New Highly Fluorinated Styrene-Based Materials with Low Surface Energy Prepared by ATRP

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Received July 7, 2003; Revised Manuscript Received October 29, 2003

ABSTRACT: 2,3,5,6-Tetrafluoro-4-(2,2,3,3,3-pentafluoropropoxy)styrene (TF(F_5)S) and 2,3,5,6-tetrafluoro-4-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctaoxy)styrene (TF(F_{15})S) are prepared by nucleophilic substitution of 2,3,4,5,6-pentafluorostyrene. The neat monomers are subjected to atom transfer radical polymerization (ATRP) at 110 °C to high conversions in relatively short times, 10−120 min; TF(F_5)S is additionally polymerized at 70 and 90 °C. Block copolymers with styrene are prepared by the macroinitiator approach. All polymers, in the number-average molecular weight range from 6000 to 35 000, have polydispersity indexes between 1.08 and 1.37. The homopolymers show glass transitions from 16 to 62 °C depending on molecular weight, whereas the block copolymers exhibit phase separation mirrored in two T_gs, which could be observed when the smallest block constitutes more than 10 mol %. The fluorinated side chains of P(TF(F_5)S) and P(TF(F_{15})S) enrich the surface of thin films, which results in an advancing water contact angle of 117° and 122°, respectively. Both XPS analyses and contact angle measurements strongly imply that the fluorinated parts of the block copolymers migrate to the surface and create low surface energy films.

Introduction

Fluoropolymers have a prominent position when demanding chemical and physical properties are in question. Among the particular fluoropolymer merits are high thermal, chemical, aging and weather resistance, oil and water repellency, excellent inertness, and low flammability and refractive index. Recent, notable applications are within such different topics as generation of low-energy surfaces,[1−11] surface-modified membranes,[12] low permittivity or low dielectric constant,[13] and low optical loss exploited in waveguide devices.[14−16]

The fluorinated block copolymers with well-defined structures applied for generation of low-energy surfaces are either polystyrene based and initially prepared by living anionic polymerization[3,4,6−8,10,11] or poly(butyl methacrylate-*co*-perfluoroalkyl acrylate)[9] synthesized by atom transfer radical polymerization (ATRP). Low critical surface tensions have also been determined in fluorinated poly(amide urethane) block copolymers with fluorinated side chains prepared from diacid chlorides.[1,2] In the styrene-based polymers the fluorination was obtained by functionalization of polystyryllithium and subsequent Williamson reactions,[6,7] by deprotection of poly(4-*tert*-butyldimethylsiloxyloxystyrene) followed by Williamson reactions,[7] or via oxidative hydroboration of isoprene blocks succeeded by esterification with perfluorinated acid chloride.[3,4,6,11] On the other hand, one example of a TEMPO-mediated controlled radical polymerization of a fluorinated alkoxymethylstyrene also exists.[11]

We have recently demonstrated[17] the fast, controlled polymerization of 2,3,4,5,6-pentafluorostyrene (FS) by use of ATRP. This technique also allows block copolymers with other monomers, e.g., styrene, to be prepared. Furthermore, the 4-methoxy-substituted analogue, 2,3,5,6-tetrafluoro-4-methoxystyrene (TFMS), can be polymerized in the same manner with controlled characteristics.[18,19] Moreover, both homo- and block copolymers of TFMS could be demethylated and the corresponding hydroxy sites derivatized with azobenzene side chains in a Williamson ether synthesis. The potential nucleophilic substitution in the *para* position of FS prompted us to attempt the preparation of novel FS monomers with 4-fluoroalkoxy side chains and subsequently investigate their polymerization potential with a view to these novel materials' self-assembly process at surfaces. This paper therefore reports on the preparation of two novel, highly fluorinated styrene monomers and how well-defined homo- as well as block copolymers with styrene and FS can be prepared by ATRP. Furthermore, we report on the preliminary investigations of the surface characteristics of these new polymers.

Experimental Section

Materials. 1*H*,1*H*-Pentafluoropropane-1-ol and 1*H*,1*H*-pentadecafluorooctane-1-ol (ABCR Chemicals, Germany) were used as received. Styrene (St) and FS (Sigma-Aldrich) were passed through a ready to use, disposable prepacked inhibitor remover column, stored over CaH_2, and vacuum-distilled before use. Tetrahydrofuran was distilled prior to use from CaH_2 over sodium metal under dry nitrogen. Cu(I)Br, 1-phenylethyl bromide (PhEBr), and bipyridine (bipy) (all from Sigma-Aldrich) were used as received. All the reactions described were carried out in an inert atmosphere.

Synthesis of Monomers: 2,3,5,6-Tetrafluoro-4-(2,2,3,3,3-pentafluoropropoxy)styrene (TF(F_5)S). In a three-neck round-bottom flask equipped with a magnetic stirrer, addition funnel, and reflux condenser, a solution of 13.0 g (67 mmol) of FS in 50 mL of dry THF was cooled to 0 °C. A solution of 12.7 g (74 mmol) of fluorinated sodium propane-1-olate in 100 mL of THF was added slowly. Stirring was continued for 1 h and then brought to reflux for 19 h. After cooling, the reaction mixture was poured into 400 mL of ice water and extracted

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10.1021/ma034952b CCC: $27.50

with diethyl ether. The organic layer was dried with sodium sulfate, and the ether was evaporated. The residue was stored over calcium hydride for 1 day and then distilled at 56 °C/1.3 mbar. Yield = 17.5 g (80%). ^{1}H NMR ($CDCl_3$): $\delta = 5.7$ (d, 1H, $J = 11.5$ Hz, $-CH{=}CH_{(1)}$), 6.05 (d, 1H, $J = 18.0$ Hz, $-CH{=}CH_{(2)}$), 6.65 (dd, 1H, $J = 18.0$ Hz and $J = 11.9$ Hz, $-CH{=}CH_2$), 4.60 (t, 2H, $J = 12.3$ Hz, $-OCH_2$). ^{13}C NMR ($CDCl_3$): $\delta = 147.0$ (m), 142.8 (m), 138.6 (m), 134.8 (m), 122.7 (t), 121.3 (t), 116.1 (m), 112.5 (m), 69.5 (t). ^{19}F NMR (C_6F_6): $\delta = -155.12$ ($2F_{ar}$), -141.26 ($2F_{ar}$), -121.73 (2F), -80.75 (3F).

2,3,5,6-Tetrafluoro-4-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctaoxy)styrene (TF(F_{15})S). Following a similar procedure by use of fluorinated sodium octane-1-olate, TF(F_{15})S was synthesized in a yield of 85% and distilled at 94 °C/1.3 mbar. ^{1}H NMR ($CDCl_3$): $\delta = 5.65$ (d, 1H, $J = 11.5$ Hz, $-CH{=}CH_{(1)}$), 6.05 (d, 1H, $J = 18.0$ Hz, $-CH{=}CH_{(2)}$), 6.60 (dd, 1H, $J = 18.0$ Hz and $J = 11.8$ Hz, $-CH{=}CH_2$), 4.70 (t, 2H, $J = 12.3$ Hz, $-OCH_2$). ^{19}F NMR (C_6F_6): $\delta = -155.15$ ($2F_{ar}$), -141.36 ($2F_{ar}$), -123.33 (2F), -120.19 (2F), -119.77 (2F), -119.01 (4F), -117.92 (2F), -78.25 (3F).

Polymerization Procedure. The polymerizations were performed in a dry Schlenk tube keeping the initiator:CuBr:bipy ratio at 1:1:3. In a typical homopolymerization experiment the tube was charged with 3.500 g (10.80 mmol) of TF(F_5)S, 0.126 g (0.68 mmol) of PhEBr, 0.097 g (0.68 mmol) of Cu(I)Br, and 0.319 g (2.04 mmol) of bipy were added. In the case of block copolymerization 1.0 g (0.159 mmol) of PTF(F_5)S1 was dissolved in 5 mL of xylene in a tube; 0.023 g of Cu(I)Br, 0.074 g of bipy, and 5.95 g (57 mmol) to 16.0 g (154 mmol) of St or 5.05 g (41.5 mmol) of FS were added. Oxygen was removed by three freeze−pump−thaw cycles by applying vacuum and backfilling with nitrogen. The tube with the polymerization mixture was immersed into a silicon oil bath, preheated to 110 °C. After the desired time, the tube was removed from the bath and cooled rapidly down to ambient temperature, and the reaction mixture was diluted with THF. The polymers were precipitated in methanol and dried under vacuum. The yields were determined gravimetrically. These homopolymers were further employed as macroinitiators for block copolymerizations with St and FS in xylene solution. The conversion of the second monomer was determined gravimetrically, too.

Measurements. ^{1}H, ^{13}C, and ^{19}F NMR were recorded on a Bruker 250 MHz spectrometer at room temperature using chloroform-*d* as the solvent if not otherwise specified. Chemical shifts for ^{1}H and ^{13}C NMR are reported in δ ppm downfield from TMS, whereas for ^{19}F NMR the values are stated downfield from hexafluorobenzene.

Molecular weights were determined by size exclusion chromatography (SEC) employing a Viscotek 200 instrument equipped with a PLguard and two PLgel mixed D columns in series from Polymer Laboratories using a RI detector. Measurements were performed in THF at room temperature with a 1 mL/min flow; molecular weights were calculated using PS narrow molecular weight standards in the range 7×10^2−4×10^5 employing the TriSEC software.

FTIR spectra of the neat, powdered samples were recorded on a Perkin-Elmer SpectrumOne FTIR spectrometer.

Thermal analyses were performed with a differential scanning calorimeter, DSC Q1000 from TA Instruments, in a temperature range of −30 to 200 °C at a heating rate of 10 °C min^{-1} under nitrogen. The glass transition temperature (T_g) was determined automatically by the instrument from the second heating trace and is reported as the midpoint of the thermal transition.

Thermal degradation was investigated by thermogravimetric analysis (TGA) performed with a TGA Q500 from TA Instruments recording the total weight loss on approximately 10−12 mg samples from room temperature to 600 °C at a rate 5 °C min^{-1} in a nitrogen flow of 90 mL/min.

XPS analysis was performed using a Sage 100 (SPECS, Berlin, Germany) instrument with an Al Kα X-ray source operated at 300 W and a pressure of $<10^{-7}$ Torr. The analysis was carried out using a takeoff angle of 90° from the surface plane. Atomic concentrations of each element were calculated from the integral peak intensities using a linear background. The systematic error was on the order of 3−5%.

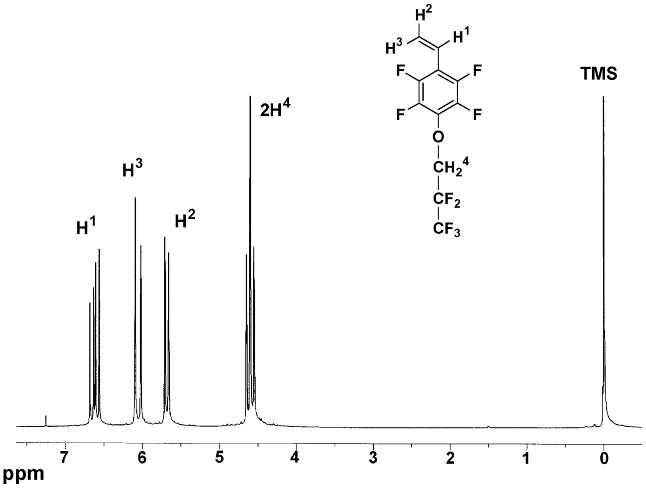
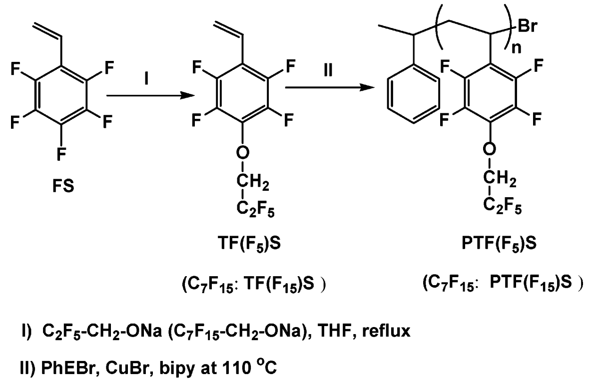


Figure 1. ^{1}H NMR spectrum of TF(F_5)S (in $CDCl_3$).

Scheme 1. Synthesis of Novel Fluorinated Monomers and Polymers



The contact angle of water toward the air side of the polymer films spin-coated on glass slides from 2 to 3% w/w solutions in THF was measured using a contact angle meter at 25 °C with an accuracy of ±2°. The reported values are the average of three measurements made at different positions of a film.

Results and Discussion

Two new, highly fluorinated monomers, 2,3,5,6-tetrafluoro-4-(2,2,3,3,3-pentafluoropropoxy)styrene (TF(F_5)S) and 2,3,5,6-tetrafluoro-4-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctaoxy)styrene (TF(F_{15})S), have been prepared by nucleophilic substitution of 2,3,4,5,6-pentafluorostyrene with the sodium alcoholates of the corresponding fluorinated alcohols, as shown in Scheme 1.

The developed procedure, which is a modification of a route[20,21] to the 4-methoxy-substituted analogue, TFMS, results in 80−85% yields of the vacuum-distilled monomers that elude as pure compounds on an OligoPore (optimized for small- and medium-sized compounds) SEC column. The structures of both monomers were confirmed by a combination of different spectroscopic techniques. FTIR spectra show strong bands at 1200 and 1103 cm^{-1} indicative of aliphatic fluorocarbons. The ^{1}H NMR spectrum of TF(F_5)S in Figure 1 confirms the presence of the three vinyl protons and furthermore shows a strongly deshielded triplet at 4.6 ppm corresponding to two protons. The methoxy protons of 2,3,5,6-tetrafluoro-4-methoxystyrene resonate

Table 1. Homopolymerization of TF(F_5)S, TF(F_{15})S, and St by ATRP in Bulk and Xylene Solution

polymer	time (min)	M_n (target^a)	M_n (NMR)	SEC M_n	SEC PDI	yield (%)	T_g (°C)
PTF(F_5)S1-Br	10	5 000	6 700	6 300	1.30	86	34
PTF(F_5)S2-Br	20	20 000	15 300	18 400	1.09	77	60
PTF(F_5)S3-Br^b	20	20 000		16 900	1.08	58	56
PTF(F_5)S4-Br	23	36 000		25 400	1.20	69	62
PTF(F_{15})S1-Br	120	50 000	28 500			74	26
PTF(F_{15})S2-Br	60	10 000	9 700			70	16
PS1-Br	135	5 000		4 000	1.26	77	81
PS2-Br	420	10 000		9 700	1.18	84	87

^{a} Assuming 100% conversion. ^{b} In 30% xylene solution.

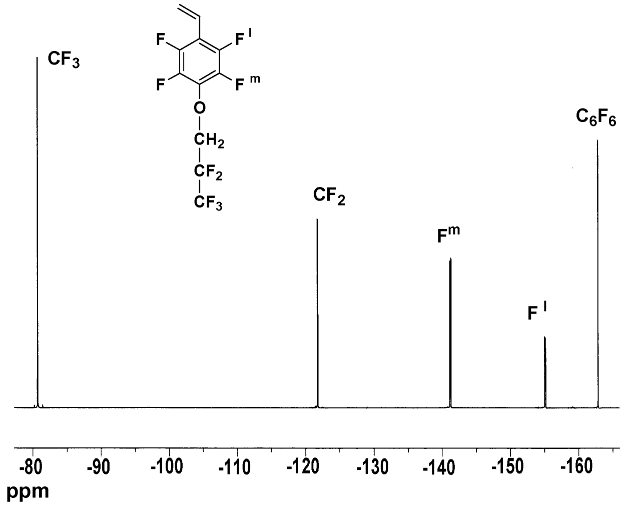


Figure 2. ^{19}F NMR spectrum of TF(F_5)S (in $CDCl_3-C_6F_6$).

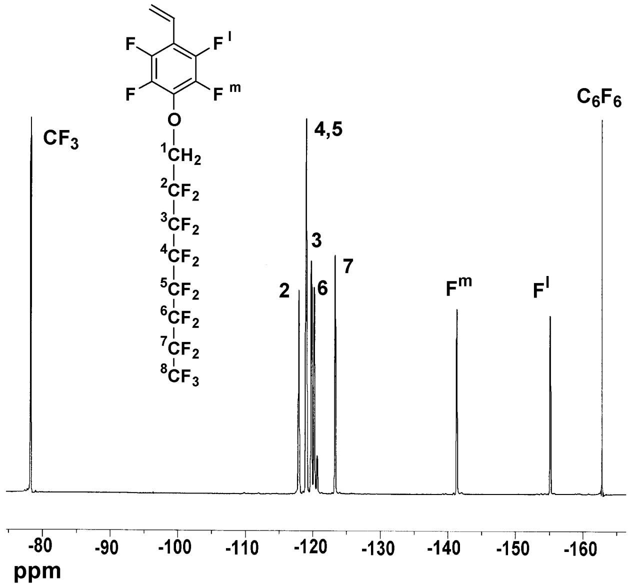


Figure 3. ^{19}F NMR spectrum of TF(F_{15})S (in $CDCl_3-C_6F_6$).

at 4.1 ppm.[19] That is close to the position (4.0 ppm) where the methyleneoxy protons of 1*H*,1*H*-pentafluoropropane-1-ol emanate. Moreover, the triplet pattern will result from the coupling with two neighbor fluorine atoms. Also, the ^{13}C NMR resonance at 69.5 ppm (Experimental Section) is indicative of a methyleneoxy carbon. The strongest evidence for the *para* substitution of the fluorocarbon chain on the phenyl ring in TF(F_5)S is obtained from the ^{19}F NMR spectrum depicted in Figure 2. This spectrum demonstrates the presence of four different types of fluorine atoms. Two types strongly imply the symmetrical 4-substition on the phenyl ring and the remaining two sets of fluorine atoms stem from the side chain.

Similar observations were made for the other monomer, TF(F_{15})S, where in fact the methyleneoxy protons are further deshielded (4.7 ppm). Again, the ^{19}F NMR spectrum depicted in Figure 3 clearly supports the *para* substitution on the phenyl ring. In addition, six different kinds of fluorine resonances originating from the seven groups of fluorine on the aliphatic fluorocarbon chain are observed. The direction of the nucleophilic substitution exclusively in the *para* position of FS is likely facilitated by a partial electron donation from the vinyl group into the phenyl ring with the four electron-withdrawing fluorine susbstituents. Moreover, the unidirectional reaction is probably assisted by the fact that the fluorine is a good leaving group in this strongly activated nucleophilic substitution.

TF(F_5)S and TF(F_{15})S were subjected to ATRP employing 1-phenylethyl bromide as the initiator with Cu(I)Br and bipyridine as the catalyst system at 110 °C. All polymerizations reported here have been performed with an initiator:Cu(I)Br:bipy ratio of 1:1:3. Both monomers polymerize rapidly in bulk as seen from Table 1, and their ATRP is faster than the corresponding ATRP of FS[17] and TFMS.[19] The obtained polydispersity index (PDI) in all cases is below 1.3, which was also observed in the cases of PFS (<1.2)[17] and PTFMS.[19] Generally, a PDI at this level is one of the benefits of a "living"/controlled polymerization. For TF(F_5)S even PDIs lower than 1.1 were achieved in some instances. The M_ns of these novel polymers were determined by SEC using PS standards; however, the M_n can additionally be estimated by ^{1}H NMR. The spectrum shown in Figure 4 includes the basic structural components of PTF(F_5)S2-Br.

Principally, both the areas of the aromatic protons (H_a) and the methyl protons (H_b) from the initiator and the areas of either the main chain protons (H_p) or the side chain protons (H_d) can be employed to calculate the degree of polymerization. The results of M_n listed in Table 1 show relatively good agreement between results obtained by the two different methods. The polymerization of TF(F_5)S in xylene solution also proceeds rapidly and controlled, although to a lower conversion.

Consequently, the ATRP of TF(F_5)S was also carried out at both 90 and 70 °C, resulting in a lower rate of polymerization, as listed in Table 2. The PDI observed at these lower temperatures was slightly broader as the reaction times were longer. This shows that the radical termination is more efficiently suppressed also for these monomers at the highest temperature when the polymerization rate is fastest. In principle, termination in any radical polymerization is unavoidable; however, by

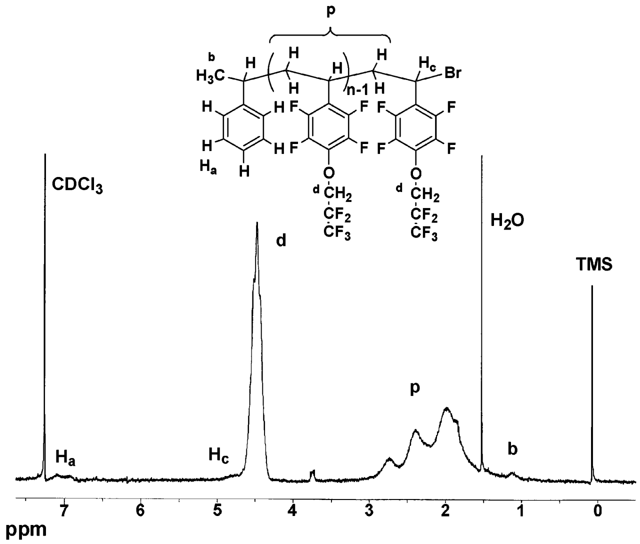


Figure 4. ^{1}H NMR spectrum of PTF(F_5)S2-Br (in $CDCl_3$).

Table 2. ATRP and Conventional Radical Polymerization of TF(F_5)S at Different Temperatures

polymer	temp (°C)	time (min)	yield (%)	SEC M_n	SEC DPI
PTF(F_5)S4-Br[a]	110	23	69	25 400	1.20
PTF(F_5)S5-Br[a]	90	75	65	23 900	1.28
PTF(F_5)S6-Br[a]	70	180	47	30 000	1.37
PTF(F_5)S7-Br[b]	70	30	86	145 900	1.60

[a] M_n (target) 36 000. [b] 0.1 wt % AiBN as the initiator.

ATRP the termination is minimized by creating a steady, low concentration of short-lived, active radical chain ends.[22]

A polymerization of TF(F_5)S was also performed with the conventional radical initiator, AiBN at 70 °C. The polymerization is fast and results in high conversion (86%) in 30 min (Table 2). The polymer had a M_n of approximately 146 000 with a relatively low PDI (1.6). We are unable to offer an explanation so far for this relatively low PDI; however, similarly low PDIs (~1.6) were also obtained for the other fluoropolymers, PFS[17] and PTFMS,[23] when prepared with AiBN in bulk. Nevertheless, the PTF(F_5)S obtained with AiBN cannot be used for synthesis of block copolymers, one of the goals of the investigation.

The ATRP of the other monomer, TF(F_{15})S, employing the same initiator and catalyst system at 110 °C, results in 74% yield in 2 h and 70% yield in 1 h when the target molecular weights are 50 000 and 10 000, respectively, as seen from Table 1. The homopolymers of TF(F_{15})S were insoluble in common organic solvents with fluorinated solvents being the exception. Therefore, it was not possible to perform a SEC analysis, while ^{1}H NMR spectra could be recorded in a C_6F_6:$CDCl_3$ mixture (3:1 v/v). The ^{1}H NMR spectrum of PTF(F_{15})S2-Br shown in Figure 5 includes the principal structural features that were employed to calculate $M_{n,NMR}$ (Table 1) in a manner similar to the one described for PTF(F_5)S2-Br.

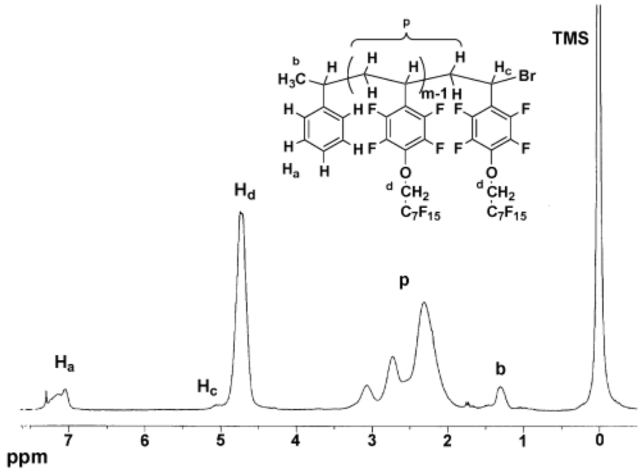


Figure 5. ^{1}H NMR spectrum of PTF(F_{15})S2-Br (in 3:1 mixture of C_6F_6 and $CDCl_3$).

The relatively low PDI of PTF(F_5)S produced by ATRP most likely implies that the majority of the polymer chains have retained the bromine end group functionality, and therefore the homopolymer can be employed as macroinitiator for the preparation of block copolymers with styrene. The macroinitiator concept for synthesis of highly fluorinated block polymers with PS has previously been demonstrated[19] to be flexible; thus, with FS, TFMS, and St the block sequences could be completely interchanged. PTF(F_5)S1-Br was employed as macroinitiator for a set of block copolymers with St; in addition, a single block copolymer with FS was prepared. The inclusion of the block copolymer initiated with PS2-Br complemented the set of PTF(F_5)S-*b*-PS polymers to a series with a PS content ranging from 51 to 89 mol %, as seen from Table 3. That the rate of copolymerization of FS is much faster than that of St is again clearly demonstrated since 55% of FS is polymerized by PTF(F_5)S1-Br in 4.5 h, whereas only 5% of St is converted at nearly the same conditions. Furthermore, the incorporation of 88 mol % of FS is accomplished in 4.5 h, whereas it lasted 17 h to achieve 89 mol % St block copolymer content under similar conditions. It should be added that the block copolymer composition was calculated from ^{1}H NMR spectroscopy.

All the block copolymers were additionally subjected to SEC analyses primarily in order to investigate the PDIs. The SEC traces of the macroinitiator, PTF(F_5)-S1-Br, and the three block copolymers with increasing

Table 3. Preparation of Block Copolymers of PTF(F_5)S or PTF(F_{15})S with St or FS by ATRP (1 g of Macroinitiator, Polymerization Temperature 110 °C, Initiator:CuBr:bipy = 1:1:3)

polymer	time (h)	M_n (target[a])	xylene (mL)	conv[b] (%)	SEC M_n	SEC PDI	PS content (mol %)	M_n (NMR)	T_g (°C)
PTF(F_5)S1-*b*-PS1	4	25 000	3.3	5	10 800	1.20	70	11 800	31; 75
PTF(F_5)S1-*b*-PS2	8	50 000	5	5	12 400	1.23	80	15 200	30; 95
PTF(F_5)S1-*b*-PS3	17	100 000	5	8	14 800	1.37	89	23 900	93
PTF(F_5)S1-*b*-PFS	4.5	50 000	5	55	34 700	1.34	88[c]	35 300	96
PS2-*b*-PTF(F_5)S	9	67 000	15	48	19 900	1.30	51	38 800	92; 53
PS1-*b*-PTF(F_{15})S	4	50 000	10	69	6 800	1.30	36	44 400	72; 34
PS2-*b*-PTF(F_{15})S	4	9 500	4	63	11 600	1.24	90	15 700	87

[a] Assuming 100% conversion of the second monomer. [b] Conversion of second monomer. [c] Content of PFS in mol %.

Table 4. Contact Angles and Glass Transition Temperatures of Styrene and *Para*-Substituted Styrene Homopolymers, Prepared by ATRP

				contact angle (deg)	
polymer	M_n (SEC)	PDI	T_g (°C)	advancing	receding
PS-Br	16 500	1.11	100	95	80
PFS-Br[a]	16 000	1.18	98	108	97
PTFMS-Br[b]	16 700	1.25	94	115	101
PTF(F_5)S3-Br	16 900	1.08	56	117	105
PTF(F_{15})S1-Br	28 500[c]		26	122	104

[a] Reference 17. [b] Reference 19. PTFMS = poly(2,3,5,6-tetrafluoro-4-methoxystyrene). [c] M_n by ^{1}H NMR in C_6F_6−$CDCl_3$.

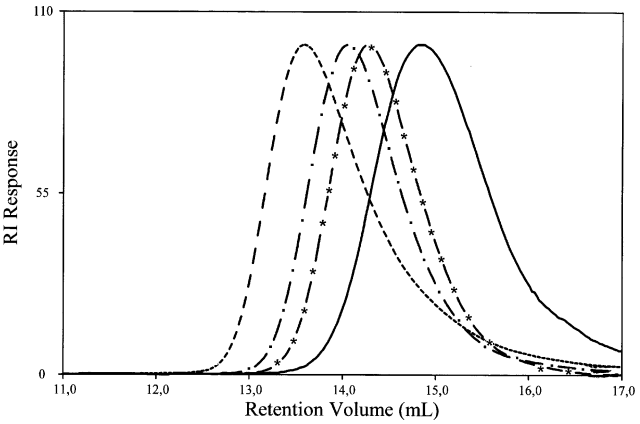


Figure 6. SEC overlays of PTF(F_5)S1-Br (—, M_n 6300, PDI 1.30) and its block copolymers, PTF(F_5)S1-*b*-PS1 (— ∗ —, M_n 10 800, PDI 1.20), PTF(F_5)S1-*b*-PS2 (— · —, M_n 12 400, PDI 1.23), and PTF(F_5)S1-*b*-PS3 (- - -, M_n 14 800, PDI 1.37) as a function of increasing PS content.

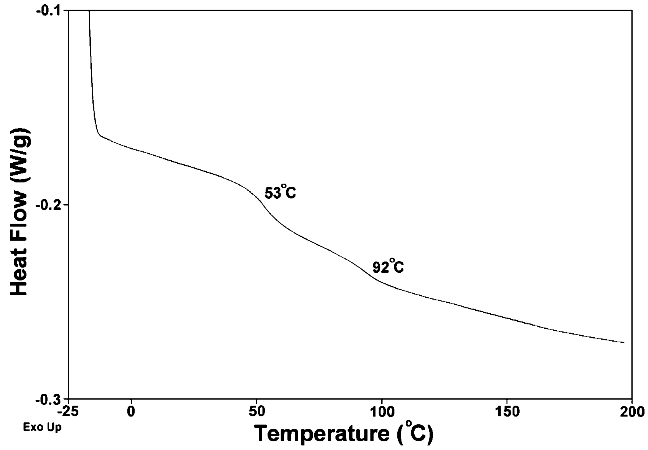


Figure 7. DSC trace of PS2-*b*-PTF(F_5)S with a heating rate of 10 °C/min.

PS content are overlayed in Figure 6. It is seen how the SEC trace of each of the block copolymers is shifted to a higher elution volume than that of the macroinitiator, strongly implying the formation of a copolymer. Moreover, the block copolymers prepared separately generally retain the PDI from the macroinitiator. It is noted that the M_n(SEC) values reported in Table 3 are only indicative due to the normal problems with assessment of M_n of copolymers by use of standard calibration.

The insolubility of PTF(F_{15})S necessitated the block copolymer route starting from the PS−Br macroinitiator. Two different block copolymers with 36 and 90 mol % PS content were synthesized in xylene solution. The introduction of the PS block in the block copolymers rendered solubility in THF and $CDCl_3$ to these block copolymers. The SEC analyses of the PS-*b*-PTF(F_{15})S polymers reveal a relatively narrow PDI (Table 3), and the observed shift in elution volume also signals the formation of block copolymers. However, the M_n by SEC of these block copolymers is very different from the theoretically predicted, whereas the NMR values are much closer to the theoretical values.

Thermal Properties. The glass transition temperatures (T_g) of all these novel polymers were determined by DSC. T_g of PTF(F_5)S is in the range 34−62 °C (Table 1) depending on M_n. PTF(F_5)S1-Br ($M_n \sim 6700$) has the lowest T_g whereas the remaining PTF(F_5)S polymers seem to approach a maximum T_g of approximately 62 °C. PTF(F_{15})S has even lower T_g (16−26 °C) also with a M_n dependence. We have previously observed a T_g dependence of M_n for PFS with a maximum value (~102 °C) similar to that of PS.[17] This strongly suggests that the introduction of alkoxy side chains in the *para* position of the fluorinated phenyl rings of the polymers results in a plasticizing effect with a corresponding decrease of the T_g. Furthermore, the length of the substituting alkoxy group seems to govern the level of T_g inasmuch as the longest alkoxy groups decreases T_g mostly. Substantial support for this claim is provided in Table 4 where T_gs of polymers of nearly the same M_n but with different and increasing alkoxy group length are compared.

The T_gs of the block copolymers listed in Table 3 show some interesting phenomena. First, copolymers with the fluorinated alkoxy side chains and PS demonstrate phase separation with two-phase morphology as reflected in two T_gs when the molar composition is not too different. Figure 7 shows a representative DSC trace of a PTF(F_5)S-*b*-PS polymer. It is also intriguing that the length of a particular block reflects the T_g typical of that block length. For example, in PTF(F_5)S1-*b*-PS1 and PTF(F_5)S1-*b*-PS2 the T_g assigned to the PTF(F_5)S block is very close to the one observed in the macroinitiator. On the other hand, in PS2-*b*-PTF(F_5)S where the PTF(F_5)S block is larger the T_g of this is recorded to 53 °C. However, when one of the blocks becomes too short typically around 10 mol % with the M_n discussed here, only the T_g of the largest block is detected. Similar observations emerge in the case of the PS1-*b*-PTF(F_{15})S polymer where a T_g of 34 °C has been assigned to the PTF(F_{15})S block, and a T_g of 72 °C is attributed to the PS block. However, in the second block copolymer where the PS block constitutes 90 mol % only a $T_g \sim 87$ °C from that block is observed.

Finally, the thermal stability of the novel homopolymers was investigated and compared to those of PS, PFS, and PTFMS. Figure 8 shows the weight loss of PTF(F_5)S and PTF(F_{15})S in a N_2 atmosphere as a function of temperature. It is seen that both polymers have almost the same thermal stability and that the stability of both is inferior to the stabilities of both PFS[17] and PTFMS;[19] the fluoroalkoxy side groups are apparently more thermally labile than the methoxy group. In fact, the thermal stability of PTF(F_5)S and PTF(F_{15})S is even lower than that of PS; thus, the beneficial fluorination on the phenyl ring,[17] which was also partly experienced in the case of PTFMS,[19] is unable to compensate for the thermal lability of the fluoroalkoxy groups.

Surface Properties. Preliminary investigations of the novel materials' surface properties were conducted by determination of the contact angles of a water drop on spin-coated surfaces. The results are listed in Table

Table 5. Results of XPS Analysis and Contact Angle Measurements Using Water Droplets on Film Surfaces of the Fluorinated Polymers

		elements (%, XPS)					contact angle (deg)	
polymer	PS (mol%)	F	C	O	F/C × 100	F/C × 100 theor	advancing	receding
PTF(F_5)S1	0	46.2	48.3	5.5	96	130	117	105
PS2-*b*-PTF(F_5)S	51	43.4	50.0	6.6	87	74	113	102
PTF(F_5)S1-*b*-PS1	70	37.7	57.7	4.6	65	54	111	104
PTF(F_5)S1-*b*-PS2	80	39.3	55.4	5.3	71	35	109	100
PTF(F_5)S1-*b*-PS3	89	31.3	63.3	5.4	49	19	105	99
PS	100						95	80
PTF(F_{15})S	0	57.0	40.1	3.0	142	188	122	104
PS1-*b*-PTF(F_{15})S	36	54.7	42.7	2.6	128	101	119	103
PS2-*b*-PTF(F_{15})S	90	36.7	61.4	1.9	60	34	111	102

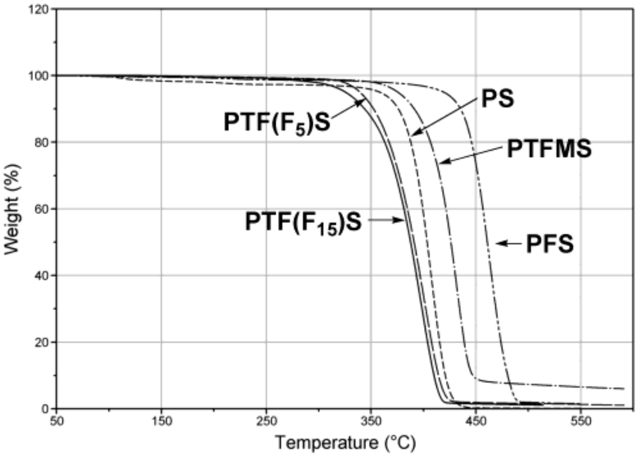


Figure 8. TGA curves of PS, PFS, PTFMS, PTF(F_5)S, and PTF(F_{15})S in a N_2 atmosphere with a heating rate of 5 °C/min.

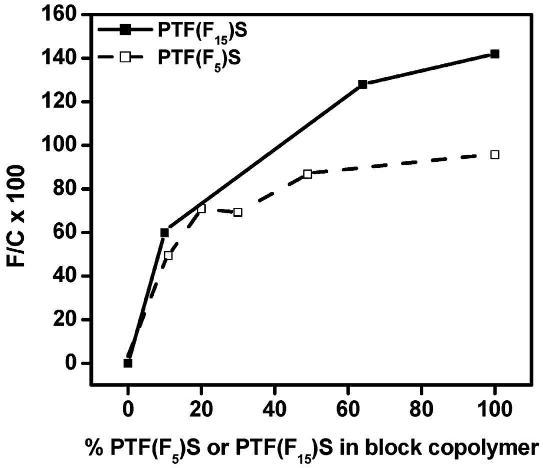


Figure 9. F/C ratio determined by XPS at the surface as a functionof % PTF(F_{15})S (■) or PTF(F_5)S (□) in block copolymers.

4 where a gradual increase in the advancing contact angle when going from PS over PFS and PTFMS to PFT(F_5)S and PFT(F_{15})S is seen. However, already the fluorination of the phenyl ring increases the hydrophobicity of the material surface as argued from the increase in contact angle. A further raise in hydrophobicity is gained when the fluorinated phenyl ring is added methoxy groups (PTFMS), whereas the substitution of methoxy groups with the fluorinated propoxy groups (PFT(F_5)S) only slightly increases the contact angle from 115° to 117°. This observation is somehow surprising since the surface tension of CH_3 groups (30 dyn/cm)[2] is much higher than that of CF_3 groups (15 dyn/cm). When even longer fluorooctaoxy groups exist on the phenyl ring (PFT(F_{15})S), an advancing water contact angle of 122° is found. Such a very large contact angle has previously been detected for surfaces of fluorinated alkyl side-chain ionenes[5] and was explained by excellent alignment of the CF_3 groups on the surface. In comparison, poly(tetrafluoroethylene) under the same conditions shows a contact angle of 115°.[5] The length of the fluorinated side chain thus seems to be critical for the packing and alignment of the CF_3 groups in order to fully exploit a material's potential for creating low-energy surfaces. A fluorinated octyl side chain on PFS is sufficient to achieve the lowest possible surface energy whereas a fluorinated propyl side chain appears to be too short. Further support for this claim is provided by XPS analysis of the films reported in Table 5. In the case of PTF(F_5)S 46% fluorine was detected on the surface whereas the surface of PTF(F_{15})S is further enriched in fluorine (57%). It should be added that the analysis seems to underestimate the fluorine content as evident from a comparison of the determined F/C ratio with the calculated, theoretical F/C ratio.

Thin films of the block copolymers of PTF(F_5)S and PTF(F_{15})S with PS were likewise investigated by XPS and subjected to contact angle measurements. Interestingly, all block copolymers show relative high fluorine content at the surfaces as seen from Table 5. Even the copolymers with the lowest content (~10 mol %) of the fluorinated block reveal fluorine contents of 31−37%. This strongly suggests that the fluorinated blocks orient toward the surfaces. As a comparison, a XPS analysis of PTFMS shows 28% fluorine on the surface. The F/C ratios in the surfaces of all the block copolymers are depicted in Figure 9.

The same dramatic effect is observed in the contact angle determinations of the block copolymer surfaces also listed in Table 5. An approximately 10 mol % block of the fluorinated monomer in the PS block copolymers increases the contact angle to 105° and 111° for TF(F_5)S and TF(F_{15})S, respectively. The contact angle dependence of the content of TF(F_{15})S in the block copolymers is shown in Figure 10. The advancing contact angle of water is also depicted in Figure 11 as a function of the detected F/C ratio in the film surfaces. The two sets of angles express that at the same F/C ratio the highest contact angle will most likely be achieved in the PTF(F_{15})S with the homopolymer PTF(F_5)S being the only exception. Furthermore, it is obvious that the highest possible contact angle, 122°, can only be obtained with the homopolymer of PTF(F_{15})S. On the other hand, the PTF(F_{15})S blocks also have a much higher F/C ratio per repeating unit of the main chain compared to the PTF(F_5)S blocks. This is due to the fluoroalkoxy side chains in the TF(F_{15})S repeating units that contain 10 more fluorine atoms than the similar side chains in the TF(F_5)S repeating units. In other words, the higher

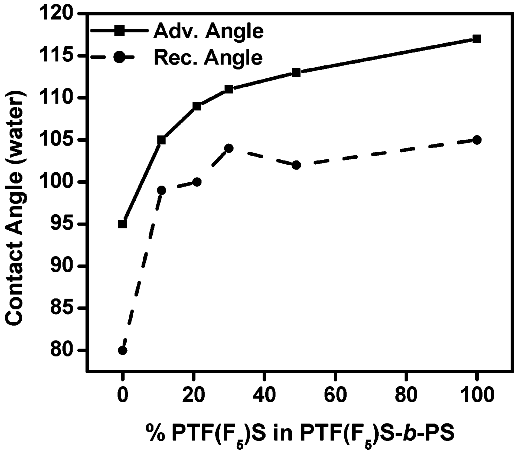


Figure 10. Advancing (■) and receding (●) contact angles of water on block copolymer surfaces as a function of % PTF-(F$_5$)S in block copolymers.

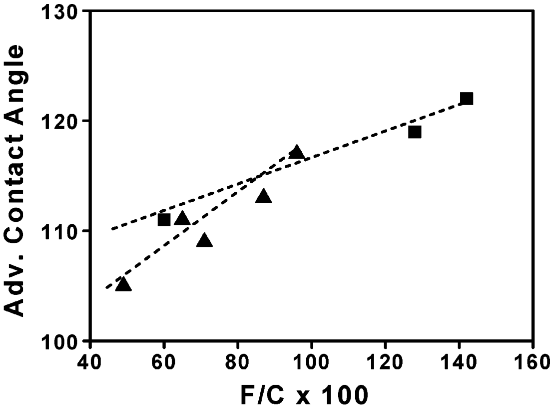


Figure 11. Advancing contact angle of water as a function of the determined F/C ratio in the film surfaces of PTF(F$_{15}$)S (■) or PTF(F$_5$)S (▲) blocks in homo- or block copolymers.

contact angle is achieved due to more than twice as many fluorine atoms per chain segment, thus at a considerably higher consumption of fluorine. However, the minimum necessary amount of fluorine in order to obtain these contact angles has not been worked out since the analysis is based on a relatively small and limited number of block copolymers with styrene. On the other hand, starting from the respective short fluoropolymer macroinitiators, the styrene block length and thus the F/C ratio of the block copolymer can to a certain extent be controlled when this is needed.

In combination, both XPS analyses and contact angle measurements strongly imply that the fluorinated blocks preferentially segregate at the air surface of the films when spin-coated. Furthermore, even a relatively small fluorinated block in a PS block copolymer significantly and effectively lowers the surface energy of the block copolymer.

Conclusions

Nucleophilic substitution on FS with the proper fluorinated alcohols provides a facile route to novel, highly fluorinated monomers. These can be polymerized in a controlled manner by ATRP. Furthermore, block copolymers with St and controlled characteristics can be prepared by the macroinitiator approach. The new homopolymers demonstrate different, but considerably lower, T_gs than PFS and PS with comparable molecular weights presumably resulting from a fluoroalkoxy side-chain plasticizing effect. The block copolymers with PS are characterized by strong phase separation reflected in two T_gs, which can be observed when the smallest block constitutes more than 10 mol %. The long fluorinated octaoxy side chain enriches surfaces of both homopolymers and block copolymers with PS. Spin-coated films containing the fluorinated octaoxy side chain obtain very low surface energy as revealed by a high advancing water contact angle on the order of 122°. The influence of mixing small amounts of these block copolymers in a PS matrix on the surface properties is under investigation.

Acknowledgment. We gratefully acknowledge the financial support from Aage and Johanne Louis-Hansen's Foundation (DK) and Materials Research, Danish Research Agency. We thank Lene Hubert, Risø National Laboratory, DK, for recording the XPS spectra.

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MA034952B