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S. S. Bae[a]; K. Chakrabarty[a]; T. A. P. Seery[a]; R. A. Weiss[ab]
[a] Polymer Science Program, [b] Department of Chemical Engineering, University of Connecticut, Storrs, CT

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THERMOPROCESSIBLE HYDROGELS. I. SYNTHESIS AND PROPERTIES OF POLYACRYLAMIDES WITH PERFLUOROALKYL SIDE CHAINS

S. S. BAE,[1] K. CHAKRABARTY,[1] T. A. P. SEERY,[1,*] and R. A. WEISS[1,2]

[1]Polymer Science Program
[2]Department of Chemical Engineering
University of Connecticut
Storrs, CT 06269

ABSTRACT

Copolymers composed of acrylamide (AM), N,N-dimethylacrylamide (DMAM), N-isopropylacrylamide (NIPAM) and 2-(N-ethyl-perfluorooctanesulfonamido) acrylamide (FOSA) were synthesized by free radical polymerization. The chemical structure of the resulting polymers was characterized with NMR spectroscopy and thermal properties were measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). ^{1}H-NMR spectra of the copolymers of NIPAM with FOSA showed that FOSA was incorporated quantitatively. The glass transition temperature (T_g) of the copolymers and the terpolymers decreased with increasing FOSA content. The T_gs, however, were higher than predicted for a random copolymer by the Fox equation, which was attributed to microphase separation of the hydrophobic, fluorinated species. Copolymers of AM and FOSA became discolored above 180°C due to formation of cyclic imide and nitrile moieties through cyclization or dehydration of amide groups. The equilibrium water sorption of the copolymers decreased with increasing FOSA content, but increasing FOSA suppressed the water desorption kinetics.

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[*] Author to whom correspondence should be addressed.

Water sorption and thermal stability were improved by terpolymerization of AM, NIPAM, DMAM and FOSA.

INTRODUCTION

Hydrophobically modified water-soluble polymers have been explored extensively in recent years because of their potential for application as viscosifying agents, drug delivery systems and additives for enhanced oil recovery [1-6]. The viscosity enhancement of these polymers in aqueous media is ascribed to physical crosslinks arising from association of hydrophobic groups. The nature of the physical crosslinks depends on the structure, concentration and location along the polymer backbone of the hydrophobic segments. The chemical structure of the water-soluble back bone, and the ionic strength and pH of the solvent also affect the association. Hogen-Esch and coworkers have reported that perfluoroalkyl-modified water-soluble polymers such as hydroxyethylcellulose, polyacrylamides and polyethylene oxide exhibit much stronger interactions when compared to the corresponding hydrocarbon derivatives[4-6, 8-9]. Their efforts with perfluoroalkyl-modified polyacrylamides involved changing the size of the perfluoroalkyl side chain and introducing spacers of different length between the back bone and perfluoroalky side group. They demonstrated that control of the physical crosslinks determined the ultimate properties of the polymers.

Chemical crosslinking is often used when hydrogels must be insoluble in water and require mechanical strength for handling. Chemical crosslinking, however, is difficult to control in a melt fabrication process, and it is not reversible. In contrast, physical crosslinks can be thermoreversible, so that common melt fabrication processes, such as injection molding, may be used. Therefore, hydrogels based on crosslinks formed from hydrophobic interactions, such as the perfluoroalkyl-modified polyacrylamides have potential as thermoformable hydrogels. For many hydrogel applications, biocompatibility is also required and the material must also have high oxygen permeability, water sorption, and wettability.[10] Most of these properties are inter-related [10, 11]. For example, oxygen permeability is largely related to water content and also influences biocompatibility.

Current efforts to develop new hydrogels are focused on manipulating each property individually by changing monomers, crosslinking agents, and formulation. For example, the copolymerization of N-vinyl pyrrolidone (NVP) and methacrylates, in the presence of a crosslinker such as allyl methacrylate, or ethylene glycol dimethacrylate, provides an important class of hydrogels [12]. However, due to poor copolymerization of NVP and methacrylate monomers, the polymeric products often have inconsistent quality, such as poor dimensional control, low modulus, and low water content. Lai synthesized methacryloxyethyl vinyl carbonate, a novel crosslinker containing a vinylcarbonate and a methacrylate group enhancing copolymerization of NVP and methacrylate and with this crosslinker improved the properties of a hydrogel composed of NVP and methacrylate [13].

Polydimethylsiloxane (PDMS), due to its low modulus of elasticity, optical transparency, and high oxygen permeability, is an ideal candidate for use in some hydrogel applications. However, PDMS is hydrophobic and attempts to form copolymers with hydrophilic monomers such as HEMA, NVP, and acrylamide have resulted in opaque, phase-separated materials due to the poor solubility of PDMS in those monomers. Kunzler and Ozark synthesized methacrylate end-capped siloxanes containing hydrophilic side chains and successfully copolymerized them with high concentration of hydrophilic monomers to give hydrogels possessing high levels of oxygen permeability [14]. They found in their work with fluoro-substituted siloxanes that higher concentrations of fluorinated side chains and fluoro-methacrylates in the copolymer formulation resulted in a dramatic reduction in protein deposition. Ammon *et al.* synthesized macro-monomers composed of octafluoropentyl-methacrylate and polyethylene glycol and copolymerized these macromonomers with HEMA to achieve high wettability and low protein deposition. They reported a significant enhancement of the surface concentration of the macromonomeric unit relative to the bulk concentration, which improved the surface properties [15].

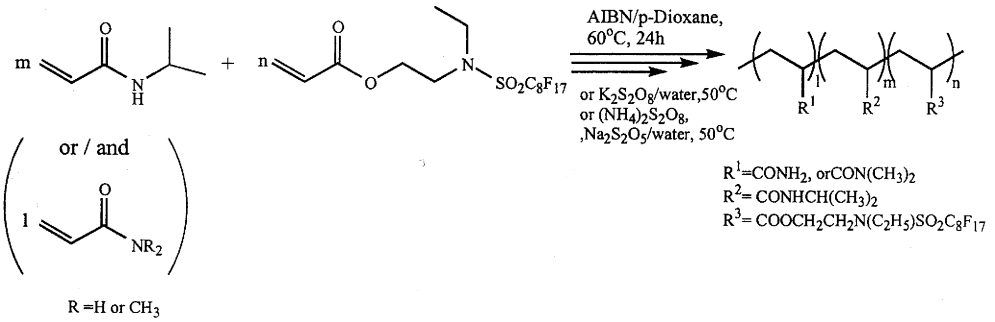
Muhlebach *et al.* modified poly (vinyl alcohol) with alkenyl azlactones to obtain water-soluble polymers with pendant methacrylate and acrylamide groups [16]. These polymers were crosslinked by UV-irradiation within seconds to form transparent networks with high water content. Krakovsky et al. incorporated a small amount of sodium methacrylate in HEMA based copolymers to achieve high water content but at the same time, the incorporation of ionic groups increased protein deposition [17]. Sassi *et al.* studied sorption of lysozyme by HEMA copolymer hydrogels as a function of gel composition [18]. They prepared three types of HEMA gel: neutral (HEMA), acidic (HEMA + acrylic acid), and basic (HEMA + dimethylamino-ethylmethacrylate). The rate of protein uptake by acidic gel was more rapid than that by the neutral gel. Lysozyme did not adsorb or partition into the basic gel. They attributed these results to electrostatic interactions between the protein and the polymer gels. In the case of the acidic gel, the carboxylic group should be negative-charged in physiological conditions (pH 7.2-8) to interact with the positively charged protein in the same conditions.

Nearly all of the prior literature on hydrogels employed covalent crosslinking, which precludes using conventional melt processes to fabricate the materials. Our approach for developing a thermoformable hydrogel started with polyacrylamide containing perfluoroalkyl side chain. In an aqueous environment, perfluoroalkyl side chains of the polymer associate inter and intramolecularly to provide strong physical crosslinking. The strength of these interactions depends on the temperature so that processing in the dry state with subsequent hydration could allow for mass production of shaped hydrogels without chemical crosslinking. We further anticipate that these fluoroalkyl side chains will reduce adventitious protein deposition. Candidate polymers were synthesized by radical polymerization (Scheme 1) and the properties of the resulting polymers such as chemical structure, solubility, thermal properties and water content were investigated.

EXPERIMENTAL

Materials and Instruments

N-isopropylacrylamide (Acros, 99%) was recrystallized twice from a mixture of hexane and benzene (v/v, 65/35). The comonomer, FOSA (obtained from 3M, tradename FX-13), was recrystallized three times from methanol before use. AIBN (1,1′-azobis-(isobutyro-nitrile)) (Aldrich, 99%) was also puri-



Scheme 1.

fied by recrystallization twice from methanol. Proton NMR spectra were recorded on a Bruker Advance DMX 500 spectrometer using $CDCl_3$ as the solvent with tetramethyl silane as an internal standard. Gel permeation chromatography measurements were made in THF at 35°C with a Waters 150C system equipped with four Waters Ultrastyragel columns (10000, 5000, 500, 100 Å) and two detectors (refractive index and ultraviolet) at a flow rate of 1 mL/min. Polystyrene standards were used for calibration. The sample solutions were prepared by dissolving the polymer in THF and filtering the solutions with a PTFE membrane filter (Millipore, pore size 0.45 um) prior to measurement. Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer DSC-7 using a heating rate of 20°C/min. To remove solvent history effects and absorbed moisture, the samples were annealed at 160°C under nitrogen for 10 minutes and then quenched to 30°C before each DSC heating scan. Dilute solution viscosity measurements were carried out using an Ubbelohde-type viscometer immersed in a water bath controlled to 0.1°C. The efflux time was measured with a digital stop-watch at a resolution of 0.1s.

Copolymerization of AM and FOSA

Acrylamide (30 g, 422.1 mmol) and FOSA (1.32 g, 2.1 mmol) were dissolved in 60 ml acetone. The solution was diluted with 300 ml of water containing sodium dodecyl sulfate (2.0 g). The mixture was purged with dry nitrogen for 30 minutes. The temperature was raised to 50°C. Ammonium persulfate (22.8 mg) and sodium metabisulfite (19.0 mg) were injected into the mixture. The reaction was terminated after 24 hours by cooling to room temperature. The viscous reaction mixture was recovered by precipitation in 2 L of acetone. The recovered polymer was dried under vacuum at 50°C for 48 hours.

Copolymerization of DMAM and FOSA

Method A

N,N-dimethylacrylamide (6.25 g, 63 mmol) and FOSA (0.197 g, 0.315 mmol) were dissolved in 15 ml of acetone. The solution was diluted with 110 ml of water containing SDS (0.125 g). The mixture was purged with dry nitrogen for 30 minutes. The temperature was raised to 40°C. Potassium persulfate (0.85 g, 3.15 mmol) dissolved in 80 ml water was injected into the mixture. The reaction was terminated after 24 hours by cooling to room temperature. The product was isolated in the same manner as the AM/FOSA polymer.

Method B

N,N-dimethylacrylamide (10 g, 100 mmol) and FOSA (0.315 g, 0.504 mmol) were dissolved in 110 ml of dioxane using a Teflon coated magnetic stirrer. The solution was purged with dry nitrogen gas for 30 minutes. The temperature was raised to 60°C. A solution of AIBN (0.04 g, 0.244 mmol) in 15 ml dioxane was injected into the reaction mixture. The reaction was terminated after 24 hours by cooling. The product solution was reduced to half its volume with a rotary evaporator. The copolymer was recovered by precipitating into 750 ml of diethyl ether and dried under vacuum at 70°C for 48 hours.

Copolymerization of NIPAM and FOSA

The monomers and initiator were dissolved in 1,4-dioxane and was purged with dry nitrogen for 30 minutes. The polymerization was run for 24 hours at 60°C. After cooling to room temperature, the polymer was precipitated in excess diethyl ether. The precipitate was dried at 60°C for 24 hours and then at 160°C under vacuum for 2 hours.

Terpolymerization

Terpolymerization procedure was the same as that used in the copolymerization of NIPAM and FOSA.

Characterization of Monomers and Polymers with ^{1}H-NMR Spectroscopy

An accurate ^{1}H-NMR spectrum of FOSA was required so that quantitative copolymer compositions could be determined. One dimensional spectra exhibited all the characteristic peaks expected for the structure reported in literatures [19, 5], but there was deviation in the predicted integration values of some of the peaks. According to the proposed structure in Scheme 1, the ratio of the integration values of the three methylene peaks at 4.4, 3.9, and 3.6 ppm, respectively should be 1 to 1 to 1 but as seen in Figure 1, the observed ratio was 2 to 1 to 3. Further study of FOSA with two-dimensional NMR spectroscopy (COSY), shown in Figure 2, reconciled the discrepancy; the methylene proton resonance at 3.9 ppm (9) had split and was overlapped with the peak at 3.6 ppm (10).

^{1}H-NMR spectra of all the copolymers of Nisopropylacrylamide and FOSA and their homopolymers were measured. As expected, the vinyl proton peaks (5.6 to 6.5 ppm) in the ^{1}H-NMR spectrum of the monomers were not present in the ^{1}H-NMR of the polymers. Even though all the peaks were broad, the

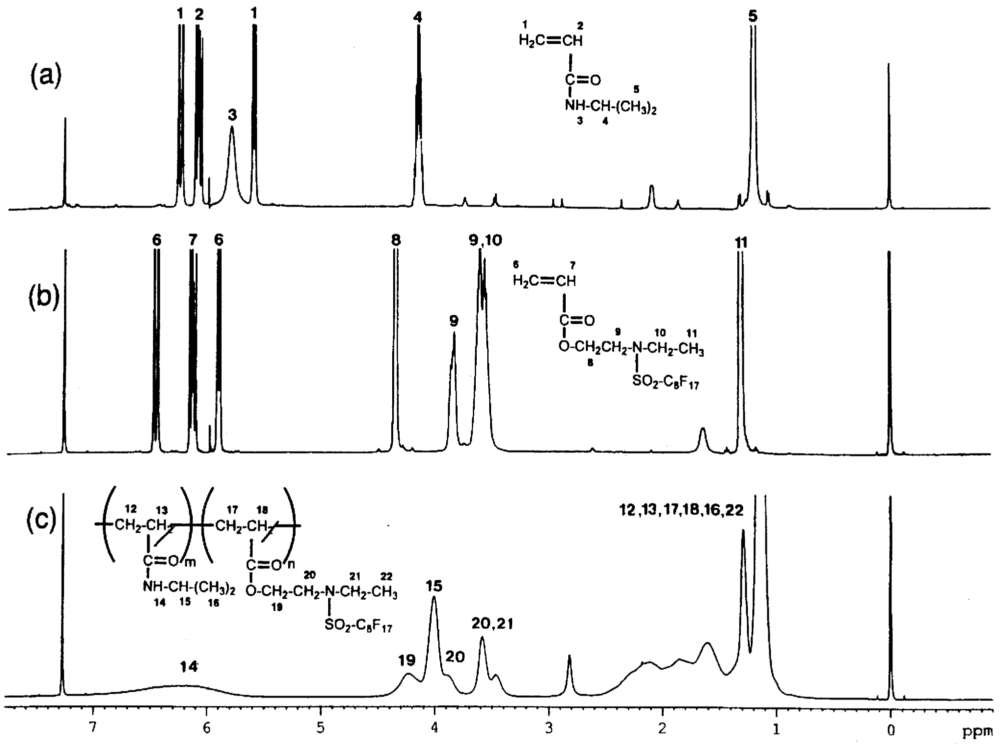


Figure 1. ^{1}H-NMR spectra of NIPAM (a), FOSA (b) and CP005 (c).

^{1}H-NMR spectra of the polymers showed all the characteristic peaks of the copolymer structure, and the composition of the copolymers was calculated from the integration values. The sum of integration values of the peaks in the range of 3.4 to 4.2 ppm account for the relative amount of the methylene protons labeled 19, 20, and 21 in the FOSA and the methine proton labeled 15 in the NIPAM. The concentration of each monomer unit in the polymers was calculated using the following equations:

$$\frac{m + 6n}{m} = X \tag{1}$$

where m is the total moles of N-isopropylacrylamide unit in copolymer and n is the total moles of FOSA and X is the integrated value between 3.4 and 4.2 ppm when the amide proton resonance (peak 14) is set to an area of 1. From Equation 1, the mol% of FOSA is calculated as follows:

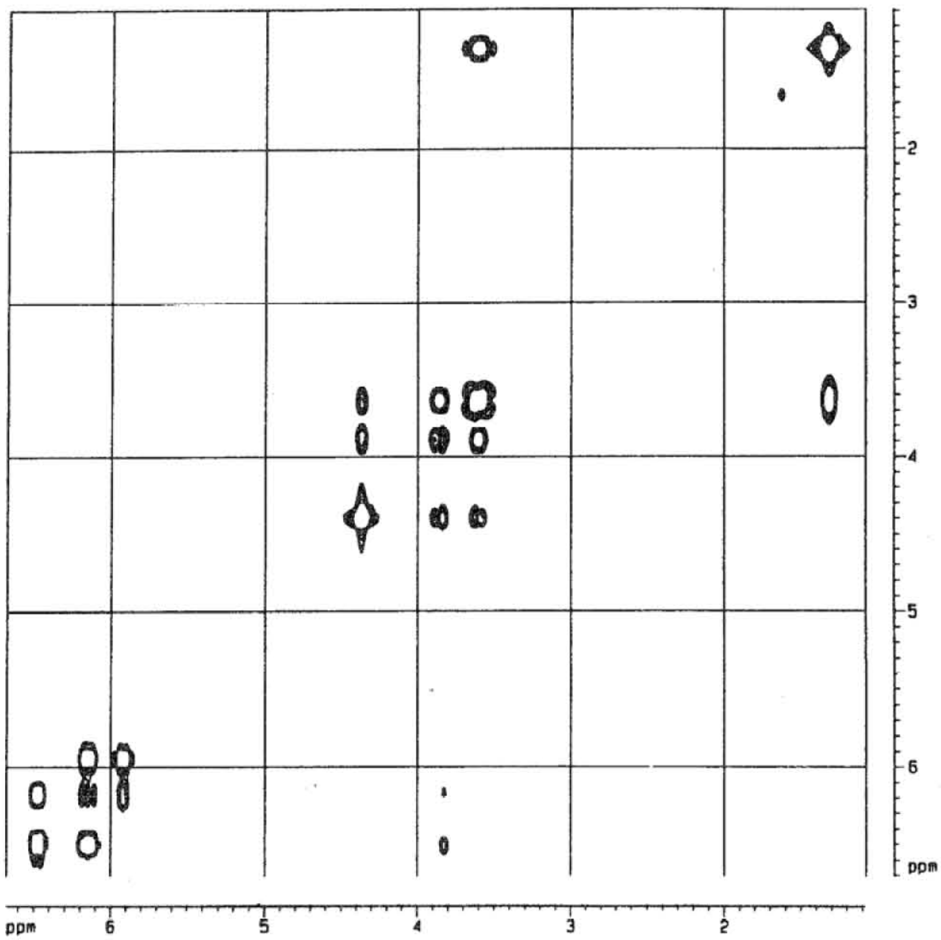


Figure 2. Proton-proton nuclear correlated spectrum of FOSA.

$$\frac{n}{m+n}=\frac{X-1}{X+5} \tag{2}$$

and the results are summarized in Table 1.

N-isopropylacrylamide ($CDCl_3$, ppm)

1.196 (d, $-CH_3$, 6H), 4.169 (m, -CH-, 1H), 5.804 (bs, -NH-, 1H), 5.618, 6.279 (d, d, CH_2=, 2H), 6.098 (q, =CH-, 1H)

TABLE 1. Characterization Results for the Copolymers of NIPAM and FOSA

Polymer ID	FOSA(mol%)		M_n[b]	M_w[b]	M_n/M_w[b]	T_g (°C)[c]	Water content (%)
	added	found[a]					
HIPAM	0	-	56,419	94,915	1.68	145.1	N/A
CP001	0.5	0.49	23,258	38,734	1.67	144.1	N/A
CP002	2.0	1.89	17,334	31,277	1.80	138.9	63
CP003	5.0	4.88	19,801	31,292	1.58	135.5	23
CP004	10.0	9.21	21,439	37.564	1.75	124.0	12
CP005	20.0	19.8	29,009	42.998	1.48	108.1	-
CP006	30.0	-	-	-	-	67.9	-
CP007	50.0	-	-	-	-	56.5	-
CP008	80.0	-	-	-	-	49.4	-
Poly(FOSA)	100.0	-	-	-	-	48.7	-

[a] Calculated from the integration values in ^{1}H-NMR spectrum-

[b] Determined by GPC in THF using polystyrene standards at 35 °C

[c] Determined by DSC

FOSA ($CDCl_3$, ppm)

1.303 (t, $-CH_3$, 3H), 3.557 – 3.615 (m, $-CH_2-N-CH_2-$, 3H), 3.836-3.865 (m, $-CH_2-C\underline{H}_2-N-$, 1H), 4.385 (t, $O-CH_2-$, 2H), 5.917, 6.480 (d,d, $CH_2=$, 2H), 6.144 (q, $=CH-$, 1H)

Poly (N-isopropylacrylamide-co-FOSA) ($CDCl_3$, ppm)

1.287-2.177 (bm,$-CH_3$,$-CH_2-$), 3.473- 4.237 (bm, $-CH_2-N-CH_2-$, $O-CH_2-$, $-CH-$),6.252 (bs, -NH-, 1H)

Water Content

Determinations of equilibrium water sorption and water loss rate were performed on films prepared by compression molding using a Carver Laboratory Press at 180-205°C. Films were saturated with phosphate buffered saline (Fisher, pH 7.4, 0.9 wt% NaCl) for 2 days at room temperature. The equilibrium water sorption, %W, was calculated using the following equation:

$$\%W = \frac{W - W_o}{W} \times 10 \tag{3}$$

where W and W_o are the mass of the saturated and dry polymer film, respectively.

Desorption Kinetics

Films saturated with the buffer solution were pinned to a cork with two centimeters between the film and the cork. This allowed the film to be quasi-freestanding and to have airflow on all sides. The pins were placed so as to minimize gross deformation or folding during the water loss measurements. The film was placed on a bench top at ambient conditions and the mass was measured at regular intervals.

RESULTS AND DISCUSSION

Copolymers of Acrylamide and FOSA

Polyacrylamides containing FOSA (0.01-0.5 mol%) were synthesized by free radical polymerization in deionized water at 50°C using either potassium persulfate or the redox couple of ammonium persulfate/sodium metabisulfite as an initiator. The molecular weights were in the range of 10^5 to 10^6 g/mol as determined by dilute solution viscosity [20]. The high molecular weight polymers formed clear gels in water. The glass transition temperatures of the homopolymer and copolymers as measured by DSC were observed to lie in the range of 185-190°C. At temperatures above 190°C, the polymer discolored to yellow. As reported in the literature [22], polyacrylamide degrades at high temperature (200-205°C) to provide cyclic imide or nitrile groups. Figure 3 shows the thermal degradation mechanism of polyacrylamide and poly (N-alkyl substituted-acrylamides). This was confirmed by the appearance of a peak at 1710 cm^{-1} that corresponds to cyclic imide groups in the IR spectrum of a polyacrylamide dried at 190°C (Figure 4).

Copolymers of N,N-dimethylacrylamide and FOSA

Copolymers of N,N-dimethylacrylamides and FOSA were synthesized in water using ammonium persulfate/sodium metabisulfite or potassium persulfate as an initiator, and in 1,4-dioxane using AIBN. The latter method is preferred, as it does not require a surfactant. Typically, the copolymers synthesized in dioxane had lower molecular weights as compared to those synthesized in water because dioxane acts as a chain transfer agent [22]. Copolymers with up to 5 mol% FOSA were synthesized. The T_gs of these copolymers were 110–120°C. Transparent films were obtained by compression molding at 150-160°C. All of the copolymers are soluble in water and common organic solvents such as THF, acetone and dioxane.

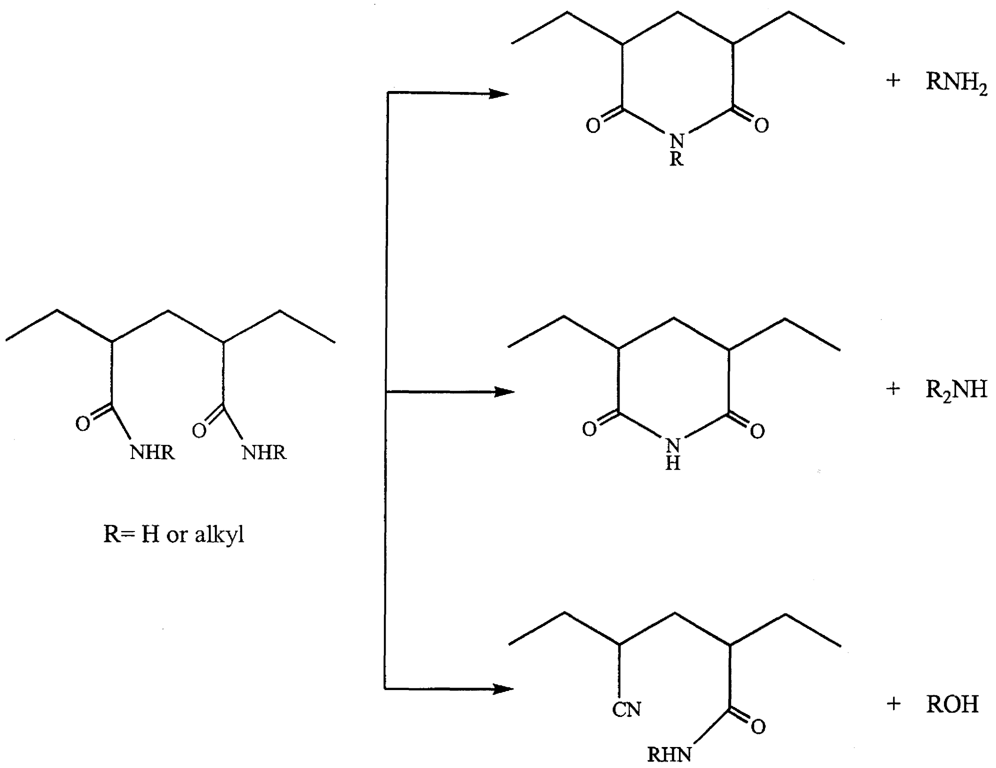


Figure 3. Degradation mechanism of polyacrylamide or poly(N-alkyl-substituted acrylamide).

Copolymers of N-isopropylacrylamide and FOSA

Copolymers of N-isopropylacrylamide and FOSA were synthesized in 1,4-dioxane using AIBN as an initiator. None of these copolymers were soluble in water. Copolymers with up to 20 mol% of FOSA were soluble in THF, acetone and chloroform. Copolymer with above 20 mol% of FOSA precipitated from p-dioxane as the polymerization progressed and the resulting polymers were not soluble in common organic solvents such as THF, acetone, chloroform and carbon tetrachloride. The content of FOSA incorporated in the chloroform soluble polymers was calculated from ^{1}H-NMR spectra and the results are summarized in Table 1. As shown in Table 1, the FOSA was incorporated quantitatively in the copolymers. The T_g of these copolymers determined by DSC was in the range of 49-145°C and decreased with content of FOSA in the copolymer. Figure 5 shows the glass transition temperature plot for the copolymers and the

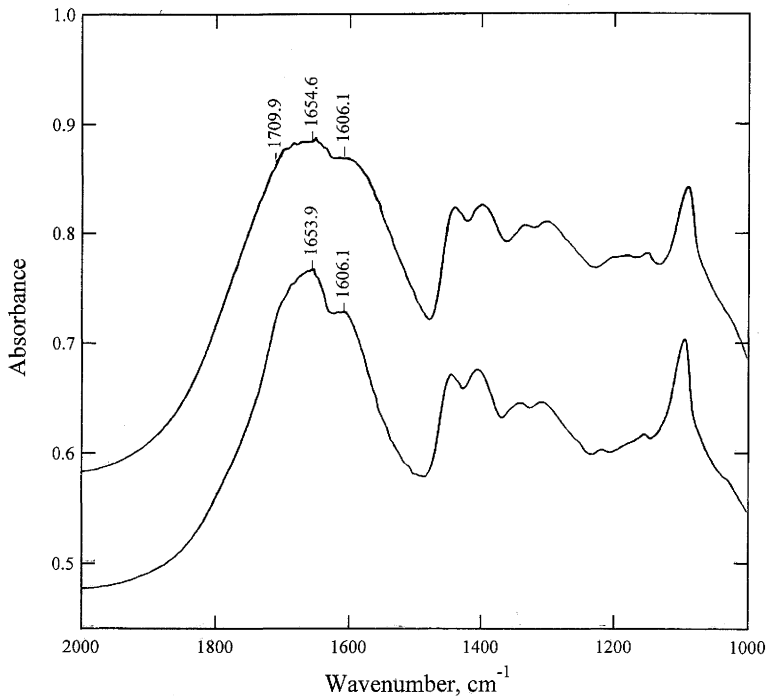


Figure 4. FTIR spectra of polyacrylamide dried under vacuum at 190°C for 15 minutes (lower) and 24 hours (upper).

values predicted from the Fox equation, $1/T_g = w_1/T_{g1} + w_2/T_{g2}$, where w_1 and w_2 are the mass fractions of NIPAM and FOSA in the copolymer and T_{g1} and T_{g2} are the glass transition temperatures of poly(NIPAM) and poly(FOSA), respectively. The T_gs of the copolymers showed positive deviation from the Fox equation. This can be explained if the perfluoroalkyl groups form a separate microphase due to hydrophobic interactions. In that case, the FOSA concentration in the continuous phase is less than the overall composition of the copolymer, which would produce a higher than expected T_g for the continuous phase. A second T_g for a perfluoroalkyl-rich microphase was not observed by DSC, but that is probably due to the relatively low volume fraction and/or the size of the microphase which would tend to significantly broaden the transition leading to low signal to noise in the thermogram. An alternative explanation for the higher than expected T_g is that the it is due to the crosslinking of the polymer by the hydrophobic interactions, though that explanation is also based on microphase separation of the polymer.

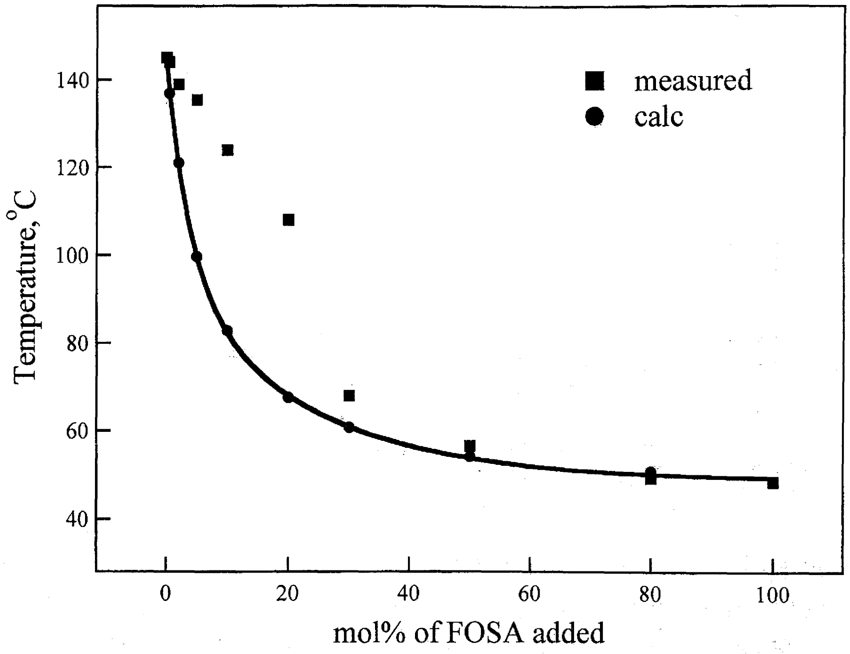


Figure 5. Glass transition temperature plot for the copolymers of NIPAM with various content of FOSA.

DSC thermograms of the poly(FOSA) showed an endothermic peak that appeared at 90°C (Figure 6), which arises from melting of the crystalline fluorocarbon side chains. Crystallization of fluoralkyl side-chains have been previously reported in the literature [23]. For example, Pittman synthesized polyfluoroalkyl-acrylates containing the alkyl groups HCF_2 $(CF_2)_nCH_2$- (where n=1,3,5,7,9) and found that side-chains crystallized when n = 7 or 9.

Equilibrium water sorption of our copolymers was measured in various phosphate buffer solutions and the results are shown in Figure 7. The water content decreased with increasing FOSA content, and the water content of the polymers was also affected by pH and ionic strength. The water content increased with decreasing pH due to the basicity of the amide group, i.e., the amide group is protonated and requires greater hydration than the conjugate base. Gel hydration decreased with increasing salt concentration in the buffer which "salts out" the fluorinated side group. Water content of the copolymers at pH 7.4, in phosphate buffer solution containing 0.9 wt% of NaCl, was in the range 12– 63%. Figure 8 shows the water desorption kinetics of the copolymers, which was measured after saturating the polymers with the buffer solution. With increasing FOSA content in the copolymers the water loss rate decreased.

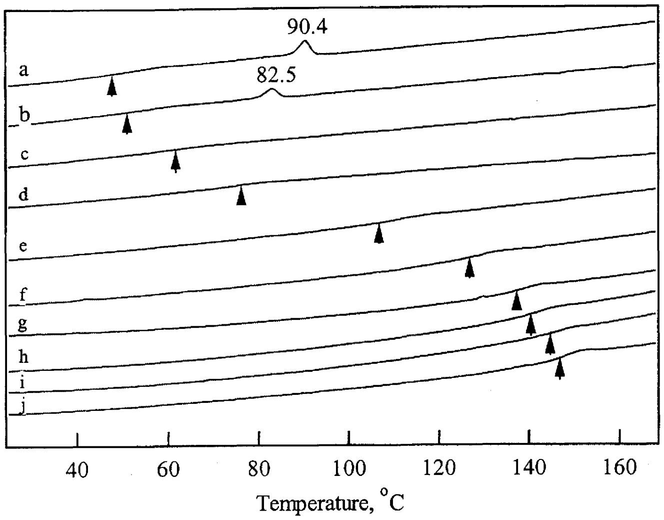


Figure 6. Differential scanning calorimetry thermogram for the copolymer of NIPAM with various content of FOSA (a; poly (FOSA), b; CP008, c; CP007, d; CP006, e; CP005, f; CP004, g; CP003, h; CP002, i; CP001, j; Poly(N-isopropylacrylamide)).

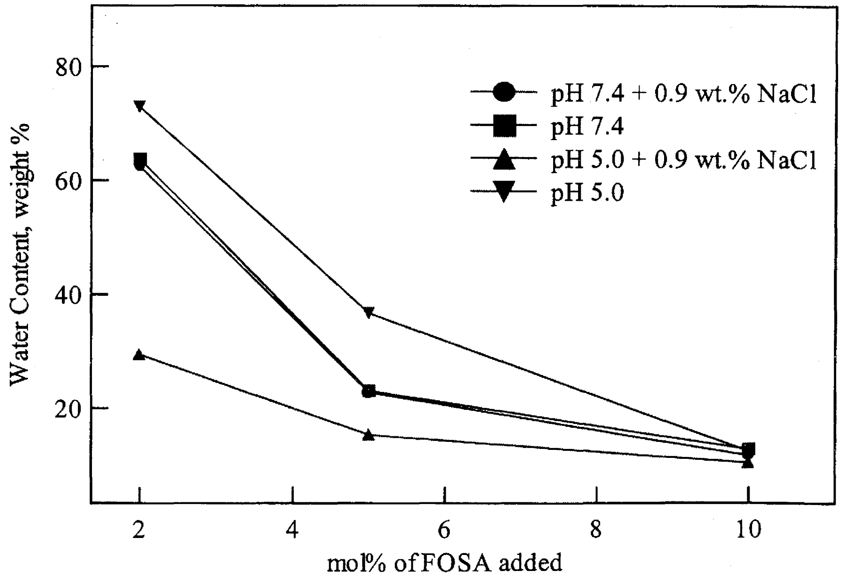


Figure 7. Water content of the copolymers of NIPAM with various content of FOSA.

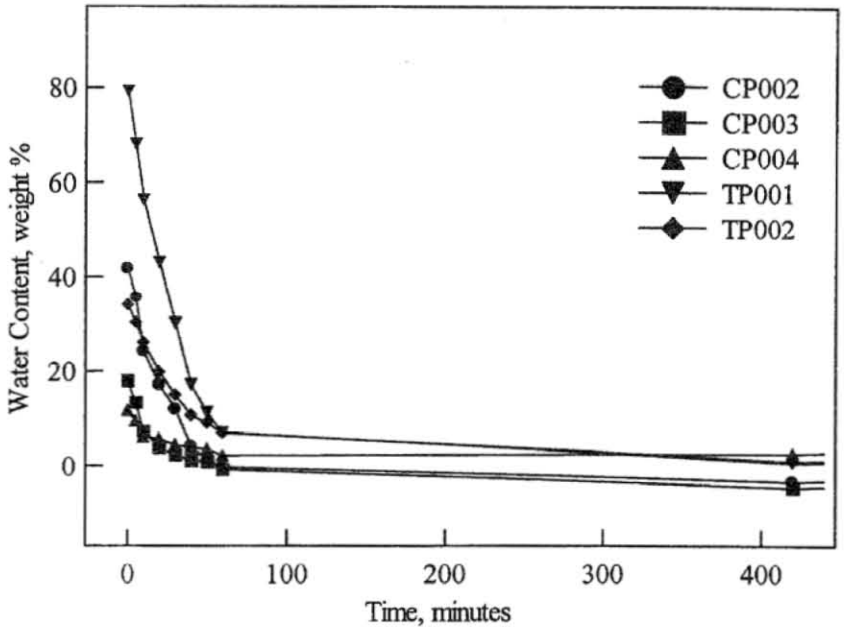


Figure 8. Water loss rate of the copolymers of NIPAM and FOSA and the terpolymers of NIPAM, DMAM, and FOSA.

Terpolymers Based on N-Isopropylacrylamide and FOSA

Two problems were identified in the synthesis and properties of copolymers of acrylamide and FOSA. First, it was difficult to synthesize copolymers with high FOSA content because of the extremely different solubility of the two monomers, and second, the high T_g of the AM/FOSA copolymers required high processing temperatures, which led to degradation of the polymers. For copolymers containing N,N-dimethylacrylamide and FOSA, it was necessary to use a large amount of FOSA in order to prepare a copolymer that was insoluble in water. However, the T_g of the resulting polymer was relatively low, which is a deficiency for any biomedical application that requires steam sterilization without significant deformation of the polymer. Copolymers of N-isopropylacrylamide with FOSA sorb less water than corresponding copolymers prepared from the other acrylamides. A combination of three types of acrylamide monomers with FOSA may provide a balance of the properties desired in a hydrogel – that is, melt processability without degradation, a sufficiently high T_g so that steam sterilization is feasible, and relatively high water sorption and oxygen permeability.

Table 2 summarizes the properties of the various terpolymers synthesized in this study. Adding AM or DMAM to a polymer based on NIPAM and

TABLE 2. Characterization Results for Terpolymers

Polymer composition	T_g (°C)	Water content (%)
NIPAM/AM/FOSA (80/20/10)	143.3	39
NIPAM/AM/FOSA (70/30/10)	155.2	56
NIPAM/MAM/FOSA (80/20/5)	132.7	64
NIPAM/MAM/FOSA (80/20/10)	128.4	56
NIPAM/MAM/FOSA (20/80/5)	108.5	80

FOSA increased the equilibrium water sorption of the polymers, and the T_g changed in accordance with the T_g of the homopolymers based on the different acrylamides. A comparison of the water contents of the NIPAM/AM/FOSA (80/20/10) and NIPAM/DMAM/FOSA (80/20/10) terpolymers indicates that incorporation of DMAM is more efficient for increasing water content.

CONCLUSION

FOSA can be quantitatively incorporated into copolymers or terpolymers of AM, DMAM and NIPAM by free radical polymerization in deionized water using ammonium persulfate/sodium metabisulfite or potassium persulfate as an initiator or in p-dioxane using AIBN. The molecular weight of copolymers of DMAM and FOSA polymerized in water were higher than when the polymerization was run in p-dioxane, because of chain transfer in p-dioxane. The T_g of the polymers decreased with increasing incorporation of FOSA, though the decrease was less than expected for a random copolymer. The higher than expected T_g is believed to be due to microphase separation of the perfluoroalkyl chains due to hydrophobic interactions, though confirmation of that hypothesis requires additional characterization of the microstructure. Small angle neutron scattering studies of these materials is currently underway and will be reported in another report.

The equilibrium water sorption of the copolymers and terpolymers was affected by the chemical composition of the polymers, pH and salt concentration. The water content increased for increasing AM or DMAM or decreasing FOSA. Water content also decreased at high pH or high salt concentration. AM and DMAM structure are capable of more hydration compared to NIPAM due to the less hydrophobic character on the nitrogen atom. The basic nature of the amide or N-alkyl substituted group results in higher water sorption in acidic solution. Increasing salt concentration is unfavorable to the fluoroalky side-chains due to the increased ionic strength of the solution and results in lower water sorption. Incorporation of AM or DMAM into the copolymer structure of NIPAM and FOSA increased the water absorption.

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