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Copolymers of *N*,*N*-Dimethylacrylamide and 2-(*N*-ethylperfluorooctanesulfonamido)ethyl Acrylate in Aqueous Media and in Bulk. Synthesis and Properties

Xiaoyi Xie and Thieo E. Hogen-Esch*

Loker Hydrocarbon Research Institute and Department of Chemistry,
University of Southern California, Los Angeles, California 90089-1661

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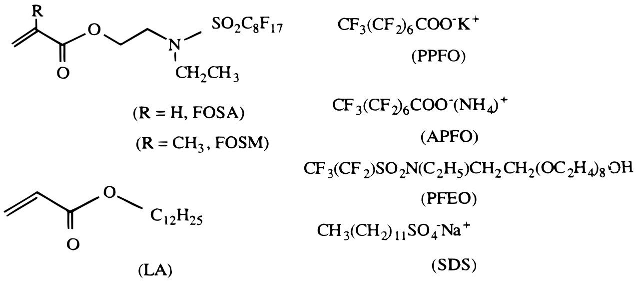
ABSTRACT: Hydrophobically modified (HM) associating water-soluble poly(*N*,*N*-dimethylacrylamide) (PDMA) polymers were prepared by free-radical copolymerizations of DMA and 2-(*N*-ethylperfluorooctanesulfonamido)ethyl acrylate (FOSA). The polymerizations were carried out in deionized water in the presence of ammonium persulfate at 50 °C or in bulk in the presence of AIBN at 65 °C. The copolymerization kinetics monitored simultaneously by ^{19}F and ^{1}H NMR spectroscopy indicates that DMA and FOSA is incorporated at the same relative rates throughout the polymerization. The viscosities of the polymer solutions were measured on a Brookfield viscometer and an Ubbelohde capillary viscometer. A large viscosity enhancement was observed in comparison with PDMA homopolymer solutions. The effects of polymer concentration, shear rate, surfactants, salts, and temperatures on the reduced and Brookfield viscosities were investigated. Interestingly, the aqueous solution of the copolymer prepared in bulk exhibits both hydrophobic interaction and polyelectrolyte effects in the presence of anionic perfluorocarbon surfactant. The resulting polymers were also characterized by size exclusion chromatography and by ^{1}H and ^{19}F NMR spectroscopy.

Introduction

Hydrophobically modified (HM) associating polymers have attracted substantial interest due to their unique rheological properties. These polymers are often referred to as the so-called "associative thickeners"[1,2] and usually consist of a water-soluble polymer containing a small fraction of hydrophobic groups.[3,4] When dissolved in water above the overlap concentration (c*),[5] they tend to self-associate by intermolecular hydrophobic interaction, generating a transient "network" via associations of the hydrophobic groups ("liaisons"), resulting in substantial viscosity increases. Upon application of shear, the networklike structures, held together by the relatively weak hydrophobic associations, are disrupted, giving rise to typical pseudoplastic behavior. However, upon removal of shear the network structures reform and the viscosities of the polymer solutions completely recover their original low shear values.

Recently we reported the synthesis of copolymers of acrylamide (AM) and perfluoroalkyl (meth)acrylate comonomers 2-(*N*-ethylperfluorooctanesulfonamido)ethyl acrylate (FOSA) or FOSM[6] (Chart 1). The polymerization of AM and FOSA or FOSM in water was initiated by $(NH_4)_2S_2O_8$ and $Na_2S_2O_5$ in the presence of perfluorocarbon surfactants and/or acetone (7−15 vol %). After dilution with water, the copolymer solutions were shown to be strongly viscosifying compared with the polyacrylamide homopolymer. Thus, the solution viscosities at 0.40 s^{-1} shear rate are from 1 to 3 orders of magnitude higher compared with the solutions of the AM copolymers of lauryl acrylate (LA) under similar copolymerization conditions. Viscosities of 0.5 wt % copolymer solutions plotted vs comonomer content showed viscosity maxima at 0.07 mol % FOSA and 0.28 mol % FOSM. Similar but significantly lower viscosity maxima were observed for the AM−LA copolymers but at much higher LA molar content (3 mol %) (Figure 1). These observations were shown to be consistent with the formation of a physical network held together by intermolecular hydrophobic associations (Scheme 1).

Chart 1. Comonomers and Surfactants



One of the difficulties in the molecular characterization of the fluorocarbon copolymers is the occurrence of very strong association of the fluorocarbon-containing copolymers. Thus, light scatterring indicates residual association of fluorocarbon groups in water at very low concentrations (~10 ppm),[7] allowing the determination of apparent molecular weights only. Formation of polymeric clusters has also been observed by light scattering techniques for hydrocarbon containing associating copolymers.[8]

Another difficulty in the characterization of the fluorocarbon- and hydrocarbon-modified acrylamides is the determination of hydrophobic comonomer content. Routine spectroscopic methods such as UV, IR, NMR, etc., are limited by the often extremely low comonomer content.[9] Valint et al.[8,9] and Schulz et al.[10] have remedied this problem by using UV-active hydrophobic groups such as *N*-(4-ethylphenyl)acrylamide. However, the incorporation of aromatic moieties modifies the structure of the hydrophobe and therefore may change the extent and nature of the hydrophobic associations occurring between simple hydrocarbons.

An even greater difficulty is the determination of comonomer sequences. Blocky comonomer sequences recently have been proposed by McCormick et al.[11,12] for copolymers of acrylamide and *N*-octylacylamide and more recently by Candau et al.[13,14] Copolymer micro-

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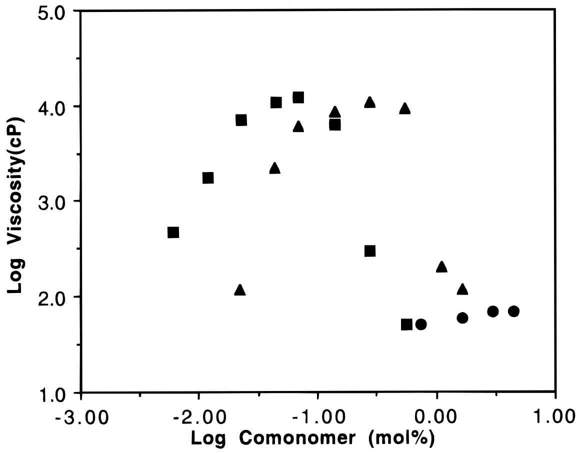
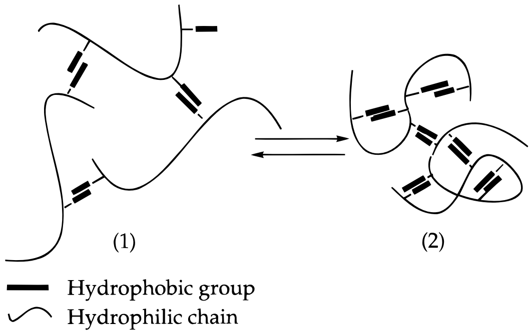


Figure 1. Brookfield viscosity at 0.4 s^{-1} shear rate as a function of FOSA (■), FOSM (▲), and LA (●) comonomer contents at 0.5 wt % polymer concentration.

Scheme 1. (1) Intermolecular and (2) Intramolecular Association of Water-Soluble Copolymers Having Pendent R_F or R_H Groups



structure has been inferred from NMR[15] and fluorescence[11,12] techniques, but no direct determination has been completely successful so far.

Poly(*N*,*N*-dimethylacrylamide) (PDMA) is well-known as a water-soluble polymer and is widely used in the paper, textile, and coatings industries. Although copolymerization of DMA with styrene and methyl methacrylate has been extensively studied by other investigators,[16−19] few reports on the preparation and characterization of hydrophobically modified PDMA have appeared.[20] However, the synthesis of such polymers would be of interest because, in contrast to hydrophobically modified polyacrylamide (PAM), PDMA copolymers would be expected to be soluble in media such as MeOH, THF, and $CHCl_3$ where hydrophobic association is expected to be absent.

Hydrophobically modified HM polymers typically are synthesized in the presence of surfactants in order to "solubilize" the hydrophobic comonomers in the aqueous media. However, the binding of surfactants to HM polymers may be typically quite strong, and consequently, polymer-bound surfactants may be difficult to completely remove from the solution by dialysis or precipitation. As a result, the synthesis of surfactant-free HM polymers is of considerable interest.

Such hydrophobically associating copolymers at least in principle may be synthesized by solution or bulk copolymerization that gives copolymers in which the comonomer distribution in the chain is determined by reactivity ratios. However, solution copolymerizations often produce HM copolymers with low molecular weight and low hydrophobe incorporation.[21] Solutions of such copolymers typically show low viscosities. Furthermore, the redissolution in water of such copolymers recovered by precipitation is often difficult.[6,22−24] In such cases attempted dissolution in water gives gellike particles that remain in suspension and do not disappear even after prolonged heating under vigorous stirring. Such behavior may be attributed to the strong hydrophobic interactions in the precipitated polymer chains.

Bulk polymerizations are a synthetic alternative provided that solubility of the comonomer in the monomer is sufficient to allow polymerization under homogeneous conditions. Since both hydrophobic comonomers, i.e., FOSA and LA are soluble in DMA, the bulk copolymerization of DMA and FOSA or LA is of interest.

Experimental Section

Reagents and Solvents. *N*,*N*-Dimethylacrylamide (Aldrich) was distilled over calcium hydride under a reduced pressure to remove the inhibitors. The comonomer 2-(*N*-ethylperfluorooctanesulfonamido)ethyl acrylate (FOSA) generously donated by the 3M Co. was recrystallized from ethanol twice and dried under vacuum to give white powder (mp 27−42 °C). The anionic fluorocarbon surfactants (PPFO, APFO) and nonionic fluorocarbon surfactant (PFEO) were obtained from the 3M Co. and used as received. Sodium dodecyl sulfate (SDS, Aldrich) was used without further purification.

Ammonium persulfate ($(NH_4)_2S_2O_8$; Aldrich), sodium metabisulfite ($Na_2S_2O_5$; Aldrich), and 2,2′-azobisisobutyronitrile (AIBN; Eastman Kodak Co.) were used without further purification. Sodium chloride was purchased from Mallinckrodt and used as received.

All of the solvents such as acetone, dimethylformamide, and methanol were obtained from Mallinckrodt (reagent grade or ACS grade) and used as received. Deionized water was obtained with use of Polymetrics water treatment system containing two mixed-bed column tanks connected in series.

Surfactant-Mediated Polymerizations. All copolymerizations of DMA were carried out at a constant DMA content (20.2 mmol) and various FOSA contents ranging from 0.0016 to 0.32 mmol (0.08−1.6 mol % relative to DMA) in the presence of redox initiators $(NH_4)_2S_2O_8$ (0.01 mmol) and $Na_2S_2O_5$ (0.01 mmol) at 50 °C. The monomer and comonomer dissolved in 4 mL of acetone and 0.05 g of PPFO surfactant were loaded into a single-neck round-bottomed flask (50 mL) capped with a rubber septum. Deionized water was added to a volume of 25 mL. The flask was placed in a mineral oil bath at 50 °C. Using two syringe needles as gas inlet and outlet, a stream of ultrapure grade argon (99.99%) was introduced to the flask for 30 min to remove oxygen and other impurities. The initiator solutions were then injected with a gas-tight syringe through the rubber septum into the flask where the reaction mixture was rapidly stirred with a magnetic stirrer. The polymerization was allowed to proceed at 50 °C for 24 h and was terminated by opening the flask to air. The homopolymer was prepared in a similar manner except that the polymerization proceeded in the absence of comonomer.

Bulk Polymerizations. The copolymerizations of DMA and FOSA or LA were carried out in bulk at 60 °C under argon, using AIBN as initiator. The DMA monomer (5 g, 0.05 mol) and 0.031−0.125 g (0.05−0.2 mmol) of FOSA (0.1−0.4 mol % relative to DMA) were loaded into a single-neck round-bottomed flask (50 mL) equipped with a magnetic stirrer. The solution of AIBN (0.002 g, 0.012 mmol) in DMA was added with a syringe to the flask which was capped with a rubber septum. The solution was then degassed by purging with argon for 10 min. The flask was placed in a thermally regulated oil bath at 60 °C. The polymerization was rapid and exothermic and was allowed to proceed for 16 h. The homopolymer was prepared in a similar manner except that the polymerization proceeded in the absence of comonomer.

The copolymerization of DMA and LA was carried out as described above for the copolymerization of DMA and FOSA except that the comonomer LA (0.12 g, 0.5 mmol) was used instead of FOSA.

Table 1. Copolymerization of DMA and FOSA at 50 °C in Water

	FOSA (mol %)							
sample code[a]	added	obsd[b]	yield[c] (%)	$[\eta]^d$ (dL/g)	$M_v{}^e$ ($\times 10^{-6}$)	$M_w{}^f$ ($\times 10^{-6}$)	$M_n{}^f$ ($\times 10^{-5}$)	MWD[f]
P-E0-000	0	0	95.5	5.35	3.9	3.2	8.2	3.90
P-E1-008	0.008		91.3	4.46	3.0	2.6	6.8	3.82
P-E2-024	0.024		93.7	5.19	3.8	3.2	8.1	3.95
P-E3-048	0.048	0.05	96.6	4.48	3.0	2.8	7.0	4.01
P-E4-100	0.100	0.10	95.1	5.20	3.8	3.1	7.8	3.96
P-E5-200	0.200	0.19	97.2	5.67	4.3	3.4	9.7	3.50
P-E6-398	0.398	0.41	99.1	4.54	3.1	3.0	8.3	3.62
P-E7-794	0.794	0.78	99.9	4.92	3.5	2.9	7.4	3.92
P-E8-1575	1.575	1.56	98.5	5.18	3.8	3.0	7.8	3.84

[a] The letters P and E refer to PDMA and emulsion polymerization, respectively, the digit following E refers to a sample series number, and the last three digits divided by 1000 refer to the comonomer content in the monomer mixture (in mol %). [b] Calculated by the integration of ^{19}F NMR in CD_3OD in the presence of CF_3SO_3Na. [c] Determined gravimetrically. [d] Measured by capillary viscometry in MeOH at 25 °C. [e] Calculated from $[\eta]$ with $K = 17.5 \times 10^{-5}$ dL/g, $\alpha = 0.68$ in MeOH.[29] [f] Determined by SEC in THF, using polystyrene standards.

Kinetic Studies. The copolymerization kinetics of DMA and FOSA was performed at 50 °C in a 10 mm NMR tube. The concentrations of the reactants in 2 mL of D_2O containing 16 vol % acetone were as follows: [DMA] = 0.8 M; [FOSA] = 8×10^{-3} M; $[(NH_4)_2S_2O_8] = 4 \times 10^{-3}$ M; $[Na_2S_2O_5] = 4 \times 10^{-3}$ M. A stream of ultrapure grade argon (99.99%) was introduced to the flask to purge the sample for 30 min. After addition of the initiator solutions with a gas-tight microsyringe, the solution was capped and the NMR measurements were carried out at 50 °C.

Preparation of Aqueous Polymer Solutions. Dilution of the resulting gellike polymers obtained by emulsion polymerizations was accomplished by adding aliquots of deionized water (25 mL) into the reaction mixture. The process was repeated several times until a homogeneous polymer solution was obtained. Occasionally, shaking of the solution by hand was necessary to assist the dissolution of the copolymers.

The polymers prepared by bulk polymerizations were obtained in the form of plasticlike solids. The sample solutions were prepared by following a procedure similar to that described for the polymers prepared by emulsion polymerizations. The polymer solutions were purified either by dialysis against deionized water, using a dialysis membrane tube (size no. 1, Spectrum Medical Industries Inc.) or by precipitation in acetone. The solid polymer obtained by precipitation was dried at 50 °C in a vacuum oven and dissolved in organic solvents such as MeOH and THF for subsequent measurements.

Viscosity Measurements. Capillary viscometry measurements were carried out using an Ubbelhode viscometer (Cannon no. 100 for water or no. 75 for MeOH). The temperature was kept at 25.0 °C with the use of a water bath and a VWR Model 1120 temperature regulator. For reduced viscosity measurements in organic solvents, the solid polymer obtained by precipitation and drying was dissolved in MeOH or THF and diluted to the desired concentrations.

Brookfield viscometry measurements were carried out by using a Wells Brookfield viscometer (LVT model) equipped with two different sizes of spindles (no. 18 and no. 34) and a temperature-control water bath at 25 °C. The viscosity in centipoise determined at different shear rates (s^{-1}) was obtained by converting the direct readout at corresponding rotational speed (rpm), using the range table supplied by the manufacturer. The shear rate was calculated from the rotational speed of the spindle.

Fluorine-19 and Proton NMR Measurements. The ^{19}F NMR spectra were recorded on a Bruker AM-360 FT-NMR spectrometer operating at 339 MHz in CD_3OD at 30 °C using CF_3SO_3Na as an internal standard. The ^{19}F NMR data for polymer samples were collected overnight. The chemical shifts of ^{19}F signals are referenced to $CFCl_3$. The acquisition parameters were as follows: spectral width, 35 715 Hz; relaxation delay, 20 s; acquisition time, 0.5 s; pulse width, 9 Hz. The T_1 value of the CF_3SO_3Na was 4 s,[25] appreciably longer than that of the CF_3 group of the polymer (<1 s).

For kinetic studies of copolymerization, the ^{19}F NMR and ^{1}H NMR spectra were recorded on a Bruker WM 270 spectrometer at 254 MHz interfacing with an Aspect 2000 computer using a dual F/H probe head. The ^{19}F NMR acquisition parameters were as follows: spectral width, 50 000 Hz; relaxation delay, 0 s; acquisition time, 0.32 s; pulse width, 16 Hz. The NMR spectrometer was programmed in a desired time interval to record alternately the ^{1}H signal of DMA and the ^{19}F signal of FOSA for the duration of the copolymerization. DMA monomer and comonomer depletion was followed up to 90% conversion.

SEC Measurements. For determination of molecular size and molecular size distribution, the samples were prepared by dissolving the purified polymer solid in HPLC grade THF. The size exclusion chromatography (SEC) measurements were performed on a Waters HPLC component system equipped with two Waters Ultra-μ-styragel columns (500, 10 000 Å), one PLgel 5 μm Mixed-C column and two detectors (refractive index and ultraviolet) at a flow rate of 1.0 mL/min in THF at 25 °C. Polystyrene standards were used for calibration.

Results and Discussion

Polymerizations. The emulsion copolymerizations of DMA and FOSA were carried out in deionized water at 50 °C in the presence of PPFO (4.5×10^{-3} M), using a redox $(NH_4)_2S_2O_8/Na_2S_2O_5$ system. The comonomer content was varied from 0 to 1.58 mol %. The total monomer concentration was kept at 8 wt %. Acetone (4 mL, 16 vol %) was added as cosolvent to help dissolve the comonomer. The presence of acetone in the polymerization lowers the molecular weight of PAM as a result of chain transfer to acetone so that careful control of acetone concentration is necessary.[22,26,27] For comparison, the PDMA homopolymer was prepared under experimental conditions identical to that for the preparation of the copolymers. The homopolymerization and copolymerizations were found to be essentially quantitative. The resulting homopolymer of DMA and its FOSA copolymers are listed in Table 1.

The bulk copolymerizations of DMA and FOSA were carried out at 60 °C under argon, using AIBN as initiator. The polymerization was rapid and exothermic and was allowed to proceed for 16 h. For the purpose of comparison, the hydrocarbon copolymers of DMA and LA were also prepared under identical conditions. The results are summarized in Table 2.

Polymer Characterization. The molecular weight of hydrophobically modified PDMA is an important parameter for the viscosity of polymer solutions. For instance, for PDMA aqueous solutions, the reduced viscosity is doubled when the molecular weight is increased by 20%.[28] Such an effect should be even more significant for HM associating polymers.

The apparent molecular weights of the DMA−FOSA copolymers were determined by intrinsic viscosity meas-

Table 2. Copolymerization of DMA with FOSA and LA at 65 °C in Bulk[a]

	FOSA (mol %)							
sample code[b]	added	obsd[c]	yield[d] (%)	$[\eta]^e$ (dL/g)	M_v^f ($\times 10^{-5}$)	M_w^g ($\times 10^{-5}$)	M_n^g ($\times 10^{-4}$)	MWD[g]
P-B0-00	0	0	91	1.24	4.6	4.0	6.9	5.78
P-B1-01	0.1	0.11	91	1.20	4.4	3.7	6.4	5.82
P-B2-02	0.2	0.17	90	1.22	4.5	4.1	7.0	5.89
P-B3-02	0.2[h]	0.18	92	0.91	2.9	2.4	4.0	5.95
P-B4-04	0.4	0.38	93	1.27	4.8	4.3	7.5	5.73
P-B5-10	1.0[i]		93	1.17	4.2	4.9	9.5	5.15

[a] DMA (5 g) with 2 mg of AIBN. [b] The letters P and B refer to PDMA and bulk polymerization, respectively, the digit following B refers to a sample series number, and the last two digits divided by 10 refer to the comonomer content in the monomer mixture (in mol %). [c] Calculated by the integration of ^{19}F NMR in CD_3OD in the presence of CF_3SO_3Na. [d] Determined gravimetrically. [e] Measured by capillary viscometry in MeOH at 25 °C. [f] Calculated from $[\eta]$ with $K = 17.5 \times 10^{-5}$ dL/g, $\alpha = 0.68$ in MeOH.[29] [g] Determined by SEC in THF, using polystyrene standards. [h] AIBN (5 mg) was added. [i] LA was used instead of FOSA.

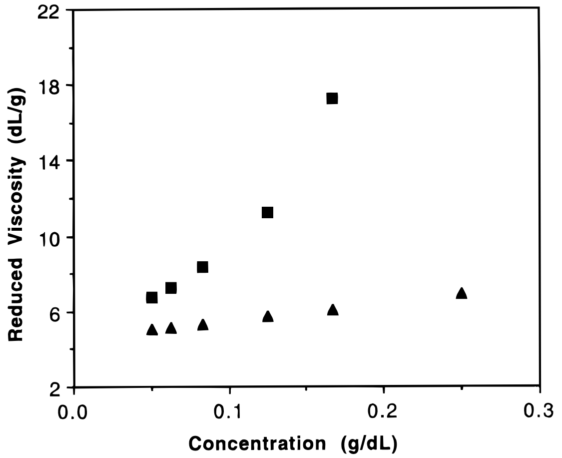


Figure 2. Reduced viscosity as a function of concentration of copolymer P-E4-100 (■) and of homopolymer P-E0-000 (▲) in water at 25.0 °C.

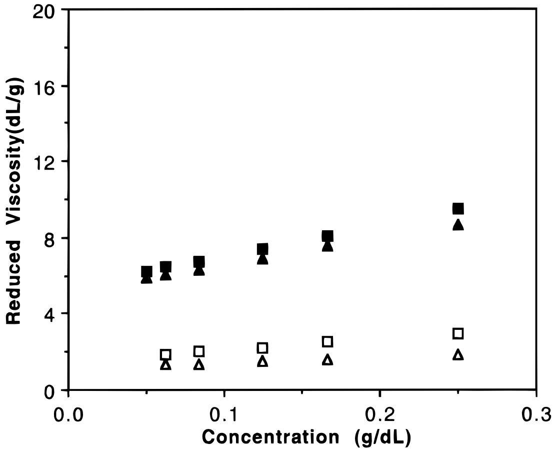


Figure 3. Reduced viscosity as a function of concentration of copolymer P-E4-100 in MeOH (■) and THF (□) and of homopolymer P-E0-000 in MeOH (▲) and THF (△) at 25.0 °C.

urements in methanol, using the relationship[29] established for the PDMA homopolymer (Tables 1 and 2). Due to the formation of supramolecular aggregates in water through strong hydrophobic associations of fluorocarbon groups even in very dilute solutions, the resulting molecular weight values are usually overestimated, and thus only apparent values are obtained. This is illustrated in Figure 2, which shows a viscosity vs concentration profile in water for the PDMA homopolymer and a copolymer PE-4-100 (Table 1) at 25 °C. An intrinsic viscosity of ~4.6 dL/g is obtained for the PDMA, and a similar value is obtained for the copolymer. However, a large viscosity enhancement for the copolymer is observed compared to the homopolymer, especially at higher polymer concentrations. For instance, at the homopolymer overlap concentration ($c^* \approx 1/[\eta]$) of ~0.20 g/dL, the reduced viscosity of the copolymer containing 0.1 mol % FOSA is ~4 times larger than that of the homopolymer. From the above, this large viscosity difference is apparently due to strong intermolecular hydrophobic association of the fluorocarbon groups. Strong copolymer association is also indicated by a sharp increase in reduced viscosity at higher concentrations compared to PDMA itself. However, in methanol or THF, the reduced and intrinsic viscosities of PDMA (P-E0-000) and of the copolymer (P-E4-100) were found to be approximately the same (Figure 3). Since hydrophobic association is greatly reduced or absent in these solvents, it is clear that the molecular weights of the copolymers are of the same order of magnitude as that of PDMA. The intrinsic viscosities in THF are smaller than those in methanol. This correlates with the lower solubility of the PDMA in THF. Thus, the large viscosity differences in water between the copolymers and the homopolymer is not caused by differences in the molecular weight but is rather due to the degree of hydrophobic association in the DMA–FOSA copolymers.

The molecular weights of these polymers have also been determined by SEC based on polystyrene standards, using THF as eluting solvent. The results are summarized in Tables 1 and 2. The apparent molecular weights of the copolymers are similar to those of the PDMA homopolymer obtained under the identical conditions. All samples have broad molecular weight distributions (MWD): MWD = 3.5–4.0 for emulsion polymerization polymers and MWD = 5.2–6.0 for bulk copolymerization polymers. The apparent M_w's determined by SEC are in close agreement with the M_v's calculated from the intrinsic viscosities (Tables 1 and 2).

Copolymer Composition. Fluorine-19 NMR because of its 100% natural abundance and high sensitivity is useful in the determination of fluorine content. The copolymer in methanol shows sharp and well-resolved ^{19}F NMR signals suitable for integration against added sodium triflate. From the ratio of the peak areas of $(CF_2)_7CF_3$ at −82.8 ppm and $NaSO_3CF_3$ at −80.8 ppm, the FOSA content could be calculated. The results are summarized in Tables 1 and 2, indicating a quantitative comonomer incorporation.

The ^{19}F NMR absorption for the copolymer in water is broadened beyond recognition probably due to low perfluorocarbon mobility resulting from strong hydrophobic association.[30] As a result of this apparent lack of a copolymer signal, in contrast to the well-resolved ^{19}F NMR peaks for the comonomer (Figure 4) it is possible to determine the comonomer polymerization

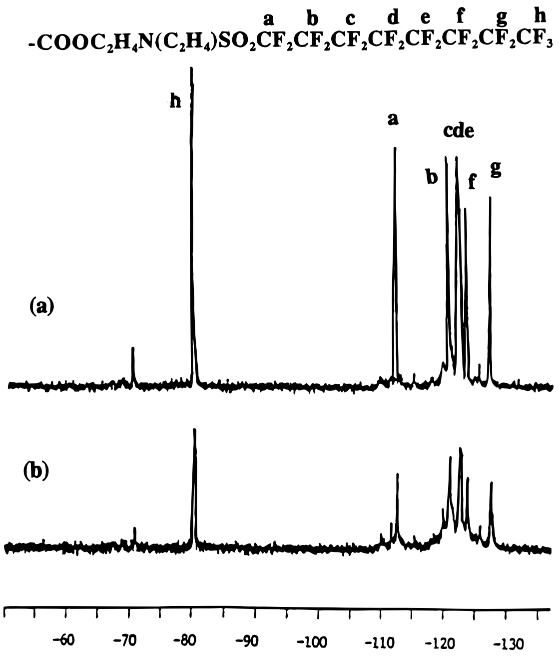


Figure 4. ^{19}F NMR spectrum of FOSA during aqueous copolymerization (P-E4-100) at 50 °C at (a) 2 and (b) 90 min.

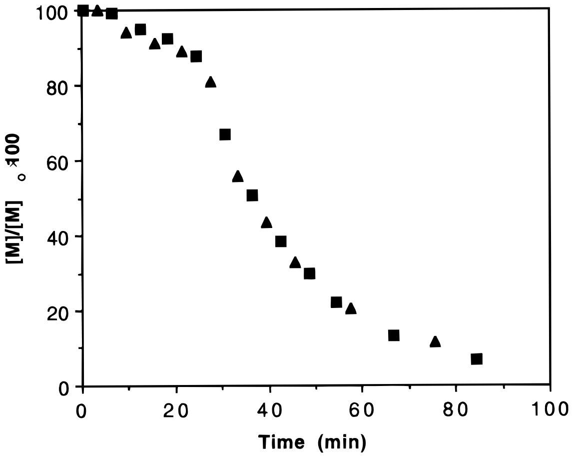


Figure 5. Monomer concentration as a function of time for the copolymerization of DMA and FOSA in 2 mL of D_2O at 50 °C: DMA (■); FOSA (▲). [FOSA] = 8 × 10^{-3} M; [AM] = 0.8 M; [acetone] = 16 vol %; $[(NH_4)_2S_2O_8]$ = 4 × 10^{-3} M; $[Na_2S_2O_5]$ = 4 × 10^{-3} M.

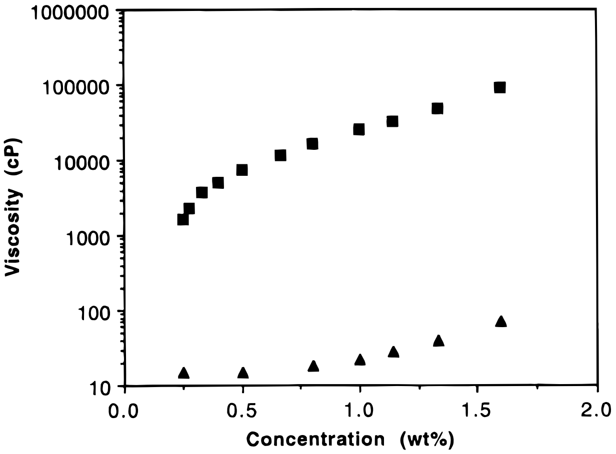


Figure 6. Brookfield viscosity at 0.4 s^{-1} shear rate as a function of concentration of copolymer P-E4-100 (■) and of homopolymer P-E0-000 (▲) in water at 25 °C.

kinetics (Figure 5). Thus, the copolymer hydrophobe content may be determined as a function of time. Kinetic studies were carried out in a 10 mm NMR tube under conditions identical to that used for the above copolymerizations. As shown in Figure 5, the disappearance of the monomer (followed by ^1H NMR) and comonomer could be followed up to 90% conversion. The relative rates of polymerization for monomer and comonomer were found to be equal throughout the polymerization. In the first 20 min, probably as a result of inhibition by small residual amounts of oxygen, the reaction rates were slow after which the polymerization was rapid before slowing down again at high conversion. The kinetic studies confirmed the quantitative comonomer incorporation in excellent agreement with the fluorine content determined by ^{19}F NMR in CD_3OD in the presence of sodium triflate as internal standard (Figure 6, Table 1). Similar results were observed for the copolymerization of AM and FOSA.[30] This is consistent with but does no prove a random incorporation of the comonomer units in the polymer chain.

Assuming homogeneous copolymerizations, and given the large excess of AM over FOSA, random comonomer sequences may be expected if the reactivity ratio of the comonomer (M_2) is low ($r_2 < 1$). For the present case, there is a lack of experimental data on the monomer reactivity ratios. Using the Q and e values (0.49 and 0.09, respectively) reported by Saini et al. for DMA (1) and assuming a similar reactivity of FOSA (2) and methyl acrylate ($Q = 0.42$, $e = 0.60$), the Alfrey-Price equations give r_1 and r_2 values of 1.22 and 0.63, respectively. Of course, the question of whether the reactivities of FOSA and MA are similar remains. However, electron-withdrawing effects of the R_F group in FOSA on the acrylate double bond should be small. Steric effects due to the large R_F group should be present, but this is expected to reduce r_2. Further support for the low value of r_2 comes from the copolymerizations of AM and FOSA in similar emulsion polymerization that yields r_1 and r_2 values of 30 and 0.80, respectively.[31] The r_1 value of DMA is expected to be smaller that that of AM.[32] It is implausible therefore that the incorporation of FOSA in the block copolymer is blocky.

Viscosities in Semidilute Solution. Figure 6 shows a Brookfield viscosity vs concentration profile of PDMA and copolymer P-E4-100 in water at 25 °C at a shear rate of 0.4 s^{-1}. Intermolecular hydrophobic association significantly contributes to the solution viscosity. The viscosity of the copolymer is between 2 and 3 orders of magnitude greater than that of the PDMA homopolymer of about the same molecular weight, consistent with strong hydrophobic association (see above).

Effect of Comonomer Content. The Brookfield viscosity of 0.5 wt % solutions of a series of copolymers measured at a shear rate of 0.4 s^{-1} in water vs comonomer content shows a viscosity maximum as a function of comonomer content (Figure 7). The viscosity maximum for the DMA–FOSA copolymer occurs at 0.1 mol % FOSA content. Similar viscosity maxima were obtained for FOSA-modified polyacrylamide, and the FOSA content at the viscosity maximum was also similar (0.07 mol %).[6] Although it is conceivable that variations in molecular weight may affect the curve somewhat, the data in Table 1 indicate that the maximum is not primarily due to differences in molecular weights but to a variation in comonomer content. The

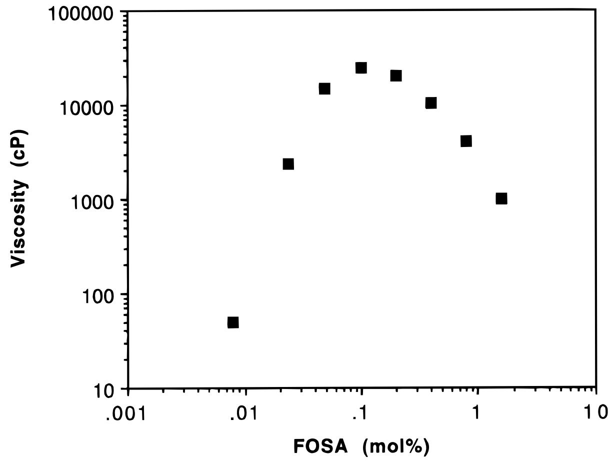


Figure 7. Brookfield viscosity of polymers P-E1−P-E8 (Table 1) at 0.4 s^{-1} shear rate as a function of FOSA comonomer content at 1.0 wt % polymer concentration.

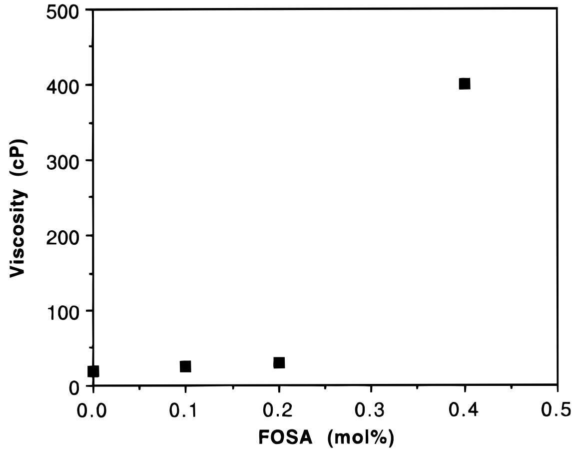


Figure 8. Brookfield viscosity as a function of concentration of FOSA comonomer content of copolymers prepared in bulk. Measurements were made at 5 wt % concentration with 0.4 s^{-1} shear rate. No surfactant present.

observation of a viscosity maximum for the case of the AM−FOSA and AM−LA copolymers was explained by competing intermolecular and intramolecular associations. At low FOSA content, the formation of a network by intermolecular association is favored. However, at higher FOSA content, intramolecular associations begin to become dominant, resulting in a decrease of the size of the coil as shown in Scheme 1.

For the copolymers prepared in bulk, the apparent constant shear viscosities of 5.0 wt % solutions of DMA−FOSA copolymers, as a function of FOSA content, are shown in Figure 8. As in the case of the emulsion copolymerization, the viscosity appears to be directly related to the hydrophobe content of the copolymer samples. The bulk copolymer solutions show much lower viscosities compared to the solutions of the copolymers prepared by emulsion copolymerizations. For instance, the viscosities of the 5.0 wt % bulk copolymers at a FOSA content of 0.2 mol % are ~200 times lower compared to that of the 1.0 wt % emulsion copolymers (Figures 7 and 8). These dramatic differences may be due to a number of factors including (i) differences in molecular weight, (ii) differences in comonomer sequence distribution, and (iii) the presence or absence of surfactants. Molecular weights of the bulk copolymer are much lower (based on M_v) than for the copolymers prepared in solution due at least in part to the high viscosities and resulting incomplete comonomer conversions in the bulk copolymerizations. This is also indicated by the much lower reduced viscosities of the PDMA homopolymer prepared in bulk compared to that prepared in the emulsion copolymerizations. The role of molecular weight in the viscosity of the copolymers is probably of great importance. Thus, highest viscosities for the emulsion copolymers are obtained at a FOSA content of ~0.1 mol % (Figure 7). At this perfluorocarbon content at molecular weights of $M_n = {\sim}1 \times 10^5$ (or DP_n ~10^3), there is an average of one FOSA unit per chain, allowing only micellar aggregation (Chart 2).

Chart 2. Micellelike Aggregation of Low Molecular Weight Copolymers Containing Single Hydrophobic Pendent Groups

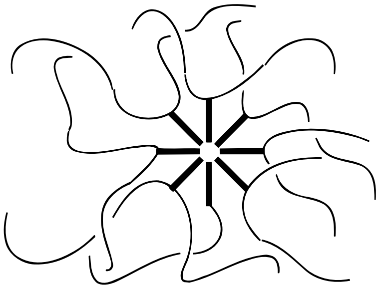
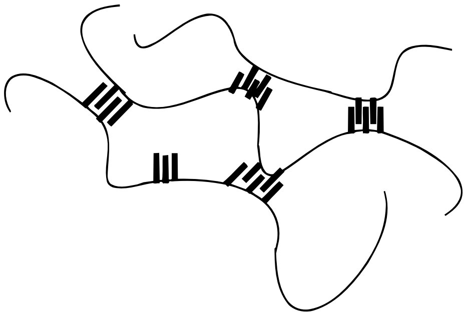


Chart 3. Hydrophobically Associating Blocky Copolymers



Since, at least for these and related systems, the occurrence of reversible interchain “liaisons” rather than micellar aggregation is the likely mechanism for viscosification, an average of at least two FOSA units per chain is required. The presence of blocky sequence distributions has been proposed by several authors as a prerequisite for hydrophobic copolymer association (Chart 3). However, at a FOSA content of 0.1 mol % or less, the relatively low molecular weight of the bulk copolymer makes the formation of blocky FOSA sequences unlikely (see above).

Alternatively, the high viscosities of the emulsion copolymers may be due to surfactant−polymer interactions leading to micellar bridging (see effects of added surfactants below).

Effect of Shear Rate. The effect of shear rate on the viscosity of 1.0 wt % solutions of copolymers P-E2-024 and P-E4-100 and PDMA is shown in Figure 9. Copolymer viscosities decrease dramatically with increasing shear rate, showing highly pseudoplastic behavior. However, the viscosity of the homopolymer does not show this shear dependence. This is again consistent with network formation in the copolymers occurring through weak hydrophobic associations between chains. At very high shear rates, the viscosities of the copolymer and homopolymer solutions converge somewhat. At a shear rate of 17 s^{-1}, network formation through intermolecular associations is disrupted but the hydrophobic associations are still contributing substantially to the

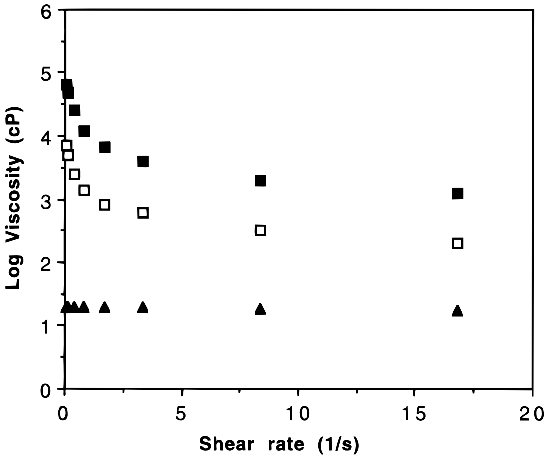


Figure 9. Effect of shear rate on solution viscosity of copolymers P-E4-100 (■) and P-E2-024 (□) and homopolymer P-E0-000 (▲) at 1.0 wt % polymer concentration.

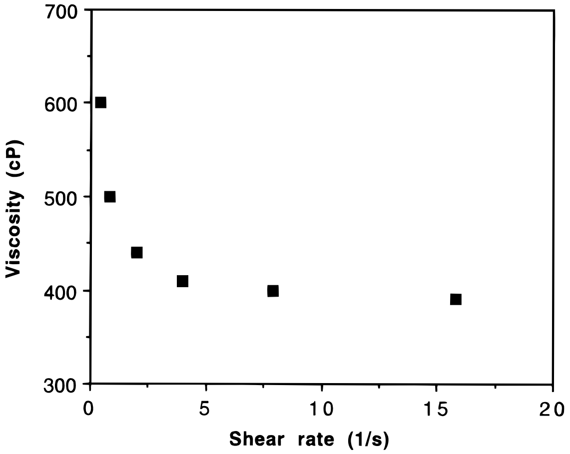


Figure 10. Brookfield viscosity of copolymer P-B4-04 as a function of shear rate at 5 wt % polymer concentration. No surfactant present.

viscosity. The viscosity is restored completely and rapidly (<1 s) when the shear is removed, indicating that networks reassemble rapidly. This rapid reforming of hydrophobic "bonds" is most likely responsible for the considerably higher viscosities (>100) times of the copolymers compared to PDMA at higher shear rates. The degree of shear thinning apparently is not strongly dependent on hydrophobic content, whereas the viscosity enhancement is much more sensitive to hydrophobic content. These typical features of shear thinning have been described for other fluorocarbon- and hydrocarbon-containing associating copolymers.[3,4,6,14,22,33,41]

The viscosity of bulk copolymer P-B4-04 as a function of shear rate is presented in Figure 10. As in the case of the emulsion copolymers, the pronounced pseudoplastic behavior is consistent with the formation of physical networks through hydrophobic associations. However, it should be noted that the bulk copolymers clearly show much less pronounced shear thinning than for the emulsion copolymers.

Effect of Added Salt. The nature of the association phenomena reported above is further demonstrated by the increase in solution viscosities upon addition of NaCl. Figure 11 shows modest viscosity increases of 0.5 and 1.0 wt % solutions of P-E2-024, P-E4-100, and P-E0-000 with increasing NaCl concentration in the range of 0−0.85 M. Such increases have been observed for the case of AM−FOSA copolymers and were attributed mainly to a "salting out" of the hydrophobic groups[34] by the salt. At higher polymer concentrations, the viscosity increases are more pronounced. These increases in viscosity upon addition of salt appear to correlate well with the salting-out effect of NaCl on hydrophobic association. For instance, the addition of a neutral electrolyte, i.e., NaCl to solutions of anionic surfactants in aqueous solution causes a decrease in cmc values and an increase in the aggregation number and volume of the micelles.[35]

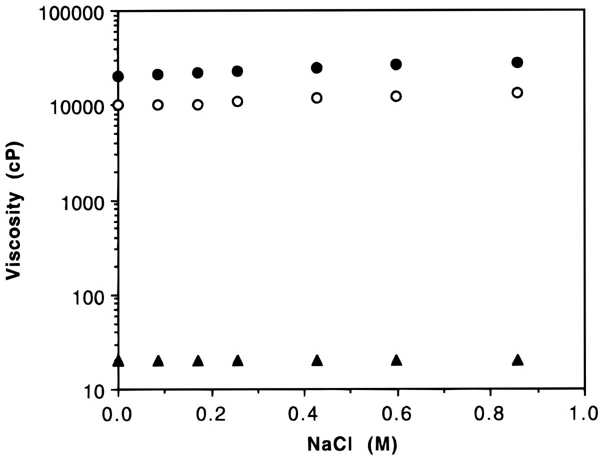


Figure 11. Brookfield viscosity, at 0.4 s^{-1} shear rate, of copolymer P-E4-100 as a function of concentration of NaCl at different polymer concentrations: 1.0 (●) and 0.5 wt % (○); and homopolymer P-E0-000 (▲) at 0.5 wt %.

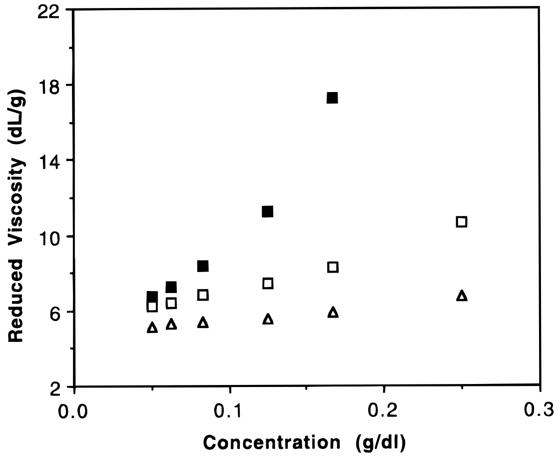


Figure 12. Reduced viscosity as a function of concentration of copolymer P-E4-100 in water (■) and DMF/water (50:50, v/v) (□); and homopolymer in DMF/water (50:50, v/v) (△) at 25.0 °C.

Effect of Additives. The effect of organic solvents on hydrophobic associations was investigated by addition of dimethylformamide (DMF) to aqueous solutions of 0.5 wt % solutions of P-E4-100 and P-E0-000. The addition of DMF (50 vol %) causes a dramatic decrease in reduced viscosity, as shown in Figure 12. For instance, in water at a concentration of 0.17 g/dL, the reduced viscosity of a solution of copolymer is ~18 dL/g. At the same polymer concentration in a 50 vol % of DMF aqueous solution, the reduced viscosity of the copolymer solution is only 7 dL/g, although the reduced viscosities of the homopolymer solutions are essentially unchanged upon DMF addition (see Figure 2 and Figure 12). This indicates that the organic solvent acts to break up hydrophobic association thereby dramatically decreasing the solution viscosity. Similar effects have been shown by reduced viscosity measurements of

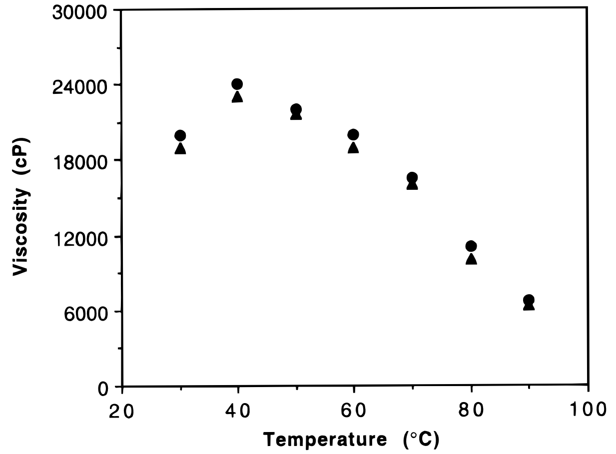


Figure 13. Brookfield viscosity vs temperature for copolymer P-E5-200: dialyzed (●) and nondialyzed (▲) at 1.0 wt % polymer concentration with 0.4 s^{-1} shear rate.

fluorocarbon-containing AM copolymers in DMF/H_2O (50 vol %).[6,22] In DMF/H_2O, higher values of the reduced viscosity and the Huggins constant are obtained for the copolymer than for the homopolymer, indicating the copolymer still undergoes aggregation particularly at higher concentrations.

Effect of Temperature. In contrast to PDMA, the viscosity of the copolymer P-E5-200 (Table 1) increases with increasing temperature, reaching a maximum at 40 °C (Figure 13). Viscosity maxima in the 60–80 °C range were also observed in FOSA containing AM copolymers[6,22] and were interpreted as being consistent with an entropy driven association process.[36] The reason for the viscosity maximum occurring at a lower temperature for the case of the PDMA–FOSA copolymers is not understood. At higher temperatures, the viscosities of all of these copolymer solutions decrease with increasing temperature, presumably as a result of the less ordered structure of water itself. Thus, in this range, water may behave again somewhat like a nonaqueous solvent producing conventional viscosity–temperature profiles. The viscosity–temperature profile is essentially the same for dialyzed and undialyzed solutions, indicating that these phenomena are not directly related to polymer–surfactant interactions. A similar complex behavior with temperature has been observed for surfactant solutions. For instance, the cmc of surfactants in water with increasing temperature first decreases and then increases,[37] due to decreased hydration of the hydrophilic group at higher temperatures, thus favoring micellization. However, the temperature increase also causes disruption of the structured water surrounding the hydrophobic group, an effect that disfavors micellization. The relative magnitude of these two opposing effects, therefore, determines whether the cmc increases or decreases over a particular temperature range.[38]

Effect of Added Surfactant. The addition of APFO surfactant to dialyzed solutions of the emulsion polymers leads first to a viscosity increase followed by a decrease at higher surfactant concentrations to a value much lower than the original value (Figure 14, Table 3). Similar viscosity changes on addition of surfactants to HM water-soluble polymers have been observed by other research groups[13,23] and have been interpreted as due to micellar bridging and surfactant-mediated polymer dissociation as the surfactant concentration increases (Scheme 2).

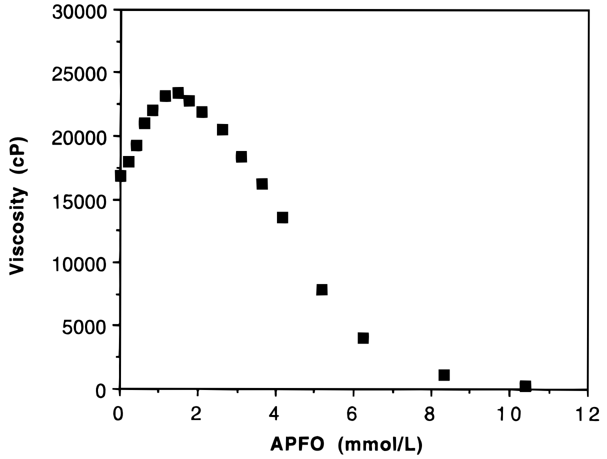


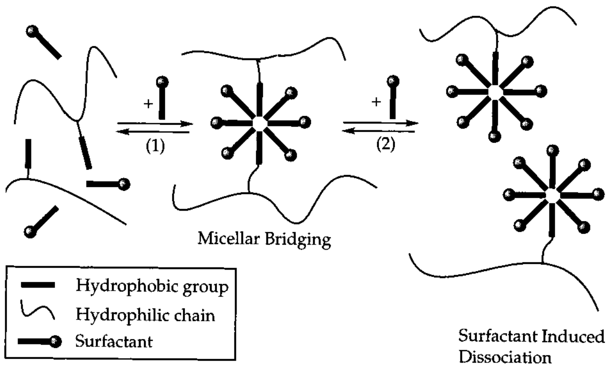
Figure 14. Brookfield viscosity vs added fluorocarbon surfactant for copolymer P-E5-200. Measurements were made at 1.0 wt % polymer concentration with 0.4 s^{-1} shear rate. The sample was dialyzed before measurement.

Table 3. Effect of Added Surfactant on Solution Viscosity (cP) of Copolymers Prepared in Bulk[a,b]

surfactant (APFO)		FOSA content (mol %)		
(wt %)	(mmol/L)	0.1	0.2	0.4
0.0	0.0	30	80	400
0.2	4.2	380	2400	14000
0.4	8.3	1000	7600	28000
0.6	12.5	1400	13600	40000
0.8	16.6	800	12000	36000
1.0	20.8	150	4000	26000
1.2	24.9		1400	12000
1.4	29.1		200	4000
1.6	33.3			800
1.8	37.4			500

[a] Samples were prepared for the copolymerization of DMA and FOSA in bulk. [b] Brookfield viscosities were measured at 5 wt % polymer concentration with 0.4 s^{-1} shear rate at room temperature.

Scheme 2. Surfactant-Mediated Copolymer Association (1) and Dissociation (2)



The viscosities of the bulk copolymers as a function of APFO concentration measured at 0.40 s^{-1} also give viscosity maxima (Figure 15). For bulk copolymers of low FOSA content ($\leq$0.1 mol %), the solution viscosity does not differ greatly from that of copolymer solutions without surfactant. However, addition of a small amount of surfactant (5×10^{-3} M) to the copolymers containing $\geq$0.2 mol % FOSA results in large viscosity enhancements. Viscosity increases dramatically ($\sim 10^3$-fold) with increasing surfactant concentrations and reaches a maximum at an APFO concentration of 12×10^{-3} M followed by appreciable viscosity decreases. Assuming that the SEC determined M_n values of the bulk copolymers are approximately correct (DP_n ~1000), it is

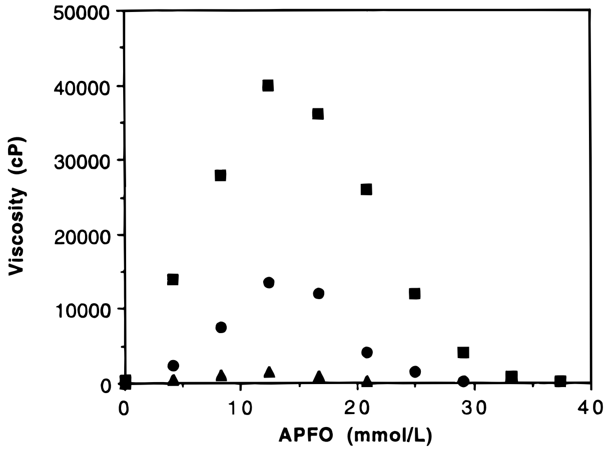


Figure 15. Effect of added surfactant on solution viscosity of bulk copolymers with different FOSA comonomer contents: 0.4 (■), 0.2 (●), 0.1 (▲) mol % at 5 wt % concentration with 0.4 s^{-1} shear rate.

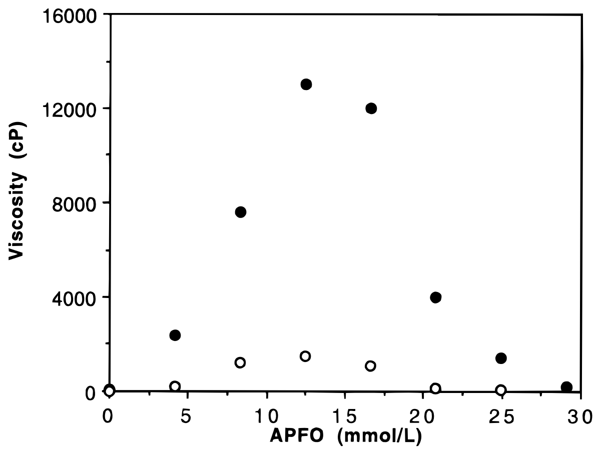


Figure 16. Effect of added surfactant on solution viscosity of copolymer P-B2-02 at different polymer concentrations: 5.0 (●) and 2.5 (○) wt % at 0.4 s^{-1} shear rate.

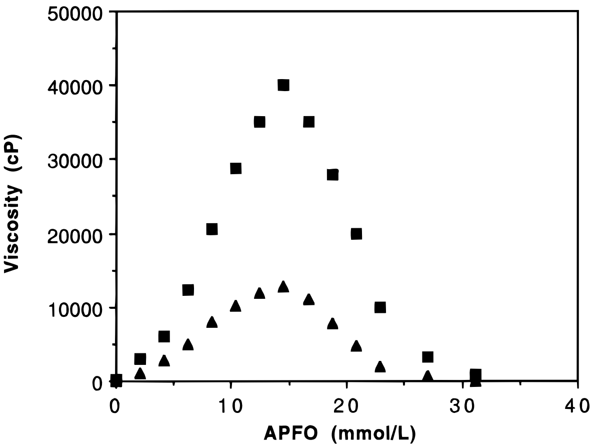


Figure 17. Effect of added surfactant on solution viscosity of copolymers P-B2-02 and P-B3-02 with different molecular weights: 4.1 × 10^5 (■) and 2.4 × 10^5 (▲) at 5 wt % polymer concentration at 0.4 s^{-1} shear rate.

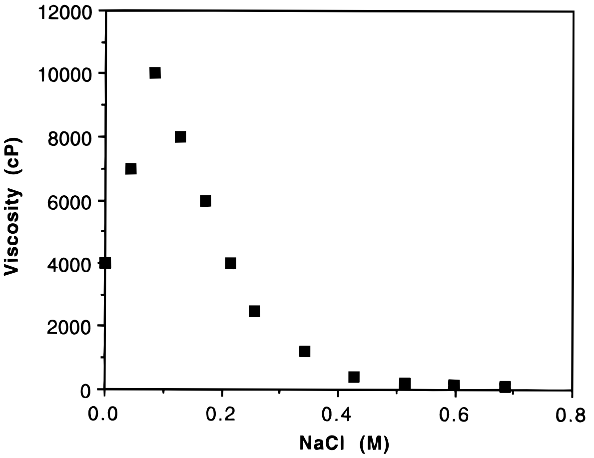


Figure 18. Brookfield viscosity as a function of added NaCl for copolymer P-B2-02 at 5 wt % polymer concentration with 0.4 s^{-1} shear rate in the presence of APFO surfactant (15 × 10^{-3} M).

interesting that at a FOSA level of ≥0.2 mol % ≥ (>2 R_F groups/chain) there is a significant visosity increase upon APFO addition consistent with micellar bridging-induced net work formation. At APFO concentrations well above the cmc (9.6 × 10^{-3} M),[39] the viscosity is observed to be approximately the same as the copolymer solution without surfactant. The maxima occur at about the same surfactant concentration independent of FOSA content. However, the magnitude of the peak viscosity is very sensitive to the amount of hydrophobe in each sample consistent with the above. Viscosity maxima have also been observed for other fluorocarbon-containing PAM copolymers[22] and for hydrocarbon copolymers of AM and *N*-(4-ethylphenyl)acrylamide.[13]

These dramatic effects are consistent with the formation of mixed aggregates through the interaction of the surfactant molecules with the fluorocarbon hydrophobic groups, e.g., micellar bridging effect[13] (Scheme 2). The surfactant associates directly with the hydrophobes of the copolymers. As the concentration of surfactant increases, a point is reached at which there is sufficient surfactant needed for effective micellar bridging. At higher surfactant concentrations, the polymer hydrophobes may become solubilized by single micelles thus leading to a decrease in the viscosity.

These effects are, as expected, polymer concentration dependent, as shown in Figure 16. The viscosities of 2.5 and 5.0 wt % solutions as a function of surfactant concentration present maxima at about the same surfactant concentrations of 12.5 × 10^{-3} M. As expected, the viscosities decrease strongly as the copolymer concentration decreases.

Figure 17 shows the viscosities for copolymers with different molecular weights but the same (0.2 mol %) FOSA content as a function of surfactant (APFO) concentration. The higher molecular weight copolymer not unexpectedly gives greater viscosity enhancement upon addition of a surfactant. The number of hydrophobes per polymer chain for the higher molecular weight copolymer is larger, greatly facilitating intermolecular cross-linking as induced by surfactant binding. It is expected that increasing molecular weight greatly contributes to viscosity as a result of an increase in the number of hydrophobes per chain and due to the increased size of the coil itself.

NaCl has long been known as a "salting-out" electrolyte promoting hydrophobic association (see above) and causing a decrease in the cmc of surfactants. Thus, in order to explore the micellar bridging in the polymer—surfactant system, the effect of addition of NaCl on the solution viscosity is of considerable interest. Figure 18 shows an interesting salt effect that differs from the results shown in Figure 11. Upon addition of NaCl in the presence of APFO (1.5 × 10^{-2} M), the solution viscosity of a 5.0 wt % copolymer solution (P-B2-02)

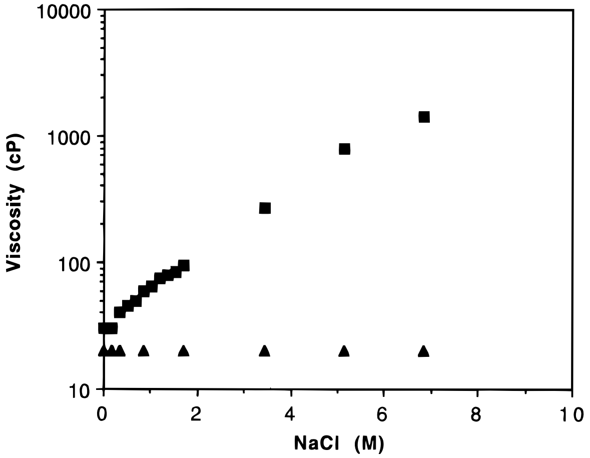


Figure 19. Brookfield viscosity as a function of added NaCl for copolymer P-B2-02 (■) and homopolymer (▲) at 5 wt % polymer concentration with 0.4 s^{-1} shear rate in the absence of surfactant.

increases $\sim$2.5-fold at a NaCl concentration of 0.1 M. However, above a NaCl concentration of 0.2 M, the viscosity of the system sharply decreases below that of the copolymer in water. Above 0.5 M NaCl, the solution show very little viscosity (<100 cP). No such effect was observed for the case of the emulsion polymers.

The cause for these viscosity changes is not fully understood. The viscosity increase could be due to the known effects of NaCl on hydrophobic association (salting out) or to increased binding of fluorocarbon carboxylate surfactant to the fluorocarbon group of the PDMA, and thus chain expansion, leading to polyelectrolyte character. The sharp decrease in viscosity with further addition of salt is consistent with such a polyelectrolyte effect. Beyond a NaCl concentration of $\sim$0.1 M, the anionic charges in the polymer chain are shielded, causing the chain to contract and hence the viscosity to decrease. Addition of NaCl in the absence of surfactant causes the viscosity to increase with increasing NaCl concentration up to 7 M whereas addition of NaCl to a solution of the PDMA homopolymer results in no viscosity enhancement (Figure 19). It is probable, therefore, that the enormous viscosity increases upon addition of APFO (Figure 15) are due to both surfactant binding to the polymer and to micellar bridging.

In order to explore the importance of polyelectrolytic effects, copolymer binding of non-ionic surfactants was of obvious interest. As illustrated in Figure 20, the addition of the nonionic surfactant PFEO to the copolymer solution shows little viscosity enhancement below 20×10^{-3} M. Upon further addition, the viscosity increases gradually, passes through a maximum at $\sim$0.1 M and then decreases. This is consistent with a micellar bridging effect, similar to that for anionic surfactants except that the apparent micellar bridging efficiency of anionic surfactant is greater than that of the nonionic surfactant. Thus a viscosity maximum of $\sim$40 000 cP is reached at $\sim 10 \times 10^{-3}$ M anionic surfactant compared to 100×10^{-3} M for the nonionic surfactant.

Figure 21 shows the shear-dependent viscosity of copolymer solutions in the presence of APFO and PFEO surfactant. Surprisingly, no shear thinning is observed for the copolymer solution in the presence of the anionic APFO surfactant. This is currently not well understood but could be related to a polyelectrolyte effect. The relatively strong shear thinning effect for the same copolymer in the presence of nonionic surfactant is consistent with the effect of micellar bridging.

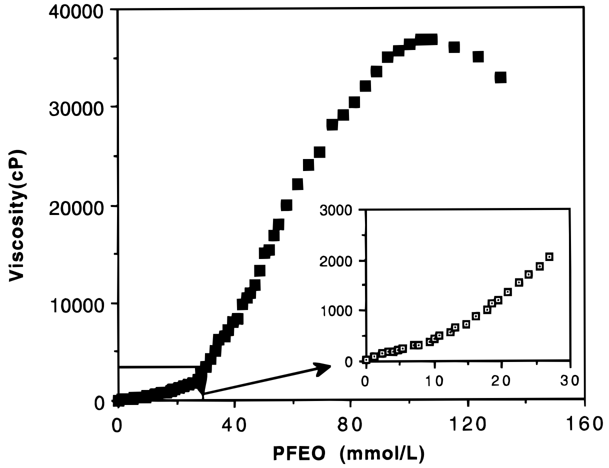


Figure 20. Brookfield viscosity as a function of added nonionic surfactant PFEO for copolymer P-B2-02 at 5 wt % polymer concentration with 0.4 s^{-1} shear rate.

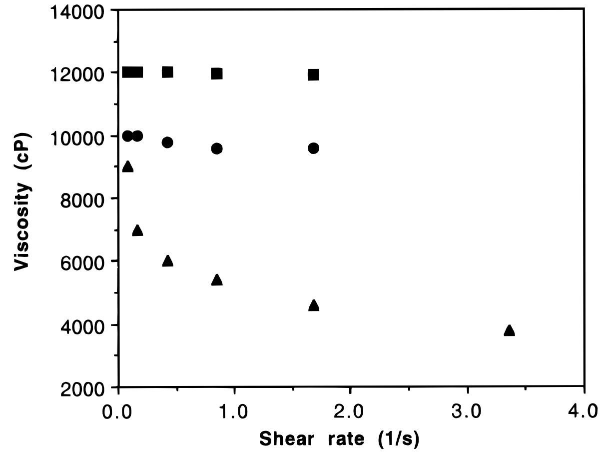


Figure 21. Effect of shear rate on solution viscosity of copolymer P-B2-02 at 5 wt % polymer concentration in the presence of 15×10^{-3} M APFO (■), 15×10^{-3} M APFO + 0.1 M NaCl (●), and 33×10^{-3} M PFEO (▲).

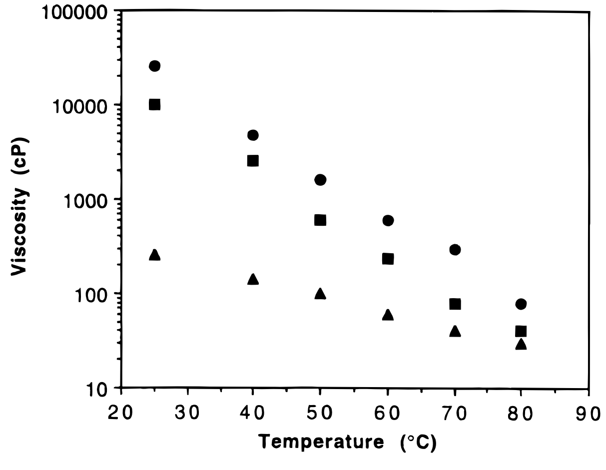


Figure 22. Effect of temperature on solution viscosity of copolymer P-B2-02 at 5 wt % polymer concentration with 0.4 s^{-1} shear rate at different APFO surfactant concentrations: 20×10^{-3} (■), 10×10^{-3} (●), and 0 (▲) M.

Figure 22 shows the effect of temperature on the viscosity of copolymer solutions at a given shear rate in the presence of 2.0×10^{-2}, 1.0×10^{-2}, and 0 M zero APFO surfactant concentration. The viscosities decrease sharply with increasing temperature especially at 2.0×10^{-2} M APFO. In the absence of surfactant, the solution shows relatively little viscosity decrease

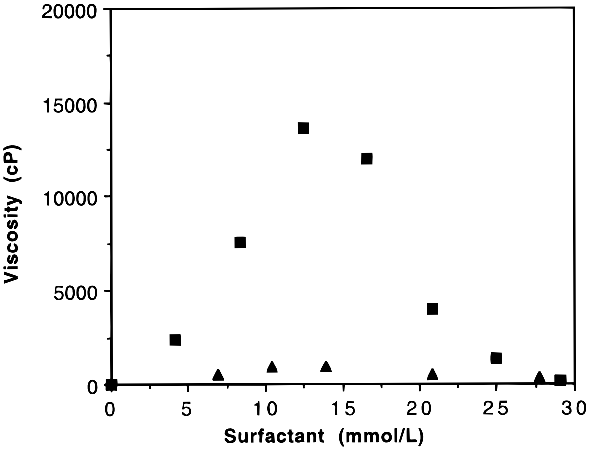


Figure 23. Brookfield viscosity as a function of added APFO (■) and SDS (▲) for copolymer P-B2-02 at 5 wt % polymer concentration with 0.4 s^{-1} shear rate.

over the range of 25–80 °C. At the highest temperatures, the copolymer solutions with and without surfactants give an almost identical viscosity of about 30–100 cP. It should be noted that these results differ from that of Figure 14 in which the viscosity–temperature profile shows a maximum. The absence of a viscosity maximum with temperature in the present case suggests again that the viscosity enhancement derives from different factors possibly including polyelectrolyte effects.

The effect of surfactant on the solution viscosity of the bulk copolymers was further explored by addition of SDS to solutions of DMA–FOSA associative polymers. Figure 23 shows a viscosity maximum as a function of SDS concentration similar to that seen for the case of APFO. The viscosity maximum occurs at a SDS concentration of 12×10^{-3} M, nearly identical to that of the maximum for APFO (12.5×10^{-3} M). However, the viscosity maximum in the presence of a hydrocarbon surfactant is much lower. This indicates that addition of the hydrocarbon surfactant also causes interchain bridging between copolymer fluorocarbon hydrophobic groups present in the copolymer. However, viscosities are much lower (~15 times) so that the interactions between the fluorocarbon groups of the copolymer and the hydrocarbon groups of the surfactant are much weaker. This is in agreement with a report of Guo and co-workers,[40] who reported the appreciably lesser stability of mixed micelles in the sodium perfluorooctanoate/SDS mixed-surfactant system compared to the micelles of either hydrocarbon or fluorocarbon surfactants.

Similar phenomena are expected for the case of addition of hydrocarbon or fluorocarbon surfactants to PDMA copolymers containing hydrocarbon pendent groups. As shown in Figure 24, addition of SDS and APFO to a DMA copolymer containing 1.0 mol % LA units results in viscosity maxima for both surfactants. The viscosity maximum for the hydrocarbon surfactant is much larger than that for the fluorocarbon surfactant. Clearly, in this case micellar bridging by fluorocarbon surfactant is much less effective than by SDS, consistent with the above lack of stability of mixed micelles. It is worth noting that the differences in micellar bridging efficiency as judged by viscosity differences are greater (14 times) for the case of the perfluorocarbon than for the hydrocarbon modified polymers (3 times) (Table 4). A tentative order for the strength of the polymer–surfactant interactions is listed as follows: $P_{RF}–S_{RF} > P_{RH}–S_{RH} > P_{RF}–S_{RH} > P_{RH}–S_{RF}$. However, mixed fluorocarbon–hydrocarbon surfactant systems of this type are expected to be complicated, and a full rationalization of these results will have to await further work.

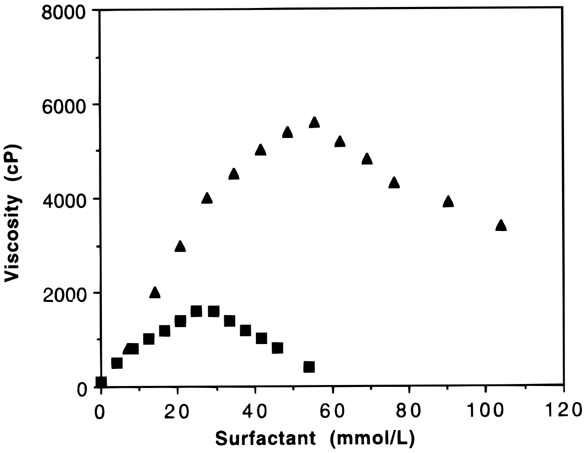


Figure 24. Brookfield viscosity as a function of added hydrocarbon surfactant SDS (▲) and fluorocarbon surfactant APFO (■) for LA-containing copolymer P-B5-10 at 5 wt % polymer concentration with 0.4 s^{-1} shear rate.

Table 4. Micellar Bridging of Polymer–Surfactant Systems[a,b]

	R_H copolymer[c] (cP)	R_F copolymer[d] (cP)
no surfactant	100	60
R_F surfactant (APFO)	1600	14000
R_H surfactant (SDS)	5600	1000

[a] R_H and R_F refer to the hydrocarbon and fluorocarbon, respectively. [b] Viscosity data were taken from the maxima of Figures 24 and 25. [c] Sample P-B2-02. [d] Sample P-B5-10.

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