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Engineering low surface energy polymers through molecular design: synthetic routes to fluorinated polystyrene-based block copolymers

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New narrow polydisperse polystyrene-based block copolymers comprising fluorinated aromatic substituents in the side chains were synthesized following two different synthetic routes: (i) TEMPO-mediated controlled radical polymerization of fluorinated styrene monomers; (ii) A sequence of polymer modification reactions on anionically formed polystyrene-*block*-polyisoprene block copolymers. Using the former route, AB diblock and ABA triblock copolymers were obtained in which a block of polystyrene bearing a fluorocarbon chain substituent with a range of $n\mathrm{CF}_2$ groups ($n = 4$, 6, or 8) was incorporated as B block. Following the latter route, polystyrene-*block*-polyisoprene AB diblock copolymers were prepared by anionic polymerization and then modification by introduction of fluorinated tails with different numbers of CF_2 groups ($n = 6$ or 8). The thermal behavior as well as the bulk microstructure of the fluorinated block copolymers were investigated and the effect of the chemical structure on the properties was evaluated. All the samples showed a tendency to form layered mesophases in the bulk, and increasing the length of the fluorocarbon tail of the side chain enhanced the degree of order of the mesophase from a disordered smectic ($n = 4$ or 6) to ordered pseudohexagonal smectic ($n = 8$). Contact angles of block copolymer films were measured using water as the wetting medium. Values of advanced contact angles up to 130° (120° receded angles) were found which were quite constant over prolonged immersion times in water.

Introduction

Fluorination of organic compounds and polymers brings about dramatic changes in their physical properties with respect to the corresponding fully hydrogenated materials. In general, perfluorinated materials show low intramolecular and intermolecular interactions which lead to low cohesive energy and therefore to low surface energy properties.[1] Moreover, fluorinated polymers possess good thermal stability as well as great chemical stability as a consequence of the perfluorination of the macromolecular chain. Other special characteristics of fluorinated polymers are represented by a low relative permittivity,[2] a low refractive index,[3] hydrophobicity and lipophobicity,[4,5] and a low friction coefficient.[6]

Due to these unique properties, fluorinated polymers may find diverse applications in electronics,[7] optics,[8] biomaterials,[9] lubricants and surfactants,[10] and coatings;[11] for more extensive references see Ref. 12. In particular, because of the special surface behavior of fluorinated polymers, the introduction of fluorine atoms on a polymer chain may represent a strategy for producing materials to be used in low surface energy, non-stick coatings.

The surface behavior, as well as the stability of the surface properties towards reconstruction in water of fluorinated liquid-crystalline block copolymers has been the subject of recent studies.[13–16] The interplay between the microphase separation of the incompatible blocks and the liquid-crystalline organization of the mesogenic molecules may be a useful means for producing highly hydrophobic, low adhesion surfaces where the fluorinated block component of the block copolymer can be selectively and efficiently driven towards the surface of a polymer coating. The liquid-crystalline assembly of the fluorinated mesogenic side groups of the polymer can in fact result in the formation of a stable, uniformly organized array of trifluoromethyl groups at the surface of the polymer film which could be used for the production of high performance non-stick coatings. Control of polydispersity of block copolymers is a necessary prerequisite for the macromolecular engineering of polymers with suitable properties for these applications.

Bearing these ideas in mind, in this work we prepared two classes of new narrow polydisperse block copolymers bearing fluorocarbon segments in the side chains of one polymer block for orderly assembly in the bulk. We followed two different synthetic routes, the former is the controlled radical polymerization of fluorinated styrene monomers, and the latter is the polymer modification of anionically prepared polystyrene-*block*-polyisoprene block copolymers with fluorocarbon chains. In general, the adopted experimental schemes were able to provide block copolymers with a fluorinated block in which the chemical structure could be controlled, and reliably correlated with the ultimate bulk and surface properties. The relative ease of preparation can be taken as a useful requisite for scaling up the process leading to fluorinated materials for advanced applications.

Experimental section

Starting materials

1*H*,1*H*,2*H*,2*H*-Perfluorohexanol (99%), 1*H*,1*H*,2*H*,2*H*-perfluorooctanol (99%), 1*H*,1*H*,2*H*,2*H*-perfluorodecanol (99%), 4-chloromethylstyrene (95%), ethyl 4-hydroxybenzoate (99%), triphenyl phosphine, diethyl azodicarboxylate (DEAD), 2,2,6,6-tetramethylpiperidin-1-yloxy radical (TEMPO), 2-fluoro-1-methylpyridinium toluene-4-sulfonate (FMPTS), 9-borabicyclo[3.3.1]nonane

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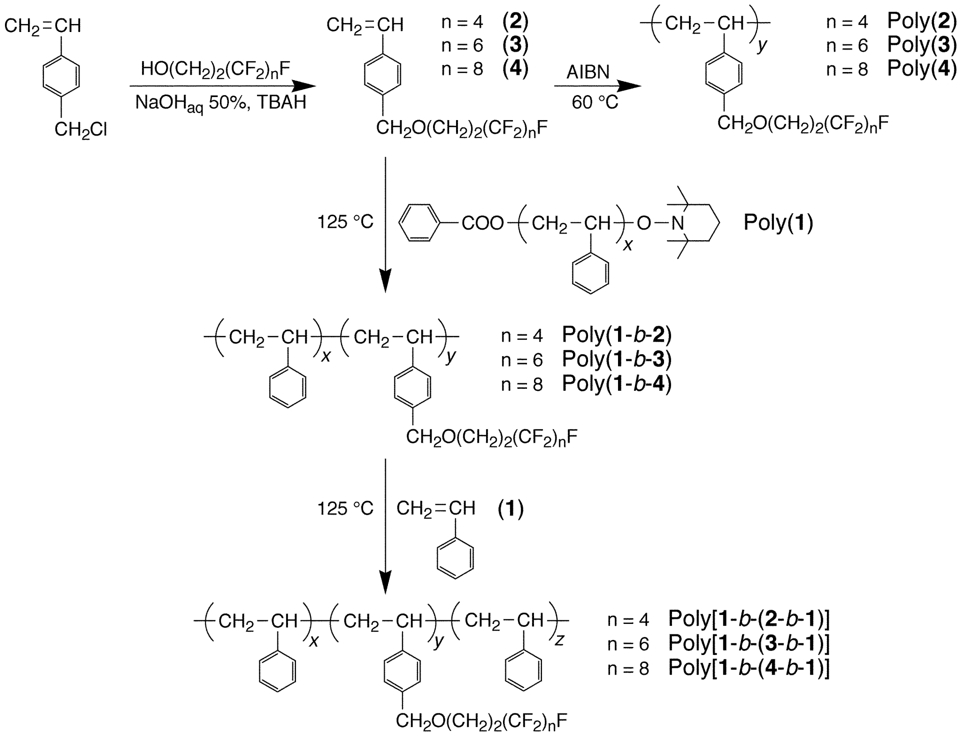


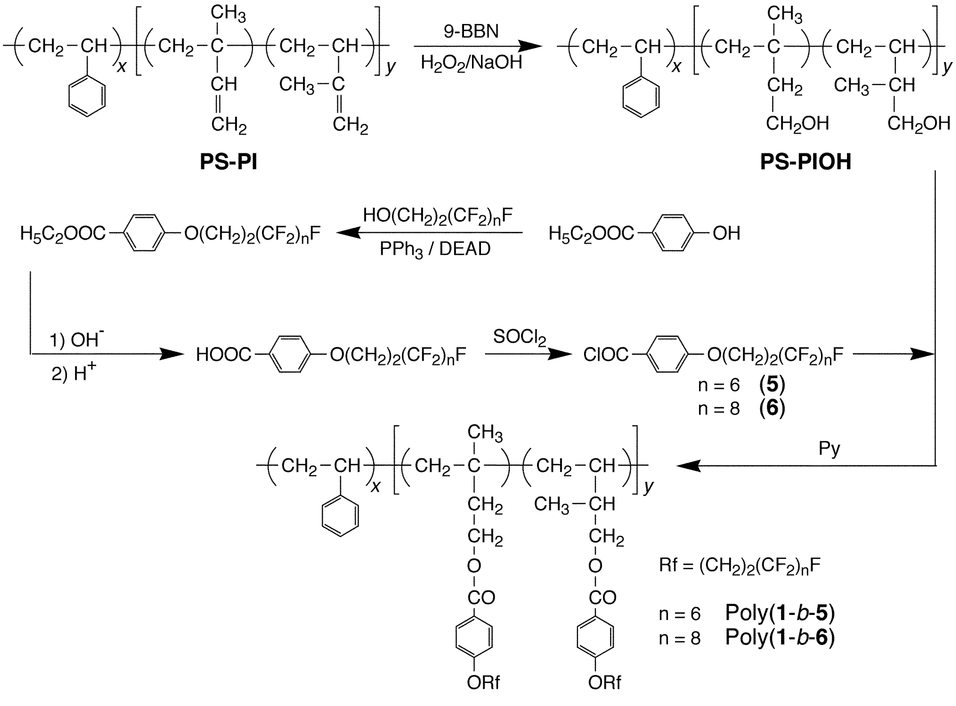
Scheme 1 Reaction scheme for the preparation of fluorinated side-chain block copolymers by controlled radical polymerization.

(9-BBN) in tetrahydrofuran solution and 1,1,2-trichlorotrifluoroethane were purchased from Aldrich and used without further purification. Styrene was washed several times with a 30% NaOH aqueous solution and then distilled over CaH_2 (bp 45 °C/30 mmHg). Benzoyl peroxide (BPO) and azobis(isobutyronitrile) (AIBN) were recrystallized from methanol. Diglyme was distilled over sodium (bp 62 °C/17 mmHg). Thionyl chloride was distilled under a nitrogen atmosphere. Pyridine was refluxed over KOH and distilled under a nitrogen atmosphere. THF was refluxed over Na/K alloy and then distilled under a nitrogen atmosphere.

The synthetic procedures for the preparation of fluorinated polystyrene-based block-copolymers are illustrated in Schemes 1 and 2. Experimental details are given below for the preparation of one representative block copolymer sample for each copolymer class.

A. Controlled radical polymerization of fluorinated styrenes (Scheme 1)

Preparation of polystyrene macroinitiator poly(1). 2.0 g (19 mmol) of freshly distilled styrene (**1**), 30 mg (13 mmol)



Scheme 2 Reaction scheme for the preparation of fluorinated side-chain block copolymers by polymer modification.

of BPO, 29 mg (19 mmol) of TEMPO and 9.0 g (32 mmol) of FMPTS were degassed by several freeze–thaw cycles in a glass vial which was then sealed off *in vacuo* and kept at 125 °C for 22 hours. The polymer poly(**1**) was purified by repeated precipitations from dichloromethane solution into methanol and finally dried *in vacuo* for several hours at room temperature (70% yield).

^{1}H-NMR ($CDCl_3$, δ in ppm from TMS): 0.23 and 0.40 (not integrable, TEMPO methyl), 1.3–2.5 (3H, CH_2CH), 6.2–7.4 (5H, aromatic).

Preparation of 4-(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)oxymethylstyrene (2). A mixture of 10.0 g (21 mmol) of 1*H*,1*H*,2*H*,2*H*-perfluorohexanol and 80 mL of 50 wt% aqueous NaOH solution was vigorously stirred at room temperature for an hour (for 1*H*,1*H*,2*H*,2*H*-perfluorodecanol stirring at 100 °C was necessary). Then 1.0 g (3 mmol) of tetrabutylammonium hydrogensulfate (TBAH) in 80 mL of CH_2Cl_2 was added. Subsequently, 6.5 g (44 mmol) of 4-chloromethylstyrene was added dropwise to the suspension. After stirring for 15 hours at 40 °C, the organic layer was separated, washed with dilute HCl, with water to neutrality and finally dried over Na_2SO_4. After evaporation of the solvent an oily residue was obtained that was purified by double elution on silica gel with hexane–ethyl acetate (30/1 v/v) as the eluent. 7.1 g of pure (**2**) (56% yield, GLC purity > 99%) as a transparent viscous liquid was obtained.

FT-IR (KBr pellet, $\bar{\nu}$ in cm^{-1}): 3060–3025 (ν C-H aromatic), 2920 (ν CH_2), 1630–1450 (ν C=C aromatic + vinyl), 1210–1030 (ν C-O-C + ν C-F), 706 (δ C-H aromatic), 666 (ω CF_2).^{1}H-NMR ($CDCl_3$, δ in ppm from TMS): 2.4 (2H, CH_2CF_2), 3.7 (2H, OCH_2), 4.4 (2H, $PhCH_2O$), 5.2 and 5.7 (2H, CH_2=), 6.7 (1H, CH=), 7.2–7.5 (4H, aromatic). ^{19}F-NMR ($CDCl_3$, δ in ppm from CF_3CO_2H): −6 (3F, CF_3), −38 (2F, CH_2CF_2), −49 (2F, CF_2), −51 (2F, CF_2). Anal. ($C_{15}H_{13}F_9O$): % calcd. C 47.37, H 3.42, F 45.00; % found C 47.51, H 3.29, F 45.1.

Preparation of AB diblock copolymer poly1-*block*-poly2. 100 mg of polystyrene macroinitiator poly(**1**) and 1.0 g of fluorinated monomer (**2**) were degassed by several freeze–thaw cycles in a glass vial which was then sealed off *in vacuo* and kept at 125 °C for 24 hours. The diblock copolymer poly**1**-*block*-poly**2** formed was purified by repeated precipitations from chloroform solution into methanol and extraction with boiling acetone and finally dried *in vacuo* for several hours at room temperature (70% yield).

FT-IR (film on KBr, $\bar{\nu}$ in cm^{-1}): 3050–3020 (ν C-H aromatic), 2930 (ν CH_2), 1620–1450 (ν C=C aromatic), 1250–1030 (ν C–O–C + ν C–F), 702 (δ C–H aromatic), 658 (ω CF_2).^{1}H-NMR ($CDCl_3$, δ in ppm from TMS): 1.3–2.7 (6.6H, CH_2CH + CH_2CF_2), 3.8 (2.0H, OCH_2), 4.5 (2.0H, $PhCH_2O$), 6.3–7.6 (4.7H, aromatic).^{19}F-NMR ($CDCl_3$, δ in ppm from CF_3CO_2H): −6 (3F, CF_3), −38 (2F, CH_2CF_2), −48 (2F, CF_2), −52 (2F, CF_2).

Preparation of ABA triblock copolymer poly1-*block*-poly2-*block*-poly1. 100 mg of poly**1**-*block*-poly**2** diblock copolymer and 1.5 mL of freshly distilled styrene (**1**) were degassed by several freeze–thaw cycles in a glass vial which was then sealed off *in vacuo* and kept at 125 °C for 3 hours. The triblock copolymer poly**1**-*block*-poly**2**-*block*-poly**1** formed was purified by repeated precipitations from chloroform solution into methanol and extraction with boiling acetone and finally dried *in vacuo* for several hours at room temperature (70% yield).

FT-IR (film on KBr, $\bar{\nu}$ in cm^{-1}): 3050–3020 (ν C–H aromatic), 2930 (ν CH_2), 1620–1450 (ν C=C aromatic), 1250–1030 (ν C-O-C + ν C-F), 702 (δ C-H aromatic), 658 (ω CF_2).^{1}H-NMR ($CDCl_3$, δ in ppm from TMS): 1.3–2.7 (16.2H, CH_2CH + CH_2CF_2), 3.8 (2.0H, OCH_2), 4.5 (2.0H, $PhCH_2O$), 6.3–7.6 (22.6H, aromatic).^{19}F-NMR ($CDCl_3$, δ in ppm from CF_3CO_2H): −6 (3F, CF_3), −38 (2F, CH_2CF_2), −48 (2F, CF_2), −52 (2F, CF_2).

Preparation of homopolymers. In a typical homopolymerization experiment, 0.5 g of fluorinated monomer (**2**), 5 mg of AIBN and 1 mL of anhydrous benzene were degassed by several freeze–thaw cycles in a glass vial that was then sealed off *in vacuo*. The polymerization was carried out at 60 °C for 24 hours. The polymer poly(**2**) was purified by repeated precipitations from chloroform solution into methanol and finally dried *in vacuo* for several hours at room temperature (55% yield).

FT-IR (film on KBr, $\bar{\nu}$ in cm^{-1}): 3050–3020 (ν C–H aromatic), 2930 (ν CH_2), 1620–1450 (ν C=C aromatic), 1250–1030 (ν C-O-C + ν C-F), 708 (δ C–H aromatic), 658 (δ CF_2). ^{1}H-NMR ($CDCl_3$, δ in ppm from TMS): 1.3–2.7 (5H, CH_2CH + CH_2CF_2), 3.8 (2H, OCH_2), 4.5 (2H, $PhCH_2O$), 6.3–7.6 (4H, aromatic).

B. Polymer modification of block copolymers (Scheme 2)

Anionic copolymerization of styrene and isoprene. Polystyrene-*block*-polyisoprene block copolymers **PS-PI**a (x = 400, y = 150) and **PS-PI**b (x = 640, y = 115) were synthesized by living anionic polymerization according to a literature procedure.[17]

Hydroboration of polystyrene-*block*-polyisoprene. 3.0 g (9 mmol of vinyl and methylvinyl groups) of **PS-PI**a was vacuum dried overnight at 50 °C in a flask equipped with a septum. After cooling, 150 mL of freshly distilled THF that had been degassed by repeated freeze–pump–N_2 purge cycles was transferred into the flask *via* a cannula. The solution was cooled to −15 °C and 22 mL (11 mmol) of a 0.5 M THF solution of 9-BBN, which had previously been degassed by repeated freeze–pump–N_2 purge cycles, was added. The solution was stirred for 24 hours at room temperature and then cooled to −25 °C before 2 mL of anhydrous methanol was injected into the solution. The solution was stirred for an additional 30 min and 2 mL (39 mmol) of 6 M NaOH (purged with N_2 for 30 min) was added. After an additional 10 min, 4 mL of 30% H_2O_2 (purged with N_2 for 30 min) was added. Precipitation occurred and stirring became difficult. After 2 additional hours at −25 °C, the temperature of the solution was slowly raised to room temperature. The suspension was stirred for 30 min and then heated to 55 °C for 1 hour to form a homogeneous solution. After cooling to room temperature, the solution phase separated. The lower layer was frozen in a liquid N_2–propan-2-ol bath and the upper organic layer was slowly poured into 800 mL of 0.25 M NaOH aqueous solution. The polymer precipitated was filtered, washed with 0.25 M NaOH aqueous solution, and dissolved in 60 mL of THF. The polymer solution was then reprecipitated into 0.25 M NaOH aqueous solution and stirred overnight. The polymer was reprecipitated three more times. Finally the polymer **PS-PIOH**a was washed with water and dried under vacuum (95% yield). FT-IR (KBr, $\bar{\nu}$ in cm^{-1}): 3500 (broad, ν O–H), 2980–2840 (ν CH_2), 1680–1450 (ν C=C aromatic), 1300–1100 (ν C–O–C), 710 (δ C–H aromatic).

Synthesis of semifluorinated acyl chlorides. A solution of 4.0 g (0.048 mol) of DEAD in 8 mL of dry diethyl ether was slowly added at room temperature under vigorous stirring to a mixture of 7.0 g (0.042 mol) of ethyl 4-hydroxybenzoate, 11.6 g (0.042 mol) and triphenyl phosphine, 20.0 g (0.043 mol) of 1*H*,1*H*,2*H*,2*H*-perfluorodecanol and 500 mL of dry diethyl ether. The reaction mixture was stirred at room temperature for 72 hours. The precipitate was filtered off and the solvent evaporated under vacuum. The crude product was purified by silica gel column chromatography with ethyl acetate–hexane (3 : 1 v/v) as the eluent. 15.6 g (25% yield) of pure ethyl 4-(1*H*,1*H*,2*H*,2*H*-perfluorodecyloxy)benzoate as a white solid was obtained.

^{1}H-NMR ($CDCl_3$, δ in ppm from TMS): 1.4 (3H, CH_3), 2.6 (2H, CH_2CF_2), 4.3 (4H, $2CH_2$), 6.9 (2H, aromatic), 8.0 (2H, aromatic).

A mixture of 7.0 g (0.011 mmol) of ethyl 4-(1*H*,1*H*,2*H*,2*H*-perfluorodecyloxy)benzoate, 0.9 g (0.017 mmol) of KOH, 80 mL of water and 110 mL of ethanol was refluxed for 5 hours. The reaction solution was then acidified with 37% HCl and extracted with CH_2Cl_2. The organic solution was finally washed with 5% $NaHCO_3$, 37% HCl and water. After evaporation of the solvent, 6.2 g (97% yield) of 4-(1*H*,1*H*,2*H*,2*H*-perfluorodecyloxy)benzoic acid was obtained (mp 201–204 °C). ^{1}H-NMR (DMSO-d$_6$, δ in ppm from TMS): 2.6 (2H, CH_2CF_2), 4.3 (2H, CH_2O), 7.0 (2H, aromatic), 8.0 (2H, aromatic). Finally, a mixture of 1.5 g (2.6 mmol) of 4-(1*H*,1*H*,2*H*,2*H*-perfluorodecyloxy)benzoic acid and 5 mL (42 mmol) of $SOCl_2$ was stirred under nitrogen atmosphere at 40 °C for 1 hour and then refluxed for 4 hours. The excess $SOCl_2$ was stripped off under vacuum and 1.5 g (96% yield) of 4-(1*H*,1*H*,2*H*,2*H*-perfluorodecyloxy)benzoyl chloride (**6**) was obtained (mp 70–72 °C). FT-IR (KBr pellet, $\bar{\nu}$ in cm^{-1}): 3100–3050 (ν C–H aromatic), 2980–2840 (ν CH_2), 1780 (ν C=O), 1680–1450 (ν C=C aromatic), 1240–1090 (ν C-O-C + ν C-F), 648 (ω CF_2). ^{1}H-NMR ($CDCl_3$, δ in ppm from TMS): 2.6 (2H, CH_2CF_2), 4.3 (2H, CH_2O), 7.0 (2H, aromatic), 8.0 (2H, aromatic). Anal ($C_{17}H_8ClF_{17}O_2$): % calcd. C 33.85, H 1.33, Cl 5.89, F 53.61; % found C 33.72, H 1.39, Cl 76.05, F 53.9.

Side-chain esterification of block copolymers. 0.3 g (0.8 mmol of CH_2OH groups) of block copolymer **PS-PIOH**a was dissolved in 3 mL of anhydrous THF and 0.08 g (1 mmol) of pyridine. Then a solution of 0.6 g (1 mmol) of (**6**) in 2 mL of anhydrous THF was slowly injected through a rubber septum into the reaction flask. The reaction mixture was kept at 50 °C for 24 hours, after which 1 mL of anhydrous methanol was injected into the flask to convert the excess acid chloride to ester. The polymer solution was poured into a large amount of a methanol–water (1 : 1 v/v) solution. The polymer poly**1**-*block*-poly**6** precipitate was filtered and dissolved in THF and reprecipitated into methanol three times. Finally the polymer was dried overnight at 60 °C in a vacuum oven (90% yield).

FT-IR (film on KBr, $\bar{\nu}$ in cm^{-1}): 3100–3050 (ν C–H aromatic), 2980–2840 (ν CH_2), 1716 (ν C=O), 1680–1450 (ν C=C aromatic), 1250–1040 (ν C–O–C + ν C–F), 710 (δ C–H aromatic), 648 (ω CF_2).^{1}H-NMR ($CDCl_3$, δ in ppm from TMS): 0.6–2.4 (15.0H, aliphatic), 2.5–2.6 (2.0H, CH_2CF_2), 3.8–4.4 (4.0H, $COOCH_2$ + $PhCH_2O$ + CH_2OH (unreacted)), 6.3–7.2 (13.3H, styrenic), 7.4–8.0 (4.0H, benzoate).

Characterization. ^{1}H-NMR and ^{19}F-NMR spectra were recorded with Varian Gemini 200 and Varian Gemini VXR 300 spectrometers, respectively. Either deuterated chloroform or deuterated chloroform–1,1,2-trichlorotrifluoroethane (2 : 1 v/v) was used as a solvent. Infrared spectra were taken with a Perkin Elmer 1600 Series FTIR spectrophotometer. Spectra were recorded on KBr pellets or on polymer films cast from solution on KBr plate.

Gel permeation chromatography (GPC) was carried out using a Jasco PU-1580 liquid chromatograph equipped with four PL gel 5 mm Mixed-C columns, a Jasco 830-RI refractive index detector and a Perkin Elmer LC75 UV detector. Molecular weights were quoted with respect to monodisperse polystyrene standards (M_n = 500–120 000). Chloroform was used as solvent and the GPC operated at 1 mL min^{-1}. 1 wt% polymer solution volumes of 20 μl were used for GPC measurements.

Differential scanning calorimetry (DSC) measurements were performed with a Mettler DSC-30 instrument. Samples of 5–15 mg were used with 5–20 °C min^{-1} scan rate. The phase transition temperatures of the polymers were taken as the maximum temperature in the DSC enthalpic peaks. The glass transition temperature was taken as the half-devitrification temperature.

Wide angle X-ray diffraction (WAXD) patterns were obtained at the Cornell High Energy Synchrotron Source (CHESS) (λ = 1.55 Å) using a charge coupled detector. The X-ray intensity and the distance between the sample and the detector were adjusted according to experimental needs. Films of thickness ≈1 mm cast from 5 wt% trifluorotoluene solutions were analyzed.

Contact angles were measured using a NRL Contact Angle Goniometer Model 100-00 (Ramé-Hart Inc.) at 20 °C. The contact angle values were averaged over four measurements. The advanced contact angle was read by injecting 4 μL liquid drop. The receded contact angle was measured by removing 3 μL of liquid from the droplet. Single-layer polymer films were prepared by casting 5 wt% trifluorotoluene polymer solutions on glass slides which were allowed to evaporate slowly for a few days and then annealed for 24 hours in a vacuum oven at 30 °C (poly**1**-*block*-poly**2** to poly**1**-*block*-poly**4**) or at 110 °C (poly**1**-*block*-poly**5** and poly**1**-*block*-poly**6**). Double-layer polymer films were prepared by casting a top layer of a 2 wt% fluorinated block copolymer trifluorotoluene solution onto a bottom layer cast from a 3 wt% SEBS (styrene-ethylene-butadiene rubber, Kraton G1652M from Shell) $CHCl_3$ solution. The solvent was allowed to evaporate slowly for a few days and subsequently the film was annealed at 110 °C for 24 hours in a vacuum oven.

Results and discussion

Synthesis by controlled radical polymerization

The TEMPO-mediated controlled radical polymerization (CRP) was chosen to prepare the first class of fluorinated polystyrene-based block copolymers. This method involves the combined use of a conventional free radical initiator, such as benzoyl peroxide (BPO) or azobis(isobutyronitrile) (AIBN), and a stable free radical such as 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO).[18–22] The latter functions as a reversible capping agent of the active site on the growing polymer chain and regulates the growth of the chain. The molar mass increase is linear with conversion and polymers with narrow polydispersities can be obtained. Furthermore, due to the "living character" of CRP, block copolymers can be prepared by sequential polymerization of different monomers. However, the difficulty in the reversible dissociation of the polymer chain-TEMPO adduct restricts the versatility of the method. Typical monomers that are polymerized by TEMPO-mediated CRP are styrene and its derivatives.[23–25] More recently, this technique has been successfully extended to alkyl methacrylates[26] and other vinyl monomers, such as vinylpyridine.[27] 2-Fluoro-1-methylpyridinium toluene-4-sulfonate (FMPTS) can be used in combination with TEMPO to provide faster reaction rates than TEMPO alone and to reduce the self-polymerization of styrene.[28,29] The organic acid would decrease the concentration of the nitroxide radicals, thus increasing the number of active growing polymer chains to be involved in the propagation step.

In this work, styrene (**1**) and 4-(1*H*,1*H*,2*H*,2*H*-perfluoroalkyl)oxymethylstyrenes (**2**)–(**4**) were selected for the preparation of fluorinated polystyrene-based block copolymers (Scheme 1). The fluorinated monomers were synthesized by a phase-transfer catalyzed etherification of fluorinated alcohols with 4-chloromethylstyrene in the presence of tetrabutylammonium hydrogensulfate (TBAH) as a phase transfer catalyst, by following a modification of a literature procedure.[6]

Table 1 Characterization data of block polymers from CRP

Sample	$M_n{}^a$ /kg mol^{-1}	$M_w/M_n{}^a$	Compn.$_{FB}{}^b$ (wt %)	Degree of polymerisation ^{b} x	y	z
Poly(**1**)	4	1.10	0	40	–	–
Poly**1**-*block*-poly**2**	18	1.30	88	40	75	–
Poly**1**-*block*-poly**3**	18	1.28	87	40	60	–
Poly**1**-*block*-poly**4**	n.d.	n.d.	92	40	110	–
Poly**1**-*block*-poly**2**-*block*-poly**1**	110	1.37	50	40	75	240
Poly**1**-*block*-poly**3**-*block*-poly**1**	65	1.35	49	40	60	260
Poly**1**-*block*-poly**4**-*block*-poly**1**	140	1.40	19	40	110	1270

[a]Determined by GPC in chloroform, with PS calibration. [b]Weight composition in fluorinated block (FB) and degree of polymerization, determined by ^{1}H-NMR.

In fact, it was necessary to preform the fluorinated alkoxide by reaction with a 50% aqueous NaOH solution prior to nucleophilic substitution of 4-chloromethylstyrene. 1*H*,1*H*,2*H*,2*H*-Perfluorohexanol and 1*H*,1*H*,2*H*,2*H*-perfluorooctanol were kept under vigorous stirring at room temperature, whereas 1*H*,1*H*,2*H*,2*H*-perfluorodecanol was reacted at 100 °C for two hours in order to achieve quantitative formation of the corresponding alkoxide. The purification of the reaction products was complicated by the presence of unreacted 4-chloromethylstyrene and distyryl by-products, which had to be carefully separated from the monomers in order to avoid cross-linking side-reaction during the polymerization.

Monomers (**2**)–(**4**) were used for the preparation of AB diblock and ABA triblock copolymers composed of a polystyrene block (block A) and a fluorinated polystyrene block (block B) (Scheme 1). This was achieved by using a "living" TEMPO-terminated polystyrene poly(**1**) as one macroinitiator (M_n = 4 000, x = 40, and M_w/M_n = 1.10) to prepare diblock copolymers poly**1**-*block*-poly**2** to poly**1**-*block*-poly**4** that in turn were used as TEMPO-terminated "living" block copolymers to polymerize styrene, thereby yielding the corresponding triblock copolymers, poly**1**-*block*-poly**2**-*block*-poly**1** to poly**1**-*block*-poly**4**-*block*-poly**1** (Scheme 1).

The polystyrene macroinitiator poly(**1**) was prepared in bulk at 125 °C in the presence of the BPO–TEMPO–FMPTS system. The polymerization of the fluorinated styrenes was performed at 125 °C in either bulk (liquid monomers (**2**) and (**3**)) or in diglyme solution (solid monomer (**4**)).

Block copolymers poly**1**-*block*-poly**2** and poly**1**-*block*-poly**3** showed an increased molar mass with respect to the macroinitiator poly(**1**) and a relatively low polydispersity ($M_w/M_n \approx$ 1.3) consistent with the occurrence of a CRP process (Table 1). They also appeared free from residual unreacted macroinitiator (see GPC trace in Fig. 1). Poly**1**-*block*-poly**4** could not be analyzed by GPC because of its limited solubility in common organic solvents for analysis. The actual copolymer structure was confirmed by ^{19}F-NMR and ^{1}H-NMR analyses. The ^{1}H-NMR data were also used to evaluate the copolymer composition and number average molar mass.

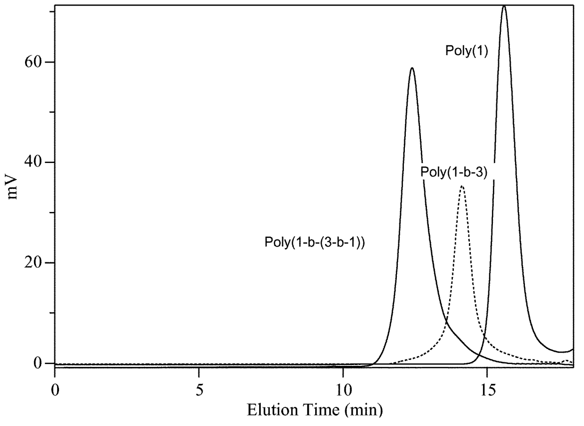


Fig. 1 GPC traces of the polystyrene macroinitiator, poly(**1**), and the derived diblock and triblock copolymers, poly**1**-*block*-poly**3** and poly**1**-*block*-poly**3**-*block*-poly**1**, respectively.

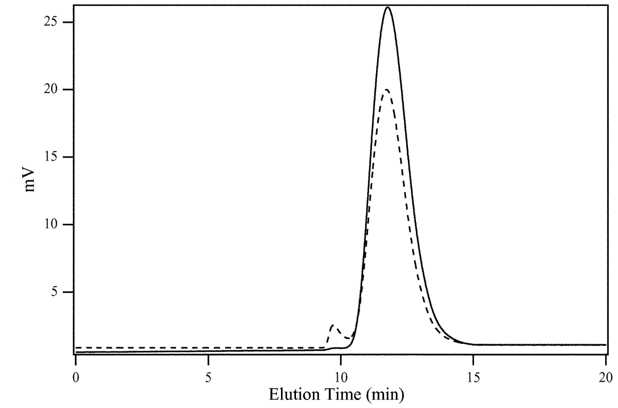


Fig. 2 GPC traces of triblock copolymer poly**1**-*block*-poly**4**-*block*-poly**1** before (dashed line) and after (solid line) extraction with boiling acetone.

Relatively narrow polydispersities were also exhibited by the triblock copolymers ($M_w/M_n \approx$ 1.4). One typical GPC curve is reported in Fig. 1. Minor amounts of "dead" polystyrene were selectively removed from triblock copolymers by extraction with boiling acetone (Fig. 2). All these findings proved that CRP was indeed successful in preparing different architectures of block copolymers with controlled block length ratios and narrow polydispersities of block lengths.

Homopolymers poly(**2**) to poly(**4**) were easily prepared by conventional free radical initiation in the presence of AIBN as a radical initiator at 60 °C to be used as model polymers in terms of both molecular characteristics and bulk properties (Table 2).

Synthesis by polymer modification

The anionic block copolymerization of styrene and isoprene followed by polymer chemical modification was the chosen method to prepare a second class of fluorinated side-chain block copolymers with narrow molar mass distributions. The overall synthetic procedure is outlined in Scheme 2. Polystyrene-*block*-polyisoprene **PS-PI** parent block copolymers were

Table 2 Characterization data of homopolymers from free radical polymerization (AIBN)

Sample	$M_n{}^a$ /kg mol^{-1}	$M_w/M_n{}^a$
Poly(**2**)	21	2.5
Poly(**3**)	15	2.5
Poly(**4**)	n.d.	n.d.

[a]By GPC in chloroform, with PS calibration.

Table 3 Characterization data of block copolymers from polymer modification

Sample	M_n[a] kg mol^{-1}	M_w/ M_n[a]	% Side chain modification[b]	Compn.$_{FB}$[c] (wt%)
PS-PIOHa	54	1.10	100	–
PS-PIOHb	83	1.10	100	–
Poly**1**-*block*-poly**5**a	64	1.12	96	64
Poly**1**-*block*-**6**a	n.d.	n.d.	94	69
Poly**1**-*block*-poly**6**b	82	1.12	95	54

[a] Determined by GPC in THF, with PS calibration. [b] By ^{1}H-NMR. [c] Weight composition in fluorinated block (FB), determined by ^{1}H-NMR.

prepared by anionic polymerization of styrene and isoprene according to a well established procedure.[17] Two copolymer samples were prepared in which the polystyrene–polyisoprene block length ratio was 40 000 : 10 000 in **PS-PI**a and 65 000 : 8 000 in **PS-PI**b. In each case the polydispersity was rather low (M_w/M_n = 1.10). The 1,2 to 3,4 isoprene units molar ratio was 40 : 60 as determined by ^{1}H-NMR.

PS-PI block copolymers were then modified, prior to attachment of fluorinated side groups, by a hydroboration reaction of the side-chain double bonds with 9-BBN.[30] Hydrolysis with H_2O_2–OH^- of the borane intermediate led to copolymers **PS-PIOH** containing hydroxy terminated side chains. Finally, the attachment of the semifluorinated side groups was carried out by esterification with a fluorinated acid chloride **5** or **6** in anhydrous pyridine. The fluorinated acid chlorides were synthesized from ethyl 4-hydroxybenzoate after a Mitsunobu reaction[31] with the fluorinated alcohol of choice (Scheme 2).

In each modification step the extent of substitution of the isoprene side chain was practically quantitative (Table 3). In particular, the FT-IR spectra of the final modified block copolymers showed that the hydroxy absorption of **PS-PIOH** in the 3500 cm^{-1} region had completely vanished with the concurrent appearance of very prominent ester group absorbances at 1716 cm^{-1} and 1195 cm^{-1}. The attachment of the fluorinated side substituent was confirmed by ^{19}F-NMR and ^{1}H-NMR analyses, which also permitted evaluation of the block copolymer composition (Table 3).

Three modified block copolymers were prepared bearing two different fluorinated alkyl tails, poly**1**-*block*-poly**5**a with a perfluorooctyl tail and poly**1**-*block*-poly**6**a-b with a perfluorodecyl tail respectively. Poly**1**-*block*-poly**6**a and poly**1**-*block*-poly**6**b possessed different block length ratios (Table 3).

The GPC traces of the hydroxylated block copolymer **PS-PIOH**a and the respective fluorinated block copolymers poly**1**-*block*-poly**5**a and poly**1**-*block*-poly**6**a are reported in Fig. 3. Solution aggregation of the fluorinated blocks was observed for the poly**1**-*block*-poly**6**a sample that contained a greater proportion of longer perfluorocarbon side-chain units. In this copolymer, the higher molar mass GPC peak was attributed to the formation of micelles in solution while the lower molar mass peak was assigned to isolated block copolymer macromolecules (Fig. 3). This was in agreement with what is reported in the literature for polystyrene-*block*-polyisoprene block copolymers having different fluoroalkyl tails in the side chains.[16]

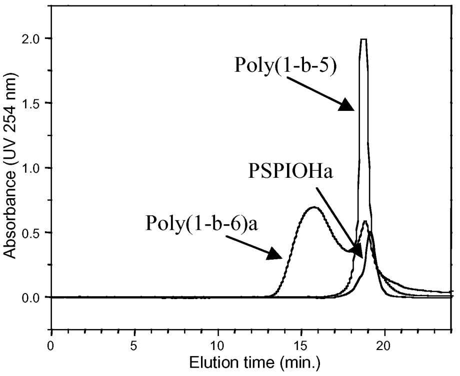


Fig. 3 GPC traces of hydroxylated block copolymer **PS-PIOH**a and derived diblock copolymers poly**1**-*block*-poly**5**a and poly**1**-*block*-poly**6**a.

Following this route, the modification with fluorinated moieties of the side chains of the isoprene block enabled the creation of fluorinated AB block copolymers in which the block length ratio and the narrow polydispersity of the starting copolymer were retained.

Thermal studies of fluorinated block copolymers

The phase transition behavior of the block copolymers was investigated by DSC and the results are summarized in Table 4. All the samples were first heated to a higher temperature than the glass transition temperature (T_g), or the isotropization temperature (T_i) when detected, in order to eliminate effects of the thermal history on sample transitions. The DSC data collected in the table were taken from the second heating scan.

Homopolymers poly(**2**) to poly(**4**) showed a glass transition temperature that increased with increasing length of the fluorocarbon group from 14 °C to 50 °C. The glass transition was detected as a weak increase in the heat capacity which might be explained by the low mobility of the fluorinated segments that are assembled in an organized structure. Poly(**4**) also underwent a first order transition at 67 °C because of an intermediate phase transition between mesophases (see below). In no case was isotropization of the mesophase detectable by DSC. Optical microscopy observations revealed weakly birefringent textures but no definite isotropization temperature.

The DSC curves of diblock copolymers poly**1**-*block*-poly**2** to poly**1**-*block*-poly**4** displayed the glass transition of the fluorinated block as a weak increase in heat capacity (T_g = 17–52 °C), but did not show the glass transition of the polystyrene block, probably due to the low styrene content. Instead, triblock copolymers poly**1**-*block*-poly**2**-*block*-poly**1** to poly**1**-*block*-poly**4**-*block*-poly**1** exhibited only the glass transition of the polystyrene block at 106 °C but not the glass transition

Table 4 Thermal (by DSC) and structural (by WAXD) data of fluorinated polymers

Sample	T_g[a] / °C	T_g[b] / °C	T_i[a] / °C	ΔH_i[a] / J g^{-1}	d[c] (±0.3 Å)	L[d] (±1 Å)
Poly(**1**)	–	85	–	–	–	–
Poly(**2**)	14	–	n.d.	n.d.	22	13
Poly(**3**)	17	–	n.d.	n.d.	26	16
Poly(**4**)	50	–	n.d.[e]	n.d.[e]	35	18
Poly**1**-*block*-poly**2**	17	n.d.	n.d.	n.d.	22	13
Poly**1**-*block*-poly**3**	17	n.d.	n.d.	n.d.	26	16
Poly**1**-*block*-poly**4**	52	n.d.	n.d.[f]	n.d.[f]	34	18
Poly**1**-*block*-poly**2**-*block*-poly**1**	n.d.	106	n.d.	n.d.	21	13
Poly**1**-*block*-poly**3**-*block*-poly**1**	n.d.	106	n.d.	n.d.	25	16
Poly**1**-*block*-poly**4**-*block*-poly**1**	n.d.	106	n.d.	n.d.	33	18
Poly**1**-*block*-poly**5**a	−32	101	207	1.1	34	21
Poly**1**-*block*-poly**6**a	−20	100	210	0.4	40	23
Poly**1**-*block*-poly**6**b	−20	100	210	0.4	40	23

[a] Glass transition temperature and isotropization temperature (and enthalpy) of the fluorinated block. [b] Glass transition temperature of the polystyrene block. [c] Measured smectic interlayer spacing. [d] Calculated length of the polymer side chain. [e] Transition between mesophases at 67 °C (ΔH = 1.5 J g^{-1}). [f] Transition between mesophases at 68 °C (ΔH = 0.7 J g^{-1}).

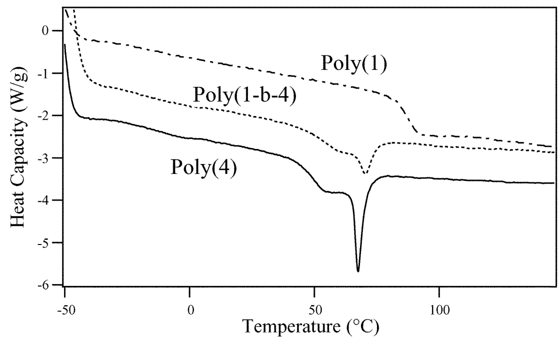


Fig. 4 DSC traces of homopolymer poly(**1**), derived diblock copolymer poly**1**-*block*-poly**4** and homopolymer poly(**4**) (10 °C min^{-1}).

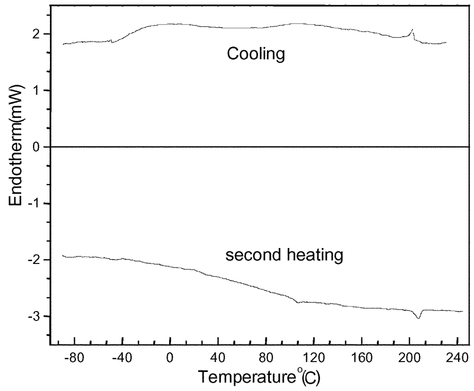


Fig. 5 DSC traces of diblock copolymer poly**1**-*block*-poly**5**a (10 °C min^{-1}).

of the fluorinated block due to the high molar content of styrene. Poly**1**-*block*-poly**4** and poly**1**-*block*-poly**4**-*block*-poly**1** also formed mesophases quite similar to the respective homopolymer poly(**4**). Representative DSC traces are shown in Fig. 4.

The side-chain modified block copolymers poly**1**-*block*-poly**5**, poly**1**-*block*-poly**6**a-b were found to have a glass transition due to the polystyrene block at about 100 °C (detected on heating) and a glass transition for the fluorinated block in the range −30 to −20 °C (detected on cooling) as is shown in Fig. 5. Furthermore, they gave rise to a broad mesophase up to a T_i of 210 °C.

These observations strongly suggested that the chemically incompatible polymer blocks were microphase separated in each block copolymer architecture, whether AB diblock or ABA triblock. The mesophase order of the fluorinated side groups was not disrupted in the separated domains. These findings were confirmed by a detailed investigation of the morphology of the block copolymers by small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). This topic will be the subject of a forthcoming paper.

X-Ray studies of fluorinated block copolymers

Wide-angle X-ray diffraction measurements were carried out at room temperature on film specimens aimed at gaining further information on the bulk microstructure of the synthesized polymers.

All the polymers exhibited one wide-angle reflection (periodicity of about 5 Å) and one or more low-angle reflections pointing to the existence of a smectic mesophase.[32] This was formed by the assembly of the side groups in a two-dimensional structure probably driven by the separation at the molecular level of their different chemical constituents. The smectic layer spacings (d) measured and the lengths (L) of the side groups calculated by molecular models in the extended planar conformation with the fluorinated tail in a twisted zig-zag (helical) conformation of span p = 2.59 Å[33] are listed in Table 4. A comparison between d and L suggested that the side groups were organized in a double layer structure in each polymer.

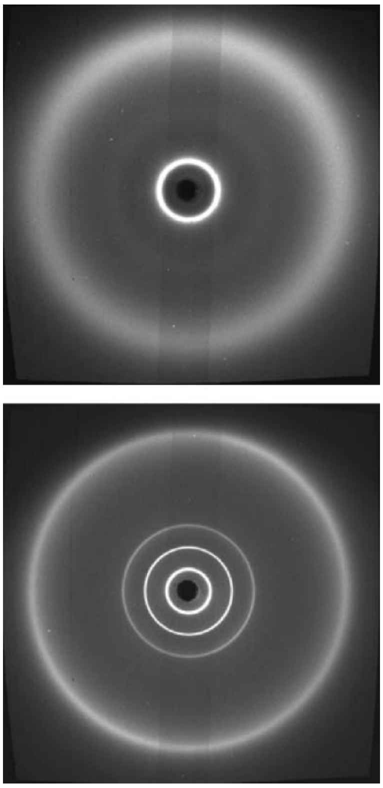


Fig. 6 WAXD patterns at 25 °C of homopolymers poly(**3**) (top) and poly(**4**) (bottom).

Homopolymers poly(**2**) through poly(**4**) were taken as simple model polymers of the fluorinated block in the corresponding block copolymers. The X-ray diffraction patterns at room temperature of poly(**3**) and poly(**4**) are shown in Fig. 6. Poly(**2**) and poly(**3**) containing shorter fluorocarbon tails, $(CF_2)_4$ and $(CF_2)_6$ respectively, formed a disordered smectic mesophase (Fig. 6 top). On the other hand, poly(**4**) containing a longer $(CF_2)_8$ tail gave rise to an ordered (pseudo-hexagonal) smectic mesophase (Fig. 6 bottom). For this last homopolymer the detection of up to 4 orders of sharp low-angle reflections evidenced the existence of a long range correlation between the smectic layers, which modulated the electronic density along the layer normal.[32]

The diblock and triblock copolymers displayed X-ray diffraction patterns similar to their corresponding homopolymers, as illustrated in Fig. 7. No significant changes of the smectic layer spacing were detected in the copolymers (d = 34 Å for poly**1**-*block*-poly**4**, d = 33 Å for poly**1**-*block*-poly**4**-*block*-poly**1**), which also confirmed that the block copolymers were phase separated and gave rise to the same kind of smectic mesophase as the respective homopolymers. In the latter block copolymer, a diffuse halo was also detected at intermediate diffraction angles originating from the amorphous polystyrene block (periodicity of 10–11 Å) (Fig. 7 bottom).

Representative X-ray patterns of block copolymers poly**1**-*block*-poly**5**a and poly**1**-*block*-poly**6**a are shown in Fig. 8. The former presented a disordered smectic mesophase (d = 34 Å), while the latter formed a pseudo-hexagonal smectic mesophase (d = 40 Å). Therefore, the lengthening of the fluorinated tail from $(CF_2)_6$ to $(CF_2)_8$ segments enhanced the order of the mesophase by favoring in-plane correlations of the side chains.

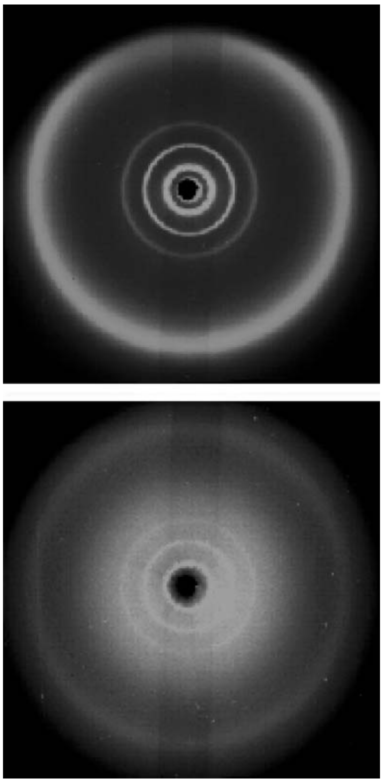


Fig. 7 WAXD patterns at 25 °C of diblock copolymer poly**1**-*block*-poly**4** (top) and triblock poly**1**-*block*-poly**4**-*block*-poly**1** copolymer (bottom).

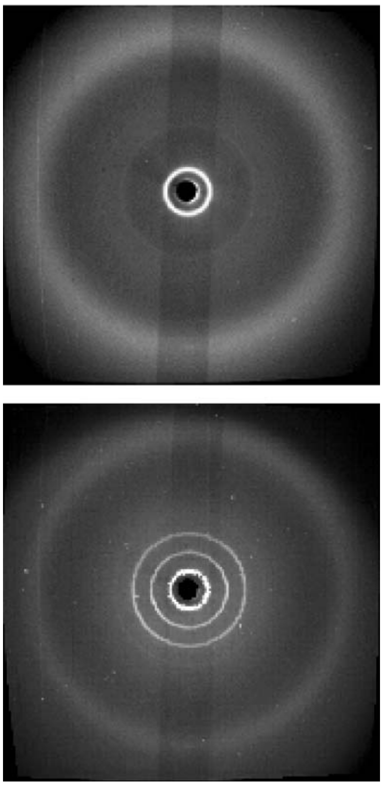


Fig. 8 WAXD patterns at 25 °C of diblock copolymers poly**1**-*block*-poly**5**a (top) and poly**1**-*block*-poly**6**a (bottom).

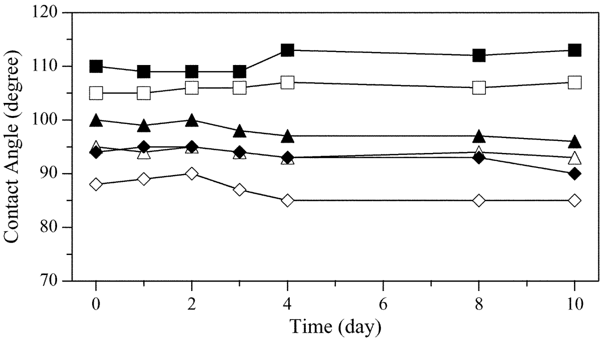


Fig. 9 Advanced (filled symbols) and receded (open symbols) contact angles (±3°) of films from block copolymers poly**1**-*block*-poly**2** (◆), poly**1**-*block*-poly**3** (▲), and poly**1**-*block*-poly**4** (■) as a function of immersion time in water.

Surface properties of block copolymer films

In order to assess the wettability of the surface of the polymer films and their stability towards reconstruction upon immersion in water, measurements of advanced and receded contact angles with water as the wetting liquid were carried out as a function of the immersion time in water. The films were prepared as single-layer films by casting from dilute (2–5 wt%) polymer solutions onto glass slides. Double-layer films of copolymers poly**1**-*block*-poly**5**a and poly**1**-*block*-poly**6**a were prepared by casting a top-layer of fluorinated block copolymer onto a SEBS film bottom-layer. This was meant to check for the possibility of achieving surface performance comparable to pure block copolymer films, by using polymer films with a smaller amount of fluorinated material.

Dry films from block copolymers poly**1**-*block*-poly**2** to poly**1**-*block*-poly**4** showed values of the advanced contact angle in the range 94–111° that depended on the length of the fluorinated side-chain tail (Fig. 9). Introduction of the longer tails resulted in higher contact angles. This was indicative of a relatively high hydrophobicity of the polymer film surfaces. In all cases the receded contact angles were lower by 5–6°, which also pointed to the formation of quite stable fluorinated surfaces. Both advanced and receded contact angles remained essentially unaffected over a 10 day exposure to water.

Single-layer dry films of poly**1**-*block*-poly**5**a and poly**1**-*block*-poly**6**a showed large advanced contact angles of about 120° and 130°, respectively (Fig. 10). These values were about 6–10° greater than the receded angles. Thus, the contact angles for the latter class of block copolymers were significantly greater than those measured for the former class, which might be due to a higher order at the film surface in the latter polymers. Both advanced and receded contact angles were quite constant over a 25 day exposure to water, consistent with the presence of non-reconstructing hydrophobic surfaces.

Double-layer dry films also showed rather high advanced contact angles of about 119° and 123° for poly**1**-*block*-poly**5**a

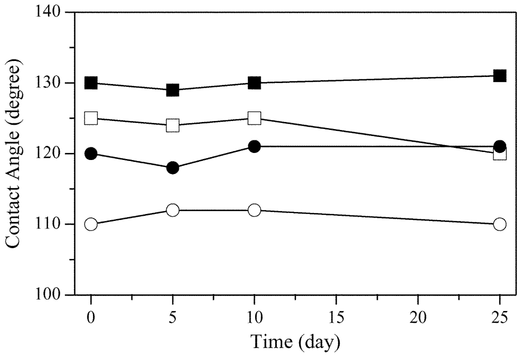


Fig. 10 Advanced (filled symbols) and receded (open symbols) contact angles (±3°) of single-layer films from block copolymers poly**1**-*block*-poly**5**a (●), poly**1**-*block*-poly**6**a (■) as a function of immersion time in water.

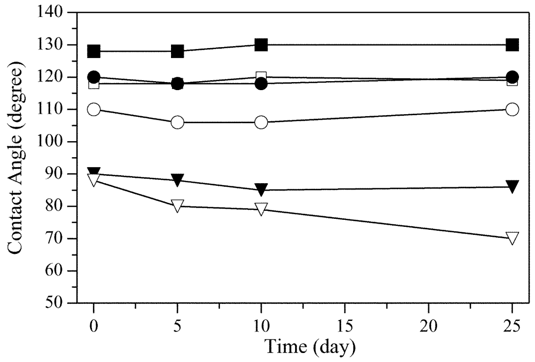


Fig. 11 Advanced (filled symbols) and receded (open symbols) contact angles ($\pm 3°$) of double-layer films with a top layer from block copolymers poly**1**-*block*-poly**5**a (●) and poly**1**-*block*-poly**6**a (■) and a bottom layer from SEBS, as a function of immersion time in water. SEBS (▼) films were used for comparison.

and poly**1**-*block*-poly**6**a, respectively (Fig. 11). These values turned out to be somewhat smaller than those of the single-layer films, but still acceptably high. Furthermore, they remained quite stable upon prolonged (up to at least 25 days) exposure to water. In contrast, SEBS films exhibited much lower contact angles (90° advanced) for which hysteresis became more appreciable after long exposures times (Fig. 11). This indicated an enrichment of the surface of the coating with the fluorinated block copolymers due to surface segregation in the double-layer films. We explained the high contact angles detected with the presence at room temperature of a liquid-crystalline surface that favors stable, close packing of the fluorinated tails at the film surface.

Conclusions

Following our strategy for engineering polymers as suitable materials for hydrophobic non-stick coatings, we prepared two classes of new fluorinated polystyrene-based block copolymers with low polydispersity by controlled radical polymerization and polymer modification. The TEMPO-mediated CRP turned out to be a rather simple and straightforward preparation method for block copolymers bearing fluorinated aromatic side chains. On the contrary, the polymer modification scheme involved a greater number of more complex synthetic steps, the anionic polymerization for the preparation of the parent copolymers to be modified was the initial stage.

The block copolymers containing a $(CF_2)_8$ tail in the side chains showed a stronger tendency to form smectic mesophases than the block copolymers bearing a $(CF_2)_4$ or a $(CF_2)_6$ tail. This can be attributed to the interplay between the rod-like nature of the fluorinated side chains and the phase separation at the molecular level of the different incompatible aromatic-fluoroaliphatic components of the polymer repeat unit.

Measurements on block copolymer films as a function of immersion time in water evidenced rather high values of contact angles that were quite constant. This suggests that the fluorinated block copolymers form fluorine-enriched surfaces that would be highly hydrophobic and quite resistant to reconstruction.

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