Water-Soluble Copolymers. 39. Synthesis and Solution Properties of Associative Acrylamido Copolymers with Pyrenesulfonamide Fluorescence Labels

Stephen A. Ezzell† and Charles L. McCormick*

Department of Polymer Science, University of Southern Mississippi, Hattiesburg, Mississippi 39406-0076

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ABSTRACT: Pyrenesulfonamide-labeled model associative polymers have been prepared via copolymerization of acrylamide with 0.5 mol % *N*-[(1-pyrenylsulfonamido)ethyl]acrylamide. Synthesis of this monomer and details of copolymerization with acrylamide via surfactant and solution copolymerization techniques are described. The microheterogeneous surfactant technique yields a copolymer which exhibits intermolecular associative behavior in aqueous media as demonstrated by rheological and steady-state fluorescence studies. Conversely, classical light scattering studies indicate the compact nature of the copolymer prepared by the homogeneous solution technique. Intramolecular hydrophobic associations, indicated by a low second virial coefficient and a small hydrodynamic volume, dominate rheological behavior.

Introduction

Microheterogeneous phase separation in hydrophobically-modified water-soluble copolymers can be achieved by appropriate structural tailoring, yielding systems with unique rheological characteristics. Among such materials are rheology modifiers known as "associative thickeners" which demonstrate significant increases in viscosity above the critical overlap concentration, C^*.[1] For example, the copolymer of acrylamide containing 0.75 mol % *n*-decylacrylamide prepared under suitable conditions[2] exhibits a 16-fold increase in apparent viscosity (Figure 1) as the copolymer concentration increases from 0.05 to 0.20 g/dL. Homopolyacrylamide, by comparison, prepared under the same reaction conditions shows only a gradual increase in viscosity with concentration.

Although associative thickeners based on hydrophobic modification of a number of polymer types including polyacrylamides, cellulosics, polyethers, etc., have been reported, the mechanisms responsible for their rheological behavior have yet to be fully elucidated. The low concentration of "hydrophobes" and the nature of the interactions preclude study by traditional spectroscopic techniques such as IR or NMR due to insufficient resolution. Photophysical techniques with appropriately labeled copolymers, however, have been used by our group and others[3,4] to study such systems.

In this paper we report synthesis and solution properties of copolymers of acrylamide with *N*-[(1-pyrenylsulfonamido)ethyl]acrylamide. The pyrenesulfonamide comonomer serves in two capacities in this study; it provides a fluorescence label for photophysical measurements, and it serves as the hydrophobic monomer. Under selected reaction conditions discussed herein associative properties are observed. The subsequent paper in this series details photophysical evidence for the associations.

Experimental Section

Materials. Acrylamide (AM) was recrystallized from acetone three times and vacuum-dried at room temperature prior to use. Pyrene was purified by flash chromatography[5] (silica gel packing; CH_2Cl_2 eluent). *N*,*N*-Dimethylformamide (DMF) was allowed to stand overnight over 4-Å molecular sieves and was then distilled at reduced pressure. H_2O was deionized and had a conductance of less than 1×10^{-7} mho/cm. Other starting materials were purchased commerically and used as received. Solvents were reagent-grade, unless otherwise noted.

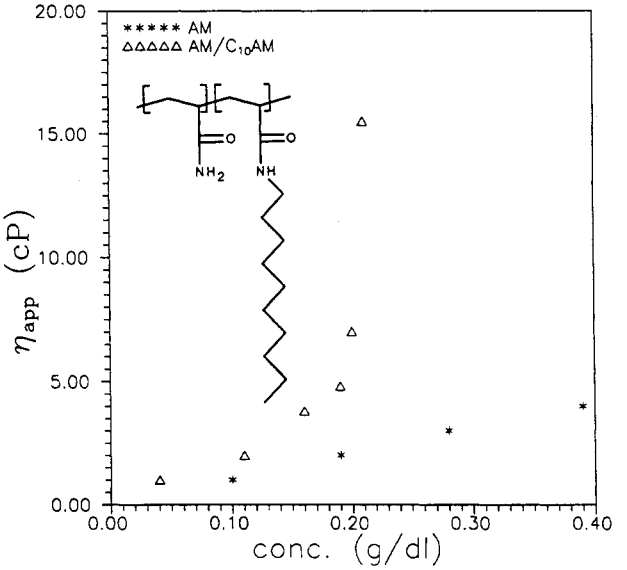

Figure 1. Illustration of associative behavior of polyacrylamide modified with 0.75 mol % *n*-decylacrylamide via surfactant polymerization.

Monomer and Model Compound Synthesis. *N*-[(1-Pyrenylsulfonamido)ethyl]acrylamide (5) and Its Precursors (Schemes I and II). Sodium 1-Pyrenesulfonate (7). A literature method[6] was modified for the preparation of sodium 1-pyrenesulfonate. Pyrene (6; 47.60 g, 0.235 mol) was dissolved in 300 mL of CH_2Cl_2. Chlorosulfonic acid (16 mL, 0.24 mol) dissolved in 50 mL of CH_2Cl_2 was added dropwise to the pyrene solution with brisk stirring, at 0 °C, under a steady nitrogen stream. The reaction progress was followed by TLC (CH_3OH eluent); 1-pyrenesulfonic acid appears at $R_f = 0$ while pyrene has a higher R_f value. The resulting dark-green solution was poured (with extreme caution) into 500 cm^3 of ice and stirred, allowing the CH_2Cl_2 to evaporate over a 2-day period. This solution was filtered twice through Celite to remove particulates; each time the Celite pads were washed with 1×150 mL of H_2O. NaOH (10.0 g, 0.25 mol) was added as an aqueous solution. Aqueous NaCl (500 cm^3) was also added. The yellow sodium salt 7 was precipitated via slow solvent evaporation, filtered, and vacuum-dried at 65 °C. Elemental analysis indicated that this product was a dihydrate and contained residual NaOH. This salt was used successfully in the subsequent reaction without further

† Present address: 3M Science Research Laboratory, St. Paul, MN 55144-1000.

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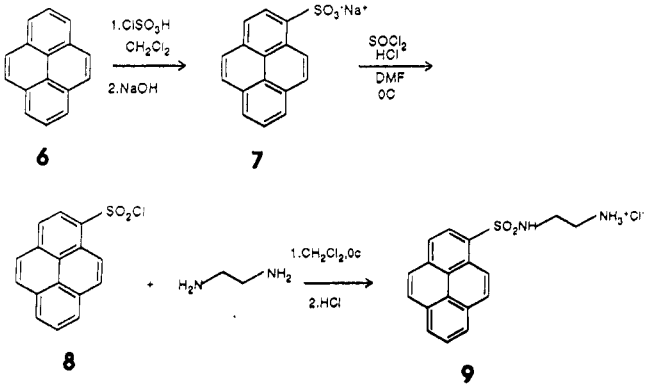
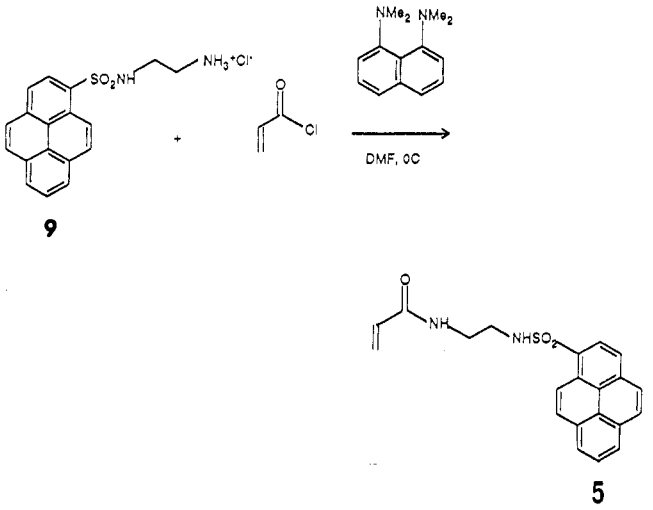
Scheme I
Synthesis of *N*-(1-Pyrenylsulfonyl)ethylenediamine Hydrochloride (9)



Scheme II
Synthesis of *N*-[(1-Pyrenylsulfonamido)ethyl]acrylamide (5)



purification. Yield: 51.0 g (71%). Anal. Calcd for $C_{16}H_{13}O_5SNa$: C, 56.46; H, 3.85; S, 9.42; Na, 6.76. Found: C, 55.64; H, 3.15; S, 9.33; Na, 8.71. IR: 3100–3700 (OH stretch due to H_2O); 3045 (aromatic CH stretch); 1194 and 1060 (asymmetric and symmetric S=O stretch) cm^{-1}. ^{13}C NMR (DMSO-d_6): δ 123.72, 124.82, 125.34, 126.26, 126.74, 126.80, 126.88, 127.29, 127.69, 130.11, 130.71, 131.29, 141.81 (all aromatic resonances).

1-Pyrenesulfonyl Chloride (8). A hydrochloric acid solution in diethyl ether (30 mL, 3×10^{-2} mol) was added to a slurry of **7** (9.1 g, 3×10^{-1} mol) in DMF (200 mL) to generate the sulfonic acid. Thionyl chloride (22 mL, 0.18 mol) was then added dropwise. TLC with 3:1 CH_2Cl_2/acetone eluent showed the disappearance of the starting material ($R_f = 0$) and the appearance of **8** ($R_f = 0.6$). Stirring was continued for 3 h, and then the solution was poured into 400 cm^3 of ice. The orange-yellow precipitate was filtered and washed with 500 mL of H_2O. This material was air-dried overnight on the filter and then vacuum-dried for 18 h at 100 °C. Yield: 7.7 g (85%). Mp: 172 °C. Anal. Calcd for $C_{16}H_9SO_2Cl$: C, 63.89; H, 3.00; S, 10.67; Cl, 11.78. Found: C, 63.85; H, 3.09; S, 10.61; Cl, 11.59. IR: 3107, 3145 (aromatic CH stretch); 1590 (SCl stretch); 1361, 1173 (asymmetric and symmetric S=O) cm^{-1}. ^{13}C NMR (DMSO-d_6): δ 123.79, 123.90, 124.34, 124.93, 125.52, 126.40, 126.73, 126.99, 127.36, 127.91, 130.19, 130.78, 131.52, 141.55 (all aromatic resonances).

***N*-(1-Pyrenylsulfonyl)ethylenediamine Hydrochloride (9).** A modification of a literature procedure for the reaction of acid chlorides with symmetrical diamines,[7] via a high-dilution technique, was used for the synthesis of **9**. Ethylenediamine (10.0 mL, 0.15 mol) was added to 1 L of CH_2Cl_2 and stirred rapidly at 0 °C under a nitrogen blanket. **8** (3.0 g, 1.0×10^{-2} mol) was dissolved in 1 L of CH_2Cl_2 and added dropwise to the stirred diamine solution. After addition was completed (about 2 h), the CH_2Cl_2 layer was extracted with 2 × 3 L of H_2O and 1 × 2 L of 5% NaCl. The CH_2Cl_2 layer was slowly filtered through a pad of $MgSO_4$ and then treated with 15 mL of 1.0 N HCl dissolved in diethyl ether. The resulting fine pale-yellow precipitate was vacuum-dried at room temperature. TLC of this material (3:1 CH_2Cl_2/acetone eluent) exhibited only one component at R_f = 0. HPLC purity was determined to be >99.9%. Anal. Calcd for $C_{18}H_{17}SO_2N_2Cl$: C, 59.92; H, 4.72; N, 7.77; S, 8.89; Cl, 9.83. Found: C, 59.92; H, 4.59; N, 7.57; S, 8.64; Cl, 9.81. IR: 2800–3600 (NH_3-Cl stretch); 3318 ($HNSO_2$ stretch); 3028 (aromatic CH stretch); 2912 (aliphatic CH stretch); 1325, 1159 (asymmetric and symmetric S=O); 1085 (SN stretch) cm^{-1}. ^{13}C NMR (DMSO-d_6): δ 38.61, 39.87 (ethylene resonances); 123.06, 123.28, 124.15, 126.77, 126.96, 129.63, 129.96, 130.40, 131.60, 134.05 (aromatic resonances).

The free amine of **9** was prepared via addition of a concentrated aqueous solution of a molar equivalent of NaOH to **9** dissolved in the minimum amount of DMF. After brief stirring, the solution was poured into H_2O, which precipitated **9** in the free amine form, designated here as **10**. This yellow solid was washed with H_2O and then vacuum-dried at room temperature. A downfield shift of the ethylene resonances was observed in the ^{13}C NMR spectrum, confirming the formation of the free amine.[8] ^{13}C NMR (DMSO-d_6): δ 42.62, 46.03 (ethylene resonances); 123.20, 123.46, 124.17, 126.77, 126.96, 129.70, 129.87, 130.53, 131.60, 134.05 (aromatic resonances).

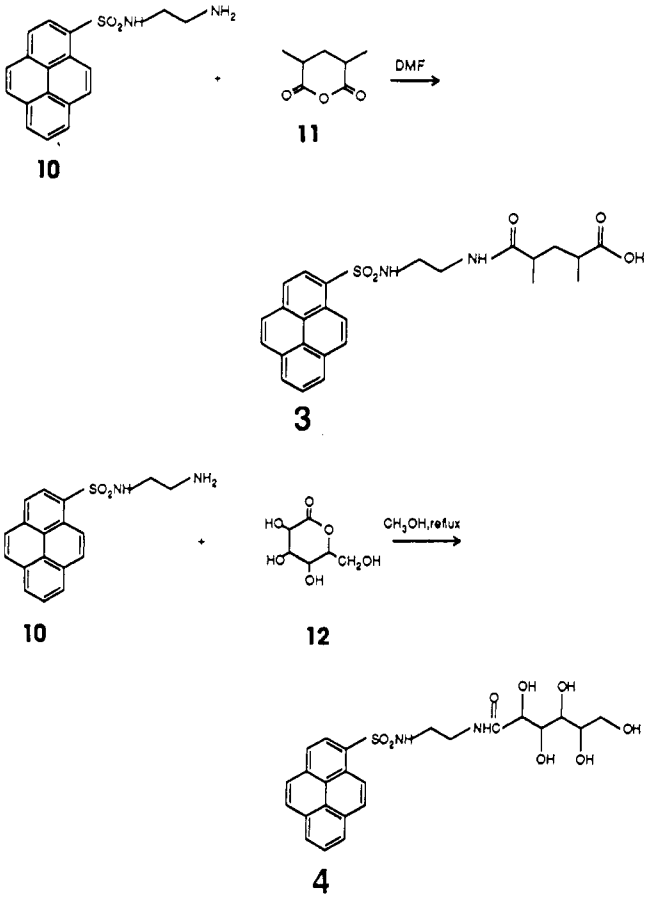
***N*-[(1-Pyrenylsulfonamido)ethyl]acrylamide (5).** The synthesis of **5** is depicted in Scheme II. The amine hydrochloride salt **9** (1.0 g, 2.8×10^{-3} mol) and 1,8-bis(dimethylamino)naphthalene (1.19 g, 5.6×10^{-3} mol) were stirred with 7 mL of DMF under a nitrogen stream for 15 min at 0 °C. Acryloyl chloride (2.2 mL, 2.8×10^{-2} mol) in 7 mL of DMF was then added dropwise to the amine solution. TLC (acetone eluent) was used to follow the depletion of the starting amine (R_f = 0) and the generation of the product (R_f = 0.70). After the addition was complete, the reaction mixture was poured into 150 cm^3 of ice. The product precipitated overnight as a yellow solid, which was subsequently filtered and vacuum-dried at room temperature. Yield: 0.90 g (88%). Product recrystallization was performed by dissolution of 0.9 g of **5** in 300 mL of boiling CH_2Cl_2, decolorization with Norit RB 1 0.6 charcoal pellets, and filtration through a Celite pad. Pale-green crystals formed, which were recovered in 69% yield. Purity of this material was determined to be >99.9% via HPLC. Anal. Calcd for $C_{21}H_{18}SO_3N_2$: C, 66.67; H, 4.76; S, 8.47; N, 7.41. Found: C, 66.83; H, 5.00; S, 8.48; N, 7.49. IR: 3050–3600 (NH stretch); 3370, 3289 ($HNSO_2$ stretch); 3084 (aromatic CH stretch); 2938, 2864 (aliphatic CH stretch); 1659, 1540 (amide I and II bands); 1312, 1159 (S=O asymmetric and symmetric stretch) cm^{-1}. ^{13}C NMR (DMSO-d_6): δ 38.77, 41.95 (ethylene carbons); 127.14, 129.58 (vinylic carbons); 123.09, 123.32, 124.07, 124.27, 125.02, 126.63, 126.79, 126.86, 129.44, 129.73, 130.36, 131.44, 132.23, 133.88 (aromatic carbons); 164.84 (acrylamido ketone carbon).

Pyrenesulfonamide Model Compounds. 2,4-Dimethyl-*N*-[(1-pyrenylsulfonamido)ethyl]glutaramide (3). Synthesis of **3** required first the preparation of 2,4-dimethylglutaric anhydride, followed by amination with **10** (Scheme III).

2,4-Dimethylglutaric Anhydride (11). 2,4-Dimethylglutaric acid (2.0 g) was added to 5 mL of acetic anhydride. Vacuum distillation of this solution at 90 °C gave acetic anhydride as the first fraction. The anhydride product **11** then distilled over as a clear liquid which cooled to form a hygroscopic, hard white solid. Although an IR of this product showed the presence of some diacid (OH stretch 2500–3500 cm^{-1}; C=O stretch due to diacid at 1698 cm^{-1}), this material was successfully used in subsequent reactions without purification. Yield: 1.1 g (62%). IR: 3500–2500 (OH stretch due to acid), 1794, 1752 (asymmetrical and symmetrical anhydride ketone stretching modes); 1698, 1459 (acid ketone stretching modes) cm^{-1}.

Synthesis of 3 (Scheme III). The amine sulfonamide **10** (0.75 g, 2.31×10^{-3} mol) was dissolved in 6 mL of DMF. This solution was added dropwise to **11** (0.41 g, 2.54×10^{-3} mol) dissolved in 2 mL of DMF under N_2 at 0 °C. The reactant mixture was stirred for 5 h and then poured into 50 mL of saturated NaCl solution, which was acidified (HCl). A yellow oil immediately formed. The H_2O was decanted and the product dissolved in 30 mL of CH_2Cl_2. Extraction of this solution with 50 mL of H_2O

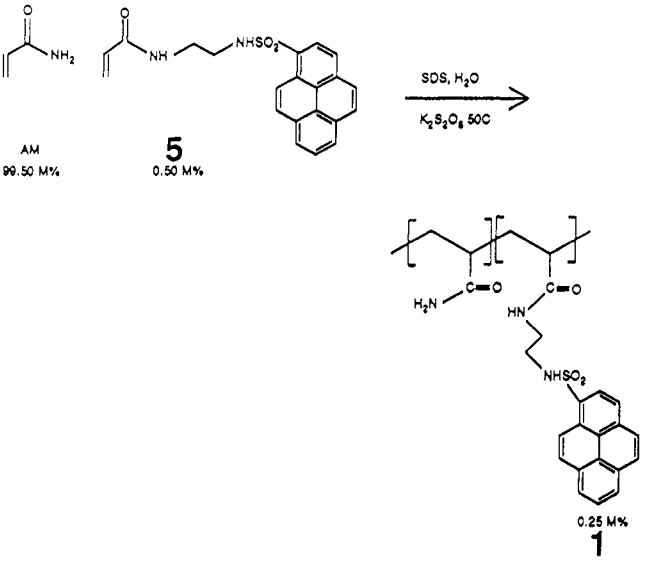
Scheme III
Synthesis of Pyrene-Containing Model Compounds 3 and 4



precipitated the product as a pale-green solid. TLC (CH_3OH eluent) gave a $R_f = 0.82$ for the product; traces of impurities near $R_f = 0$ were also present. Purification of **3** was performed via dissolution of 0.61 g in DMF, followed by flash chromatography on 250 mL of silica gel, with CH_3OH as the eluent. This procedure was tedious since the product was very slow to elute. Vacuum solvent removal from the pure fractions gave about a 0.2-g (33%) yield of a pale-yellow-green product. The HPLC purity of this material was determined to be >99.9%. Anal. Calcd: C, 64.35; H, 5.63; N, 6.01; S, 6.87. Found: C, 64.20; H, 5.69; N, 5.94; S, 6.73. IR: 3500–2500 (acid OH stretch); 3378, 3284 (*HN*SO_2 stretching); 1737 (asymmetric C=O stretch of the acid residue); 1684 (amide I); 1549 (amide II); 1302, 1167 (asymmetric and symmetric S=O stretch). ^{13}C NMR (DMSO-d_6): 20.37, 21.13, 21.56 (aliphatic resonances of the glutaric residue); 42.84, 45.30 (aliphatic resonances of the ethylenediamine residue); 126.94, 127.92, 130.63, 133.23, 135.99, 137.62 (aromatic resonances); 179.01, 180.80 (ketone resonances of the glutaric residue).

***N*-[(1-Pyrenylsulfonamido)ethyl]gluconamide Heptahydrate (4).** Synthesis of **4** is depicted in Scheme III. The free amine of **10** (0.44 g, 1.36×10^{-3} mol) was added to δ-gluconolactone (**12**; 0.30 g, 1.68×10^{-3} mol) in 2 mL of CH_3OH. A clear green solution was obtained upon heating; a reflux was maintained for 18 h. Compound **4** precipitated from solution as a yellow-green solid. After filtration and washing with CH_3OH, **4** was vacuum-dried overnight at room temperature. The HPLC purity of this compound was determined to be 99.9%. Elemental analysis determined **4** to be a heptahydrate. Yield: 0.31 g (45%). Mp: 171–173 °C. Anal. Calcd (heptahydrate): C, 46.67; H, 4.90; N, 4.53; S, 5.19. Found: C, 46.16; H, 4.55; N, 4.24; S, 5.31. IR: 3600–3000 (OH stretch); 3379 (*HN*SO_2 stretch); 1657 (amide I); 1533 (amide II); 1419 (CN stretch); 1307, 1161 (asymmetric and symmetric S=O) cm^{-1}. ^{13}C NMR (DMSO-d_6): δ 38.24, 41.20 (ethylene resonances); 63.27 (1′*C*OH); 69.89, 71.44, 72.25, 73.45 (2′*C*OH); 123.17, 123.35, 124.22, 126.65, 126.81, 127.09, 129.51, 129.68, 129.62, 130.51, 133.93 (aromatic resonances); 172.77 (amide ketone).

Scheme IV
Synthesis of Copolymer 1 via the Surfactant Polymerization Technique



Synthesis of Pyrenesulfonamide-Labeled Polymers. Poly[*N*-[(1-pyrenylsulfonamido)ethyl]acrylamide-*co*-acrylamide] 1. Surfactant Polymerization Technique. The general method of Turner et al. was employed (Scheme IV).[9] Monomer feed ratio in this copolymerization was 99.50 mol % AM to 0.50 mol % **5**. The polymerization was performed by adding 7.38 g (0.105 mol) of AM, 7.92 g (2.74×10^{-2} mol) of sodium dodecyl sulfate, 0.20 g (5.29×10^{-4} mol) of **5**, and 235 g of H_2O to a 500-mL flask equipped with a mechanical stirrer, nitrogen inlet, condenser, bubbler, and heating bath. This mixture was heated to 50 °C under a nitrogen purge. The stirring rate was maintained at approximately 60 rpm. All of the monomer **5** had dissolved after 15 min; polymerization was then initiated via syringe addition of 9.25×10^{-6} mol of $K_2S_2O_8$ as a deaerated solution in 2 mL of H_2O. Polymerization was allowed to continue at 50 °C for 12 h, after which time the polymer was recovered via precipitation into acetone. Purification was accomplished by redissolving the polymer in H_2O and dialyzing against H_2O using 12 000–14 000 molecular weight cutoff dialysis tubing. The polymer was recovered by freeze-drying. Conversion was 22%.

Poly[*N*-[(1-pyrenylsulfonamido)ethyl]acrylamide-*co*-acrylamide] 2. Solution Polymerization Technique. Monomer feed ratios, quantities, and equipment in this preparation (Scheme V) were the same as in the previous procedure. Comonomers were dissolved in a mixture of 130 mL of DMF and 100 mL of H_2O. Three freeze–pump–thaw cycles were performed to remove residual oxygen. The initiation procedure was as described for the surfactant polymerization. In this case, polymer precipitated from the solution as the polymerization continued (12 h). Pouring the suspension into acetone allowed recovery of the polymer product. Purification procedures were as described for the surfactant polymerization. Conversion was 21%. UV analysis determined **2** to contain 0.35 mol % **5** (70% incorporation).

Characterization Methods. Pyrenesulfonamide Derivatives. ^{13}C NMR spectra were recorded with a Bruker AC-300 instrument. Most samples were dissolved in DMSO-d_6; chemical shift assignments are relative to the central DMSO peak (^{13}C, 39.50 ppm). UV–vis spectra were recorded with a Perkin-Elmer Lambda 6 spectrophotometer. A Mattson Model 2020 FTIR was used to obtain infrared spectra.

Sample purities were determined in most cases by both TLC and HPLC. TLC was performed on Merck Kieselgel 60 silica gel plates. Developed plates were generally viewed under 325-nm light for pyrene derivatives. HPLC was performed on a Hewlett-Packard Model 1050 system equipped with a photodiode-array detector. A Waters μ-Bondapak C18 column was employed with methanol as the mobile phase. The sample effluent was typically monitored at 220 and 350 nm. Alternately, multiple wavelengths

Scheme V
Synthesis of Copolymer 2 in DMF/H_2O

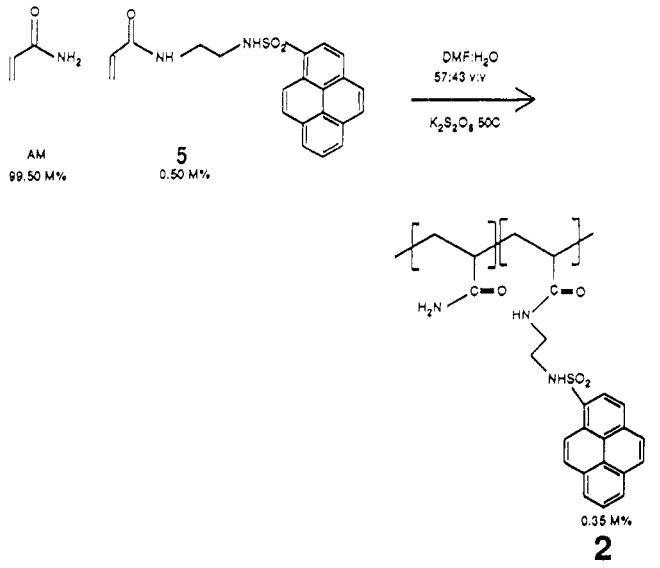


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Table I
Stock Solutions of Labeled Polymers

polymer	polym conc, mg/dL	fluorophore conc, mol/L
1	218	7.13×10^{-5}
2	193	9.28×10^{-5}

were monitored—depending on the nature of the suspected impurities.

Solution Preparation. Polymer stock solutions were prepared in H_2O or 2% (w/w) NaCl at ca. 200 mg/dL. Several weeks of constant mechanical shaking were required for complete solubilization. Solutions were filtered through an 8-μm filter; a peristaltic pump was employed to pump the solution at a low flow rate. Polymer and fluorophore concentrations of stock solutions are shown in Table I.

Copolymer Composition. The copolymer composition was determined by UV analysis of the aqueous copolymer solutions. The pyrenesulfonamide chromophore was determined to have $\epsilon = 24120\ M^{-1}\ cm^{-1}$.

Rheological Studies. Viscosity measurements were performed on solutions ranging from 20 to 200 mg/dL in concentration. Measurements were recorded with a Contraves low-shear 30 rheometer at 25 °C and a shear rate of 6.0 s^{-1}.

Classical Light Scattering. Classical light scattering measurements were performed on a Chromatix KMX-6 instrument. A 1.2-μm filter was used in the filter loop. Measurements were made at 25 °C. d_n/d_c measurements were taken on a Chromatix KMX-16 differential refractometer also at 25 °C.

Results and Discussion

The synthetic objective of this work was to prepare a pyrene-containing monomer which could be copolymerized with acrylamide to yield a copolymer with associative thickening behavior. Our concept was to utilize a hydrolytically stable monomer with both the necessary hydrophobic characteristics and photophysical response. Although fluorescence probes and labels have been used to study organization, we know of no other reports utilizing the fluorescence label as the sole hydrophobic moiety for domain formation.

The monomer *N*-[(1-pyrenylsulfonamido)ethyl]acrylamide (**5**) proved to have the necessary properties to achieve our synthetic objective. This monomer was initially synthesized and a small quantity provided by Winnik's group.[10] Subsequently we modified synthetic procedures and scaled up the reaction sequence to provide sufficient quantities of purified monomer for polymerization and photophysical investigations.

Several features of **5** should be noted. The acrylamido functionality of the monomer allows rapid copolymerization with the acrylamide monomers. Monomers of this type have large ratios of (k_p^2/k_t) where k_p and k_t represent the rate constants for propagation and termination in free-radical polymerization. The amide and sulfonamide linkages are hydrolytically stable in aqueous media and thus protect the integrity of the label during photophysical analysis. The monomer **5** has no benzylic hydrogens for chain transfer as do most pyrene labels reported in the literature. The spacer length (in this case, ethylene) can be altered in the synthetic procedure to decouple the pyrene from the polymer backbone. Finally the pyrenesulfonamide chromophore has a high molar absorptivity value and a high quantum yield of fluorescence.[11]

The synthesis of **5** deserves some comment. The first synthetic step (Scheme I), chlorosulfonation of pyrene, proceeded smoothly. Product **7**, sodium 1-pyrenesulfonate, contained a small amount of NaOH but was used without further purification. The compound was isolated as a dihydrate; similar compounds have been reported to exist as hydrates—for example, 1-pyrenesulfonic acid.[12] Transformation to pyrenesulfonyl chloride (**8**) was also facile.

The reaction of **8** with ethylenediamine to give *N*-(1-pyrenylsulfonyl)ethylenediamine hydrochloride (**9**) was problematic. Initial attempts, despite dilute reaction conditions, led to production of significant amounts of the ethylenediamine bis(sulfonamide) which was difficult to separate from **9**. Apparently, the reaction is diffusion-controlled. Reaction of **8** with ethylenediamine is quite rapid, and if the desired monosulfonamide product **10** encounters another molecule of **8**, the sequential reaction will occur.

Recent literature has addressed control of such reactions. Monoacylation of symmetrical diamines can be achieved by a "high-dilution" technique.[7,13] Therefore, a very dilute solution of **8** was added dropwise to a solution of excess ethylenediamine with rapid mixing to reduce the disubstitution reaction. A pure product was obtained by extraction in methylene chloride and conversion to the amine hydrochloride **9** by addition of HCl in diethyl ether.

Reaction of **9** with acryloyl chloride (Scheme II) was facilitated by using 2 equiv of the acid scavenger 1,8-bis(dimethylamino)naphthalene. This base is sterically hindered[14] and will not deprotonate the sulfonamide proton **5**. The sulfonamide proton of **5** is acidic; triethylamine and other bases deprotonate **5** to give the sulfonamide salt, which is nonfluorescent. The pyrenesulfonamide monomer **5** was recrystallized from methylene chloride. HPLC analysis utilizing dual ultraviolet detection at 330 and 220 nm indicated a sample purity greater than 99.9%.

In addition to the desired sample purity, monomer **5** is soluble in aprotic solvents such as dimethylformamide and dimethylacetamide. It is insoluble in water but, importantly, is readily solubilized by sodium dodecyl sulfate micelles.

Model compounds **3** [2,4-dimethyl-*N*-[(1-pyrenylsulfonamido)ethyl]glutaramide] and **4** [*N*-[(1-pyrenylsulfonamido)ethyl]gluconamide heptahydrate] were synthesized as water-soluble species bearing the pyrenesulfonamide moiety for model studies (Scheme III). Neither **3** nor **4** has been previously reported. Structural and purity evaluations of both were satisfactory. Interestingly, despite extended drying, **3** remained a heptahy-

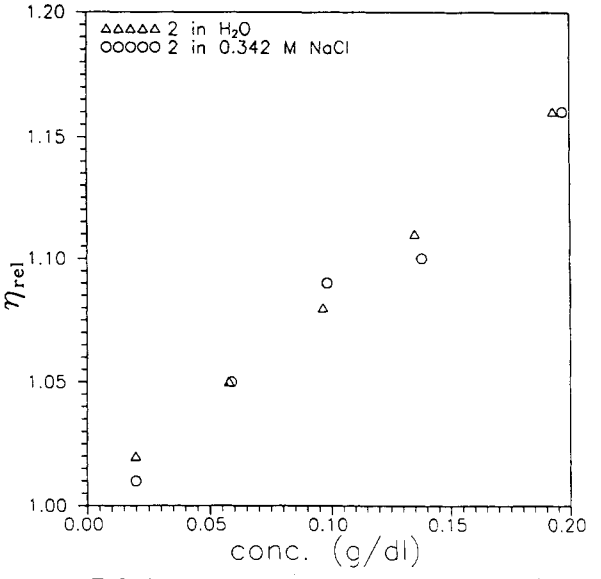

Figure 2. Relative viscosity vs concentration for copolymer 2 in H_2O (Δ) and in NaCl (O).

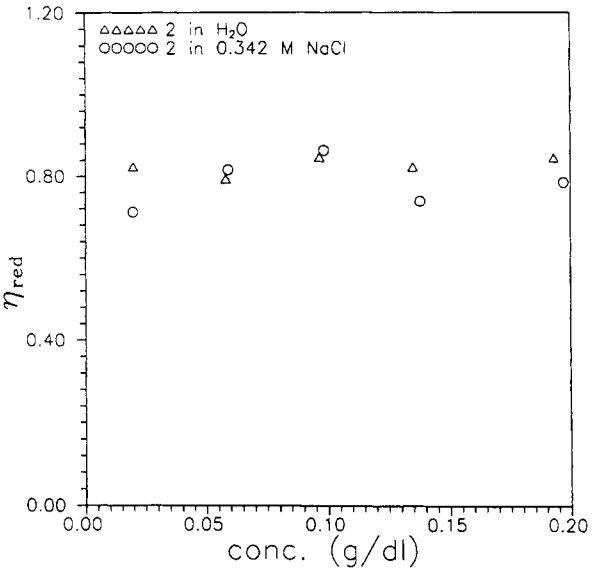

Figure 3. Reduced viscosity vs concentration for copolymer 2 in H_2O (Δ) and in NaCl (O).

drate. Other hydrophobic gluconamides have also been reported to have highly hydrated structures.[15]

Synthesis of Model Polymers. Two synthetic methods were chosen to prepare copolymers with approximately 0.5 mol % **5** but different microstructures. In the first procedure, often called the "micellar technique", 99.5 mol % acrylamide and 0.5 mol % **5** were copolymerized in aqueous solution in the presence of sodium dodecyl sulfate at concentrations well above its critical micelle concentration (Scheme IV). Potassium persulfate was used as the initiator.

Concurrent studies in our laboratories with phenyl and naphthyl chromophore-containing monomers have shown that in this microheterogeneous procedure the surfactant/hydrophobic monomer ratio is important in dictating final rheological properties.[16] These findings are consistent with a proposed mechanism of successive chain propagation of hydrophobic monomers present in the separate SDS micelles and solution polymerization of acrylamide resulting in short runs of the comonomer randomly distributed along the polymer backbone. The importance of this distribution will be addressed later in this report.

In a second synthetic procedure (Scheme V) the two monomers in the same molar ratios were copolymerized under homogeneous reaction conditions in a DMF/H_2O mixture again with potassium persulfate initiation. This polymerization might be expected to occur in a more random fashion than the micellar polymerization with monomers of **5** randomly distributed along the backbone.

Copolymer Characterization. The micellar copolymer 1 was purified by successive precipitation into acetone, redissolution into water, dialysis to remove the surfactant, and freeze drying. Verification of the removal of SDS was obtained using the $BaCl_2$ reagent. Copolymer 2 precipitated as a suspension during polymerization and was purified by sequential addition to acetone, filtration, redissolution into water, and lyophilization.

Copolymer compositions were determined by ultraviolet spectroscopic analysis in water of the pyrenesulfonamide chromophore at 351 nm ($\epsilon = 24\,120\ M^{-1}\ cm^{-1}$). Copolymer 1 was found to contain 0.25 mol % **5** (50% incorporation), while copolymer 2 contained 0.35 mol % (70% incorporation). Fluorescence studies which include characterization of the microstructure of copolymers 1 and 2 are reported in the following paper in this issue.

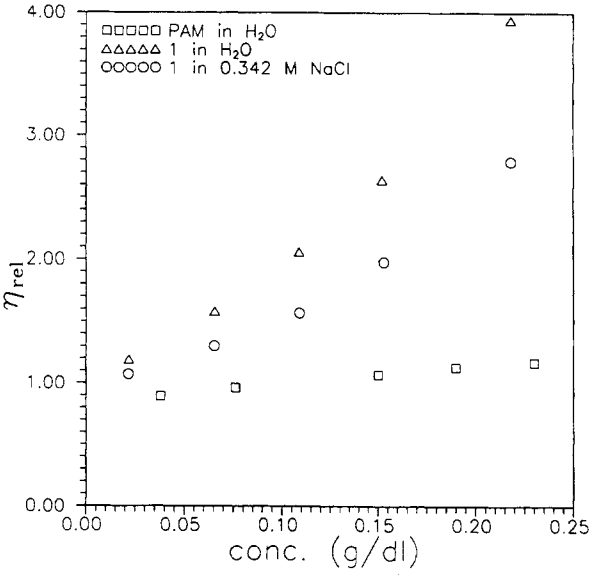

Figure 4. Relative viscosity vs concentration for copolymer 1 in H_2O (Δ) and in NaCl (O) and for homopolyacrylamide in H_2O (□).

Rheological Studies

Rheological studies were performed on diluted stock solutions (Table I). Copolymer 1 prepared by the micellar technique, like many other associative copolymers synthesized previously in our labs, required several weeks with continuous shaking for complete dissolution. A Contraves low-shear 30 rheometer operating at 6 s^{-1} was utilized for viscometric studies.

Equations 1 (the Huggins equation) and 2 (the "modified Einstein–Simha" equation) are often utilized to study polymer solution behavior. The utility of the Huggins

$$\eta_{red} = [\eta] + k'[\eta]^2 C \quad (1)$$

$$\eta_{rel} = 1 + [\eta]C \quad (2)$$

equation (eq 1) is well recognized for solvated polymers; alternately, eq 2 has been proposed for the analysis of polymers which behave as suspensions in solution.[17] Plots of the relative viscosity versus concentration for **2**, the solution-polymerized system, are illustrated in Figure 2

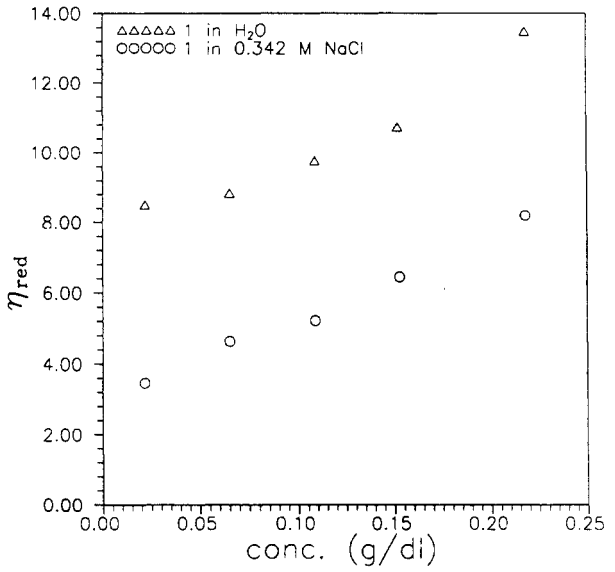

Figure 5. Reduced viscosity vs concentration for copolymer 1 in H_2O (△) and in NaCl (○).

in deionized H_2O and 2% NaCl. The linearity of the data and an intercept value of 1 suggest that this polymer behaves as a suspension in solution. The higher order terms of the Huggins equation, which account for interpolymer interactions, appear to be unimportant here. Huggins plots of these data in water and NaCl are given in Figure 3. The reduced viscosity is insensitive to the polymer concentration (within experimental error), giving a value of zero for the Huggins constant.

These data and fluorescence data to be presented later suggest the presence of intramolecular hydrophobic associations of the pyrenesulfonamide label. Such associations could result in compaction of the polymer coil, giving the observed suspensionlike behavior. Classical light scattering was performed on copolymer 2 in deionized H_2O indicating $M_w = 1.6 \times 10^5$ with $A_2 \approx 0$.

Structure 1 is representative of copolymers of 5 with AM prepared by the micellar polymerization technique. Relative viscosity profiles are illustrated in Figure 4 for deionized water and NaCl solutions. At low concentrations (<0.10 g/dL), intermolecular association is apparent. Increased ionic strength (2% NaCl) contracts the polymer coil, yielding a lower viscosity. The low C^* value likely represents the onset of intermolecular hydrophobic associations of the pyrenesulfonamide moieties. By comparison, a homopolymer of acrylamide exhibits linear viscosity behavior throughout this concentration range. Attempts at Huggins plots for 1 are given in Figure 5. The nonlinearity of the profiles indicates the first two terms of the Huggins equation are insufficient to model these data. Such a nonlinear response is strong evidence for intermolecular associative behavior. It should also be noted that the associative tendencies at copolymer 1 in solution preclude analysis by light scattering.

Conclusions

Our objectives in the synthesis and study of model associative polymers necessitated the synthesis of a fluorophore-containing hydrophobic monomer and model compounds. These materials were purified for polymerization and subsequent photophysical studies. The hydrolytically stable, pyrenesulfonamide-labeled monomers are readily copolymerizable with acrylamide via homogeneous (solution) and heterogeneous (micellar) polymerization techniques. Labeled copolymers prepared by the two procedures have significantly different rheological behaviors. The surfactant-polymerized copolymer 1 in aqueous media exhibits a low critical overlap concentration—typical of associative thickener behavior. Conversely, the solution copolymerization yields copolymer 2, which is more spherical in nature. The Huggins profile of this copolymer in aqueous solutions has zero slope, demonstrating a compact conformation. Light-scattering analysis of this copolymer in H_2O gives a second virial coefficient value of zero. Photophysical analysis of these systems has been conducted and is reported in the next paper in this series.

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