ANNUAL 1994

DOE Progress Report ... 11/15/93 - 11/15/94

DOE/ER/45407--77

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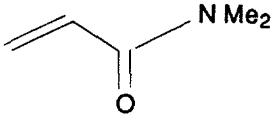
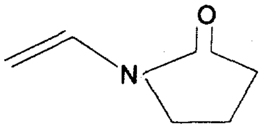
1. Summary of Research Progress

A) Synthesis of DMA - FOSA and NVP - FOSA copolymers

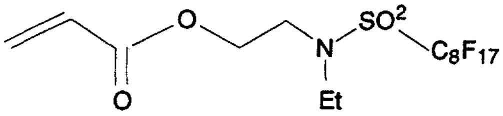
A large number of hydrophobically associating copolymers of N-vinylpyrolidone (NVP) or N,N-dimethyl acrylamide (DMA) with perfluoroalkyl acrylates (FOSA) containing between .01 and 1.0 mole % FOSA (with respect to DMA) were synthesized by emulsion and by bulk copolymerization. In contrast with the acrylamide (AM) FOSA copolymers the corresponding NVP and DMA copolymers are soluble in THF and CH_3OH in addition to water. This is expected to be of help in the characterization.



DMA



NVP



FOSA

The kinetics of DMA (NVP) copolymerizations, followed by ^{1}H and ^{19}F NMR, showed quantitative conversion of monomer and FOSA comonomer that polymerized at the same relative rates throughout the polymerization. The emulsion polymerizations carried out in the presence of perfluorocarbon surfactants gave higher molecular weights than the bulk copolymerizations as indicated by reduced viscosity measurements in CH_3OH. The intrinsic viscosities in CH_3OH of PDMA and the DMA - FOSA copolymers were identical indicating little or no association below 1000 ppm. Molecular weights of the copolymers were in the order of $\sim 10^6$.

The Brookfield viscosity of 1.0 wt % DMA - FOSA aqueous copolymer solutions plotted as a function of FOSA content showed a bell shaped curve with a viscosity maximum of 20,000 cP at about .10 mole % FOSA. This behavior was also observed for the NVP - FOSA copolymers for the acrylamide - FOSA copolymers synthesized earlier. In contrast to PDMA, the DMA - FOSA copolymers show large viscosity decreases with increasing shear and viscosity increases with addition of NaCl. Temperature increases (25 → 40°) give rise to viscosity increases thus supporting hydrophobic association. However, the DMA - FOSA copolymers being soluble in non-aqueous solvents such as

HH

CH_3OH and THF could be characterized more readily compared to the AM - FOSA copolymers.

The above results are important in that they show that PDMA homo and copolymers have essentially identical molecular weights and that the rheological differences in water are largely due to hydrophobic association. The occurence of viscosity maxima of 0.5 weight % PDMA copolymer solutions at .10 mole % FOSA and appreciable viscosities (~ 10^3 cP) at .02 mole % FOSA corresponds to the presence of 30 and 7 FOSA units/chain respectively. Such low numbers appear to preclude blocky FOSA sequences in the chain. This is also shown by the kinetic measurements that indicate the same relative rates of DMA and FOSA polymerization throughout the course of reaction.

Kinetics of AM - FOSA copolymerization

Polymerization carried out in H_2O and monitored by ^1H and ^{19}F NMR in the presence of > 6.0 wt % acetone (or perfluorocarbon surfactants) shows the same relative rates of disappearance throughout the reaction. Below about 6 wt % acetone or in the absence of perfluorocarbon surfactants the FOSA comonomer reacts at a lower rate than that of AM.

Solutions of this kind show the presence of two ^{19}F NMR absorptions for the CF_3 group: a sharp absorption at about -36 ppm along with a broader absorption at -37 ppm. Polymerization under these conditions results in a rapid disappearance of the peak at -36 ppm whereas the -37 ppm is not affected. These results document the existence of unreactive FOSA aggregates (droplets) along with more reactive form of FOSA and this is in accord with the kinetics observed. These results again suggest random rather than blocky incorporation of FOSA into the copolymers and are in accord with the viscosity dependence on comonomer content that are also consistent with the formation of random copolymers.

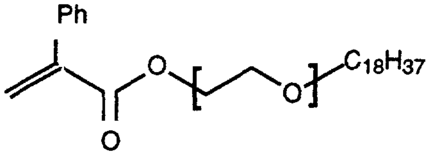
C) Synthesis of model associating polymers

The synthesis was recently carried out of end funtionalized perfluorocarbon derivatives 1 of PDMA by anionic polymerization of DMA followed by reaction with $C_7F_{15}COCl$. (eq 1) However, viscometric studies on these polymers and the non functionalized precursors showed no hydrophobic association at all. We had reasons to believe that this failure to associate was due to strong coupling between the highly mobile R_F groups and the hydrophilic chain. Thus, we synthesized end functionalized PDMA polymers (B) by reaction of difunctional anionic PDMA with a single C_{18} functionalized alpha-phenyl acrylate (**2**) containing a water-soluble "spacer" having 10 oxyethylene units.

$$R-\underset{\underset{O}{\|}}{C}-PDMA-\underset{\underset{O}{\|}}{C}-R$$

1 a $R = C_7F_{15}$

b $R = C_{18}H_{37}$



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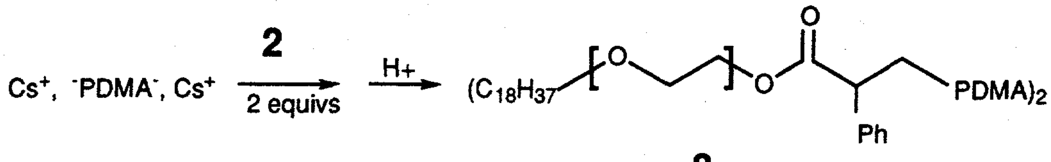
$$\text{Cesium Naphtalene} \xrightarrow{DMA} Cs^+,\ {}^-PDMA^-,\ Cs^+ \xrightarrow{R\,COCl} \mathbf{1}$$

(eqn 1)



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In contrast to polymers **1a** and **1b** polymers **3** gave effective viscosity enhancement in water indicating hydrophobic association. This important result shows the importance of the oligo oxyethylene "spacer" in the decoupling of the water-soluble polymer and the hydrophobic group thus promoting hydrophobic association.

B. Characterization

The physical chemistry work on the fluorocarbon associating polymers has focused on light scattering and viscosity studies of the modified polyacrylamide copolymers and on some special model systems incorporating the same perfluoroalkyl hydrophobic units. One of the most significant issues for the copolymerization is characterization of the microstructure of the copolymer and the influences on various conditions of the polymerization on the microstructure. The nature of incorporation of the hydrophobic comonomers into the polymer, blocky vs. random, spacing between hydrophobic segments, influence of overall chain molecular weight relative to incorporation ratio of hydrophobes, all have been shown or can be expected, to influence the physical properties such as viscosity.

In the absence of specific rigorous control of the microstructure in the random polymerization, we have supplemented the work on the polyacrylamide copolymers with very productive new studies of model polymers where we can control the placement of the hydrophobic units. While it is doubtful that such model systems will have properties which are better than have been achieved with the random copolymers, the model systems have allowed us to quantify the influence of several key parameters. The models have also allowed us to make contact with recent theoretical work specifically addressing transient associations by Tanaka and Edwards, Annable et al., and Tanaka and Stockmayer.

The model systems are of two types: first, polyethylene oxide with perfluoroalkyl units on each end ("telechelics") and second, copolymers made by a condensation of macromers which consist of PEO chains with linking units on each end with the perfluoroalkyl groups as side chains ("combs"). We have varied size of the perfluoroalkyl units, the length of the PEO subchains, and, for the combs, the overall chain molecular weight. In agreement with the basic Tanaka and Edwards model, formulated specifically for telechelic molecules, we have shown Arrhenius temperature dependence of viscosity with the activation energy proportional to the hydrophobe length. Similarly we have confirmed the expectation from the theory for the independence of the activation barrier to polymer molecular weight or hydrophobe spacing.

On the other hand, we have confirmed Annable's result that loop formation by the associating polymers, neglected by the simple model, is a significant influence decreasing the viscosity at lower concentrations. In a new finding, made possible by the comparison between the telechelic and comb polymers, we have demonstrated that both of the previous models overestimate the viscosity effects for telechelics, and the molecular weight dependence of the viscosity, because they neglect binary junctions of two hydrophobes which only lead to chain extension and do not contribute to network formation. This effect is not significant for comb polymers of reasonable length since nearly every junction, even binary interactions, lead to active network strands. Combined with the enormous activation energy barrier given by the fluorocarbon hydrophobes this is probably the key to the exceptional effectiveness of the random fluorocarbon copolymers. That is, to account for the enormous viscosities there is no need to invoke mechanisms involving cooperativity of "blocky" hydrophobe sequences. In fact, we can speculate that it is likely that with the low comonomer fractions of our most effective copolymers, any grouping of the hydrophobes would reduce the number of effectigve network strands and thereby reduce the viscosity effect.

2. Research Plans

The simultaneous ^1H and ^{19}F NMR measurements on AM and FOSA copolymerization kinetics have given important clues on the details of the copolymerization of these monomers (see above). We believe that further studies aimed at the detailed copolymerization mechanism will provide us with the final data needed to elucidate the FOSA comonomer sequences in the above copolymers.

We plan to extend these studies to the hydrocarbon acrylate -AM or hydrocarbon acrylamide -AM copolymers in order to elucidate the comonomer sequences in these important types of hydrophobically associating polymers. A number of investigators have claimed "blocky" structures but these claims appear to be controversial. The above kinetic studies are intended to help resolve these issues.

In collaboration with Dr. Y-X Zhang, Academia Sinica, Shanghai, we have started the synthesis of R_F modified poly(acrylamide-2-acrylamide, 0-2-methyl propane sulfonate). These perfluorocarbon-modified polymers are expected to show characteristics of both polyelectrolytes and -R_F containing water-soluble polymers.

We will also complete the synthesis and characterization by viscometry and lightscattering of model R_H and R_F-modified polymers. These will include one- and two-end functionalized PDMA containing R_H and R_F groups. These studies are expected to greatly enhance our understanding of hydrophobic association of R_F and R_H- modified water-soluble polymers.

Talks Presented

Thieo E. Hogen-Esch

1993	ACS National Meeting, Denver, Co.	*Effects of Water Soluble Spacers on the Hydrophobic Association of Fluorocarbon Modified Polyacrylamides.*
1993	ACS National Meeting, Denver, Co.	*Synthesis of Well-Defined Poly(N,N-dimethylacrylamide) Containing Perfluorooctanoyl End Groups.*
1993	American Cyanamide, Stamford, CT	*Hydrophobic Association in Water-Soluble Copolymers*
1993	Hercules-Aqualon, Wilmington, Del	*Synthesis of Perfluorocarbon-Containing Water-Soluble Polymers*
1993	Dupont Central Research, Wilmington, Del	*Synthesis and Properties of Perfluorocarbon-Modified Polyacrylamides*
1993	Hoechst-Kalle Albert, Mainz, Germany	*Hydrophobic Association in Water-Soluble Polymers*
1994	ACS National Meeting, San Diego, CA	*Fluorine-Containg Hydrophobically Assciating Water-Soluble Polymers. Kinetics of Polymerization by NMR.*
1994	ACS National Meeting, San Diego, CA	*Synthesis and Characterization of Hydrophobically Associating Poly(N,N-dimethylacrylamide)*
1994	Department of Chemical Engineering, University of Southern California	*Perfluorocarbon-modified Hydrophobically Associating Polyacrylamides*
1994	Department of Chemistry, Clark Atlanta University	*Hydrophobic Association of Perfluoroalkyl Modified Water-Soluble Polymers*

1993

Gordon Research Conference, Polymers, Ventura, 1993	*Polymer Associations: solutions to gels*
International Symposium on Polymers & Complex Fluids, Korean Chemical Society, Seoul, Korea, 1993	*Structure & Dynamics of associating polymer solutions*
Pohang Institute of Science & Technology, Department of Chemistry, Pohang, Korea, 1993	*Structure & dynamics of associating polymer solutions*
Korea Institute of Science & Technology, Seoul, Korea, 1993	*Structure & dynamics of associating polymer solutions*
American Physical Society National Meeting, High Polymer Physics Division, Seattle, 1993	*Viscoelasticity of associating polymer solutions*
Union Carbide, Charleston, WV, 1993	*Structure and dynamics of associative polymeric systems*

1994

ACS National Meeting, Symposium on Polymer Dynamics & Thermodynamics in Solutions, San Diego, 1994	*Structure & dynamics of associating polymers in solution*
APS National Meeting, Ford Prize Symposium, Pittsburgh, 1994	*Investigations of polymer interactions in solution by scattering and viscoelasticity*
University of Southern Mississippi, Department of Polymer Science, Hattiesburg, 1994	*Investigations of strong polymer interactions in solution by scattering and viscoelasticity*
Louisiana State University, Department of Chemistry, Baton Rouge, 1994	*Investigations of strong polymer interactions in solution by scattering and viscoelasticity*
Networks '94, Biannual International Symposium on Polymer Networks and Gels, Prague, Czech Republic, 1994	*Transient gels of associating polymers*
Polymers Division, National Institute of Standards and Technology, 1994	*Structure and Dynamics of Polymeric Systems with Specific Interactions*

Future Invitations

ACS National Meeting, Symposium on Physical Chemistry of Polymers and Complex Liquids, Anaheim, 1995	*Associating polymers and transient gels*
Associating Polymers: Symposium on structure interaction & dynamics in systems containing associating polymers, Loen, Norway, 1995	*Associations with fluorocarbon hydrophobes*
Faraday Discussion #101: Gels, Paris, 1995	*Dynamics of transient gels of mdel polymers formed by strong fluorocarbon associations*

Publications

X. Xie and T.E. Hogen-Esch, Polymer Preprints, **1994, 35(1), 498-499**	*Synthesis and Characterization of Hydrophobically Associating Poly(N,N-dimethylacrylamide)*
M. Yassini and T.E. Hogen-Esch, Polymer Preprints, **1994, 35(1), 478-479**	*Fluorine Containing Hydrophobically Associating Water-Soluble Polymers. Kinetics of Polymerization by 19F NMR.*
F. Hwang and T.E. Hogen-Esch, Macromolecules, Accepted.	*Self Assembling Fluorocarbon-Containing Polyacrylamides. Effects of Hydrophilic Spacers.*
E.J. Amis and N. Hu, Polymer Preprints, 1994, 35(1), 102-103	*Structure and Dynamics of Associating Polymers In Solution*
E.J. Amis, N. Hu, T.A.P. Seery, T.E. Hogen-Esch, M.Yassini, and F.Hwang,Hydrophilic Polymers: Performance with Environmental Acceptance, E. Glass, Ed., Amer. Chem. Soc., **1994**, in press.	*Associating Polymers with Fluorocarbon Hydrophobic Units*
T.E. Hogen-Esch and E.J. Amis, Trends in Polymer Science, **1994**, in press	*Hydrophobic Associations in Perfluorocarbon-Containing Water-soluble Polymers*