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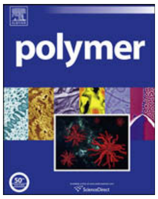

Tailored surface properties of semi-fluorinated block copolymers by electrospinning

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ABSTRACT

Diblock copolymers based on polystyrene (PS) macroinitiators and four different fluorinated monomers (perfluorooctyl ethyl methacrylate (FMA), pentafluorostyrene (FS), perfluorooctyl-ethylene oxymethyl styrene (EMS), 2,3,5,6-tetrafluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecaoxy)styrene (FSF)) were synthesized via atom transfer radical polymerization (ATRP). The lengths of the PS and fluorinated blocks were altered and the surface and self-assembling properties of the polymers were compared with respect to the fluorinated monomer used and the fluorine content. The surface properties, contact angles and surface tension, were enhanced by the existence of the CF_3 groups at the end of the alkyl chains compared with poly(pentafluorostyrene). Hydrophobicity of the surfaces was further enhanced by electrospinning the polymer solutions, which yielded superhydrophobic surfaces with water contact angles $>150^\circ$ for polymers having CF_3 groups.

1. Introduction

Fluorinated polymers composed of flexible backbones and perfluoro- or semifluoro-alkyl side chains have attracted much attention due to the unique and interesting characteristics originating from the C–F bond as well as the F atom [1–4]. Perfluoro- and semifluoro-alkyl groups are incompatible with water and with most organic solvents. A viable method to make soluble materials is copolymerization with non-fluorinated monomers, which has resulted in a number of different copolymer architectures having functional chain ends, random or block distribution of the fluorinated monomers or different topologies such as star-like or hyperbranched architecture. The development of living/controlled polymerization techniques has allowed straightforward synthesis of various block copolymers with fluorinated segments. Especially atom transfer radical polymerization (ATRP) has been successfully used to synthesize various fluorinated (meth)acrylic and styrenic block copolymers with low polydispersities and tailored molecular architectures [2]. On the other hand, a class of fluorinated copolymers are polymers whose side group is aromatic fluorinated ring, such as side group on pentafluorobenzene, FS [5], instead of a fluorinated alkyl chain. These polymers share the common properties of the C–F bonds and fluorine atoms. However, as the aromatic structure does not contain the most surface active CF_3 groups, the polymers based on pentafluorostyrene tend to be more soluble. The aromatic groups may also be functionalized with fluorinated alkyls, resulting in highly fluorinated monomers [6–8]. Similarly as the fluoroalkyl polymers, the block copolymers based on fluorinated polystyrenes tend to microphase separate due to the incompatibility of the blocks.

The strong segregation at the molecular level is often followed by self-organization to form well oriented phases at surfaces as well as in the bulk. The resulting surfaces exhibit excellent chemical and thermal stability, low adhesion, low friction coefficient, and extremely low surface energy that differs substantially from surfaces of conventional hydrocarbon-based polymers. The fluoroalkyl groups also induce self-organization in selective solvents to form various molecular assemblies such as monolayers, bilayers, regular and reversed micelles and vesicles. The formed self-assemblies may have interesting morphologies, as the rigid fluorinated polymer parts or segments may form not only spherical micelles [9], but also non-spherical structures varying in their aggregation states depending on the length of the blocks, concentration and the nature of the fluorinated units [10–17].

These properties have stimulated research on a number of different potential applications, ranging from use of the polymers

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as surfactants in emulsion polymerization in supercritical carbon dioxide [18], emulsifiers in fluorous–organic mixtures with emphasis on catalysis [6,19,20] as well as templates for preparation of inorganic nanoparticles [14,21,22]. Recently an application that has raised interest for fluorocarbon materials is hydrophobic surface coating [23,24]. Partially due to the specific properties of fluorocarbon materials these surfaces display repellent properties and could be utilised as coatings with anti-fouling or self-cleaning activity.

Electrospinning or electrospray is a process by which either submicron polymer fibres or polymeric particles can be deposited on a surface using electrostatically driven jet of a polymer solution [25,26]. If the molecular weight of the polymer is sufficiently high and viscosity of the solution is appropriate, mats of solid polymer nanofibers on the surface of choice can be achieved. Lower molecular weight polymers typically form micron sized particles instead of fibres due to the lack of chain entanglements during the process. These electrostatically coated surfaces typically have the surface roughness that is needed to observe superhydrophobicity, i.e. a lotus leaf effect. Although lotus leaf effect can be achieved without non-fluorinated materials, as observed in nature and shown by various groups by careful optimization of the surface structures of different materials, use of fluorinated compounds has some advantages. By using fluorinated materials superhydrophobicity could be achieved without as stringent structure optimization due to their inherent hydrophobicity. Furthermore, fluorinated surfaces are expected to retain their hydrophobicity even if the surface structure is destroyed for example by wear.

In the present study we have synthesized several different fluorinated diblock copolymers via ATRP. The polymers have polystyrene (PS) blocks but differ in the used fluorinated monomer and the lengths of the blocks. The aim is to compare the effect of the different monomers with respect to the properties of the polymers. A conventional electrospinning device was used to deposit some of the fluorinated block copolymers on a surface either as pure solutions or as blends with polystyrene homopolymer.

2. Experimental

2.1. Materials

Phenyl 2-bromopropionate was synthesized as described by Haddleton and Waterson [27] using phenol (Merck, 99.5%) and 2-bromopropionyl bromide (Aldrich Chemicals, 98%), dichloromethane (Lab-Scan, HPLC), 2,2-bipyridine (bipy, Aldrich Chemicals 99+%), dimethyl 2,6-dibromoheptadioate (Aldrich Chemicals, 97%), 1H,1H,2H,2H-perfluoro-1-decanol (Fluka), tetrabutylammonium-hydrogensulphate (TBAH, Fluka, >99%), 4-chloromethylstyrene (Fluka, 90%), p-xylene (Merck), toluene (Lab-Scan, HPLC), methanol (J.T. Baker, HPLC) and tetrahydrofuran (THF, Lab-Scan, HPLC) were used as received. Cu(I)Br was washed with glacial acetic acid (AppliChem, 96%). Anisol (Reagent Plus, 99%), Styrene (Merck) and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, Aldrich Chemicals, 98%) were vacuum distilled before use. Perfluorooctyl ethyl methacrylate (FMA, Aldrich Chemicals, 97%) and pentafluorostyrene (FS, Aldrich Chemicals, 99%) were vacuum distilled to remove the stabilizers. Polystyrene (PS123) used for blends in electrospinning was prepared by homopolymerization of styrene (Aldrich) in benzene ($c_{\text{styrene}} = 8$ M, $c_{\text{AIBN}} = 5.8$ mM, $T = 70$ °C, 20 h). The reaction mixture was precipitated into methanol and further purified with reprecipitation from chloroform to diethylether. Weight average molecular weight was 123 000 g/mol and PDI 1.5.

2.2. Synthesis of FSF monomer

Synthesis of 2,3,5,6-tetrafluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecaoxy)styrene (FSF) was as follows. 1H,1H,2H,2H-perfluorodecanol (16 mmol) was mixed with 32 ml of 50% aqueous NaOH. Amounts of 32 ml dichloromethane and 1.6 mmol tetrabutylammonium hydrogen sulphate (TBAH) were added, and the resulting suspension was vigorously stirred. Upon addition of pentafluorostyrene (18 mmol), the reaction mixture turned slightly yellow. After stirring for 72 h at 40 °C, the organic layer was separated and washed with 0.1 M HCl and with water and dried over sodium sulphate. After evaporating of solvent the product was crystallized in methanol. Yield was ~30%. ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm: 2.6 (2H, $-OCH_2CH_2C_8F_{17}$), 4.45 (2H, $-OCH_2CH_2C_8F_{17}$), 5.7 (1H, $-CH{=}CH_{(1)}$), 6.05 (1H, $-CH{=}CH_{(2)}$), 6.65 (1H, $-CH{=}CH_2$).

2.3. Synthesis of EMS monomer

The procedure described by Höpken and Möller [28] was used to obtain the perfluorooctyl-ethylene oxymethyl styrene (EMS). 1H,1H,2H,2H-perfluorodecanol (10.9 mmol) was mixed with 20 ml of 50% aqueous NaOH. 20 ml dichloromethane and 1.6 mmol tetrabutylammonium hydrogen sulphate (TBAH) were added and the resulting suspension was vigorously stirred. Upon addition of 4-chloromethylstyrene (11 mmol) the reaction mixture turned brown. After stirring for 24 h at 40 °C organic layer was separated and washed with 0.1 M HCl and with water, and dried over sodium sulphate. After evaporating of solvent the product was crystallized twice in methanol. Yield was 50%. ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm: 2.45 (2H, $-OCH_2CH_2C_8F_{17}$), 3.77 (2H, t, $-OCH_2CH_2C_8F_{17}$), 4.54 (2H, $OCH_2C_6H_4$), 5.26 (1H, $-CH{=}CH_{(1)}$), 5.76 (1H, $-CH{=}CH_{(2)}$), 6.73 (1H, $-CH{=}CH_2$), 7.36 (4H, aromatic protons).

2.4. General ATRP procedure for macroinitiators

Bromine terminated polystyrene, PS-Br, macroinitiators were prepared as follows. Solution of styrene, phenyl 2-bromopropionate, Cu(I)Br and PMDETA were weighed in round bottomed flask using monomer:initiator:Cu(I)Br:ligand molar ratio 100:1:1:2. Solution was degassed by five freeze–thaw cycles and the sealed polymerization mixture was immersed into a silicon oil bath at 80 °C. After 180 min reaction time, the mixture was cooled down to ambient temperature, diluted with THF and filtered through silica and Al_2O_3 column. After filtering, the polymer was precipitated in methanol and dried under vacuum. The purity of the sample was ascertained by ^{1}H NMR spectroscopy. SEC against PS standards was used in the calculation of molar mass and molar mass distribution.

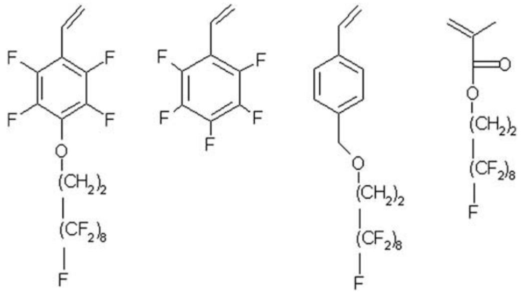
2.5. General procedure for ATRP of the fluorinated monomers

The monomer, macroinitiator, Cu(I)Br and PMDETA and anisol or xylene as solvent were weighed in round bottomed flask using monomer:initiator:Cu(I)Br:ligand molar ratio 30:1:1:2, see Table 1. Solution was degassed by five freeze–thaw cycles and the sealed polymerization mixture was immersed into a silicon oil bath at 110 °C. After 60–420 min reaction time the mixture was cooled down to ambient temperature, diluted with THF and filtered through silica and Al_2O_3 column. After filtering, the polymer was precipitated in methanol and dried under vacuum. The purity of the samples was ascertained by ^{1}H NMR spectroscopy. The molar masses were determined from the ^{1}H NMR spectra and polydispersity from SEC.

Table 1
Synthesis of block copolymers.

Sample[a]	M (mmol)	I (mmol)	CuBr (mmol)	Ligand (mmol)	Solvent	Time (min)	Yield (%)
PS$_{2900}$-*b*-PFSF	0.9	0.2	0.21	0.4[b]	Anisol (5 ml)	180	75
PS$_{9300}$-*b*-PFSF	0.4	0.07	0.07	0.17[b]	Anisol (3 ml)	180	76
PS$_{2900}$-*b*-PEMS	0.9	0.2	0.14	0.17[b]	Anisol (5 ml)	180	49
PS$_{9300}$-*b*-PEMS	0.5	0.07	0.07	0.23[b]	Anisol (5 ml)	180	54
PS$_{2900}$-*b*-PFMA	6.7	0.2	0.07	0.17[b]	Anisol (4 ml)	60	17
PS$_{9300}$-*b*-PFMA	3.4	0.07	0.07	0.12[b]	Anisol (3 ml)	60	34
PS$_{3700}$-*b*-PFS	10.3	0.14	0.14	0.22[c]	Xylene (5 ml)	240	68
PS$_{3700}$-*b*-PFS	5.2	0.14	0.14	0.22[c]	Xylene (5 ml)	180	69
PS$_{5600}$-*b*-PFS	5.2	0.09	0.09	0.18[c]	Xylene (5 ml)	180	74

[a] Subscript denotes molar mass in g/mol.
[b] PMDETA.
[c] 2,2-Bipyridine.



Scheme 1. Chemical structures of the monomers. From left to right FSF, FS, EMS, FMA.

2.6. ^{1}H NMR spectroscopy

The structure and purity analyses were carried out at room temperature using a Varian Gemini 2000 spectrometer operating at 200 MHz for protons. The samples were dissolved in deuterated chloroform or in a mixture of deuterated chloroform and perfluorobenzene. The ratio of styrene to fluorinated monomer was calculated from the integrals of the protons in the polymer backbone (1.7–2.6 ppm) and the proton signals at 4–5 ppm arising from the –CH$_2$– groups next to aromatic ether linkage in the case of PEMS and PFSF and the –CH$_2$– groups next to the ester linkage in the case of PFMA. For the PS-*b*-PFS polymers the molar masses were determined by comparing the integrals of aromatic protons from styrene to the total number of CH and CH$_2$ protons from the polymer chain.

2.7. Size exclusion chromatography (SEC)

SEC was performed with a Waters chromatograph equipped with three Styragel columns (HR2, HR4, HR6), and a 410 differential refractometer (Waters Instruments, Rochester, MN). THF was used as an eluent with a flow rate of 0.8 ml/min. PS standards (PSS Polymer Standards Service GmbH) were used for the calibration.

2.8. Dynamic light scattering (DLS)

Samples were dissolved overnight in toluene at 20 °C before measurements. Measurements were conducted with a Brookhaven Instruments BI-200SM goniometer and a BI-9000AT digital correlator. Ar laser (LEXEL 85, $l = 488$ nm) was used as a light source, the laser power being typically ~45 mW. In DLS experiments, autocorrelation functions of intensity of scattered light, $G_2(t)$, were collected at scattering angle of 90° unless otherwise indicated. The correlation function was then analyzed by inverse Laplace transform program CONTIN to obtain the apparent hydrodynamic diameter and the distributions of hydrodynamic diameter.

2.9. Electrospinning and electron microscopy

For electrospinning fluorinated block copolymers PS35-*b*-PFS35, PS28-*b*-PFSF4 and PS89-*b*-PFMA11 were dissolved in chloroform (30% w/v). PS123 was also dissolved in chloroform (20% w/v) as such or as a mixture with above mentioned fluorinated block copolymers having fluorinated polymer content in mixtures 10 or 30 wt.% of PS123. Homemade electrospinning device consisted of a syringe infusion pump, a positively charged stainless steel HPLC capillary (0.51 mm ID, 1.59 mm OD, Supelco), and a negatively charged collector. Stainless steel plate covered with aluminum foil was used as the collector. The +15 kV positive charge was achieved with Spellman SL30P30/220 high voltage generator (Spellman High Voltage Electronics Corp.) with a low current output (limited to a few mA). −5 kV negative charge on the collector was achieved with Philip Harris 15 kV high voltage generator (Philip Harris Ltd.) The polymer solution was delivered to metal capillary via a syringe pump (KDS-100-CE) with flow rate of 1 ml/h. The distance between blunt-end capillary and collector was 25 cm. The electrostatically coated substrates were stored in vacuum desiccator prior to the contact angle measurements and electron microscopy. Scanning electron microscopy (SEM) experiments were made with Hitachi S-4800 field emission scanning electron microscope from the samples coated with Pt. To investigate the fluorine distribution, element mapping

Table 2
Molecular characteristics and surface properties of block copolymers.

Code	Sample	$M_{n_{NMR}}$ (g/mol)	$M_{n_{SEC}}$ (g/mol)	PDI	F mol-fraction[a]	Elemental F (%)[b]	Surface tension (mN/m)[c]	Contact angle solvent casted (°)	Contact angle electrospun (°)
PS28-*b*-PFSF4	PS$_{2900}$-*b*-PFSF	5500	4000	1.3	0.14	13.2	20	120	160
PS89-*b*-PFSF4	PS$_{9300}$-*b*-PFSF	11 900	11 400	1.4	0.04	5.2	23.2		
PS28-*b*-PEMS2	PS$_{2900}$-*b*-PEMS	4100	4300	1.2	0.07	6.2	23.5		
PS89-*b*-PEMS2	PS$_{9300}$-*b*-PEMS	10 500	10 000	1.2	0.02	2.2	25.3		
PS28-*b*-PFMA6	PS$_{2900}$-*b*-PFMA	6100	3200	1.3	0.22	15.0	19.2		
PS89-*b*-PFMA11	PS$_{9300}$-*b*-PFMA	15 200	9600	1.1	0.12	10.1	21.4	117	150
PS35-*b*-PFS35	PS$_{3700}$-*b*-PFS	10 500	12 000	1.29	0.51	15.6	28.6	108	127
PS35-*b*-PFS49	PS$_{3700}$-*b*-PFS	13 200	16 000	1.36	0.58	18.2	28.6		
PS53-*b*-PFS35	PS$_{5600}$-*b*-PFS	12 400	12 000	1.27	0.40	12.4	28.7		

[a] Refers to molar fraction of fluorinated monomer compared to styrene.
[b] Elemental fluorine calculated based on the polymer composition.
[c] Surface tension in toluene for 1 wt.% solutions. PS-*b*-PFS by du Nouy ring method and others by pendant drop method.

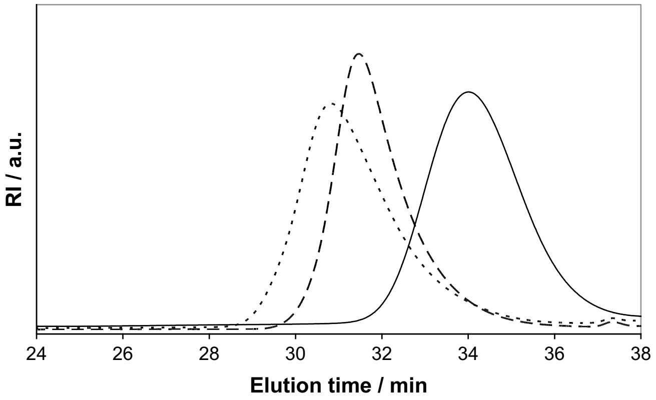


Fig. 1. SEC elution chromatograms of PS35 (line), PS35-*b*-PFS35 (dashed line) and PS35-*b*-PFS49 (dotted line).

using energy dispersive spectroscopy (EDS) was performed. The fluorine distribution was studied on the SEM scanned area.

2.10. Surface tension and contact angle measurements

Surface tensions were measured either by pendant drop method using KSV CAM 200 instrument or with a KSV Sigma 7^{03} system using du Nouy ring. Known amounts of polymers were dissolved in toluene 24 h before measurements with concentrations between 0.0025 and 3 wt.%. Five parallels for each concentration were measured and the average and standard deviations were calculated from the parallels. Contact angle measurements were made with a KSV CAM 200 instrument using distilled water. The contact angles were measured either from the electrospun aluminum foils or films prepared by solvent casting on aluminum foil using the same solutions as used in electrospinning and drying overnight.

3. Results and discussion

3.1. Synthesis of polymers

Bromine terminated polystyrenes, PS-Br, were synthesized using CuBr/PMDETA as the catalyst and phenyl 2-bromopropionate as the initiator. The conversions were kept below 60% in order to keep all the chain ends brominated. Syntheses afforded polystyrene macroinitiators with molar masses of 2900–9300 g/mol according to SEC. These macroinitiators were consequently used in the polymerization of fluorinated monomers perfluorooctyl ethyl methacrylate (FMA), pentafluorostyrene (FS), perfluorooctylethylene oxymethyl styrene (EMS) and 2,3,5,6-tetrafluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecaoxy)styrene (FSF), see Scheme 1. In the following, the structures of the polymers are given either by using the determined number-averaged molar mass for the macroinitiators (*e.g.* PS_{2900}-*b*-PFSF) and by code which refers to number of repeating units per polymeric block (*e.g.* PS28-*b*-PFS4), see Tables 1 and 2.

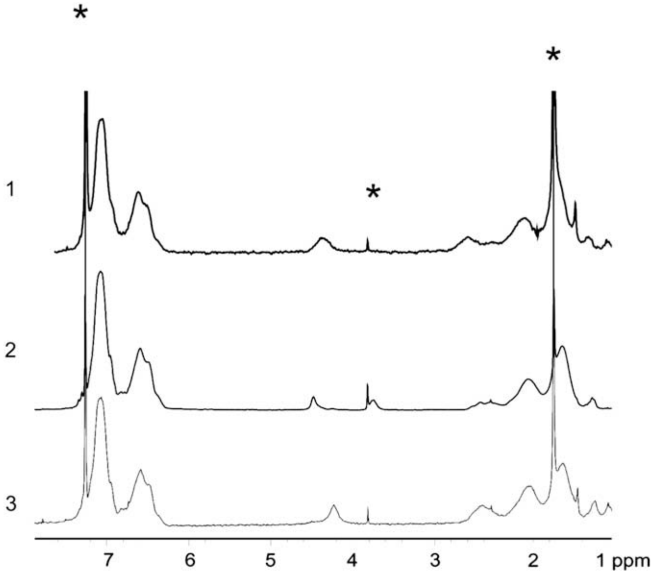


Fig. 2. ^{1}H NMR spectra of the 1) PS28-*b*-PFSF4, 2) PS28-*b*-PEMS2 and 3) PS28-*b*-PFMA6. Solvent signals marked with asterisk.

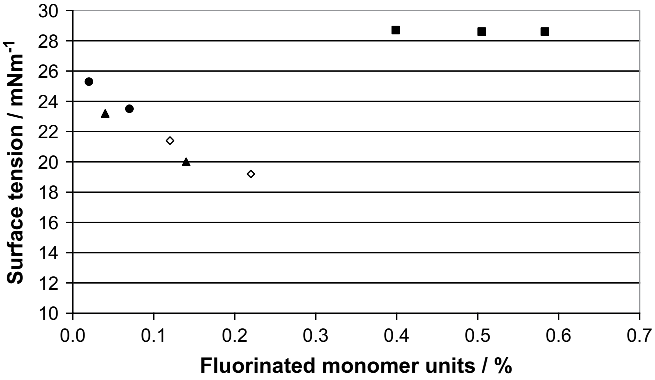


Fig. 3. Surface tensions of 1 wt.% the block copolymer solutions in toluene plotted against fraction of fluorinated monomers. PS-*b*-PFS (■), PS-*b*-PFSF (▲), PS-*b*-PEMS (●) and PS-*b*-PFMA (◇).

Tables 1 and 2 collect the synthesis conditions, molecular characteristics and surface properties of the polymers. The structural characterisation of semi-fluorinated polymers by SEC is often complicated by the tendency of the molecules to associate due to the fluorinated segments [5]. In the present study this was seen in the case of the polymers with fluorinated alkyl chains, where the apparent molar mass according to SEC shows a tendency for lower M_n values compared with the NMR analysis. For the polymers with PFS as the fluorinated block, such effect was typically not observed. Monomodal SEC elution curves, see example of SEC chromatograms in Fig. 1, together with NMR signals from the fluorinated blocks, shown in Fig. 2, enable calculation of the number of fluorinated units for the different block copolymers and estimation of the polydispersity of the products.

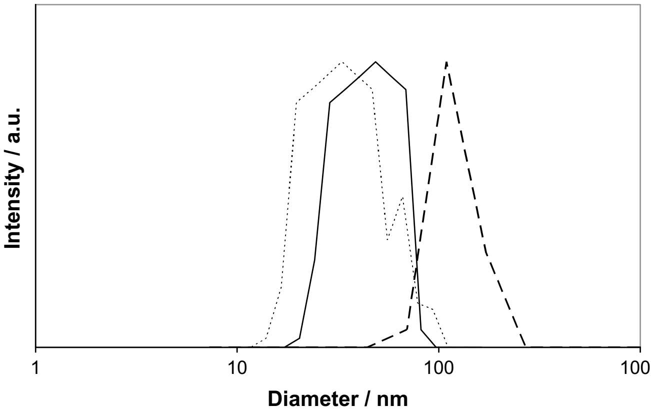


Fig. 4. Size distributions of the aggregated solutions, PS89-*b*-PFMA11 (full line), PS28-*b*-PFMA6 (dashed line) and PS35-*b*-PFS35 (dotted line).

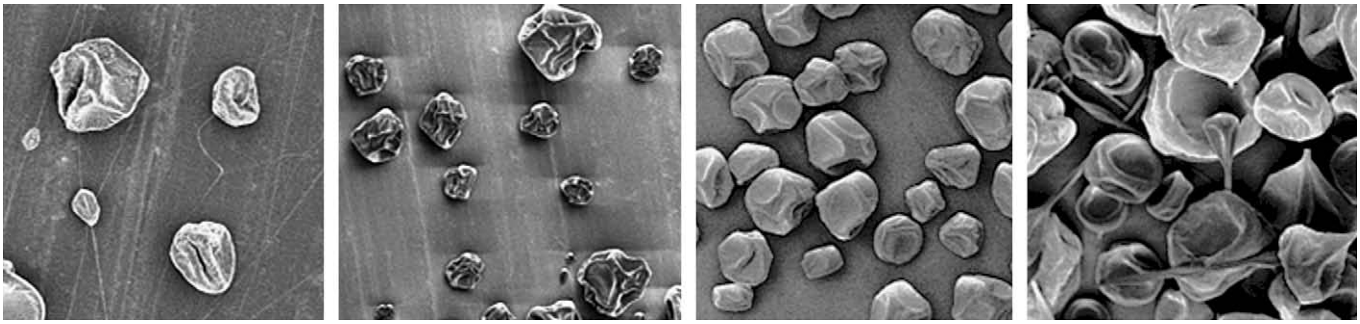


Fig. 5. SEM micrographs (100 μm × 100 μm) of electrospun polymers. From left to right PS123, PS35-*b*-PFS35, PS89-*b*-PFMA11 and PS28-*b*-PFSF4.

As is evident from Table 2 the polymers bearing fluorinated alkyl substituted monomers, EMS, FSF and FMA, have low degrees of polymerization of the fluorinated block, only a few monomer units. This is most probably due to the conditions chosen for polymerization including the bulkiness of the monomers. Nevertheless, the weight fraction of the fluorinated monomers is high compared to their degree of polymerization due to the high molar mass of the fluorinated monomers. In contrast, the polymerization of FS showed faster kinetics when compared with styrene as reported previously [16]. Consequently polymers with higher degree of polymerization of the fluorinated block to the macroinitiator were obtained for the PS-*b*-PFS polymers in contrast to the other fluorinated monomers.

3.2. Surface tension in toluene

PS homopolymers did not affect the surface tension of toluene (32 mN m^{-1}) in the studied concentration range while the fluorinated polymers clearly decrease the surface tension as shown in Table 2. Tests made with different polymers showed decreasing surface tension with increasing polymer concentration to 0.5–0.6 wt.% after which no significant change was noticed, similarly as in a previous publication on FMA containing eicosanyl methacrylates [12]. Thus, a reference concentration, 1 wt.%, was chosen to compare the surface properties of different polymers.

All of the studied PS-*b*-PFS polymers show a similar surface tension regardless of the polymer composition. This shows that the effect of the lengths of PS macroinitiator or the fluorinated block is negligible on the resulting surface tension. The situation is different in the case of the polymers bearing fluorinated alkyl chains, which first of all show a much more pronounced effect on the surface tension than the block copolymers based on poly(pentafluorostyrene), but also the fraction of fluorinated units has an effect. When the minimum surface tensions obtained for different polymers are compared, correlation of the fraction of fluorinated groups to the observed reference surface tension is found, see Fig. 3. It is clear that the increasing fraction of fluorinated alkyl groups, especially the CF_3 groups, is responsible for the enhanced surface activity. The reference surface tensions found for PS-*b*-PFSF, PS-*b*-PEMS and PS-*b*-PFMA are comparable to the ones found for other fluorinated acrylate copolymers in toluene. For example, corresponding values have been observed for poly(methyl methacrylate)-*b*-poly(1H,1H,2H,2H-perfluorohexyl methacrylate) and poly(methyl methacrylate)-*b*-poly(1H,1H,2H,2H-perfluorooctyl methacrylate) copolymers by Krupers and Möller [10].

3.3. Aggregate analysis

It is of interest now to study the aggregates formed in solution by the different polymers. Although the fluorinated blocks should phase separate efficiently from the PS blocks in solution, no aggregates were detected for PS-*b*-PFSF and PS-*b*-PEMS polymers in toluene by DLS. The absence of aggregates was also indicated by the low intensity of scattered light from these solutions. Thus the polystyrene block solubilises the polymers with short fluorinated blocks sufficiently in order to keep them molecularly dissolved in toluene. On the other hand, solutions of polymers with other fluorinated blocks, PS-*b*-PFMA and PS-*b*-PFS, clearly aggregate and hence, strongly scatter light. The different size distributions obtained this way are shown in Fig. 4. The PS89-*b*-PFMA11 polymer shows aggregates with average diameter ~40 nm. When a shorter PFMA block is used in the case of PS28-*b*-PFMA6, the aggregates are

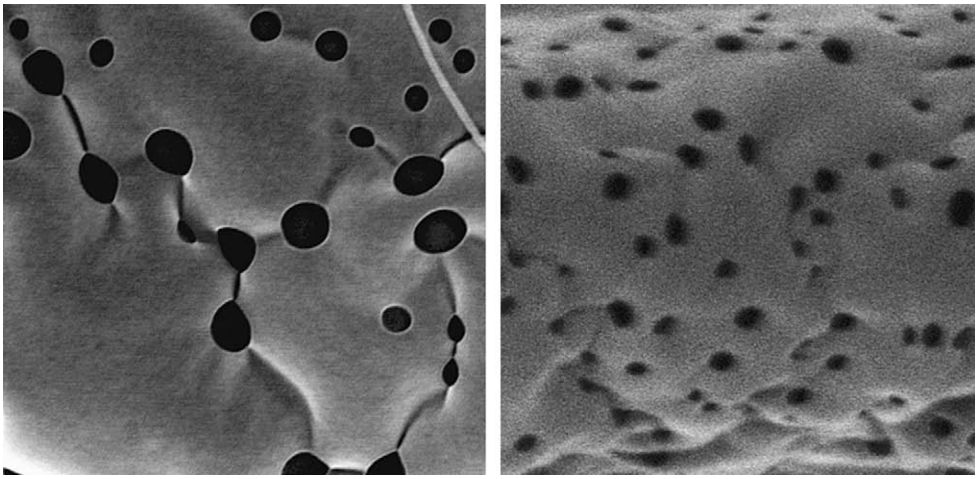


Fig. 6. SEM micrographs (2 μm × 2 μm) of electrospun polymers PS123 (left) and PS89-*b*-PFMA11 (right).

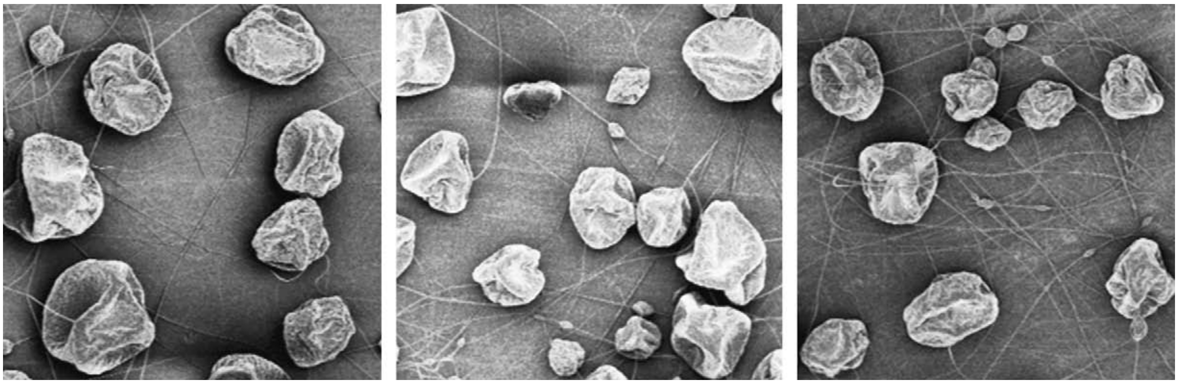


Fig. 7. SEM micrographs (100 μm × 100 μm) of electrospun polymer mixtures of PS123 containing 10 wt.% fluorinated polymer. From left to right PS35-*b*-PFS35, PS89-*b*-PFMA11 and PS28-*b*-PFSF4.

significantly larger, with mean diameter ∼120 nm. This naturally means that the aggregation number for the PS28-*b*-PFMA6 polymer is higher than what it is for PS89-*b*-PFMA11. This can be understood on the basis of the properties and length of the fluorinated block. When the rigid fluorinated block is long enough, it limits the curvature of the core of the micelles and thus results in lower aggregation number. In PS-*b*-PFS polymers the fluorine containing blocks are much longer than in the other studied polymers and although the poly(pentafluorostyrene) does not have as high surface activity as the polymers having CF_3 groups, the length of the blocks induces phase separation. The length of the PFS block does not influence the size distribution of the aggregates significantly and thus also for these polymers the aggregation number tends to decrease slightly for the polymers having longer PFS blocks.

3.4. *Electrospinning*

The relatively low molar mass and the tendency to aggregate are challenging with respect to the electrospinning process, since sufficient viscosity and viscoelastic properties are needed in the process to provide stable jets and to make mats with even sized fibres. For an aggregated system the viscosity tends to be lower and this complicates the formation of electrospun nanofibers and the optimization of the process.

In the electrostatic coating process with polystyrene, PS123, a mixture of nanofibers with diameter of 200–300 nm and particles with diameter around 10–20 μm was formed, see Fig. 5 for scanning electron micrograph. The studied fluorinated block copolymers, PS35-*b*-PFS35, PS28-*b*-PFSF4 and PS89-*b*-PFMA11 electrospun as such formed 10–20 μm particles as shown in Fig. 5, completely without the formation of nanofibers. This effect is most likely due to the rather low molar mass of the polymers and the aggregation tendency which results in insufficient viscoelasticity. It can be seen that in all cases the polymer particles have a shape of shrunken spheres, which originates from the solvent-containing polymer spheres collapsing after the spinning process as chloroform evaporates. This explanation is further confirmed upon higher magnification on the surface, shown in Fig. 6, where the surfaces of the fibres or particles show evenly distributed holes of the order of tens of nanometers which have formed after the electrospinning process upon solvent drying.

Mixed solutions of PS123 and fluorinated block copolymers formed similar collapsed spheres as in the case of PS123 or fluorinated block copolymers, but also nanofibers with a diameter of 200–300 nm were created, see Fig. 7. The formation of nanofibers is caused by the higher molecular weight polystyrene component, which allows the formation of chain entanglement in the whipping process during the electrospinning. However, as particles were formed also during the electrospinning of PS123 itself and the electron micrographs resemble very much the case with pure PS123, we conclude that mixing the fluorinated block copolymer does not change the behaviour under the electrospinning conditions.

Elemental mapping using EDS on the pure fluorinated block copolymers shows intense fluorine concentration on the edges of the microparticles in the case of PS89-*b*-PFMA11 and PS28-*b*-PFSF4, see Fig. 8. On the other hand, mixing fluorinated block copolymer with PS123 results in rather even distribution of fluorine throughout the sample. This means that the polystyrene block in the fluorinated block copolymers enables intimate mixing with the pure polystyrene PS123 in the case of mixtures.

3.5. *Contact angle measurements*

Comparison of the surfaces by contact angle measurements shows that neat fluorinated block copolymer surfaces have very different surface characteristics depending on the fluorinated

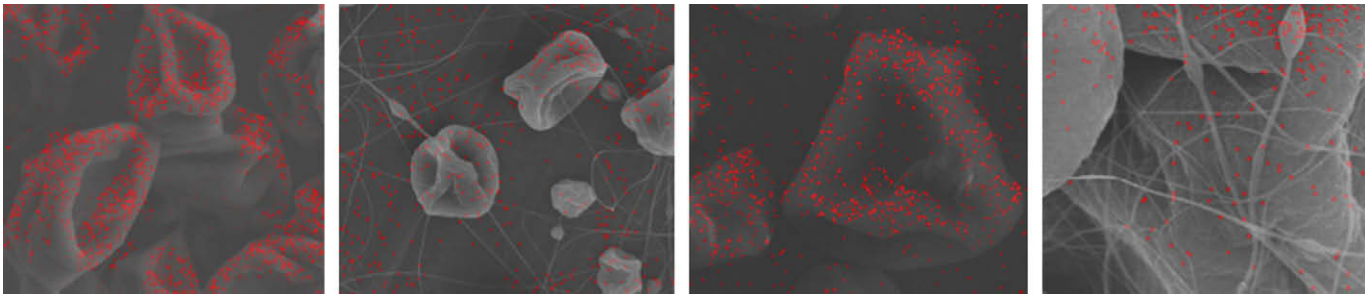


Fig. 8. Fluorine element maps from SEM micrographs of electrospun polymers and polymer mixtures with PS123 containing 30 wt.% fluorinated polymer. From left to right PS28-*b*-PFSF4, PS123 mixed with 30 wt.% PS28-*b*-PFSF4, PS89-*b*-PFMA11, and PS123 mixed with 30 wt.% PS89-*b*-PFMA11.

monomer used and the deposition technique, see Fig. 9. The most hydrophobic surfaces are formed by electrospinning using the polymers based on CF_3 containing monomers, PS28-*b*-PFSF4 and PS89-*b*-PFMA11. Both polymers exhibit a contact angle above 150°. On the other hand, solvent casted films of these polymers show much smaller contact angles, of the order of 115–120°. Although it is likely that the fluorinated groups concentrate on the surfaces of the solvent casted samples, the experiments manifest that the surface roughness plays an important role in the surface hydrophobicity. The electrospun polystyrene PS123 shows increased CA ($\sim$130°) compared with the solvent casted sample (CA $\sim$ 100°) as well as the block copolymer having poly(pentafluorostyrene) block, PS35-*b*-PFS35 (CA $\sim$ 108° for solvent casted, 127° for electrospun). Thus it is clear that in addition to surface roughness, the enrichment of the CF_3 groups is responsible for the enhanced hydrophobicity in the present case.

The tendency of fluorinated units to enrich on the formed surfaces encouraged us to try to electrospin materials containing only a fraction of fluorinated material, which would be beneficial also cost-wise taking into account the high cost of fluorinated materials. In order to achieve this, polymer solutions containing fluorinated block copolymers were mixed with a solution of polystyrene. Fig. 10 shows how the concentration of the fluorinated block copolymer affects the contact angles of the electrospun surfaces. It is seen how the CF_3 containing polymers, PS28-*b*-PFSF4 and PS89-*b*-PFMA11, retain the hydrophobicity to a large degree although the weight fraction of the fluorinated material is decreased to 10 wt.%. This indicates the fluorinated units enriching on the surface and the effect of preserved surface roughness, which was also shown in Figs. 5 and 7. For practical uses of fluorinated polymers in electrospinning this shows that the amounts of fluorinated compounds can be reduced significantly while retaining the properties, thus making the use of these materials more commercially viable.

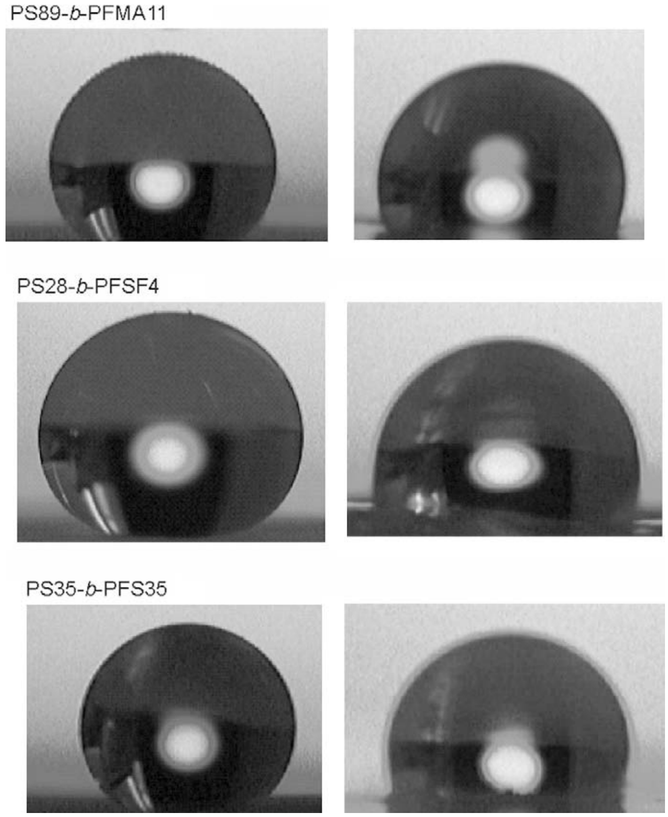


Fig. 9. Photographs of water droplets on electrospun materials (left) and solution casted surfaces (right) for different neat block copolymer solutions.

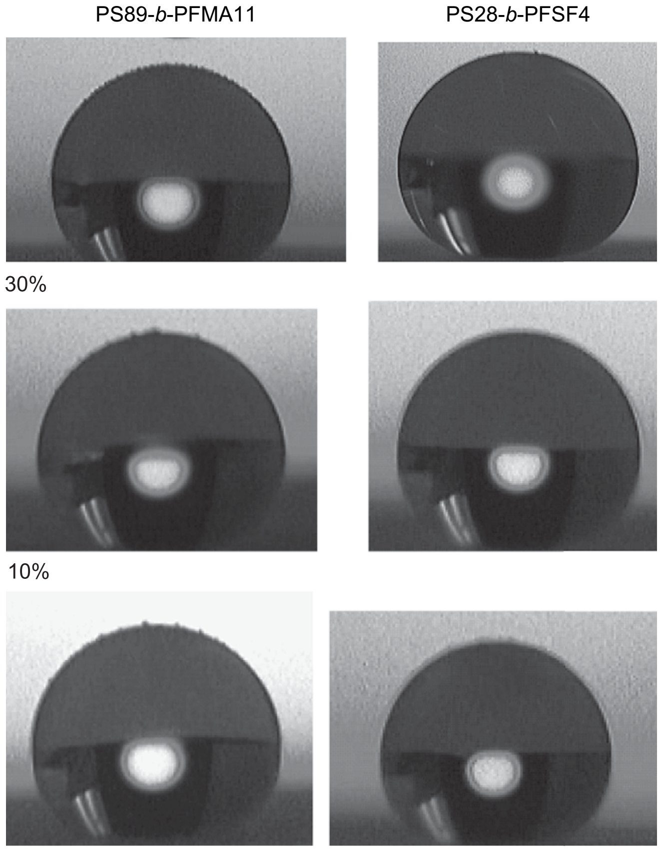


Fig. 10. Photographs of water droplets on electrospun mixed solutions of PS123 and fluorinated block copolymer with different block copolymer weight fractions (in wt.% of block copolymer to PS123).

4. Conclusions

Diblock copolymers based on polystyrene and various fluorinated blocks were polymerized via ATRP and the properties of different monomers on polymer properties compared. These organosoluble polymers showed enhanced surface activity in toluene due to the fluorinated blocks. The polymers having CF_3 groups at the ends of the fluorinated alkyl side chains had notably higher surface activity compared with materials having poly(pentafluorostyrene) as the fluorinated block. Due to the incompatibility of the fluorinated blocks with polystyrene or the solvent medium, aggregation of the polymers was observed in most cases when the fluorinated block was long enough. Selected polymers were used in electrospinning to produce electrospun surfaces and their surface properties were compared with those of solvent casted films. Superior surface hydrophobicity, exceeding contact angle of 150° for water was observed for electrospun polymers bearing CF_3 groups, while solvent casted films had contact angles typical for surface enriched fluorinated compounds, $\sim$120°. Additionally, solution mixtures of these fluorinated block copolymers and polystyrene were electrospun. The surfaces were found to retain their hydrophobicity nearly on a constant level down to fluorinated block copolymer concentration of 10 wt.% to polystyrene.

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