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## Complex Formation of $\beta$ -Cyclodextrin- and Perfluorocarbon-Modified Water-Soluble Polymers

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The complex formation has been studied by  $^{19}\text{F}$  NMR and viscometry of  $\beta$ -cyclodextrin ( $\beta$ -CD) and water-soluble telechelic and one-ended perfluorocarbon derivatives ( $\text{C}_6\text{F}_{13}$  and  $\text{C}_8\text{F}_{17}$ ) of poly(ethylene glycol)s (PEGs) of molecular weights of 5000 and 10000 and poly(dimethylacrylamide)s containing  $\text{C}_8\text{F}_{17}$  pendent groups. Fluorine-19 NMR of the PEG derivatives shows  $\text{CF}_3$  resonances at about  $-80$  and  $-82$  ppm corresponding to monomeric and associated structures, respectively. For the case of the one-ended  $\text{C}_6\text{F}_{13}$  PEG ( $M = 5000$ ) derivatives, a formation constant on the order of  $10^4$  was determined. Addition of  $\beta$ -CD to this polymer leads to the formation of 1:1  $\beta$ -CD- $\text{R}_\text{F}$  complexes that gives  $\text{CF}_3$  resonances that are very close to that of the monomeric  $\text{RF}$  groups. Essentially quantitative complex formation with  $\beta$ -CD was observed in the presence of free  $\beta$ -CD concentrations larger than about  $10^{-2}$ – $10^{-3}$  M. The reduced viscosity of 1.0 wt % aqueous solutions of the telechelic PEG of MW of 10 000 containing  $\text{C}_8\text{F}_{17}$  end groups is greatly reduced as a result of intermolecular hydrophobic association. Addition of stoichiometric  $\beta$ -CD completely suppresses hydrophobic association in this solution, as demonstrated by a virtually complete loss of viscosity due to association. Similar reductions in viscosity were observed for the case of poly-(dimethylacrylamide) containing pendent groups. In this case a larger excess of  $\beta$ -CD was required to completely suppress  $\text{R}_\text{F}$  association.

### Introduction

Over the past few years we have synthesized fluorocarbon derivatives of water-soluble polymers such as polyacrylamide,<sup>1,2</sup> poly(*N,N*-dimethylacrylamide),<sup>3</sup> and (hydroxyethyl)cellulose.<sup>4</sup> In all of these cases hydrophobic intermolecular association of the  $\text{R}_\text{F}$  groups was demonstrated to be much stronger than for the corresponding hydrocarbon derivatives of the same carbon number.<sup>5</sup> However, the detailed structure of these polymers, particularly those synthesized in micellar systems,<sup>1,2</sup> is not yet well established. For this reason the behavior of model PEGs end-functionalized with perfluorocarbons is of interest.<sup>5–8</sup>

Association of hydrophobically modified water-soluble polymers has been the subject of intense scrutiny in recent

years.<sup>9–25</sup> Some of this activity has been focused on the relationship between the structure of such polymers and their association in aqueous media.

Because such relationships are often complex, the association of well-defined poly(ethylene glycol)s (PEGs) end-functionalized with long hydrocarbon groups has been the subject of considerable recent work.<sup>13–20</sup> However, such structure–property relationships are not necessarily transferable to associating polymers with pendent hydrophobic groups.<sup>21–25</sup>

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Thus the loss of entropy incurred upon association of end-functionalized PEGs is expected to be larger than that in associating polymers containing pendent groups because of the greater mobility of end groups generally and because inter- and intramolecular association in pendent type polymers typically involves multiple cooperative associations of hydrophobic groups along the polymer backbone that tend to decrease entropic losses upon association. Thus it would be of interest to develop methods allowing a better comparison between associating polymers having terminal and those with pendent groups.

An indication that there may be qualitative differences in the association of end-functionalized and pendent type perfluorocarbon associating polymers is provided by the observation that well-defined  $^{19}\text{F}$  NMR resonances are visible in  $\text{R}_\text{F}$  end-functionalized PEGs whereas for the corresponding pendent type polymers such resonances are broadened beyond recognition.<sup>2,3,5</sup>

Through monitoring of the complex formation of  $\beta$ -cyclodextrins with the  $\text{R}_\text{F}$  groups of the above and similar polymers, it may be possible to assess the type and perhaps the degree of the hydrophobic association of such polymers. Thus, in the presence of  $\beta$ -CD, the associated perfluorocarbon aggregates may be disrupted by the competitive formation of  $\beta$ -CD-perfluorocarbon complexes and, in turn, this could provide information on the mutual association of the  $\text{R}_\text{F}$  groups.

One of the most characteristic features of cyclodextrins (CDs) is their ability to form inclusion complexes with various hydrophobic or amphiphilic species by capturing different guest molecules inside their hydrophobic cavities.<sup>26</sup> Depending on the diameter sizes and volumes,  $\alpha$ ,  $\beta$ , and  $\gamma$ -cyclodextrins, can selectively complex molecules of various sizes.<sup>17</sup>

$\beta$ -Cyclodextrin ( $\beta$ -CD) has been shown to complex fluorocarbon surfactants more strongly than hydrocarbon surfactants due to a better fit of the larger  $\text{R}_\text{F}$  group in the relatively large CD cavity.<sup>28–31</sup> Thus 1:1 complexes of  $\beta$ -CD and perfluorocarbon surfactants are observed at low  $\beta$ -CD concentrations, with formation constants depending on

**Table 1. Fluorocarbon-Modified Polymers**

samples	type	$\text{R}_\text{F}$	$M_\text{p}$ <sup>a</sup>	end functionalization (%) <sup>b</sup>
FP810T	telechelic PEG derivative	$\text{C}_8\text{F}_{17}$	11300	96
FP605M	one-ended PEG derivative	$\text{C}_6\text{F}_{13}$	5840	92
FPM	DMA/FOSA copolymer	$\text{C}_8\text{F}_{17}$		FOSA content (0.1 mol %)

<sup>a</sup> Determined by SEC in THF calibrated by PEG standards.

<sup>b</sup> Determined by  $^{19}\text{F}$  NMR in methanol using  $\text{CF}_3\text{SO}_3\text{Na}$  as an internal standard.

perfluorocarbon length, the largest value being observed for  $\text{C}_7\text{F}_{15}$  derivatives.<sup>31</sup> At high  $\beta$ -CD concentrations 2:1 (CD: $\text{R}_\text{F}$ ) complexes have been demonstrated for longer chain  $\text{R}_\text{F}$  surfactants  $\text{C}_n\text{F}_{2n+1}\text{COONa}$  ( $n > 6$ ).<sup>31</sup>

In the following we report on the formation of  $\beta$ -CD complexes of PEGs end-functionalized with  $\text{C}_6\text{F}_{13}$  and  $\text{C}_8\text{F}_{17}$  groups and of poly(*N,N*-dimethylacrylamide) (PDMA) containing pendent  $\text{C}_8\text{F}_{17}$  groups.<sup>6</sup>

## Experimental Section

**Reagents.**  $\beta$ -Cyclodextrin ( $\beta$ -CD),  $\text{NaSO}_3\text{CF}_3$ , *N,N*-dimethylacrylamide (DMA), poly(ethylene glycol) (PEG), and isophorone diisocyanate (IDI) (Aldrich) were used as received. DMA and IDI were distilled under reduced pressure prior to use. The 2-(*N*-ethylperfluorooctanesulfonamido)-ethyl acrylate (FOSA) comonomer and the anionic  $\text{CF}_3(\text{CF})_6\text{COONH}_4$  (APFO) surfactant were donated by the 3M Co.<sup>32</sup> Acetone, diethyl ether (DEE), DMF, methanol and THF (Mallinckrodt, reagent grade or ACS grade) were used as received. Deionized water was obtained with a "Polymetric" Water Treatment System containing two mixed column tanks connected in series.

**Synthesis of Fluorocarbon-Modified PEGs and PDMA.** *Telechelic PEG Derivative (FP810T).* PEG ( $M_n = 10\,000$ ;  $M_w/M_n = 1.3$ ) was reacted with a large excess of  $\text{C}_8\text{F}_{17}\text{C}_2\text{H}_4\text{COCl}$  obtained from the reaction of  $\text{C}_8\text{F}_{17}\text{C}_2\text{H}_4\text{COOH}$  and  $\text{PCl}_5$ .<sup>33</sup> The PEG precursor was heated at 70 °C under a continuous flow of argon to remove HCl, and the  $\text{C}_8\text{F}_{17}\text{C}_2\text{H}_4\text{COCl}$  was added slowly in small portions. Near the end of the reaction (3–4 h), the temperature was increased to 100 °C in order to complete the reaction. The product, named FP810T, with the first digit indicating the number of carbons in the  $\text{R}_\text{F}$  group and the second two digits indicating the approximate molecular weight in thousands, was dissolved in  $\text{CHCl}_3$  and precipitated in petroleum ether followed by drying on the vacuum line at ambient temperature.

*One-Ended PEG Derivative (FP605M).* Poly(ethylene glycol) monomethyl ether (5 g) ( $M_n = 5300$ , Polysciences) was dried under vacuum overnight and then heated at 60 °C under high vacuum ( $10^{-5}$  Torr) for 2–3 h to remove residual water. It was first reacted with 50 equiv of IDI under argon in 100 mL of dry THF at 45 °C for 48 h (Chart 1). The reaction mixture was precipitated in DEE to remove unreacted IDI, and the product after drying was further reacted with 1*H*,1*H*,2*H*,2*H*-perfluorooctanol (5 equiv) in THF for 48 h, with addition 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 of the perfluoro alcohol.

*PDMA Copolymer (FPM).* The copolymerization of DMA and FOSA (DMA = 0.8 M, FOSA =  $8 \times 10^{-4}$  M, and 23 mL of  $\text{H}_2\text{O}$ ) was performed in a 50 mL round-bottom flask in the presence of 0.035 M APFO surfactant. The flask was placed in a mineral oil bath at 50 °C. Using two syringe needles as gas inlet and outlet, a stream of ultrapure grade argon (99.99%) was introduced into the flask for 30 min to remove oxygen. A  $\text{K}_2\text{S}_2\text{O}_8$  initiator

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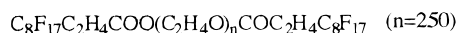
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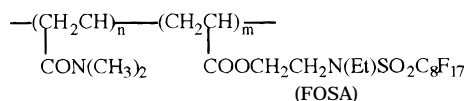
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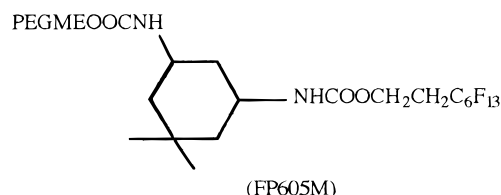
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**Chart 1. Structures of Perfluorocarbon Polymer Derivatives**

(FP810T)



(FPM)



(FP605M)

solution (0.0075 mmol) was then injected with a gastight syringe through the rubber septum into the flask containing the rapidly stirred reaction mixture. The polymerization was allowed to proceed at 50 °C for 24 h and was terminated by exposure to air followed by precipitation in acetone at −78 °C. The copolymer aqueous solution was dialyzed against a mixture of deionized water and methanol (50v/50v) to remove the last traces of surfactant.

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

Brookfield viscometry measurements were carried out by using a Wells Brookfield viscometer (LVT model) equipped with two different sizes of spindles (No. 18 and No. 34) and a temperature-control water bath at 25 °C. The viscosity in centipoise (cP) determined at different shear rates ( $\text{s}^{-1}$ ) was obtained by converting the direct readout at the corresponding rotational speed (rpm), using the range table supplied by the manufacturer. The shear rate was calculated from the rotational speed of the spindle.

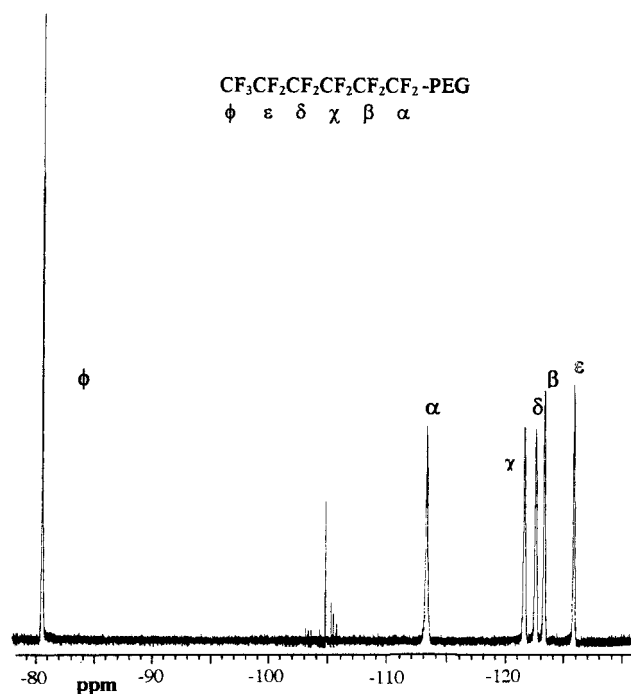
**Fluorine-19 NMR Measurements.** The  $^{19}\text{F}$  NMR spectra were recorded either on a Bruker AM-360 FT-NMR spectrometer operating at 339 MHz using a 5 mm quadrinuclear probe ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$ ) or on a Bruker WM 270 spectrometer at 254 MHz using a 10 mm dual probe ( $^1\text{H}$  and  $^{19}\text{F}$ ). The chemical shifts of the  $^{19}\text{F}$  signals were referenced to aqueous solutions of  $\text{NaSO}_3\text{CF}_3$  at −78.25 ppm. Since the  $T_1$  value of the internal standard is 4 s, a 20 s relaxation delay was used for the spectra requiring quantitative data. The acquisition parameters were as follows: spectral width, 30 000 Hz; acquisition time, 0.56 s; pulse width, 9  $\mu\text{s}$  at 360 MHz and 16  $\mu\text{s}$  at 270 MHz. The number of acquisitions varied from 8 to 4000 depending on the sample concentration.

The peak assignment of  $^{19}\text{F}$  FP605M was confirmed by COSY (Figure 1). Because the four-bond  $^{19}\text{F}$  couplings were larger,<sup>34</sup> these were used instead of three-bond couplings for the purpose of identifying the peaks.

**SEC Measurements.** The samples were analyzed on a "Waters" HPLC component system (600E) equipped with two "Waters" ultra- $\mu$ -Styragel columns (500, 10 000 Å) and RI and UV detectors at a flow rate of 1.0 mL/min in THF at 25 °C using narrow distribution PEG calibration standards (Polysciences). They were also analyzed on a Waters SEC equipped with three Shodex columns (OH Pak SB-804HQ, SB-806HQ, and a guard column OH Pak SB-800P) and a RI (Waters) detector at a flow rate of 0.8 mL/min in a 0.05 N solution of sodium acetate in deionized water filtered before use on a 0.10  $\mu\text{m}$  filter (Durapore).

**Results and Discussion****Fluorocarbon-Modified Water-Soluble Polymers.**

Well-defined structures and high degrees of functional-



**Figure 1.**  $^{19}\text{F}$  NMR peak assignments of the  $\text{C}_6\text{F}_{13}$  end group of FP605M in  $\text{CHCl}_3$ .

ization (>90%) were obtained for the end-functionalized PEG derivatives, as indicated by  $^{19}\text{F}$  NMR.<sup>11</sup> Hydrophobic association of the  $\text{R}_\text{F}$  end groups was studied by viscometry and  $^{19}\text{F}$  NMR. For aqueous solutions of the one-ended modified PEG derivative (FP605M) in the  $10^{-5}$ – $10^{-3}$  M concentration range, dimeric association prevails with an association constant of  $1.8 \times 10^4 \text{ M}^{-1}$ .<sup>6,35</sup> This dimeric association is also clearly seen by aqueous SEC. Figure 1b shows the presence of the unimer (a), dimer (b), and multimers (c) with apparent molecular weights of 5000, 10 000, and 30 000.

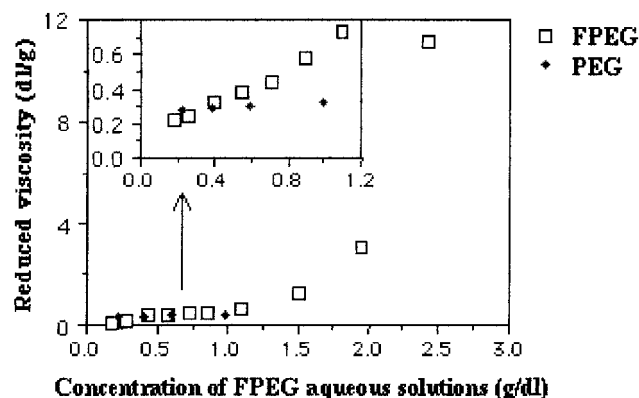
The DMA–FOSA copolymer FPM was synthesized by an APFO surfactant-mediated copolymerization of DMA and FOSA. The copolymerization kinetics indicated that the relative rates of reaction of acrylamide and FOSA were identical and remained the same throughout the polymerization, consistent with random incorporation of the comonomer.<sup>3</sup> The copolymer FOSA content (0.11 mol %) was determined in methanol by  $^{19}\text{F}$  NMR using  $\text{CF}_3\text{SO}_3\text{Na}$  as an internal standard and was found to be close to the calculated value.

**Complex formation of  $\beta$ -cyclodextrin and FP810T.** The hydrophobic association of the telechelic FP810T in aqueous solution was investigated by capillary viscometry. The reduced viscosity–concentration profile of FP810T above about 1.5 g/dL ( $1.4 \times 10^{-3}$  M) in water shows large increases, indicating intermolecular hydrophobic association through the  $\text{R}_\text{F}$  end groups (Figure 2). The reduced viscosities of the FP810T solutions begin to exceed that of the PEG precursor at a concentration of around 0.4 g/dL ( $2.8 \times 10^{-4}$  M), which is about 1 order of magnitude lower than the overlap concentration  $c^*$  (about 4 g/dL). The larger Huggins constant of FP810T compared with that of the PEG precursor (25 vs 1.1), obtained between 0.2 and 1.0 dL/g, is also consistent with strong intermolecular association, as well as with the lower intrinsic viscosity of FP810T (0.14 g/dL) is consistent with a strong intramolecular association of FP810T at very low concentration.

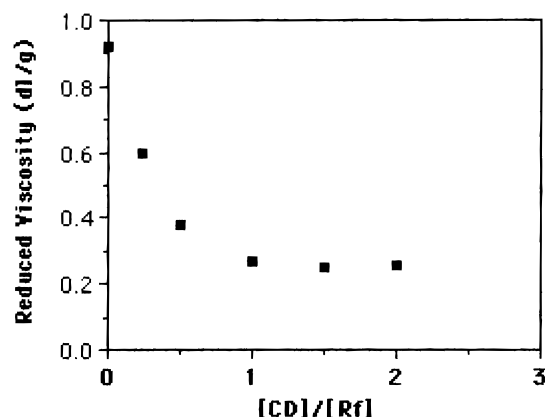
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**Figure 2.** Reduced viscosity vs concentration profile of an aqueous solution of FP810T.



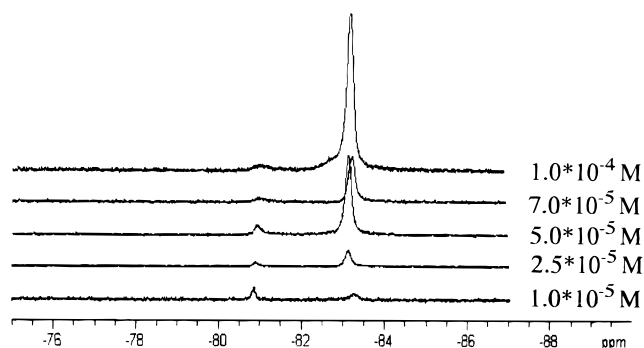
**Figure 3.** Effect of the  $\beta$ -CD/ $R_F$  ratio on the reduced viscosity of a 1 wt % FP810T aqueous solution.

Upon addition of  $\beta$ -CD to a  $8.9 \times 10^{-4}$  molar aqueous solution of this  $R_F$ -functionalized telechelic PEG, the reduced viscosity sharply decreased and leveled off at a CD/ $R_F$  molar ratio of about 1 (Figure 3). This indicates 1:1 complex formation of the  $R_F$  group of FP810T and the  $\beta$ -CD, resulting in the dissociation of the aggregates formed by intermolecular hydrophobic association of the  $R_F$  groups. The reduced viscosity (0.27 g/dL) at  $\beta$ -CD/ $R_F$  mole ratios exceeding 1 is essentially identical to that of the unfunctionalized PEG precursor (0.28 g/dL), indicating that hydrophobic association of this polymer, under these conditions, can be completely eliminated by the addition of a stoichiometric amount of  $\beta$ -CD. Thus, complex formation of  $\beta$ -CD and the  $C_8F_{17}$  group appears to be quantitative.

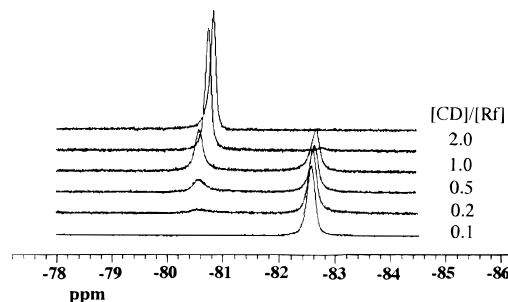
It should be pointed out that reduced viscosity measurements in this case only provide semiquantitative information. Thus, since association in this case has been shown to be dimeric, even at only 80% complex formation, the statistical probability of dimer formation is reduced to 4%.

The  $^{19}F$  NMR resonances of the  $CF_3$  group of FP810T between  $10^{-4}$  and  $10^{-5}$  M are shown in Figure 4. Above a polymer concentration of  $5 \times 10^{-4}$  M only a single  $CF_3$  absorption at  $\delta = -83.0$  ppm is observed. However, a second downfield resonance ( $\delta = -81.0$  ppm) appears below  $5 \times 10^{-4}$  M.

Similar changes are observed for the  $CF_2$  resonances. The ratio of the low- and high-field  $CF_3$  resonances is concentration dependent, increasing with decreasing polymer concentrations. The presence of two  $CF_3$  resonances indicates the existence of at least two types of  $R_F$  groups exchanging slowly on the  $^{19}F$  NMR scale. The



**Figure 4.** Concentration dependence of the  $^{19}F$  NMR resonances of the  $CF_3$  groups of FP810T in water.



**Figure 5.** Changes in  $CF_3$  resonance of the  $^{19}F$  NMR spectra of a  $1.7 \times 10^{-2}$  M aqueous solution of FP810T as a function of the concentration of  $\beta$ -CD.

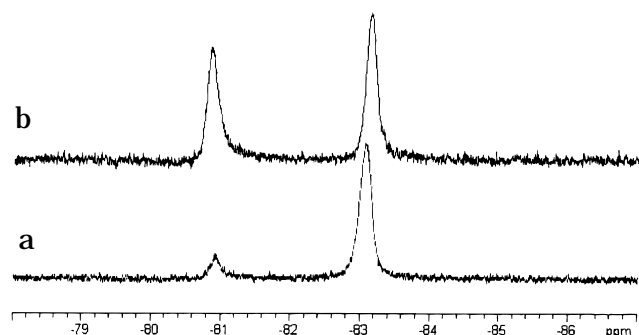
upfield resonance appears to represent an associated polymer, while the downfield resonance may represent a dissociated—probably monomeric—form. The concentration of the species corresponding to the low-field peak is approximately constant in the  $10^{-4}$ – $10^{-5}$  M range, consistent with micellar association of the  $R_F$  groups.

Upon addition of  $\beta$ -CD to a  $1.7 \times 10^{-2}$  M aqueous solution of this polymer, a new downfield  $CF_3$  resonance appears with about the same chemical shift as the monomeric form of FP810T at about  $-81$  ppm. The changes in the relative magnitude of the downfield resonances increased with increasing amounts of  $\beta$ -CD, as shown in Figure 5.

Below a  $\beta$ -CD/ $R_F$  molar ratio of 1.0, the magnitude of the downfield resonance approximately corresponds to the concentration of the added  $\beta$ -CD, and this indicates a 1:1 stoichiometry of  $\beta$ -CD and the  $R_F$  end groups consistent with the above viscosity data and with previous work demonstrating a 1:1 complex of  $\beta$ -CD and a  $C_8F_{17}$  perfluorocarbon surfactant.<sup>31</sup>

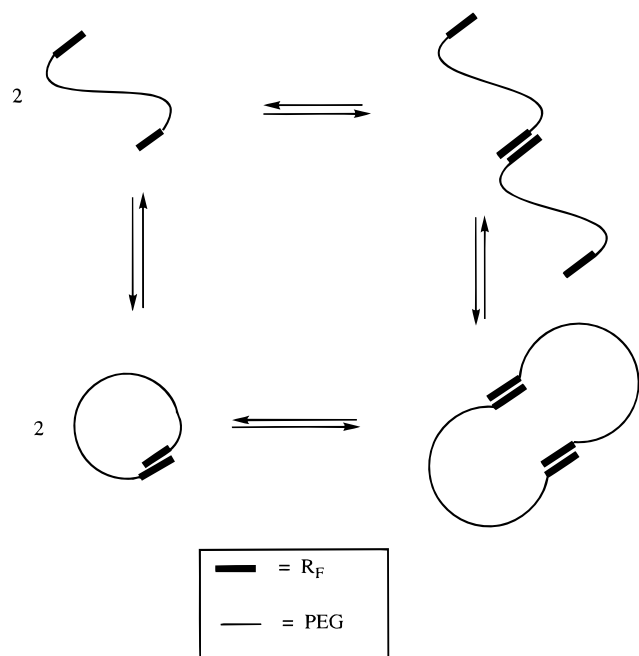
At a  $\beta$ -CD/ $R_F$  molar ratio of 1.0, a small upfield  $CF_3$  resonance is still visible but disappears at a ratio of 2. The incomplete complex formation at CD/ $R_F$  molar ratios between 1 and 2 apparently reflects the competitive equilibria of CD– $R_F$  complex formation and hydrophobic association of  $R_F$  groups into dimeric and possibly higher aggregates as well as rosette-like cyclized structures that have been postulated for telechelic PEGs end-functionalized with hydrocarbons (Scheme 1).<sup>18</sup>

Upon addition of  $\beta$ -CD to a  $5 \times 10^{-5}$  M aqueous solution of FP810T where both the dissociated (around  $-81.0$  ppm) and associated (at  $-83.00$  ppm) forms of the  $R_F$  end group are present, an increase in the magnitude of the downfield resonance and a decrease in the upfield resonance is observed with the magnitude of the downfield peak corresponding approximately to the concentration of the added  $\beta$ -CD (Figure 6). The near quantitative conversion into the  $\beta$ -CD– $R_F$ –FP810T complex at this low concentration indicates a high value of the binding constant.



**Figure 6.** Effect of the  $\beta$ -CD on the  $\text{CF}_3$  resonance of  $^{19}\text{F}$  NMR spectra of a  $5 \times 10^{-5}$  M aqueous solution of FP810T: (a) absence of  $\beta$ -CD; (b) Addition of  $2.5 \times 10^{-5}$  M  $\beta$ -CD.

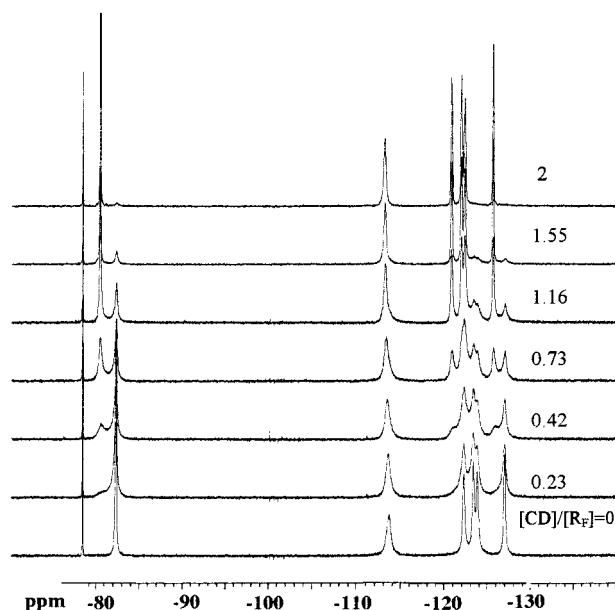
**Scheme 1. Competitive Inter- and Intramolecular Association of Telechelic  $\text{R}_\text{F}$ -Functionalized PEGs**



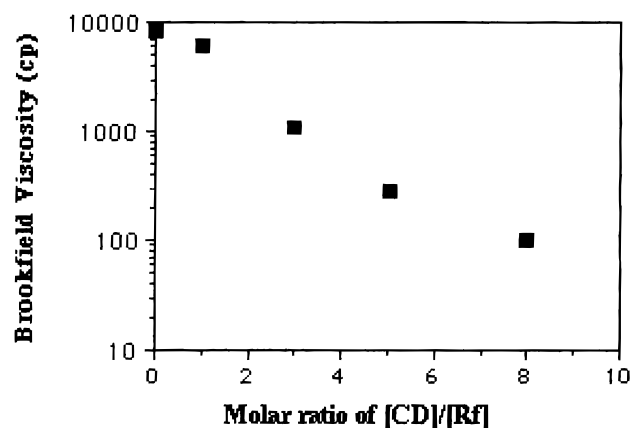
However in this case the association of the perfluorooctyl groups can be intramolecular as well as intermolecular, the degree of association being unknown, and this would appear to preclude a convenient analysis allowing a straightforward determination of the binding constant of  $\beta$ -CD and monomeric FP810T. No significant chemical shift difference is observed for the  $\text{CF}_3$  resonance, upon formation of the  $\beta$ -CD complex, in agreement with work by Guo et al. (Figure 6).<sup>31</sup>

The spectra in Figure 6 allow a rough estimation of the formation constant of the  $\beta$ -CD inclusion complex of monomeric FP810T. On the basis of Figure 4, the concentration of monomeric FP810T does not vary much with concentration and should therefore have approximately the same value as in the absence of  $\beta$ -CD (about  $7 \times 10^{-5}$  M). The downfield resonance then provides the concentration of the  $\beta$ -CD- $\text{R}_\text{F}$  complex, and this in turn gives the concentration of the uncomplexed  $\beta$ -CD; therefore the formation constant of the monomeric FP810T and  $\beta$ -CD can be estimated as on the order of  $10^5 \text{ M}^{-1}$ .

The observation of separate resonances for the micellar and the  $\beta$ -CD-complexed forms of the  $\text{R}_\text{F}$  groups indicates that their exchange is slow on the NMR time scale. Since the separation between the two forms is about 2 ppm, the time scale of exchange between the two forms is on the order of  $1.5 \times 10^{-3}$  s or greater.



**Figure 7.** Effect of addition of  $\beta$ -CD on the  $^{19}\text{F}$  NMR spectra of a  $5.7 \times 10^{-3}$  M aqueous solution of FP605M.



**Figure 8.** Effect of  $\beta$ -CD on the Brookfield viscosity of an aqueous solution (1 wt %) of a PDMA-FOSA copolymer.

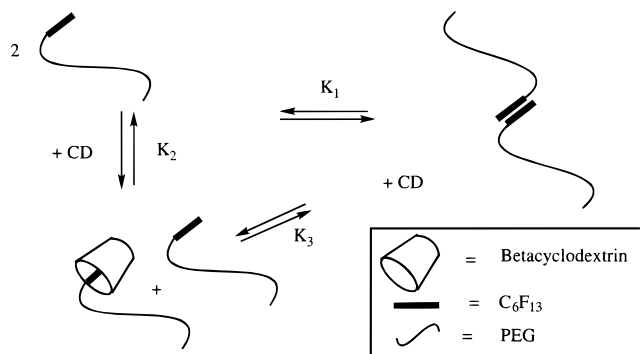
**Complex Formation of FP605M.** Complex formation of  $\beta$ -CD with a one-ended  $\text{C}_6\text{F}_{13}$ -end-functionalized PEG (FP605M) was studied by  $^{19}\text{F}$  NMR at a polymer concentration of  $5.7 \times 10^{-3}$  M (Figure 7).

As in the case of FP810T, upon addition of  $\beta$ -CD, the  $\text{CF}_3$  resonance due to the upfield dimer at  $-82.2$  ppm decreases and a new  $\text{CF}_3$  downfield resonance at  $-80.3$  ppm is observed. At about 1 equiv of added  $\beta$ -CD the ratio of the downfield over the upfield resonance is about 3 and at 2.0 equiv of  $\beta$ -CD the resonance at  $-82.2$  ppm has virtually disappeared.

A new distinct downfield resonance is also observed for the  $\epsilon$ - $\text{CF}_2$  group upon addition of  $\beta$ -CD and the ratios of the two  $\epsilon$ -resonances at a given concentration of  $\beta$ -CD are identical to that of the  $\text{CF}_3$  ( $\phi$ ) resonances. For the other  $\text{CF}_2$  groups only downfield shifts are observed, but broadened resonances are visible in the intermediate range that sharpen at  $\beta$ -CD/FP605M ratios exceeding 1.5. The data are thus consistent with the formation of a 1:1  $\beta$ -CD-FP605M inclusion complex that exchanges slowly with the associated form on the  $^{19}\text{F}$  NMR time scale.

As was shown previously, at high concentration ( $> 10^{-3}$  M) the  $\text{CF}_3$  resonance in the absence of  $\beta$ -CD corresponds to a dimeric form of the polymeric surfactant. The monomeric FP605M begins to form below about  $10^{-3}$  M

**Scheme 2. Binding by  $\beta$ -Cyclodextrin of Aqueous Poly(ethylene glycol) End-Functionalized with  $C_6F_{13}$  Groups**



and predominates at  $10^{-4}$  M, and the corresponding monomer–dimer association constant was determined as  $1.8 \times 10^4 \text{ M}^{-1}$ .<sup>6,35</sup>

The spectra in Figure 7 appear to reflect two competing equilibria, as shown in eqs 1 and 2. Thus the formation constant  $K_2$  based on this dimeric association may be calculated using eqs 1–4, where  $[CD]_t$ ,  $[CD]$ ,  $[R_F]$ ,  $[(R_F)_2]$ ,



$$[R_F]_t = [R_F] + [CD-R_F] \quad (3)$$

$$[CD]_t = [CD] + [CD-R_F] \quad (4)$$

and  $[CD-R_F]$  are the concentrations of the total and free  $\beta$ -CD, that of the monomeric and dimeric  $R_F$  groups, and that of the 1:1  $\beta$ -CD– $R_F$  complex, respectively. The concentrations of  $R_F$  and  $CD-R_F$  corresponding to the downfield resonance,  $[R_F]_t$ , and that of the dimer,  $[(R_F)_2]$ , are calculated from the relative magnitudes of the downfield and upfield resonances of the  $CF_3$  groups, respectively, and from the association constant  $K_1$ . The calculated constant  $K_2$  is  $(7.0 \pm 1.0) \times 10^3 \text{ M}^{-1}$ , which is quite close to the reported formation constant ( $7.8 \times 10^3 \text{ M}^{-1}$ ) for the complex of  $\beta$ -CD with  $C_6F_{13}COONa$ .<sup>31</sup> It should be pointed out that the constant  $K_3$  (Scheme 2) representing the  $\beta$ -CD mediated dissociation of the dimer

by binding to one of the  $R_F$  groups equals  $K_2/K_1$  and is found to be quite small ( $3.9 \times 10^{-1}$ ).

Upon addition of  $\beta$ -CD to very dilute (about  $10^{-5}$  M) solutions of FP605M, no separate resonances are observed but changes in chemical shifts are apparent that are similar to that observed by Guo et al. for complex formation of  $\beta$ -CD with  $C_6F_{13}CO_2Na$ .<sup>31</sup> Thus the  $CF_3$  group gives an upfield shift whereas the shifts of the  $CF_2$  groups are downfield.

**Complex Formation of  $\beta$ -CD with the Fluorocarbon-Modified Poly(*N,N*-dimethyl acrylamide) (FPM).** Upon addition of  $\beta$ -CD, the Brookfield viscosity of a 1.0 wt % FPM aqueous solution decreases, indicating that the hydrophobic association between the copolymer FOSA units has been disrupted as in the case of the fluorocarbon-modified PEG derivatives (Figure 8).

However, in this case, a larger concentration of  $\beta$ -CD was needed in order to completely eliminate hydrophobic association between the FOSA units. Thus, at a 1:1 mole ratio of  $[CD]/[FOSA]$ , a large residual viscosity is still observed, attributable to associated structures. Only at a  $CD/R_F$  molar ratio of 8, corresponding to a concentration of free CD of about  $7 \times 10^{-4}$  M, is a viscosity observed that is comparable to that of the PDMA homopolymer. This suggests that the hydrophobic association of the FOSA units in FPM is stronger than in the fluorocarbon-modified PEG derivatives.

It is possible that the apparently weaker binding of the pendent FOSA groups by  $\beta$ -CD than of the FP605M  $R_F$  end groups is due to steric interference by the PDMA chain backbone. More likely, the competing inter- or intramolecular association of the pendent FOSA groups is stronger due to the cooperativity of the multiple intermolecular interactions between the  $R_F$  groups of the polymers.

Such stronger perfluorocarbon association is also consistent with earlier  $^{19}F$  NMR measurements on the DMA–FOSA and acrylamide–FOSA copolymers that fail to detect  $R_F$  resonances in aqueous solutions presumably due to a tight mutual association that appears to immobilize the  $R_F$  groups. This is in sharp contrast with the above end-functionalized  $R_F$ –PEG derivatives or with ionic perfluoro surfactants where the  $^{19}F$  NMR resonances are readily detectable.

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