

Toward the Replacement of Long-Chain Perfluoroalkyl Compounds: Perfluoropolyether-Based Low Surface Energy Grafted Nanocoatings

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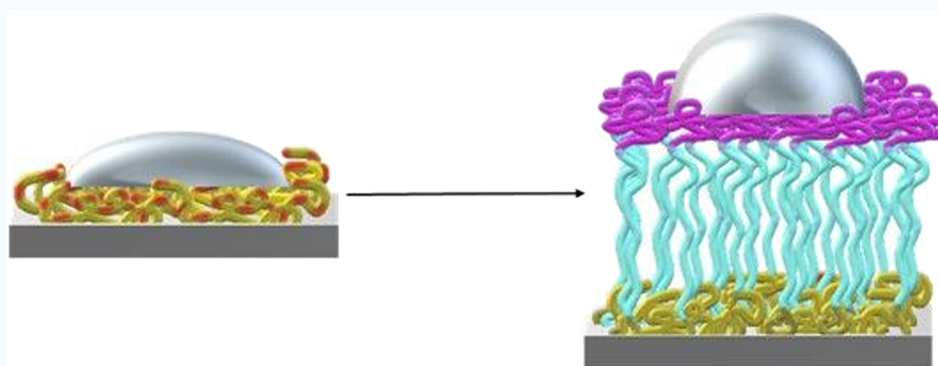
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ABSTRACT: We describe a straightforward approach to fabricating perfluoropolyether (PFPE)-based nanocoatings, significantly decreasing the spreading of oil and water on coated surfaces. In the fabrication, polyglycidyl methacrylate (PGMA) is used as an anchoring layer deposited on the silicon surface before PFPE attachment. Perfluoropolyether-based polyester acid (PFPE-COOH) is then grafted to the PGMA surface to reduce its surface energy and, consequently, wettability. The grafted surface demonstrates a hexadecane contact angle of 40–46° and a water contact angle of 80–98°. The surface's wettability strongly depends on the grafted layer thickness, where grafting of the thicker PFPE layers results in lower oil and water wettability. We expect that the employment of PFPE-based grafted nanocoatings will eliminate the health and environmental concerns of long perfluoroalkyls, which are typically used to obtain surfaces with decreased spreading of oil and water.

KEYWORDS: water repellency, oil repellency, perfluoropolyether, polymer grafting, nanocoatings, surface modification

1. INTRODUCTION

Low surface energy coatings, decreasing/preventing the spreading of oil and water, have drawn considerable interest for numerous practical applications, including self-cleaning surfaces, antifouling and anticorrosion coatings, oil/water separation, and textiles.^{1–8} The preparation of surfaces with low oil wettability is more challenging than the fabrication of hydrophobic ones because the surface tension (ST) of water (72 mN/m) is much higher than ST of oils (25–40 mN/m), resulting in the virtually complete spreading of oils on practically any nonfluorinated substrate. Only when the surface energy of substrates or coatings is lower than that of oils the substrates/coatings exhibit various degrees of oil repellency.^{2,9–11}

Thus, for the fabrication of oil-repellent surfaces, fluorocarbon groups (–CF₂ and –CF₃) are used since they reduce the surface tension of the materials more than hydrocarbons do (CF₃ < CF₂H < CF₂ < CH₃ < CH₂).^{12–15} For decades, long-chain perfluoroalkyl compounds (C_nF_{2n+1}–, *n* ≥ 7, LCPFAs) have been used to obtain water- and oil-repellent

surfaces in a number of applications, including membranes and polymer films, as well as surfactants.^{4,12,16–19} However, LCPFAs (frequently mentioned as “forever chemicals”²⁰ in popular media), owing to their bioaccumulative and toxicological effect on the environment, humans, and wildlife, have been phased out of production and applications.^{21–24} Currently, low surface energy perfluoropolyethers (PFPEs) are being considered as the replacement for long-chain perfluoroalkyl substances because of the presence of oxygen between the fluorinated units in their backbone.^{9,10,22,25–27} Perfluoropolyethers are projected to be safer than LCPFAs because of the materials’ low toxicity and high oxidative/thermal

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stability.^{22,28–30} PFPEs are biocompatible and present on the FDA list for food contact products.³¹ In addition, during the thermal degradation, PFPEs release in the environment significantly fewer compounds in comparison with other fluoropolymers.³²

To this end, PFPE-based (co)polymers, oligomers, and cross-linked materials were demonstrated in our preceding works and those of others to have the capability to serve as hydrophobic/lyophobic materials and interfaces.^{10,25–28,33–38} However, to the best of our knowledge, grafting of PFPE-based oligomers to an inorganic surface to obtain low surface energy nanocoatings, decreasing the spreading of oil and water, has not yet been reported in the scientific literature. With this in mind, we fabricated nanocoatings obtained through the grafting of PFPE-based polyesters. Specifically, a silicon substrate was first modified with an anchoring polyglycidyl methacrylate (PGMA) layer to render an epoxy terminated surface, and then it was modified with a PFPE-based polyester terminated with $-\text{COOH}$ and C_4F_9 -PFPE- end-groups. The surface wettability and the morphology of coatings were analyzed using contact angle measurements and atomic force microscopy (AFM), respectively.

2. EXPERIMENTAL SECTION

2.1. Materials. PGMA ($M_n = 176\text{ k g/mol}$) was synthesized using the procedure reported elsewhere.³⁹ In our preceding publications, we reported the synthesis of PFPE-isophthalate polyester acid (PFPE-COOH) in detail.²⁵ The synthetic procedure for the PFPE-COOH polymer oligomer (Figure 1) is also described in the online

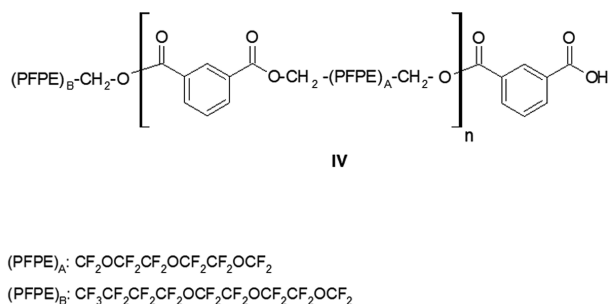


Figure 1. Chemical structure of PFPE-COOH.

Supporting Information (SI) for the manuscript (SI: S1). Silicon wafers were used as substrates (Semiconductor Processing Co.). To clean Si wafers, concentrated sulfuric acid and hydrogen peroxide (VWR International) were used to prepare a "piranha" solution (3:1 concentrated sulfuric acid and 30% hydrogen peroxide). Isophthaloyl chloride (IsoCl) was obtained from Sigma-Aldrich. PFPE-based alcohols (1*H*,1*H*,11*H*,11*H*-fluorinated-3,6,9-trioxaundecane-1,11-diol and 1*H*,1*H*-fluorinated-3,6,9-trioxatridecan-1-ol) from Synquest Laboratories were used in the synthesis. Triethylamine (Et_3N) and methyl ethyl ketone (MEK) were acquired from Sigma Aldrich.

2.2. Nanocoating Fabrication. PGMA films were deposited on a Si wafer surface by dip-coating (using a Mayer Fientechnik D-3400 dip-coater) from 0.05, 0.25, 0.5, and 1.0% wt% solution in MEK at a withdrawal rate of 300 mm/min. Before polymer deposition, the wafers were cleaned with the piranha solution at 80 °C for 1 h and rinsed several times with high-purity DI water. Finally, substrates were dried with nitrogen. The wafers were coated with PGMA and then annealed at 120 °C for 1 h in a vacuum oven. Subsequently, they were rinsed with fresh MEK four times to remove unbounded polymer from surfaces and dried at room temperature overnight. Next, the layer of PFPE-COOH was cast on the wafers dropwise from the MEK solution. Grafting of PFPE-COOH was conducted from the melt at 150 °C overnight in a laboratory oven. The grafted wafers were rinsed

with fresh MEK at least four times to remove ungrafted PFPE-COOH.

2.3. Characterization Techniques. A COMPEL automatic ellipsometer from InOmTech, Inc., was used (at an angle of incidence of 70° and wavelength of 653 nm) to determine the thickness of the nanocoatings obtained. A refractive index of 1.525 was assumed for the coatings, which is the refractive index for PGMA.³⁹ A Dimension 3100 microscope (Digital Instruments, Inc.) was used for the AFM imaging. The AFM scanning was conducted over a 10 by 10 μm area of the coatings in tapping mode using NSC16 tips. The scan rate was 1 Hz. The films' root-mean-square (RMS) roughness was determined from the recorded AFM images. The sessile drop method was used to measure the water and hexadecane contact angles at room temperature. The contact angle measurements were conducted with a drop shape analysis instrument (DSA10, Kruss, Germany). Equilibrating time for the liquid drops was 60 s.

3. RESULTS AND DISCUSSION

The nanocoatings were fabricated in two major steps. First, PGMA was deposited on silicon wafers. Then, PFPE-COOH was attached to the wafers modified with PGMA via an epoxy-carboxylic acid reaction^{40,41} (Figure 2). Specifically, nanocoatings with different PFPE/PGMA thicknesses were prepared to determine how the films' structure influences water and oil spreading on the modified surfaces.

3.1. Preparation of PGMA Anchoring Layer. It is well established that PGMA is a highly reactive polymer since it can react with a number of nucleophilic groups through the epoxy ring-opening.^{40,41} Thus, the polymer can covalently bind to surfaces of different chemical nature. PGMA is used to generate a highly reactive anchoring layer that can be available for further treatment. Essentially, the PGMA anchoring layer is produced as a nanoscale internally self-cross-linked coating covalently bound to a substrate boundary via its epoxy functional groups. At the same time, a significant number of unreacted epoxy groups in the anchoring layer (Figure 3) are available for subsequent grafting reactions.^{40,42–46}

Si wafers were dip-coated from 0.05, 0.25, 0.5, and 1.0 wt% PGMA solutions in MEK; subsequently annealed at 120 °C for 1 h; and rinsed with the solvent. Figure 4 illustrates the relation between the thickness of the annealed PGMA layer and the concentration of the PGMA solution before and after the solvent treatment. With increasing concentrations of the PGMA solution, the layer thickness increases from ~ 7 to ~ 65 nm. The thickness of the annealed PGMA layer changes by less than 20% due to the vigorous solvent rinse. Therefore, the majority of PGMA macromolecules were covalently attached to the Si wafer via reaction with the surface and cross-linking.

Swelling experiments were conducted to investigate the cross-linking density of the annealed PGMA layers. For this purpose, the PGMA layers were exposed to saturated chloroform vapor to swell. During the swelling, their thickness was measured by ellipsometry. The cross-linking density of PGMA layers was calculated using the modified Flory–Rehner equation (SI: S2).⁴⁷ Figure 5 shows the swelling behavior of PGMA films with different thicknesses and the corresponding calculated cross-linking density. It was found that the film thickness in chloroform (swollen thickness) increases with the increase in the dry thickness of the PGMA layer. It was determined that a larger fraction of epoxy groups were cross-linked in the thinner PGMA layers, providing a more rigid structure with greater cross-linking density (Figure 5b). Therefore, the concentration of the epoxy groups available

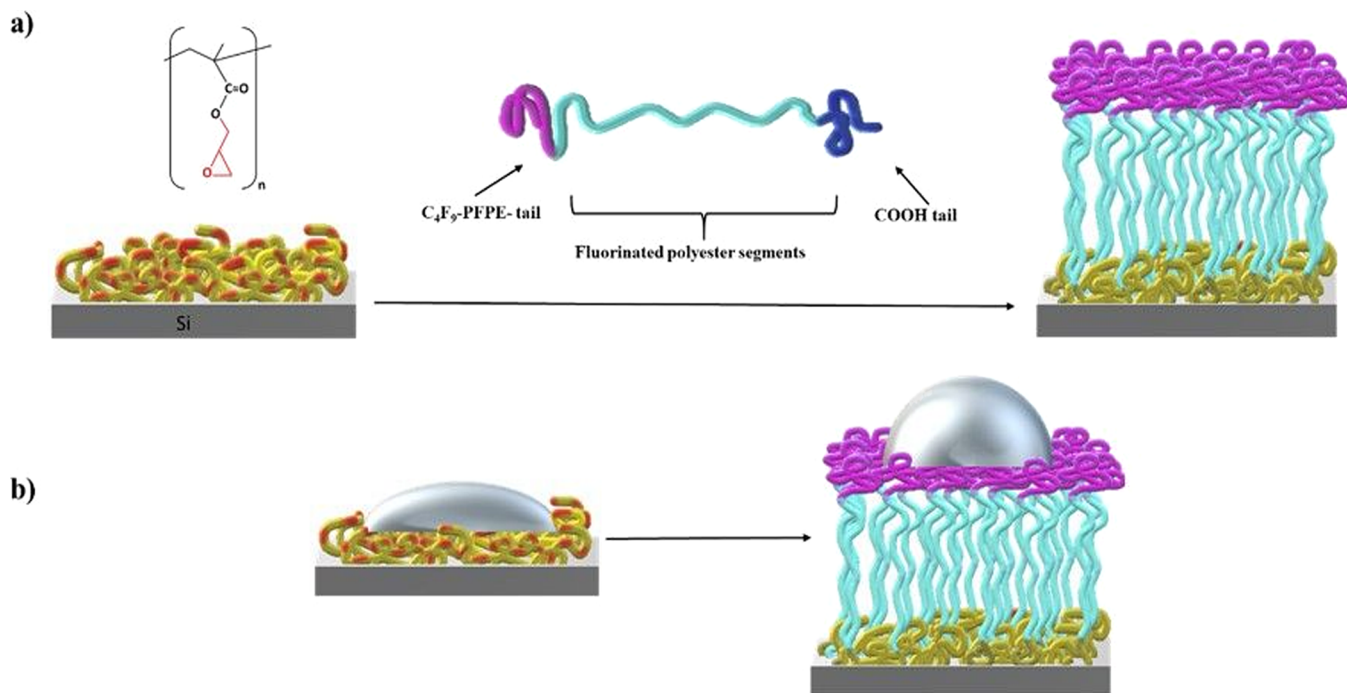


Figure 2. Schematic of (a) grafting of PFPE-COOH with C₄F₉-PFPE and -COOH tails to PGMA anchoring layer and (b) PFPE brushes grafted on PGMA and contacting wetting liquid.

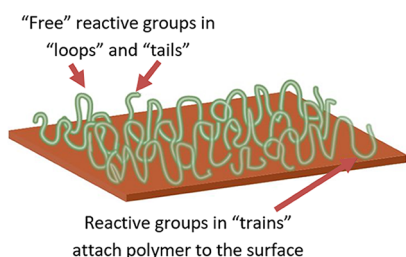


Figure 3. Schematic representation of reactive epoxy groups of PGMA attached to the Si wafer.

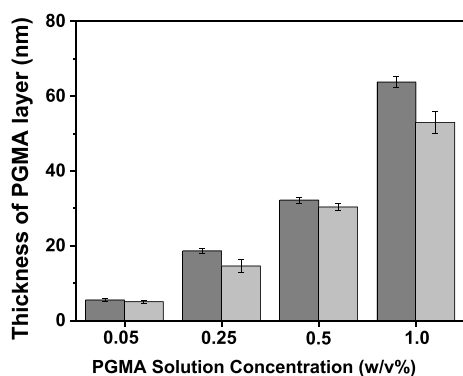


Figure 4. The thickness of PGMA layer as a function of the polymer concentration in MEK used in the dip-coating: before (dark) and after (light) the solvent treatment. The samples were annealed at 120 °C for 1 h.

for the PFPE grafting was expected to be much lower in the thinner layers than that in the thicker layers. We estimated the concentration of epoxy groups in the anchoring layer from the cross-linking density (SI: S3). The data summarized in Table 1 show that there are 25 times more epoxy groups in the thickest layer than in the thinnest one.

3.2. PEPE-COOH Grafting. PGMA coated Si wafers were grafted with PFPE-COOH from the melt at 150 °C overnight. To determine the amount of PFPE attached to the PGMA layer, the thickness of the grafted layer was measured using ellipsometry (Figure 6). It was found that the amount of PFPE anchored to the surface increases in a nearly linear fashion with the rise in the anchoring layer thickness. This increase was expected since the thicker PGMA layers have more free epoxy groups to react with PFPE-COOH. However, it appeared that the cross-linking density and concentration of epoxy groups of the PGMA layer do not significantly influence this relationship. Thus, a substantial amount of epoxy groups is available for grafting in all anchoring layers, irrespective of the number of the groups used for cross-linking. In fact, a significant number of the groups are still present in all layers after the grafting (Table 1 and SI: S3).

It is known that when the surface is enriched with fluorocarbon groups, the wettability of surfaces decreases, resulting in a lower spreading of water and oil. Therefore, the wettability of the grafted surface depends on the degree of screening of PGMA macromolecules with C₄F₉-PFPE chains. When PFPE chains are grafted to PGMA, they are organized in a brush-like structure. In this structure, isophthalic acid ends are anchored to epoxy groups of PGMA, whereas C₄F₉-PFPE tails are exposed to the air interface (Figure 2). The parameters of the brush layer such as the grafting density (Σ) of both PGMA layer and PFPE brushes, their surface coverage (Γ), the radius of gyration (R_g), and the average distance (L) between PGMA and PFPE chains in the brush layers were determined using known relationships (detailed in SI: S3). The parameters are presented in Table 1. From R_g and L , we can estimate the level of the overlap between PFPE chains in the brush-like nanocoating using the straightforward geometrical model (Figure 7).^{48,49}

Three regimes are considered for surface shielding effects within the geometrical model. The chains are far away in

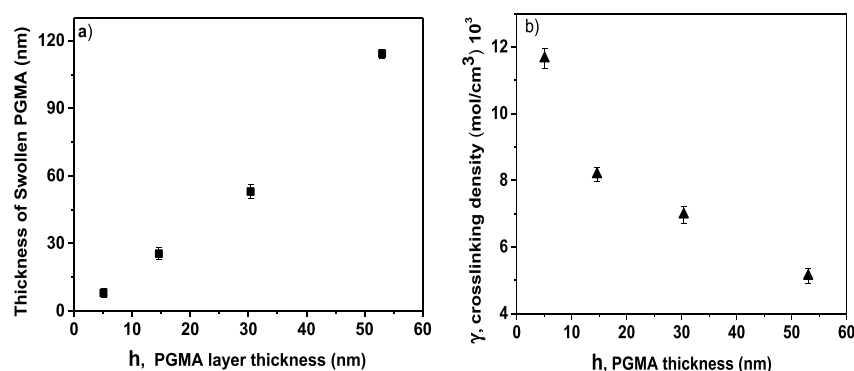


Figure 5. Swelling behavior of PGMA films in saturated chloroform vapor: (a) thickness of swollen PGMA layers and (b) cross-linking density as a function of the PGMA thickness.

Table 1. Parameters of PGMA and PFPE Layers^a

	R_g (nm)	h (nm)	Σ (chains/ nm ²)	Γ (mg/ m ²)	C ($\times 10^5$ mol/m ²)	L (nm)
PGMA	8.6	5.1	0.02	5.48	1.5	7.30
		14.6	0.05	15.78	6.3	4.30
		30.4	0.11	32.82	15	2.98
		53.0	0.20	57.26	38	2.26
PFPE	1.1	3.8	0.81	7.04	0.4	1.11
		9.6	2.05	17.76	3.4	0.70
		20.4	4.37	37.91	9	0.48
		32.6	7.00	60.67	28	0.38

^a R_g , radius of gyration; h , thickness; Σ , grafting density; Γ , surface coverage; C , concentration of epoxy groups; and L , distance between grafting sites.

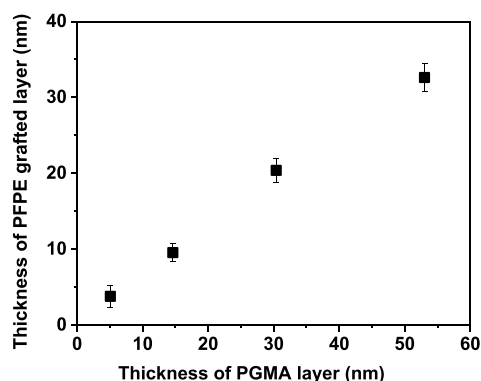


Figure 6. The thickness of the PFPE grafted layer versus the thickness of the PGMA anchoring layer.

regime I ($L > 2R_g$). Thus, they do not overlap. In regime II ($R_g \geq L > \sqrt{2}R_g$), PFPE chains start to overlap as their grafting density on PGMA increases. However, the grafting density of the chains is still not sufficient to cover the whole surface. In regime III ($L \leq \sqrt{2}R_g$), there is no open space between chains, and overlapped chains are forced to stretch away from the interface.

We compared the R_g (~ 1.1 nm) and $\sqrt{2}R_g$ (~ 1.5 nm) values for PFPE-COOH with different L values presented in Table 1. It was found that all but one PFPE layer are in regime III, whereas the thinnest grafted layer (3.8 nm) is in regime II. Therefore, it was expected that the PGMA layer grafted with the thinnest PFPE layer would exhibit the highest degree of oil and water spreadability.

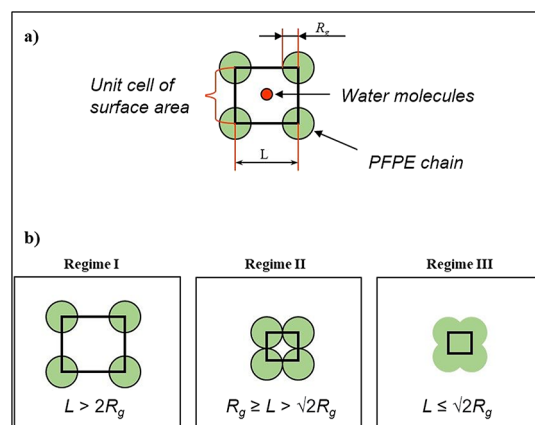


Figure 7. A geometric model of PFPE surface coverage. (a) The disc radius is equal to the radius of gyration of the PFPE macromolecule. (b) A mathematical representation of three different regimes for PFPE surface coverage.

3.3. Morphology of PGMA and PFPE Grafted Layers.

AFM imaging was conducted to determine the surface morphology of the nanocoatings before and after the PFPE grafting. As seen in Figure 8, smooth and homogeneous PGMA anchoring layers were obtained via dip-coating and annealing. When PFPE was grafted to PGMA, the surface morphology changed significantly. Dark areas on the image (ascribed to PGMA) and brighter domains (ascribed to PFPE) are clearly visible on images of the grafted layers. The PFPE grafting does not influence surface roughness significantly. After the grafting, film surfaces are still smooth on the nanoscale level (root-mean-square (RMS) roughness < 2 nm).

3.4. Wettability of the Nanocoatings.

The contact angles of water (WCA) and hexadecane (HCA) were measured for PFPE/PGMA nanocoatings to determine the level of water and oil spreadability on the grafted substrates. The substrate (silicon wafer) was completely wettable with water and oil (WCA and HCA $< 5^\circ$). Figures 9a,b shows that the PGMA anchoring layer (irrespective of thickness) is partially wettable with water (WCA $\approx 65^\circ$) but completely wettable with hexadecane (HCA $< 5^\circ$). When PFPE was grafted to PGMA, water and oil spreadability on the surface was significantly decreased. Even with grafting of a 3.8 nm thick layer, HCA and WCA were raised to the level of 42 and 80° , respectively. When more PFPE (33 nm) was attached, HCA and WCA further increased to ~ 46 and $\sim 98^\circ$, respectively.

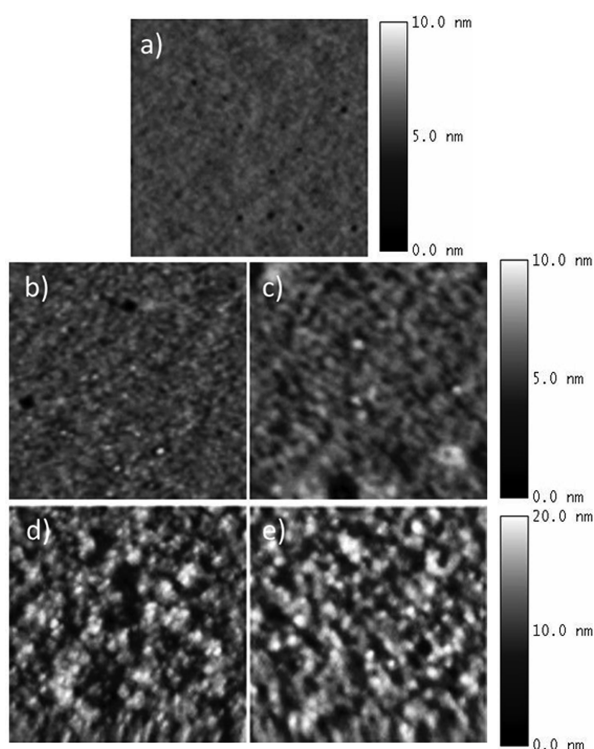


Figure 8. AFM ($10 \times 10 \mu\text{m}$) topographical images of PGMA and PFPE/PGMA surfaces. Pure PGMA surface (5 nm thick layer) (a) and PFPE/PGMA surfaces (b–e). Thickness of PFPE/PGMA layers: (b) 4/5 nm (RMS = 0.5 nm), (c) 10/15 nm (RMS = 0.8 nm), (d) 20/30 nm (RMS = 1.9 nm), and (e) 33/53 nm (RMS = 1.7 nm). Vertical scale: a–c = 10 nm and d–e = 20 nm.

It is well established that polytetrafluoroethylene (PTFE) is considered to be a water-/oil-repellent polymer. Thus, the oil and water repellency of PFPE/PGMA nanocoatings and PTFE film was compared. We measured the WCA and HCA of PTFE film as 118° and 51° , respectively. These values are close to those reported in the scientific literature by others.^{50,51} We can conclude that the water and oil wettability level for all PGMA/ PFPE nanocoatings is approaching but still somewhat lower than that of PTFE.

3.5. Surface Energy Estimation. Surface energy (γ) was also determined for the PFPE/PGMA nanocoatings. The WCA and HCA data provided the base for quantitative evaluations of the surface energy of the polymer films using the Owens–Wendt method (SI: S4), which was previously used by us and others for the characterization of PFPE-based surfaces.^{10,25,27,52–55} Figure 9c shows that the PGMA film has relatively high surface energy (41.5 mN/m). However, PFPE grafted surfaces possessed much lower surface energy.

Specifically, when only a 3.8 nm thick PFPE layer was grafted on PGMA, surface energy became 30 mN/m. Furthermore, the surface energy of the PFPE/PGMA coating decreased from 30 to 21 mN/m, indicating that a significant amount of $-\text{CF}_2-$ and $-\text{CF}_3$ groups is present on the surface. This value is significantly lower than the surface tension of typical oils. The surface energy of PFPE/PGMA nanocoatings was slightly higher than that of PTFE ($\gamma_s \approx 18.5 \text{ mN/m}$). It can be expected since PTFE consisted only of fluorocarbon groups ($-\text{CF}_2-$), while the PFPE grafted layer included, besides fluorocarbon groups, the hydrocarbon and ester groups in its structure. However, as the thickness of the PFPE layer

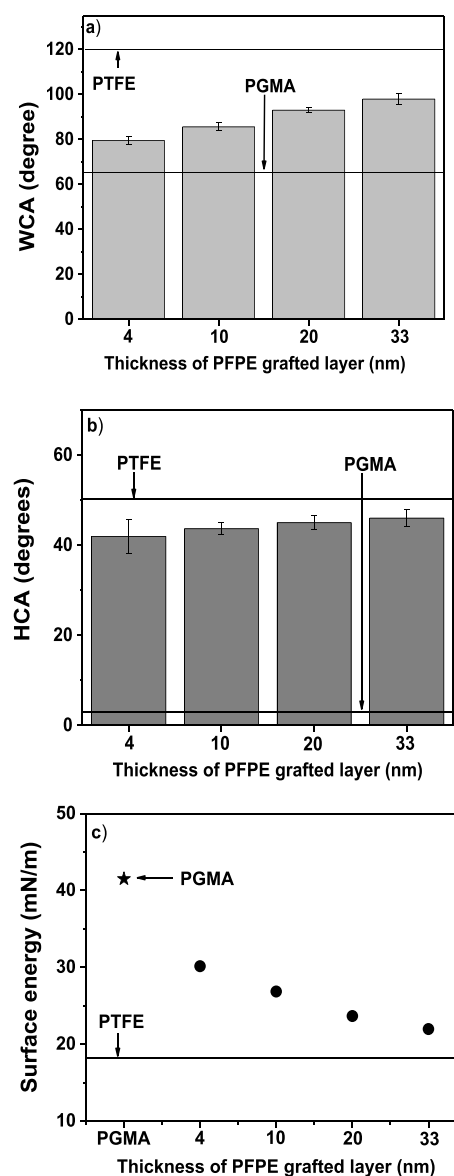


Figure 9. WCA (a) and HCA (b) for PFPE/PGMA nanocoatings. Contact angles for PGMA and PTFE are given for comparison. (c): The surface energy of PGMA and PFPE/PGMA nanocoatings. Line for PTFE ($\gamma_s = 18.5 \text{ mN/m}$).

was increased (up to 33 nm), its surface energy was reduced to $\sim 21 \text{ mN/m}$, which is close to the surface energy of PTFE.

4. CONCLUSIONS

We demonstrate that original PFPE-based oligomers can be used as an oil- and water-repellent component of low surface energy nanoscale coatings. Namely, it is shown that when PFPE-COOH is grafted on the PGMA anchoring layer, it blooms to the surface, leading to low water and oil wettability of the modified surface. The wettability of the PFPE/PGMA coating depends on the thickness of the anchoring and grafted layers. The thickest PFPE/PGMA layer obtained demonstrates a level of water and oil spreadability comparable to PTFE.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsapm.1c01438>.

Synthesis of PFPE-COOH (S1); calculation of cross-linking density (S2); characterization of PGMA and PFPE grafted layers (S3); and calculation of surface energy of PFPE/PGMA nanocoatings (S4) (PDF)

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Notes

The authors declare no competing financial interest.

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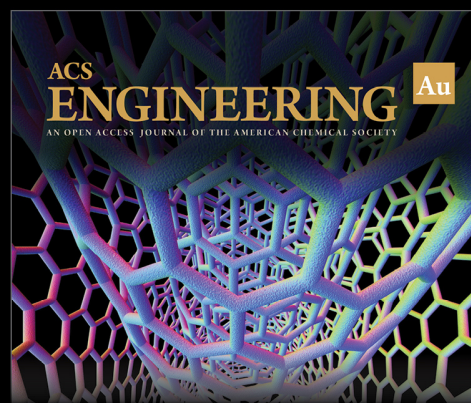
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