glycol), with hydrophobic groups.[7,10,14,15]

We have previously[35,36] synthesized a series of fluorocarbon (R_F)-modified poly(acrylamides) and found that the copolymers containing fluorocarbon acrylate derivatives **2**, **3a**, and **3b** are much more effective viscosifiers compared with the corresponding hydrocarbon (R_H) derivatives such as the copolymers of **5a** (see Scheme 1).

Furthermore, the comonomer molar content of the most effectively viscosifying copolymers tended to be much smaller (0.10–0.50 mol %) for the copolymers of **3a** and **3b**, compared with that of **5a** (~1–3 mol %).

Scheme 1. Hydrophobic Comonomers and Fluorocarbon Surfactant



The copolymers of **3a** and **3b** were found to be more effective viscosifiers compared with **2**.[35] This interesting observation was tentatively ascribed to the presence of the hydrophilic ($-CH_2CH_2NEtSO_2-$) spacers. The occurrence of spacer effects in promoting hydrophobic association has been documented.[8] However, there may be other reasons such as the slight difference in hydrophobe length, the presence of a highly polar sulfonamide group, etc. We now report a more systematic study of such possible "spacer effects" on fluorocarbon-modified, as well as hydrocarbon-modified, hydrophobically associating water-soluble polymers.

Experimental Section

Reagents and Solvents. Acrylamide (ultrapure electrophoresis grade from Polysciences Inc.) was used without further purification. The fluorine-containing surfactant **1** and monomers **3a** and **3b** were donated by the 3M Co. The comonomer was recrystallized twice from methanol before use (mp = 35 °C). The purified comonomer was shown to contain small amounts of branched perfluorocarbon acrylates (~15% by GC). The 1,1-dihydroperfluorooctyl acrylate (**2**) and dodecyl acrylate (**5a**) were purchased from Monomer–Polymer Laboratories and distilled before use. 1,1-Dihydroperfluorooctanol, 2-chloroethanol, 2-(2-chloroethoxy)ethanol, 2-[2-(2-chloroethoxy)ethoxy]ethanol, acryloyl chloride, triethylamine, sodium hydride, dodecyl mono-/bis-/tris(ethyleneoxy) alcohols, and hydrocarbon surfactant SDS (sodium dodecyl sulfate) were

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commercial materials supplied by Aldrich Chemical Co. 1,1-Dihydroperfluorooctanol was dried under vacuum for at least 2 days before use.

Solvents, such as diethyl ether, acetone, toluene, and diglyme, were obtained from Mallinckrodt and were used as received. Deionized water was used in all cases.

Synthesis of Comonomers. 1,1-Dihydroperfluorooctylmono-/bis-/tris(ethyleneoxy) Alcohol Precursors. In a typical experiment, 3.5 g of a 60% sodium hydride dispersion in mineral oil (0.0875 mol) was washed with three portions each of 40 mL of anhydrous diethyl ether. This treated sodium hydride was transferred to a three-necked, 300-mL round-bottom reactor furnished with a dropping funnel, a nitrogen gas inlet/outlet, and a refluxing condenser. To the slurry of the NaH and 150 mL of fresh anhydrous diethyl ether was added with stirring at room temperature over a period of 20 min 25 g (0.0625 mol) of 1,1-dihydroperfluorooctanol, $CF_3(CF_2)_6CH_2OH$, dissolved in 80 mL of diethyl ether. The mixture was stirred for another 6 h under nitrogen, and the temperature was then raised to the boiling point of diethyl ether while applying a nitrogen flow until about half of the diethyl ether was removed. A mixed solvent (60 mL of toluene and 20 mL of diglyme) was added slowly into the mixture. The temperature was then raised slowly to the reflux temperature (about 110 °C) during a 1-h period. To this refluxing solution was added very slowly a solution of 0.08 mol of 2-chloroethanol ($ClCH_2CH_2OH$) dissolved in 80 mL of toluene over a period of about 15 h. The mixture was then kept refluxing for another 24 h. The cooled mixture was neutralized by adding dilute acetic acid and filtered to remove the salt. 1,1-Dihydroperfluorooctylmono(ethyleneoxy) alcohol was obtained in about 45% yield by reduced pressure distillation (bp 75−80 °C) at 0.01 mmHg. ^1H NMR ($CDCl_3$) shows peaks at δ 2.22 (s, 1H, $-OH$), 3.73−3.80 (m, 4H, $-OCH_2CH_2O-$), and 4.03 (t, 2H, $-OCH_2R_F$).

1,1-Dihydroperfluorooctylbis(ethyleneoxy) alcohol was similarly prepared by reaction of the potassium salt of 1,1-dihydroperfluorooctanol and 2-(2-chloroethoxy)ethanol in 40% yield. The boiling point is 105−110 °C at 0.01 mmHg. ^1H NMR ($CDCl_3$) shows peaks at δ 2.43 (s, 1H, $-OH$), 3.60−3.83 (m, 8H, $-OCH_2CH_2OCH_2CH_2O-$), and 4.04 (t, 2H, $-OCH_2R_F$).

1,1-Dihydroperfluorooctyltris(ethyleneoxy) alcohol was obtained, using 2−[2−(2−chloroethoxy)ethoxy]ethanol and 1,1-dihydroperfluorooctyltris(ethyleneoxy) alcohol, by a similar procedure with 32% yield. The boiling point is 130−140 °C at 0.01 mmHg, and ^1H NMR shows peaks at δ 2.62 (s, 1H, $-OH$), 3.60−3.82 (m, 12H, $-(OCH_2CH_2)_3O-$), and 4.03 (t, 2H, $-OCH_2R_F$).

1,1-Dihydroperfluorooctylmono-/bis-/tris(ethyleneoxy) acrylates (Comonomers 4a/4b/4c). A mixture of 1,1-dihydroperfluorooctylmono(ethyleneoxy) alcohol (0.0135 mol, 6.0 g), acryloyl chloride (0.0167 mol, 1.5 g), hydroquinone (0.05 g, inhibitor), and 15 mL of diethyl ether was prepared in a three-necked, 50-mL flask equipped with a nitrogen inlet/outlet, a thermometer, a dropping funnel, and a water-cooled reflux condenser fitted with a calcium chloride drying tube. To this cooled (ice−water bath) and well-stirred solution was added dropwise as nitrogen was passed slowly through the system a solution of triethylamine in 8 mL of ether. The resulting slurry was stirred for several hours at room temperature and then refluxed for another 2 h, after which it was cooled and filtered. The filtrate was then washed successively with water, aqueous sodium bicarbonate, and water. The washed ether layer was then dried over magnesium sulfate and distilled to produce essentially pure 1,1-dihydroperfluorooctylmono(ethyleneoxy)acrylate (**4a**) (bp 47−52 °C at 0.01 mmHg) with 82% yield. ^1H NMR ($CDCl_3$) shows peaks at δ 3.88 (t, 2H, $-COOCH_2C\mathbf{H_2}OCH_2C_7F_{15}$), 4.34 (t, 2H, $-COOC\mathbf{H_2}CH_2O-$), 4.02 (t, 2H, $-OC\mathbf{H_2}C_7F_{15}$), 5.86 (q, 1H, $CH_a\mathbf{H_b}{=}CHCOO-$), 6.44 (q, 1H, $C\mathbf{H_a}H_b{=}CHCOO-$), and 6.14 (q, 1H, $CH_2{=}C\mathbf{H}COO-$). ^{13}C NMR shows peaks at δ 63.2 (s, $-COO\mathbf{C}H_2CH_2OCH_2C_7F_{15}$), 68.2 (t, $-O\mathbf{C}H_2C_7F_{15}$), 70.8 (s, $-COOCH_2\mathbf{C}H_2OCH_2C_7F_{15}$), 110−120 (m, $-OCH_2\mathbf{C_7}F_{15}$), 128 (s, $\mathbf{C}H_2{=}CHCOO-$), 131 (s, $CH_2{=}\mathbf{C}HCOO-$), and 166 (s, $CH_2{=}CH\mathbf{C}OO-$). Elem anal. (Galbraith Laboratories, Knoxville, TN) of **4a**. Calcd for $C_{13}F_{15}H_9O_3$: C, 31.32; F, 57.23; H, 1.81. Found: C, 31.54; F, 57.05; H, 1.78.

1,1-Dihydroperfluorooctylbis/tris(ethyleneoxy) acrylates (**4b**/**4c**) were prepared in a similar procedure with 78% and 72% yields, respectively. These products were further purified by preparative column chromatography (eluent AcOEt/MeOH/hexane 80/10/10), and their structures were confirmed by ^1H, ^{13}C, and ^{19}F NMR and elemental analysis (Galbraith Laboratories, Knoxville, TN). ^1H NMR of **4b** shows peaks at δ 3.67−3.81 (m, 6H, $-COOCH_2C\mathbf{H_2}OC\mathbf{H_2}C\mathbf{H_2}OCH_2C_7F_{15}$), 4.32 (t, 2H, $\mathbf{COOCH_2}CH_2O-$), 4.04 (t, 2H, $-OC\mathbf{H_2}C_7F_{15}$), 5.84 (q, 1H, $CH_a\mathbf{H_b}{=}CHCOO-$), 6.43 (q, 1H, $C\mathbf{H_a}H_b{=}CHCOO-$) and 6.15 (q, 1H, $CH_2{=}C\mathbf{H}COO-$). ^{13}C NMR shows peaks at δ 63.5 (s, $-COO\mathbf{C}H_2CH_2OCH_2CH_2OCH_2C_7F_{15}$), 68.3 (t, $-O\mathbf{C}H_2C_7F_{15}$), 69.3 (s, $-COOCH_2CH_2OCH_2\mathbf{C}H_2OCH_2C_7F_{15}$), 7.07 (s, $-COOCH_2CH_2O\mathbf{C}H_2CH_2OCH_2C_7F_{15}$), 110−120 (m, $-OCH_2\mathbf{C_7}F_{15}$), 128 (s, $-\mathbf{C}H_2{=}CHCOO-$), 131 (s, $CH_2{=}\mathbf{C}HCOO-$), and 168 (s, $CH_2{=}CH\mathbf{C}OO-$). Elem anal. (Galbraith Laboratories, Knoxville, TN) of **4b**. Calcd for $C_{15}F_{15}H_{13}O_4$: C, 33.21; F, 52.58; H, 2.40. Found: C, 32.74; F, 52.25; H, 2.32.

^1H NMR of **4c** shows peaks at δ 3.60−3.81 (m, 10H, $-COOCH_2C\mathbf{H_2}OC\mathbf{H_2}C\mathbf{H_2}OC\mathbf{H_2}C\mathbf{H_2}OCH_2C_7F_{15}$), 4.32 (t, 2H, $-COOC\mathbf{H_2}CH_2O-$), 4.04 (t, 2H, $-OC\mathbf{H_2}C_7F_{15}$), 5.83 (q, 1H, $CH_a\mathbf{H_b}{=}CHCOO-$), 6.43 (q, 1H, $C\mathbf{H_a}H_b{=}CHCOO-$), and 6.15 (q, 1H, $CH_2{=}C\mathbf{H}COO-$). ^{13}C NMR shows peaks at δ 63.6 (s, $-COO\mathbf{C}H_2CH_2OCH_2CH_2OCH_2CH_2OCH_2C_7F_{15}$), 68.3 (t, $-O\mathbf{C}H_2C_7F_{15}$), 69.1 (s, $-COOCH_2CH_2OCH_2CH_2OCH_2\mathbf{C}H_2OCH_2C_7F_{15}$), 70.6−70.7 (t, $-COOCH_2CH_2O\mathbf{C}H_2\mathbf{C}H_2O\mathbf{C}H_2CH_2OCH_2C_7F_{15}$), 72.3 (s, $-COOCH_2\mathbf{C}H_2OCH_2CH_2OCH_2CH_2OCH_2C_7F_{15}$), 110−120 (m, $-OCH_2\mathbf{C_7}F_{15}$), 128 (s, $\mathbf{C}H_2{=}CHCOO-$), 131 (s, $CH_2{=}\mathbf{C}HCOO-$), and 166 (s, $CH_2{=}CH\mathbf{C}OO-$). Elem anal. (Galbraith laboratories, Knoxville, TN) of **4c**. Calcd for $C_{17}F_{15}H_{17}O_5$: C, 34.81; F, 48.63; H, 2.90. Found: C, 34.64; F, 48.38; H, 2.76.

^{19}F NMR ($CFCl_3$) spectra of **4a**, **4b**, and **4c** are almost identical, showing peaks (for the carbons numbered as $-OCH_2C^{(1)}F_2C^{(2)}F_2C^{(3)}F_2C^{(4)}F_2C^{(5)}F_2C^{(6)}F_2C^{(7)}F_3$) at δ −126 ($-C^{(1)}\mathbf{F_2}-$), −124 ($-C^{(2)}\mathbf{F_2}-$), −123 ($-C^{(3)}\mathbf{F_2}-$), −122 ($-C^{(4)}\mathbf{F_2}C^{(5)}\mathbf{F_2}-$), −120 ($-C^{(6)}\mathbf{F_2}-$), and −81 ($-C^{(7)}\mathbf{F_3}$).

Dodecylmono-/bis-/tris(ethyleneoxy) Acrylates (Comonomers 5a/5b/5c). The hydrocarbon-containing comonomers with hydrophilic spacer, **5a**−**c**, were also prepared with the same procedure as described above except using dodecylmono-/bis/tris(ethyleneoxy) alcohols as the starting materials. The ^1H NMR spectrum of **5c** shows peaks at δ 0.88 (t, 3H, $-O(CH_2)_{11}C\mathbf{H_3}$), 1.18−1.27 (m, 20H, $-OCH_2(C\mathbf{H_2})_{10}CH_3$), 1.57 (t, 2H, $-OC\mathbf{H_2}(CH_2)_{10}CH_3$), 3.47 (t, 2H, $-OCH_2C\mathbf{H_2}OC_{12}H_{25}$), 3.56−3.68 (m, 6H, $-COOCH_2CH_2OC\mathbf{H_2}C\mathbf{H_2}OC\mathbf{H_2}CH_2OC_{12}H_{25}$), 3.76 (t, 2H, $-COOCH_2C\mathbf{H_2}OCH_2CH_2OCH_2CH_2OC_{12}H_{25}$), 4.32 (t, 2H, $-COOC\mathbf{H_2}CH_2OCH_2CH_2OCH_2CH_2OC_{12}H_{25}$), 5.83 (q, 1H, $CH_a\mathbf{H_b}{=}CHCOO-$), 6.43 (q, 1H, $C\mathbf{H_a}H_b{=}CHCOO-$), and 6.15 (q, 1H, $CH_2{=}C\mathbf{H}COO-$).

^1H NMR spectra of **5a** and **5b** show the same characteristic peaks as those of **5c**.

Polymerizations. A series of polymerizations was carried out using the same stock solution of surfactant **1**, dissolved in deionized water. To a set of 50-mL capped round-bottomed flasks containing 1g of acrylamide, 13.0 mL of deionized water, and 30 mg of surfactant **1** were transferred varying amounts of comonomer (**2**, **3a**, **4a**, **4b**, or **4c**) dissolved in acetone using a gas-tight syringe capable of accurate dosage of about 1 μL. The final volume of acetone in each flask was brought to exactly 1.50 mL, and the final concentration of surfactant **1** was kept at 3.50 mM. These mixtures were then degassed by applying a very slow but constant flow (the flow rate was kept at 2−5 mL/min using a flow indicator) of pure (99.99%) argon gas using needles as gas inlet and outlet. After purging the solution at 60 ± 1.0 °C with argon for 30 min, 0.25 mL of a 1.0×10^{-2} M solution of sodium metabisulfite and 0.25 mL of a 1.0×10^{-2}M solution of ammonium persulfate were injected using a gas-tight syringe into the rapidly stirred contents of the flask. The final total volume was kept constant at 15 mL. Each polymerization was carried out for 24 h at 60 ± 1.0 °C and was quenched by exposure to O_2. Gels of various consistencies were obtained at periods between 1 and 20 h. The homopolymer was prepared using the same procedures, except that no comonomer was present during polymerization.

Table 1. Brookfield Viscosity[a] of Fluorocarbon-Modified Poly(acrylamides)[b]

	copolymer				
comonomer (mol %)	**4a**	**4b**	**4c**	**3a**	**2**
0	40	40	40	40	
0.003	60	60	80	60	
0.006	80	120	260	160	
0.010	180	280	1800	640	40
0.030	680	3200	9000	6700	
0.06	7400	11500	19200	8800	80
0.08	11000	16000	24600	8200	
0.12	14000	18000	46000	6000	180
0.25	14080	16200	26000	300	660
0.50	4400	6000	7200		960
1.00	60	80	1200		540
1.50					180
2.00					60

[a] Shear rate = 0.42 s^{-1}. Viscosities were measured at 25 °C. [b] Polymer concentration = 0.50 g/dL.

Copolymerizations of acrylamide and comonomers **1** and **5a–d** were also carried out under the same conditions except using (8.68 mM) sodium dodecyl sulfate.

Polymer Dissolution and Viscosity Measurements. The hydrophobically modified poly(acrylamide) solutions were prepared by dilution of the contents (~6.7 wt % polymer solutions) of the flask with appropriate volumes of deionized water and allowed to stand for periods varying from 24 h to several weeks in order to obtain homogeneous solutions prior to viscosity measurements. The solutions were then dialyzed against deionized water for 2–3 days in order to remove initiator and surfactant traces. The final weight of the polymer solutions was brought to 200 g so that the final polymer concentration was obtained at 0.5 wt %.

Brookfield viscometer measurements were carried out, by using a Wells Brookfield equipped with different sizes of spindles and a temperature-control water bath. The Brookfield viscosity (cP) and shear rate were obtained by direct readout and rotational speed (rpm), using the range table supplied by the manufacturer. The apparent intrinsic viscosities of the resulting polymers were also measured at 30 °C by capillary viscometry using an Ubbelohde viscometer.

Results

Eight series of copolymers containing varying fractions of comonomers were synthesized by emulsion copolymerization of acrylamide and the hydrocarbon- or fluorocarbon-containing comonomers, using $(NH_4)_2S_2O_8$ and $Na_2S_2O_5$ as initiators and SDS or **1** needed to disperse the hydrophobic comonomers in micellar form. These copolymerizations were found to be essentially quantitative. Copolymerization kinetics carried out by simultaneous ^1H and ^{19}F NMR in conditions similar to that in the copolymer syntheses indicates that the copolymerization of AM and FOSA is quantitative and is proceeding with the same relative rates.[38] Thus, copolymer composition does not appear to change during the reaction. Acrylamide homopolymers were also prepared under conditions identical to those for the preparation of the copolymers but without the presence of comonomer. Tables 1 and 2 show the Brookfield viscosities of 0.5 wt % solutions of the resulting copolymers as a function of comonomer content and structure.

In all cases, viscosity maxima were observed in the plots of viscosity versus comonomer content at constant polymer concentration (0.5 wt %) (Figures 1–3).[35] First, the introduction of the $-CH_2CH_2O-$ spacer into **2** raises the viscosity maxima of the corresponding solutions more than 20-fold (Figure 1). Increasing the length of the spacer (n = 2, 3) further raises the viscosity maxima (30% and 200%, respectively) (Figure 2). Increasing viscosities with increasing spacer lengths have been observed for water-soluble copolymers containing hydrocarbon acrylates.[8]

Table 2. Brookfield Viscosity[a] of Hydrocarbon-Modified Poly(acrylamides)[b]

	copolymer			
comonomer (mol %)[c]	**5d**	**5c**	**5b**	**5a**
0.03	1420	260	80	
0.10	3860	1040	360	25
0.50	9680	2200	1220	
0.75				50
1.0	7600	4040	1840	
1.5				100
2.0	4800	3200	2240	
3.0	1880	1020	740	120
4.5	660	240	130	40

[a] Shear rate = 0.42 s^{-1}. Viscosities were measured at 25 °C. [b] Polymer concentration = 0.50 g/dL. [c] With respect to acrylamide units.

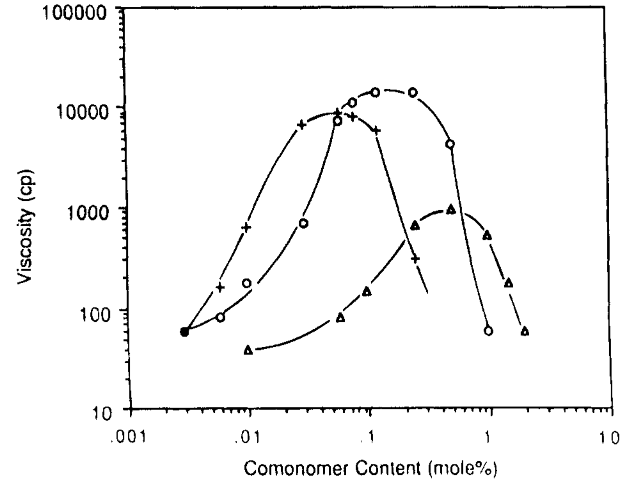


Figure 1. Effect of the comonomer content of comonomers **2** (△), **3a** (+), and **4a** (○) on the viscosity of 0.50 wt % copolymer solutions at 0.42 s^{-1} shear at 30.0 °C.

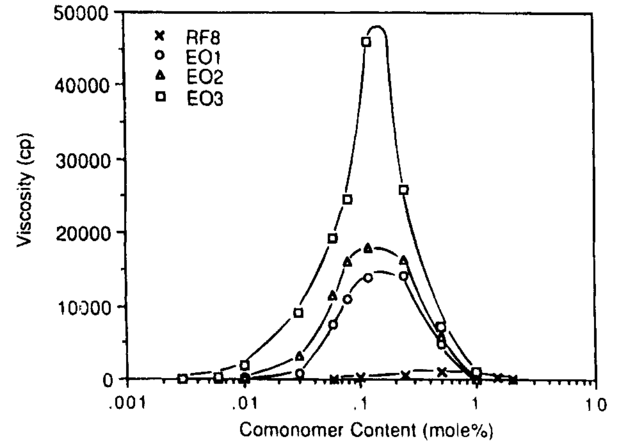


Figure 2. Effect of the contents of comonomers **2** (×) **4a** (○), **4b** (△), and **4c** (□) on the viscosities of 0.50 wt % copolymer solutions at 0.42 s^{-1} shear at 30.0 °C.

The comonomer content of the R_F copolymers at the viscosity maximum is also of interest. This maximum occurs at 0.60 mol % for zero spacer length but is significantly lower (~0.1 mol %) for a spacer length of n = 1 (Figure 1). However, the comonomer content at the viscosity maximum does not appear to change much as the spacer length is increased further (Figure 2).

In the case of hydrocarbon comonomers **5a–d** (Table 2), longer hydrophilic spacers also appear to strongly

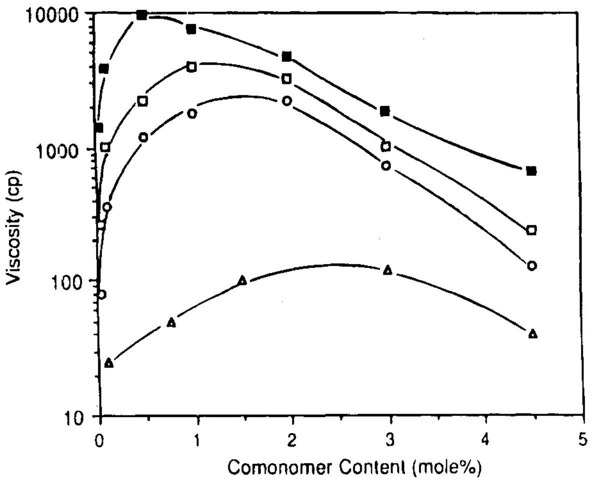
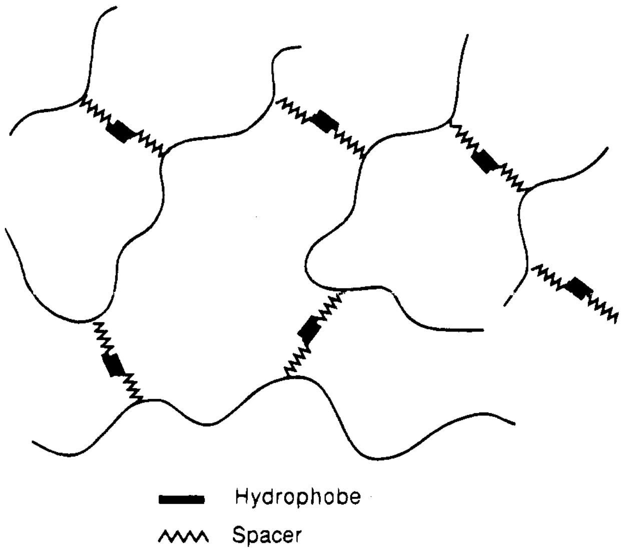


Figure 3. Effect of the contents of comonomers **5a** (△), **5b** (○), **5c** (□), and **5d** (■) on the viscosities of 0.50 wt % copolymer solutions at 0.42 s^{-1} shear at 30.0 °C.

Chart 1



enhance the viscosities of the resulting copolymer solutions up to 100-fold in going from $n = 0$ to 3 (Figure 3). Furthermore, the comonomer content at the viscosity maximum is decreased. Figure 3 shows the values of the comonomer contents at the viscosity maxima for hydrocarbon acrylates **5a–d** as about 2.5, 1.5, 1.0, and 0.5 mol %, respectively (see below).

We believe that the viscosity enhancements due to spacer effects may be due to two possible causes. The first of these may be the excluded-volume effect involving the close proximity of large polymer coils that are joined through intermolecular hydrophobic association of the pendent hydrophobic moieties (Chart 1). This excluded-volume effect, at least for the case of intermolecular association, should be less important for longer spacer lengths. Thus, the hydrophilicity and flexibility of the (CH_2CH_2O) spacer may help in increasing the distance between the polymer coils, thus facilitating intermolecular association (Chart 1).

A second possible effect is the decoupling of the motions of the hydrophobic moieties in the aggregate from that of the chain to which the hydrophobe is attached. This effect would be analogous to that observed in side-chain liquid crystalline polymers in which polymethylene or similar spacers, separating pendent mesogenic groups from the polymer backbone, decouple the motions of the mesogens from that of the backbone.

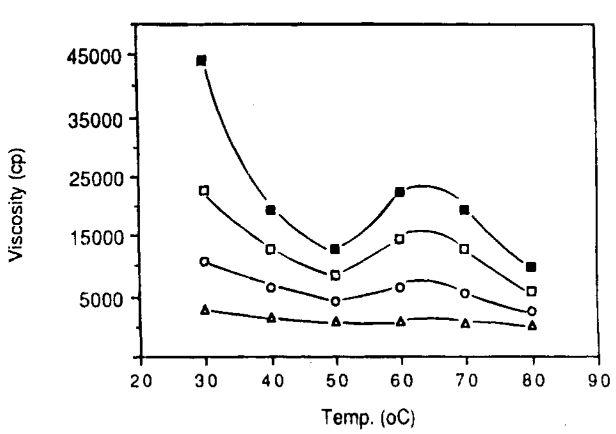


Figure 4. Temperature-dependent viscosities of 0.50 wt % copolymer solutions at 0.84 s^{-1} shear. Comonomers **2** (△), **4a** (○), **4b** (□), and **4c** (■).

Of the two possible causes for the sharp viscosity increases with spacer length, we believe the second is more plausible. First, excluded-volume effects are difficult to reconcile with the pronounced effects of increasing the spacer length from $n = 0$ to 1 and the much smaller effects in increasing n to 2 and 3. On the other hand, the decoupling effects account quite well for our observations. The ^{19}F NMR data[38] suggest a large degree of immobilization of the perfluorocarbon moieties in the hydrophobe aggregate, whereas the polymer backbone is relatively flexible. In the absence of a spacer, this coupling is expected to cause a decrease in copolymer entropy upon formation of the hydrophobic aggregates. The insertion of the hydrophilic spacers would tend to decrease this loss of entropy.

It is of some interest to note that the comonomer content at the viscosity maximum is slightly lower for comonomer **3a** compared with that of comonomers **4a–c** (0.07 vs 0.15 mol %). The reason for this is not clear but may correlate with the fact that the fluorocarbon moiety of **3a** is longer than that of **4a–c** (C_8F_{18} vs C_7F_{15}).

The temperature-dependent viscosities (at shear rate 0.084 s^{-1}) of the fluorocarbon-modified copolymer solutions are shown in Figure 4. From 30 to 50 °C, there is a viscosity decrease followed by an increase and a maximum at about 65 °C. Similar Brookfield viscosity–temperature profiles were previously observed for **3a** containing poly(acrylamides).[35]

The viscosity increases observed upon heating (from 50 to 65 °C) are consistent with entropy-driven hydrophobic association.

The viscosity increase from 50 to 60 °C is more pronounced for the copolymers of **4c** and **4b** than that for **4a** and **2**, consistent with the observation that a longer hydrophilic spacer is more effective in promoting the formation of intermolecular hydrophobic aggregates. For the homopoly(acrylamide) prepared under identical conditions, the viscosity versus temperature behavior is completely different and shows a monotonous decline in viscosity with increasing temperature. This indicates again that the viscosity–temperature profile of the fluorocarbon-modified water-soluble poly(acrylamides) is related to hydrophobic association.

At higher temperature (65–80 °C) the viscosity decreases with increasing temperature presumably as a result of the less ordered structure of water itself. Thus, in this range, hydrophobic association is no longer

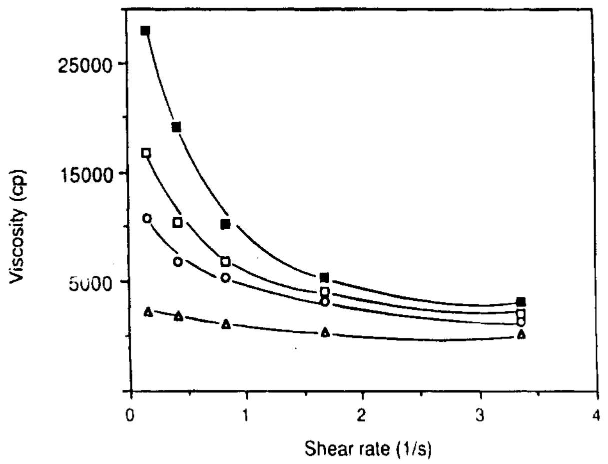


Figure 5. Dependence of the viscosity of copolymer solutions (0.50 wt %) on shear at 30.0 °C. Comonomers **2** (△), **4a** (○), **4b** (□), and **4c** (■) at 0.6 mol % content.

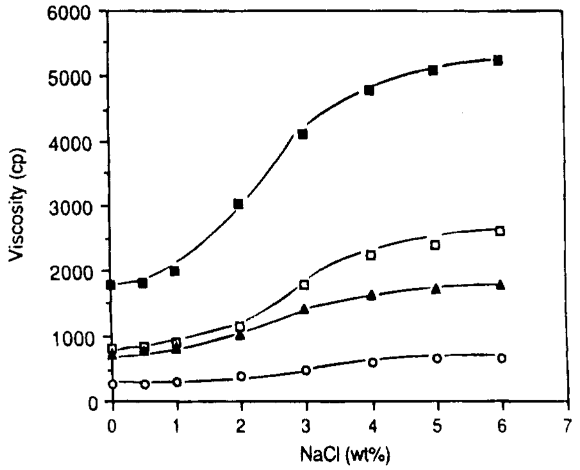


Figure 6. Effect of the NaCl concentration on viscosities of 0.25 wt % copolymer solutions. Comonomers **3a** (▲), **4a** (○), **4b** (□), and **4c** (■) at 0.03 mol % content. The temperature is 30.0 °C.

strongly entropy-driven and conventional viscosity–temperature profiles result. The decrease in viscosity from 30 to 50 °C is not well understood.

The 0.5 wt % aqueous solutions of copolymers of acrylamide and **2** and **4a–c** were found to be highly pseudoplastic. This was also observed earlier for the copolymers of **3a**. The sharp decreases of viscosity with increasing shear (see Figure 5) are clearly due to the shear-induced disruption of the network formed by the weakly associating hydrophobic groups. When the shear was removed, the viscosities of the solutions recovered rapidly and completely, indicating that the hydrophobic association is reversible.

Figure 6 shows viscosity increases (up to 3-fold) with increasing NaCl concentration in the 1–6 wt % range. The increases in viscosity with NaCl concentration are sigmoidal, changing little in going from 0 to 1%, followed by a sizable increase in going from 1 to 3 wt % NaCl and finally a small increase at higher NaCl concentration. These increases appear to correlate well with the known effects of NaCl on hydrophobic association ("salting out").[39] For instance, for the case of hydrophobic association involving micelles, Ray et al. having shown that the presence of a (water) "structure-marking" electrolyte such as NaCl lowers the cmc values of nonionic surfactants.[39]

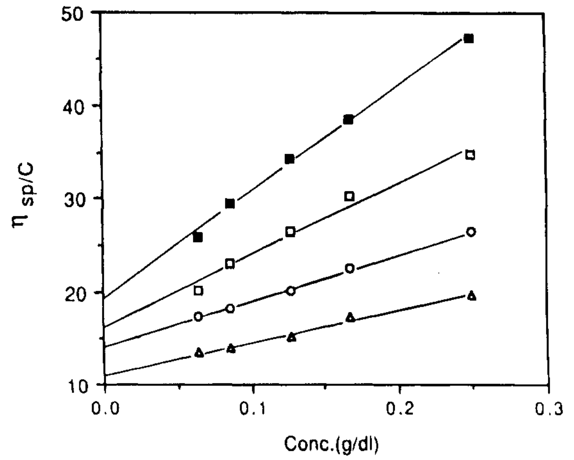


Figure 7. Reduced viscosities of copolymer containing 0.03 mol % of **3a** (▲), **4a** (○), **4b** (□), and **4c** (■) in water at 30.0 °C.

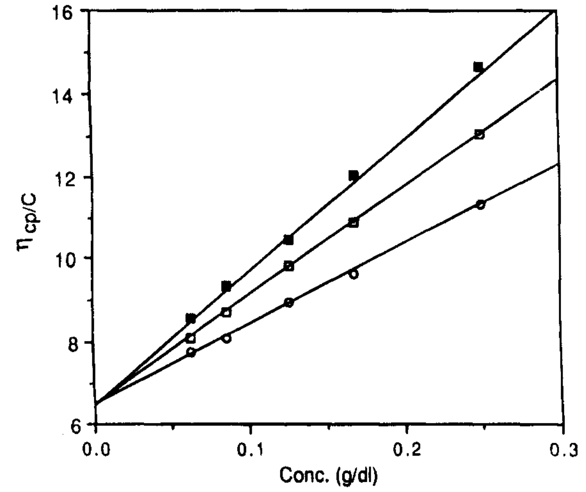


Figure 8. Reduced viscosity–concentration profiles of copolymers containing 0.03 mol % of comonomers **4a** (○), **4b** (□), and **4c** (■) in DMF/H_2O (~50/50, v/v) at 30.0 °C.

Reduced viscosity measurements in water (see Figure 7) show that the copolymers containing longer hydrophilic spacers possess appreciably higher apparent intrinsic viscosities than the copolymers containing shorter or no spacers, indicating residual association even at extremely low concentrations (<0.05 wt %). The intrinsic viscosities vary from 10 to 20 dL/g, indicating strong residual polymer association at these concentrations. This has also been demonstrated by recent dynamic light scattering measurements of the FOSA acrylamide copolymers in water indicating significant residual associations at concentrations above 10 ppm.[36,40]

Figure 8 shows the reduced viscosity–concentration profiles of fluorocarbon-containing acrylamide copolymers of **4a–c** (containing 0.03 mol % comonomer) in DMF/H_2O (50/50 by volume). In this medium the poly(acrylamide) copolymers of **4a–c** show much lower and similar intrinsic viscosities.[35] Furthermore, the intrinsic viscosity of poly(acrylamide) homopolymer formed under identical conditions is similar also. This similarity in intrinsic viscosities in this medium where hydrophobic association is much reduced indicates that the large variation among the apparent intrinsic viscosities of the three copolymer in water is probably not caused primarily by differences in the molecular weights of the individual chains but is rather due to the differing degrees of hydrophobic association. From the K and α values[41] reported for the Mark–Houwink–Sakurada

Table 3. Apparent Intrinsic Viscosities ([η])[a] and Huggins Constants (K_H)[a] of the Fluorocarbon-Modified Copolymers in Water and in DMF/H_2O (50/50, v/v) from Figures 8 and 9

		in DMF/H_2O (50/50, v/v)	
comonomer[b]	[η] in H_2O (dL/g)	[η] (dL/g)	K_H
4c	19.31	6.45	0.79
4b	16.21	6.46	0.63
4a	14.27	6.50	0.45
2	11.18		
4a[c]		5.79	0.53
4a[d]		5.27	0.80

[a] Obtained from $\eta_{sp}/c = [\eta] + K_H[\eta]^2c$ at 30 °C. [b] Comonomer content is 0.03 mol %. [c] Comonomer content is 0.003 mol %. [d] Comonomer content is 1.0 mol %.

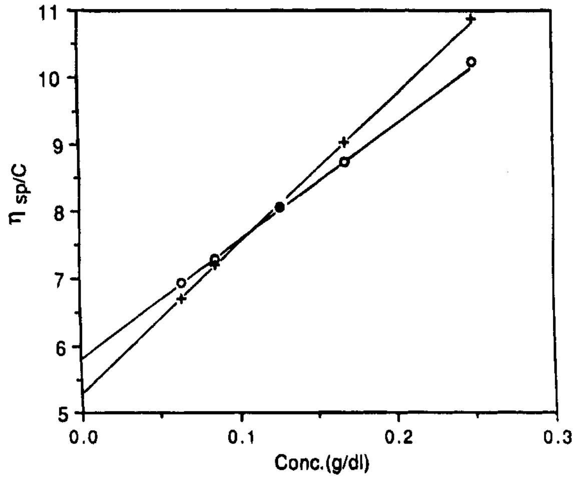


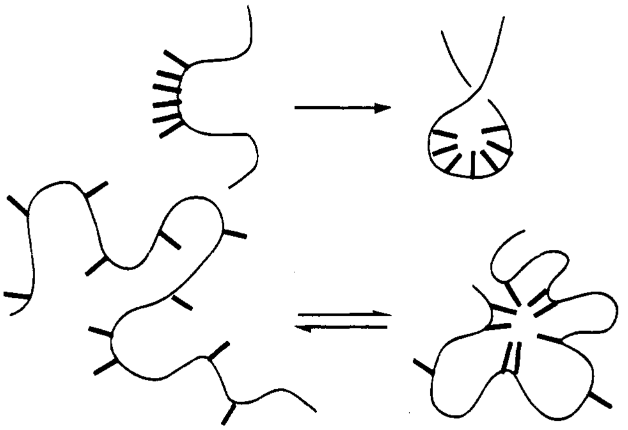
Figure 9. Reduced viscosity–concentration profiles of copolymers containing **4a** at 0.003 mol % (○) and 1.0 mol % (+) in DMF/H_2O (50/50, v/v) at 30.0 °C.

relationship of poly(acryamide) in water at 30 °C, an intrinsic viscosity of about 6 dL/g corresponds to a viscosity-average molecular weight of ~10^6, corresponding to a degree of polymerization of about 1.4 × 10^4. For a comonomer content of 0.03 mol %, this corresponds to about four comonomer units/chain. The poly(acrylamides) with this comonomer content still show substantial viscosification. This low number of comonomer units/chain would seem to suggest random incorporation of the comonomers into the poly(acrylamide) chain (see below).

The Huggins constants K_H calculated from Figure 8 are found to increase with spacer length. Thus the values for the copolymers of **4c**, **4b**, and **4a** are found to be 0.79, 0.63, and 0.45 respectively (Table 3). This may indicate again a greater residual tendency for the longer spacer length polymers to associate at higher concentrations even in DMF/H_2O (50/50 by volume).

The finding that copolymers of **4a**, **4b**, and **4c** have similar intrinsic viscosities in DMF/H_2O is not very surprising in view of the fact that they contain the same very low mole fraction (0.03 mol %) of comonomer. However, one may expect to find variations in MW as the comonomer content is varied appreciably. Accordingly, the [η] values of copolymers **4a** containing 0.003 and 1.0 mol % of comonomer **4a**, prepared under identical conditions, were measured in 50/50 DMF/H_2O (Figure 9). The value of [η] of the copolymer containing only 0.003 mol % of **4a** is essentially identical to that of poly(acrylamide) formed under these conditions ([η] = 5.8 dL/g), but the copolymer containing 1.0 mol % of **4a** has a somewhat lower intrinsic viscosity ([η] = 5.4 dL/g). This is consistent with the lower intrinsic viscosities in DMF/H_2O of acrylamide copolymers containing a greater fraction of acrylates.[42,43] As the acrylate concentration increases, chain termination increases (acrylate polymerization leads to much lower molecular weight), so that copolymer molecular weight is decreased. At the same time, since comonomer content increases, intramolecular hydrophobic association at high dilution is increased, resulting in chain contraction.

Scheme 2



Discussion

Any accounting of the properties of hydrophobically modified water-soluble polymers should start with the structure of such polymers. For the case of the above and similar copolymers, this is not a simple issue. Even the total content of hydrophobic groups in the polymer is difficult to determine, especially for simple hydrocarbon groups. Thus, for the hydrocarbon-modified polymers, hydrocarbon content is generally small (1–3 wt %) so that ^1H NMR is not suitable for quantitative determination. Furthermore, such groups, at least in this case, do not possess other spectroscopic (UV, IR) properties that allow quantitative determination of such low comonomer content.

However, this is different with the fluorocarbon-containing comonomers. Copolymerization kinetics of acrylamide and comonomer **3a** were carried out under polymerization conditions similar to those employed in the present case by following the disappearance of the ^{19}F NMR signals of the fluorocarbon moiety of the comonomer.[38]

Since the corresponding ^{19}F NMR signal of the copolymer is broadened beyond recognition, such measurements are readily carried out. They show that under these conditions the disappearance of the acrylate comonomer **3a** occurs at a relative rate which does not differ from that of acrylamide itself. Since copolymer yields are essentially quantitative, copolymer compositions appear to directly reflect comonomer content in the reaction mixture.

Since the copolymerizations of the acrylamide and perfluorocarbon acrylate comonomers are generally carried out in the presence of a perfluorocarbon surfactant, such an "emulsion copolymerization" could produce essentially two types of copolymer structures, blocky or random (see Scheme 2), by two different mechanisms.

First, there is the possibility of a dual polymerization mechanism (M1) in which acrylamide polymerizes in an aqueous medium while the hydrophobic comonomer is incorporated into the chain through a type of micellar polymerization process. Thus, the resulting polymer would be expected to have a structure in which the comonomer is incorporated into the polymer chain in a blocky fashion.[9b]

In a second mechanism (M2), the copolymerization occurs in the aqueous medium. The micelles in this case only serve as a "reservoir", continuously releasing the hydrophobic comonomer into the aqueous medium. In this case the structure of the resulting copolymer is essentially determined by the comonomer concentration in the aqueous medium and by its reactivity ratios. For the acrylamide (1)–methyl acrylate (2) comonomer pair the reactivity ratios are reported as $r_1 = 1.30$ and $r_2 = 0.05$.[44] Although these reactivity ratios will probably be somewhat different for the acrylates in this study, the relatively large separation between the hydrophobic group and the acrylate double bond suggests that the reactivity ratios in the present case are probably not too different. This indicates that, for homogeneous copolymerization (M2) involving very low comonomer mole fractions, comonomer incorporation into the poly(acrylamide) chain should be random. On the other hand, if mechanism M1 prevailed in the copolymerization, a copolymer with a blocky structure (small blocks) could be formed. The actual mechanism involved is not clear. However, as indicated above, for a 0.03 mol % comonomer content and a molecular weight of $\sim 10^6$, there are an average of roughly 4 hydrophobes per polymer chain. It is of interest to note that for the copolymers of **3a** and **4a–c** significant viscosification occurs at a comonomer content that is 3 times lower (0.01 mol %) (Figures 1 and 2). It seems unlikely that effective viscosification could occur in these cases if comonomer incorporation occurred in a blocky fashion. Our data on the R_F-containing copolymers thus seem to favor homogeneous copolymerization.

As pointed out above, we believe that the principal cause for the viscosity maxima (Figures 1–3) is the competition between the formation of intra- and intermolecular hydrophobic interactions.[35] A possible reason for this is that the number of hydrophobes per hydrophobic "cluster" is likely to be larger for intra- than for intermolecular association. Thus, although this number in the latter case is probably quite low, the number involved in intramolecular association is likely to be larger since the corresponding intramolecular excluded volume is plausibly much less serious. As a result the predominant formation of intramolecular micelles is plausible for the copolymers having higher mole fractions of hydrophobes (>1 mol %) (Scheme 2). If the hydrophobic groups are present in blocky sequences, such intramolecular association is expected to be even more pronounced (Scheme 2).

As pointed out above, for both the R_F and R_H systems large increases in viscosity resulting from increases in spacer length are generally accompanied by large decreases in comonomer content at the viscosity maximum (Figures 1–3). For both R_F and R_H copolymers there is an approximately 20-fold increase in viscosity by increasing the hydrophilic $(CH_2CH_2O)_n$ spacer from $n = 0$ to 1. As shown in Figures 1 and 3, the decreases in comonomer content at the viscosity maximum with spacer length are also similar ($\sim 3\times$ and $5\times$, respectively). In going to longer spacers (from $n = 1$ to 3) the increases in viscosity are somewhat larger for the R_H than the R_F acrylates (factors of 5 and 3, respectively). For longer spacers, the corresponding decreases in comonomer content at the viscosity maximum for the R_H acrylates are substantial ($\sim 3\times$), but there is little change for the R_F acrylates, possibly because the viscosity increases for the R_F acrylates also are smaller.

It would appear that these observations are consistent with the following. As hydrophobe association becomes stronger (as a result of longer spacers, for example), both inter- and intramolecular hydrophobe association increases. This would then allow the fraction of hydrophobes in the chain to decrease, and this in turn decreases competition due to intramolecular association, making intermolecular associatino even stronger. Conversely, as the mole fraction of hydrophobes increases beyond a certain value, intermolecular polymer association increases but intramolecular association increases even more. Thus even as polymer association increases, polymer coil contraction increases even further. This would then lead to a comonomer content for which the overall size of the polymer cluster is maximized.

As was discussed above, longer spacers may mitigate excluded-volume effects. However, it is more likely that weaker coupling between the hydrophobic groups and the polymer backbone for the case of longer spacers is expected to greatly enhance hydrophobic association. This latter effect can be understood as follows. The association of hydrophobes into hydrophobic aggregates requires a certain degree of "order" (see above). This ordering process then affects the polymer segments attached to the hydrophobes, leading to lower entropy. Longer spacers serve to minimize this loss of entropy by helping to decouple the motions of the chain segments and the hydrophobe aggregates. The relatively large increases in viscosity observed in going from spacers of $n = 0$ to $n = 1$ suggest the second mechanism as the more plausible one.

Analogous spacer effects have been observed in surfactants of the structure $C_{12}H_{25}(CH_2CH_2O)_nSO_3Na$, where increases in the value of n have been shown to increase the degree of hydrophobe association reflected in lower cmc values as n increases from 1 to 4.[45] As n increases from 0 to 1, the cmc decreases from 8.0 to 0.5 mM, a factor of 16. Further increases in n ($n = 2$ and 4) result in more modest decreases in cmc (0.3 and 0.2 mM, respectively). No satisfactory explanation of such effects appears to have been offered thus far.[46] The resemblance of these surfactant spacer effects with our data is striking and suggests a similar rationalization.

Conclusions

Water-soluble copolymers of acrylamide and fluorocarbon or hydrocarbon-containing acrylates with hydrophilic spacers of varying lengths separating the hydrophobe from the acrylate functionality were synthesized using radical polymerization in the presence of surfactants. The data indicate that the existence of a hydrophilic spacer between the hydrophobic group and the polymer backbone helps in promoting the formation of hydrophobic "cross-links" forming a transient "network", resulting in dramatic viscosity enhancements. The results show that a longer hydrophilic spacer leads to more effectively viscosifying copolymers than copolymers containing comonomers with shorter spacers or no spacer at all. This is consistent with an "excluded-volume effect" but more plausibly to a "decoupling effect". The comonomer content required for maximum viscosity decreases with increasing spacer length.

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