②

Office of Naval Research

End-of-Year Report

Publications/Patents/Presentations/Honors/Students Report

for

Contract Number N00014-89-J-1893
R & T Code: 4132055

Copolymers for Drag Reduction in Marine Propulsion:
New Molecular Structures with Enhanced Effectiveness

Annual Report for the Period
June 1, 1990 - May 31, 1991

Principal Investigators

Charles L. McCormick
Roger D. Hester
University of Southern Mississippi
S.S. Box 10076
Hattiesburg, MS 39401

May 31, 1991

PART I

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

R&T Number: 4132055
Contract/Grant Number: N00014-89-J-1893
Contract/Grant Title: Copolymers for Drag Reduction in Marine Propulsion: New Molecular Structures with Enhanced Effectiveness
Principal Investigator: Charles L. McCormick
Roger D. Hester
Mailing Address: Southern Station Box 10076
Hattiesburg, MS 39406-0076
Phone Number: (601) 266-4872 Fax Number: (601) 266-5504
E-Mail Address: 2609 West 4th Street, Hattiesburg, MS 39406

a. Number of papers submitted to refereed journals, but not published: 6
b. Number of papers published in refereed journals (list attached): 5
c. Number of books or chapters submitted, but not yet published: 9
d. Number of books or chapters published (list attached): 4
e. Number of preprints: 10
f. Number of patents files: 0
g. Number of patents granted: 0
h. Number of invited presentations at workshops/professional meetings: 7
i. Number of presentations at workshops or professional meetings: 20
j. Honors/Awards/Prizes for contract/grant employees: 2
k. Total number of Graduate Students and Post-Doctoral associates supported <u>by at least 25%</u> during this period, under <u>this</u> R&T project number:
    Graduate Students 13
    Post-Doctoral Associates: 0
  including the number of,
    Female Graduate Students: 0
    Minority Graduate Students: 1
    Asian Graduate Students: 2
l. Other funding (list attached)

A. Technical Papers Submitted

"Water-Soluble Copolymers. 26. Fluorescence Probe Studies of Hydrophobically-Modified Maleic Acid-Ethyl Vinyl Ether Copolymers," Charles. L. McCormick, Charles E. Hoyle, and Mark D. Clark, to be published in Polymer (1990).

"A Comparison of Apparent Solubilities of a Group of Copolymers Possessing a Common Comonomer," Charles L. McCormick, Charles E. Hoyle, Mark D. Clark, and Teresa A. Schott, submitted to Polymer International (1990).

"Water-Soluble Copolymers. 37. Synthesis and Characterization of Hydrophobically Modified, Acrylamide-Based Polyelectrolytes," Charles L. McCormick, J. C. Middleton, D. F. Cummins, submitted for publication (1990).

"Water-Soluble Copolymers. 38. Synthesis and Characterization of Terpolymers of Acrylamide, N-(4-Butyl)Phenylacrylamide, and Sodium Acrylate, Sodium-2-Acrylamido-2-Methylpropanesulfonate or Sodium-3-Acrylamido-3-Methylbutanoate," Charles L. McCormick, J. C. Middleton and C. E. Grady, submitted for publication (1990).

"Water Soluble Copolymers. 39. Synthesis and Solution Properties of Associative Acrylamido Copolymers with Pyrenesulfonamide Fluorescence Labels," Charles L. McCormick and Stephen A. Ezzell. submitted for publication (1990).

"Water Soluble Copolymers. 40. Photophysical Studies of the Solution Behavior of Associative Pyrenesulfomide-Labelled Polyacrylamides," Charles L. McCormick, Charles E. Hoyle, David Creed and Stephen Ezzell, submitted for publication (1990).

B. Technical Papers Published

"Water-Soluble Copolymers. XXXII. Macromolecular Drag Reduction, A Review of Predictive Theories and the Effects of Polymer Structure," S. E. Morgan and C. L. McCormick, *Progress in Polymer Science*, *15(3)*, 507-549 (1989).

"Water-Soluble Polymers. XXXIII. Ampholytic Terpolymers of Sodium 2-Acrylamido-2-Methylpropanesulfonate with 2-Acrylamido-2-Methylpropane-Dimethylammonium Chloride and Acrylamide: Synthesis and Aqueous Solution Behavior," C. L. McCormick and C. B. Johnson, *Polymer*, *31*, 1100 (1990).

"Water-Soluble Polymers. XXXIV. Ampholytic Terpolymers of Sodium 2-Acrylamido-2-Methylpropanesulfonate with 2-Acrylamido-2-Methylpropane-Dimethylammonium Chloride and Acrylamide: Synthesis and Absorbency Behavior," C. L. McCormick and C. B. Johnson, *J. Macromol. Sci., Chem., A27(5)*, 539 (1990).

"Water-Soluble Copolymers. XXXV. Photophysical and Rheological Studies of the Copolymer of Methacrylic Acid with 2-(1-naphthylacetyl) ethylacrylate," Charles L. McCormick, Charles E. Hoyle and Mark D. Clark, *Macromolecules*, 23(12), 3124 (1990).

"Water-Soluble Copolymers. XXXVI. Photophysical Investigations of Water-Soluble Copolymers of 2-(1-naphthylacetamido)ethylacrylamide," C. L. McCormick, C. E. Hoyle and M. D. Clark, *Macromolecules*, 24(9) 2397 (1991).

C. Books or Chapters Submitted

Water-Soluble Polymers, Charles L. McCormick, co-editor, from American Chemical Society National Meeting, Miami, FL, September 1989, Accepted for Publication (1990) in ACS Symposium Series.

"Structural Design of Water-Soluble Copolymers," C. L. McCormick, *Water Soluble Polymers: Synthesis, Solution Properties, and Applications*, ACS Symposium Series 467, Chapter 1, page 2 (1991).

"Copolymers of Acrylamide and a Novel Sulfobetaine Amphoteric Monomer," L. C. Salazar and C. L. McCormick, *Water Soluble Polymers: Synthesis, Solution Properties, and Applications*, ACS Symposium Series 467, Chapter 7, page 119 (1991).

"Synthesis and Solution Characterization of Pyrene-Labeled Polyacrylamides," S. A. Ezzell and C. L. McCormick, *Water Soluble Polymers: Synthesis, Solution Properties, and Applications*, ACS Symposium Series 467, Chapter 8, page 130 (1991).

"Photophysical and Rheological Studies of the Aqueous Solution Properties of Naphthalene-Pendent Acrylic Acid Copolymers," M. D. Clark, C. L. McCormick and C. E. Hoyle, *Water Soluble Polymers: Synthesis, Solution Properties, and Applications*, ACS Symposium Series 467, Chapter 19, page 291 (1991).

"The Roles of Molecular Structure and Solvation on Drag Reduction in Aqueous Solutions," C. L. McCormick, S. E. Morgan and R. D. Hester, *Water Soluble Polymers: Synthesis, Solution Properties, and Applications*, ACS Symposium Series 467, Chapter 21, page 320 (1991).

"The Rheological Properties of Hydrophobically Modified Acrylamide-Based Polyelectrolytes," J. C. Middleton, D. F. Cummins and C. L. McCormick, *Water Soluble Polymers: Synthesis, Solution Properties, and Applications*, ACS Symposium Series 467, Chapter 22, page 338 (1991).

"Molecular-Weight-Distribution Determination of Water-Soluble Macromolecules by Dynamic Light Scattering," *Water Soluble Polymers: Synthesis, Solution Properties, and Applications*, ACS Symposium Series 467, Chapter 18, page 276 (1991).

"Synthesis and Solution Behavior of Electrolyte - Responsive Polyampholytes," Luis C. Salazar, Ph.D. Dissertation, University of Southern Mississippi, June 1991.

D. Books or Chapters Published

"Photophysical Investigations of Hydrophobically-Modified Water-Soluble Polymers," M. D. Clark, Ph.D. Dissertation, University of Southern Mississippi, December 1990.

"Synthesis and Solution Properties of Pyrene-Labelled Water-Soluble Polymers," S. A. Ezzell, Ph.D. Dissertation, University of Southern Mississippi, December 1990.

"Synthesis and Characterization of Hydrophobically-Modified Polyacrylamides," J. C. Middleton, Ph.D. Dissertation, University of Southern Mississippi, December 1990.

"Effects of Polymer Parameters on Drag Reduction," Abbas Safieddine, Ph.D. Dissertation, University of Southern Mississippi, December 1990.

E. Preprints

"Synthesis and Characterization of Potassium Salts of Poly(Maleic Anhydride-Alt-Ethyl Vinyl Ethers) Modified with Pendent Hydrophobic Alkyl Amine Groups," Charles L. McCormick and Y. Chang, Polymer Preprints, 31(2), 462 (1990).

"Concepts in Polymer Education: IV. Perspectives on Research Challenges for Water-Soluble Polymers," Charles L. McCormick, Polymer Preprints, 31(2), 416 (1990).

"Copolymers of Sodium 2-Acrylamido-2-Methyl-Propane-Sulfonate with (2-Acrylamido-2-Methyl-Propyl) Trimethyl-Amonium Chloride," C. L. McCormick, E. E. Kathman and L.C. Salazar, Polymer Preprints, 32(1), 98 (1991).

"Spin Traps as Probes of Hydrophobicity in Poly(Maleic Anhydride-ALT-Ethyl Vinyl Ethers) Modified with Pendent Hydrophobic Alkyl Amine Groups," Polymer Preprints, C. L. McCormick and J. K. Newman, 31(1), 100 (1991).

"Synthesis and Characterization of N-Isopropylacrylamide Copolymers for the Study of Drag Reduction," C. L. McCormick and P. S. Mumick, Polymer Preprints, 31(1), 102 (1991).

"Microstructure Studies of Hydrophobically-modified Maleic Anhydride-Ethyl Vinyl Ether Copolymers," C. L. McCormick and Y. Chang, Polymer Preprints, 31(1), 104 (1991).

"Photophysical and Rheological Properties of Naphthalene-Labelled Water-Soluble Copolymers Polymerized in Surfactant Solutions," C. L. McCormick, J. C. Middleton and K. D. Branham, Polymer Preprints, 31(1), 106 (1991).

"Synthetic, Photophysical and Viscometric Studies of Pyrene-Labelled Acrylamide Copolymers," C. L. McCormick, M.C. Kramer and S. A. Ezzell, Polymer Preprints, 31(1), 108 (1991).

"Properties of Hydrophobically-Modified Water-Soluble Polymers Prepared by Synthetic and Recombinant Techniques," C. L. McCormick, J. C. Middleton and M. J. Logan, Polymer Preprints, 31(1), 110 (1991).

"Rheological and Photophysical Evidence for Hydrophobic Associations in Water-Soluble Polymers," C. L. McCormick, S. A. Ezzell, J. C. Middleton, Polymer Preprints, 31(1), 573 (1991).

H. Invited Presentations at Workshops or Professional Society Meetings

"Synthesis and Structural Organization of Hydrophobically Modified Ion-Containing Polymers in Aqueous Solution," Charles L. McCormick, J. Middleton and L. Salazar, Abstracts 33rd IUPAC International Symposium on Macromolecules, 1.3.5 (1990).

"Photophysical and Rheological Studies of Naphthalene and Pyrene-Labeled Copolymers in Aqueous Solution," Charles L. McCormick, M. Clark and S. Ezzell, Abstracts 33rd IUPAC International Symposium on Macromolecules, 2.3.1 (1990).

"Dilute Solution and Drag Reduction Properties of Acrylamide-Co-N-Isopropylacrylamide Polymers," C. L. McCormick and P. S. Mumick, Abstracts of the 42nd Southeast-46th Southwest Regional ACS Meeting, 223 (1990).

"Synthesis and Characterization of Potassium Salts of Poly(Maleic Anhydride-Alt-Ethyl Vinyl Ethers) Modified with Pendent Hydrophobic Alkyl Amine Groups," Charles L. McCormick and Y. Chang, National ACS Meeting, Washington, D.C., August 1990.

"Concepts in Polymer Education: IV. Perspectives on Research Challenges for Water-Soluble Polymers," Charles L. McCormick, National ACS Meeting, Washington, D.C., August 1990.

"Structural Design of Water-Soluble Copolymers," C. L. McCormick, Eighteenth Annual Water-Borne, Higher-Solids, and Powder Coatings Symposium, New Orleans, LA, February 1991.

"Rheological and Photophysical Evidence for Hydrophobic Associations in Water-Soluble Polymers," S. A. Ezzell, J. C. Middleton and C. L. McCormick, National ACS Meeting, Atlanta, GA, April 1991.

I. Presentations at Workshops or Professional Society Meetings

"Molecular Design of Associating Copolymers in Aqueous Solution," C. L. McCormick, J. C. Middleton and M. J. Logan, Abstracts of the 42nd Southeast-46th Southwest Regional ACS Meeting, 219 (1990).

"Solution Properties of Pyrene Sulfonamide-Labelled Water-Soluble Polymers," C. L. McCormick, S. A. Ezzell and M. C. Kramer, Abstracts of the 42nd Southeast 46th Southwest Regional ACS Meeting, 219 (1990).

"Photophysical Investigations of Water-Soluble Copolymers of 2-(1-Naphthylacetamido)-Ethylacrylamide," C. L. McCormick, C. E. Hoyle, M. D. Clark and K. D. Branham, Abstracts of the 42nd Southeast-46th Southwest Regional ACS Meeting, 219 (1990).

"Synthesis and Characterization of Water-Soluble Polyampholyte Based on a Novel Zwitterionic Betaine Monomer," C. L. McCormick, L. C. Salazar and E. E. Kathman, Abstracts of the 42nd Southeast-46th Southwest Regional ACS Meeting, 218 (1990).

"Solution Behavior Studies of Hydrophobically-Modified Maleic Anhydride-Ethyl Vinyl Ether Copolymers," C. L. McCormick and Y. Chang, Abstracts of the 42nd Southeast-46th Southwest Regional ACS Meeting, 220 (1990).

"^{13}C NMR of Spin Traps as Probes of Hydrophobic Domains in Hydrophobically-Modified Maleic Anhydride-Ethyl Vinyl Ether Copolymers," C. L. McCormick and J. K. Newman, Abstracts of the 42nd Southeast-46th Southwest Regional ACS Meeting, 222 (1990).

"Intramolecular Association of Hydrophobically-Modified Maleic Anhydride-Ethyl Vinyl Ether Copolymers," Y. Chang and C. L. McCormick, 55th Annual Meeting of the Mississippi Academy of Sciences, Jackson, MS, February 1991.

"Copolymers of Acrylamide for the Study of Drag Reduction," P. S. Mumick and C. L. McCormick, 55th Annual Meeting of the Mississippi Academy of Sciences, Jackson, MS, February 1991.

"Solution Properties of High Charge Density Polyampholytes," E. E. Kathman, L. C. Salazar and C. L. McCormick, 55th Annual Meeting of the Mississippi Academy of Sciences, Jackson, MS, February 1991.

"Photophysical and Viscometric Studies of Pyrene-Labelled Acrylamide Copolymers: Development of Structure-Property Relationships," M. C. Kramer, S. A. Ezzell and C. L. McCormick, 55th Annual Meeting of the Mississippi Academy of Sciences, Jackson, MS, February 1991.

"Effects of Copolymer Microstructure on Photophysical and Rheological Properties of Naphthalene Labelled Water-Soluble Copolymers," K. D. Branham, J. C. Middleton and C. L. McCormick, 55th Annual Meeting of the Mississippi Academy of Sciences, Jackson, MS, February 1991.

"Water-Soluble Polymers Prepared by Synthetic and Recombinant Techniques," M. J. Logan, J. C. Middleton and C. L. McCormick, 55th Annual Meeting of the Mississippi Academy of Sciences, Jackson, MS, February 1991.

"^{13}C NMR of Spin Traps as Probes of Hydrophobic Domains in Maleic Anhydride-Ethyl Vinyl Ether Copolymers Modified with Pendent Alkyl Groups," J. K. Newman and C. L. McCormick, 55th Annual Meeting of the Mississippi Academy of Sciences, Jackson, MS, February 1991.

"Photophysical and Rheological Properties of Naphthalene-Labelled Water-Soluble Copolymers Polymerized in Surfactant Solution," K. D Branham, J. C. Middleton and C. L. McCormick, National ACS Meeting, Atlanta, GA, April 1991.

"Microstructure Studies of Hydrophobically-Modified Maleic Anhydride-Ethyl Vinyl Ether Copolymers," Y. Chang and C. L. McCormick, National ACS Meeting, Atlanta, GA, April 1991.

"Copolymers of Sodium 2-Acrylamido-2-Methyl-Propanesulfonate with (2-Acrylamido-2-Methyl-Propyl)Trimethylammonium Chloride," E. E. Kathman, L. C. Salazar and C. L. McCormick, National ACS Meeting, Atlanta, GA, April 1991.

"Synthetic, Photophysical and Viscometric Studies of Pyrene-Labelled Acrylamide Copolymers," M. C. Kramer, S. A. Ezzell and C. L. McCormick, National ACS Meeting, Atlanta, GA, April 1991.

"Properties of Hydrophobically-Modified Water-Soluble Polymers Prepared by Synthetic and Recombinant Techniques," M. J. Logan, J. C. Middleton and C. L. McCormick, National ACS Meeting, Atlanta, GA, April 1991.

"Synthesis and Characterization of N-Isopropylacrylamide Copolymers for the Study of Drag Reduction," P. S. Mumick and C. L. McCormick, National ACS Meeting, Atlanta, GA, April 1991.

"Spin Traps as Probes of Hydrophobicity in Poly(Maleic-Anhydride-Alt-Ethyl Vinyl Ethers) Modified with Pendent Hydrophobic Alkyl Amine Groups," J. K. Newman and C. L. McCormick, National ACS Meeting, Atlanta, GA, April 1991.

J. Honors/Awards/Prizes for Contract Grant Employees

Charles L. McCormick, Invited to give lecture at Gordon Research Conference, August 1991.

Steve Ezzell, Finalist for Unilever Graduate Research Award, Polymer Division American Chemical Society.

K. Graduate Students

Dr. Mark D. Clark - graduated December 1990
joined Eastman Kodak

Dr. John C. Middleton - graduated December 1990
joined Monsanto

Dr. Steve Ezzell - graduated December 1990
joined 3-M Corporation

Dr. Abbas Saffieddine - graduated December 1990
joined General Electric

L. E. Salazar
K. D. Branham
E. E. Kathman
M. Kramer
M. J. Logan
P. S. Mumick
Y. Chang
J. K. Newman
J. C. Dickerson

Undergraduates

Kelly Anderson
Paul Welch
Cindy Farmer
Andy Simm
Pablo Dopico
Michael Flesher
Thomas Cotton
Michelle Mapp

L. Other Funding

$52,000 from Air Products.

$5,845.25 received from MS-AL Sea Grant Consortium for student fellowship.

$30,000 received from Union Carbide.

$19,000 received from B. F. Goodrich.

$12,000 received from Unilever for chemistry fellowship.

Continuing Research Grants:
  Sun Oil Company, $55,000
  B.P. Americas, $15,000

PART II

Charles L. McCormick
Department of Polymer Science
University of Southern Mississippi
(601) 266-4872

Scientific Officers - Dr. JoAnn Milliken
Dr. Kenneth Wynne

Description of Project

Responsive synthetic copolymers are being tailored with specific microstructural features in order to elucidate drag reduction behavior and acoustical attenuation in aqueous media. Recent studies suggest that the major role of the polymer may be that of ordering the solvent in the immediate vicinity of the macromolecular coil. The key to varying fluid response under flow conditions lies in synthesizing specific microstructural runs by appropriate mer organization. Resulting microphase separation appears to alter solvation characteristics upon extension in fluid flow. New methods of data analysis allow for the first time direct comparisons of polymer type by assessing drag reduction efficiency as a function of polymer volume fraction. A master curve has been developed from this approach which yields an extensibility parameter suggested by a number of theoretical drag reduction models. Rheological measurements, dynamic light scattering studies, and photophysical techniques are being employed to study microphase organization.

Significant Results During the Last Year

During the past year the role of local solvent ordering on drag reduction efficiency has emerged as a major consideration for a large number of our synthetic models. Clearly viscosity alone is not the most important factor; in fact copolymers with compact conformations (intramolecular modes of association) exert a much more profound influence on frictional reduction than extended polyelectrolytes. Hydrophobically-modified copolymers such as diacetone acrylamide or isopropylacrylamide (the latter in the presence of surfactant below CMC) show significantly greater drag reduction efficiency than polyethyleneoxide. Under quiescent conditions hydrophobically associated groups (microphase separated) have an "ice-like", ordered water structure in their immediate vicinity. Clearly extensional flow changes the nature of the water ordering and the draining characteristics of the polymer.

Research Planned from June 1, 1991-May 30, 1992

Studies during the next twelve months will focus on solution behaviors of the large number of synthetic models prepared to date in our laboratories. Intensive focus will be placed on those microstructurally tailored systems with hydrophobic and ampholytic moieties situated strategically along the macromolecular backbone. Particular emphasis will be placed on the water structural changes brought about by addition of electrolytes, urea, and ionic and nonionic surfactant below CMC. Recent studies have shown dramatic increases in drag reduction with addition of small quantities of sodium dodecyl sulfate to diacetone acrylamide and isopropyl acrylamide copolymers with acrylamide. Interestingly these copolymers are near their lower critical solution temperature (LCST) and are in compact configuration at room temperature. By heating these polymers, we can induce macrophase separation and can measure thermodynamic parameters (ΔH, ΔS, ΔG) associated with water reordering at the endothermic transition. Additionally water ordering times will be measured in model polymers utilizing capillary magnetic resonance imaging techniques with a Bruker 400 MH_z NMR. Finally, a student from our laboratories is studying with Dr. R. A. Pethrick at the University of Strathclyde for three months. Upon his return we will construct a swept frequency acoustic resonant interferometer for measuring polymer-solvent interaction in both static and turbulent fluid conditions.

Graduate Students Working on Project

Kelly Branham
Erich Kathman
Mark Logan
Pavneet Mumick
Yihua Chang
Michael Kramer
Kent Newman
Jimmy Dickerson
Paul Ferguson

Postdoctoral Fellow

Dr. Paul Ferguson

COPOLYMERS FOR DRAG REDUCTION IN MARINE PROPULSION

University of Southern Mississippi
Department of Polymer Science
Charles L. McCormick and Roger D. Hester

OBJECTIVES

- Synthesis of water-soluble copolymers with energy dissipative modes of action in shear fields.
- Characterization of copolymer microstructure
- Study of dilute solution properties including associative properties
- Determination of rheological properties and the role of hydration in turbulent flow
- Development of surface-grafted and ablative coatings
- Training of U.S. graduate students

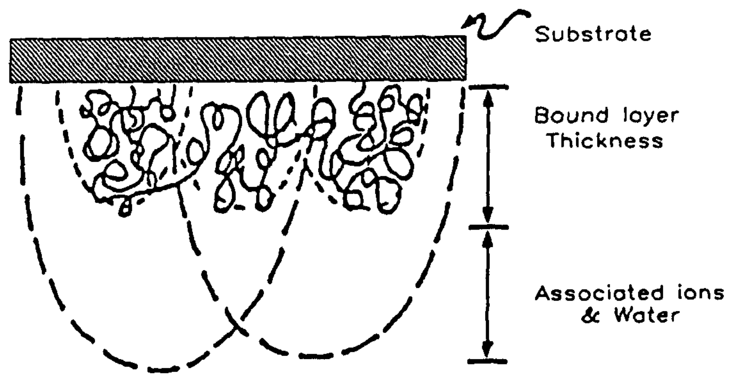
APPROACH

- Explore the drag reduction efficiency of carefully tailored copolymers with intra- and intermolecular associations in aqueous solutions
- Develop analytical procedures to relate drag reduction effectiveness to fundamental parameters of hydrodynamic volume and volume fraction
- Study changes in polymer conformation and solvation in flow fields utilizing fluorophore-labeled copolymers
- Develop controlled surface-grafted copolymers with potential energy dissipative function

RELATED TECHNOLOGY

- The effects of aqueous drag reducing fluids on cavitation characteristics are under study. The extent to which acoustic detection and signature identification can be masked is of interest.

REPRESENTATION OF SUBSTRATE WITH LONG-CHAIN HYDROPHILIC GRAFTS



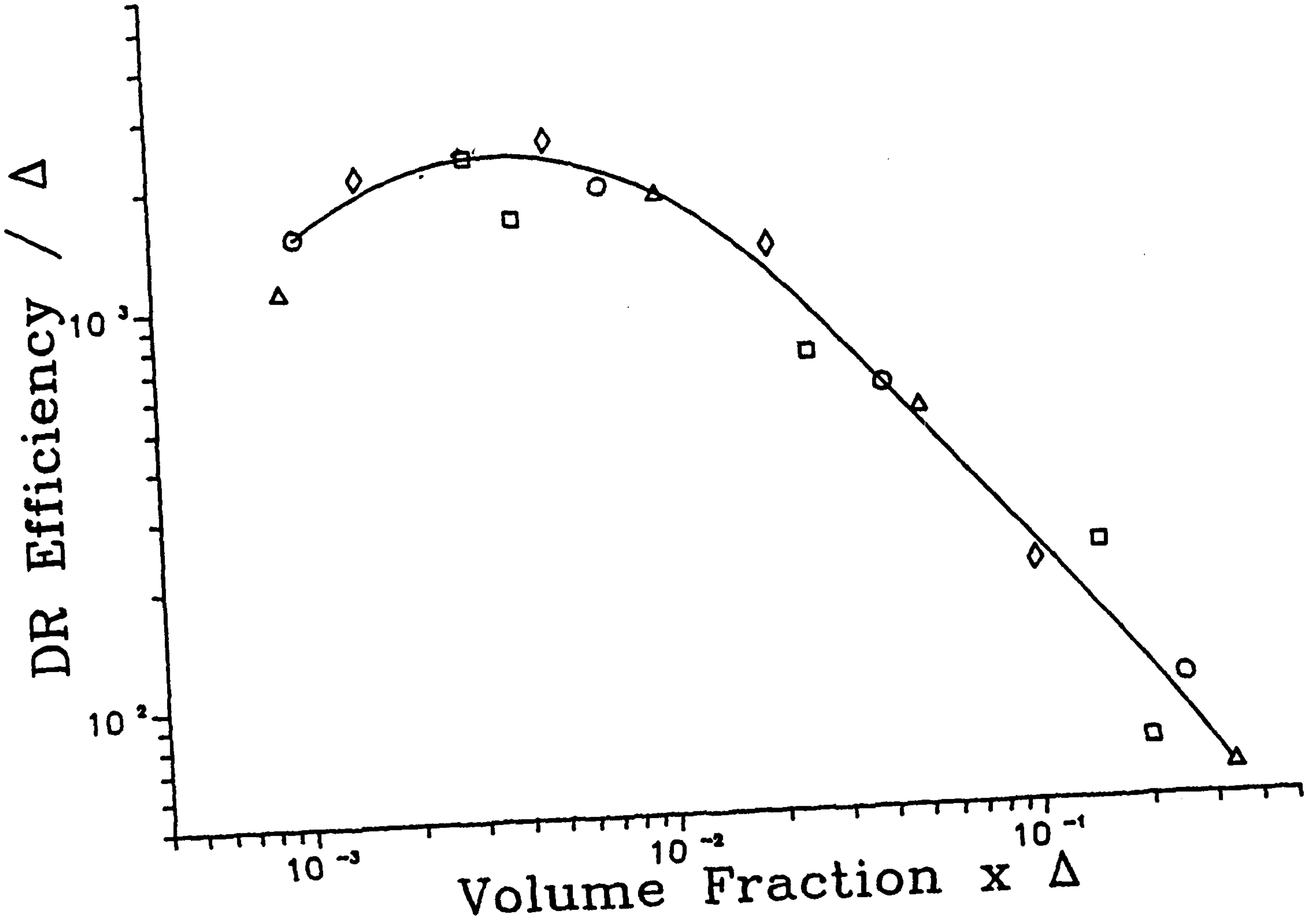

DR Efficiency / Δ
10³
10²
10⁻³
10⁻²
10⁻¹
Volume Fraction x Δ

TABLE III

Polymer Shift Factors

Polymer	Shift Factors in Disk Flow
Homopolymers:	
PEO WSR-301	1.0
PAM-4	2.0
Copolymers:	
DAAM 15	1.3
DAAM 20	2.2
DAAM 25	6.5
DAAM 30	8.0
DAAM 35	10.0
NaA 5	3.0
NaA 10	3.0
NaA 20	8.0
NaA 35	0.35
NaAMB 5	3.5
NaAMB 10	3.5
NaAMB 25	3.5
NaAMB 40	3.5
NaAMB 100	0.075
NaAMPS 5	2.1
NaAMPS 10	2.1
NaAMPS 15	2.1
NaAMPS 20	2.1
NaAMPS 35	2.1
NaAMPS 100	0.09

Research Highlights

Responsive Microphase Copolymer Fluids for Drag Reduction

A research team headed by Drs. Charles L. McCormick and Roger D. Hester from the University of Southern Mississippi is developing a series of responsive copolymers for utilization in drag reduction and acoustical attenuation applications. The key to responsive fluid behavior under flow conditions lies in microstructural organization of mers along the copolymer backbone and changes in solvation characteristics upon extension. A new method of data analysis from rotational disk flow and tube flow experiments allows determination of drag reduction efficiency as a function of volume fraction. Further normalization using an empirical shift factor allows, for the first time, meaningful comparisons of copolymer types from experimental data. The empirical shift factor is related to extensibility parameters suggested in a number of theoretical drag reduction models and appears to be the key to construction of optimally responsive fluids. Theological measurements, dynamic light scattering studies, and photophysical techniques are being employed to study microphase domain organization.

ECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

a. REPORT SECURITY CLASSIFICATION
NONE

1b. RESTRICTIVE MARKINGS
NONE

a. SECURITY CLASSIFICATION AUTHORITY
NONE

b. DECLASSIFICATION / DOWNGRADING SCHEDULE
NONE

3. DISTRIBUTION / AVAILABILITY OF REPORT
UNLIMITED

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
90-91-1

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
University of Southern
Mississippi

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
Office of Naval Research

6c. ADDRESS *(City, State, and ZIP Code)*
University of Southern Mississippi
Polymer Science Department
Southern Station Box 10076
Hattiesburg, MS 39406-0076

7b. ADDRESS *(City, State, and ZIP Code)*
800 North Quincy Avenue
Arlington, VA 22217

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
Office of Naval Research

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS *(City, State, and ZIP Code)*
800 N. Quincy Avenue
Arlington , VA 22217

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO

11. TITLE *(Include Security Classification)*
Synthesis and Characterization of Potassium Salts of Poly(Maleic Anhydride-Alt-Ethyl Vinyl Ethers)Modified with Pendent Hydrophobic Alkyl Amine Groups

12. PERSONAL AUTHOR(S)
Yihua Chang and Charles L. McCormick

13a. TYPE OF REPORT
Journal article

13b. TIME COVERED
FROM ________ TO ________

14. DATE OF REPORT *(Year, Month, Day)*

15. PAGE COUNT

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

22a. NAME OF RESPONSIBLE INDIVIDUAL
Charles L. McCormick

22b. TELEPHONE *(Include Area Code)*
(601)266-4868

22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

SYNTHESIS AND CHARACTERIZATION OF POTASSIUM SALTS OF POLY(MALEIC ANHYDRIDE-ALT-ETHYL VINYL ETHERS) MODIFIED WITH PENDENT HYDROPHOBIC ALKYL AMINE GROUPS

Yihua Chang and Charles L. McCormick

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

Introduction

Polymeric soaps represent an interesting class of synthetic polymers containing both hydrophilic groups and long, non-polar side chains. Polysoaps differ considerably in their physical properties from the conventional synthetic polyelectrolytes due to the presence of the long hydrophobic side chains in the polymer molecules which have the potential to form hydrophobic domains.[1,2] The properties of the polysoap depend on the number and nature of the groups introduced. It has been shown that hydrolyzed copolymers of maleic anhydride and n-alkyl vinyl ethers (n = 4, 5, 6, 8) in aqueous solutions undergo a conformational transition from a hypercoiled to a random coil form as the degree of deprotonation is increased by the addition of base. The transition, however, is shifted to a higher value of deprotonation with increasing alkyl group size.[3]

A series of studies have been carried out in our laboratory to investigate the intra- and intermolecular association of various polymers. Recent work has been directed toward synthesis and characterization of copolymers of maleic anhydride and ethyl vinyl ether which were subsequently reacted with various amounts of n-alkyl amines (n = 8, 12) to form amides. Hydrolysis of the remaining anhydride groups yields water-soluble polymers with degrees of amidation from 8% to 60%. This series of copolymers provides a useful model system for elucidating the nature of hydrophobic bonding in polysoap molecules. Our initial work focuses on the differences in the viscosity behavior of the members of this series in aqueous solutions having varying pH and added electrolyte concentration.

Experimental

n-Alkyl amines were used as received. Ethyl vinyl ether was distilled prior to use. Maleic anhydride was recrystallized twice from chloroform at 50-52°C prior to use. (Benzoyl peroxide (BPO) was recrystallized in chloroform/methanol and dried under vacuum.) Benzene was purified by mixing with calcium hydride for 72 hours and then distilled under nitrogen atmosphere. FTIR, ^{1}H and ^{13}C NMR were used for microstructural identification of the polymers.

Copolymerization of Maleic Anhydride with Ethyl Vinyl Ether

Maleic anhydride (10.77 g, 0.1098 mol) and benzoyl peroxide (0.04514 g, 1.863×10^{-4} mol) were dissolved in benzene (100 ml) in a 250 ml 3-neck round bottom flask with a magnetic bar. The flask was sealed and fitted with a thermometer, a condenser, a long gas delivery needle and a short needle on the top of the condenser to serve as a gas escape valve. Dry, oxygen-free nitrogen was flushed through the flask for 45 min. The short needle was then removed and ethyl vinyl ether (9.110 g, 0.1214 mol) was injected into the solution. The system was heated at 59-61°C for 8 hours. The white precipitate was filtered and dissolved in acetone (125 ml). The product was precipitated from acetone by gradually adding up to 200 ml ethyl ether, filtered, and then dried under vacuum. The copolymer was purified by reprecipitating the acetone solution (125 ml) into diethyl ether (150 ml). The precipitate was cut to small pieces which were then immersed in ethyl ether overnight. The polymer was filtered, dried under vacuum and stored in desiccator.

Amidation of Copolymer

The solution of copolymer (10.20 g, 5.99×10^{-2} mol) in methyl ethyl ketone (150 ml) was reacted under nitrogen with octylamine (the amount added depends upon the degree of amidation that one expects) at 80°C for 16 hours. The purple solution was then poured into ethyl ether (1200 ml) with vigorous stirring. The pink precipitate was placed in 400 ml of ethyl ether with stirred overnight, filtered and dried under vacuum.

Hydrolysis of Polymers

The hydrolysis of the polymers was carried out in basic solution. The polymer salts were prepared by hydrolysis of amide copolymers in 1N aqueous KOH solution at room temperature for 24 hours. These solutions were then dialyzed for a week against water at room temperature to remove low molecular weight polymers and excess KOH. The final products were obtained by freeze-drying.

Viscometry

The appropriate amount of dried polymer was weighed and then dissolved in water in a volumetric flask from which further dilutions of this stock solution could be made. Viscosity measurements were conducted on a Contraves LS 30 low shear rheometer at a shear rate of 6 reciprocal seconds at 25°C.

Results and Discussion

Polymer Synthesis and Characterization

The synthetic routes and structures of the polymers are shown in Scheme 1. The purity of the product was indicated by ^{13}C NMR spectrum showing no C=C absorption.[4] The structure of the intermediate obtained from the reaction of copolymer with alkyl amines was somewhat difficult to identify. To verify if a charge-transfer complex shown in Figure 1 was formed (perhaps the reason for the purple color), we examined some model reactions. Reaction of succinic anhydride with dodecylamine did not involve any color change under conditions analogous to the polymer reaction. The product was shown to be the corresponding amide by NMR and FTIR spectra. The formation of color, however, was observed when the copolymer was reacted with N,N-dimethyldodecylamine. It has been reported that the succinyl 4-(dimethylamino)-pyridinium ion is formed in the reaction of succinic anhydride with 4-(dimethylamino) pyridine.[5] In our experiment, the concentrated solution of succinic anhydride and N,N-*dimethyldodecyl amine in methyl ethyl ketone* exhibits a color change from pink to brown at room temperature. UV spectra of polymers obtained from the reactions of the copolymer with primary and tertiary amines show the same absorption maximum at 562nm (the absorption intensity of latter was stronger for the same feed ratio of amine to acid anhydride than that of the former). This might be explained by partial dodecylamine conversion to the amide lowering the concentration of the charge-transfer complex. This is consistent with the observation that the color of the intermediates changes from pink to purple when the degree of amidation increases from 8% to 60%.

The hydrolysis of the polymers was carried out in 1N aqueous KOH solution at room temperature. It is known that alkaline hydrolysis induces only the hydrolysis of the acid anhydride to acid groups without attacking amide group.[6] Complete hydrolysis was verified by the FTIR spectrum which shows no C=O stretching vibration of acid anhydride.

Viscometric Studies

The way in which the number of n-alkyl groups attached to the polymer chain affects the viscometric behavior in deionized water is shown in Figures 2 and 3. A familiar pattern typical for polyelectrolytes is found: the reduced viscosities, which are very large at high dilutions due to the highly extended conformation of the flexible polyions, decrease with increasing polymer concentration. It is noteworthy, however, that the reduced viscosities of all polyions having n-alkyl side chains drop significantly. These decreases may be explained in terms of the intramolecular associations between the long hydrophobic side chains. This is a consequence of the fact that the hydrophobic side chains are compelled to form an intramolecular micelle from which solvent is excluded. The large contraction of the polysoap molecules, indicated by the viscosity change, decreases the hydrodynamic volume of the polysoap molecule and hence the opportunities for intermolecular contacts.

Figure 4 illustrates the behavior of a polysoap containing 12.4 mole % of n-octyl groups in a plot of reduced viscosity versus concentration at various pH values. Addition of HCl affects the conformation of the polymer molecules in aqueous solutions in two ways. First, addition of electrolyte makes the solution more polar and leads to more compact structures due to the intramolecular interactions of hydrophobic side chains in dilute solution. Secondly, the charge density along the polymer chain decreases upon the neutralization, promoting the compactness of the macromolecules. A similar effect is observed when a small amount of KCl is added to the solutions of polyions.

Conclusions

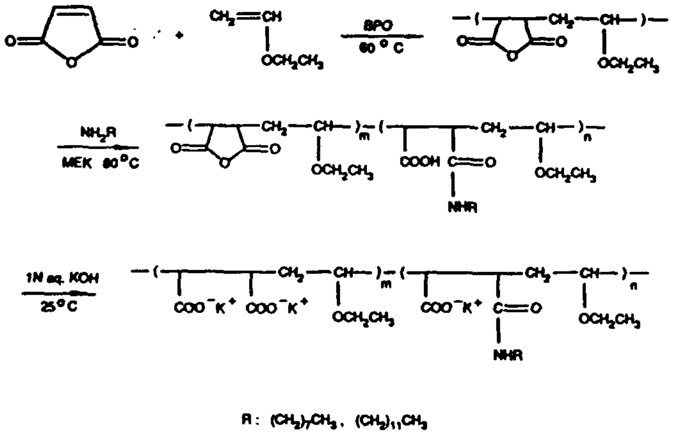
Polysoap molecules with low-to-moderate n-alkyl group content display associative behavior in aqueous solutions with varying pH and ionic strength. The polymers with higher alkyl group content tend to be more compact. These polymer systems show little tendency for intermolecular associations at the concentrations investigated.

Acknowledgements

Funding of portions of this research by the U.S. Department of Energy, the Office of Naval Research, the Defense Advanced Research Projects Agency, and BP America Inc. is gratefully acknowledged.

References

1. U. P. Struass and N. L. Gershfeld, J. Phys. Chem., 58, 747 (1954).
2. U. P. Struass, etc., J. Phys. Chem., 577 (1956).
3. U. P. Strauss and M. S. Schlesinger, J. Phys. Chem., 28(14), 1627 (1978).
4. K. E. Koenig, Macromolecules, 16, 99 (1983).
5. R. Kliger and J. C. Hunt, JACS, 111, 3325 (1989).
6. J. Furukama, et al., J. Polym. Sci., Polym. Chem. Ed., 17, 255 (1979).



Scheme 1. Polymer synthesis.

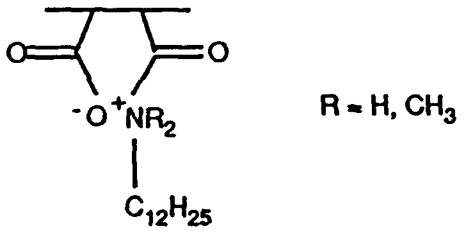


Figure 1. Proposed structure of charge-transfer complex.

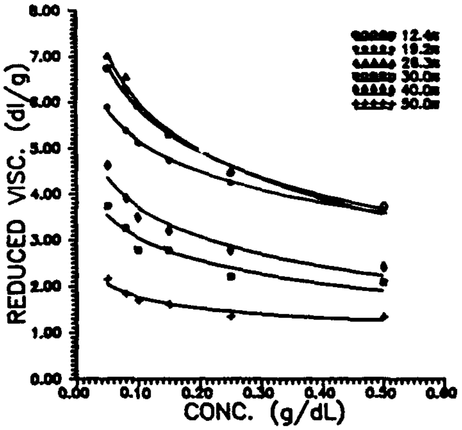


Figure 2. Effect of octyl group content on reduced viscosity of polyelectrolytes in DI water.

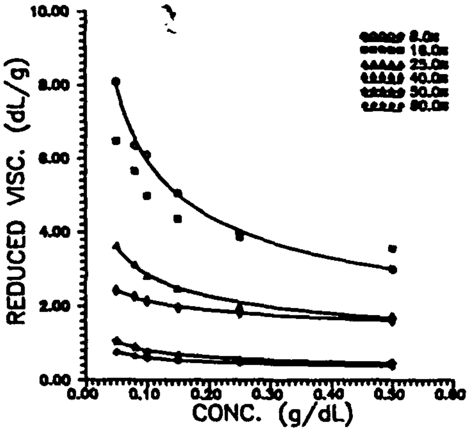


Figure 3. Effect of dodecyl group content on reduced viscosity of polyelectrolytes in DI water.

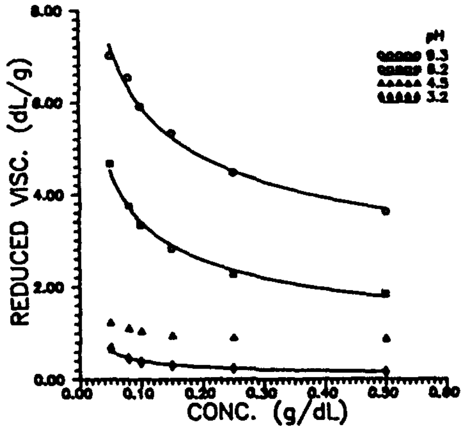


Figure 4. Effect of pH on reduced viscosity of polyelectrolyte containing 12.4% octyl groups.

URITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

. REPORT SECURITY CLASSIFICATION NONE	1b. RESTRICTIVE MARKINGS NONE
. SECURITY CLASSIFICATION AUTHORITY NONE . DECLASSIFICATION / DOWNGRADING SCHEDULE NONE	3. DISTRIBUTION / AVAILABILITY OF REPORT UNLIMITED
PERFORMING ORGANIZATION REPORT NUMBER(S) 90-91-2	5. MONITORING ORGANIZATION REPORT NUMBER(S)
. NAME OF PERFORMING ORGANIZATION University of Southern Mississippi 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research
. ADDRESS (City, State, and ZIP Code) University of Southern Mississippi Polymer Science Department Southern Station Box 10076 Hattiesburg, MS 39406-0076	7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Avenue Arlington, VA 22217
a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
c. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Avenue Arlington , VA 22217	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
Rheological and Photophysical Evidence for Hydrophobic Associations in Water-Soluble Polymers

12. PERSONAL AUTHOR(S)
Stephen A. Ezzell, John C. Middleton and Charles L. McCormick

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
journal article	FROM ______ TO ______		

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL
Charles L. McCormick	(601)266-4868	

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

Rheological and Photophysical Evidence for Hydrophobic Associations in Water-Soluble Polymers

by
Stephen A. Ezzell, John C. Middleton
and Charles L. McCormick

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

Introduction

Studies in our laboratories have focused on developing macromolecules that can maintain or increase the viscosity of aqueous systems in the presence of mono- or multivalent electrolytes. Recent work concentrated on the synthesis and characterization of copolymers of acrylamide with *n*-decylacrylamide (C10 AM). These polymers show unique solution behavior with the incorporation of less than 1 mol % of the n-alkylacrylamide group.[1,2] Polymer association occurs intermolecularly through the pendent hydrophobic groups above a critical polymer concentration (C*). Above C* a rapid increase in apparent viscosity is observed as the polymers form networks with the hydrophobic groups acting as transient crosslinks. Research in our labs has shown these polymers to be very slow to redissolve from the dry state.[3] Additionally, determination of the actual amount of the C10 AM present in the polymer was not possible due to the low amount of incorporation. To overcome this difficulty, we used the hydrophobic monomer N-(4-butyl)phenylacrylamide[4], which has a ultraviolet chromophore, in our polymerization. This enables us to fully characterize the resulting polymer composition by a combination of ultraviolet analysis and elemental analysis. In order to enhance dissolution and provide electrolyte character, a series of terpolymers containing acrylamide (AM), N-*n*-decylacrylamide (C-10 AM) as the hydrophobic group, and sodium-3-acrylamido-3-methylbutanoate (NaAMB), sodium acrylate (NaA), or sodium-2-acrylamido-2-methylpropanesulfonate (NaAMPS) have been synthesized. These monomers appear in Figure 1. Our focus with these materials is on the interplay of hydrophobic and electrostatic interactions as reflected by rheological studies.

We have also employed pyrene-labelled poly(acrylamides) as model systems for polymeric associative behavior. Copolymerization of pyrene derivative APS (Figure 2) with acrylamide via a surfactant polymerization technique gives a pyrene-containing water-soluble polymer (AM-APS). Photophysical investigations of this system lend insight into its microscopic solution characteristics.

Experimental

Acrylamide and AMPS were obtained commercially from Aldrich Chemical Co. and purified by recrystallization from acetone. Acrylic acid was also obtained commercially from Aldrich and purified by vacuum distillation to remove inhibitor before use. N-(4-butyl)phenylacrylamide[5] and NaAMB[6] were synthesized by previously reported methods.

A series of terpolymers was prepared with monomer feeds of 0.5 mole percent of the 4BPAM and 5 and 25 mole percent of each of the ionizable groups. The remaining polymer backbone was composed of acrylamide. The incorporation of water-soluble and water-insoluble monomers into a polymer backbone was accomplished using a surfactant polymerization method.[6] This technique utilizes an aqueous solution of surfactant above its CMC to solubilize the hydrophobic monomer. Sodium dodecyl sulfate was the surfactant in this instance. A water-soluble initiator, potassium persulfate, was used to induce free-radical polymerization.

Ultraviolet spectroscopy was used in determining polymer composition. Beer's law plots were obtained for water-soluble model compound and compared against polymer absorption to verify absorption similarity at 250 nm. Polyacrylamide was used as a reference to remove any background absorption. Elemental analysis (EA) was used to determine carbon and nitrogen present and a combination of UV and EA used to fully characterize the terpolymer composition.

Stock solutions were prepared by dissolving the appropriate amount of salt in deionized water contained in volumetric flasks. The appropriate amount of dried polymer was weighed into a glass container and solvent added. Typical polymer concentrations were 0.2 g/dL. The polymers were dissolved by gentle shaking on an orbital shaker for 14 days to allow complete hydration before further dilutions of these stock solutions were made. Viscosity experiments were conducted on a thermostatically controlled Contraves LS 30 low shear rheometer at variable shear rates. The upper limit of the Contraves was 250 cP. Several polymers had viscosities above the upper limit of the Contraves (250 cP). Graphs have an upper limit of 250 cP and polymers with higher values were considered gels.

The preparation of AM-APS has been previously reported.[7] APS content of this copolymer is 0.25 mol %. Steady-state fluorescence spectra were obtained with a Spex Fluorolog 2 instrument; spectra were taken in the front-face mode. I_E/I_M ratios were obtained from fluorescence intensities measured at 400 nm (monomer emission, I_M) and 510 nm (excimer emission, I_E).

Results

Hydrophobic Polyelectrolytes

Figures 2-4 illustrate the viscosity response of the hydrophobic polyelectrolytes as a function of (1) polymer concentration and (2) salt concentration. These polymer systems are observed to show good salt tolerance. These systems all display typical polyelectrolyte behavior at low salt concentration and maintain their viscosity with increasing salt concentration by means of hydrophobic associations above C*. Terpolymers containing NaA display the best behavior (Figure 5). The more pendent NaAMPS and NaAMB appear to interfere more with hydrophobic association than the NaA which is nearer the polymer backbone.

Pyrene-Labelled Associative Thickeners

The viscosity response and I_E/I_M ratios of AM-APS are shown in Figure 6 as a function of polymer concentration in DI H_2O. A low value of C* is observed for the viscosity response (a -1.1 value of the concentration axis corresponds to 0.8 ppT). I_E/I_M values of the pyrenesulfonamide label are also enhanced above C*. From these trends, we believe the viscosity of this polymer is driven by the hydrophobic associations of the pyrenesulfonamide label. Intermolecular associations are observable at the microscopic level by I_E/I_M measurements; these molecular interactions are reflected on a macroscopic level by the rheological C*.

Acknowledgements

Support for this research by the United States Department of Energy, the Office of Naval Research and the Defense Advanced Research Projects Agency is gratefully acknowledged.

References

1. McCormick, C. L. and Johnson, C. B. *PMSE, 55*, 366 (1986).
2. McCormick, C. L.; Johnson, C. B. and Nonaka, T. *Polymer, 29(4)*, 731 (1988).
3. McCormick, C. L.; Middleton, J. C. and Cummins, D. F. *Polymer Preprints, 30(2)*, 348 (1989).
4. Valint, P. L., Jr.; Bock, J. and Schulz, D. N. *PMSE*, 482 (1987).
5. McCormick, C. L. and Blackmon, K. P. *J. Polym. Sci. Polym. Chem., A24*, 2635 (1986).
6. Turner, S. R.; Siano, D. B. and Bock, J. U. S. Patent 4,520,182.
7. Ezzell, S. A. and McCormick, C. L. *Polymer Preprints, 30(2)*, 340 (1989).

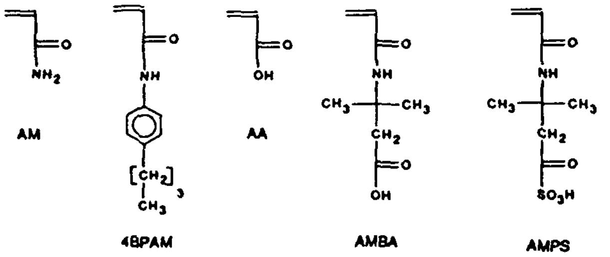


Figure 1. Monomers used to prepare terpolymers.

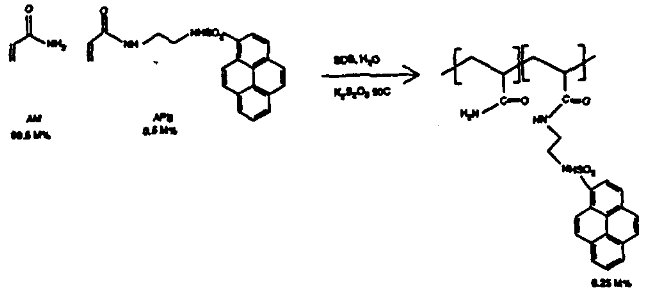


Figure 2. AM-APS Synthesis.

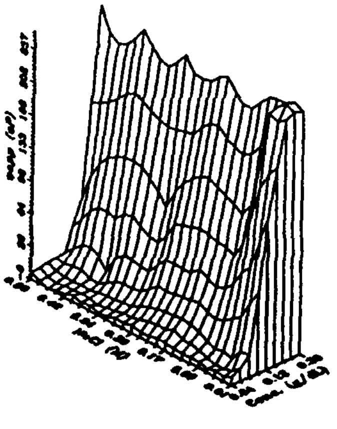


Figure 3. Apparent viscosity as a function of polymer concentration and NaCl ionic strength for a terpolymer of 4BPAM (0.46 mol%), NaAMPS (6.2 mol%), and AM (93.4 mol%).

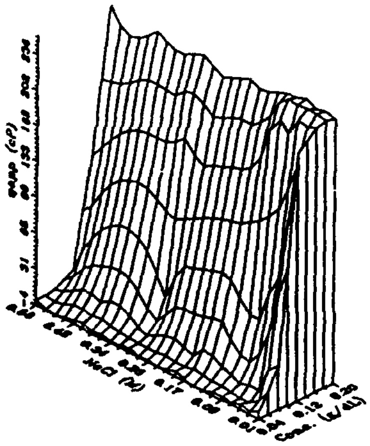


Figure 4. Apparent viscosity as a function of polymer concentration and NaCl ionic strength for a terpolymer of 4BPAM (0.46 mol%), NaAMB (7.7 mol%), and AM (91.8 mol%).

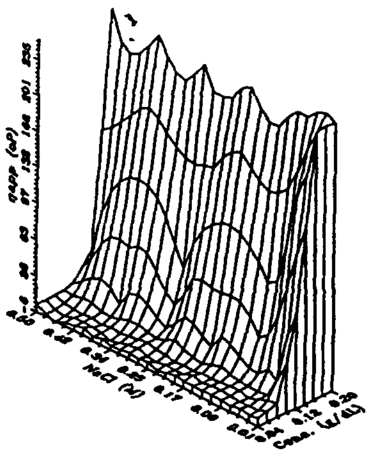


Figure 5. Apparent viscosity as a function of polymer concentration and NaCl ionic strength for a terpolymer of 4BPAM (0.45 mol%), NaA (8.9 mol%), and AM (90.7 mol%).

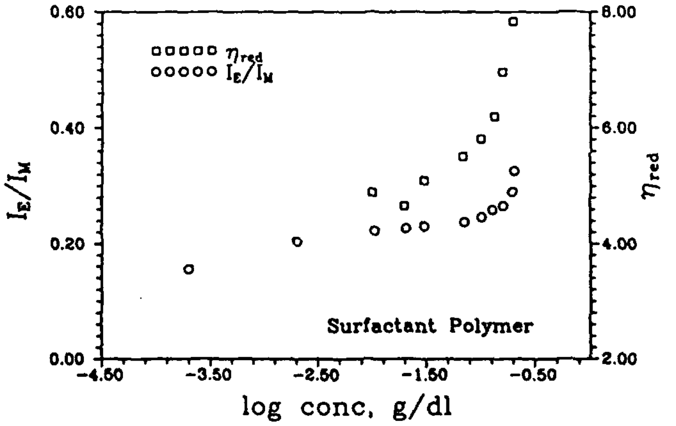


Figure 6. Viscosity response and I_E/I_M for AM-APS in DI H_2O.

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
NONE

1b. RESTRICTIVE MARKINGS
NONE

2a. SECURITY CLASSIFICATION AUTHORITY
NONE

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE
NONE

3. DISTRIBUTION / AVAILABILITY OF REPORT
UNLIMITED

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
90-91-3

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
University of Southern Mississippi

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
Office of Naval Research

6c. ADDRESS *(City, State, and ZIP Code)*
University of Southern Mississippi
Polymer Science Department
Southern Station Box 10076
Hattiesburg, MS 39406-0076

7b. ADDRESS *(City, State, and ZIP Code)*
800 North Quincy Avenue
Arlington, VA 22217

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
Office of Naval Research

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS *(City, State, and ZIP Code)*
800 N. Quincy Avenue
Arlington , VA 22217

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE *(Include Security Classification)*
Properties of Hydrophobically-Modified Water-Soluble Polymers Prepared by Synthetic and Recombinant Techniques

12. PERSONAL AUTHOR(S)
Mark J. Logan, John C. Middleton and Charles L. McCormick

13a. TYPE OF REPORT
journal article

13b. TIME COVERED
FROM ________ TO ________

14. DATE OF REPORT *(Year, Month, Day)*

15. PAGE COUNT

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

22a. NAME OF RESPONSIBLE INDIVIDUAL
, Charles L. McCormick

22b. TELEPHONE *(Include Area Code)*
(601)266-4868

22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

Properties of Hydrophobically-Modified Water-Soluble Polymers Prepared by Synthetic and Recombinant Techniques

by
Mark J. Logan, John C. Middleton
and Charles L. McCormick

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

Introduction

For some time now research in our laboratory has been concentrated on water soluble polymers, in particular acrylamide copolymers. Acrylamide copolymers find use as water-soluble viscosifiers and displacement fluids in enhanced oil recovery. Several studies were conducted by our laboratory with regard to copolymers of acrylamide (AM) and N-(1,1-dimethyl-3-oxobutyl)-N-(n-propyl)acrylamide (PDAAM), Figure 1. As a result, it was observed that AM-PDAAM copolymers experienced a decrease in viscosity in comparison to AM homopolymers of similar molecular weight.[1] At that time we postulated that this phenomenon was due to intrachain associations of the hydrophobic PDAAM units along the polymer chain. Interestingly, in at least one instance, the formation of polymeric emulsions was observed; these became extremely viscous and were stable with time upon the addition of a hydrocarbon (cyclohexane). The formation of this emulsion is believed to be the result of hydrocarbon associating with the hydrophobic domains within the AM-PDAAM copolymer. The propyl group on the amide nitrogen is believed to be responsible for the hydrophobicity of PDAAM; therefore, we are tailoring monomers with successive increases in the length of the alkyl group from propyl to hexyl. We wish to maximize the intramolecular interactions in acrylamide copolymers without significantly reducing performance as a water-soluble, microheterogeneous copolymer. Upon finding this maximum in properties we will utilize this data base to produce pH responsive micellar polymers using charged comonomers.

In conjunction with the investigation of acrylamide copolymers, the hydrophobic associations of de novo proteins are being examined. Proteins can be classified into three main categories: globular, membrane and fibrous. Ultimately, these tertiary structures are the product of the interactions of the secondary structures: alpha-helices, beta-sheets and random coil regions. The formation of these secondary structures can be attributed to a careful balance of several molecular forces along the protein backbone. Most notable of these forces are hydrogen bonding, hydrophobic interactions and electrostatic effects. Through these interactions we would initially like to explore the development of a de novo protein which would demonstrate properties similar to that of ionic surfactants.

Experimental

PDAAM Synthesis

The synthesis for PDAAM is found in reference 1. Synthesis of the hydrophobic monomers of increasing alkyl chain length is not changed significantly from that of PDAAM. Polymerization of the acrylamide copolymers utilizes a micellar technique reported by Peer.[2] Elemental analysis is used to determine copolymer structure. Molecular weight measurements are obtained using membrane osmometry. Viscosity data are obtained using a Contraves Low Shear 30 rheometer.

De Novo Protein

Secondary structure is predicted using the Chou and Fasman method[3] of conformation prediction. Oligonucleotide synthesis is performed using a Milligen/Biosearch Cyclone Plus DNA synthesizer. Expression vectors were obtained from Stratagene; NH8a, NH16a and NH18a are the expression vectors used. Characterization consists of ^{13}C-NMR, ^{1}H-NMR, membrane osmometry, and FT-IR.

Discussion

Polymeric micelles have gained much attention recently. Much of the attention has been devoted to the understanding of molecular forces and solution properties of amphiphilic polymer micelles in water. The hydrophobic side-chain length, length of the hydrophobic backbone sequences and electrostatic forces affect the formation of the polymeric micelle. It has also been demonstrated that the length of the alkyl group, more so than the charge density, affects the onset of micelle formation. For this reason, we wish to explore the effects of alkyl chain length on the formation of a polymeric micelle.

In addition to the length of the alkyl chain, the length of the hydrophobic sequence in the polymer is also believed to affect the strength of intramolecular hydrophobic interactions. In an attempt to explore the effect of length of the hydrophobic sequence in the polymer backbone, a micellar polymerization scheme will be utilized as reported by Peer.[2] In this way it is possible to increase the length of the hydrophobic segment by the sue of cosurfactant; varying the concentration of hydrophilic co-monomer and finally the length of the alkyl chain on the hydrophobic monomer may also alter the length of the hydrophobic segment in the polymer chain.

The formation of micelles is not exclusive to synthetic molecules; nature also produces a multitude of systems that aggregate to form micelles. Indeed these aggregations are essential for many complex chemical reactions and biological processes. These micelles may be formed by phospholipids as well as proteins. Due to recent advances in both recombinant DNA technology and de novo protein design, it seems that now the ability to produce a protein with a predicted structure from first principles is a possibility.

Presently, there are a plethora of schemes to predict the secondary and tertiary structure of proteins from their amino acid composition. Many of these use complex algorithms to calculate minimal energy conformations, accessibility of solvent, hydrophobicities of the amino acids, and hydrophobic moments. These methods have all demonstrated some level of success in predicting protein conformations. One of the most widely used techniques of secondary structure prediction is that of Chou and Fasman[3]; this was subsequently refined by Chou.[4] The method uses parameters obtained from the analysis of known sequences and structures to predict the secondary structure of a protein. Briefly, the X-ray structure of 64 different proteins were analyzed in terms of their alpha-helical and beta-sheet regions as well as their amino acid composition. Distinct classes of proteins were shown to possess significantly different amino acid compositions. Through the use of their computerized algorithm proteins have been assigned to their correct structural class with 80% accuracy.

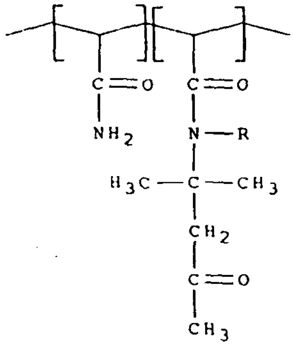
By using the Chou and Fasman method of structure prediction, it is hoped that a protein of a low molecular weight can be designed and produced which displays surfactant-like properties.

Acknowledgements

Support of this research by the United States Department of Energy, the Office of Naval Research and the Defense Advanced Research Projects Agency is gratefully acknowledged.

References

1. McCormick, C. L. and Blackmon, K. P. *Agnew, Makromol.*, *144*, 87-99 (1986).
2. Peer, W. J. *Polymers in Aqueous Media*, Advances in Science Series No. 223; J. E. Glass, Ed.; American Chemical Society: Washington, DC, 1987; p. 381-397.
3. Chou, P. Y. and Fasman, G. D. *Adv. Enzymology*, *47*, 45-148 (1978).
4. Chou, P. Y. *Prediction of Protein Structure and the Principles of Protein Conformation*; G. D. Fasman, Ed.; Plenum Press: New York, 1989; p. 549-587.



R: Propyl, Butyl, Pentyl, Hexyl

Figure 1. Acrylamide copolymer.

CURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

a. REPORT SECURITY CLASSIFICATION
NONE

1b. RESTRICTIVE MARKINGS
NONE

a. SECURITY CLASSIFICATION AUTHORITY
NONE

b. DECLASSIFICATION / DOWNGRADING SCHEDULE
NONE

3. DISTRIBUTION / AVAILABILITY OF REPORT
UNLIMITED

. PERFORMING ORGANIZATION REPORT NUMBER(S)
90-91-4

5. MONITORING ORGANIZATION REPORT NUMBER(S)

a. NAME OF PERFORMING ORGANIZATION
University of Southern
Mississippi

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
Office of Naval Research

c. ADDRESS *(City, State, and ZIP Code)*
University of Southern Mississippi
Polymer Science Department
Southern Station Box 10076
Hattiesburg, MS 39406-0076

7b. ADDRESS *(City, State, and ZIP Code)*
800 North Quincy Avenue
Arlington, VA 22217

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
Office of Naval Research

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS *(City, State, and ZIP Code)*
800 N. Quincy Avenue
Arlington , VA 22217

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE *(Include Security Classification)*
Synthetic, Photophysical and Viscometric Studies of Pyrene-Labelled Acrylamid
Copolymers

12. PERSONAL AUTHOR(S)
Michael C. Kramer, Stephen A. Ezzell and Charles L. McCormick

13a. TYPE OF REPORT
journal article

13b. TIME COVERED
FROM ________ TO ________

14. DATE OF REPORT *(Year, Month, Day)*

15. PAGE COUNT

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

22a NAME OF RESPONSIBLE INDIVIDUAL
Charles L. McCormick

22b. TELEPHONE *(Include Area Code)*
(601)266-4868

22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

Synthetic, Photophysical and Viscometric Studies of Pyrene-Labelled Acrylamide Copolymers

by
Michael C. Kramer, Stephen A. Ezzell
and Charles L. McCormick

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

Introduction

Our research group has investigated the solution properties of water-soluble copolymers capable of forming hydrophobic microdomains.[1,2] These hydrophobically modified polymers are of interest for utility as rheology modifiers, drilling fluids for enhanced oil recovery, and as controlled-release media for pharmaceuticals and pesticides. We are interested in evaluation of the microscopic behavior of these systems via photophysical studies. Comparison of rheological and photophysical studies can offer insight into the structure-property relationships of these systems.[3]

Experimental

The synthesis of [(1-(β-aminoethyl) sulfonamidopyrene)] acrylamide (APS) and copolymerization with acrylamide (AM) has been previously reported utilizing both solution and micellar polymerization techniques (Figures 1 and 2).[4] Steady-state fluorescence spectra were recorded with a Spex Fluorolog 2 fluorescence spectrometer, taken in front-face mode, with slits set at 0.5 nm. The excitation wavelength was 340 nm; emission was recorded in the range of 350-600 nm. Fluorescence decay curves were measured with a Photochemical Associates single-photon counting instrument with a H_2-filled 510-B flashlamp. A digital micro PDP-11 and PRA software were used to fit decay profiles using the noniterative deconvolution technique. Decay times were measured by excitation set at 340 nm and monomer emission at 400 nm. Viscometric measurements were made using a Contraves LS-30 low-shear rheometer at 25°C with a constant shear rate of 6 sec^{-1}.

AM-APS Copolymerization

As previously reported, AM and APS were successfully copolymerized by solution and micellar techniques. These two techniques yield 0.35 and 0.25 mol. % APS incorporation, respectively (Figures 1 and 2). It was found that these two techniques yielded two entirely different microstructures, the APS units randomly incorporated into solution-polymerized AM-APS and micellar polymerization giving a block-like microstructure. This blockiness for copolymers synthesized in the presence of surfactant has been reported by others.[5]

Results and Discussion

The ratio of excimer to monomer emission (I_E/I_M) and reduced viscosity (η_{red}) as a function of concentration for solution and micellar-polymerized AM-APS are shown in Figures 3 and 4. For the case of solution-polymerized AM-APS, fluorescence data indicates there is no change with concentration in polymer conformation on the microscopic level. The viscosity response is likewise independent of concentration. We believe this is a result of the random incorporation of APS units. Hydrophobic intramolecular associations of the randomly-spaced pyrenesulfonamide label may collapse the polymer coil. Viscometry of micellar-polymerized AM-APS shows a low critical overlap concentration (C*), and I_E/I_M measurements are enhanced above C*. The viscosity response above C* seems to be driven by intermolecular hydrophobic interactions of the pyrenesulfonamide labels as reflected by I_E/I_M. Fluorescence lifetime studies (Table 1) show a double-exponential decay for both copolymers. These lifetimes are similar in value to those of the water-soluble pyrene-labelled model compounds PSGA and PSGL (Figure 5). These data indicate that the APS units are in an aqueous microenvironment. Fluorescence quenching studies with nitromethane, a hydrophilic quencher, give Stern-Volmer quenching constants (K_{SV}) indicative of a diffusion-controlled process. This indicates the absence of microdomains, excepting microheterogeneity resulting from interaction of the pyrene moieties to form excimer.

Conclusions

Photophysical and viscometric studies of solution and micellar-polymerized AM-APS indicate that the molecular solution behavior can effectively be probed via fluorescence studies. Observed trends parallel those encountered in viscometry, allowing development of structure-property relationships. Fluorescence lifetime and quenching studies suggest that the APS labels are in an aqueous microenvironment. This intriguing copolymer series is currently being further investigated and additional APS-labelled systems are also under investigation.

Acknowledgements

Support from the United States Department of Energy, the Office of Naval Research, the Defense Advanced Research Projects Agency, and Unilever is gratefully acknowledged.

References

1. McCormick, C. L.; Nonaka, T.; and Johnson, C. B. *Polymer*, *29*, 738 (1988).
2. McCormick, C. L.; Hutchinson, B. H.; and Morgan, S. E., *Makromol. Chem.*, *188*, 357 (1987).
3. Clark, M. D.; McCormick, C. L.; and Hoyle, C. E., *Macromolecules*, *23*, 3124 (1990).
4. Ezzell, S. A.; and McCormick, C. L., *Polym. Prepr.*, *30(2)*, 340 (1989).
5. Peer, W. J., *PMSE*, *57*, 492 (1987).

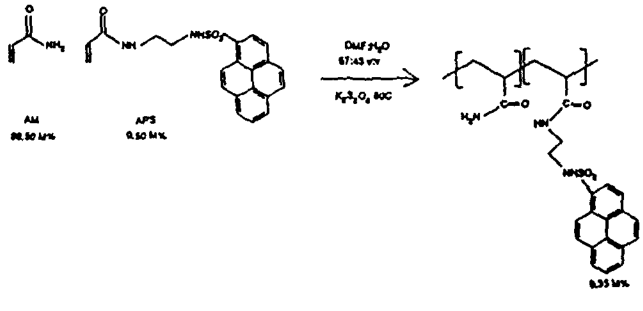


Figure 1. Solution polymerization scheme.

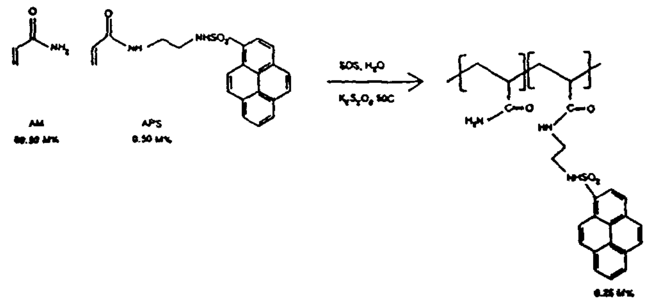


Figure 2. Surfactant polymerization scheme.

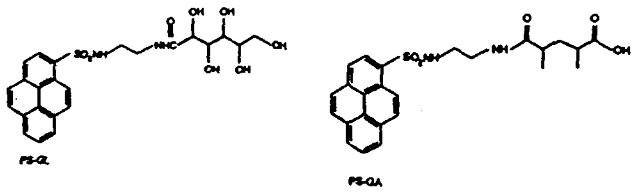


Figure 5. Model compounds PSGA and PSGL.

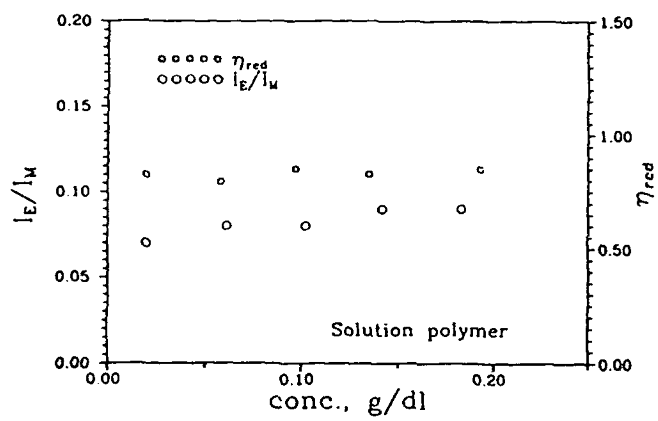


Figure 3. Excimer:monomer emission ratios (I_E/I_M) and reduced viscosity (η_{red}) vs. concentration, solution-polymerized AM-APS in deionized H_2O.

Table I
Nitromethane Quenching Studies in Deionized H_2O

Model Compounds

	C, $\overline{m}$	Ksv, μm^{-1}	T, ns
PSGL	3.1×10^{-7}	5.8×10^{4}	13.4
PSGA	2.5×10^{-7}	4.9×10^{4}	13.3

Solution-Polymerized AM-APS

Polymer C g/dl	APS C $\overline{m}$	Ksv μm^{-1}	T_1	T_2
1.93×10^{-1}	9.3×10^{-5}	1.2×10^{4}	12.9	18.7
1.93×10^{-3}	9.3×10^{-7}	1.7×10^{4}	8.6	13.3

Surfactant-Polymerized AM-APS

Polymer C g/dl	APS C $\overline{m}$	Ksv μm^{-1}	T_1	T_2
2.18×10^{-1}	7.1×10^{-5}	1.1×10^{4}	7.7	13.5
2.18×10^{-3}	7.1×10^{-7}	2.3×10^{4}	7.8	13.8

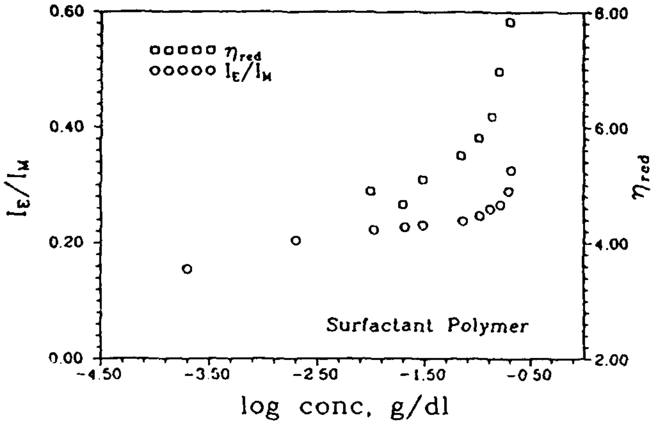


Figure 4. Excimer:monomer emission *ratios* (I_E/I_M) and reduced viscosity (η_{red}) vs. concentration, surfactant-polymerized AM-APS in deionized H_2O.

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION NONE	1b. RESTRICTIVE MARKINGS NONE
2a. SECURITY CLASSIFICATION AUTHORITY NONE	3. DISTRIBUTION/AVAILABILITY OF REPORT UNLIMITED
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE NONE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) 90-91-5	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION University of Southern Mississippi	6b. OFFICE SYMBOL *(If applicable)*
7a. NAME OF MONITORING ORGANIZATION Office of Naval Research	
6c. ADDRESS (City, State, and ZIP Code) University of Southern Mississippi Polymer Science Department Southern Station Box 10076 Hattiesburg, MS 39406-0076	7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Avenue Arlington, VA 22217
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL *(If applicable)*
9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Avenue Arlington , VA 22217	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO.

11. TITLE *(Include Security Classification)*
Photophysical and Rheological Properties of Naphthalene-Labelled Water-Soluble Copolymers Polymerized in Surfactant Solution

12. PERSONAL AUTHOR(S)
Kelly D. Branham, John C. Middleton and Charles L. McCormick

13a. TYPE OF REPORT journal article	13b. TIME COVERED FROM ______ TO ______	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION
22a. NAME OF RESPONSIBLE INDIVIDUAL Charles L. McCormick	22b. TELEPHONE *(Include Area Code)* (601)266-4868 / 22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

Photophysical and Rheological Properties of Naphthalene-Labelled Water-Soluble Copolymers *Polymerized in Surfactant Solution*

by
Kelly D. Branham, John C. Middleton
and Charles L. McCormick

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

Introduction

Research in our labs has recently focused on the synthesis and characterization of intra- and intermolecularly associating, water-soluble copolymers. Probing of microenvironmental and microstructural properties of these polymers by photophysical methods has proven to be a useful tool in determining structure-property relationships of these polymers in solution. Solution properties of a copolymer of acrylamide (Am) containing less than one mole percent of n-decylacrylamide polymerized under micellar conditions has been previously reported. This copolymer showed interesting associative properties.[1] Hydrophobically-modified copolymers of acrylamide, associations of which can be monitored by both viscometry and fluorescence spectroscopy, represent the next step in our studies of polymeric associations.

Polymer microstructure has been shown to play an important role in the photophysical properties of polymers synthesized under solution and micellar conditions.[2] Also, the extent of hydrophobe incorporation and microstructural heterogeneity of copolymers has been reported as a function of the concentration of surfactant used in micellar polymerizations.[3] In this paper we wish to report the synthesis of a series of water-soluble copolymers of acrylamide with less than one mole percent of 4-(1-naphthylacetamido)butyl acrylamide (NABAm) (Figure 1) which are polymerized under micellar conditions. The photophysical and rheological properties of these systems indicate microstructural differences based on the surfactant-to-hydrophobe ratio used in the synthesis of each copolymer.

Experimental

NABAm Synthesis

All materials were obtained from Aldrich in the highest purity available and were used as received unless otherwise noted. NABAm was prepared via a four step synthesis as shown in Figure 2. The dicyclohexylcarbodiimide coupling agent (0.16 mole) was dissolved in chloroform (100ml) and added rapidly to a slurry of 1-naphthylacetic acid (0.16 mole) and n-hydroxysuccinimide (0.16 mole) in chloroform (400ml). The hydroxysuccinimide ester was diluted to a volume of 1.2l and reacted with butylamine (2.26 mole in 300ml chloroform) via a modified high dilution technique for the monosubstitution of symmetrical diamines.[4] The monosubstituted product was obtained, with only a trace of the disubstituted product present. UV analysis indicated 0.08 mole (50% yield) of the reaction product was present. This solution was concentrated to 170ml by rotary evaporation. "Proton Sponge" (0.085 mole) was added as an acid scavenger and the solution was diluted to 400ml. Acryloyl chloride (0.08 mole) was dissolved in chloroform (50ml) and added dropwise to the solution. All steps were carried out in an ice/salt bath below 0 °C. The resulting product was recrystallized twice from a methanol:chloroform mixture.

Copolymer Synthesis

Acrylamide was obtained from Aldrich and recrystallized twice from acetone. The copolymers were synthesized in deionized water at 50 °C using a micellar polymerization technique previously described in the literature.[5] A typical synthesis used 0.1089 moles of Am, 0.0011 moles of NABAm, and 3.67 x 10^{-5} moles $K_2O_8S_2$ as the initiator. This technique employs a surfactant above its CMC to solubilize the hydrophobic NABAm. Sodium dodecyl sulfate (SDS) was used in this study, varying the molar ratios to NABAm from 20:1 to 80:1. Polymerizations were allowed to proceed for approximately four hours after which the polymers were precipitated into acetone and vacuum dried. The copolymers were redissolved in deionized water, purified by dialysis and freeze dried. The NABAm content of the copolymers was determined by UV analysis at 280nm; these results appear in Table I along with the SDS to NABAm ratios.

Fluorescence Spectra

Steady-state emission spectra were obtained on a Spex Fluorolog-2 fluorescence spectrophotometer. Samples (0.4 g/L) were deaerated with helium. Excitation wavelength was 280nm and the monomer intensities (I_M) and excimer intensities (I_E) were measured at 330 and 400nm, respectively.

Viscosimetric Studies

Solution viscosities were measured at 30 °C on a Contraves LS-30 low shear rheometer at a shear rate of 6 s^{-1} after dissolving the appropriate amount of polymer in 0.5 M NaCl water with gentle shaking over the period of several days. Polymer concentration ranged from 0.20 to 0.04 g/dL.

Results and Discussion

Varying the SDS to NABAm concentration ratios from 20:1 to 80:1 in the synthesis of the copolymers effects both the degree of hydrophobe incorporation and the fluorescence properties of this series of copolymers. The steady-state spectra (Figure 2), as well as the I_E/I_M ratios listed in Table I, indicate that the steady-state fluorescence properties can be correlated with copolymer microstructure. As the surfactant-to-hydrophobe ratio decreases, an increase in I_E/I_M is observed. The data indicate increased hydrophobic associations of the NABAm moieties. As the SDS to NABAm ratio is decreased, the number of hydrophobic groups per micelle is increased. This apparently results in a more blocky microstructure, as reflected by the enhanced values of I_E/I_M.

These results agree with recent reports. Valint et al. report drifts in hydrophobe incorporation as well as changes in polymer microstructural heterogeneity, as a function of the SDS concentration employed in polymerization.[3] Also, Dowling and Thomas used steady state and transient fluorescence measurements to determine block lengths of styrene in a water-soluble styrene/acrylamide copolymer polymerized under micellar conditions.[2] They report that the block length of styrene increases, with decreasing surfactant-to-styrene ratios.

Plots of reduced viscosity verses concentration (Figure 3) show that reduced viscosity tends to increase as the SDS-to-NABAm molar ratio decreases, indicating a correlation between NABAm block length and intermolecular polymer association. Peer has pointed out that hydrophobic interactions depend on the sequence length of the hydrophobic blocks.[6] Longer hydrophobic blocks, fewer of which are on the polymer chain would tend to favor inter- over intramolecular interactions. Further rheological studies are currently underway.

Conclusions

Naphthalene-labelled polyacrylamides have been synthesized via a micellar technique, with varied molar ratios of surfactant-to-hydrophobic naphthalene monomer. Blocky microstructural characteristics are suggested by the I_e/I_m values. As the SDS-to-NABAm molar ratio is decreased, fewer micelles with higher NABAm content are formed. This results in longer blocks of NABAm and higher degrees of hydrophobe incorporation. Also, reduced viscosity appears to increase with increasing block length and hydrophobe content.

Acknowledgements

Support of this research by the United States Department of Energy, the Office of Naval Research and the Defense Advanced Research Projects Agency is gratefully acknowledged.

References

1. McCormick, C. L.; Johnson, C. B; Nonaka, T. *Polymer*, *29*, 731 (1988).
2. Dowling, K. C. and Thomas, J. K. *Macromolecules*, *23*, 1059 (1990).
3. Valint, P. L., Jr.; Bock, J.; Ogletree, J.; Zushma, S. and Pace, S. J. *Polymer Preprints*, *31*, 67 (1990).
4. Jacobson, A. R.; Makris, A. N. and Sayre, L. M. *J. Org. Chem.*, *52*, 2592 (1987).
5. Turner, S. R.; Siano, D. B. and Bock, J. U.S. Patent 4,520,182.
6. Peer, W. J. *Polymers in Aqueous Media*, ACS Advances in Science Series No. 223; J. E. Glass, Ed.; American Chemical Society: Washington, DC, 1987.

Table I. Excimer to Monomer Ratios and NABAm Content of AM/NABAm Copolymers

SDS:NABAm	Mole% NABAm	I_e/I_m
20:1	0.92	0.53
35:1	0.75	0.36
50:1	0.73	0.29
65:1	0.61	0.26
80:1	0.67	0.22

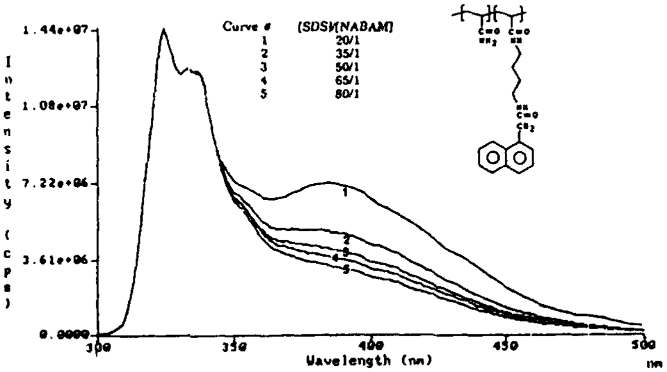


Figure 1. Steady-state fluorescence emission spectra of Am/NABAm copolymers.

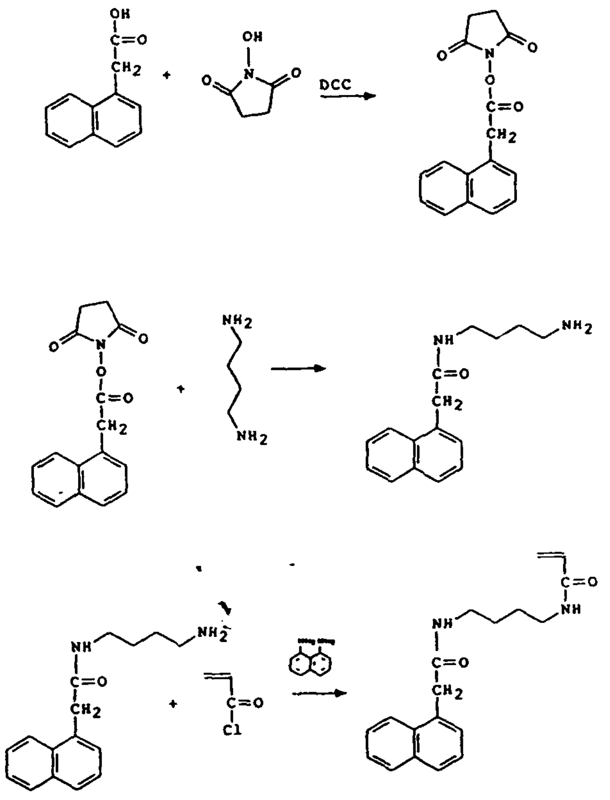


Figure 2. Synthetic scheme for NABAm.

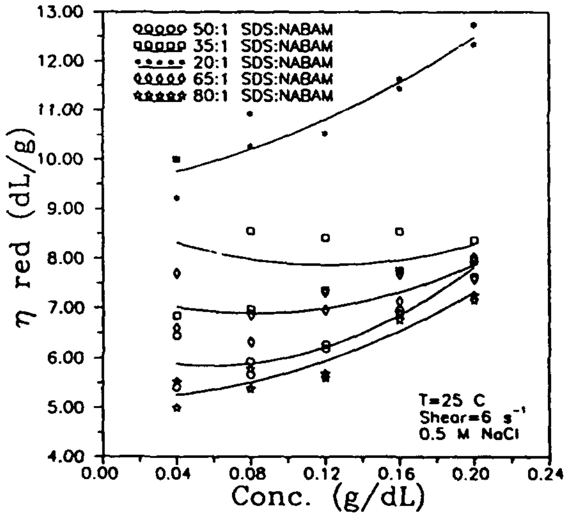


Figure 3. Plots of reduced viscosity vs. concentration for AM/NABAm copolymers.

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
NONE

1b. RESTRICTIVE MARKINGS
NONE

2a. SECURITY CLASSIFICATION AUTHORITY
NONE

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE
NONE

3. DISTRIBUTION / AVAILABILITY OF REPORT
UNLIMITED

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
90-91-6

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
University of Southern
Mississippi

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
Office of Naval Research

6c. ADDRESS *(City, State, and ZIP Code)*
University of Southern Mississippi
Polymer Science Department
Southern Station Box 10076
Hattiesburg, MS 39406-0076

7b. ADDRESS *(City, State, and ZIP Code)*
800 North Quincy Avenue
Arlington, VA 22217

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
Office of Naval Research

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS *(City, State, and ZIP Code)*
800 N. Quincy Avenue
Arlington , VA 22217

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE *(Include Security Classification)*
Copolymers of Sodium 2-Acrylamido-2-Methyl-Propanesulfonate with (2-Acrylamido-2-Methylpropyl)trimethylammonium Chloride

12. PERSONAL AUTHOR(S)
Erich E. Kathman, Luis C. Salazar and Charles L. McCormick

13a. TYPE OF REPORT
journal article

13b. TIME COVERED
FROM ________ TO ________

14. DATE OF REPORT *(Year, Month, Day)*

15. PAGE COUNT

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

22a. NAME OF RESPONSIBLE INDIVIDUAL
Charles L. McCormick

22b. TELEPHONE *(Include Area Code)*
(601)266-4868

22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

Copolymers of Sodium 2-Acrylamido-2-Methyl-Propanesulfonate with (2-Acrylamido-2-Methylpropyl)trimethylammonium Chloride

by

Erich E. Kathmann, Luis C. Salazar
and Charles L. McCormick

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

Introduction

Polyelectrolytes and polyampholytes have been the subject of study in our laboratories for the past several years. Using monomers designed specifically for incorporation into water soluble polymers, we have been able to tailor the properties of aqueous systems. Negatively charged monomers such as sodium 2-Acrylamido-2-methylpropanesulfonate (NaAMPS) 1 can be homopolymerized or copolymerized with a neutral monomer such as acrylamide to yield anionic polyelectrolytes. Likewise, a positively charged monomer such as 2-acrylamido-2-methylpropyltrimethylammonium chloride (AMPTAC) 2 can be homopolymerized or copolymerized to yield a cationic polyelectrolyte. When equal molar concentrations of negatively charged monomers and cationically charged monomers are polymerized, the resulting macromolecule is referred to as a polyampholyte.

This paper reports the study of a series of copolymers that have varying ratios of NaAMPS and AMPTAC. The resulting systems exhibit solution behavior typical of polyanions, polycations, and polyampholytes dependent upon copolymer structure and characteristics of the solvating medium. Previous work in our laboratories has dealt with the comonomer AMPDAC (2-acrylamido-2-methylpropyldimethylammonium chloride) 3[1] which was capable of reducing its cationic character by loss of HCl. In the case of copolymers of AMPDAC and acrylamide, such neutralization resulted in polymer precipitation as the charge disappeared. AMPTAC was specifically designed to solve this problem.

Experimental

Monomer Synthesis

2-Acrylamido-2-methylpropyltrimethylammonium chloride (AMPTAC) 2 was synthesized by reacting 2-acrylamido-2-methylpropanedimethyl-amine (AMPDA) with a ten-fold excess of methyl iodide in diethyl ether. Methyl iodide was obtained from the Aldrich Chemical Co. and was used without further purification. The synthesis of AMPDA has been previously reported.[2] This initial reaction gave the quaternized monomer with an I^- counterion. The iodide ion was then ion-exchanged using Dowex Cl^- resin to obtain the desired AMPTAC 2. 2-Acrylamido-2-methylpropanesulfonic acid was obtained from the Fluka Chemical Co. and recrystallized using a methanol/2-propanol solvent system before use. Potassium persulfate from J. T. Baker Co. was recrystallized twice from deionized water.

Copolymer Synthesis

The homopolymers of NaAMPS and AMPTAC and the copolymers of AMPTAC with NaAMPS, the ATAS series, were synthesized free radically in a 0.512-M NaCl aqueous solution under nitrogen at 30°C using 0.1 mol % potassium persulfate as the initiator. The monomer concentration was held at 0.45 M and the pH adjusted to 7.0 ± 0.1 with sodium hydroxide to convert the neutral sulfonic acid moiety to the charged sodium sulfonate moiety. The reaction was terminated at <30% conversion due to the high viscosity of the reaction medium and as a precaution against copolymer feed drift. The polymers were precipitated in acetone, redissolved in deionized water, dialyzed against water, and then lyophilized. All copolymers were soluble in deionized water except for ATAS-50. This copolymer precipitated from solution during dialysis and remained insoluble until NaCl was added. Conversions were determined gravimetrically.

Copolymer Characterization

Elemental analyses for carbon, hydrogen, nitrogen, and sulfur were conducted by M-H-W Laboratories of Phoenix, AZ on both the low and high conversion copolymer samples. ^{13}C NMR studies were performed on the ATAS copolymers at 22.5 MHz on a JEOL FX-90Q Spectrometer to confirm the elemental analysis results. The procedure for quantitatively determining copolymer compositions from ^{13}C NMR has been discussed in detail elsewhere.[3] Light scattering studies were performed on a Chromatix KMX-6 low-angle laser light scattering spectrophotometer. Refractive index increments were obtained using a Chromatix KMX-16 laser differential refractometer.

Viscosity Measurements

Stock solutions of sodium chloride (0.10, 0.20, 0.30, 0.50 and 0.75M NaCl) were prepared by dissolving the appropriate amount of salt and a small amount of sodium azide in deionized water in volumetric flasks. Polymer stock solutions were made by dissolving the appropriate amount of polymer in these salt solutions. The solutions were then diluted to appropriate concentrations and allowed to age for two to three weeks before being analyzed with a Contraves LS-30 rheometer. Triplicate samples were prepared of each concentration to reduce experimental error.

Results and Discussion

Macromolecular Structure

The ratio of 1 and 2 in the polymerizations was varied in the feed to obtain the series of ATAS copolymers. The number appended to the acronym ATAS refers to the amount of 2 in the feed. For example ATAS-40 represents a polymer made with 60% 1 and 40% 2 in the feed.

The compositions of the ATAS copolymers determined using ^{13}C NMR and elemental analysis are presented in Table 1. Differences in the compositions may be due to the loss of NaCl upon the formation of 1:2 monomer pairs. Salmone et al.[4,5] have synthesized and polymerized cationic-anionic monomer salt pairs into alternating copolymers. As was shown in our labs with the ADAS series[1], AMPDAC and NaAMPS likewise form ion pair associations. We expect the same behavior for the ATAS series. Figure 2 illustrate the feed verses copolymer composition for the ATAS and ADAS copolymer series. Both copolymer series exhibit alternating tendencies.

Effects of Copolymer Composition

The effects of copolymer composition on the intrinsic viscosities of the ATAS and ADAS copolymers in 0.10 M NaCl are shown in Figure 3. Both copolymer series exhibit viscosity minima when there is an equal molar amount of each charged monomer in the copolymers. This is characteristic of polyampholyte behavior. Attractive electrostatic interactions reduce the hydrodynamic volume of the polymer coils. As the copolymer compositions develop charge imbalances, an increase in the solution viscosity is observed due to repulsive electrostatic interactions which increase the hydrodynamic volume. The low viscosities for ATAS-100 and ADAS-100 are due to low molecular weights.

Effects of Added Electrolytes

The effects of sodium chloride on the intrinsic viscosities of the ATAS copolymers and the NaAMPS and AMPTAC homopolymers were determined at a shear rate of 5.96 sec^{-1}. The solutions of these polymers show decreasing intrinsic viscosities with increasing ionic strength. ATAS-0, an anionic homopolymer of NaAMPS, shows the greatest decrease in viscosity as the salt concentration is increased. As more AMPTAC is incorporated this effect is less pronounced due to the transition of the copolymers from polyelectrolytes to polyampholytes. At equal concentration of each monomer in the copolymers, (ATAS-50) there is little change in the viscosity.

Conclusions

A series of high charge density polyelectrolytes and polyampholytes has been synthesized. The homopolymers of NaAMPS and AMPTAC and the copolymers of NaAMPS and AMPTAC have been synthesized and are currently being characterized. As the amount of AMPTAC in the copolymers increases to an equal balance with the NaAMPS, the copolymers behave less like polyelectrolytes and more as polyampholytes. This behavior is reflected in the increased viscosity with added electrolytes.

Acknowledgements

Support of this research by the United States Department of Energy, the Office of Naval Research and the Defense Advanced Research Projects Agency is gratefully acknowledged.

References

1. McCormick, C. L. and Johnson, C. B. *Macromolecules*, *21*, 686 (1988).
2. McCormick, C. L. and Blackmon, K. P. *Polymer*, *27*, 1971 (1986).
3. McCormick, C. L. and Hutchinson, B. H. *Polymer*, *27(4)*, 623 (1986).
4. Salmone, J. C.; Tsai, C. C.; and Watterson, A. C. In *Ions in Polymers*, Advances in Chemistry Series No. 187; American Chemical Society: Washington, DC, 1980; p 337.
5. Salmone, J. C.; Mahmud, N. A.; Mahmud, M. U.; Nagabhushanam, T.; and Watterson, A. C. *Polymer*, *23*, 843 (1988).

Table I
Compositions of the ATAS Copolymers as
Determined by Elemental Analysis^a and ^{13}C NMR^b.

Sample	AMPTAC^a %	NaAMPS^a %	AMPTAC^b %	NaAMPS^b %
ATAS-10	14.68	85.32	21.02	78.98
ATAS-25	36.04	63.96	36.38	63.62
ATAS-40	45.30	54.70	40.03	59.97
ATAS-50	51.65	48.35	49.05	50.95
ATAS-70	65.69	34.31	62.00	38.00

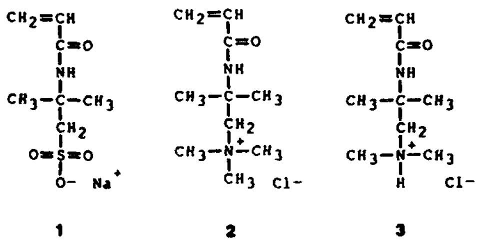


Figure 1.

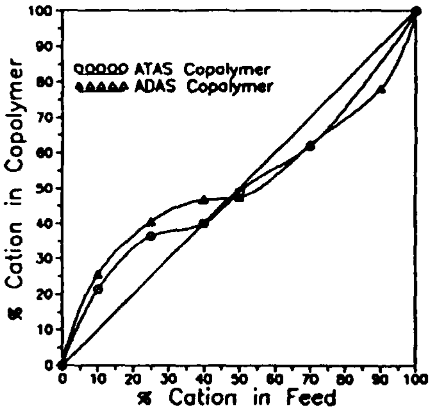


Figure 2. Compositions of the ADAS and ATAS copolymers as a function of feed.

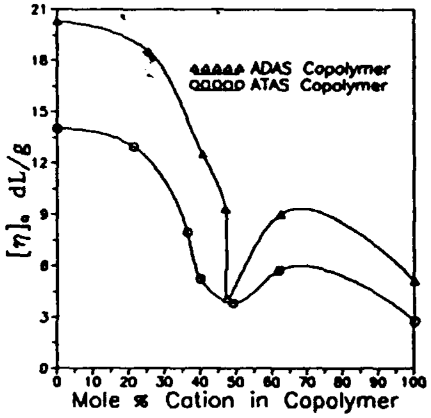


Figure 3. Dependence of the ATAS and ADAS copolymer series on composition in 0.1 M NaCl determined at 25°C with a shear rate of 5.96 sec^{-1}.

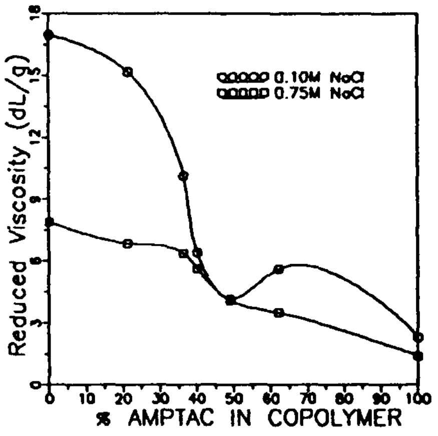


Figure 4. Reduced viscosities for the ATAS copolymer series as a function of composition in 0.01M and 0.75M NaCl. Determined with a polymer concentration of 0.05 g/dL at a shear rate of 5.96 sec^{-1} at 25°C.

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
NONE

1b. RESTRICTIVE MARKINGS
NONE

2a. SECURITY CLASSIFICATION AUTHORITY
NONE

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE
NONE

3. DISTRIBUTION / AVAILABILITY OF REPORT
UNLIMITED

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
90-91-7

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
University of Southern
Mississippi

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
Office of Naval Research

6c. ADDRESS *(City, State, and ZIP Code)*
University of Southern Mississippi
Polymer Science Department
Southern Station Box 10076
Hattiesburg, MS 39406-0076

7b. ADDRESS *(City, State, and ZIP Code)*
800 North Quincy Avenue
Arlington, VA 22217

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
Office of Naval Research

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS *(City, State, and ZIP Code)*
800 N. Quincy Avenue
Arlington , VA 22217

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE *(Include Security Classification)*
Spin Traps as Probes of Hydrophobicity in Poly(Maleic Anhydride-Alt-Ethyl Vinyl Ethers) Modified with Pendent Hydrophobic Alkyl Amine Groups

12. PERSONAL AUTHOR(S)
J. Kent Newman and Charles L. McCormick

13a. TYPE OF REPORT
journal article

13b. TIME COVERED
FROM ________ TO ________

14. DATE OF REPORT *(Year, Month, Day)*

15. PAGE COUNT

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

22a NAME OF RESPONSIBLE INDIVIDUAL
Charles L. McCormick

22b. TELEPHONE *(Include Area Code)*
(601)266-4868

22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

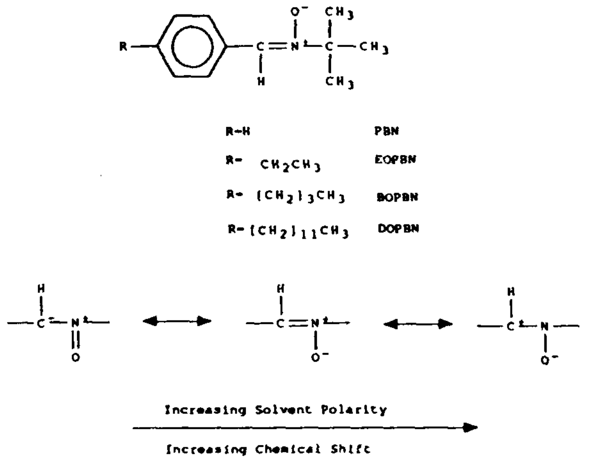
Spin Traps as Probes of Hydrophobicity in Poly(Maleic Anhydride-Alt-Ethyl Vinyl Ethers) Modified with Pendent Hydrophobic Alkyl Amine Groups

by
J. Kent Newman and Charles L. McCormick

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

Introduction

Alternating copolymers of maleic anhydride and ethyl vinyl ether (MAEVE) have been hydrophobically-modified with pendant alkyl moieties and hydrolyzed to obtain water-soluble polysoaps. Spin-label probes such as N-tert-butyl-α-phenylnitrone (PBN) exhibit chemical shifts of the benzyl carbon in MAEVE polymers and provide a method for investigation of hydrophobic associations in aqueous polymer solutions. The ^{13}C chemical shift, δ_c, of the benzyl-nitrone carbon has been studied in a range of varying solvents and was found to be a indicator of the polarity of the environment in which the nitrone is solubilized. Synthesis of hydrophobically modified PBN derivatives such as dodecyl-PBN (DOPBN) allow for tailoring the spin probe to the system under study. Chemical shift changes have been monitored as a function of polymer concentration and temperature.



Experimental

Alternating copolymers of maleic anhydride (MA) and ethyl vinyl ether (EVE) were synthesized[2,3] in benzene at 70°C using a 1:2 molar ratio of MA:EVE with 0.1 mole% AIBN as an initiator. The polymer was precipitated into diethyl ether, dried in a vacuum oven at 40°C, and redissolved into acetone followed by precipitation into ether. Hydrophobic modification was accomplished by reaction of the appropriate molar ratio of alkyl amine with a 0.02 molar solution of MAEVE in ethyl acetate. The MAEVE solution was cooled to 0°C, purged with N_2, and the amine added dropwise. The solution was heated to 65°C and allowed to react for 10 hours. The solution was concentrated by rotary evaporation, precipitated into diethyl ether, and dried under vacuum. Hydrolysis of the MA moiety to generate the polyelectrolyte was conducted in 1M KOH at room temperature on a 4% w/w solution of MAEVE. The reaction was allowed to proceed until complete dissolution of the polymer occurs (16-18 hours). The polymer was precipitated into MeOH, redissolved into H_2O, and freeze-dried. Specific polymers are denoted as $MAEVEC_{18}$-60, referring to 60 mole% modification of MAEVE with the C_{18} alkyl moiety.

Results and Discussion

Solutions of PBN with hydrophobically-modified MAEVE polymers were studied at various concentrations and temperatures and were shown to exhibit shifts of the nitrone carbon (see table below). In aqueous solutions of PBN (0.028M), the nitrone chemical shift (δ_c) is 138.2 ± 0.1 ppm and in $CHCl_3$, δ_c is 131.0 ppm at 30°C. Upon addition of sufficient SDS to form micelles, the chemical shift decreases to 135.7 ppm indicating that the PBN is residing in a less polar environment. In a 2% w/w solution of MAEVE in H_2O, δ_c is 138.2. With 2% w/w $MAEVEC_{18}$-60, the shift decreases to 137.5 ppm and is 137.4 ppm at a 4% polymer concentration.

Solution	δ_c, ppm
$CHCl_3$	131.0 ± 0.2
H_2O	138.2
SDS	135.7
MAEVE	138.2
$MAEVEC_{18}$-60, 2%	137.5
$MAEVEC_{18}$-60, 4%	137.4

In the following table, the nitrone chemical shift values indicate lower polarity as temperature increases for a 2% w/w solution of $MAEVEC_{18}$-60. The decrease in δ_c indicates that an increased number of probe molecules are solubilized in the hydrophobic domains, suggesting either an increase in size or an increased number of hydrophobic regions. These limited data at present may not reflect the behavior of individual polymer molecules since these studies were conducted at polymer concentrations where polymer-polymer entanglements may occur. The overlap concentration of these polymers is estimated to be in the range of 1-2% w/w. Although the MAEVE polymers are of relatively low molecular weight (approx. 250,000), the effects of hydrophobic modifications on the overlap concentration is not clear.

Temperature, °C	δ_c, ppm
30	137.4
40	137.1
50	137.2
60	136.9
70	136.6
80	136.7
90	136.7

Although the chemical shifts of the benzyl carbons are small, the utility of the method has been established and may provide complementary information to the fluorescence probe studies of hydrophobic interactions also being investigated in our research group. Synthesis of more hydrophobic spin-traps such as EOPBN, BOPBN, and DOPBN may allow for a wider range of chemical shift values than those observed with the more hydrophilic PBN spin trap.

Acknowledgements

Financial support of this research by the United States Department of Energy, the Office of Naval Research and the Defense Advanced Research Projects Agency is gratefully acknowledged.

References

1. Janzen, E. G.; Haire, D. L.; Coulter, G. A.; Stronks, H. J.; Krygsman, P. H.; Towner, R. A.; and Hilborn, J.W. *J. Org. Chem.*, *54(12)*, 2915 (1989).
2. Chang, Y. and McCormick, C. L. *Polymer Preprints*, *31(2)*, 462 (1990).
3. Clark, M. D. Ph.D. Dissertation, The University of Southern Mississippi, Hattiesburg, MS, 1990.

ECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

a. REPORT SECURITY CLASSIFICATION NONE	1b. RESTRICTIVE MARKINGS NONE
a. SECURITY CLASSIFICATION AUTHORITY NONE b. DECLASSIFICATION / DOWNGRADING SCHEDULE NONE	3. DISTRIBUTION / AVAILABILITY OF REPORT UNLIMITED
PERFORMING ORGANIZATION REPORT NUMBER(S) 90-91-8	5. MONITORING ORGANIZATION REPORT NUMBER(S)

a. NAME OF PERFORMING ORGANIZATION University of Southern Mississippi	6b. OFFICE SYMBOL *(If applicable)*	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research
c. ADDRESS *(City, State, and ZIP Code)* University of Southern Mississippi Polymer Science Department Southern Station Box 10076 Hattiesburg, MS 39406-0076		7b. ADDRESS *(City, State, and ZIP Code)* 800 North Quincy Avenue Arlington, VA 22217
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL *(If applicable)*	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS *(City, State, and ZIP Code)* 800 N. Quincy Avenue Arlington , VA 22217	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE *(Include Security Classification)*
Synthesis and Characterization of N-Isopropylacrylamide Copolymers for the Study of Drag Reduction

12. PERSONAL AUTHOR(S)
Pavneet S. Mumick and Charles L. McCormick

13a. TYPE OF REPORT journal article	13b. TIME COVERED FROM ________ TO ________	14. DATE OF REPORT *(Year, Month, Day)*	15. PAGE COUNT

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION

22a. NAME OF RESPONSIBLE INDIVIDUAL Charles L. McCormick	22b. TELEPHONE *(Include Area Code)* (601)266-4868	22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

Synthesis and Characterization of N-Isopropylacrylamide Copolymers for the Study of Drag Reduction

by
Pavneet S. Mumick and Charles L. McCormick

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

Introduction

Frictional resistance in turbulent flow can be reduced to as little as one-quarter that of the pure solvent by the addition of extremely small concentrations of soluble polymers. This drag reduction phenomenon shown by polymeric additives has been known since 1949, when it was first reported by B.A.Toms.[1] There has been considerable research in this area over the last three decades but there is no universally accepted model that explains the mechanism by which macromolecules act to bring about frictional reduction. Some quantitative models have accurately predicted the drag reduction behavior of water-soluble homopolymers such as poly(ethylene oxide) and polyacrylamide. Our research group is the first to have undertaken extensive analyses of polymers of widely differing structures and compositions.[2-5] All polymers were found to conform to a universal curve, when normalized for volume fraction of polymer in solution.[3,5]

We hypothesize that polymer solvation affects drag reduction efficiency. Recent work in our laboratory has indicated that slight changes in the polymer structure and associated solvent affect solvation and therefore, affect drag reduction behavior.[2-5] Figure 1 (from Ref. 4) shows the variation of friction factors versus Reynolds number for DAAM 15 polymers (i.e., the copolymer made from 15 mole% diacetone acrylamide and 85 mole% acrylamide in the feed) as a function of solvent.

Copolymers showing hydrophobic inter- and intramolecular interactions have proven to be the most efficient drag reducers studied in our laboratory. Therefore, a new series of hydrophobically associating copolymers, poly(acrylamide-co-N-isopropylacrylamide) (AM-co-IPAM), has been synthesized and characterized. The solution properties of these copolymers are extremely sensitive to sodium dodecyl sulfate (SDS) and salt (NaCl) concentration as well as temperature. Thus, these polymers are good models to assess the effect of solvation on drag reduction performance.

Experimental

Polymer Synthesis

All chemicals were obtained commercially. The monomers were purified by recrystallization from suitable solvents. The polymerizations were performed in aqueous solution using 0.2 mole % potassium persulfate free radical initiator at 30°C under a nitrogen atmosphere. Total monomer concentration was 0.45 M. The reactions were terminated by the addition of catechol after approximately 4.5 hours of polymerization time. Polymer conversions of 50% to 60% were obtained. Copolymers were purified by dialysis. The dialyzed copolymer solutions were freeze-dried.

Copolymer Composition and Solution Properties

^{13}C NMR (JEOL FX90Q, Carbon 22.5 MHz) and elemental analysis (M-H-W Laboratories, Phoenix, AZ) were used to determine copolymer compositions. A standard temperature controlled turbidimeter was used for the turbidimetric studies. 0.2 g/dL polymer solutions were used for the studies. The measurements were within ± 0.5°C. The viscometric studies were performed on a Cannon-Ubbelohde four-bulb shear dilution viscometer.

Drag Reduction Measurements

The drag reduction performance is being tested in a rotating disk and a tube flow apparatus. These instruments have been described elsewhere.[3]

Results and Discussion

The reactivity ratios (Table I) were calculated from the feed ratios of the monomers and the copolymer compositions, at low conversion (~ 10%), using the Kelen-Tudos[6] and the Fineman-Ross[7] techniques. The reactivity ratios indicate random copolymerization.

The viscometric studies were conducted as a function of solvent and temperature. All copolymers conform to the Huggins and the Kraemer equations. As reported in Table II, the intrinsic viscosities are lower in 0.514 M NaCl and 1 M urea (Fig. 2) as compared to those in deionized water for all the copolymers except IPAM-40. Therefore, these polymers show hydrophobic associations. In 0.2% SDS, the alkyl chain of the surfactant molecules associates with the polymer backbone. Consequently, very high intrinsic viscosities are realized (Table II) due to the charge-charge repulsion between adjacent surfactant molecules and/or disruption of intramolecular hydrophobic associations.

Figure 3 shows the effect of temperature on reduced viscosity for IPAM-85. As the temperature approaches the phase separation temperature or the lower critical solution temperature (LCST), the copolymers exhibit lower hydrodynamic volumes. The LCST of IPAM-85 is 42°C in deionized water (Table III).

The turbidimetric studies were also performed as a function of solvent and temperature. The results are given in Table III. The phase separation temperatures are lower in 0.514 M NaCl as compared to those in deionized water for all copolymers. Urea increases the LCST of IPAM-70 and IPAM-55 as compared to their LCST in deionized water. No phase separation occurs below 100°C in 0.2% SDS for all copolymers.

The effect of salt concentration on the solution properties of IPAM-55 can be seen in Figure 4. At low salt concentrations the LCST is lowered by 4°C for every 1% increase in salt concentration. At high salt concentrations (> 15%) the LCST is lowered by 2°C for every 1% increase in salt concentration.

The drag reduction studies of these copolymers, as a function of solvent, are currently in progress. This copolymer series lends us a great opportunity to study the effect of polymer microstructure and associated solvent on drag reduction.

Acknowledgements

Financial support from the United States Department of Energy, the Office of Naval Research and the Defense Advanced Research Projects Agency is gratefully acknowledged.

References

1. Toms, B. A. *Proceedings International Congress on Rheology*, **2**, 135 (1949).
2. Morgan, S. E. Ph.D. Dissertation, The University of Southern Mississippi, Hattiesburg, Mississippi, 1988.
3. McCormick, C. L.; Hester, R. D.; Morgan, S. E. and Safieddine, A. M. *Macromolecules*, *23*, 2124 (1990).
4. McCormick, C. L.; Hester, R. D.; Morgan, S. E. and Safieddine, A. M. *Macromolecules*, *23*, 2132 (1990).
5. Mumick, P. S.; Morgan, S. E. and McCormick, C. L. *Polym. Prepr.*, *30(2)*, 256 (1989).
6. Kelen, T. and Tudos, F. *J. Macromol. Sci.-Chem.*, *A9*, 1 (1975).
7. Fineman, M. and Ross, S. *J. Polym. Sci.*, *5*, 259 (1950).

Table I. Reactivity Ratios

Method	r_1	r_2	r_1r_2
Kelen-Tudos	0.95	1.04	0.99
Fineman-Ross	0.98	1.06	1.04

Monomer 1 = Acrylamide (AM).
Monomer 2 = N-isopropylacrylamide (IPAM).

Table II. Zero-shear Intrinsic Viscosities (dl/g) in Different Solvents at 30°C

Sample	DI Water	0.514 M NaCl	1 M Urea	0.2% SDS
IPAM-100	4.73 8.16 (at 20°C)	*	3.37	20.10
IPAM-85	7.26 3.74 (at 40°C)	5.05	5.65	20.92
IPAM-70	6.41	5.32	5.24	27.95
IPAM-55	9.66	9.27	7.04	31.77
IPAM-40	8.16	7.86	9.24	27.37

* Phase separation occurs at 27.5°C.

Table III. Turbidimetric Studies
[Phase separation occurs at the temperatures indicated (°C)]

Sample	In DI Water	In 0.514 M NaCl	In 1 M Urea
IPAM-100	34.0	27.5	33.5
IPAM-85	42.0	35.0	42.0
IPAM-70	53.0	45.0	54.0
IPAM-55	74.0	62.0	79.0
IPAM-40	#	#	#

\# No phase separation up to 100°C.
No phase separation occurs in 0.2% SDS up to 100°C for all copolymers.

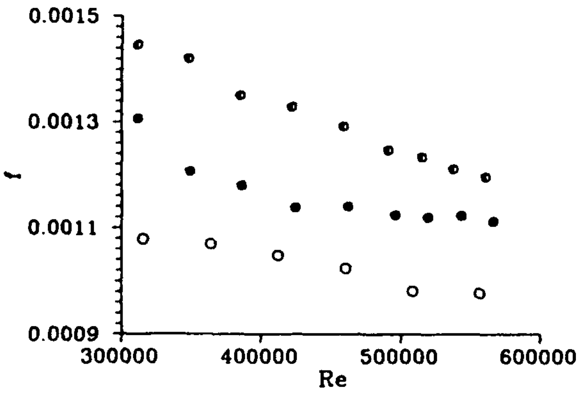


Figure 1. Friction factor versus Reynolds number for DAAM-15 in different solvents at 3 ppm concentration tested with a rotating disk. 1 M Urea (◐); Deionized water (●); 0.514 M NaCl (○).

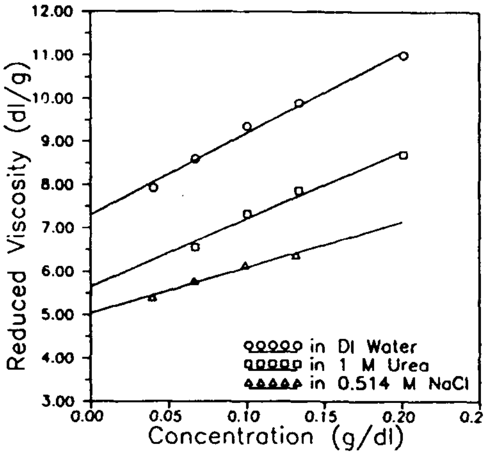


Figure 2. Huggins plot for IPAM-85 in different solvents at 30°C.

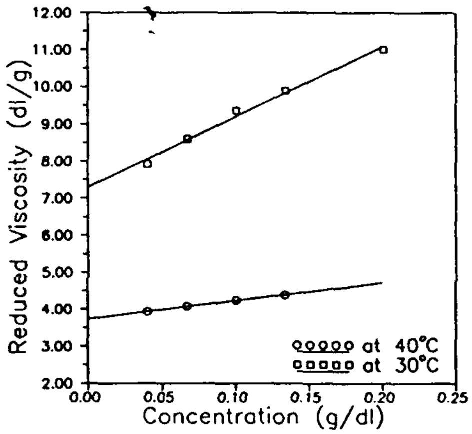


Figure 3. Huggins plots for IPAM-85 in deionized water at different temperatures.

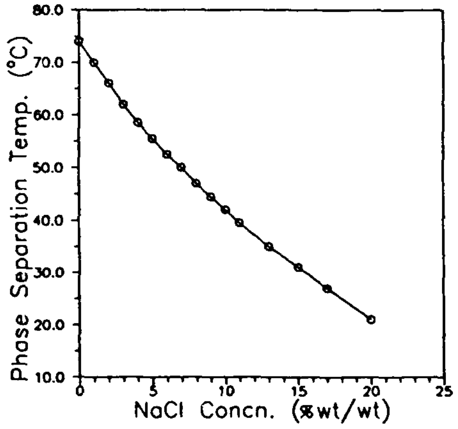


Figure 4. Effect of NaCl concentration on the phase separation temperature of IPAM-55.

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
NONE

1b. RESTRICTIVE MARKINGS
NONE

2a. SECURITY CLASSIFICATION AUTHORITY
NONE

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE
NONE

3. DISTRIBUTION / AVAILABILITY OF REPORT
UNLIMITED

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
90-91-9

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
University of Southern
Mississippi

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
Office of Naval Research

6c. ADDRESS *(City, State, and ZIP Code)*
University of Southern Mississippi
Polymer Science Department
Southern Station Box 10076
Hattiesburg, MS 39406-0076

7b. ADDRESS *(City, State, and ZIP Code)*
800 North Quincy Avenue
Arlington, VA 22217

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
Office of Naval Research

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS *(City, State, and ZIP Code)*
800 N. Quincy Avenue
Arlington , VA 22217

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE *(Include Security Classification)*
Microstructure Studies of Hydrophobically-Modified Maleic Anhydride-Ethyl Vinyl Ether Copolymers

12. PERSONAL AUTHOR(S)
Yihua Chang and Charles L. McCormick

13a. TYPE OF REPORT
Journal article

13b. TIME COVERED
FROM ________ TO ________

14. DATE OF REPORT *(Year, Month, Day)*

15. PAGE COUNT

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

22a. NAME OF RESPONSIBLE INDIVIDUAL

22b. TELEPHONE *(Include Area Code)*
(601)266-4868

22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

Microstructure Studies of Hydrophobically-Modified Maleic Anhydride-Ethyl Vinyl Ether Copolymers

by
Yihua Chang and Charles L. McCormick

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

Introduction

Polyelectrolytes containing relatively large amounts of pendant hydrophobic groups are interesting in that they have a tendency to form intramolecular hydrophobic bonds in aqueous solutions. The conformation of the polymer chain in solution depends critically on the macromolecular composition. Strauss and the coworkers have shown the effects of the number and length of the hydrophobic groups attached to maleic anhydride and alkyl vinyl ether copolymers.[1,2] If the alkyl groups are few or very short, the polymer exhibits typical polyelectrolyte behavior. A transition from a random conformation to a compact coil may occur with increasing content and/or length of the alkyl branches as a result of intramolecular aggregation.

In previous studies[3], we have synthesized the potassium salt of maleic anhydride and ethyl vinyl ether copolymers modified with a series of pendant n-octyl and n-dodecyl amine groups (HMAEVE), as shown in Figure 1. These water-soluble copolymers exhibit a strong tendency for intramolecular association in aqueous solutions. The polymers with higher alkyl group content tend to have a more compact conformation. Here we report the effects of varying pH and electrolyte concentration on the resulting rheological properties of these hydrophobically-modified polyelectrolytes. The qualitative comparison of viscosities of these polymers in different aqueous media provides a better understanding of microheterogeneous associations in aqueous solution.

Experimental

The preparation of HMAEVE has been described elsewhere.[3] The mole percentages of hydrophobe substitution are indicated in the appropriate figures. Viscosity measurements were conducted on a Contraves LS 30 low shear rheometer at a shear rate of 6 s^{-1} at 25°C.

Results and Discussion

Inter- and Intramolecular Associations

It has been shown that HMAEVE polymers in the dilute aqueous solutions exhibit intramolecular association.[3] In the concentrated regime where the overlap of the polymer molecules is possible, the thermodynamic equilibrium still favors the attraction between hydrophobic groups belonging to the same polymer. This argument is based on the observation that the apparent viscosity of freshly prepared 2 g/dL solution of the polymer containing 40% dodecyl group in deionized water at 25°C decreases for a considerable time. The decrease of the viscosity of the solution may be caused by the decrease of the extent of the intermolecular association of the hydrophobic groups and the simultaneous increase of intramolecular association.

This assumption is further confirmed by examining the viscosity aging studies. The data in Figure 2 were obtained one day and 20 days after the solution preparation. Reduced viscosity initially decreases slightly in the low concentration region and then increases at higher concentration for the freshly prepared sample. The steep rise of the curve in the high concentration region indicates increased intermolecular associations of polymer. The reduced viscosities of the same polymer solutions measured after twenty days exhibit slight decreases as the concentration increases. These viscosity responses are consistent with polymer conformational changes from opened association (intermolecular) to closed association (intramolecular) as a function of solution aging.

Effect of pH on Viscosity of Polymer Solutions

Figure 3 illustrates the viscosity behavior of the polymers containing various amounts of n-octyl moieties at different pH values. The reduced viscosities of all the polymer solutions increase with increasing pH before reaching a maximum and then decreasing. At low pH, the charge density along the polymer chain is low, promoting intramolecular associations. Also, addition of electrolyte increases ionic strength of the solution and leads to a more compact structure of the macromolecules due to a suppression of the electrostatic repulsions between the ionic groups.

Above a certain pH value, the reduced viscosity decreases. At this point, addition of KOH, which shields the interaction between the charged groups along the polymer backbone, causes the polymer collapse.

Effect of KCl on Viscosity of Polymer Solutions

A similar effect as that discussed for the changes of pH, was observed when KCl was added to the dodecyl polymer solutions (Figure 4). For the reduced viscosity decreases as the KCl concentration increases. A different type of behavior is indicated for the polymer containing 60% hydrophobic groups. While the reduced viscosity initially decreases with increasing KCl concentration, it reaches a minimum and increases again. Since the viscosity rise with added KCl occurs only in the polymer solution with greatest hydrophobe content, this may be ascribed to intermolecular interactions of hydrophobic groups on separate polymer molecules.

Conclusions

These hydrophobically-modified polymers display intramolecular association behavior in aqueous solutions as a function of pH and ionic strength. The reduced viscosity of the polymer solution decreases considerably when KCl is added, due to electrostatic interactions. However, the reduced viscosity of the polymer with 60% dodecyl group decreases first and then increases upon increasing the KCl concentration. In the concentrated regime, these polymers show preference for intramolecular association to intermolecular association. Efforts are being directed at the preparation of pyrene-containing polymers for photophysical characterization of the hydrophobic microdomains.

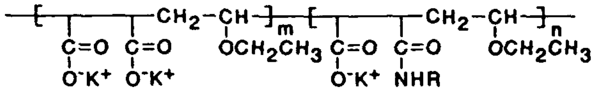
Acknowledgements

Financial support of this research by the U.S. Department of Energy, the Office of Naval Research, the Defense Advanced Research Projects Agency, and BP America Inc. is gratefully acknowledged.

References

1. Strauss, U. P. and Dubin, P. L. *J. Phys. Chem.*, *71*, 2757 (1967).
2. Strauss, U. P. and Dubin, P. L. *J. Phys. Chem.*, *74*, 2848 (1970).

3. McCormick, C. L. and Chang, Y. *Polym. Prep.*, *31(2)*, 462 (1990).



R : $[CH_2]_7CH_3$, $[CH_2]_{11}CH_3$

Figure 1. Polymer Structure

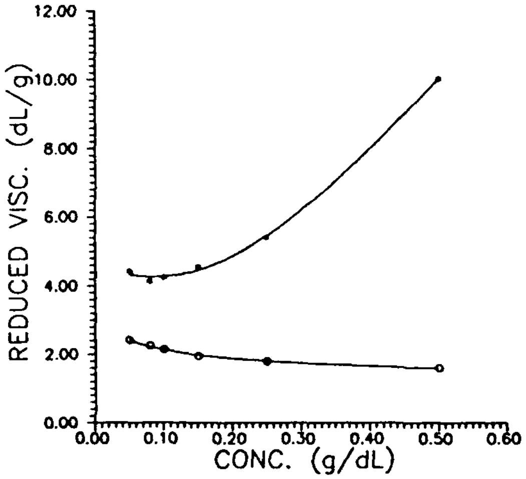


Figure 2. Comparison of reduced viscosity vs. concentration of 40% dodecyl modified HMAEVE at various times. One day after the sample preparation (*); 20 days after the sample preparation (o).

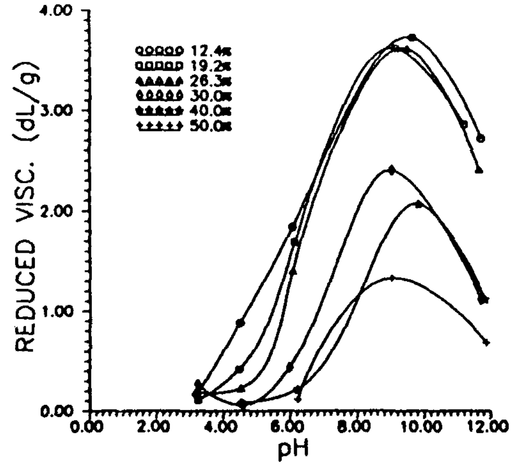


Figure 3. Effect of pH on the reduced viscosity of octyl modified HMAEVE at 25°C.

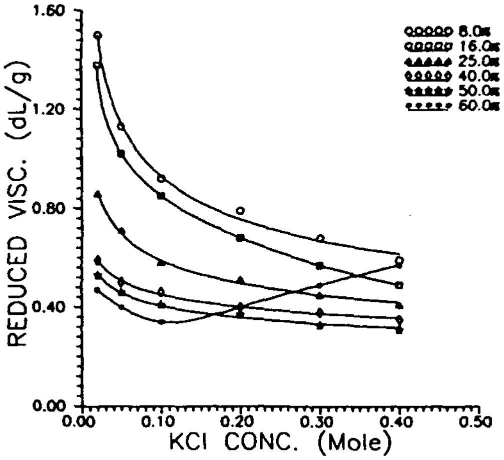


Figure 4. Effect of KCl concentration on the reduced viscosity of dodecyl modified HMAEVE.

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
NONE

1b. RESTRICTIVE MARKINGS
NONE

2a. SECURITY CLASSIFICATION AUTHORITY
NONE

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE
NONE

3. DISTRIBUTION / AVAILABILITY OF REPORT
UNLIMITED

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
90-91-10

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
University of Southern Mississippi

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
Office of Naval Research

6c. ADDRESS *(City, State, and ZIP Code)*
University of Southern Mississippi
Polymer Science Department
Southern Station Box 10076
Hattiesburg, MS 39406-0076

7b. ADDRESS *(City, State, and ZIP Code)*
800 North Quincy Avenue
Arlington, VA 22217

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
Office of Naval Research

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS *(City, State, and ZIP Code)*
800 N. Quincy Avenue
Arlington , VA 22217

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE *(Include Security Classification)*
Water-soluble polymers:33. Ampholytic terpolymers of sodium 2-acrylamido-2-methylpropanesulphonate with 2-acrylamido-2-methylpropanedimethylammonium chloride and acrylamide: synthesis and aqueous-solution behavior

12. PERSONAL AUTHOR(S)
Charles L. McCormick and C. Brent Johnson

13a. TYPE OF REPORT
journal article

13b. TIME COVERED
FROM ________ TO ________

14. DATE OF REPORT *(Year, Month, Day)*

15. PAGE COUNT

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

22a. NAME OF RESPONSIBLE INDIVIDUAL
Charles L. McCormick

22b. TELEPHONE *(Include Area Code)*
(601)266-4868

22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

Water-soluble polymers: 33. Ampholytic terpolymers of sodium 2-acrylamido-2-methylpropanesulphonate with 2-acrylamido-2-methylpropanedimethylammonium chloride and acrylamide: synthesis and aqueous-solution behaviour

Charles L. McCormick* and C. Brent Johnson
Department of Polymer Science, University of Southern Mississippi,
Hattiesburg, Mississippi 39406, USA

(Received 30 May 1989; revised 7 August 1989; accepted 7 August 1989)

Synthesis and viscometric studies of a series of moderate-to-low charge-density terpolymers of acrylamide (AM) with sodium 2-acrylamido-2-methylpropanesulphonate (NaAMPS) and 2-acrylamido-2-methylpropanedimethylammonium chloride (AMPDAC) have been conducted. Plots of apparent viscosity *versus* polymer concentration revealed critical overlap concentrations (C^*) in the range 0.10–0.14 g dl^{-1}. The dependence of the reduced viscosity of the terpolymers on temperature was minimal, with only a slight decrease in viscosity observed with increasing temperature. Reduced viscosity was shown to be a function of polymer composition, charge distribution and molecular weight of the terpolymers. The low-to-moderate charge-density terpolymers of NaAMPS with AMPDAC displayed viscosities over 100% greater than the high charge-density copolymers. The superior viscometric characteristics of the terpolymers became more evident as the polymer concentration approaches C^*.

(Keywords: synthesis; water-soluble polymers; terpolymers; viscosity; solution behaviour)

INTRODUCTION

Water-soluble polymers are used in a number of applications, including enhanced oil recovery, drag reduction and absorbency, in which electrolyte tolerance is necessary for efficient performance. Polyampholytes have received relatively little attention despite their potential in such applications. These polymers offer unique properties as a result of ionic interactions, both intra- and intermolecular in nature, which affect hydrodynamic volume. Polyampholytes differ from conventional polyelectrolytes in that they contain both positive and negative charges distributed in some fashion along the polymer backbone.

Salamone *et al.* reported the synthesis of polyampholytes derived from cationic–anionic monomer pairs[1]. High charge-density copolymers with 1:1 molar ratios of the respective comonomers displayed viscosity behaviour in salt solution unlike that of normal polyelectrolytes. Later, the same group reported the spontaneous polymerization of several ion-pair comonomers[2,3]. The viscosities of the copolymers increased with potassium chloride concentration. Several studies have also been conducted on aliphatic and aromatic sulphobetaine polyampholytes, which incorporate positive and negative charges within the mer unit. Several of these inner salt polymers possess hydrogel characteristics. Peiffer and Lundberg recently reported the importance of incorporating non-charged monomers into ampholytic polymers for optimum viscosity behaviour[4].

Series of high charge-density copolymers of 2-acrylamido-2-methylpropanedimethylammonium chloride (AMPDAC) with sodium 2-acrylamido-2-methylpropanesulphonate (NaAMPS) have been studied previously in our laboratories[5,6]. The solution properties of these polymers are determined by a number of parameters including charge type and distribution, polymer microstructure, molecular weight, hydrophobic/hydrophilic balance, solvent type, pH and ionic strength. Intramolecular ionic interactions dominate solution behaviour of copolymers with 1:1 molar compositions of AMPDAC and AMPS respectively.

In this work we report the synthesis and viscometric characterization of a series of low-to-moderate charge-density ampholytic terpolymers of AMPDAC, NaAMPS and acrylamide (AM). These have been synthesized and characterized with the goal of elucidating on a molecular level the effects that dictate macroscopic solution properties.

EXPERIMENTAL

Materials and monomer synthesis

2-Acrylamido-2-methylpropanedimethylammonium chloride (AMPDAC) was synthesized as previously described[7]. AMPDAC was converted to the base, 2-acrylamido-2-methylpropanedimethylamine (AMPDA) prior to purification. AMPDAC was found to be prone to spontaneous polymerization if stored in the acid form. To accomplish the deprotonation, AMPDAC was placed

---

* To whom correspondence should be addressed

0032-3861/90/061100-08

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
NONE

1b. RESTRICTIVE MARKINGS
NONE

2a. SECURITY CLASSIFICATION AUTHORITY
NONE

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE
NONE

3. DISTRIBUTION / AVAILABILITY OF REPORT
UNLIMITED

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
90-91-11

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
University of Southern Mississippi

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
Office of Naval Research

6c. ADDRESS *(City, State, and ZIP Code)*
University of Southern Mississippi
Polymer Science Department
Southern Station Box 10076
Hattiesburg, MS 39406-0076

7b. ADDRESS *(City, State, and ZIP Code)*
800 North Quincy Avenue
Arlington, VA 22217

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
Office of Naval Research

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS *(City, State, and ZIP Code)*
800 N. Quincy Avenue
Arlington , VA 22217

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE *(Include Security Classification)*
Water-soluble Copolymers. 36. Photophyscial Investigations of Water-Soluble Copolymers of 2-(1-Naphthylacetamido)ethylacrylamide

12. PERSONAL AUTHOR(S)
C. L. McCormick, C. E. Hoyle and M.D. Clark

13a. TYPE OF REPORT
journal article

13b. TIME COVERED
FROM ________ TO ________

14. DATE OF REPORT *(Year, Month, Day)*

15. PAGE COUNT

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

22a. NAME OF RESPONSIBLE INDIVIDUAL
Charles L. McCormick

22b. TELEPHONE *(Include Area Code)*
(601)266-4868

22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

Macromolecules 1991, *24*, 2397–2403

Water-Soluble Copolymers. 36. Photophysical Investigations of Water-Soluble Copolymers of 2-(1-Naphthylacetamido)ethylacrylamide

C. L. McCormick,* C. E. Hoyle, and M. D. Clark

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

Received July 26, 1990; Revised Manuscript Received November 26, 1990

ABSTRACT: A hydrolytically stable monomer, 2-(1-naphthylacetamido)ethylacrylamide (NAEAm), has been synthesized to utilize as a label in photophysical studies of copolymers with methacrylic and acrylic acid. An increase in excimer emission relative to monomer emission (I_E/I_M) is observed upon increasing solution pH. The hydrophobic character of both the naphthyl chromophores and the pendent methyl groups of MAA and the effective decoupling of the naphthyl chromophores from the polymer backbone via a spacer linkage are responsible for this behavior. The effects of NaCl, urea, and Triton X-100 surfactant on solution properties indicate that hydrophobic interactions among naphthyl chromophores are responsible for formation of an intramolecular "hypercoil" at high pH. Fluorescence measurements confirm the importance of coil dimensions and ion binding on quenching by nitromethane and copper(II) ions.

Introduction

The covalent attachment of hydrophobic chromophores such as naphthalene and pyrene to polyelectrolytes can result in microheterogeneous water-soluble systems that are in some respects micellelike. The chromophores within these copolymers may be protected from the bulk solution via hydrophobic self-association,[1–4] and, in some instances, large hydrophobic compounds may be solubilized within such microenvironments.[5,6] The photophysical behavior of pendent chromophores is dependent on whether the polymer coil is expanded or micellelike. For example, excimer formation in amphiphilic polyelectrolytes is dependent on the degree of ionization of the polymer (pH of the solution).[7] Generally, as the degree of ionization (pH) increases, segmental Coulombic repulsions cause the polymer coil to expand, increasing the separation between chromophores and decreasing the degree of excimer formation. However, we have recently reported an amphiphilic copolyelectrolyte in which expansion of the polymer coil with increasing pH causes an increase in excimer intensity.[8] We have proposed that this behavior is due, at least in part, to the "decoupling" of the chromophore from the polymer backbone by a relatively long, flexible spacer group. Unfortunately, inherent hydrolytic instability of the chromophore[9] hindered further investigations of this system.

This paper reports the synthesis of a hydrolytically stable analogue of the previously studied chromophore, copolymerization with both acrylic and methacrylic acid, and initial studies of the photophysical properties of the resulting water-soluble copolymers. The goals of this work are (1) to understand how changes in polymer conformation affect the environment of the chromophore and (2) to elucidate the effect of chromophore concentration on polymer conformation.

Experimental Section

Materials. All chemicals used in the preparation of the monomers, polymers, and model compound were purchased from Aldrich Chemical Co. and were purified using previously reported methods.[10] Reagent-grade solvents were used without further purification, with the exception of *N,N*-dimethylformamide (DMF), which was dried over 4A molecular sieves and distilled under reduced pressure.

Instrumentation. The UV absorption spectra of the samples were measured using a Perkin-Elmer Lamda 6 spectrophotometer.

IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrophotometer.

NMR spectra were recorded with a Bruker AC-300 spectrometer.

Steady-state fluorescence spectra of the polymer solutions were measured at room temperature with a SPEX Fluorolog-2 fluorescence spectrometer equipped with a DM3000F data station.

Fluorescence decay curves were measured with a Photochemical Research Associates single-photon-counting instrument. The nonlinear iterative deconvolution technique was used to fit the decay profiles.

Synthesis of 2-(1-Naphthylacetamido)ethylacrylamide (NAEAm). 2-(1-Naphthylacetamido)ethylacrylamide (NAEAm) was prepared from 1-naphthylacetic acid (NAA) in a three-step process. The first step involved the formation of the activated succinimide ester of NAA (NAA–NHS) (Scheme I), the second, monoacylation of ethylenediamine with NAA–NHS (NAA–EDA) (Scheme II), and the third, the preparation of 2-(1-naphthylacetamido)ethylacrylamide (NAEAm) (Scheme III).

1-Naphthylacetic acid (NAA; 5.00 g, 27.0 mmol) and *N*-hydroxysuccinimide (NHS; 3.10 g, 27.0 mmol) were slurried in 60 mL of $CHCl_3$ at room temperature. Dicyclohexylcarbodiimide (DCC; 5.58 g, 27.0 mmol), a coupling agent, in $CHCl_3$ (20 mL) was added slowly to this suspension with rapid stirring. Addition of DCC gradually solubilized *N*-hydroxysuccinimide. Upon complete dissolution of NHS, a white precipitate (DCC–urea) was immediately formed. After addition of DCC was complete, the reaction was allowed to continue for 1 h. The product was filtered, and the filtrate, analyzed via thin-layer chromatography (silica, CH_3CN eluent). Near-quantitative conversion of the acid to the succinimide ester (NAA–NHS) was observed.

2-(1-Naphthylacetamido)ethylenediamine (NAA–EDA) was prepared via modification of a high-dilution procedure for the monosubstitution of symmetrical diamines with acid derivatives.[11] NAA–NHS (7.64 g, 27.0 mmol) was diluted with $CHCl_3$ to a volume of 350 mL and was added dropwise with vigorous stirring to a solution of ethylenediamine (19.45 g, 324 mmol) and $CHCl_3$ (50 mL) at 0 °C. The reaction was allowed to continue at room temperature overnight. The solution was filtered, concentrated under vacuum to approximately 75 mL, washed four times with a 10% sodium chloride solution (35 mL), and dried over magnesium sulfate. Thin-layer chromatography (silica, CH_3CN eluent) indicated that the primary reaction product was the monoacylated derivative, with only a trace amount of the disubstituted product. For the subsequent reaction, the amount

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
NONE

1b. RESTRICTIVE MARKINGS
NONE

2a. SECURITY CLASSIFICATION AUTHORITY
NONE

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE
NONE

3. DISTRIBUTION / AVAILABILITY OF REPORT
UNLIMITED

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
90-91-12

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
University of Southern
Mississippi

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
Office of Naval Research

6c. ADDRESS *(City, State, and ZIP Code)*
University of Southern Mississippi
Polymer Science Department
Southern Station Box 10076
Hattiesburg, MS 39406-0076

7b. ADDRESS *(City, State, and ZIP Code)*
800 North Quincy Avenue
Arlington, VA 22217

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
Office of Naval Research

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS *(City, State, and ZIP Code)*
800 N. Quincy Avenue
Arlington , VA 22217

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE *(Include Security Classification)* Water-Soluble Polymers. XXXIV. Ampholytic Terpolymers of Sodium 3-Acrylamido-3-Methylbutanoate with 2-Acrylamido-2-Methylpropane-Dimethylammonium Chloride and Acrylamide: Synthesis and Absorbency Behavior

12. PERSONAL AUTHOR(S) Charles L. McCormick and C. Brent Johnson

13a. TYPE OF REPORT
journal article

13b. TIME COVERED
FROM ________ TO ________

14. DATE OF REPORT *(Year, Month, Day)*

15. PAGE COUNT

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

22a. NAME OF RESPONSIBLE INDIVIDUAL
Charles L. McCormick

22b. TELEPHONE *(Include Area Code)*
(601)266-4868

22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

J. MACROMOL. SCI.—CHEM., A27(5), pp. 539–547 (1990)

WATER-SOLUBLE POLYMERS. XXXIV. AMPHOLYTIC TERPOLYMERS OF SODIUM 3-ACRYLAMIDO-3-METHYLBUTANOATE WITH 2-ACRYLAMIDO-2-METHYLPROPANE-DIMETHYLAMMONIUM CHLORIDE AND ACRYLAMIDE: SYNTHESIS AND ABSORBENCY BEHAVIOR

CHARLES L. McCORMICK* and C. BRENT JOHNSON

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

ABSTRACT

Synthesis and absorbency studies of a series of terpolymers of acrylamide (AM) with sodium 3-acrylamido-3-methylbutanoate (NaAMB) and 2-acrylamido-2-methylpropanedimethylammonium chloride (AMPDAC) are reported. Terpolymers were synthesized with varying molar feed ratios of the three monomers; those containing greater than 1% charged groups were not water soluble but formed hydrogels. Ampholytic terpolymers synthesized from monomer mixtures of 5% AMPDAC, 10% NaAMB, and 85% AM exhibit a 230-fold weight gain in pure water and a 30-fold gain in 0.514 *M* NaCl. Enhanced water absorbency of terpolymers with a charge imbalance is consistent with operative osmotic forces in crosslinked polyelectrolytes. The good absorbency in NaCl solutions can be attributed to hydration of paired cationic and anionic mer units in this terpolymer series.

INTRODUCTION

Inter- and intramolecular ionic interactions are known to influence the solution behavior of polyelectrolytes. Polyampholytes exhibit unusual properties relative to conventional polyelectrolytes as a result of attractive ionic forces between oppositely charged mer units. Although polyampholytes have not received the attention that conventional polyelectrolytes have, several recent studies illustrate the utility of ampholytic polymers [1–7]. Salamone et al. reported the synthesis of

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
NONE

1b. RESTRICTIVE MARKINGS
NONE

2a. SECURITY CLASSIFICATION AUTHORITY
NONE

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE
NONE

3. DISTRIBUTION / AVAILABILITY OF REPORT
UNLIMITED

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
90-91-13

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
University of Southern
Mississippi

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
Office of Naval Research

6c. ADDRESS *(City, State, and ZIP Code)*
University of Southern Mississippi
Polymer Science Department
Southern Station Box 10076
Hattiesburg, MS 39406-0076

7b. ADDRESS *(City, State, and ZIP Code)*
800 North Quincy Avenue
Arlington, VA 22217

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
Office of Naval Research

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS *(City, State, and ZIP Code)*
800 N. Quincy Avenue
Arlington , VA 22217

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO

11. TITLE *(Include Security Classification)*
Water-Soluble Copolymers.35. Photophysical and Rheological Studies of the Co-polymer of Methacrylic Acid with 2-(1-Naphthylacetyl)ethyl Acrylate

12. PERSONAL AUTHOR(S)
C. L. McCormick, C.E. Hoyle, and M.D. Clark

13a. TYPE OF REPORT
journal article

13b. TIME COVERED
FROM ________ TO ________

14. DATE OF REPORT *(Year, Month, Day)*

15. PAGE COUNT

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

22a. NAME OF RESPONSIBLE INDIVIDUAL
Charles L. McCormick

22b. TELEPHONE *(Include Area Code)*
(601)266-4868

22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

Macromolecules 1990, *23*, 3124–3129

(23) Moore, D. R.; Mathias, L. J. *J. Appl. Polym. Sci.* 1986, *32*, 6299.
(24) Moore, D. R.; Mathias, L. J. *Polym. Compos.* 1988, *9*, 144.
(25) Vandenberg, E. J.; Diveley, W. R.; Filar, L. J.; Patel, S. R.; Barth, H. G. *Polym. Mater. Sci. Eng.* 1987, *57*, 139.
(26) Salamone, J. C.; Krauser, S. F.; Richard, R. E.; Clough, S. B.; Waterson, A. C.; Vandenburg, E. J.; Dively, W. R.; Filar, L. J. *Polym. Mater. Sci. Eng.* 1987, *57*, 144.
(27) Salamone, J. C.; Li, C. K.; Clough, S. B.; Bennett, S. L.; Watterson, A. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1988, *29*, 273.
(28) Takayangi, M. *Pure Appl. Chem.* 1983, *55*, 819.
(29) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 324.
(30) Sundaresan, N. S.; Basak, S.; Pomerantz, M.; Reynolds, J. R. *J. Chem. Soc., Chem. Commun.* 1987, 621.

Water-Soluble Copolymers. 35. Photophysical and Rheological Studies of the Copolymer of Methacrylic Acid with 2-(1-Naphthylacetyl)ethyl Acrylate

C. L. McCormick,* C. E. Hoyle, and M. D. Clark

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

Received October 2, 1989; Revised Manuscript Received January 22, 1990

ABSTRACT: Fluorescence and dilute solution viscosity behavior of a 20:80 mol % copolymer of 2-(1-naphthylacetyl)ethyl acrylate (NAEA) and methacrylic acid (MAA), respectively, have been studied. The fluorescence spectra of this copolymer showed an almost 4-fold increase in excimer emission relative to monomer emission (I_E/I_M) upon increasing from pH 5 to 9. Similarly, as the pH of the medium increases, reduced viscosity increases, indicating a transition from a compact coil to a more expanded coil at pH 7.5. This behavior is unlike that previously reported presumably due to the extent of naphthyl group substitution, the hydrophobic character of both the naphthyl groups and the pendant methyl groups of MAA, and effective decoupling of the chromophore from the polymer backbone by a spacer group. The effects of urea, a water-structure breaker, and of polymer concentration indicate that, at high pH, NAEA–MAA forms an intramolecular "hypercoil". High quenching efficiencies of both monomer and excimer fluorescence by copper(II) ions result from ionic binding of the quencher ions with the copolymer.

Introduction

Recently, polyelectrolytes containing pendant aromatic chromophores such as naphthalene or phenanthrene have attracted a great deal of attention, particularly as models for artificial photosynthetic systems.[1–4] These polymers have been reported to exist in dilute aqueous solution as "hypercoils", which are characterized by hydrophobic aromatic groups clustered toward the center of the coil and hydrophilic ionic groups located in the aqueous boundary.[5–7] The microenvironment produced by the polyelectrolytes to which the hydrophobic chromophores are covalently attached often dramatically affects both the photophysical and photochemical properties of the chromophore. Most investigations to date have primarily been conducted on solutions of polymers in the electrolyte form. To date few comprehensive studies directed toward understanding the effect of pH on the conformation, and consequently the photophysical and rheological properties, of these "pseudomicellar" polymers have been conducted.

In this paper, we report the results of both fluorescence emission and viscosity studies of a polymer of methacrylic acid containing 20 mol % of 2-(1-naphthylacetyl)ethyl acrylate. Data suggest that the observed behavior relates, at least in part, to hydrophobic naphthyl group associations along the polymer chain.

Experimental Section

Materials. The synthesis of 2-(1-naphthylacetyl)ethyl acrylate (NAEA) has been outlined elsewhere.[8] Poly[2-(1-naphthylacetyl)ethyl acrylate-*co*-methacrylic acid) (NAEA–MAA) was prepared by 2,2′-azobis(isobutyronitrile) (AIBN) (1.0 mol %) initiated radical polymerization of NAEA (20 mol %) and MAA (80 mol %) in degassed *N,N*-dimethylformamide (DMF) solution at 65. After 6 h, the sample was precipitated into diethyl ether, redissolved into DMF, and reprecipitated into diethyl ether. A dialysis/HPLC technique indicated <0.1 mol % residual NAEA in the copolymer. The composition of the polymer was determined from both elemental analysis (MHW Laboratories, Phoenix, AZ) and the UV absorption spectrum of NAEA–MAA in DMF (ϵ = 6745 M^{-1} cm^{-1} at 280 nm). The polymer consists of 20.5 mol % NAEA and 79.5 mol % MAA.

Urea (Aldrich, 99+%) was recrystallized three times from methanol. Copper nitrate (Aldrich 99.99%) was used as received.

The polymer solutions were prepared in deionized water. Due to the inherent hydrolytic instability of NAEA,[8] solutions were discarded after 48 h and fresh solutions prepared for subsequent studies.

Methods. Polymer Characterization. UV absorbance measurements (Perkin-Elmer Lambda 6B) and elemental analysis (MHW Laboratories, Phoenix, AZ) were used to determine the composition of the copolymer. The copolymer contained 20.5 mol % NAEA and 79.5 mol % MAA. The number average molecular weight, M_n, of the copolymer was estimated to be 140 000, based on osmotic pressure measurements (Knauer Osmometer with 600W membrane, Arro Laboratories, Inc.) in *N,N*-dimethylacetamide.

Fluorescence Spectroscopy. The concentration of polymer in solution was ca. 0.01 g/dL (unless otherwise noted) such that the concentration of naphthyl moieties in solution was always <10^{-4}. Sample solutions were degassed with N_2 *for 15 min prior* to emission measurements. Steady-state fluorescence spectra were measured on a Perkin-Elmer 650-10B spectrophotometer;

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
NONE

1b. RESTRICTIVE MARKINGS
NONE

2a. SECURITY CLASSIFICATION AUTHORITY
NONE

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE
NONE

3. DISTRIBUTION / AVAILABILITY OF REPORT
UNLIMITED

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
90-91-14

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
University of Southern
Mississippi

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
Office of Naval Research

6c. ADDRESS *(City, State, and ZIP Code)*
University of Southern Mississippi
Polymer Science Department
Southern Station Box 10076
Hattiesburg, MS 39406-0076

7b. ADDRESS *(City, State, and ZIP Code)*
800 North Quincy Avenue
Arlington, VA 22217

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
Office of Naval Research

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS *(City, State, and ZIP Code)*
800 N. Quincy Avenue
Arlington , VA 22217

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE *(Include Security Classification)* Water-Soluble Copolymers XXXII: Macromolecular Drag Reduction. A Review of Predictive theories and the Effects of Polymer Structure.

12. PERSONAL AUTHOR(S)
Sarah E. Morgan and Charles L. McCormick

13a. TYPE OF REPORT
journal article

13b. TIME COVERED
FROM ________ TO ________

14. DATE OF REPORT *(Year, Month, Day)*

15. PAGE COUNT

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

22a NAME OF RESPONSIBLE INDIVIDUAL
Charles L. McCormick

22b. TELEPHONE *(Include Area Code)*
(601)266-4868

22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

Prog. Polym. Sci., Vol. 15, 507–549, 1990
0079-6700/90 $0.00 + .50

WATER-SOLUBLE COPOLYMERS XXXII: MACROMOLECULAR DRAG REDUCTION. A REVIEW OF PREDICTIVE THEORIES AND THE EFFECTS OF POLYMER STRUCTURE

Sarah E. Morgan and Charles L. McCormick[*]
Department of Polymer Science, University of Southern Mississippi, Box 10076, S.S., Hattiesburg, MS 39406, U.S.A.

CONTENTS

1. INTRODUCTION: THE DRAG REDUCTION PHENOMENON

1.1. *Discovery and definition*

Frictional resistance in turbulent flow can be reduced to as little as one-quarter that of the pure solvent by the addition of certain flow modifiers. This turbulent drag reduction may be manifested in a smaller value of the measured friction

---

[*] Please address all correspondence to this author.

[†] This article was originally published under the erroneous title "Water-Soluble Polymers in Enhanced Oil Recovery" in *Progress in Polymer Science*, Vol. 15, No. 1, pp. 103–145. The publishers apologise to the authors of the article for this error.

coefficient, as a decrease in pressure drop per unit length of pipe, or as a decrease in energy required to pump a fluid or propel an object through a fluid.

Toms[1] was the first to publish drag reduction data (the phenomenon is also known as the "Toms effect"). He reported unusually low friction factors for dilute solutions of poly(methyl methacrylate) in monochlorobenzene in turbulent pipe flow. Mysels[2] observed a similar effect for gasoline thickened with aluminium soaps. Experiments performed at Edgewood Arsenal during the Second World War demonstrated much smaller pressure drops for gasoline/soap mixtures than for pure gasoline flowing through pipelines.

In the late fifties and early sixties the study of drag reduction began in earnest. In 1959 the results of Ph.D. dissertations of D. W. Dodge under Professor A. B. Metzner at Delaware[3,4] and R. G. Shaver under E. W. Merrill at MIT[5] appeared simultaneously. Both described unusually low friction factors for dilute polymer solutions. Soon afterward, researchers in the petroleum industry noticed friction reduction in guar gum, sand, and water suspensions used in oil-well fracturing.[6,7] The research of Crawford[8] and Savins[9] spurred the Navy's interest in the phenomenon for possible military applications. Early significant contributions from Navy researchers were made by Hoyt, Fabula, and coworkers.[10,11] Fabula *et al.*[12] are credited with the discovery of the drag-reducing properties of poly(ethylene oxide), the most widely studied and commercially utilized drag reducer.[13]

These early studies laid the framework for the myriad of drag reduction investigations, both theoretical and experimental, which have appeared over the past forty years. However, the phenomenon is not completely understood, and a number of the chemical, mechanistic, and hydrodynamic aspects of drag reduction remain to be studied. The large number of recent publications in the area (i.e. Refs 14, 15 and 16) attest to the fact that drag reduction remains an important topic for research.

1.2. *Types of drag reducing additives*

Drag reduction has been reported for several solvent/additive systems, including dilute solutions of high molecular weight, soluble polymers,[1,13] surfactants and micellar systems,[17] suspensions of insoluble particles such as fine grains or fibers,[18,19] and for polymer solutions mixed with soaps or fibers.[20-24] It has also been found that modified surfaces, such as compliant surfaces, heated surfaces, and surfaces covered with "riblets" (small triangular ribs) aligned with the flow, can provide drag reduction of varying degrees.

To date, polymer solutions are the most widely studied and most often employed of the drag reducing systems.[25] A partial listing of polymeric drag reducing fluids is found in Table 1.

In general, the research indicates that any soluble polymer which is of a sufficiently high molecular weight (greater than 1 × 10^5), or which is capable