ThE FuTuRe iS NoW!

Directed by Ericson L. Mata Z

Langmuir

Adhesion and Friction Properties of Fluoropolymer Brushes: On the Tribological Inertness of Fluorine

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Propiedades de adhesión y fricción de cepillos fluoropoliméricos: sobre la inactividad tribológica del flúor

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LET’S GO TO THE PAST!

Biomacromolecules **2004**, *5*, 869−876

Thermodynamic Studies on the Adsorption of Fibronectin Adhesion-Promoting Peptide on Nanothin Films of Poly(2-vinylpyridine) by SPR

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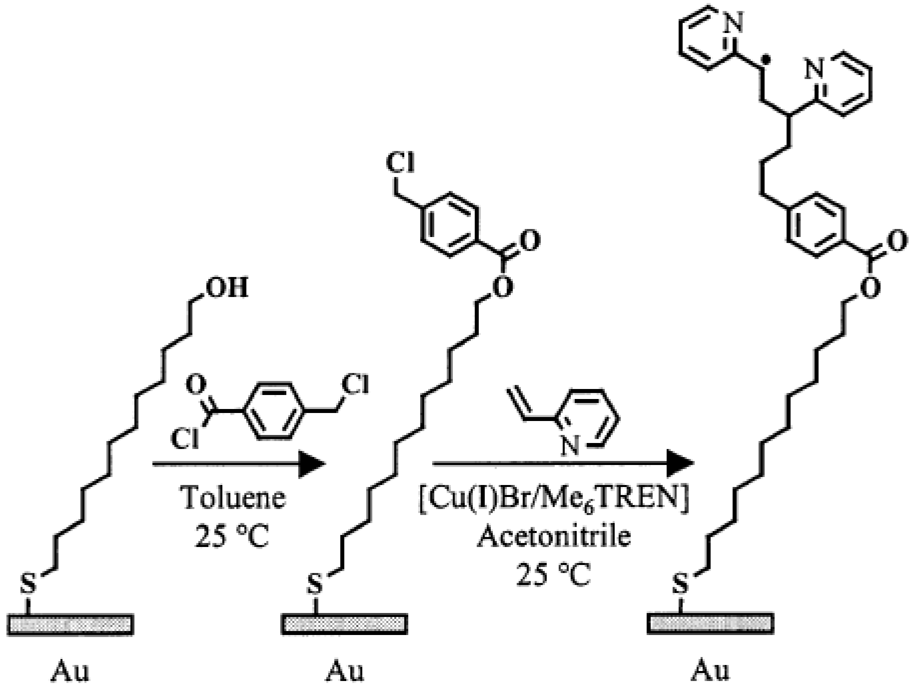
Scheme 1. Synthetic Pathway to Surface-Confined Poly(2-vinylpyridine)



Results and Discussion

surface plasmon resonance (SPR)

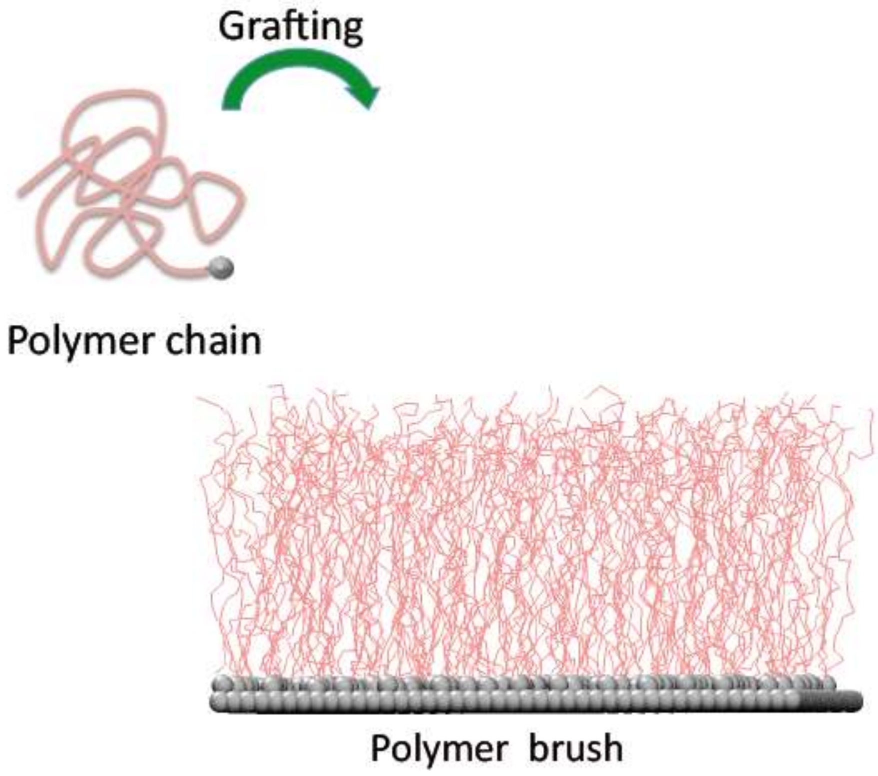
WHAT ARE MEMS/NEMS?

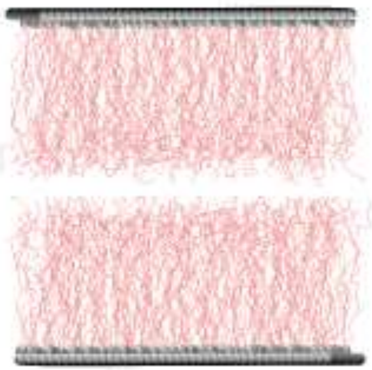
MEMS-microelectromechanical systems

NEMS-nanoelectromechanical systems

¿WHAT ARE POLYMER BRUSHES?

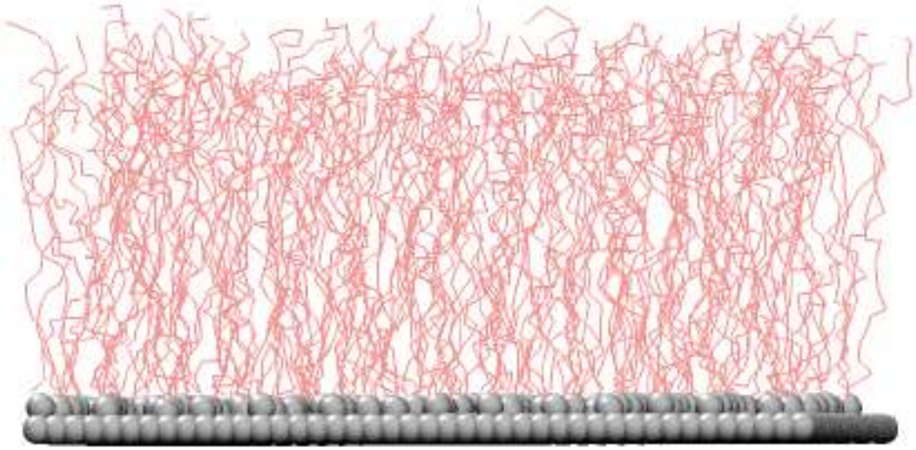
Fuente: http://www.thebabyshop.com.mx/producto1.php/producto/CEPILLO-PARA-BIBERONES-C-DISPENSADOR-DE-JABON/p/7560





Fuente: http://sites.northwestern.edu/erbas/

POLYMER BRUSHES-FORMAL DEFINITION



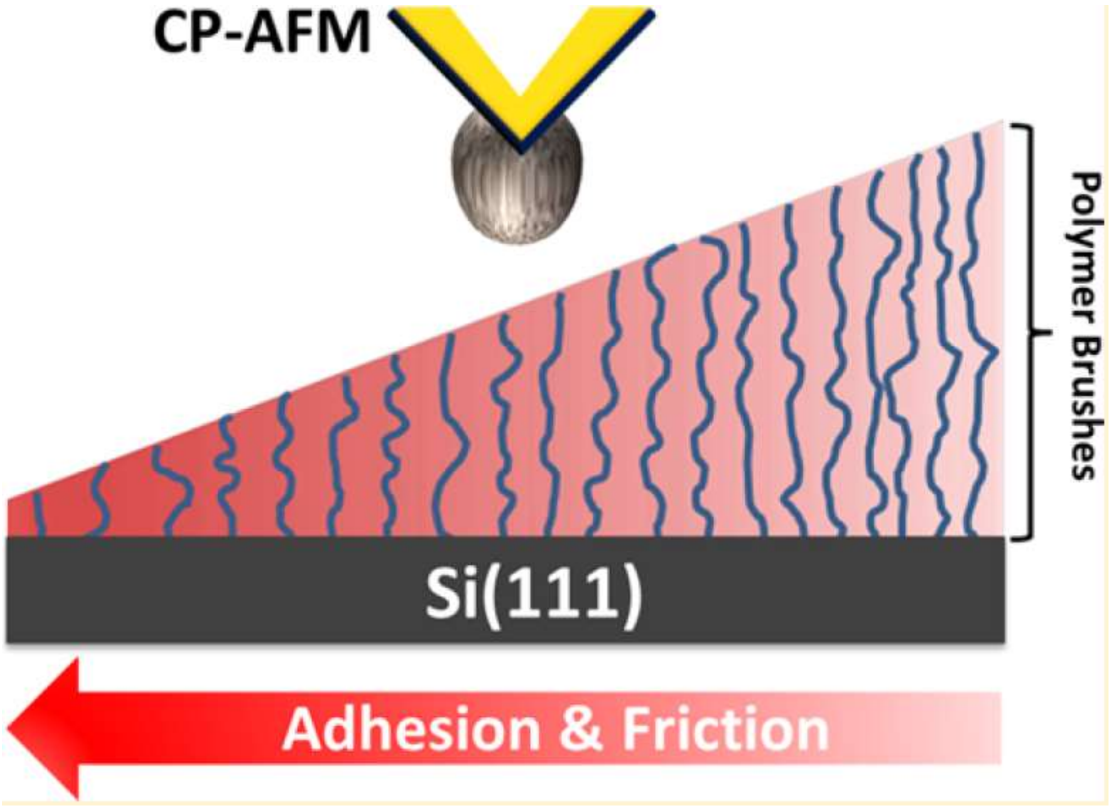
Polymer brush

Polymer brushes — tightly packed, surface-bound polymers[1] — are increasingly used due to their unique properties, which make them amenable for a wide range of applications. Their potential becomes evident from the range of fields in which they are currently studied: antifouling surfaces,[2] reversible switching behavior (depending on, e.g., pH, heat, or light),[3,4] multivalent functionalization,[5] tunable wettability[6,7] and lubrication,[8] and so forth. Therefore, polymer brushes find application in sensors,[9,10] drug delivery,[9] and micro and nano fluidic devices.[11] Polymer brushes can be obtained quite easily

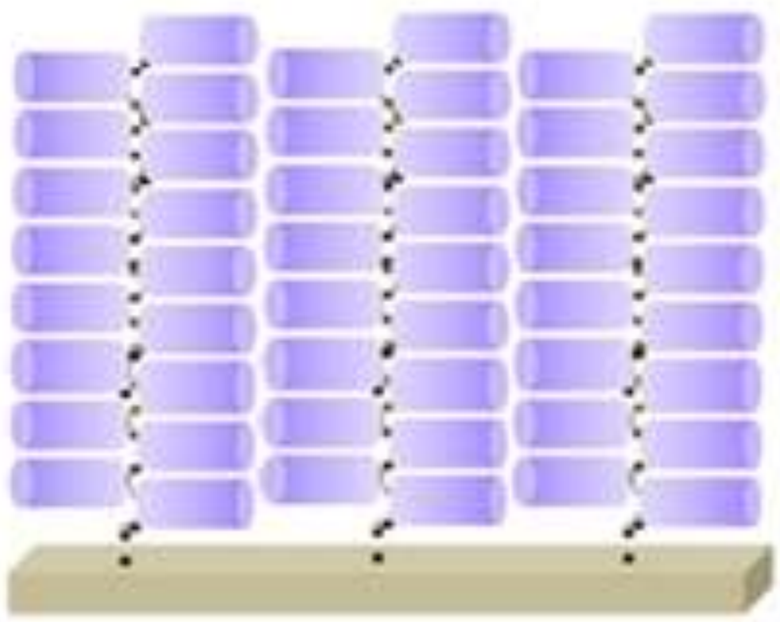
WHAT IS CONECTION BETWEEN NEMS/MEMS-PEPTIDE-POLYMER BRUSHES?

PREVIOUS RESEARCH

Adhesion and Friction Properties of Fluoropolymer Brushes: On theTribological Inertness of Fluorine (2014)
Varying thickness & using until SPF3



¡LET'S GO TO THE PRESENT!



SPF17

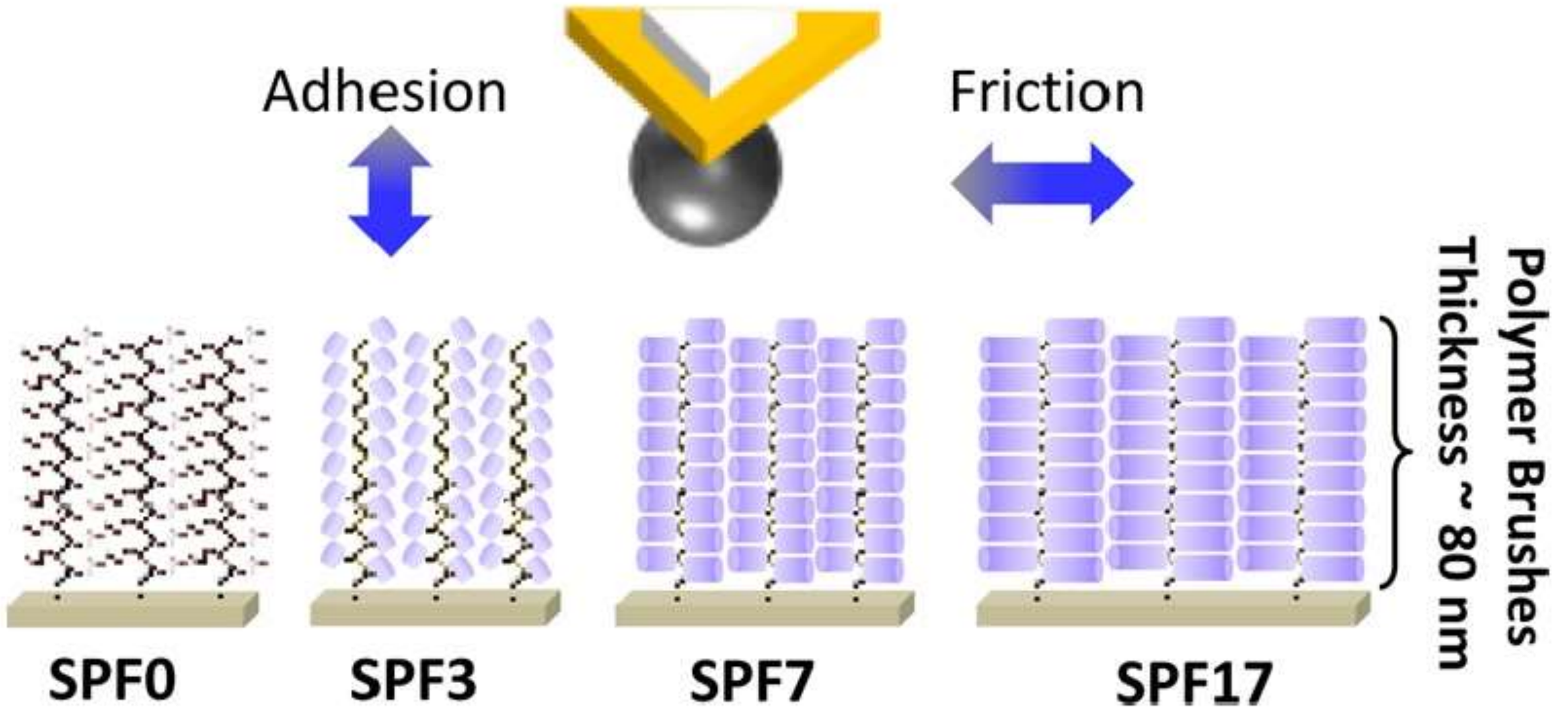
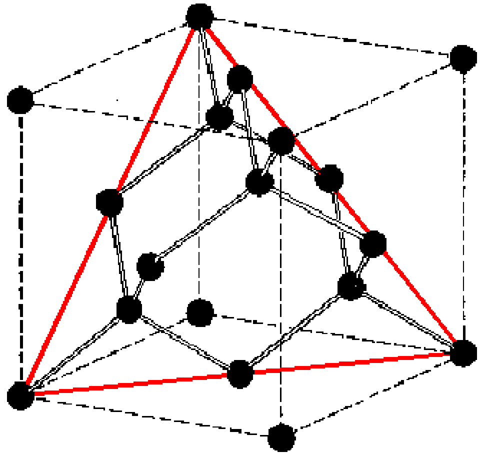


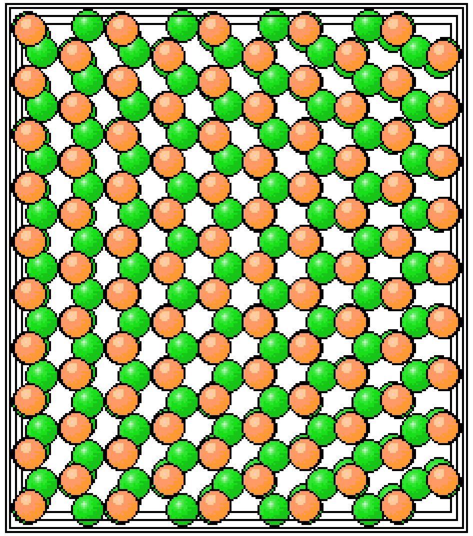
Figure 1. Schematic representation of covalently bound fluorinated polymer brushes at constant thickness (~80 nm) but with varying fluorine content to study the effects of fluorination in polymer on the adhesion and friction properties.

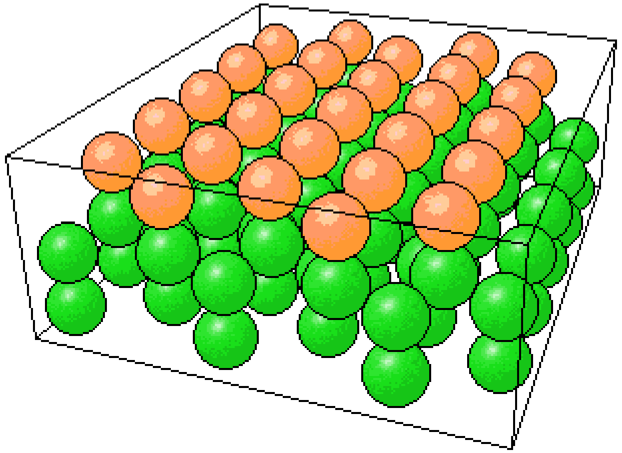


Silicon has a crystal lattice of the **diamond lattice** structure (see the schematic view on the left).
Si(111) notation refers to a specific set of atomic planes in that structure. In the cube shown on the left it corresponds to the plane outlined with red. Another way to see what the (111) crystal planes in diamond lattice look like is provided by the "cork-ball" models shown below.

Si(111) Surface

The left image shows a top view of the atomic arrangement for the (111) plane. The right image shows a 3-dimensional view of the same surface. In both cases atoms are color-coded: orange for the top layer, green for all the deeper layers





These two images have been generated with the help of the Surface Explorer web-based tool. http://nanowiz.tripod.com/sisteps/si111.htm

LET'S UNDERSTAND Si(111)

Surface Characterization.

Kruss Drop Shape Analyzer – DSA100
Photo from http://www.kruss.de/products/contact-angle/dsa100/drop-shape-analyzer-dsa100/

Goniometer
Photo from: https://es.wikipedia.org/wiki/Goni%C3%B3metro

LET'S WATCH A MOVIE

Bruker Tensor 27 FT-IR spectrometer
Photos from https://www.bruker.com/products/infrared-near-infrared-and-raman-spectroscopy/ft-ir-routine-spectrometers/tensor/overview.html

SENTECH Laser ellipsometer SE 400adv PV
Foto tomada de http://www.sentech.com/en/SE-400adv-PV__2229/

JEOL JPS-9200 X-ray photoelectron spectroscopy (XPS) http://www.jeol.co.jp/en/products/detail/JPS-9200.html

Adhesion and Friction Measurements.

As**ylum Research MFP-3D atomic force microscope (AFM),**
Photo from www.asylumresearch.com

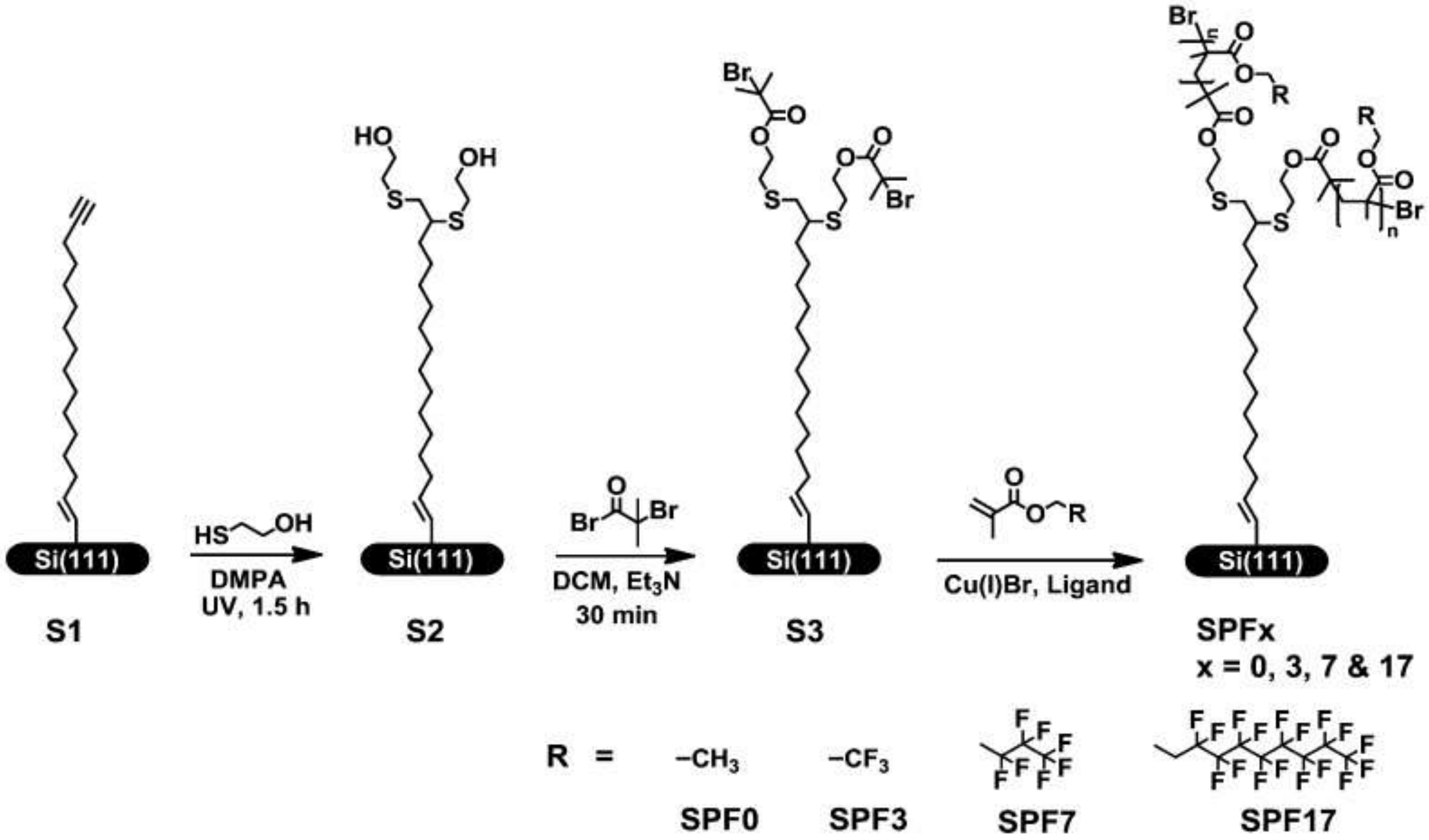


Figure 2. Schematic representation of the preparation of the polymer brushes.

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EXPERIMENTAL METHODS

Materials. 1,15-Hexadecadiyne was synthesized following previously reported procedure.[23,27] α,α,α-Trifluorotoluene (TFT), dichloromethane (DCM), chlorobenzene, tetrahydrofuran (THF), mercaptoethanol, acetone (semiconductor grade VLSI PURANAL), hexafluoroisopropanol (HFP), nonafluorobutyl methyl ether (NFE), α-bromoisobutyryl bromide, 2,2-dimethoxy-2-phenylacetophenone (DMPA), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA), 4,4′-dinonyl-2,2′-bipyridine (dNbpy), α-bromoisobutyryl bromide, copper(I) bromide (Cu(I)Br), ethyl methacrylate (EMA), 2,2,2-trifluoroethyl methacrylate (TFEMA), 2,2,3,3,4,4,4-heptafluorobutyl methacrylate (HFMA), and 2-perfluorooctylethyl methacrylate (FOEMA) were purchased from Sigma-Aldrich and used without further purification unless otherwise specified. DCM and THF were distilled before use. The inhibitors from monomers EMA, TFEMA, HFMA, and FOEMA were removed by passing through a basic alumina column.

RESULTS AND DISCUSSION

Preparation and Characterization of Polymer Brushes.

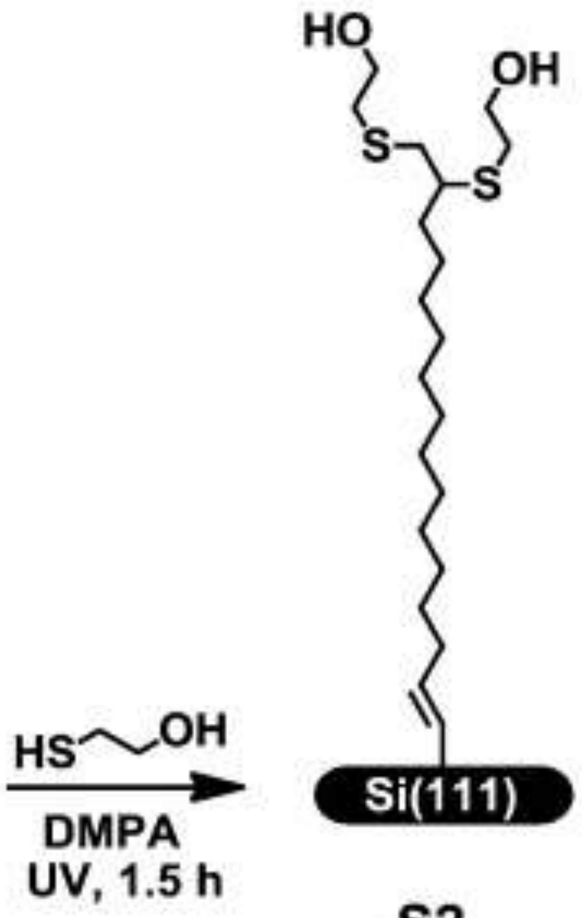
First, Si(111) surfaces were functionalized with 1,15-hexadecadiyne to obtain alkyne-terminated surfaces (S1).

S1

RESULTS AND DISCUSSION

Preparation and Characterization of Polymer Brushes.

Further functionalized
via a TYC reaction with
mercaptoethanol to obtain a
high surface coverage of
covalently bound hydroxyl-
terminated
surfaces.

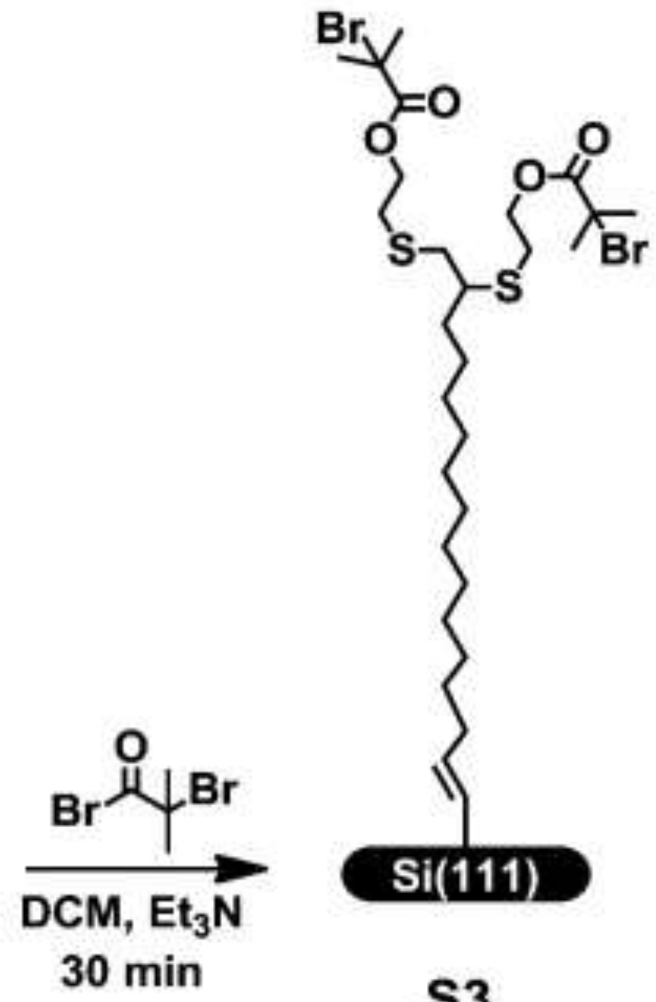


S2

RESULTS AND DISCUSSION

Preparation and Characterization of Polymer Brushes.

The resultant hydroxyl-terminated surfaces were treated with α-bromoisobutyryl bromide to obtain initiator-functionalized surfaces



S3

Biomacromolecules **2004,** *5,* 869−876

Thermodynamic Studies on the Adsorption of Fibronectin Adhesion-Promoting Peptide on Nanothin Films of Poly(2-vinylpyridine) by SPR

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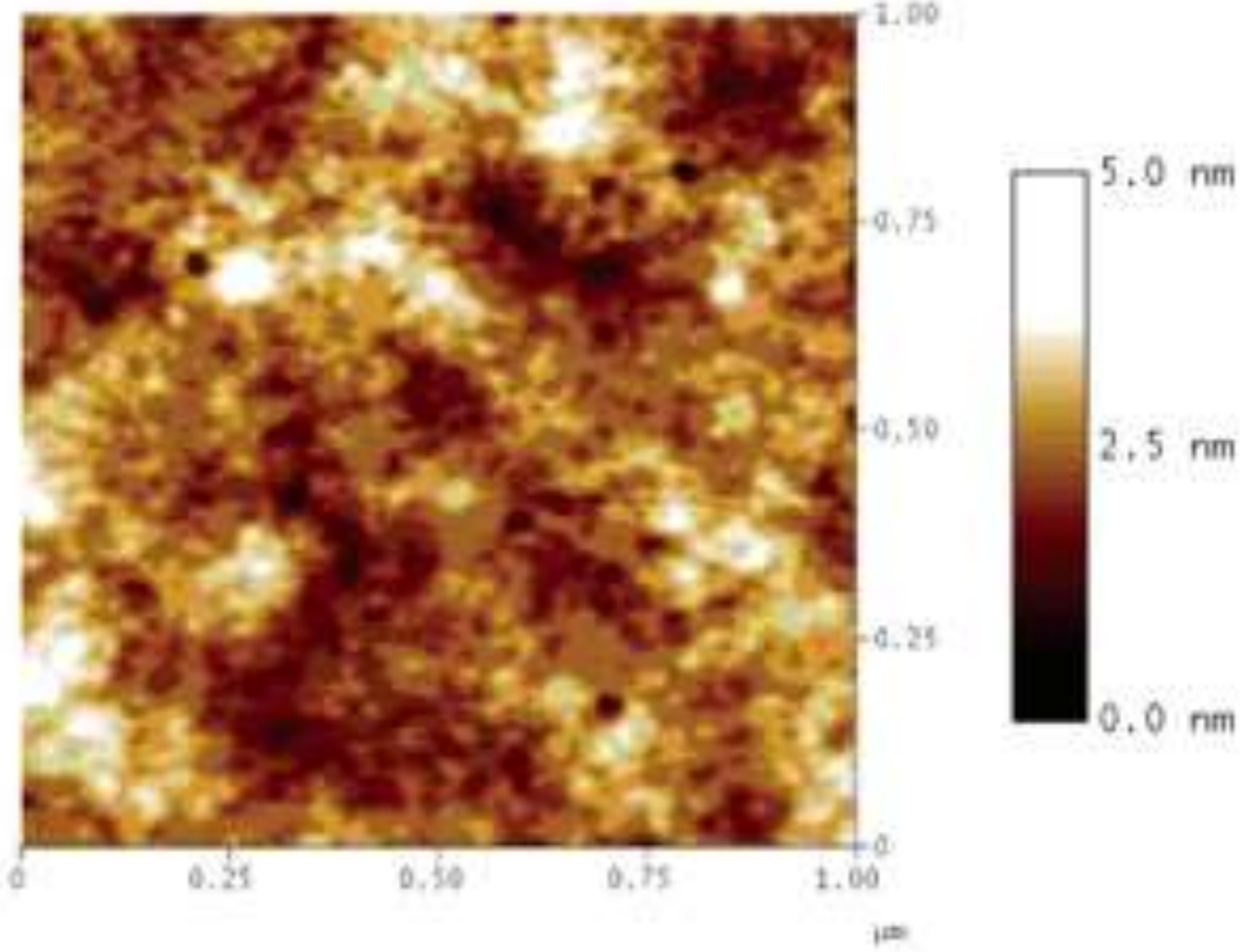
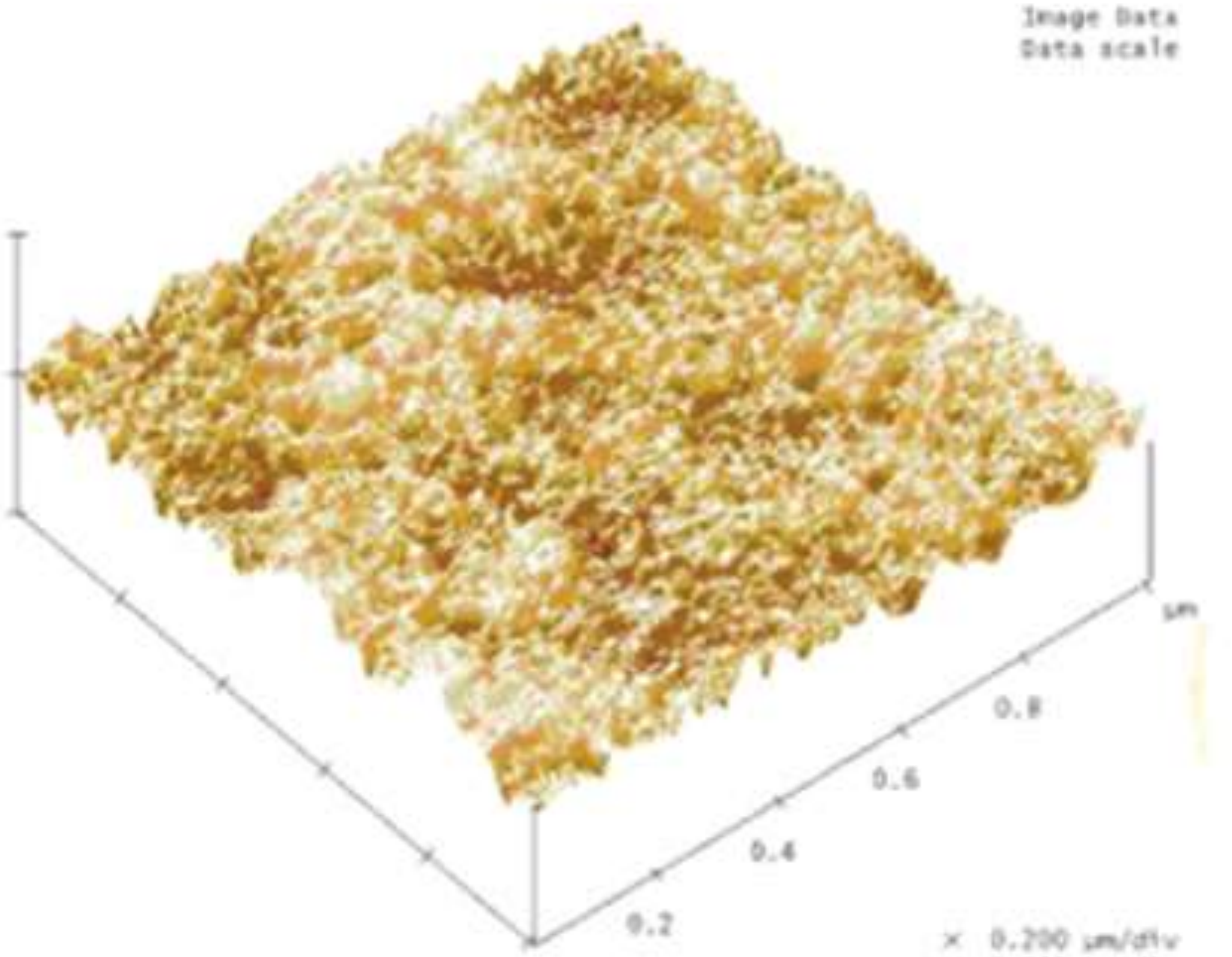


Figure 2. AFM 2D and 3D images (1 μm square) of poly(2-vinylpyridine) layer with 55 Å thickness, showing the topography of the surface used subsequently for SPR measurements. RMS roughness is 0.518 nm. The *z*-axis scale for the lower image is 5 nm per division.



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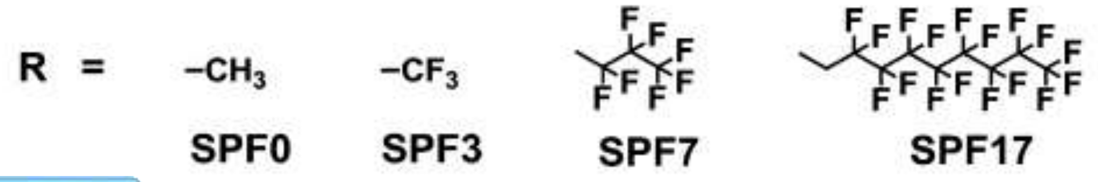
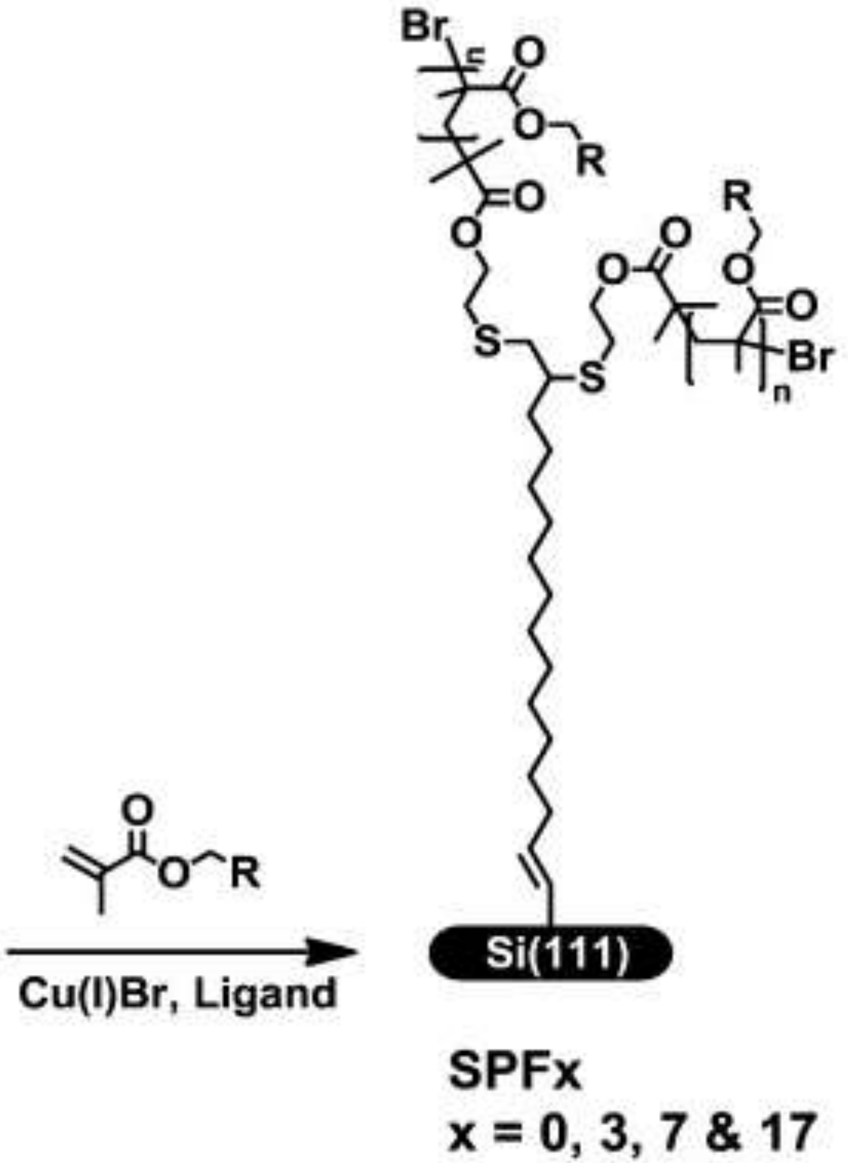
RESULTS AND DISCUSSION

Preparation and Characterization of Polymer Brushes.

Using these S3 surfaces in a SI-ATRP (SI-ATRP surface initated atom-transfer radical polymerization) reaction in combination with the indicated methyl acrylate derivatives yielded the nonfluoropolymer surface SPF0 and the three fluorinated polymer brush surfaces SPF3, SPF7, and SPF17, which have 3, 7, and 17 fluorine atoms per monomer, respectively.





RESULTS AND DISCUSSION

Preparation and Characterization of Polymer Brushes. ANGULOS DE CONTACTO

Table 1. Static (θ) Contact Angle Measured on Polymer Brushes Using Polar and Nonpolar Solvents, Ellipsometric Thickness, and AFM-Determined Surface Roughness of Dry Polymer Brushes

polymer brushes	thickness (nm)	reaction time (h)	θ_{H_2O} (deg)	θ_{HD} (deg)	$\theta_{FC\text{-}40}$ (deg)	RMS (nm)
SPF0	75	24	88		<20	0.8
SPF3	80	60	98	50		0.7
SPF7	78	72	110	66		0.6
SPF17	80	96	121	71		1.8

A dry film thickness of ~80 nm as measured with ellipsometry was achieved by stopping the polymerization after a specific reaction time (Table 1). The roughness of polymer brushes was between 0.8 and 1.8 nm, Indicating the uniform growth of polymer brushes

RESULTS AND DISCUSSION

Preparation and Characterization of Polymer Brushes. IRRA XPS

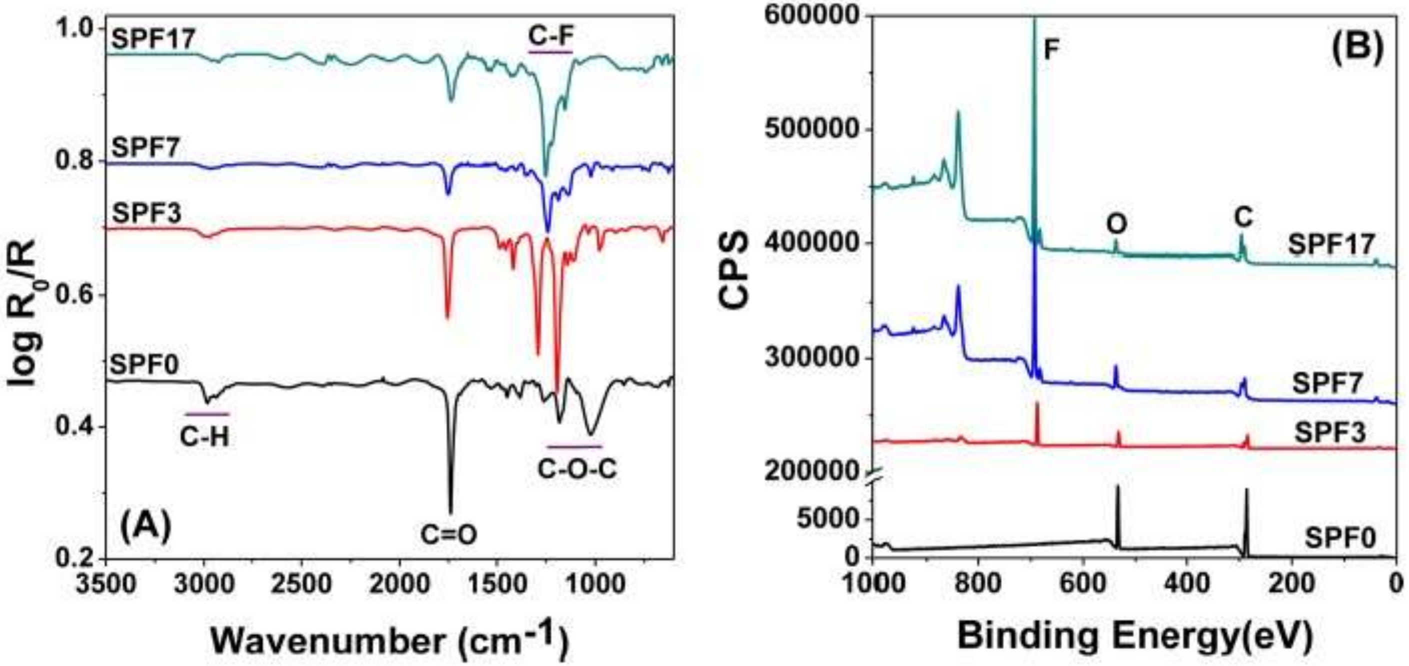


Figure 3. IRRA spectra (A) and (B) XPS survey scan of SPF0, SPF3, SPF7, and SPF17 polymer brushes.

peaks between 2818 and 3070 cm−1 that can be assigned to the aliphatic CH and CH2 stretching vibrations, whereas the intense peak at ∼1751 cm−1 corresponds to the C�O moiety from ester carbonyl groups. Characteristic C−F peaks for fluoropolymers SPF3, SPF7, and SPF17 were observed between 1094 and 1382 cm−1.

RESULTS AND DISCUSSION

Preparation and Characterization of Polymer Brushes. IRRA XPS par SPF7 (A) y SPF17 (B)

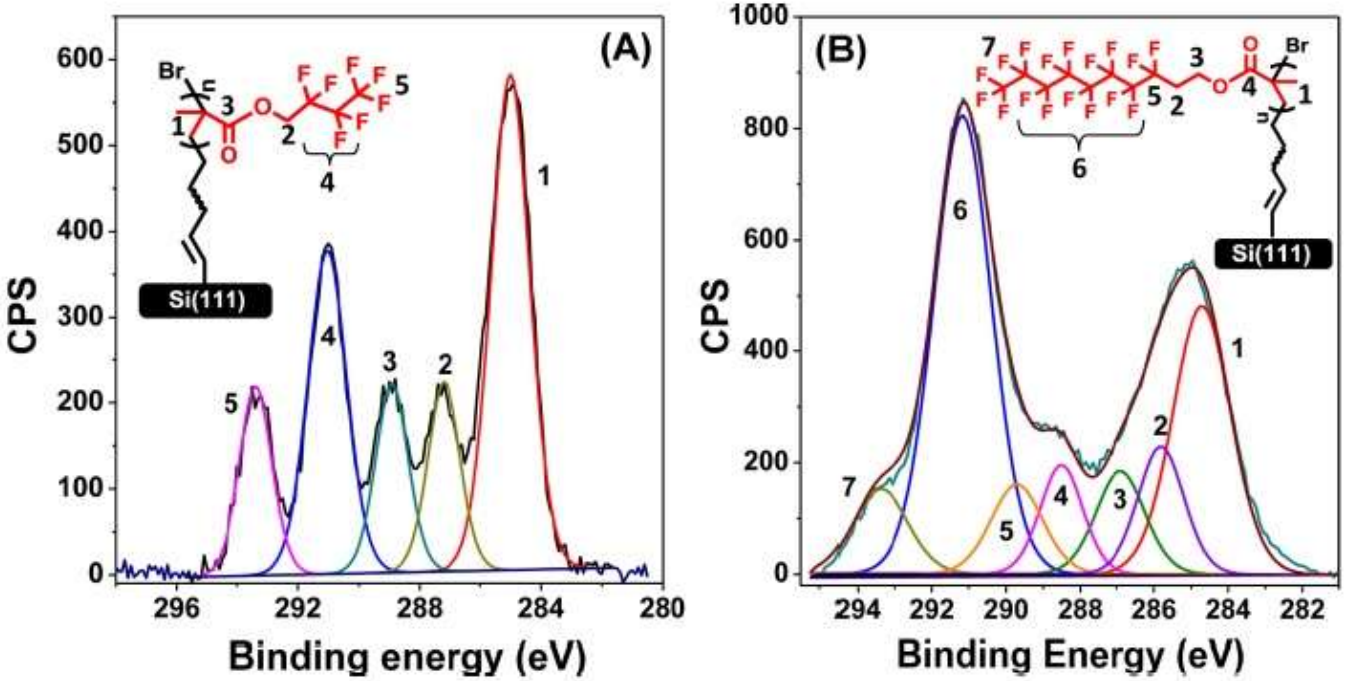


Figure 4. XPS C 1s spectra of SPF7 (A) and SPF17 (B) polymer brushes.

The XPS C 1s narrow scan of SPF7 (Figure 4A) can be deconvoluted in five peaks at 285.0, 287.2, 288.9, 290.9, and 293.4 eV, corresponding to CH_2−C−CH_3, CH_2−CF_2, C=O, CF_2 and CF_3, respectively.

(Figure 4B): Analogously, the XPS C 1s spectrum of SPF17 was also deconvoluted; here seven peaks could be discerned correspondingto carbons having different chemical environments 285.0 eV (CH_2−C−CH_3), 286.9 eV (CH_2−O), 285.8 eV (CH_2−CF_2), 288.5 eV (C□O), 289.6 (−CF_2−CF_2−CH_2−), 291.1 (CF_2), and 293.3 eV (CF_3).

$$\alpha = \left(\frac{d}{a}\right)^{3-1/\nu} \quad (1)$$

where α is the swollen ratio (h_{swell}/h_{dry}, where h = polymer layer thickness (in nm) measured with ellipsometry) of polymer brushes in different solvents, $1/d^2$ is the grafting density, with an average distance d between tethered points of neighboring polymer chains, and a is the monomer size (EMA = 0.57 nm, TFEMA = 0.58 nm, HFMA = 0.76 nm, and FOEMA = 1.58 nm, obtained from their respective modeled structures at there lowest energy configuration as in a polymer backbone in ChemBio3D Ultra 13.0), while finally the exponent ν was assumed to be 1/2 for theta solvent behavior for densely grafted polymer brushes, according to Malhan et al.[38] The

$$M_w = \frac{h_{dry}\rho N_A}{1/d^2} \quad (2)$$

where ρ is the bulk density of the polymer (1.11 g/cm^3 for SPF0, 1.18 g/cm^3 for SPF3, 1.34 and 1.60 g/cm^3 for SPF17), and N_A is Avogadro's number.

Table 2. Swelling Ratio, Grafting Density (Chains/nm^2), and Molecular Weight (g/mol) As Determined for Polymer Brushes by Swelling in Different Solvents

polymer brushes	solvents	swelling ratio (α)	grafting density[a] (chains/nm^2)	mol wt[b] (g/mol)
SPF0	acetone	2.17	0.64	78 000
	HFP	2.40	0.53	94 000
	NFE	2.13	0.68	74 000
	FC-40	2.17	0.65	77 000
SPF3	acetone	2.21	0.60	95 000
	HFP	2.29	0.57	100 000
	NFE	2.15	0.64	74 000
	FC-40	2.08	0.69	83 000
SPF7	acetone	1.78	0.55	115 000
	HFP	2.56	0.26	246 000
	NFE	2.00	0.43	149 000
	FC-40	2.99	0.19	330 000
SPF17	acetone	1.36	0.22	360 000
	HFP	2.44	0.07	1 140 000
	NFE	2.16	0.09	890 000
	FC-40	2.04	0.10	800 000

[a]Estimated from eq 1. [b]Estimated from eq 2 after determining polymer grafting density.

RESULTS AND DISCUSSION

ADHESION

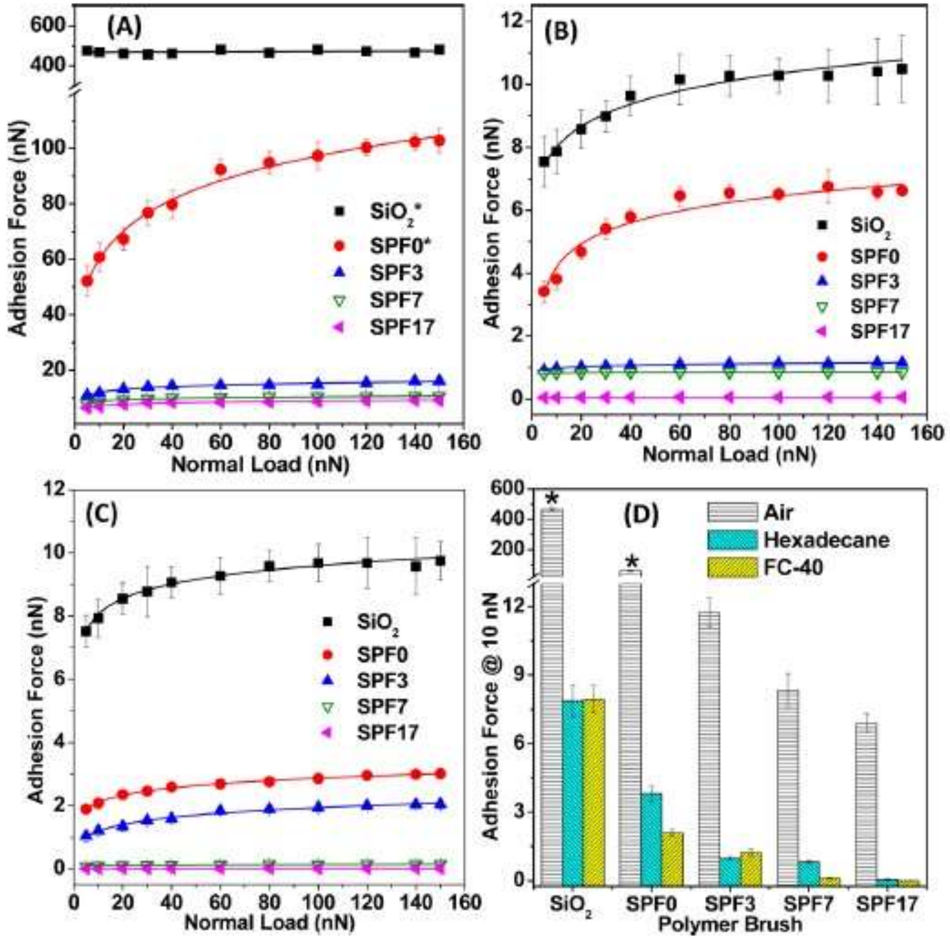


Figure 5. Adhesion (pull-off) forces at various applied normal load (5−150 nN) obtained on polymer brushes under (A) ambient (RH = 44 ± 2%) [*dry (RH < 5%)], (B) hexadecane, and (C) FC-40. (D) Adhesion forces obtained at 10 nN applied normal load.

RESULTS AND DISCUSSION

FRICTION

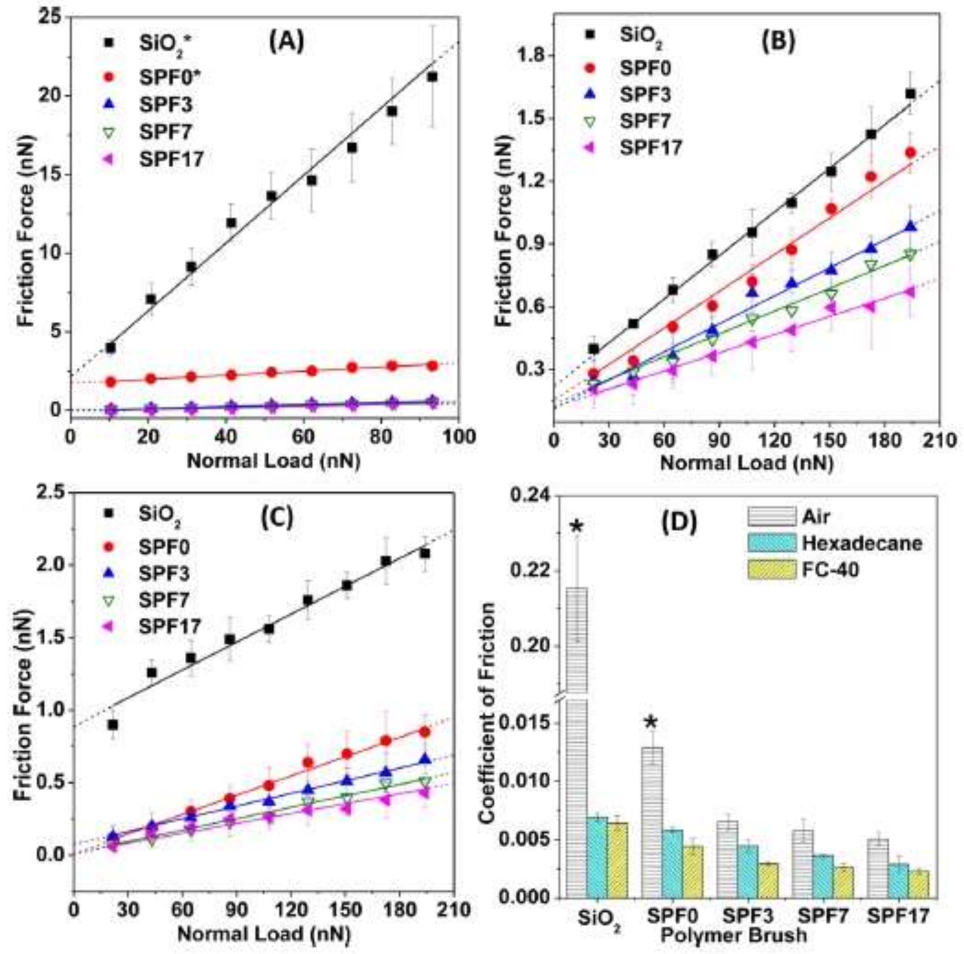


Figure 6. Friction forces versus applied normal load obtained under (A) ambient conditions (RH = 44 ± 2%) [*dry conditions; RH < 5%], (B) in hexadecane, and (C) in FC-40. (D) Friction coefficient under all above conditions obtained from the slope of plots of the friction force versus normal load.

CONCLUSIONS

High-density covalently bound fluoro and non-fluoropolymer brushes (SPFx with x = 0, 3, 7, and 17 F atoms per monomer) can be grown by SI-ATRP on Si(111) surfaces via thiol−yne click chemistry.

The adhesion and friction forces of such polymer brushes can be tuned to progressively smaller values with increasing fluorine content.

Therefore, these SPF17 polymer brushes have great potential as dry lubricants.

!ThE FuTuRe iS NoW!

Directed by Ericson L. Mata Z

Consequences:

Dry lubricants!

WELCOME TO THE FUTURE!

Thanks a lot…

A present for you!

¡Los SOW!