

Surface activity of perfluorodecanoyl end-capped poly(ethylene oxide) and associated adsorption behavior to the air–water interface

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The structure and adsorption kinetics of poly(ethylene oxide) end-capped with perfluorodecanoyl groups either at one or both ends have been characterized. These nearly monodisperse polymers with molecular weights in the range of 400–16 K g/mol are effective nonionic surfactants with very high surface activity. For aqueous solutions with concentrations in the range of 2–8 mg/ml, surface tensions determined by the drop-volume method are as low as 13.6–18.0 mN/m at 20°C. At high surface coverage, close-packed PEO chains with one end capped form a brush-like structure at the interface. Polarized infrared reflectance spectroscopy showed that perfluoroalkyl groups were nearly perpendicular to the air–water interface. The molecular area per chain was 30–32 Å² for poly(ethylene oxide) capped only at one end and 36–40 Å² for poly(ethylene oxide) with both ends capped. Only 22% of poly(ethylene oxide) chains with both ends capped form loops at the interface, while the remaining chains form an extended structure at high surface coverage. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Specifically modified poly(ethylene oxide) chains have proven to be some of the most important nonionic surfactants available^{1,2}. These polymers are relatively simple in structure, consisting of water-soluble low molecular weight poly(ethylene oxide) modified with hydrophobic end groups, which may be residues of alcohols, alkylphenols, esters of fatty acids, mercaptans, alkylamines, or alkylamides². As most surfactants, although the functions of these specifically modified polymers are known, the structure and associated changes have yet to be defined. In these nonionic surfactants, the average number of oxyethylene units generally is greater than 5 or 6 in order for the samples to be soluble in water. For a particular series with the same hydrophobic end group, the critical micellar concentration (cmc) increases with increasing number of oxyethylene groups. Molecules that incorporate a larger number of oxyethylene groups are quite soluble, but the surface activity is depressed. Therefore, for most applications, the number of oxyethylene groups is chosen in the range of 9–18, a number much smaller than typically occurs in polymers³. The chemical nature and the length of the hydrophobic end group can also affect the activity of the surfactant. The surface tension of these nonionic surfactants in aqueous solutions can vary over the range of 25–40 mN/m at the cmc, depending on the specifics of chemical structures. The highest surface activity at the cmc (at 25°C) has been

measured for poly(ethylene oxide) incorporating either fluorinated (19 mN/m)⁴ or siloxane (20 mN/m)⁵ terminal groups. Polymeric surfactants can be synthesized as specific block copolymers, by grafting or as comb-like structures⁶. The surface activity of a number of these surfactants is generally less than that of their low-molecular-weight analogues, with surface tensions at cmc never lower than 30–35 mN/m.

In this study, the structure at the air–water interface, of adsorbed end-capped poly(ethylene oxide) with extremely high surface activity has been characterized. Since functional groups incorporating fluorocarbons are the most effective surface active agents^{7,8}, the perfluoroalkyl group was chosen as the terminal substituent. For example, the best nonionic low molecular weight fluorocarbon surfactants can decrease the surface tension of aqueous solutions to 12–15 mN/m⁹. The compounds used in the current study, which have one or both end groups replaced by perfluorodecanoyl groups, all have high surface activity.

In the theories first presented by de Gennes^{10–12} and Alexander¹³, the adsorbed chains possess a mushroom conformation at low surface coverage and transform to brushes at high coverage. Milner reviewed several polymer systems¹⁴, including (1) polymers that form colloids stabilized by an end-grafted chain; (2) polymer surfactants; (3) polymer compatibilizers, and (4) copolymer microphases, that were used to test the theoretical predictions. Unfortunately, for poly(ethylene oxide)-based polymeric surfactants, few experimental data are available for comparing theoretical predictions with experimental results,

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owing to the lack of availability of both suitable model compounds or sensitive characterization techniques. The most commonly used experimental techniques for structural determination at the air–solution interfaces for aqueous solutions of poly(ethylene oxide) are ellipsometry¹⁵, X-ray fluorescence¹⁶, NMR¹⁷ or neutron reflection¹⁸.

Recently, attention has been directed to the aggregation of soluble hydrophobically end-capped poly(ethylene oxide) chains at the air–solution interface^{19–21}. The behaviour of end-capped poly(ethylene oxide) is very different from that of unmodified poly(ethylene oxide)²². Infrared reflectance spectroscopy has been developed and applied to the characterization of a variety of polymers adsorbed to the air–solution interface^{23,24}. Based on the presence of various infrared features, Ren *et al.* found that poly(ethylene oxide) with perfluoroalkyl end groups have a very high ability to form a brush-like structure at the air–solution interface, especially at high surface coverage²³. The small cross-sectional area measured suggested that the perfluoroalkyl groups were oriented nearly perpendicular to the surface at the high coverage. Poly(ethylene oxide) chains with one end capped by perfluoroalkyl groups are thus expected to form a brush-like structure at the air–solution interface, while poly(ethylene oxide) with both ends modified may also form loops that allow both end-capped ends to lie in the surface. We have systematically examined the surface tension of these newly synthesized polymers and have characterized their monolayer structure by infrared spectroscopy. Our results are reported here.

EXPERIMENTAL SECTION

Materials

Chloroform, methanol and hexane (Fisher HPLC grade) were used as received. Benzene (Fisher HPLC grade) was distilled over CaH₂. Tetrahydrofuran (Aldrich, 99.9% anhydrous) was distilled from sodium benzophenone dianion. Poly(ethylene oxide) diol samples were purchased from American Polymer Standards Corporation and Poly-sciences. Monohydroxy poly(ethylene oxide) was purchased from Polymer Laboratories. The synthetic procedures have been described previously²⁵. The six poly(ethylene oxide) studied had either one or both ends substituted with perfluorodecanoyl groups, and are listed in Table 1.

Measurement of surface tension

The surface tension, γ , was measured using the drop-

volume technique^{26,27} and analysed with the following expression:

$$\gamma = \frac{V\rho g}{r}F \quad (1)$$

where V is the volume of drop, ρ is the density of the solution, r is the tip radius, g is the gravitational acceleration, and F is the correction factor used in previous studies²⁸. The accuracy and reproducibility of this method are 0.1 mN/m²⁹. An aerometer was used to determine the densities of the solutions. It is known that surface tension varies as a function of time for both molecular and polymeric surfactants. For pure liquids, variation of surface tension with respect to the detachment time of the droplet is known very accurately³⁰. The value of surface tension at detachment time (50–60 s) is the same as the extrapolated value at infinity. Owing to the hydrodynamics of forming a drop, the volume and surface area may change during the measurement²⁹. This complexity introduces some uncertainty into data analysis. In addition, the time dependence of the surface tension can be further complicated due to the kinetics of adsorption of surface active substances. In some cases, extremely long times are needed in order for samples to reach equilibrium^{30,31}. Approximately ten measurements were made at detachment times that varied from 0.1 s to 1 h for every polymeric surfactant solution, allowing extrapolation to the equilibrium value.

The time-dependent drop volume for the solution of ⁸KPEO^{F2} ($c = 0.16$ mg/ml) as a function of time is shown in Figure 1. This set of data is characteristic of all the samples studied. If equation (1) is to be employed to calculate surface tension, it is necessary to obtain an equilibrium value of volume drop. The most frequently used semi-empirical extrapolation method of obtaining the equilibrium value is shown below^{32–34}:

$$V_e = V(t) - K_V t^{-3/4}, \quad (2)$$

where t is the time, K_V is a constant, $V(t)$ is the time-dependent drop volume, and V_e is the equilibrium value. When the value of V_e is obtained, a corresponding value of surface tension can be calculated from equation (1) as done previously^{32–34}. In this study, the dynamic volume data cannot be fitted to one single line, as shown in Figure 1. In fact a discontinuity for long time dependence, i.e., longer than a certain detachment time (500 s for this example), is observed in every sample studied. We have therefore fit two straight lines to the data obtained, one for data for the period typically below 500 seconds, and take the equilibrium value fitted to the data obtained at times longer than 500 s. By repeating the procedure for data of different concentrations, the variation of equilibrium surface tension was obtained as a function of the concentration for each sample. The surface tensions obtained for the samples studied are summarized in Figures 2 and 3.

External reflection infrared spectroscopy

The model compound methoxy tri(ethylene glycol) perfluorodecanoyl ester (MTEG^F) was dissolved in *n*-hexane at 0.250 mg/ml. ⁸KPEO^{F2} (see Table 1) was dissolved in Milli-Q water (resistance 18.2 M Ω) at 0.50 mg/ml. The micro-syringe used to spread the film on the water surface was rinsed with hexane several times before each film was spread. Each film was allowed to stand for 15 min before measurements began. Infrared spectra were collected with a Perkin-Elmer System 2000 FTi.r. spectrometer equipped with a narrow band MCT detector

Table 1 Sample characterizations, surface concentrations Γ (10⁻¹⁰ mol cm⁻²) at cmc, and molecular areas a_0 (Å²) per chain of perfluorodecanoyl end capped poly(ethylene oxide)

Sample	⁴⁰⁰ PEO ^F	² KPEO ^F	¹⁶ KPEO ^F	³ KPEO ^{F2}	⁸ KPEO ^{F2}	¹⁵ KPEO ^{F2}
M_n	400	1.90×10^3	1.64×10^4	3.10×10^3	7.72×10^3	1.53×10^4
PDI	not available	1.05	1.02	1.06	1.04	1.18
Γ	5.2	5.6	5.3	4.2	4.6	4.3
a_0	32	30	32	40	36	38

PDI, polydispersity index, M_w/M_n ; ⁴⁰⁰PEO^F, ²KPEO^F and ¹⁶KPEO^F are poly(ethylene oxide) chains with one end capped with perfluorodecanoyl groups; ³KPEO^{F2}, ⁸KPEO^{F2} and ¹⁵KPEO^{F2} have both ends capped with perfluorodecanoyl groups. The leading superscripts represent the approximate molecular weights shown

(Infrared Associates) using a commercial external reflection cell (Specac Ltd), with the incident angle set at 30° in all measurements. The cell was equipped with a grid polarizer (Graseby Specac) and a removable Teflon trough. All spectra were collected in s-polarization by coadding 512 scans at 4 cm⁻¹ resolution.

RESULTS AND DISCUSSION

As shown in Figures 2 and 3, the surface tension as a function of bulk concentration demonstrates that all the

poly(ethylene oxide) end-capped with perfluorodecanoyl groups either at one or both ends are among the most effective surfactants, exhibiting unusually high values of surface activity. For aqueous solutions with concentrations greater than 1 mg/ml, the surface tensions measured were found to be less than 18 mN/m at 20°C. When concentrations of aqueous solutions for perfluoroalkyl end-capped poly(ethylene oxide) are in the range of 2–8 mg/ml, the surface tension of the aqueous solutions determined by the drop-volume technique may decline to values as low as 13.6–18.0 mN/m, the highest surface activity for polymeric

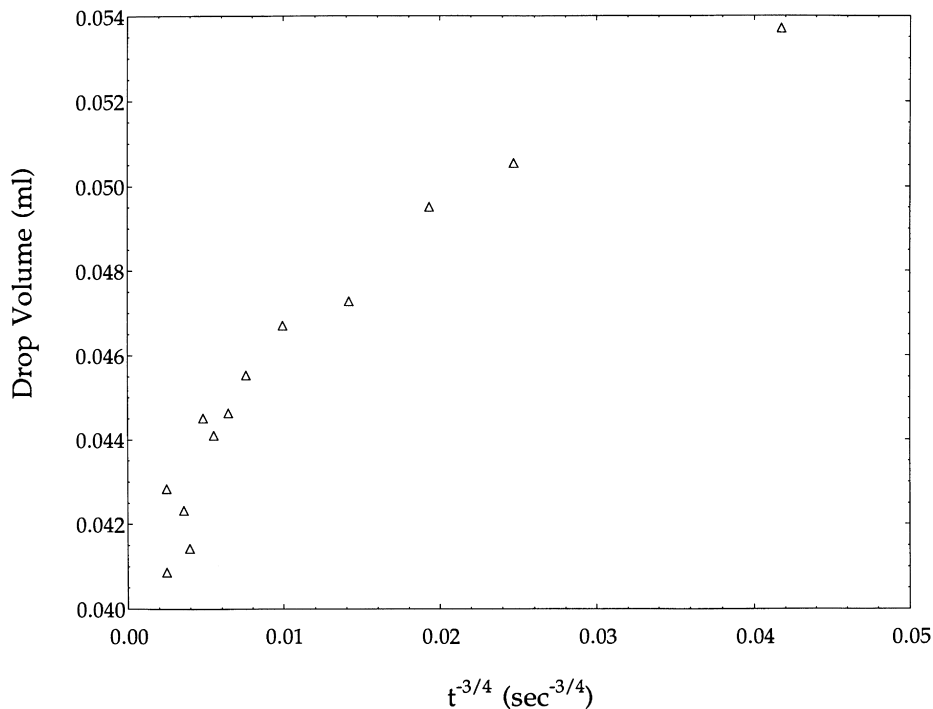


Figure 1 Drop volume of aqueous solution for ⁸KPEO^{F2} (*c* = 1.62 × 10⁻⁴ g/ml) versus *t*^{-3/4} at 20°C

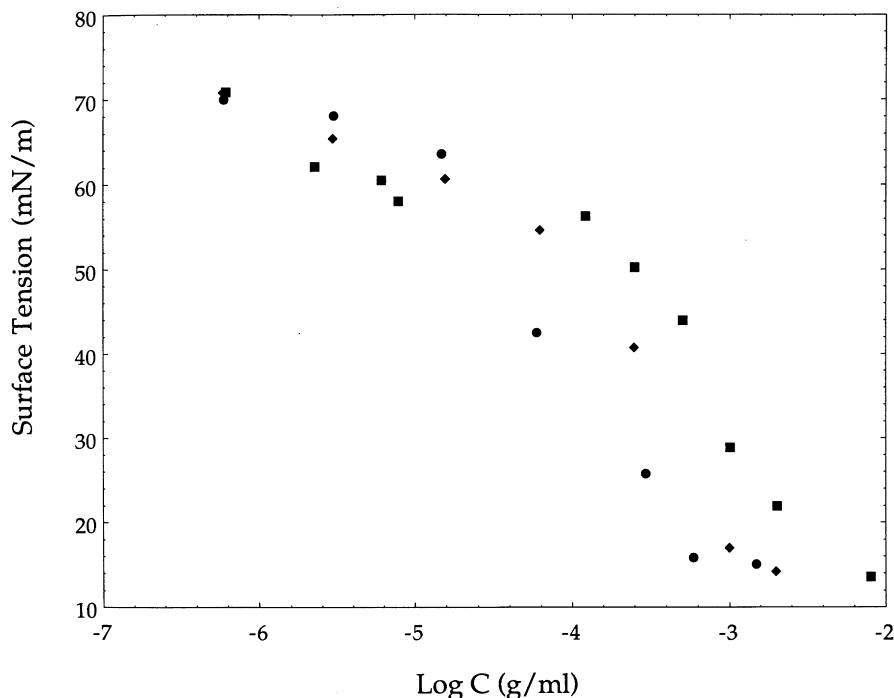


Figure 2 Equilibrium surface tension versus logarithmic concentration at 20°C for aqueous solutions of ⁴⁰⁰PEO^F (●), ^{2K}PEO^F (◆), and ^{16K}PEO^F (■)

surfactants known. This is very similar to the behaviour found for low-molecular-weight fluorinated surfactants³⁵. The cmc is less than 10 mg/ml and the surface tension at the cmc is approximately in the range of 13.6–18.0 mN/m at 20°C.

Fluorocarbon chains attached to a hydrophilic functional group form surfactants with high surface activity. Samples at less than 1% concentration can reduce the surface tension of water from 72 mN/m to between 15 and 20 mN/m. The fluorinated ionic surfactant having the greatest surface activity is a perfluoroalkyl acid, i.e. C₇F₁₅COOH. In that case, the surface tension of the aqueous solution is 15.2 mN/m at the cmc (2.8 mM) and 30°C⁹. Another fluorinated nonionic surfactant C₈F₁₇CH₂CON((C₂H₄O)₃CH₃)₂ can reduce the surface tension to 19 mN/m at 25°C at the cmc (0.012 mM)⁴. The high surface activity of fluorinated surfactants can be explained by the strong hydrophobic nature of fluorinated groups³⁵. For monolayers of fluorocompounds, the CF₃ group has the lowest value of critical surface tension, i.e., 6 mN/m and the value for the CF₂ group is 18 mN/m. These values are much lower than the critical surface energies of any other functional group. For comparison, the critical surface energy of the oxyethylene group is ~40 mN/m.

The results obtained from the drop-volume method depend on the hydrodynamics governing the speed of drop formation. For pure liquids, extrapolation to the equilibrium value can be established empirically based on the data obtained at different dropping speeds. It has been found that a retention time of 50–60 s is sufficient for equilibrium for pure water or organic liquids. For solutions containing a surface active component, the result is more complicated because the diffusion of the solute from the bulk state into the air–solution interface typically occurs at a slow rate. The time dependence of the surface tension of end-capped poly(ethylene oxide) chains is displayed in *Figures 4 and 5*, which show the surface tension as a function of detachment time. The equilibrium values are shown at the rightmost edge of *Figures 4 and 5*. The equilibration time for the

surface tension of a polymer solution may be on the order of hours, depending on solution concentration, the molecular weight of surfactants, and the nature of the hydrophilic end groups. Because of the high surface activity associated with fluorinated end groups, the adsorption rate of a perfluoroalkyl end-capped poly(ethylene oxide) is much faster than that of the unmodified poly(ethylene oxide).

The Gibbs adsorption isotherm relates the amount of adsorbed surfactant per unit area, Γ , to the change of the surface tension γ as a function of the bulk concentration c :

$$\Gamma = \frac{1}{RT} \frac{\partial \gamma}{\partial \ln c} \quad (3)$$

where R is the gas constant and T is the absolute temperature. On a semilog plot relating γ to concentration, the number of adsorbed molecules per unit area can be obtained. It is then possible to calculate area per surfactant molecule, a_0 , at the air–water interface using the expression:

$$a_0 = 1/(N_{av}\Gamma) \quad (4)$$

where N_{av} is Avogadro's number. The a_0 values obtained by the above method based on the surface tension data for concentrations higher than 0.1 mg/ml are listed in *Table 1*.

In the consideration of cross-sectional areas obtained, the orientation of end groups relative to the air–water surface needs to be analysed. The two extremes in orientation of the end groups are either perpendicular or parallel to the interface. The cross-sectional area occupied by the perfluorocarbon chain end is ~28 Å² based on the X-ray determination for crystalline perfluoro-*n*-eicosane³⁶ or 27.7 Å² for perfluorinated alkyl chain³⁷. Both these values are very close to the cross-sectional area of 25 Å² per molecule of a closely packed state^{38,39}. In the second case, the cross-sectional area for the perfluorodecanoyl group lying in the surface is 78 Å² obtained from the density (2.0 g/cm³) and unit cell of the perfluorocarbon²⁵. The other type of experiment capable of yielding the molecular area at the

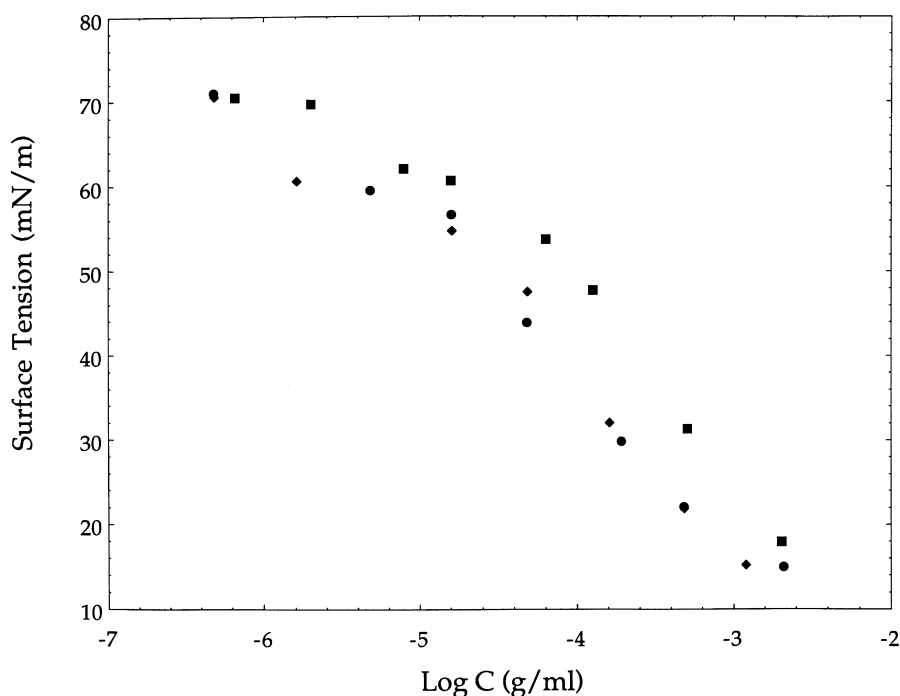


Figure 3 Equilibrium surface tension versus logarithmic concentration at 20°C for aqueous solutions of ³KPEO F₂ (●), ⁸KPEO F₂ (◆) and ¹⁵KPEO F₂ (■)

surface is one in which the surface pressure *versus* area isotherm of a Langmuir film is measured. It was shown from such experiments that the area per perfluorinated alkyl end group is $\sim 29 \text{ \AA}^2$ for $\text{F}(\text{CF}_2)_{10}\text{CH}_2\text{COOH}$ ⁴⁰, $28\text{--}33 \text{ \AA}^2$ for several fluorinated fatty acids³⁹, 30.9 \AA^2 for perfluorododecyl aspartate⁴¹ and $\sim 30 \text{ \AA}^2$ for a non-polar molecule

perfluoro-n-eicosane⁴². In all these cases, the end groups are oriented perpendicular relative to the air–water interface.

The measured cross-sectional area of perfluorodecanoyl end groups for the one end capped poly(ethylene oxide) are summarized in *Table 1*. The data suggest that poly(ethylene oxide) chains with different chain lengths occupy nearly the

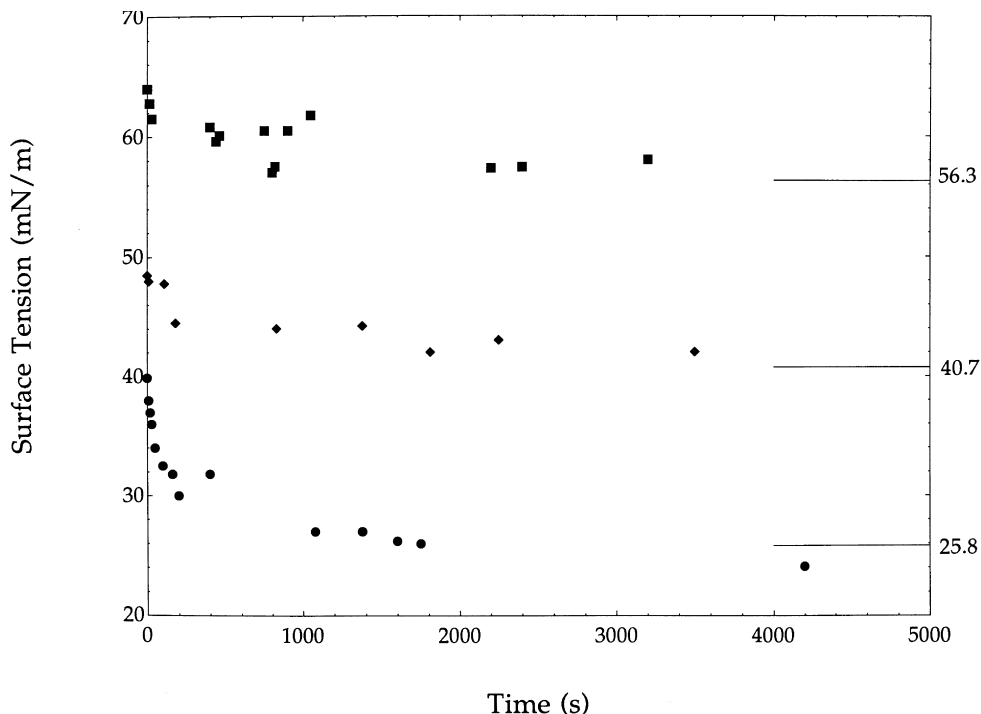


Figure 4 Dynamic surface tension *versus* drop detachment time at 20°C for aqueous solutions of ⁴⁰⁰PEO^F ($c = 2.98 \times 10^{-4} \text{ g/ml}$), ^{2K}PEO^F ($c = 2.50 \times 10^{-4} \text{ g/ml}$) and ^{16K}PEO^F ($c = 1.23 \times 10^{-4} \text{ g/ml}$)

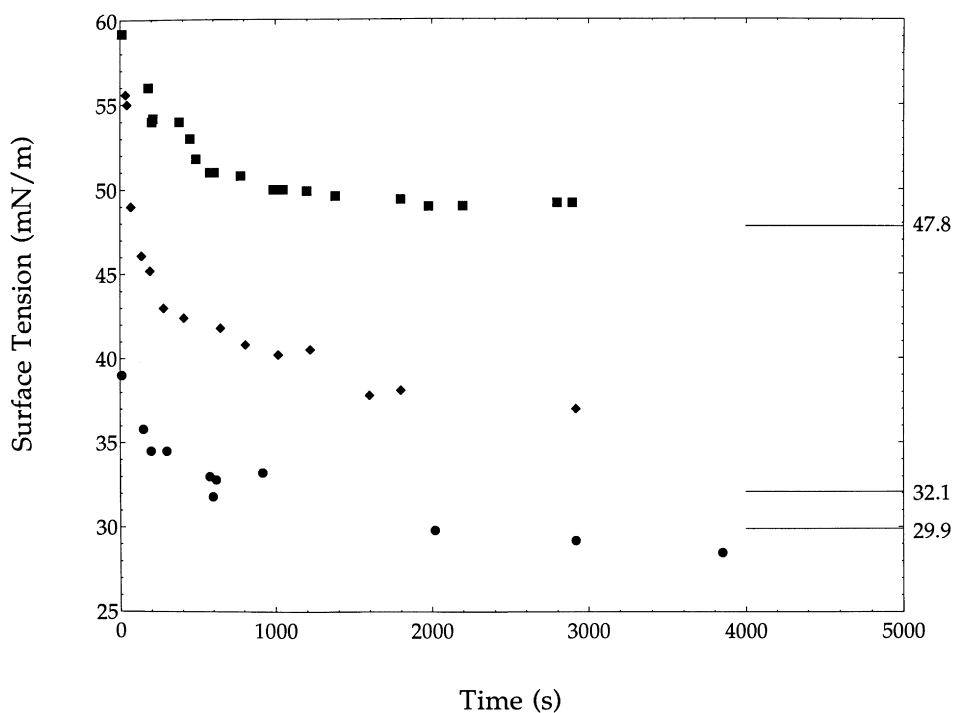


Figure 5 Dynamic surface tension *versus* drop detachment time at 20°C for aqueous solutions of ^{3K}PEO^{F2} ($c = 1.93 \times 10^{-4} \text{ g/ml}$), ^{8K}PEO^{F2} ($c = 1.62 \times 10^{-4} \text{ g/ml}$) and ^{15K}PEO^{F2} ($c = 1.27 \times 10^{-4} \text{ g/ml}$)

same area at the air–water interface. For these samples, the areas per molecule obtained by the Gibbs adsorption isotherm are in the range 30–32 Å², nearly identical to that expected for the end group standing perpendicular to the interface. In order to explain this observation, it could be imagined that almost all of the end groups are perpendicular to the surface and the molecular conformation of poly(ethylene oxide) chains adsorbed at the surface exist as brush. Similarly, as shown also in *Table 1* for poly(ethylene oxide) with both ends capped, the cross-sectional area per molecule was also insensitive to the molecular weight. The values are obviously higher than those for poly(ethylene oxide) with one end capped. The reason for this is that some molecules are able to form loops with both ends adsorbed to the surface simultaneously, so each chain with both ends capped can occupy more area at the surface.

It is interesting to note that the area occupied on water by an adsorbed perfluoroalkyl end-capped poly(ethylene oxide) is much smaller than the cross-sectional area of the unmodified poly(ethylene oxide) of the same molecular weight at the same temperature, as shown in *Figure 6*. This indicates that the conformational distribution of fluoroalkyl end-capped poly(ethylene oxide) chains is significantly different from unmodified poly(ethylene oxide) when adsorbed in the air–water interface, forming the extended brush structure. A large number of surface tension measurements for poly(ethylene oxide) alcohol have appeared in the literature². The surface tensions above the cmc are in the range of 25–40 mN/m, depending on the number of ethylene oxide groups in these nonionic surfactants. The shorter the poly(ethylene oxide) block, the lower the surface tension. The cross-sectional area, a_0 , per poly(ethylene oxide) chain adsorbed at the surface has been shown to increase progressively with increasing poly(ethylene oxide) chain length. Based on the molecular area, a_0 , at the cmc for polyoxyethylene dodecanols^{43,44}, hexadecanols⁴⁵, and nonylphenol⁴⁶, it was also found that a_0

increases continuously with increasing number of oxyethylene groups, and scales as $N^{1/2}$. This functional form suggests that the disturbance in chain conformation for the poly(ethylene oxide) adsorbed at the air–water interface is significant. The relation between the molecular area and N was explained by assuming that, at saturation adsorption, the hydrated ether groups pack closely at the interface and the thickness of the interface is proportional to $N^{1/2}$ ⁴⁷.

The best description for flexible polymer chains in a good solvent is a loose coil with the molecular configuration obeying the statistics associated with self-avoiding walk⁴⁸. An aqueous solution of poly(ethylene oxide) belongs to this category. The characteristic size in terms of the radius R of the coil, is a power function of the chain length, N , i.e., $R \sim N^n$, where n is the scaling index, typically about 0.6⁴⁸. Hence, the cross-sectional area of a free chain of poly(ethylene oxide) in the bulk of water changes with varying chain length approximately as $N^{1.2}$. At a surface with very low coverage of adsorbed chains, each chain is isolated, and exists in a mushroom conformation. The cross-sectional area changes insignificantly compared with that expected in the bulk state^{49,50}. With increasing surface coverage, the adsorbed chains pack closer to each other. The chains can overlap and possibly interpenetrate, distorting the overall shape gradually. When the concentration of the polymeric surfactants is at the cmc, the surface coverage is high and the molecular shape of adsorbed chains must change. The relationship between the cross-sectional area measured as a function of molecular weight can be an indicator to describe the degree of distortion for adsorbed polymers at the surface. For polyoxyethylene nonylphenols, dodecanols, and hexadecanols, the molecular areas were related to the ethylene oxide number in the chain as $N^{0.51}$, $N^{0.54}$, and $N^{0.64}$, respectively^{43–46}. For perfluorodecanoyl end-capped poly(ethylene oxide), this dependence of the molecular area on the molecular weight reduces to N^0 . This

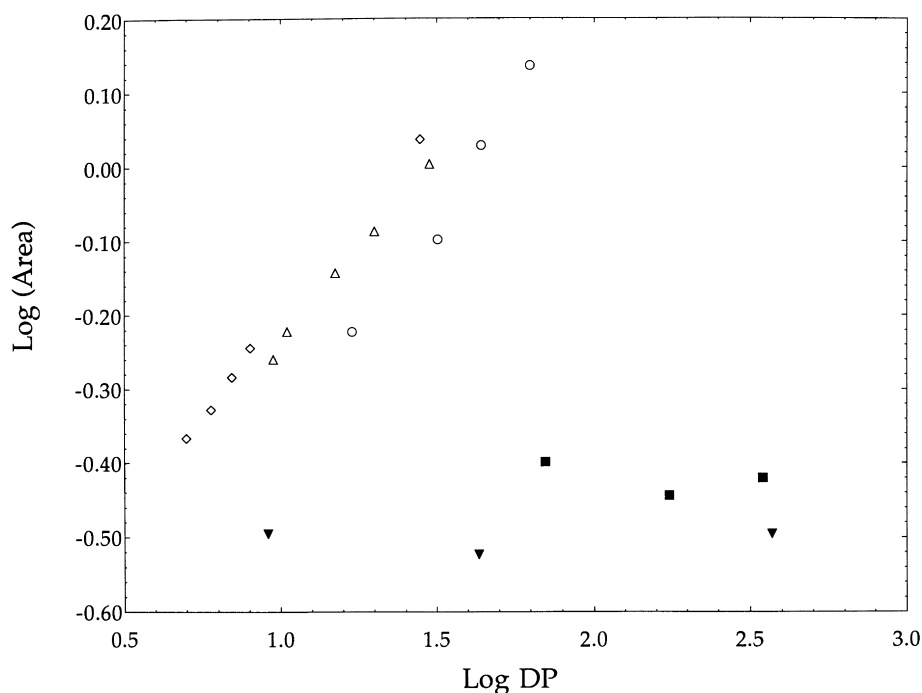


Figure 6 Molecular area per chain at the surface versus degree of polymerization for perfluoroalkyl and alkyl end-capped PEO. End groups: dodecanol (◇), nonylphenol (△), hexadecanol (○), one end perfluorodecanoyl (▼), and both ends perfluorodecanoyls (■)

implies that when these polymeric surfactants transfer from the bulk state to the surface at the cmc, their shapes change significantly from the random coil ($a_0 \sim N^{1.2}$) to the brush ($a_0 \sim N^0$), as Ren suggested earlier²³.

The perturbation of poly(ethylene oxide) chain conformation caused by the introduction of perfluoroalkyl end groups is much larger than that produced by alkyl end groups due to the exceedingly hydrophobic character of the fluorocarbon terminal group. The cross-sectional area per molecular chain is much smaller than for the coils formed by poly(ethylene oxide) chains in water. The type of end group is extremely important in governing the chain conformation of adsorbed end-capped poly(ethylene oxide) chains.

Because of the extremely hydrophobic perfluoroalkyl end groups, poly(ethylene oxide) capped at one end effectively form brush structures when physically adsorbed to the air–water surface. It has generally been assumed that poly(ethylene oxide) with both ends capped are suitable for forming loops when chains are adsorbed to the surface. The possibility of forming the loops is limited, however, by both thermodynamics and kinetics. Even with the presence of surface active perfluoroalkyl end groups, the probability of forming loops by simultaneous adsorption of both ends in the same chain is still low. Based on *Table 1* and as shown in *Figure 6*, similar to one end-capped poly(ethylene oxide), the end groups of PEO^{F2} adsorbed to the surface also have a nearly perpendicular orientation relative to the air–water interface.

The average value of the molecular cross-sectional area per chain at the cmc is 31 \AA^2 for poly(ethylene oxide) with one end capped, and 38 \AA^2 for poly(ethylene oxide) with both ends capped. The percentage of chains with both ends capped that form loops can then be estimated by assuming that the area occupied per looped chain is exactly twice that for chains with only one end capped. In this way, we estimate that about 22% of poly(ethylene oxide) chains with

both ends capped form loops at the surface and 78% maintain the extended brush conformation.

The structure of the adsorbed end-functionalized poly(ethylene oxide) at the air–solution interface was further studied by external reflection infrared spectroscopy. It has been shown that the adsorption of this type of fluoroalkyl end-capped poly(ethylene oxide) at the air–solution interface can be quantified by comparing the reflectance absorbance of the C–F vibrational bands with that of an insoluble fluorinated alcohol²³. The model compound we chose was methoxy tri(ethylene glycol) perfluorodecanoyl ester (MTEG^F), which is essentially the end-functionalized ethylene oxide trimer. The fluorinated functional end of this compound is identical to that of the six end-capped poly(ethylene oxide) polymers. The surface pressure isotherm measured on a Langmuir trough of this model compound spread from chloroform on water surface is included in *Figure 7*. The area occupied by each molecule is determined to be 29 \AA^2 by extrapolating the last stage of the pressure curve to zero pressure. This value agrees with the value reported in the literature for fluorocarbon surfactants^{44,46,47}.

A reflection infrared spectrum of MTEG^F film spread on the water surface with a packing density of $30 \text{ \AA}^2/\text{molecule}$ is shown in *Figure 8*. The surface pressure isotherm shows that the fluorocarbons are closely packed at this density, with the chain axis perpendicular to the water surface. The reflection spectrum of ⁸KPEO^{2F} adsorbed from aqueous solution (2.0 mg/ml) is also included in *Figure 9*. It can be seen that the features of the C–F bands in the 1200–1300 cm^{-1} region of ⁸KPEO^{2F} resemble those of the MPEG^F. The relative intensities of the two perpendicular bands at 1152 and 1207 cm^{-1} are the same, but the 1238 cm^{-1} band, which contains a parallel component⁵¹, is slightly stronger in the spectrum of ⁸KPEO^{2F}. This indicates that the packing of the fluorinated chain ends of ⁸KPEO^{2F} is very similar to the packing of the MPEG^F, but

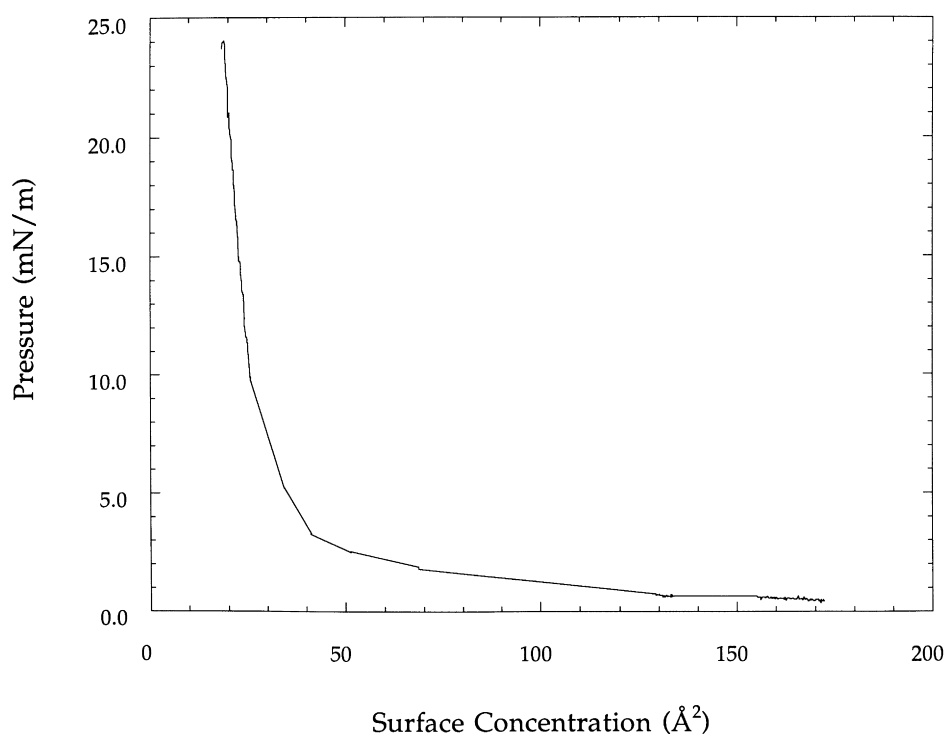


Figure 7 Surface pressure isotherm of MTEG^F monolayer spread on water surface

the average orientation of the fluoroalkyl chain ends may deviate slightly from 90°. A possible reason for this deviation is that the 2.0 mg/ml concentration used is much less than the cmc and the molecular cross-sectional area occupied by each end group is larger than the value associated with close packing. As a result, the perfluoroalkyl end group has more space to move and thus is less well oriented. In fact, the molecular area per fluoroalkyl end group can be estimated by the spectroscopic data as well.

Assuming that the orientation of the fluorinated chain ends of $^{8k}\text{PEO}^{2F}$ is 90° as is that of MPEG^F , the relative reflectance at constant incidence angle is proportional to the number of absorbing molecules at the surface. Therefore, the surface density of the adsorbed fluorinated chain ends can be determined by:

$$\frac{A_P}{A_M} = \frac{S_M}{S_P} \quad (5)$$

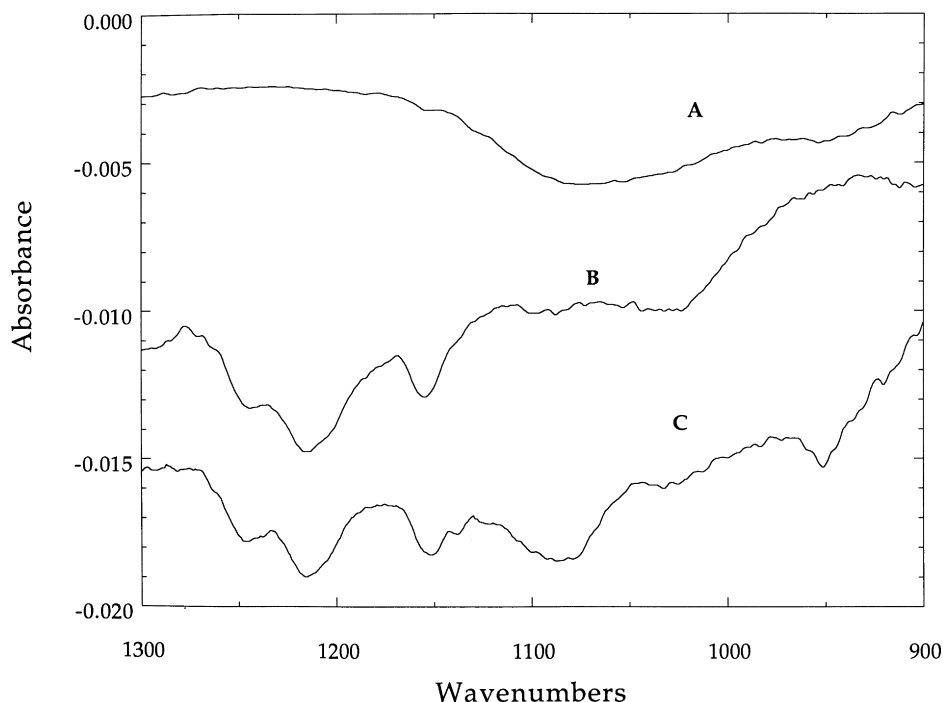


Figure 8 External reflectance IR spectra obtained using s-polarization of (A) PEO solution; (B) a monolayer of MTEG^F spread on water surface (30 Å/molecule); and (C) $^{8k}\text{PEO}^{2F}$ solution (2.0 mg/ml)

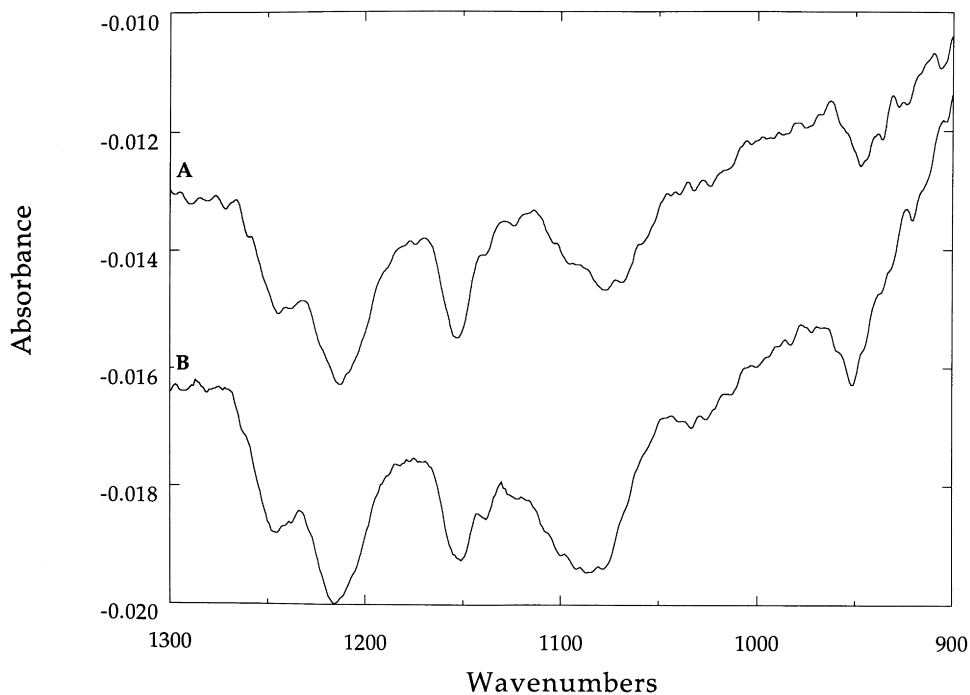


Figure 9 Comparison of s-polarization reflectance spectra of (A) $^{5k}\text{PEO}^F$ solution (4.16 mg/ml); and (B) $^{8k}\text{PEO}^{2F}$ solution (2.0 mg/ml)

where S_M is the area occupied by one fluorinated chain end for the MPEGF, A_M is the absorbance of the s polarized reflectance of the corresponding film, S_p is the area occupied by one fluorinated chain end for the $^{8K}PEO^{2F}$, and A_p is the s polarized reflectance from the surface of the polymer solution. The result thus obtained suggest that the cross-sectional area is 40 \AA^2 for the adsorbed $^{8K}PEO^{2F}$ chains.

It has been pointed out that the absorbance in a reflection infrared spectrum is dependent on the orientation of the transition moment as it is in the transmittance infrared. Theoretical calculations have been conducted to quantify the relationship between the orientation and the absorbance⁵¹. If the dependence of absorbance on the orientation angle is included, equation (6) becomes:

$$\frac{A_p}{A_M} = \frac{S_M}{S_p} k(\nu) = k(\nu) \sin^2 \nu \quad (6)$$

where θ is the angle between the chain axis and the surface. Based on the $k(\theta)$ versus θ relationship calculated, the orientation angle θ is 69° , and the packing density of the perfluoroalkyl chain ends is a 34 \AA^2 for the cross-sectional area. This surface density value agrees very well with the results obtained by surface tension measurements as described above. Based on this combination of spectroscopic and surface tension measurements, we conclude that the perfluoroalkyl chain ends for the functionalized poly(ethylene oxide) form an relatively ordered structure at the air-solution interface.

Polymer chains with one end functionalized form a 'tail' conformation when they adsorb to the interface, while the poly(ethylene oxide) homopolymers with both ends functionalized can assume either 'loop' or 'tail' conformations depending on the surface affinity of the end group and the surface coverage^{52,53}. Additional structural information for adsorbed $^{8K}PEO^{2F}$ chains at the air-solution interface can be obtained by studying the poly(ethylene oxide) backbone vibration region. Compared with the reflection spectrum of the $^{5K}PEO^F$ solution shown in Figure 9, it can be seen that if we normalize these two spectra with respect to the 1207 cm^{-1} C-F stretching vibrational band, the poly(ethylene oxide) backbone vibrations at 1050 and 930 cm^{-1} for the $^{8K}PEO^{2F}$ are stronger than the corresponding bands for the $^{5K}PEO^F$. This indicates that for each adsorbed $^{8K}PEO^{2F}$ chain, the average poly(ethylene oxide) chain attached to each adsorbed fluorinated tail is longer than the tail for $^{5K}PEO^F$. If both of the fluorinated chain ends of a $^{8K}PEO^{2F}$ molecule adsorb to the interface, i.e., it is in 'loop' conformation, the chain can be considered as two $^{4K}PEO^F$ chains. The average poly(ethylene oxide) chain attached to each fluorinated chain end, with molecule weight ~ 4000 , would be smaller than the poly(ethylene oxide) chain attached to each perfluoro chain end for $^{5K}PEO^F$, and the relative band intensity of the poly(ethylene oxide) backbone vibrations normalized to the number of chain end should be higher for $^{5K}PEO^F$ than that of $^{8K}PEO^{2F}$. The opposite is observed, indicating that for $^{8K}PEO^{2F}$ chains adsorbed to the air-water interface, the loop conformation is not the predominant structure. These results are in agreement with results obtained from the Gibbs adsorption isotherm.

CONCLUSIONS

We have synthesized poly(ethylene oxide) end-capped with perfluorodecanoyl groups at one or both ends, as a new type of polymeric surfactant with very high surface activity. These samples are the most efficient surfactants measured as

compared with other polymeric or nonionic species. The end-capped poly(ethylene oxide) are a good molecular model to test the formation of 'tail' or 'loop' conformations at the air-water surface owing to the extremely hydrophobic nature of the perfluoroalkyl end groups. A very high ability to self-organize at the air-water interface was characterized by the determination of surface tension and infrared reflectance spectroscopy. At high surface coverage, the molecular orientation of the perfluoroalkyl end group is nearly perpendicular to the air-water interface and close packing is approached. For poly(ethylene oxide) with one end capped, the chain forms a brush conformation with the perfluoroalkyl end group. Most of the poly(ethylene oxide) chains with both ends capped also form a brush conformation and only a small percentage of these chains form extended loops.

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