Fabrication of the Superhydrophobic Surface Inspired from Lotus-Effect

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연꽃잎을 모사한 초소수성 표면 제작

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Abstract

Wettability of solid surfaces with liquids is governed by the chemical properties and the microstructure of the surfaces. We report on the preparation of liquid-repellent surfaces using surface-attached monolayers of perfluorinated polymer molecules on porous silica substrates. A covalent attachment of the polymer molecules to the substrate is achieved by generation of the polymer chains through starting a surface-initiated radical-chain polymerization of a fluorinated monomer. To this, self-assembled monolayers of azo initiators are attached to silica substrates, which are used to kick off the polymerization reaction in situ. The growth of the fluorinated polymer films and the characterization of the obtained surfaces by surface plasmon spectroscopy, XPS, and contact angle measurements is described. It is shown that perfluorinated polymer films can be grown with controlled thicknesses on flat and even on porous silica surfaces, essentially without changing the surface roughness. The combination of the low surface energy coating and the surface porosity allows generation of materials which are both water and oil repellent.

1. Introduction

The hydrophobicity of a surface can be enhanced by a chemical modification that lowers the surface energy. This modification leads to an increase in the contact angle of a water drop. Fluorinated polymers have unique surface properties such as extremely low surface energy, chemical inertness, low friction coefficients, and relatively low permeability for most gases. These interesting properties allow for much utilization of fluorinated polymers as the prevention of the adhesion of snow to antennas and windows, self-cleaning traffic indicators, metal refining, and stain-resistant textiles. Random or multiphase copolymers have been used either as pure compounds or as additives to base polymers in

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film formation in order to give hydrophobic surface properties on various substrates such as metals, inorganic compounds, polymers, and so forth. But extremely low surface energy of the fluorinated polymer in a thin film on a surface raises problems for the physical adhesion of the coating to the substrate, and films are separated easily from the solid surfaces even due to external weak stress. Therefore, an important challenge is to prepare fluorinated polymer films which adhere strongly to solid surfaces and retain hydrophobic surface properties for long periods of time even upon mechanical/thermal stress exposure.

For the preparation of fluorinated polymer films on solid surfaces, most methods are based on physisorption. However, in this case, the interaction between the polymer film and the solid surface is not very strong as the adhesion is based only on van der Waals forces. To circumvent these limitations, polymers have been grown at surfaces using the immobilization of an initiator at the substrate

surface and radical-chain polymerization in situ ("grafting-from" method). In this case, the self-assembled initiator molecules can be immobilized on the surface by a one-step reaction. Subsequent polymerization in situ leads to films with high grafting densities and easily controlled thickness.

The contact angle of a liquid on a substrate however, depends not only on the surface tension of the liquid and the substrate but also on the surface roughness of the substrate. An example of the importance of the surface roughness is the wetting behavior of leaves of the lotus plant ("lotus-effect"). A superhydrophobic surface results from the increase of the surface roughness, so that the local geometry provides a large geometric area for a relatively small projected area. This effect can be observed in nature on the leaves of the sacred lotus. The surfaces of these leaves have micrometer-scale roughness, resulting in water contact angles up to 170°, because air that is trapped between the droplets and the wax crystals at the plant surface minimizes the contact area.

In this paper, we try to combine the two strategies discussed above and describe a chemical pathway to coat rough substrates with a firmly adhering monolayer of a perfluorinated polymer. We report on the preparation and surface characteristics of porous silica surfaces with surface-attached perfluorinated polymer brushes. As a first step, a selfassembled monolayer of an azo initiator is formed on a rough silica surface, and a perfluorinated polymer monolayer is prepared by the grafting-from approach. After this, the wetting of the obtained surface-modified materials by water and oil and various other test liquids is measured.

2. Experimental Section

2.1. Materials and characterizations.

Porous silica substrates were dried by heating to 110 °C at 10^{-2} mbar overnight. The average pore diameters were 1 μm (S1) and 20 μm (S20), and the specific areas were 0.87 and 2.24 m^2/g, respectively. The specific area was determined by nitrogen adsorption according to the Brunauer-Emmett-Teller (BET) technique. Perfluoroalkylethyl acrylate (FA) [F(CF$_2$)$_8$CH$_2$CH$_2$-COOCH=CH$_2$, Hoechst] was purified chromatographically over neutral AlOx, distilled in a vacuum from copper(I) chloride, and stored at -30 °C. Toluene was distilled from sodium after refluxing overnight using benzophenone as an indicator. Triethylamine and 1,1,2-trichloro-trifluoroethane (TTFE) were dried by distillation

from CaH$_2$ and CaCl$_2$, respectively. Dimethylchlorosilane was purified by distillation. All reagents described above were purified under an argon atmosphere. The other chemicals were used as received.

Thicknesses of deposited Ag, SiOx, and synthesized polymer brushes were measured by SPS. The film thickness was calculated from the experimental data using the Fresnel theory and a simple box profile. X-ray photoelectron spectroscopy (XPS) spectra were obtained with an Al Kα X-ray source (15 keV), a filament current of 20 mA, and a takeoff angle of 90°. Contact angles were measured using an optical goniometer. Two groups of contact liquids were used. To obtain the critical surface tension by Zisman's plot, n-alkanes were used. In a second set of experiments, water/methanol mixtures were used in which the surface tension of the liquid was varied from 22.6 dyn/cm for absolute methanol to 72.8 dyn/cm for pure water, depending upon the concentration of methanol. The roughness of the porous materials was measured using Surftest SV-402 (Mitutoyo). To obtain an image of the cross section of the porous silica substrates, an epoxy resin was cast onto the substrates, the sample was cut, and the cross section was polished by SiC paper and diamond cloth.

2.2. Grafting-From Polymerization.

Fig 1 shows the schematic diagram for the grafting-from polymerization. 4,4′-Azobis-(4-cyanopentanoic acid-(3′-chlorodimethylsilyl) propyl-ester) (ADS) was prepared according to the literature by hydrosylation of 4-(3-allyl oxycarbonyl-1-cyano-methyl-propyazo)-4-cyano-4-methylbutyric acid allyl ester and dimethylchlorosilane with a hexachloroplatinic acid catalyst. Grafting-from polymerizations were carried out after immobilization of ADS on the silica substrates, through subsequent radical polymerization with FA. Double side polished silicon wafers and BK7 glass slides onto which a 50 nm thick Ag layer and a 30 nm thick SiOx layer had been evaporated were used as substrates for the Fourier transform infrared (FTIR) and surface plasmon spectroscopy (SPS) experiments. Immobilization of the initiator onto porous silica and onto planar substrates was performed under an argon atmosphere by adding 0.1 g of ADS and 0.5 mL of triethylamine to the SiO$_2$ substrates inserted into a solution of 50 mL of dry toluene. After degassing at ca. 1 mbar until no gas evolution from
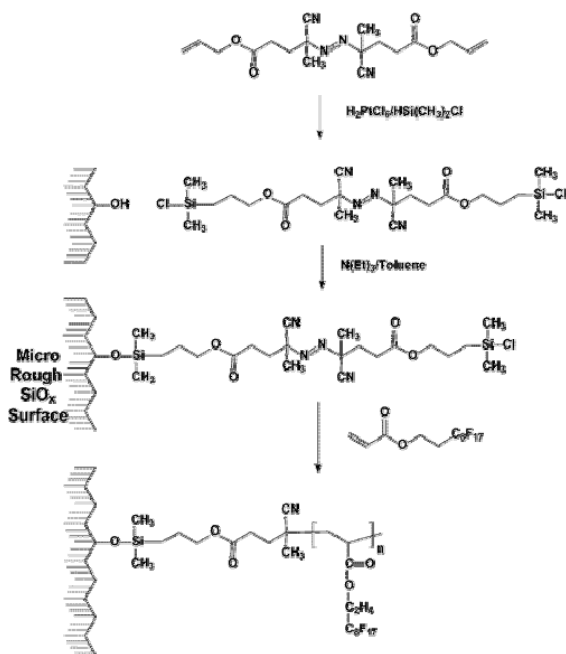
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Fig. 1 Schematic diagram of the generation of fluorinated surface-attached polymer monolayers on microrough substrates.

micropores of the silica substrate could be observed, the mixture was stirred for 15 h. The initiator modified substrates were washed with toluene, methanol, and acetone and dried under a vacuum at 10^{-2} mbar. Radical polymerization was carried out at 60 °C under a reduced pressure argon atmosphere after degassing by repeated freeze-thaw cycles. After polymerization was stopped, the polymer-modified substrates were removed, and free polymer adsorbed on the surface was washed away through extraction with TTFE for 16 h.

3. Results and Discussion

3.1. Preparationof Poly(perfluoroalkylethyl acrylate) (PFA) Films by Grafting-From Polymerization.

The preparation of the initiator layer covalently attached to the porous silica surface, as illustrated in Fig 1, is an important first step to obtain the surface-fluorinated polymer layers. The azochlorosilane initiator has been prepared according to literature procedures (Prucker, O.; Rü̈he, J. Macromolecules 1998, 31, 592). The synthesized initiator mixture was immobilized onto porous silica substrates under inert conditions in the presence of triethylamine, yielding the initiator-modified substrate in a one-step reaction. In the second step, the attached
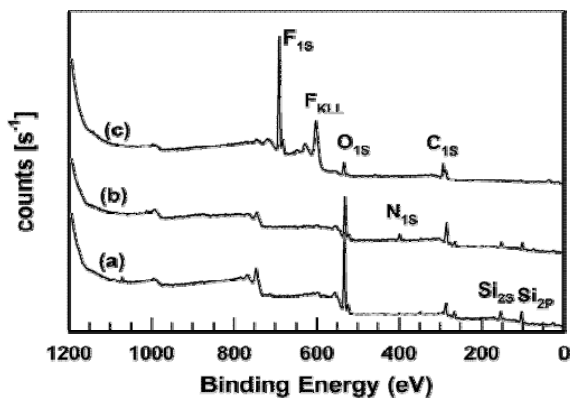

Fig. 2 XPS spectra of (a) the unmodified porous silica surface and the surface (b) after ADS immobilization and (c) after growth of the fluorinated polymer monolayer.
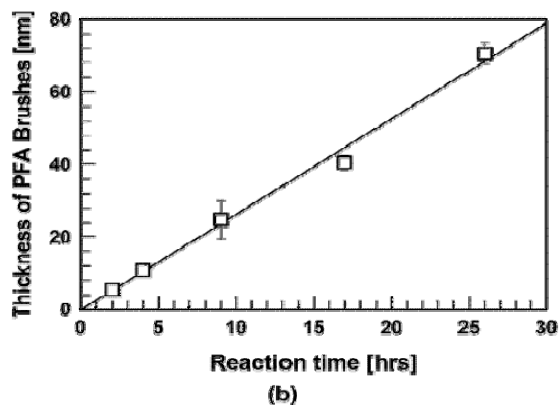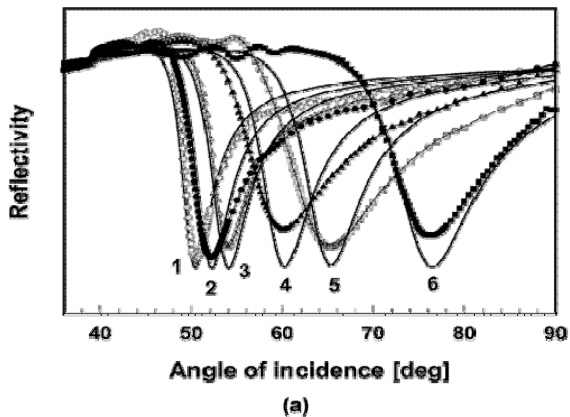

Fig. 3 (a) Reflectivity curves of PFA brushes obtained after different polymerization times: (1) 0 (◖), (2) 2 h (●), (3) 4 h (△), (4) 9 h (▲), (5) 17 h (□), and (6) 27 h (■); symbols represent measured data, and straight lines represent model fit calculations according to Fresnel theory assuming a simple box model. (b) Thicknesses of the PFA brushes from (a) as a function of the polymerization time.

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initiator is thermally activated through cleavage of the azo group, and thermal radical polymerization is initiated with the fluorinated monomer FA yielding PFA chains grown from the surface.

The chemical identification of each stage of the grafting from polymerization was carried out by XPS analysis as shown in Fig 2. The XP spectrum of the as-obtained porous silica surface shows Si_{2S}, Si_{2P}, and O_{1S} signals at 154.0, 102.5, and 531.8 eV. After immobilization of ADS, a N_{1S} signal, which can be attributed to the azo groups, appeared at 399.7 eV. The N_{1S} signal disappeared after polymerization, and a strong F_{1S} signal at 688.2 eV can be observed because of the perfluoroalkyl side chains of the PFA layer. The spectrum is in good agreement with that of bulk polymer measured in previous studies. The absence of any signals due to the substrate shows that it is possible to prepare a homogeneous PFA layer on a rough silica surface by grafting-from polymerization.

To determine the thicknesses of PFA films attached to substrates, SPS measurements were carried out simultaneously on porous and planar substrates. For the preparation of these samples, neat FA was polymerized starting from a porous silica surface and on SiOx/Ag-coated glass slides for varying reaction times. Fig 3a shows the SPS spectra from the films obtained in this way. The minimum of the reflectivity curve shifts from an incident angle of 50° after immobilization of the initiator to higher angles after polymerization. The polymer film thickness is calculated from the angular shift of the resonance signal according to Fresnel theory. The thicknesses of the obtained PFA layers as a function of the polymerization time are shown in Fig 3b. The measurements were carried out on three different spots on each substrate. The results of the SPS experiments demonstrate that the thickness of the PFA layer can be precisely controlled by adjusting the conversion of the initiator through choosing an appropriate polymerization time, and the film formation can be carried out in a well-reproducible manner.

3.2. Determination of the Surface Geometry.

To investigate the influence of the surface geometry on the contact angle, the surface roughness of the microporous samples was measured before and after formation of the PFA monolayer. To do this, the cross sections of the modified and unmodified silica were determined for materials with two different pores sizes (1 and 20

Table. 1 Comparison of the Roughness Factors of Porous Silica Substrates before and after Grafting-From Polymerization

roughness parameter [μm]	sample S1		sample S20	
	unmodified	modified	unmodified	modified
R_a	3.4	3.4	31.0	30.0
R_q	4.3	4.3	37.8	36.8
R_y	25.3	23.6	170.8	161.4
S	61.6	61.3	245.2	237.8
S_m	290.8	273.1	682.5	648.6

μm pore diameter). To avoid artifacts due to structure changes during cutting of the substrate, it was coated with epoxy before cutting. As the ratio between peak spacing and height is very similar before and after grafting-from polymerization (Table 1), it can be concluded that the films on the rough substrates are also quite homogeneous. To further substantiate this point, the length scale dependence of the porosity was measured also for the different samples. Clogging of small pores would show up as a change in the slope of the $N(r)$ versus r curves. To obtain this information, the cross sections of the samples before and after surface modification were analyzed on length scales between 0.3 and 3 μm by SEM using the box counting method (Fig 4).

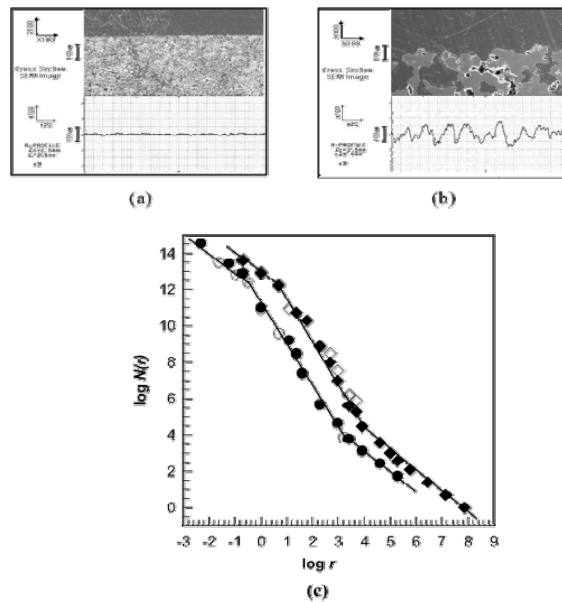Fig. 4 SEM images and roughness profiles of modified substrates (a) S1 and (b) S20 and (c) a plot of log N[r] vs log r for the cross-sectional trace curves of S1 (unmodified, ○; modified, ● and S20 (unmodified, ◇; modified, ◆).

Without attempting a detailed analysis of the length scale dependence of the roughness of the individual samples, it can be concluded from the similarity of the shape and slope of the modified and unmodified samples that the layer coats the surface in a very even manner and no change in the porosity can be observed.

3.3. Contact Angles of Liquids on Flat and Rough Silica Surfaces.

Fig 5 shows a Zisman plot for a PFA film on a flat and a rough SiO_2 surface obtained using a series of n-alkanes of different chain lengths. The PFA brushes on rough surfaces were prepared using bulk FA and a reaction time of 2 h. To allow a comparison with a rough surface, a flat film was prepared by spin casting of PFA polymer on a glass slide with a thickness of about 1 μm. The Zisman plot gives a critical surface energy of 7.9 ± 1.0 dyn/cm for the flat surface and within the experimental error the same value for the PFA-brush-modified rough surface (7.8 ± 2.9 dyn/cm)which is comparable to one obtained in previous studies. The similarity of the two values suggests that the surface chemistry of the two samples is very close to each other. However, the contact angles of the test liquids on the rough substrate increase much more strongly with increasing surface tension. This can be directly seen when the slopes of the cosθ versus γ curves of the two samples are compared in Fig 8. While the test liquid with a surface tension of 25.4
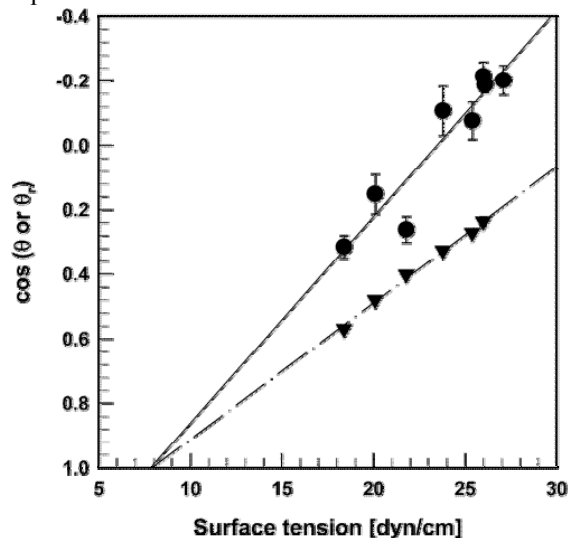
dyn/cm exhibits on the flat substrate a contact angle of about 76°, the contact angle of the same liquid on the rough substrate is 101°. Such an increase of the contact angle with increasing surface roughness of the substrate is in good agreement with theoretical expectations.

Even though the influence of the graft density on the surface free energy is straightforward, the wetting behavior of the substrates which are inhomogeneously covered with PFA brushes is quite complicated. If the surface tension of the liquid drops below a certain critical value, the liquid disperses into the pores of the substrates so that it appears to wet the surface completely. At higher surface tensions, the droplet no longer wets the surface and high contact angles are observed. While the incompletely modified surfaces exhibit generally lower contact angles than for the completely modified surfaces, the general trend of the wetting behavior of the different samples is very similar. In addition, the difference in surface roughness between the two samples S1 and S20 has no significant influence on the wetting behavior of the materials (Fig 6). Although this seems to be at first sight somewhat surprising, the fractal structure of the two surfaces is very similar as can be concluded from the similarity of the N(r) versus r curves of the two samples (Fig 4c). Not only the absolute roughness value but also the type and shape of the roughness profile are of great importance for the wetting properties.
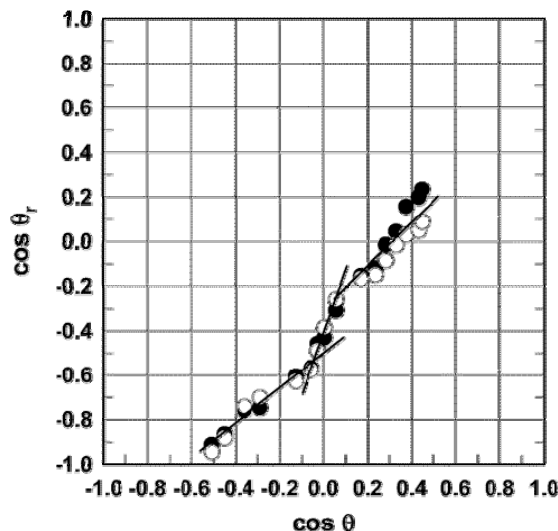

Fig. 5 Zisman plot of alkane test liquids on a flat (▼) and PFA-modified rough surface (●) (initiator concentration, 29.75 mg/m²).

Fig. 6 Comparison of contact angles of PFA-modified rough surfaces (cos θr) (S1, ○; S20, ● with flat surfaces (cos θ).
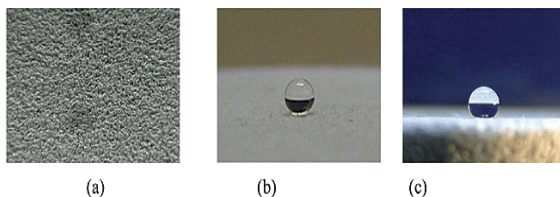
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Fig. 7 Water and oil drops on rough silica surfaces: (a) unmodified surface and (b, c) PFA-brush-modified surface.

The dramatic changes of the wetting behavior of the material induced by the surface modification can be directly observed when the images of droplets on an unmodified and a PFA-brush-modified rough SiO_2 surface are compared (Fig 7). On the native SiO_2 surface, the water spreads completely and is rapidly absorbed into the inner part of the porous silica (Fig 7a). In contrast to this, on the PFA brush a water contact angle of more than 160° is obtained and an almost perfectly round drop is formed on the surface (Fig 7b). It was indeed quite difficult to obtain such images as due to the very small liquid-surface interaction the water drop has a very strong tendency to roll off the surface. The drop can be kept on the surface only if the substrate is leveled very carefully. Similar experiments with an oil droplet (methylene iodide) on the same surface also give an oil contact angle of larger than 100° (Fig 7c).

4. Conclusions

In this paper, it has been shown that perfluorinated monolayers can be covalently attached to planar and rough surfaces in such a way that a homogeneous coverage of the surface can be obtained. Even on very rough surfaces, no changes in the surface roughness can be observed and the molecularly thin films conform nicely with the surface structure. Through the chemical attachment of the fluorinated polymers to porous substrates, materials with ultrahydrophobic and oil-repellent properties can be obtained. Measurements of the critical surface tension obtained from a Zisman plot for these materials give a value of only 7.8 dyn/cm, which is considerably lower than even that of Teflon (19.2 dyn/cm).

A combination of the generation of surface-attached monolayers from low surface energy polymers with the concept of controlling the wetting properties of a material through microstructuring of the surface seems to be an attractive pathway for the generation of water- and oil repellent materials.

6. Notes and References

This paper is an excerpt from the following writed by these authors.

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