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Synthesis and Characterization of One-Ended Perfluorocarbon-Functionalized Derivatives of Poly(ethylene glycol)s

Huashi Zhang, Jing Pan, and Thieo E. Hogen-Esch*

Loker Hydrocarbon Research Institute, University of Southern California,
Los Angeles, California 90089

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ABSTRACT: PEG derivatives of molecular weights of approximately 5K and 10K and end-functionalized with C_6F_{13} groups in aqueous solutions show strong association of the perfluorocarbon end groups into dimers as indicated by ^{19}F NMR and reduced viscosity studies. In sharp contrast, the C_8F_{17} derivatives in aqueous media appear to associate into micelles. Association of the C_6F_{13} groups is favored by a lower PEG molecular weight, presumably due to excluded volume interactions. Addition of NaCl and increasing temperature favors association of the 5K C_6F_{13} derivative, consistent with hydrophobic association. Increasing temperature also promotes hydrophobic association into dimers as indicated by a positive change in the entropy of association, ΔS, of 21 cal mol^{-1} K^{-1} and a relatively large positive value of the change in the enthalpy of association, ΔH, of 3.5 kcal/mol. Viscometric studies appear to be consistent with the fluorine-19 NMR studies but additionally suggest the occurrence of hydrophobic interactions of the perfluorocarbon groups with the PEG surfactants.

Introduction

Associative thickeners are water-soluble polymers containing hydrophobic substituents that undergo hydrophobic association in aqueous solution.[1−3] A well-known class of these polymers is that of the telechelic hydrophobic ethoxylated urethane (HEUR) polymers, which are poly(ethylene glycol)s (PEGs) end-functionalized through urethane linkages with hydrophobic end groups.[4] Because of their relatively well-defined structures, HEUR polymers have been used as models in molecular studies of hydrophobic association processes. Most of the early studies of HEUR thickeners were focused on rheological measurements.[2−7] More recently physicochemical characterizations have included static and dynamic fluorescence,[3−11] static and dynamic light scattering,[12,13] surface tension,[14−16] and NMR self-diffusion.[14−16] However, most of these studies were carried out on HEUR-segmented copolymers prepared by polycondensation of PEG of low molecular weight with a diisocyanate. The association behavior of such polymers is difficult to interpret because of the possible occurrence of both inter- and intramolecular hydrophobic association and because of the wide molecular weight distributions of these polymers. More recently, PEGs of low polydispersities prepared by a direct modification of the hydroxyl groups of PEG were synthesized and studied by small-angle X-ray scattering (SAXS), small-angle neutron scattering (SANS), NMR relaxation, self-diffusion, and ESR measurements.[17−21]

Recently we have shown that fluorocarbon (R_F) functionalized polyacrylamides, polydimethylacrylamides and similar polymers synthesized by copolymerization of hydrophilic monomers and perfluorocarbon -containing comonomers exhibit much stronger hydrophobic association than that of the corresponding hydrocarbon derivatives.[22−24] However because the perfluorocarbon groups in these cases are pendent, the distribution of such groups unavoidably varies making interpretation of association behavior difficult. Thus better-defined models are of interest. Hydrophobic association of R_F-functionalized PEGs has been studied, and as expected stronger hydrophobic association was observed for the R_F end-functionalized PEGs than the corresponding hydrocarbon (R_H) derivatives.[25,26] However, hydrophobic association of telechelic end-functionalized PEGs involves both intermolecular and intramolecular association, thus complicating the studies.

We now describe the synthesis and characterization by ^{19}F NMR and viscometry of narrow molecular weight distribution PEG derivatives having nominal molecular weights of 5000 or 10000 and end-functionalized with C_6F_{13} or C_8F_{17} groups. The effects of (a) the PEG molecular weight, (b) the size of the R_F groups, (c) the presence of NaCl or methanol, and (d) the effect of temperature on the association of these PEG derivatives are reported.

Experimental Section

Reagents and Solvents. Poly(ethylene glycol) monomethyl ether (MW = 5000 M_w/M_n = 1.10) was obtained from Fluka, Poly(ethylene glycol) monomethyl ether (MW = 10,000 M_w/M_n = 1.10) was obtained from Shearwater. Isophorone diisocyanate (IDI, Aldrich) was freshly distilled under vacuum. The hydrophobic alcohols, 1*H*,1*H*,2*H*,2*H*−perfluorooctanol and 1*H*,1*H*,2*H*,2*H*−perfluorodecanol (PCR) were dried by evacuation on the vacuum line (10^{-5} Torr) before use. Dibutyltin diacetate (Aldrich) was used without further purification.

Acetone, dimethylformamide (DMF), methanol, hexane, diethyl ether (DEE), and THF were obtained from Mallinckrodt (reagent grade or ACS grade) and used as received. THF was dried by distillation over Na/K alloy in cases where this was necessary. Deionized water was obtained with the use of a "Polymetric" water treatment system containing two mixed column tanks connected in series.

Synthesis of the One-Ended Fluorocarbon-Functionalized PEGs. Poly (ethylene glycol) monomethyl ether (5 g) samples with DP values of 120 and 250 were dried under vacuum overnight and then heated at 60 °C with vigorous stirring under high vacuum (10^{-5} Torr**)** for 2−3 h to remove residual water. They were then reacted with 50 equiv of IDI under argon in 100 mL of dry THF at 45 °C for 48 h. The reaction mixture was precipitated in ethyl ether to give a product that was shown by SEC to contain one IDI moiety per PEG. This product was reacted with 1*H*,1*H*,2*H*,2*H*-perfluoro-

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Scheme 1. Synthesis of One-Ended Fluorocarbon-Functionalized PEG Derivatives

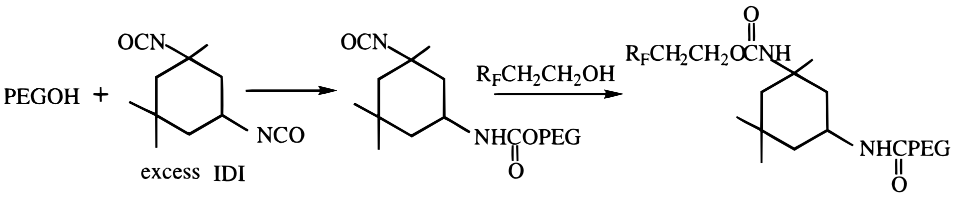


Table 1. Fluorocarbon-Functionalized PEG Derivatives

Samples[a]	R_F	M_p of PEG Precusors[b]	M_p[b]	PDI[b]	F (%)[c]
FP605M	C_6F_{13}	5250	5840	1.10	92
FP805M	C_8F_{17}	5250	6020	1.09	98
FP610M	C_6F_{13}	10500	11200	1.10	90
FP810M	C_8F_{17}	10500	11500	1.10	95

[a] Sample codes are as follows: FP stands for fluorocarbon modified PEG; the first number (6 or 8) stands for C_6F_{13} or C_8F_{17}; the next two numbers stand for the MW of PEG (in thousand) and M is one-ended functionalization. [b] Determined by SEC in THF calibrated by PEG standards. [c] Degree of the functionalization determined by ^{19}F NMR in methanol using CF_3SO_3Na as internal standard.

octanol or 1*H*,1*H*,2*H*,2*H*-perfluorodecanol (5 equiv) in THF for 48 h, in the presence of two drops of dibutyltin diacetate solution as the catalyst. The reaction mixture was precipitated in DEE followed by dissolution in THF and reprecipitation in DEE to remove the excess perfluoro alcohol (Scheme 1).

Viscosity Measurements. Capillary viscometry measurements were carried out using an Ubbelhode viscometer (Cannon no. 100). The temperature was kept at 25.0 °C with the use of a VWR model 1120 temperature regulator.

SEC Measurements. The samples were analyzed on a "Waters" HPLC component system (600E) equipped with two "Waters" ultra-u-styragel columns (500, 10 000 A) and two detectors (refractive index and ultraviolet) at a flow rate of 1.0 mL/min in THF at 25 °C using narrow distribution PEG calibration standards (Polysciences).

Fluorine-19 NMR Studies. Fluorine-19 NMR spectra were recorded either on a Bruker AM-360 FT-NMR spectrometer operating at 339 MHz using a 5 mm quadrinuclear probe (^1H, ^{13}C, ^{19}F, and ^{31}P) or on a Bruker WM 270 spectrometer at 254 MHz using a 10 mm dual nuclear probe (^1H and ^{19}F). Chemical shifts were referenced to aqueous $NaSO_3CF_3$ at −78.25 ppm. Since the T_1 value of the internal standard $NaSO_3CF_3$ is 4 s,[27] a 20 s relaxation delay was used for the spectra requiring quantitative data. Acquisition parameters were as follows: spectral width, 30 000 Hz; acquisition time, 0.56 s; pulse widths, 9 ms at 360 MHz and 16 ms at 270 MHz. The number of acquisitions varied from 8 to 4000 depending on the sample concentration.

Fluorine-19 assignments for FP605M (see Table 1 for code names) were obtained by COSY (Figure 1). Because of the larger four bond ^{19}F coupling constants,[28] these were used instead of three bond couplings for the purpose of identifying the peaks.

Results and Discussion

Synthesis of the One-Ended Fluorocarbon-Functionalized PEGs. The synthesis of one-ended fluorocarbon functionalized PEG derivatives is similar to that described by Glass et al.[29] for hydrocarbon-functionalized PEG derivatives except that fluorocarbon alcohols ($R_FCH_2CH_2OH$) were used in our case (Scheme 1). Thus the C_6F_{13} and C_8F_{17} derivatives (FP605M, FP805M, FP610M, and FP810M (the first digit gives the carbon number of the R_F group and the second two digits give the molecular weights in thousands) were synthesized from narrow molecular weight distribution PEGs (PDI = 1.1) with nominal molecular weights of 5000 and 10 000 (Table 1). SEC analysis indicated the complete absence of the coupled polymer containing two PEG chains. The degree of functionalization of the R_F derivatives was determined by ^{19}F NMR in methanol with $NaSO_3CF_3$ as internal standard. High degrees of functionalization (>90%) were obtained in all four samples.

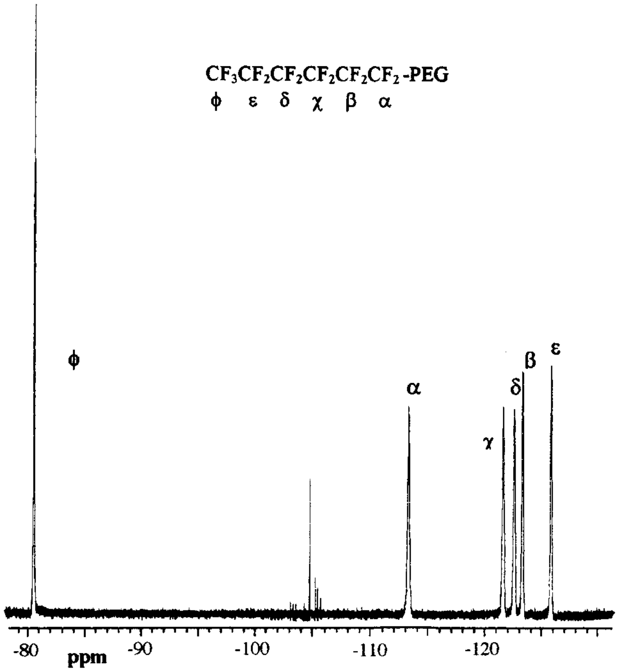


Figure 1. Fluorine-19 NMR assignments of the C_6F_{13} end-group of FP605M in $CHCl_3$.

Fluorine-19 NMR Studies. Effects of Concentration and PEG Molecular Weight. The ^{19}F NMR spectrum of the CF_3 group of FP605M in aqueous solutions shows a pronounced concentration dependence. Above 1.7×10^{-3} M, only a single broad absorption is visible at about −82.1 ppm (Figure 2).

At a lower concentration (1.7×10^{-3}M) the presence of a second species is revealed by the broadening and the asymmetry of the peak due to the presence of a shoulder corresponding to a lower MW species. Upon further dilution a distinct second downfield absorption (at −80.2 ppm) appears the relative magnitude of which increases at lower concentration. At about 5×10^{-5} M, the relative magnitude of the downfield absorption is about 5 times larger than that of the upfield absorption. The absorption at −80.2 ppm is assigned as the dissociated form of FP605M, while the upfield absorption (−82.1 ppm) appears to represent the associated form.

These changes are fully reversible and reproducible and appear to indicate changes in the degree of association upon dilution. For a simple association of nR_F

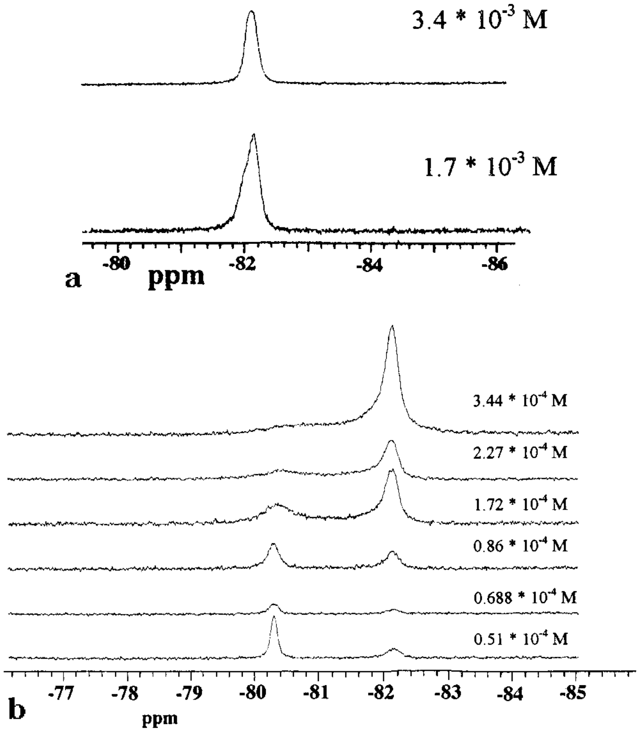


Figure 2. (a) ^{19}F CF_3 absorptions of aqueous FP605M solution with internal standard $NaSO_3CF_3$ ($\delta = -78.25$ ppm). (b) Concentration dependence of the ^{19}F NMR resonances of the CF_3 group in aqueous solutions of FP605M.

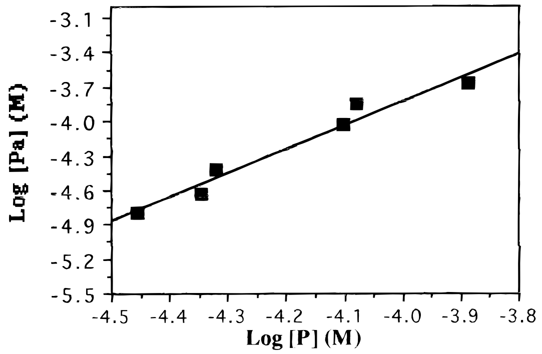


Figure 3. Double logarithmic plot of the relative magnitude of the up- and downfield CF_3 resonances of sample FP605M.

functionalized PEG's (P) into a micellar aggregate (P_n) we can write

$$nP \overset{K}{\rightleftharpoons} P_n$$

$$K = [P_n]/[P]^n \tag{1}$$

$$[P_n] = [P_a]/n = K[P]^n \tag{2}$$

$$\log[P_a] = n \log[P] + \log(Kn) \tag{3}$$

where $[P_n]$, and [P] represent the concentrations of the aggregated and nonaggregated PEG's, respectively, and K is the equilibrium constant. The concentration of P_n is evaluated from the magnitude of the upfield resonance, $[P_a]$ (eq 2). Thus, a plot of log $[P_a]$ versus log [P] is expected to give a straight line with a slope equal to the association number (n). As shown in Figure 3, the data of Figure 2 gives a slope of close to 2, consistent with a monomeric-dimeric equilibrium in the low concentration region (10^{-5}–10^{-3} M). The corresponding value of K is equal to $(1.8 \pm 0.5) \times 10^4$ M^{-1} (Table 2).

Table 2. Association Numbers, Association Constants and Cmc of Fluorocarbon-Modified PEG Derivatives

	NaCl (M)	association constant (K)	association no. (n)	cmc (M)
FP605M	0	1.8×10^4	2	
	0.4	4.1×10^4		
	0.6	1.0×10^5		
FP610M	0	8×10^2	2	
FP805M	0		>10	1.5×10^{-6}
FP810M	0		>10	7.0×10^{-6}

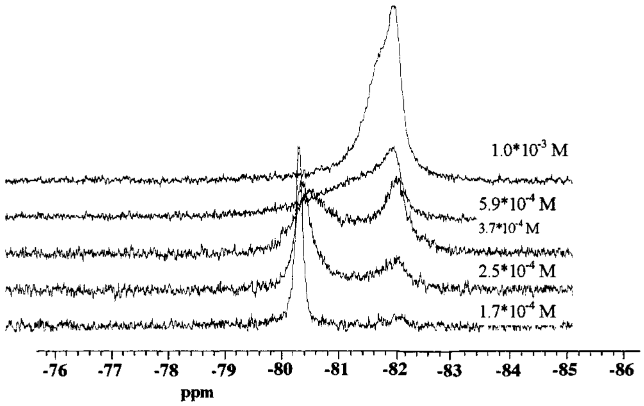


Figure 4. Concentration dependence of the ^{19}F NMR resonances of the CF_3 group in aqueous solutions of FP610M.

The ^{19}F NMR spectra for FP610M gives the same characteristic −82.1 and −80.2 ppm absorptions as observed for the lower MW derivative (FP605M) and a similar concentration dependence of the relative magnitudes of the two absorptions was observed (Figure 4). However, in this case the extent of association at a given concentration was found to be lower than for FP605M, consistent with a greater excluded volume due to the larger hydrodynamic size of the longer chain of FP610M.

For instance at about 1×10^{-4} M., the downfield absorption at −80.3 ppm dominates, and at 1×10^{-3} M, there still appears to be an absorption corresponding to the dissociated polymer although the absorption has shifted to higher field. The association number (n) and the association constant (K) of FP610M were determined based on the same method used for FP605M. A value for the association number of about 2 was obtained.

The association constant of about 800 M^{-1} is more than 20 times lower than for FP605M (Table 2). The lower association constant of FP610M compared to FP605M is consistent with the expected greater excluded volume upon formation of this dimer. Similar effects have been observed for hydrocarbon PEG surfactants. Thus for surfactants of the structure: $C_9H_{19}C_6H_4(OCH_2CH_2)_nOH$ the cmc of the surfactant with $n = 50$ was 2.8×10^{-4} M whereas that of the surfactant containing PEG of a higher molecular weight ($n = 100$) was about 4 times higher.[30]

As the concentration of FP610M increases, the downfield resonances broaden and move upfield. This is also observed in the ^{19}F spectra of FP605M (Figure 2), but it is somewhat less pronounced. We tentatively interpret this interesting behavior as due to exchange between the monomeric and dimeric species on the NMR time scale. Since the formation of the dimer (P_2) from the monomer (P) is bimolecular, the lifetime of the monomeric species, being inversely proportional to both the concentration of P and the rate constant of dimer-

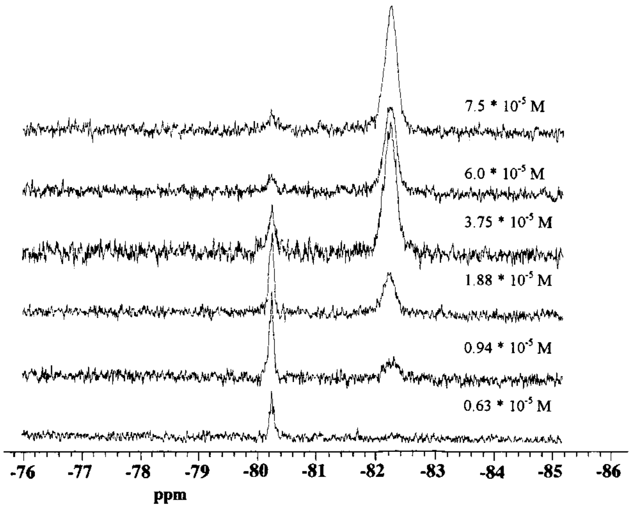


Figure 5. Concentration dependence of the ^{19}F NMR resonances of the CF_3 group in aqueous solutions of FP810M.

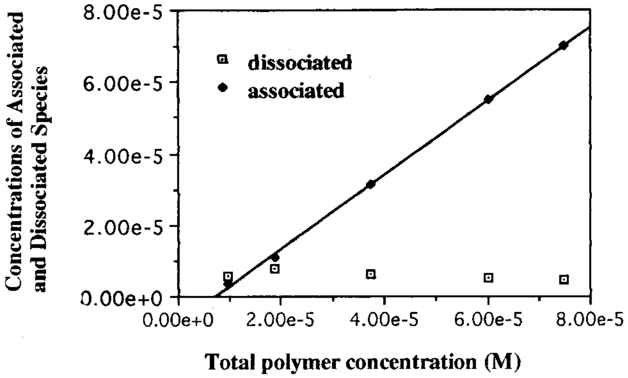
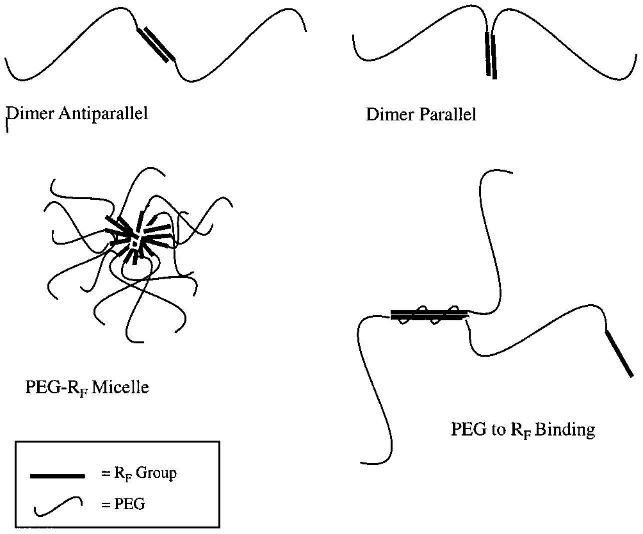


Figure 6. Concentration dependence of the fractions of disscociated and associated forms of FP810M.

Scheme 2. Modes of Association of R_F End-Functionalized PEGs



ization, decreases with increasing concentration of the monomer P and thus with the total polymer concentration. However, because the dissociation of the dimer into monomer is unimolecular, the half-life ($t_{1/2}$) of the dimer is concentration independent. Thus at higher polymer concentrations the chemical shift of the monomeric species is expected to shift upfield.[31]

Perfluorocarbon Group Effects. In contrast to the C_6F_{13} derivatives, the concentration of the dissociated form of FP810M corresponding to the downfield resonance was observed to be *independent* of the total polymer concentration whereas the concentration of the associated form increased with total polymer concentration (Figures 5 and 6). This behavior is also observed for typical surfactant systems, where the concentration of the monomeric surfactant above the cmc is independent of the total surfactant concentration, and equal to the cmc.[32] This indicates that FP810M behaves as a typical surfactant with a cmc value of 7×10^{-6} M which equals the concentration of the dissociated species. Above a concentration of 10^{-4}M, this PEG surfactant therefore should exist as a micelle (Scheme 2). Although the data do not allow an estimation of the degree of aggregation, the constant concentration of the dissociated species [P] suggests a large association number ($n > 10$) as indicated by eq 3.

As was the case for the C_6F_{13} derivatives, the hydrophobic association of FP805M having a lower PEG molecular weight than FP810M occurs at an even lower concentration. Only at a total polymer concentration of about 1×10^{-5} M does the resonance of the dissociated form become visible (about 10%), with an estimated concentration of about 1×10^{-6} M. Because of NMR sensitivity limitations the ^{19}F spectra of FP805M below 10^{-5} M could not be obtained. However, the line shapes of the two characteristic absorptions ($\delta = -80.2$ and -82.1 ppm) of FP805M judging from its ^{19}F spectrum at 1.4×10^{-5} M are similar to that of FP810M. Assuming that, as for the case for FP810M, the magnitude of the downfield resonance is concentration independent, the cmc of FP805M thus is estimated as about 1×10^{-6} M (Table 2). The greater apparent degree of association of the C_8F_{17} compared to that of the C_6F_{17} PEG derivatives is consistent with stronger hydrophobic association of these longer perfluorocarbon chains. As in the case of the C_6F_{13} derivatives the degree of association of the C_8F_{17} polymer surfactants decreases with increasing PEG length presumably as a result of greater excluded volume interactions.

As shown in Figure 5, and in sharp contrast with the C_6F_{13} derivatives, the ^{19}F resonances and chemical shifts of FP810M are concentration independent and less broad. The same is the case for the other resonances of this polymer and for the CF_3 resonances of FP805M. This would be consistent with a slower monomer–aggregate exchange on the NMR time scale and a slower rate of micellar dissociation due to the stronger interaction between the longer perfluorocarbons (see below).

Effects of Addition of NaCl. The effect of addition of NaCl on the intermolecular association of FP605M is illustrated in Figure 7. The relative magnitudes of the CF_3 upfield absorption over the downfield absorption increases with increasing NaCl concentrations. Clearly the monomer–dimer equilibrium shifts toward the dimer (P_2) at higher salt concentrations consistent with the salt effects expected for hydrophobic association and in agreement with our previous results in other hydrophobically associating fluorocarbon-modified water-soluble polymer systems.[22–24] The corresponding association constants using an association number of 2.0 are listed in Table 2.

Temperature Effects. The effect of temperature on the association of a 1.3×10^{-4} M. aqueous solution of FP605M is shown in Figure 8. As shown above, two separate CF_3 absorptions are observed at 4.8 °C repre-

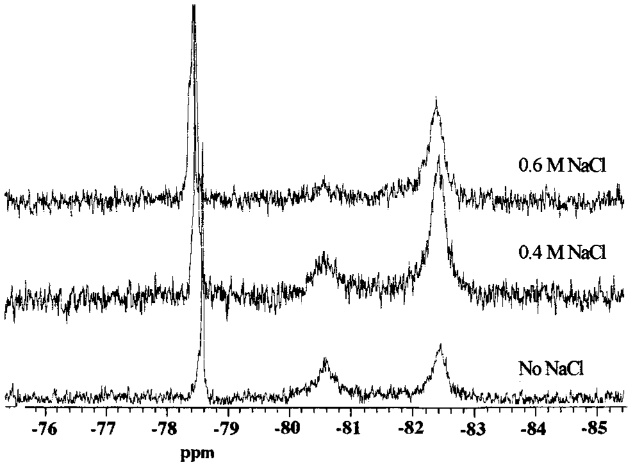


Figure 7. Effect of addition of NaCl on the fractions of associated and dissociated forms of aqueous solutions of FP605M.

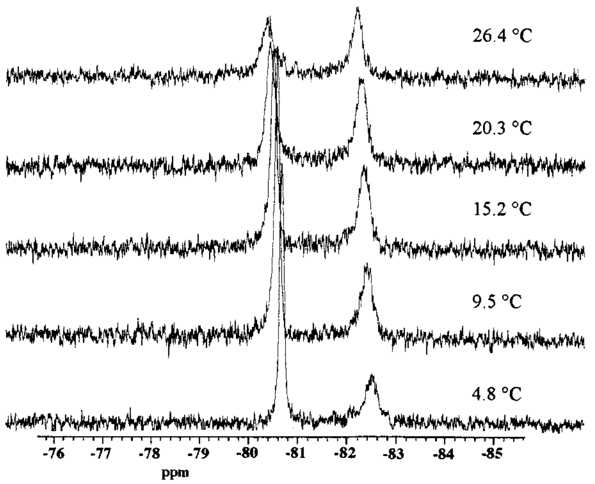


Figure 8. Effect of temperature on the ^{19}F NMR resonances of the CF_3 group of FP605M in aqueous solutions.

senting the unassociated and dimeric form of FP605M. Upon heating, the relative magnitude of upfield absorption increases, consistent with an entropy driven aqueous hydrophobic association process.[33,34] The association constants (K) at various temperatures are calculated by the relative magnitudes of the upfield and downfield absorptions using an association number of 2.0, and a plot of ln K versus $1/T$ gives a ΔH value for the change in enthalpy of the formation of the dimer of + 6.9 kcal mol^{-1} K^{-1} and a corresponding ΔS value of + 42 cal mol^{-1} K^{-1} corresponding to values of +3.45 kcal and +21 cal mol^{-1} K^{-1} per polymeric surfactant. (Figure 9). The large positive value of ΔS confirms the hydrophobic nature of the entropy driven association process. The value of ΔS is comparable to that of fluorocarbon nonionic surfactants (30−33 cal mol^{-1} K^{-1}), but the magnitude of ΔH is significantly higher than that of nonionic fluorocarbon surfactants that are on the order of 0−2 kcal mol^{-1} K^{-1}.[33] The exact reason for the unusually high value of the ΔH value is currently unclear.

Effect of Organic Solvents. As shown in Figure 10 upon addition of methanol to aqueous solutions of FP605M, the broad upfield CF_3 absorption (−82.2 ppm) gives way to several narrower downfield absorptions, and eventually a CF_3 absorption is observed similar to that seen in pure methanol. Clearly, as the methanol content increases, the relative magnitude of the upfield absorption decreases and multiple new downfield resonances appear, the nature of which is not understood in detail. However, it is clear that the extent of association decreases with increasing methanol content, consistent with the breakup of the micellar polymers into more dissociated species and consistent with the largely hydrophobic nature of the interactions.

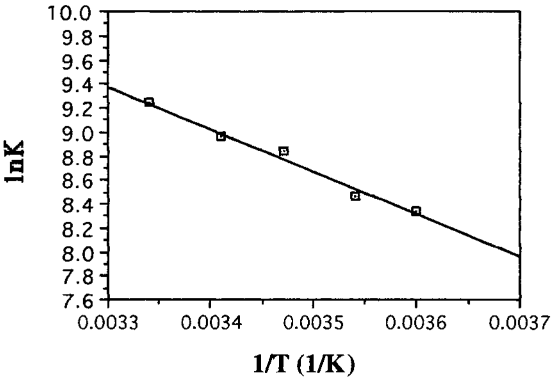


Figure 9. Temperature dependence of the fractions of associated and dissociated forms of aqueous solutions of FP605M.

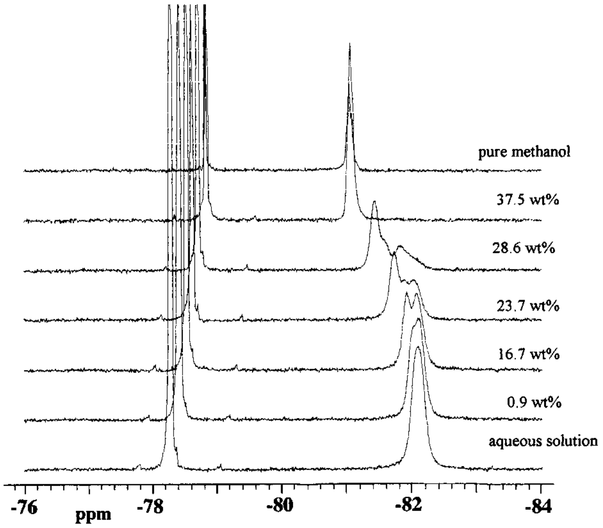


Figure 10. Effect of methanol concentration on the ^{19}F NMR resonances of the CF_3 group in aqueous solutions of FP605M.

Viscosity Studies. As shown in Figure 11, the end functionalized PEGs (FP605M and FP805M) have higher reduced viscosities than the unmodified precursors, indicating the existence of hydrophobic association. Below 2.0 g/dL, (3.4×10^{-3} M) FP605M shows a reduced viscosity that is similar to that of the corresponding unmodified PEG (MW = 10 000), but at higher concentration, the reduced viscosity increases sharply. Apparently, at about 2.0 g/dL, FP605M has a hydrodynamic size that is similar to that of PEG of a molecular weight of 10 000, confirming predominantly dimeric association in agreement with the ^{19}F NMR results. This is in good agreement with the NMR spectra that indicate that dimerization is largely complete at this concentration (about 3.3×10^{-3}M.)

It is remarkable that the association into dimers appears to occur far below the critical concentration, c^*, for the PEG precursor (molecular weight of 5000) that would be expected to be on the order of 6 g/dL. Above about 2.5 g/dL the reduced viscosity of FP605M increases sharply. This increase would appear to be

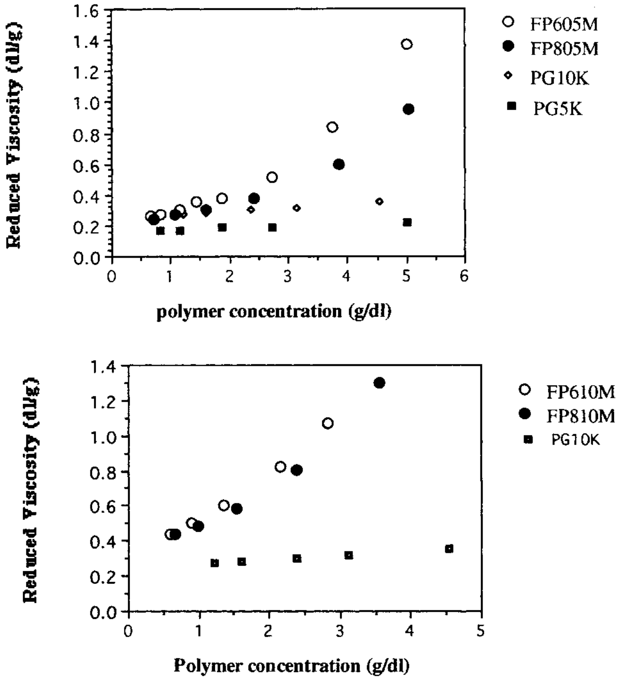


Figure 11. (a) Reduced viscosity vs concentration profiles of FP605M, FP805M, and unmodified PEGs. (b) Reduced viscosity vs concentration profiles of FP6110M, FP810M, and PEG precursor.

inconsistent with micellization into trimers or higher aggregates since the reduced viscosity of such a species would be *lower* than that of the dimer.[35] It is possible that this increase is due to hydrophobic binding of PEG segments to the dimeric perfluorocarbon moieties thus leading to chain extension (Scheme 2).

Above about 2.5 g/dL the reduced viscosity of FP805M, having a larger C_8F_{17} end group, surprisingly, is *smaller* compared to that of the C_6F_{13} one-ended derivative. This difference could be due to the formation of star-shaped polymers by micellization of FP805M. The formation of micelles containing a sizable number of polymeric surfactants is consistent with this (see above NMR results).[35] However, the reduced viscosities of FP805M above 2.5 g/dL are larger than the estimated value of the PEG of a molecular weight of 10 000, and this again would be inconsistent with only micellization.

As pointed out above, the marked viscosity increases with concentration might perhaps be due to intermolecular interactions between the perfluorocarbon groups and the PEG chains. Such interactions between PEG and hydrocarbon surfactants have been documented and appear to be at least partially hydrophobic in nature.[32]

Similar but less pronounced reduced viscosity vs concentration profiles are seen for the FP610M and FP810M polymers. In this case the reduced viscosities of the two polymeric surfactants are essentially identical over the concentration range studied. Both exhibit higher reduced viscosities compared with the unmodified PEG precursor (Figure 11b) and consistent with the occurrence of intermolecular interactions of associated R_F groups and the PEG chains.

The nature of—what would appear to be- the intermolecular dimers of FP605M and FP610M is of considerable interest since such dimers could exist in parallel—and antiparallel—forms and analogous intramolecular cyclic forms may exist also (Scheme 2). The present data do not allow us to distinguish between these isomers. A consideration of such structures formed from polymeric water-soluble end-functionalized fluorocarbon derivatives would lead to the prediction that the antiparallel forms would be preferred since it would allow a greater distance between the two hydrophilic chains thus minimizing excluded volume interactions. However, in the present case the situation is more complicated since the present polymers have a cyclohexyl moiety positioned between the PEG and the R_F groups. Since hydrocarbons and perfluorocarbons do not mix readily,[36] in this case the parallel dimer would be favored by the "matching" hydrocarbon and perfluorocarbon segments. In this respect a comparison of the association properties of the present polymers and polymers lacking such hydrocarbon segments would be of interest.

The influence of perfluorocarbon size on the hydrophobic association of one-ended fluorocarbon modified PEG derivatives is larger than expected. However, other rheology studies of similar telechelic C_6F_{13} and C_8F_{17} modified PEG (MW = 35 000) derivatives indicate that the C_6F_{13} derivative has a much faster relaxation time (1.4 vs 66 ms)[37] than that of the C_8F_{17} derivative, in agreement with the results obtained from the above ^{19}F NMR studies (see above). The relaxation time corresponds to exit of the hydrophobic group from the micelle and is the slowest step in the rearrangement of the network, an idea developed by Annable in terms of a transient network model and consistent with the above.[38]

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