Surface Engineering of Styrene/PEGylated-Fluoroalkyl Styrene Block Copolymer Thin Films

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ABSTRACT: A series of diblock copolymers prepared from styrenic monomers was synthesized using atom transfer radical polymerization. One block was derived from styrene, whereas the second block was prepared from a styrene modified with an amphiphilic PEGylated-fluoroalkyl side chain. The surface properties of the resulting polymer films were carefully characterized using dynamic contact angle, XPS, and NEXAFS measurements. The polymer morphology was investigated using atomic force microscope and GISAXS studies. The block copolymers possess surfaces dominated by the fluorinated unit in the dry state and a distinct phase separated microstructure in the thin film. The microstructure of these polymers is strongly influenced by the thin film structure in which it is investigated. © 2008 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 47: 267–284, 2009

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INTRODUCTION

Fluoropolymers have a prominent position when low values of cohesive energy and surface energy are required.¹ The low surface free energy is a key property of these polymers and may prevent attachment and adhesion, and attack or solvation by aqueous solution and most organic solvents. The strength of the C—F bond increases with the extent of adjacent carbon fluorination, meaning that the longer the fluoroalkyl group, the higher its stability, and hydrophobicity. Therefore, films and coatings from fluorinated polymers have been investigated for a variety of applications ranging from low friction alignment layers in electro-optic devices² to surface-modified membranes³ and to biologically inert coronary stent coatings.⁴

More complex structures of fluorinated block copolymers have been prepared by cationic, 5 anionic, 6 and group transfer polymerization. 7

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However, these techniques have been limited by the need for high-purity monomers and solvents, reactive initiators, and anhydrous conditions. In contrast, the controlled radical polymerization process is easier to carry out and can be performed in bulk or in solution. Several examples exist of fluorinated homo-8 and block copolymers^{9,10} produced by TEMPO-mediated controlled radical polymerization. Atom transfer radical polymerization (ATRP) has been successfully used for the polymerization of a different set of fluorinated monomers^{11–18} (usually acrylates and methacrylates) in either conventional solvents or supercritical carbon dioxide¹⁹ to obtain diverse polymer architectures with controlled molecular weights, dispersities, terminal functionalities, and compositions.

ATRP has also been used for the synthesis of amphiphilic block copolymers comprised of a hydrophilic block and a hydrophobic, and lipophobic, semifluorinated block. Such polymer systems include ionic block copolymers carrying carboxylic or sulfonic groups,²⁰ and nonionic block copolymers containing a poly(ethylene glycol) macroinitiator block.^{21,22} Amphiphilic diblock and triblock molecules and oligomers containing poly(ethylene glycol) (PEG) and poly(perfluoroethylene) chain segments are widely investigated as building blocks of micelles and other nanoaggregates.²³ However, they are rarely incorporated into block copolymers, for example, as PEGylated-fluoroalkyl side-chain substituents²⁴ or main-chain macroinitiators.^{25,26} In one recent example, an amphiphilic block copolymer was prepared by chemical modification of a preformed poly(styrene-b-acrylic acid) copolymer with the commercially available fluorosufactant Zonyl FSO-100.²⁷

In this work, we focused on the ATRP synthesis and surface characterization of novel AB diblock copolymers with a polystyrene component (block A) and a polystyrene component carrying a PEGylated-fluoroalkyl side chain (block B). Using this controlled procedure, we have made full use of the capabilities of the ATRP technique to design block copolymers with predetermined molecular and macromolecular parameters and to minimize chemical structural defects in the final product, which cannot be equally ensured by using polymer-analogous reactions on block copolymers. The block copolymer architecture permits the ready solution based processing of a variety of substituents including fluorinated units that are suitable for specific surface interactions.²⁸ Furthermore, the block copolymer approach, through its phase separated structure, directs the formation of a brush-like polymer surface that has been shown to be a superior surface for optimal cell-surface interactions.²⁹

Although it is well known that block copolymers microphase separate to a preferred microstructure, we anticipated that surface and interface segregation will also take place to enhance further organization in the surface region when a low surface energy block was incorporated.^{12,30} In particular, we found that the presence of a fluorinated block selectively and effectively led to segregation to the surface of polymer films driven there by its low surface energy. Therefore, by incorporating a fluorinated component into the architecture of the target polymers, the surface (and bulk) properties of block copolymers could be appropriately engineered.

EXPERIMENTAL

Materials

THF was refluxed over Na/K alloy and distilled at atmospheric pressure under nitrogen. CH_2Cl_2 was refluxed over CaH_2 and distilled at atmospheric pressure under nitrogen. Anisole and diethylene glycol dimethyl ether (diglyme) were kept at 100 °C over sodium for 4 h and then distilled under reduced pressure.

4-Vinylbenzoic acid, (1) the ethoxylated (PEGylated)-fluoroalkyl surfactant, Zonyl FSO-100 (2) (registered trademark of E. I. du Pont de Nemours and Co), 4-(dimethylamino)pyridine (DMAP, \geq 99%), *N,N'*-dicyclohexylcarbodiimide (DCC, 99%), 2,2'-bipyridine (Bipy, \geq 99%), copper(I) bromide (99.999%), and 1-phenylethyl bromide (1-(PE)Br, 98%) were purchased from Aldrich and used without further purification.

Styrene (S) (from Fluka) was washed with 5% NaOH and water. After drying over Na_2SO_4 , it was distilled under reduced pressure.

 α, α' -Azobis(isobutyronitrile) (AIBN) (from Fluka) was recrystallized from methanol.

Synthesis of Monomers and Polymers

Monomer Sz

0.500 g (3.375 mmol) of 4-vinylbenzoic acid and 0.041 g (0.337 mmol) of DMAP were dissolved in 20 mL of anhydrous CH_2Cl_2 under nitrogen atmosphere. The solution was cooled to 0 °C, and 0.695 g (3.368 mmol) of DCC in 20 mL of

anhydrous CH_2Cl_2 was slowly added. The mixture was kept under stirring for 15 min at 0 °C and for 1 h at room temperature. Then, a solution of 2.33 g (3.37 mmol) of Zonyl FSO-100 in 10 mL of CH_2Cl_2 was added dropwise. The reaction mixture was kept under stirring at room temperature for 62 h. The white precipitate formed during the reaction was filtered off and the organic solution was sequentially washed with 5% NaHCO₃, 5% HCl, and water, and finally dried over Na₂SO₄. The solvent was then evaporated under vacuum and the residue was eluted on silica gel with dichloromethane/methanol (98/2 vol/vol) to give 2.53 g (yield 92%) of monomer Sz as a yellow semisolid material.

¹H NMR (CDCl₃): δ (ppm) = 2.5 (1.9H, CH₂CF₂), 3.2–4.2 (20.3H, CH₂O), 4.5 (2.0H, COOCH₂), 5.4 and 5.9 (2.1H, CH₂=), 6.7 (1.0H, CH=), 7.5 and 8.0 (4.1H, aromatic).

FTIR (film): \overline{v} (cm⁻¹) = 3090–3044 (v C—H aromatic), 2874 (v C—H aliphatic), 1716 (v C=O), 1608 (v C=C aromatic), 1508 and 1455 (δ C—H aliphatic), 1400–1000 (v C—O and v C—F), 653 (ω CF₂).

Homopolymer P(Sz)

0.500 g (0.61 mmol) of Sz, 5 mg of AIBN, 2.5 mL of distilled diglyme, and 1 mL of trifluorotoluene were introduced into a Pyrex vial and degassed by several freeze-thaw pump cycles. The polymerization was carried out at 65 °C for 48 h. The polymer was purified by several precipitations into *n*-hexane from THF solutions giving 0.345 g (yield 69%) of a viscous yellowish polymer.

 $^{1}\mathrm{H}$ NMR (CDCl_3): δ (ppm) = 1.0–2.0 (3.1H, CH_2CH), 2.4 (1.9H, CH_2CF_2), 3.0–4.2 (20.4H, CH_2O), 4.4 (2.0H, COOCH_2), 6.4 and 7.6 (4.0H, aromatic).

FTIR (film): \overline{v} (cm⁻¹) = 3034 (v C–H aromatic), 2878 (v C–H aliphatic), 1722 (v C=O), 1609 (v C=C aromatic), 1509 and 1454 (δ C–H aliphatic), 1400–1000 (v C–O and v C–F), 654 (ω CF₂).

Bromo-Terminated Polystyrene

In a typical preparation, 5.00 mL (43.70 mmol) of S, 0.255 g (1.635 mmol) of Bipy, and 0.74 mL (0.54 mmol) of 1-(PE)Br were introduced into a dry Schlenk flask under nitrogen. The solution was purged with nitrogen for 15 min and then 0.078 g (0.544 mmol) of CuBr was added. After four freeze-thaw pump cycles, the polymerization was let to proceed for 330 min at 110 °C. After cooling

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to room temperature, the polymer mixture was dissolved in THF and then eluted on neutral alumina to remove CuBr catalyst. The solvent was removed under vacuum, and the polymer was purified by repeated precipitations from THF into methanol (yield 73%). The resulting polymer, with an average degree of polymerization of 51 is denoted by S51.

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Styrene/PEGylated-Fluoroalkyl Styrene Block Copolymers

In a typical preparation, 1.50 g (0.28 mmol) of Brterminated polystyrene S51 and 0.466 g (2.983 mmol) of Bipy were introduced into a dry Schlenk flask, which was then evacuated and flushed with nitrogen three times. A solution of 4.66 g (5.7 mmol) of Sz in 20 mL of anisole was added under nitrogen. After purging with nitrogen for 30 min, 0.142 g (0.989 mmol) of CuBr was added and the solution was finally degassed by four freeze-thaw pump cycles. The polymerization was let to proceed for 66 h at 115 °C. When the reaction was stopped, the polymer mixture was dissolved in THF and then eluted on neutral alumina to remove the catalyst. The solvent was removed under vacuum and the crude polymer was purified by repeated precipitations from chloroform into methanol (yield 71%). The resulting diblock copolymer, with an average degree of polymerization of the amphiphilic styrene block equal to 20, is denoted by S51Sz20.

¹H NMR (CDCl₃): δ (ppm) = 1.0–2.2 (10.7H, CH₂CH), 2.4 (1.9H, CH₂CF₂), 3.0–4.2 (20.3H, CH₂O), 4.4 (2.0H, COOCH₂), 6.1–8.1 (16.8H aromatic).

¹⁹F NMR (CDCl₃/CF₃COOH): δ (ppm) = -6 (3.0F, CF₃), -38 (2.0F, CF₂CH₂), -45 to -48 (9.8F, CF₂), -51 (2.0F, CF₂CF₃).

FTIR (film): \overline{v} (cm⁻¹) = 3080–3000 (v C—H aromatic), 2922 (v C—H aliphatic), 1722 (v C=O), 1608 (v C=C aromatic), 1493 and 1454 (δ C—H aliphatic), 1400–1000 (v C—O and v C—F), 759 and 699 (δ C—H aromatic), 654 (ω CF₂).

Film Deposition

The thinner polymer films (thickness 200–400 nm) were obtained by spin coating 3 wt % solutions of the polymer in CHCl₃ or THF on glass slides (for static contact angle and X-ray photoelectron spectroscopy measurements) and Si wafers (for atomic force microscopy, near-edge X-ray absorption fine structure spectroscopy, and

grazing-incidence small angle X-ray scattering measurements). The thicker polymer films (thickness 500–1000 nm) were obtained by dip coating glass cover slips in a 1.5 wt/v solution of the polymers in CHCl₃ or THF (for measurements of advancing and receding contact angles). Unless otherwise specified, the films were vacuum dried overnight at room temperature and then annealed at 120 °C, to favor the formation of an equilibrium structure. The films were studied in as-prepared specimens ("dry" films) and after immersion in distilled water at room temperature for 3–9 days ("wet" films).

Characterization

 1 H (versus TMS) and 19 F (versus CF₃COOH) spectra were recorded on Varian Gemini VRX 200 and Varian Gemini VRX 300 spectrometers, respectively.

Infrared spectra were recorded with a Spectrum One Perkin–Elmer Fourier Transform infrared spectrophotometer with 4 cm⁻¹ resolution. Polymer films were cast on KBr crystal plates.

Size exclusion chromatography (SEC) was carried out with a Jasco PU-1580 liquid chromatograph equipped with two PL gel 5 μ m Mixed-D columns, a Jasco 830-RI refractive index detector, and a Perkin–Elmer LC75 UV detector. Polystyrene standards (0.4–400 kg/mol) were used for calibration.

Differential scanning calorimetry (DSC) measurements were performed with a Mettler DSC-30 instrument (10 °C/min). The glass transition temperature ($T_{\rm g}$) was set at the half-devitrification temperature.

Static contact angle measurements were carried out with a FTA200 Camtel goniometer using several contact liquids of the highest purity commercially available. Water advancing and receding contact angle experiments were carried out by the Wilhelmy balance method using a Dataphysics tensiometer DCAT-11 with immersion-withdrawal rates of 200 μ m/s. In this method, a glass plate hangs from a balance which measures the vertical force, F, acting on it. Assuming that the viscous force acting on the plate as it moves in the liquid bath is negligible,³¹ F is given by F = W $+ 2(L + e)\gamma\cos\theta - B$, where W and 2(L + e) are the weight and perimeter (e = 0.1 mm and L)= 24 mm) of the solid plate, γ is the water surface tension (72 mN/m), θ is the contact angle, and B the buoyancy force. During the detecting process, F varies with the variation of B, which is proportional to the immersion depth of the plate. Thus a linear relationship is obtained as far as the friction force acting along the plate is negligible. The computing software of the DCA calculates F at a zero depth of immersion (where B = 0) from a linear regression. The contact angles are then obtained by $\cos\theta = (F - W)/2\gamma(L + e)$.

Two different experiments were performed: (i) three immersion cycles at 6 mm immersion depth, with dwell times between immersion and with-drawal of 10 s; (ii) one immersion cycle at 6 mm immersion depth with a dwell time of 1000 s, followed by two immersion cycles at 12 mm immersion depth and a dwell time of 10 s.

X-ray photoelectron spectroscopy (XPS) spectra were recorded with a Perkin-Elmer PHI 5600 spectrometer with a standard Al-Ka source (1486.6 eV) operating at 350 W. The working pressure was less than 10^{-8} Pa. The spectrometer was calibrated by assuming the binding energy (BE) of the Au $4f_{7/2}$ line to be 84.0 eV with respect to the Fermi level. Extended spectra (survey) were collected in the range 0-1350 eV (187.85 eV pass energy, 0.5 eV step, 0.025 s/step). Detailed spectra were recorded for the C (1s), O (1s), and F (1s) regions (11.75 eV pass energy, 0.1 eV step, 0.1 s/ step). The standard deviation in the BE values of the XPS line was 0.10 eV. The atomic percentage, after a Shirley type background subtraction, was evaluated using the PHI sensitivity factors.³³ To take into account charging problems, the hydrocarbon peak was adjusted to a position of 285.0 eV, and the subpeak BE differences were evaluated.

Near-edge X-ray absorption fine structure (NEXAFS) experiments were carried out on the U7A NIST/Dow materials characterization endstation at the National Synchrotron Light Source at Brookhaven National Laboratory. Partial electron yield carbon K-edge NEXAFS spectra were acquired and normalized as discussed in Krishnan et al.²⁷

Grazing incidence small angle X-ray scattering (GISAXS) experiments were carried out at the G1 station of the Cornell High Energy Synchrotron Source (CHESS) using a $\lambda = 0.124$ nm X-ray beam. The beam was collimated to a height of 250 μ m and a width of 250 μ m by three sets of slits. Two beam stops were used in front of the detector: (i) a blade to block the direct beam and (ii) a tantalum rod 1.25 mm wide to block the intense specular reflection.³⁴ Images of the scattered intensity were recorded with a fiber optically coupled CCD camera (Quantum 1 by ADSC).



Scheme 1. Synthesis of monomer Sz.

The surface morphology of polymer thin films was studied using Veeco Dimension 3100 atomic force microscope (AFM) in the tapping mode.

RESULTS AND DISCUSSION

Synthesis

The AB diblock copolymers consisted of a block of polystyrene and a block of polystyrene carrying a PEGylated-fluoroalkyl side chain. Thus, an unusual amphiphilic character was achieved by use of the hydrophilic-hydrophobic chain substituents on the second block. The PEGylated-fluoroalkyl 4vinylbenzoate monomer (Sz) was prepared by the direct esterification of 4-vinylbenzoic acid (1) with the commercially available PEGylated fluorosurfactant Zonyl FSO-100 (2) (Scheme 1). The reaction was carried out at room temperature using N,N'-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP). The reaction took place with high yields (>80%), although the by-product N,N'-dicyclohexylurea was difficult to remove from the desired monomer.

The fluorinated PEG (2), $F(CF_2CF_2)_y(CH_2-CH_2O)_xCH_2CH_2OH$, has a broad distribution of molecular weights. On the basis of the areas of $-CF_2-CH_2-$ protons and $-CF_2-$ fluorines in the ¹H and ¹⁹F NMR spectra of monomer Sz, we evaluated the average number of oxyethylene groups in the PEG segment, *x*, to be 5 and that of the perfluoroethylene groups in the fluorinated segment, *y*, to be 4.

The amphiphilic block copolymers were prepared by a two-step procedure based on two sequential ATRP (Scheme 2). In the first step, bromo-terminated polystyrene macroinitiators having molecular weights of 8.4, 5.3, and 2.7 kg/ mol were prepared by ATRP of styrene, S, in bulk in the presence of 1-phenylethyl bromide/CuBr/ 2,2'-bipyridine (1:1:3 M ratio) at 110 °C. The experimental molecular weights and molecular weight distributions of the macroinitiators are listed in Table 1.

In the second step, the copolymerizations for attachment of the block of amphiphilic styrene monomer, Sz, to the polystyrene block were carried out in anisole or diglyme solutions at 115 °C. Starting from the same polystyrene macroinitiators, we prepared different sets of block copolymers in which the length of the amphiphilic block was appropriately tuned either by changing the initial monomer/macroinitiator molar ratio, while keeping the reaction time constant, or by fixing the initial ratio and changing the reaction time (Table 2). Block copolymers are denoted by the code SnSzm, where *n* indicates the polymerization degree of the polystyrene block and *m* that of the amphiphilic polystyrene block.

The formation of block copolymer structures was confirmed by ¹⁹F NMR spectroscopy investigations which clearly proved the insertion of the semifluorinated component as a second block in the diblock copolymers. The relative S and Sz content was evaluated from the integrated areas of the ¹H NMR signals at 4.4 ppm (COOCH₂ of Sz)



Scheme 2. Synthesis of diblock copolymers SnSzm by ATRP.

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MI ^a	S:I:CuBr:Bipy ^b	t _r ^c (min)	$M_{\rm n}{}^{\rm d}$ (g/mol)	$M_{ m w}/M_{ m n}^{ m d}$	n ^c
S81 S51 S26	160:1:1:3 80:1:1:3 60:1:1:3	330 330 90	$8400 \\ 5300 \\ 2700$	$1.27 \\ 1.35 \\ 1.52$	81 51 26

Table 1. Experimental Conditions for the Synthesisand Physical–Chemical Properties of PolystyreneMacroinitiators

^aBr-terminated polystyrene macroinitiator.

^b Styrene/1-(PE)Br/CuBr/Bipy molar ratio.

^cReaction time.

^dNumber average molecular weight, polydispersity, and degree of polymerization by SEC.

and between 6 and 8 ppm (aromatic rings of S and Sz). Consistently, the length of the Sz block was calculated from the known length of the S block.

Figure 1 illustrates the SEC traces of the S81 macroinitiator and the block copolymer S81Sz19 derived therefrom. The monomodal shape of the block copolymer curve suggested the absence of residual homopolymers and the complete initiation of the macroinitiator during the ATRP process. However, the dispersity values were quite high $(1.3 < M_w/M_n < 1.8)$, probably because of the inherently high dispersity of the side chain in the monomer Sz ($M_w/M_n = 1.31$). Moreover, although ATRP is a controlled radical polymerization, permanent deactivation of propagating species via termination or chain transfer cannot be completely avoided. The apparent partial agreement between the values of the molecular weights evaluated by SEC and NMR results from the fact that the former technique provided approximate values of $M_{\rm n}$ as the block copolymers have different hydrodynamic volumes from those of the polystyrene standards used for calibration.

Differential Scanning Calorimetry

The thermal behavior of the block copolymers was studied by DSC. Only copolymers S81Sz6, S51Sz6, and S26Sz4 showed two glass transition temperatures at about -35 °C, typical of the amphiphilic polystyrene block, and close to 85 °C, typical of the polystyrene block. The presence of two glass transitions was due to the phase separation of the chemically incompatible blocks in separate domains. For all the other block copolymers, only the single glass transition temperature of the Sz block was detected near -35 °C. Consistent with the thermal behavior of the block copolymers rich in S units, we assume that the two blocks were separated in copolymers having higher molar percentages of Sz as well, although it was not possible to detect the $T_{\rm g}$ of the polystyrene block by DSC.

Static Contact Angles and Surface Energy

Static contact angle measurements were performed on thin polymer films, which were spin coated onto glass slides from a 3 wt % solution and then annealed for one night at 120 °C to achieve equilibrium morphologies. In fact, previous XPS and NEXAFS measurements carried out on similar amphiphilic surfaces²⁷ showed that annealing influenced the chemical composition of the surface. In particular, it was found that the abundance of fluorinated carbon species ($-CF_2-$, $-CF_3$) increased with increasing annealing

Copolymer	$Sz:MI^{a}$	$t_{\rm r}^{\rm \ b}({\rm h})$	M_n^c (g/mol) (SEC)	$M_{ m w}\!/\!M_{ m n}^{ m c}$	$M_{\rm n}{}^{\rm d}$ (g/mol) (NMR)	m^{d}
S81Sz6	10:1	66	17,400	1.62	13,300	6
S81Sz19	50:1	66	21,300	1.50	23,900	18
S81Sz39	100:1	66	27,300	1.73	40,100	39
S51Sz6	10:1	64	13,300	1.50	10,200	6
S51Sz17	20:1	24	16,000	1.51	19,100	17
S51Sz20	20:1	66	22,800	1.77	21,600	20
S26Sz4	5:1	66	9300	1.65	6000	4
S26Sz8	10:1	24	13,200	1.69	9200	8
S26Sz13	10:1	66	10,100	1.63	13,300	13

Table 2. Experimental Conditions for the Synthesis and Physical-Chemical Properties of Block Copolymers

^aAmphiphilic styrene monomer/macroinitiator molar ratio.

^bReaction time.

^cNumber average molecular weight and polydispersity by SEC.

^dNumber average molecular weight and degree of polymerization by ¹H NMR.



Figure 1. SEC traces of macroinitiator S81 and block copolymer S81Sz19.

temperature owing to a more effective segregation of the surface morphology.

AFM root mean square roughness $R_{\rm q} = (\Sigma_i Z_i^2/N)^{0.5}$, where Z_i are heights relative to the mean, and N is the number of points measured on the analyzed surface, ranged between 2 and 4 nm. Because the surfaces were very smooth, the effect of surface roughness on contact angle measurements would be negligible.³⁵

The measured contact angles for the block copolymers are collected in Table 3. The values of contact angle θ with water and *n*-hexadecane are conventionally regarded as indicators of hydrophobicity ($\theta_{\rm w} > \sim 90^{\circ}$) and lipophobicity ($\theta_{\rm h}$ $> \sim 60^{\circ}$), respectively. According to this criterion, all of the polymer surfaces were both hydrophobic $(\theta_{\rm w} \ge 99^{\circ})$ and lipophobic $(\theta_{\rm h} \ge 62^{\circ})$. As seen in Table 3, for all probe liquids, the values of static contact angles did not show any specific dependence on the degree of fluorination of the polymers, not even when the molar content of the fluorinated monomer was relatively low (e.g., 7 mol % in S81Sz6). The static contact angles were more or less constant for each probe liquid: $\theta_{\rm w} \sim 104^{\circ}$, $heta_{
m h}\sim\,66^\circ,\ heta_{
m DI}\sim\,85^\circ,\ {
m and}\ heta_{
m EG}\sim\,92^\circ.$ We suppose that a threshold of surface concentration of fluorinated chains may exist, above which an increase in Sz units in the copolymer did not lead to an increase in contact angle.³⁶ This could be effectively achieved in a microphase separated block copolymer system (see below, chemical and microphase structure analyses).

Measurements of liquid-solid contact angles are commonly used to evaluate solid surface tension, $\gamma_{\rm S}$. However, the correlation between θ and $\gamma_{\rm S}$ is still a controversial question and none of the different methods proposed are generally

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accepted.³⁷ Accordingly, we followed the surface tension component approaches of Owens, Wendt, and Kaelble (OWK)^{38,39} and of van Oss, Chaudhury, and Good (vOCG),^{40,41} which both rely on Fowkes' model that assumes the total surface energy is the sum of different interaction components (van der Waals dispersive, dipole, hydrogen bonding, etc.) at the liquid–solid interface and postulates a geometric mean relationship for both of the solid–liquid and liquid–liquid interfacial tensions.⁴² In particular, in the former approach the solid surface tension

$$\gamma_{\rm S} = \gamma_{\rm S}^{\rm d} + \gamma_{\rm S}^{\rm p} \tag{1}$$

combined with the Young's equation yields

$$\gamma_{\rm L}(1+\cos\theta) = 2\left[\left(\gamma_{\rm S}^{\rm d}\gamma_{\rm L}^{\rm d}\right)^{1/2} + \left(\gamma_{\rm S}^{\rm p}\gamma_{\rm L}^{\rm p}\right)^{1/2}\right] \qquad (2)$$

where γ^{d} and γ^{p} are the dispersion and the polar components, respectively, of the solid, $\gamma_{\rm S}$, and liquid, $\gamma_{\rm L}$, surface tensions; vapor adsorption is assumed to be negligible. By measuring the contact angles of at least two liquids, one polar and one nonpolar, on the same surface two equations can be obtained from which the two unknowns ($\gamma_{\rm S}^{d}$ and $\gamma_{\rm S}^{\rm p}$) of the solid can be calculated. The total surface energy of the polymer is computed as the sum of the $\gamma_{\rm S}^{d}$ and $\gamma_{\rm S}^{\rm p}$ terms (eq 1). The latter approach involves three different surface tension components, that is, the Lifshitz-van der Waals dispersive component, $\gamma^{\rm LW}$, the polar electron-donor (Lewis base) component, γ^{-} , and the polar electron-acceptor (Lewis acid) component, γ^{+} (eq 3):

$$\gamma_{\rm S} = \gamma_{\rm S}^{\rm LW} + 2\left(\gamma_{\rm S}^+ \gamma_{\rm S}^-\right)^{1/2} \tag{3}$$

Table 3. Static Contact Angles of the BlockCopolymer Films with Different InterrogatingLiquids^a

Polymer Film	$\theta_{\mathbf{w}} \ (^{\circ})$	$\theta_{\rm h}(^\circ)$	$\theta_{\rm DI}(^\circ)$	$\theta_{\rm EG} \ (^\circ)$
P(Sz)	103 ± 1	64 ± 1	81 ± 3	88 ± 2
S81Sz6	106 ± 1	67 ± 1	87 ± 1	92 ± 1
S81Sz19	107 ± 1	66 ± 1	92 ± 2	92 ± 1
S81Sz39	104 ± 1	63 ± 1	81 ± 2	94 ± 1
S51Sz20	100 ± 1	66 ± 1	84 ± 1	93 ± 2
S26Sz4	103 ± 1	66 ± 1	n.d.	92 ± 1
S26Sz8	108 ± 1	69 ± 1	91 ± 1	92 ± 1
S26Sz13	102 ± 1	66 ± 1	81 ± 2	95 ± 1

 $^{\rm a}$ Contact angles measured with water, *n*-hexadecane, diiodomethane, and ethylene glycol.

Polymer Film	$\gamma_{\rm S}^{\rm d}~({\rm mN/m})$	$\gamma^{\rm p}_{\rm S}$ (mN/m)	$\gamma_{\rm S}^{\rm OWK~a}~(mN\!/\!m)$	$\gamma_{\rm S}^{\rm LW}$ (mN/m)	$\gamma_{\rm S}^-$ (mN/m)	$\gamma_{\rm S}^+$ (mN/m)	$\gamma_{\rm S}^{\rm vOCG~b}$ (mN/m)
P(Sz)	14.4	2.2	16.6	16.7	3.04	$7.6 imes\cdot10^{-3}$	17.0
S81Sz6	13.3	1.7	15.0	14.1	2.52	$1.8 imes10^{-2}$	14.5
S81Sz19	13.7	1.3	15.0	11.8	2.30	$1.1 imes10^{-1}$	12.9
S81Sz39	14.5	1.9	16.4	17.1	4.14	$1.5 imes10^{-1}$	18.6
S51Sz20	13.5	3.9	17.4	15.6	8.58	$1.5 imes10^{-1}$	17.9
S26Sz8	12.7	1.5	14.2	12.4	2.21	$8.5 imes10^{-2}$	13.2
S26Sz13	13.6	2.7	16.3	16.6	6.20	$2.7 imes10^{-1}$	19.2

Table 4. Surface Tensions of the Block Copolymer Films Calculated by Two Different Additive-Component Methods

^a Calculated with the Owens–Wendt–Kaelble method: γ_S^d dispersion component, γ_S^p polar component. ^b Calculated with the van Oss–Chaudhury–Good method: γ_S^+ Lewis acid component, γ_S^- Lewis base component, γ_S^{LW} Lifshitz– van der Waals component.

which leads to a Young's equation of the form:

$$\begin{split} \gamma_{\rm L}(1+\cos\theta) &= 2 \Big[(\gamma_{\rm S}^{\rm LW} \gamma_{\rm L}^{\rm LW})^{1/2} + (\gamma_{\rm S}^+ \gamma_{\rm L}^-)^{1/2} \\ &+ (\gamma_{\rm S}^- \gamma_{\rm L}^+)^{1/2} \Big] \ (4) \end{split}$$

In this case at least three different liquids, two polar and one nonpolar, are necessary to obtain the three equations that can be solved for the unknowns $\gamma_{\rm S}^{\rm LW}$, $\gamma_{\rm S}^+$, and $\gamma_{\rm S}^-$. Thus, the dispersion contribution $\gamma^{\rm d}$ corresponds to $\gamma^{\rm LW}$, whereas the polar contribution of $\hat{\gamma}^{d}$ is further split into the two Lewis acid and base components γ^{\pm} . In this study, n-hexadecane and water were chosen as the nonpolar and polar liquids, respectively, for the OWK method. Diidomethane was chosen as the nonpolar liquid, whereas water and ethylene glycol were chosen as the polar liquids, for the vOCG method. The polymer surface tension and the related components calculated for the homopolymer and the block copolymer films according to the two different additive-component approaches are collected in Table 4.

The use of Young's equation, which describes the equilibrium state, for determining surface energies of dynamic surfaces that undergo environment-dependent surface reconstruction (cf. Section 3.4) is complex. Because of surface reconstruction, the surface composition is expected to be different for each probe liquid, depending on polarity of the liquid. In contact with water or ethylene glycol, which are polar liquids, the hydrophilic PEG groups will preferentially segregate to the surface. On the other hand, the PEG groups will not show preferential surface segregation when in contact with nonpolar probe liquid such as hexane. Essentially, a different surface is being probed with each probe liquid. Nevertheless, the values of the solid surface energy obtained by the two methods, $\gamma_{\rm S}^{\rm OWK}$ and $\gamma_{\rm S}^{\rm vOCG}$, were surprisingly in agreement with each other. More importantly, the values of $\gamma_{\rm S}$ (lower than 19 mN/m) for polymers containing Sz units were consistent with the low surface energy expected of these fluorinated polymers. It should be noted that diblock copolymers of polystyrene and para-substituted perfluorodecyloxymethyl styrene are known to exhibit much lower surface energies ($\sim 11 \text{ mN/m}$),⁹ which did not increase even when a para-substituted polyethyleneoxymethyl styrene block¹⁰ was inserted as a central or terminal third block in triblock copolymers. In the case of the side-chain amphiphilic polymers of the present study, however, the presence of the PEGylated segment directly linked to the fluorinated chain leads to an increase in surface energy.

As expected of nonpolar, nonhydrogen bonding surfaces such as fluorinated surfaces, the dispersion contribution ($\gamma_S^d \approx 12-15 \text{ mN/m}$) to γ_S^{OWK} was largely dominant, with γ_S^p being minimal ($\gamma_S^p \approx 1-$ 4 mN/m). However, the polar component was significantly higher than that calculated for other fluorinated block copolymers,¹⁰ likely because PEG segments of Sz units participate in polar hydrogen-bonding interactions. Similarly, the nonpolar parameter $\gamma_{\rm S}^{\rm LW}$ provided the major contribution to $\gamma_{\rm S}^{\rm vOCG}$ with respect to the acid–base components $\gamma_{\rm S}^{\pm}$. The Lewis acid contribution was found to be insignificant ($\gamma_{\rm S}^+ \approx 1.4 \ 10^{-3}$ to 1.5 10^{-1} mN(m), such as the small number of electron mN/m), owing to the small number of electron acceptor -CH₂CF₂- groups on the surfaces of these materials. On the other hand, the electrondonor (Lewis base) component was high ($\gamma_{\rm S}^- \approx 2-$ 9 mN/m), mainly because of the ability of the oxygen atoms in the ethylene glycol group $(-OCH_2CH_2-)$ to form hydrogen bonds. The

influence of the PEG content on the wettability in general, and on the basic component in particular, of a fluorinated surface has also been shown for crosslinked hyperbranched fluoropolymer-poly (ethylene glycol) amphiphilic network coatings.⁴³ In fact, the basic contribution increased by increasing the amount of PEG in the polymer net-

reasing the amount of PEG in the polymer network and thus by decreasing the hydrophobic/ hydrophilic balance. In the present copolymers, it was not possible to establish a monotonic trend of $\gamma_{\overline{S}}$ with the nominal content of PEG units. The hydrophobic/hydrophilic balance mostly depends on the ratio of tetrafluoroethylene and oxyethylene segment lengths, which was the same per repeat unit, independent of the length of the Sz block.

From Table 4, it may appear that the overall surface energy, $\gamma_{\rm S}^{\rm OWK}$ or $\gamma_{\rm S}^{\rm vOCG}$, showed no correlation with the block copolymer composition or microphase formation. For example, using the OWK method, the block copolymer S81Sz6, which has a lamellar morphology in thin films (cf. section on microphase structure) is estimated to have the same surface energy as the block copolymer S81Sz19, which has a cylindrical morphology. We believe that the apparent inconsistency is because of the fact that both methods are not strictly applicable for $\gamma_{\rm S}$ determination of surfaces that exhibit environment-dependent surface composition. The values of surface energy estimated using these methods are inadequate in characterizing the influence of block copolymer architecture on surface composition and surface segregation. Detailed comparison of homopolymer, block copolymer, and random copolymer surfaces, using X-ray absorption spectroscopic techniques, will be reported in a separate paper.⁴⁴ It may be argued that dynamic contact angles should be used for the determination of solid surface tensions, as discussed by Kwok et al.⁴⁵ We found that dynamic contact angle values themselves depended on the measurement technique, for example, the sessile drop method or the Wilhelmy plate method. Dynamic surface wettability experiments, nevertheless, provided critical information in understanding the time scale of surface reconstruction, as will be discussed in the following section.

Dynamic Surface Wettability

Experiments on polymer films using water as wetting liquid were carried out to assess the effect of the wetting medium on surface stability. A 1.5 wt % toluene solution of the block copolymers was dip coated onto glass cover slips and dried at 120 °C for 15 h.

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Table 5. Advancing and Receding Contact Angles^afor Block Copolymer Films

Polymer Film	$\theta_{a}\left(^{\circ} ight)$	$\theta_{\mathbf{r}}$ (°)	Δ (°) ^b
P(Sz) S81Sz6 S81Sz19 S51Sz6 S51Sz17 S51Sz20 S26Sz8 S26Sz13	$egin{array}{c} 101\pm 1 \ 97\pm 1 \ 106\pm 1 \ 102\pm 2 \ 106\pm 1 \ 106\pm 106\pm 1 \ 106\pm 106\pm 106\pm 106\pm 106\pm 106\pm 106\pm 106\pm$	$egin{array}{c} 34 \pm 2 \ 54 \pm 1 \ 51 \pm 2 \ 40 \pm 1 \ 41 \pm 2 \ 41 \pm 1 \ 42 \pm 1 \ 42 \pm 1 \ 44 \pm 2 \end{array}$	66 43 55 62 65 65 61 62

 a Calculated as an average on the three immersion cycles. b Hysteresis: Δ = θ_a – θ_r

Two sets of measurements were performed. The first experiment consisted of three immersion cycles at 6 mm immersion depth with dwell times between immersion and withdrawal of 10 s. In the second experiment, the coated slide was advanced by 6 mm and kept immersed for 1000 s. Then the slide was reversed to the start position and finally advanced by 12 mm, so that an additional 6 mm of fresh surface was exposed to water. This was followed by another 12-mm immersionwithdrawal cycle with a short dwell time of 10 s.

In the first experiment, with only 10 s dwell time between each immersion and withdrawal, neither the advancing angle, $\theta_{\rm a}$, nor the receding angle, $\theta_{\rm r}$, changed significantly during the three advancing and receding cycles. Thus, average values of the three cycles are reported in Table 5.

The $\theta_{\rm a}$ values were quite high (96° < $\theta_{\rm a}$ < 107°), whereas θ_r were lower and generally below 55°. As a consequence, large values of hysteresis ($40^{\circ} < \Delta < 70^{\circ}$) were found. Hysteresis of contact angles is usually due to the existence of metastable states at the solid-liquid-vapor interface. The surface energy difference $\gamma_{\rm L}(\cos\theta_{\rm r}$ – $\cos\theta_{\rm a}$) is attributed to the fact that the free energy required to separate the liquid from the solid is greater than the energy released during contact. Contact angle hysteresis is caused by factors such as surface roughness, chemical heterogeneity of the topmost layer, and surface reconstruction of the polymer film after contact with the liquid.⁴⁶ The investigated block copolymer films showed a fairly low AFM roughness ($R_q = 5-7$ nm) and its effect on hysteresis would be negligible. Therefore, the experimentally observed values of Δ are most likely due to a combination of chemical heterogeneity and restructuring of the surface.

The advancing water contact angles on the block copolymer surfaces were strongly influenced by the fluoroalkyl segments in the PEGylated fluoroalkyl side chains and were generally within the range of 100 to 107° , with the exception of the S81Sz6 surface that showed a lower $\theta_{\rm a}$, of about 97° .

The advancing water contact angles on all surfaces were lower than that on a perfluoromethyl terminated perfluoroalkyl surface ($\theta_a > 120^\circ$) due to the influence of the PS block and the polar groups in the block copolymer, including PEG. Polystyrene has an advancing water contact angle of 88°, which is low when compared with perfluoroalkyl covered surfaces.

The polymer S81Sz6 showed the lowest θ_a of about 97°. As discussed below, block copolymer S81Sz6 has a lamellar morphology, with the lamellae oriented parallel to the substrate. Hence, the surface is expected to be covered by the PSz block, and the contact angles are expected to be close to those on the PSz homopolymer ($\theta_a = 101^\circ$ and $\theta_r = 34^\circ$). Nevertheless, the lower advancing water contact angle (97°) and higher receding contact angle (54°) can be attributed to the fact that the top PSz layer is fairly thin, and the underlying PS block has a stronger influence on the wetting behavior. The lamellar *d*-spacing, determined using GISAXS, was correspondingly the lowest for this block copolymer (equal to about 14 nm). Evidently, the underlying PS layer not only lowers θ_{a} but also increases θ_r . On the other hand, the lamellar block copolymer S51Sz6, with thicker lamellae (24 nm d-spacing), has advancing and receding water contact angles closer to those on the homopolymer surface.

The higher $\theta_{\rm r}$ on the block copolymer surfaces, in comparison to the PSz homopolymer surface, is because of the PS block. The influence of the PS block on $\theta_{\rm r}$ is clear when data for block copolymers prepared from the S81 macroinitiator (S81Sz6 and S81Sz19) are compared with those for block copolymers containing the S51 and S26 PS blocks. The receding contact angle was higher (52 \pm 3°) on the block copolymers with the longer S81 PS blocks, and lower (42 \pm 3°) on block copolymers with the shorter S51 and S26 PS blocks.

To investigate the dependence of the contact angle values on the film history in immersionwithdrawal cycles a second set of measurements was carried out. The weight versus immersion depth plot showed that in the first 6 mm of the second cycle (after 1000 s of immersion in water) $\theta_{\rm a}$ and $\theta_{\rm r}$ were lower than the respective contact



Figure 2. Force-immersion depth curves for the polymer S81Sz19: 1st cycle 6 mm depth/1000 s dwell time, 2nd and 3rd cycles 12 mm depth/10 s dwell time. (For the meaning of the force F, see Experimental).

angles for the second 6 mm, when fresh surface was exposed, thereby causing a net discontinuity in the graph. For example, in the case of S81Sz19 coating, $heta_{
m a}=107^\circ$ and $heta_{
m r}=52^\circ$ for the fresh surface, and $heta_{
m a}=102^\circ$ and $heta_{
m r}=49^\circ$ for the immersed surface (after 1000 s dwell time). Moreover, the θ_a over the top half of the second immersion cycle were same as that for the first cycle (Fig. 2). The θ_r over the top half of the immersed surface (with only 10 s dwell time in water) was higher than the θ_r on the bottom half that was immersed in water for 1000 s (52° versus 49°). However, it quickly reached the 1000 s immersion value, during the third cycle, after another short dwell time of 10 s. These results suggest that a rearrangement of the outer molecular layers happened upon short immersion time in water.⁴⁷

It is, in general, difficult to investigate on a molecular scale how the structure of fluorinated surfaces may evolve upon contact with water,48 but surface reconstruction of the present polymer films likely occurred by a mechanism similar to that proposed for a related amphiphilic block copolymer.²⁷ The high advancing water contact angle and low receding contact angle, even after repeated immersion-withdrawal cycles indicates that the mechanism of surface reconstruction consists of "flipping" of the PEGylated-fluoroalkyl side chains, that made the perfluorinated chain segments point inwards and exposed the PEG chain segments outwards when the surface is in contact with water. Such a molecular reorganization favors the chemical interaction between the hydrophilic portions and reduces the contact with water of the hydrophobic-lipophobic portions.



Figure 3. Water contact angle versus immersion time in water for S51Sz20.

Moreover, measurements of static water contact angle, $\theta_{\rm w}$, carried out on the amphiphilic polymer films completely immersed in water for various times up to 14 days, showed that $\theta_{\rm w}$ decreased as the immersion time increased. This descending trend was generally more pronounced initially (typically the first 24–48 h), and more gradual later, until $\theta_{\rm w}$ reached a plateau value. Although this steady value depended on the specific copolymer, $\theta_{\rm w}$ remained larger than 70°–75°. Figure 3 illustrates the trend of $\theta_{\rm w}$ with immersion time for block copolymer S51Sz20.

The findings suggest that the surface underwent another reorganization process spanning over a longer time scale than the previous one. Thus, molecular reorganization could indeed occur by at least two different mechanisms: (i) the migration of the polystyrene block away from the water-polymer interface, and (ii) the reorientation of the Sz chains by reversible "flipping." The two processes likely occur simultaneously, but with different kinetics. Reconstruction at the macromolecular level requires long immersion times (days according to measurements of contact angle θ_w), whereas reconstruction of the side chains occurred over a short time scale (seconds according to measurements of θ_a and θ_r).

Chemical Analysis by XPS

Information about the chemical composition of the surface of the polymer films was obtained by means of X-ray photoelectron spectroscopy (XPS). The films were analyzed before ("dry" film) and after 9 days of immersion in water ("wet" film); the XPS analyses were carried out at room temperature under typical high vacuum conditions. The surface composition of the "wet" films is expected to be that corresponding to a kinetically trapped condition, rather than the equilibrium state when in contact with water. However, as is evident from Figure 3, reorganization of blocks occurs rather slowly at room temperature. The XPS spectra of the "wet" surface can, therefore, be considered indicative of chemical composition when the surface has equilibrated with water.

XPS spectra were acquired at different photoelectron emission angles ϕ (the angle between the surface normal and the path taken by the electrons toward the detector) corresponding to sampling depths of ~3–10 nm.^{49,50} We illustrate the general XPS findings for the films of S51Sz20 taken here as a representative example. The survey spectra of the polymer did not show the presence of elements other than C, O, and F. The elemental analysis data for the different emission angles ϕ are summarized in Table 6, where they are also compared with the corresponding values calculated from the known stoichiometric ratios of the block copolymer components.

The atomic percentage dependence on ϕ showed that there was a composition gradient normal to the film surface into the bulk. In fact, the experimental C atomic percentage was lower than the stoichiometric value (67%) and increased from 50.2% to 64.1% with increasing sampling depth from $\phi = 70^{\circ}$ to $\phi = 20^{\circ}$. By contrast, the F

Table 6. XPS Atomic Composition of the "Dry" and the "Wet" Surfaces of Block Copolymer S51Sz20 at Different Photoemission Angles ϕ

S51Sz20 FILM				"Dry"		"Wet"		
	ϕ (°)		C (%)	0 (%)	F (%)	C (%)	0 (%)	F (%)
		Stoichiometric	67	10	23	67	10	23
	70		50.2	11.3	38.5	60.0	16.6	23.4
	50		55.4	12.7	31.9	55.1	14.9	30.0
	20		64.1	13.3	22.6	65.3	14.5	20.2

atomic percentage was higher than the stoichiometric value (23%) and decreased from 38.5% at ϕ = 70° to 22.6% at ϕ = 20°. Thus, the polymer surface was enriched in F content because of the tendency of the fluorinated chains to migrate to the surface driven by their low surface energy. The O atomic percentage was slightly higher than the stoichiometric percentage (10%) and increased with increasing depth up to 13.3% at ϕ = 20°. This finding is consistent with the increment of oxyethylene segments in the bulk of the segregated amphiphilic block copolymer film.

In the "wet" samples the F atomic percentage was significantly lower as compared to the corresponding "dry" samples, 23.4% at $\phi = 70^{\circ}$ (i.e., at the lower sampling depth). On the contrary, the O atomic percentage rose in passing from "dry" to "wet" surface, 16.6% at $\phi = 70^{\circ}$. Therefore, the concentration of PEG segments at the surface was higher after exposure to water, as a consequence of the rearrangement of the amphiphilic side chains. Moreover, one can also note that the C atomic percentage increased in changing "dry" to "wet" samples, being 50.2% and 60.0% at ϕ $= 70^{\circ}$, respectively. This increase likely was affected by a greater population of both the PEGylated chains and the styrene backbone in the Sz block, which became more exposed at the outer surface as a consequence of the flipping process, rather than by the polystyrene block, which instead tended to migrate into the bulk because of its hydrophobic nature. All these findings agreed very well with the results obtained from contact angle measurements and were supported by NEXAFS analyses, see below.

The C(1s) peak revealed a complex shape and the fitting procedure indicated the presence of at least five main contributions: those at 292 eV and 294 eV corresponded to the $-CF_2$ and $-CF_3$ moieties of the perfluorinated chains, respectively; the peak at 289 eV was attributed to the C=O of the ester group, and the partially resolved peaks at 285 eV and 287 eV were due to the sum of more components. In particular, the former was attributed to C atoms in the aromatic rings and in the polymer backbone, whereas the latter depended on several carbons of the oxyethylene units. Figure 4 shows the C(1s) XPS spectra of surfaces before and after immersion in water, detected using a photoelectron emission angle of 70° . The results show a depletion of $-CF_2$ - and -CF₃ carbon atoms of the amphiphilic side chains from 21.6% and 4.1%, respectively, for the "dry" samples to 14.9% and 1.5% for the "wet" samples.



Figure 4. Area-normalized C(1s) XPS signals for "dry" and "wet" surfaces of S51Sz20 at $\phi = 70^{\circ}$.

Consistently, the perfluorinated segments had turned inwards in the "wet" films, the terminal $-CF_3$ groups being more hidden and barely detectable.

Analysis by NEXAFS

Near-edge X-ray absorption fine structure spectroscopy (NEXAFS) was also used to probe molecular reconstruction at the surface of the block copolymer after immersion in water. Polymer thin films were prepared by spin coating a 3% (w/v) solution of the amphiphilic block copolymer in CHCl₃ on Si wafers, drying in a vacuum oven at 60 °C and further annealing at 120 °C for 12 h. These films are referred to as "dry" surfaces. To study under-water surface reconstruction, the thermally annealed surfaces were immersed in distilled water for 3 days at room temperature and then for 12 h at 70 °C. The surfaces were kept immersed in water at room temperature until NEXAFS measurement, whereupon they were removed from water and dried under vacuum at room temperature. These surfaces are referred to as "wet." NEXAFS spectra obtained at X-ray incident angles, θ , of 50° and 130° (with respect to the sample surface) were compared. Spectra for the "dry" and "wet" block copolymer films were also compared notably at the C K-edge (Fig. 5). The NEXAFS spectra were qualitatively similar to the XPS spectra, and the most significant resonance peaks were identified individually. Moreover, the resonance peak of the phenyl ring carbons was highly resolved at 285 eV, in contrast to XPS that normally does not allow for such a resolution and quantitative analysis. The C 1s- σ^*_{C-F} resonance intensities did not show a monotonic



Figure 5. C(1s) NEXAFS spectra of "dry" and "wet" films of the block copolymer S51Sz20, obtained at X-ray incident angles θ of (a) 50° and (b) 130°. "D" denotes the channeltron electron detector.

dependence on $\sin^2\theta$, indicating that the fluoroalkyl segments of the side chains were not oriented at the surface.⁵¹ This is in accord with the behavior of previous acrylic amphiphilic polymers.²⁷ This is expected of the polydisperse fluoroalkyl segments that were moreover decoupled from the polymer main chain by polydisperse PEG spacer segments. By contrast, block copolymers of a closely related polystyrene block carry-1*H*,1*H*,2*H*,2*H*-perfluorodecyl ing chain side groups were found to present a relatively high orientational order of the fluoroalkyl chains that self-assembled in a smectic surface mesophase.⁵² The orientation of the side chains is, however, of no consequence to the discussion that follows, because the X-ray incident angle of 50° is close to the "magic angle" of 51.2° (for a X-ray degree of polarization equal to 0.85) at which the measured intensity is independent of molecular orientation. The same is true for the supplementary incident angle of 130° . The incident angles of 50° and 130° correspond to photoelectron emission angles, ϕ , of about 4° and 76° , respectively. Thus, the spectra acquired at 50° incidence probe deeper into the film, whereas those obtained at 130° are highly surface sensitive. Figure 5 shows the partial electron yield (PEY) NEXAFS spectra in the C(1s) region for the amphiphilic block copolymer S51Sz20.

The effect of water immersion on molecular composition at the block copolymer surface is

clearly evident from the spectra in Figure 5(a). The "wet" surface showed a lower intensity of the C 1s- π_{Φ}^* resonance at 285 eV indicating that water immersion resulted in a migration of phenyl rings, in the backbones of the amphiphilic styrene block and those in the styrene block, away from the polymer surface. There was a similar decrease in the intensity of the C 1s- σ^*_{C-F} resonance at 292 eV, indicating that the hydrophobic fluoroalkyl segments migrated as expected away from the surface. An increase in the C 1s- σ^*_{C-H} resonance at 287 eV is observed, which can be attributed to the surface migration of the hydrophilic PEG segments, or the alkyl backbone, after contact with water. Figure 5(b) compares the C(1s) NEXAFS spectra of the "dry" and "wet" surfaces acquired at an X-ray incident angle of 130° ($\phi = 76^{\circ}$). The weak intensity of the C 1s- π_{Φ}^* resonance is immediately evident, indicating that the surface of the block copolymer thin film is predominantly populated by the amphiphilic side chains, in both the "dry" and the "wet" samples. The phenyl rings, including those in the styrenic backbone of the amphiphilic block, are buried below the PEGylated-fluoroalkyl segments. The C 1s- σ^*_{C-F} and C 1s- σ^*_{C-H} resonances are prominent in these spectra, with the former diminishing in intensity and the latter increasing in intensity after the surface has contacted water. Block copolymer thin films of S51Sz20 have a spherical microstructure. Compodepth profiling using sitional NEXAFS

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Figure 6. 2-Dimensional GISAXS map of block copolymer S51Sz6 acquired at an X-ray incidence angle of (a) 0.12° and (b) 0.135° ; $\alpha_{cP} = 0.115^{\circ}$.

spectroscopy was used to investigate molecular composition and molecular reconstruction in block copolymer films with different microstructures. These results will be discussed separately in future.⁴⁴

Microphase Structure by GISAXS and AFM

The surface microphase structure in amphiphilic block copolymers was investigated using grazing incidence small angle X-ray scattering (GISAXS) and corroborated by atomic force microscopy (AFM). Thin films of fluorinated block copolymers were prepared on silicon wafers by spin coating 3% (w/v) solutions of the polymers in chloroform. The films were dried at 60 °C in a vacuum oven overnight and annealed at 120 °C for 12 h.

Figure 6(a) shows a 2-dimensional GISAXS image of block copolymer S51Sz6 at an X-ray incidence angle α_i of 0.12°. The scattering pattern along the q_z axis is clearly indicative of a lamellar morphology in which the lamellae are oriented parallel to the substrate.

To determine the lamellar spacing, D_{lam} , along with the critical angle (for total external reflection), α_{cP} the GISAXS images were acquired at a series of X-ray incidence angles ranging from 0.06° to 0.22° . Line slices were taken along the q_z axis as close to the beam stop as possible. When α_{i} $> \alpha_{\text{cP}}$ the peak in scattering intensity appears as a doublet [Fig. 6(b)], and is modeled using the distorted-wave Born approximation⁵³:

$$\begin{aligned} q_{z}^{*}(\alpha_{\rm i}) &= \frac{2\pi}{\lambda} \left[\sin \alpha_{\rm i} \right. \\ &\left. + \sqrt{\sin^{2} \alpha_{\rm cP} + \left(\frac{n\lambda}{D_{\rm lam}} \pm \sqrt{\sin^{2} \alpha_{\rm i} - \sin^{2} \alpha_{\rm cP}} \right)^{2}} \right] (5) \end{aligned}$$

where, q_z^* is the z-component of the scattering vector at which the scattering intensity is a maximum, λ is the wavelength of the incident X-rays, and n is a positive integer. At X-ray incidence angles that were significantly below the critical angle, the scattering peaks were very weak. Figure 7 shows the experimental values of q_z^* (first



Figure 7. Experimental peak positions versus angle of X-ray incidence for S51Sz6. Data were fitted using eq 5 to determine the critical angle and lamellar spacing.



Figure 8. 2-Dimensional GISAXS map of polymer S51Sz17 acquired at an X-ray incident angle of (a) 0.11° and (b) 0.15° . The hexagonal cylinder lattice is indicated in (a). At higher incident angles diffraction spots are split up due to reflection from the substrate. The sharp spots clearly indicate a well-aligned hexagonal lattice with a (10) plane parallel to the substrate. (For more detail see text and Table 7). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

order peak) as a function of α_i . The data were fitted using eq 5 to obtain $\alpha_{cP} = 0.115^{\circ}$ and $D_{lam} = 13.5$ nm.

Figure 8 shows the GISAXS maps of the S51Sz17 thin films acquired at two different X-ray incident angles. For an X-ray incident angle of 0.11°, which is slightly below the critical angle, indexing of the peaks was done by modeling the morphology as hexagonally packed cylinders lying parallel to the substrate, as the peaks appear to align well to an equilateral triangular grid.^{54,55}

By defining the real space lattice vectors towards the nearest neighboring cylinders, a comparison can be made between the experimental and theoretical peak positions as shown in Table 7. A lattice parameter of 20.3 nm was used in the calculations. The peaks R1 and R2 appear from scattering from the (01) and (10) planes, respectively. The peak R3 is assumed to originate from scattering of cylinders rotated 30° , similar to what was observed by Lee et al.⁵⁴ Also, the R4 peak should theoretically appear below the Yoneda band. This peak is most likely the Yoneda enhancement of the tail of the actual peak which is inaccessible. To determine the critical angle of the film, a similar analysis was done for this polymer as for the polymer S51Sz6. Figure 9 shows

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the experimental values of q_z^* (first order peak) as a function of α_i . The data were fitted using eq 5 to obtain $\alpha_{cP} = 0.125^{\circ}$.

Figure 10 shows tapping mode AFM phase image of the surface of polymer S51Sz17. The image suggests a lying-cylinder morphology with a nearest neighbor spacing of 20 nm, which is in agreement with the cylinder domain size determined by GISAXS.

In contrast, polymer S51Sz6 showed a featureless phase image that is characteristic of a uniform lamellar morphology (Fig. 11), which agreed well with GISAXS results, as the surface was

Table 7. Experimental and Theoretical Peak Values for Block Copolymer S51Sz17 at an Incident Angle of 0.11°

Peak	Experimental	Theoretical	Index
R1	(0, 0.510)	(0, 0.516)	(0 1)
R2	(0.310, 0.329)	(0.310, 0.337)	(1 0)
R3	(0.360, 0.239)	(0.357, 0.232)	30 deg rotated
R4	(0.623, 0.235)	(0.619, 0.159)	(2-1)
R5	(0.313, 0.702)	(0.310, 0.695)	(11)
R6	(0, 0.899)	(0, 0.874)	$(0\ 2)$
R7	(0.619, 0.510)	(0.619, 0.516)	(2 0)



Figure 9. Experimental peak positions versus angle of X-ray incidence for S51Sz17. Data were fitted using eq 5 to determine the critical angle. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

completely and homogeneously covered by lamellar phase of the fluorinated, lowest surface energy block. The spots in the AFM phase images correspond to holes or depressions in the corresponding height images (not shown). Island or hole formation is expected for symmetric diblock copolymer thin films when the film thickness is not an integral multiple of the lamellae spacing.⁵⁶

Thus, we identified the morphology and the nanodomain periodicity of the films from amphiphilic block copolymers comprised of two blocks with differing relative compositions by a combination of GISAXS and AFM analyses. By varying the volumetric fraction, $\phi_{\rm Sz}$, of the amphiphilic block (Table 8), diverse surface morphologies from spherical to cylindrical and to lamellar could be created by the macromolecular engineering of the block copolymers, having relatively well controlled molar masses and compositions of the constituent blocks.

CONCLUSIONS

The phenomenon of self-assembly and self-segregation is exhibited by a variety of fluorinated polymers, blends, and crosslinked networks and is generally regarded as a useful tool to construct a low surface energy material. A series of block copolymers were readily prepared from styrenic monomers using ATRP reactions. By pairing a nonpolar fluorinated unit with a polar ethylene glycol unit to form an amphiphilic surface moiety, it is possible to create a complex, dynamic surface well suited for applications such as coatings that



Figure 10. AFM phase image of block copolymer S51Sz17 surface. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

can resist biofouling. Such an amphiphilic group is delivered to the surface of a polymer film, because surface segregation of the fluorinated group carries it to the surface. Detailed contact angle measurements showed the importance of both components to the surface properties. Careful XPS and NEXAFS measurements also showed that the surface is dominated by the fluorinated component in the dry or vacuum state with the ethylene glycol unit located just below the surface. The important role of the thin film structure on



Figure 11. AFM phase image of block copolymer S51Sz6 surface. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

Polymer Film	$\phi_{\mathrm{Sz}}{}^{\mathrm{a}}$ (vol %)	Morphology	AFM Periodicity (nm)	GISAXS Periodicity (nm)
S51Sz6	${\sim}37$	Parallel lamellae		14
S51Sz17	${\sim}63$	Lying cylinders	20	20
S51Sz20	${\sim}67$	Disordered spheres	23	22
S81Sz6	${\sim}27$	Parallel lamellae		24
S81Sz19	${\sim}54$	Lying cylinders	25	24

Table 8. Morphological Parameters of the Surface of Block Copolymer Films

^aEstimated volume fraction of the amphiphilic polystyrene block.

microstructure development was demonstrated by GISAXS and AFM measurements.

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