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Synthesis and Self-Assembly of Fluorocarbon- and Hydrocarbon-Modified Hydrophilic Polymers

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Research Summary

Department of Energy Office of Basic Energy Sciences

Introduction:

Over the past three years we have worked in several areas.

1.1 Effect of spacer lengths on the degree of association of hydrophobically modified polyacrylamides.

Studies on copolymers of acrylamide (AM) and comonomers 2 - 9 and other hydrophobically modified polymers have shown that the reduced and Brookfield viscosities sharply increase with increasing lengths of the "spacers" separating the perfluorocarbon (R_F) or hydrocarbon (R_H) pendent groups from the hydrophilic backbone (Figs 1,2). These increases are tentatively attributed to a decreased loss of entropy of the water-soluble backbone, upon formation of the R_H or R_F hydrophobic aggregate¹⁻⁶. Thus the spacers would appear to enhance association by decoupling the motion of the chain from that of the hydrophobic aggregate. Longer spacers may also mitigate excluded volume effects of the hydrophilic chains or chain segments upon $R_F(R_H)$ aggregation.

Scheme-1 Structures of monomers and comonomers

1.2 Fluorocarbon mediated association of R_F -substituted polyacrylamide-AMPS copolymers

In collaboration with Dr. Y. X. Zhang (Institute of Organic Chemistry, Academia Sinica Shanghai, PRC) a series of acrylamide copolymers of -2- (acrylamido)-2-methyl- propane sodiumsulfonate (AMPS) was synthesized containing from 0 to 1.0 mole % of R_F -comonomer **1a**.⁷ In all cases strong R_F hydrophobic association was observed manifested in large Brookfield viscosity increases over that of copolymers without pendent R_F -groups. The plots of viscosity against molar content of **1**, as seen in most of these systems, showed bell-shaped curves reflecting a competition between inter and intra- molecular association. Thus at very high R_F content intramolecular hydrophobic interactions begin to dominate over inter-molecular interactions resulting in a shrinkage of the polymer coils leading to a viscosity decrease. The extent of R_F mediated polymer association was found to be lower than for the AM copolymers of **1** possibly because intermolecular association formation is resisted by repulsive electrostatic interactions between chains..

1.3 Hydrophobic association in R_F (R_H)-modified poly(N,N-dimethylacrylamide)(PDMA) and polyvinylpyrrolidone (PVP)

An investigation of these polymers and copolymers was of particular interest because of good copolymer solubility in several non aqueous solvents such as methanol and THF facilitating SEC analysis. Thus in contrast with PAM copolymers a correlation of physical properties with molecular weight is possible.

1.3.1 Effects of comonomer content and molecular weight

We have shown that for PDMA copolymers of **1a**, prepared by aqueous emulsion and bulk copolymerizations, dramatic aqueous viscosity increases are observed compared to the corresponding homopolymers prepared under identical reaction conditions (Figs 3 and 4)⁸. Lower viscosities were observed for the bulk copolymers compared to the emulsion copolymers and this is at least partially due to significantly lower molecular weights of the bulk copolymers ($DP_n \sim 4000$) compared to the emulsion copolymers ($DP_n \sim 30,000$). These and other results are difficult to explain in terms of differences in comonomer sequence distributions between the bulk and emulsion copolymers but (see section 1.4) appear to be consistent with both types of copolymers having random comonomer sequences. In contrast with the corresponding polyacrylamide copolymers all of the PDMA copolymers could be analyzed by SEC in THF allowing the determination of molecular weights and molecular weight distributions. This represents a considerable advantage of the PDMA and PVP copolymers. (Tables 1,2) Viscosity average molecular weights of PDMA were also determined in methanol and are generally in good agreement with the M_n values obtained from SEC.

1.3.2 Addition of surfactants

Upon addition of $C_7F_{15}CO_2K$ and $C_{12}H_{25}O_5O_3Na$ surfactants to surfactant-free PDMA bulk copolymers of **1a** and **6** dramatic viscosity enhancements are observed especially for the addition of R_F surfactants to the R_F copolymer (Fig 5).⁸ These viscosity enhancements are consistent with intermolecular micellar bridging (Scheme-2) with the following order in the effectiveness of micellar bridging depending on the nature of the polymer-surfactant combination: $R_F-R_F > R_H-R_H > R_F-R_H > R_H-R_F$ in qualitative agreement with what is known for the relative incompatibility of hydrocarbon and fluorocarbons. Furthermore it is plausible that binding of the surfactant to the neutral polymer gives rise polyelectrolyte effects. Thus upon addition of NaCl; viscosities increase and then decrease dramatically.(Fig 6) Furthermore addition of nonionic R_F surfactants gives viscosity increases that are smaller and are not affected by salt addition.

1.3.3 Copolymerization kinetics of DMA and NVP and fluorocarbon comonomers

The kinetics of emulsion copolymerization of acrylamide, N,N-dimethylacrylamide and N-vinyl pyrrolidone with comonomer **1** has shown that under carefully chosen reaction conditions monomer and comonomer conversion are quantitative and that the relative rates of monomer- and comonomer- depletion are identical (Fig 7)^{8,9}. This important finding indicates that in these cases the copolymer composition is time-independent. These data again are consistent with, but do not prove, random copolymerization.

1.4 Synthesis of R_F -containing poly(N-isopropyl acrylamide)'s

A series of copolymers were synthesized of N-isopropylacrylamide (NIA) and FOSA and of NIA and FOSM (**1b**) containing between .080 and 1.25 mole % of the R_F comonomers. The

viscosity versus polymer concentration profile revealed that solutions of these copolymers gave much higher (100-1000 times) low shear viscosities compared to the $C_{12}H_{25}$ copolymers. In contrast to the AM copolymers the FOSM (1b) copolymers of NIA gave higher viscosities than the FOSA (1a) copolymers. Interestingly the viscosities of these copolymer solutions were found to be unusually temperature dependent compared to the corresponding polyacrylamide copolymers. Thus for solutions of the FOSA acrylamide copolymers of the viscosity-temperature profile shows a maximum between 60° and 80°C but does not greatly change (factor of 5) whereas some of the NIA copolymer solutions show a reversible thousand fold viscosity decrease in going from 10° to 30°C. Apparently the lower critical solution temperature (about 30°) brings on polymer aggregation thus causing coil collapse that in turn prevents R_F -mediated inter-polymer association. These enormous viscosity changes may be of interest in a number of applications.

1.5 Synthesis of HM narrow MWD telechelics PDMA and PDMA block copolymers

1.5.1 Telechelic polymers

Narrow molecular weight distribution water soluble PDMA has been prepared by anionic polymerization initiated by a number of K and Cs initiators in THF at -78° C.¹⁰ Furthermore, the corresponding telechelic fluorocarbon (C_7F_{15}) and hydrocarbon ($C_{12}H_{25}$) functionalized PDMA's 15, 16, and 17 have been prepared by anionic polymerization of DMA initiated with naphthalene cesium in THF at -78° followed by reaction with $C_7F_{17}COCl$, $C_{17}H_{35}COCl$ or monomer 10a.^{5,11}

In contrast to 15 and 16 polymer 17 showed strong intermolecular association even at low concentrations.¹¹ This indicates again (see Section 1.1) that water-soluble spacers play an important role in enhancing hydrophobic association of HM R_F and R_H polymers.

1.5.2 Block copolymers

Narrow MWD PDMA-PMMA hydrophilic-hydrophobic block copolymers were synthesized by anionic polymerization of DMA followed by addition of MMA.¹² Interestingly the sequence could be reversed without increasing MWD's. Excellent agreement was obtained between calculated and experimentally determined molecular weights and relative block lengths

1.6. Studies of Telechelic R_F (R_H) Derivatives of Polyethyleneglycols

1.6.1 Viscometric and light-scattering studies¹³

The aggregation of telechelic R_F and R_H PEO derivatives was studied by viscometry and static and dynamic light scattering in methanol and water.¹³ In contrast to methanol, in water the $R_F(\text{R}_H)$ PEO derivatives were shown to be extensively aggregated even at very low polymer concentration (<100 ppm).

The presence of the C_8F_{17} group caused stronger aggregation than the shorter perfluorocarbons as shown by the much higher (factor of 10) viscosities than the C_7F_{15} derivatives of the same PEO (MW = 8000) that in turn were more strongly (factor 10-100) viscosifying than the C_6F_{13} derivatives.

The viscosifying ability of the C_7F_{15} PEO derivatives were shown to be comparable to that of $C_{16}H_{33}$ PEO derivatives illustrating the extraordinary tendency toward aqueous aggregation of the R_F groups.

Static and dynamic light scattering studies indicated that the $(C_8F_{17})_2\text{PEO}$ (MW = 35,000) is associated into large polymer clusters (MW = 800,000) containing an average of 23 chains. Comparison of the hydrodynamic and gyration radii indicated the polymer cluster to be highly branched and consistent with R_F aggregates containing an average of four C_8F_{17} groups.

1.6. Fluorine-¹⁹NMR studies

In collaboration with Professor A Margaillan (Universite' de Toulon, France) we have synthesized and studied hydrophobic association in aqueous solutions of C_8F_{17} end functionalized telechelic polyethylene glycol, $(C_8F_{17}-PEG-C_8F_{17})$ with a MW of about 10^4 and have studied hydrophobic association by ^{19}F NMR viscometry and size exclusion chromatography.¹⁴

Both the reduced viscosity and ^{19}F NMR data point to an R_F aggregation numbers in excess of 2. Thus at high molar R_F concentrations ($C > 10^{-2}$ M) the ^{19}F NMR shows a strong resonance at -83 ppm. At 10^{-3} M there is an additional downfield resonance at -81 ppm and at 10^{-4} M the downfield resonance predominates. These observations indicate a concentration dependent equilibrium between a more highly aggregated species at -83 ppm and a less aggregated species at -81 ppm but inconsistent with a simple pair-wise inter-or intramolecular association of R_F groups. The upfield resonance is also appreciably broader than the down field resonance indicating a lower degree of mobility of the R_F group in this aggregate. (see Proposed Research) SEC analysis of very dilute solutions shows the prescence of highly aggregated polymer clusters (cluster size of about 20 polymers) in agreement with our earlier data on similar systems.(Section 1.6.1)

1.6.2 Effect addition of beta-cyclodextrin

Addition of beta-cyclodextrin to aqueous solutions of the R_F PEG R_F leads to dramatically lowered reduced viscosities that are similar to that of the unfunctionalized PEG.¹⁵ Significantly the ^{19}F upfield resonance is now replaced by a strong down field resonance indicating that the fluorocarbon group hydrophobically binds to the CD cavity and that this binding disrupts the R_F aggregate.(see Proposed Research)

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Figure 1. Effect of the contents of comonomers 2(x 3 (O), 4 (Δ), and 5 ($\square$) on the viscosities of 0.50 wt % copolymer solutions at 0.42 s⁻¹ shear at 30.0°C.

Figure 2. Effect of the contents of comonomers 6 (Δ), 7 (O), 8 ($\square$) and 9 ($\blacksquare$) on the viscosities of 0.50 wt % copolymer solutions at 0.42 s⁻¹ shear at 30.0°C.

Figure 3 Reduced viscosity as a function of concentration of copolymer P-E4-100 ($\blacksquare$) and of homopolymer P-E0-000 (Δ) in water at 25.0°C

Figure 4 Brookfield viscosity at 0.4 s⁻¹ shear rate as a function of concentration of copolymer P-E4-100 ($\blacksquare$) and of homopolymer P-E0-000 (Δ) in water at 25°C.

Figure 5 Effect of added surfactant on solution viscosity of bulk copolymers with different FOSA comonomer contents: 0.4 ($\blacksquare$), 0.2 ($\bullet$), 0.1 (Δ) mol % at 5 wt % concentration with 0.4 s⁻¹ shear rate.

Figure 6. Brookfield viscosity as a function of added NaCl for copolymer P-B2-02 at 5 wt % polymer concentration with 0.4 s⁻¹ shear rate in the presence of APFO surfactant (15 x 10⁻³ M).

Figure 7 Monomer concentration as a function of time for the copolymerization of DMA and FOSA in 2 mL of D₂O at 50 °C: DMA (■); FOSA (▲). [FOSA] = 8×10^{-3} M; [AM] = 0.8 M; [acetone] = 16 vol %; [(NH₄)₂S₂O₈] = 4×10^{-3} M; [Na₂S₂O₃] = 4×10^{-3} M.

Scheme 2. Surfactant-Mediated Copolymer Association (1) and Dissociation (2)

Table 1. Copolymerization of DMA and FOSA at 50 °C in Water

sample code ^a	FOSA (mol %)		yield ^c (%)	[η] ^d (dL/g)	M_n^e ($\times 10^{-6}$)	M_w^f ($\times 10^{-6}$)	M_n^g ($\times 10^{-5}$)	MWD ^h
	added	obsd ^b						
P-E0-000	0	0	95.5	5.35	3.9	3.2	8.2	3.90
P-E1-008	0.008		91.3	4.46	3.0	2.6	6.8	3.82
P-E2-024	0.024		93.7	5.19	3.8	3.2	8.1	3.95
P-E3-048	0.048	0.05	96.6	4.48	3.0	2.8	7.0	4.01
P-E4-100	0.100	0.10	95.1	5.20	3.8	3.1	7.8	3.96
P-E5-200	0.200	0.19	97.2	5.67	4.3	3.4	9.7	3.50
P-E6-398	0.398	0.41	99.1	4.54	3.1	3.0	8.3	3.62
P-E7-794	0.794	0.78	99.9	4.92	3.5	2.9	7.4	3.92
P-E8-1575	1.575	1.56	98.5	5.18	3.8	3.0	7.8	3.84

^a The letters P and E refer to PDMA and emulsion polymerization, respectively, the digit following E refers to a sample series number, and the last three digits divided by 1000 refer to the comonomer content in the monomer mixture (in mol %). ^b Calculated by the integration of ¹⁹F NMR in CD₃OD in the presence of CF₃SO₃Na. ^c Determined gravimetrically. ^d Measured by capillary viscometry in MeOH at 25 °C. ^e Calculated from [η] with $K = 17.5 \times 10^{-5}$ dL/g, $\alpha = 0.68$ in MeOH.²⁹ ^f Determined by SEC in THF, using polystyrene standards.

Table 2. Copolymerization of DMA with FOSA and LA at 65 °C in Bulk^a

sample code ^b	FOSA (mol %)		yield ^d (%)	[η] ^e (dL/g)	M_n^f ($\times 10^{-5}$)	M_w^g ($\times 10^{-5}$)	M_n^h ($\times 10^{-4}$)	MWD ⁱ
	added	obsd ^c						
P-B0-00	0	0	91	1.24	4.6	4.0	6.9	5.78
P-B1-01	0.1	0.11	91	1.20	4.4	3.7	6.4	5.92
P-B2-02	0.2	0.17	90	1.22	4.5	4.1	7.0	5.89
P-B3-02	0.2 ^a	0.18	92	0.91	2.9	2.4	4.0	5.95
P-B4-04	0.4	0.38	93	1.27	4.8	4.3	7.5	5.73
P-B5-10	1.0 ^a		93	1.17	4.2	4.9	9.5	5.15

^a DMA (5 g) with 2 mg of AIBN. ^b The letters P and B refer to PDMA and bulk polymerization, respectively, the digit following B refers to a sample series number, and the last two digits divided by 10 refer to the comonomer content in the monomer mixture (in mol %). ^c Calculated by the integration of ¹⁹F NMR in CD₃OD in the presence of CF₃SO₃Na. ^d Determined gravimetrically. ^e Measured by capillary viscometry in MeOH at 25 °C. ^f Calculated from [η] with $K = 17.5 \times 10^{-5}$ dL/g, $\alpha = 0.68$ in MeOH.²⁹ ^g Determined by SEC in THF, using polystyrene standards. ^h AIBN (5 mg) was added. ⁱ LA was used instead of FOSA.

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