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Office of Naval Research

End-of-the-Year Report

Publications/Patents/Presentations/Honors/Students Report

for

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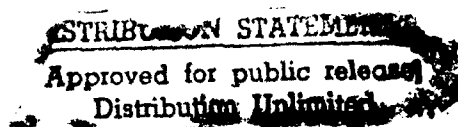
R & T Code: 4132055

Copolymers for Drag Reduction in Marine Propulsion:

New Molecular Structures with Enhanced Effectiveness

Annual Report for the Period

June 1, 1992 - May 31, 1993



Principal Investigators

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May 31, 1993

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Part I

Office of Naval Research
Publications/Patents/Presentations/Honors Report

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Marine Propulsion: New Molecular
Structures with Enhanced
Effectiveness
Principal Investigator: Charles L. McCormick
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- a. Number of papers submitted to refereed journals, but not published: 6
- b. Number of papers published in refereed journals, (list attached): 7
- c. Number of books or chapters submitted, but not yet published: 0
- d. Number of books or chapters published (list attached): 0
- e. Number of preprints: 3
- f. Number of patents filed: 0
- g. Number of patents granted: 0
- h. Number of invited presentations at workshops/professional meetings: 0
- i. Number of presentations at workshops or professional meetings: 19
- j. Honors/Awards/Prized for contract/grant employees: 0
- k. Total number of Graduate Students and Post-Doctoral associates supported by
at least 25% during this period, under this R&T project number:
Graduate Students 11
Post-Doctoral Associates 0
including the number of,
Female graduate students 2
Minority Graduate students 0
Asian Graduate Students 1
- l. Other funding (list attached)

A. Technical Papers Submitted

"Water Soluble Copolymers. 47. Copolymerization of Maleic Anhydride and N-Vinylformamide: Charge Transfer Complexation of the Monomers and Their Reactivity Ratios," Y. Chang and C. L. McCormick, submitted to *Macromolecules* (March 1993).

"Water Soluble Copolymers. 48. Reactivity Ratios of N-vinylformamide with Acrylamide, Sodium Acrylate, and n-Butyl Acrylate," submitted to *Macromolecules* (April 1993).

"Water Soluble Copolymers. 49. Effect of the Distribution of the Hydrophobic Cationic Monomer DAMAB on Solution Behavior of Associating Acrylamide Copolymers," Y. Chang and C. L. McCormick, submitted to *Macromolecules* (March 1993).

"Water Soluble Copolymers LI: Copolymer Compositions of High-Molecular Weight Functional Acrylamido Water-Soluble Polymers Using Direct Polarization Magic-Angle Spinning ^{13}C NMR," J. Kent Newman and C. L. McCormick, submitted to *Polymer* (May 1993).

"Water Soluble Copolymers. 52: ^{23}Na NMR Studies of Hydrophobically-Modified Polyacids: Copolymers of 2-(1-Naphthylacetamido)-ethylacrylamide with Acrylic acid and Methacrylic acid," J. Kent Newman and C. L. McCormick, submitted to *Macromolecules* (May 1993).

"Water Soluble Copolymers LIII: ^{23}Na NMR Studies of Ion-Binding to Anionic Polyelectrolytes: Poly(sodium 2-acrylamido-2-methylpropanesulfonate), Poly(sodium 3-acrylamido-3-methylbutanoate), Poly(sodium acrylate) and Poly(sodium galacturonate)," J. Kent Newman and C. L. McCormick, submitted to *Macromolecules* (May 1993).

B. Technical Papers Published

"Water-Soluble Copolymers: 26. Fluorescence Probe Studies of Hydrophobically-Modified Maleic Acid-Ethyl Vinyl Ether Copolymers," C. L. McCormick, C. E. Hoyle and M. D. Clark, *Polymer*, 33(2), 243-247 (1992).

"Water-Soluble Copolymers. 39. Synthesis and Solution Properties of Associative Acrylamido Copolymers with Pyrenesulfonamide Fluorescence Labels," C. L. McCormick and S. A. Ezzell, *Macromolecules*, 25(7), 1881-1886 (1992).

"Water Soluble Copolymers: 44. Ampholytic Terpolymers of Acrylamide with Sodium 2-Acrylamido-2-Methylpropanesulfonate and 2-Acrylamido-2-Methylpropanetrimethylammonium Chloride," C. L. McCormick and L. C. Salazar, *Polymer*, 33(20), 4384-4387 (1992).

"Water Soluble Copolymers 46. Hydrophilic Sulfobetaine Copolymers of Acrylamide and 3-(2-Acrylamido-2-Methylpropanedimethylammonio)-1-Propanesulfonate," C. L. McCormick and L. C. Salazar, *Polymer*, 33(21), 4617-4624 (1992).

"Water Soluble Copolymers. XLII. Cationic Polyelectrolytes of Acrylamide and 2-Acrylamido-2-Methylpropanetrimethylammonium Chloride," C. L. McCormick and L. C. Salazar, *J. Poly. Sci.: Part A—Poly. Chem.*, 31, 1099-1104 (1993).

"Water Soluble Copolymers 45. Ampholytic Terpolymers of Acrylamide with Sodium 3-Acrylamido-3-Methylbutanoate and 2-acrylamido-2-Methylpropanetrimethylammonium Chloride," C. L. McCormick and L. C. Salazar, to be published in *J. Appl. Poly. Sci.* (July 1993).

"Analysis of Hydrophobically Modified Copolymers Utilizing Spectroscopic Probes and Labels," to be published in *Soluble Polymer Complexes*, C. L. McCormick, K. D. Branham, R. Varadaraj, and J. Bock; Springer Verlag: 1993.

E. Preprints

"²³Na NMR Studies of Ion Binding to Anionic Polyelectrolytes," J. K. Newman and C. L. McCormick, *Polymer Preprints*, 33(2), 361 (1992).

"Synthesis and Solution Characterization of Cationic, Hydrophobically-Modified Acrylamide Copolymers," Y. Chang and C. L. McCormick, *Polymer Preprints*, 33(2), 202 (1992).

"Water Soluble Polyampholytes for the Study of Drag Reduction," P. S. Mumick, P. M. Welch and C. L. McCormick, *Polymer Preprints*, 33(2), 337 (1992).

I. Presentations

"²³Na NMR Studies of Ion Binding to Anionic Polyelectrolytes," J. K. Newman and C. L. McCormick, 204th National ACS Meeting, Washington, DC, August 1992.

"Synthesis and Solution Characterization of Cationic, Hydrophobically-Modified Acrylamide Copolymers," Y. Chang and C. L. McCormick, 204th National ACS Meeting, Washington, DC, August 1992.

"Water Soluble Polyampholytes for the Study of Drag Reduction," P. S. Mumick, P. M. Welch and C. L. McCormick, 204th National ACS Meeting, Washington, DC, August 1992.

"Drag Reduction in Marine Propulsion: Impact of Start-Up Funds on Advanced Technologies," C. L. McCormick, Mississippi-Alabama Sea Grant Consortium Program Review, Biloxi, MS, September 15-17, 1992.

"Synthesis and Design of *Denovo* Hydrophobically Associating Polypeptides," M. Logan, G. Cannon, S. Heinhorst, and C. McCormick, National ACS Meeting, Denver, CO, March 1993.

"Derivatization of Chitin and Cellulose Utilizing LiCl/N,N-Dimethylacetamide Solvent System," S. L. Williamson and C. L. McCormick, National ACS Meeting, Denver, CO, March 1993.

"Controlled Activity Polymers: Synthesis, Characterization and Reactivity Ratios of β -Naphthyl Acrylate, 5-Acrylamido(β -Naphthyl)Valerate, and 6-Acrylamido(β -Naphthyl) Caproate Copolymers," C. Boudreaux, D. Sellers and C. L. McCormick, National ACS Meeting, Denver, CO, March 1993.

"Effect of Surfactants on the Solution Properties of Hydrophobically Modified, Cationic Polyacrylamides," Y. Chang and C. L. McCormick, National ACS Meeting, Denver, CO, March 1993.

"Rheological and Photophysical Investigation of Domain-Forming Hydrophobic Polyelectrolytes Based on Sodium 11-Acrylamidoundecanoate," M. C. Kramer, C. G. Farmer-Welch and C. L. McCormick, National ACS Meeting, Denver, CO, March 1993.

" ^{23}Na NMR Studies of Ion-Binding to Anionic Polyelectrolytes: Sodium 2-Acrylamido-2-Methylpropanesulfonate (NaAMPS) and Sodium 3-Acrylamido-3-Methylbutaneioic Acid (NaAMB)," J. Kahalley, J. K. Newman and C. L. McCormick, National ACS Meeting, Denver, CO, March 1993.

"Synthesis and Solution Behavior of Polyelectrolyte/Polyampholyte Terpolymers Based on 3-(2-Acrylamido-2 methylpropanedimethylammonio)-1-propanesulfonate, Acrylic Acid, and Acrylamide," E. E. L. Kathmann, D. L. Davis and C. L. McCormick, National ACS Meeting, Denver, CO, March 1993.

"Synthesis and Aqueous Solution Properties of Responsive Polyelectrolytes and Polyampholytes," C. L. McCormick, M. C. Kramer, Y. Chang, K. D. Branham, and E. L. Kathmann, National ACS Meeting, Denver, CO, March 1993.

"Tailored Copolymer Structures: Effects on Drag Reduction in Aqueous Media," C. L. McCormick and P. S. Mumick, National ACS Meeting, Denver, CO, March 1993.

"A New Generation of Electrolyte and pH Responsive Water-Soluble Polymers for Mobility Control," C. L. McCormick, K. D. Branham, D. L. Davis, and J. C. Middleton, National ACS Meeting, Petroleum Chemistry Division, Denver, CO, March 1993.

"Hydrophobically-Modified Polyelectrolytes: Rheological Properties in Aqueous Solution," E. Kathmann, Y. Chang, and C. L. McCormick, National ACS Meeting, Polyelectrolytes Symposium, Denver, CO, March 1993.

"Synthesis and Solution Characterization of Cationic, Hydrophobically Modified Acrylamide Copolymers," Y. Chang and C. L. McCormick, ANTEC, New Orleans, LA, May 1993.

"Investigation of Domain-Forming Hydrophobic Polyelectrolytes Via Rheological and Photophysical Studies," M.C. Kramer, C. L. McCormick, 5th Annual Graduate Polymer Conference Georgia Tech., Univ. April 1993.

"Structure/Property Relationships in Associative Polyelectrolytes: Effects of Synthetic Parameters on Polymer Microstructure and Solution Properties," K.D. Branham, G. L. Shafer, D. L. Davis, and C. L. McCormick, 5th Annual Graduate Polymer Conference Georgia Tech., Univ. April 1993.

K. Graduate Students

Dr. J. Kent Newman - will graduate August 1993
joined Geotechnical Division/U.S. Army Corp of Engineers

Dr. Pavneet Mumick - graduated May 1993
joined Kimberly-Clark

James P. Dickerson - graduate August 1993
joined Eastman Chemical

C. Boudreaux
K.D. Branham
E.E. Kathman
M. Kramer
M. J. Logan
Y. Chang
S. Williamson
K. Johnson

Undergraduates

D. Sellers
D. Davis
G. Shafer
S. Manning
T. Posey
T. Boykin

L. Other Funding

"DOE/EPSCoR Traineeship," DOE/EPSCoR, \$15,625/year (1992-1994)

"Responsive Copolymers for Enhanced Oil Recovery," Department of Energy, \$273,400 (1992).

Unilever Research Fellowship, \$15,000 (1993).

Exxon Chemical Company, \$10,000 (1993).

Gillette Research Institute, \$15,000 (1993).

PART II

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Roger D. Hester
The University of Southern Mississippi
(601) 266-4872*

Scientific Officers: Dr. JoAnn Milliken
 Dr. Kenneth Wynne

Project Description/Significant Results for 6/1/92-5/31/93

Responsive synthetic copolymers have been tailored with specific microstructural features in order to elucidate drag reduction behavior in aqueous media. Our studies have clearly shown the role of the polymer in ordering of solvent in the vicinity of the macromolecular coil. Specific "runs" of hydrophobic units spaced by hydrophilic units are necessary for macrophase organization in aqueous media. We have prepared pH- and salt-responsive drag reducing systems based on zwitterionic and ionic polymer structures which have the best drag reducing properties reported to date. The copolymers of acrylamide with 3-(2-acrylamido-2-methylpropanedimethylammonio)-1-propane sulfonate (AMPDAPS) showed the highest drag reduction efficiency as measured by a rotating disk apparatus. The polymer can be prepared by inverse emulsion or microemulsion techniques for rapid dispersion. The automated display system constructed in our laboratory indicates that polymer solutions of this copolymer system reach maximum drag reduction in an extremely short time frame.

A kinetic model has been proposed by our group that explains the major features of the drag reduction phenomenon. The model considers the collision of fluid disturbances in turbulent flow with the polymer coils in solution based on volume fraction of the latter. Experimental measurements of drag reduction efficiency can be related to molecular parameters of our extensively characterized polymers. The model gives explanations for inconsistencies that arise in drag reduction measurement using different flow geometries and is consistent with previously obtained data and empirically derived relationships. The model shows that increasing the molecular weight (or degree of polymerization) increases the polymer hydrodynamic coil size which increases the chance of collision between a polymer coil and a turbulent flow region. Increasing molecular weight and controlled alteration of macromolecular structure also increases the effectiveness of a collision to reduce turbulence which may be related to the extensional viscosity of the polymer solution.

Major Success of Work to Date

- discovery of salt-water effective drag reducing polymers
- new polymerization/dispersion technology
- rapid response DR fluid with low volume/low weight
- rapid measurement apparatus for small quantities of material

Important Consequences are Development of

- an empirical relationship relating DR efficiency to polymer structure--including salt water systems where most polymers are inefficient
- a kinetic model consistent with theoretical model and experimental measurements
- techniques which should allow accurate prediction of behavior in flat plate and tube geometries based on rotating disk data.

The Important Breakthroughs in This Research Should be Followed by Continued R&D on

- rapid delivery emulsions
- measurement techniques/automation
- the role of the new DR systems in signature alteration

Project Goals for the last quarter of the contract June 1 - August 31, 1993

During the last three months of the project, the final technical publications will be written from the recently completed laboratory measurements.

Needs

The fundamental concepts developed in this project could have a dramatic impact on the technology of drag reduction. We continue to seek those program coordinators within DOD who could help in implementation of dual use technologies arising from our substantial research efforts.

REPORT DOCUMENTATION PAGE

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Water-soluble copolymers: 26. Fluorescence probe studies of hydrophobically modified maleic acid-ethyl vinyl ether copolymers

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39406-0076, USA

(Received 13 August 1990; accepted 19 October 1990)

Pyrene fluorescence spectra and lifetimes have been employed to study the pH-induced conformational transitions of maleic acid-ethyl vinyl ether copolymers that have been hydrophobically modified with varying amounts of 4-butylaniline (4-BA). Results indicate that those copolymers containing up to 50 mol% 4-BA (relative to the total number of maleic acid groups) undergo a transition from a highly collapsed 'hypercoil' conformation at low degrees of ionization (α) to an open, hydrated conformation at high α . In contrast, a copolymer containing 70 mol% 4-BA moieties forms compact, hydrophobic microdomains over the entire range of α . Fluorescence quenching of the pyrene probe by Ti^{3+} and nitromethane indicates that the accessibility of these microdomains is related to α and/or the degree of hydrophobe incorporation. Diffusion coefficients and effective coil diameters of these polymers as determined via dynamic light scattering measurements indicate an increasing degree of intramolecular association with increasing hydrophobe content at high α , while fluorescence measurements indicate no such interactions. It is suggested that, though the pyrene probe may associate with the hydrophobic regions of these polymers, it is not adequately 'protected' from the bulk aqueous solution for fluorescence enhancement to occur.

(Keywords: copolymers; fluorescence spectroscopy; conformation; maleic acid; ethyl vinyl ether; hydrophobic modification)

INTRODUCTION

In recent years, considerable interest in microdomain-forming polyelectrolytes or 'polysoaps' has arisen. Owing to the presence of such microdomains, these polymers are capable of solubilizing large, water-insoluble hydrocarbons in much the same way as surfactant micelles. One class of polysoaps consists of alternating maleic anhydride/alkyl vinyl ether copolymers. Strauss and others demonstrated that for alkyl groups of length n (where $3 < n < 10$), at low degree of ionization α , the observed fluorescence intensity of a dansyl label is large, indicating that the label molecules are surrounded by non-polar alkyl groups¹⁻⁵. As α is increased, the fluorescence intensity drops sharply, indicating a transition from a collapsed 'micelle-like' conformation to an expanded coil in which the probe is surrounded by a polar aqueous environment. Furthermore, as alkyl group size increases, the relative hydrophobicity within the coil at low α is increased as is the degree to which the polyacid must be ionized in order to destabilize the compact conformation⁵⁻⁹.

We have conducted a photophysical study of the effects of the relative hydrophobicity of a polysoap on the stabilization of the collapsed polymer coil at high α . The polysoaps were 4-butylaniline-modified copolymers of maleic acid-ethyl vinyl ether (MA-EVE), with aqueous solution behaviour typical of a polyelectrolyte¹⁻³. In this

paper, we report preliminary results on the utility and apparent limitations of pyrene as a fluorescence probe to study changes in the conformation of the polysoaps with increasing α .

EXPERIMENTAL

Synthesis

The preparation of a series of hydrophobically modified MA-EVE copolymers was carried out in a three-step process. First, an alternating parent polymer of maleic anhydride and ethyl vinyl ether was synthesized. Next, the parent polymer was derivatized to varying degrees with a long-chain, primary amine. Finally, these derivatized copolymers were hydrolysed to form the corresponding water-soluble polymers.

Maleic anhydride-co-ethyl vinyl ether (MA-EVE)
Maleic anhydride (12.26 g, 0.125 mol), ethyl vinyl ether (18.02 g, 0.250 mol) and 2,2-azobisisobutyronitrile (0.022 g, 1.25×10^{-4} mol) were dissolved in 250 ml of benzene and degassed with N_2 bubbling for 30 min. The solution was then heated to 65°C. After approximately 30 min, the polymer had begun to precipitate. After 16 h, both the precipitated polymer and the benzene solution were poured into 1 litre of ethyl ether to yield a white, powdery precipitate. The precipitate was redissolved into 100 ml acetone, reprecipitated into 750 ml ethyl ether, and dried under vacuum at 50°C; yield 19.35 g (91.0%).

* To whom correspondence should be addressed.

Methyl esterification of MA-EVE. Esterification of the copolymer for molecular-weight studies was carried out as follows. The copolymer was slurried in ~50 ml of methanol. Upon complete dissolution of the copolymer, 0.02 vol% of concentrated H_2SO_4 was added and the mixture heated to 50°C for 8 h. The esterified polymer was purified by repeated precipitation from benzene into ether, and finally dried under vacuum at 40°C.

Modification of MA-EVE with 4-butylaniline. Maleic anhydride-co-ethyl vinyl ether (3.5 g, 2.06×10^{-2} mol of anhydride units) was dissolved in 100 ml of ethyl acetate. The solution was cooled to 0°C with an ice bath and degassed with N_2 for 20 min. An appropriate amount of freshly distilled 4-butylaniline (4-BA) was dissolved in 50 ml of ethyl acetate and placed in an addition funnel. With continued N_2 bubbling, the aniline solution was added dropwise to the polymer solution, keeping the temperature below 5°C. The nitrogen purge was removed, and the solution was heated to 65°C for 10 h, at which time the polymer was precipitated into 600 ml of ethyl ether. The white, powdery precipitate was dissolved in 75 ml of acetone, reprecipitated into 600 ml of ethyl ether, and dried under vacuum at room temperature.

Hydrolysis of hydrophobically modified MA-EVE. The modified MA-EVE copolymers (2.0 g) were slurried in 50 ml of 1.0 N aqueous KOH. This mixture was stirred at room temperature until complete dissolution of the polymers occurred. The polymers were precipitated into 700 ml of methanol and immediately redissolved in water. The solutions were dialysed against deionized water (Spectra/Por 4 membranes, MW cut-off 12000–14000) and freeze-dried. The degree of 4-butylaniline incorporation in each of the copolymers was determined via u.v. absorption methods using the extinction coefficient determined for a model compound in water ($\epsilon = 11\,800 \text{ M}^{-1} \text{ cm}^{-1}$ at 250 nm). The resulting compositions are summarized in Table I.

Characterization

From the molecular-weight estimate of the parent polymer and a calculated average molecular weight per repeat unit (u.v. compositional studies), molecular weights of each polymer were calculated such that the concentration of each modified copolymer in solution could be maintained at approximately $6.3 \times 10^{-2} \text{ mol l}^{-1}$.

Molecular-weight determination of esterified polymer. A qualitative molecular-weight estimate of 3.17×10^5

(approx. $DP = 1450$) was made from gel permeation chromatography (g.p.c.) measurements on a Waters system employing a bank of 100, 500, 10^4 and 10^5 Å μ -Styragel columns and a differential refractometer. Monodisperse poly(methyl methacrylate) standards (Scientific Polymer Products) were used to establish the calibration curve.

Fluorescence emission studies of pyrene probe. Solutions of modified MA-EVE copolymers were 'doped' with pyrene by adding microlitre quantities of a concentrated pyrene/methanol solution to the polymer solution. Typically, 1 μl of a 10^{-2} M pyrene solution was added to 10 ml of polymer solution to give a final pyrene concentration of 10^{-6} M . Samples were degassed by bubbling with helium.

Pyrene steady-state emission spectra were recorded with a SPEX Fluorolog-2 fluorescence spectrometer. The spectra were corrected for the wavelength dependence of the detector response using an internal correction function provided by the manufacturer. All samples were excited at 324 nm, and the intensities of the first and third vibronic bands were measured at approximately 372 and 382 nm, respectively.

Fluorescence decay curves were measured with a Photochemical Research Associates single-photon counting instrument using an N_2 -filled S10-B flashlamp. An IBM-PC was employed along with PRA software to fit the decay profiles using the non-linear iterative deconvolution technique. In those cases where non-exponential decays were observed, only the long-lived portion of the decay curves was fitted.

Dynamic light scattering. Photon correlation spectroscopy studies were conducted using a Brookhaven model BI-DS with a Spectra-Physics 127 laser operating at 653.6 nm. The sample chamber was in a thermostated index-matching bath (toluene) and a Brookhaven model BI-2030AT autocorrelator and associated software were used to process signals. All data presented are for a 90° scattering angle at 25°C.

Much care was taken during sample preparation in order to remove all traces of dust. Deionized, filtered water was used for initial sample preparation. Solutions were then filtered in line for several hours using Gelman Acrodisc filters (0.45, 1.2, or 3.0 μm pore size). Contaminated samples were easily identified by their erratic non-reproducible scattering signals.

RESULTS AND DISCUSSION

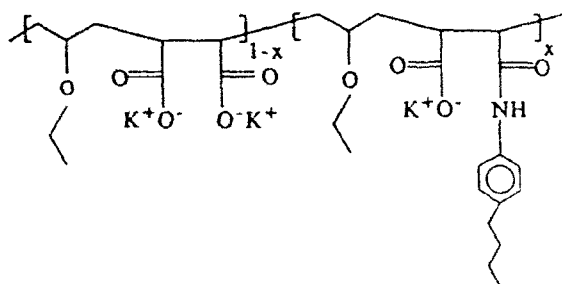
The 'parent' polymer of maleic anhydride-co-ethyl vinyl ether (MA-EVE) was prepared by free-radical polymerization in benzene ($M_n = 317\,000$, $DP = 1450$). Each of the hydrophobically modified polymers was prepared by reaction of the parent copolymer with an appropriate amount of 4-BA and subsequent hydrolysis in dilute aqueous KOH. U.v. compositional analysis was employed to determine the mole percentage of maleic anhydride units that had been derivatized, e.g. 4-BA-50 denotes a copolymer in which one-half of the total available maleic anhydride units were derivatized with 4-BA. The general structure of 4-BA-modified MA-EVE

Table I Composition of 4-BA copolymers

Polymer	4-BA* (mol%)
4-BA-10	9.3
4-BA-25	22.1
4-BA-50	46.9
4-BA-70	71.1

*As determined via u.v. absorption

copolymers is shown below:



The low water-solubility and long lifetime (200 ns in water and 400 ns in organic solvents) of pyrene make it an excellent probe of micelles or microdomain-forming polymers¹⁰. The fluorescence spectrum and lifetime of the pyrene molecule yield information about the polarity of the local environment (micropolarity) and the change in polarity when the medium is modified. The ratio of the third and first vibronic peaks of the steady-state emission spectrum of pyrene (I_3/I_1) and the fluorescence lifetime serve as a sensitive indicator of the polarity of the microenvironment. Higher values of I_3/I_1 indicate a more hydrophobic environment.

Effects of pH

Figure 1 depicts the dependence of I_3/I_1 on pH in aqueous solutions of the hydrophobically modified 4-BA-maleic acid-ethyl vinyl ether copolymers. For copolymers containing 10–50 mol% 4-BA, changes in I_3/I_1 are qualitatively similar to those observed for poly(methacrylic acid) (PMA)^{11–13} and maleic acid-alkyl vinyl ether copolymers where the alkyl group size is less than 10 carbons^{1–3}. This implies the presence of a conformational transition from a collapsed hydrophobic coil to one that is highly expanded and hydrated with increasing pH. Also, as the degree of incorporation of the hydrophobic group in the copolymers is increased, the degree to which the polymer must be ionized in order to induce this transition also increases. These results are also similar to those previously reported for maleic acid-alkyl vinyl ether copolymers in which the relative hydrophobicity of the polymer coil is varied by the length of the hydrophobic alkyl chain rather than by the degree of hydrophobe incorporation⁴. Furthermore, it is worth noting that for 4-BA-50, I_3/I_1

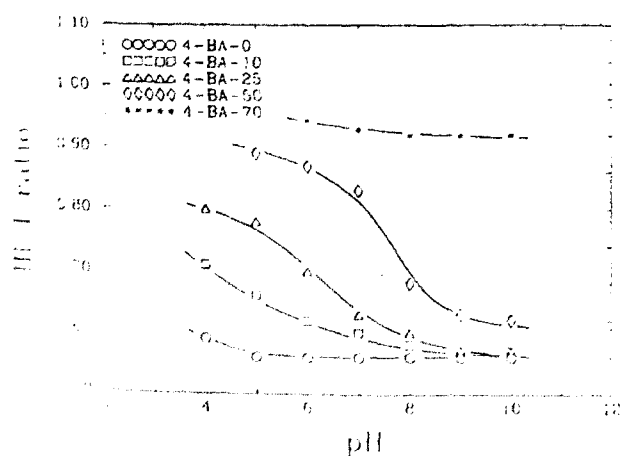


Figure 1 Effect of pH on I_3/I_1 for pyrene probe solubilized in 4-BA copolymers.

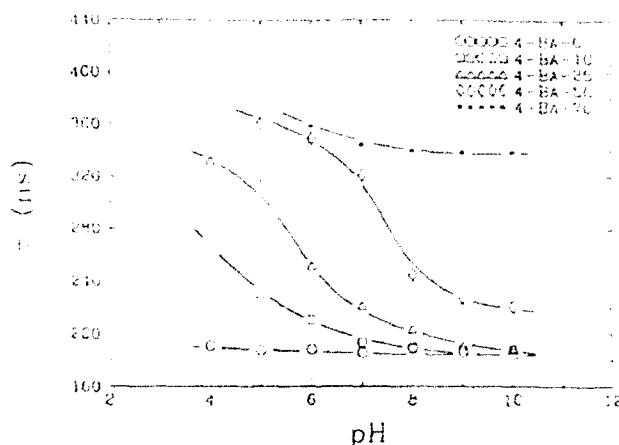


Figure 2 Effect of pH on the fluorescence lifetime τ for pyrene probe solubilized in 4-BA copolymers

at high pH is significantly larger than in pure water but is still low enough to indicate a strong hydrophilic environment. This behaviour suggests that, though the coil is highly expanded and hydrated, the pyrene probe continues to interact with the hydrophobic butyl-phenyl side groups rather than remaining in the bulk aqueous phase. This point will be addressed further in the discussion of the fluorescence quenching data.

In 4-BA-0, a low I_3/I_1 (about 0.56) reflects an essentially aqueous environment and is invariant with changes in pH. This behaviour suggests a relatively expanded conformation for the polymer over the entire pH range. In contrast, a high (~ 0.93) and relatively pH-insensitive I_3/I_1 of pyrene in solutions of 4-BA-70 reflects the presence of microdomains even at high degrees of ionization of the polymer. These data indicate stabilization of the collapsed polymer coil via hydrophobic interactions between 4-BA moieties and are once again similar to those observed in analogous systems.

The effects of pH on the pyrene fluorescence lifetime τ are depicted in Figure 2. At this time, it should be pointed out that only the fluorescence decay curves of pyrene in those solutions whose I_3/I_1 indicate a totally aqueous environment could be satisfactorily fitted to a single exponential. Numerous efforts to fit the remaining decay curves to a sum of exponentials (either two or three) proved to be unsuccessful. Thus, values of τ were estimated by fitting the long-lived portion of these decay curves to a single exponential. In the interest of consistency, the same number of data channels were fitted for each decay. Nonetheless, for each of the 4-BA copolymers, τ changes with pH in very much the same way as does I_3/I_1 , thus confirming the role of hydrophobic interactions in forming and maintaining the collapsed hypercoil structures of these polymers.

The non-exponential character of the pyrene fluorescence decay in non-aqueous environments could possibly be affected by the formation of a non-emissive exciplex between pyrene and the acetanilino group of the 4-BA copolymers and/or a distribution of hydrophobic host sites for the pyrene probe. Using model compounds, an inefficient ($k_a = 3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$), but nonetheless significant, quenching of pyrene fluorescence in methanol by a small-molecule acetanilide model compound occurs; no emissive complex is formed. A slight deviation from exponential decay is observed for pyrene in the presence of the model compound, suggesting that a non-

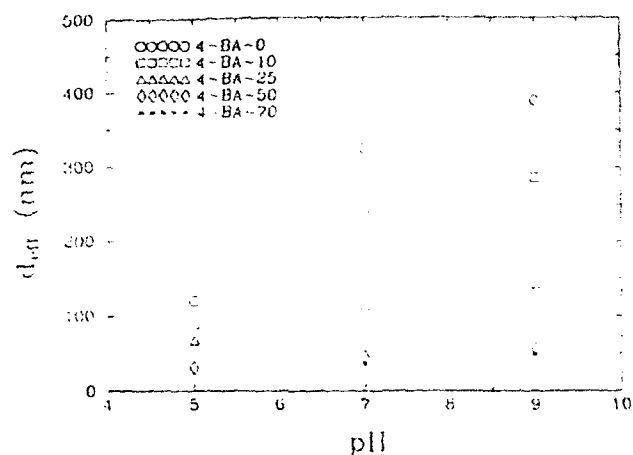


Figure 3 Effect of pH on the effective diameter of the polymer coil d_{eff} for 4-BA copolymers

fluorescing reversible complex could be present. However, since the deviation from non-linearity is minimal, complex formation, if occurring, could be only a minor contributing factor in the non-exponential decays observed for pyrene in solutions of the 4-BA copolymers. Perhaps more applicable to the present case is the fact that the rate of emission decay of the pyrene probe becomes multiexponential when the probe molecules are partitioned between/among different environments¹³. If a continuous distribution of microenvironments exists within the polymer coil, the fluorescence lifetimes of the probes associated with these different environments should be described by a function that comprises the sum of several exponential decay functions. Therefore, it is suggested that the hydrophobic characters of the discrete heterogeneous microenvironments associated with the 4-BA copolymers are non-uniform throughout the solution and that the fluorescence lifetimes (Figure 2) as measured describe the most hydrophobic regions of the polymer coil.

The effects of pH on the effective diameter of the polymer molecules d_{eff} as measured by quasielastic light scattering are shown in Figure 3. Assuming minimal degradation of the copolymers on hydrolysis, the degree of polymerization of each of the copolymers is the same ($DP \approx 1450$). Therefore, any variations of d_{eff} that occur within the copolymer series may safely be considered to be due to hydrophobic interactions between 4-BA groups rather than due to differences in molecular weight. As might be expected, as the degree of hydrophobic substitution increases, the degree to which the polymer coil expands on increasing pH is dramatically decreased. Furthermore, a decrease in d_{eff} with increasing 4-BA substitution at each value of pH indicates that these associations are largely intramolecular in nature. Apparently, a minimum value of d_{eff} is reached at high hydrophobe content (> 50 mol%), indicating that the polymer has assumed the smallest coil dimensions possible without macroscopically phase-separating. These data are again indicative that stabilization of the collapsed coil at high degrees of ionization occurs via hydrophobic aggregation along the polymer chain.

An interesting phenomenon is observed on comparison of the effective diameters of the copolymers containing 0, 10 and 25 mol% 4-BA groups with the fluorescence data, both steady-state and transient, at pH 9.

Fluorescence measurements for each of the three copolymers indicate that the pyrene probe is exposed to an aqueous environment, i.e. there are no hydrophobic aggregates in the solution. However, significant decreases in d_{eff} as the mole percentage of 4-BA is increased indicate that intramolecular hydrophobic interactions are indeed present in the system. We have obtained similar results in numerous efforts to employ fluorescence probe techniques to study a number of other water-soluble polymer systems in our laboratories. Though solution methods such as viscometry and light scattering indicate that hydrophobic interactions are indeed a factor in observed polymer solution properties¹⁴⁻¹⁷, such interactions are not always reflected by pyrene probe photophysics. Polymer solution characteristics may be influenced considerably by the presence of hydrophobic interactions within the solution; however, these interactions or associations may not be in the form of aggregates of sufficient size or propensity to 'protect' a probe molecule from the bulk aqueous solution. This also suggests that, though the pyrene probe is a very effective tool in the study of hydrophobic interactions in water-soluble polymer systems, caution must be exercised in interpreting the absence of fluorescence enhancement of a probe molecule as a complete absence of hydrophobic associations.

Fluorescence quenching

The bimolecular quenching rate constants, k_q , for quenching of pyrene steady-state fluorescence intensity in water and the various copolymer systems are presented in Table 2. The values of k_q obtained from linear Stern-Volmer intensity quenching with the neutral quencher nitromethane in the 4-BA copolymer solutions are lower than those observed in water, suggesting that, even in the case of 4-BA-0, penetration of the quencher molecule is inhibited by the main chain of the host polymer. At low pH, this restrictive effect is particularly sensitive to the degree of incorporation of hydrophobe in the copolymer; increased hydrophobe content leads to a more highly collapsed coil, which in turn slows diffusion of the quencher to the probe and lowers k_q . As with I_0/I_1 and τ , the quenching rate constants at high pH for 4-BA-0, 4-BA-10 and 4-BA-25 are similar, again suggesting the absence of hydrophobic interactions capable of sequestering a pyrene probe from the aqueous environment.

Table 2 Fluorescence quenching rate constants* for pyrene in aqueous solutions of 4-BA copolymers

Quencher	Polymer	pH 8.0	pH 5.0
CH_3NO_2	Water	8.5×10^9	8.4×10^9
	4-BA-0	5.2×10^9	6.2×10^9
	4-BA-10	5.1×10^9	2.8×10^9
	4-BA-25	5.1×10^9	3.7×10^9
	4-BA-50	1.9×10^9	1.4×10^9
	4-BA-70	1.2×10^9	insoluble
TiNO_2	Water	6.1×10^9	5.9×10^9
	4-BA-0	7.9×10^9	7.8×10^9
	4-BA-10	7.9×10^9	3.7×10^9
	4-BA-25	8.1×10^9	1.8×10^9
	4-BA-50	2.8×10^9	1.1×10^9
	4-BA-70	1.4×10^9	insoluble

*Changes in fluorescence intensity measured at 25°C in air.

The electrostatic binding of the cationic quencher Ti^+ to the negatively charged 4-BA copolymers results in relatively higher quenching efficiencies, perhaps due to static quenching, than those observed for the non-interactive quencher nitromethane. This phenomenon is particularly prominent for the 4-BA-70 copolymer. Similar decreases in k_q , but less substantial than those observed for quenching with nitromethane, with increasing hydrophobe content also suggest that the degree to which the polymer coil collapses at a given pH is related to its degree of hydrophobicity. An interesting feature of the Ti^+ quenching experiments at high pH involves the three copolymers for which pyrene shows no appreciable hydrophobic aggregation, 4-BA-0, 4-BA-10 and 4-BA-25. As with nitromethane, the k_q values for each of the three copolymers are approximately equivalent, indicating an open, hydrated structure. However, unlike nitromethane, the k_q values for Ti^+ quenching are higher (slightly) than in water. Since it is well known that cationic quenchers interact strongly with anionic polymers such as the 4-BA series, these data suggest that the pyrene probes may also be associated with the more hydrophobic regions of these three copolymers, regions which, as previously mentioned, apparently do not form micelle-like domains capable of protecting the pyrene molecule from the aqueous phase.

CONCLUSIONS

Photophysical studies of the pyrene probe molecule solubilized by the 4-BA copolymers indicate that these polymers are capable of forming hydrophobic microdomains in aqueous solution. The stability and relative hydrophobicity of these domains are related to both the degree of ionization and the extent of hydrophobic modification of the polymer. Direct comparison of photophysical characteristics of the pyrene probe (steady-state and transient) with effective molecular size of the copolymers as determined by dynamic light scattering as a function of pH suggests that hydrophobic interactions that may alter the solution characteristics of a polymer rather dramatically may not significantly enhance the photoproperties of a probe molecule.

Fluorescence quenching measurements indicate that, in the absence of microdomains (high α , low hydrophobe content), the pyrene probe nonetheless associates with the hydrophobic segments of the expanded polymer coil. It is suggested that, while these segments are capable of hydrophobic interactions with each other as well as with the pyrene probe, they do not form discrete microdomains that are capable of 'protecting' the probe molecule from the bulk aqueous phase.

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

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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 conditions² 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, cellulose, 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 chromatography⁵ (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

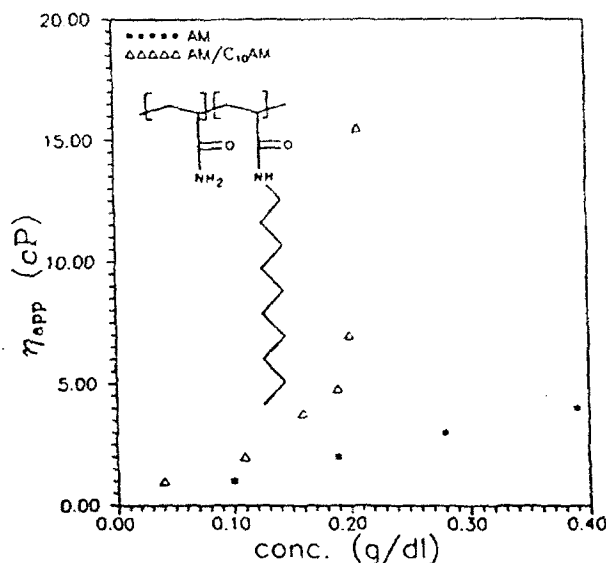


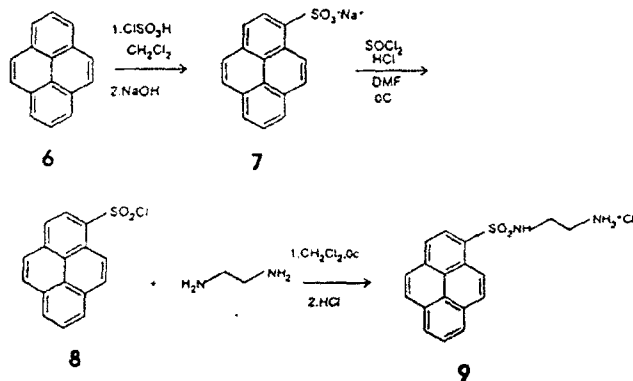
Figure 1. Illustration of associative behavior of polyacrylamide modified with 0.75 mol % *n*-decylacrylamide via surfactant polymerization.

of less than 1×10^{-7} mho/cm. Other starting materials were purchased commercially and used as received. Solvents were reagent-grade, unless otherwise noted.

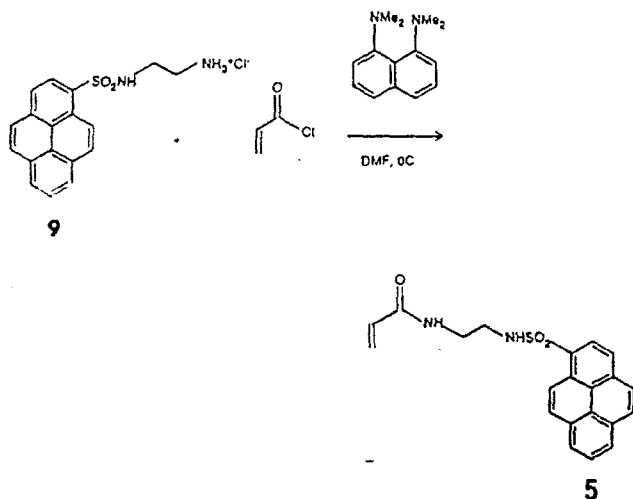
Monomer and Model Compound Synthesis. *N*-[(1-Pyrenylsulfonamido)ethyl]acrylamide (5) and Its Precursors (Schemes I and II). Sodium 1-Pyrenesulfonate (7). A literature method⁶ was modified for the preparation of sodium 1-pyrenesulfonate. Pyrene (6; 47.60 g, 0.235 mol) was dissolved in 300 mL of CH_2Cl_2 . 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 cm³ 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 cm³) 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

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



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



purification. Yield: 51.0 g (71%). Anal. Calcd for $C_{16}H_{13}O_6SNa$: 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 (S=O stretch); 1361, 1173 (asymmetric and symmetric S=O stretch) 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^+ 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).

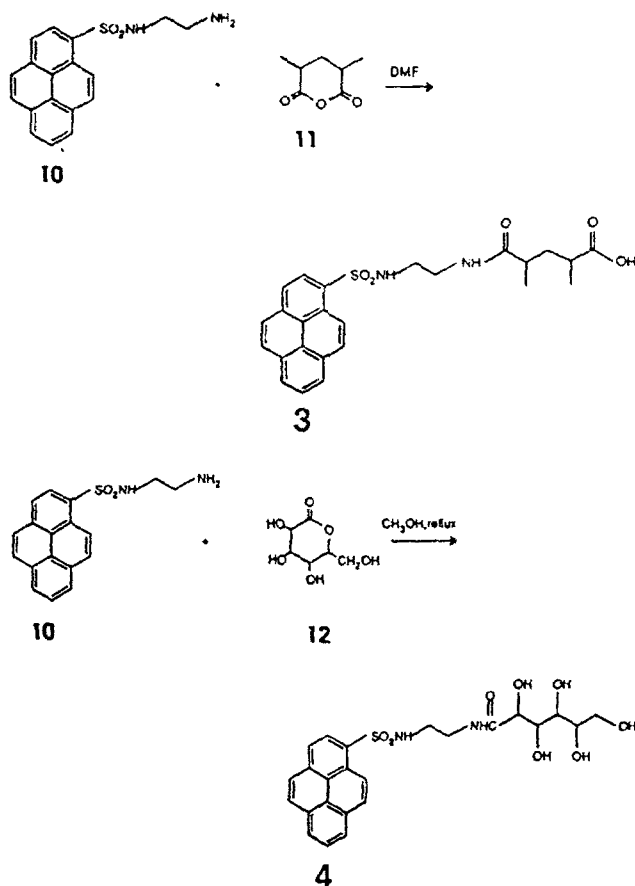
***N*-[(1-Pyrenylsulfonylamido)ethyl]acrylamide (5).** The synthesis of 5 is depicted in Scheme II. The amine hydrochloride salt 9 (1.0 g, 2.8×10^{-3} mol) and 1,8-bis(dimethylamino)naphthalene (1.19 g, 5.6×10^{-3} mol) were stirred with 7 mL of DMF under a nitrogen stream for 15 min at 0 °C. Acryloyl 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 $C_{21}H_{19}SO_2N_3$: 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 (vinyl 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 (acrylamide ketone carbon).

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

2,4-Dimethylglutamic Anhydride (11). 2,4-Dimethylglutamic 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

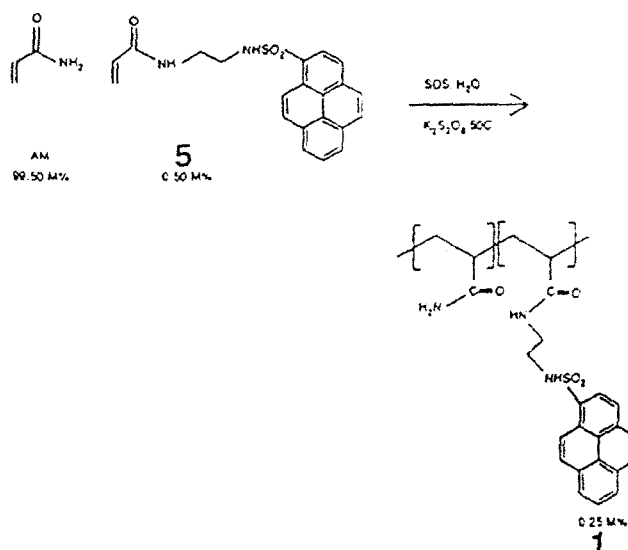
Scheme III
Synthesis of Pyrene-Containing Model Compounds 3 and 4



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 (HNSO_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 ($\text{DMSO}-d_6$): 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 (HNSO_2 stretch); 1657 (amide I); 1533 (amide II); 1419 (CN stretch); 1307, 1161 (asymmetric and symmetric S=O) cm^{-1} . ^{13}C NMR ($\text{DMSO}-d_6$): δ 38.24, 41.20 (ethylene resonances); 63.27 (1'COH); 69.89, 71.44, 72.25, 73.45 (2'COH); 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

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 $\text{K}_2\text{S}_2\text{O}_8$ 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 $\text{DMSO}-d_6$; 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/H₂O

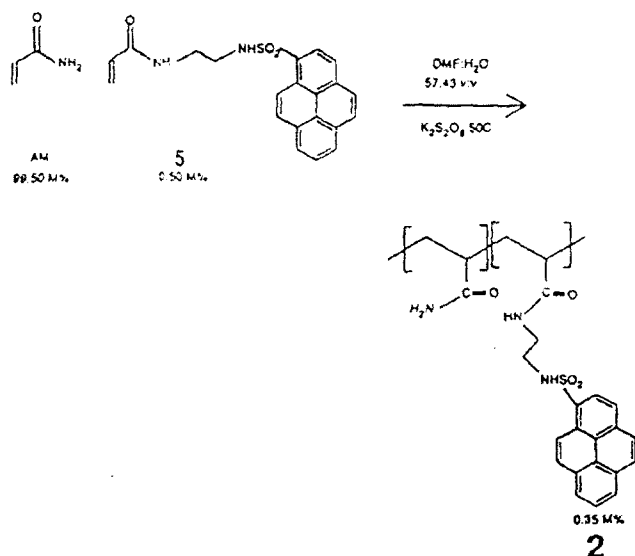


Table I
Stock Solutions of Labeled Polymers

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 H₂O 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- μ m 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 $\epsilon = 24120 \text{ M}^{-1} \text{ cm}^{-1}$.

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- μ m 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

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 pyrene-sulfonamide 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 hindered¹⁴ 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 pyrene-sulfonamide moiety for model studies (Scheme III). Neither 3 nor 4 has been previously reported. Structural and purity evaluations of both were satisfactory. Inter-

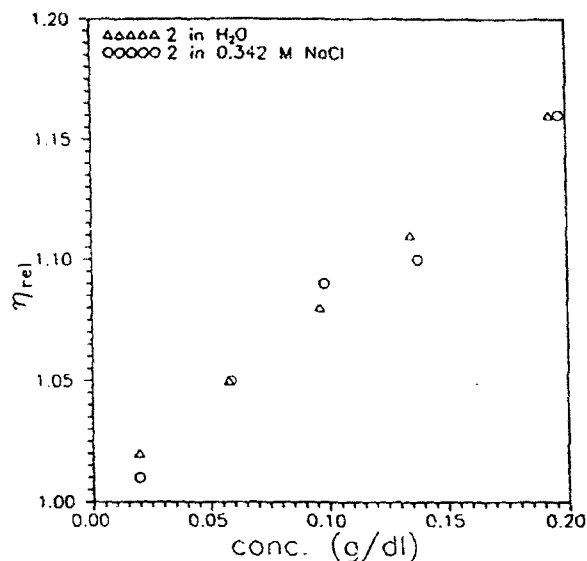


Figure 2. Relative viscosity vs concentration for copolymer 2 in H₂O (Δ) and in NaCl (O).

drate. Other hydrophobic gluconamides have also been reported to have highly hydrated structures.¹⁶

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/H₂O 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 BaCl₂ 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 ($\epsilon = 24\,120\text{ M}^{-1}\text{ cm}^{-1}$). 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

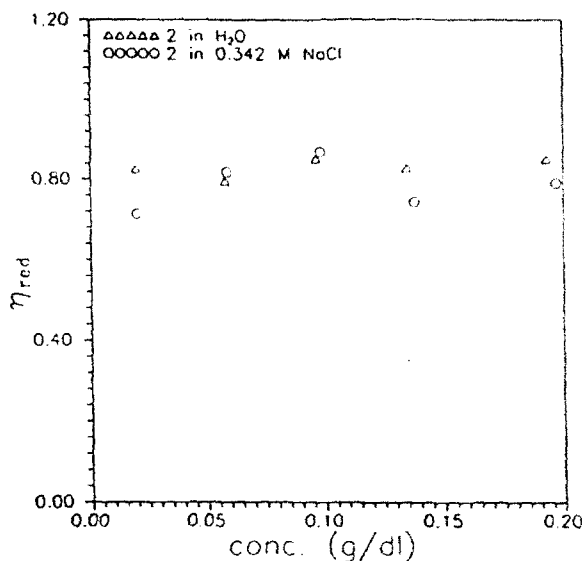


Figure 3. Reduced viscosity vs concentration for copolymer 2 in H₂O (Δ) and in NaCl (O).

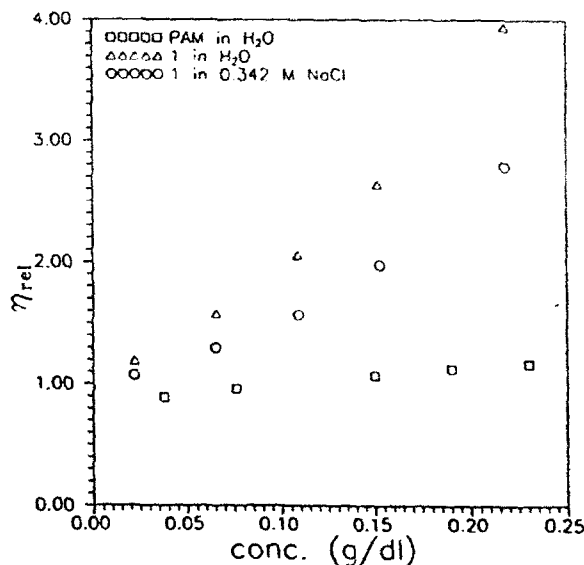


Figure 4. Relative viscosity vs concentration for copolymer 1 in H₂O (Δ) and in NaCl (O) and for homopolyacrylamide in H₂O (□).

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

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

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

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

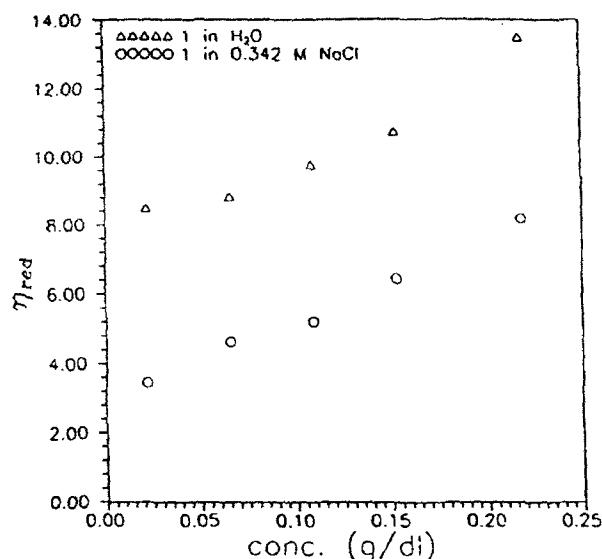


Figure 5. Reduced viscosity vs concentration for copolymer 1 in H₂O (Δ) and in NaCl (O).

in deionized H₂O 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 H₂O 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 flu-

orophore-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 H₂O 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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Water soluble copolymers: 44. Ampholytic terpolymers of acrylamide with sodium 2-acrylamido-2-methylpropanesulphonate and 2-acrylamido-2-methylpropanetrimethylammonium chloride

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Low charge density ampholytic terpolymers of acrylamide with random distributions of sodium 2-acrylamido-2-methylpropanesulphonate and 2-acrylamido-2-methylpropanetrimethylammonium chloride have been synthesized by free radical polymerization in 0.5 M NaCl aqueous solutions. Terpolymer compositions were obtained by ^{13}C n.m.r. Low angle laser light scattering provided molecular weights and second virial coefficients which varied from 2.78×10^5 to $6.77 \times 10^5 \text{ g mol}^{-1}$ and 1.31 to 2.95 ml mol^{-1} respectively. Dilute solution properties of the terpolymers were measured with respect to composition concentration and added electrolytes. Polyampholyte behaviour was observed for the polymer with as little as 0.5 mol% of each charged group and became significant when 7 mol% of each charged monomer was incorporated. At 12 and 15 mol% incorporation of each charged monomer, solution behaviour became complex consistent with the existence of intermolecular interactions at low ionic strengths and intramolecular associations at medium salt concentrations.

(Keywords: copolymer; terpolymer; free radical polymerization)

INTRODUCTION

Few studies have been reported for polyampholytes with low charge densities¹⁻⁸ although copolymers and terpolymers of this type have great potential as rheology modifiers. Applications include drag reduction, enhanced oil recovery, personal care and coatings formulations. The 'antipolyelectrolyte' effect or increased viscosity in salt solutions has not been commercially exploited. Microstructural charge placement, polymer concentration and ionic strength are important in determining viscosity behaviour. For polyampholytes with hydrophilic mers, the lower the charge density the greater the solubility in deionized water and the less added electrolyte necessary for dissolution^{2-4,7}.

Peiffer *et al.*^{7,8} studied polyampholytes with low charge densities by incorporating the neutral monomer acrylamide (AM) along with methacrylamidopropyltrimethylammonium chloride and sodium styrene sulphonate yielding properties not readily attainable with the high charge density polyampholytes. Polymers were soluble in deionized water as well as in the presence of added electrolytes. In the absence of added electrolytes, the low charge density polyampholytes (< 10 mol%) showed intermolecular associations while the polymers with higher charge densities favoured intramolecular ionic associations. The rheology of high ionic strength aqueous solutions could be controlled by adjusting the net

charge and the anion/cation charge density of the polyampholytes.

Our laboratories have previously explored polyampholyte behaviour using high charge density copolymers^{9,10} and low charge density terpolymers¹¹⁻¹³. Low charge density terpolymers (the ADASAM terpolymer series) were made using AM as a neutral hydrophilic monomer along with sodium 2-acrylamido-2-methylpropanesulphonate (NaAMPS) and 2-acrylamido-2-methylpropanedimethylammonium hydrochloride (AMPDAC) as the charged monomers (Figure 1). The terpolymers were soluble in deionized water and exhibited enhanced viscosity as electrolytes were added. Both intra- and intermolecular associations could be observed in rheological studies.

This paper reports the study of a new series of terpolymers (the ATASAM series) made with 2-acrylamido-2-methylpropanetrimethylammonium chloride

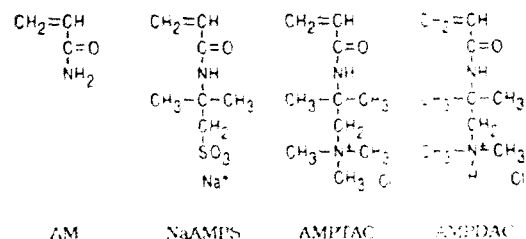


Figure 1. Structures for the monomers.

* To whom correspondence should be addressed.

(AMPTAC) as the cationic monomer. This monomer features a quaternized ammonium functionality which is resistant to hydrolysis and readily copolymerizable^{2,12}. The methods used to synthesize these terpolymers and their dilute solution behaviour are discussed and compared to the previously studied ADASAM series.

EXPERIMENTAL

Monomer synthesis

NaAMPS obtained from Fluka was purified by recrystallization from a methanol/2-propanol solvent system followed by drying under vacuum at room temperature. Synthesis of AMPTAC by a multistep procedure has been previously reported¹². Briefly, 2-acrylamido-2-methylpropanedimethylamine was reacted with a 10-fold excess of methyl iodide in refluxing diethyl ether then ion-exchanged to yield the product AMPTAC.

Synthesis of terpolymers of AM with NaAMPS and AMPTAC

Terpolymers of AM with NaAMPS and AMPTAC (the ATASAM series) were synthesized by free radical polymerization in 0.5 M NaCl aqueous solutions under nitrogen at 30 °C using 0.1 mol% potassium persulphate as the initiator. The feed ratio of AM:NaAMPS:AMPTAC was varied from 99.0:0.5:0.5 to 70:15:15 mol% with the total monomer concentration held constant at 0.45 M. The use of 0.5 M NaCl as the reaction medium ensured that the terpolymers remained in solution during polymerization.

In a typical synthesis, specified quantities of each monomer were dissolved in small volumes of NaCl solution. After the pH was adjusted to 7, the separate solutions were combined and diluted to a 0.45 M total monomer concentration. The reaction mixture was sparged with nitrogen for 20 min then initiated with 0.1 mol% potassium persulphate. The reaction was usually terminated at <30% conversion due to the high viscosity of the reaction medium and as a precaution against terpolymer compositional drift. The polymers were precipitated in acetone, redissolved in deionized water, then dialysed using Spectra/Por 4 dialysis bags with molecular weight cut-offs of 12 000–14 000 g mol⁻¹. After isolation by lyophilization, the polymers were stored in desiccators with a nitrogen atmosphere.

All terpolymers were soluble in deionized water except for ATASAM 10-10 and ATASAM 15-15. These terpolymers precipitated from solution during dialysis.

These hydrogel-like materials were washed repeatedly with deionized water to remove any remaining salt, or monomer, and then lyophilized. Conversions were determined gravimetrically. Table 1 lists reaction parameters for the terpolymerization of AM with NaAMPS and AMPTAC. FTIR, typical terpolymer: ATASAM 15-15. N-H 3515–3200 cm⁻¹ (s); C-H 2933 cm⁻¹ (m); C=O 1674–1658 cm⁻¹ (s); S-O 1208 cm⁻¹ (s). ¹³C n.m.r., ATASAM 15-15, AM C=O 181.1 ppm; AMPTAC C=O 179.2 ppm; NaAMPS C=O 178.0 ppm; chain CH 45.0 ppm; chain CH₂ 38.0 ppm; quat. CH₃ 57.1 ppm; gem CH₃ 29.5 ppm.

Terpolymer characterization

Terpolymer compositions were determined from ¹³C n.m.r. by integration of the amide carbonyl peaks¹³. ¹³C n.m.r. spectra were obtained using 10 wt. wt% aqueous (D₂O) polymer solutions with 3-(trimethylsilyl)-1-propanesulphonic acid, sodium salt (DSS) as the reference. FTIR spectra were acquired using a Perkin-Elmer 1600 series FTIR spectrophotometer. Molecular weight studies were performed on a Chromatix KMX-6 low angle laser light scattering instrument. Refractive index increments were obtained using a Chromatix KMX-16 laser differential refractometer. For quasielastic light scattering a Langley-Ford model LF1-64 channel digital correlator was used in conjunction with the KMX-6. All measurements were conducted at 25 °C in 1 M NaCl.

Viscosity measurement

Stock solutions of sodium chloride were prepared by dissolving the appropriate amount of salt in deionized water. Polymer stock solutions were made by dissolving a specified amount of polymer in solvent from these salt solutions. The solutions were then diluted to required concentrations and allowed to age for 2–3 weeks before being analysed with a Contraves LS-30 rheometer. Triplicate samples were prepared of each concentration to reduce experimental error. Intrinsic viscosities were evaluated using the Huggins equation¹⁴.

RESULTS AND DISCUSSION

The ATASAM terpolymers were synthesized by varying the ratio of AM:NaAMPS:AMPTAC from 99.0:0.5:0.5 to 70:15:15 mol% in the feed. Reaction parameters and the resulting compositions for the polymers are given in Table 1. The number appended to the acronym ATASAM refers to the concentration of NaAMPS and AMPTAC in the feed, respectively. This series differs from the

Table 1 Reaction parameters for the terpolymerization of AM with NaAMPS and AMPTAC

Sample number	Feed composition (mol%)		Reaction time (hr)	Conversion (%)	Terpolymer composition (mol%) AM NaAMPS AMPTAC
	AM	NaAMPS AMPTAC			
ATASAM 0-5-0.5	99.9	0.5 0.5	2.5	100	99.9:0.5:0.5
ATASAM 2.5-2.5	95.0	2.5 2.5	2.5	100	95.0:2.5:2.5
ATASAM 5.0-5.0	90.0	5.0 5.0	2.5	100	89.0:6.0:5.0
ATASAM 10-10	80.0	10.0 10.0	2.5	90.0	90.0:10.0:10.0
ATASAM 15-15	70.0	15.0 15.0	2.5	100	66.5:28.5:15.0
ATASAM 5-10	85.0	5.0 10.0	3.0	100	83.7:6.4:11.0

(Determined from ¹³C n.m.r.)

(Theoretical)

previously studied ADASAM series in that AMPTAC replaces AMPDAC as the cationic monomer. The quaternary ammonium of AMPTAC has been shown to provide a hydrolytically stable cationic moiety which remains charged regardless of solvent pH¹².

Compositional studies

Terpolymer compositions were determined by the integration of acrylamido carbonyl peaks obtained from ¹³C n.m.r. This method gave the mol% AM, NaAMPS and AMPTAC in the terpolymers with the exception of ATASAM 0.5-0.5 and ATASAM 2.5-2.5 which were assumed to have compositions equivalent to their feed. Previous studies of AM copolymers with NaAMPS or AMPTAC showed low concentrations of charged monomers in the feed provided random incorporation regardless of the conversion^{2,12,15}. The terpolymerizations were terminated at low conversion (<30% except for ATASAM 0.5-0.5) as an added precaution against compositional drift. Relatively good agreement between the feed compositions and the terpolymer compositions is shown in Table 1.

In these terpolymerizations it is unlikely that the charged units exist in pairs along the polymer chain. Previous studies have demonstrated that addition of sodium chloride lowers monomer-monomer and monomer-polymer electrostatic interactions during polymerization^{2,16,17}. A similar shielding effect would be expected to eliminate monomer pairing thus producing polyampholytes with charged monomers distributed randomly along the polymer chain. It is also interesting that attempts to synthesize these polyampholytes without added electrolytes were not successful due to phase separation of the reaction mixture.

Light scattering studies

Classical and quasielastic light scattering data for the ATASAM series are presented in Table 2. Molecular weights range from 2.78×10^6 to $6.77 \times 10^6 \text{ g mol}^{-1}$. Terpolymers with similar degrees of polymerization show decreasing second virial coefficient (A_2) values with increasing charge density. This trend is consistent with that of recently prepared sulphobetaine copolymers of AM with the zwitterionic monomer 3-(2-acrylamido-2-methylpropanedimethylammonio)-1-propanesulphonate^{3,4}.

The mean polymer diffusion coefficients (D_0) and hydrodynamic diameters (d_h) are consistent with degrees of polymerization and A_2 values. Decreasing solvation is indicated by decreasing A_2 , lower d_h and larger D_0 values. The terpolymer ATASAM 5-5 has a degree of polymerization similar to ATASAM 10-10 but has greater A_2 and d_h values.

Viscometric studies

The dilute solution behaviour of the ATASAM series was studied in relationship to copolymer composition and added electrolyte concentration. Apparent viscosities of the polymers were measured at polymer concentrations below C^* , the critical overlap concentration, using a Contraves LS-30 low shear rheometer. The solutions were aged 2-3 weeks to allow complete solvation. Intrinsic viscosities were calculated using the Huggins relationship

Effects of terpolymer composition. The terpolymers with approximately balanced molar concentrations of NaAMPS and AMPTAC exhibit polyampholyte behaviour. ATASAM 5-10 displays polyelectrolyte behaviour as a direct result of the charge imbalance. For ATASAM 0.5-0.5 and ATASAM 2.5-2.5 the charge density is not sufficient to produce major changes in viscosity, however slight increases in intrinsic viscosity were observed with increasing salt concentration.

Effects of added electrolytes. The effects of sodium chloride on the intrinsic viscosities of the ATASAM terpolymers were measured at a shear rate of 5.96 s^{-1} at 25°C as shown in Figure 2. ATASAM 5-5 displays a dramatic increase in viscosity with the addition of a small amount of sodium chloride. This is indicative of the elimination of intramolecular interactions and the resulting coil expansion.

The terpolymers ATASAM 10-10 and ATASAM 15-15 display complex behaviour with increasing salt concentration. The presence of a small amount of electrolyte is

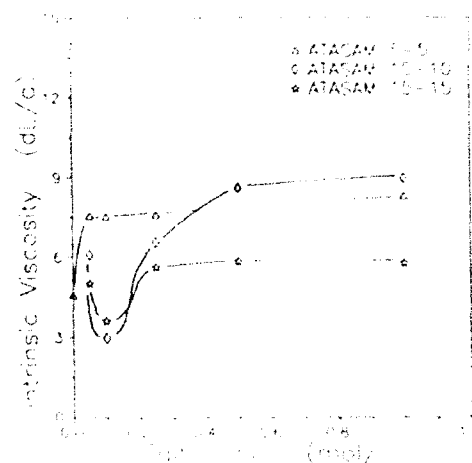


Figure 2. Effects of sodium chloride on the intrinsic viscosities of ATASAM terpolymers determined at a shear rate of 5.96 s^{-1} at 25°C.

Table 2. Classical and quasielastic light scattering data for terpolymers of AM with NaAMPS and AMPTAC

Sample number	d_h (Å)	$M_w (\times 10^{-6})$ (g mol^{-1})	$A_2 (\times 10^4)$ ($\text{ml}^2 \text{mol}^{-2}$)	$D_0 (\times 10^5)$ ($\text{cm}^2 \text{s}^{-1}$)	α (Å)	$[DP] (\times 10^{-2})$
ATASAM 0.5-0.5	0.1476	6.03	2.90	3.52	100	8.25
ATASAM 2.5-2.5	0.1281	7.78	1.6	3.45	85	7.61
ATASAM 5-5	0.1510	5.07	2.66	3.61	120	8.48
ATASAM 10-10	0.1395	5.87	1.57	3.47	100	8.44
ATASAM 15-15	0.1341	6.77	1.31	3.73	104	7.74
ATASAM 10-5	0.1316	3.88	1.59	3.43	100	5.48

^a Determined in 0.01 M NaCl at 25°C.

^b $[DP]$ degree of polymerization.

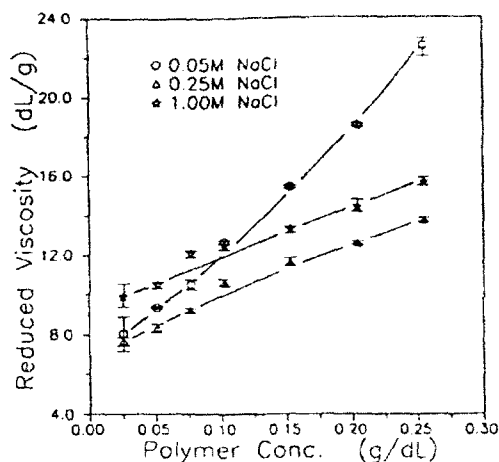


Figure 3 Reduced viscosities of the ATASAM 10-10 terpolymer as a function of polymer concentration at various ionic strengths determined at a shear rate of 5.96 s^{-1} at 25°C . The bars represent the distribution of the data

required to solubilize both terpolymers. A slight increase in the ionic strength initially produces a decrease in intrinsic viscosity, likely due to the elimination of intermolecular molecular interactions with increasing ionic strength²⁻⁷. As the ionic strength increases further, the intrinsic viscosities increase as intramolecular interactions are reduced and chain solvation is enhanced.

Figure 3 displays the reduced viscosity of ATASAM 10-10 as a function of polymer concentration at three ionic strengths. Intermolecular interactions exist in 0.05 M NaCl as suggested by the large reduced viscosities above C^* ($\sim 0.15 \text{ g/dL}$ polymer concentration). Polymer aggregation is likely occurring at low salt concentration. In 0.25 M NaCl the reduced viscosities above C^* decrease as intermolecular interactions are disrupted. Remaining intramolecular interactions in 0.25 M NaCl are eliminated resulting in increased reduced viscosity at 1.0 M NaCl .

CONCLUSIONS

Synthesis of the ampholytic ATASAM terpolymers in NaCl solutions allowed the incorporation of charged monomers in equal amounts and in random sequences. Molecular weights and $\bar{M}_w$ values varied from 2.78×10^4 to $6.77 \times 10^4 \text{ g/mol}$ and 1.31 to $2.95 \text{ ml/mol g}^{-1}$, respectively. Solution properties were studied as functions of terpolymer composition as determined by

^{13}C n.m.r. and ionic strength. Polyampholyte behaviour was observed for the polymer with as little as $0.5 \text{ mol\%}$ of each charged group and became significant when $7 \text{ mol\%}$ of each charged monomer was incorporated. ATASAM 5-5 displayed an 80% increase in intrinsic viscosity in 1 M NaCl compared to deionized water. At 12 and $15 \text{ mol\%}$ incorporation of each charged monomer, the solution behaviour was complex with increasing ionic strength. These polymers were insoluble in deionized water but dissolved in 0.05 M NaCl . Increasing the ionic strength to 0.1 M NaCl led to a decrease in intrinsic viscosity, the result of elimination of intermolecular interactions, i.e. aggregates. Further increases in ionic strength led to disruption of intramolecular interactions and an increase in intrinsic viscosity.

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Water soluble copolymers: 46. Hydrophilic sulphobetaine copolymers of acrylamide and 3-(2-acrylamido-2-methylpropanedimethylammonio)-1-propanesulphonate

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The free radical copolymerization of acrylamide (AM) with 3-(2-acrylamido-2-methylpropanedimethylammonio)-1-propanesulphonate (AMPDAPS) has been studied in the range from 99 to 25% AM in the feed. Copolymer compositions obtained by elemental analysis and ^{13}C n.m.r. reflect the monomer feed concentrations. The value of $r_1 r_2$ has been determined to be 0.60 for the AM-AMPDAPS pair. Copolymer microstructures, including run numbers and sequence distributions, were calculated from the reactivity ratios. Molecular weights for the series range from 3.0×10^6 to $21.5 \times 10^6 \text{ g mol}^{-1}$. Second virial coefficients decrease from 2.67 to $0.21 \text{ ml mol g}^{-2}$ as charge density increases. Intrinsic viscosities decrease with increasing AMPDAPS content, but increase with increasing temperature (in the range of 25–60°C) and added electrolytes (NaCl and/or CaCl_2). The solution behaviour of the homopolymer of AMPDAPS is independent of pH. The observed properties are consistent with the charge density of the polymers and the sulphobetaine structure of the AMPDAPS monomer.

(Keywords: copolymers; free radicals; acrylamide)

INTRODUCTION

Synthetic polyampholytes can be prepared from zwitterionic monomers which exhibit the requisite net charge of zero at appropriate pH. The positive charge is provided by a quaternary ammonium functionality and the negative charge is provided by a carboxylate or sulphonate group (betaine and sulphobetaine). A number of investigations have focused on the unusual properties of zwitterionic polyampholytes.

Ladenheim and Morawetz reported the reaction poly(4-vinyl pyridine) with ethyl bromoacetate followed by hydrolysis of the ester to give high charge density polyampholytes¹. Hart and Timmerman prepared sulphobetaine polyampholytes by reacting poly(2-pyridine) with sultones or by polymerizing the sultone derivative of 4-vinylpyridine². Salamone *et al.* synthesized a variety of sulphobetaines based on vinylimidazole³.

Galin and co-workers conducted an elegant study of poly(sulphobetaines) with various structures^{4–7}. They described the synthesis of a series of polyampholytes by the quaternization of vinylamines with 1,3-propanesultone. Utilizing the Mark–Howink–Sakurada relationship, the existence of specific dipolar intramolecular interactions between lateral zwitterions was established. They concluded that in the presence of electrolytes, a polyampholyte behaved like a random coil of moderate flexibility in a thermodynamically very poor solvent.

Schulz *et al.*⁸ have examined the phase behaviour and solution properties of the homopolymer of the commercially available monomer *N*-(3-sulphopropyl)-*N*-methacroyloxyethyl-*N,N*-dimethylammonium betaine (SPE). Negative A_2 values were found for the polyampholyte in solutions of low ionic strength; positive values were found as the ionic strength increased. Highly alternating copolymers of *N*-vinylpyrrolidone (NVP) with SPE which showed polyampholyte behaviour in solution were also researched⁹.

Wielma studied the synthesis and solution properties of zwitterionic betaine and sulphobetaine polymers with one, two or three methylene units between the charged groups¹⁰. Varying degrees of ionization were achieved for the carboxylate groups by controlling the pH. At high pH values the polymers behaved as polyampholytes while at low pH values, polyelectrolyte behaviour was observed. It was concluded that strong intramolecular coulombic interactions were the dominant factor in the solubility behaviour of zwitterionic polymers.

Previous research in our laboratories focused on polyampholyte co- and terpolymers prepared by incorporation of cationic and anionic monomers^{11–15}. Rheological characteristics, particularly pH and electrolyte responsiveness, can be readily changed by microstructural manipulation during synthesis. Recently we have initiated studies of polyampholytes prepared from zwitterionic monomers which would have similar structural characteristics^{16–17}. In this paper we report the synthesis and characterization of a series of

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copolymers of acrylamide with the novel amphoteric monomer 3-(2-acrylamido-2-methylpropanedimethylammonio)-1-propanesulphonate (AMPDAPS).

EXPERIMENTAL

Materials and monomer synthesis

AMPDAPS was synthesized by the ring opening reaction of 1,3-cyclopropanesultone (PS) with 2-acrylamido-2-methylpropanedimethylamine (AMPDA; Figure 1). 1,3-Cyclopropanesultone (Aldrich) was used without further purification. The synthesis of AMPDA has been previously reported by our laboratories¹⁹. In a typical monomer synthesis, 0.144 mol AMPDA and 0.156 mol PS were reacted in 500 ml propylene carbonate under N₂ at 55 °C for 4 days. During this period the product formed as a white precipitate. This was then filtered and washed with diethyl ether until all the propylene carbonate was removed. AMPDAPS (m.p. 220–224 °C) was obtained in 80% yield. Analysis for C₁₂H₂₄N₂O₄S. Calculated: C, 49.29%; H, 8.29%; N, 9.58%; S, 10.96%. Found: C, 49.07%; H, 8.27%; N, 9.56%; S, 11.12%. I.r.: N–H, 3280 cm⁻¹ (m); C=C–H, 2990 cm⁻¹; aliphatic C–H, 2940 cm⁻¹; amide C=O, 1660 cm⁻¹ (s) and 1550 cm⁻¹ (s); S–O, 1200 cm⁻¹ (s).

Acrylamide (AM; Aldrich) was recrystallized twice from acetone and vacuum dried at room temperature. Potassium persulphate (J. T. Baker) was recrystallized twice from deionized water.

Synthesis of copolymers of AMPDAPS with AM

The homopolymer of AMPDAPS and the copolymers of AMPDAPS with AM (the DAPSAM series) were synthesized by free radical polymerization in a 0.5 M NaCl aqueous solution under nitrogen at 30 °C using 0.1 mol% potassium persulphate as the initiator. The feed ratio of AM:AMPDAPS was varied from 99:1 to 25:75 mol% with the total monomer concentration held constant at 0.45 M. The use of 0.5 M NaCl as the reaction medium ensured that polymers with high AMPDAPS content remained homogeneous during polymerization.

In a typical synthesis, specified quantities of each monomer were dissolved in small volumes of NaCl solution. The separate solutions were then combined and diluted to a 0.45 M monomer concentration. After the pH was adjusted to 7, the reaction mixture was sparged with nitrogen for 20 min then initiated with 0.1 mol% potassium persulphate. A low conversion sample was always analysed to allow reactivity ratio studies. The reaction was usually terminated at <30% conversion due to the high viscosity of the reaction medium and as

a precaution against copolymer drift. The polymers were precipitated in acetone, redissolved in deionized water, then dialysed using Spectra Por 4 dialysis bags with molecular weight cutoffs of 12 000–14 000 g mol⁻¹. After isolation by lyophilization the polymers were stored in desiccators with a nitrogen atmosphere.

When more than 40 mol% AMPDAPS was incorporated in the copolymers swelling but not dissolution could be achieved in deionized water. These 'hydrogels' were washed repeatedly with deionized water to remove any remaining salt or monomer and then lyophilized. Conversions were determined gravimetrically. Table 1 lists reaction parameters for the copolymerization of AMPDAPS with AM and the homopolymerization of AMPDAPS. I.r.: DAPSAM-100 homopolymer: N–H 3200 cm⁻¹ (s); C–H 3050 cm⁻¹ (m) and 2980 cm⁻¹ (m); C=O 1650 cm⁻¹ (s); S–O 1200 cm⁻¹ (s). Typical copolymer: DAPSAM-75: N–H 3290 cm⁻¹ (s); C–H 3050 cm⁻¹ (m) and 2980 cm⁻¹ (m); C=O 1670 cm⁻¹ (s); S–O 1200 cm⁻¹ (s).

Copolymer characterization

Elemental analyses for carbon, hydrogen and nitrogen were conducted by M-H-W Laboratories (Phoenix, AZ) on both the low and high conversion copolymer samples. ¹³C n.m.r. spectra of the DAPSAM polymers were obtained using 5–10 wt% aqueous (D₂O) polymer solutions with DSS as the reference. The procedure for quantitatively determining copolymer compositions from ¹³C n.m.r. has been discussed in detail elsewhere²⁰. I.T.I.r. spectra for all materials synthesized were obtained using a Perkin-Elmer 1600 Series I.T.I.r. spectrophotometer. Molecular weight studies were performed on a Chromatix KMX-6 low angle laser light scattering instrument. Refractive index increments were obtained using a Chromatix KMX-16 laser differential refractometer. For quasielastic light scattering a Langley-Ford Model LFI-64 channel digital correlator was used in conjunction with the KMX-6. All measurements were conducted at 25 °C in 1 M NaCl at pH 7.0 ± 0.1.

Viscosity measurements

Stock solutions of sodium chloride were prepared by dissolving the appropriate amount of salt in deionized water in volumetric flasks. Polymer stock solutions were made by dissolving designated amounts of polymer in the salt solutions. The solutions were then diluted to appropriate concentrations and allowed to age for 2–3 weeks before being analysed with a Contraves LS-30 rheometer. Triplicate samples were prepared of each concentration to reduce experimental error. Intrinsic viscosities were evaluated using the Huggins equation²¹. The modified Einstein-Simha equation was used to calculate the intrinsic viscosities for DAPSAM-40-3 as a function of temperature²².

RESULTS AND DISCUSSION

Compositional analysis

The copolymers of AMPDAPS with AM (the DAPSAM series) were synthesized by varying the feed ratios of AM:AMPDAPS from 99:1 to 25:75 mol%. Reaction parameters and the resulting compositions for the polymers are given in Table 1. Copolymer compositions were determined from ¹³C n.m.r. and

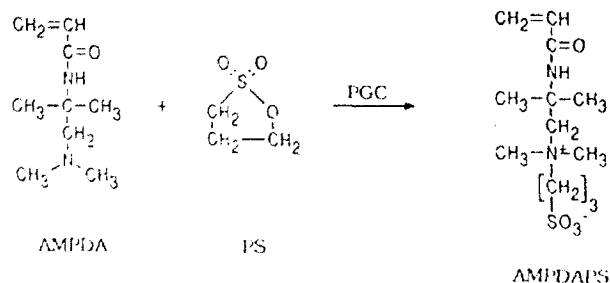
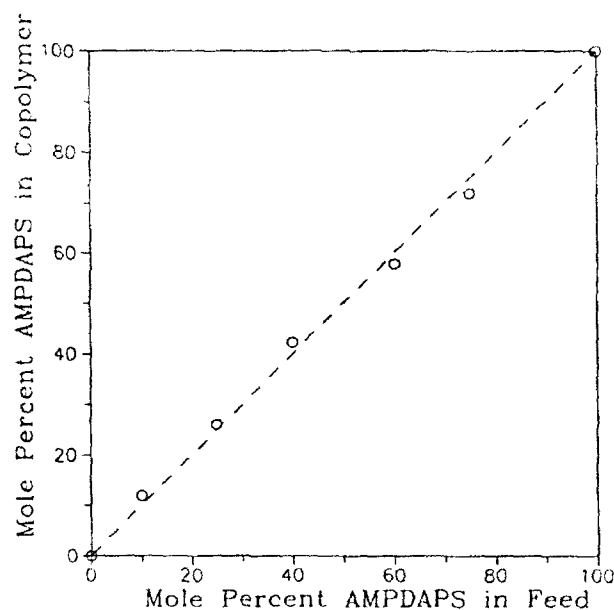


Figure 1. Synthesis of 3-(2-acrylamido-2-methylpropanedimethylammonio)-1-propanesulphonate (AMPDAPS).

Table 1 Reaction parameters for the copolymerization of acrylamide (AM) with 3-(2-acrylamido-2-methylpropanedimethylammonio)-1-propanesulphonate (AMPDAPS)

Sample number	Feed ratio AM:AMPDAPS	Reaction time (h)	Conversion (%)	C (wt%)	N (wt%)	AMPDAPS in copolymer (mol%) ^a	AMPDAPS in copolymer (mol%) ^b
DAPSAM-1	99:1	5.0	28.8	—	—	1 ^c	1 ^c
DAPSAM-5	95:5	5.0	27.4	—	—	5 ^c	5 ^c
DAPSAM-10-1	90:10	2.8	12.9	45.47	14.59	11.9 ± 0.4	10.0 ± 0.6
DAPSAM-10-2	90:10	4.5	22.1	—	—	—	9.6 ± 0.6
DAPSAM-10-3	90:10	3.0	23.4	—	—	—	10.0 ± 0.8
DAPSAM-25-1	75:25	4.5	3.4	43.74	12.04	26.0 ± 0.8	26.0 ± 1.6
DAPSAM-25-2	75:25	23	44.9	41.04	11.13	27.7 ± 0.8	—
DAPSAM-40-1	60:40	2.0	9.2	44.11	10.77	42.1 ± 1.3	38.3 ± 2.3
DAPSAM-40-2	60:40	4.8	16.7	43.95	10.77	38.9 ± 1.2	—
DAPSAM-40-3	60:40	3.3	38.2	—	—	—	40.0 ± 2.4
DAPSAM-60-1	40:60	2.0	9.2	44.39	9.96	57.9 ± 1.7	57.3 ± 3.4
DAPSAM-60-2	40:60	4.8	16.7	44.44	9.93	58.8 ± 1.7	—
DAPSAM-75-1	25:75	3.0	12.2	44.35	9.39	71.9 ± 2.2	69.2 ± 4.2
DAPSAM-75-2	25:75	7.0	24.7	44.43	9.47	70.1 ± 2.2	—
DAPSAM-100	0:100	10	56.8	—	—	100 ^c	100 ^c

^a Determined from elemental analysis^b Determined from ¹³C n.m.r.^c Theoretical value**Figure 2** Mole percent AMPDAPS incorporated into the copolymers as a function of comonomer feed ratio

elemental analysis data. Integration of ¹³C carbonyl peaks gave the mol% of AM and AMPDAPS in the copolymers, which agrees favourably with that derived from elemental analysis. The copolymer compositions as a function of feed composition for the DAPSAM series are shown in *Figure 2*. The copolymerization curve follows closely that of an ideally random system represented by the dashed line.

Reactivity ratio and microstructure studies

Reactivity ratio values for the AMPDAPS series were determined from monomer feed ratios and resultant

copolymer compositions obtained at low conversions. Fineman-Ross²³ and Kelen-Tüdös²⁴ methods were used to determine the monomer reactivity ratios. The Fineman-Ross method yielded reactivity ratios for AM and AMPDAPS of $r_1 = 0.79$ and $r_2 = 0.73$. The Kelen-Tüdös method gave reactivity ratios of 0.79 and 0.75 for r_1 and r_2 , respectively and $r_1 r_2 = 0.60$. The experimental data indicate random comonomer incorporation with a slight alternating tendency.

To elucidate the microstructural features of these copolymers, the equations of Igarashi²⁵ and Pyun²⁶ were employed. The fractions of AM-AM, AMPDAPS-AMPDAPS, and AM-AMPDAPS units (the mol% blockiness, the mol% alternation, and the mean sequence length) in the copolymers were calculated from the reactivity ratios and the copolymer compositions (*Table 2*). The mean sequence lengths of AM and AMPDAPS reverse in value when the amount of AMPDAPS in the copolymers increases from 25 and 40 mol% to 60 and 75 mol%. This behaviour is indicative of a random microstructure.

Low angle laser light scattering

Weight-average molecular weights were determined by classical low-angle laser light scattering. *Table 3* shows the data obtained at 25 °C in 1 M NaCl. The molecular weights vary from 3.0×10^6 to 21.5×10^6 g mol⁻¹. For polymers prepared under similar conditions (initiator concentration, reaction conversion, etc.), the more AMPDAPS in the feed, the lower the molecular weight of the resulting polymer. The similar molecular weights of DAPSAM-10 and -25, and DAPSAM-60 and -75 allow meaningful assessments of the effects of copolymer composition on solution behaviour.

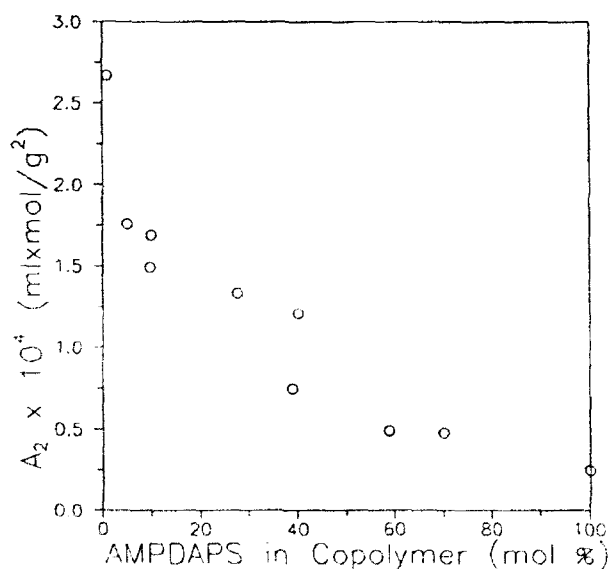
The second virial coefficients (A_2) decrease with increasing AMPDAPS content in the copolymers, as shown in *Figure 3*. This is the opposite of polyelectrolytes which have increasing A_2 values with increasing charge

Table 2 Structural data calculated for the copolymers of acrylamide M_1 (AM) with 3-(2-acrylamido-2-methylpropanedimethylammonio)-1-propanesulphonate M_2 (AMPDAPS)^a

Sample number	M_2 in copolymer (mol%) ^b	Blockiness (mol%)		Alternation (mol%) M_1-M_2	Mean sequence length	
		M_1-M_2	M_2-M_2		M_1	M_2
DAPSAM-10-1	11.9	77.2	0.9	21.9	8.2	1.1
DAPSAM-25-1	26.0	53.0	5.0	42.0	3.4	1.3
DAPSAM-40-1	42.9	30.4	14.8	54.8	2.2	1.5
DAPSAM-60-1	57.9	14.7	30.5	54.8	1.5	2.1
DAPSAM-75-1	71.9	6.0	49.7	44.4	1.3	3.3

^a Determined with $r_1 = 0.79$ and $r_2 = 0.75$ ^b Determined from elemental analysis**Table 3** Classical and quasielastic light scattering data for copolymers of acrylamide (AM) with 3-(2-acrylamido-2-methylpropanedimethylammonio)-1-propanesulphonate (AMPDAPS)

Sample number	AMPDAPS in copolymer (mol%) ^a	dn/dc	M_w ($\times 10^{-6}$ g mol ⁻¹)	A_2 ($\times 10^4$ ml mol ⁻² g ⁻²)	$D_w \times 10^8$ (cm ² s ⁻¹)	d_w (Å)	DP ($\times 10^{-4}$)
DAPSAM-1	1 ^c	0.1450	3.2	2.67	5.05	1170	4.45
DAPSAM-5	5 ^c	0.1520	12.4	1.76	3.16	1650	15.1
DAPSAM-10-2	9.6	0.1385	7.0	1.49	4.01	1380	7.50
DAPSAM-10-3	10 ^b	0.1436	21.5	1.69	3.20	1530	23.0
DAPSAM-25-2	27.7	0.1395	8.2	1.33	3.97	1180	6.35
DAPSAM-40-2	38.9	0.1224	15.1	0.78	3.62	1420	9.57
DAPSAM-40-3	40 ^b	0.1546	17.5	1.21	3.24	1560	11.0
DAPSAM-60-2	58.8	0.1480	5.4	0.49	3.60	1430	2.71
DAPSAM-75-2	70.1	0.1293	6.2	0.48	4.90	1060	2.63
DAPSAM-100	100 ^c	0.1322	3.0	0.25	6.28	870	1.67

^a Determined from elemental analysis^b Determined from ¹³C n.m.r.^c Theoretical**Figure 3** Dependence of the second virial coefficient (A_2) on the composition of the DAPSAM polymers (determined in 1 M NaCl at 25 °C)

density. In deionized water, copolymers with compositions greater than 40 mol% AMPDAPS are insoluble. Solubility is achieved in the presence of electrolytes; however, even in 1 M NaCl, A_2 values are

less than those of DAPSAM-1 which approximates a neutral polyacrylamide sample.

Quasielastic light scattering (q.l.s.) data are presented in Table 3 and illustrated in Figures 4 and 5. The mean polymer diffusion coefficients (D_w) and diameters (d_w) for all copolymer systems in 1 M NaCl show some dependence on the degree of polymerization and on the weight-average molecular weight. As degree of polymerization and molecular weight increase, D_w values decrease (d_w increase). The scatter in the data is, of course, due to solvation differences with compositional changes, a conclusion clearly supported by A_2 values.

Dilute solution properties

Effects of copolymer composition. The effects of copolymer composition on the intrinsic viscosities of the DAPSAM copolymers (Table 2) in 0.514 M NaCl are shown in Figure 6. The decrease in the intrinsic viscosities is due to decreases in molecular weight as well as increasing intramolecular interactions which constrict the polymer coils. The presence of the AMPDAPS monomer units is responsible for the latter, as demonstrated by the second virial coefficients. For DAPSAM-60 and -75, which have similar molecular weights and degrees of polymerization, increasing AMPDAPS concentration decreases the respective intrinsic viscosities. Schulz *et al.* postulated these interactions to be based on electrostatic attractions between opposite charges of different sulphobetaine units⁸. One might expect such effects to

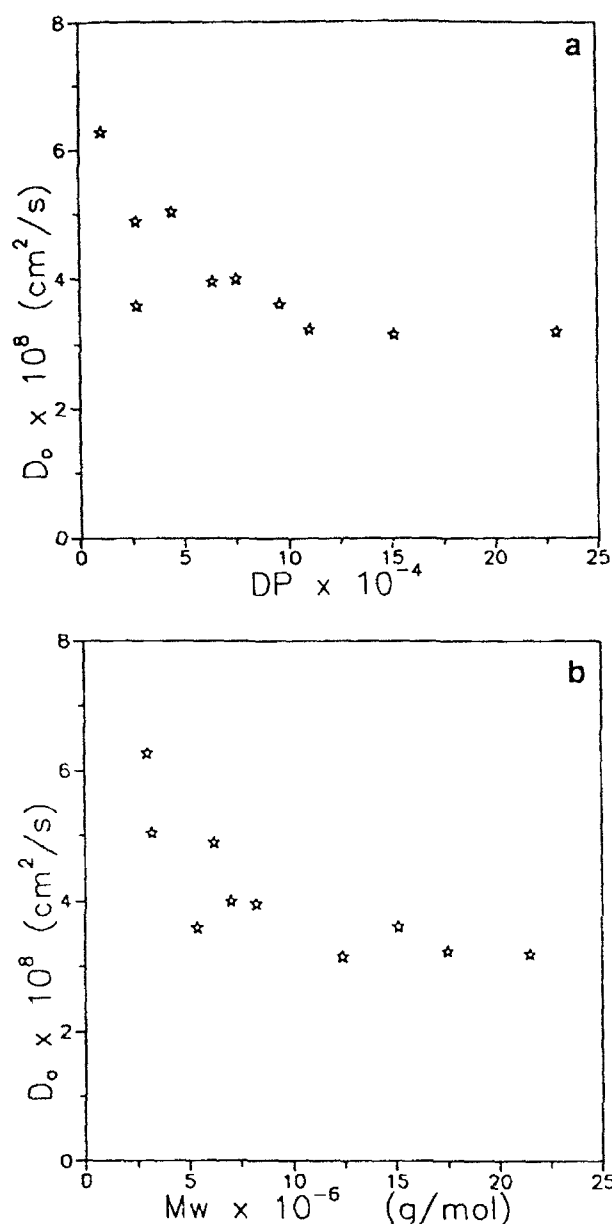


Figure 4 Dependence of the diffusion coefficient (D_o) on (a) degree of polymerization and (b) molecular weight of the DAPSAM copolymers (determined by q.l.s. in 1 M NaCl at 25 °C)

be especially strong as microheterogeneous associations lead to local decreases in dielectric constant of the domains.

Effects of added electrolytes. The effects of sodium chloride on the intrinsic viscosities of the DAPSAM copolymers and the AMPDAPS homopolymer were determined at a shear rate of 1.75 s^{-1} as shown in Figure 7. The polymer solutions show increasing intrinsic viscosities as the amount of salt in the solutions increases. Some of the polymers do not dissolve unless salt is present. DAPSAM-60 and DAPSAM-75 require 0.0428 M NaCl, and DAPSAM-100 needs 0.257 M NaCl for dissolution. Attempts to remove the salt from the polymers by dialysis result in phase separation of the polymers from solution.

The initial decreases in intrinsic viscosity for DAPSAM-10 and DAPSAM-25 are due to the elimination of intermolecular interactions with increasing ionic strength. This behaviour has been observed with other polyampholyte systems^{1,15,17,18}. DAPSAM-40, which possesses a higher charge density, experiences a disruption of intramolecular interactions with increasing ionic strength. In all cases the intrinsic viscosities increase significantly.

Figure 8 demonstrates the effects of adding the divalent salt calcium chloride to solutions of the DAPSAM copolymers and the AMPDAPS homopolymer. DAPSAM-60, -70, and the AMPDAPS homopolymer are insoluble up to a critical concentration.

A number of studies by other research groups have attempted to find evidence for the existence of

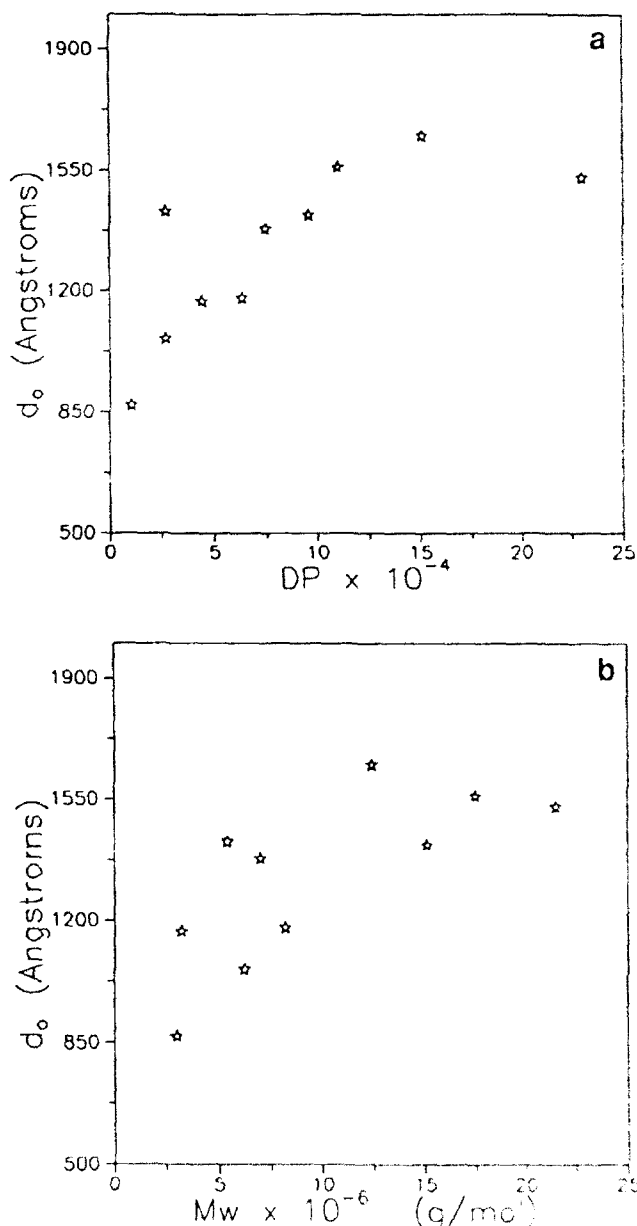


Figure 5 Dependence of copolymer mean diameter (d_o) on (a) degree of polymerization and (b) molecular weight (determined by q.l.s. in 1 M NaCl at 25 °C)

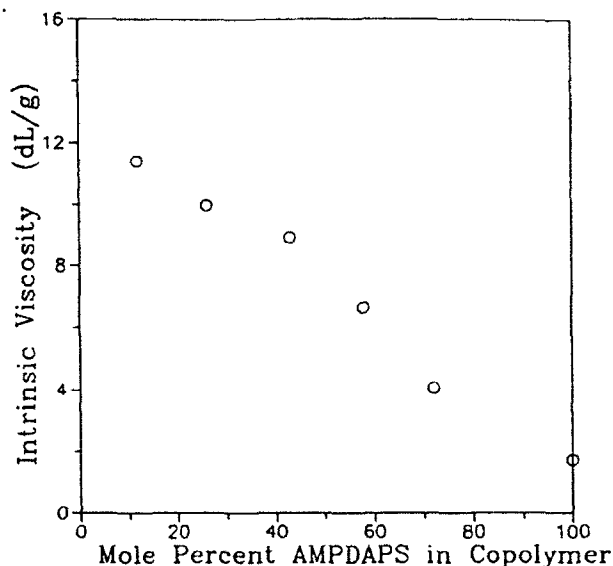


Figure 6 Intrinsic viscosity of DAPSAM copolymers as a function of AMPDAPS incorporated (determined in 0.514 M NaCl at a shear rate of 1.25 s^{-1})

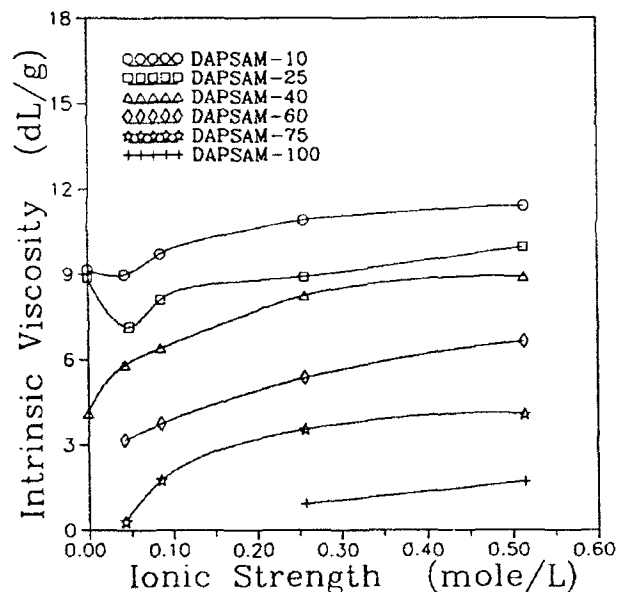


Figure 7 Dependence of the intrinsic viscosity of DAPSAM copolymers on NaCl ionic strength (determined at 25°C at a shear rate of 1.75 s^{-1})

hydrophobic domains within polyampholytes. For sulphobetaine and betaine polyampholytes, it is conceivable that intramer and intramolecular charge-charge associations may lead to such domains. Zheng *et al.* utilized reporter anionic probes to find a polyampholytic environment with the same relative hydrophobicity of methanol⁷. Wielma was unsuccessful in using fluorescent labels on polysulphobetaines to relate macroscopic behaviour, such as increases in solution viscosity, to changes in the microenvironment along the polyampholyte backbone¹⁰.

Our research group is currently active in developing fluorescent probe and label technology^{27,28}. For this

study, however, a simple approach was utilized to assess the presence of hydrophobic domains in the DAPSAM polymers. Urea is a water structure breaker which solubilizes certain molecules by disrupting hydrophobic domains. It follows that if hydrophobic domains exist within polyampholytes, the presence of urea should alter solution behaviour.

Solutions of the copolymers DAPSAM-10-3 and DAPSAM-40-3 were studied in deionized water, 1 M NaCl, 1 M urea, and a mixture of 1 M NaCl and 1 M urea. Figures 9 and 10 show the reduced viscosity for each copolymer as a function of polymer concentration. For each copolymer, the solution in deionized water has

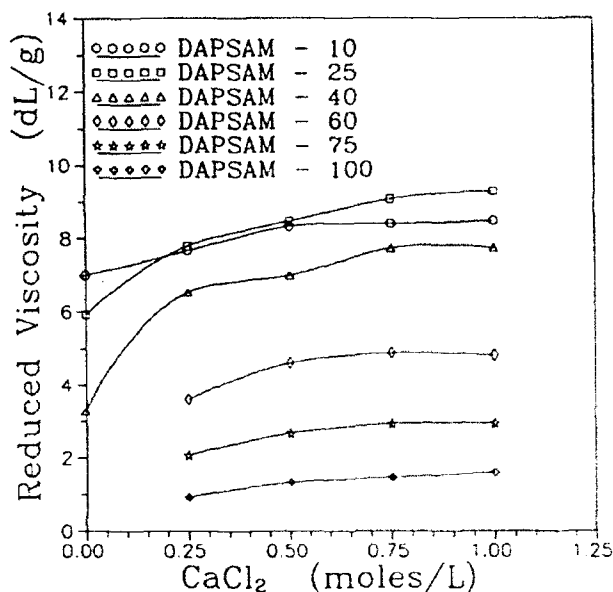


Figure 8 Reduced viscosity of DAPSAM copolymers as a function of CaCl_2 concentration (determined at 25°C at a shear rate of 1.75 s^{-1})

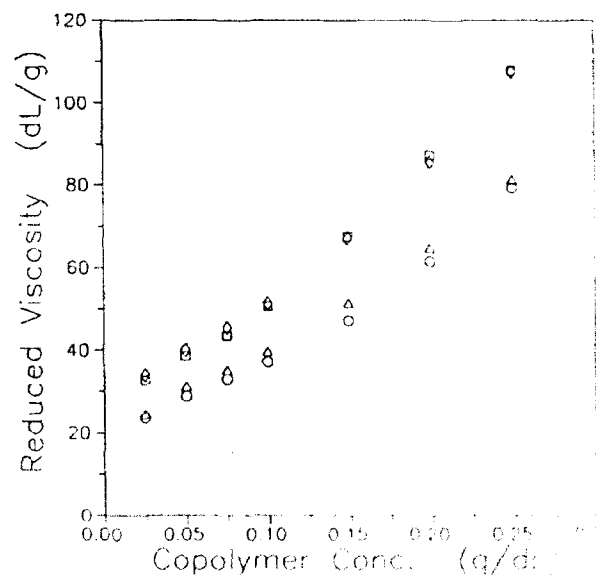


Figure 9 Changes in reduced viscosity of DAPSAM-10 as a function of solvent (determined at 25°C with a shear rate of 5.96 s^{-1}). Deionized water, $\circ$; 1 M NaCl, $\square$; 1 M urea, $\triangle$; 1 M NaCl + 1 M urea, $\diamond$

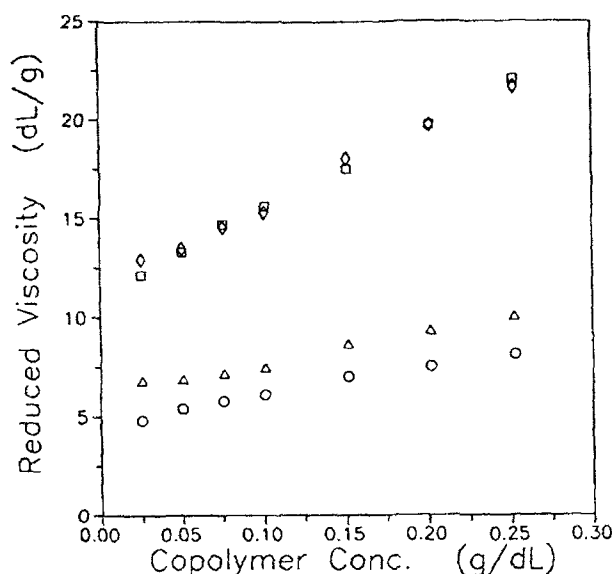


Figure 10 Changes in reduced viscosity of DAPSAM-40 as a function of solvent (determined at 25 °C with a shear rate of 5.96 s^{-1}). ○, Deionized water; □, 1 M NaCl; △, 1 M urea; ◇, 1 M NaCl + 1 M urea

the lowest viscosity. The addition of 1 M urea increases reduced viscosity by only a small amount relative to that produced by the addition of 1 M NaCl. The combination of NaCl and urea yields the same viscosity increase as that attained by 1 M NaCl alone. As a reference, homopolyacrylamide solution shows no change in viscosity in the presence of salt or urea. The slight increase in reduced viscosity for both DAPSAM-10-3 and DAPSAM-40-3 in the presence of urea is most likely due to enhanced hydrogen bonding between the polymers and the solvent. The major effect dominating rheological behaviour appears to be charge screening upon addition of NaCl, yielding better solvated chains. Transition from dilute to semidilute behaviour is more readily observed for the DAPSAM-10-3 sample which is initially less compact than DAPSAM-40-3.

Effects of temperature. Intrinsic viscosities for DAPSAM-40-3 increase with increasing temperature (Figure 11). The copolymer was tested in deionized water in the range 25–60 °C. Most neutral polymers and polyelectrolytes exhibit reductions in viscosity as a function of increasing temperature. In deionized water this behavior exists in a compact conformation as evidenced by second virial coefficients and viscosity data. Temperature increases obviously allow accessibility to more extended conformations and better solvation. Copolymers which were insoluble in deionized water, however, could not be solubilized by the application of heat, apparently as a result of strong intramolecular ionic effects. Interestingly, the DAPSAM copolymers are phase stable to 100 °C in the presence of added electrolytes.

Effects of pH. Although acrylamide can be used as a comonomer to obtain very high molecular weights, hydrolysis can be problematic. Figure 12 shows the effects of pH on DAPSAM-25 in deionized water and in 0.512 M NaCl. At high pH the acrylamide unit is hydrolysed to

the carboxylate ion and a corresponding increase in viscosity is observed for the polymer in deionized water. The presence of salt negates the polyelectrolyte effect and disrupts zwitterionic intramolecular interactions. The solution viscosities of the DAPSAM-100 homopolymer are independent of pH in 0.512 M NaCl. Resistance of the AMPDAPS monomer to hydrolysis is due to the presence of geminal methyl groups next to the amide functionality. This protecting group has been used in other hydrolytically stable monomers such as sodium 2-acrylamido-2-methylpropanesulphonate (NaAMPS)²⁹ and sodium 3-acrylamido-3-methylbutanoate (NaAMB)³⁰

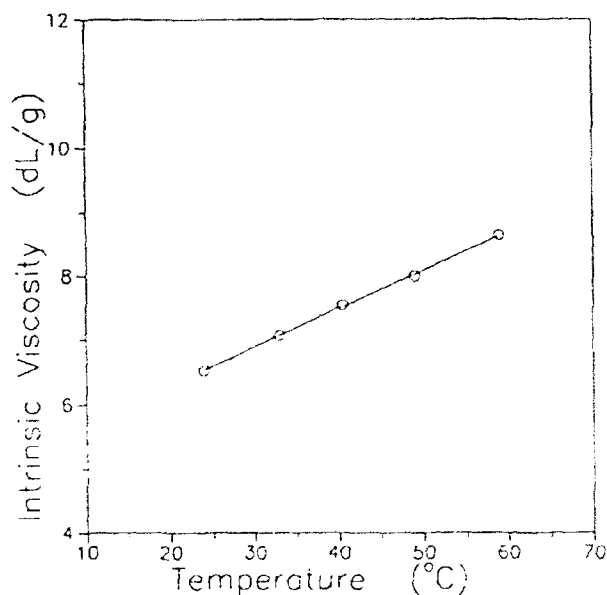


Figure 11 Intrinsic viscosity of the DAPSAM-40-3 copolymer as a function of temperature (determined in deionized water at a shear rate of 5.96 s^{-1})

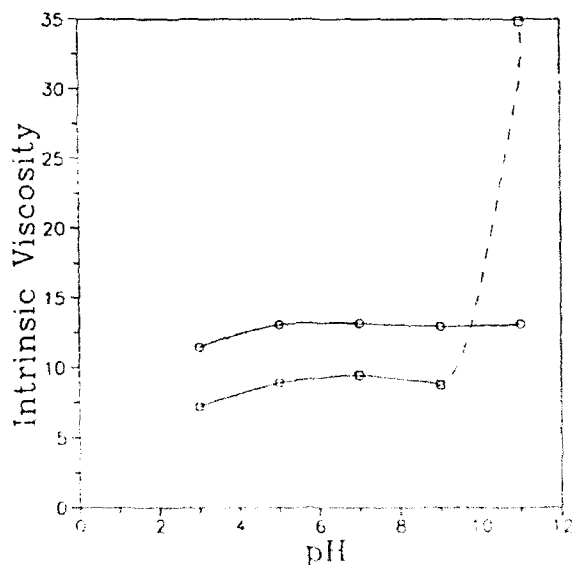


Figure 12 Intrinsic viscosity of DAPSAM-25 as a function of pH in (○) deionized water; (□) 0.512 M NaCl (determined at 20 °C with a shear rate of 1.25 s^{-1})

CONCLUSIONS

The new sulphobetaine monomer 3-(2-acrylamido-2-methylpropanedimethylammonio)-1-propanesulphonate (AMPDAPS) has been synthesized and incorporated into a series of copolymers (the DAPSAM series) with AM as the comonomer. The polymers were examined by ^{13}C n.m.r., FTi.r., elemental analysis and low angle laser light scattering. Elemental analysis data from low conversion samples gave $r_1 r_2 = 0.60$ for the AM-AMPDAPS monomer pair. Copolymer microstructures were statistically determined from reactivity ratios and found to be random with a slight alternating tendency. Weight-average molecular weights in the range of 3.0×10^6 to $21.5 \times 10^6 \text{ g mol}^{-1}$ have been determined for the polymers. Second virial coefficients were found to decrease in value as the zwitterion content of the copolymers increased.

Increasing concentrations of AMPDAPS decrease the intrinsic viscosities of the copolymers. Copolymers containing more than 40 mol% AMPDAPS are insoluble in deionized water but readily dissolve in the presence of NaCl. The copolymers display increased viscosity upon addition of NaCl and CaCl_2 ; intramolecular interactions are responsible for this effect. Intrinsic viscosities increase in the temperature range 25–60°C.

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Water-Soluble Copolymers. XLII. Cationic Polyelectrolytes of Acrylamide and 2-Acrylamido-2-methylpropanetrimethylammonium Chloride

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SYNOPSIS

The new monomer 2-acrylamido-2-methylpropanetrimethylammonium chloride (AMPTAC, M_2) has been synthesized. Free radical copolymerization with acrylamide (AM, M_1) in feed ratios varying from 10 to 50 mol % AMPTAC gave the cationic ATAM series. Copolymer compositions were determined from ^{13}C -NMR. The reactivity ratio product r_1r_2 was found to be 0.62. Molecular weights varied from 1.4 to 16.5×10^6 g/mol for the copolymers. Turbidimetric studies showed aqueous solutions of the copolymers to be phase stable in the presence of CaCl_2 and Na_2CO_3 up to 100°C . Solution behavior was independent of pH in the range of 3 to 11, and temperature in the range of 25 to 60°C . Intrinsic viscosities of the cationic copolymers decreased with the addition of electrolytes; however, some samples showed curvature in plots of intrinsic viscosity versus the inverse square root of ionic strength. © 1993 John Wiley & Sons, Inc.

Keywords: polyelectrolyte • polycation • acrylamide • water soluble • phase stability

INTRODUCTION

Acrylamide based polyelectrolytes are of increasing interest for a wide variety of industrial applications. Several examples of the uses of cationic polymers are in such areas as paper products, flocculation, film coatings, and membranes.¹ Polymers containing the cationic monomer 2-acrylamido-2-methylpropanedimethylammonium hydrochloride (AMPDAC) have been studied in our laboratories by McCormick et al.²⁻⁷ Depending on pH and local microstructure the number of protonated and free amine units varied under different solvation conditions. The new monomer 2-acrylamido-2-methylpropanetrimethylammonium chloride (AMPTAC, M_2) has been synthesized which features a quaternized ammonium moiety stabilized from hydrolysis by a gem-dimethyl group.^{8,9} The monomer possess

an acrylamido functionality which readily polymerizes in aqueous solution.

Copolymers of this new monomer with acrylamide (the ATAM series) have been synthesized with a variety of compositions. Experiments were conducted to determine reactivity ratios which were (in turn) used to statistically elucidate the microstructure of the copolymers. Dilute solution viscosity behavior was examined as a function of composition, pH, temperature, and added electrolytes. Phase behavior was also studied as a function of added electrolytes.

EXPERIMENTAL

Materials and Monomer Synthesis

The synthesis of 2-acrylamido-2-methylpropanetrimethylammonium chloride (AMPTAC) involved a multistep procedure (Fig. 1). In the first step 2-acrylamido-2-methylpropanedimethylamine (AMPDA) was synthesized using the procedure of McCormick and Blackmon.² This precursor was

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further reacted with methyl iodide and then ion-exchanged to yield the product AMPTAC.

Acryloyl chloride obtained from Aldrich and 1-dimethylamino-2-amino-2-methylpropane supplied by Angus were used without further purification. A typical synthesis involved the dissolution of 0.5 mol of diamine precursor in 400 mL of tetrahydrofuran (THF) in a 1000 mL flask equipped with a mechanical stirrer and an addition funnel. After cooling the reaction mixture to 5–10°C, 0.5 mol of acryloyl chloride were added dropwise over a period of 1–1.5 h. On completion of the addition, the reaction was allowed to proceed for another 5 h at room temperature. The product AMPDAC, a white precipitate, was filtered and dried under vacuum; THF was completely removed to avoid complications in the next step. The crude AMPDAC was dissolved in deionized water and the pH adjusted to 12–13 by the addition of concentrated NaOH. Extraction with chloroform, followed by concentration, provided the uncharged precursor AMPDA. For purification, AMPDA was recrystallized twice using a chloroform/petroleum ether solvent system. Pure AMPDA was then reacted with a 10-fold excess of methyl iodide in diethyl ether. Typically methyl iodide (2.5 mol) from Aldrich was added to 0.25 mol AMPDA in 200 mL of diethyl ether. The reaction was allowed to reflux with stirring for 20 h. This initial reaction gave the quaternarized monomer precursor 2-acrylamido-2-methylpropanetrimethylammonium iodide (AMPTAI) as an off-white precipitate. After isolation by filtration, the precipitate was purified by two recrystallizations employing a 2-propanol/diethyl ether solvent system.

The iodide ion was then ion-exchanged using Dowex Cl^- resin to obtain the desired AMPTAC. Usually the monomer AMPTAC was not isolated but used in solution obtained directly from the ion-exchange column. The quantitative conversion of AMPTAI to AMPTAC allowed the concentration of AMPTAC to be determined from the amount of AMPTAI used and the amount of solution (water/monomer) collected. If isolation was required, a dilute solution of the ion-exchange eluent could be lyophilized to yield AMPTAC. Isolation was avoided if possible due to the occurrence of autopolymerization during lyophilization and the very hygroscopic nature of AMPTAC.

Acrylamide (AM) from Aldrich was recrystallized twice from an acetone/petroleum ether solvent system and vacuum-dried at room temperature prior to use. Potassium persulfate from J. T. Baker was recrystallized twice from deionized water prior to use.

Synthesis of Copolymers of 2-Acrylamido-2-methylpropanetrimethylammonium Chloride with Acrylamide

The ATAM series of copolymers was synthesized by free radical polymerization of 2-acrylamido-2-methylpropanetrimethylammonium chloride (AMPTAC) with acrylamide (AM) in aqueous solution at 30°C using 0.1 mol % potassium persulfate as the initiator. The feed ratio of AM : AMPTAC was varied from 90 : 10 to 50 : 50 with the total monomer concentration held constant at 0.46M.

In a typical synthesis, separate solutions with specific concentrations of each monomer were combined. The pH was adjusted to 7 and the reaction mixture was transferred to a 1000 mL three-necked flask equipped with a mechanical stirrer, nitrogen inlet, and a gas bubbler. The mixture was placed in a 30°C water bath, sparged with nitrogen for 20 min, then initiated with 0.1 mol % of potassium persulfate. The reaction was terminated by precipitating the polymer with acetone at less than 50% conversion. The polymers were purified by dialysis in Spectra/Por 4 dialysis bags with molecular weight cutoffs of 12,000–14,000 Da. After isolation by lyophilization, the copolymers were stored in desiccators under nitrogen.

IR: homopolymer, ATAM-100, $\text{N}-\text{H}$ (broad), 3426–3297 cm^{-1} ; $\text{C}-\text{H}$, 3047–2939 cm^{-1} ; $\text{C}=\text{O}$, 1658 cm^{-1} (s), 1542 cm^{-1} (m); N^+-R_4 , 966 cm^{-1} . Typical copolymer: ATAM-50, $\text{N}-\text{H}$ (broad), 3423 cm^{-1} ; $\text{C}-\text{H}$ 2068–2934 cm^{-1} ; $\text{C}=\text{O}$ 1666 cm^{-1} (s), 1542 cm^{-1} (m); N^+-R_4 , 965 cm^{-1} .

^{13}C -NMR: homopolymer, ATAM-100, $\text{C}=\text{O}$, 178.8 ppm; chain CH_2 , 37.3 ppm; chain CH , 44.6 ppm; CH_2-N^+ , 73.0 ppm; C , 56.8 ppm; gem CH_3 , 30.0 ppm; N^+-CH_3 , 57.9 ppm.

Copolymer Characterization

Copolymer compositions were determined from ^{13}C -NMR by the integration of acrylamido carbonyl peaks.¹⁰ ^{13}C -NMR spectra were obtained using 10 wt/wt % aqueous (D_2O) polymer solutions with DSS as the reference. FT-IR spectra were obtained using a Perkin-Elmer 1600 Series FT-IR spectrophotometer. Molecular weight studies were performed on a Chromatix KMX-6 low angle laser light scattering instrument. Refractive index increments were obtained using a Chromatix KMX-16 laser differential refractometer. For quasielastic light scattering a Langley-Ford Model LF1-64 channel digital correlator was used in conjunction with the KMX-6. All measurements were conducted at 25°C in 1M NaCl.

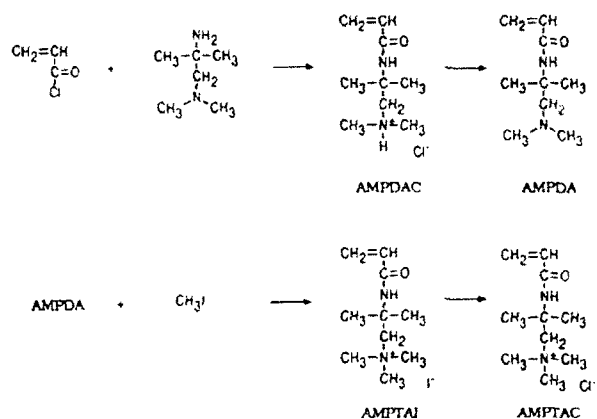


Figure 1. Multistep synthesis of the cationic monomer 2-acrylamido-2-methylpropanetrimethylammonium chloride (AMPTAC).

Viscosity Measurements

Stock solutions of sodium chloride (0.042, 0.086, 0.257, and 0.514 M NaCl) were prepared by dissolving the appropriate amount of salt in deionized water in volumetric flasks. Polymer stock solutions were then made by dissolving the appropriate amount of polymer in these solutions. The solutions were then diluted to final concentrations and allowed to age for 2–3 weeks before being analyzed with a Contraves LS-30 rheometer.

Turbidimetry

A phototurbidimeter was employed for measuring the critical phase separation temperature of the polymers. Polymer solutions with concentrations of 0.20 g/dL in various solvents were stirred by a magnetic stirrer, and heated slowly at a rate not exceeding 3°C/min by an air heating system. A thermometer was used to monitor the temperature to

within 0.2°C. A decrease in photoelectric current caused by a decrease in the transmittance of light was used to identify the onset of polymer precipitation. The cloud point (critical temperature) could be assessed with an accuracy of 0.5°C.

RESULTS AND DISCUSSION

The synthesis (Fig. 1) of the new monomer 2-acrylamido-2-methylpropanetrimethylammonium chloride (AMPTAC) has allowed the preparation of a series of cationic polyelectrolytes (the ATAM series). These copolymers are analogous to the previously studied copolymers (the ADAM series) of acrylamide with 2-acrylamido-2-methylpropanedimethylammonium hydrochloride (AMPDAC). Quaternization of the cationic moiety by a fourth alkyl group yields a monomer which is pH stable in aqueous solution. The effect of this added methyl substituent on copolymerization behavior was studied by examining the microstructure of the copolymers using reactivity ratios to calculate monomer sequence distributions. Changes in polymer-solvent interaction were assessed by studying the dilute solution properties and the phase behavior of the copolymers as a function of composition, pH, temperature and added electrolytes.

Compositional Analysis

The ATAM copolymers were synthesized by varying the feed ratios of AM : AMPTAC from 90 : 10 to 50 : 50 mol %. Structural characterization was achieved by integration of the ¹³C-NMR amide carbonyl peaks. Reaction parameters and the resulting compositions for the ATAM series are given in Table I. The reactions were usually terminated at < 50% conversion due to high viscosity of the reaction me-

Table I. Reaction Parameters for the Copolymerization of Acrylamide (AM) with 2-Acrylamido-2-methylpropanetrimethylammonium Chloride (AMPTAC)

Sample Number	Feed Ratio AM : AMPTAC	Reaction Time (h)	Conversion (%)	AMPTAC in Copolymer ^a (mol %)
ATAM-9	91 : 9	3.0	10.8	9 ± 0.6
ATAM-20	80 : 20	6.4	20.5	20 ± 1.2
ATAM-30	70 : 30	6.4	45.9	32 ± 1.6
ATAM-50	50 : 50	6.5	33.1	49 ± 2.5
ATAM-100	0 : 100	24	38.8	100 ^b

^a Determined from ¹³C NMR.

^b Theoretical value.

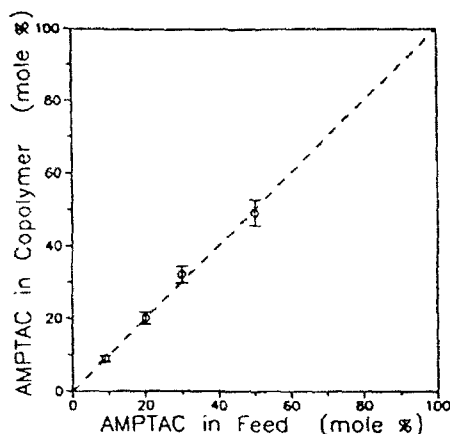


Figure 2. Mole percent AMPTAC incorporated into the copolymers as a function of comonomer feed ratio. The dashed line represents ideal random incorporation.

dium and as a precaution against compositional drift. Copolymer compositions as a function of feed composition are shown in Figure 2. The data lie close to the dashed line which represents completely random incorporation.

Reactivity Ratio and Microstructure Studies

The feed ratios and the resultant copolymer compositions were used to calculate reactivity ratios for the AM : AMPTAC pair. A linear least-squares evaluation of the high conversion method of Kelen et al. yielded values with 95% confidence.¹¹ AM (M_1) and AMPTAC (M_2) comonomers gave reactivity ratios $r_1 = 0.95 \pm 0.03$ and $r_2 = 0.66 \pm 0.08$ ($r_1 r_2 = 0.62$). This indicates a more random incorporation than the AM : AMPDAC monomer pair which had $r_1 r_2 = 0.19$.² This increased randomness may signify that the quaternary ammonium moiety forms a tighter ion pair with the chloride counter ion and therefore is not as electrostatically active as the am-

monium hydrochloride monomer. Alternatively the additional hydrophobicity of AMPTAC may play a role in collision frequency during polymerization.

Microstructural information was obtained statistically using the equations of Igarashi¹² and Pyun¹³ and is presented in Table II. The fractions of AM-AM, AMPTAC-AMPTAC, and AM-AMPTAC units in the copolymers and the mean sequence length of the monomers in each copolymer were calculated from reactivity ratio data. The data are indicative of random monomer sequencing. For the ADAM copolymer with composition similar to ATAM-50, the mole percent alternation was 25% higher while the mean sequence length of the cationic monomer was 24% less. This information is in accord with the reactivity ratios and the data of Figure 2.

Light Scattering Studies

Classical and quasielastic light scattering data for the ATAM series are presented in Table III. With the exception of ATAM-50, the copolymers have a narrow range of molecular weights ranging from 1.5×10^6 g/mol for the homopolymer ATAM-100 to 4.0×10^6 g/mol for ATAM-20. The values determined for the high molecular weight of ATAM-50 were reproducible but may be the result of polymer chains remaining entangled after dissolution. Weight-average molecular weights determined by classical light scattering are skewed in favor of large molecules (or aggregates). Quasielastic light scattering is not as sensitive to the presence of large molecules (or aggregates). Hence the diffusion coefficient data and the average diameters do not reflect a significant deviation in size from the other copolymers for ATAM-50. The second virial coefficients indicate increasing polymer/solvent interactions as the amount of AMPTAC in the polymers increased.

Table II. Structural Data for the Copolymers of Acrylamide (M_1) with 2-Acrylamido-2-methylpropanetrimethylammonium Chloride (M_2)

Sample Number	AMPTAC in Copolymer* (mol %)	Blockiness (mol %)		Alternation (mol %)	Mean Sequence Length	
		M_1-M_1	M_2-M_2		M_1	M_2
ATAM-9	9.0	82.3	0.6	17.1	10.6	1.1
ATAM-20	22.0	63.7	2.8	33.5	4.8	1.2
ATAM-30	32.3	49.3	6.3	44.5	3.2	1.3
ATAM-50	49.0	26.3	18.3	55.4	2.0	1.7

* Determined from ^{13}C -NMR.

Table III. Classical and Quasielastic Light Scattering Data for Copolymers of Acrylamide (AM) with 2-Acrylamido-2-methylpropanetrिमethylammonium Chloride (AMPTAC)

Sample Number	AMPTAC in Copolymer (mol %) ^a	M_w ($\times 10^{-6}$ g/mol)	A_2 ($\times 10^4$ mL $\cdot$ mol/g ²)	$D_0 \times 10^8$ (cm ² /s)	d_0 (Å)	DP $\times 10^{-4}$
ATAM-9	9.0	1.37	0.90	5.19	1061	1.65
ATAM-20	22.0	3.97	1.12	3.45	1503	4.05
ATAM-30	32.3	3.08	1.38	3.51	1770	2.76
ATAM-50	49.0	16.47	2.02	2.96	1723	11.90
ATAM-100	100	1.47	2.12	6.37	916	0.71

^a Determined from ¹³C-NMR.

Effects of quaternizing the ammonium moiety are manifested in the values of the second virial coefficients. Those previously reported for the ADAM series² were an order of magnitude ($0.32\text{--}1.6 \times 10^{-3}$ mL mol/g²) larger than those for the ATAM series ($0.90\text{--}2.12 \times 10^{-4}$ mL mol/g²). Again, this provides more evidence for increased hydrophobicity or ion condensation of quaternary AMPTAC monomer.

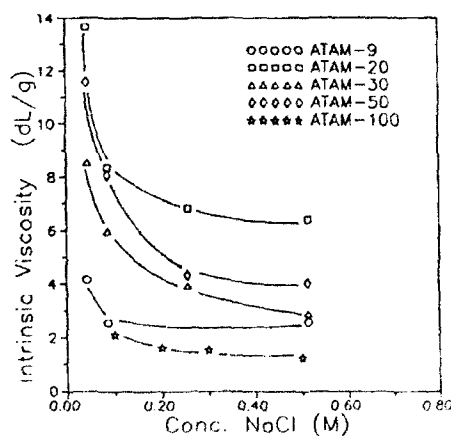
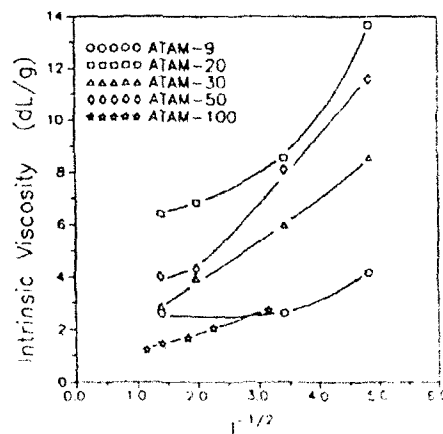
Viscometric Studies

The solution behavior of the homopolymer ATAM-100 was examined in the pH range of 3 to 11 in 0.1M NaCl. No dependence in apparent viscosity was observed. This is expected since there is no facile mechanism by which AMPTAC may lose its charge as is the case with the AMPDAC monomer.

Intrinsic viscosities for the ATAM series polymers are independent of temperature. The polymers were tested in deionized water and in 0.5M NaCl in the temperature range of 25 to 60°C. Most polymers

and polyelectrolytes exhibit reductions in viscosity as a function of increasing temperature. This is due to the elimination of rotational hinderances allowing the polymer coils to occupy smaller volumes in solution. The polymers of the ADAM series display viscosity reduction with increasing temperature.³ Second virial coefficients show however that the ATAM series are poorly solvated with compact conformations over all temperatures studied. Changes in solution temperature may alter polymer conformations but not significantly enough to change solution behavior.

The ATAM polymers act as cationic polyelectrolytes with reduction of intrinsic viscosities with the addition of electrolytes (Fig. 3). To further demonstrate this behavior, the intrinsic viscosities were plotted as a function of the reciprocal square-root of the ionic strength (Fig. 4). Only ATAM-30 exhibits the linear dependence which is typical of polyelectrolytes. The curvature of the data indicates an enhanced sensitivity to ionic strength relative to

**Figure 3.** Intrinsic viscosities for the ATAM copolymer series as a function of NaCl concentration determined at a shear rate of 5.96 s^{-1} at 30°C.**Figure 4.** Intrinsic viscosities for the ATAM copolymers plotted as a function of the inverse square root of ionic strength.

other polyelectrolytes. This may be due to the hydrophobicity of the cationic monomer AMPTAC and the resulting site electrostatic binding of the chloride counterion (decreased dielectric constant).

Turbidimetry

AMPTAC is designed to be a cationic monomer stable to changes in pH. An added benefit is superior phase stability. Aqueous solutions of the ATAM copolymers remain soluble to 100°C in presence of 3.5% Na₂CO₃. The ADAM copolymers by contrast exhibited phase separation as the amount of Na₂CO₃ and the solution temperatures increased.³ Due to the cationic nature of the ATAM polymers, divalent cations such as CaCl₂ have little effect on phase behavior.

CONCLUSIONS

The new monomer 2-acrylamido-2-methylpropane-trimethylammonium chloride has been synthesized and incorporated into copolymers with acrylamide. ¹³C-NMR was used to determine the copolymer compositions. Reactivity ratios determined from a method from Kelen et al. were found to have $r_1r_2 = 0.62$. Copolymer microstructures have been statistically predicted, utilizing the methods of Igarashi and of Pyun, to be nearly random. Aqueous solutions of the copolymers exhibit phase stability in the presence of CaCl₂ and Na₂CO₃ up to 100°C. Intrinsic viscosities decrease with the addition of electrolytes. Linear dependence of intrinsic viscosities on the reciprocal square-root of ionic strength was not observed. This sensitivity to electrolytes at low ionic strengths is due to the increased hydrophobicity of

the ammonium moiety once counter ion condensation has occurred.

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Water-Soluble Copolymers. XLV. Ampholytic Terpolymers of Acrylamide with Sodium 3-Acrylamido-3-Methylbutanoate and 2-Acrylamido-2-Methylpropanetrimethylammonium Chloride

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SYNOPSIS

Water-soluble, low charge density polyampholytes have been synthesized by free-radical terpolymerization of acrylamide (AM) with sodium 3-acrylamido-3-methylbutanoate (NaAMB) and 2-acrylamido-2-methylpropanetrimethylammonium chloride (AMPTAC). Terpolymer compositions obtained by ^{13}C -NMR reflect monomer feed concentrations. Molecular weights and second virial coefficients range from 3.43 to 19.4×10^6 g/mol and from 1.63 to 3.61 mL mol/g $^{-2}$, respectively, as determined by low-angle laser light scattering. Ionic associations were explored by investigating the dilute solution properties as a function of terpolymer concentration, terpolymer charge density, and added electrolytes. Terpolymers with 0.5, 2.5, and 5.0 mol % of both of the cationic (AMTAC) and anionic (NaAMB) monomers were soluble in deionized water, whereas those with 10 and 15 mol % of each monomer required electrolyte addition. The higher-density terpolymers undergo a 700% increase in intrinsic viscosity upon changing NaCl concentration from 0.05 to 1 M. Polyelectrolyte behavior could be induced by decreasing solution pH below the pK_a of the NaAMB mer. Intermolecular ionic associations resulting in gel networks were studied utilizing dynamic mechanical analysis. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Only a limited number of synthetic polyampholytes have been reported in the literature that possess the carboxylate moiety as the anionic group. Early studies incorporated methacrylic acid and various ammonium species that provided high charge density polymers that were polyampholytes at their isoelectric points.¹⁻³ The polymers were polyanions in alkaline solution and polycations in acid solution. Nonaka and Egawa⁴ treated potassium polymethacrylate with 3-chloro-2-hydroxypropanetrimethylammonium chloride to obtain polymers with various amine/acid ratios. Merle et al.⁵ compared polyampholytes prepared by the hydrolysis or acidolysis of poly(*N,N*-dimethylaminoethyl methacrylate to

polymers made by the copolymerization of *N,N*-dimethylaminoethyl methacrylate and methacrylic acid.

Polyampholytes with regular structures have also been reported that incorporated the carboxylate group, but solution properties were rarely mentioned.⁶⁻⁸ Zwitterionic polyampholytes have been made with the carboxylate as part of a betaine functionality.⁹ Wielma studied the synthesis and solubility of zwitterionic polymers with carboxylate moieties.⁹ Varying degrees of ionization were achieved for the carboxylate groups by controlling the pH. At high pH values, the polymers behaved as polyampholytes, whereas at low pH values, polyelectrolyte behavior was observed.

Previously we reported ampholytic terpolymers containing the carboxylate group as the negatively charged moiety.¹⁰⁻¹² Sodium 3-acrylamido-3-methylbutanoate (NaAMB) was polymerized with 2-acrylamido-2-methyldimethylammonium hydrochloride

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ride (AMPDAC) and acrylamide (AM) as a neutral spacer. The superabsorbing terpolymers formed highly swollen gels even with added electrolytes due to strong intermolecular interactions. By contrast, structurally homologous terpolymers synthesized with the sulfonate monomer were soluble in deionized water and exhibited viscosity increases as electrolytes were added.¹⁰ Both intra- and intermolecular associations were observed in agreement with other literature reports on similar structures.¹⁴ In this study, we report electrolyte-soluble ampholytic terpolymers of acrylamide with the anionic monomer NaAMB and the cationic monomer AMPTAC.

EXPERIMENTAL

Materials and Monomer Synthesis

Sodium 3-acrylamido-3-methylbutanoate (NaAMB) monomer was synthesized via a Ritter reaction of equimolar amounts of 3,3-dimethylacrylic acid with acrylonitrile as reported by Hoke and Robins¹⁵ and as modified by McCormick and Blackmon.¹⁶ Synthesis of 2-acrylamido-2-methylpropanetrimethylammonium chloride (AMPTAC) by a multistep procedure has been previously reported.^{12,17} Briefly, 2-acrylamido-2-methylpropanedimethylamine was reacted with a 10-fold excess of methyl iodide in refluxing diethyl ether, then ion-exchanged to yield AMPTAC.

Synthesis of Terpolymers of NaAMB with AMPTAC and AM

Terpolymers of AMPTAC with NaAMB and AM (the ATABAM series) were synthesized by free-radical polymerization in a 0.5M NaCl aqueous so-

lution under nitrogen at 30°C using 0.1 mol % potassium persulfate as the initiator. The feed ratio of AM:NaAMB:AMPTAC was varied from 99.0 : 0.5 : 0.5 to 70 : 15 : 15 mol % with the total monomer concentration held constant at 0.45M. The synthesis and purification procedures have been reported previously.^{17,18} Table I lists reaction parameters for the terpolymerization of AM with NaAMB and AMPTAC. IR: Terpolymer: ATABAM 15-15, N—H 3401–3200 cm⁻¹ (s); C—H 2930 cm⁻¹ (m); C=O 1685–1653 cm⁻¹ (s); N⁺—R₄ 966 cm⁻¹. ¹³C-NMR: ATABAM 5-5, AM C=O, 180.8 ppm; NaAMB C=O, 176.9 ppm; AMPTAC C=O, 178.3 ppm; chain CH, 43.1 ppm; chain CH₂, 36.1 ppm; gem CH₃, 27.9 ppm.

Terpolymer Characterization

Terpolymer compositions were determined from ¹³C-NMR by integration of the acrylamido carbonyl peaks.¹⁹ ¹³C-NMR spectra were obtained using 10 wt/wt % aqueous (D₂O) polymer solutions with DSS as the reference. FTIR spectra were acquired using a Perkin-Elmer 1600 Series FTIR spectrophotometer. Molecular weight studies were performed on a Chromatix KMX-6 low-angle laser light-scattering instrument. Refractive index increments were obtained using a Chromatix KMX-16 laser differential refractometer. A Langley-Ford Model LF1-64 channel digital correlator was used in conjunction with the KMX-6 to obtain quasi-elastic light-scattering data. All measurements were conducted at 25°C in 1M NaCl.

Viscosity Measurement

A 1 g/dL stock solution of each terpolymer was made in deionized water. Aliquots were taken and

Table I Reaction Parameters for Terpolymerization of AM with NaAMB, and AMPTAC

Sample No.	Feed Composition (mol %) AM : NaAMB : AMPTAC	Reaction Time (h)	Conversion (%)	Terpolymer Composition* (mol %) AM : NaAMB : AMPTAC
ATABAM 0.5-0.5	99.0 : 0.0 : 0.5	2.5	20.8	99 ^b : 0.5 ^b : 0.5 ^b
ATABAM 2.5-2.5	95.0 : 2.5 : 2.5	4.0	41.0	89.1 : 5.1 : 5.8
ATABAM 5.0-5.0	90.0 : 5.0 : 5.0	4.0	47.8	85.9 : 7.9 : 6.2
ATABAM 10-10	80.0 : 10.0 : 10.0	6.0	22.3	80.5 : 9.7 : 9.8
ATABAM 15-15	70.0 : 15.0 : 15.0	4.0	25.6	74.6 : 11.5 : 14.0
ATABAM 10-5	85.0 : 10.0 : 5.0	3.0	20.2	75.7 : 13.6 : 10.7
ATABAM 5-10	85.0 : 5.0 : 10.0	3.0	14.5	85.3 : 4.5 : 10.2

* Determined by ¹³C-NMR.

^b Theoretical.

diluted with salt solutions to designated ionic strength and a polymer concentration of approximately 0.3 g/dL. These were further diluted to give polymer solutions with concentrations above and below C^* (0.025–0.3 g/dL). After aging for 2–3 weeks, the solutions were analyzed with a Contraves LS-30 rheometer. Triplicate samples were prepared of each concentration to reduce experimental error. Intrinsic viscosities were evaluated using the Huggins equation.²⁰

Dynamic Mechanical Analysis

A Rheometrics RMS-800 dynamic mechanical spectrometer was used to examine G' (storage modulus) and G'' (loss modulus) as a function of frequency for 1 g/dL solutions of ATABAM 2.5–2.5 in various salt concentrations. Measurements were obtained using a Couette test geometry with 50% constant strain at 25°C.

RESULTS AND DISCUSSION

The previously studied ADABAM terpolymer series that contained AM, NaAMB, and AMPDAC (Fig. 1) formed highly swollen gels in aqueous solutions even in the presence of electrolytes. Strong hydrogen bonding between the carboxylate and the tertiary ammonium hydrochloride groups led to intermolecular cross-links that persisted even in 1M NaCl. Substitution of the protonated tertiary amine monomer AMPDAC by a quaternized monomer AMPTAC allows formation of soluble ampholytic terpolymers.

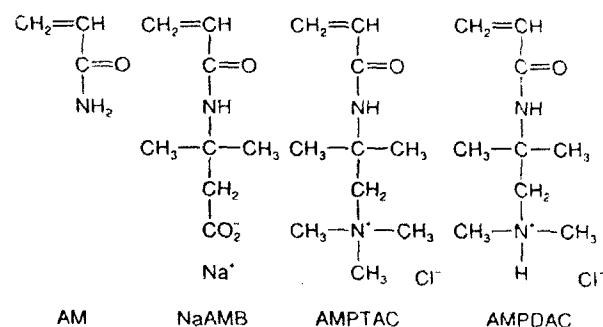


Figure 1 Structures for the monomers Acrylamide (AM), Sodium 3-Acrylamido-3-methylbutanoate (NaAMB), 2-Acrylamido-2-methylpropanetrimethylammonium Chloride (AMPTAC), and 2-Acrylamido-2-methylpropanedimethylammonium Hydrochloride (AMPDAC).

Compositional Studies

Compositions for the ATABAM series of terpolymers were determined by integration of ^{13}C -NMR acrylamido carbonyl peaks (Table I). Much like the previously studied ATASAM series,²¹ synthesis of the terpolymers in 0.5M NaCl led to random incorporation of the charged groups such that the resulting compositions approximate the feed compositions. The presence of added electrolytes during polymerization shields the charged groups from each other so that monomer pairing is not favored. Such random distribution of ionic mers along the backbone would be predicted to result in significantly different properties when compared to terpolymers with large numbers of neighboring group associations. The terpolymers ATABAM 10–5 and 5–10 were synthesized with charge imbalances in the feed, resulting in polyelectrolyte solution behavior.

Light-scattering Studies

Low-angle laser light scattering was employed to obtain the molecular weight and second virial coefficient (A_2) data shown in Table II. The molecular weights range from 3.43 to 19.4×10^6 g/mol for ATABAM 0.5–0.5 and ATABAM 10–5, respectively. The terpolymers ATABAM 10–10, 15–15, and 5–10 have very similar degrees of polymerization and therefore can be used for comparative structure/property assessments. Except for ATABAM 0.5–0.5, the A_2 values range from 1.63 to 2.06×10^{-4} mL mol/g² for the charge-balanced systems. ATABAM 0.5–0.5 remains well solvated in 1M NaCl as indicated by the A_2 value of 3.63 mL mol/g².

Quasi-elastic light scattering was used to obtain the diffusion coefficients (D_0) and hydrodynamic volumes (d_0) shown in Table II. ATABAM 10–10 has the largest d_0 value of 2160 Å, reflecting good solvation and high molecular weight. ATABAM 5–5 possesses a molecular weight and hydrodynamic volume approximately equal to that of ATABAM 0.5–0.5, although its second virial coefficient is much smaller. A similar effect is observed for ATABAM 10–5, which has 73% the molecular weight of ATABAM 5–10, yet, due to the presence of three times as much NaAMB, has approximately the same hydrodynamic volume.

Viscometric Studies

Effects of Terpolymer Composition

The terpolymers ATABAM 2.5–2.5, 5–5, 10–10, and 15–15 exhibit polyampholyte behavior as expected

Table II Classical and Quasi-elastic Light-Scattering Data for Terpolymers of AM with NaAMB with AMPTAC

Sample No.	dn/dc	$MW \times 10^{-6}$ (g/mol)	$A_2 \times 10^4$ (ml mol/g ²)	$D_0 \times 10^5$ (cm ² /g)	a_0 (Å)	$DP \times 10^{-3}$
ATABAM 0.5-0.5	0.1543	3.43	3.61	4.98	1024	4.82
ATABAM 2.5-2.5	0.1372	13.9	1.66	3.13	1873	15.0
ATABAM 5-5	0.1386	3.45	1.63	4.76	1003	4.02
ATABAM 10-10	0.1395	10.8	2.06	2.64	2159	11.0
ATABAM 15-15	0.1308	12.2	1.75	3.13	1630	11.5
ATABAM 5-10	0.1460	11.2	1.84	3.61	1330	10.8
ATABAM 10-5	0.1399	19.4	1.85	3.89	1440	21.1

for equal (or near equal) concentrations of NaAMB and AMPTAC. ATABAM 0.5-0.5, 2.5-2.5, and 5-5 have charge densities low enough to allow solubilization in the absence of added electrolytes. At slightly higher charge densities, however, ATABAM 10-10 and 15-15 are insoluble in deionized water. The net charge of ATABAM 5-10 and 10-5 polyelectrolytes allow solubility in electrolyte-free water.

Charge density also controls the type of macromolecular associations present. ATABAM 2.5-2.5 displays very strong intermolecular associations that "gel" semidilute polymer solutions at low ionic strengths. The high charge density ampholyte terpolymers possess both inter- and intramolecular associations under the same conditions.

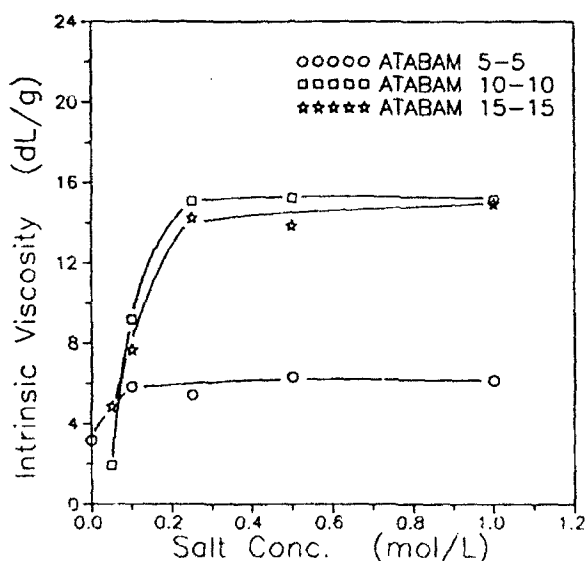


Figure 2 Intrinsic viscosities of ATABAM 5-5, 10-10, and 15-15 plotted as function of NaCl concentration determined at 25°C at a shear rate of 5.96 s⁻¹.

Effects of Added Electrolytes

Figure 2 displays the intrinsic viscosity of a number of the terpolymers as a function of NaCl concentration obtained using the Huggins equation.²⁰ The data are indicative of classic "antipolyelectrolyte" behavior. Increases in solution ionic strength disrupt intramolecular ionic associations, thus producing increases in polymer hydrodynamic volume. ATABAM 10-10 undergoes a 700% increase in intrinsic viscosity going from 0.05 to 1M NaCl. ATABAM 10-10 and 15-15, which have similar molecular weight, attain the same intrinsic viscosity in 1M NaCl.

The data parallel the behavior observed for the previously examined ADASAM low charge density terpolymers.¹³ For example, ADASAM 10-10 (76.7 mol % AM, 12.6 mol % NaAMPS, and 10.7 mol % AMPDAC) displayed a 330% increase in intrinsic viscosity from deionized water to 1M NaCl. The complex solution behavior of the ATASAM terpolymers was not observed.²¹

Effects of pH

The reduced viscosities for ATABAM 10-10 obtained in neutral and acidic pH values are shown in Figure 3. Above pH 7.5, the polymers behave as polyampholytes since all NaAMB units possess a negative charge. Intramolecular charge-charge interactions initially constrict the coils but disappear as solvent ionic strength is increased. At pH 3, the polymers behave as polyelectrolytes. The NaAMB units are protonated so that only the cationic charge of AMPTAC remains. Like typical polyelectrolytes, the coils expand in the absence of added electrolytes but collapse in their presence.

It is interesting that the polyelectrolyte form of ATABAM 10-10 has smaller dimensions in 1M NaCl than does the polyampholyte form. This may

be due to the relative hydrophobicity of the acid form of NaAMB. For example, copolymers of NaAMB with AM precipitate from aqueous solution below pH 5.¹² The presence of this relatively hydrophobic monomer may constrict the polymer to dimensions smaller than those of a random coil, thus producing the effect observed in Figure 3. Also, the extent of counterion condensation may differ for the two forms at high NaCl concentrations.

Dynamic Mechanical Analysis

The intermolecular associations of ATABAM 2.5-2.5 are strong enough to produce gels with elastic properties in solvents of low ionic strengths. The storage modulus G' and the loss modulus G'' were examined on a Rheometrics RMS-800 spectrometer using a couette test configuration. Solutions of varying ionic strengths at constant polymer concentrations (1 g/dL) were analyzed at 50% strain in the frequency range of 0.1–100 rad/s. The frequencies at which G' and G'' intersect, i.e., $\tan \delta = G''/G' = 1$, are plotted as a function of ionic strength in Figure 4. At NaCl concentrations above 0.05 M, the frequency at which $\tan \delta$ is unity becomes independent of ionic strength. This implies the complete disappearance of intermolecular associations.

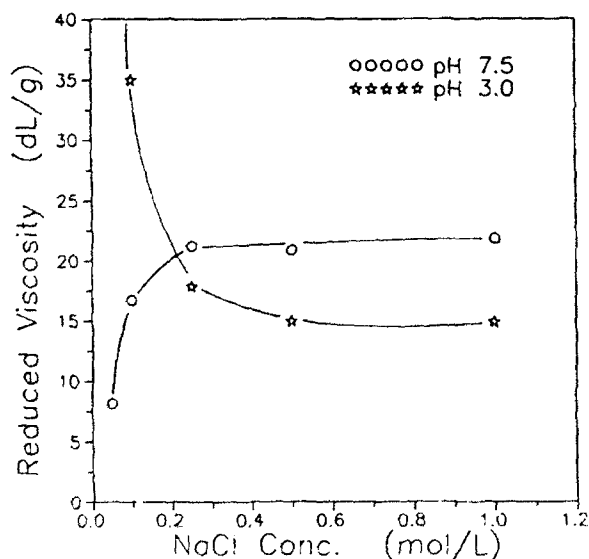


Figure 3 Reduced viscosity for ATABAM 10-10 in the polyampholyte form (pH 7.5) and in the polyelectrolyte form (pH 3.0). Determined with a polymer concentration of 0.10 g/dL at 25°C at a shear rate of 5.96 s^{-1} .

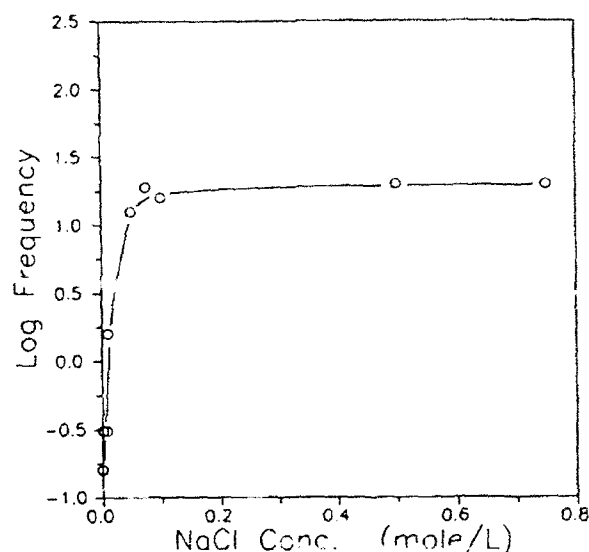


Figure 4 Log frequency at which $\tan \delta$ is unity as a function of NaCl concentration for 1 g/dL solutions of ATABAM 2.5-2.5.

CONCLUSIONS

The ATABAM series of low charge density polyampholytes has been synthesized by free-radical terpolymerization of AM with NaAMB and AMPTAC. Unlike the analogous terpolymers containing the tertiary amine hydrochloride monomer AMPDAC, this series dissolves in aqueous solutions provided enough salt is present to disrupt ionic associations. The terpolymers have been characterized by ^{13}C -NMR, FTIR, and classical and quasi-elastic low-angle laser light-scattering techniques. The terpolymer compositions reflect the monomer feed concentrations. Molecular weights range from 3.43 to $19.4 \times 10^6 \text{ g/mol}$ for the series.

Increases in solution ionic strength disrupt intramolecular ionic associations, thus producing increases in polymer hydrodynamic volume. ATABAM 10-10 undergoes a 700% increase in intrinsic viscosity, going from 0.05 to 1 M NaCl. Intermolecular ionic associations, studied utilizing dynamic mechanical analysis, were observed to be very sensitive to the presence of added electrolytes.

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