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Fluorocarbon Surfactant Polymers: Effect of Perfluorocarbon Branch Density on Surface Active Properties

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ABSTRACT: We describe a series of fluorocarbon surfactant polymers designed for modifying fluorocarbon surfaces such as poly(tetrafluoroethylene). Novel fluorocarbon surfactant polymers poly(*N*-vinyldextranaldonamide-*co*-*N*-vinylperfluoroundecanamide), in which hydrophilic dextran oligosaccharides and hydrophobic perfluoroundecanoyl groups were incorporated sequentially onto a poly(vinylamine) backbone, were synthesized and characterized by FT-IR, NMR, and XPS spectroscopy. By adjusting the feed ratio of dextran to fluorocarbon branches, surfactant polymers with different hydrophilic/hydrophobic balances were prepared. The surface activity of the surfactants at the air/water interface was demonstrated by significant reductions in water surface tension. Surfactant adsorption and adhesion at the solid PTFE/aqueous interface were examined under well-defined dynamic flow conditions, using a rotating disk system. The surface activity at the air/water interface and adhesion stability on PTFE under an applied shear stress both increase with increasing density of fluorocarbon branches on the polymer backbone. The results show that stable surfactant adhesion on PTFE can be achieved by adjusting the hydrophilic dextran to hydrophobic fluorocarbon branch ratio.

Introduction

The properties of poly(tetrafluoroethylene) (PTFE), including its mechanical strength, chemical inertness, nonadhesiveness, thermal stability, and low coefficient of friction, make it very useful for a variety of applications.[1−3] For many biomedical applications, however, it would be useful if the PTFE surface could be easily modified to facilitate surface modification with bioactive molecules like heparin[4,5] or cell adhesive peptide/proteins[6−8] to improve interfacial biocompatibility. However, the chemical inertness of PTFE makes it difficult to modify the surface in order to introduce chemically useful organic moieties. The only successful approaches have involved highly energetic reactions like glow discharge[9−11] or chemical etching using methylene lithium or benzoin dianion.[12−14] Unfortunately, such approaches do not produce a surface with well-defined chemistry.

An alternative approach for effective surface modification of PTFE, which we examine in this report, is to investigate physisorption of surfactants.[15−18] Surfactant adsorption can provide a well-defined surface modification that is nondestructive to the PTFE surface and easier to perform than high-energy reactions. One concern, as with any approach to surface modification that involves noncovalent interactions, is the adhesion stability of the surfactant on the solid substrate. Adhesion stability can be improved by increasing the molecular weight of the surfactant, such as moving from classical molecular diblock surfactant structures[19] to polymeric systems, decreasing the entropy of the surfactant by adopting a branch or comblike structure, or by increasing hydrophobic−hydrophilic balance.[20,21] These options are also consistent with the results from Fleer's self-consistent-field theory on polymer adsorption.[22−24]

Our previous work[25,26] on nonionic dextran surfactant polymers demonstrated effective surface assembly at a solid/aqueous interface and useful interfacial properties, such as suppression of protein adsorption, which are highly beneficial for blood-contacting medical devices.[27] The polymer surfactants are composed of poly(vinylamine) with pendant dextran and alkanoyl groups. When adsorbed on a hydrophobic surface such as polyethylene, the alkanoyl side chains adhere to the hydrophobic substrate, while the dextran side chains are oriented into the aqueous environment to provide a biocompatible oligosaccharide interface.

However, the existing surfactant polymers with hydrocarbon side chains readily adsorb on PTFE but do not show stable adhesion. This observation suggests that favorable enthalpic, as well as entropic, changes may be important for achieving stable surfactant−PTFE adhesion. Accordingly, we have designed surfactant polymers with fluorocarbon side chains, which would be expected to favor adsorption and strong adhesion on PTFE under aqueous solutions. Fluorocarbon chains have similar chemical structure to the PTFE substrate.[28] They are also more hydrophobic[29] and have a larger molecular cross section than hydrocarbons.

Here, we describe fluorocarbon surfactant polymers that adhere to PTFE surface under aqueous conditions and provide a stable oligosaccharide interface suitable for biomedical applications. The polymers, consisting of a poly(vinylamine) backbone with dextran and fluorocarbon side chains, were characterized by FT-IR, NMR, and XPS, with surface activity demonstrated by significant reductions in water surface tension at the air−water interface, and by XPS after modification and exposure to dynamic flow conditions over the shear stress range of 0−20 dyn/cm^2. In particular, we examine the relationship between fluorocarbon branch density

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and the hydrophobic−hydrophilic balance on adhesion stability.

Experimental Section

Materials. Perfluoroundecanoic acid, *N*-hydroxysuccinimide, and dicyclohexylcarbodiimide (DCC) were purchased from Aldrich and used as received. Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were purchased from Aldrich and purified by vacuum distillation before use. Water was purified through a Millipore filtration system producing water with resistivity higher than 18.2 MΩ cm. PVAm and Dextran lactone ($M_n = 1500$, $M_w/M_n = 1.16$, DP = 9) were prepared according to the methods reported previously.[19,25] Regenerated cellulose dialysis membrane (MWCO = 3500 Da) was purchased from Fisher. Poly(tetrafluoroethylene) (PTFE, skived thin sheet) was obtained from Enflo Inc. (Bristol, CT). All other reagents and solvents were used as received, unless otherwise specified.

Polymer Analysis. ^{1}H NMR spectra were obtained on a Varian Germini-300 MHz spectrometer using D_2O or DMSO-d_6 as solvent, in parts per million downfield from tetramethysilane (TMS) as a reference. FT-IR spectra in the range 4000−800 cm^{-1} were recorded using a Bio-Rad Digilab FTS-40 IR spectrometer. The materials were ground with KBr and pressed into pellets. For each sample, 100 scans were collected with a resolution of 8 cm^{-1}. XPS spectra were collected on a Physical Electronics PHI-5400 X-ray photoelectron spectrometer with monochromatic Al Kα radiation source at 1487 eV. All spectra were calibrated in reference to the aliphatic C_{1s} carbon at a binding energy of 285.0 eV.

Gel permeation chromatography (GPC) was carried out on a Waters 2690 Alliance system equipped with HEMA-Bio100 column, working at room temperature with distilled water as elutent at a flow rate of 1 mL/min. A Waters 410 differential refractometer and a Mini Dawn light scattering detector were used, and molecular weight (M_n and M_w) of poly(*N*-vinylformamide) (PNVF) was deduced with dn/dc for the polymer set at 0.17.

Surface tensions of aqueous surfactant polymer solutions were measured by the Du Nouy ring method, using a Sigma 703 surface tensiometer at 25 °C. The tensiometer was calibrated with pure water before each use. The surface tension of each surfactant solution was measured 20 min after each dilution to allow time for equilibration. Surface tension was measured three times at each concentration, and the degree of reproducibility was within ±1.0 dyn/cm.

Surface Modification and Characterization Methods. PTFE was modified by immersing in surfactant solution (1−2 mg/mL) for 48 h. The surfactant solution was diluted several times with pure water before samples were removed and air-dried overnight.

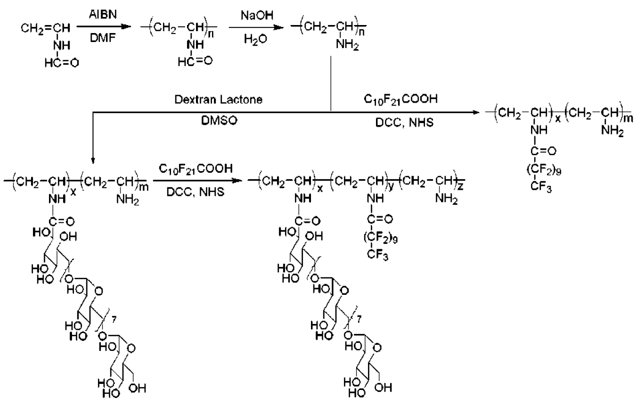
A rotating disk system was used to simulate laminar flow over a shear stress range of 0−20 dyn/cm^2 in phosphate buffer saline (PBS).[30] A thin PTFE (Teflon) sheet was cut into 17 mm diameter disk, attached to the rotating disk sample mount, and rotated in the PBS solution. The typical duration time for each experiment was 1 h. The shear stress (τ_{ss}, dyn/cm^2) experienced at the surface of the disk is a linear function of the radial distance from the center of the disk (r) as described by

$$\tau_{ss} = 0.8\eta r\left(\frac{\omega^3}{\nu}\right)^{1/2} \tag{1}$$

where η is the absolute viscosity of the testing medium (poise), ν is the kinetic viscosity (stokes), and ω is the angular velocity (rad/s).

Data Analysis. The structural data from NMR and XPS were analyzed using two approaches: (1) using ^{1}H NMR to determine the dextran percentage and using XPS to determine the fluorocarbon percentage; (2) using XPS data itself to determine the structural information. For quantification, the surfactant structure is described as (PVAm-Dex)$_x$-(PVAm−FC11)$_y$-(PVAm)$_z$, where x, y, and z are molar percentage of dextran, fluorocarbon, and free amines, respectively, and they are related by $x + y + z = 1$.

Scheme 1. Synthetic Route to Poly(vinylamine) and Derivatization of Poly(vinylamine) with Dextran Lactone and *N*-(Perfluoroundecanoyloxy)succinimide



In the first approach, the composition of the surfactant is calculated as follows:

$$x = \frac{A_{Dex}/9}{A_{CH_2}/2} \tag{2}$$

$$y = \frac{\varphi_F/21}{\varphi_N/2} \tag{3}$$

$$z = 1 - x - y \tag{4}$$

where A_{Dex} is the peak integral associated with dextran protons at glycosidic linkage, A_{CH_2} is the peak integral associated with PVAm backbone, and φ_F and φ_N are the fluorine and nitrogen percentage measured from XPS, respectively.

In the second approach, a surfactant polymer was deposited as a thin film on polyethylene (PE), and F_{1s}, N_{1s}, and O_{1s} were recorded to derive the structural information. The structural information x, y, and z was solved by minimizing the function $(\varphi_N - \varphi_N^*)^2 + (\varphi_O - \varphi_O^*)^2 + (\varphi_F - \varphi_F^*)^2$, where φ_N, $\varphi_{O,}$ and φ_F are nitrogen, oxygen, and fluorine percentage measured from XPS, respectively, and φ_N^*, φ_O^*, and φ_F^* are the calculated nitrogen, oxygen, and fluorine percentage, respectively. The atom percentage and structure composition are related by

$$\varphi_N^* = \frac{1}{46x + 22y + 1} \tag{5}$$

$$\varphi_O^* = \frac{46x + y}{46x + 22y + 1} \tag{6}$$

$$\varphi_F^* = \frac{21y}{46x + 22y + 1} \tag{7}$$

Minimization was accomplished using Optimization toolbox of MatLab.

Synthesis. The general synthetic route for branched fluorocarbon surfactant polymers is summarized in Scheme 1. The general strategy for the synthesis is based on poly(vinylamine) (PVAm) chemistry. PVAm is synthesized according to methods reported previously.[25] Briefly, PVAm is obtained from basic hydrolysis of poly(*N*-vinylformamide) (PNVF), which is obtained by free radical polymerization of *N*-vinylformamide in DMF with AIBN as the initiator. The molecular weight of PVAm ($M_n \sim 35\,000$, $M_w/M_n \sim 1.3$) was deduced from that of PNVF assuming 100% hydrolysis and no loss in the purification process. PVAm can be easily modified with a variety of functional groups, such as carboxylic acid, lactone, isocyanate, or aldehyde. In this report, dextran molecules were attached to PVAm by reacting the amino groups with dextran lactone. Fluorocarbon branches were attached to the backbone by reacting the amino groups with perfluorocarbon succinimide.

***N*-(Perfluoroundecanoyloxy)succinimide.** To a solution of perfluoroundecanoic acid (2 g, 3.5 mmol) and *N*-hydroxysuccinimide (0.48 g, 4.2 mmol) in DMF (5 mL) was added dicyclohexylcarbodiimide (DCC) (0.86 g, 4.2 mmol). The mixture was stirred at ice bath temperature. After 5 h the reaction mixture was filtered to remove the dicyclohexyl urea, and the precipitate was washed with cold DMF (10 mL). The solvent in the filtrate was removed by vacuum rotary evaporation. The yellow oil residue was washed with water and chloroform to yield a white solid, which was vacuum-dried at room temperature to give 1.64 g (70%) of *N*-(perfluoroundecanoyloxy)-succinimide. IR (KBr, cm^{-1}): 1774 (ν(C═O) of ester), 1705 and 1659 (ν (C═O) of imide), 1214 and 1152 (ν(−CF$_2$−)).

Poly(*N*-vinylperfluoroundecanamide) (PVAm-FC11). PVAm-FC11 was prepared by reacting the amino groups of PVAm with *N*-(perfluoroundecanoyloxy)succinimide. PVAm (5 mg, 0.12 mmol) was added to a methanol solution (2 mL) of *N*-(perfluoroundeanoyloxy)succinimide (76.9 mg, 0.12 mmol). The reaction mixture was stirred for 5 h. The precipitate was filtered, washed several times with methanol, and vacuum-dried at 78 °C to give 34.3 mg (50%) of PVAm-FC11. IR (KBr, cm^{-1}): 1681 (ν(C═O) of amide), 1549 (ν(N−H) of amide), 1239, 1212 and 1153 (ν(−CF$_2$−) of side chain).

Poly(*N*-vinyldextranaldonamide) (PVAm-Dex). PVAm-Dex was prepared by reacting the amino groups of PVAm with dextran lactone. Dextran lactone was prepared according to the methods prescribed previously.[25] A solution of PVAm (5 mg, 0.12 mmol amino groups) and dextran lactone (0.16 g, 0.12 mmol) in 5 mL of DMSO/methanol (10/1) was stirred at 70 °C for 48 h. The product was precipitated by the addition of acetone. The precipitate was filtered and dried under vacuum at 78 °C overnight to give 0.13 g (80%) of PVAm-Dex. IR (KBr, cm^{-1}): 1643 (ν(C═O) of amide), 1559 (ν(N−H) of amide), 1153 (ν(C−O) in dextran).

Poly(*N*-vinyldextranaldonamide-*co*-*N*-vinylperfluoroundecanamide) (PVAm(Dex:FC11)). Surfactant polymers PVAm(Dex:FC11) were prepared by reacting the amino groups of PVAm with dextran lactone and *N*-(prefluoroundecanoyloxy)succinimide sequentially. Surfactant polymers with dextran-to-fluorocarbon ratio 1:0.5, 1:1, and 1:2 were synthesized. As an example, to prepare PVAm(Dex:FC11) 1:1, a solution of dextran lactone (78 mg, 0.06 mmol), PVAm (5 mg, 0.12 mmol) in 5 mL of DMSO/methanol (10/1) was stirred at 70 °C for 48 h. The reaction mixture was precipitated by the addition of acetone, and the raw material was dried to give 70 mg (80%) of PVAm-Dex.

To a DMSO solution (2 mL) of PVAm-Dex (21.6 mg) was added *N*-(perfluoroundecanoyloxy)succinimide (10 mg). The mixture was stirred for 5 h. The solution was concentrated by vacuum distillation, and the product was precipitated by the addition of acetone. The precipitate was filtered and dried under vacuum at 78 °C overnight to give 20 mg of raw product, which was purified by extensive dialysis against water using a Spectr/Por 3 regenerated cellulose membrane with 3500 molecular weight cutoff. The same procedure was followed to synthesize the PVAm(Dex:FC11) 1:0.5 and 1:2 by varying the amount of *N*-(perfluoroundecanoyloxy)succinimide reacting with the PVAm-Dex. IR (KBr, cm^{-1}): 1671 and 1640 (ν(C═O) of amide), 1557 (ν(N−H) of amide), 1238 and 1211 (ν(CF$_2$) of side chain), 1153 (ν(C−O) in dextran and ν(−CF$_2$−). ^{1}H NMR (D$_2$O, δ): 1−1.6 (CH$_2$ of PVAm), 3.0−4.1 (−CH− of PVAm backbone and all dextran CH and CH$_2$ except the ones at glycosidic linkages), 5.0 (dextran CH at glycosidic linkages).

Results and Discussion

The general design for the surfactant synthesis is based on poly(vinylamine) (PVAm) chemistry. In consideration of surfactant adhesion on a solid PTFE surface, a higher molecular weight PVAm backbone is important for increasing the number of fluorocarbon branches per unit molecule. On the other hand, a lower molecular weight backbone allows the adsorbed polymer to more easily undergo conformational changes that are needed to approach the lowest energy conformational state on the PTFE surface. From our previous work on surfactant polymers with hydrocarbon branches, a molecular weight (M_n) of 5000−40 000 for the PVAm provides stable adsorption on polymers such as low-density polyethylene.

In addition to the initiator:monomer ratio and reaction temperature, the choice of solvent can have a major impact on the molecular weight of PNVF because of the difference in chain transfer constant to solvent. Typically, 2-propanol is used as solvent to produce PNVF with relatively low molecular weight ($M_n \sim 10\,000$), while DMF is used to obtain a higher molecular weight PNVF ($M_n \sim 40\,000$) as in this study. The molecular weight was determined by GPC/light scattering, and the molecular weight for PVAm ($M_n \sim 35\,000$, $M_w/M_n \sim 1.3$) was calculated from that of PNVF.

FT-IR spectra of PVAm and the branched derivatives are shown in Figure 1. In Figure 1a, the ν(N−H) around 3417 cm^{-1} and δ(N−H) around 1597 cm^{-1} indicate the presence of amino groups in the PVAm. However, the shape of ν(N−H) is broadened considerably compared with small organic amines, like octylamine, because of the extensive intramolecular and intermolecular hydrogen binding that occurs in the polymeric systems.

Derivatization of PVAm. Graft polymers with either hydrophobic fluorocarbon branches or hydrophilic dextran branches were synthesized, as well the complete fluorocarbon surfactant polymer. PVAm-FC11 was prepared by reacting the amine groups of PVAm with *N*-(perfluoroundecanoyloxyl)succinimide in methanol. The reaction of succinimide with amine is selective, so that hydroxyl groups on dextran do not need protection. PVAm-FC11 was insoluble in methanol and has poor solubility in most common solvents. The appearance of the amide I and II, ν(−CF$_3$), and ν(−CF$_2$−) indicates new amide bond formation, as shown in Figure 1c. A weak shoulder around 1590 cm^{-1} is attributed to unreacted amino groups. It is interesting to note that the amide I peak of PVAm-FC11 was shifted to higher wavenumber (1681 cm^{-1}) compared with the amide I (~1643 cm^{-1}) for surfactants with hydrocarbon branches. This shift may be caused by the strong inductive effect of the perfluorocarbon chain. Similar shifts also have been reported for small fluorocarbon molecules such as trifluoroacetamide, in which the amide I absorbance appears at 1709 cm^{-1}.[31]

The ^{1}H NMR of dextran and dextran lactone dissolved in D$_2$O is shown in Figure 2. The anomeric proton of dextran in solution can adopt one of two positions (α or β), which are in equilibrium, but can be distinguished by the different chemical shifts (4.33 and 4.93 ppm) (Figure 2a). When dextran is oxidized to dextran aldonic acid, the signal coming from anomeric protons becomes nondetectable (Figure 2b), suggesting complete oxidation.

PVAm-Dex was prepared by reacting the amino groups of PVAm with dextran lactone as described previously.[25] The solubility of PVAm in DMSO is enhanced by the addition of methanol. The aminolysis of dextran hydroxyl groups is selective, so that protection of dextran lactone is not necessary. Dextran was attached successfully to PVAm through amide bonds,

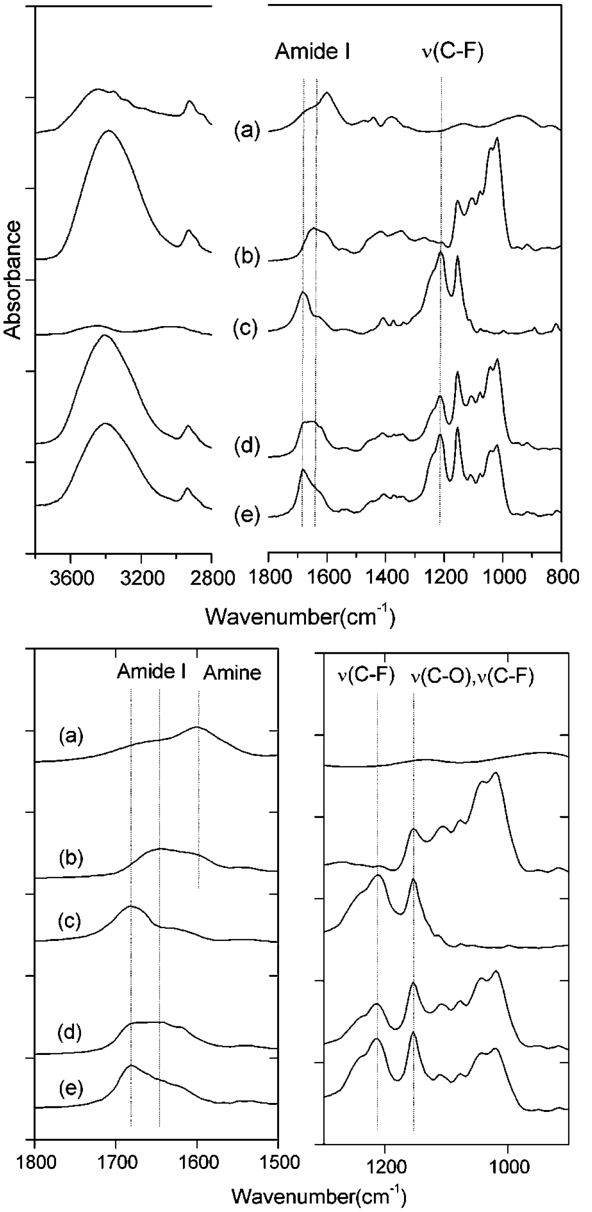


Figure 1. IR spectra of (a) PVAm, (b) PVAm-Dex, (c) PVAm-FC11, (d) PVAm(Dex:FC11) 1:1, and (e) PVAm(Dex:FC11) 1:2.

as shown by the amide I, amide II, and ν(C−O) peaks in the IR spectra (Figure 1b).

PVAm-Dex also was characterized by ^{1}H NMR in D_2O, as shown in Figure 3. Compared with DMSO-d_6, D_2O simplifies the hydroxyl groups of dextran and gives a more accurate estimate of the dextran content in the polymer. The methylene group in PVAm backbone appeared in a broad peak around 1−2 ppm. The dextran branches appeared at two regions: at 5 ppm, due to protons at the α(1−6) glycosidic linkage and at 3−4 ppm region due to all the other protons, except hydroxyl protons. Dextran attachment was determined to be around 22%. This was determined by comparing the protons at glycosidic linkages to the protons in the PVAm backbone in PVAm-Dex. The broad peak in PVAm backbone indicates restricted chain motion after dextran attachment. The shape of proton peaks in dextran branches is the same as that for pure dextran, indicating that molecular freedom of dextran is not restricted by attachment to PVAm. This finding has important implications, since useful biomedical properties like protein resistance and protection from surface "fouling" depend on the rotational motion of attached hydrophilic molecules.

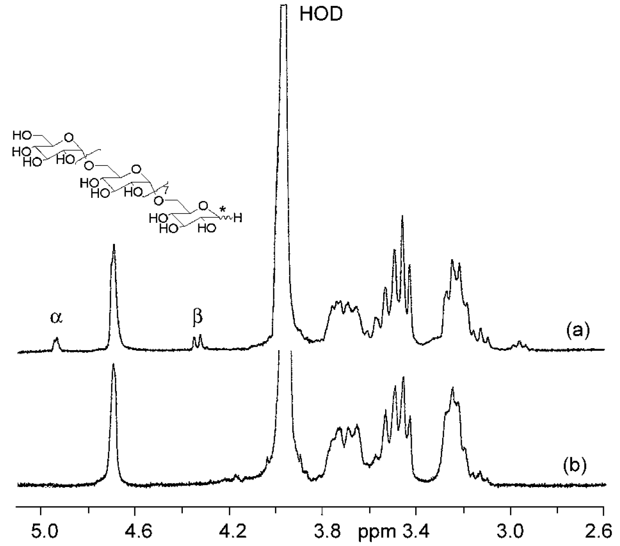


Figure 2. ^{1}H NMR of (a) dextran and (b) dextran aldonic acid in D_2O. The disappearnce of anomeric protons in dextran aldonic acid indicates the terminal oxidation reaction is complete.

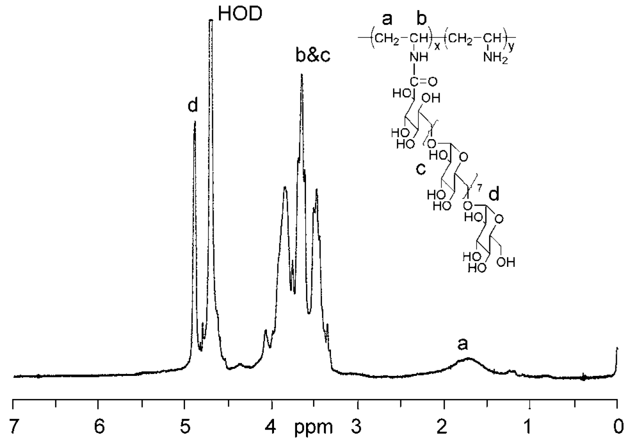


Figure 3. ^{1}H NMR of PVAm-Dex in D_2O by comparing the integral area (d) of glycosidic linkage with the protons in PVAm backbone (a), the density of dextran attachment can be determined.

Synthesis of PVAm(Dex:FC11). Unlike the synthesis of analogous hydrocarbon surfactant polymers, fluorocarbon surfactants cannot be synthesized by reacting PVAm with dextran lactone and succinimide simultaneously. Since the fluorosuccinimide reacts much faster with PVAm than does dextran lactone, the resulting PVAm-FC11 would precipitate, thus preventing further attachment of the hydrophilic dextran.

Similar to PVAm-FC11, the amide bond (1678 cm^{-1}) formed between PVAm and the fluorocarbon appears at higher IR wavenumber compared with the amide bond formed between PVAm and dextran lactone (1640 cm^{-1}). This frequency shift is attributed to inductive effects of the perfluorocarbon chain. As a result, the relative absorbance for the two peaks varies with the ratio of fluorocarbon to dextran on the polymer backbone. As shown in Figure 1d,e, the peaks at 1678 and 1640 cm^{-1} for PVA(Dex-FC11) 1:1 are approximately the same height, while the relative peak height at 1678 cm^{-1} is ~1.7 times greater than the 1640 cm^{-1} absorbance for PVA(Dex:FC11) 1:2.

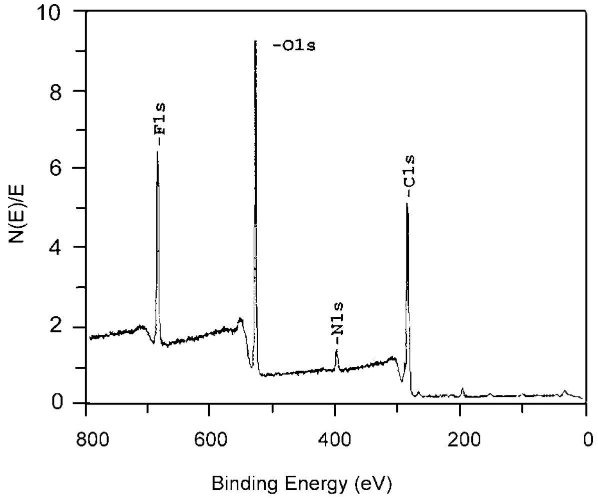


Figure 4. XPS spectra of surfactant PVA(Dex:FC11) 1:1 on PE. The fluorocarbon branch density is estimated by two methods: (1) by comparing fluorine to nitrogen percentage or (2) by least-squares fitting of F, N, and O to surfactant composition. Percentage (%) C, 52.3 (contributed part by substrate); O, 29.4; F, 15.1; N, 3.2.

The results from the infrared analysis demonstrate that successful control of the surfactant polymer structure was achieved by adjusting the hydrophobic to hydrophilic feed ratios. The amide I, amide II, ν(C−O), ν($-CF_2-$), and v($-CF_3$) show successful attachment of both perfluorocarbon and dextran to the PVAm backbone through amide bonds. However, numerous overlapping peaks from amide, amine, and possibly water in the nearby region preclude accurate quantitative analysis by FT-IR.

The composition of each surfactant was determined quantitatively by combining the results from the ^{1}H NMR and XPS. The dextran branch density was obtained through the ^{1}H NMR analysis, while the fluorocarbon branch density was deduced from XPS analysis (Figure 4). By comparing the F_{1s} fluorine peak from the hydrophobic branch and the N_{1s} nitrogen peak from the backbone, the fluorocarbon branch density can be quantified. XPS data also can be processed using a least-squares method to fit nitrogen, fluorine, and oxygen percentages to the surfactant structure. The carbon percentage is not used in the calculation, since it contains contributions from the PE substrate. The results quantify the dextran density on the polymer backbone for each surfactant polymer to be about 21%, very similar to the result determined from the NMR analysis. While the dextran content is a constant for each surfactant polymer, the fluorocarbon branch density, determined by XPS analysis, increases from 15 to 45 mol % of reacted amines in the polymer backbone, as shown in Table 1. The structural information (x, y, and z) determined using XPS itself is in excellent agreement (±2 mol %) with the data in Table 1 obtained using the combination of NMR and XPS. In addition, there are many unreacted amine groups along the polymer backbone. This is attributed to steric inhibition effects of the attached bulky dextran molecules. However, any remaining unreacted amine groups can be capped by reaction with smaller molecules such as glucolactone or acetic succinimide, as was demonstrated in a previous report.[25]

Table 1. Fluorocarbon Surfactant Composition

composition	PVAm(Dex:FC11) dextran:perfluoroundecanoyl ratio 1:0.5	1:1	1:2
mol wt[a] (M_n)			
PVAm	35000	35000	35000
surfactant	370000	397000	504000
composition (mol %)			
dextran[b]	22	22	22
perfluoroundecanoyl[c]	15	21	45
amine	63	57	33
groups per surfactant			
dextran	179	179	179
perfluoroundecanoyl	122	171	366
amine	512	464	269

[a] Based on GPC/light scattering of poly(N-vinylformamide) ($M_w/M_n \sim 1.3$). [b] Based on NMR data. [c] Based on XPS data.

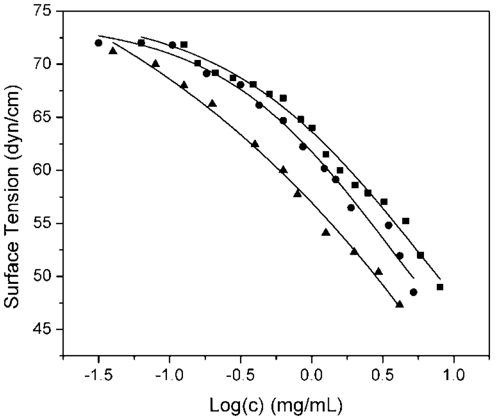


Figure 5. Surface tension of fluorocarbon surfactant polymers in aqeuous solutions. The dextran to fluorocarbon branch ratio in PVAm(Dex:FC11) is held constant at three different values: 1:0.5 (■); 1:1 (●); 1:2 (▲).

Surface-Active Properties. The surface-active properties of fluorocarbon surfactants at the air/water interface were obtained from surface tension measurements. The surface tension data were plotted against the logarithm of concentration, as shown in Figure 5. Surfactant efficiency, defined as $\log(1/C)_{\pi=20}$, where C is the bulk concentration in mol/L, measures the surfactant concentration needed to lower water surface tension by 20 dyn/cm. The efficiency for surfactants 1:0.5, 1:1, and 1:2 is estimated to be around 4.7, 4.8, and 5.2, respectively, as determined from the data in Figure 5 and the surfactant molecular weight shown in Table 1. The increased content of fluorocarbon branches in surfactant 1:2 provides a greater thermodynamic driving force for surfactant assembly at the air/water interface and thus is more efficient in reducing water surface tension. In terms of effectiveness, defined by the minimum surface tension, all three polymers are very similar up to the solubility limit. This suggests similar fluorocarbon coverage at the interface, since effectiveness depends on the van der Waals attractions of the hydrophobic groups in the surfactants.[32] No critical micelle phenomenon for all three surfactants was observed over the measured concentration range. This result is consistent with previous observations for hydrocarbon surfactant polymers.[25]

Surfactant Adsorption and Adhesion on PTFE. In the presence of a solid surface, surfactants in water can minimize interfacial energy by forming micelles, assembling at air−water interface, and by adsorbing at the solid/water interface. XPS analysis (Figure 6) shows surfactant adsorption on PTFE obtained under different shear stress conditions. For comparisons between each

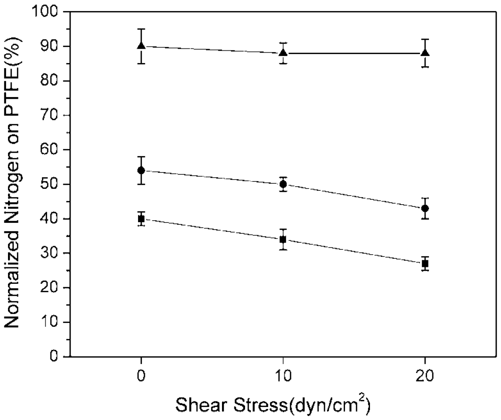


Figure 6. Normalized nitrogen percentage on PTFE as a function of shear stress experienced by the surfactant polymer. The dextran to fluorocarbon branch ratio in PVAm(Dex:FC11) is held constant at three different values: 1:0.5 (■), 1:1 (●), and 1:2 (▲).

surfactant, the N_{1s} atomic percent is normalized against the value obtained for the respective bulk polymer. For surfactant polymer PVAm(Dex:FC11) with branch ratios ranging from 1:0.5 to 1:2, the nitrogen percentage at 0 dyn/cm^2 increases monotonically from 40% to 90%, indicating increasing amount of adsorbed surfactant. This follows the same order as the results obtained for surface activity at the air/water interface. These finding also are consistent with previous reports and theoretical considerations, which show adsorption increases with increased hydrophobic content.[22−24] Electrostatic interaction is not a significant factor in controlling surfactant adsorption, since zeta potentials for all three surfactants measured in PBS solution are close to 0 mV.

The adhesion of surfactants on PTFE was investigated by exposing surface adsorbed surfactant to different applied shear stress for 1 h. For the surfactant with a dextran:fluorocarbon branch ratio of 1:2, there is no significant change in the amount of adsorbed surfactant polymer after exposure to shear stress ranging from 0 to 20 dyn/cm^2. This indicates that the adsorption was not kinetically reversible on the time scale of the measurements. In contrast, the amount of adsorbed surfactant decreases by 32% and 20% for surfactants with branch ratios of 1:0.5 and 1:1, respectively, over the same shear stress range. The results obtained under applied shear stress suggests that increasing the fluorocarbon branch density correlates with increasing surfactant adhesion on PTFE. Consequently, the fluorocarbon branch density appears to be an important factor in controlling surfactant polymer adsorption and adhesion on PTFE.

The stability of adsorbed comblike polymer surfactants on solid polymer substrates will depend on many factors, including polymer backbone molecular weight, the length and ratios of the hydrophobic and hydrophilic branches, and surfactant−surfactant and surfactant−substrate intermolecular interactions. The chemical similarity between the fluorocarbon branches and the PTFE is designed to improve the thermodynamic compatibility between the surfactant and the substrate compared with the hydrocarbon branches used previously. The fluorocarbon branch also possesses a symmetric cylindrical shape, which should match the geometry of surface fluorocarbon chains in PTFE and increase adhesive intermolecular contact. Further iteration of this approach should assist in identifying important structure−property correlations needed to achieve optimal surfactant−substrate adhesive interactions.

Conclusions

We describe a synthetic approach to prepare a variety of fluorocarbon surfactant polymers with well-defined structures. The comblike surfactant polymers with fluorocarbon and dextran branches described in this report are surface-active at both the air/water and PTFE/aqueous interface. Increasing the fluorocarbon branch density from 15 to 45 mol % in the polymer backbone increases the surface activity of the polymer at both the air/water and the PTFE/aqueous interface. This was demonstrated by significant reductions in surface tension obtained from aqueous surfactant solution, by increased adsorption on PTFE, and by increased adhesion stability under applied shear stresses of up to 20 dyn/cm^2.

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References and Notes

(1) Veith, F. J.; Ascer, E.; Gupta, S. K. In *Vascular Graft Update: Safety and Performance*; Kambic, H. E., Kantrowitz, A., Sung, P., Eds.; ASTM: Philadelphia, PA, 1986; pp 25−32.
(2) Ku, D. N.; Allen, R. C. In *Biomedical Engineering Handbook*; Bronzino, J. D., Ed.; CRC Press: Boca Raton, FL, 1995; pp 1871−1878.
(3) Brewster, D. C. In *Vascular Surgery*, 5th ed.; Rutherford, R. B., Ed.; W.B. Saunders: Philadelphia, PA, 2000; Vol. 1, pp 559−584.
(4) Hoffman, J.; Larm, O.; Scholander, E. *Carbohydr. Res.* **1983**, *117*, 328−331.
(5) Shankar, H.; Senatore, F.; Wu, D. R.; Avantsa, S. *Biomater., Artif. Cells, Artif. Organs* **1990**, *18*, 59−73.
(6) Dekker, A.; Reitsma, K.; Beugeling, T.; Bantjes, A.; Feijen, J.; Vanaken, W. G. *Biomaterials* **1991**, *12*, 130−138.
(7) Ito, Y.; Kajihara, M.; Imanishi, Y. *J. Biomed. Mater. Res.* **1991**, *25*, 1325−1337.
(8) Deutsch, M.; Meinhart, J.; Fischlein, T.; Preiss, P.; Zilla, P. *Surgery* **1999**, *126*, 847−855.
(9) Vargo, T. G.; Gardella, J. A.; Meyer, A. E.; Baier, R. E. *J. Polym. Sci., Polym. Chem.* **1991**, *29*, 555−570.
(10) Sipehia, R.; Martucci, G.; Barbarosie, M.; Wu, C. *Biomater. Artif. Cells, Immobilization Biotechnol.* **1993**, *21*, 455−468.
(11) Baquey, C.; Palumbo, F.; Porte-Durrieu, M. C.; Legeay, G.; Tressaud, A.; d'Agostino, R. *Nucl. Instrum. Methods Phys. Res., Sect. B: Beam Interact. Mater. Atoms* **1999**, *151*, 255−262.
(12) Daubendiek, R. L.; Calvert, J. G. *Environ. Lett.* **1974**, *6*, 253−272.
(13) Costello, C. A.; McCarthy, T. J. *Macromolecules* **1984**, *17*, 2940−2942.
(14) Costello, C. A.; McCarthy, T. J. *Macromolecules* **1987**, *20*, 2819−2828.
(15) Shults, M.; Updike, S.; Busby, M.; Sokol, L.; Garber, C. *Trans. ASAIO* **1979**, *25*, 66−70.
(16) Danielson, N. D.; Siergiej, R. W. *Biotechnol. Bioeng.* **1981**, *23*, 1913−1917.
(17) Kobos, R. K.; Eveleigh, J. W.; Stepler, M. L.; Haley, B. J.; Papa, S. L. *Anal. Chem.* **1988**, *60*, 1996−1998.
(18) Rucka, M.; Turkiewicz, B.; Zuk, J. S. *J. Am. Oil Chem. Soc.* **1990**, *67*, 887−889.
(19) Zhang, T. H.; Marchant, R. E. *Macromolecules* **1994**, *27*, 7302−7308.
(20) Lee, J. H.; Kopecek, J.; Andrade, J. D. *J. Biomed. Mater. Res.* **1989**, *23*, 351−368.
(21) Lee, J. H.; Kopeckova, P.; Kopecek, J.; Andrade, J. D. *Biomaterials* **1990**, *11*, 455−464.

(22) Scheutjens, J. M. H. M.; Fleer, G. J. *J. Phys. Chem.* **1979**, *83*, 1619−1635.

(23) Evers, O. A.; Scheutjens, J. M. H. M.; Fleer, G. J. *Macromolecules* **1990**, *23*, 5221−5233.

(24) van der Linden, C. C.; Leermakers, F. A. M.; Fleer, G. J. *Macromolecules* **1996**, *29*, 1000−1005.

(25) Qiu, Y. X.; Zhang, T. H.; Ruegsegger, M.; Marchant, R. E. *Macromolecules* **1998**, *31*, 165−171.

(26) Holland, N. B.; Qiu, Y.; Ruegsegger, M.; Marchant, R. E. *Nature (London)* **1998**, *392*, 799−801.

(27) Horbett, T. A. *Cardiovasc. Pathol.* **1993**, *2*, 137S−148S.

(28) Ishikawa, Y.; Kuwahara, H.; Kunitake, T. *J. Am. Chem. Soc.* **1994**, *116*, 5579−5591.

(29) Javis, N. L.; Zisman, W. A. In *Kirk-Ohmer Encyclopedia of Chemical Engineering*, 2nd ed.; Standen, A., Ed.; Interscience Publishers: New York, 1966; Vol. 9, pp 686−738.

(30) Vacheethasanee, K.; Marchant, R. E. *J. Biomed. Mater. Res.* **2000**, *50*, 302−312.

(31) Pouchert, C. J. *The Aldrich Library of Infrared Spectra*, 2nd ed.; Aldrich Chemical Co.: Milwaukee, WI, 1975.

(32) Rosen, M. J. *J. Am. Oil Chem. Soc.* **1972**, *49*, 293−297.

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