

A Novel Fluorinated Polymeric Product for Photoreversibly Switchable Hydrophobic Surface

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A new chemical product, that is, photoreversibly switchable hydrophobic surface coating, was synthesized by atom transfer radical polymerization and graft-from method based on molecular design. Focusing on the strategy of new product development from the chemical product engineering perspective, the product characterization, switching mechanism analysis, performance evaluation, and model interpretation were carried out to confirm the new product manufacture and to ensure the product application with a following aging test. The results show that the product enables surfaces to have reversibly switchable wettability and excellent stability after a month-long test with eight irradiation cycles. Additionally, the wetting behavior of silicon surface can be tuned between hydrophilicity and hydrophobicity based on blank sample using the surface engineering technique (decorated with functional film and surface roughening). The product presented here can be utilized for constructing a hydrophobic surface with photo-induced controllable wettability in moisture-resistance, and it also offers a new technique for the manipulation of liquids in microfluidic devices.

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Introduction

Over the past decade, chemical product engineering as a new field in the chemical engineering discipline has gained a lot of attention. The main reason for this attractive emerging paradigm is to satisfy the rapidly evolving industrial demands for the growing specialty of chemical products.^{1–8} The first book on chemical product design by Cussler and Moggridge provided the insight for chemical engineers to manufacture products with customer demand.¹ To be specific, product engineering was defined as “the whole science and art of creating chemical products with desired function” by Moggridge et al.⁴ More recently, Guo et al. designed and developed a novel drug-delivery system with potential applications in cancer drug delivery following the viewpoint of product engineering and design.^{7,8} In addition, our group provided guidelines toward the development of inorganic-organic nanocomposites with multiple properties from the chemical product viewpoint.⁹ We also used a systematic multiscale method to achieve the correlation of structure-performance-methodology on the basis of Ca^{2+} responsive brush copolymers with promising application in water softening.¹⁰

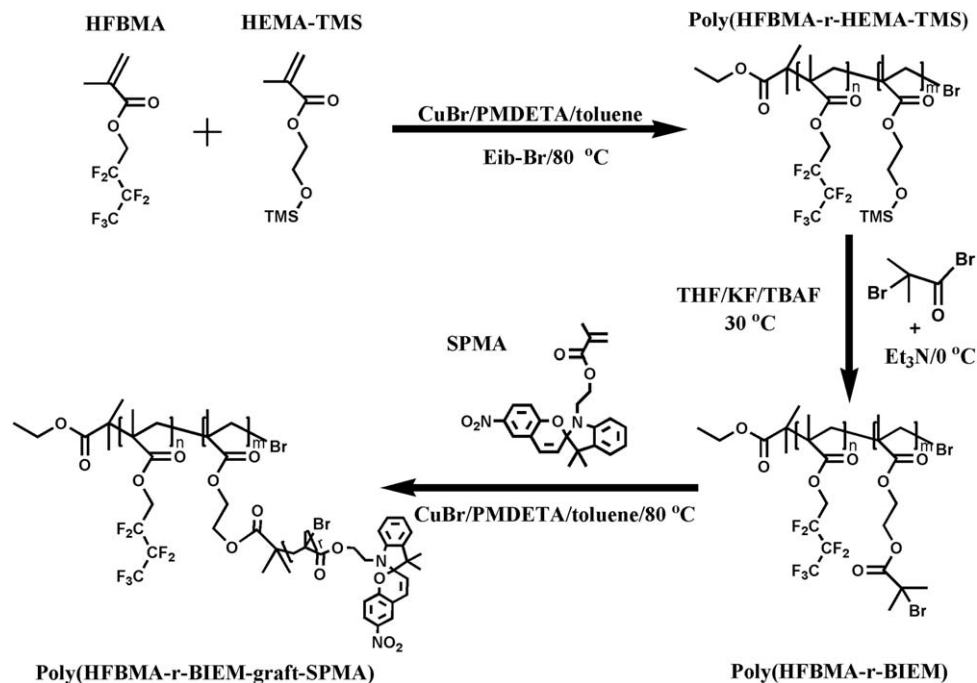
Functional surfaces and surface coatings as a key area of concern in almost all industrial fields have attracted increasing attention in the past few years, which include easy-cleaning and/or self-cleaning properties, switchable properties responding to external stimuli, and long-term stability.^{11,12} Among them, smart surfaces or smart coatings with tunable wettability induced by external environment are interesting^{13,14} and have applications in separators,¹⁵ chemical valves,¹⁶ sensors,¹⁷ microfluidic devices,¹⁸ and so forth. Up to now, various external stimuli, including light irradiation,^{19–29} electric potential,^{30–32} temperature,^{33–36} and pH^{37–42} can be utilized to control the wettability of surfaces. Among them, light illumination is usually chosen as a control factor due to its facile operation, low cost, and limited environmental impact.^{19,20} For example, photo-induced switchable surfaces can be used to fabricate direct pumping devices and valves with no moving mechanical parts in microfluidics system, which has a larger surface area-to-volume ratio and dominated by surface forces.⁴³

To fabricate a light-controlled smart surface, inorganic oxides (e.g., TiO_2 , ZnO , and V_2O_5) and photochromic organic compounds (e.g., azobenzene and spiropyran) are thought as rational choices for surface modification. In general, inorganic oxides have higher photoactivity than organic molecules in one direction, but the inverse process of the former is much slower. The recovery will even take more than 10 days.^{21,22} Conversely, the photochromic molecules of spiropyran (Sp) can be isomerized to polar hydrophilic merocyanine (Mc) upon UV light irradiation and revert to hydrophobic Sp form when responding to visible-light

Additional Supporting Information may be found in the online version of this article.

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Scheme 1. Synthetic route of poly(HFBMA-r-BIEM-graft-SPMA).

irradiation, and thus is applied to control the surface wettability.⁴⁴

To obtain the desired functions, the development of new or advanced coating materials and construction of micro-structured and nanostructured surfaces through surface engineering are necessary. Fluorinated copolymers are usually selected as modifiers for hydrophobic surface because of their high chemical and thermal resistance as well as low surface energy.⁴⁵ In addition, it should be pointed out that the roughness of substrate surface is another key factor on governing surface wettability. Consequently, novel photoreversibly switchable hydrophobic surfaces with or without texturization were fabricated by random copolymer with fluoroalkyl and spiropyran side chains in the present work. The copolymer is named poly(2,2,3,3,4,4,4-heptafluorobutyl methacrylate-random-2-(2-bromoisobutyryloxy)ethyl methacrylate-graft-[1'-(2-methacryloxyethyl)-3',3'-dimethyl-6-nitrospiro-(2H-1-benzo-pyran-2,2'-indoline)]) [abbreviated as poly(HFBMA-r-BIEM-graft-SPMA)] and was synthesized via atom transfer radical polymerization (ATRP) as demonstrated in Scheme 1.

The aim of this work is to develop a novel product, that is, the photoreversibly switchable hydrophobic surface coating. We focus on the strategy of the new product development from the chemical product engineering perspective, which includes product design, product characterization and analysis, and product application study as shown in Scheme 2. After preparing the designed product, basic characterizations of the copolymer product are carried out. Next, the product performance in terms of the photoreversibly switchable hydrophobicity is evaluated. This includes the isomerization of the Sp moieties incorporated in solvent and copolymer film, switchable water contact angle (WCA) characterization, the surface composition and morphology of smart surfaces. These issues are directly linked to the mechanism of switchable hydrophobic property and physicochemical characteristics of the surface decorated by designed polymeric material. Finally, the application of a new product

should stand the test of time, and thus an aging test for a month long is also conducted.

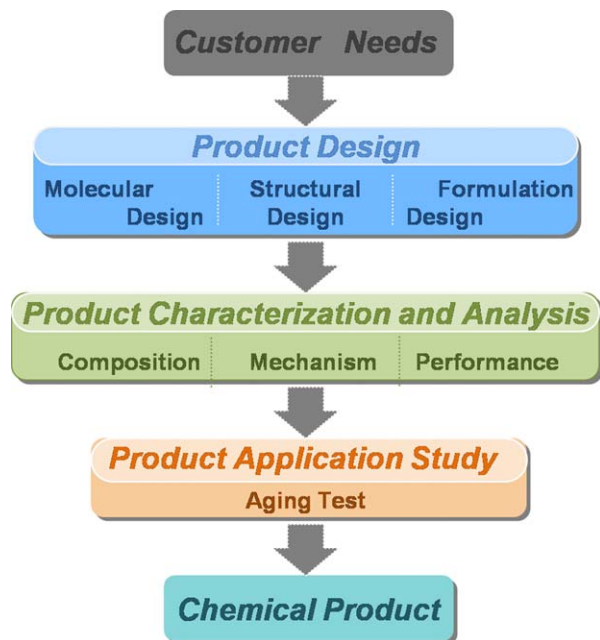
Experimental

Materials

2,2,3,3,4,4,4-Heptafluorobutyl methacrylate (HFBMA, J&K (Beijing) Chemical, 97%) was rinsed with aqueous NaOH (5 wt %) solution prior to use. 2-Hydroxyethyl methacrylate (HEMA, 95%), ethyl 2-bromoisobutyrate (Eib-Br, 98%), 2-bromoisobutyryl bromide (98%), 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, 98%), and tetrabutylammonium fluoride [TBAF, 1 M in tetrahydrofuran (THF)] were received from TCI (Shanghai) Development Co. HEMA was purified as in previous work.⁴⁵ 1'-(2-methacryloxyethyl)-3',3'-dimethyl-6-nitrospiro-(2H-1-benzo-pyran-2,2'-indoline) (SPMA) was synthesized according to previously reported work.^{46,47} THF [99%, Sinopharm Chemical Reagent Co. (SCRC)] was refluxed and distilled from sodium naphthalenide solution. All other reagents and solvents were used as obtained from SCRC.

Synthesis of 2-(trimethylsilyloxy)ethyl methacrylate (HEMA-TMS)

The synthesis of HEMA-TMS was referred to the previous work.⁴⁸ First, purified HEMA (10 mL, 76 mmol, 1 equ.), triethylamine (15.9 mL, 114 mmol, 1.5 equ.), and 250 mL of ethyl ether were added in to a dry flask and cooled to 0°C. Then, trimethyl chlorosilane (TMS-Cl, 14.7 mL, 114 mmol, 1.5 equ.) was added dropwise over 10 min. A white precipitate formed immediately. The mixture was stirred at 0°C for 2 h then filtered to remove the solids. The filtrate was then washed with deionized water for three times and dried overnight using anhydrous MgSO₄. The protected monomer was obtained by removal of ether under vacuum and distilled at 50°C under 0.06 Torr.



Scheme 2. The idea of chemical product design used in this work.

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Synthesis of poly(HFBMA-*r*-HEMA-TMS) random copolymer

A typical procedure for the synthesis of random copolymer by ATRP is as follows: toluene (5 mL), catalyst system (0.15 mmol CuBr, 0.3 mmol PMDETA), HFBMA (15 mmol), and HEMA-TMS (10 mmol) were added into a dried reaction flask. After three freeze-pump-thaw cycles, initiator (Eib-Br, 0.15 mmol) was added into the mixture. The reaction was carried out at 80°C and stopped after 10 h. The resulting copolymer was obtained by removing the catalyst, precipitating in petroleum ether (60–90°C), and finally drying under vacuum.

Preparation of poly(HFBMA-*r*-BIEM) random copolymer

The poly(HFBMA-*r*-HEMA-TMS) copolymer (2 g) was dissolved in 50 mL dry THF. KF (3 mmol) and TBAF (0.03 mmol) were added into the polymer solution and stirred for 12 h at 30°C. After the deprotection, triethylamine (9 mmol) was added into the solution, followed by slow addition of 2-bromoisobutyl bromide (4.5 mmol) at 0°C and stirred at room temperature for 12 h. The esterified copolymer poly(HFBMA-*r*-BIEM) was obtained through precipitating the polymer solution into methanol and dried under vacuum.

Preparation of poly(HFBMA-*r*-BIEM-graft-SPMA) random brush copolymer

The poly(HFBMA-*r*-BIEM-graft-SPMA) was obtained by ATRP of SPMA using poly(HFBMA-*r*-BIEM) as macroinitiator based on graft-from method.⁴⁹ A typical procedure is described as follows: toluene (10 mL), poly(HFBMA-*r*-BIEM) (435 mg, with 0.6 mmol initiative sites), PMDETA (0.6 mmol), and CuBr (0.3 mmol) were added into a reaction flask. After deoxygenation, the deoxygenated SPMA solution (1.2 mmol, 0.504 g in 2 mL toluene) was added under N₂

protection. The reactions were carried out at 80°C and stopped after 10 h. The resulting polymers were obtained by removing the catalyst, precipitating twice in methanol and finally drying under vacuum. Monomer conversion was measured by gravimetry.

Texturization of silicon wafer

Before use, the silicon wafers and glass slide were carefully cleaned in a beaker of 10% HCl and KF solution for 24 h and followed by successive acetone, ethyl alcohol, and deionized water placed in an ultrasonic bath for at least 20 min at room temperature and then dried with nitrogen stream. The etched silicon wafer was obtained by the following texturization process⁵⁰: the silicon wafers were etched in a solution consisting of 2% NaOH and 20% isopropyl alcohol by volume at 80°C under reflux condition for 15 min. After that, the wafers were washed again with deionized water and dried with nitrogen stream. All the global root-mean-square (RMS) roughness of blank substrates (RMS_{flat glass} = 2.21 nm, RMS_{flat silicon} = 2.11 nm, and RMS_{etched silicon} = 151 nm) were analyzed by atomic force microscope (AFM) as shown in Supporting Information Figure S1.

Preparation of the copolymers films

The polymer solution (3 wt % in THF) was spin-casted onto clean glass slide or clean silicon wafer at 3000 rpm for 30 s, and then dried naturally for 24 h. The thickness of as-prepared films is 200 nm.

Light sources

The UV light source was a high pressure mercury lamp equipped with a band pass filter to get an emission wavelength at 365 nm. The intensity of the UV light was 3 mW cm⁻². The source of visible light (620 nm) was a tungsten 40 W lamp that generated a power of 2 mW cm⁻². The samples were placed at a distance of 5 cm from the light source at room temperature.

Measurements

¹H NMR. The copolymer composition was determined by nuclear magnetic resonance (¹H NMR) spectroscopy (Varian Mercury plus 400, 400 MHz) in CDCl₃ with tetramethylsilane (TMS) internal standard.

Gel Permeation Chromatograph. Molecular weights (M_n) and molecular weight distributions (M_w/M_n) of polymer were determined on a gel permeation chromatograph (GPC, Tosoh Corporation) equipped with two HLC-8320 columns (TSK gel Super AWM-H, pore size: 9 μm; 6 × 150 mm, Tosoh Corporation) and a refractive index detector (Bryce) consisting of double-path, double-flow system at 30°C. The elution phase was DMF (0.01 mol/L LiBr, elution rate: 0.6 mL/min). A series of poly methyl methacrylate were used as the universal calibration standard.

UV-Vis Spectra. The UV-vis spectra were recorded on a UV-2550 spectrophotometer (Shimadzu, Japan). The concentration of polymer solution was 0.25 mg/mL in THF.

Atomic Force Microscope. The surface morphology and roughness of the spin-coated films were acquired on a Nanoscan E-Sweep (SII, Japan) AFM in the tapping mode at room temperature.

Static Water Contact Angle. The static water contact angles were recorded on a Contact Angle Measuring Instrument (KRÜSS, DSA30) by the sessile drop method with a

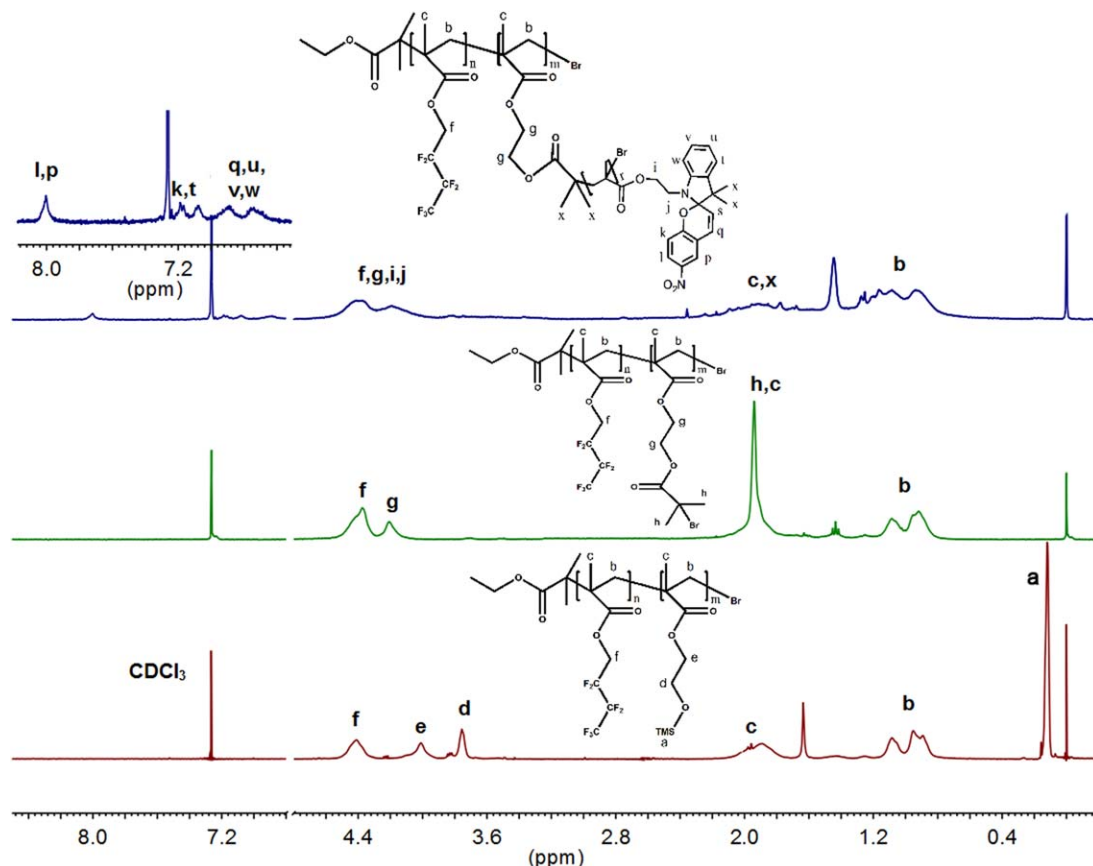


Figure 1. ^1H NMR spectra of poly(HFBMA-*r*-BIEM-graft-SPMA) (in blue, top), poly(HFBMA-*r*-BIEM) (in green, middle), and poly(HFBMA-*r*-HEMA-TMS) (in dark red, bottom).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

microsyringe at room temperature. The injection volume of liquid is 5 μL . The reported angle is an average value of five readings from different locations.

X-Ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy (XPS) spectra were recorded to determine the surface composition of the resulting polymer films using an AXIS Ultra DLD system (Kratos Co., Japan), equipped with an Al K α monochromatic source of 1486.60 eV.

Results and Discussion

Synthesis of fluorinated random copolymer with spiropyran brushes

Similar to our previous work,⁴⁹ the protected HEMA, HEMA-TMS, was used for synthesizing backbone copolymer due to its large dissolvability in low-polarity solvents. In addition, the resulting copolymers are more compatible with organic media, especially after copolymerization with hydrophobic monomers. After the deprotection and transesterification with 2-bromoisobutyryl bromide, they can be prepared into graft copolymers.

In this work, poly(HFBMA-*r*-HEMA-TMS) was successfully synthesized by ATRP, which was confirmed by ^1H NMR spectroscopy (Figure 1, dark red line, bottom). By comparing the peak area ratio of characteristic signals for HFBMA ($\delta=4.4$ ppm 2H, $-\text{OCH}_2(\text{CF}_2)_2\text{CF}_3$) and PHEMA-TMS ($\delta=0.05$ – 0.16 ppm, 9H, $-\text{Si}(\text{CH}_3)_3$), their overall composition can be obtained. According to the result, the degrees of polymerization for HFBMA and HEMA-TMS are

50 and 30, respectively. The theoretically calculated M_n of random copolymer [poly(HFBMA-*r*-HEMA-TMS)] is 19,476 g/mol. The GPC results shown in Figure 2 are 21,300 g/mol for M_n and 1.21 for M_w/M_n , which indicate good agreement with theoretical M_n and controllable feature.

To further functionalize the fluorinated copolymers, deprotection and esterification were carried out to obtain macromolecular initiator with multi-initiative sites. As depicted in Figure 1 (green line, middle), one can find that the characteristic peak of $-\text{O-TMS}$ resonance is absent, as well as the strengthened characteristic peak ($\delta=1.97$ ppm) for $-\text{C}(\text{CH}_3)_2\text{-Br}$ is present. Both of them indicate that the TMS groups on the copolymers were fully removed and the macromolecular initiator was successfully synthesized. In addition, Figure 2 shows that the GPC trace moves toward high molecule weight side (23,700 g/mol) without broadening the polydispersity ($M_w/M_n=1.19$), and the $M_{n,\text{GPC}}$ is close to theoretical M_n (21,783 g/mol), which also indicate the successful esterification.

Finally, the fluorinated random copolymers with spiropyran brushes, poly(HFBMA-*r*-BIEM-graft-SPMA), were successfully synthesized by graft polymerization. On one hand, the characteristic signals ($\delta=8.01$ – 8.03 ppm, $\delta=6.70$ – 7.25 ppm) for the proton of benzopyran phenyl group were clearly observed in Figure 1 (blue line, top). On the other hand, the peak at 1.97 ppm assigned to the methyl protons of BIEM disappeared, indicating almost 100% initiation efficiency. Additionally, the GPC results in Figure 2 illustrate that the molecular weight of obtained graft copolymer is 36,500 g/mol, and the molecular

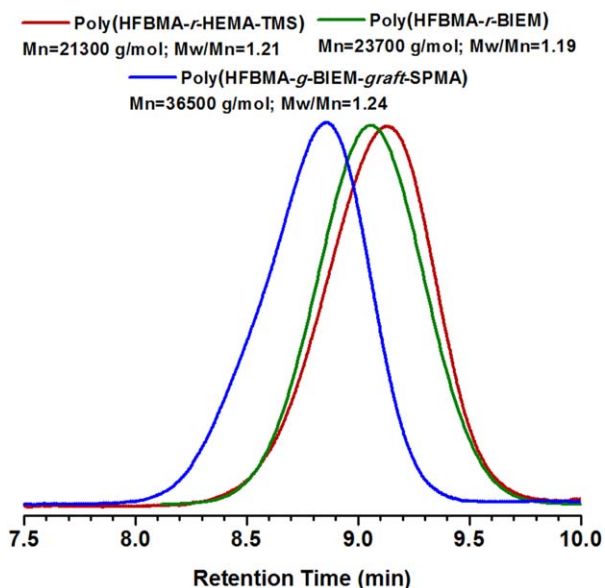


Figure 2. GPC traces for the synthesized copolymers.

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weight distribution is 1.24, proving that the graft polymerization of SPMA is well controlled. The theoretical M_n (34,386 g/mol) calculated from the degree of graft reaction based on monomer conversion (ca. 50%) also agrees quite well with $M_{n,GPC}$.

It worth noting that direct preparation of functional copolymers using copolymerization HFBMA and SPMA functional monomers is difficult to achieve due to the low activity of SPMA monomers containing photochromic spiropyran moieties, and thus the graft polymerization was chosen in this work. Interestingly, all of the alkyl bromides on copolymer main chains maintain activity and the ratio of monomer and initiator sites (2:1) is rather small, and thus makes the graft reaction as effective as clickable chemistry method.⁵¹

Photoisomerization of the spiropyran moieties

The spiropyran units in the copolymers can be transformed between the Sp and Mc form upon light irradiation with different wavelengths.²⁵ The photochemical isomerization of spiropyran units in THF solvent is schematically illustrated and measured by UV-vis spectroscopy as shown in Figure 3A. The appearance of absorption band at 570 nm indicates that spiropyran in brush copolymer converts from the Sp to Mc isomer responding to UV irradiation at a wavelength of 365 nm, and thus the solution appears violet. When irradiated with visible light (620 nm), the Mc form can be switched back to Sp form. However, the color of copolymer solution is yellow instead of colorless, which might be attributed to H-type Sp-Mc and intramolecular Mc_n stacks as confirmed by the shoulder absorption band at 490 nm.

It is known that the switchable wettability of as-prepared spin-coated film induced by irradiation is a result of the different hydrophilicity corresponding to Sp and Mc isomer. As shown in Figure 3B, the spectrum also exhibits the characteristic absorption band at 570 nm for Mc form, and the band vanishes after 30 min of visible light irradiation. It should be noted that the lower absorbance intensity at 570 nm in UV-vis spectrum of spin coated film implies that the isomerization of bulky Sp moieties has been restrained by limited available free volume and restricted conformational freedom in solid even after prolonging irradiation time. Besides, the WCA measurements were carried out to monitor the switchable wetting behavior upon different light stimulus. As expected with the fluorinated random brushes copolymer film, the wettability of glass slide has been greatly improved from hydrophilic (WCA = 49.5°) to hydrophobic (WCA = 103.0°). From the inset of Figure 3B, one can find that the WCA changes from 103.0 to 95.4° for flat glass substrate, and the variation ($\Delta WCA = 7.6^\circ$) is comparable to that ($\Delta WCA = 5\text{--}15^\circ$) of surface-grafted polymer brushes with different Sp moieties grafting density as previously reported.²⁵ Due to the importance of surface free energy (γ) in predicting a liquid wettability on solid surface and estimating the type of intermolecular interactions, the relevant values based on Li-Neumann equation⁵² were calculated as listed in Table 1. The results show that the spin-

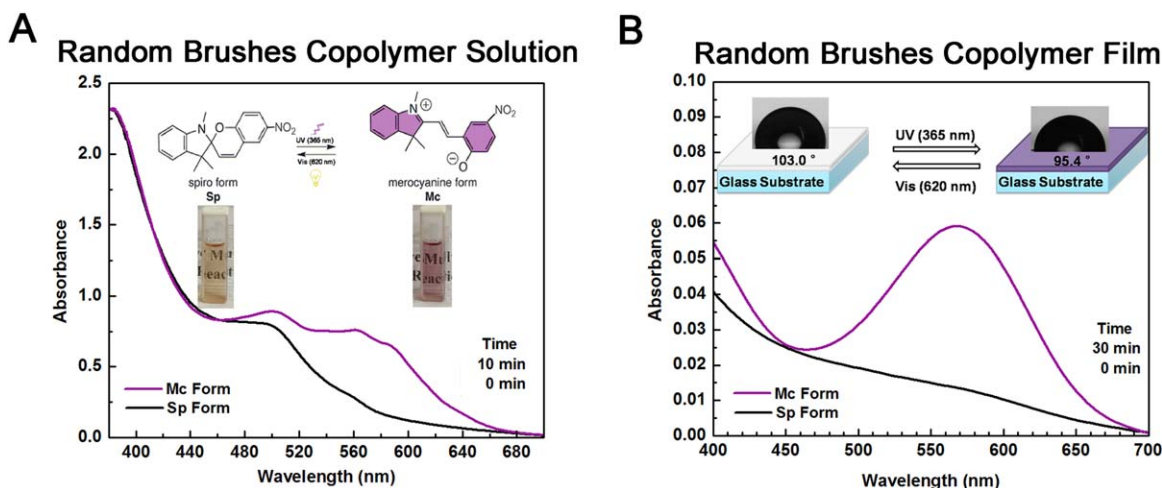


Figure 3. UV-vis spectra of poly(HFBMA-*r*-BIEM-graft-SPMA) random brushes copolymer solution (A) and spin-coated film on glass slide upon UV light irradiation (B).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 1. Surface Free Energy of Different Substrates (mN/m)^a

Substrate	Energy		
	Blank	Spin-Coated Film	Spin-Coated Film After UV Irradiation
Glass	54.0	21.2	25.8
Flat Silicon	30.4	18.9	27.0

^aThe data are calculated from a new equation: $1 + \cos\theta = 2(\gamma_s/\gamma_L)^{1/2} \exp[-\beta(\gamma_L - \gamma_s)^2]$ derived by Li and Neumann based on Young's model, where γ_s , γ_L , and θ represents the surface energy of solid, water, and the static water angel, respectively. $B = 0.1247 \times 10^{-3}$; $\gamma_L = 72.8$ mN/m.

coated film on glass substrate allows reducing the value of γ from 54.0 to 21.2 mN/m and switching it between 21.2 and 25.8 mN/m upon light stimulus.

Switchable hydrophobicity of silicon surface

To further study the switchable wetting behavior, the random brushes copolymer was spin-coated onto silicon substrate. Figures 4A1, A2 show an improvement of hydrophobicity of flat silicon surface based on the as-prepared hydrophobic coating, where WCA changes from 88.0 to 106.8° and γ decreases from 30.4 to 18.9 mN/m. The WCA changes from 106.8 to 93.5° as a consequence of photoisomerization of Sp when the sample is illuminated with UV light (Figure 4A3). However, comparing the results of both copolymer modified flat surfaces (WCA = 103.0° and $\Delta WCA = 7.6^\circ$ for glass slide; WCA = 106.8° and $\Delta WCA = 13.3^\circ$ for silicon wafer), we find that the difference between them is not significant. It can be summarized that the improvement of maximum limit of surface hydrophobicity through surface chemical composition decoration (surface polarity and conformational change) has been reached.

Conversely, surface roughness is another key parameter governing surface wettability. Therefore, the as-prepared copolymer film was spin-coated onto an etched silicon substrate aiming to obtain a better photoreversibly switchable hydropho-

bic surface. Figure 4B1 shows that the WCA of etched silicon surface reaches 109.2°, which is even higher than that of flat silicon surface decorated by copolymer film (WCA = 106.8°). It indicates that the influence of surface roughness is more effective than chemical composition in this work. As shown in Figure 4B2, the hydrophobicity of silicon surface has been improved with the WCA increased from 106.8 to 120.8° on the basis of the combined effect of chemical composition (surface polarity and conformational change) and surface roughness. Meanwhile, WCA of the sample changed from 120.8 to 100.9° ($\Delta WCA = 19.9^\circ$) when it was exposed to UV light for 30 min. To the best of our knowledge, this is an excellent result concerning smart surface fabricated by copolymer containing Sp moieties. It is worth noting that the as-prepared smart surface has achieved the photoreversibly switching between hydrophilicity and hydrophobicity based on blank sample (109.2°) in response to subsequent irradiation with 365 nm UV light and 620 nm visual light.

To further understand the phenomenon, model interpretation was presented. Wenzel model⁵³ and Cassie–Baxter model⁵⁴ are two classical hypotheses that are usually proposed to explain the effect of roughness on the surface wettability. The Wenzel model can be expressed as follows

$$\cos \theta_r = r \cos \theta_Y \quad (1)$$

where θ_r is the apparent contact angle on a rough substrate the surface, θ_Y is Young's contact angle, and $r(>1)$ is the ratio of actual wetted surface area over the geometric surface area.

The Cassie–Baxter model can be given by Eq. 2

$$\cos \theta_r = f_s(1 + r \cos \theta_Y) - 1 \quad (2)$$

where $f_s(<1)$ is the ratio of solid–liquid interface area over the total area.

In this work, the WCA of flat silicon wafer is 88.0° (slight hydrophilicity), while that of etched silicon substrate is

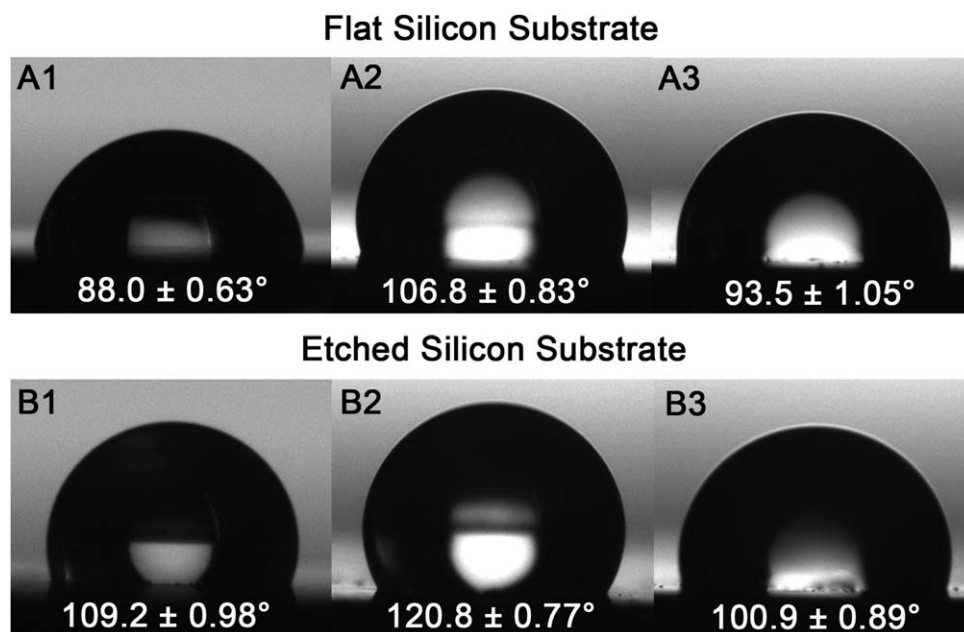


Figure 4. Photographs of WCA on flat silicon and etched silicon substrates: blank (A1 and B1); decorated by random brushes copolymer before UV irradiation (A2 and B2); decorated by random brushes copolymer after UV irradiation for 30 min (A3 and B3).

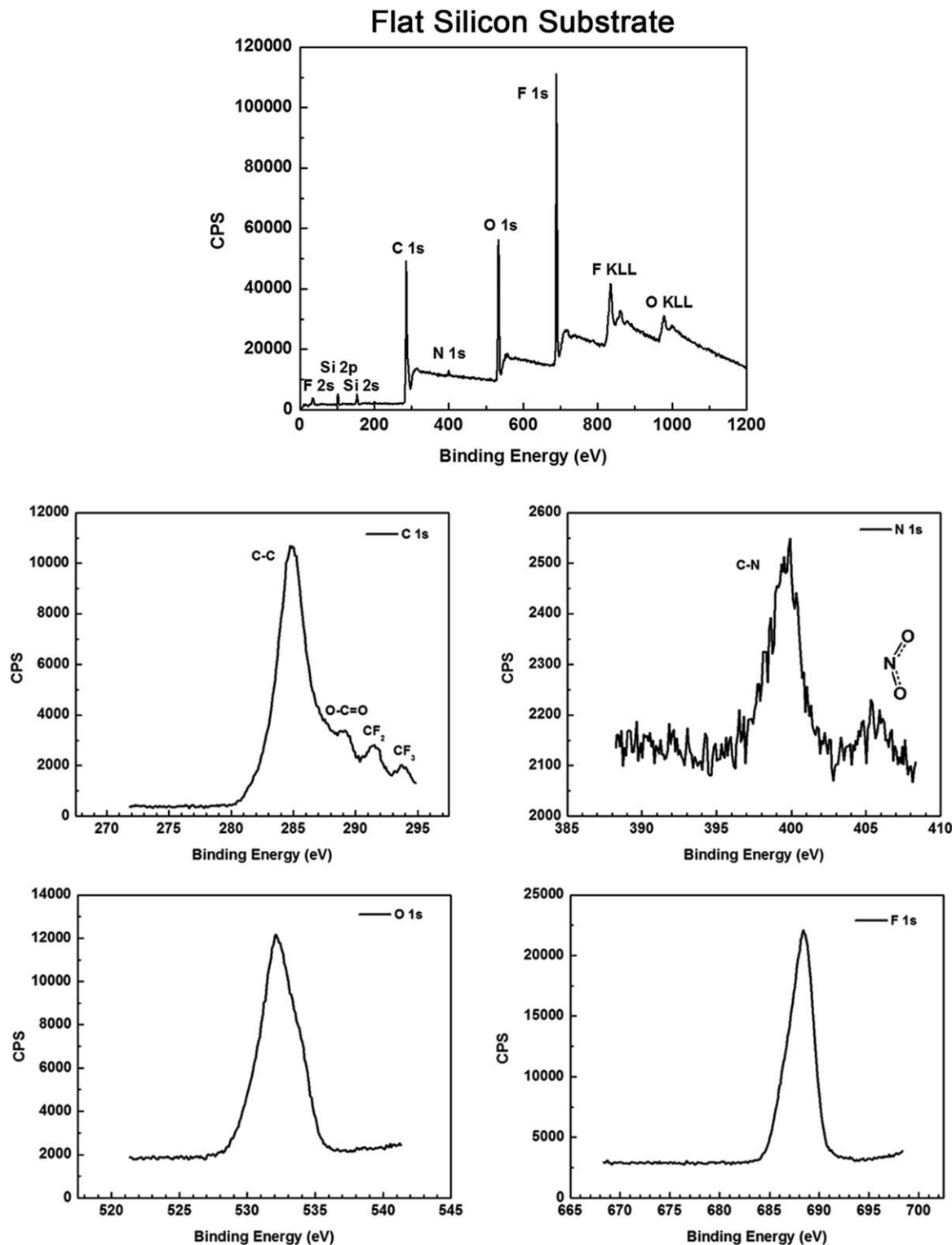


Figure 5. Surface composition of flat silicon substrate decorated by random brushes copolymer film.

109.2° (hydrophobicity). This result does not agree well with Wenzel model which explains the fact that hydrophilic surfaces ($\theta < 90^\circ$) become more hydrophilic, and hydrophobic surfaces ($\theta > 90^\circ$) become more hydrophobic after surface roughening. Therefore, we assume that the result belongs to Cassie and Baxter behavior, which supports the water drop by trapped air and asperities on the surface. The trapped air makes the surface exhibit an enhanced hydrophobic behavior. Furthermore, one can calculate the value of f_s (=0.65)

according to Eq. 2 and both WCAs of blank samples. As for the silicon substrates decorated by copolymer film, the value of f_s is given by 0.68, which is nearly equal to that of blank sample. This indicates that the Cassie and Baxter model is valid for present phenomenon. Consequently, the surface free energy of roughed silicon substrate should be similar to that of flat silicon wafer.

Another intriguing result in this work is that the ΔWCA (19.9°) for roughed silicon substrate is larger than that

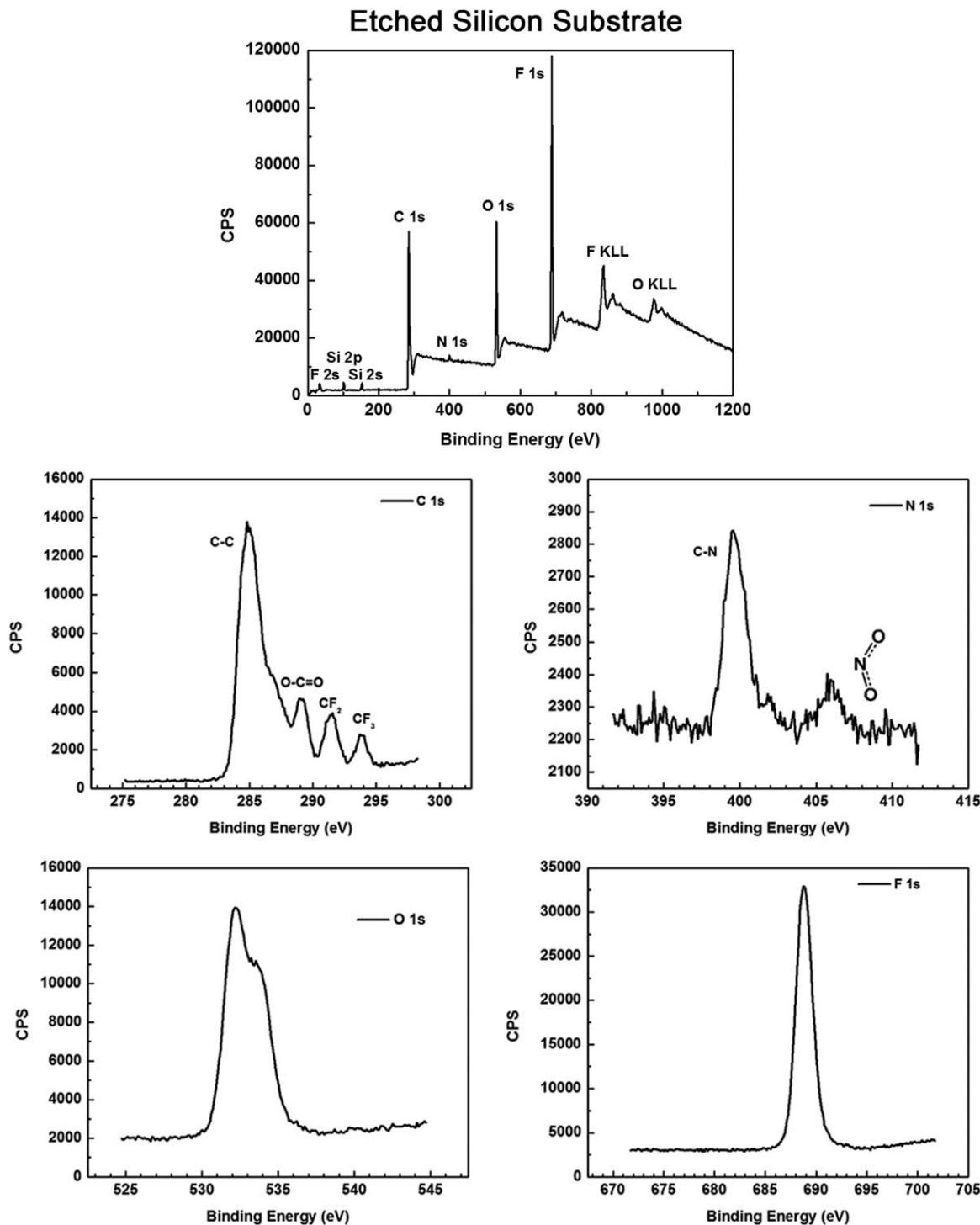


Figure 6. Surface composition of etched silicon substrate decorated by random brushes copolymer film.

Table 2. XPS Quantification of Silicon Substrates Modified by Random Brushes Copolymer Film (% Atom)

Substrate	Element				W_F (%) ^a (in bulk)
	C 1s	N 1s	O 1s	F 1s	
Flat silicon	62.30	1.48	16.24	19.98	19.34
Etched silicon	61.20	1.47	16.32	21.01	

^a W_F is the weight percent of fluorine obtained from the equations: $F\% = (7 \times 19 \times DP_n)/(M_n(\text{Calc.}))$, where each fluorinated monomer HFBMA contains seven fluorine atoms and the fluorine atomic weight is 19 and DP_n is polymerization degree of the PHFBMA.

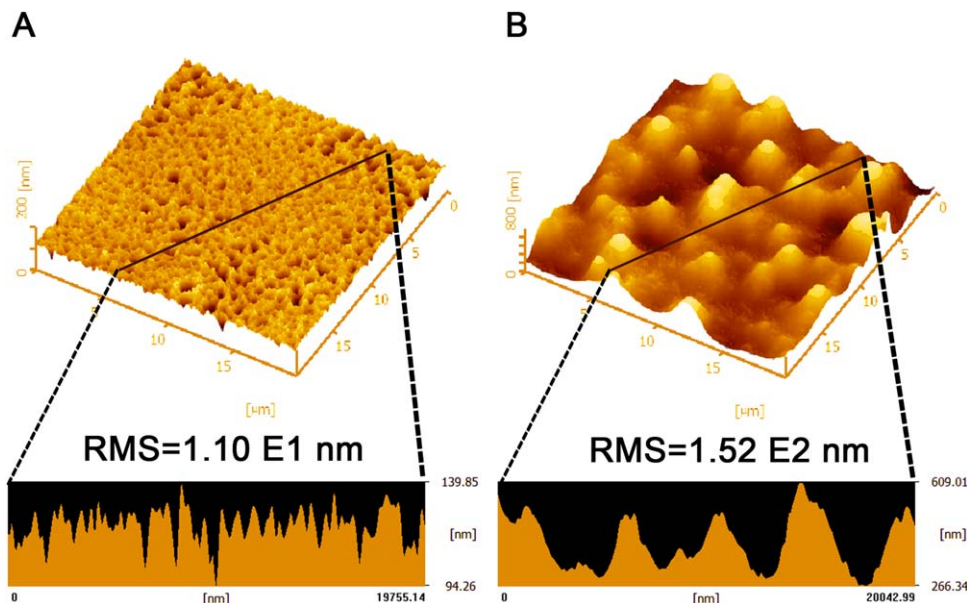


Figure 7. AFM three-dimensional images, global RMS roughness (RMS), and corresponding section (black line) profiles of flat silicon (A) and etched silicon (B) substrates decorated by random brushes copolymer film.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(13.3°) of flat silicon wafer. Why can the similar copolymer composite make them different? We also can get some information from the Cassie and Baxter model. After UV irradiation, the WCA of etched silicon substrate is 100.9° and that of flat one is 93.5°. The f_s value in this situation is 0.86, which is higher than before. Higher f_s indicates that the water drop has sunken down into the groove resulting from photoisomerization of the hydrophobic Sp to hydrophilic Mc form on etched substrate. This, therefore, leads to a higher solid–liquid interface area.

Surface composition and morphology of the films

After evaluating the photoreversibly switchable hydrophobicity performance of production on silicon substrates, the

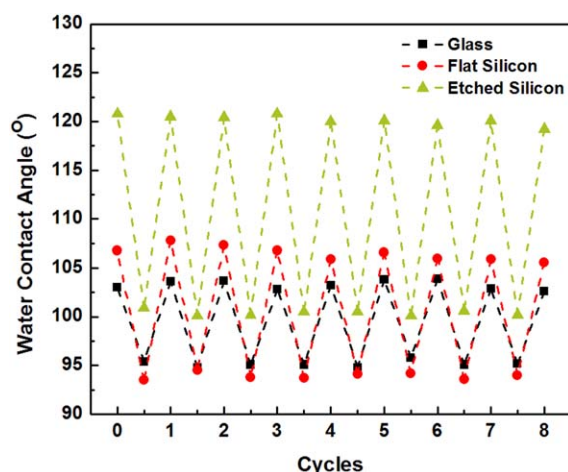


Figure 8. Reversibly photoresponsive wettability of flat glass slide, flat silicon, and etched silicon substrates decorated by random brushes copolymer film.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

composition and morphology of smart surfaces were analyzed by XPS and AFM. The XPS survey scan spectra in Figures 5 and 6 present the same characteristic signals of carbon, nitrogen, oxygen, and fluorine for flat and etched surfaces. The peaks at 978, 832, 685, 531, 398, 285, and 30 eV correspond to the direct photoionization from O KLL, F KLL, F 1s, O 1s, N 1s, C 1s, and F 2s core levels, respectively. And, the weak signals of Si 2s and Si 2p are assigned to the substrates. In addition, the high resolution C 1s spectrum shows a complex pattern of peaks, which indicates four different carbon bonds of CF₃ at 294.7 eV, CF₂ at 292.1 eV, O—C=O at 289.4 eV, and C—C at 284.8 eV, respectively. The XPS survey scan spectra of as-fabricated surfaces after UV irradiation are similar to that before as shown in Supporting Information Figures S2 and S3. This might result from the inconspicuous difference of characteristic single peak of O 1s in copolymer during photoisomerization process. To be specific, the spiropyran molecule comprises an indoline and a chromene moiety bound together via a spiro junction and oriented perpendicular with respect to one another. During the transformation, the cleavage of the C_{spiro}—O bond results in the formation MC under UV irradiation.

To obtain more information about the composition before and after UV irradiation, the quantification of C, N, O, and F by software is summarized in Table 2 and Supporting Information Table S1. Both surfaces do not show distinct difference in the contents of elements, which verifies the similar surface compositions of as-prepared films and similar surface energy of both surfaces. Indeed, the surface composition without change is a clear indication that the switchable wetting effects observed are due to the existence of spiropyran. Generally, the selective segregation of semifluorinated chains makes the fluorine enrich on surfaces on the basis of its low surface energy and self-assembly behavior. When comparing the contents of F in surface and bulk, however, we find that there is only a small increase. This result probably arises from the microstructure of the random

copolymer, which is of excellent component compatibility at the nanoscale.⁴⁵ As a whole, the relative lower surface energy of both functional surfaces might result from the stretching out of semifluorinated segments at the polymer-air interface rather than surface enrichment, and the switchable property of as-fabricated surfaces results from the physicochemical characteristics rather than composition change.

As mentioned earlier, the roughness of surface is another factor affecting the wetting behavior. From the AFM three-dimensional images of both silicon surfaces (Figure 7A), the flat silicon substrate with as-prepared film appears relatively smooth with global RMS roughness of 11 nm based on spin-coating technique. But, the pyramid topography with copolymer film depicted in Figure 7B demonstrates that the improvement of surface roughness has been achieved and the global RMS reaches as high as 152 nm. In addition, the corresponding section (black line) profiles indicate that both of functional surfaces have uniform macrostructures and nanostructures. In a word, by means of surface engineering (surface modification and texturization), the hydrophobicity and controllable wettability of silicon surface have been greatly enhanced. These results give insight into the mechanism of switchable hydrophobic property and physicochemical characteristics of the surface decorated by designed polymeric material.

Practical engineering application study

The aim of this work is to design a new engineering material (smart surface coating) with novel functionality and good performance for customers. The above sections have confirmed the advent of the product based on the basic characterizations, the evaluation of the photoreversibly switchable hydrophobicity performance, and the insight of switching mechanism. But beyond that, the lifetime of product is another issue that customers concern. In the present work, a repetitive month-long experiment was carried out to monitor the performance of as-prepared coating. The result presented in Figure 8 shows that the different smart surfaces undergo a reversible light-induced wettability switching with excellent stability by alternately irradiation with UV and visible light, and the controllability is improved in the order of flat glass slide, flat silicon, and etched silicon substrates. Compared with the traditional coating product used in nowadays, the alternative product in this study has unique advantage and can be applied in moisture-resistance field and microanalytical devices via controlling the spread of liquids on a surface.

Conclusions

To sum up, a new chemical product with novel photoreversibly switchable hydrophobicity based on molecular design was synthesized via ATRP and graft-from method. The graft reaction carried out at a small ratio of monomer and initiator sites (2:1) makes itself as effective as a clickable chemistry method. The obtained copolymer product was confirmed by ¹H NMR spectroscopy and GPC measurement. The photoisomerizations of spiropyran units in the copolymers in THF solvent and spin-coated film were monitored by UV-vis spectra. The results give insight into the switching mechanism concerning the switchable wettability of as-prepared spin-coated film induced by irradiation.

Thanks to the surface engineering technique (decorated with functional film or/and surface roughening), the product

was applied for developing smart surfaces that show hydrophobicity and reversibly switchable wettability. In specific, WCA is 103.0° and ΔWCA is 7.6° for glass surface; WCA is 106.8° and ΔWCA is 13.3° for silicon surface; WCA is 120.8° and ΔWCA is 19.9° for etched silicon surface. Note that, the wetting behavior of etched silicon surface decorated with functional film can be tuned between hydrophilicity and hydrophobicity based on blank sample. As a whole, these interesting results were successfully explained by experiments and the Cassie and Baxter model.

Furthermore, the performance of the surface still remains well after a month-long experiment with eight irradiation cycles. This result of aging test shows that the product enables surfaces to have excellent stability. Over all, the new product presented here can be developed for a hydrophobic surface with low surface free energy in moisture-resistant field. Meanwhile, it also offers an application with photo-induced controllable wettability in coating as well as a new technique for the manipulation of liquids in microfluidic devices based on the viewpoint of chemical product engineering.

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