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SYNTHESIS AND CHARACTERIZATION OF SELF-ASSEMBLING WATER-SOLUBLE POLYMERS

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Publications

11-89 - Present

1. M. Yassini and T.E. Hogen-Esch, *Polymer Preprints*, **33**, (1), 933 (1992).	Fluorine-Containing Hydrophobically Associating Polymers
2. X. Xie and T.E. Hogen-Esch, *Polymer Preprints*, **33**, (1), 241 (1992).	Anionic Polymerization of N,N-Dialkyl Acrylamides and Methacrylamides
3. T.A. Seery, M. Yassini, T.E. Hogen-Esch and E. J. Amis, *Polymer Preprints*, **33**, (1), 935 (1992).	Static and Dynamic Light Scattering Characterization of Solutions of Hydrophobically Associating Fluorocarbons-Containing Polymers
4. Y-X. Zhang, F.S. Hwang and T.E. Hogen-Esch, P. Dubin, D.N. Schulz, Eds., Springer Verlag, 1992.	Fluorocarbon-Modified Water-Soluble Polymers, Chapter in "Hydrophobically Modified Associating Polymers",
5. Y-X. Zhang, A-H. Da, G.B. Butler and T.E. Hogen-Esch, *J. Polym. Sci., (Chem. Ed.)*, **32**, 000 (1992).	A Fluorine-Containing Hydrophobically Associating Polymer. 1. Synthesis and Solution Properties of Copolymers of Acrylamide and Fluorine Containing Acrylates or Methacrylates
6. T.A. Seery, M. Yassini, T.E. Hogen-Esch and E. J. Amis, *Macromolecules*, **00**,000 (1992).	Static and Dynamic Light Scattering Characterization of Solutions of Hydrophobically Associating Fluorocarbons-Containing Polymers
7. F. Hwang and T.E. Hogen-Esch, *Polym. Preprts.*, **32** (1), 581 (1991).	Fluorocarbon Modified Water-Soluble Cellulose Derivatives.
8. Y-X. Zhang, A-H. Da, T.E. Hogen-Esch, and G./B. Butler, Chapter 10, ACS Symposium Series No. 467, 1991, "Water Soluble Polymers", pages 159-174, S. Shalaby, C.L. McCormick, and G.B. Butler, Editors.	New Fluorocarbon Containing Hydrophobically Associating Polyacrylamide Copolymers.
9. S. Gopal Krishnan, G.B. Butler, T.E. Hogen--Esch and N-Z. Zhang, Chapter 11, ACS Symposium Series, No. 467,1991, pages 175-188, "Water-Soluble Polymers", S. Shalaby, C.L. McCormick, and G.B. Butler, Editors.	Hydrophobically Associating Ionic Copolymers of Methyldiallyl-1,1-dihydropentadecafluorooctoxyethyl-ammonium Chloride.
10. Y-X. Zhang. A-H. Da., G.B. Butler, and T.E. Hogen-Esch. *J. Polym. Sci.*, Polym. Ltrs., **28**, 213 (1990).	A Fluorocarbon-Containing Hydrophobically Associating Polymer.

11. 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.
12. 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.
13. Y-X. Zhang, A-H Da, G.B. Butler, and T.E. Hogen-Esch, Proceed. 33rd IUPAC Symposium on Macromolecules, Montreal, 1990.	Water-Soluble Graft Copolymers of 2,3-Dihydroxypropyl Cellulose With Acrylamide and Sodium-2-Acrylamido Propane Sulfonate.
14. Y-X. Zhang, A-H. Da, G.B. Butler, and T.E. Hogen-Esch, *Polym. Preprs.*, **30** (2), 338 (1989).	A New Fluorocarbon Containing Hydrophobically Associating Polyacrylamide Copolymer.

Presentations (1990-1991)

1. M. Yassini and E.E. Hogen-Esch, ACS National Meeting, San Francisco, CA, April 1992.	Fluorine--Containing Hydrophobically Associating Polymers
2. X. Xie and T.E. Hogen-Esch, ACS National Meeting, San Francisco, CA, April 1992.	Anionic Polymerization of N,N-Dialkyl Acrylamides and Methacrylamides
3. T.A. Seery, M. Yassini, T.E. Hogen-Esch ,and E.J. Amis, ACS National Meeting, San Francisco, CA, April 1992.	Static and Dynamic Light Scattering Characterization of Solutions of Hydrophobically Associating Fluorocarbon-Containing Polyacrylamides
4. T.E. Hogen-Esch, Y-X. Zhang, A-H. Da, E.J. Amis, M. Yassini, and T. Seery, Symposium on Supramolecular Aspects of Polymer Synthesis and Polymer Structures, Max Planck Institut fur Polymers, Forschung, Mainz, FRG., Septermber,1991.	Synthesis and Properties of Fluorocarbon Containing Associating Aqueous Polymers
5. E.J. Amis, Procter and Gamble Company, Cincinnati, 1991	Structure and Dynamics of Hydrophobically Associating Polymer Solutions
6. E.J. Amis, Applied Biosystems, Inc., Foster City, CA, 1991	Structure and Dynamics of Hydrophobically Associating Polymer Solutions
7. F. Hwang and T.E. Hogen-Esch, Spring ACS Meeting, Atlanta, Georgia April 1991,	Fluorocarbon-Modified Water-Soluble Cellulose Derivatives
8. T.E. Hogen-Esch, DuPont, July 1991.	Fluorocarbon Containing Hydrophobically Associating Polymers
9. T.E. Hogen-Esch, Aqualon-Hercules, August, 1991.	Hydrophobically Modified Water-Soluble Polymers
10. T.E. Hogen-Esch, University of Aachen, Germany, May 1991.	Fluorocarbon-Modified Polyacrylamides
11. T.E. Hogen-Esch, University of Bordeau, June 1991.	Hydrophobically Modified Water-Soluble Polymers
12. T.E. Hogen-Esch, Polish Academy of Sciences, Lodz. Poland, August, 1991.	Fluorocarbon-Containing Associating Water-Soluble Polymers

13. 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
14. 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
15. E.J. Amis, American Chemical Society National Meeting, Innovative Rheological Techniques, Atlanta, GA, 1991	Gel transitions at a Molecular Level
16. E.J. Amis, CNRS, Laboratoire de Spectrometrie et D'Imagerie Ultrasonores, Strasbourg, 1991	Dynamic Viscoelesticity During Chemical and Physical Gel Transitions
17. E.J. Amis, Albert-Ludwigs Universitat, Institute fur Makromolekulare Chemie, Frieburg, 1991	Dynamic Viscoelesticity During Chemical and Physical Gel Transitions
18. E.J. Amis, American Physical Society National Meeting, High Polymer Physics Division, Indianapolis, 1991 (presented by T. Seery)	Structure and Dynamics of Associating Polymers in Solution
19. Y-X. Zhang, A-H. Da, T.E. Hogen-Esch and G.B. Butler, Thirty-third IUPAC International Symposium on Macromolecules, Montreal, Canada, July 8-13, 1990	Water-Soluble Graft Copolymers of 2,3-Dihydroxypropylcellulose with Acrylamide and Sodium-2-acrylamido-2-methylpropanesulfonate
20. E.J. Amis, Gordon Research Conference, Polymer Physics, Rhode Island, 1990.	Light Scattering and Viscosity of Associating Polymers in Solution
21. T.E. Hogen-Esch, M. Yassini, Y-X. Zhang, F. Hwang, E.J. Amis, and T. Seery, Washington ACS Meeting, August, 1990	Synthesis and Characterization of Fluorocarbon-Containing Polyacrylamides
22. E.J. Amis, Gordon Research Conference, Complex Fluids, Volterra, Italy, 1990	Viscoelestic Studies of Physical and Chemical Gel Transitions

Abstract
Proposed Research

The synthesis is proposed of water-soluble vinyl and other polymers capable of self-assembly through hydrophobic bonding of pendent fluorocarbon and other hydrophobic groups. The self-assembly process will be studied by viscometry and dynamic viscoelasticity, and by static and dynamic light scattering. These investigations are aimed at identifying the structural features of polymers that are important in enhancing the viscosity of aqueous polymer solutions at very low polymer concentrations (<1000 ppm). We will also initiate small angle neutron scattering (SANS) measurements aimed at the determination of the size of the fluorocarbon-containing hydrophobic aggregates.

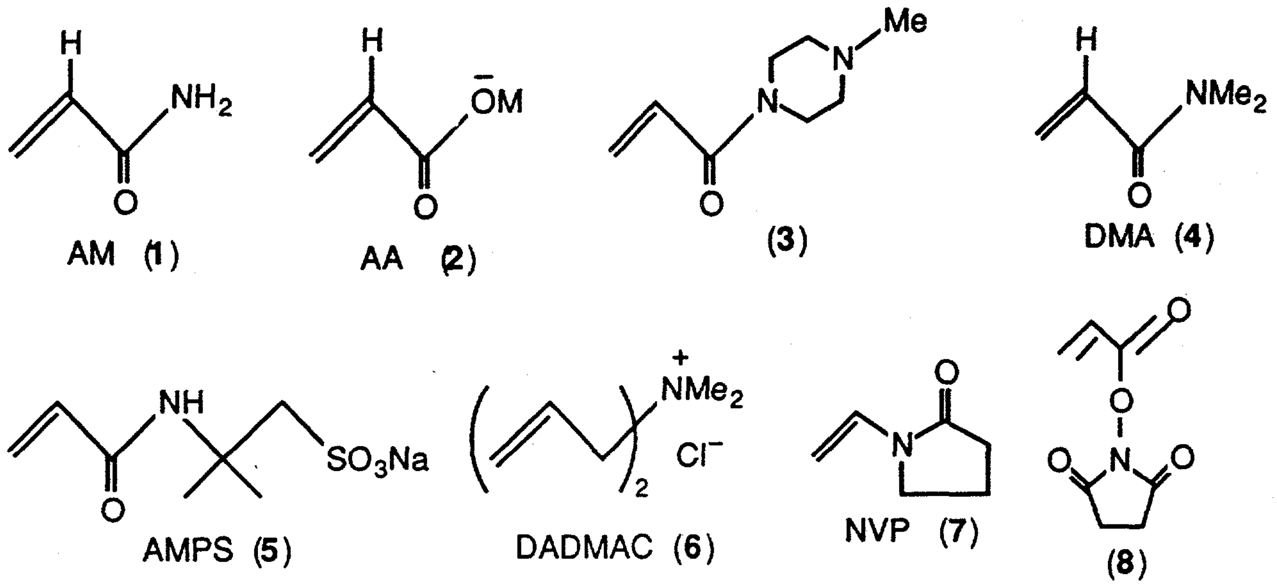
We will be interested in the degree of self assembly as a function of the type and length of the hydrophobic groups and of the type and length of the flexible spacer group linking the hydrophobic to the polymer backbone. The nature of the hydrophilic chain will also be of interest. Thus, we will investigate a number of hydrophilic comonomers such as acrylamide, N-vinylpyrrolidone and anionic or cationic vinyl monomers. Surface interactions of these interesting copolymers will be studied by adsorption onto appropriately modified latex spheres.

Finally, we propose to explore the synthesis of water-soluble polymers capable of self assembly through interactions of pendent polyanions and polycations.

1. Research Summary (November 1989 to Present)

1.1. Introduction

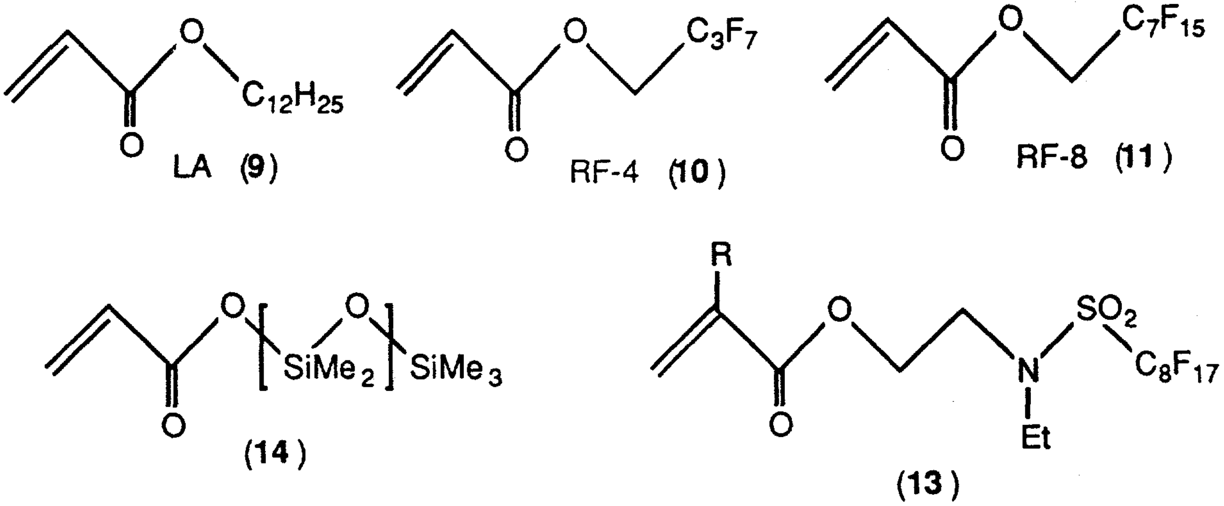
Over the past three years, we have further documented the very large viscosities obtained for perfluorocarbon derivatives of polyacrylamide (PAM) prepared by aqueous copolymerization of hydrophilic vinyl monomers such as AM (Scheme 1) and hydrophobic comonomers shown in Scheme 2.[1-13]



AM (1) AA (2) (3) DMA (4)

AMPS (5) DADMAC (6) NVP (7) (8)

Scheme 1. Water-soluble vinyl monomers.

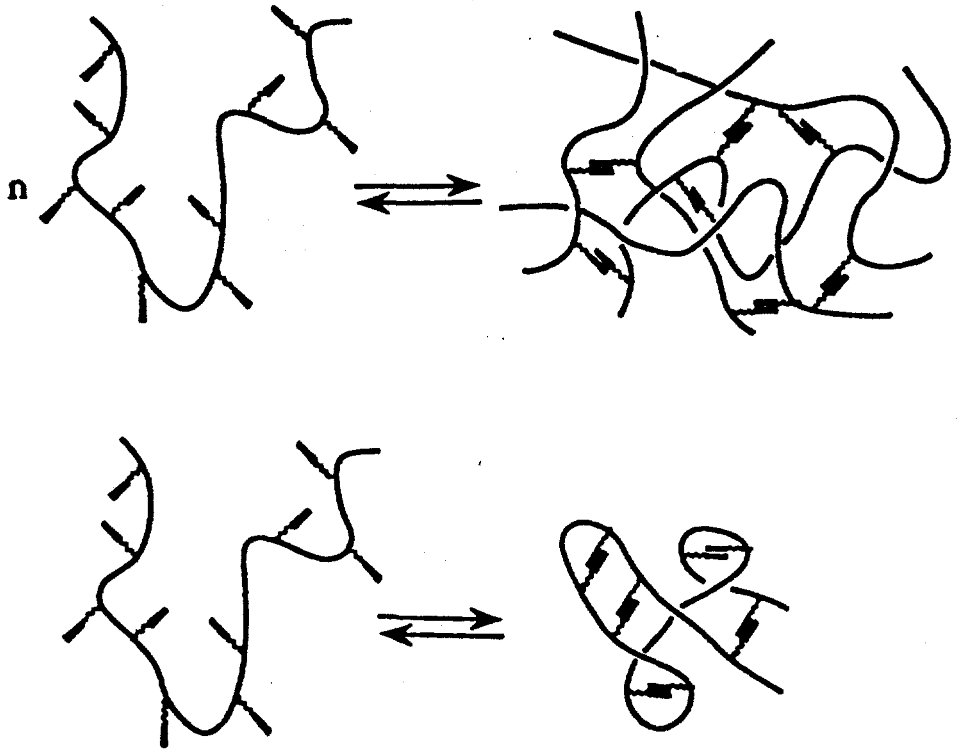


LA (9) RF-4 (10) RF-8 (11)

(14) (13)

Scheme 2. Hydrophobic Comonomers of current interest.

These large viscosities were previously shown to result from strong hydrophobic intermolecular association of hydrophobic fluorocarbon groups as schematically depicted in Scheme 3. This is the case, particularly with comonomer **13** where Brookfield (BF) viscosities of the copolymers solutions (.5 wt %) were typically from 1 - 2 orders of magnitude greater than the solutions of the copolymers containing laurylacrylate prepared under identical conditions. The perfluoroalkyl containing copolymers were also shown to have other properties consistent with very strongly hydrophobically associating polymers. Thus, large viscosity decreases were demonstrated upon addition of organic solvents such as acetone and DMF and upon addition of perfluorocarbon surfactants. Viscosity increases were shown to occur upon addition of common salts and upon increasing the temperature. The BF viscosities were shown to decrease sharply with increasing rates of shear. Such properties are of interest in several applications (see Proposed Research).



Scheme 3. Hydrophobic association of water-soluble copolymers containing pendent hydrophobic groups.

We also studied the effects of perfluorocarbon substitution for the case of hydroxyethylcellulose (HEC). In this case also, it could be shown that perfluoroalkyl substitution gives rise to self associative behavior that is stronger than that obtained for the hydrocarbon derivatives of HEC with the same hydrophobe lengths.

In the following, we briefly summarize some of the most important results obtained over the previous funding period.

1.2. Acrylamide Copolymerizations

More than 120 acrylamide copolymers were synthesized during the last funding period.[1-6,8-10,12-17] Comonomers (Scheme 2) have included acrylate-containing fluorocarbons, hydrocarbons and silicones as hydrophobic groups. Several fluorocarbon containing acrylates were used without and with hydrophilic "spacers" between the hydrophobic group and the vinyl group.

1.2.1. Acrylamide Copolymers Containing Comonomers 13 (Yassini, Hwang, Xie)

Studies were undertaken in order to more firmly establish preliminary results obtained in the preceding funding period, especially the Brookfield (BF) viscosity-comonomer (**13a**)-content profile. In agreement with previous results,[1,2,3] the BF viscosity vs comonomer content plot shows a bell-shaped curve with a viscosity maximum at around .07 mole %. Appreciable viscosity increases over that of the homopolymer were noted at mole fractions as low $\sim 1\times10^{-4}$. This demonstrates the extraordinary effectiveness of fluorocarbon comonomers **13** in the promoting hydrophobic association.

We have also explored polymerization methods aimed at reducing the time needed to dissolve the polymer gels formed in the polymerization.[13] The time needed was reduced from typical values of several weeks or more to a few days. Furthermore, we have been able to scale up preparations from about 2 grams to about 10 grams by increasing surfactant concentration and by decreasing acrylamide concentration.

The effects of organic cosolvents in the polymerizations was briefly explored (Fig. 1). Below 8 vol % acetone, the polymerization gives hard gels that are difficult to dissolve. At higher acetone concentrations, there is a rapid decrease in viscosity, presumably as a result of chain transfer to acetone. We have shown that acetone content may be lowered and that polymerizations without acetone are possible by using lower AM concentrations. However, for optimal viscosification behavior, the presence of some acetone appears to be necessary.

1.2.2. Kinetics of Copolymerization of 13a by ^{19}F NMR (M. Yassini)[14]

We have now been able to use ^{19}F NMR to accurately determine comonomer concentration during copolymerization.[12] This was possible due to the fact that the ^{19}F signal of the copolymer is extremely broad and does not appear to contribute at all to the comonomer peak. The CF_3 peak of the comonomer is particularly convenient to determine. We have also carried out simultaneous ^{19}F and ^{1}H NMR on the disappearance of **13a** and of **1** (vinyl protons) respectively. The results of such a study (Fig. 2) show that the conversion of **1** and **13a** proceeds in parallel fashion.[12] Thus, the composition of the chain, at least in these cases, is not substantially affected by conversion. This would appear consistent with the copolymerization proceeding in the aqueous phase although a micellar process cannot be ruled out. Addition of water-soluble chain-transfer agents such as 2-mercapto ethanol was shown to lead to large decreases in solution viscosity probably as a result of chain transfer to the thiol in the aqueous phase.

1.2.3. Synthesis of Terpolymers of Acrylamide, Sodium-2-acrylamido-2-methyl propane sulfonate and Fluorocarbon Containing Acrylate 13a (Y-X. Zhang and Coworkers)[15]

Twenty-one copolymerizations of **1** and comonomers **5** and **13a** were carried out. Three series of terpolymers were prepared in which the AMPS content was held constant at about 10, 30 or 70 mole % respectively. For each AM/AMPS composition, 7 runs were performed in which the content of hydrophobic comonomer **13a** was varied between 0 and .4 mole %. For the AM/AMPS 70/30 and 30/70 series the apparent intrinsic viscosities determined in 1.0 M. NaCl plotted against the mole content of comonomer **13a** showed a maximum occuring at .08 and 0.11 mole % respectively. This result would appear to be similar to that obtained for copolymers of **1** and **13a**. Surprisingly, this was not observed for the AM/AMPS 90/10 series where intrinsic viscosities did not appear to vary much with the content of **13a**.

1.2.4. Copolymerizations with Polydimethylsiloxane (PDMS) Containing Acrylates (X-Y. Zhang)[17]

In addition to the copolymerization of fluorocarbon- and hydrocarbon acrylates, we also investigated polydimethylsiloxane acrylate derivatives (comonomer **14**, Scheme 2). As was observed with the other comonomers, a bell shaped curve was obtained in plotting the BF viscosity of 0.5 wt % copolymer solutions as a function of comonomer content (Fig. 3). Such a bell curve was observed previously for PAM copolymers containing perfluorocarbon and hydrocarbon acrylates and appears to result from competing inter- and intramolecular hydrophobic association. Thus, at higher comonomer content, intramolecular association prevails leading to partial chain collapse. The BF viscosities of solutions (0.5 wt %) of the PAM copolymers containing **14** are lower than that of the copolymers of the perfluorocarbon comonomers **13** but were found to be higher than the copolymers containing laurylacrylate. The apparent relative hydrophobicities in the order perfluorocarbons > polydimethylsiloxanes > hydrocarbons are parallelled in the association of the corresponding surfactant giving cmc's that are decreasing in the order perfluorocarbons < PDMS < hydrocarbons.

1.3. Solution Properties of Acrylamide Copolymers

1.3.1. Effects of Temperature, Cosolvents, Surfactants and Addition of Salts (M. Yassini, X. X. Xie, F. Hwang)[13]

We have characterized some of the most effectively viscosifying copolymers by capillary viscometry (Fig. 4).[2] The very high intrinsic viscosity at about 23 dl/gr of sample 12 - 65 is only apparent. Viscometry in water-DMF mixtures shows large decreases in $[\eta]$ giving values of around 3 dl/gr in 50 % H_2O/DMF. The intrinsic viscosity of polyacrylamide itself is only slightly decreased in going from H_2O to 50 % H_2O/DMF.[1,2] These results document the substantial dissociation of the polymer clusters in the presence of organic solvents. Similar effects are shown in Figure 5 for the effects of addition of acetone. Decreases in viscosity are not observed until addition of about 5.0 wt % and a substantial decrease is not observed until about 10 %. Similar effects are shown upon addition of a perfluorocarbon surfactant ($F(CF_2)_7COOK$). Figure 6 shows clearly the onset of polymer cluster dissociation. Apparently this is occuring by competitive association of the fluorocarbon surfactants with the perfluorocarbon groups in the copolymer. Such a process could be represented by equation 1:

$$PS_m \underset{K_2}{\overset{S}{\rightleftharpoons}} nP \underset{K_1}{\rightleftharpoons} P_n \qquad (1)$$

Figure 6 shows a decrease of surfactant concentration necessary for the onset of a BF viscosity decrease at lower copolymer concentration. This would appear to be consistent with the above process.

We have also studied the effect of addition of salts (MX) on the BF viscosity and, at least for some of the systems, have found very large viscosity increases upon addition of relatively low amounts of salt[15] (Fig. 7). Other systems however, show much smaller increases, particularly the most effectively viscosifying copolymers. The reason for these differences is not quite clear. Studies on these systems are in progress.

The effects of different cations and anions were briefly investigated. The differences between anions were found to be larger than between cations. The results are consistent with "salting-out" effects that increase hydrophobic association.[18] Support for this is provided by the fact that "salting-in" salts such as $(n\text{-Bu})_4N^+Cl^-$ give viscosity decreases.

The effects of temperature on the viscosity of AM copolymers of **13a** was unusual and very interesting (Fig. 8). Depending on the method of preparation, various viscosity-temperature profiles were obtained with maxima varying from 60° - 80°C. We believe that such viscosity increases are related to the fact that hydrophobic association is exoentropic (ΔS = positive) but a detailed understanding of this interesting effect is still missing. Further work on this is in progress.

1.3.2. Rheology of Hydrophobically Modified Acrylamide Copolymers (X-Y Zhang and Coworkers)[19]

The shear dependent viscosity of the acrylamide copolymers containing comonomers **9, 10, 11** and **13** was measured. Above shear rates (γ) of about 1.0 sec^{-1}, the 0.5 wt % copolymers solutions were found to conform to the Ostwald-De Waele equation 2:

$$\eta = m\,\gamma^{n-1} \qquad (2)$$

In all cases, the copolymers were found to be pseudoplastic ($n<1$). However, for the copolymers of **13a**, this behavior was especially pronounced as shown in Tables 1 and 2. The polyacrylamide homopolymer solutions were found to be somewhat pseudoplastic ($n < .90$) but the values of n were found to sharply decrease with increasing comonomer content reaching a minimum value of .20 and .12 at around .045 and .060 mole % for the copolymers of **13a** and **13b** respectively. Upon increasing the comonomer content further, the values of n increased and, above about 1 mole %, reached values comparable to that of the homopolymer . Similar behavior was found for the copolymers of **11** but here the values of n were generally higher with a minimum of about .35 at about .50 mole % comonomer. For the copolymers of **9** and **10**, the values of n tended to be similar to that of polyacrylamides synthesized under identical conditions.

These results appear consistent with pronounced intermolecular hydrophobic association at low comonomer **13** content (< .1 mole %). The very large sized aggregates readily fall apart as the result of shear. At higher comonomer content, hydrophobic association is intra-molecular[1,2] and is plausibly not easily disrupted by shear. The much decreased tendency of comonomers **9** and **10** to promote hydrophobic association is again consistent with the higher value of n.

The effect of the presence of organic cosolvents on rheology was also briefly examined (Table 3). For 0.5 wt % solutions of copolymer RFA-18 (content of comonomer **13a** is .023 mole %) increasing the DMF content from zero to 30 volume percent led to an increase in the value of n from .23 to .60. This is again consistent with a decrease in hydrophobic association documented earlier (Section 1.3.1).

1.3.3. Static and Dynamic Light Scattering Determination of Acrylamide Copolymer Molecular Weight (T.Seery)[9]

Because of the unique synthesis of the materials in this project, fundamental characterization of molecular weights, chain topology, and conformations of the molecules in solution, was not available. Any reasonable understanding of the mechanism that produces the dramatic viscosity effects requires this basic information. The physical chemical component of this project focussed initially on these issues.

Static and dynamic light scattering measurements (SLS and DLS) have been performed on solutions of a polyacrylamide containing small amounts of the comonomer, 2-(N-ethylperfluorooctanesulfonamido) ethyl acrylate (**13a**) in order to characterize absolute molecular weight. Three samples of the copolymers were used in light scattering studies over 3 decades of concentration from 10 - 10000 ppm. The measurements were designed to establish the behavior of single chains by diluting the associating molecules so that osmotic forces would cause the clusters to disassociate. This did not occur and our studies demonstrate large aggregates even at concentrations as low as 10 ppm.

Dynamic light scattering from these solutions was extremely complicated, as discussed below, and as a result the static light scattering and Zimm plots were difficult to interpret. Figures 9 and 10 show a typical comparison between the Zimm plot for homopolyacrylamide and a copolymer with only 0.007 mol % of comonomer. The most dramatic influence is the shift of apparent solvent quality from good solvent to poor solvent as shown by the change from a strong positive second virial coefficient A_2, to one that is zero or slightly negative (from the slope of the concentration extrapolation). Typical apparent molecular weights for these materials were in the range 2 - 9 x 10^6. Because the DLS showed that the solution structure was not simple, we could not rely on these molecular weight determinations without further efforts to reduce the aggregation effects.

Single chain behavior in the DLS was observed with the addition of a structurally matched fluorocarbon surfactant. The hydrophobic end of the surfactant was chemically identical to the fluorocarbon pendent groups in the copolymers. Under these conditions the correlation functions could be fit with a single relaxation time corresponding to a hydrodynamic radius of 70 - 80 nm. The absence of other contributions to the scattering indicates that the surfactants completely disrupt both inter- and intramolecular associations to eliminate both aggregates and collapsed chains. In the SLS the effect was to improve the quality of the data and to recover the positive A_2 value (Figures 11 and 12). These results clearly demonstrate the shielding of hydrophobic associations by the added surfactant and they further support our interpretation of the effect of surfactant to reduce the viscosity enhancement. Section (1.3.1)

Similar investigations with DMF and acetone as cosolvents did not eliminate the associated clusters from the DLS experiment or significantly improve the static light scattering.

1.3.4 Dynamic Light Scattering for Semidilute Solutions of Associated Copolymers. (T. Seery)[9]

For DLS measurements across an expanded concentration range (10 ppm to 1%) the correlation functions exhibited multiple relaxation. The angular dependence of the relaxations demonstrated that the modes correspond in general to diffusion processes. At low concentrations, modes were identified with aggregates and collapsed single chains while at higher concentration, gel-like modes typical of semi-dilute polymer solutions were seen.

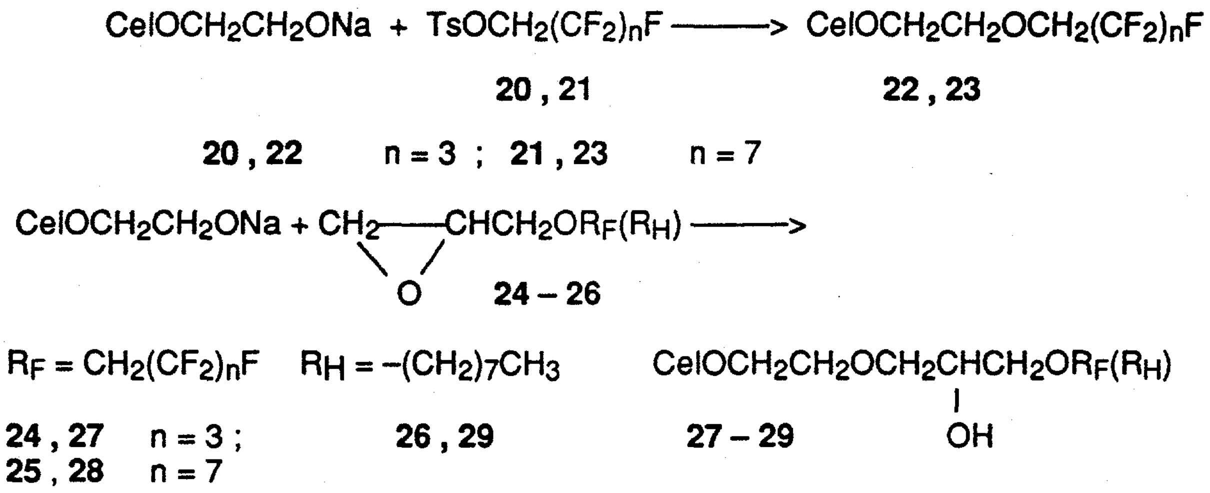
Figure 13 shows this behavior where the filled points follow the growth of associated clusters from the dilute regime into the semidilute regime with the formation of a pseudo gel. This sample has 0.07 mol % of comonomer **13** and shows enormous viscosification accompanying the transition to the semidilute regime. The open symbols show the result of addition of 0.1 or 1.0% of FC129 surfactant which breaks the associations to give single chain scattering as anticipated from the viscosity results.

Also present at low concentration was a temperature dependent and angle independent slow relaxation. The lack of angular dependence indicates that this relaxation is not diffusive. The temperature dependence is very strong with the relaxation rate increasing by a factor of 35 for a 30° increase in temperature. The relaxation rate slows at higher polymer concentrations. Observation of this mode has been hindered by its slow correlation times (50 ms to 7 s) which requires long data collections. We have recently acquired a correlator with an extended dynamic range that will allow further investigation of this process.

1.4. Synthesis and Characterization of Fluorocarbon-Modified Hydroxyethylcellulose (F. Hwang)[7,11]

Incorporation of perfluorocarbon groups in hydroxyethylcellulose (HEC) was carried out by reaction of an HEC Na salt with 1,1-dihydroperfluorocarbon tosylates and with epoxy derivatives as shown in Scheme 4.[7,11] The HEC derivatives **22** and **23** were insoluble or marginally soluble.

Fluorocarbon derivative **27** likewise was only partially soluble. However, surprisingly, **28** was shown to have good solubility. The fluorocarbon content of this polymer in contrast with the corresponding AM copolymers of **13** could be determined by ^{19}F NMR using an internal standard. This indicates that the type of hydrophobic association may differ from that involved in the AM-13a copolymers. This polymer moreover, was found to be substantially more effective in viscosification compared with a C_8 hydrocarbon derivative **29** consistent with the superior performance of fluorocarbons in promoting hydrophobic association. However, the effect was less dramatic than that demonstrated for the acrylamide copolymers where the viscosity of the fluorocarbon containing copolymers was found to be 1 - 2 orders of magnitude higher than that of the hydrocarbon analogs.[1-3] The associative character of the HEC derivative **28** was demonstrated by the very steep increase of viscosity with concentration (Fig. 14). Furthermore, as was observed for the hydrocarbon derivatives of HEC by Landoll and others,[20] the viscosity of polymers **28** showed a pronounced maximum when plotted against degree of substitution (Fig. 15). The most likely explanation is similar to that invoked for the hydrocarbon HEC derivatives involving intra- and intermolecular hydrophobic association.[20]



Scheme 4. Modification of HEC Using Tosylates 20, 21, and Epoxy Derivatives **24 –26**.

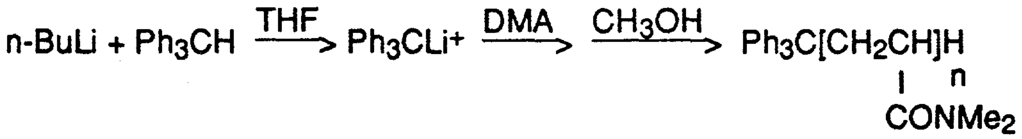
The pronounced shear thinning behavior of the viscosity of solutions of **28** is again consistent with extensive hydrophobic association and appears to be similar to that of the acrylamide copolymers. Addition of salt (NaCl ~ 2 wt %) was found to lead to modest increases in viscosity (10 - 20 %).

1.5. Synthesis by Anionic Polymerization of Well Defined Hydrophobically Modified Water-Soluble Polymers (X. Xie)[21]

The anionic polymerization of N,N-dimethylacrylamide (DMA) (**4**) and of 1-acryloyl-4-methylpiperazine (AMP) (**3**, Scheme 1) was explored in order to obtain monodisperse water-soluble polymers with hydrophobic groups placed at well defined locations along the chain. This would include hydrophobic groups placed at the ends or the center of the chain.

AMP was prepared using literature procedures and DMA was purchased. The two monomers were first polymerized by standard radical polymerization techniques in water

using persulfates as initiators. The PDMA and PAMP polymers were water-soluble and were analyzed by SEC and by ^1H and ^{13}C NMR. The molecular weight distributions of these polymers were typical of vinyl polymers prepared by radical polymerization. The corresponding alkyllithium or lithium carbanion initiated anionic polymerization of DMA in THF using vacuum line techniques according to equation 3 led to polymers that were rather insoluble in THF in contrast to the PDMA samples prepared by radical polymerization. The solubilities of the two polymers in a variety of solvents are shown in Table 4. The differences in solubilities between the PDMA samples prepared by radical and anionic polymerization are curious and are almost certainly due to differences in stereochemistry.



$$\text{n-BuLi} + \text{Ph}_3\text{CH} \xrightarrow{\text{THF}} \text{Ph}_3\text{CLi}^+ \xrightarrow{\text{DMA}} \xrightarrow{\text{CH}_3\text{OH}} \text{Ph}_3\text{C}[\underset{\text{CONMe}_2}{\text{CH}_2\text{CH}}]_n\text{H} \qquad (3)$$

In the presence of Cs^+ ions, however, the anionic polymerization of **3** and **4** leads to reasonably high MW polymers (MW > 10^5 Daltons) that were soluble in THF (Table 5). In order to synthesize water-soluble polymers containing hydrophobic chain segments, anionic block copolymerization of DMA and methylmethacrylate (MMA) was carried out as shown in equation 4.

$$\text{PH}_3\text{CCs}^+ \xrightarrow{\text{DMA}} \text{PH}_3\text{C}- \text{PDMA}^-\text{Cs}^+ \xrightarrow[\text{2) H}^+]{\text{1) MMA}} \text{Ph}_3\text{C}-\text{PDMA}-\text{PMMA} \qquad (4)$$

Although block copolymers were formed they were not completely monodisperse.

Better results were achieved by reaction of anionic PDMA with hydrocarbon or perfluorocarbon acid chlorides (eq. 5).

$$\text{RCs} \xrightarrow[-70^\circ\text{THF}]{\text{DMA}} \text{PDMA}^-,\text{Cs}^+ \; + \xrightarrow[\text{R}_\text{F}\text{COCl}]{} \text{R}-\text{PDMA}-\text{R}_\text{F} \qquad (5)$$

The perfluoro PDMA derivatives were water-soluble. The synthesis of the potentially more interesting bis-substituted PDMA (PAMP) polymer according to eq 6 is in progress. (See Proposed Research, Section 2.5.)

$$\text{DMA} \xrightarrow{\text{Cs}^+\text{Naph}^{o-}} {}^-\text{PDMA}^-, 2\text{Cs}^+ \xrightarrow{\text{R}_\text{F}\text{COCl}} \text{R}_\text{F}\,\text{PDMA}\,\text{R}_\text{f} \qquad (6)$$

References - Research Summary

1. Y-X. Zhang, A-H. Da, G.B. Butler and T.E. Hogen-Esch, *J. Polym. Sci., Polymer Letters,* **28**, 213 (1990).
2. Y-X. Zhang, A-H. Da, G.B. Butler and T.E. Hogen-Esch, *J. Polym. Sci., (Chem. Ed.),* **32**, 000 (1992).
3. Y-X. Zhang, A-H. Da, G.B. Butler and T.E. Hogen-Esch, *Polym. Preprts.,* **30**, (2), 338 (1989).
4. T.E. Hogen-Esch, M. Yassini, Y-X. Zhang, F.S. Hwang, E.J. Amis and T.A. Seery, *Polym. Preprts.,* **31**, (2), 460 (1990).
5. Y-X. Zhang, A-H. Da, T.E. Hogen-Esch and G.B. Butler, Chapter 10, ACS Symposium Series No. 467, "Water Soluble Polymers" (1991) pages 159-174, S. Shalaby, C.L. McCormick and G.B. Butler, Editors.
6. S.G. Krishnan, G.B. Butler, T.E. Hogen-Esch and N-Z. Zhang, Chapter 11, ACS Symposium Series No. 467, "Water Soluble Polymers" (1991) pages 175-188, S. Shalaby, C.L. McCormick and G.B. Butler, Editors.
7. F.S. Hwang and T.E. Hogen-Esch, *Polym. Preprts.,* **32**, (1), 581 (1991).
8. T.E. Hogen-Esch, M. Yassini, Y-X. Zhang, F.S. Hwang, E.J. Amis and T.A. Seery, *Polym. Preprts.,* **31**, (2), 460 (1990).
9. T.A. Seery, M. Yassini, T.E. Hogen-Esch and E.J. Amis, *Macromolecules,* **00**, 000 (1992).
10. T.A. Seery, M. Yassini, T.E. Hogen-Esch and E.J. Amis, *Polym. Preprts.,* **33**, (1), 935 (1992).
11. Y-X. Zhang, F.S. Hwang and T.E. Hogen-Esch, "Fluorocarbon-Modified Water-Soluble Polymers", Chapter in "Hydrophobically Modified Associating Polymers", P. Dubin, D.N. Schulz, Eds., Springer Verlag, 1992.
12. M. Yassini , F.S. Hwang, X.X. Xie, and T.E. Hogen-Esch, *Polymer Preprts.,* **33**, (1) 933 (1992).
13. M. Yassini and T.E. Hogen-Esch, To be published.
14. M. Yassini and T.E. Hogen-Esch, Manuscript in preparation.
15. Y-X. Zhang, J. Yang, A-H. Da, Y-Q. Fu and T.E. Hogen-Esch, In preparation.
16. Y-X. Zhang, A-H. Da, N. Li, L-C. Zhang and T.E. Hogen-Esch, In preparation.
17. Y-X. Zhang and T.E. Hogen-Esch, Manuscript in preparation.
18. S. Saito, *J. Pol. Sci.*, A., Vol 1, 1789 (1969).
19. Y-X. Zhang, A-H. Da, Y-Q. Fu and T.E. Hogen-Esch, In preparation.
20. L.M. Landoll, *J. Polym. Sci., Chem. Ed.,* **20**, 443 (1982); A.C. Sau, *Prep. Polym. Mat. Sci. Eng.,* **57**, 497 (1987).
21. X. Xie and T.E. Hogen-Esch, *Polymer Preprints,* **33**, (1), 241 (1992).

Effect of Reaction Medium on Polymer Viscosity

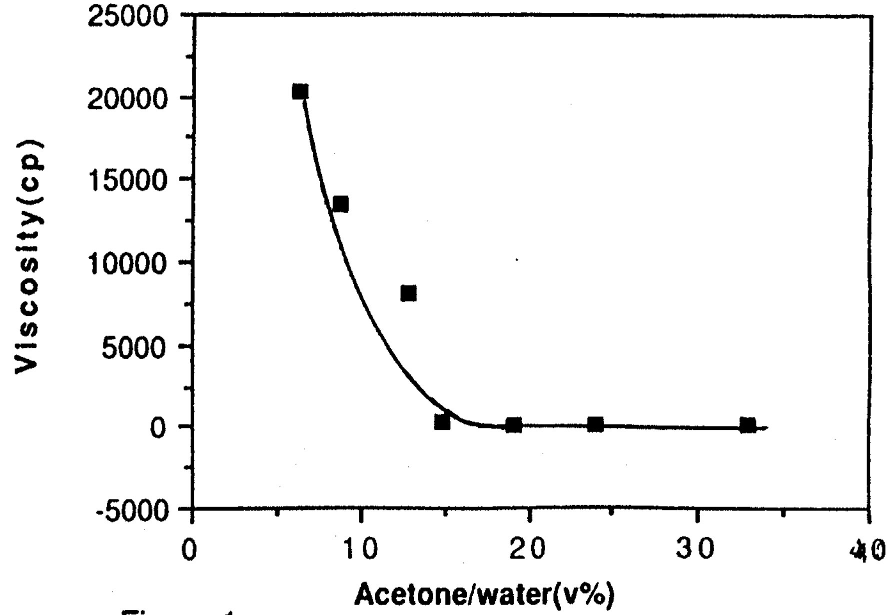


Figure 1

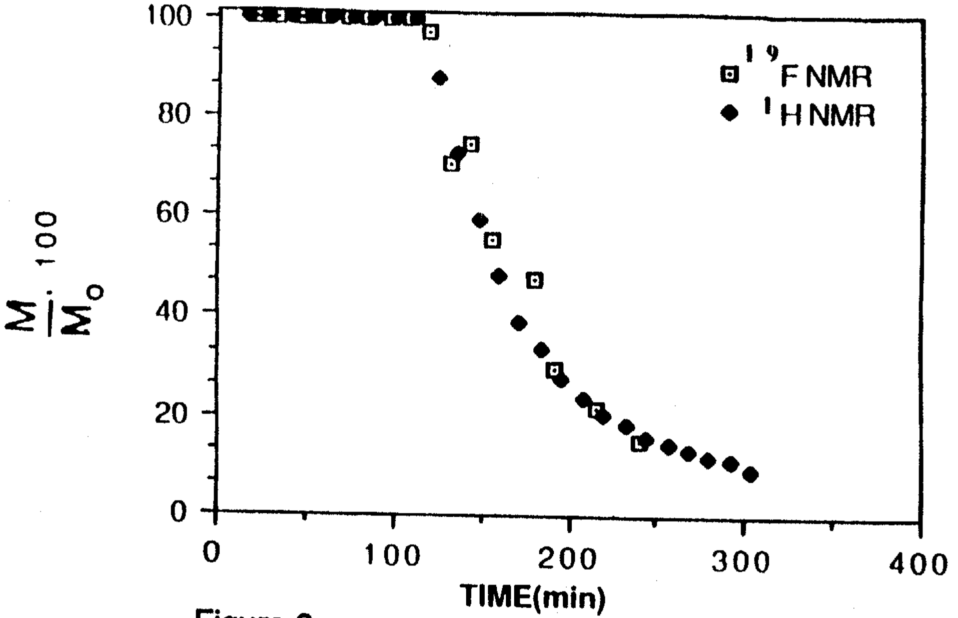
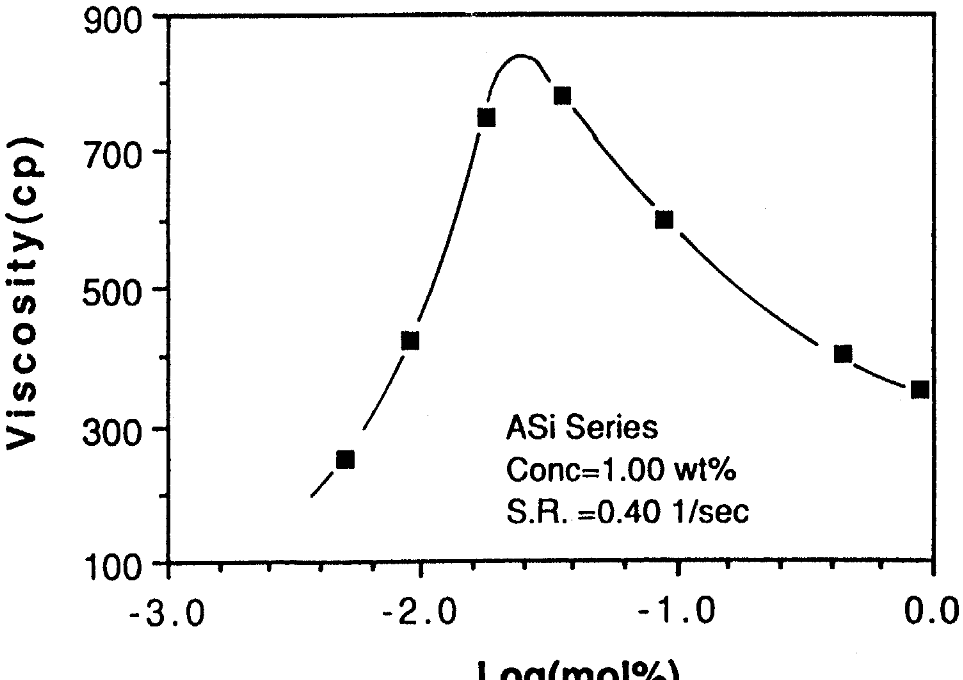


Figure 2



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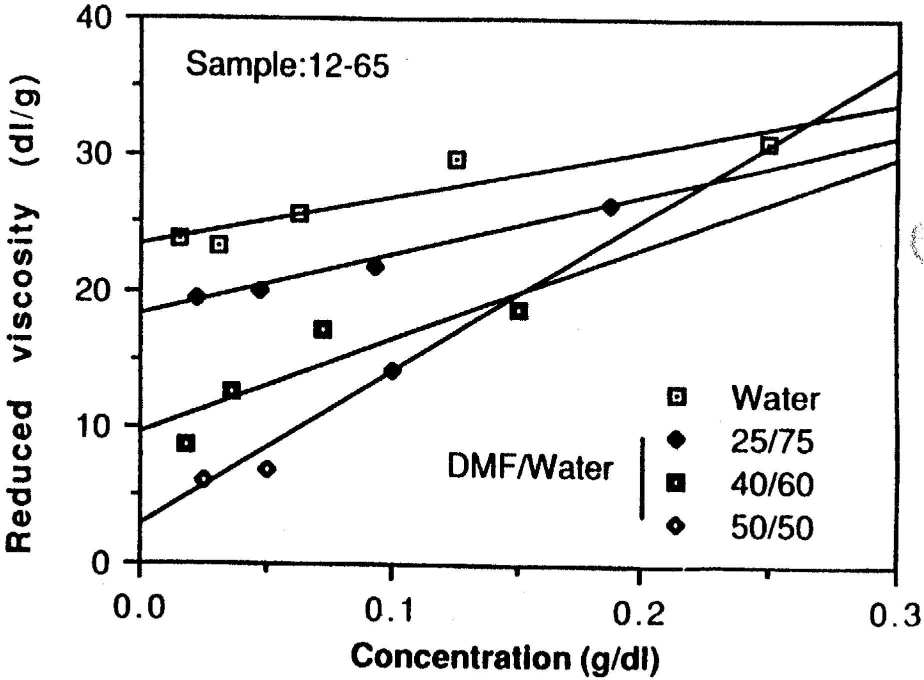

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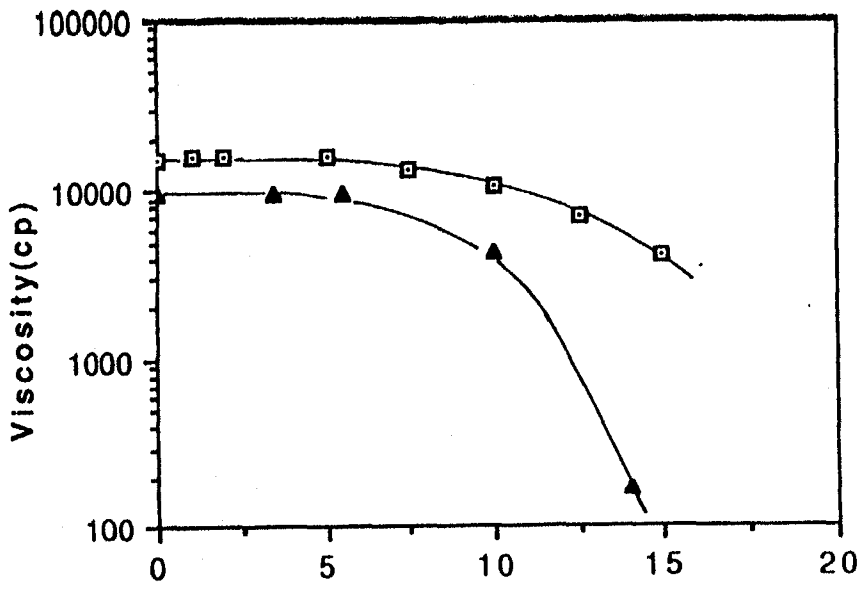

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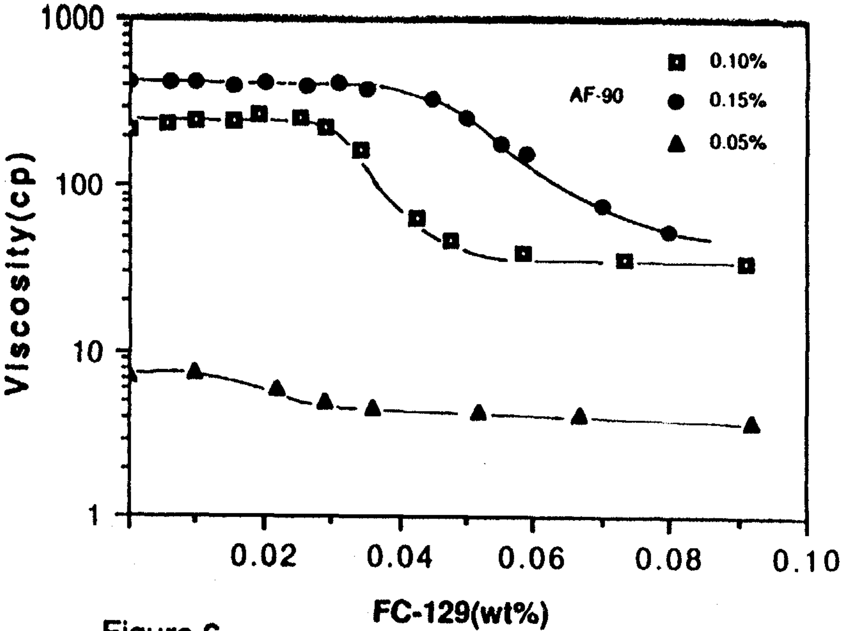

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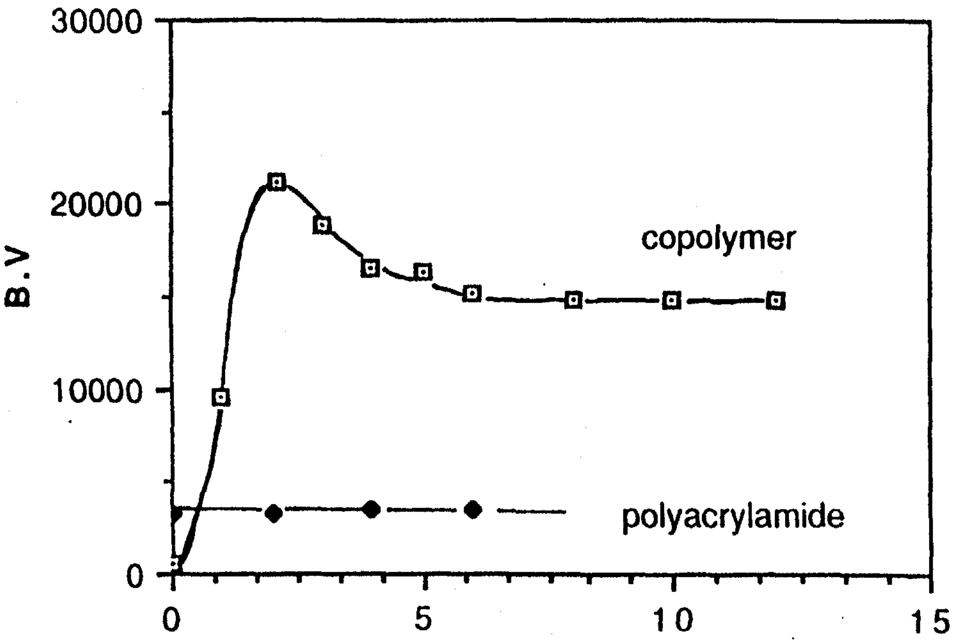

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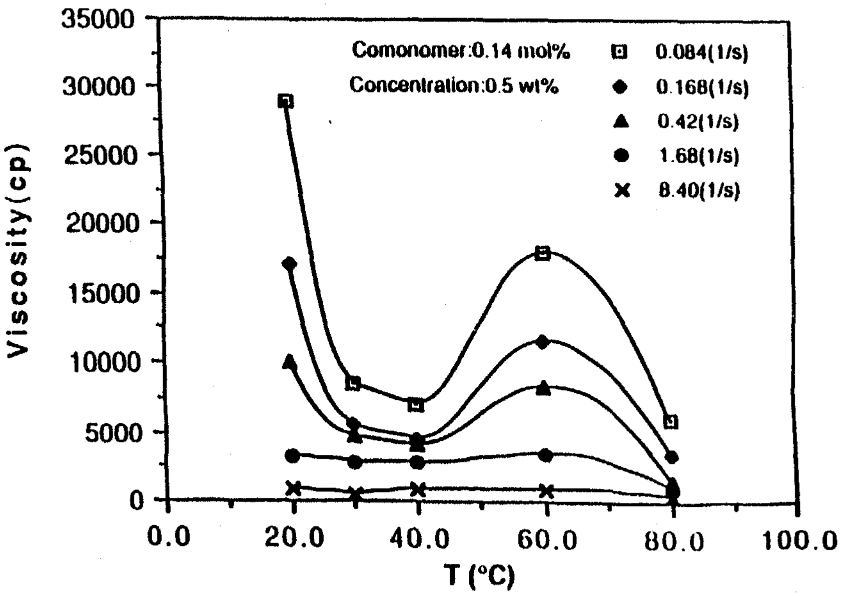

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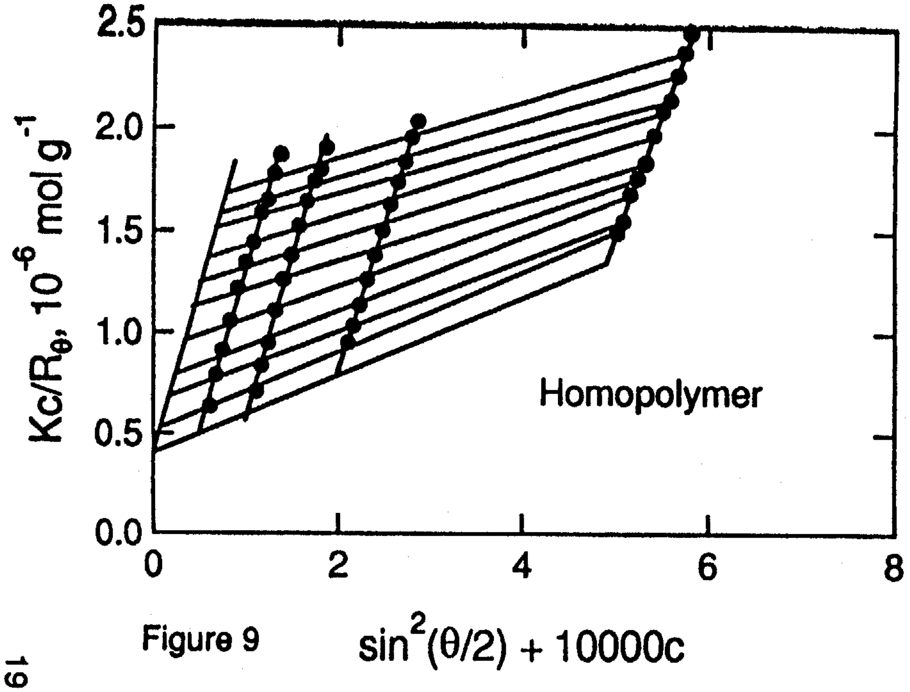

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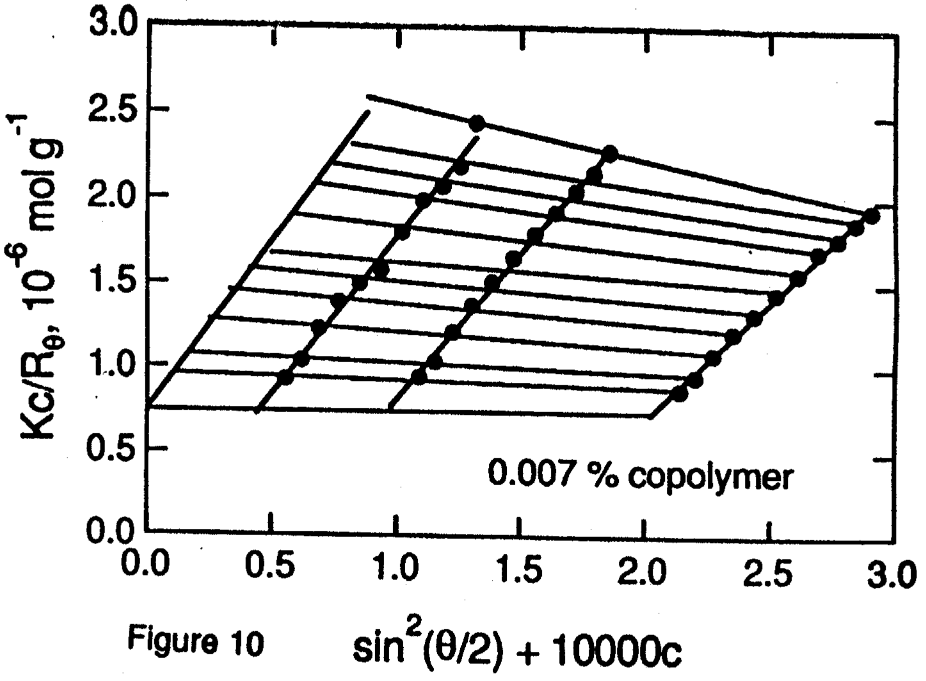
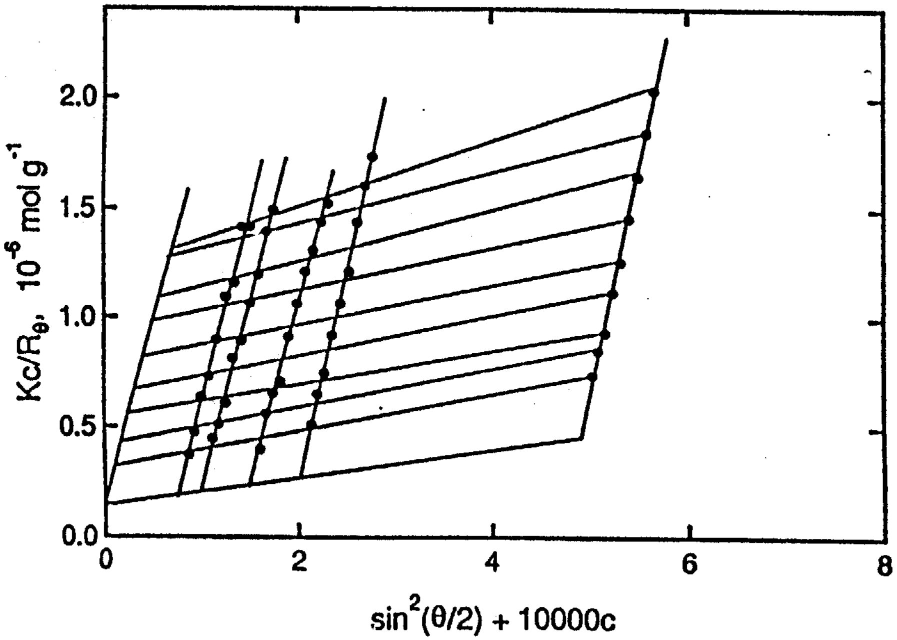


Figure 10



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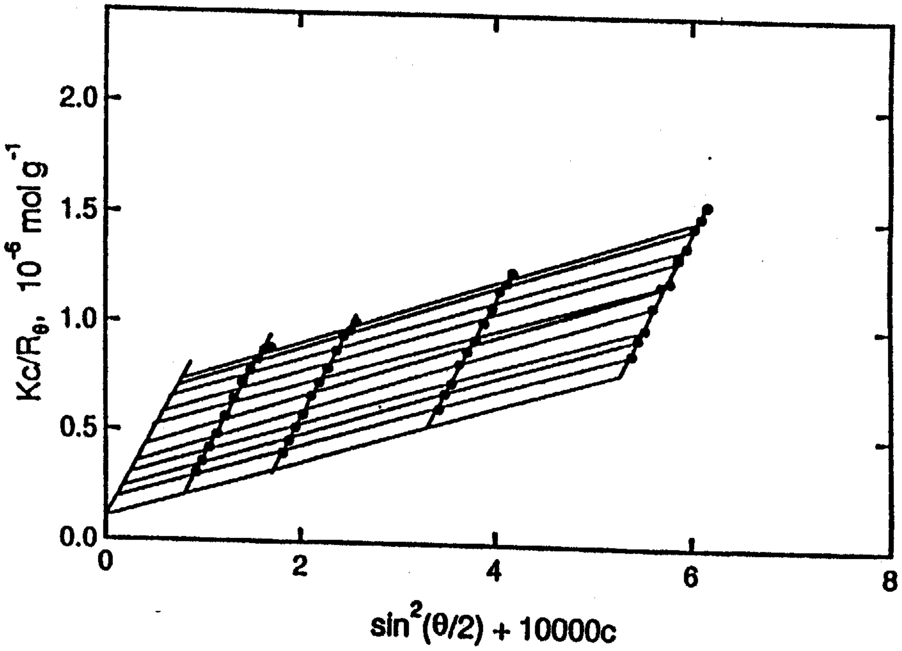

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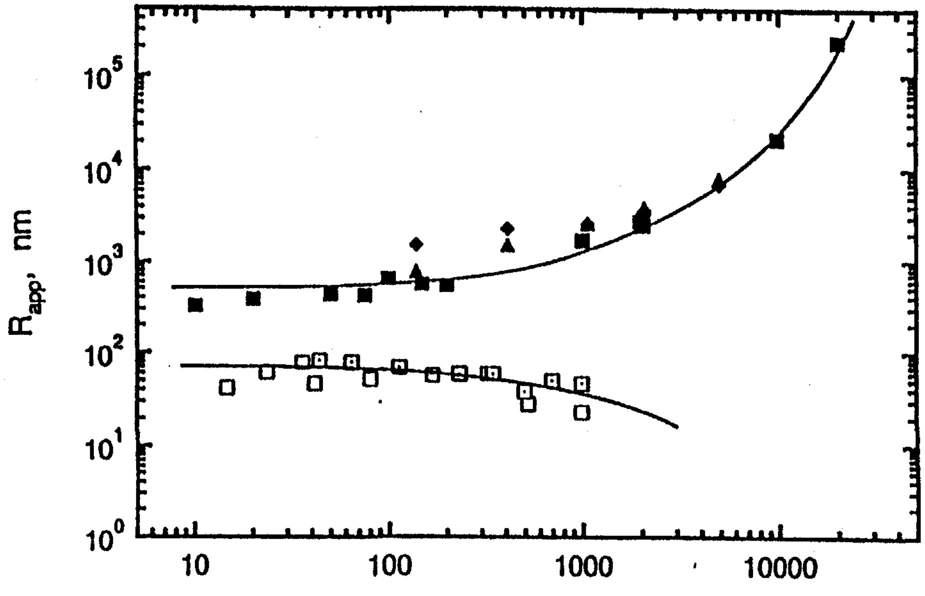
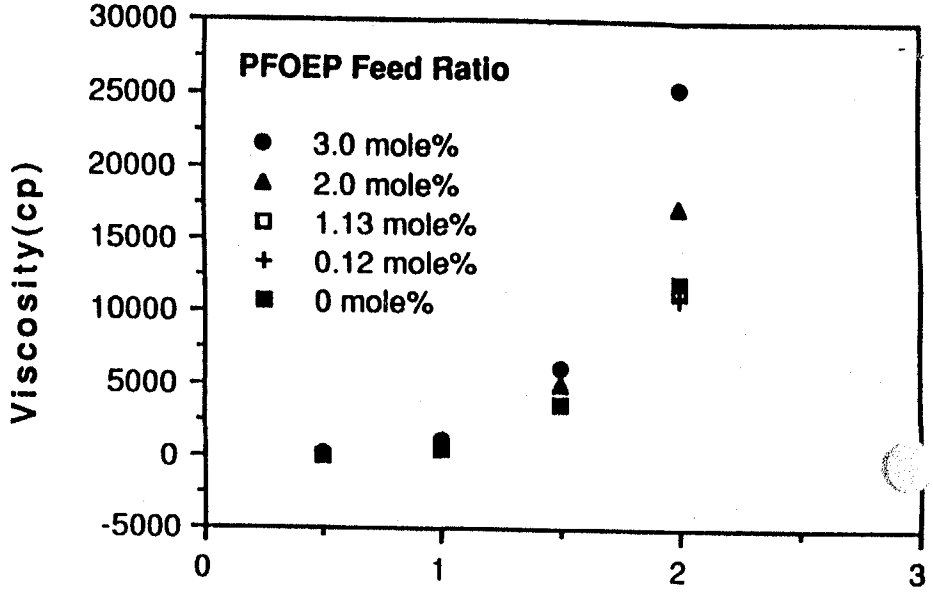


Figure 13



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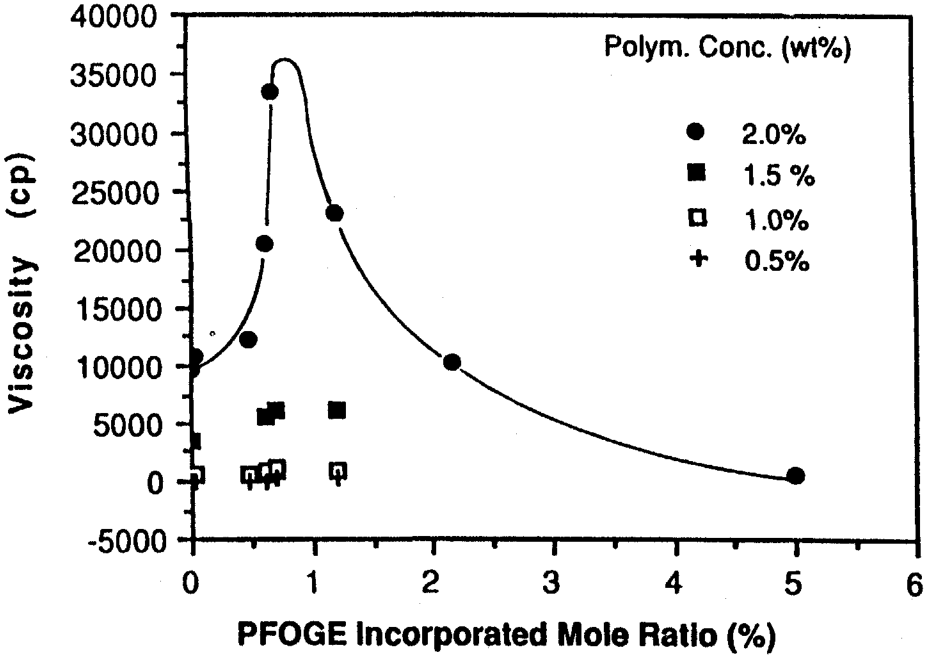


Figure 15

Table 1. Parameters for the Power-Law Model: $\eta = m\gamma^{n-1}$ for 0.5 wt% Aqueous Solutions of Copolymers of **13a** and **13b**

	Comonomer mol%	n	m	Correlation
13a Series:				
RFA-22	0.006	0.461	373	-0.991
21	0.012	0.398	1086	-0.996
18	0.023	0.293	2897	-0.993
17	0.045	0.202	5623	-0.999
12	0.07	0.385	4898	-0.978
10	0.14	0.351	2851	-0.999
9	0.28	0.618	1910	-0.981
8	0.56	0.809	40	-0.987
7	1.12	0.796	33	-0.993
13b. Series:				
RFM-24	0.022	0.732	110	-0.986
23	0.044	0.387	1119	-0.997
15	0.069	0.116	3648	-0.999
16	0.14	0.246	5902	-0.999
19	0.28	0.243	4519	-0.989
20	0.55	0.323	4508	-0.998
22	1.11	0.779	110	-0.985
23	1.66	0.817	73	-0.997

Table 2. Parameters for the Power-Law Model: $\eta = m\gamma^{n-1}$ for 0.5 wt% Aqueous Solutions of Copolymers of **10** and **11**

	Comonomer mol%	n	m	Correlation
Comonomer 10				
RF4-42	4.22	0.822	26.1	-0.993
43	2.81	0.828	45.3	-0.997
44	1.41	0.846	37.7	-0.999
45	0.71	0.862	32.6	-0.986
46	0.38	0.859	37.4	-0.973
47	0.16	0.842	34.3	-0.997
Comonomer 11				
RF8-39	2.36	0.867	40.9	-0.984
33	1.57	0.768	85.1	-0.993
35	1.06	0.682	236.7	-0.997
40	0.51	0.345	706.3	-0.996
34	0.27	0.566	287.5	-0.999
36	0.11	0.849	149.4	-0.991
37	0.06	0.768	84.5	-0.997
41	0.03	0.795	80.2	-0.999

Table 3. Parameters for the Power-Law Model: $\eta = m\gamma^{n-1}$ for 0.5 wt% Solutions of RFA-18 at Different DMF-Water Compositions

DMF/H20 v/v	n	m	Correlation
0	0.234	5688	-0.999
5:95	0.208	6053	-0.998
8:92	0.22	5998	-0.999
11:89	0.234	5888	-0.999
13:87	0.254	5675	-0.998
16:84	0.275	4841	-0.999
20:80	0.313	2704	-0.999
24:76	0.382	2163	-0.997
29:71	0.598	643	-0.982

Table 4 Solubility of PDMA and PAMP polymers

Samples	Initiator	MeOH	H_2O	TOL	THF	CHCl3	CH_2Cl_2	DMF	DOX
PDMA	Radical	S	S	I	S	S	S	I	I
PDMA	RLi	S	P	I	I	P	P	I	I
PDMA	TPMLi	S	P	I	I	P	P	I	I
PDMA	TPMLi*	S	S	I	P	S	S	-	-
PDMA	$DD^{2-}K_2^+$	S	S	I	P	S	S	-	-
PDMA	$DD^{2-}Cs_2^+$	S	S	I	S	S	S	-	-
PDMA	TPMCs	S	S	I	S	S	S	-	-
PAMP	Radical	S	S	I	S	S	S	I	I
PAMP	RLi	S	S	I	I	S	S	I	I
PAMP	TPMLi	S	S	I	I	S	S	I	I
PAMP	TPMLi*	S	S	P	S	S	S	-	-
PAMP	$DD^{2-}Cs_2^+$	S	S	S	S	S	S	-	-

* Tetramethylethylenediamine(TMEDA) was added as a complexing agent.
S=soluble P=partially soluble I=insoluble R=n-butyl, s-butyl, t-butyl
TPMLi = triphenylmethyllithium TPMCs = triphenylmethylcesium
DMF=dimethylformamide TOL=toluene DOX=dioxane

Table 5 Anionic polymerization of DMA, AMP and MAMP in THF

Sample	Initiator	T°C	Mn(Calc)	Mn(SEC)**	MWD	Yield(%)
PDMA0611	radical	50	-	243,000	2.92	-
PDMA0730	$DD^{2-}K_2^+$	-78	-	32,800	1.31	68
PDMA0116	$DD^{2-}Cs_2^+$	-15	64,100	53,500	2.44	50
PDMA0123	$DD^{2-}Cs_2^+$	-78	160,300	135,00	1.52	75
PDMA0723	TPMLi*	-78	12,400	-	-	80
PDMA1201	TPMCs	-78	20,000	22,700	1.02	83
PAMP0313	$DD^{2-}Cs_2^+$	-15	50,700	53,000	2.69	84
PAMP0530	TPMCs	-15	11,400	13,000	2.10	83
PAMP0603	TPMCs	-78	4,800	6,900	1.26	66
PAMP0613	TPMCs	-78	12,800	10,700	1.52	75
PAMP0626	TPMLi*	-78	12,400	13,800	2.03	57
PAMP0716	TPMLi*	-100	12,400	5,900	1.56	81
PAMP0319	FL^-Cs^+	-15	-	-	-	0
PMAMP1102	TPMLi	-78	-	-	-	0
PMAMP1112	TPMLi	-15	-	-	-	0
PMAMP1212	t-BuLi	-78	-	-	-	0

* TMEDA was added as a complexing agent.

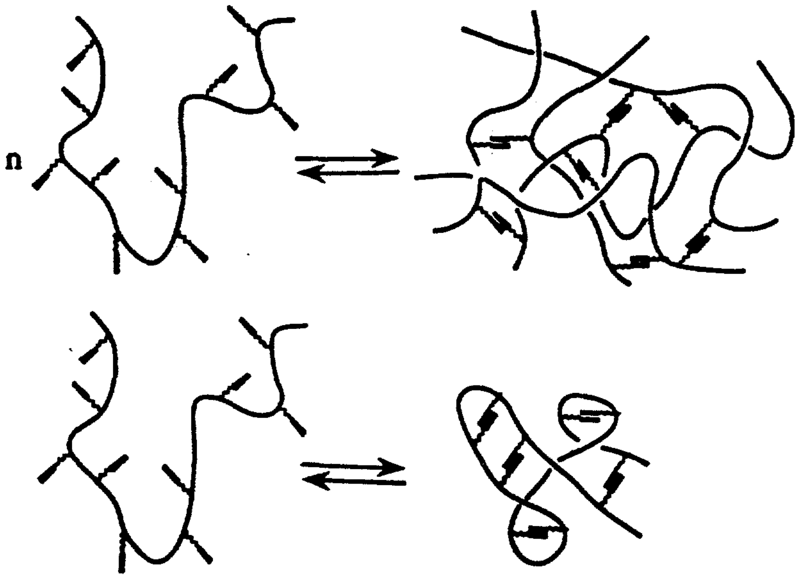
** Calibrated by polystyrene standard samples.

FL^-Cs^+ is fluorenyl cesium.

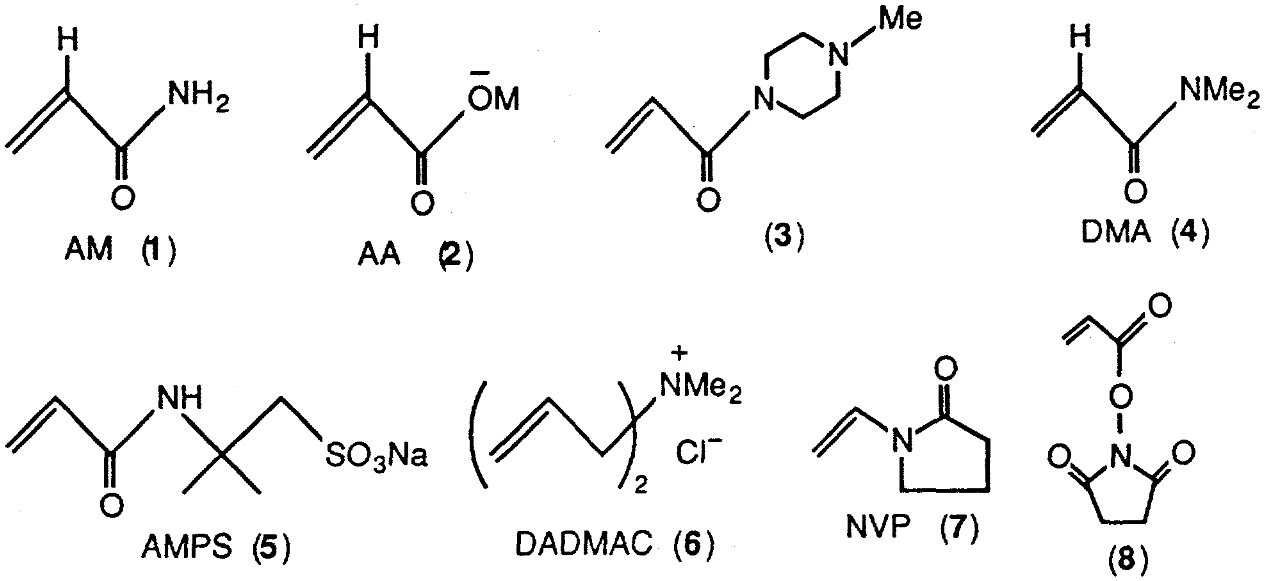
2. Proposed Research

2.1. Introduction

Over the past few years, we have been interested in the synthesis and characterization of water-soluble polymers endowed with hydrophobic groups.[1-20] These polymers in aqueous media are capable of associating into polymer clusters through interaction of the hydrophobic groups (Scheme 1). The "carrier" polymers have included typical water-soluble polymers based on vinyl monomers such as acrylamide (AM), and analogous electrolyte monomers such as acrylates, methacrylates, AMPS, DADMAC, etc. (Scheme 2), and other water-soluble polymers such as hydroxyethyl cellulose (HEC).

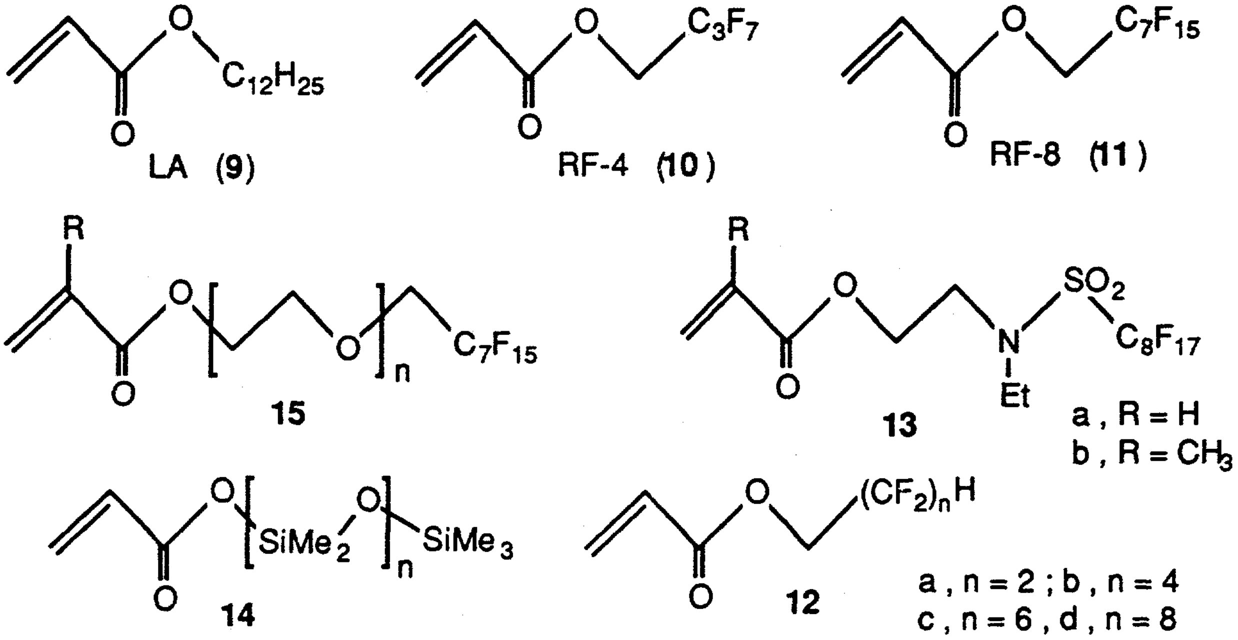


Scheme 1. Schematic Representation of Intra- and Intermolecular Association of Water-Soluble Copolymers Containing Hydrophobic Comonomers.



Scheme 2. Water-soluble vinyl monomers.

The incorporation of hydrophobic groups into the carrier vinyl polymers is achieved by copolymerization of hydrophobic comonomers (Scheme 3) with the water-soluble mono-mer in aqueous media containing surfactants and/or water-miscible organic cosolvents in order to help solubilize the hydrophobic comonomers.[6] Typical water-soluble initiators such as persulfates are used to initiate polymerization at near-ambient conditions.



Scheme 3. Hydrophobic Comonomers of current interest.

As described in the "Research Summary", the incorporation of fluorocarbon containing comonomers such as **11**, but especially **13a** or **13b** (Scheme 2), was shown to result in copolymers that were substantially more viscosifying compared to hydrocarbon containing comonomers such as laurylacrylate (LA, Scheme 3). Furthermore, the optimum molar content of comonomer for the case of **13a** or **13b** was shown to be much lower compared with the copolymers containing laurylacrylate (Research Summary).

The detailed mode of polymer association, especially the structure and composition of the hydrophobic aggregates is currently unknown.[21] It is generally recognized that these structures are probably not micelles and contain a smaller number of hydrophobic groups.[21]

As outlined in the "Research Summary", the perfluorocarbon containing polyacrylamides have a number of interesting properties. These include a) effective viscosification of aqueous solutions at very low polymer concentrations (<100 ppm), b) increases in the viscosity of the aqueous polymer solutions upon addition of common inorganic salts such as NaCl, or upon increasing the temperature and pronounced decreases in viscosity resulting from shear (pseudoplastic behavior). These properties are now well documented to result from polymer association due to aggregation of the perfluorocarbon side chains.[6,9-20] Thus, there are sharp viscosity decreases upon addition of water miscible organic solvents such as acetone DMF and DMSO or of fluorocarbon surfactants. In these cases, the organic moiety appears to associate with the perfluorocarbon groups or to decrease the hydrophilic character of the aqueous medium or both .

The proposed research is aimed at a better understanding of these interesting aqueous polymer systems. It seems reasonable that a thorough understanding of polymer association will lead to the development of a new generation of rheology modifiers.

Several important questions need resolution. These include (a) the copolymer structure, especially the number of hydrophobic groups per chain (b) the placement of the comonomer in the chain (isolated or blocky) (c) the molecular weight and MW distribution of the individual chains, etc. Furthermore, (d) the chemical structure of the carrier polymer and (e) that of the hydrophobic comonomer will be of obvious interest. Thus, we will investigate the effect(s) of type and length of the hydrophobic group and the length of the water-soluble spacers. We also propose to investigate the role of the structure of the carrier polymer through the synthesis and characterization of hydrophobically modified copolymers based on other water-soluble monomers as shown in Scheme 2 (see below).

A second set of questions concerns the nature of the association process. Here we will be interested in the degree of association (number of chains/cluster) and the number of hydrophobic groups per aggregate particularly as it relates to the structure of the associating polymers. We will also be interested in the interaction of the associating coils (effects on segment density for instance). In all of these cases, these structures will be examined by light scattering viscosity and other techniques as a function of independent variables such as polymer concentration, presence of salt(s) or surfactants, temperature, shear, etc. (see below).

A third and more exploratory question concerns the possibility of interactions other than hydrophobic that may be of interest in promoting polymer-polymer association in aqueous media. Such interactions would involve specific multiple interactions, especially polyanion-polycation interactions. Some of these could involve hydrophobic bonding as well.

In the following, we outline the specifics of the proposed research.

2.2 Synthesis and Determination of Copolymer Structure.

2.2.1. Comonomer Content and Distribution.

Although the question of comonomer content and distribution has received attention, this issue has not been fully resolved. Hydrocarbon containing comonomers are very difficult to detect by ^1H or ^{13}C NMR or other spectroscopic techniques due to low comonomer content in the hydrophilic chain (.3 - 3.0 mole %). As a result, studies have been conducted with hydrophobic comonomers containing UV absorbing moieties.[22] However, the behavior of these comonomers may differ substantially from simple comonomers containing long alkyl chains.

The case of the perfluorocarbon containing comonomers is even more problematic because of the extremely low mole fractions in the chain ($\sim 10^{-4} - 10^{-3}$) of comonomer typical of the most effectively associating copolymers. For instance, polyacrylamide containing extremely low molar fractions ($10^{-3} - 10^{-4}$) of comonomers **13a** or **13b** is a highly effective associa[illegible] copolymer. However, determina[illegible]n of the comonomer content of the copolymer, for instance by fluorine elemental analysis of the polymer, is quite difficult because of the low fluorine content of the copolymers. Furthermore, the ^{19}F NMR absorption of the polymer cannot be observed in aqueous media.[20] Very weak ^{19}F polymer NMR signals are observed in DMF-D_2O mixtures but the accurate determination of the comonomer content of the chain under these conditions is questionable.

We have recently found that the content of fluorine-containing comonomers in polyacrylamide copolymers may be determined indirectly by ^{19}F NMR by following comonomer depletion during polymerization through observation of an appropriate ^{19}F signal such as the terminal CF_3 group of the monomer perfluoroalkyl chain.[20] As a result, the incorporation of the comonomer into the chain may be determined accurately even at very low comonomer concentrations (~ 10^{-2} mole %).

With regard to hydrocarbon comonomers, such studies of course, are much more difficult as a result of interference by ^{1}H signals arising from other proton sources such as solvent and polymer. Furthermore, comonomer sequence distribution of either fluorine or hydrocarbon containing monomers is of substantial interest since blocks of hydrophobic comonomers in the water-soluble carrier are expected to exhibit different association behavior from that of isolated hydrophobic comonomers.

It has recently been proposed by several researchers that a copolymer structure containing blocks of comonomer units is likely on the basis of fluorescent and other spectroscopic observations.[23] Such a structure is consistent with an emulsion polymerization involving the presence of the hydrophobic comonomers in the surfactant micelles. Thus, the formation of copolymers could involve a dual polymerization mechanism[23] involving the polymerization of acrylamide or other aqueous vinyl monomer in the aqueous phase interrupted by brief intervals in which the polymeric radicals would enter the micelle resulting in the sequential incorporation of a number of hydrophobic comonomers into the chain. This would result in a blocky structure as illustrated in Scheme 4.

$$P^\bullet \xrightarrow[\text{aqueous polymerization}]{nM_1} P{\sim}(M_1)^\bullet_n \xrightarrow[\text{micellar polymerization}]{mM_2}$$

$$P(M_1)_n(M_2)^\bullet_m \xrightarrow[\text{aqueous polymerization}]{p\,M_1} \text{etc.} \quad {\sim}{\sim}{\sim}{\sim}(M_1)_n\ (M_2)_m\ (M_1)_p^\bullet$$

Dual Mechanism Polymerization

$$P^\bullet \xrightarrow{M_1} P(M_1)_n^\bullet \xrightarrow{M_2} P_o(M_1)_n\,M_2^\bullet \xrightarrow{mM_1} \xrightarrow{M_2} \xrightarrow{pM_1}$$

$$\longrightarrow P\,(M_1)_n\,M_2\,(M_1)_m\,M_2\,(M_1)_p$$

Single Mechanism Aqueous Phase

Scheme 4. Dual- and Single-Mechanism Vinyl Copolymerization of Hydrophilic-Hydrophobic Monomers In Micellar Systems.

On the other hand, the polymerization may take place exclusively in the aqueous phase. In this case, the concentration of the hydrophobic comonomer in the aqueous phase is maintained by comonomer diffusion from the micellar into the aqueous phase. As a result, comonomer incorporation will be determined by reactivity ratio's of the two monomers. For the acrylates, this will most likely lead to esentially random comonomer distributions.[24] Resolution of this question is not simple, especially because of the low mole fractions of comonomer in the copolymers. Thus, standard NMR spectroscopic techniques suitable for the determination of comonomer sequence are not readily applicable in these cases. Therefore, we propose to synthesize appropriate ^{13}C labelled hydrophobic comonomers of the type $H_2{}^{13}C = {}^{13}CH\ CO - S\ R$ where S and R refer to a hydrophilic spacer and the hydrocarbon- or fluorocarbon groups respectively. Carbon-13 NMR studies of the corresponding copolymer are expected to allow unambiguous determination of the question of detailed comonomer sequences (Section 3.)

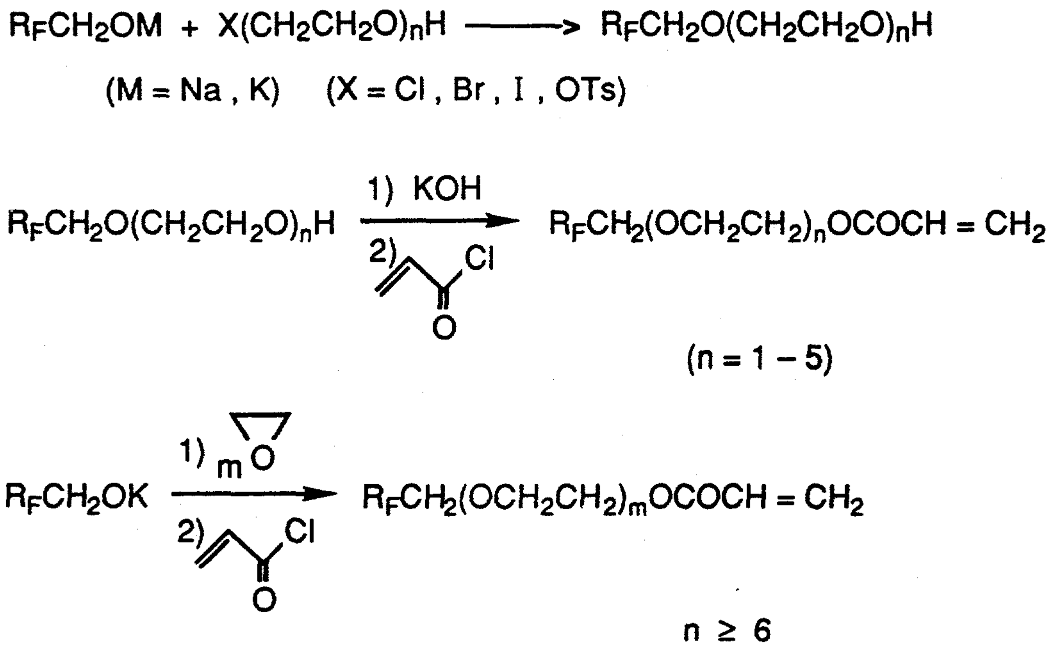
The synthesis of these labeled comonomers would involve the reaction of the appropriate alcohols with the corresponding carbon labeled acryloylchloride ($^{13}CH_2 = {}^{13}CHCOCl$).

2.3. Comonomer Structure

2.3.1. Effect of Spacers

The dramatic enhancement in the hydrophobic association of acrylamide copolymers based on comonomers **13**, compared to comonomer **11**, that does not contain a hydrophilic spacer is of considerable interest.[25] We have previously believed that this enhanced comonomer effectiveness is due to the decoupling of the motions of the carrier chains from that in the hydrophobic aggregate. Support for this view was provided by the fact that hydroxyethylcellulose (HEC) containing perfluorocarbons attached via longer hydrophilic spacers[7,11] was found to be much more strongly associating than HEC of the same length containing shorter hydrophilic spacers or lacking hydrophilic spacers altogether. Furthermore, we have recently succeeded in preparing comonomers **15**, in which hydrophilic spacers $(CH_2CH_2O)_n$ ($n = 1 - 3$) connect the perfluorocarbon group $CF_3(CF_2)_6$ to the carrier polymer. Preliminary investigations have shown these comonomers to be highly efficient in imparting strongly associative behavior to the corresponding acrylamide copolymers. It is too early to tell whether these new comonomers are superior to comonomers **13**, both with regard to viscosity enhancement (effectiveness) and to efficiency (viscosity enhancement divided by comonomer content). However, these promising results prompt us to propose a synthesis program aimed at elucidating fully the role of the spacer length in these systems. Thus, we propose to investigate extending the spacer lengths (from 3 to about 20 – 40 EO units).

The lower homologues of comonomer **15**, ($n = 1 - 5$) will be prepared by the reactions shown in Scheme 5. The higher homologues will be synthesized by anionic polymerization of EO initiated by the potassium salt of R_FCH_2OH followed by reaction with acryloyl- or methacryloylchloride. Particularly for the longer spacers ($n \geq 6$ EO units) a distribution of spacer lengths is probably unavoidable but attempts will be made to keep the distribution as narrow as possible.



Scheme 5. *Synthesis of comonomers,* **15.**

2.3.2. Hydrophobe Type and Length

Our hunch that fluorocarbon should be more effective than hydrocarbons as hydrophobic groups in water-soluble polymers is now reasonably well established on the basis of our results over the past three years.[9-20] Perhaps the greater apparent hydrophobic character of fluorocarbons is not too surprising in view of the low surface energy of fluorocarbons[7] and the demonstrated very low critical micelle concentrations of fluorocarbon surfactants.[26] Another factor in the greater apparent hydrophobicity may be the greater surface area of perfluoroalkyls compared to hydrocarbons of the same chain length. Previous results have shown that polydimethylsiloxanes (PDMS) containing acrylates are more effective than hydrocarbon acrylates as comonomers in associating polyacrylamide copolymers and this seems to correlate with very low surface energies of polydimethylsiloxane.

Enhanced hydrophobic association with increased hydrophobe chain length has been well documented for both hydrocarbons and fluorocarbons.[5,26,28] For instance, 1,1-dihydroperfluorobutylacrylate at about 3 mole % (9.0 wt %) gives an acrylamide copolymer solution (0.5 wt %) having a Brookfield viscosity of about 50 cp but the 1,1-dihydroperfluorooctylacrylate at .50 mole % (~3 wt %) produces a copolymer having a viscosity of 1400 cp for a 0.5 wt % copolymer solution.[10-12]

We would therefore be interested in preparing fluorocarbon-containing acrylates or similar comonomers having longer perfluorocarbon lengths.

Our collaborating group at the Institute for Organic Chemistry Academia Sinica, Shanghai, PRC headed by Dr. X-Y. Zhang will prepare fluorocarbon-containing alcohols of the type **16** and **17.**

$F(CF_2)_nCH_2OH$ $n = 7-20$ **(16)**

$H(CF_2)_mCH_2OH$ $m = 7-20$ **(17)**

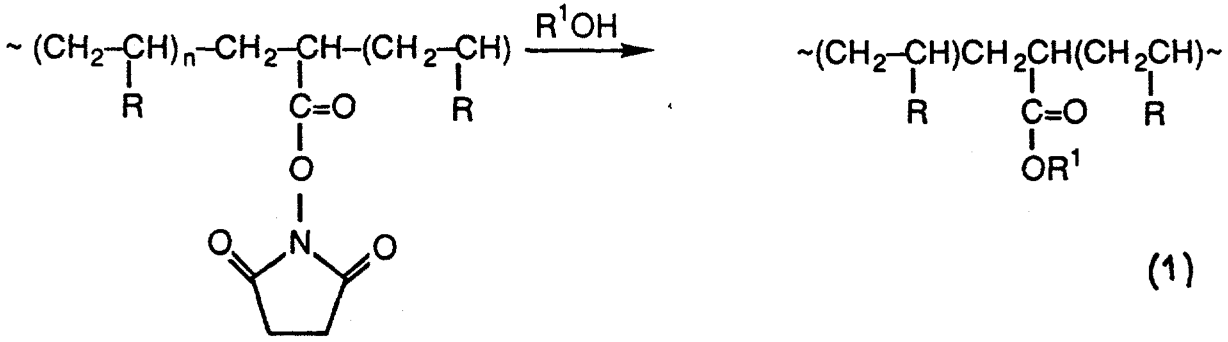
$F(CF_2)_p(CH_2)_qOH$ **(18)**

They will also prepare some of the corresponding acrylates or similar comonomers.

Another type of hydrophobic moiety of interest are perfluorocarbon-hydrocarbon structures. Alcohols, **18**, incorporating such structures have recently been synthesized by the group of Professor Moeller and coworkers at the University of Twente (Netherlands).[29] This group has kindly agreed to make samples of these alcohols available for the synthesis of the corresponding comonomers by the usual route (reaction with acryloylchloride). The availability of this comonomer will be of considerable interest since in this case, the "spacer" connecting fluorocarbon to the carrier polymer is a hydrocarbon instead of a hydrophilic polyethyleneoxide. Since hydrocarbons and fluorocarbons are incompatible, the hydrocarbon most likely will not be incorporated into the fluorocarbon aggregate. In such a case, the hydrocarbon moiety may form aggregates with other hydrocarbon "spacers" or it may simply function similar to the hydrophilic spacers.

2.4. Precursor Comonomers

In this case, a comonomer after copolymerization is capable of being transformed by transesterification or transamidation into hydrophobic monomer units. For example, N-hydroxy succinimide upon reaction with acryloyl chloride gives N-acrylolysuccinimide (comonomer **8**, Scheme 2) which is capable of radical copolymeriza-tion with acrylamide or other hydrophilic monomers such as N-vinylpyrrolidone.[30] After copolymerization, the comonomer unit may be converted to a hydrophobic unit by reaction with hydrophobic alcohols or amines (equation 1). If such procedures could be developed, this would have enormous advantages in establishing convincing structure-property correlations.



(1)

For instance, it should then be possible to prepare a series of copolymers of the same degree of polymerization, but with different hydrophobic content. This could be done, at least in principle, by reacting the same precursor polymer with mixtures of NH_3 and hydrophobic alcohols. Since NH_3 converts the N–oxysuccinimido acrylate (**8**) or similar activated esters into the $\sim CH_2CHCONH_2$ unit and because the hydrophobic alcohol or -amine transesterifies **8** into a hydrophobic acrylate or acrylamide group, control of the extent of hydrophobic substitution is possible, in principle, at constant chain length.

Furthermore, by reacting the same prepolymer with several types of hydrophobic alcohols or amines, it should be possible, at least in principle, to prepare a series of copolymers with the same molar content and sequence distribution of different hydrophobic groups. Thus, for the first time, a rigorous comparison of copolymers of various degrees of substitution and of different hydrophobes would be possible.

2.4. Effect of Carrier Polymer

The studies on hydrocarbon and fluorocarbon modified HEC's have shown that the carrier polymer plays an important role in the expression of the hydrophobic effects. For instance, viscosity enhancement in fluorocarbon modified HEC is much less pronounced than for the PAM copolymers. Furthermore, in contrast with the fluorocarbon containing PAM copolymers, ^{19}F NMR studies of the fluorocarbon modified HEC shows clear and well defined ^{19}F absorptions. This may indicate either incomplete association or the formation of hydrophobic aggregates of a different nature. For instance, it is conceivable that hydrophobic association of HEC derivatives is less pronounced because HEC itself has greater hydrophobic character causing intramolecular association of the hydrophobic group with HEC, the carrier polymer.

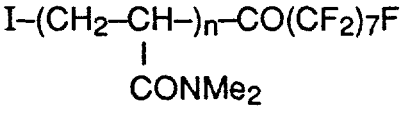
Therefore, we intend to synthesize a number of copolymers of several hydrophobic comonomers with water-soluble monomers of varying hydrophilic character. Carrier polymers with enhanced lipophilic character would include polymers of methacrylamide, N-vinylpyrrolidone or N-alkylacrylamide.

The presence of both hydrophobic and charged groups in the carrier polymer is expected to be of special interest because of the documented increase of the reduced viscosities of polyelectrolytes at low concentration in media of low ionic strength. If hydrophobic association can be maintained under such conditions, elevated viscosities at very low polymer concentrations may be possible. Therefore, we will synthesize a number of terpolymers containing acrylamide hydrophobic comonomers and ionic comonomers such as AMPS.

2.6. Synthesis of Model Hydrophobically Associating Polymers

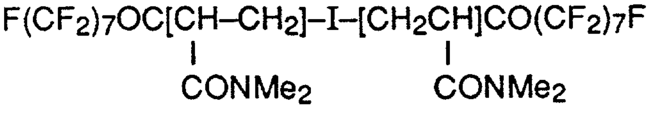
The synthesis of hydrophobically associating water-soluble polymers with well defined structure, architecture, molecular weight distribution and placement of hydrophobes provides opportunities for insight into much needed structure-property relationships.

Over the past few months, we have prepared by anionic polymerization, a monodisperse water-soluble poly(N,N-dimethylacrylamides), **19,** having a perfluorocarbon terminal group (Research Summary) and similar polymers, **20**, having two terminal perfluoro groups are currently being synthesized by anionic polymerization using difunctional (I^{2-}) carbanions as initiators.



$$I{-}(CH_2{-}\underset{CONMe_2}{CH}{-})_n{-}CO(CF_2)_7F$$

19



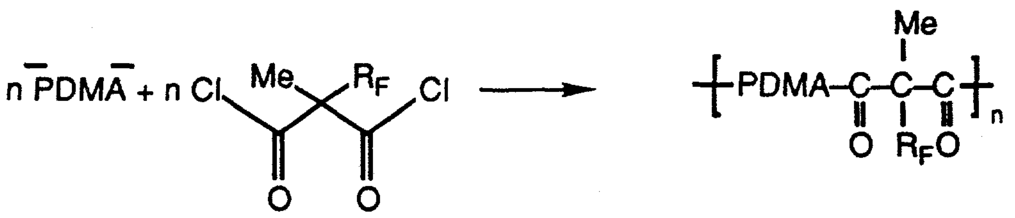
$$F(CF_2)_7OC[\underset{CONMe_2}{CH}{-}CH_2]{-}I{-}[CH_2\underset{CONMe_2}{CH}]CO(CF_2)_7F$$

20

Preliminary observations suggest that polymers of this type are extremely surface active even when the molecular weight of the polymer is high ($MW \geq 30{,}000$). The characterization of these polymers and investigations of their properties are currently underway.

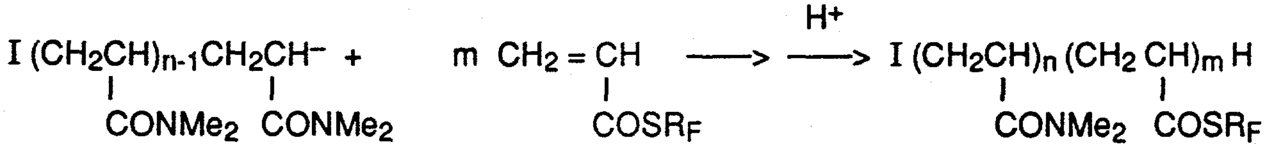
We propose to extend the structural scope of these polymers further by the synthesis of hydrophilic polymers having perfluorocarbon groups spaced at constant distance throughout the chain, for instance, by reacting a dianionic "living" precursor

(-PDMA-) with fluorocarbon-containing malonylchlorides (eq 2).



(2)

Another interesting approach toward the synthesis of well defined fluorocarbon containing polymers involves the anionic block copolymerization of DMA with hydrophobic comonomers (Scheme 3) according to equation (3):



$$\underset{\text{CONMe}_2}{\mathrm{I\,(CH_2CH)_{n-1}}}\underset{\text{CONMe}_2}{\mathrm{CH_2CH^-}} + \quad m\ \mathrm{CH_2 = }\underset{\text{COSR}_F}{\mathrm{CH}} \longrightarrow \xrightarrow{H^+} \mathrm{I\,}\underset{\text{CONMe}_2}{\mathrm{(CH_2CH)_n}}\,\underset{\text{COSR}_F}{\mathrm{(CH_2\,CH)_m}}\,\mathrm{H}$$

(3)

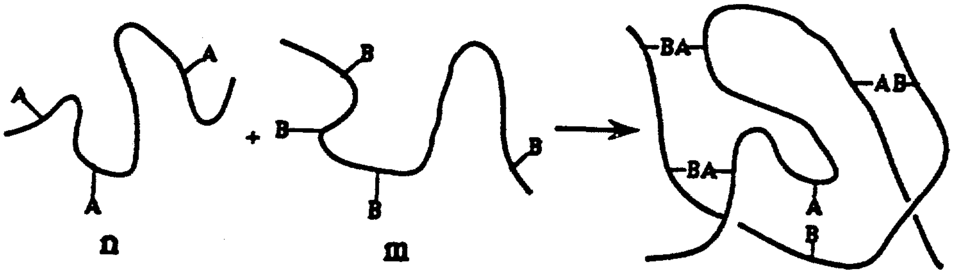
where S = – $OCH_2CH_2N(Et)SO_2$–, –$O(CH_2CH_2O)_pCH_2$⁻ or other spacer and R_F is a perfluorocarbon hydrophobic group. Preliminary experiments indicate that addition of **13a** to living PDMA is indeed possible.

The advantage of this method is that the number of R_F groups/chain may be changed by variation of the molar ratio of DMA the comonomer. Furthermore, the synthesis of blocky R_F–containing structures would make possible experimental evidence for the effectiveness of such structures in promoting inter-polymer association.

2.7. Alternative Approaches Toward Polymer Association In Aqueous Media

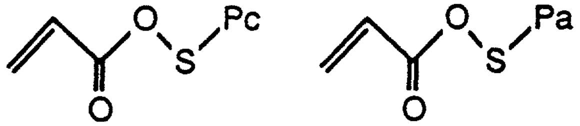
The introduction of perfluorocarbons into water-soluble polymers has been shown to lead to dramatically enhanced polymer association occurring well below the polymer overlap concentration at least in the PAM copolymers. It is clear that much work remains to be done in fully evaluating the considerable potential of these systems in enhanced oil recovery and in other areas where mobility control is of interest.

Since the cost of using polymers is high, the mobility control potential of polymers at extremely low concentrations is of great interest. However much greater is the degree of association of the perfluoroalkyl containing PAM copolymers, the fact remains that intramolecular association will increasingly compete with intermolecular association at extremely low concentration (<100 ppm). Therefore, the synthesis of polymers capable of association through a different mechanism will be of special interest. The association process should preferably be of the A-B (Scheme 6) rather than the A-A type as in the case of hydrophobically modified polymers since this would avoid coil collapse at very low concentration. Furthermore, high viscosity solutions could be prepared at the required time by simply mixing the two relativel y low viscosity solutions of the non-associated polymers.

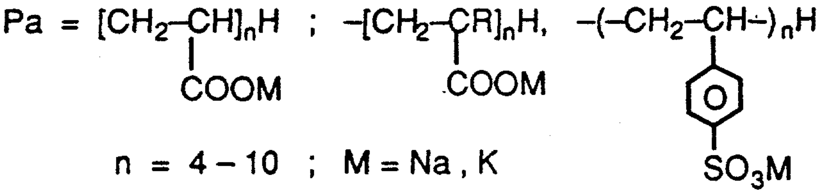


Scheme 6. Polymer Association Based On Association Processes of the A-B type.

The association constant should be large to insure extensive association at very low concentration but should be controllable through variation of group A or/and B. Furthermore, the incorporation of groups A and B in the polymer should be readily carried out preferably as a copolymerization with typical water-soluble commercial monomers with mobility control potential such as acrylamide. Given the above requirements, the synthesis and copolymerization of macromonomers, of the type shown in Scheme 7,

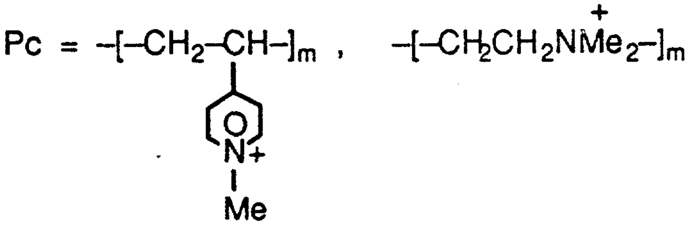


S = Spacer, Pa = polyanion, Pc = polycation



$$\mathrm{Pa} = [\mathrm{CH_2}-\underset{\mathrm{COOM}}{\mathrm{CH}}]_n\mathrm{H}\ ;\ -[\mathrm{CH_2}-\underset{\mathrm{COOM}}{\mathrm{CR}}]_n\mathrm{H},\ -(-\mathrm{CH_2}-\underset{\mathrm{C_6H_4SO_3M}}{\mathrm{CH}}-)_n\mathrm{H}$$

$n = 4-10$; $M = Na, K$



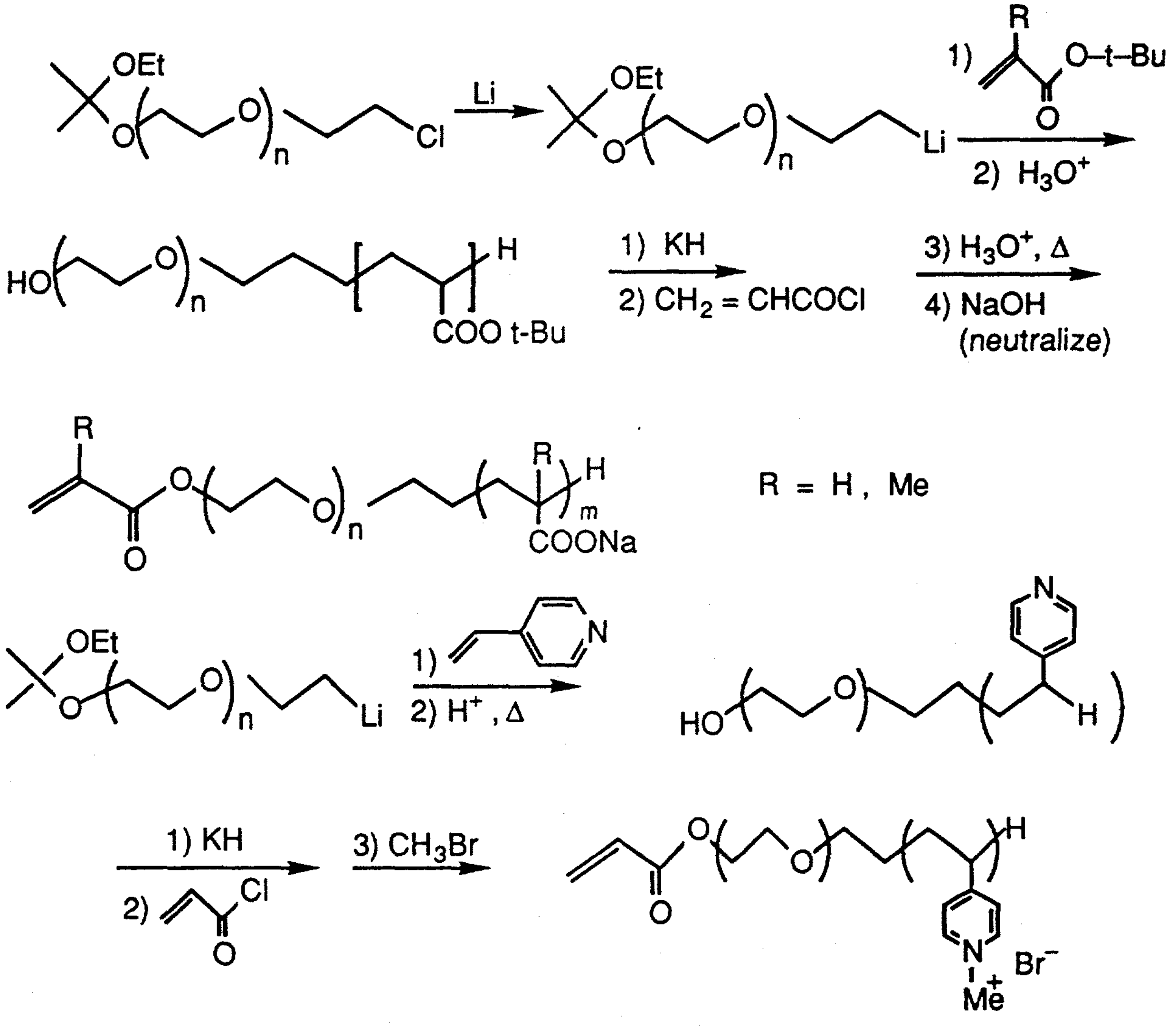
$$\mathrm{Pc} = -[-\mathrm{CH_2}-\mathrm{CH}-]_m\ ,\quad -[-\mathrm{CH_2CH_2}\overset{+}{\mathrm{N}}\mathrm{Me_2}-]_m$$

Scheme 7. Macromonomers containing polyanion or polycations as pendent groups.

would be of interest. Low DP polyanion-polycation interactions of this type would be attractive for several reasons. Although anion-cation ion pairs are generally fully dissociated in aqueous media, this is not the case for polyanion-polycation interactions.[31] Thus, stable aqueous complexes are formed between alkali salts of polymethacrylic acid and quaternized polyethylene imines having degrees of polymerization as low as four.

The reasons for these strong polyanion-polycation interactions are no doubt complex involving cooperative Coulombic forces, ion pairing with counter ions, dielectric saturation, etc. Furthermore, hydrophobic bonding most likely also contributes to some degree to the stability of such complexes.

Typically in these cases, the association constants increase sharply at higher degrees of oligomerization as a result of cooperative interactions. Thus, the formation constants are subject to control by variation of polyanion or polycation chain lengths. In order to evaluate the feasibility of these ideas, we propose the synthesis of the macromonomers primarily using anionic polymerization. Examples of the synthesis are shown in Scheme 8.



Scheme 8. Synthesis of Polyelectrolyte Macromonomers Capable of Copolymerization with Acrylamides.

The anionic oligomerizations similar to that shown in Scheme 8, have been carried out in our laboratories in the context of other research and should not present serious problems. The water-soluble macromonomers should have excellent water-solubility and radical copolymerization with acrylamides in aqueous media is expected to proceed readily. Because of the expected very strong polyanion-polycation association, the molar content of the macromonomers in the copolymers is expected to be quite low. ($<10^{-2}$ mole %)

3. Characterization and Rheology

3.1 Molecular Weight Determination

The light scattering methods for determining molecular weight, radius of gyration, and virial coefficients have been developed so that they are now almost routine analyses. This makes it convenient to consider what effects the various changes in the polymerization conditions have on the MW of polymer produced. These measurements are essential as new comonomers are incorporated or their placements modified and changes in viscosifications are observed. Particularly in cases where materials are being optimized for cost effective use of expensive comonomers we must know if a simple increase in overall chain molecular weight, with the accompanying change in number of hydrophobic groups per chain can substitute for an increase in comonomer mole fraction. Because the evidence suggests that increasing comonomer content may actually reduce their effectiveness by intramolecular associations, optimization of the comonomer content by controling chain molecular weight may be a feasible route. At this time we have no information on the influence of chain length polydispersity on the viscosification. The presence of a significant fraction of low molecular weight copolymers with a small number of comonomers per chain would presumably be detrimental as they would be ineffective in providing intermolecular associations. As methods develop to control polydispersity or fractionate we will be able to address this effect.

3.2. NMR Studies

3.2.1. Carbon-13 NMR Studies of ^{13}C Labeled Copolymers

The availability of acrylates of the structure: $^{13}CH_2 = {}^{13}CHCOSR_F$ (R_H) where S and R_F (or R_H) denote the hydrophilic spacer and the perfluorocarbon or hydrocarbon groups respectively and similar comonomers such as N-substituted acrylamides, will be of considerable interest in the determination of comonomer sequence distributions (Section 2.1). The presence of sequences of two or more such units in the chain would generate ^{13}C-methylene and -methine triplets arising from $^{13}C{-}^{13}C$ coupling in addition to the expected doublets arising from isolated units or from "external" $-^{13}CH_2-$ or $-^{13}CHR-$ units having only one ^{13}C neighbor. Fine splitting resulting from the stereochemistry of adjacent vinyl units may affect the results.[32] However, the $^{13}C{-}^{13}C$ one bond couplings are rather large (30-40 cps)[33] and this should allow unambiguous analysis of the occurrence of blocky structures. Signals due to the occurrence of ^{13}C absorptions of CH_2 or CH acrylamide signals may be eliminated by appropriate filtering procedures that remove all but ^{13}C signals involving the presence of two or more adjacent ^{13}C nuclei.[34,35]

It is expected that studies of this type will clarify unresolved issues with regard to the distribution of the hydrophobic comonomers in hydrophobically associating water-soluble copolymers.

3.2.2. Fluorine–19 NMR Studies

These studies have been described in some detail in Section 2.2.1. and will provide information on the overall comonomer content of the copolymer by determination of the comonomer concentration during the copolymerization process. Thus, the kinetics of copolymerization is monitored as well and this is expected to provide additional information on the nature of these copolymerization processes. The ^{19}F NMR absorptions of the CF_3 groups of the monomers **13** are most convenient for ^{19}F NMR studies since they absorb well downfield of the envelope of the closely spaced CF_2 absorptions of the perfluoroalkyl group. Currently, available fluorocarbon-containing surfactants have the structure $CF_3(CF_2)_6COO^-K^+$. As a result, the CF_3 absorptions of the surfactant interfere with that of the monomer. Especially at low comonomer concentrations, this could lead to substantial errors. Therefore, we will synthesize ^{19}F-containing surfactants without the CF_3 group by oxidation of the corresponding alcohols **17** containing the CH_2OH head group followed by neutralization. This also should allow ^{19}F NMR studies of interactions of perfluorocarbon containing copolymers with this surfactant. Addition of surfactants is expected to lead to dissociation of the copolymer aggregates by competitive hydrophobic bonding to the copolymer by the surfactant. Such processes have been demonstrated by viscometry and by dynamic light scattering. It is hoped that studies of this type will provide information on the nature of the very strong perfluorocarbon-perfluorocarbon interactions and perhaps to the determination of the number of hydrophobes/aggregate.

For the fluorine containing copolymers synthesized by chemical modification (Section 2.3) it is expected that direct ^{19}F NMR analysis of the copolymers will be difficult because of excessive broadening. In such a case, we will analyze the depletion of the perfluorocarbon containing reagents by ^{19}F NMR. In combination with the molecular weight determination, knowledge of the comonomer content will give us the average number of hydrophobes per chain.

3.3. Static and Dynamic Light Scattering Studies

The physical chemical investigations will focus on the assembly process of the associated polymers and on the coupling of energy from external perturbations into the macromolecular structures. Useful purposes for polymers of this type will require this knowledge and optimizing a system for particular applications will be efficient if these characterizations can be related to the synthetic options.

New scattering investigations will be initiated by small angle neutron scattering using the National Cold Neutron Scattering Facility at the National Institute of Standards and Technology. We have established collaborations with Dr. Charles C. Han at NIST who will provide beam time for preliminary experiments on the NIST Polymer Division 8-meter SANS instrument. These initial measurements will allow us to compete favorably for beam time on the two new 30 meter SANS instruments at NIST coming on line in 1992. We have consulted with Professor Julia Higgins of Imperial College, one of the world's experts on these types of SANS measurements, and she has been quite encouraging about the prospects for successfully using SANS to measure cluster sizes of the associated hydrophobes.[1] The experimental protocol requires that we increase sample concentrations by freeze drying and compacting the associated polymer clusters from solutions and thereby increase the density of scattering cross sections. A similar procedure has been used successfully by Higgins and co-workers for a similarly associated ionomer system.

3.4 Viscoelesticity and Dynamic Relaxations

As mentioned in the report on previous results, a slow non-diffusive mode in the DLS has been observed and we speculate that it is related to "sticker migration". We will continue to pursue these studies in the course of the DLS work and will correlate the strength of this dynamic interaction with viscometric work. We have initiated preliminary studies of a strongly associating sample as a function of concentration using our multiple lumped resonator instrument.[2-3] This device allows measurement of dynamic viscoelasticity, (storage and loss moduli), over a frequency range of 50 to 9000 Hz. Previous extensive investigations under other support has demonstrated that G"/G' becomes frequency independent just at the gel point even for an exceedingly dilute gel.[4] This is an extremely sensitive method to characterize gelation. Preliminary work on the associating polymer system shows the same sharp demarkation of gelation when investigated as a function of concentration. These viscoelastic studies will be pursued for various levels and types of comonomers to characterize the factors that control the onset of gel formation.

Also along these lines, a recently constructed a magnetically levitated sphere viscometer allows viscosity measurements at extremely low shear rates.[5] Current work with a lower limit of 0.4 s^{-1} has shown that reliable extrapolations to zero shear viscosities are not possible for this system because of a sharp increase in viscosity at lower shear rates. The new instrument provides shear rates as low as 0.002 s^{-1} without compromising sensitivity. The temperature range on this instrument provides a window to look at the unusual temperature dependences discussed previously. These studies will complement the DLS and viscoelastic work to help analyze the dynamics of the chains forming the associated clusters.

3.5 Surface Activity

In a different vein, there is interest in using the hydrophobic effect which causes the copolymers to attach to surfaces.[6] An observation was made by us previously that in contrast with usual aqueous solutions, dilute solutions of these copolymers can be filtered rather easily through Teflon membrane filters. This suggests that the copolymer coats the hydrophobic membrane and makes it hydrophilic. One avenue which others have explored in studies of polymer interactions with surfaces has been to use monodisperse polystyrene latex particles as substrates to absorb copolymers. Previous workers have considered hydrophilic and hydrophobic diblock copolymers. Similar work for our system will require preparation of latex spheres with fluorocarbon modified surfaces. A very significant difference between this work and previous studies with hydrocarbon hydrophobes is that, as our work has demonstrated convincingly, the fluorocarbon interaction is so strong, that the amounts of hydrophobic component can be reduced to almost trace levels while still anchoring a long hydrophilic polymer. This enormous interaction energy could provide a system with unique surface activity. A study of surface effects generally could be useful because such effects are relevant to EOR applications.

3.6. Rheology

The viscosity of the copolymer solutions will continue to be of interest for two main reasons. On the one hand, Brookfield (BF) viscometry is a convenient and rapid technique that is qualitatively diagnostic for changes in copolymer clustering. Examples are sharp BF viscosity decreases observed with increasing shear and with addition of substances (salts, acetone, DMF, etc.) that change the nature of the medium and/or complete with chain-chain hydrophobic interactions (surfactants).

Viscosity increases observed at higher temperature likewise are consistent with entropy driven hydrophobic association processes.

Because of its speed and convenience, BF viscosity will continue to be used as a convenient way to reveal changes in copolymer association resulting from addition of other substance changes in temperature, etc. Changes in BF viscosity resulting from changes in comonomer structure, -content and -sequence distribution will be of interest especially since comonomer content and -sequence distribution are subject to experimental verification (Section 2.1.)

Furthermore, we will have the possibility of studying BF viscosity changes resulting from changes in comonomer-structure or -content at constant molecular weight and MW distribution (Section 2.3).

References

1. C. Tanford, *The Hydrophobic Effect,* 2nd Ed., Wiley, New York, 1980; A. Ben-Naim, *Hydrophobic Interactions,* Plenum, New York, 1980.
2. S. Evani, G.D. Rose, *Polym. Mat. Eng. Prepr.,* **57**, 477 (1987).
3. "Polymers in Aqueous Media", J.E. Glass, Ed., ACS Advances in Chemistry, **223**, Washington, DC, 1989.
4. "Water-Soluble Polymers For Petroleum Recovery", G.A. Stahl and D.N. Schulz, Eds., Plenum Press, New York 1988; P. Molyneux "Water-Soluble Synthetic Polymers, Vol. 1 and 2, CRC Press, Inc., Boca Ratan, Florida, 1982.
5. L.M. Landoll, *J. Polym. Sci. Polym. Chem. Ed.,* **20**, 443 (1982); A.C. Sau, *Polym. Mat. Sci. Eng. Prepr.,* **57**, 497 (1987); S. Evani, U.S. Pat. 4,432,881 (1984); V.G. Constien and M.T. King, U.S. Pat. 4,541,935 (1985).
6. For hydrocarbon containing polyacrylamides, see: D.N. Schulz, J.J. Kaladas, J.J. Maurer, J. Bock, S.J. Pace, W.W. Schulz, *Polymer,* **28**, 2110 (1987); C.L. McCormick, C.E. Hoyle, D. Clark, *Proc. Polym. Mat. Sci. Eng.,* **57**, 643 (1987); J.C. Middleton, D. Cummins, C.L. McCormick, *Polym. Prepr.,* **30**(2), 348 (1989); J. Bock, S.J. Pace, P.L. Valint, *Polym. Prepr.,* **30**(2), 386 (1989); C.E. Flynn, J.W. Goodwin, *Proc. Polym. Mat. Sci. Eng.,* **61**, 522 (1989); S.R. Turner, D.N. Schulz, D.B. Siano, J. Bock, *Proc. Mat. Sci. Eng., 55*(2), 355 (1986).
7. V.P. Schonfeld, H. Selibt, *z. Chem.,* **16**(12), 497 (1976).
8. P. Muederjee, Handa, *J. Phys. Chem.,* **85**, 2298 (1981).
9. Y-X. Zhang, A-H. Da, G.B. Butler, T.E. Hogen-Esch, *J. Polym. Sci., Polymer Letters,* **28**, 213 (1990).
10. Y-X. Zhang, A-H. Da, G.B. Butler, T.E. Hogen-Esch, *J. Polym. Sci., (Chem. Ed.),* **32**, 000 (1992).
11. Y-X. Zhang, A-H. Da, G.B. Butler, T.E. Hogen-Esch, *Polym. Preprts.,* **30**, (2), 338 (1989).
12. T.E. Hogen-Esch, M. Yassini, Y-X. Zhang, F.S. Hwang, E.J. Amis, T.A. Seery, *Polym. Preprts.,* **31,** (2), 460 (1990).
13. Y-X. Zhang, A-H. Da, T.E. Hogen-Esch, 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.
14. S.G. Krishnan, G.B. Butler, T.E. Hogen-Esch, N-Z. Zhang, Chapter 11, ACS Symposium Series No. 467, "Water Soluble Polymers", pages 175-188 , S. Shalaby, C.L. McCormick and G.B. Butler, Editors.
15. F.S. Hwang, T.E. Hogen-Esch, *Polym. Preprts.,* **32,** (1), 581 (1991).
16. T.E. Hogen-Esch, M. Yassini, Y-X. Zhang, F.S. Hwang, E.J. Amis, T.A. Seery, *Polym. Preprts.,* **31**, (2), 460 (1990).
17. T.A. Seery, M. Yassini, T.E. Hogen-Esch, E.J. Amis, *Macromolecules,* **00**, 000 (1992).
18. T.A. Seery, M. Yassini, T.E. Hogen-Esch, E.J. Amis, *Polym. Preprts.,* **33,** (1), 935 (1992).
19. Y-X. Zhang, F.S. Hwang, T.E. Hogen-Esch, "Fluorocarbon-Modified Water-Soluble Polymers", Chapter in "Hydrophobically Modified Associating Polymers", P. Dubin, D.N. Schulz, Eds., Springer Verlag, 1992.
20. M. Yassini, T.E. Hogen-Esch, *Polym. Preprts.,* **33**, (1), 933 (1992).
21. X-K. Jiang, *Acc. Chem. Res.,* 362 (1988).
22. P.L. Valint Jr., J. Bock, D.N. Schulz, (UV) *Proc. Polym. Mat. Sci. and Eng.,* **57**, 482 (1987).

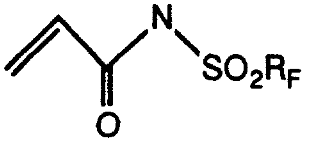
23. W. Peer, *Proc. Polym. Mat. Sci. and Eng.*, **57**, 492 (1987); S. Evani, G.D. Rose, *Ibid.*, **57**, 477 (1987); S.A. Ezzell and C.L. McCormick, "Water Soluble Polymers", W. Shalaby, C.L. McCormick, G.B. Butler, Eds., ACS Symposium Series, Vol. 467, Chapter 8 (1991).
24. J. Brandrup and E.H. Immergut, Eds., "*Polymer Handbook,* 1975, Second Ed., Chapter 2.
25. See also D.N. Schulz, T.J. Kaladas, J.J. Maurer, J. Bock, S.J. Pace, W.W. Schultz, *Polymer,* **20**, 2110 (1987).
26. D. Myers, "Surfactant Science and Technology", VCH Publishers, Inc., New York, 1988, Chapter 3.
27. a. A.C. Sau, L.M. Landoll, "Polymers in Aqueous Media", J.E. Glass, Ed., *Adv. Chem. Series,* 223, pp. 343-364; b. P. L. Valint, Jr., J. Bock, D.N. Schulz, Ibid, Chapter 21, pp. 399-410; c. J. Bock, D.B. Siano, P.L. Valint, Jr., S.J. Pace, Ibid, Chapter 22, pp. 411-424.
28. H. Ringsdorf, J. Venzmer, F.M. Winnik, *Macromolecules,* **24,** 1678 (1991).
29. J. Hopken, S. Shuko, Y. Czech and M. Moller, *Polym. Preprts.,* **33(1),** 937 (1992).
30. A. Polak et al., *J. Am. Chem. Soc.,* **102**, 6324 (1980).
31. E. Tsuchida, K. Abe, "Interactions Between Macromolecules in Solution and Intermacromolecular Complexes", Advances in Polymer Science, **45**, Springer-Verlag, New York, 1982.
32. E. Lippman, T. Pehk, K. Anderson, C. Rappe, *Org. Magn. Reson.,* **2**, (2), 109 (1970).
33. H. Gunther, "NMR Spectroscopy, Wiley Publ. Co., New York, 1987, Chapter 10.
34. R. Ramachandron, C.J. Blake, B.N. Gray, L.R. Brown, *J. Magn. Reson.,* **79**, (2), 357 (1988).
35. M.H. Levitt, R.R. Ernst, *Mol. Phys.,* **50**, (6), 1109 (1983).
36. J.S. Higgins, Personal Communication 1991.

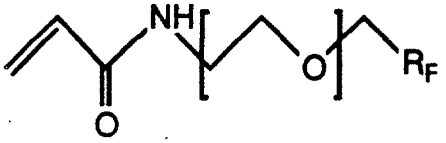
37. D.W. Hair, F.J. Niertit, D.F. Hodgson, E.J. Amis, *J. Rev. Sci. Instr.,* **60**, 2789 (1989).
38. J.L. Shrag, R.M. Johnson, *Rev. Sci. Instr.,* **42,** 224 (1971).
39. D.F. Hodgson, E.J. Amis, *J. Non-Cryst. Solids,* **913,** 131-133 (1991).
40. M. Adam, M. Delsanti, P. Pieransky, R. Meyer, *Rev. Phys. Appl.,* **19**, 253 (1984).
41. D.H. Napper, *Polymeric Stabilization of Colloidal Dispersions;* Academic Press, London, 1983.

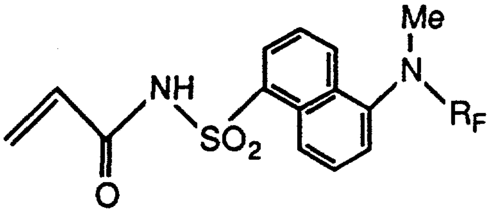
Collaborative Research

Dr. X-Y. Zhang (Shanghai)

The research group at the Institute of Organic Chemistry, Academia Sinica, Shanghai, PRC headed by Dr. X-Y. Zhang, is currently engaged in collaborative research involving the synthesis of perfluorocarbon-containing alcohols of the corresponding acrylates or -methacrylates (Section 2.2.2.). These monomers will then be used in copolymerization studies and the copolymers will be characterized and evaluated by the techniques outlined above. In addition, this group will prepare several additional acrylamide-type monomers shown below.







The fluorocarbon-containing naphtalene derivative will be used in acrylamide copolymerizations. The resulting polymers will be investigated by the group of Professor Winnik (see below.)

Dr. M. Winnik (Toronto)

Discussions with Professor Winnik during the ACS Atlanta meeting have led to collaborations in the area of fluorocarbon-modified water-soluble polymers. The group of Dr. Winnik is interested in such polymers containing fluorescent probes. Thus, fluorocarbon-containing water-solubles polymers containing such probes (see above) will be synthesized in collaboration with the group of Dr. Y-X. Zhang.

Dr. C. C. Han (National Institute of Standards and Technology)

E. J. Amis and his students will carry out small angle neutron scattering (SANS) in collaboration with Dr. Charles Han (NIST). The objective of this work is to measure cluster sizes of the associated fluorocarbons. Of interest will be the cluster size as a function of perfluorocarbon-hydrophobic content. We will also be interested in the relative sizes of inter- and intromolecular hydrophobe clusters. Since the excluded volume effects of intramolecular hydrophobic association will be smaller, this may be expected to lead to larger cluster sizes.

Significance of Research

Our work to date has documented the extraordinary effects of suitably placed perfluoroalkyl groups on the degree of association of perfluoroalkyl-containing polyacrylamides. This is reflected in the persistence of polymer clusters at polymer concentrations below 10 ppm and in very high viscosities (10,000 - 30,000 cp at shear rate of 0.4 sec^{-1}) of relatively dilute solutions (0.5 wt %).

Even more impressive is the extremely low level of fluorocarbon-containing comonomer necessary to generate this highly associative behavior. Thus, levels around .1 mole % are optimal, but very good viscosification still occurs at .01 mole %. This indicates possible commercial potential in applications varying from enhanced oil recovery and drag reduction to waste water floculation.

Since our initial report on the effects of fluorocarbon substitution in water-soluble polymers, there has been considerable interest in this work, especially from industry. Examples are extensive consultations held with the 3 M Company on the possibility of patenting some of this work. Research by this company on aspects of this work is in progress. There also has been interest in this work on the part of several other companies including Aqualon-Hercules, American Cyanamide and DuPont. This has taken the form of invited seminars (Hercules-Aqualon, DuPont, Applied Biosystems, and Procter and Gamble) and/or consultations on this research at USC (Cyanamid, Exxon).

Several University research groups have expressed interest in this work and have told the PI or co-PI that they are currently doing work on perfluoro-containing water-soluble polymers or that they intend to do so. Examples are work in progress at the University of Toronto (Winnik) and at the University of Lowell (Watterson).

Budget removed

Current and Pending Support

Investigator(s)	Source	Project Title	Award	Period
T.E. Hogen-Esch	NSF-DMR Polymer Program	Synthesis of Topologically and Stereochemically Well-Defined Polymers	$308,700	4-91 to 3-94
T.E. Hogen-Esch (E.J. Amis, Co-PI)	Dept. of Energy, Office of Basic Energy Sciences	Synthesis of Novel Associating Water-Soluble Polymers	$315,488	8-89 to 7-92
T.E. Hogen-Esch	NSF-Materials CBTE-MCCP	Solution Properties and Membrane Formation of New Block Copolymers	$154,900	7-89 to 6-92
T.E. Hogen-Esch (Collaboration with Prof. S. Penczek, Lodz, Poland)	NSF Eastern Europe Travel Support	Spectroscopic Determination of Polymer Macrostructure...	$4,000	5-90 to 4-93
T.E. Hogen-Esch (L. Dalton, R. Salovey,USC)	NSF	Synthesis and Processing of Chemically Derivatized Polymer Microspheres for Use in Photonics and Electronics Applications	$896,731	submitted
E.J Amis (J.J. Aklonis)	ONR (Chemistry)	Processing of Polymers Using Supercritical Fluids	$785,000	11-89 to 11-92
E.J. Amis, Co-PI T. Hogen-Esch, PI	Dept. of Energy	Synthesis of Novel Associating Water-Soluble Polymers	$315,488	8-89 to 7-92
E.J. Amis	PRF (ACS)	Kinetics of Polymer Crystallization from Solution	$40,000	5-91 to 8-93
E.J. Amis	Applied Biosystems	Characterization of Novel Gels for DNA Sequencing Applications	$68,919	3-92 to 2-93
Weber, Olah, Dalton, Prakash, Casanova, Amis	NSF	Conjugated Polymers	$539771	submitted
E.J. Amis	Dow Chemical	Viscoeleastic Studies of Rodlike Polymers	$15,000	submitted
E.J. Amis	NSF (East Europe)	Polyelectrolyte Structure and Dynamics	$20,000	submitted

Available Facilities

Several NMR instruments are available in the department including a Bruker 270 MHz and 300 MHz NMR wiith multinuclear capability, and several lower field instruments. A new 500 MHz Bruker NMR will be in place in September of this year. Routine mass spectrometry measurements may be carried out on two GC-MS instruments. Other major departmental instrumentation includes: a pulsed EPR spectrometer, an automated X-ray deffractometer, an automated atomic absorption spectrometer, a CD spectrometer, a time resolved photo acoustic calorimeter. Routine IR and UV/ViS spectrometers are available in the polymer laboratories, as well as routing GC equipped with capillary and packed columns.

The major equipment for polymer characterization includes: three Waters liquid chromatographs, two lightscattering spectrophotometers and refractometers, three digital autocorrelators (two with log time capabilities), a unique multiple lumped resonator viscoelastic instrument, a levitated sphere viscometer, equipment for thermogravimetric analysis and DSC (2), a creep extensiometer, a rheovibron, and various conventional viscometers.

Ten vacuum lines are now available in the polymer synthesis laboratories. These lines, capable of producing a vacuum of less than 10^{-5} mm Hg, will be used in the polymer synthesis program.

BIOGRAPHICAL DATA

THIEO ELTJO HOGEN-ESCH

PERSONAL

Social Security	[redacted]
Date of Birth	[redacted]
Place of Birth	
Marital Status	Married to Cheryl E.
Children	John, 1967; Tom, 1968; Christopher, 1972

PRESENT POSITION AND ADDRESS

Professor of Chemistry
Department of Chemistry
University of Southern California
University Park
Los Angeles, CA 90089-1661

EDUCATION

Institution	Dates	Major Field	Degree
University of Leiden,		Chemistry	B.Sc.
Netherlands	1958-61	Physical Polymer Chemistry	M.Sc.
State University of New York (Syracuse)	1963-66	Polymer Chemistry Physical Organic Chemistry	
University of Leiden	1967	Physical Organic Chemistry	Ph.D. (Cum Laude)

EMPLOYMENT

1988-Present	Professor, Department of Chemistry, University of Southern California
1979-1988	Professor, Department of Chemistry, University of Florida
1975-1979	Associate Professor, Department of Chemistry, University of Florida
1970-1975	Assistant Professor, Department of Chemistry, University of Florida.
1969-1970	Visiting Professor, College of Environmental Science and Forestry, Syracuse, NY.
1968-1969	Postdoctoral Research Associate, College of Environmental Science and Forestry, Syracuse, NY.
1967-1968	Advising Technologist, Shell Nederland Chemie NV, Rotterdam, Netherlands.

AWARDS

Fellow Japanese Society for the Promotion of Science, May 1987.
University of Florida, Sigma Xhi Award, 1983-84.
Who's Who in Science and Technology.
Visiting Professor, Johannes Gutenberg University, Mainz, West Germany.May-June, 1982.
Visiting Professor, Laboratorium Voor Macromoleculaire en Organische Scheikunde, University of Leuven, Belgium, May-June 1977.
Visiting Scientist, Centre des Recherches sur les Macromolecules, Strasbourg, France, Sept. and Oct. 1977.
Visiting Professor, Universite Pierre it Marie Curie, Paris VI and Universite Paris-Nord, Nov. and Dec. 1977.
Visiting Professor, University of Leiden, Netherlands, April-Sept. 1975

PROFESSIONAL ACTIVITIES

ACS Polymer Division, Member Program Committee, 1981-1988; Organizer (with Prof. J. Smid) of International Symposium on "Advances in Anionic Polymerization", New York, NY, April 13-18, 1986.

Editorial Board, Journal of Polymer Science, 1985-1989.

Associate Director, Center for Macromolecular Science, University of Florida, 1971-1987. Director 1987-1988.

Chairman, Gainesville ACS Section, 1976.

University of Florida Patent Committee: Physical Sciences Review Committee, 1982.

Utrecht-Florida University Exchange Committee, 1981-1983.

University of Florida, Department of Chemistry: Graduate Advisory and Curriculum Committee, Seminar Committee, Space Committee, Industrial and Alumni Relations Committee, Language Committee.

Consulting: SCM Corporation, 1976-1977; Millchem, Inc., 1979-1980;
Cooper Distributors, 1979-1980; Frontier Contact Lenses, Inc. 1980-1981;
DuPont, 1982-1983; Dow Chemical, 1984-present;
W. R. Grace and Company, 1989-Present.

RESEARCH INTERESTS

1. Mechanism and stereochemistry of anionic oligomerization and polymerization of vinyl monomers.
2. Synthesis of star-cyclic polymers of well-defined structure.
3. Synthesis, structure determination and properties of associating water-soluble polymers and copolymers.
4. Synthesis and properties of block copolymers.

TEACHING

Course Teaching	Institution/Year	Level
Physical Chemistry of Polymers Laboratory	University of Leiden, 1960	Undergraduate
Organic Chemistry, CHM 3210/3211	University of Florida, 1971-80	Undergraduate
Quantum Applications to Organic Chemistry	University of Florida, 1972-73	Graduate
Organic Chemistry, CHM 5224	University of Florida, 1980	Beginning Graduate
Physical Chemistry of Polymers, CHM 5511	University of Florida, 1974-88	Advanced/Undergrad./Graduate
The Organic Chemistry of Polymers, CHM 5272	University of Florida, 1985	Advanced/Undergrad/Graduate
Polymer Synthesis, Chem. 561	Univ. of Southern Calif., 1989	Graduate
Organic Chem., Chem. 322aL/325aL	Univ. of Southern Calif., 1989	Graduate

SHORT COURSES

Ion Pairing in Carbanion Reactions	University of Louvain, 1977	Graduate
Anionic Polymerization	Univ. of Paris, Univ. of Paris-Nord, 1977	Graduate
Carbanions in Organic Reaction	Johannes Gutenberg University Mainz, France, June 1979	Graduate
Institute in Science and Technology Short Course	State University of New York at New Paltz, 1981	Graduate
Recent Developments in Organic Chemistry (PT Catalysis) for Industrial Chemists	University of Florida, 1981, 1982, (1 Lecture)	Graduate

Polymer Physical Chemistry Service Course for SCM	SCM Corp., Jacksonville, FL 1983 (6 Lectures)	Graduate/Advanced Undergraduates
Institute in Science and Technology Short Course, Water-Soluble Polymers	State University of New York at New Paltz, 1983 (1 Lecture)	Graduate

Ph.D. DISSERTATIONS AND M.Sc. THESES DIRECTED

M. J. Plodinec, "Ion Pairing and Hydrogen Bonding in the Excited State of Alkali Carbanion Salts", Ph.D., University of Florida, December 1974.

R. E. Cambron, "Alkali Cation Binding to Nonionic Polymers", Ph.D., University of Florida, December 1976.

W. L. Jenkins, "Ion Pair Structure and Beta Carbon Stereochemistry in the Anionic Oligomerization of Vinyl Pyridines", Ph.D., University of Florida, June 1978.

R. A. Smith, "Methylation and Alpha-Carbon Stereochemistry in the Anionic Oligomerization and Polymerization of 2-(2-Pyridyl)propene", M.Sc., University of Florida, March 1981.

S. S. Huang, "Stereochemistry of Anionic Oligomerization of 2-Vinylpyridine. Preparation and Analyses by NMR and Chromatography", Ph.D., University of Florida, June 1981.

C. R. Wince, "The Synthesis and Interactions of Oligopeptide Bis Intercalators with DNA", M.S., University of Florida, August 1982.

M. A. Buese, "Stereoselection and Stereoelection in the Anionic Oligomerization and Polymerization of Vinylphenylsulfoxide", Ph.D., University of Florida, September 1982.

C. C. Meverden, "Stereochemical and Mechanistic Studies on the Anionic Oligomerization of 2- and 4-Vinyl Pyridines", Ph.D., University of Florida, August 1983.

M. A. Doherty, "Synthesis and Characterization of Stereoblock Polymers of Poly-(methylmethacrylate)", Ph.D., University of Florida, December 1984.

I. M. Khan, "Anionic Polymerization of 2-Vinyl Pyridines: Studies of Intermediate Carbanions and Their Role in the Stereochemistry of Polymerization", Ph.D., University of Florida, December 1984.

B. C. Bell, "Stereochemistry of Anionic Oligomerization of t-Butylvinylketone", Ph.D., University of Florida, June 1986.

William Toreki, "Synthesis of Well-Defined Cyclic Branched and Water-Soluble Polymers Via the Anionic Polymerization of 2-Vinylpyridine", Ph.D., University of Florida, May 1988.

R. S. Kanga, "Thermal Elimination of Poly(phenylvinylsulfoxide) and Its Styrene Block Copolymers", Ph.D., University of Florida, August 1988.

K. G. Bannerjee, "The Stereochemistry of Group Transfer Polymerization of Methyl-Diphenylmethyl and Triphenylmethylmethacrylates", Ph.D., University of Florida, August 1988.

J. P. Mason, "The Synthesis and Characterization of Monodisperse Polydimethylsiloxane-Poly(methylmethacrylate) AB, ABA and Star Block Copolymers. Stereocomplex Formation with Isotactic Poly(methylmethacrylate)", Ph.D., Univ. of Southern California, December 1989.

B. J. Ladd, "Synthesis and Characterization of Polybutadiene-PMMA Block Copolymers Stereocomplex Formation with Isotactic PMMA", Ph.D., University of Southern California, February 1990.

J. Sundararajan, "Synthesis and Characterization of Macrocyclic Poly(2-vinylpyridine) and Polystyrene", Ph.D., University of Southern California, May 1991.

124.	T.E. Hogen-Esch, B.J. Ladd, J.P. Mason, J. Helary and G. Belorgey, *Polym. Preprts.,* **31** (2), 405 (1990).	Stereocomplex Formation of PMMA-Containing Block Copolymers. Synthesis and Properties.
125.	T.E. Hogen-Esch, M. Yassini, Y-X Zhang, F. Huang, E.J. Amis and T. Seery, *Polym. Preprts.,* **31**(2), 460 (1990).	Synthesis and Characterization of Fluorocarbon Containing Polyacrylamides.
126.	Y-X Zhang, A-H Da, G.B. Butler and T.E. Hogen-Esch, *Proceed. 33rd IUPAC Symp. Macromolecules,* 1990.	Water-Soluble Graft Copolymer of 2,3-Dihydroxypropylcellulose With Acrylamide and Sodium 2-Acrylamido-2-Methylpropane Sulfonate.
127.	T.E. Hogen-Esch and B.J. Ladd, *Proceed. 33rd IUPAC Symp. Macromolecules*, 1990.	Synthesis and Properties of Polybutadiene-Syndiotactic PMMA. Block- and Star-Block Copolymers.
128.	T.E. Hogen-Esch and J.P. Mason, *Proceed. 33rd IUPAC Symp. Macromolecules,* 1990.	Synthesis and Stereocomplex Formation of Polydimethylsiloxane-PMMA Block- and Star-Block-Copolymers.
129.	Y-X. Zhang, A-H. Da, T.E. Hogen-Esch and G.B. Butler, *J. Polym. Sci., Chem. Ed.,* Accepted.	Copolymers of Acrylamide and Acrylate Comonomers Containing Perfluoroalkyl Groups.
130.	R. Kanga, T.E. Hogen-Esch, C.D. Batich and R. Crockett, *J. Polym. Sci., (Chem. Ed.),* Submitted.	An XPS Study of Thermal Elimination in Poly(phenylvinylsulfoxide) and Their Block Copolymers.
131.	J. Baumgarten, A.H. Mueller and T.E. Hogen-Esch, *Macromolecules,* **24**, 353 (1991).	Determination of E/Z and Meso-Racemic End Group Stereochemistry in the Anionic Polymerization of Methylmethacrylate in THF.
132.	T.E. Hogen-Esch, J. Sundararajan and W. Toreki, *Makromol. Chem.*, Macromol. Symp., **47,** 23 (1991).	Synthesis and Characterization of Topologically Interesting Vinyl Polymers.
133.	Y-X Zhang, A-H Da and T.E. Hogen-Esch, Chapter 10, ACS Symposium Series, No. 467, "Water-Soluble Polymers", S. Shalaby, C.L. McCormick and G.B. Butler, Eds., pages 159-174.	New Fluorocarbon-Containing Hydrophobically-Associating Polyacrylamide Copolymers.
134.	S. Gopalkrishnan, G.B. Butler, T.E. Hogen-Esch and N.Z. Zhang, Chapter 11, ACS Symposium Series, No. 467, "Water-Soluble Polymers", S. Shalaby, C.L. McCormick and G.B. Butler, Eds., pages 175-188.	Hydrophobically Associating Ionic Copolymers of Methyl Diallyl 1,1-dihydropentadecafluorooctoxyethylammonium Chloride.

135.	F. Huang and T.E. Hogen-Esch, *Polym. Preprts.,* **32** (1), 581 (1991).	Fluorocarbon-Modified Water-Soluble Cellulose Derivatives.
136.	J. Sundararajan and T.E. Hogen-Esch, *Polym. Preprts.,* **32** (1), 63 (1991).	Synthesis and Characterization of Macrocyclic Poly(2-vinylpyridine).
137.	Q. Jin, D. Dimov and T.E. Hogen-Esch, *Polym. Preprts.,* **32** (1), 465 (1991).	Lithium Alkoxides As Modifiers for the Synthesis of Isotactic Poly(2-vinylpyridine).
138.	R. Yin and T.E. Hogen-Esch, *Polym. Preprts.,* **32** (1), 539 (1991).	Synthesis and Characterization of Poly(2-vinylpyridine) b-t-Butylmethacrylate Copolymers.
139.	T.E. Hogen-Esch, J.R. Mason, B.J. Ladd, G. Helary and G. Belorgey, ACS Symposium Series, No. J. Riffle, Editor, In preparation.	Crosslinking of PMMA Elastomer Block Copolymers Through PMMA Stereocomplexes.
140.	G. Helary, G. Belorgey, B. Ladd and T.E. Hogen-Esch, *Polymer,* accepted.	Stereocomplex Formation in Polybutadiene-Syndiotactic Polymethylmethacrylate Block Copolymers Blended with Isotactic PMMA.
141.	J. Sundararajan and T.E. Hogen-Esch, *Polym. Preprts.*, **32** (2) 604 (1991).	Synthesis and Characterization of Macrocyclic Polystyrene Effect of Molecular Weight on Glass Transition Temperature.
142.	R. Yin and T.E. Hogen-Esch, *Polym. Preprts.,* **33** (1), 000 (1991).	First Synthesis of a Macrocyclic Block Copolymer Macrocyclic Polystyrene-b-Polydimethylsiloxane.
143.	M. Yassini and T.E. Hogen-Esch, *Polym. Preprts.,* **33** (1), 000 (1992).	Fluorine Containing Hydrophobically Associating Polymers.
144.	X. Xie and T.E. Hogen-Esch, *Polym. Preprts.,* **33** (1), 000 (1992).	Anionic Polymerization of N,N-Dialkylacrylamide and -methacrylamide.
145.	E.J. Amis, T.A. Seery, M. Yassini and T.E. Hogen-Esch, *Polym. Preprts.,* **33** (1), 000 (1992).	Static and Dynamic Lightscattering Characterization of Hydrophobically Associating Fluorocarbon Containing Polymers.
146.	J. Sundararajan and T.E. Hogen-Esch, *Polym. Preprts.,* **33** (1), 000	Synthesis and Characterization of Poly(2-vinylpyridine) Macrocycles. Effect of Coupling Agent.
147.	J. Sundararajan and T.E. Hogen-Esch, (Ft. Lauderdale Symp. Book Chapter).	Synthesis and Characterization of Macrocyclic Poly(2-vinylpyridine) and the Effect of a Rigid Couplint Agent on its Properties.
148.	K. Bannerjee and T.E. Hogen-Esch, *Macromolecules,* Submitted, (1-92)	Stereochemistry of Polymerization of Triphenylmethyl and Diphenylmethylmethacrylate Under GTP Conditions.
149.	R. Volpe, T.E. Hogen-Esch, F. Gores and A.H. Mueller, *Macromolecules,* Submitted (2-92).	Stereochemistry of Living PMMA Anions As Determined by NMR Analysis of Carbon-13 Labeled Methyl End Groups.

Eric J. Amis
Curriculum Vitae

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Culver City, CA 90230
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Department of Chemistry
University of Southern California
Los Angeles, CA 90089-0482
(213) 740-4113

Education

Ph.D. in Chemistry, 5/81, University of Wisconsin, Madison, Wisconsin
Major: Physical Chemistry; Thesis Advisor: Professor Hyuk Yu

B.S. in Chemistry, 5/76, Willamette University, Salem, Oregon
Research Advisor: Professor Arthur D. Payton

Professional Experience

9/90 – present	Associate Professor of Chemistry Faculty Associate Fellow of the Loker Hydrocarbon Institute University of Southern California, Los Angeles, California
6/92 - present	Editor, Journal of Polymer Science: Polymer Physics, Wiley-Interscience
8/86 – present	Guest Researcher, Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland
8/84 – 8/90	Assistant Professor of Chemistry University of Southern California, Los Angeles, California
12/82 – 7/84	Project Associate with Professor John D. Ferry Department of Chemistry, University of Wisconsin–Madison
8/81 – 11/82	National Research Council Postdoctoral Associate with Dr. Charles C. Han, Polymer Division National Bureau of Standards, Washington, D.C.
4/81 – 7/81	Research Associate with Professor John D. Ferry Department of Chemistry, University of Wisconsin–Madison
9/76 – 3/81	Teaching Assistant and Research Assistant with Professor Hyuk Yu Department of Chemistry, University of Wisconsin–Madison

Honors and Awards

Burlington Northern Foundation Faculty Achievement Award for Excellence in Teaching, University of Southern California, 1989
Chemistry Department Alumni Teaching Award, University of Southern California, 1988
National Research Council Postdoctoral Fellowship, 1981
Outstanding Teaching Assistant Award, University of Wisconsin, 1978
Mary L. Collins Graduate Scholarship, Willamette University, 1976
Cum laude Graduate, Willamette University, 1976
Mary L. Collins and Oregon State Scholar, Willamette University, 1972-1976

Memberships

American Chemical Society, American Physical Society, Society of Rheology, Materials Research Society, Sigma Xi, AAAS

Personal

[redacted]
Married 16 years; one daughter, 11 years old

Professional Activities

USC Loker Hydrocarbon Institute Symposium Honoring John D. Ferry, Organizer and Chair: Advances in Polymer Dynamics, Los Angeles, 1990

American Physical Society, Materials Physics Group Focus, Session Organizer and Co-Chair: Complex Fluids and Sol-Gel Systems, National Meeting, Anaheim, 1990

American Physical Society, Division of High Polymer Physics, Publications Committee Chairman, 1991-92, Guest Editor, December 1992 issue Journal of Polymer Science, Polymer Physics Edition

American Physical Society, Division of High Polymer Physics, Co-Organizer: Demonstrations of Concepts in Polymer Physics, Indianapolis, 1992

Editor, Journal of Polymer Science: Polymer Physics Edition, 1992-present

American Chemical Society, Polymer Division, Symposium Co-Organizer and Chair: Polyelectrolytes, National Meeting, Denver, (1993)

Invited Lectures – National and International Meetings

American Chemical Society National Meeting, Lecture Series on Polymer Characterization, Anaheim, 1986	*Characterization of macromolecules in solution by viscosity measurements*
American Chemical Society National Meeting, Polymer Self-Diffusion and Related Problems, Denver, 1987	*Self diffusion of polymer, solvent, and ternary probe molecules through dilute, semidilute, and entangled polystyrene solutions*
Gordon Research Conference, Polymers, Ventura, 1989	*The use of dynamic light scattering to follow the initiation and growth of polymer crystals*
American Chemical Society National Meeting, Molecular Aspects of Rheology, Dallas, 1989	*Viscoelasticity of polyelectrolytes in dilute solution*
Gordon Research Conference, Dynamics of Macromolecular and Polyelectrolyte Solutions, Oxnard, 1990	*Dilute solution viscoelasticity of polyelectrolytes*
International Discussion Meeting on Relaxations in Complex Systems, Crete, 1990	*Dynamic viscoelasticity during sol-gel reactions*
American Chemical Society National Meeting, Innovative Rheological Techniques, Atlanta, 1991	*Gel transitions at a molecular level*
American Chemical Society National Meeting, Thermoreversible Gelation, New York, 1991	*Dynamic viscoelasticity during thermoreversible gelatin gelation*
American Chemical Society National Meeting, Polymers of Geometrical Beauty: Rings, Combs, Stars and Dendrimers, New York, 1991	*Light scattering and viscoelasticity of linear and ring polyelectrolytes*

Invited Lectures – National and International Meetings (continued)

Speciality Polymers '91: Supramolecular Aspects of Polymer Synthesis and Polymer Structure, Max-Planck-Institut für Polymerforschung, Mainz, FRG, 1991	*Synthesis and properties of fluorocarbon containing associating aqueous polymers*
CNRS, Laboratoire de Spectrometrie et D'Imagerie Ultrasonores, Strasbourg, 1991	*Dynamic viscoelasticity during chemical and physical gel transitions*
Albert-Ludwigs-Universität, Institut für Makromolekulare Chemie, Freiburg, 1991	*Dynamic viscoelasticity during chemical and physical gel transitions*
Networks '92, Biannual International Symposium on Polymer Networks and Gels, San Diego, (1992)	*Dynamics of chemical and physical gels during gelation*
Gordon Research Conference, Polymers, Ventura, (1993)	*Polymer Associations: Solutions to Gels*
Gordon Research Conference, Ion Containing Polymers, New Hampshire, (1993)	*Dynamics of polyelectrolytes in solution*

Publications, 1989 to present

19. T.A.P. Seery, J.A. Shorter, and E.J. Amis,
"Concurrent Static and Dynamic Light Scattering from Macromolecular Solutions. I. Model Systems in the Low q Regime",
Polymer, 1989, **30**, 1197-1203.

20. D.F. Hodgson and E.J. Amis,
"Viscometric Titration of a Linear Polyelectrolyte",
J. Chem. Phys., 1989, **91**, 2635-2642.

21. D.W. Hair, F.J. Niertit, D.F. Hodgson, and E.J. Amis,
"High Speed Signal Averager for Characterizing Periodic Signals in the Time Domain",
Rev. Sci. Inst., 1989, **60**, 2780-2784.

22. N. Ding, E.J. Amis, R. Salovey, and R.M. Briber,
"Preparation of Polymer Crystal Nuclei",
J. Polym. Sci.: Prt. C: Polym. Lett., 1989, **27**, 489-496.

23. D.W. Hair and E.J. Amis,
"Intrinsic Dynamic Viscoelasticity of Polystyrene in Theta and Good Solvents",
Macromolecules, 1989, **22**, 4528-4536.

24. A. Ngam-ek, T.A.P. Seery, E.J. Amis, and S.D. Grover,
"Malate-Induced Hysteresis of Phosphoenolpyruvate Carboxylase From *Crassula argentea*",
Plant Physiology, 1989, **91**, 954-960.

25. D.F. Hodgson and E.J. Amis,
"Dynamic Viscoelasticity During a Sol-Gel Reaction",
Phys. Rev. A, 1990, **41**, 1182-1185.