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Wetting Behavior of Oleophobic Polymer Coatings Synthesized from Fluorosurfactant-Macromers

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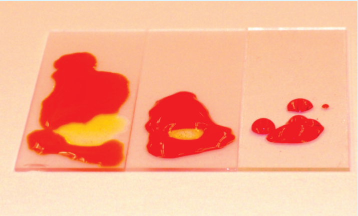
Supporting Information



ABSTRACT: Architecturally similar monomers were copolymerized with a water–oil discriminate fluorosurfactant to create hydrophilic–oleophobic coatings. Acrylic acid, hydroxyethyl methacrylate, and methyl methacrylate were used as comonomers with the fluorosurfactant macromer. The homopolymers of the selected comonomers are water-soluble, water-swellable, and water-insoluble, respectively, thus coupling the surfactant monomer in varying concentration within polymers of varying hydrophilicity. Wetting behavior of water and hexadecane were examined as a function of copolymer composition, thus revealing critical structure–property relationships for the surfactant-based system. Acrylic acid copolymers and hydroxyethyl methacrylate copolymers both exhibited a hexadecane contact angle which exceeded the water contact angle. This condition predicted an ability to "self-clean" oil-based foulants. The most oleophobic of the self-cleaning copolymers had an advancing hexadecane contact angle of 73° and an advancing water contact angle of 40°. It was determined that the advancing and receding water and hexadecane contact angle response varies montonically for each copolymer type as the surface concentration of the surfactant is varied. Comparing between copolymer types revealed large differences in wetting response. Methyl methacrylate copolymers with 2.8 mol % surfactant had advancing water contact angle 82° and advancing hexadecane contact angle 26°, which is neither oleophobic nor self-cleaning. In contrast, acrylic acid copolymers with 3.1 mol % surfactant had advancing water contact angle of 44° and advancing hexadecane contact angle of 52°, creating a self-cleaning coating. Thus, the nature of the comonomer exerts a greater influence than the surfactant content on the wetting behavior and self-cleaning ability of the final coating.

KEYWORDS: oleophobic, self-cleaning, hydrophilic, copolymer, coating, wetting, antifog

INTRODUCTION

Hydrocarbon fouling is a problem of critical interest for both industrial and environmental reasons, as oils and other organic matter have the propensity to preferentially coat and potentially ruin many surfaces. Considerable efforts are applied to prevention and removal of fouling for fabrics,[1−4] membranes,[5−7] and food industry applications,[8,9] among other devices and surfaces.[10] Rather than relying on external cleaning treatments, tailored surface treatments designed for oleophobicity have shown success in creating materials which inherently resist fouling. Such materials are potentially capable of extending the passive service life due to self-cleaning nature and fouling resistance. Strategies for creating robust oleophobic surfaces are often bioinspired,[3,11] and can specifically include the physical manipulation of surface structures,[12−14] or unique chemical modification in the form of selectively amphiphilic macromolecules.[15,16] In the former case, the surfaces are often permanently oleophobic whereas the latter strategy can include "switchable-wetting" based on molecular reconstruction in the presence of various fluids.[10,17] Many oleophobic surfaces are also hydrophobic[18] or even superhydrophobic[19,20] which may be desirable for specific applications. A more challenging case is the hydrophilic–oleophobic surface where water will wet the surface, but oil will not. Stimuli-responsive surfaces have been created by other laboratories[21−24] and previously by the authors[25−27] which simultaneously display hydrophilicity and oleophobicity based on a favorable interaction with polar liquids and an unfavorable interaction with nonpolar liquids. Surface bound surfactants can be employed for such a purpose. Plasma polymerized polymer, such as maleic anhydride[21] or poly(acrylic acid)[23] complexed with a cationic fluorosurfactant displayed low water contact angle ∼20° and high hexadecane contact angle ∼80°, for example. Hydrophilicity of these surfaces is only possible through a two step deposition process in which the plasma polymer surface is first created followed by surface functionalization by the fluorinated surfactant. If the anhydride/acrylic acid-fluorosurfactant polymer is created prior to deposition a hydrophobic-oleophobic surface is formed. It is thought that the fluorosurfactant-plasma polymer maintains hydrophilicity because the fluorinated constituents remain in a relatively mobile state at the film surface. Thus the fluorinated moieties may be able to reorganize to allow for penetration of water molecules into the hydrophilic subsurface. Recent NEXAFS studies have concluded that similar amphiphilic polymers exhibit surface reconstruction when switching from the dry to wet state.[28]

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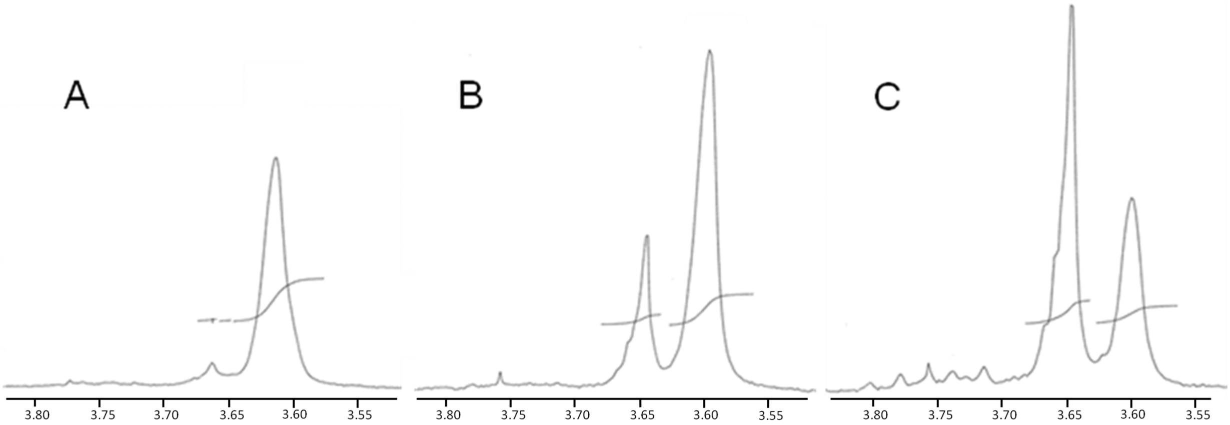

Figure 1. Partial H^1 NMR spectra (3.55−3.8 ppm) of methyl methacrylate copolymer showing peaks of PEG (3.65 ppm) and methacrylate (3.60 ppm) constituents for f-PEG feed content of (A) 1, (B) 10, and (C) 25 mol %.

For water to wet the surface, defects in the fluorinated surface must be present to allow access to the hydrophilic underlayer. Once water molecules are able penetrate the fluorinated end groups, the hydrophilic underlayer is able to wick water across the surface. If the fluoropolymer does not have clear segregation of hydrophilic and hydrophobic constituents, the wicking phenomena is prevented from occurring as beneath the outermost fluorinated surface there is more fluorinated material. There is no longer a hydrophilic underlayer to promote the wetting by water, and the surface is shown to be uniformly hydrophobic.

Widespread adoption of novel oleophobic surfaces is often limited by processing demands relating to either cost or scalability from the laboratory to industrial use. To this end, we have translated concepts from previous work[25−27] into the design of surfactant based copolymers which may be synthesized in bulk quantities and applied to surfaces in separate processing steps. Thus, the application of the copolymer coating can be separated from the synthesis in a laboratory environment. Here, we present the synthesis of surfactant based copolymers with varying mol % of the active surfactant moiety. Additionally, three commodity monomer types were used to elicit the contribution of the comonomer to the hydrophilic−oleophobic response.

EXPERIMENTAL SECTION

Materials. Perfluorinated surfactants (commercial f-PEG) were purchased from DuPont (trade name Zonyl FSN). Zonyl FSN has a reported molecular weight of 950 g/mol. Perfluorinated surfactants were dried using $MgSO_4$ in anhydrous toluene in a sealed nitrogen environment. The following chemicals were purchased from Sigma-Aldrich Co. (Milwaukee, USA) and used as received: anhydrous toluene, methanol, hexane, chloroform, hexadecane, ethylene glycol dimethacrylate, $MgSO_4$, and 2,2′-azobisisobutyronitrile (AIBN) The following monomers were purchased from Sigma-Aldrich and were purified using trap-to-trap distillation to remove any inhibitors: methacryloyl chloride, methyl methacrylate, hydroxyethyl methacrylate, acrylic acid.

Polymer Synthesis. Methacryloyl chloride in slight excess was reacted with dried commercial f-PEG in anhydrous toluene overnight to create f-PEG monomer (shown schematically in Figure 1A). Unreacted methacryloyl chloride and inhibitor were separated from the f-PEG monomer via column chromatography using silica gel and methanol. The f-PEG monomer was further concentrated via rotary evaporator. NMR spectra of the f-PEG monomer confirmed the successful reaction of methacryloyl chloride with the terminal alcohol group of the initial f-PEG molecule (not shown). The ratio of PEG units to methyl units in the f-PEG monomer was calculated to be 9.3 based on the NMR spectra of f-PEG monomer.

Random copolymers were synthesized from feed mixtures of f-PEG monomer and either acrylic acid, methyl methacrylate, or hydroxyethyl methacrylate with feed ratios of 1:99 mol %, 10:90 mol % and 25:75 mol %. A full synthesis protocol is shown in the Supporting Information. A brief description follows here. All polymers were synthesized in 1:2 volume ratio of monomer to solvent at 70 °C for 72 h with AIBN as the initiator. Acrylic acid (AA) copolymers were synthesized in methanol and precipitated in toluene. Methyl methacrylate (MMA) copolymers were synthesized in toluene and precipitated in hexane. Hydroxymethyl methacrylate (HEMA) copolymers were synthesized in methanol and precipitated in chloroform. Molecular weight of copolymers was not characterized because of incompatibility with GPC columns. Homopolymers of f-PEG, methyl methacrylate, hydroxymethyl methacrylate, and acrylic acid were also synthesized as controls.

Polymer Characterization. Dynamic contact angle measurements were taken using a Ramé-Hart Advanced Automated Model 500 goniometer. Water and hexadecane were used as model fluids to characterize oleic fouling and self-cleaning via dynamic contact angle. Water was deionized to a resistivity of 18.3 M-ohm-cm using a Barnstead Nanopure Infinity filtration system. Proton NMR spectra were measured using a Varian Inova300−1. A Kratos Axis Ultra II was used for X-ray photoelectron spectroscopy as a method of surface sensitive chemical characterization. Polymer films, several hundred nm thick, were created by spin-casting at 3000 rpm from a 3 wt % solution followed by a 24 h anneal at 120 °C. This temperature was chosen as it exceeds the glass transition temperature of the constituent homopolymers (106 °C for PAA, 105 °C for PMMA, 86 °C for PHEMA).[29] The f-PEG homopolymer is a soft wax at room temperature, thus we assume that the inclusion of f-PEG in the copolymers will lower the T_g and that annealing at 120 °C is adequate for all polymer compositions. Toluene was preferred solvent for methyl methacrylate copolymers; methanol was preferred solvent for both hydroxyethyl methacrylate and acrylic acid copolymers.

Two performance tests were also conducted on select copolymers. A self-cleaning test was performed in which droplets of both water and hexadecane were simulataneously placed in contact with the surface. Once on the surface, the two fluids are brought into contact with each other and the interaction between the droplets is observed. On conventional surfaces hexadecane will spread more aggressively and displace the water at the surface, whereas self-cleaning surfaces are sufficiently oleophobic that water is able to displace the hexadecane. In addition, antifog tests were performed on the spin-cast surfaces in two different conditions. Room temperature copolymer coatings were held 10 cm above steam bath for 30 s. Copolymer coatings were also placed in a −20° freezer for 30 min and then removed into humid laboratory air. In both cases, the nature of the condensed water was observed as either "fogged" or "clear vision".

RESULTS

The bulk polymerization model was initially explored with methyl methacrylate as a representative comonomer to combine with the f-PEG monomer. Methyl methacrylate was chosen primarily because of its structural similarity to methacryloyl chloride, the precursor to the f-PEG monomer. The primary question to be addressed was the feasibility of creating a reactive f-PEG monomer and the ability to incorporate this monomer into a polymerization reaction with methyl methacrylate. The polymers created from feed composition of 1, 10, and 25 mol % f-PEG monomer with the balance being methyl methacrylate, were measured using NMR.

NMR was used to determine final composition of each methyl methacrylate copolymer as compared to the respective molar feed ratio. The copolymers composed of f-PEG and methyl methacrylate exhibit two distinct peaks centered at 3.60 ppm and 3.65 ppm. The three terminal hydrogen atoms on the methacrylate group (which is not present in the f-PEG monomer) have a peak centered at 3.60 ppm which is distinct from the four hydrogen atoms on the ethylene groups which has a peak centered at 3.65 ppm (Figure 1). For feed composition of 1, 10, and 25 mol % f-PEG the resultant methyl methacrylate copolymers had final compositions of 0.5, 2.8, and 12.8 mol % f-PEG, respectively.

Subsequent compositional characterization was performed using XPS as discussed below. XPS was the preferred method of characterization because we were primarily concerned with the composition at the surface of the polymers in thin film geometries. XPS being surface sensitive to the first several nm of material was ideally suited to measure the composition of polymer that would determine the hydro-and oleophobic behavior. Additionally, methyl methacrylate copolymers were very amenable to NMR measurements based on solubility and clarity of distinct peaks for quantitative characterization; for nonmethyl methacrylate copolymers the fidelity of NMR characterization was diminished.

XPS analysis of f-PEG homopolymer indicated that the average molecular formula for the f-PEG monomer was $F_{19}C_{35}O_{12}H_{49}$. Molecular formula was determined from the high resolution carbon spectra (representative spectra shown for acrylic acid copolymers in Figure 2, peak assignments are identical). Five peaks were used to fit the f-PEG carbon spectra: aliphatic carbon at 285.0 eV, ethylene glycol carbon at 286.2 eV, carboxylic carbon at 288.8 eV, main chain difluoro-carbon at 291.65 eV, and terminal trifluoro-carbon at 294.0 eV. Each surfactant molecule contains only one trifluoro carbon, using this constraint, the molecular composition of the fluorinated end was determined from the ratio of difluoro carbon to trifluoro carbon which was 8.02 ± 0.18 to 1. The ratio is based on 23 high-resolution carbon spectra from f-PEG containing copolymers and f-PEG homopolymer. The f-PEG monomer is likely to be polydisperse with a majority of species having fluorinated components of either eight or ten total fluorinated carbons. The carbon to fluorine ratio as measured in the XPS survey spectra for f-PEG homopolymer was 1.86 ± 0.05 to 1. Assuming 19 fluorine and 9 carbon atoms in the fluorinated constituent, 26 carbon atoms remain; 4 carbon atoms are accounted by the methocryloyl chloride modification (Scheme 1A) and 22 carbon atoms comprise the polyethylene glycol component of f-PEG. The polyethylene glycol component, just as with the fluorinated component, is also likely to be polydisperse with an average of 11 (C−C−O) monomer units. The XPS based compositional analysis ($F_{19}C_{35}O_{12}H_{49}$, 1022 g/mol) is consistent with the calculated molecule weight (1018 g/mol) of the presynthesized f-PEG components as reported by suppliers (see Experimental Section). Full XPS characterization of the f-PEG polymer was needed to establish a method of quantifying final copolymer composition based on high resolution XPS spectra of carbon. The spectra of three acrylic acid copolymers are shown in Figure 2 as an example.

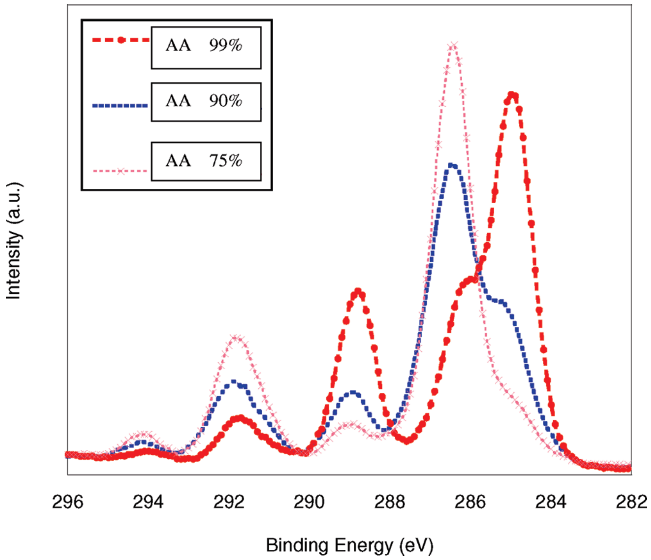

Figure 2. High-resolution XPS spectra for three acrylic acid-f-PEG copolymers varied by monomer feed ratio. High f-PEG (25 mol % feed) spectra is thin dotted line with (x) markers, medium f-PEG (10 mol % feed) is blue dotted line, low f-PEG (1 mol % feed) is double thick dotted line with (circle) markers. Five peaks were used to fit the f-PEG carbon spectra: aliphatic carbon at 285.0 eV, ethylene glycol carbon at 286.2 eV, carboxylic carbon at 288.8 eV, main chain difluoro-carbon at 291.65 eV, and terminal trifluoro-carbon at 294.0 eV.

Scheme 1. Synthesis of (A) f-PEG Monomer from Methacryolyl Chloride and Commercial Fluorosurfactant, (B) Methyl Methacrylate, (C) Acrylic Acid, (D) Hydroxyethyl Methacrylate

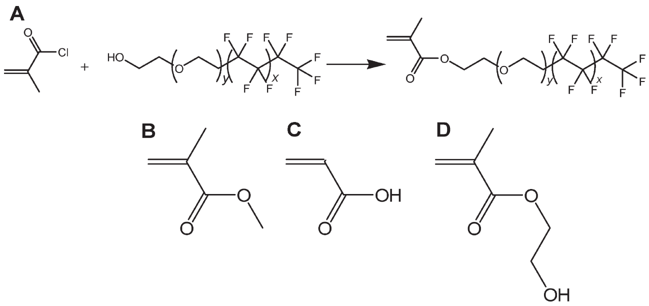

Table 1. Molar Composition and Weight Composition of Copolymers As Measured by XPS (* denotes composition determined by NMR) Compared to Molar Feed Ratio for Synthesis Reaction

molar composition in feed	molar % f-PEG measured in copolymer	wt % f-PEG measured in copolymer
acrylic acid	0	0
99% AA 1% f-PEG	3.1	31.1
90% AA 10% f-PEG	17.2	74.6
75% AA 25% f-PEG	43.9	91.7
hydroxyethyl methacrylate	0	0
99% HEMA 1% f-PEG	4.9	28.7
90% HEMA 10% f-PEG	7.8	39.8
75% HEMA 25% f-PEG	12.4	52.5
methyl methacrylate	0	0
99% MMA 1% f-PEG	0.5*, 0.58	5.6
90% MMA 10% f-PEG	2.8*, 2.7	22.7
75% MMA 25% f-PEG	12.8*	59.9

The fluorinated constituent of the f-PEG copolymers can be measured unambiguously in the XPS high resolution carbon spectra.[30,31] Thus, by clarifying the specific composition of the f-PEG monomer, the high resolution carbon spectra can be used to measure the composition of random f-PEG copolymers. Here the fluorinated carbon peak is directly compared with the carboxylic carbon peak. The energy envelop for the carboxylic carbon peak conveniently does not overlap either the fluorinated carbon peak or the ethylene glycol carbon peak. Furthermore, each monomer used contains exactly one carboxylic carbon atom, making this peak ideal for compositional measurement. Compositional measurements for the random copolymers are critical to revealing structure−property relationships as variations in monomer reactivity render the feed composition an unreliable guide to copolymer composition. Copolymer composition in mol % and wt % compared to initial molar feed ratio is shown in Table 1.

The method of using XPS and NMR interchangeably for surface grafted polymers has been well-established.[32] The composition of the methyl methacrylate copolymer synthesized at 1 mol % and 10 mol % feed ratio was measured with both NMR and XPS. The XPS and NMR methods were in close agreement with regard to determining copolymer composition. The 25:75 mol % methyl methacrylate copolymer did not yield enough material to prepare a spin-cast film for XPS analysis; however, NMR analysis was sufficient to characterize the composition. For all three copolymer types, the final composition as measured with either XPS or NMR greatly varied from the feed composition. For acrylic acid copolymers, the copolymer had more f-PEG than represented in the feed; in contrast the methyl methacrylate copolymer contained less f-PEG than represented in the feed in all cases. The hydroxyethyl methacrylate copolymer contained more f-PEG compared to the feed content for the 1 mol % reaction, but less f-PEG in the copolymer compared to the feed content for the 10 and 25 mol % reaction. It is currently unclear why there is so much variation between the final compositions of the three copolymer types. The variation may be due to differences in monomer reactivity in relation to f-PEG or possibly related to changes in solubility as a function of copolymer composition. Changes in solubility could cause in situ phase segregation of the copolymers and the unreacted monomers, thus altering the final copolymer composition. Further study in this vein is warranted, but beyond the scope of this paper.

Copolymer solubility was initially screened at concentrations of 20 mg/mL for a variety of solvents as it was expected that the introduction of surfactant moieties would potentially render some compositions to be mildly water-soluble. Water, ethanol, methanol, and isopropyl alcohol were used as is. Notably, although poly(acrylic acid) is itself water-soluble, the addition of f-PEG constituents into the bulk polymer resulted in non-water-soluble polymers. Likewise, hydroxyethyl methacrylate and methyl methacrylate copolymers were insoluble in water. Lack of water solubility was ideal for the end application of a coating, as laboratory testing (for example, water contact angle) could be performed on simple spin-cast surfaces without the need for additional cross-linking steps to prevent dissolution. Methyl methacrylate based copolymers were found to only be soluble in toluene and at very low concentrations in chloroform. Acrylic acid and hydroxyethyl methacrylate copolymers were soluble at low concentrations in water with added base when the f-PEG was less than 5% mol of the entire polymer composition. Although poly(acrylic acid) is known to have pH sensitive solubility due to its ability to ionize, polyhydroxyethyl methacrylate is not. The hydroxyethyl methacrylate copolymer solubility at high pH may be related to electrolyte strength or effects from the f-PEG. All compositions of acrylic acid and hydroxyethyl methacrylate copolymers were soluble in methanol. The addition of f-PEG clearly affected solubility of the resulting copolymers as compared to the respective homopolymers.

The wetting behavior of the f-PEG copolymers was measured on films which were spin-cast on silicon wafers and annealed at 120 °C. Water and hexadecane were used as representative fluids to characterize hydrophilicity and oleophobicity respectively via advancing and receding contact angle (Figure 3). Hexadecane was used as a representative foulant, as it has very low surface energy and is prone to aggressively wet surfaces.[33] The self-cleaning ability of the polymers was assessed by measuring the water contact angle and the hexadecane contact angle on surfaces, which has been spin-cast from solution.

The overall wetting trends in terms of f-PEG wt % are shown in Figure 4. From this treatment of the data, it is evident that the water contact angles are more significantly influenced by the copolymer type whereas hexadecane contact angles are more significantly influenced by the amount of f-PEG in the copolymer. Further discussion of wetting behavior will be in terms of mol %; however, Table 1 catalogs the copolymer composition in both wt % and mol %. The contact angle data for the acrylic acid copolymers shows water contact angles increasing with the addition of f-PEG, however the water contact angle behavior is not strongly affected by changes in the final composition of the copolymer as all advancing contact angles are between 40° and 50°. The hexadecane advancing and receding contact angle behavior is significantly enhanced with the addition of the f-PEG molecule. Advancing hexadecane contact angles increase with the addition of more f-PEG; the receding contact angles do not experience similar increases with increase f-PEG content. There is a significant increase in hexadecane contact angle as f-PEG content increased from zero to 3.1 mol % and again from 3.1 to 17.2 mol %. Further increasing the f-PEG surface content beyond 17.2 mol % appears to have little effect on wetting behavior.

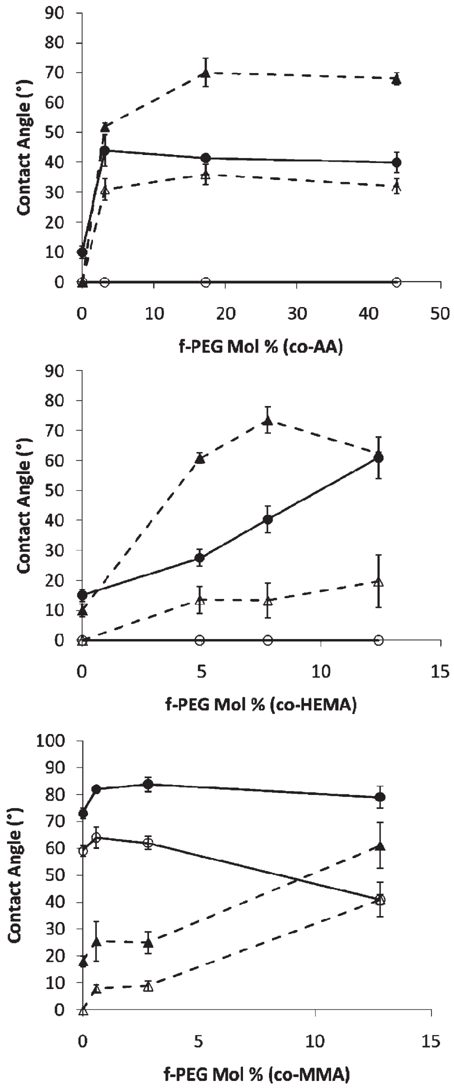

Figure 3. Contact angles on acrylic acid (top), hydroxyethyl methacrylate (middle), and methyl methacrylate (bottom) copolymers presented as a function of f-PEG composition in mol %. Advancing (closed circle) and receding (open circle) water angles and advancing (closed triangle) and receding (open triangle) hexadecane angles are presented. Data are average measurements on at least three surfaces.

The contact angle data for the hydroxyethyl methacrylate copolymers show advancing water contact angles increasing linearly with the addition of f-PEG. The advancing water contact angle of the 12.4 mol % hydroxyethyl methacrylate copolymer exceeded that of the 17.2 mol % acrylic acid copolymers, which indicates that the substrate (or comonomer) exerts a strong influence over the hydrophilicity. The hexadecane advancing contact angle behavior is significantly enhanced with the addition of the f-PEG, though there is minimal difference in the contact angles with regard to varying the composition. The hexadecane receding contact angles were also unaffected by composition, though the presence of f-PEG did enhance the receding hexadecane contact angles to a measurable 13−14° as compared to 0° of pure hydroxyethyl methacrylate.

Methyl methacrylate copolymers exhibited much higher water contact angles than the acrylic acid or hydroxyethyl methacrylate copolymers. Methyl methacrylate homopolymer has a relatively high water contact angle of 73°; the addition of f-PEG as a comonomer further increased the advancing water contact angle. Likewise, receding water contact angle was greater than 40° for all methyl methacrylate copolymers. In contrast, receding water contact angle was <10° for all acrylic acid and hydroxyethyl methacylate copolymers indicating that while there is some resistance to complete wetting, once these surfaces are wetted the water layer interacts strongly with the surface. Although the addition of f-PEG also increased the hexadecane contact angle, in no instance was the hexadecane contact angle greater than the water contact angle for the methyl methacrylate copolymers. Methyl methacrylate copolymers have an elevated hexadecane contact angle as compared to neat PMMA on which hexadecane spreads. In stark contrast, for both hydroxyethyl methacrylate and acrylic acid copolymers, the hexadecane contact angle is greatly enhanced, while maintaining hydrophilicity. Using the simple self-cleaning test described in the Experimental Section, the acrylic acid copolymers with 3.3 mol % f-PEG and greater exhibited robust self-cleaning, where no external agitation was required for oil displacement. See Video S1 in the Supporting Information. The hydroxyethyl methacrylate copolymers should have also been robustly self-cleaning at intermediate f-PEG compositions based on the water and hexadecane contact angles. However, the self-cleaning behavior was less robust than the acrylic acid copolymers. Although hexadecane could still be macroscopically displaced on the surface, additional mechanical agitation was sometimes required.

■ DISCUSSION

The water contact angle of the unmodified homopolymers appears to have a strong correlation with the water contact angle behavior of the corresponding f-PEG copolymers. The hexadecane contact angle behavior is not as strongly influenced by the character of the unmodified polymer. This observation has some implications with respect to the proposed mechanism of stimuli responsive behavior for these surfactant based coatings. In previous studies with the hydrophilic−oleophobic surfaces created on silica surfaces,[25,26] the surfactant molecules were covalently anchored on silicon wafers. In that work, surfactant molecules were attached via a monolayer of isocyanate reactive sites, and thus the surfactant molecules were highly constrained and uniformly distributed at the surface. Any disorder on the surface was due to either incomplete reactions between the isocyanate and the surfactants or disorder could also be due to the inherent polydispersity of the surfactants. As described here in the Experimental Section, the surfactant is unlikely to be monodisperse. With the surfactant-based copolymers, the f-PEG molecules may be distributed throughout the depth of the polymer coating. Thus the locations of the hydrophilic and oleophobic constituents are intercalated with each other. The implication of this structural difference is that there is likely significant surface reordering as the copolymers undergo solvent induced molecular rearrangement such that in the presence of water, the hydrophilic moieties are located at the interface. Similarly, in the absence of water, the low-surface-energy component (fluorine) is then positioned at the interface. For such a system to be successful in discriminating between different fluids, a critical amount of hydrophilic material must be present in order to mask the hydrophobic material in the presence of water. This is not the case in the example of the methyl methacrylate copolymers, which are relatively hydrophobic and oleophilic—the

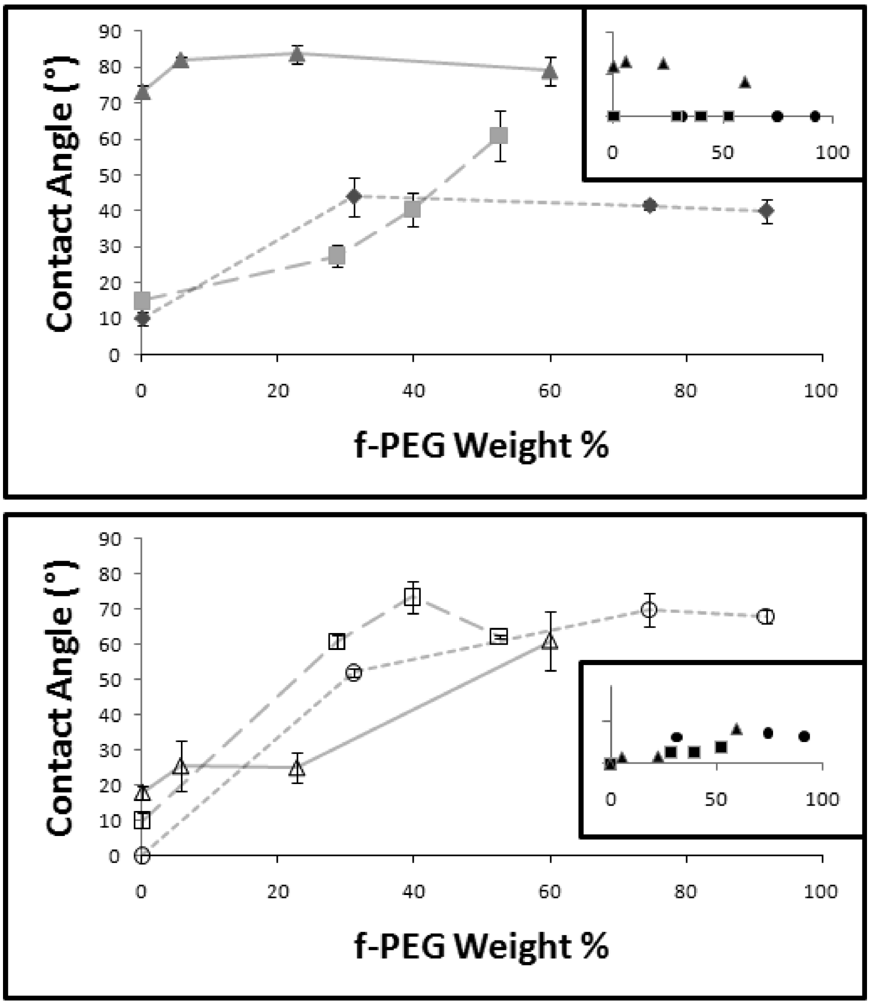

Figure 4. Top: Advancing water contact angles on acrylic acid (circle), hydroxyethyl methacrylate (squares), and methyl methacrylate (triangles) copolymers presented as a function of f-PEG composition in wt %; inset plot is receding water contact angle for the same surfaces. Bottom: Advancing hexadecane contact angles on acrylic acid (circle), hydroxyethyl methacrylate (squares), and methyl methacrylate (triangles) copolymers presented as a function of f-PEG composition in wt %; inset plot is receding hexadecane contact angle for the same surfaces. Data are same as presented in Figure 3. Lines drawn to aid the eye.

opposite character of the hydroxyethyl methacrylate and acrylic acid copolymers. The specific interaction of water with the copolymer should also be considered. In the experiments presented all three copolymers are well below their glass transition temperature which range between 86 °C and 106 °C.[29] Therefore, significant surface restructuring should be severely impeded outside of the individual f-PEG molecules. However, although none of the copolymers were water-soluble, water should effectively act as a plasticizer for the acrylic acid and hydroxyethyl methacrylate moieties, thus providing a mechanism for some amount of structural mobility sufficient to expose a hydrophilic surface.

The hydroxyethyl methacrylate and acrylic acid copolymers show optimal behavior at relatively low fluorosurfactant compositions. In the case of hydroxyethyl methacrylate, the surfaces at 4.92 mol % f-PEG have a difference in water/hexadecane advancing contact angles of 33° in favor of hexadecane. Increasing the f-PEG content to 7.8 mol % resulted in an increase of both contact angles by 12°, the difference in water/hexadecane advancing contact angles remains 33°; further increases caused a more hydrophobic surface, with little change in the oleophobicity. The same trend is observed in the acrylic acid copolymers, where increased f-PEG content resulted in greater oleophobicity up to 17.2 mol %, further increases yielded no net benefit in wetting behavior. Notably for both hydroxyethyl methacrylate and acrylic acid copolymers, the receding water contact angle was consistently 0° irrespective of composition. As a result, these surfaces had high water contact angle hysteresis. In contrast, the methyl methacrylate copolymers had a measurable receding water contact angle, and subsequently low water contact angle hysteresis. It has been demonstrated that the water contact angle hysteresis strongly determines the fouling-release properties of a surface.[34] For this reason, advancing and receding contact angles for water and hexadecane are useful for predicting hydrophilicity and oleophobicity and likewise any potential for self-cleaning of foulants in aqueous systems.

When considering the ability of water to displace oil on the surface, there was no net benefit by increasing the f-PEG composition past a compositional threshold which varied based on the copolymer material. Similar trends in material design where "less is more" have been observed, specifically in regard to oleophobic coatings.[35] As such, it is likely that by increasing the

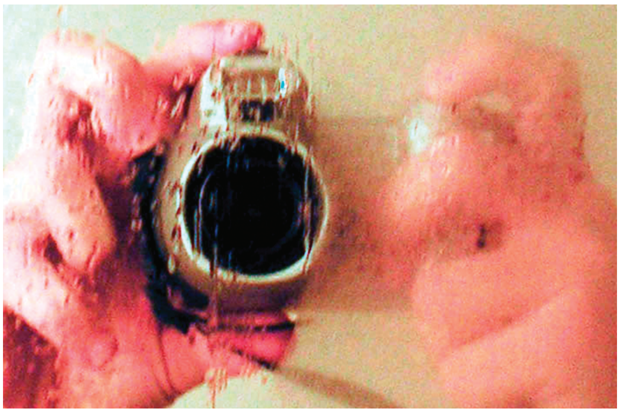

Figure 5. Mirror glass coated with acrylic acid copolymer on the left and uncoated glass on the right exposed to saturated water vapor environment.

fluorosurfactant content, there is some degree of structural or cooperative arrangement unrelated to the introduction of wetting fluids. At higher fluorosurfactant composition, it may be possible for micelle-like clusters to form that would impede the ability of the material to be as solvent-responsive as observed in compositional amounts.

The most oleophobic surface created by the copolymerization method had an advancing hexadecane contact angle of 73° and an advancing water contact angle of 40°. This is similar to results observed on surfaces previously created with the same f-PEG oligomer by a direct grafting method.[25,26] It seems that a difference in advancing contact angles of 33° is the maximum achievable in this system without resorting to manipulating the physical surface structure or increasing the roughness. We have shown in previous work that by grafting to microporous silica membranes the advancing hexadecane contact angle increased to 104°, with a corresponding drop in hydrophilicity indicating that the 73° ceiling observed in this work is not an absolute limit for this type of system.[27] Similarly, other studies have shown net increases in hexadecane contact angle of 45° simply by introducing porosity to the system.[36]

Self-cleaning by fluid displacement may occur by many possible mechanisms. In cases where the contact angle of the foulant (hexadecane) is greater than the contact angle of water, which is the "cleaning" fluid the surface can exhibit robust self-cleaning.[16,17,21] In the event that this is true, water has an energetic driving force to displace the foulant on the surface, as the water will more aggressively wet the surface. Characterizing self-cleaning behavior simply by relying on contact angle measurements alone is limiting in that each solvent is measured individually in air. In contrast, most self-cleaning applications involve contact with mixed fluids or in a submerged environment. Many examples exist of wetting behavior transitioning based on the testing environment, a simple example being in dry and humidified air.[37] To this end, a simple self-cleaning test was performed in which droplets of both water and hexadecane were placed in contact with the surface. Once on the surface, the two fluids are brought into contact with each other. On conventional surfaces hexadecane will spread more aggressively and displace the water at the surface, which is typically predicted from analysis of contact angle measurements. Here again we observed a significant difference in the performance of the copolymers distinguished by the nature of the constituent homopolymer where the methyl methacrylate copolymer had poor self-cleaning ability, hydroxyethyl methacrylate copolymer had moderate self-cleaning with some agitation and acrylic acid copolymers had excellent self-cleaning.

The hydrophilic f-PEG copolymers also have a potential application as antifog surfaces. Many efforts at designing antifog coatings have focused on creating superhydrophilic composite surfaces[38−41] as the ability to mitigate fog-formation is strongly correlated with a low water contact angle.[42,43] Fog will not develop on hydrophilic surfaces, as the water condensed and wets the surface forming a transparent sheet as opposed to discrete droplets which scatter light. Antifog surfaces that are oleophobic are especially useful for long-lifetime coatings, as contaminates will ruin the hydrophilicity of a coating and cause it to again fog in the presence of condensate. The spin-cast surfaces were tested for fogging in two environments: held above steam bath and removed from −20° freezer into humid laboratory air. Acrylic acid copolymers performed the best in both tests showing no fogging in either case. Hydroxyethyl methacrylate copolymers were prone to fogging, however, which was surprising as their measured contact angles were lower than those of the acrylic acid copolymers. It is not currently understood why this is the case.

An additional test was performed for acrylic acid copolymer with 17.2 mol % f-PEG in which the copolymer was deposited from a slightly basic isopropyl alcohol solution onto a mirror glass. For comparison the remainder of the mirror glass was cleaned with basic isopropyl alcohol solution containing no polymer. The mirror glass was exposed to saturated water vapor for 10 min in a steam chamber. As shown in Figure 5, the polymer coated glass did not fog, whereas the unmodified glass showed significant fogging. The fogging test was aggressive enough to result in macroscopic condensation on the modified glass; however, clear vision was still maintained.

The intercalated surfactants present in the copolymer coatings may also provide enhanced wear resistance. With the modification of the flat silica, the surfactants are present only in a single layer. Any damage to this outermost surface will forever ruin the hydrophilic-oleophobic nature of the surface. However, with the copolymer coating the surfactant is present at the surface and throughout the bulk of the film. Thus the degradation of a portion of the surface will merely result in the exposure of an identical layer present below the first potentially enhancing the functional lifetime of such a coating. Currently no tribological studies have been performed on the copolymer systems; this remains a topic of further investigation. Likewise, alternative polymer synthesis methods are currently being investigated to control the distribution and location of surfactant moieties along the polymer chain in contrast to the random radical polymerization presented here. Additionally, with regard to the minimum fluorine content on the surface, introducing a third comonomer comprised of nonfluorinated PEG oligomers along with the surfactant may be a method to enhance the antifogging or hydrophilic nature of the surfaces while minimizing the use of the actual surfactant.

CONCLUSION

Bulk copolymers of perfluorinated polyethylene glycol and acrylic acid, methyl methacrylate or hydroxyethyl methacrylate were synthesized; the synthesis method was confirmed using NMR and final composition was established with XPS. Water and hexadecane contact angles were measured to establish any potential for self-cleaning surfaces using the paradigm of covalently attached f-PEG brushes as a benchmark comparison. Antifog ability was also characterized. Acrylic acid copolymers performed the best as antifog coatings. Both the hydroxyethyl methacrylate and acrylic acid copolymer coatings showed good performance as self-cleaning surfaces as both had hexadecane contact angles ~33° greater than their water contact angles; interestingly, the ideal self-cleaning behavior was determined to be at an intermediate fluorosurfactant composition.

Thus our work with varying copolymer composition provides evidence that fluorine content is not the most important factor in achieving hydrophilic-oleophobic behavior. Likewise the nature of the commodity copolymer (MMA, HEMA, AA) had a strong influence over the wetting behavior of the final coating. The copolymer acted in concert with the PEG constituent to enhance the hydrophilicity in the case of acrylic acid and hydroxyethyl methacrylate with only slight detriment in some cases to the oleophobicity. The addition of methyl methacrylate had a severely detrimental effect on the hydrophilicity.

The f-PEG system, which has been previously applied as grafted brushes on silica surfaces[25,26] and to silica membranes for solvent selective separation[27] was further translated to bulk copolymers, which have many advantages with regard to material processing and ease of application as compared to the grafting method. The f-PEG copolymer coatings were shown to be simultaneously oleophobic and hydrophilic which has direct application for self-cleaning antifog surfaces. The wetting behavior of the f-PEG copolymers was found to be primarily dependent on the nature of the second copolymer and secondarily dependent on the mol % of f-PEG in the copolymer.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Details concerning polymer synthesis method and a video demonstrating self-cleaning in oil/water systems. This material is available free of charge via the Internet at http://pubs.acs.org.

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