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Polystyrene–Polyperfluorooctylethyl acrylate Diblock Copolymers: The Effect of Dilution of the Fluorinated Mesogenic Chains on Bulk and Surface Properties

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Summary: Three smectic poly(styrene-*b*-perfluorooctylethyl acrylate) block copolymers (S-*b*-AF8) with different degrees of polymerization (n, m) of the relative blocks were synthesized by atom transfer radical polymerization (S, $n = 25$; AF8 $m = 2, 6, 23$). The mesophase structure and transition temperatures were investigated by DSC and WAXD. The block copolymer having the shortest fluorinated block was blended with a thermoplastic elastomer SEBS in different proportions, in order to look at the effect of a further dilution of the perfluorinated groups on non-wetting properties. Thin films of the block copolymers as well as the blends exhibited large contact angles with both water and *n*-hexadecane, which resulted in low solid surface tensions. XPS findings at different photoemission angles confirmed the effective surface segregation of the mesogenic chains of the fluorinated polymer block.

Keywords: block copolymers; fluoropolymers; mesophase; polymer blends; surface segregation

Introduction

Liquid crystalline block copolymers can form hierarchical structures, which extend over several spatial length scales, from the morphological level typical of block copolymers down to molecular dimensions distinctive of liquid crystalline mesophases.[1,2] One special case is that of diblock copolymers carrying perfluorinated side chain mesogens. In fact, relatively long pendent perfluorocarbon groups ($-(CF_2)_xF$, $x \geq 8$) self-assemble in smectic-like structures at the surface of thin films, which exhibit high order parameters.[3-5] Such a surface order can be a manifestation of the bulk mesophase order. The formation of this mesophase state is due to the intramolecular phase segregation of the strongly incompatible hydrocarbon – fluorocarbon constituents of the polymer repeat units that spontaneously organize in an orderly fashion. The ability to self-assemble is also enhanced by the intrinsic low surface energy of perfluorinated chains that are driven to the solid – air interface.[6,7] Thus, the wettability of fluorinated polymers is markedly influenced by their packing order, and liquid crystalline polymers generally present lower surface tensions than amorphous polymers. Because of the inherent non-stick behavior fluorinated polymers are candidates as lubricant, wear control, antisoiling and anti(bio)fouling materials.[8–15]

In this work, we synthesized well-defined poly(styrene-*b*-2-perfluorooctylethyl acrylate) copolymers, in order to study how the different chemical composition can affect the bulk and surface properties of the polymeric films. The liquid

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crystalline copolymer with the shortest fluorinated block was then incorporated into blends with a commercial thermoplastic elastomer SEBS. We found that such blends retain the non-wetting behavior of the pristine block copolymer, irrespective of composition and dilution.

Experimental Part

Materials

Trifluorotoluene (TFT), hexafluorobenzene, 2,2'-bipyridine (Bipy), CuBr, 1-phenylethyl bromide (1-(PE)Br) and monomer 2-perfluorooctylethyl acrylate (AF8) (Aldrich) were used without further purification. Styrene (S) (Fluka) was washed with 5% NaOH and water, dried over Na_2SO_4 and distilled under reduced pressure. α,α'-Azobis(isobutyronitrile) (AIBN) (Fluka) was recrystallized from methanol. Polystyrene-*b*-poly(ethylene-*co*-butylene)-*b*-polystyrene (SEBS) triblock elastomer (Kraton G1652M) was kindly provided by Kraton Polymers. The styrene content of SEBS was ~ 30 wt %.

Polystyrene–Polyperfluorooctylethyl acrylate Block Copolymers

Diblock copolymers were prepared according to a two step procedure described in[16] (Figure 1). In the first step, a solution of 30.00 mL (261.83 mmol) of S, 2.049 g (13.12 mmol) of Bipy, and 0.60 mL (4.37 mmol) of 1-(PE)Br was purged with nitrogen for 15 min and then 0.625 g (4.36 mmol) of CuBr was added. After four freeze – thaw pump cycles, the polymerization was let to proceed for 90 min at 110 °C. After cooling to room temperature, the polymer solution was diluted with THF and then eluted on neutral alumina. The polymer was purified by repeated precipitations from THF solutions in methanol (yield 48%). The resulting Br-terminated polystyrene (average degree of polymerization, $n = 25$) is denoted by P(S).

In the second step, 1.028 g (0.38 mmol) of macroinitiator P(S) and 179 mg (1.148 mmol) of Bipy were flushed with nitrogen three times. A solution of 1.978 g (3.817 mmol) of AF8 in 11 mL of TFT was added under nitrogen. After four freeze – thaw pump cycles, 54 mg (0.379 mmol) of CuBr was added and the solution was subjected to four freeze – thaw pump cycles. The polymerization was let to proceed for 66 h at 115 °C. When the reaction was stopped the polymer solution was diluted with TFT and washed with water until the disappearance of greenish color. The solvent was removed under vacuum and the polymer was precipitated from TFT solution in methanol (yield 58%). The resulting diblock copolymer, containing 8 mol % AF8 (average degree of polymerization, $m = 2$), is denoted by (S-*b*-AF8)8.

^{1}H NMR ($CDCl_3$): δ (ppm) $= 1.2 - 2.6$ (37.6H, CH_2CH, CH_2CF_2), 4.5 (2.0H, $COOCH_2$), $6.2 - 7.3$ (54.3H aromatic).

^{19}F NMR ($CDCl_3$/hexafluorobenzene): δ (ppm) $= 36$ (2.0F, CF_2), $38 - 41$ (10.0F, CF_2), 48 (2.0F, CF_2CH_2), 81 (3.0F, CF_3).

FT-IR (film): $\overline{\nu}$ (cm^{-1}) $= 3150 - 3990$ (νC – H aromatic), 1739 (ν C = O), 1602 (ν C = C aromatic), $1400 - 1000$ (νC – O and ν C – F), 757 and 699 (δC – H aromatic), 658 (ω CF_2).

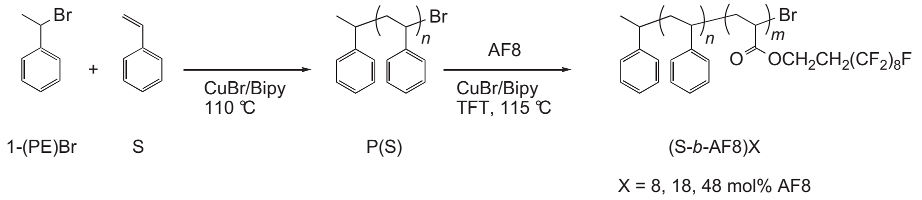

Figure 1.
Synthesis of block copolymers (S-*b*-AF8)X by ATRP.

Polymer Blends

Blends were prepared by co-precipitation of 1 wt % chloroform solutions of (S-*b*-AF8)8 and SEBS in methanol. They are denoted as (S-*b*-AF8)8/Y, where Y is the wt % content of block copolymer ($Y = 10 - 90$) in the blend.

Film Deposition

The polymer films were obtained by spin coating 3 wt % TFT solutions of the polymer alone or blended with SEBS (10–90 wt %) on glass slides. They were vacuum dried overnight and then annealed at 120 °C for 15 h (thickness 200 – 400 nm).

Characterization

^1H (vs. TMS) and ^{19}F (vs. hexafluorobenzene) spectra were recorded on Varian Gemini VRX 200 and Varian Gemini VRX 300 spectrometers, respectively.

Number (M_n) and weight (M_w) average molecular weights and dispersities (M_w/M_n) were measured by size exclusion chromatography (SEC) using a Jasco PU-1580 liquid chromatograph equipped with two PL gel 5 μm Mixed-D columns, a Jasco 830-RI refractive index detector and a Perkin-Elmer LC75 UV detector. Polystyrene standards ($4.0 \cdot 10^2$–$4.0 \cdot 10^5$ g/mol) were used for calibration.

Differential scanning calorimetry (DSC) measurements were performed with a Mettler DSC-30 instrument (10 °C/min). The isotropization transition temperature (T_i) was taken at the maximum temperature in the DSC enthalpic peak of the second heating cycle. The glass transition temperature (T_g) was set at the half-devitrification temperature.

Wide angle X-ray diffraction (WAXD) patterns were recorded with a home made diffractometer equipped with a flat film camera. The Ni-filtered CuK_α radiation was used ($\lambda = 1.54$ Å). Polymer powder samples were studied from room temperature up to T_i, taken as the temperature of disappearance of the low-angle diffraction signal. The experimental smectic interlayer periodicity (d) was compared with the length (L) of the AF8 repeat unit in its limit fully extended conformation ($L = 34 \pm 1$ Å).

Contact angle measurements were carried out with a FTA200 Camtel goniometer using water, *n*-hexadecane and ethylene glycol as interrogating liquids (purity > 99%).

Atomic force microscopy (AFM) experiments were done in the tapping mode ($A_{sp}/A_0 = 0.7$) on a commercial microscope (Multimode) system equipped with a Nanoscope IV controller (Veeco Instruments) using silicon cantilevers with a nominal force constant of ~ 30 N/m from Nanosensor (type RTESP) at a resonance frequency of about 320 kHz. Root-mean-square roughness ($R_q = (\Sigma_i Z_i^2/N)^{0.5}$, where Z_i are heights relative to the mean, and N is the number of points measured on the analyzed surface) was determined over regions of 1×1 μm^2 size and averaged over at least five measurements.

X-ray photoelectron spectroscopy (XPS) spectra were recorded with a Perkin-Elmer PHI 5600 spectrometer with a standard Al-Kα 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,[17] was evaluated using the PHI sensitivity factors.[18] To take into account charging problems, the hydrocarbon carbon peak was adjusted to a position of 285.0 eV and the sub-peak BE differences were evaluated.

Results and Discussion

Synthesis

The polystyrene – polyperfluorooctylethyl acrylate diblock copolymers (S-*b*-AF8)X (X = 8, 18, 48 mol% AF8) were prepared by a two-step procedure based on two successive atom transfer radical polymerizations (ATRP)[16] (Figure 1).

In the first step, a bromo-terminated polystyrene macroinitiator P(S) ($n = 25$) was prepared by ATRP of styrene in bulk with 1-phenylethyl bromide as an initiator and CuBr/2,2'-bipyridine as a catalyst (1:1:3 molar ratio) at 110 °C. In the second step, the copolymerization for attachment of the block of fluorinated acrylate monomer AF8 to the polystyrene block was carried out in TFT solution at 115 °C. The length of the AF8 block was varied ($m = 2$, 6, 23) by changing the AF8/P(S) feed molar ratio in the range 10 – 50 and keeping constant the reaction time ($t = 66$ h) (Table 1).

The block copolymer with the shortest AF8 block ($m = 2$) was used as a surface active component to prepare blends (S-*b*-AF8)8/Y with the thermoplastic elastomer SEBS in varied proportions (Y = 10 – 90 wt % block copolymer). Our strategy to combine a low surface energy component with a low elastic modulus matrix has the final objective to construct non-biocidal polymer coatings for antifouling/fouling release applications in the marine environment.[19,20]

Thermal and Mesophase Behavior

The thermal properties of the block copolymers were studied by DSC, with particular attention to detection of thermotropic mesophases and their phase transitions. As is evident from Table 2, they exhibited different thermal behavior depending on chemical composition. The copolymer (S-*b*-AF8)48, with the longest AF8 block ($m = 23$) showed only the transition peak at 70 °C, associated with the isotropization of a mesophase of the fluorinated block. On the other hand, the block copolymer (S-*b*-AF8)8, with the lowest content of AF8 ($m = 2$) presented only the glass transition temperature at 81 °C, without the detection of mesophase formation. In between the two previous examples, the copolymer (S-*b*-AF8)18 ($m = 6$) presented a clear peak at 60 °C due to the smectic – isotropic phase transition of the fluorinated block and a glass transition temperature at 79 °C associated with the devitrification of polystyrene block. In no case was the glass transition temperature of the fluorinated block detected in the expected region around 50 °C, see homopolymer P(AF8) in Table 2.

Block copolymers (S-*b*-AF8) represent a relatively rare example of microphase separated materials in which a soft mesophase

Table 2.
Thermal transitions of block copolymers (S-*b*-AF8)X and homopolymer P(AF8).

Sample	T_g [a]	T_i [b]	ΔH_i [b]	ΔS_i [b]	T_i [c]
	(°C)	(°C)	(J/g)	(J/gK)	(°C)
(S-*b*-AF8)8	81	n.d. [d]	n.d. [d]	n.d. [d]	50
(S-*b*-AF8)18	79	60	5.6	$1.7 \cdot 10^{-2}$	70
(S-*b*-AF8)48	n.d. [d]	70	9.9	$2.9 \cdot 10^{-2}$	80
P(AF8)	50[e]	76	14.3	$4.1 \cdot 10^{-2}$	80

[a] Glass transition temperature of the polystyrene block by DSC.
[b] Isotropization temperature, enthalpy and entropy of the fluorinated block by DSC.
[c] Isotropization temperature by WAXD.
[d] Not detected by DSC.
[e] Glass transition temperature of the fluorinated block by DSC.

Table 1.
Physical-chemical properties of (S-*b*-AF8)X block copolymers.

Sample	AF8/P(S) [a]	AF8	AF8	m [b]	M_n [c]	M_w/M_n [d]
		(mol%)	(wt%)		(kg/mol)	
(S-*b*-AF8)8	10:1	8	27	2	3.5	1.2
(S-*b*-AF8)18	20:1	18	53	6	6.0	1.2
(S-*b*-AF8)48	50:1	48	81	23	14.5	1.2

[a] AF8 monomer/P(S) macroinitiator molar ratio.
[b] Polymerization degree of AF8 block.
[c] Number average molecular weight by ^{1}H NMR.
[d] Dispersity by SEC.

of one block coexists with the rigid glassy phase of the other block.

The liquid crystal behavior was also investigated by WAXD studies. Interestingly, the (S-*b*-AF8)8 copolymer, for which the isotropization peak was not detected by DSC, displayed an ordered smectic mesophase (periodicity $d = 32.6$ Å), in which the fluorocarbon chains were arranged on a pseudo-hexagonal lattice (side of the hexagon $a_H = 5.6$ Å) and tilted with respect to the layer normal by an angle of ~ 16° (SmI_2 or SmF_2 mesophase) (Figure 2 left). This result suggests that two just mesogenic fluorocarbon pendant chains are sufficient to self-assemble in an ordered structure, which remains stable up to the isotropization temperature. The mesophase of the other block copolymers presented the same lattice parameters d and a_H, indicating that the chemical composition influenced T_i but not the mesophase structure (Figure 2 right).

Wetting Behavior and Surface Energy

The wetting behavior of the copolymers was studied by measurements of the contact angle θ of thin films (200 – 400 nm thickness) using water, ethylene glycol and *n*-hexadecane as wetting liquids (Table 3). The AFM root-mean-square roughness R_q of the films ranged between 2 and 4 nm, and the effect of surface roughness on contact angle would be negligible.[11]

The values of θ with water and *n*-hexadecane are conventionally used to estimate qualitatively hydrophobicity ($\theta_w > \sim 90°$) and lipophobicity ($\theta_h > \sim 60°$), respectively. The block copolymers showed large contact angles with all the interrogating liquids, exhibiting in particular strong hydrophobic ($\theta_w \geq 118°$) and lipophobic ($\theta_h \geq 83°$) properties. This two-fold character is typical of fluorinated polymers, as opposed to most other polymers, like polyolefins, that are hydrophobic, but not lipophobic at the same time.

One can also note that the contact angle values did not significantly depend on the chemical composition of the block copolymers, not even for (S-*b*-AF8)8 with the shortest fluorinated block. This is a clear evidence that a saturation in perfluorocarbon chains at the surface exists, above which an increase in fluorine content does not produce an increase in the contact angles.

Contact angle values measured for the thin films of the (S-*b*-AF8)8/Y blends with SEBS were also very high (e.g. $\theta_w = 119°$, $\theta_h = 81°$ and $\theta_{EG} = 99°$ for (S-*b*-AF8)8/50) and similar to those of the pristine block copolymer (Table 3). Thus, the blends retained a distinct lipophobic/hydrophobic character, even at contents of SEBS as high as 90 wt%. This suggests that the dilution effects are offset by the chemical incompatibility between the dispersed fluorinated block copolymer and the SEBS matrix, which on the other hand enhances the self-assembly process of the fluorinated chains at the outer surface of the films. The

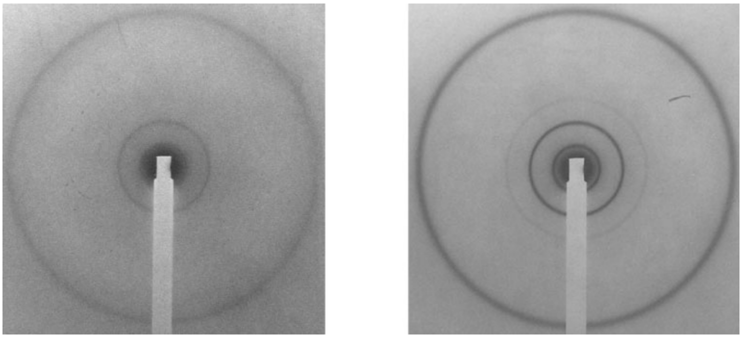

Figure 2.
WAXD pattern of the smectic mesophase of (S-*b*-AF8)8 (left) and (S-*b*-AF8)48 (right) at room temperature.

Table 3.
Contact angles[a)] and surface tensions[b)] of block copolymers and blends with SEBS.

Film	θ_w	θ_h	θ_{EG}	γ_S^{OWK} b)	γ_S^d b)	γ_S^p b)
	(°)	(°)	(°)	(mN/m)	(mN/m)	(mN/m)
(S-*b*-AF8)8	118 ± 1	85 ± 1	96 ± 1	8.9	8.2	0.7
(S-*b*-AF8)18	120 ± 1	83 ± 1	99 ± 1	9.1	8.7	0.4
(S-*b*-AF8)48	122 ± 1	86 ± 1	99 ± 2	8.2	7.9	0.3
(S-*b*-AF8)8/90	119 ± 1	80 ± 1	99 ± 1	9.9	9.5	0.4
(S-*b*-AF8)8/70	118 ± 1	79 ± 1	99 ± 1	10.2	9.8	0.4
(S-*b*-AF8)8/50	119 ± 1	81 ± 1	99 ± 1	9.6	9.2	0.4
(S-*b*-AF8)8/30	118 ± 1	81 ± 1	99 ± 1	9.7	9.2	0.5
(S-*b*-AF8)8/10	117 ± 1	80 ± 1	100 ± 1	10.1	9.5	0.6

[a)] Contact angles measured with water, *n*-hexadecane, and ethylene glycol.
[b)] Calculated with the Owens–Wendt–Kaelble method: γ_S^d dispersion component, γ_S^p polar component.

phenomenon of surface segregation is known for a variety of fluorinated polymers,[21,22] polymer blends and networks[16,23,24] and is here pursued as a tool to construct low surface energy, non-wetting polymer coatings.

To evaluate the stability of the polymeric films in water, the contact angle measurements with the same interrogating liquids were repeated after 7 days of immersion in water. The data obtained for (S-*b*-AF8)8 and some of its blends are reported in Table 4. Both θ_w and θ_h decreased after water exposure, even though the decrease was less marked for the pristine block copolymer and progressively became more pronounced for the blends with lower AF8 contents.

The measurements of solid–liquid contact angles were used to evaluate solid surface tension γ_S with the additive method of Owens, Wendt and Kaelble (OWK),[25,26] by using water and *n*-hexadecane as wetting liquids of known surface tension γ_L. In this approach the solid surface tension:

$$\gamma_S = \gamma_S^d + \gamma_S^p \tag{1}$$

combined with the Young's equation yields:

$$\gamma_L(1 + \cos\theta) = 2\left[(\gamma_S^d \gamma_L^d)^{1/2} + (\gamma_S^p \gamma_L^p)^{1/2}\right] \tag{2}$$

where γ^d and γ^p are the dispersion and the polar components of surface tension, respectively. Since there are two unknowns (γ_S^d, γ_S^p), it is necessary to use at least two probing liquids of known γ_L^d and γ_L^p.

The surface tensions and the related components calculated for the copolymers and the blends before water immersion are collected in Table 3. In any case, the block copolymer films exhibited very low surface tensions ($\gamma_S^{OWK} \leq 9.1\,\text{mN/m}$). The dispersion component overwhelmed the associated polar component in determining the total surface tension. This behavior is typical of fluorinated surfaces which experi-

Table 4.
Contact angles [a)] and surface tensions [b)] of (S-*b*-AF8)8 and its blends with SEBS after 7 days of immersion in water.

Film	θ_w	θ_h	θ_{EG}	γ_S^{OWK} b)	γ_S^d b)	γ_S^p b)
	(°)	(°)	(°)	(mN/m)	(mN/m)	(mN/m)
(S-*b*-AF8)8	106 ± 1	73 ± 1	77 ± 3	13.7	11.5	2.2
(S-*b*-AF8)8/90	107 ± 1	64 ± 1	87 ± 1	15.6	14.3	1.3
(S-*b*-AF8)8/50	100 ± 2	59 ± 1	80 ± 2	18.4	15.8	2.6
(S-*b*-AF8)8/10	101 ± 1	59 ± 2	55 ± 2	18.1	15.8	2.3

[a)] Measured with water, *n*-hexadecane, and ethylene glycol.
[b)] Calculated with the Owens–Wendt–Kaelble method: γ_S^d dispersion component, γ_S^p polar component.

ence dispersion forces but prevent polar, e.g. dipole–dipole or hydrogen bonding, interactions. The surface tensions of the blends ($\gamma_S^{OWK} \leq 10.2\,mN/m$) were similar to that of the block copolymer (S-*b*-AF8)8 ($\gamma_S^{OWK} = 8.9\,mN/m$), indicating that the surface properties were dictated by the fluorinated copolymer.

Consistent with the increase in θ_w and θ_h after contact with water, the calculated surface energy values were higher than those of the related dry samples, e.g. γ_S^{OWK} passed from 8.9 mN/m to 13.7 mN/m for (S-*b*-AF8)8 and from 10.1 mN/m to 18.1 mN/m for (S-*b*-AF8)8/10. These results may be due to a surface modification which can lead to a partial disgregation of the (liquid crystalline) surface structure by chemical interactions between the polar components of the perfluorooctyl ester side chains with water.

Surface Analysis

To substantiate better the surface segregation of the fluorinated block we started an analysis of the chemical composition of the film surface by angle-dependent X-ray photoelectron spectroscopy (XPS) measurements. Spectra were recorded at different photoemission angles $\phi = 70°$, $50°$, and $20°$, that corresponded to increasing sampling depths in the range $3 - 10\,nm$.

We focus our attention on the films of the block copolymer (S-*b*-AF8)18 before and after contact with water for 7 days. The survey spectra demonstrated the presence of no other elements than C, O and F (Figure 3 left).[27] The C(1s) peak revealed a complex shape, and the fitting procedure indicated the presence of several contributions at ~ 285 eV (CH, CH_2, CH=), ~ 287 eV (CH_2O, $\underline{C}H_2CF_2$), ~ 290 eV (COO, $CH_2\underline{C}F_2$), ~ 292 eV (CF_2) and ~ 294 eV (CF_3) (Figure 3 right).

The elemental analysis data for the film before immersion ('dry') at different angles ϕ are summarized in Table 5, where they are also compared with the corresponding values calculated from the known 'stoichiometric' composition of the block copolymer. The atomic percentages changed with angle ϕ, consistent with a composition gradient normal to the film surface into the bulk. In particular, the F atomic percentage was markedly higher (59.8%) than the stoichiometric one (25%) and decreased with decreasing ϕ, whereas the C atomic percentage followed the opposite trend. Thus, the outermost surface of the films was selectively enriched by the low energy fluorinated block. The O atomic percentage was generally comparable with the anticipated nominal composition and slightly increased with increasing sampling depth, according to the increment of the ester group concentration in the underlying molecular layers of the polymer films.

In the film after immersion ('wet') the F atomic percentage was still significantly higher (56.4% at $\phi = 70°$) than the nominal one, but slightly lower than the corresponding 'dry' sample (59.8% at $\phi = 70°$). On the

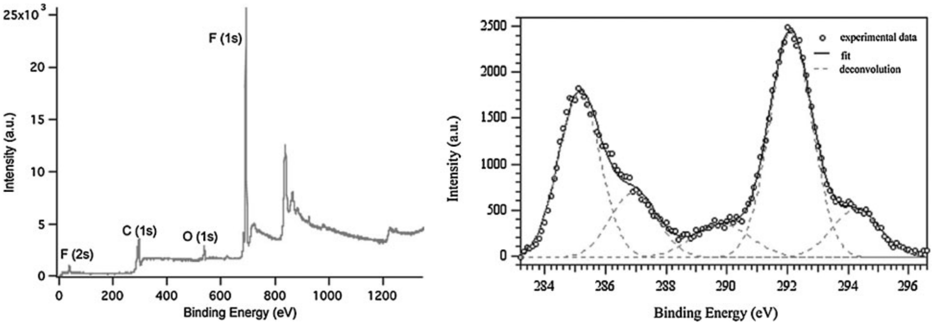

Figure 3.
XPS survey (left) and C(1s) (right) spectra at $\phi = 70°$ for (S-*b*-AF8)18.

Table 5.
XPS atomic composition of (S-*b*-AF8)18 before ('dry') and after ('wet') water immersion.

Film	ϕ		'dry'			'wet'		
	(°)		C (%)	O (%)	F (%)	C (%)	O (%)	F (%)
(S-*b*-AF8)18		stoichiometric [a]	72	3	25	72	3	25
	70	experimental	35.7	4.5	59.8	38.2	5.4	56.4
	50		38.5	4.8	56.7	42.0	5.9	52.1
	20		40.8	5.4	53.8	47.2	5.8	47.0

[a] Calculated on the basis of the known degrees of polymerization *n* and *m*.

other hand the C atomic percentage increased in changing from 'dry' to 'wet' samples, being 40.8% and 47.2% at $\phi = 70°$, respectively. These data may be interpreted assuming that a reorientation process of the outermost surface took place after prolonged contact with water. Partial disordering of the surface structure due to the polar interactions with water is in agreement with the above findings on contact angles and the related surface tensions. However, the depletion in fluorine was modest with respect to other examples of fluorinated polymer films,[28] indicating that the restructuring process is not massive and mainly involves the fluorinated side chains. This higher compositional stability of the surface structure is favored by the block nature of the copolymer in virtue of the phase segregation and self-organization of the fluorinated mesogens in an ordered phase structure. The bulk smectic structure possibly mediates and stabilizes the surface structure of the films.

Conclusion

In the three block copolymers (S-*b*-AF8) the investigated bulk and surface properties are essentially equal, irrespective of the chemical composition. Therefore, minimal amounts of AF8 repeat units in the fluorinated block (two repeat units in (S-*b*-AF8)8) are enough to ensure a liquid crystalline behavior and a marked hydrophobic/lipophobic character to the material. Such non-wetting properties are retained even when the fluorinated units are further diluted within the SEBS matrix (up to 90 wt% SEBS), owing to the strong segregation of the mesogenic side chains of the fluorinated polymer block to the outer surface.

The blend films can combine the low surface energy of fluorinated copolymer and the low elastic modulus of elastomer SEBS.

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