

Synthesis, characterization, thermal and surface properties of co- and terpolymers based on fluorinated α -methylstyrenes and styrene

Justyna Walkowiak-Kulikowska,^{1,} Anna Sz wajca,¹ Véronique Gouverneur,² Bruno Ameduri,^{3,*}*

¹ Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznań, Poland

² Chemistry Research Laboratory, University of Oxford, Oxford OX1 3TA, United Kingdom

³ Institut Charles Gerhardt, Ingénierie et Architectures Macromoléculaires, UMR CNS 5253, Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'Ecole Normale, 34296 Montpellier, France

*Corresponding authors. Dr Bruno Ameduri,
Phone: +33 467 144 368, Fax: +33 467 147 720
e-mail: Bruno.ameduri@enscm.fr

Dr Justyna Walkowiak-Kulikowska,
Phone: +48 61 829 1821, Fax: +48 61 829 1555
e-mail: Justyna.A.Walkowiak@amu.edu.pl

ABSTRACT

Conventional bulk radical co- and terpolymerizations of α -fluoromethylstyrene (FMST) or/and α -trifluoromethylstyrene (TFMST) with styrene (ST) initiated by α,α' -azobis(isobutyronitrile) (AIBN) are presented. The resulting poly(F-ST-*co*-ST) copolymers and poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers were characterized by ^1H , ^{19}F and/or ^{13}C NMR spectroscopy that evidenced the incorporation of fluorinated α -methylstyrenes and enabled to assess the molar percentages of base units (in copolymers, 10.2-49.7 mol% of FMST and 10.6-48.3 mol% of TFMST and in terpolymers, F-ST mol% ranging between 5.2-38.4 and 3.7-14.5 for FMST and TFMST, respectively). Molecular weights were in the range of $1,500\text{-}23,700\text{g}\cdot\text{mol}^{-1}$, $1,500\text{-}14,600\text{g}\cdot\text{mol}^{-1}$ and $6,900\text{-}10,900\text{g}\cdot\text{mol}^{-1}$ for poly(FMST-*co*-ST), poly(TFMST-*co*-ST) copolymers and poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers, respectively. Bulkier CF_3 group induced a lower reactivity of TFMST comonomer. From the extended Kelen-Tudos (EK-T) linear method, the kinetics of the copolymerizations led to the determination of the reactivity ratios, r_i , of both comonomers for each copolymerization system ($r_{\text{FMST}} = 0.08 \pm 0.02$ and $r_{\text{ST}} = 0.72 \pm 0.04$, $r_{\text{TFMST}} = 0.00$ and $r_{\text{ST}} = 0.64 \pm 0.01$ at $70\text{ }^\circ\text{C}$) showing that F-ST monomers were less reactive than ST, thus retarding the rate of polymerization, and thus reduced the molecular weights. However, in the case of terpolymerizations where all three monomers were incorporated into polymer chains, the retarding effects of F-STs was less noticeable indicating that a termonomer induced copolymerization occurred. Finally, the thermal properties of these copolymers showed that the presence of fluorinated monomer units incorporated into polystyrenic structure promoted a rise of the glass transition temperatures of the resulting copolymers up to $114\text{ }^\circ\text{C}$ [poly(TFMST-*co*-ST) copolymer] and a slightly better thermal stability than that of polystyrene. Furthermore, the relationships between surface structure of varied fluorinated copolymers and their wetting and oleophobic properties displayed that below 80 mol% of styrene repeating units, incorporation of 20-40 mol% of FMST or 10-20 mol% of TFMST in the copolymer structure caused a major change in the contact angle (CA) of copolymers and unexpectedly high water CA reached up to 147° .

KEYWORDS: Fluorinated α -methylstyrenes (FMST, TFMST), radical co- and terpolymerization, termonomer induced copolymerization (TIC), ^{19}F and ^1H NMR spectroscopy, thermal and surface properties.

INTRODUCTION

Fluoropolymers are very interesting materials which exhibit a unique combination of outstanding properties,¹⁻⁵ such as high thermostability and chemical inertness (to acids, bases, solvents, and petroleum), low dielectric constants and dissipation factors, low refractive index and friction coefficient, low water absorptivities, excellent surface characteristics. Hence, these high added-value products can find relevant applications in many fields of high technology: engineering, chemical and automobile industries,⁶ optics,⁷⁻¹⁰ microelectronics, textile finishing,¹¹ aeronautics,¹² and military¹³. However, these products can still be difficult to process since some of them exhibit very high melting points or even cannot be melted, while others are not soluble in common solvents. Nevertheless, the specific properties of fluoropolymers can be brought by the nature of the functional side groups of the copolymer backbone. In addition, involving other fluorinated or nonfluorinated monomers in co- or terpolymerization could lead to the formation of fluoropolymers possessing peculiar properties.

Fluorinated aromatic polymers represent an interesting family of fluoropolymers, that may gain a unique combination of high performance properties due to the characteristic effects of the aromatic group (e.g., increasing the polymer T_g and enhancing its thermostability), as well as fluorine substituent/s on the physico-chemical characteristics.¹⁴ Thomas and O'Shaughnessy¹⁵ studied the kinetics of the radical copolymerization of styrene (ST) with chlorotrifluoroethylene (CTFE). The reactivity ratios were assessed and found to be $r_{\text{ST}} = 7.0$ and $r_{\text{CTFE}} = 0.001$ at 60 °C. As expected, ST ($Q = 1$) was much more reactive than CTFE ($Q = 0.025$), and thus, the composition of poly(CTFE-*co*-ST) copolymers always contained much higher amount of ST than that of the feed.¹⁶ More recently, Kyulavska et al.¹⁷ reported the unexpected alternating radical copolymerization of CTFE with 3-isopropenyl- α,α' -dimethylbenzyl isocyanate (*m*-TMI). The average values of the

monomer reactivity ratios, r_{CTFE} and $r_{m\text{-TMI}}$, were 0.08 and 0.03 at 130 °C, respectively, depending on the monomer conversions and the applied calculation methods. In all cases, poly(CTFE-*co-m*-TMI) copolymers exhibited a high tendency toward alternation, that was confirmed by the Igarashi's theory¹⁸ which revealed a high content of CTFE-*m*-TMI heterodyads.

In the past decades, much attention has been focused on the synthesis and polymerization studies of styrenic monomers either bearing fluorine atoms/fluorinated substituents on the aromatic ring or possessing mono-, di- and trifluorinated vinyl moiety.¹⁹ Moreover, Souzy *et al.*^{19,20} studied radical co- and terpolymerizations of aromatic perfluorovinyl ether monomers i.e. 4-[(α,β,β -trifluorovinyl)oxy]bromobenzene²⁰ and 4-[(α,β,β -trifluorovinyl)oxy]benzenesulfonic acid²¹ with various fluoroolefins (vinylidene fluoride - VDF, CTFE, hexafluoropropene - HFP) and the application of the resultant functional polymers for fuel cell membranes^{22,23}. Only a few examples of radical copolymerization of fluoroolefins with fluorinated α -methylstyrenic monomers have been reported, so far. Among them, a radical copolymerization of CTFE with [1-(fluoromethyl)vinyl]benzene (FMB) as a representative styrenic comonomer with an allyl fluoride functionality was achieved successfully.²⁴ Moreover recently, Walkowiak-Kulikowska *et al.*²⁵ studied the successful radical terpolymerizations of α -trifluoromethylstyrene (TFMST) with CTFE and VDF. It is known that fluorinated α -methylstyrene (F-ST) is difficult to polymerize under radical polymerization conditions although the hydrocarbon analogue such as α -methylstyrene (MST) is easily polymerized under moderate radical and anionic polymerization conditions.^{26,27} The radical copolymerisations of α -fluoromethylstyrene (FMST) with methyl methacrylate (MMA) or styrene (ST), reported by Baldwin and Reed,²⁸ demonstrated that the fluorinated aromatic compound is an active comonomer, although it retarded the rate of polymerization of both hydrocarbon monomers, but had a greater effect on MMA than on styrene. On the other hand, the investigations on the reactivity of TFMST have mainly been focused on the reason why the monomer yields no homopolymer. Ito *et al.*²⁹ studied the initiation reaction of TFMST while Narita's team³⁰ discussed the propagation reaction, evidencing its inability to form homopolymer.

In spite of its high e and Q -values (0.90 and 0.43, respectively),^{31,32} TFMST is reluctant to undergo radical and anionic homopolymerization. However, a radical polymerization of *p*-methyl- α -trifluoromethylstyrene and α -difluoromethylstyrene initiated by AIBN to yield corresponding homooligomers was achieved by Narita et al.^{33,34} Ueda and Ito³¹, who reported the kinetics of radical copolymerization of TFMST with ST, supplied their monomer reactivity ratios ($r_{\text{TFMST}} = 0.00$ and $r_{\text{ST}} = 0.60$ at 60 °C) which confirm that TFMST does not self-propagate. Although TFMST retards the polymerization rates and significantly increases the reaction time in conventional radical copolymerization with styrene, successful iodine transfer copolymerization of both monomers (FMST and TFMST) led to fluorinated copolymers with predetermined molar masses and narrow polydispersities.³⁵

The presence of bulky and electron-withdrawing trifluoromethyl group in α -position of styrene plays the same issue in making an inefficient homopolymerization, under radical conditions, of α -trifluoromethacrylic acid.^{32–34,36–39} However, recent copolymerizations^{37–41} of such a later monomer with VDF were successfully achieved. With the objective to prepare new functional fluoropolymers for fuel cell membranes, convenient and cost-effective routes to access various non-commercially available fluorinated styrenic monomers of increasing fluorine content were developed.^{42–44} Among then, α -fluoromethylstyrene (FMST) and α -trifluoromethylstyrene (TFMST), were identified as prime candidates for further studies. Therefore, it was of interest to revisit in-depth the conventional radical copolymerizations of F-STs with styrene (ST) and further investigate the terpolymerizations of the three monomers (FMST, TFMST and ST).

EXPERIMENTAL PROCEDURES

Materials. Styrene (ST, 99.9% containing 4-*tert*-butylcatechol as inhibitor from Sigma-Aldrich) was washed with sodium hydroxide solution, rinsed with deionized water, dried, and distilled under reduced pressure before use. The radical initiator, α,α' -azobis(isobutyronitrile) (AIBN, >98% from Fluka) was recrystallized from methanol. Following reagents: octadecyltrichlorosilane (OTS, $\geq 96\%$ from Sigma-Aldrich), sulfuric acid (H_2SO_4 96% POCH), hydrogen peroxide (H_2O_2 30% POCH)

and common organic solvents (anhydrous tetrahydrofuran, THF, acetonitrile, and anhydrous toluene from Sigma-Aldrich), were used as received.

Measurements. *Nuclear Magnetic Resonance* (NMR) spectra were recorded on Bruker AC 400 instruments. Coupling constants and chemical shifts are given in Hz and ppm, respectively. The experimental conditions for ^1H (or ^{19}F) NMR spectra were as follows: flip angle 90° (or 30°), acquisition time 4.5 s (or 0.7 s), pulse delay 2 s (or 5 s), number of scans 16 (or 64), and a pulse width of 5 μs for ^{19}F NMR.

Thermogravimetric analysis (TGA) experiments were performed with a TGA 51 apparatus from TA Instruments, under nitrogen, at the heating rate of $10^\circ\text{C}.\text{min}^{-1}$ from room temperature up to a maximum of 550°C . The sample size varied between 10 and 15 mg.

Size Exclusion Chromatography (SEC) measurements were conducted using a GPC 50 from Polymer Labs (Now Varian) equipped with both refractive index (RI) and UV detectors and its corresponding software (Cirrus). The system uses two columns PL Gel Mixed C ($200 < M_w < 20,000,000$ g/mol) with THF as the eluent with a flow rate of 1.0 mL/min at room temperature. Monodispersed poly(styrene) standards were used for calibration. Aliquots were sampled from the reaction medium, diluted with tetrahydrofuran up to a known concentration ($C_{p,t}$) $\sim 4\%$ wt.%, filtered through a 20 μm PTFE Chromafil Membrane, and finally analyzed by SEC under the conditions described above.

Advancing and Receding Contact Angle (ARCA). The surface dynamic wetting angles i.e. advancing and receding drop contact angles of the covered glass surfaces were measured using the OCA 15+ contact angle measurement system. Measurements were performed as a function of time. The final values were averages of at least five CA measurements on the same sample. A drop (2 μL) of water was deposited using a micro syringe. The CAs were measured using Ellipse Fitting function. Measurements were taken over different areas on each surface. The three series of fluorinated copolymer films were obtained as previously described (detailed in Supporting Information, Scheme S47).³⁵

Synthesis of Fluorostyrenic monomers (F-STs). Noncommercially available fluorinated monomers, α -fluoromethylstyrene (FMST) and α -trifluoromethylstyrene (TFMST), were synthesized according to literature procedures (Supporting Information, section 1).^{42,43}

Radical Copolymerizations and Terpolymerizations of F-STs with ST

The batch co- and terpolymerizations of styrene (ST) with fluorinated α -methylstyrenes (F-STs) were carried out at 70 °C for 14 hours in sealed Schlenk tubes beforehand degassed by five freeze-thaw cycles until no bubbling occurred. AIBN was used as the radical initiator. Afterwise, the tube was cooled to room temperature, opened, and the content was analyzed. Part of the mixture was analyzed by ¹H and ¹⁹F NMR spectroscopy, while the remaining part of the mixture was precipitated from cold pentane. The resulting white, light powders were isolated by filtration and dried under vacuum at 80 °C until constant weight. Conversion was determined by ¹H, ¹⁹F and/or ¹³C NMR spectroscopy, and molecular weights were determined by size exclusion chromatography (SEC). The kinetics of radical copolymerizations that enabled to determine the reactivity ratios of comonomers are detailed in the Supporting Information (Table S3 and Figures S17-S22).

RESULTS AND DISCUSSION

In the synthesis of targeted fluorinated monomers, the following key-step reactions were employed: (i) a nucleophilic selective fluorination of suitable substrate with oxygen functions to enable FMST synthesis^{43,45} and (ii) palladium-mediated Suzuki cross-coupling^{46–52} for the synthesis of TFMST^{42,43}. The synthetic routes were then implemented for gram-scale preparation of the monomers, detailed in the Supporting Information (Schemes S1 and S2).

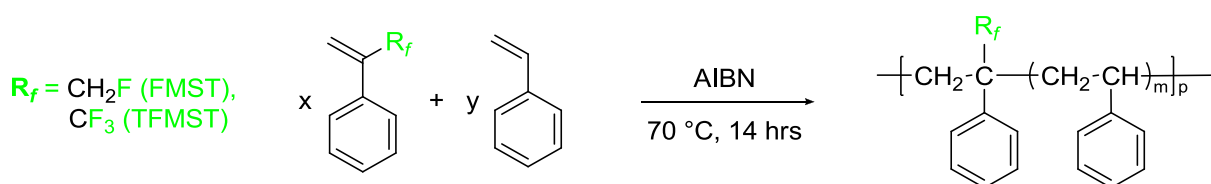
Reactivity of fluorinated α -methylstyrenes (F-STs) in radical polymerizations

In general, the radical bulk homopolymerizations of fluorinated α -methylstyrenes initiated by α,α' -azobis(isobutyronitrile) (AIBN) reported by Baldwin and Reed,²⁸ Ito et al.,^{29,32} Ueda,³¹ Kostov et al.²⁴ and the authors of present study^{25,35} were unsuccessful and did not even lead to any

oligomer. However, the first three of above mentioned authors reported that both FMST and TFMST are the efficient monomers in radical copolymerization with styrene, although the fluorinated aromatic monomers retarded the polymerization rate of styrene.

Radical copolymerizations of F-ST with ST

The conventional radical bulk copolymerizations of styrene (ST) with fluorinated α -methylstyrene (FMST or TFMST) using an initial 2,2'-azobisisobutyronitrile (AIBN) concentration of $0.01 \text{ mol} \cdot \text{L}^{-1}$ were performed at 70°C for 14 hours as illustrated in Scheme 1.



Scheme 1. Bulk radical copolymerizations of styrene (ST) with fluorinated α -methylstyrene (FMST or TFMST) initiated by AIBN at 70°C .

The resulting *poly*(FMST-*co*-ST) and *poly*(TFMST-*co*-ST) copolymers of different molecular weights (ranging from 1,500 to 23,800 $\text{g} \cdot \text{mol}^{-1}$ and 1,500 to 14,600 $\text{g} \cdot \text{mol}^{-1}$, respectively, with a F-ST mol% varying between 10.6-49.7 for FMST and 10.2-48.3 for TFMST, Table 1) were characterized by ^1H (Figures S1 and S9) and ^{19}F (Figures S2 and S10) NMR spectroscopy, detailed in the Supporting Information.

The comparison of ^1H NMR spectra (cascade A) of ST and FMST monomers with *poly*(FMST-*co*-ST) copolymer with a composition of 44.7/55.3 mol% and ^{19}F NMR spectra (cascade B) of FMST monomer with *poly*(FMST-*co*-ST) copolymer (44.7/55.3 mol%) is illustrated in Figure 1. The ^1H NMR spectrum of *poly*(FMST-*co*-ST) copolymer (—) exhibits broad signals centered at 1.72, 3.75 and 6.88 ppm attributed to secondary and tertiary aliphatic backbone protons of FMST and ST copolymer units (H_{B}' , H_{B} , H_{A}), side chain primary protons of $-\text{CH}_2\text{F}$ group of FMST (H_{A}') and aromatic protons of ST and FMST copolymer units (H_{C} , H_{D} , H_{E} , H_{C}' , H_{D}' , H_{E}'), respectively. Most probably, due to the absence of vinyl moieties, signals of aromatic protons in copolymer underwent high field shift to 6.88 ppm in comparison to H_{Ar} multiplets at 7.45, 7.52, 7.62 and 7.35,

7.46 ppm observed in NMR spectra of ST and FMST monomers, respectively. ^{19}F NMR spectrum of FMST monomer (—) exhibited a characteristic triplet at -212.7 ppm ($^2J_{\text{F-H}}=47.1$ Hz) assigned to $-\text{CH}_2\text{F}$ moiety of FMST monomer, whereas that of poly(FMST-*co*-ST) copolymer (—) displays a broad high field shifted multiplet at -223.5 ppm attributed to $-\text{CH}_2\text{F}$ moiety attached to the polymer chain.

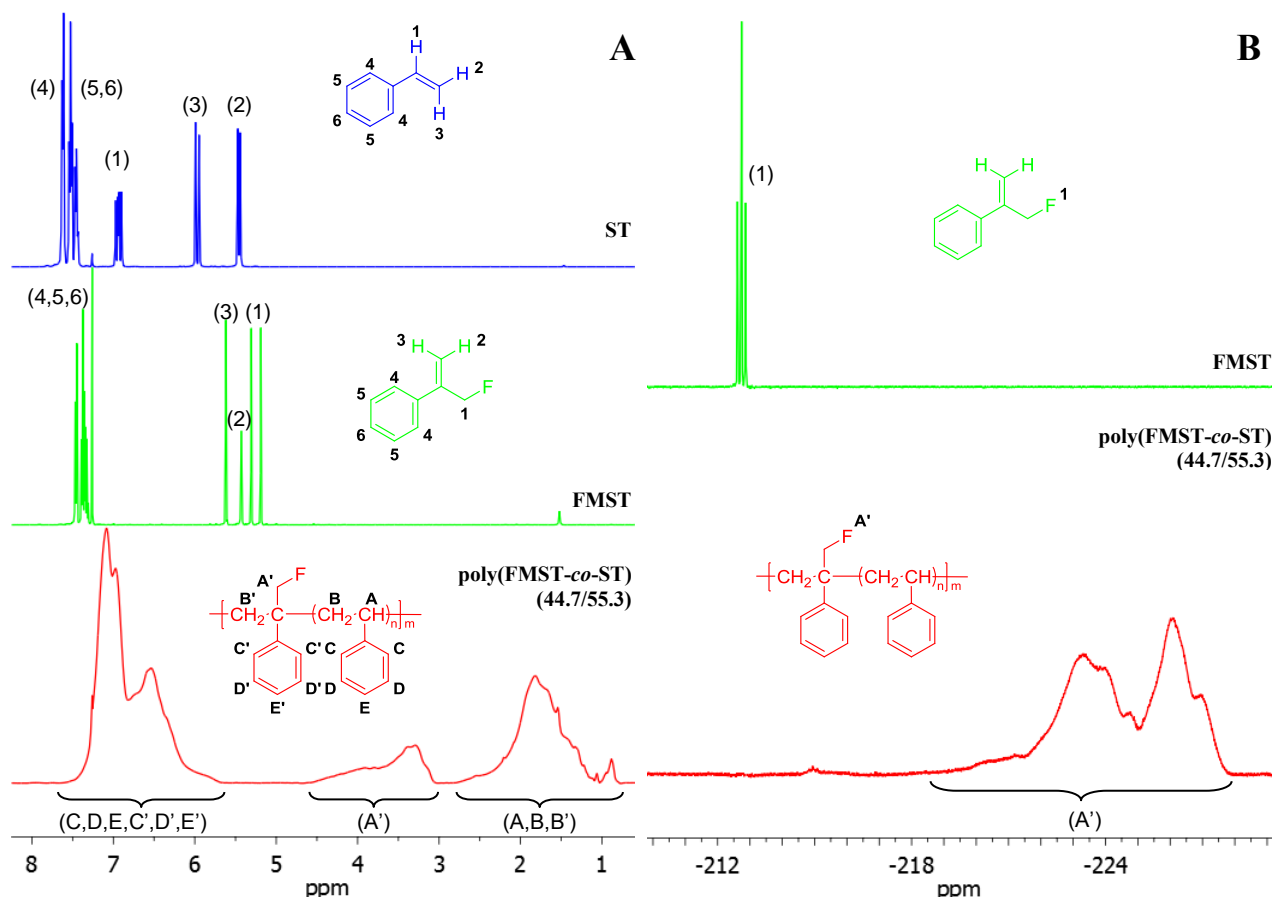


Figure 1. Comparison of ^1H and ^{19}F NMR spectra (recorded in CDCl_3) of monomers and poly(FMST-*co*-ST) copolymer. *Left-hand cascade A:* ^1H NMR spectrum of (—) styrene (ST), (—) α -fluoromethylstyrene (FMST), and (—) poly(FMST-*co*-ST) copolymer (44.7:55.3, $M_n = 2,900$ g mol $^{-1}$), respectively; *right-hand cascade B:* ^{19}F NMR spectrum of (—) α -fluoromethylstyrene (FMST) and (—) poly(FMST-*co*-ST) copolymer (44.7:55.3, $M_n = 2,900$ g mol $^{-1}$, Table 1, Entry 5).

The integrals of the characteristic proton signals (Figures S3-S8 in Supporting Information) assigned to aliphatic backbone of ST and FMST (signal centered at 1.72 ppm, marked as A, B, and B') and to fluoromethyl moiety of FMST (signal centered at 3.75 ppm, marked as A') base units

incorporated in the copolymers allowed to determine the content of ST and FMST comonomers in the copolymer (Table S1 in Supporting Information) by the following equations:

$$\text{mol}\%_{\text{ST}} = [(I_{\text{A,B,B'}} - I_{\text{A'}})/3] / \{[(I_{\text{A,B,B'}} - I_{\text{A'}})/3] + (I_{\text{A'}/2})\}$$

$$\text{mol}\%_{\text{FMST}} = (I_{\text{A'}/2}) / \{[(I_{\text{A,B,B'}} - I_{\text{A'}})/3] + (I_{\text{A'}/2})\}$$

where $I_{\text{A,B,B'}}$ and $I_{\text{A'}}$ stand for the integrals of signals centered at 1.72 and 3.75 ppm, respectively.

Moreover, the comparison of ^1H NMR spectra (cascade A) of ST and TFMST monomers with poly(TFMST-*co*-ST) copolymer with a composition of 43.7/56.3 mol% and ^{19}F NMR spectra (cascade B) of TFMST monomer with poly(TFMST-*co*-ST) copolymer (43.7/56.3 mol%) is illustrated in Figure 2 (detailed description in the Supporting Information, subchapter 3.1).

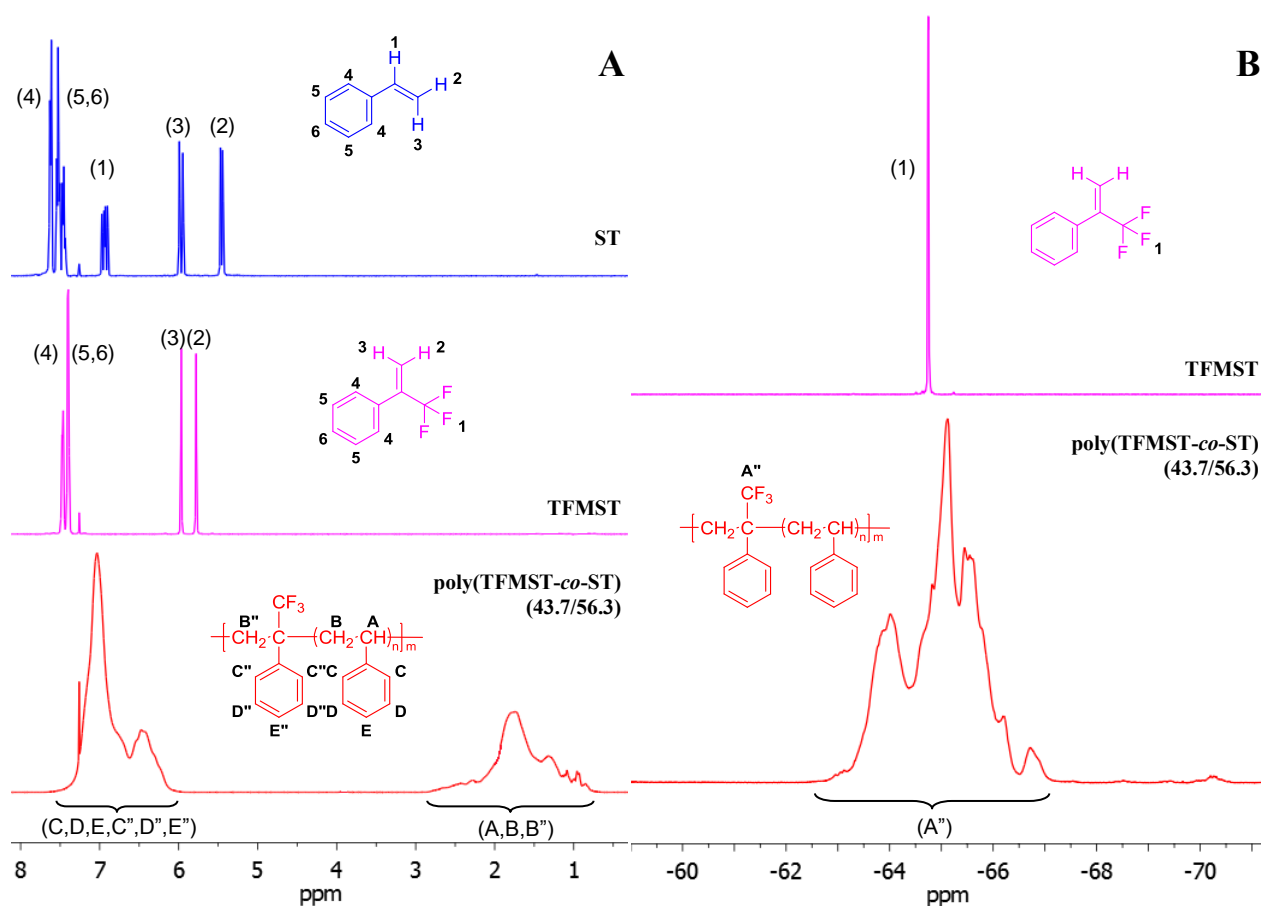


Figure 2. Comparison of ^1H and ^{19}F NMR spectra (recorded in CDCl_3) of monomers and poly(TFMST-*co*-ST) copolymer. *Left-hand cascade A:* ^1H NMR spectrum of (—) styrene (ST), (—) α -trifluoromethylstyrene (TFMST), and (—) poly(TFMST-*co*-ST) copolymer (43.7:56.3, $M_n = 6,500 \text{ g mol}^{-1}$), respectively; *right-hand cascade B:* ^{19}F NMR spectrum of (—) α -

trifluoromethylstyrene (TFMST) and (–) poly(TFMST-*co*-ST) copolymer (43.7:56.3, $M_n = 6,500$ g mol⁻¹, Table 1, Entry 10).

Table 1. Monomer conversions, yields, molecular weights (M_n), and polydispersities (\bar{D}) from the radical copolymerization and terpolymerization of F-STs with styrene at different initial monomer ratios.

Entry	Molar ratio [mol%]						Conversion [%]			Yield [wt%]	M_n^c [g/mol]	\bar{D}^c
	in feed		in polymer									
	TFMST	ST	FMST	TFMST	ST	FMST	TFMST	ST	FMST			
poly(FMST- <i>co</i> -ST)												
1	-	89.8	10.2	-	89.4 ^a	10.6 ^a	-	83.6 ^a	87.5 ^a	84	23700	3.66
2	-	80.0	20.0	-	79.8 ^a	20.2 ^a	-	83.4 ^a	84.3 ^a	83	18900	3.07
3	-	69.7	30.3	-	70.0 ^a	30.0 ^a	-	48.4 ^a	48.4 ^a	49	6600	1.88
4	-	59.8	40.2	-	69.0 ^a	31.0 ^a	-	35.3 ^a	23.2 ^a	30	4800	1.77
5	-	49.8	50.2	-	55.3 ^a	44.7 ^a	-	23.5 ^a	18.8 ^a	21	2900	1.93
6	-	21.7	78.3	-	50.3 ^a	49.7 ^a	-	19.9 ^a	5.5 ^a	8	1500	1.35
poly(TFMST- <i>co</i> -ST)												
7	10.1	89.9	-	10.6 ^b	89.4 ^b	-	46.1 ^b	43.5 ^b	-	44	14600	1.70
8	20.0	80.0	-	20.8 ^b	79.2 ^b	-	37.3 ^b	35.4 ^b	-	36	10800	1.51
9	30.1	69.9	-	28.7 ^b	71.3 ^b	-	24.6 ^b	26.3 ^b	-	26	8900	1.45
10	49.9	50.1	-	43.7 ^b	56.3 ^b	-	13.9 ^b	17.4 ^b	-	15	6500	1.36
11	70.0	30.0	-	46.9 ^b	53.1 ^b	-	8.9 ^b	15.7 ^b	-	8	2600	1.45
12	89.8	10.2	-	48.3 ^b	51.7 ^b	-	7.8 ^b	12.1 ^b	-	4	1500	1.58
poly(TFMST- <i>ter</i> -ST- <i>ter</i> -FMST)												
13	15.1	79.7	5.2	14.5 ^a	80.3 ^a	5.2 ^a	42.4 ^a	44.4 ^a	44.8 ^a	44	10700	1.61
14	11.9	76.2	11.9	9.3 ^a	79.7 ^a	11.0 ^a	39.9 ^a	53.1 ^a	46.7 ^a	50	9200	1.83
15	5.3	79.7	15.0	5.1 ^a	79.7 ^a	15.2 ^a	39.8 ^a	40.5 ^a	41.1 ^a	41	10900	1.58
16	5.0	74.9	20.1	5.0 ^a	74.0 ^a	21.0 ^a	37.5 ^a	36.9 ^a	39.1 ^a	37	9400	1.71
17	5.2	65.0	29.8	4.2 ^a	67.8 ^a	28.0 ^a	29.1 ^a	37.9 ^a	34.1 ^a	36	8000	1.61
18	5.1	55.0	39.9	3.7 ^a	57.9 ^a	38.4 ^a	21.5 ^a	30.8 ^a	28.1 ^a	29	6900	1.56

^a determined by ¹H NMR or/and ¹⁹F NMR spectroscopy.

^b determined by ¹H NMR or/and ¹⁹F NMR using pentafluorophenol (PFPhOH) as internal standard.

^c average molecular weights (M_n , M_w) and polydispersity index (\bar{D}) assessed from GPC (THF, RI) with poly(styrene) standards.

Unlike in the case of poly(FMST-*co*-ST) copolymers, the determination of ST and TFMST comonomers content in poly(TFMST-*co*-ST) copolymers was more complex and required the use of pentafluorophenol as an internal standard for NMR studies (detailed in Supporting Information, Figures S11-S16, Table S2).

Thorough, combinative NMR and SEC analyses enabled us to ascertain the comonomer conversion and the molecular weights of copolymers (Table 1). As expected, the higher fluorinated monomer content (FMST or TFMST) in the feed, the lower the efficiency of copolymerizations with styrene (i.e. the conversion of monomers), the yield, and the molecular weights of copolymers. The copolymer composition curves for FMST-ST and TFMST-ST are presented in Figure 3, demonstrating that a high F-STs concentration in the feed results in the formation of a copolymer with 1:1 alternation. However, copolymers with greater than 50 mol% F-ST units cannot be obtained under these conditions, confirming the non-homopolymerizations of such fluorinated monomers. In addition, the decrease in both molecular weight of the product and/or rate of polymerization can also be explained by the presence of chain transfer reactions to monomer, initiator, solvent, polymer.

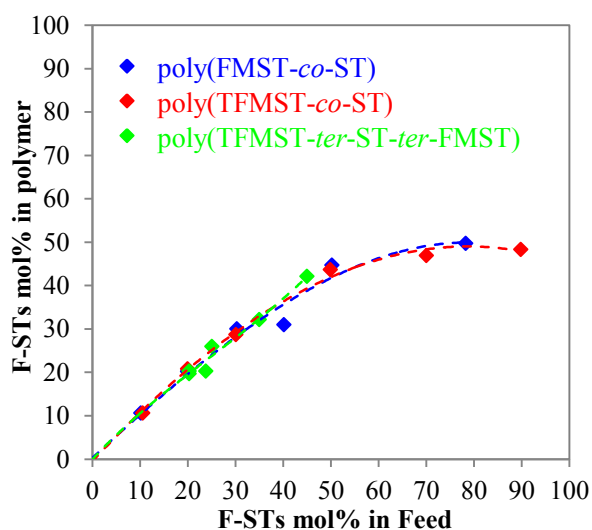


Figure 3. Co- and terpolymers composition vs. fluorinated styrene (F-ST) monomer feed of F-ST: (♦ ---) poly(TFMST-*co*-ST) copolymers, (♦ ---) poly(FMST-*co*-ST) copolymers, and (♦ ---) poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers.

Determination of monomer reactivity ratios of F-ST and ST by extended Kelen-Tüdös method

It is accepted that linear least-squares (LLS) methods, such as those proposed by Fineman and Ross (F-R)⁵³, and by Kelen and Tüdös (K-T)⁵⁴, can only be applied to experimental data at sufficiently low conversion. The only exception is the extended Kelen-Tüdös LLS method (EK-T)⁵⁴, which involves a rather more complex calculation, and can be applied to higher conversion experimental data without a significant systematic error. Therefore, in order to determine the monomer reactivity ratios of both (FMST;ST) and (TFMST;ST) couples, the EK-T LLS method was employed leading to the following values: $r_{\text{FMST}} = 0.08 \pm 0.02$ and $r_{\text{ST}} = 0.72 \pm 0.04$, $r_{\text{TFMST}} = 0.00$ and $r_{\text{ST}} = 0.64 \pm 0.01$, at 70 °C, respectively (Figure 4, details in Supporting Information, Table S3, Figures S17-S22). The reactivity ratios of TFMST and ST comonomers are in good agreement with those reported by Ueda and Ito³¹ ($r_{\text{TFMST}} = 0$, $r_{\text{ST}} = 0.60$ at 60 °C) indicating that TFMST does not self-propagate. Furthermore, since the polymer $\text{R-CH}_2(\text{Ph})(\text{CF}_3)\text{C}^\bullet$ radical does not react with its own fluorinated monomer ($k_{11}=0$) and the latter is 1.6 times more reactive than ST toward the polystyrene $\text{R-CH}_2(\text{Ph})\text{CH}^\bullet$ radical ($1/r_{\text{ST}} = 1.6$), the poly(TFMST-*co*-ST) copolymers, most probably, contain only oligomeric PST blocks intercalated between two single TFMST units, even when the TFMST feed content remains relatively low (up to 20 mol%). Poly(FMST-*co*-ST) copolymers followed a similar trend in polymer microstructure since $\text{R-CH}_2(\text{Ph})(\text{CH}_2\text{F})\text{C}^\bullet$ macroradical is reluctant to react with FMST and the monomer is 1.4 times more reactive than ST toward the polystyrene $\text{R-CH}_2(\text{Ph})\text{CH}^\bullet$ radical ($1/r_{\text{ST}} = 1.4$). Additionally, $\text{R-CH}_2(\text{Ph})(\text{CH}_2\text{F})\text{C}^\bullet$ radical adds onto ST monomer 13.2 times faster than its own polymer $\text{R-CH}_2(\text{Ph})\text{CH}^\bullet$ radical ($1/r_{\text{FMST}} = 13.2$), thereby preventing the formation of long blocks of the ST units in the copolymer chain. The high reactivity of ST and low reactivity of FMST towards fluorinated $\text{R-CH}_2(\text{Ph})(\text{CH}_2\text{F})\text{C}^\bullet$ radical may also explain why the formation of copolymers with greater than 50% FMST units cannot be obtained under radical conditions for such a copolymerization system. Interestingly, Kostov *et al.*²⁴ reported the incorporation of higher content of FMST into the

poly(CTFE-*co*-FMST) copolymer and therefore proved that the formation of oligomeric blocks of FMST units is possible.

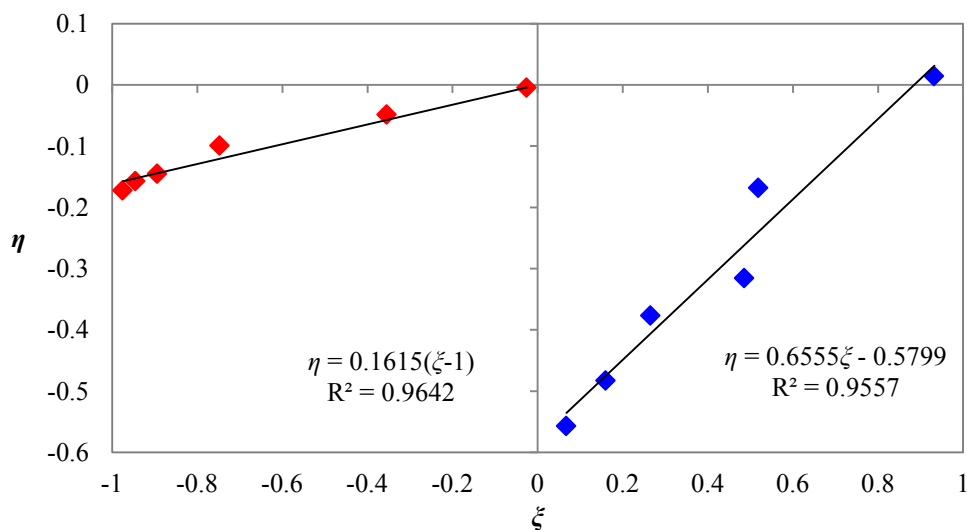


Figure 4. Determination of the monomer reactivity ratios of F-STs and ST by extended Kelen-Tüdös linear method: (♦) poly(TFMST-*co*-ST) copolymers, (♦) poly(FMST-*co*-ST) copolymers. Details are supplied in the Supporting Information.

All the observations confirm that both FMST and TFMST monomers are rather unreactive species under radical polymerization conditions. On the other hand, the fact that satisfactory amounts of fluorinated units are incorporated within the copolymers (almost as that inserted in the feed, especially when maintained up to 30 and 20 mol% for FMST and TFMST, respectively), further supports that such F-ST monomers behave as active comonomers, though retarding the rate of polymerization of other comonomer (ST). The results and conclusions are in line with those already reported by Baldwin and Reed²⁸, Narita^{26,27,30,33,34}, Ueda and Ito.^{29,31,32} The comparison of both fluorinated α -methylstyrenes shows the substantial decelerating effect of TFMST on the rate of copolymerization. The F-STs can be considered as captodative monomers since they bear both an electron-withdrawing group EWG ($-\text{CF}_3$, $-\text{CH}_2\text{F}$) and an electron-donating group EDG (phenyl) and this may give a peculiar reactivity. To explain the observed retarding effect, one should consider electronic and steric factors that influence the stability or/and reactivity of tertiary $\text{R}-\text{CH}_2(\text{Ph})(\text{R}_f)\text{C}^\bullet$

radical (R_f stands for CH_2F or CF_3) formed by addition across a double bond of F-ST of radical species generated either from an initiator or a growing polymer chain. Inducing and conjugating effects of EDG such as phenyl ring lower the energy of Single Occupied Molecular Orbital (SOMO) and thus, do stabilize the resulting macroradical. Moreover, the EWGs are known to lower orbital energies and therefore, in principal, the high electronegativity of fluorine should also lower the orbital energy of an attached carbon radical centre ($\text{X}_2\text{C}^\bullet\text{-F}$, $\text{X}=\text{H}, \text{F}$).⁵⁵ However, the effect of fluorine substituents, that are not directly attached to the radical centre, is more difficult to define. In fact, calculations reported by Pasto *et al.*⁵⁶ and Pross and Radom⁵⁷ suggest the following decreasing order of stability: $\text{CH}_3\text{CH}_2^\bullet > \text{FCH}_2\text{CH}_2^\bullet > \text{F}_2\text{CHCH}_2^\bullet > \text{CH}_3^\bullet > \text{CF}_3\text{CH}_2^\bullet$ which is, intuitively, the opposite of what might be anticipated. Therefore, most probably the presence of single, fluorinated methyl group, CF_3 in particular, attached to the carbon radical center destabilizes the systems. However, electronic factors alone are not sufficient to clarify the lower reactivity of such tertiary $\text{R-CH}_2(\text{Ph})(\text{R}_f)\text{C}^\bullet$ radical. In fact, the central carbon atom which bears most of the radical character is sterically hindered with relatively bulky groups such as $\text{RCH}_2\text{-}$ polymer chain, phenyl ring, and CF_3 or CH_2F moieties. Therefore, the addition of $\text{R-CH}_2(\text{Ph})(\text{R}_f)\text{C}^\bullet$ radical onto another monomer unit is somewhat restricted. Moreover, unavoidable side-chain transfer reactions that occur during radical polymerizations may also disturb the propagation process decreasing the molecular weight of the copolymers. Consequently, fluorinated α -methylstyrenes delay the rates of polymerization and increase unacceptably the polymerization time. Nevertheless, this deficiency can be overcome by restraining the insertion of fluorinated monomers in the feed (up to 20 mol%). By this way, resulting fluorinated copolymers that exhibit low molecular weights could be obtained in satisfactory yields (Table 1).

Radical terpolymerizations of F-ST monomers with ST

In the next step of conventional polymerization studies, our concerns focused on the radical bulk terpolymerization of FMST and TFMST with ST as displayed in Scheme 2.



Scheme 2. Bulk radical terpolymerizations of styrene (ST) with α -fluoromethylstyrene (FMST) and α -trifluoromethylstyrene (TFMST) initiated by AIBN at 70 °C.

The resulting poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers of different molar masses (ranging from 6,900 to 10,900 g·mol⁻¹, with a F-ST mol% ranging between 5.2-38.4 and 3.7-14.5 for FMST and TFMST, respectively, Table 1) were obtained in average to fair yields (Table 1) and characterized by ¹H (Figure S25), ¹³C (Figures S23 and S26) and ¹⁹F (Figures S24 and S27) NMR spectroscopy, detailed in the Supporting Information.

The comparison of ¹H NMR spectra of ST (—), FMST (—) and TFMST (—) monomers with poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers of different compositions 14.5/80.3/5.2 mol% (—) and 3.7/57.9/38.4 mol% (—) is illustrated in Figure 5. ¹H NMR spectra of monomers exhibited characteristic signals attributed to aromatic and vinyl protons already described above (Cascades A in Figures 1 and 2).

Similarly to copolymers, ¹H NMR spectra of all poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers (Figure S25) exhibited broad signals centered at 1.72, 3.75 and 6.88 ppm attributed to secondary and tertiary aliphatic backbone protons of all three base units (H_A, H_B, H_{B'}, H_{B''}), side chain primary protons of fluoromethyl group of FMST (H_{A'}), and aromatic protons of ST and FMST or TFMST termonomer units (H_{C-E}, H_{C'-E'}, H_{C''-E''}), respectively. However, the intensity of signals assigned to —CH₂F moiety depended on the FMST content incorporated in the polymer chain. Furthermore, signals of aromatic protons in terpolymers were high field shifted to 6.88 ppm in comparison to H_{Ar} multiplets at 7.45, 7.52, 7.62 and 7.35, 7.46 or 7.44, 7.52 ppm noted in spectra of ST and FMST or TFMST monomers, respectively.

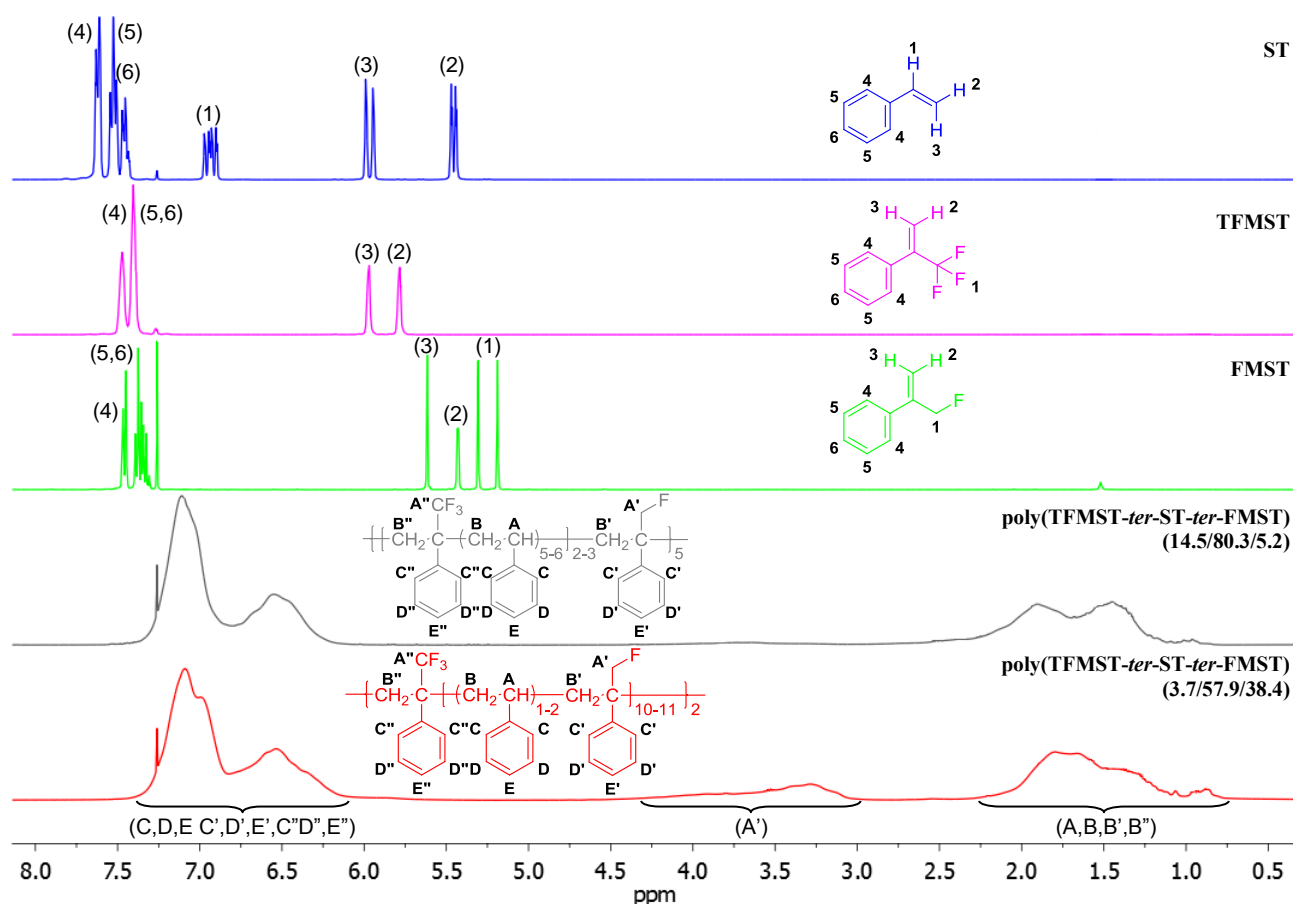


Figure 5. Comparison of ^1H NMR spectra (recorded in CDCl_3) of monomers: (—) styrene (ST), (—) α -trifluoromethylstyrene (TFMST), (—) α -fluoromethylstyrene (FMST), and poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers: (—) poly(TFMST-*ter*-ST-*ter*-FMST) terpolymer (14.5/80.3/5.2, $M_n = 10,700 \text{ g mol}^{-1}$, Table 1, Entry 13), and (—) poly(TFMST-*ter*-ST-*ter*-FMST) terpolymer (3.7/57.9/38.4, $M_n = 6,900 \text{ g mol}^{-1}$, Table 1, Entry 18).

Complementary analyses of the integrals of the characteristic proton signals (Figures S28, S30, S32, S34, S36, S38 in Supporting Information) together with the integrals of the characteristic fluorine signals (Figures S29, S31, S33, S35, S37 and S39 in Supporting Information) allowed to determine the content of ST, FMST and TFMST units in the terpolymers (Table S4 in Supporting Information). The proton signals were assigned to aliphatic backbone of ST, FMST and TFMST (signal centered at 1.72 ppm, named as A, B, B', and B'') and to fluoromethyl moiety of FMST (signal centered at 3.75 ppm, named as A') base units incorporated in the terpolymers. Whereas the fluorine signals were attributed to $-\text{CF}_3$ (signal centered at -65.0 ppm, named as A'') and $-\text{CH}_2\text{F}$

group (signal centered at -225.5 ppm, marked as A'). The terpolymer compositions were calculated in accordance with following equations:

$$\text{mol\%}_{\text{ST}} = \{[I_{\text{I}} - I_{\text{II}} - ((I_{\text{II}} * I_{\text{III}})/(3 * I_{\text{IV}}))]/3\} / \{[I_{\text{I}} - I_{\text{II}} - ((I_{\text{II}} * I_{\text{III}})/(3 * I_{\text{IV}}))]/3 + (I_{\text{II}}/2) + [((I_{\text{II}} * I_{\text{III}})/(3 * I_{\text{IV}}))/2]\}$$

$$\text{mol\%}_{\text{FMST}} = (I_{\text{II}}/2) / \{[I_{\text{I}} - I_{\text{II}} - ((I_{\text{II}} * I_{\text{III}})/(3 * I_{\text{IV}}))]/3 + (I_{\text{II}}/2) + [((I_{\text{II}} * I_{\text{III}})/(3 * I_{\text{IV}}))/2]\}$$

$$\text{mol\%}_{\text{TFMST}} = \{[(I_{\text{II}} * I_{\text{III}})/(3 * I_{\text{IV}})]/2\} / \{[I_{\text{I}} - I_{\text{II}} - ((I_{\text{II}} * I_{\text{III}})/(3 * I_{\text{IV}}))]/3 + (I_{\text{II}}/2) + [((I_{\text{II}} * I_{\text{III}})/(3 * I_{\text{IV}}))/2]\}$$

where I_{I} , I_{II} and I_{III} , I_{IV} stand for the integrals of signals centered at 1.72 ppm (H_{A} , H_{B} , $H_{\text{B'}}$, and $H_{\text{B''}}$), 3.75 ppm ($H_{\text{A'}}$) in ^1H NMR spectra and the integrals of signals centered at -65.0 ppm ($F_{\text{A''}}$) and -225.5 ppm ($F_{\text{A'}}$) in ^{19}F NMR spectra, respectively.

Combinative NMR and SEC analyses allowed us to determine the conversion of individual monomers involved in radical bulk terpolymerizations (Table 1). The terpolymer composition curve for F-ST-ST is presented in Figure 3, demonstrating that introduction of 45 mol% of F-STs in the feed (5.1 mol% of TFMST and 39.9 mol% of FMST) results in the formation of a terpolymer with 42.1 mol% content of fluoromonomers (3.7 mol% of TFMST and 38.4 mol% of FMST) that is higher than that of respective copolymers obtained under comparable reaction conditions. Moreover, similarly to copolymerization systems, increasing the fluorinated monomers (FMST and TFMST) in the feed induces a decrease in efficiency of terpolymerizations with styrene. Furthermore, the conversion of monomers, the yields, as well as molecular weights of terpolymers are slightly higher than those of corresponding poly(TFMST-*co*-ST) or even poly(TFMST-*co*-ST) copolymers. The results indicate that the reduction in efficiency of terpolymerizations is not as drastic as in case of copolymerizations. Moreover, we can anticipate the terpolymers possess structures where different monomeric FMST and TFMST units are randomly distributed between oligostyrene microblocks. Formation of such a microstructure can occur due to retarding effect of both fluorinated comonomers or the facts that they do not homopolymerize under free radical initiation, as well as the higher reactivity of polystyrene $\text{R-CH}_2(\text{Ph})\text{CH}^{\bullet}$ radical towards FMST and TFMST molecules than ST monomer (1.4 and 1.6 times, respectively). All the results suggest that the terpolymerization might be an example of termonomer induced copolymerization,⁵⁸ which

associates monomers that do not copolymerize (TFMST and FMST), and a termonomer (ST) that exhibits a good reactivity with both others.

Thermal properties

The thermal properties of the prepared co- and terpolymers were assessed by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC), and compared to those of polystyrene homopolymer (Figure 6 and in Supporting Information Table S8).

The temperatures at 10% weight loss (T_{d10}) of the polymers with F-STs content up to 20 and 25 mol% for co- and terpolymers, respectively, were higher than 320 °C (Figures S44, S46, S48 in Supporting Information). The results indicate that fluorinated polymers exhibit thermal stabilities slightly higher than those of the corresponding PST (Figures 6A). As expected, the higher the molecular weights, the better the thermal stability and with the increase of the content of TFMST or/and FMST units into the polymer structure, a substantial decrease in molecular weight is observed. Thus, the resulting copolymers are more susceptible to thermal degradation (Figure 6B). Interestingly, poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers and poly(TFMST-*co*-ST) copolymers exhibit enhanced thermal properties in comparison to poly(FMST-*co*-ST) or PST. However, restraining the insertion of fluorinated monomers in the feed (up to 20 mol%) and employing controlled radical polymerization (or RDRP) methodology such as Iodine Transfer Copolymerization enabled to produce higher molar mass poly(F-ST-*co*-ST) copolymers of considerably better thermal stabilities in comparison to the corresponding polystyrene homopolymers.³⁵ Such a difference in the thermal stability of polymer TFMST derivatives might be attributed to the presence of CF₃ group in α position that enables to reduce the thermo-oxidation.^{59–63}

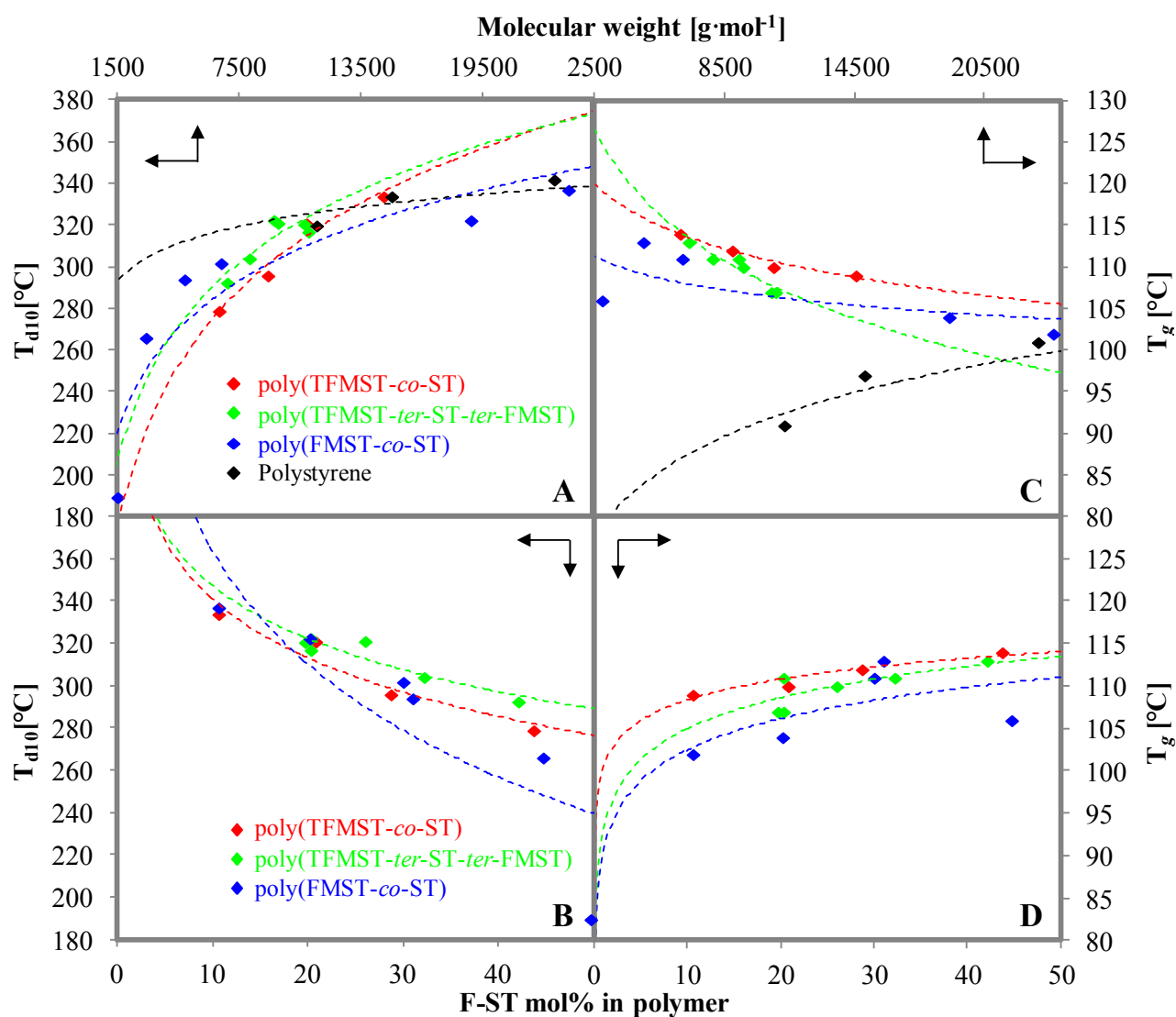


Figure 6. Thermal stabilities of the polymers obtained in bulk co- and terpolymerizations [Polystyrene, poly(TFMST-co-ST), poly(FMST-co-ST), poly(TFMST-ter-ST-ter-FMST)]; (A) 10 %wt loss decomposition temperatures (T_{d10}) versus number-average molecular weights (M_n); (B) 10 %wt loss decomposition temperatures (T_{d10}) versus molar content of F-ST units incorporated in polymers (F-STs mol%); (C) glass transition temperatures (T_g) versus number-average molecular weights (M_n); (D) glass transition temperatures (T_g) versus molar content of F-ST units incorporated in polymers (F-STs mol%)

The glass transition temperatures of these copolymers were evaluated by differential scanning calorimetry (Figures S43, S45, S47 and Table S8). The obtained values are plotted versus molecular weights (Figure 6C) and F-ST polymer content (Figure 6D). The glass transition temperatures

increased notably (up to 113/114 °C and 113 °C for co- and terpolymers, respectively) with the decreasing molecular weights of examined polymers as well as increasing F-ST mol% in their structure. In addition, in all cases and whatever the molecular weights, T_g s were higher than those of the corresponding styrene homopolymers. The comparison of co- and terpolymers of same ST content reveals that the poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers and poly(TFMST-*ter*-ST) copolymer containing ca. 80 ST mol% have T_g values of 107-111 and 110 °C, respectively. Whereas poly(FMST-*co*-ST) copolymer with 80 mol% of ST exhibits a T_g of 104 °C. This observation may indicate that the introduction of reasonable amount of fluorinated monomer units promotes an increase in the glass transition temperature of the resulting polymer by the presence of bulky CH₂F or/and CF₃ side groups.

Contact angle measurements

The dependence of advancing water contact angle AWCA (deg) on M_n (g·mol⁻¹) of such fluorinated copolymers obtained with water is presented in Table 2 and Figure S50 in the Supporting Information. In general, for all measurement series, the higher the molecular weights of polymers, the lower the contact angle. The distribution of all points proves that the values of advancing contact angle of these fluorinated copolymers increase when the content of the styrene repeating units was lower than 80 mol% (Table 2), from 112° to 147°. The exceptions were poly(TFMST-*co*-ST) copolymers which are not surprising since the replacement of H by CF₃ was expected to decrease the wettability of polymers.

As displayed in Figure 7, despite the high styrene content, the fluorine atoms in CH₂F and CF₃ groups change the hydrophobicity of the covered surface. The obtained results were in satisfactory agreement with those of previous studies on the chemical modifications of copolymers.³⁵ Moreover, for the five different copolymers compared in Figure 7 with the same (20%) molar F-ST ratio, large differences were observed between their obtained advancing CAs. This behavior confirms observations reported by Montefusco et al.⁶⁴ when a few amounts of a fluorinated acrylate were

incorporated into a hydrogenated bis(acrylate) prior to photopolymerization leading to a higher hydrophobicity of the resulting materials.

Table 2. Comparison of the Advancing Contact Angles (ACA) and molecular weights (M_n), molar ratio of ST and F-ST of polyfluorinated copolymers.

Molar ratio (mol%)		M_n	ACA [deg]
ST	F-ST	[g·mol ⁻¹]	H ₂ O(CA hysteresis)/CH ₂ I ₂
poly(FMST- <i>co</i> -ST) copolymers			
69.0	31.0	4800	117(4)/79
70.0	30.0	6600	117(5)/76
79.8	20.2	18900	112(4)/79
89.4	10.6	23700	104(4)/70
poly(TFMST- <i>co</i> -ST) copolymers			
79.2	20.8	10800	147(2)/90
89.4	10.6	14600	115(3)/75
poly(TFMST- <i>ter</i> -ST- <i>ter</i> -FMST) terpolymers			
57.9	42.1	6900	125(4)/84
67.8	32.2	8000	125(1)/83
79.7	20.3	9200	104(4)/70
74.0	26.0	9400	112(3)/77
80.3	19.7	10700	104(3)/70
79.7	20.3	10900	105(3)/71

The wettability depends on the fluorinated monomer concentration and the fluorinated additive is effective only on the air side of the films as if a migration of the fluorinated F-ST units toward the extreme surface occurred.⁶⁴ The same behavior was observed in terpolymers. Indeed, for poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers ($M_n = 9200, 10700$ and 10900 g·mol⁻¹) with almost

the same molar content of F-STs, i.e. 20 mol% and for poly(FMST-*co*-ST) copolymers ($M_n = 4800$, $6600 \text{ g}\cdot\text{mol}^{-1}$ and around 30 mol% of F-STs), the contact angles of wetting were the same (Table 2). Only one deviation was noted from this. In addition, similar water CAs were observed for poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers ($M_n = 6900$, $8000 \text{ g}\cdot\text{mol}^{-1}$) despite the difference in the F-ST contents (42 mol% and 32 mol%). Both terpolymers also displayed a different ST content (58 and 68 mol%). In this case, the CA values depend on the F-ST contents. Similar results were reported even for photocured materials containing less than 1% fluorinated acrylate for which the wettability depends on the fluorinated monomer concentration and the length of non-fluorinated spacer between the ester function and the fluorinated group.⁶⁵

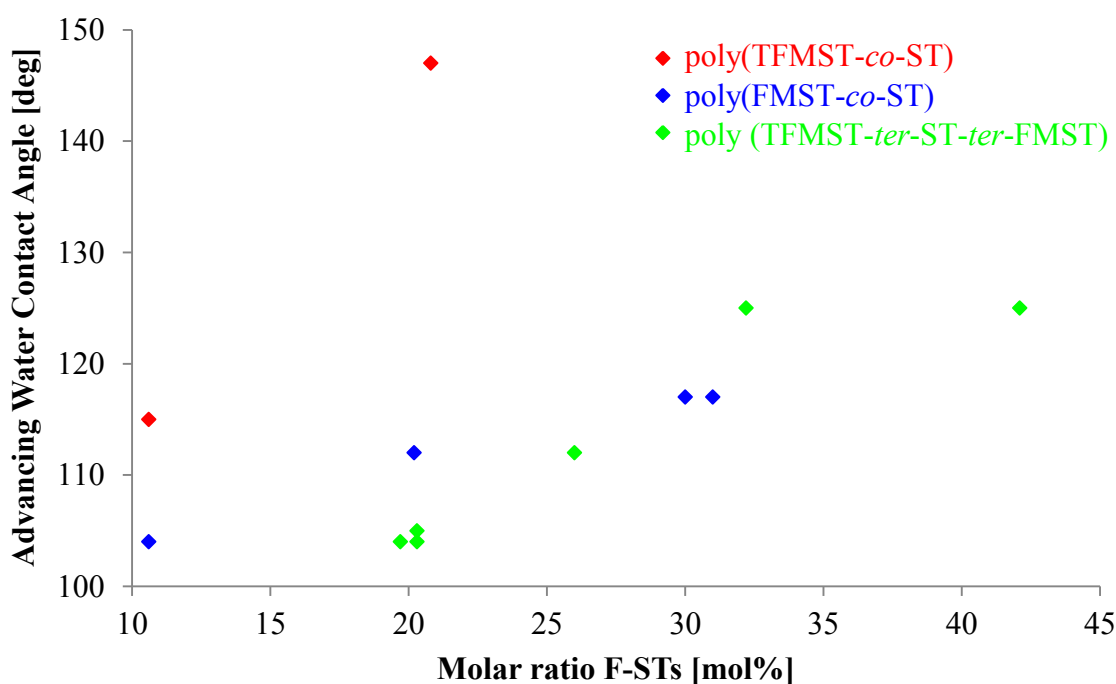


Figure 7. Advancing Water Contact Angles *versus* the molar ratio (%) of copolymers based on F-styrenes.

CH_2F and CF_3 groups in polymers were segregated at the top surface and it was reflected by the change in the contact angles. The observations of CAs values for terpolymers and copolymers indicate that the terpolymer with two fluorinated groups (CF_3 and CH_2F) are sometimes more wettable than the copolymers, in spite of the 20% F-ST. A primary reason regarding such various terpolymer surface properties arises from the difference of the chemical arrangement of their layers

on the surface. The components of the chemical structure of polystyrene is relatively simple: the benzene ring, the tertiary carbon atom bearing a single hydrogen atom and the methylene connecting bridges. Replacement of H by CH₂F and CF₃ leads to the changes in fluorinated polystyrene. The fluorinated groups, especially CF₃ group^{66,67} is located at the outer surface layer, thus inducing hydrophobic properties. As may be expected, the high contact angle value (147 °) was measured for poly(TFMST-*co*-ST) copolymer ($M_n = 10800 \text{ g}\cdot\text{mol}^{-1}$) (Supporting Information Figures S51 and S52). In all of the cases studied here, the hydrophobic effect of terpolymers depended upon the presence of all groups (CF₃, CH₂F) located at the surface.⁶⁸ Moreover, considering the results obtained for copolymers and terpolymers over the same M_n range 4800-8000 $\text{g}\cdot\text{mol}^{-1}$, low amounts of CF₃-group is enough to turn surface more hydrophobic (Table 2 and Figure S50). The observation of a hysteresis range for all of the samples indicated that the surface exhibited a similar chemical heterogeneity (Table 2). The CH₂I₂ contact angles (Table 2 and Figure S50 in the Supporting Information) on fluorinated polystyrene were also achieved as well and the values were more sensitive to the apolar parts of a surface. The CH₂I₂ CA value of the poly(TFMST-*co*-ST) copolymer ($M_n = 10800 \text{ g}\cdot\text{mol}^{-1}$) was 90°, indicating oleophobic properties of this surface.

CONCLUSIONS

Conventional bulk radical co- and terpolymerizations of styrene (ST) with α -fluoromethylstyrene (FMST) or/and α -trifluoromethylstyrene (TFMST) successfully led to fluorinated aromatic copolymers. Detailed NMR spectroscopic and SEC analyses enabled to determine the F-ST and ST monomer conversions, the composition, and molecular weights of the resulting copolymers, respectively. The maximum incorporations of FMST and TFMST in the copolymers could reach ca. 50 mol%. Moreover, a decrease in efficiency of copolymerization (with an increase of the F-ST in the feed) as well as results of kinetic studies confirmed that both TFMST and FMST retard the polymerization rate of ST. Additionally, reactivity ratios confirmed lower reactivities of both fluorinated styrenes. Low reactivity of F-STs and retarding effect in radical polymerizations may

result from the energy of the tertiary $\text{R-CH}_2\text{C}^*(\text{CF}_3)(\text{Ph})$ macroradical formed when a growing polymer attacked the F-ST monomer. As F-STs can be regarded as captodative species, the steric-hindered $\text{R-CH}_2(\text{Ph})(\text{R}_f)\text{C}^*$ macroradical is stabilized by phenyl ring and destabilized by $-\text{CH}_2\text{F}$ or $-\text{CF}_3$ electron withdrawing group. The combined steric and destabilizing effects reduce the ability of the macroradical to add onto another monomer unit and consequently decrease the rate of the propagation. However, when all three monomers were involved in terpolymerizations the retarding effect was less significant. Such a terpolymerization might be an example of “termonomer induced copolymerization”.

As expected, the assessment of the thermal properties pointed out that the incorporation of a small amount of fluorinated monomer units in the polystyrenic structure enabled to increase the glass transition temperatures significantly and promoted a slight rise of the thermal stability. In particular, copolymers based on TFMST exhibited enhanced thermal properties despite of their low molecular weights.

In addition, based on preliminary results, the surface properties of polymer coatings were estimated using dynamic contact angle measurements. The 20 mol% of F-STs units in co- and terpolymers of styrene preferentially migrated toward the surface and thus increased the hydrophobicity. When considering environmental standpoints, a low amount of CF_3 groups in co- and terpolymers was sufficient to turn the surface non-wettable and therefore of potential applications as hydrophobic coatings.

Supporting Information Available: Synthesis and spectral characterizations of fluorinated styrene monomers; ^1H and ^{19}F NMR spectra of poly(F-ST-*co*-ST) copolymers; ^1H , ^{13}C , and ^{19}F NMR spectra of poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers; determination of comonomer content in poly(F-ST-*co*-ST) copolymers and poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers; determination of comonomer reactivity ratios, comparisons of glass transition temperatures (T_g) and TGA thermograms for series of poly(F-ST-*co*-ST) copolymers and poly(TFMST-*ter*-ST-*ter*-FMST)

terpolymers of different molecular weights and compositions; and schematic formation of a glass/OTS substrate and behaviour of water and diiodomethane droplets on co- and terpolymer surfaces.

AUTHOR INFORMATION

Corresponding Authors

* Dr Bruno Ameduri, Institut Charles Gerhardt, Ingénierie et Architectures Macromoléculaires, UMR CNRS 5253, Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'Ecole Normale, 34296 Montpellier, France

* Dr Justyna Walkowiak-Kulikowska, Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznan, Poland

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENTS

The authors gratefully thank the European Community for funding through a Marie Curie Fellowship (PIEF-GA-2008-220323 for JWK). Financial support of this work was also provided by National Science Centre Poland (grant N N204 277240 to JWK and grant N N204 444740 to AS). Prof. Georgi Kostov (University Burgas, Bulgaria) and Dr Frédéric Boschet (Inovyn, Brussels, Belgium) are also acknowledged for their valuable help and fruitful discussions. French Fluorine Network (GIS) is also acknowledged.

References and Notes

- 1 J. Scheirs, *Modern Fluoropolymers: High Performance Polymers for Diverse Applications*, Wiley, New York, 1997.
- 2 G. G. Hougham, P. E. Cassidy, K. Johns and T. Davidson, *Fluoropolymers*, Springer US,

Kluwer Academic Publishers, New York, 1999.

- 3 B. Ameduri and B. Boutevin, *Well-Architected Fluoropolymers: Synthesis, Properties and Applications*, Elsevier B.V., Amsterdam, 2004.
- 4 A. L. Moore, *Fluoroelastomers Handbook The Definitive User's Guide and Databook*, William Andrew Publishing, Norwich, NY, 2006.
- 5 D. W. Smith, S. T. Iacono and S. S. Iyer, *Handbook of Fluoropolymer Science and Technology*, Wiley, 2014.
- 6 B. Ameduri and H. Sawada, *Fluorinated Polymers: Volume 1: Synthesis, Properties, Processing and Simulations*, Royal Society of Chemistry, Oxford, 2016.
- 7 B. J. Skutnik, US4511209 A, 1985(Ensign-Bickford Optics Company, United States).
- 8 S. Kobayashi, S. Munekata, M. Unoki, T. Iwamoto, EP0239935 A2, 1987(Asahi Glass Company Ltd., Japan).
- 9 T. Yamamoto, T. Matsumoto, K. Shimada, Y. Uozu, R. Murata, EP0256765 A1, 1988 (Mitsubishi Rayon Co., Ltd., Japan).
- 10 T. Yamamoto, S. Matsumoto, R. Murata, JP,01-033506,A, 1989 (Mitsubishi Rayon Co., Ltd., Japan).
- 11 B. Boutevin and Y. Pietrasanta, *Les acrylates et polyacrylates fluorés, dérivés et applications Fluorinated acrylates and polyacrylates, derivatives and applications*, EREC, Puteaux, 1988.
- 12 B. A. Banks, in *Modern fluoropolymers : high performance polymers for diverse applications*, ed. J. Scheirs, Wiley and Sons, New York, 1997, pp. 103–114.
- 13 R. F. Brady Jr., *Chem. Br.*, 1990, **26**, 427–430.
- 14 S. Banerjee, *Handbook of Specialty Fluorinated Polymers 1st Edition Preparation, Properties, and Applications*, Elsevier B.V., Amsterdam, 2015.
- 15 W. M. Thomas and M. T. O'Shaughnessy, 1953, **11**, 455–470.
- 16 F. Boschet and B. Ameduri, *Chem. Rev.*, 2014, **114**, 927–980.
- 17 M. Kyulavska, G. Kostov, B. Ameduri and R. Mateva, *J. Polym. Sci. Part A Polym. Chem.*,

2010, **48**, 2681–2697.

- 18 S. Ignarshi, *J. Polym. Sci. Part B Polym. Lett.*, 1963, **1**, 359–363.
- 19 R. Souzy, B. Ameduri and B. Boutevin, *Prog. Polym. Sci.*, 2004, **29**, 75–106.
- 20 R. Souzy, B. Ameduri and B. Boutevin, *J. Polym. Sci. Part A Polym. Chem.*, 2004, **42**, 5077–5097.
- 21 R. Souzy, B. Ameduri, B. Boutevin, P. Capron, D. Marsacq and G. Gebel, *Fuel Cells*, 2005, **5**, 383–397.
- 22 R. Souzy and B. Ameduri, *Prog. Polym. Sci.*, 2005, **30**, 469–511.
- 23 R. Souzy, B. Ameduri, B. Boutevin, G. Gebel and P. Capron, *Solid State Ionics*, 2005, **176**, 2839–2848.
- 24 G. Kostov, M. Tredwell, V. Gouverneur and B. Ameduri, *J. Polym. Sci. Part A Polym. Chem.*, 2007, **45**, 3843–3850.
- 25 J. Walkowiak-Kulikowska, F. Boschet, G. Kostov, V. Gouverneur and B. Ameduri, *Eur. Polym. J.*, 2016, **84**, 612–621.
- 26 T. Narita, *Macromol. Rapid Commun.*, 2000, **21**, 613–627.
- 27 T. Narita, *Prog. Polym. Sci.*, 1999, **24**, 1095–1148.
- 28 N. G. Baldwin and S. F. Reed, *J. Polym. Sci. Part A-1*, 1968, **6**, 2627–2635.
- 29 H. Ito, A. F. Renaldo and M. Ueda, *Macromolecules*, 1989, **22**, 45–51.
- 30 T. Narita, T. Hagiwara and H. Hamana, *Polym. Prepr. Japan*, 1986, **35**, 222.
- 31 M. Ueda and H. Ito, *J. Polym. Sci. Part A Polym. Chem.*, 1988, **26**, 89–98.
- 32 H. Ito, B. Giese and R. Engelbrecht, *Macromolecules*, 1984, **17**, 2204–2205.
- 33 T. Narita, T. Hagiwara, H. Hamana and T. Kojima, in *69th Annual Meeting of Chemical Society of Japan, Abstr.*, 1995, p. 675.
- 34 T. Narita, T. Hagiwara and H. Hamana, *Polym. Prepr. Japan*, 1996, **45**, 136.
- 35 J. Walkowiak-Kulikowska, A. Szwajca, F. Boschet, V. Gouverneur and B. Ameduri, *Macromolecules*, 2014, **47**, 8634–8644.

- 36 K. T. McElroy, S. T. Purrington, C. L. Bumgardner and J. P. Burgess, *J. Fluor. Chem.*, 1999, **95**, 117–120.
- 37 R. Souzy, B. Ameduri and B. Boutevin, *Macromol. Chem. Phys.*, 2004, **205**, 476–485.
- 38 C. Boyer and B. Ameduri, *J. Polym. Sci. Part A Polym. Chem.*, 2009, **47**, 4710–4722.
- 39 Y. Patil and B. Ameduri, *Prog. Polym. Sci.*, 2013, **38**, 703–739.
- 40 Y. Patil and B. Ameduri, *Polym. Chem.*, 2013, **4**, 2783–2799.
- 41 Y. Patil, A. Alaaeddine, T. Ono and B. Ameduri, *Macromolecules*, 2013, **46**, 3092–3106.
- 42 R. Pan, X. Liu and M. Deng, *J. Fluor. Chem.*, 1999, **95**, 167–170.
- 43 J. Walkowiak, T. Martinez del Campo, B. Ameduri and V. Gouverneur, *Synthesis (Stuttg.)*, 2010, 1883–1890.
- 44 J. Walkowiak-Kulikowska, J. Kanigowska and H. Koroniak, *J. Fluor. Chem.*, 2015, **179**, 175–178.
- 45 S. Bresciani, A. M. Z. Slawin and D. O'Hagan, *J. Fluor. Chem.*, 2009, **130**, 537–543.
- 46 N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457–2483.
- 47 T. Watanabe, N. Miyaura and A. Suzuki, *Synlett*, 2014, 207–210.
- 48 A. Sykes, J. C. Tatlow and C. R. Thomas, *J. Chem. Soc.*, 1956, 835–839.
- 49 P. Tarrant and R. E. Taylor, *J. Org. Chem.*, 1959, **24**, 238–239.
- 50 K. M. Koshy, R. Danielle and T. T. Tidwell, *J. Am. Chem. Soc.*, 1979, **101**, 357–363.
- 51 B. Jiang and Y. Xu, *J. Org. Chem.*, 1991, **56**, 7336–7340.
- 52 B. Jiang, Q. F. Wang, C. G. Yang and M. Xu, *Tetrahedron Lett.*, 2001, **42**, 4083–4085.
- 53 M. Fineman and S. D. Ross, *J. Polym. Sci. Lett. to Ed.*, 1950, **V**, 259–262.
- 54 T. Kelen and F. Tudos, *J. Macromol. Sci. Part A - Chem. Pure Appl. Chem.*, 1975, **A9**, 1–27.
- 55 R. D. Chambers, *Fluorine in Organic Chemistry*, Blackwell Publishing Ltd, Oxford, 2004.
- 56 D. J. Pasto, R. Krasnansky and C. Zercher, *J. Org. Chem.*, 1987, **52**, 3062–3072.
- 57 A. Pross and L. Radom, *Tetrahedron*, 1980, **36**, 1999–2003.
- 58 J. K. Weiss, *Polym. Prepr.*, 1971, **12**, 512–520.

- 59 R. B. Hodgdon Jr., *J. Polym. Sci. Part A-1*, 1968, **6**, 171–191.
- 60 R. A. Assink, C. Arnold and R. P. Hollandsworth, *J. Memb. Sci.*, 1991, **56**, 143–151.
- 61 F. N. Büchi, B. Gupta, O. Haas and G. G. Scherer, *Electrochim. Acta*, 1995, **40**, 345–353.
- 62 J. M. Serpico, S. G. Ehrenberg, J. J. Fontanella, K. A. McGrady, D. Perahia, X. Jiao, E. H. Sanders, T. J. Wallen and G. E. Wnek, *PMSE Prepr.*, 2002, **86**, 32–33.
- 63 J. Yu, B. Yi, D. Xing, F. Liu, Z. Shao, Y. Fu and H. Zhang, *Phys. Chem. Chem. Phys.*, 2003, **5**, 611–615.
- 64 F. Montefusco, R. Bongiovanni, A. Priola and B. Ameduri, *Macromolecules*, 2004, **37**, 9804–9813.
- 65 B. Ameduri, R. Bongiovanni, V. Lombardi, A. Pollicino, A. Priola and A. Recca, *J. Polym. Sci. Part A Polym. Chem.*, 2001, **39**, 4227–4235.
- 66 P. Mach, C. C. Huang, T. Stoebe, E. D. Wedell, T. Nguyen, W. H. De Jeu, F. Guittard, J. Naciri, R. Shashidhar, N. Clark, I. M. Jiang, F. J. Kao, H. Liu and H. Nohira, *Langmuir*, 1998, **7463**, 4330–4341.
- 67 T. Nishino, M. Meguro, K. Nakamae, M. Matsushita and Y. Ueda, *Langmuir*, 1999, **15**, 4321–4323.
- 68 T. Hayakawa, J. Wang, M. Xiang, X. Li, M. Ueda, C. K. Ober, J. Genzer, E. Sivaniah, E. J. Kramer and D. A. Fischer, *Macromolecules*, 2000, **33**, 8012–8019.