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RESEARCH REPORT

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Title of Project: Synthesis of Novel Associating Water-Soluble Copolymers

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by

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Participating Personnel

"Synthesis of Novel Associating Water-Soluble Copolymers"

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Synthesis of Novel Associating Water-Soluble Copolymers

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List of Publications

1. Y-X. Zhang, A-H. Da, G. B Butler and T.E. Hogen-Esch, *J. Polym. Sci. (Chem. Ed.)*, **31** (), 000, 1991. A Fluorine Containing Hydrophobically Associating Polymer Synthesis and Solution Properties of Copolymers of Acrylamide and Fluorine Containing Acrylates and Methacrylates.
2. Y-X. Zhang, A-H. Da, Y-C. Chen, G.B. Butler and T.E. Hogen-Esch, *J. Macromol. Sci.*, **A 27** (5), 593 (1990). Synthesis and Solution Properties of Water-Soluble Sulfonated Cellulose-Based Polymers and Their Polyacrylamide Graft Copolymers.
3. T.E. Hogen-Esch, M. Yassini, Y-X. Zhang, F. Hwang, E.J. Amis and T.A.P. Seery, *Polym. Preprts.*, **31** (2), 460 (1990). Synthesis and Characterization of Fluorocarbon Containing Polyacrylamides.
4. Y-X. Zhang, A-H. Da, T.E. Hogen-Esch and G.B. Butler, Chapter 10, ACS Symposium Series No.467, "Water Soluble Polymers", pages 159-174, S. Shalaby, C.L. McCormick and G.B. Butler, Editors. New Fluorocarbon Containing Hydrophobically Associating Polyacrylamide Copolymers.
5. S. Gopal Krishnan, G.B. Butler, T.E. Hogen-Esch and N-Z. Zhang, Chapter 11, ACS Symposium Series, No. 467, pages 175-188, "Water-Soluble Polymers", S. Shalaby, C.L. McCormick and G.B. Butler, Editors. Hydrophobically Associating Ionic Copolymers of Methylallyl-1,1-dihydro-pentadecafluorooctoxyethylammonium Chloride.
6. F. Hwang and T.E. Hogen-Esch, *Polym. Preprts.*, **32** (1), 581 (1991). Fluorocarbon Modified Water-Soluble Cellulose Derivatives.
7. T.A.P. Seery, M. Yassini, T.E. Hogen-Esch and E.J. Amis, *Macromolecules*, Submitted. Static and Dynamic Light Scattering Characterization of Solutions of Hydrophobically Associating Fluorocarbon-Containing Polymers.
8. E.J. Amis and T.A.P. Seery, *Polymer Preprts*, **32** (2), 000 (1991). Static and Dynamic Light Scattering Characterization of Hydrophobically Associating Polymers.
9. T.A.P. Seery, J.A. Shorter and E.J. Amis, *Polymer*, **30**, 1197-1203 (1989). Concurrent Static and Dynamic Light Scattering from Macromolecular Solutions. I. Model Systems in the Low q Regime.
10. D.F. Hodgson and E.J. Amis, invited chapter in *Polyelectrolytes: Science and Technologies*, M. Hara, Ed., Marcel-Dekker, New York, N.Y. 1991, in press. Polyelectrolyte Dynamics.

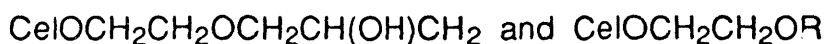
Synthesis of Novel Associating Water-Soluble Polymers

Presentations (1990-1991)

- F. Hwang and T.E. Hogen-Esch, April 1991, Spring ACS Meeting, Atlanta, Georgia. Fluorocarbon-Modified Water-Soluble Cellulose Derivatives.
- T. E. Hogen-Esch, M. Yassini, Y-X. Zhang, F. Hwang, E.J. Amis and T. Seery, August 1990 Washington ACS Meeting. Synthesis and Characterization of Fluorocarbon Containing Polyacrylamides.
- Y-X. Zhang, A-H. Da, T.E. Hogen-Esch and G.B. Butler, Thirty-third IUPAC International Symposium on Macromolecules, July 8-13, 1990, Montreal, Canada. Water-Soluble Graft Copolymers of 2,3-Dihydroxypropylcellulose With Acrylamide and Sodium-2-acrylamido-2-methylpropanesulfonate.
- Y-X. Zhang, M. Yassini, F. Hwang and T.E. Hogen-Esch, Dupont de Nemours, Wilmington, Delaware, July 15, 1991. A Fluorine-Containing Hydrophobically Associating Polymer.
- Y-X. Zhang, M. Yassini, F. Hwang and T.E. Hogen-Esch, Aqualon-Hercules, Wilmington, Delaware, August 8, 1991. Fluorocarbon-Containing Water-Soluble Polymers.
- M. Yassini, Y-X. Zhang and T.E. Hogen-Esch, Temple University, July 16, 1991. Fluorocarbon-Containing Polyacrylamides.
- T.E. Hogen-Esch, Institut for Wool Research, Aachen, Germany, May 15, 1991. Hydrophobic Association of Fluorocarbon Containing Water-Soluble Copolymers".
- E.J. Amis, Gordon Research Conference, Polymer Physics, Rhode Island, 1990. Light Scattering and Viscosity of Associating Polymers in Solution.
- E.J. Amis, Tethered Chains I: International Symposium on the Science of Polymer Surfactants, Minneapolis and Brainerd, MN 1991. Structure and Dynamics of Hydrophobically Associating Polymer Solutions.
- T.A.P. Seery and E.J. Amis, APS National Meeting, High Polymer Physics Division, Cincinnati, OH, 1991. Light Scattering and Viscosity of Associating Polymers in Solution.

Research Summary

- Fluorine-19 NMR studies were undertaken in order to determine the content of fluorine-containing comonomer in a series of acrylamide copolymers. The results indicated that comonomer conversion is essentially quantitative.
- Addition of water-soluble (HOCH₂CH₂SH) and water-insoluble (C₁₂H₂₅SH) radical scavengers indicates that the water-soluble scavenger is effective in reducing molecular weight. The water-insoluble scavenger essentially has no effect. This appears to indicate that the polymerization occurs exclusively in the aqueous phase (see also "Proposed Research").
- We have found that in certain instances, addition of as little as 1 percent salt causes huge increases (~ 20 fold) in low shear Brookfield viscosity. In other systems, the increases in viscosity are much smaller. It appears that in the former systems viscosities are lower to start with than in the latter systems. This would indicate that addition of salts may lead to strongly enhanced hydrophobic association. The reason for these interesting differences between various solutions is under investigation (see "Proposed Research").
- Perfluorocarbon containing hydroxyethylcellulose (HEC) derivatives were prepared with the structures:



(1)

(2)



Surprisingly, derivatives **1b**, **2b** and **2c** were wholly or partially insoluble. Derivatives **1a** and **1c** are effective viscosifying polymers for which the Brookfield viscosity vs degree of substitution profile goes through a maximum. Derivative **1c** is substantially more effective compared with **1a** consistent with the stronger hydrophobic character of the perfluoroalkyl groups.

- Poly(N,N-dimethylacrylamide) (4 samples) and Poly(N-acryl-N-methylpiperazine) (10 samples) were prepared by anionic polymerization in THF at -78° in the presence of Cs or coordinated Li counter cations. Molecular weights (SEC) range from 3800 - 250,000. The polymers are soluble in methanol, H₂O and chloroform and to a lesser extent, in THF and CH₂Cl₂. Molecular weight distributions were found to be fairly monodisperse ($1.11 < D < 2.69$). (See "Proposed Research").
- Static and dynamic light scattering experiments performed on solutions of hydrophobically associating polyacrylamide copolymers illuminate the underlying molecular basis for the previous observations. Aggregation effects for these polymers are observed at polymer concentrations as low as 10 ppm. These effects are manifest by large radii of multichain aggregates as well as small radii attributed to collapsed chains. The aggregates are, apparently, denser structures than random coils; comparable to microgels observed by others. With the addition of a potassium perfluorooctyl carboxylate surfactant, single chains are observed which exhibit less dense structures reflecting random coil configurations. A previously unreported temperature and concentration dependent slow relaxation mode which is independent of scattering vector was observed.

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