
ANNEX 2B

Summary of professional accomplishment in English

**Synthesis of fluorinated styrene derivatives
and its application for preparing aromatic fluoropolymers**

dr Justyna Walkowiak-Kulikowska

Adam Mickiewicz University in Poznań
Faculty of Chemistry
Department of Synthesis and Structure of Organic Compounds

Table of content

- 1.** Personal Data
- 2.** Diplomas and Scientific Degrees
- 3.** Employment History
- 4.** The Scientific Achievement
 - 4.1.** List of single issue publications presenting the scientific achievement
 - 4.2.** The research objectives and discussion of main results and achievements presented in the above mentioned scientific publications
 - 4.3.** Summary of significant results
- 5.** Other scientific achievements and future scientific plans

- 1. Name, Surname:** Justyna Walkowiak-Kulikowska
Workplace: Adam Mickiewicz University in Poznań
Faculty of Chemistry
Department of Synthesis and Structure of Organic Compound

2. Diplomas and Scientific Degrees

- 2006 *Ph. D. in Chemical Sciences*; Adam Mickiewicz University in Poznań, Faculty of Chemistry; thesis entitled: „*Synthesis and fluorinating properties of secondary amines and 1,1,3,3,3-pentafluoropropene adducts*”;
Supervisor: prof. dr hab. Henryk Koroniak
- 2002 *Master of Science in Chemistry*; Adam Mickiewicz University in Poznań, Faculty of Chemistry; thesis entitled: „*Synthesis and application of 1,1,3,3,3-pentafluoropropyl-N,N-diethyloamine–selective fluorinating agent*”;
Supervisor: prof. dr hab. Henryk Koroniak

3. Employment History

- 2018-present Senior lecturer, Adam Mickiewicz University in Poznań, Faculty of Chemistry, Department of Synthesis and Structure of Organic Compounds
- 2008-2010 Marie-Curie Fellowship, Post-doctoral position (2 years), in Prof. Véronique Gouverneur’s research group, Chemistry Research Laboratory (CRL), University of Oxford (UK) in collaboration with Dr Bruno Ameduri’s research group, Ingénierie et Architectures Macromoléculaires Institut Charles Gerhardt, Ecole Nationale Supérieure de Chemie de Montpellier (France)
- 2006 Short-term Post-doctoral position (3 months), in Prof. Günter Haufe’s research group, Organisch-Chemisches Institut, Westfälische Wilhelms-Universität, Münster (Germany)
- 2006-2018 Assistant professor, Adam Mickiewicz University in Poznań, Faculty of Chemistry, Department of Synthesis and Structure of Organic Compounds
01.08.2012-01.05.2013 a break in professional duties due to pregnancy and maternity leave

4. The Scientific Achievement

The scientific achievement following article 16 par. 2 of act from 14 March 2003 on scientific degrees and title and on degrees and title in arts (Journal of Laws no. 65, pos. 595 with changes.) is a series of single issue scientific publications entitled:

„Synthesis of fluorinated styrene derivative
and its application for preparing aromatic fluoropolymers”

4.1. List of single issue publications representing the scientific achievement

List of publications from the Journal Citation Reports (JCR) base

No.	Publication	Impact Factor 5-year Impact Factor Points of MSHE Contribution
H1	<p>Walkowiak, J.; Martinez del Campo, T.; Ameduri, B.; Gouverneur, V. “Syntheses of Mono-, Di- and Trifluorinated Styrenic Monomers” <i>SYNTHESIS</i>, 2010, <i>11</i>, 1883-1890. DOI: 10.1055/s-0029-1218785</p>	<p>IF₂₀₁₀ = 2,260 IF_{5Y} = 2,184 MSHE = 30 80%</p>
<p><i>My contribution to the paper was: developing the concept of the work and planning all the synthetic routes, coordinating the course of works, synthesizing and fully characterising most of the monomers, interpreting the results and participating in discussion, collecting cited literature, preparing and correcting the manuscript and also participating in correspondence with the reviewers.</i></p>		
H2	<p>Walkowiak, J.; Marciniak, B.; Koroniak, H. “Halofluorination of alkenes mediated by 1,1,3,3,3-pentafluoro-propene-diethylamine adduct” <i>Journal of Fluorine Chemistry</i>, 2012, <i>143</i>, 287-291. DOI: 10.1016/j.jfluchem.2012.07.012</p>	<p>IF₂₀₁₂ = 1,939 IF_{5Y} = 1,949 MSHE = 30 55%</p>
<p><i>My contribution to the paper was: developing the concept of the work, planning and coordinating the course of works, conducting thorough spectral characterization of resulting compounds, interpreting the results and participating in discussion, collecting cited literature, preparing and correcting the manuscript. I was responsible for the whole correspondence during the paper submission, handling the revision and resubmission of revised manuscripts up to the acceptance of the manuscripts. I am the corresponding author.</i></p>		
H3	<p>Walkowiak-Kulikowska, J.; Szwajca, A.; Boschet, F.; Gouverneur, V.; Ameduri, B. “Iodine Transfer Copolymerization of Fluorinated α-Methylstyrenes with Styrene Using 1-Iodoperfluorohexane as the Chain Transfer Agent” <i>Macromolecules</i>, 2014, <i>47</i>, 8634-8644. DOI: 10.1021/ma501828w</p>	<p>IF₂₀₁₄ = 5,800 IF_{5Y} = 5,654 MSHE = 45 60%</p>

My contribution to the paper was: formulating the research concept, scheduling and carrying out the synthesis of novel fluorinated styrenic copolymers using Iodine Transfer Copolymerization (ITP) and its characterization by means of available physicochemical methods, scheduling and performing experiments to prove suggested mechanism and the efficiency of the method in the synthesis of such polymer materials, scheduling and carrying out the synthesis that aimed at modifying of resultant copolymers, conducting thermal stability measurements, the results interpreting, preparing and correcting the manuscript, contributing to discussion with reviewers.

- | | | |
|-----------|--|---|
| H4 | Walkowiak-Kulikowska, J.; Kanigowska, J.; Koroniak, H.
“ α -(Difluoromethyl)styrene: Improved Approach to Grams Scale Synthesis”
<i>Journal of Fluorine Chemistry</i> , 2015 , 179, 175-178.
DOI: 10.1016/j.jfluchem.2015.07.008 | IF ₂₀₁₅ = 2,213
IF _{5Y} = 2,284
MSHE = 30
65% |
|-----------|--|---|

My contribution to the paper was: formulating the research concept, planning the alternative monomer synthetic route, interpreting the results and participating in discussion, collecting cited literature, preparing and correcting the manuscript. I was responsible for the whole correspondence during the paper submission, handling the revision and resubmission of revised manuscripts up to the acceptance of the manuscripts. I am the corresponding author.

- | | | |
|-----------|---|---|
| H5 | Walkowiak-Kulikowska, J.; Boschet, F.; Kostov, G.;
Gouverneur, V.; Ameduri, B.
“On the Reactivity of α -Trifluoromethylstyrene in Radical Copolymerizations with Various Fluoroalkenes”
<i>European Polymer Journal</i> , 2016 , 84, 612-621.
DOI: 10.1016/j.eurpolymj.2016.09.038 | IF ₂₀₁₆ = 3,531
IF _{5Y} = 3,658
MSHE = 35
70% |
|-----------|---|---|

My contribution to the paper was: formulating the research concept, synthesizing fluorinated styrenic monomers in gram scale, planning and carrying out the co- and terpolymerization reactions with fluorinated alkenes, interpreting and discussing the results, preparing and correcting the manuscript, contributing to discussion with reviewers. I am the corresponding author.

- | | | |
|-----------|---|---|
| H6 | Walkowiak-Kulikowska, J.; Szwajca, A., Gouverneur, V.,
Ameduri, B.
“Synthesis, characterization, and thermal and surface properties of co- and terpolymers based on fluorinated α -methylstyrenes and styrene”
<i>Polymer Chemistry</i> , 2017 , vol. 8, pp 6558-6569.
DOI: 10.1039/c7py01529a | IF ₂₀₁₇ = 4,927
IF _{5Y} = 4,927
MSHE = 45
70% |
|-----------|---|---|

My contribution to the paper was: formulating the research concept, synthesizing fluorinated styrenic monomers (FMST i TFMST) in gram scale, planning and carrying out the co- and terpolymerization reactions using conventional radical polymerization with styrene and its characterization by means of available physicochemical methods, scheduling and performing kinetic experiment in order to determine monomers reactivity ratios r_i of each polymerization system, conducting thermal stability measurements, the results interpreting, selecting cited literature, preparing and correcting the manuscript, contributing to discussion with reviewers. I am the corresponding author.

	Wolska, J., Walkowiak-Kulikowska, J. , Szwajca, A., Koroniak, H., Ameduri, B.	IF* ₍₂₀₁₇₎ = 2,936
H7	“Aromatic fluorocopolymers based on α -(difluoromethyl)styrene and styrene: Synthesis, characterization, and thermal and surface properties” <i>RSC Advances</i> , 2018 , vol. 8, pp 41836-41849. DOI: 10.1039/c8ra09340g	IF _{5Y} = 3,096 MSHE = 35 30%

My contribution to the paper was: participating in formulation of the research concept, coordinating the course of works on the synthesis of α -(difluoromethyl)styrene monomer, supervising the research on its reactivity under radical polymerization conditions as well as kinetic studies of the copolymerization processes and thermal stability measurements, interpreting and contributing to the results discussion, correcting the manuscript and contributing to discussion with reviewers. I am the corresponding author

List of publications and monographs in international and domestic journals from outside the Journal Citation Reports (JCR) base

No.	Publication	Contribution
H8	Kanigowska, J.; Walkowiak-Kulikowska, J. „Sulfon difluorometylofenylowy, jako uniwersalny i skuteczny odczynnik difluorometylujący” <i>Na pograniczu chemii i biologii</i> , 2014 , Vol. XXXIII, 343-360. ISBN: 978-83-232-2803-5	60%
	<i>My contribution to the paper was: formulating the research concept, planning and coordinating the course of works, interpreting and discussing the results, selecting cited literature, preparing and correcting the manuscript. I was responsible for the whole correspondence during the paper submission, handling the revision and resubmission of revised manuscripts up to the acceptance of the manuscripts. I am the corresponding author.</i>	
H9	Walkowiak-Kulikowska, J. ; Wolska, J.; Koroniak, H. “Polymers application in Proton Exchange Membranes for Fuel Cells (PEMFCs)” <i>Physical Sciences Reviews</i> , 2017 , accepted. DOI: 10.1515/psr-2017-0018	70%

My contribution to the paper was: formulating the research concept, coordinating the course of works, selecting cited literature, preparing and correcting the manuscript. I was responsible for the whole correspondence during the paper submission, handling the revision and resubmission of revised manuscripts up to the acceptance of the manuscripts. I am the corresponding author.

Total Impact Factor from Web of Science base	23,606
Total 5-year Impact Factor według bazy Web of Science base	23,749
Total points of MSHE	250
Average Impact Factor (5-year Impact Factor) per paper from JCR list	3,372 (3,393)
Average points of MSHE per paper from JCR list	35,714
Average percentage contribution to the paper	62,22

* IF adopted from 2017 according to JCR (Clarivate Analytics 2018)

4.2. The research objectives and discussion of main results and achievements presented in the above mentioned scientific publications

The presented habilitation dissertation covers the results of conducted researches described in the series publications H1-H9 under the common title: „Synthesis of fluorinated styrene derivatives and its application for preparing aromatic fluoropolymers”. Articles H1-H8 concern own research, whereas publication in *Physical Sciences Reviews* H9 extensively reviews the most important research on alternative polymer membranes with ionic groups attached, provides examples of materials with a well-defined chemical structure that are described in the literature. Furthermore, it elaborates on the synthetic methods used for preparing PEMs and the current status of fuel cell technology and its application. It also briefly discusses the development the PEMFC market. These issues were also discussed in more detail in the chapter of the book *Polymer engineering* written at the editor’s invitation (see Annex 3, point 2.2.5). Part of the results presented were received in cooperation with J. Wolska MA (née Kanigowska) as part of her PhD thesis - auxiliary supervisor, and her individual contribution to the publication is presented in Annex 5. Statements of other co-authors of the work together with determining the individual contribution each of them in the creation of individual works are also included in Annex 5.

Introduction and the research objectives

The current technology supports production of polymers with excellent mechanical, thermal, electroinsulating, or ion-conducting properties. Ion-conducting fluoropolymers that belong to superionic conductors are of particular interest for their suitability to make thin and flexible membranes of high ionic conductivity. Common themes critical to proton exchange membranes used as electrolytes include: high ionic (ca. 10 S/m) and low electron conductivities, adequate mechanical properties, allowing to obtain as thin as possible membrane (thickness approximately 10-250 μm), low fuel and oxidants permeability, thermal, hydrolytic and oxidative stability, long lifetime and low cost [1]. A milestone achievement in the development of electrolytic materials employed in *Proton Exchange Membrane Fuel Cells* (PEMFC, or *Polymer Electrolyte Membrane Fuel Cells*) was invented in the late 1960s by DuPont the first membrane based on polytetrafluoroethylene and perfluorovinyl ether, known under the tradename Nafion[®] [2].

Fluoropolymers are materials exhibiting a unique combination of outstanding properties, such as high thermostability and chemical or electrochemical inertness, low refractive index and friction coefficient, low dielectric constant and dissipation factor, low water absorptivity, excellent weather abilities and surface characteristics [3]. These high value products have therefore found applications in various fields of advanced technology, e.g. chemical and automobile industries, engineering, microelectronics, optics, textile finishing aeronautics or military [4, 5]. Although, the diversity of fluoropolymer applications is enormous, these products can still be difficult to process since some of them are not soluble in common solvents while others cannot be melted or exhibit very high melting points. Nevertheless, the specific properties of fluoropolymers especially solubility as well as adhesion, curability, surface properties, good hydrophilicity, heat and chemical resistance can be brought by the nature of the functional groups in a lateral position 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 ring on mechanical strength and thermal properties (e.g. increasing the polymer T_g and enhancing its thermostability), as well as fluorine substituent/s on the thermal and surface properties of the resultant polymers. The incorporation of both ie. phenyl ring and fluoro substituent into the polymeric chain can significantly improve physicochemical properties of the material. It is also expected that thermal stabilities higher than that of polystyrene can be achieved by the presence of fluoromethyl groups which should not undergo undesirable β -scission [6]. Degradation triggered by β -scission may result in local chain depolymerization, subsequent macromolecular structure damage and finally loss of material characteristic properties. Furthermore, fluoropolymers with aromatic functional groups in the lateral position to the polymer backbone can be modified by the introduction of functional groups (e.g. sulfonic). Postsulfonation is one of the methods that allows to convert the existing fluoropolymers into ionomeric materials for application as membranes for PEMFCs. Membranes based on fluoropolymer foils activated physically [7-12] or chemically [13], subsequently grafted with styrene and then sulfonated [14], exhibited proton conductivity comparable to those of Nafion[®]-type commercial membranes. However, a serious drawback of these membranes is a lack of stability under fuel cell conditions (supplied with pure hydrogens and oxygen at temperature higher than 60 °C). Most probably, degradation of polystyrene chains lowers thermostability of the membrane.

Fluorinated α -methylstyrene derivatives are difficult to polymerize under radical polymerization conditions. Studies on the reactivity of α -monofluoromethylstyrene [15] and α -trifluoromethylstyrene [16, 17] in radical polymerizations with styrene, allowed to obtain aromatic copolymer structures with fluoromethylstyrenic units. However, only few examples of radical copolymerization of fluoroolefins with these monomers have been reported, so far [18]. Among them, a radical copolymerization of chlorotrifluoroethylene (CTFE) with α -fluoromethylstyrene (FMST) as a representative styrenic comonomer with an allyl fluoride functionality was achieved successfully [19].

The objective of presented dissertaion was to prepare new functional aromatic fluoropolymers and study its structure, morphology, as well as influence of fluorinated groups on its physical and chemical properties. The programme of my habilitation included the researches aimed at improving already established and developing new convenient and cost-effective routes to access various fluorinated styrenic monomers either unsubstituted at the aryl group or possessing a substituent at the para position, as well as studies on reactivity of the fluorinated monomers in radical co- and terpolymerizations. Equally important was to fully characterize the resultant polymers and to modify them in order to prepare novel functional polymer materials.

Synthesis of fluorinated styrene derivatives (H1, H2, H4, H8)

An important issue of the conducted research was to develop convenient and cost-effective routes to access four class of non-commercially available fluorinated styrenic monomers (Figure 1): **I** α -fluorostyrenes (FST derivatives) [H2], **II** α -monofluoromethylstyrenes (FMST derivatives) [H1], **III** α -difluoromethylstyrenes (DFMST derivatives) [H1, H4, H8], **IV** α -trifluoromethylstyrenes (TFMST derivatives) [H1]. It required an extensive work on selecting the most convenient methodology for the introduction of fluorine atom(s) into the organic molecules. In the synthesis of target fluoroorganic monomers of various tested methods I used following key-step reactions: a regioselective halofluorination of alkenes, a nucleophilic selective fluorination of suitable substrate with oxygen functions, a nucleophilic difluoromethylation reaction and palladium-mediated Suzuki cross-coupling. The synthetic routes were then implemented for gram-scale preparation of FMST, DFMST oraz TFMST monomers.

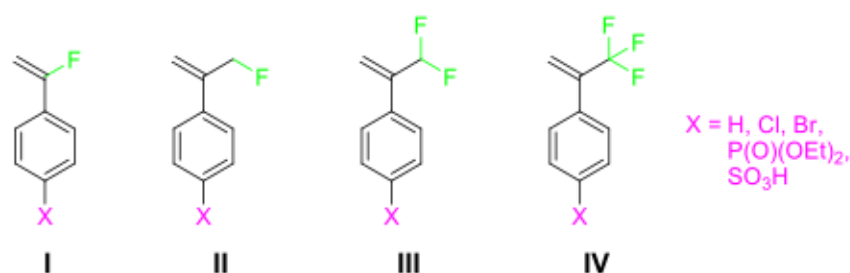
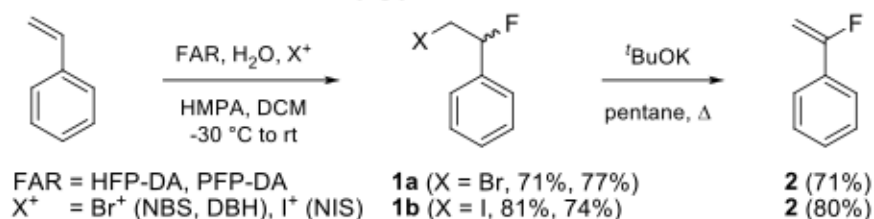


Figure 1. Four classes of fluorinated styrene derivatives: α -fluorostyrenes **I** (FST), α -monofluoromethylstyrenes **II** (FMST), α -difluoromethylstyrenes **III** (DFMST), α -trifluoromethylstyrenes **IV** (TFMST).

α -FLUOROSTYRENE DERIVATIVES

Monofluorinated alkenes proved to be valuable building blocks for the synthesis of new fluorinated compounds of potential biological activity, as well as monomers in the processes of functional fluoropolymers production. They can be easily available by two-step synthetic route with halofluorination of relevant alkene as a key-step. Thus formed vicinal bromo- and iodoalkyl fluorides in basic conditions undergo subsequent dehydrobromination/dehydroiodation leading to the formation of unsaturated derivatives possessing fluoride substituent at vinyl position. Regioselective and stereospecific halofluorination (“XF” addition) of systems with carbon-carbon unsaturated double bond is one of the most convenient reaction allowing the selective introduction of fluorine atom into organic compound. The publication H2 presented investigations on the efficiency of nucleophilic fluorinating reagent (PFP-DA) in halofluorination of a series mono- and disubstituted alkenes: 1-decene, 1-hexadecene, 1-octadecene, styrene (Scheme 1), cyclohexene, 2,5-norbomadiene, *trans*-stilbene and 2-vinylpyridine.



Scheme 1. Sequence of reactions towards the synthesis of α -fluorostyrene **2** [H2].

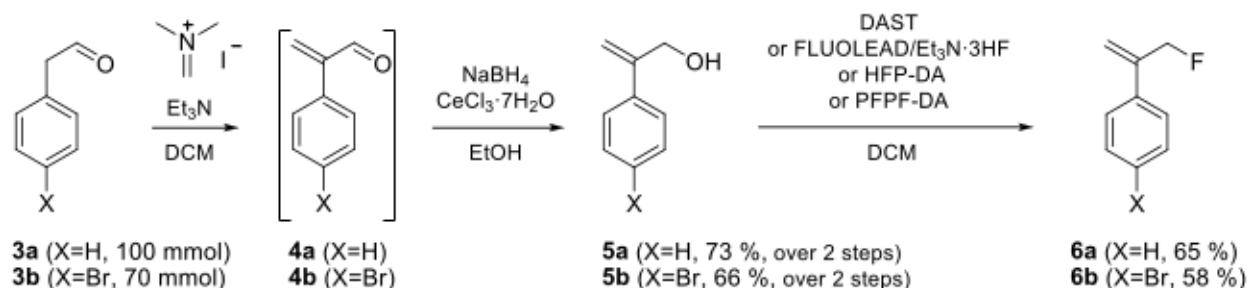
Bromo- and iodofluorination reactions of styrene enabled the gram-scale synthesis of corresponding halofluorinated aromatic derivatives in good yields (71-81% depending on a source of electrophilic halogens X^+ and applied fluorinating reagent as a source of nucleophilic fluoride). Each reaction gave only one regioisomer (2-bromo-1-fluoroethyl)benzene **1a** or (2-iodo-1-fluoroethyl)benzene **1b**, proving that the additions of “XF” towards a double bond are regioselective and follow Markovnikov’s rule. In next step, from the halofluorides by treatment with potassium *tert*-butoxide I have prepared expected monomer **2** in good yields comparable with those already reported. A colourless liquid of pure α -fluorostyrene (FST) after an exposure to light became turbid and with the time turned violet. The analyses of a resulting material revealed that fluorinated monomer **2** underwent photopolymerization and immediate HF elimination. Most likely, as a result of this process, polyphenylacetylene (pPA) was formed, which in the presence of HF undergoes subsequent degradation processes. pPA belongs to a large group of organic conductive polymers. Such materials have found application in the construction of electroluminescent diodes (PLED, OLED, PMLED, AMOLED) and are quite extensively described in the literature [20-23]. In addition, pPA can be easily obtained from commercially available phenylacetylene, e.g. in polymerization processes catalyzed by transition metals complexes. For the reasons mentioned above, the study on FST monomer reactivity under radical polymerization conditions were therefore abandoned.

α -MONOFLUOROMETHYLSTYRENE DERIVATIVES

Chemical synthesis leading to the formation of fluoroorganic derivatives do not follow general rules and methods of typical organic synthesis, due to specific chemical character of fluorine and its compounds. Effective and efficient ways enabling a selective introduction of fluorine into organic compounds are fluorination reactions both in nucleophilic and electrophilic manner. The publication **H1** presents part of the research on developing methodology suitable for production of monofluorinated monomers (FMST) using selective fluorination of relevant substrates. Initial studies were aimed at probing the efficiency of literature procedures [24, 25] for the preparation of larger quantities of material (up to 40 mmol scale). Selectfluor[®] [*1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate)*] is one of the most efficient reagent commonly used for electrophilic introduction of fluorine into organic molecules. It is a stable, easy to use, solid electrophilic *N-F reagent* enabling fluorination in mild conditions with very high yields. Therefore, first investigations followed a two-step process involving electrophilic fluorodesilylation (S_E2') of suitable allyltrimethylsilanes with Selectfluor[®] as a source of electrophilic fluorine “F⁺”. However, any attempts to improve the reaction scale resulted in significant decrease of overall yields for this sequence. Similarly, a reduction in efficiency was observed when up-scaling a one-step direct electrophilic fluorination of α -methylstyrene with Selectfluor[®]. In this case, the fluorination led to the formation of significant amount of by-products identified as the isomerised fluoroalkenes, that impeded purification and lowered by half the yield of isolated product. At this stage, the availability of reagents suitable for nucleophilic fluorination prompted me to examine alternative route for the preparation of α -fluoromethylstyrene derivatives.

The monofluorinated monomers **6** were prepared following a three-step process (Scheme 2). The reaction of aldehydes **3** with the Eschenmoser’s salt (*N,N*-dimethylmethyleammonium iodide) in the presence of a large excess of triethylamine led to the formation of α,β -unsaturated

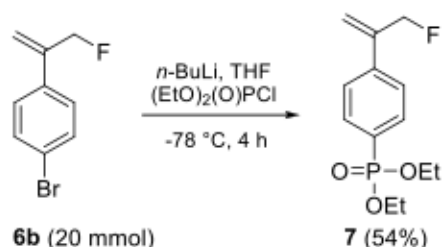
derivatives **4**. Without isolation, the resulting aldehydes **4** were reduced with sodium borohydride, leading uneventfully to the desired allylic alcohols **5**. These alcohols were converted into corresponding fluorides **6** by direct nucleophilic fluorination using alkylsulphur trifluorides and α -fluoroamines. In comparative studies, four reagents useful in organic synthesis for conversion of hydroxyl groups into fluorides: diethylaminosulphur trifluoride (DAST), 4-*tert*-butyl-2,6-dimethylphenylsulphur trifluoride (FLUOLEAD™), *N,N*-diethylamino-1,1,2,3,3,3-hexafluoropropane (HFP-DA, Ishikawa's reagent) and *N,N*-diethylamino-1,3,3,3-tetrafluoropropene (PFP-DA), were employed. The yields for the fluorination were good, consistent and comparable ($Y_{\text{DAST}} = 65\%$, $Y_{\text{FLUOLEAD}^{\text{TM}}} = 67\%$, $Y_{\text{HFP-DA}} = 65\%$, $Y_{\text{PFP-DA}} = 64\%$ and $Y_{\text{DAST}} = 58\%$, $Y_{\text{FLUOLEAD}^{\text{TM}}} = 59\%$, $Y_{\text{HFP-DA}} = 59\%$, $Y_{\text{PFP-DA}} = 58\%$, for **6a** and **6b**, respectively).



Scheme 2. Synthesis of monofluorinated α -methylstyrenes **6** by direct nucleophilic deoxyfluorination of the allylic alcohols **5** [H1].

This gram-scale synthetic route towards monofluoromethyl styrenes using a direct nucleophilic fluorination was found to be easy to implement, selective and cost-effective (in comparison to electrophilic methods) giving the desired monomers **6a** (X=H) and **6b** (X=Br) in 47% (**3a** \rightarrow **6a**) and 38% (**3b** \rightarrow **6b**) overall yield, respectively.

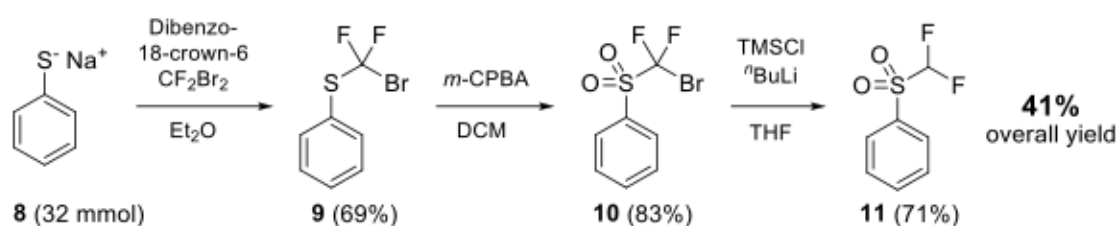
The monofluorinated styrenic monomer **6b** was further manipulated taking advantage of the presence of the bromo substituent. The introduction of a phosphonate group was elected as a suitable post-modification. To form the necessary aryl C-P bond, different approaches were considered inclusive of the classical Michaelis-Arbuzov or Michaelis-Becker reaction as well as NiCl_2 or $\text{Pd}(\text{PPh}_3)_4$ mediated cross-coupling processes. However, the reaction of the *in situ* generated aryl lithium intermediate derived from **6b** with diethyl chlorophosphonate proved to be the most efficient protocol to produce the desired aryl phosphonate **7** (**4-PFMST**, Scheme 3.).



Scheme 3. Synthesis of diethyl 4-(3-fluoroprop-1-en-2-yl)phenylphosphonate **7** [H1].

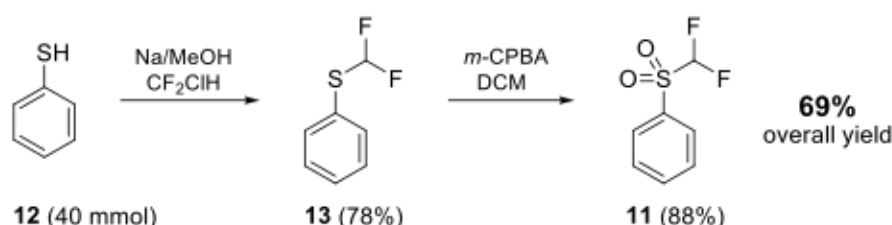
α -DIFLUOROMETHYLSTYRENE DERIVATIVES

Several research groups are focusing their efforts on the development of suitable method for introducing difluoromethyl group into organic compounds, due to a potential application of such difluoromethylated derivatives in medicine, agriculture and polymer chemistry [26]. In order to develop an effective method for preparing α -difluoromethylstyrene analogues (DFMST), I conducted a series of test reactions. Attempts to access this monomer by direct fluorination of the aldehyde **4** 1,3-dithiolane derivative (see Scheme 2) using DAST in the presence of either 1,3-dibromo-5,5-dimethylhydantoin or *N*-bromosuccinimide were not successful [27, 28]. I therefore examined an alternative strategy based on a nucleophilic difluoromethylation process using the difluoromethyl phenyl sulfone **11** [H1]. Initially, this reagent was prepared applying a three-step literature protocol (Scheme 4). The reaction of sodium thiophenolate **8** with dibromodifluoromethane in the presence of catalytic amount of dibenzo-18-crown-6 ether resulted in the formation of bromodifluoromethyl sulfide **9**. Oxidation of **9** with an excess of *meta*-chloroperoxybenzoic acid (*m*-CPBA) gave the desired sulfone **10**, that was converted in the next step into corresponding difluoromethylating reagent **11** using *n*-butyllithium as a strong base in the presence of trimethylsilyl chloride (route A).



Scheme 4. Sequence of reactions towards the synthesis of difluoromethyl phenyl sulfone **11** (route A) [H1].

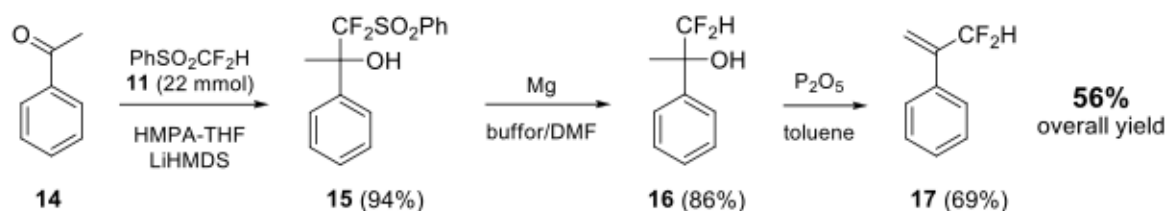
Overall yield of this three-step sequence was relatively low (41%) and I therefore investigated another strategy to obtain a desired nucleophilic difluoromethylating reagent **11** (Scheme 5) [H4, H8]. At this stage, the first step of synthesis required an *in situ* generation of sodium thiophenolate formed in the reaction of thiophenol **12** with sodium methanolate. Chlorodifluoromethane (Freon 22) was used as fluorinated building block. As in the route A, isolated sulphide **13** was subsequently oxidized with *m*-CPBA. The resulting nucleophilic difluoromethylating reagent was isolated in 69% overall yield (route B).



Scheme 5. Alternative strategy for the synthesis of difluoromethyl phenyl sulfone **11** (route B). [H4, H8]

The reactivity of difluoromethylphenyl sulfone **11** as difluoromethylating agent was studied in base-induced difluoromethylation coupling of $\text{PhSO}_2\text{CF}_2\text{H}$ with acetophenone **14** in the presence of lithium bis(trimethylsilyl)amide (LiHMDS) as a base [H8]. The resultant tertiary alcohol **15** was isolated with excellent yield, and converted in the next step into 1,1-difluoro-2-phenylpropan-

2-ol **16** using reductive desulfonylation, i.e. the cleavage of $-\text{SO}_2\text{Ph}$ group. Metallic magnesium used as a reducing agent, was activated by acetate buffer. Concentration of the buffer and composition of solvents used in the reaction influenced considerably the process yield. Dehydration of resulting carbinol **16** using phosphorus pentoxide at elevated temperature afforded the desired α -(difluoromethyl)styrene **17** (Scheme 6) [H4].

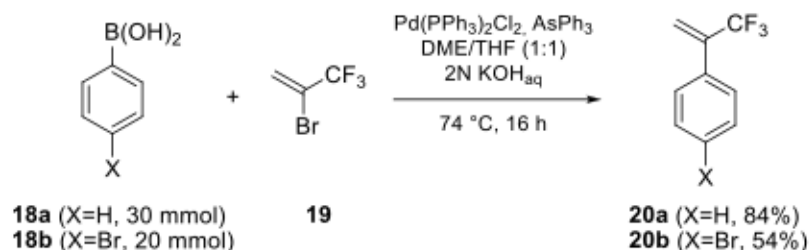


Scheme 6. Three-step synthesis of α -difluoromethylstyrene monomer DFMST **17** [H4, H8].

The synthetic routes towards both nucleophilic difluoromethylating reagent and difluoromethylstyrene was found to be selective, cost-effective, easy to implement and easily scalable giving the desired gem-difluorinated styrenic monomer DFMST **17** in 56% overall yield.

α -TRIFLUOROMETHYLSTYRENE DERIVATIVES

With the objectives to examine the influence of the fluorine content of styrenic monomers on both reactivity and copolymer composition, it was particularly interesting to investigate polymerization ability of trifluorinated α -methylstyrene analogues. The Suzuki reaction [29, 30] was selected from a number of reported synthetic methods for the introduction of trifluoromethyl groups into organic compounds. It is a reaction between boronic acids and vinyl or aryl halides catalysed with palladium [31-34]. High efficiency, mild reaction conditions, nontoxicity, stability, easy access to many boronic acids and the ability to remain unaffected in the presence of water contributed to make this method one of the best for the synthesis of simple organic compounds, as well as highly functionalized compounds [35]. α -Trifluoromethylstyrene derivatives TFMST **20** were successfully synthesized in the palladium-catalysed cross-coupling reaction of organoborons **18** with 2-bromo-3,3,3-trifluoropropene **19** (Scheme 7) [H1].



Scheme 7. Synthesis of trifluoromethyl styrenes **20** by palladium(II)-catalysed Suzuki-Miyaura coupling of the phenylboronic acids **18** with 2-bromo-3,3,3-trifluoropropene **19** [H1].

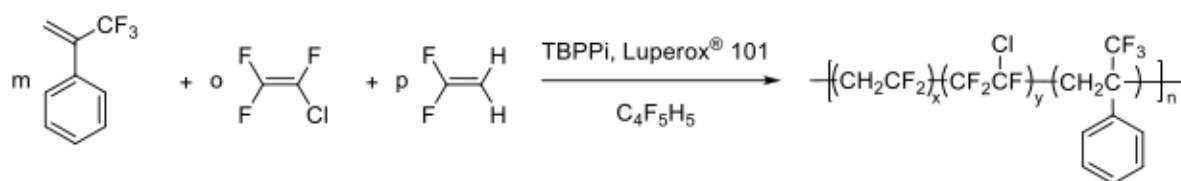
Structures of all presented above monomers were confirmed by means of available physicochemical methods (^1H NMR, ^{13}C NMR, ^{19}F NMR, MS). All developed routes to novel functional aromatic fluorinated monomers are efficient, reproducible and enable its synthesis in gram-scales. Various fluorinated methylstyrene analogues were made available in gram quantities allowing for subsequent studies of its reactivity in radical polymerization conditions.

Reactivity of the fluorinated styrene monomers in radical polymerization conditions (H3, H5, H6, H7, H9)

CONVENTIONAL RADICAL POLYMERIZATION WITH FLUORINATED AND NON-FLUORINATED OLEFINS

In general, the radical bulk homopolymerizations of fluorinated α -methylstyrenes initiated by α, α' -azobis(isobutyronitrile) (AIBN) were unsuccessful and did not even lead to any oligomer. 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 chlorotrifluoroethylene (CTFE) with α -fluoromethylstyrene (FMST) as a representative styrenic comonomer with an allyl fluoride functionality was achieved successfully [19]. The publication H5 presents the radical co- and terpolymerizations of α -trifluoromethylstyrene (TFMST) with various olefins: fluorinated (vinylidene fluoride, VDF; chlorotrifluoroethylene, CTFE; 3,3,3-trifluoropropene, TFP; 1*H*,1*H*,2*H*,2*H*-perfluorodecyl-vinyl ether, FAVE-8) and hydrogenated (eter etylovo-winylovy, EVE). The radical copolymerizations of TFMST with mentioned above olefins were carried out in 1,1,1,3,3-pentafluorobutane (solvent that does not lead to any transfer in the course of radical polymerizations) and initiated by *tert*-butyl peroxyvalate (TBPPi). Unexpectedly, all approaches to obtain copolymers containing trifluoromethyl functionalized aromatic units have failed, and did not even lead to any oligomer, totally inhibiting all copolymerization reactions.

Therefore, I decided to enhance the reactivity of TFMST using so-called Induced terpolymerization. I introduced a reactive monomer couple, ie. vinylidene fluoride, VDF and chlorotrifluoroethylene CTFE since they are known to copolymerize efficiently. Such reactions enable the induction of the reactivity to unreactive monomer resulting its (TFMST) incorporation in the VDF-*co*-CTFE copolymer A series of autoclave terpolymerizations of TFMST with VDF and CTFE was carried out in 1,1,1,3,3-pentafluorobutane and initiated by *tert*-butyl peroxyvalate (TBPPi) and 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (Luperox® 101) (Scheme 8).



Scheme 8. Radical terpolymerization reaction of vinylidene fluoride (VDF) and chlorotrifluoroethylene (CTFE) with α -trifluoromethylstyrene (TFMST); Conditions of polymerization in solution: $([\text{Luperox}^{\text{®}} 101]_0 + [\text{TBPPi}]_0) / ([\text{CTFE}]_0 + [\text{VDF}]_0 + [\text{TFMST}]_0) = 4 \text{ mol}\%$; solvent- $\text{C}_4\text{F}_9\text{H}_5$; $T = 75 \text{ }^{\circ}\text{C}$ (3 h), then $142 \text{ }^{\circ}\text{C}$ (10 h) [H5].

The ^{19}F NMR spectrum (Figure 2) of poly(VDF-*ter*-CTFE-*ter*-TFMST) terpolymer exhibited signal at -92.15 ppm (marked as $F_{\text{B(H-T)}}$) characteristic for VDF-VDF head-to-tail sequence $(\text{CH}_2\text{-CF}_2)_n$ (formed by “normal” additions in the VDF microblocks) and several signals in the range from: -95.49 to -96.79 , -114.02 to -115.19 and -116.48 to -117.95 ppm attributed to VDF-VDF head-to-head microstructures (formed by “reversed” additions of the VDF monomers) noted as F_{B} . Furthermore, in the range from: -106.03 to -120.48 ppm (F_{C}), and -120.48 to -137.25 ppm (F_{D}), appeared characteristic signals difluoro- or chlorofluoromethylene moieties of CTFE units. Additionally, ^{19}F NMR spectrum exhibited also some signals in the region of -65.40 to -76.31 ppm

(F_A) characteristic for trifluoromethyl group, evidencing incorporation of TFMST monomer units into the fluorinated polymer chain. All the signal observed in ¹⁹F NMR confirmed that induced terpolymerization led to the formation of fluoropolymer with trifluoromethylstyrene units incorporated.

The VDF, CTFE and TFMST contents in the terpolymers (Table 1) were determined according to the ¹⁹F NMR integrals of the characteristic signals of VDF, CTFE and TFMST base units incorporated in the cooligomers by the equations 1-3 as follows:

$$\text{mol\% VDF in terpolymer} = (I_{F-B}/2)/[(I_{F-B}/2)+((I_{F-C}+I_{F-D})/3)+(I_{F-A}/3)] \quad (1)$$

$$\text{mol\% CTFE in terpolymer} = [(I_{F-C}+I_{F-D})/3]/[(I_{F-B}/2)+((I_{F-C}+I_{F-D})/3)+(I_{F-A}/3)] \quad (2)$$

$$\text{mol\% TFMST in terpolymer} = (I_{F-A}/3)/[(I_{F-B}/2)+((I_{F-C}+I_{F-D})/3)+(I_{F-A}/3)] \quad (3)$$

where I_{F-A} , I_{F-B} and $I_{F-C}+I_{F-D}$ are the integrals of characteristic fluorine signals of TFMST, VDF or CTFE, respectively.

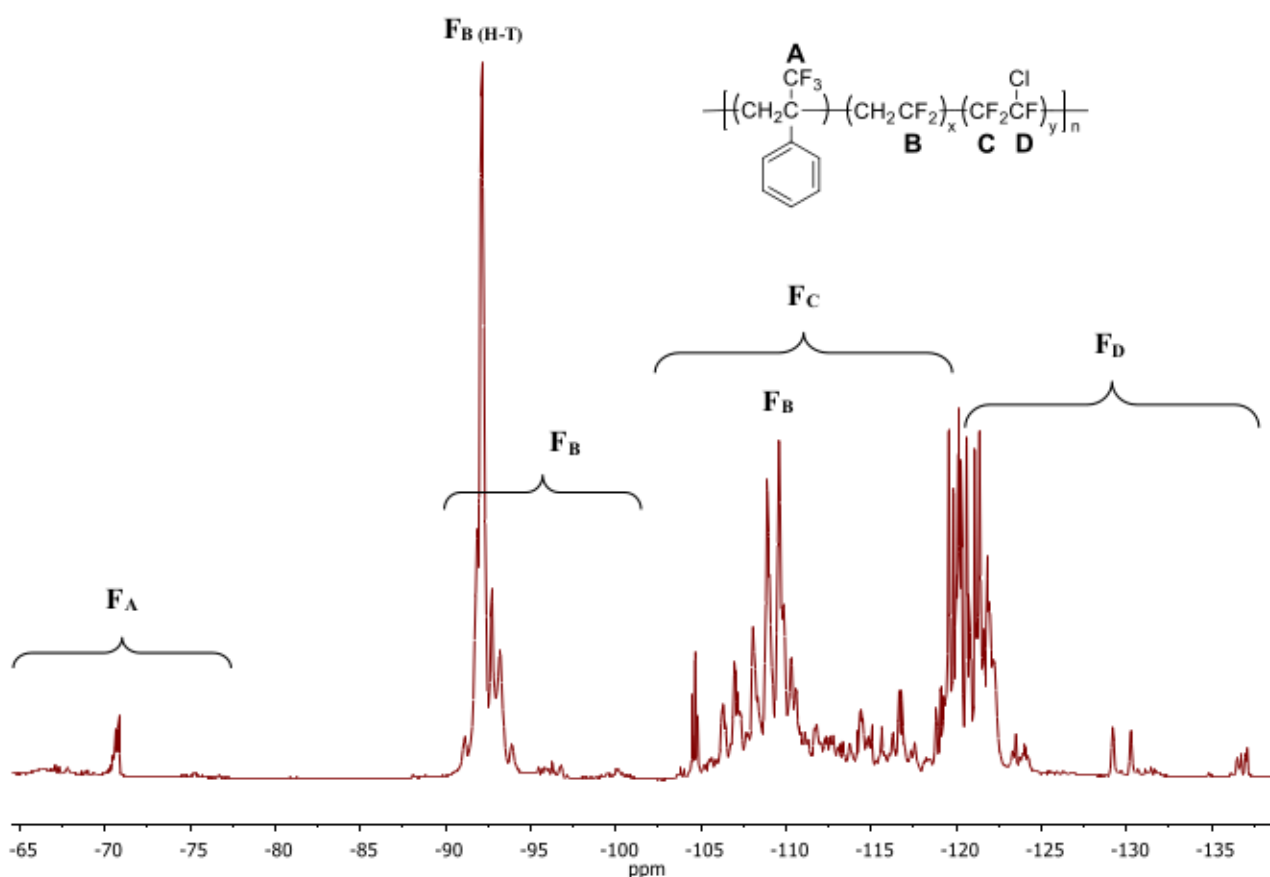


Figure 2. ¹⁹F NMR spectrum (acetone-d₆) of poly(CTFE-*ter*-VDF-*ter*-TFMST) terpolymer prepared by direct radical terpolymerization reaction, containing 51.9 mol% CTFE, 46.1 mol% VDF and 2.0 mol% TFMST (Table 1, entry 1) [H5].

Table 1. Radical polymerization of α -trifluoromethylstyrene (TFMST) with vinylidene fluoride (VDF) and chlorotrifluoroethylene (CTFE) in the presence of *tert*-butyl peroxyvalate (TBPPi) oraz 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (Luperox® 101) as radical initiators [H5].

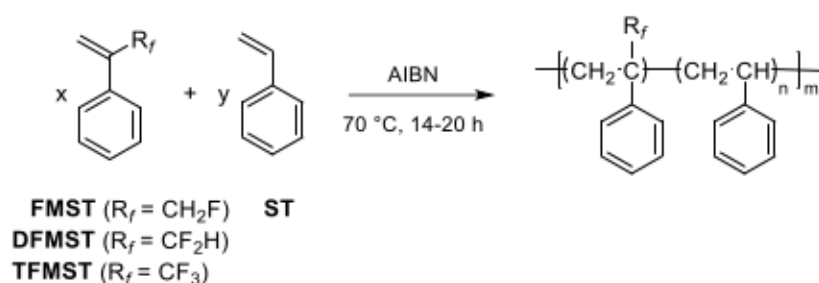
Entry	Molar ratio (mol%)						Yield ^b (wt%)	M_n^c	M_w^c	\bar{D}^c
	in feed			in terpolymer ^a						
	VDF	CTFE	TFMST	VDF	CTFE	TFMST				
1	64.9	30.5	4.6	46.1	51.9	2.0	39	4400	6600	1.5
2	64.5	29.5	6.0	42.4	52.8	4.8	80	2900	3800	1.3
3	58.3	32.0	9.7	no terpolymerization						

^a determined by ¹⁹F NMR spectroscopy; ^b yield by mass; ^c average molecular weights (M_n , M_w) and dispersity indices (\bar{D}) assessed from GPC (with polystyrene standard).

α -Trifluoromethylstyrene (TFMST) failed to homopolymerize and copolymerize with monomers such as VDF, CTFE, TFP, FAVE-8 or EVE in radical reaction conditions. However, the radical terpolymerization of TFMST with VDF and CTFE led to a successful synthesis of poly(VDF-*ter*-CTFE-*ter*-TFMST) terpolymers when the feed mol% of TFMST was lower than 10%.

CONVENTIONAL RADICAL POLYMERIZATION WITH STYRENE

α -Monofluoromethylstyrene (FMST) [15] and α -trifluoromethylstyrene (TFMST) [16, 17] (ST) are known to be efficient monomers in radical copolymerization with styrene (ST). Although, few pioneer studies demonstrated that such fluorinated aromatic monomers retarded the polymerization rate of styrene and increased unacceptably the reaction time. In order to: compare reactivity of fluorinated α -methylstyrene towards styrene in radical reaction conditions, discover the applications capabilities as well as learn more about polymerization retarding effect, I revisited conventional radical copolymerizations of FMST or DFMST or TFMST with ST. The articles H6 and H7 presents results of conducted research on conventional bulk polymerizations of FMST [H6], DFMST [H7] and TFMST [H6] with ST using 2,2'-azobis(izobutyronitrylu) (AIBN) as initiator (Scheme 9).



Scheme 9. Conventional bulk copolymerization of α -fluoromethylstyrene (FMST) and α -trifluoromethylstyrene (TFMST) with styrene (ST) initiated by AIBN at 70 °C.

The procedure enabled the synthesis of 19 poly(FMST-*co*-ST), poly(DFMST-*co*-ST) and poly(TFMST-*co*-ST) copolymers with a F-ST mol% varying between 10.6-49.7 for FMST, 10.4-48.2 for DFMST and 10.6-48.3 for TFMST, respectively and different molecular weights ranging from 23,700 to 1,500 for FMST, 17,200 to 1900 for DFMST and 14,600 to 1,500 TFMST. Thorough combinative of nuclear magnetic resonance (¹H and ¹⁹F NMR) and gel permeation chromatography (GPC) analysis of all obtained aromatic fluoropolymers enabled not only

identification of poly(F- α -MST-co-ST) copolymers structures, but also conducting appropriate calculations to determine their final composition and conversions of individual monomers. Figures 3-5 present a comparison of ^1H NMR spectra (*Cascades A*) for ST and fluorinated styrene monomers (F- α -MST), with the spectrum of exemplary poly(F- α -MST-co-ST) copolymers and a comparison of ^{19}F NMR spectra (*Cascades B*) of particular F-MST monomers with the spectrum of the same poly(F- α -MST-co-ST) copolymers.

The ^1H NMR spectra of all isolated poly(F- α -MST-co-ST) copolymers, exhibit two main broad signals in the range of 0.9 to 2.6 ppm (marked in the spectra as H_A, H_B, H_{B'}, H_{B''}) assigned to aliphatic backbone protons of methylene and methine groups of ST units and methylene moieties of F- α -MST units, as well as in the range of 6.0 to 7.5 ppm (marked in the spectra as H_C, H_D, H_E, H_{C'}, H_{D'}, H_{E'}, H_{C''}, H_{D''}, H_{E''}) attributed to aromatic protons of the phenyl substituents of both monomers (ST and F- α -MST) embedded in the copolymer structure. Most probably, due to the absence of vinyl moieties, the signals of the aromatic protons in the copolymer underwent a high field shift in comparison with the H_{Ar} multiplets observed in the NMR spectra of ST and F- α -MST monomers. In addition, in the ^1H NMR spectra of poly(FMST-co-ST) and poly(DFMST-co-ST) copolymers, the broad signals of lower intensity were observed at approx. 3.75 or 5.00 ppm, confirming the presence of protons of the -CH₂F group (FMST base units) or -CF₂H (DFMST base units), respectively.

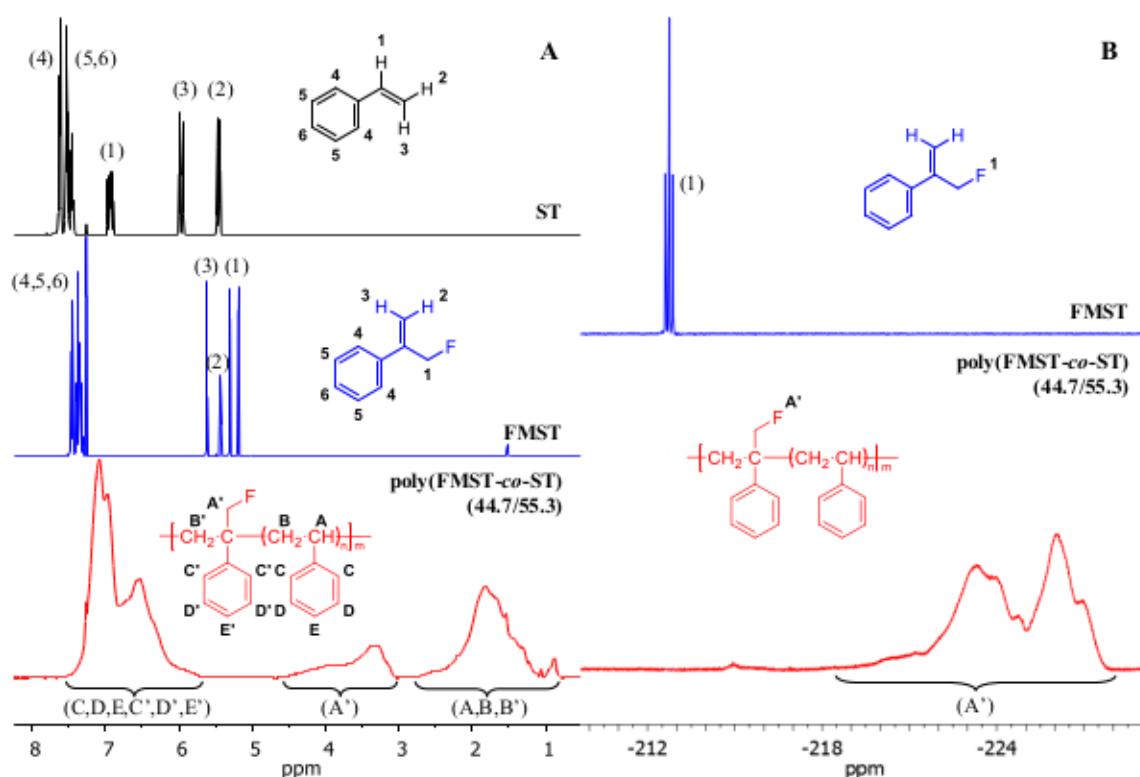


Figure 3. Comparison of ^1H i ^{19}F NMR spectra (recoded in CDCl_3) of monomers (ST i FMST) with poly(FMST-co-ST) copolymer. *Cascade A*: ^1H NMR spectra of styrene (ST) (—), α -fluoromethylstyrene (FMST) (—) and poly(FMST-co-ST) copolymer (—) (44.7/55.3, $\bar{M}_n = 2,900$, Table 2, Entry 5); *Cascade B*: ^{19}F NMR spectra of α -fluoromethylstyrene (FMST) (—) and poly(FMST-co-ST) copolymer (—) (44.7/55.3, $\bar{M}_n = 2,900$, Table 2, Entry 5) [H6].

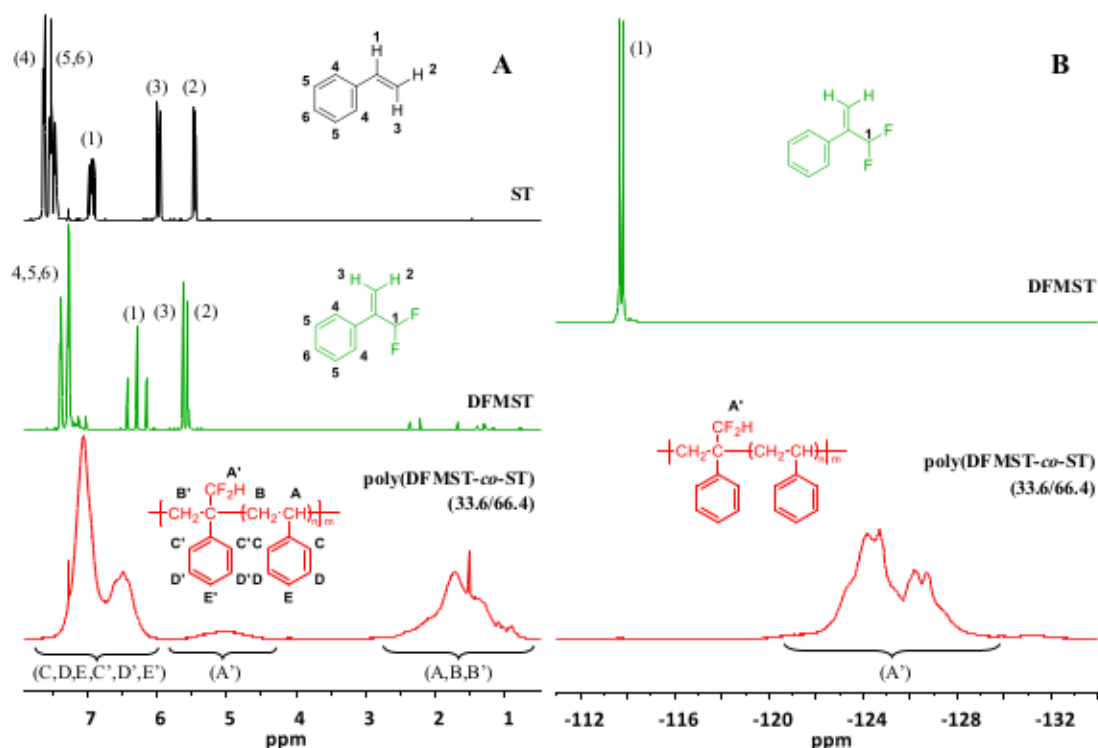


Figure 4. Comparison of ^1H i ^{19}F NMR spectra (recorded in CDCl_3) of monomers (ST i DFMST) with poly(DFMST-co-ST) copolymer. **Cascade A:** ^1H NMR spectra of styrene (ST) (—), α -difluoromethylstyrene (DFMST) (—) and poly(DFMST-co-ST) copolymer (—) (33.6/66.4, $\bar{M}_n = 5,400$, Table 2, Entry 10); **Cascade B:** ^{19}F NMR spectra of α -difluoromethylstyrene (DFMST) (—) i kopolymeru poly(DFMST-co-ST) (—) (33.6/66.4, $\bar{M}_n = 5,400$, Table 2, Entry 10) [H7].

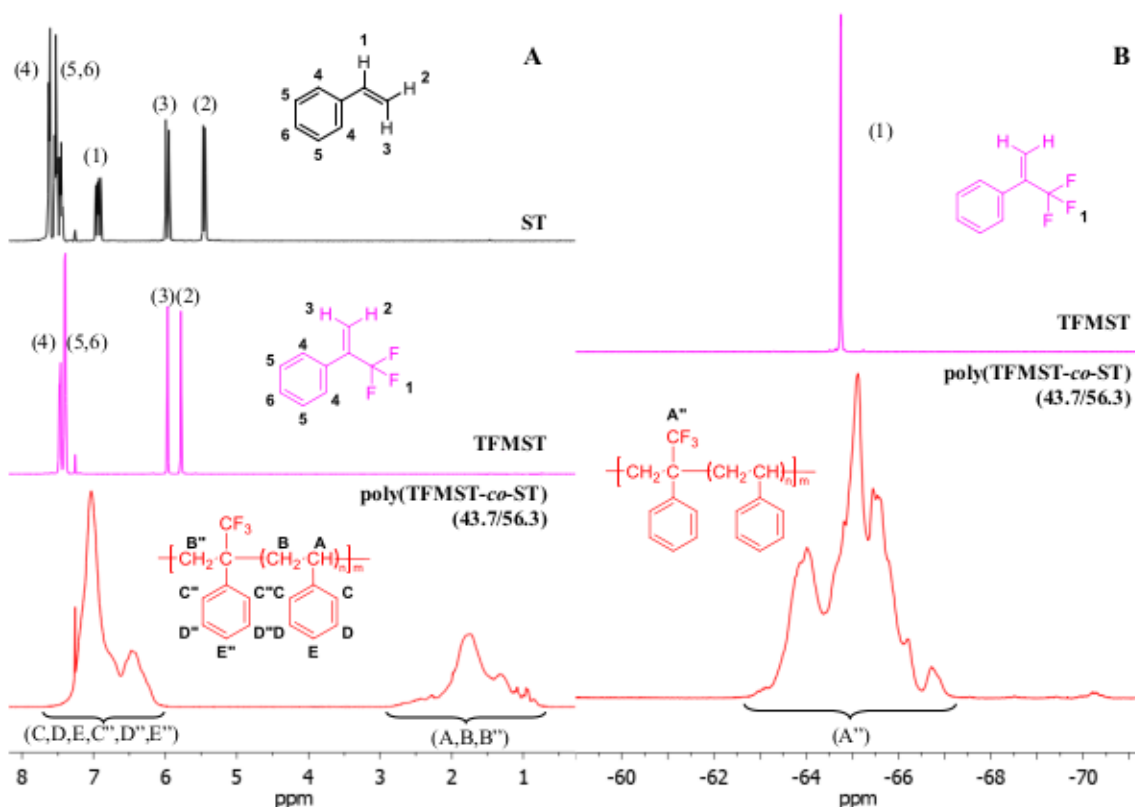


Figure 5. Comparison of ^1H i ^{19}F NMR spectra (recorded in CDCl_3) of monomers (ST i TFMST) with poly(TFMST-co-ST) copolymer. **Cascade A:** ^1H NMR spectra of styrene (ST) (—), α -trifluoromethylstyrene (TFMST) (—) and poly(TFMST-co-ST) copolymer (—) (43.7/56.3, $\bar{M}_n = 6,500$, Table 2, Entry 17); **Cascade B:** widma ^{19}F NMR (CDCl_3) α -trifluorometylostyrenu (TFMST) (—) i kopolymeru poly(TFMST-co-ST) (—) (43.7/56.3, $\bar{M}_n = 6,500$, Table 2, Entry 17) [H6].

The integrals of characteristic proton signals assigned to corresponding structural units of ST, FMST or DFMST, embedded in the chains of respective polymers allowed to determine the molar ratios of ST-FMST and ST-DFMST in copolymers (Table 2) using the following mathematical equations (Equations 4-7):

for poly(FMST-co-ST) copolymers

$$\text{mol\% ST in copolymer} = [(I_{H-A,B,B'} - I_{H-A'})/3] / \{[(I_{H-A,B,B'} - I_{H-A'})/3] + (I_{H-A'}/2)\} \quad (4)$$

$$\text{mol\% FMST in copolymer} = (I_{H-A'}/2) / \{[(I_{H-A,B,B'} - I_{H-A'})/3] + (I_{H-A'}/2)\} \quad (5)$$

where $I_{H-A,B,B'}$ and $I_{H-A'}$ stand for the integrals of the signals centered at 1.59 and 3.75 ppm, assigned to the aliphatic backbone base units of ST (H_A i H_B) and FMST ($H_{B'}$) and to the $-CH_2F$ moiety of FMST base units ($H_{A'}$), respectively (Figure 3);

for poly(DFMST-co-ST) copolymers

$$\text{mol\% ST in copolymer} = [(I_{H-A,B,B'} - I_{H-A'})/3] / \{[(I_{H-A,B,B'} - I_{H-A'})/3] + I_{H-A'}\} \quad (6)$$

$$\text{mol\% DFMST in copolymer} = (I_{H-A'}) / \{[(I_{H-A,B,B'} - I_{H-A'})/3] + (I_{H-A'}/2)\} \quad (7)$$

where $I_{H-A,B,B'}$ and $I_{H-A'}$ stand for the integrals of the signals centered at 1.59 and 5.00 ppm, assigned to the aliphatic backbone base units of ST (H_A i H_B) and FMST ($H_{B'}$) and to $-CF_2H$ moiety of DFMST base units ($H_{A'}$), respectively (Figure 4).

Unlike in the case of poly(FMST-co-ST) copolymers, the determination of the ST and TFMST comonomer contents in the poly(TFMST-co-ST) copolymers was more complex and required the use of pentafluorophenol (PFPhOH) as an internal standard for ^{19}F NMR studies. The integrals of signals assigned to $-CF_3$ groups embedded in the polymer chains and fluorine atoms of aromatic ring of internal standard allowed to determine the molar ratios of ST-TFMST in copolymers (Table 2) using the following mathematical equations (Equations 8-13):

$$n_{TFMST} = (I_{F-A'}/3) / (I_{PFPhOH}/5) * n_{PFPhOH} \quad (8)$$

$$m_{TFMST} = n_{TFMST} * M_{TFMST} \quad (9)$$

$$m_{ST} = m_{\text{copolymer}} - m_{TFMST} \quad (10)$$

$$n_{ST} = m_{ST} / M_{ST} \quad (11)$$

$$\text{mol\% ST in copolymer} = [n_{ST} / (n_{ST} + n_{TFMST})] * 100 \quad (12)$$

$$\text{mol\% TFMST in copolymer} = [n_{TFMST} / (n_{ST} + n_{TFMST})] * 100 \quad (13)$$

where $I_{F-A'}$ and I_{PFPhOH} stand for the integrals of the signals assigned to $-CF_3$ groups of TFMST base units and fluorine atoms of PFPhOH aromatic ring determined by ^{19}F NMR, n_{PFPhOH} and $m_{\text{copolymer}}$ are the number of moles of the internal standard and the weight of the copolymer weighed to prepare the NMR sample, while n_{ST} , n_{TFMST} , m_{ST} , m_{TFMST} , M_{ST} and M_{TFMST} are the numbers of moles and masses of ST and TFMST mers embedded in the structure of polymers and molar masses of styrene ($104,15 \text{ g} \cdot \text{mol}^{-1}$) i α -trifluoromethylstyrene ($172,15 \text{ g} \cdot \text{mol}^{-1}$), respectively.

Table 2. Studies on radical block copolymerizations of fluorinated α -methylstyrene derivatives: α -fluoromethylstyrene (FMST), α -difluoromethylstyrene (DFMST), α -trifluoromethylstyrene (TFMST) with styrenem (ST) initiated by AIBN at 70 °C [H6, H7].

Entry	Molar ratio(% mol)				Conversion [%]		Yield ^b (wt%)	\bar{M}_n^c	\bar{D}^c
	In feed		In copolymer		F-MST	ST			
	F-MST	ST	F-MST	ST					
poly(FMST- <i>co</i> -ST)									
1	10.2	89.8	10.6 ^a	89.4 ^a	87.5 ^a	83.6 ^a	84	23,700	3.66
2	20.0	80.0	20.2 ^a	79.8 ^a	84.3 ^a	83.4 ^a	83	18,900	3.07
3	30.3	69.7	30.0 ^a	70.0 ^a	48.4 ^a	48.4 ^a	49	6,600	1.88
4	40.2	59.8	31.0 ^a	69.0 ^a	23.2 ^a	35.3 ^a	30	4,800	1.77
5	50.2	49.8	44.7 ^a	55.3 ^a	18.8 ^a	23.5 ^a	21	2,900	1.93
6	78.3	21.7	49.7 ^a	50.3 ^a	5.5 ^a	19.9 ^a	8	1,500	1.35
poly(DFMST- <i>co</i> -ST)									
7	10.0	90.0	10.4 ^a	89.6 ^a	84.0 ^a	81.0 ^a	88	17,200	3.07
8	20.0	80.0	20.3 ^a	79.7 ^a	54.7 ^a	53.7 ^a	55	12,300	2.07
9	30.0	70.0	29.2 ^a	70.8 ^a	44.6 ^a	46.4 ^a	50	7,800	1.86
10	40.0	60.0	33.6 ^a	66.4 ^a	30.6 ^a	40.3 ^a	42	5,400	1.59
11	50.0	50.0	39.9 ^a	60.1 ^a	24.8 ^a	38.3 ^a	31	2,700	1.51
12	60.0	40.0	43.9 ^a	56.1 ^a	8.4 ^a	16.0 ^a	11	2,300	2.02
13	80.0	20.0	48.2 ^a	51.8 ^a	0.9 ^a	4.0 ^a	1	1,900	1.24
poly(TFMST- <i>co</i> -ST)									
14	10.1	89.9	10.6 ^b	89.4 ^b	46.1 ^b	43.5 ^b	44	14,600	1.70
15	20.0	80.0	20.8 ^b	79.2 ^b	37.3 ^b	35.4 ^b	36	10,800	1.51
16	30.1	69.9	28.7 ^b	71.3 ^b	24.6 ^b	26.3 ^b	26	8,900	1.45
17	49.9	50.1	43.7 ^b	56.3 ^b	13.9 ^b	17.4 ^b	15	6,500	1.36
18	70.0	30.0	46.9 ^b	53.1 ^b	8.9 ^b	15.7 ^b	8	2,600	1.45
19	89.8	10.2	48.3 ^b	51.7 ^b	7.8 ^b	12.1 ^b	4	1,500	1.58

^a Determined by ¹H NMR and ¹⁹F NMR spectroscopy; ^b Determined by ¹H NMR and ¹⁹F NMR using pentafluorophenol (PFPhOH) as the internal standard; ^c Average molecular weights (\bar{M}_n , \bar{M}_w) and the dispersity index (\bar{D}) assessed from GPC (THF, RI) with poly(styrene) standards.

Figure 6 shows the copolymerization and terpolymerization curves for the tested systems: FMST-ST, DFMST-ST, TFMST-ST and TFMST-ST-FMST (discussed below), respectively, i.e. diagrams of dependence of the copolymer composition on the amount of fluorinated styrene monomer used in the feed FMST (◆ ---), DFMST (◆ ---), TFMST (◆ ---) oraz TFMST + FMST (◆ ---).

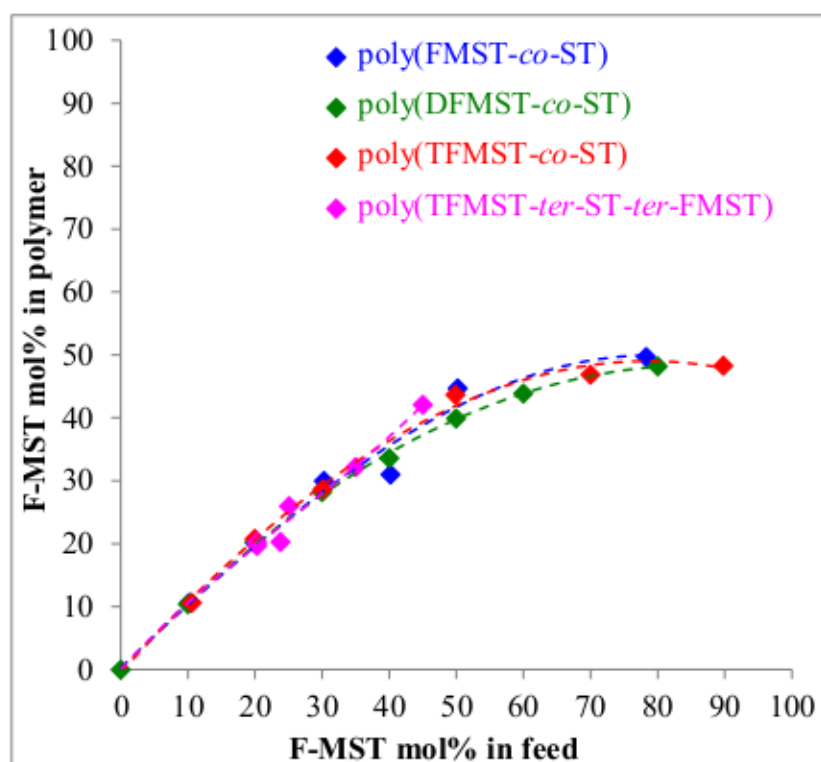


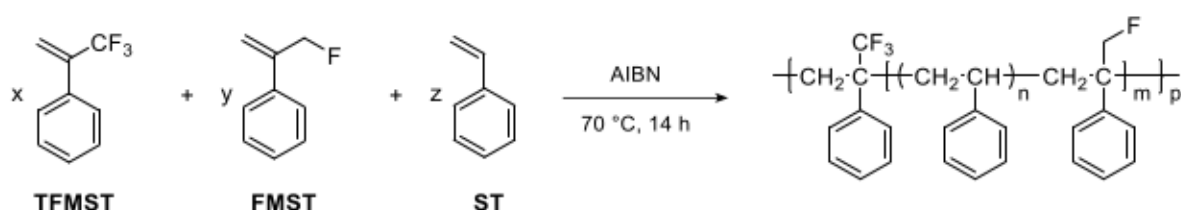
Figure 6. Co- and terpolymer composition vs. fluorinated styrene (F-ST) monomer feed of F-ST: (◆ ---) poly(FMST-co-ST) copolymers, (◆ ---) poly(DFMST-co-ST) copolymers, (◆ ---) poly(TFMST-co-ST) copolymers, and (◆ ---) poly(TFMST-ter-ST-ter-FMST) terpolymers [H6, H7].

As expected, the higher fluorinated monomers 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 average molecular weight of copolymers. Only a high F-ST 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 the molecular weight of the product and/or the rate of polymerization can also be explained by the presence of side-chain transfer reactions towards the monomer, initiator, and polymer.

Based on kinetics studies, the monomer reactivity ratios for each system (FMST;ST), (DFMST;ST) and (TFMST;ST), are as follows: $r_{ST} = 0.72 \pm 0.04$ and $r_{FMST} = 0.08 \pm 0.02$, $r_{ST} = 0.69 \pm 0.04$ and $r_{DFMST} = 0.00$, $r_{ST} = 0.64 \pm 0.01$ and $r_{TFMST} = 0.00$, at 70 °C, respectively. The computational method used was the extended Kelen-Tüdös linear least-squares method (EK-T) [36], that allows to determine reactivity ratios of monomer at high conversions and the obtained results are very similar to those obtained by nonlinear methods. The analysis of the results obtained shows that the macroradical $R-CH_2(Ph)(R_f)C^*$ reluctantly or not at all reacts with its corresponding fluorinated monomer F- α -MST ($k_{22}=0,08 \times k_{21}$ for FMST and $k_{22}=0$ for DFMST i TFMST), and adds more readily ST monomers than polystyrene $R-CH_2(Ph)CH^*$ radical ($k_{21}=12,5 \times k_{22}$ for FMST). Moreover, respective fluorinated comonomers are approx. 1,39 (for FMST), 1,45 (for DFMST) and 1,56 (for TFMST) times more reactive toward $R-CH_2(Ph)CH^*$ radical than ST comonomers ($k_{12}=1,4 \times k_{11}$ for FMST, $k_{12}=1,5 \times k_{11}$ for DFMST and $k_{12}=1,6 \times k_{11}$ for TFMST), that prevents the formation of long blocks of the ST units in the copolymer. Additionally, much higher reactivity of ST compared to F- α -MSTs toward fluorinated macroradicals $R-CH_2(Ph)(R_f)C^*$, may explain why

the formation of copolymers with greater than 50 mol% F- α -MST units cannot be obtained under radical conditions. When comparing the values of the reactivity ratios of the three fluorinated α -methylstyrene derivatives, it is clear that DFMST and TFMST show similar very low reactivity, whereas FMST is a slightly more reactive comonomer. Based on the above observations, the following reactivity order of fluorinated α -methylstyrene have been proposed: FMST > DFMST \approx TFMST. According to kinetics of the copolymerizations, and retarding effect of each fluorinated comonomers (FMST, DFMST, TFMST), as well as, the fact that they do not homopolymerize under free radical initiation, one can anticipate the copolymers possess structures where different monomeric FMST and TFMST units are randomly distributed between oligostyrenic microblocks. Microstructure of polymeric materials may have direct impact on its physicochemical parameters, and consequently on its applicability. To explain the observed retarding effect, in articles **H6** and **H7** are presented consideration on the electronic and steric factors that influence the stability or/and reactivity of the tertiary R-CH₂(Ph)(R_f)C^{*} radical that is undoubtedly formed in copolymerization reactions. In the structure of such a macroradical, beside the polymer chain, there are two groups that exhibit different electronic behavior, a fluorinated methyl group (-CH₂F, -CF₂H, -CF₃), inductively, depending on the number of fluorine atoms, withdraws electrons and the phenyl ring, which is their donor. The inducing and conjugating effects of EDGs, such as a phenyl ring lower the energy of the single occupied molecular orbital (SOMO), and thus stabilize the resulting macroradical. Moreover, the electron withdrawing groups are known to lower the orbital energies and therefore, in principal, the high electronegative fluorine should also lower the orbital energy being attached to carbon radical centre (X₂C^{*}-F, X = H and F) [37]. However, the effect of fluorine substituents, that are not directly attached to the radical centre is more difficult to define. Suggested in the literature the following decreasing order of stability: CH₃CH₂^{*} > FCH₂CH₂^{*} > F₂CHCH₂^{*} > CH₃^{*} > CF₃CH₂^{*} indicates that fluorinated methyl group, attached to the carbon radical center destabilizes the systems. However, the electronic factors alone are not sufficient to clarify the lower reactivity of such a tertiary R-CH₂(Ph)(R_f)C^{*} radical. In fact, the central carbon atom which bears most of the radical character is sterically hindered with relatively bulky groups such as RCH₂-polymer chain, phenyl ring, and -R_f moiety. Therefore, the addition of the R-CH₂(Ph)(R_f)C^{*} radical onto another monomer unit is somewhat restricted.

At this stage of the research, the possibility to incorporate two fluorinated monomers into the structure of one polymer was considered and how this can affect the process efficiency, reaction time and the size of the polymer chains formed. Publication **H6** presents the research on conventional bulk terpolymerization of FMST, TFMST and ST, using AIBN as initiator (Scheme 20, Table 3).



Schemat 10. Conventional bulk terpolymerization of α -fluoromethylstyrene (FMST) i α -trifluoromethylstyrene (TFMST) with styrene (ST) initiated by AIBN at 70 °C [**H6**].

The procedure enabled to obtain 6 novel poly(TFMST-*ter*-ST-*ter*-ST) terpolymers in average to fair yields (Table 1), with F-ST mol% varying between 5.2-38.4 mol% of FMST and 14.5-3.7 mol% of TFMST, respectively and different average molecular weights ranging from 10,900 to 6,900 (Table 10). Thorough combinative analysis (^1H and ^{19}F NMR, GPC) of all obtained aromatic fluoropolymers enabled not only identification of poly(TFMST-*ter*-ST-*ter*-ST) terpolymers structures, but also conducting appropriate calculations to determine their final composition and conversions of individual monomers. Figure 7 presents a comparison of ^1H NMR spectra (*Cascades A*) for ST, FMST and TFMST, with the spectra of exemplary poly(TFMST-*ter*-ST-*ter*-ST) terpolymers and a comparison of ^{19}F NMR spectra (*Cascades B*) of FMST and TFMST monomers with the spectra of the same poly(F- α -MST-*co*-ST) terpolymers.

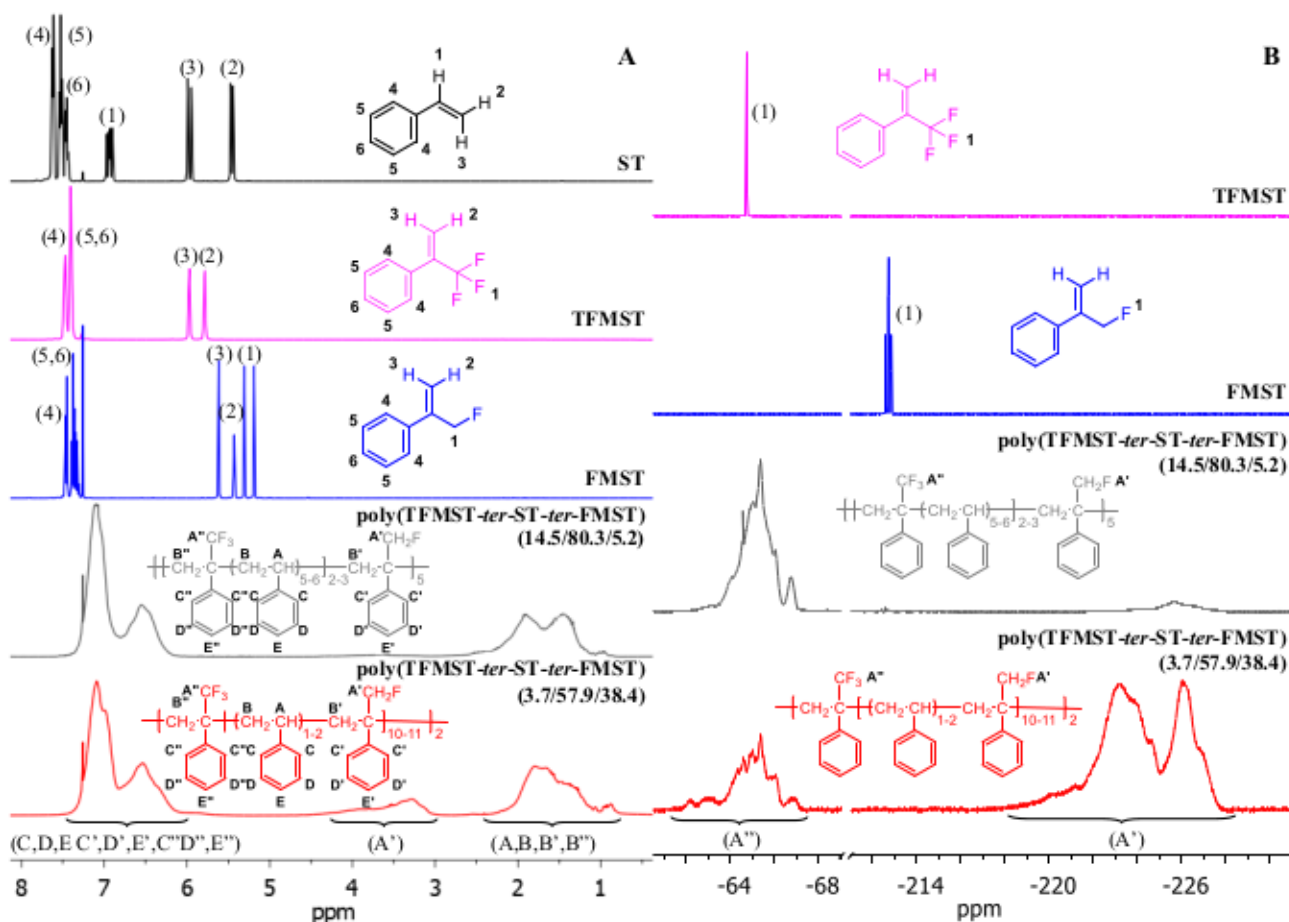


Figure 7. Comparison of the ^1H i ^{19}F NMR (recorded in CDCl_3) of monomers (ST, TFMST i FMST) and poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers: ^1H NMR spectra of styrene (ST) (—), α -trifluoromethylstyrene (TFMST) (—), α -fluoromethylstyrene (FMST) (—) and terpolymers poly(TFMST-*ter*-ST-*ter*-FMST) (—) (14.5/80.3/5.2, $\bar{M}_n = 10,700$, Tabela 3, l.p. 1) and poly(TFMST-*ter*-ST-*ter*-FMST) (—) (3.7/57.9/38.4, $\bar{M}_n = 6,900$, Tabela 3, l.p. 6).

The ^1H NMR spectra of all obtained poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers exhibited broad signals centered at 1.59 and 3.75 ppm attributed to protons of the methylene and methine moieties of backbone of all three base units and the fluoromethyl group ($-\text{CH}_2\text{F}$) of FMST. Moreover, broad signals observed in ^{19}F NMR at approx. -65.0 ppm ($-\text{CF}_3$) and -223.5 ppm ($-\text{CH}_2\text{F}$) are undeniable prove of incorporation of both fluorocomonomers into the structure of poly(TFMST-*ter*-ST-*ter*-ST) terpolymers. The integrals of signals assigned to particular structures of polymer base units (FMST, DFMST, TFMST) allowed to determine the molar ratios of TFMST-ST-FMST in terpolymers (Table 3) using the following mathematical equations (Equations 14-16):

$$\text{mol\% ST} = \{[I_{\text{I}} - I_{\text{II}} - ((I_{\text{III}} * I_{\text{IV}}) / (3 * I_{\text{IV}}))] / 3\} / \{[[I_{\text{I}} - I_{\text{II}} - ((I_{\text{III}} * I_{\text{IV}}) / (3 * I_{\text{IV}}))] / 3] + (I_{\text{II}} / 2) + [((I_{\text{III}} * I_{\text{IV}}) / (3 * I_{\text{IV}})) / 2]\} \quad (14)$$

$$\text{mol\% FMST} = (I_{\text{II}} / 2) / \{[[I_{\text{I}} - I_{\text{II}} - ((I_{\text{III}} * I_{\text{IV}}) / (3 * I_{\text{IV}}))] / 3] + (I_{\text{II}} / 2) + [((I_{\text{III}} * I_{\text{IV}}) / (3 * I_{\text{IV}})) / 2]\} \quad (15)$$

$$\text{mol\% TFMST} = \{[(I_{\text{III}} * I_{\text{IV}}) / (3 * I_{\text{IV}})] / 2\} / \{[[I_{\text{I}} - I_{\text{II}} - ((I_{\text{III}} * I_{\text{IV}}) / (3 * I_{\text{IV}}))] / 3] + (I_{\text{II}} / 2) + [((I_{\text{III}} * I_{\text{IV}}) / (3 * I_{\text{IV}})) / 2]\} \quad (16)$$

where $I_{\text{I}} = I_{\text{H-A,B,B'}}$ and $I_{\text{II}} = I_{\text{H-A'}}$ stand for the integrals of the signals centered at 1.59 and 3.75 ppm in ^1H NMR spectra, assigned to the aliphatic backbone base units of ST (H_{A} i H_{B}) and FMST ($\text{H}_{\text{B'}}$) and $-\text{CH}_2\text{F}$ moiety of FMST base units ($\text{H}_{\text{A'}}$), respectively, while $I_{\text{III}} = I_{\text{F-A''}}$ and $I_{\text{IV}} = I_{\text{F-A'}}$ stand for the integrals of the signals centered at -65,0 and -223.500 ppm in ^{19}F NMR spectra, attributed to fluorine atoms of $-\text{CF}_3$ group of TFMST base units ($\text{F}_{\text{A''}}$) and $-\text{CH}_2\text{F}$ group of FMST base units ($\text{F}_{\text{A'}}$), respectively (Figure 7).

Table 3. Studies on radical bulk terpolymerizations of fluorinated α -methylstyrene derivatives: α -fluoromethylstyrene (FMST) and α -trifluoromethylstyrene (TFMST) with styrene (ST) initiated by AIBN at 70 °C [H6].

Entry	Molar ratio in feed (mol%)			Molar ratio in terpolymer ^a (mol%)			Conversion ^a [%]			Wyd. (wt%)	\bar{M}_n^b	\bar{D}^b
	TFMST	ST	FMST	TFMST	ST	FMST	TFMST	ST	FMST			
	poly(TFMST- <i>ter</i> -ST- <i>ter</i> -FMST)											
1	15.1	79.7	5.2	14.5	80.3	5.2	42.4	44.4	44.8	44	10,700	1.61
2	11.9	76.2	11.9	9.3	79.7	11.0	39.9	53.1	46.7	50	9,200	1.83
3	5.3	79.7	15.0	5.1	79.7	15.2	39.8	40.5	41.1	41	10,900	1.58
4	5.0	74.9	20.1	5.0	74.0	21.0	37.5	36.9	39.1	37	9,400	1.71
5	5.2	65.0	29.8	4.2	67.8	28.0	29.1	37.9	34.1	36	8,000	1.61
6	5.1	55.0	39.9	3.7	57.9	38.4	21.5	30.8	28.1	29	6,900	1.56

^a Determined by ^1H NMR and ^{19}F NMR spectroscopy; ^b Average molecular weights (\bar{M}_n) and the dispersity index (\bar{D}) assessed from GPC (THF, RI) with poly(styrene) standards.

These results indicate that increasing the fluorinated monomers content (FMST and TFMST) in the feed induces a decrease in the efficiency of terpolymerizations with styrene and molecular weights of isolated products, however this effect is not as drastic as in the case of copolymerizations. Therefore, the terpolymerizations might be considered as an example of termonomer induced copolymerization (TIC) [40], which combines monomers that do not copolymerize (TFMST and FMST), and a termonomer (ST) that exhibits good reactivity with both monomers.

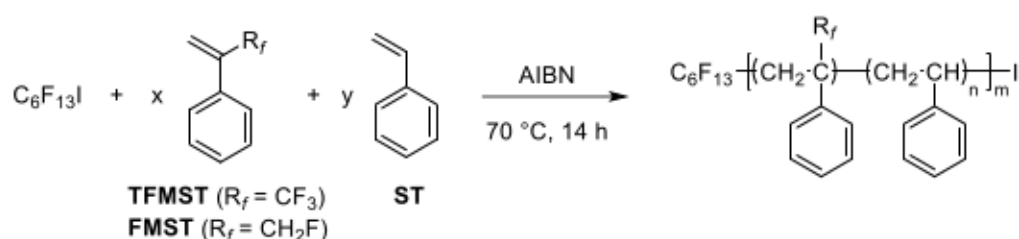
Similarly to copolymerization systems, the terpolymers possess structures where different monomeric FMST and TFMST units are randomly distributed between oligostyrene microblocks. The formation of such a microstructure can occur due to the retarding effect of both fluorinated comonomers or due to the fact that they do not homopolymerize under free radical initiation, as well as the higher reactivity of the polystyrene $\text{R-CH}_2(\text{Ph})\text{CH}^{\bullet}$ radical towards FMST and TFMST molecules than that of the ST monomer (1.4 and 1.6 times, respectively).

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 30 and 40 mol% for co- and terpolymerization, respectively. In this way, the resulting fluorinated copolymers that exhibit low molecular weights could be obtained in satisfactory yields (Table 2, Entry 1-3, 7-9, 15-16, Table 3, Entry 1-5).

The values of average molar masses of poly(FMST-*co*-ST) and poly(TFMST-*co*-ST) were unsatisfactory, I therefore decided to conduct researches on synthesis of corresponding macromolecules using the controlled radical polymerization.

CONTROLLED RADICAL POLYMERIZATION WITH STYRENE

There are different methods of controlled free-radical polymerization (CPR) extensively reported in literature. They are based either on a reversible termination reaction such as atom transfer radical polymerization (ATRP) [41], nitroxide mediated polymerization (NMP) [42, 43], or on a reversible chain transfer reaction such as reversible addition fragmentation transfer (RAFT) [44], macromolecular design for interchange of xanthate (MADIX) [45], (reversible) iodine transfer polymerization ((R)ITP) [46]. CPR processes enable to apply free-radical polymerization to the synthesis of well defined polymers with predictable molar masses, narrow molecular weight distributions and complex architectures [47]. Until now, little has been reported on the controlled radical (co)polymerization of fluorinated monomers, and its analysis reveals that iodine transfer polymerization (ITP) enables to reach such a control [46, 48]. However, fluorinated α -methylstyrene monomers (F-ST) have never been involved in the preparation of well-defined polymers by free radical copolymerization in controlled manner and therefore it was of interest to investigate such polymerization systematically. The publication **H3** presents studies on iodine transfer copolymerizations (ITcoPs) of styrene (ST) with either α -fluoromethylstyrene (FMST) or α -trifluoromethylstyrene (TFMST) (Scheme 10). A series of statistical C_6F_{13} poly(FMST-*co*-ST)I and C_6F_{13} poly(TFMST-*co*-ST)I copolymers were obtained in bulk copolymerization of ST with FMST or TFMST performed at 70 °C using AIBN as initiator and $C_6F_{13}I$ as a chain transfer agent. The introduction of fluorinated monomers was restrained at the constant value of 10 mol% compared to styrene concentration.



Scheme 10. ITP bulk copolymerizations of α -fluoromethylstyrene (FMST) and α -trifluoromethylstyrene (TFMST) with styrene (ST) in the presence of $C_6F_{13}I$ initiated AIBN at 70 °C [**H3**].

The kinetic investigations of the reaction were performed for both copolymerization systems. Using the classical Mayo equation, characteristic constants (C_{T1} , C_{ex}) were assessed for the controlled radical bulk copolymerization of styrene with fluorinated α -methylstyrenes. The first one known as the transfer constant C_{T1} actually measures the activity of the iodinated transfer agent ($C_6F_{13}I$). The second one known as exchange constant C_{ex} characterizes one of the polymerization process so-called *degenerative transfer* DT (i.e. the evolution of the molecular weight distribution versus monomer conversion). The values of transfer constants were $C_{T1(FMST)} = 1.4$ and $C_{T1(TFMST)} = 1.8$, respectively, indicating that perfluorohexyl iodide was more efficient in controlled copolymerization of ST with TFMST. Nevertheless, these values are still not high enough to

consider the living polymerizations. In addition, the calculated values of the constants characteristic to the DT reaction ($C_{\text{ex(FMST)}} = 1.9$ and $C_{\text{ex(TFMST)}} = 1.7$) are lower than that for controlled bulk homopolymerization of styrene at 80 °C. This noticeable difference reveals that the introduction of fluoromethylstyrene decreases the level of control of the copolymerization by iodine DT reaction between active and dormant chains. Nevertheless, the linear increase of molecular weight together with slight decrease of polydispersity index values observed with the monomer conversion evidenced the *pseudo*-living character of the polymerization (Figure 3).

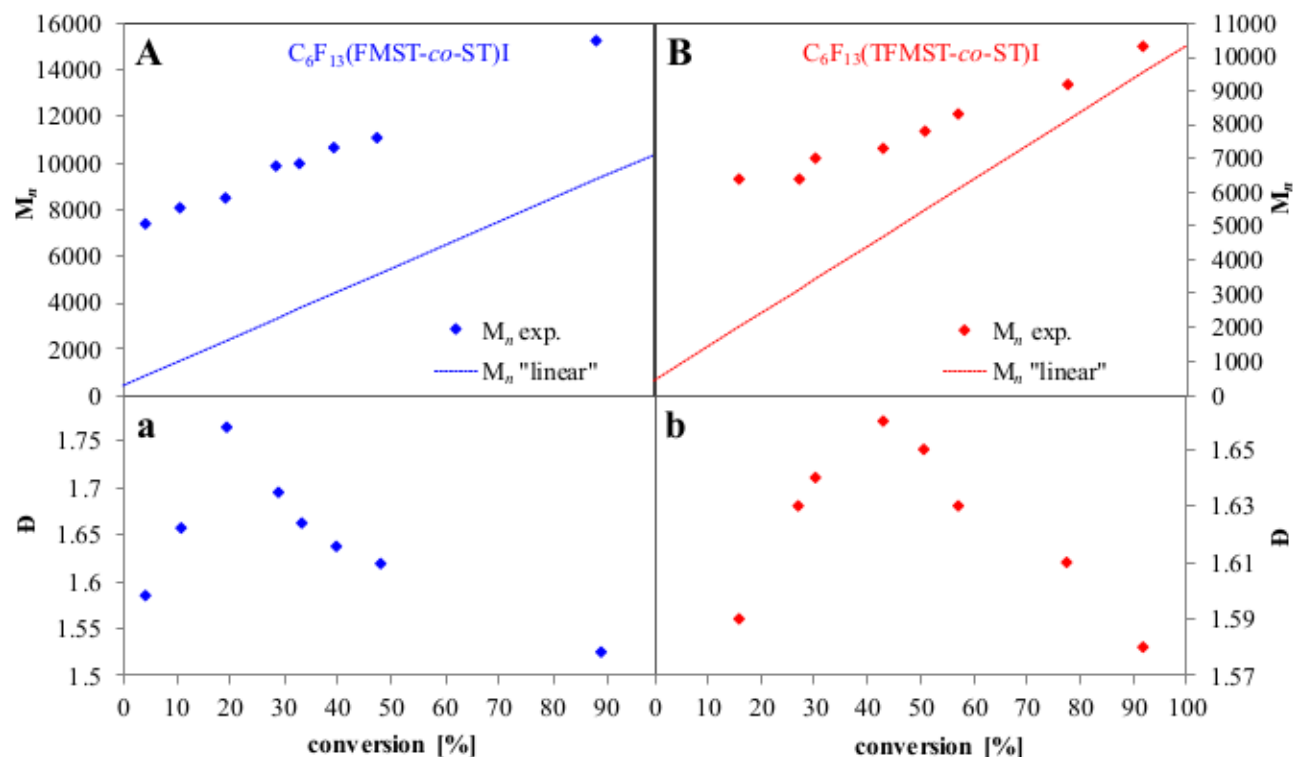


Figure 3. Plots of number-average molar masses (M_n , diagrams A and B) and polydispersity indices (\bar{D} , diagrams a and b) versus the conversion of the monomers during the iodine transfer copolymerization of styrene with fluorinated α -methylstyrenes (\blacklozenge ST-FMST, \blacklozenge ST-TFMST) at 70 °C (with a feed composition $[\text{ST}]_0:[\text{F-ST}]_0 = [90]:[10]$, $C_6F_{13}\text{I} = 0.10 \text{ mol}\cdot\text{L}^{-1}$, and $\text{AIBN} = 0.03 \text{ mol}\cdot\text{L}^{-1}$). The dotted line represents the theoretical curve: for ST-FMST system “Linear” $M_n = \text{conversion} \times 107([\text{M}]_0/[\text{C}_6\text{F}_{13}\text{I}]_0)$ (diagram A) and “Linear” $M_n = \text{conversion} \times 111([\text{M}]_0/[\text{C}_6\text{F}_{13}\text{I}]_0)$ (diagram B) [H3].

The linear increase of molecular weights observed with the monomer conversions evidenced controlled character of the radical copolymerization. Thus, it was likely that the $C_6F_{13}(\text{FMST-co-ST})\text{I}$ and $C_6F_{13}(\text{TFMST-co-ST})\text{I}$ copolymers exhibited an ω -iodine atom at the end of the chains, and the resulting copolymers could be extended by a further ITP with the addition of a second load of monomers. Actually, a chain extension by degenerative transfer was observed as depicted in Figure 4. The tailing on the low molar mass side of the chromatogram might be triggered by the existence of dead chains, which cannot be avoided when using a reversible transfer process.

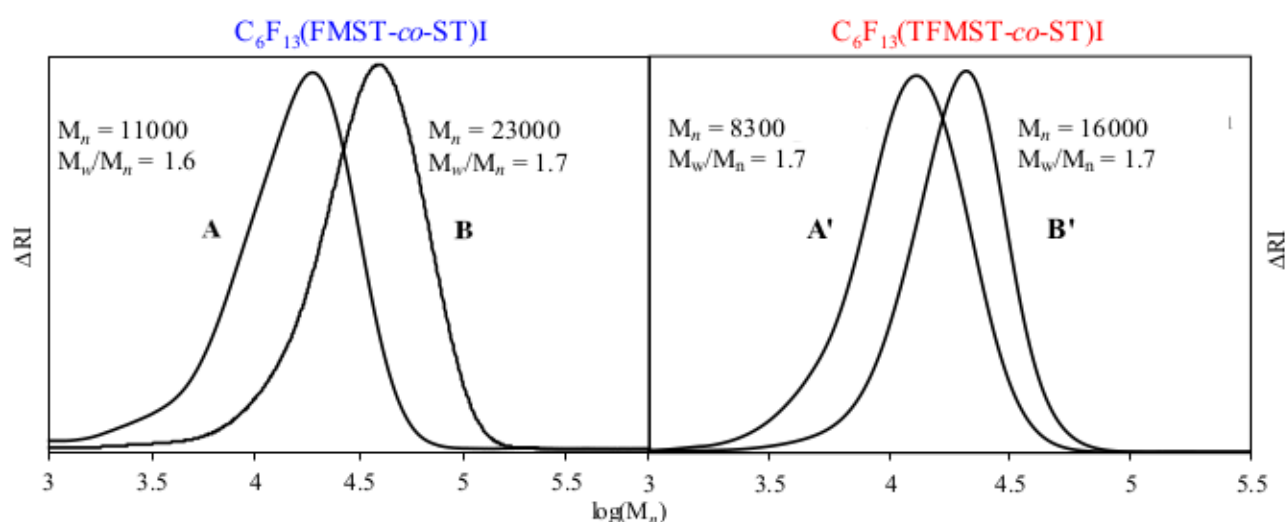


Figure 4. Size exclusion chromatograms of chain extension in bulk iodine transfer copolymerization of styrene with: **FMST** (left diagram) *first step* (A): reaction conditions were $[C_6F_{13}I]_0 = 0.10 \text{ mol}\cdot\text{L}^{-1}$, $[AIBN]_0 = 0.03 \text{ mol}\cdot\text{L}^{-1}$, $[ST]_0 = 16.9 \text{ mol}\cdot\text{L}^{-1}$, $[FMST]_0 = 1.89 \text{ mol}\cdot\text{L}^{-1}$ performed until 52% conversion; *second step* (B): addition of monomers (same amount as for the first step). For the second step, the copolymerization was stopped at 50% conversion; and **TFMST** (right diagram) *first step* (A'): reaction conditions were $[C_6F_{13}I]_0 = 0.1 \text{ mol L}^{-1}$, $[AIBN]_0 = 0.03 \text{ mol L}^{-1}$, $[ST]_0 = 15.9 \text{ mol L}^{-1}$ and $[TFMST]_0 = 1.77 \text{ mol L}^{-1}$ performed until 61% conversion; *second step* (B'): addition of monomers (same amount as for the first step). For the second step, the polymerization was stopped at 72% conversion [H3].

Consequently, these two series of experiments enabled us to demonstrate the controlled/*pseudoliving* character of the copolymerization of styrene with fluorinated α -methylstyrenes using ITP methodology. To reach C_6F_{13} poly(TFMST-*co*-ST)I, C_6F_{13} poly(FMST-*co*-ST)I high molecular weights-copolymers, a series of experiments was performed in order to vary the molecular weights from 10,000 to 43,000 and 15,000 to 65,000 (Table 2) [H3].

Table 2. Radical bulk iodine transfer copolymerization of α -fluoromethylstyrene (FMST) and α -trifluoromethylstyrene (TFMST) with styrene (ST) in the presence of $C_6F_{13}I$ initiated by AIBN at 70°C ; $[F-ST]_0/[ST]_0 \approx 1:9$.

l.p.	$[F-ST]_0/[ST]_0/[C_6F_{13}I]_0/[AIBN]_0$	Conversion ^a [%]	Yield [wt%]	M_n calc. ^b	M_n exp. ^c	\bar{D} ^c
<i>Controlled copolymerization of FMST with ST</i>						
1	31/281/3.4/1.0	89	57	9000	15000	1.5
2	63/563/3.4/1.0	80	44	16000	18000	1.5
3	125/1125/3.4/1.0	64	31	26000	24000	1.5
4	273/2228/3.5/1.0	60	20	48000	51000	1.6
5	500/4500/3.5/1.0	35	19	56000	65000	1.7
<i>Controlled copolymerization of TFMST with ST</i>						
6	30/273/3.4/1	83	43	8700	10000	1.6
7	59/529/3.3/1	74	31	15100	15000	1.6
8	111/1000/3.1/1	49	25	20100	20000	1.6
9	273/2228/3.5/1	43	15	34800	34000	1.6
10	500/4500/3.5/1	27	9	42600	43000	1.6

^a determined by ^1H i ^{19}F NMR spectroscopy; ^b calculated number-average molecular weights (M_n) calculated allowing for conversion; ^c number-average molecular weights (M_n) and polydispersity index (\bar{D}) assessed from SEC with poly(styrene) standards

PHYSICOCHEMICAL PROPERTIES OF FLUORINATED AROMATIC POLYMERS

The long-term objective was to examine the influence of the fluorinated methyl groups as the side-chains of the polymer on thermal and surface properties of the resulting C_6F_{13} (TFMST-*co*-ST)I, C_6F_{13} (FMST-*co*-ST)I copolymers [H3, H6, H7]. One of the requirements for polymer materials is the defined thermal stability under its processing and usage conditions. In the articles H6 and H7 the results of thermal degradation experiments of nonpolar copolymers poly(FMST-*co*-ST), poly(DFMST-*co*-ST), poly(TFMST-*co*-ST) and terpolymers poly(TFMST-*ter*-ST-*ter*-FMST) obtained by conventional radical polymerization, using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were presented. For comparison, TGA and DSC analyses of commercially available styrene homopolymers poly(PS) ($M_n = 11,300-23,000$) were performed (Figure 10).

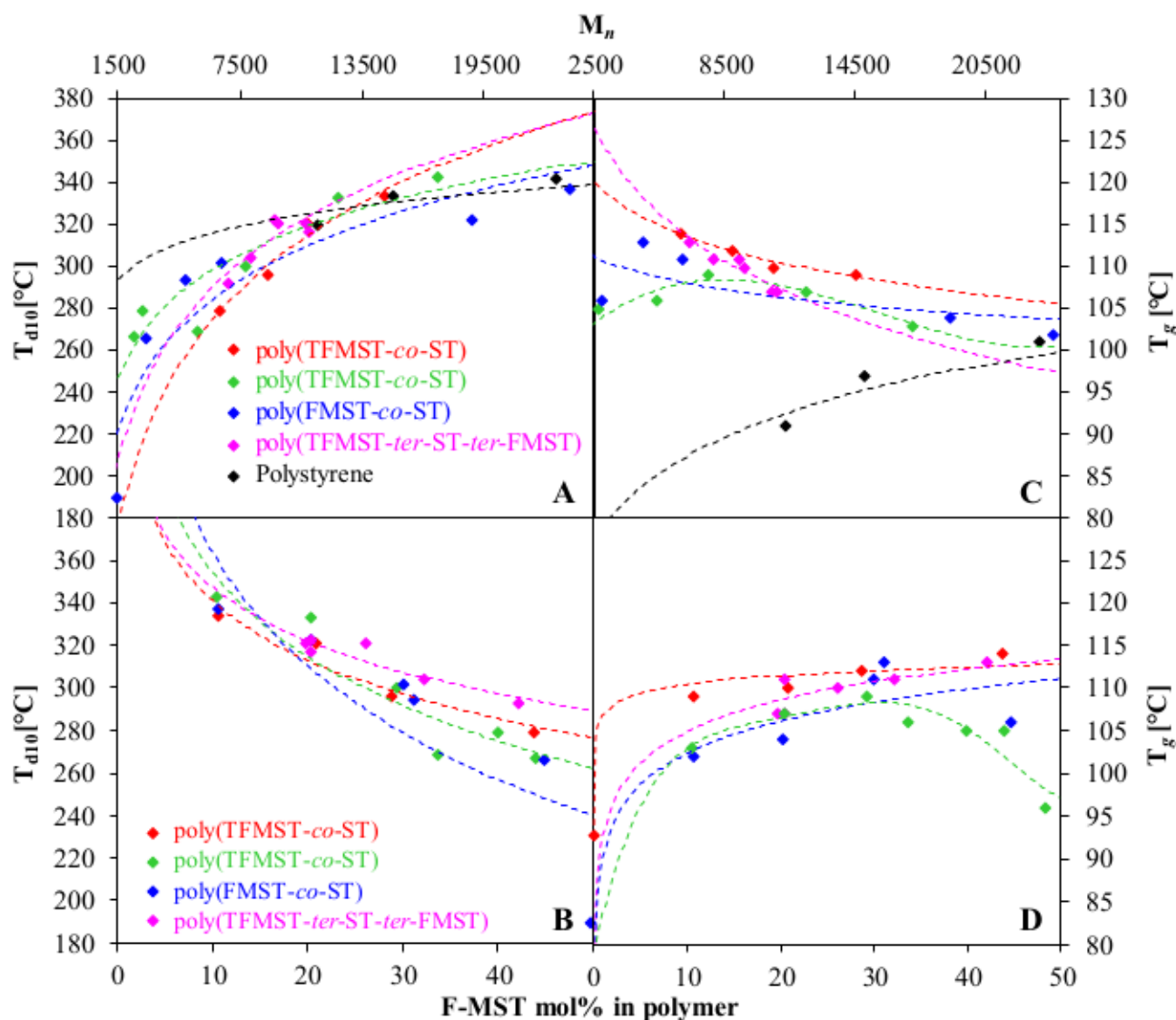
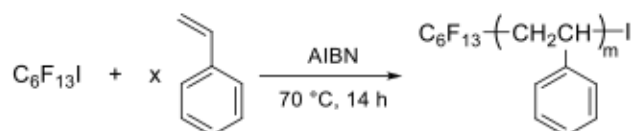


Figure 10. Thermal stabilities of fluorinated co- and terpolymers [poly(TFMST-*co*-ST), poly(DFMST-*co*-ST), poly(FMST-*co*-ST), poly(TFMST-*ter*-ST-*ter*-FMST)] and styrene homopolymer [poly(ST)]: (diagram A) Comparison of 10 %wt loss decomposition temperatures (T_{d10}) versus number-average molecular weights (M_n); (diagram B) Comparison of 10 %wt loss decomposition temperatures (T_{d10}) versus molar content of F-ST units incorporated in polymers; (diagram C) Comparison of glass transition temperatures (T_g) versus number-average molecular weights (M_n); (diagram D) Comparison of glass transition temperatures (T_g) versus molar content of F-ST units incorporated in polymers [H6, H7].

The results of this part of the thermal studies showed that the presence of fluorinated methyl groups in macromolecules do not improve substantially its thermal stability compared to the styrene homopolymer, as indicated by the temperature values at which the polymer loses 10% of its weight (T_{d10} , Figure 10, Diagrams A and B). Poly(F- α -MST-*co*-ST) copolymers and poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers containing up to 20 and 25 mol% of F- α -MST, respectively, were characterized by T_{d10} s above 320 °C. In contrast, fluorinated aromatic units embedded in the polymer structures significantly increase their glass transition temperatures (T_g , Figure 10, Diagrams C and D). An increase in the T_g temperature was observed along with the increasing content of fluorine in the structure of poly(TFMST-*co*-ST) copolymers and poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers, reaching the maximum T_g equal to 114 °C (43.7 mol% TFMST) and 113 °C (3.7 mol% TFMST and 38.4 mol% FMST), respectively. On the other hand, in the case of poly(FMST-*co*-ST) and poly(DFMST-*co*-ST) copolymers, the relatively low F-ST content in the copolymer promoted an increase of its T_g values. By reaching 30 mol% of FMST and DFMST units in the copolymer chain, maximum T_g values of 113 °C and 109 °C were obtained, respectively. Exceeding the degree of incorporation of FMST and DFMST base units resulted in lowering the glass transition temperature values, due to the decreasing number-average molecular weights of the copolymers. In general, with an increase of polymer molecular weight, the proportion of free chain-ends decreases, and its mobility significantly influences the glass transition temperature. The mobility of free chain-ends strongly depends on the molecular weight polymer.

Additionally, for selected fluorocopolymers poly(FMST-*co*-ST), poly(DFMST-*co*-ST) [H7], poly(TFMST-*co*-ST), analyses combined with the identification of volatile products released during their thermal decomposition were carried out. Results of simultaneous thermal analysis coupled with Fourier transform infrared spectroscopy (STA/FTIR) and thermogravimetric analysis coupled with mass spectrometry (TGA/MS) confirmed that in addition to low molecular volatile components i.e. CO₂, H₂O and methane, aromatic hydrocarbons like toluene, styrene, methylstyrene or F-MST are also released. Most importantly, in the process of thermodegradation of fluoropolymers no evolution of hydrogen fluoride was observed, which confirms their thermostability.

In the next stage, my researches focused on determination of thermal properties of copolymers with a similar content of fluorinated methyl groups in the polymer side chain, but exhibiting different molecular weights. The publication H3 presents the results of thermal stability tests on the series of the prepared C₆F₁₃(TFMST-*co*-ST)I, C₆F₁₃(FMST-*co*-ST)I ω -iodocopolymers was assessed by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC), and compared to those of polystyrene homopolymer C₆F₁₃(PS)I. For this purpose, it was necessary to perform a series of bulk iodine transfer homopolymerizations of styrene (ST, Scheme 11), leading to the synthesis of C₆F₁₃(PS)I homopolymers with defined average molar masses ranging from 5000 to 55000.



Scheme 11. Bulk ITP polymerization of styrene in the presence of C₆F₁₃I initiated by AIBN at 70 °C.

The obtained results revealed that the insertion of a small amount of fluorinated monomeric units promoted a significant rise of both the glass transition temperatures (T_g), as well as the temperatures at 10% weight loss (T_d^{10}). Both temperatures (T_g i T_d^{10}) increased with increasing fluorine content in polymers and their average molar masses. Interestingly, C_6F_{13} (TFMST-*co*-ST)I copolymers were much more thermally stable in comparison to C_6F_{13} (FMST-*co*-ST)I or C_6F_{13} (PS)I. Such an increase of the thermal stability might be attributed to thermo-oxidative resistance of styrene carbon α bearing CF_3 group, what could not be observed in the case of polystyrene or poly(α -fluorostyrene) [H3].

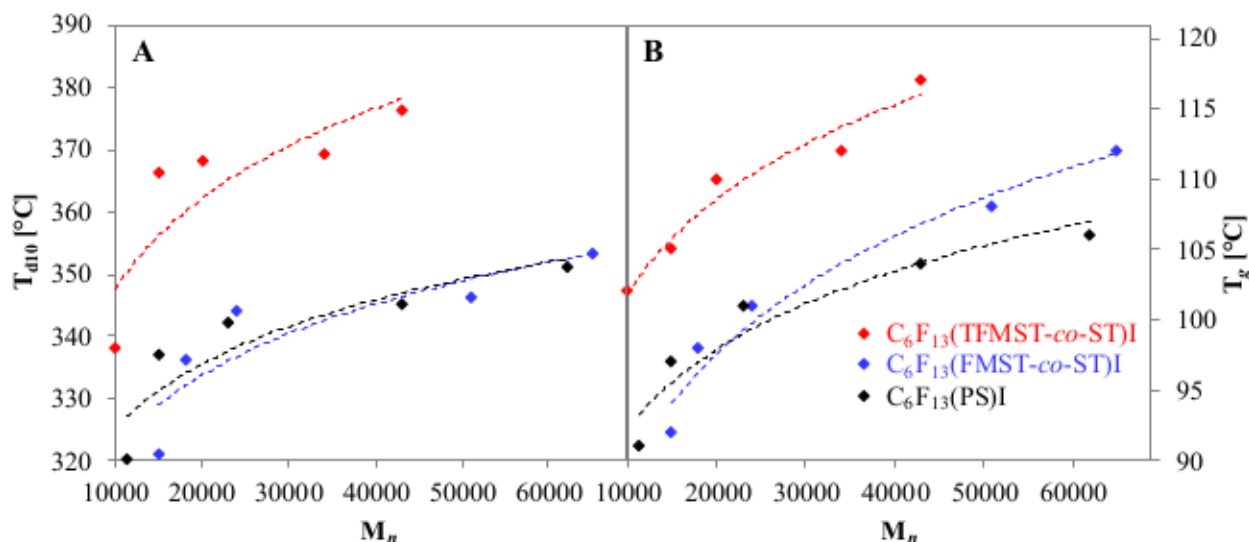
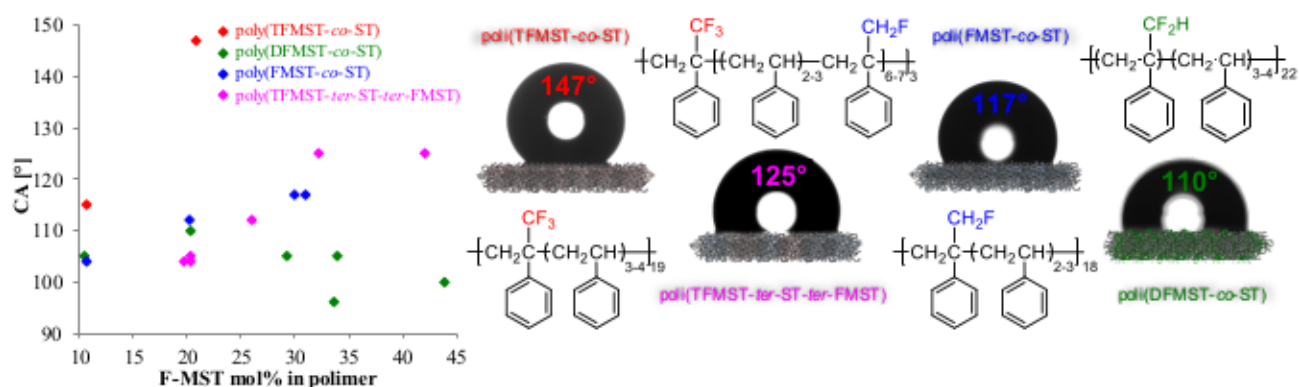


Figure 11. Thermal stabilities of copolymers obtained by ITP [C_6F_{13} (TFMST-*co*-ST)I, C_6F_{13} (FMST-*co*-ST)I, C_6F_{13} (PS)I]; (diagram A) Comparison of 10 wt.% loss decomposition temperatures (T_d^{10}) versus number-average molecular weights (M_n); (diagram B) Comparison of the glass transition temperatures (T_g) versus number-average molecular weights (M_n) [H3].

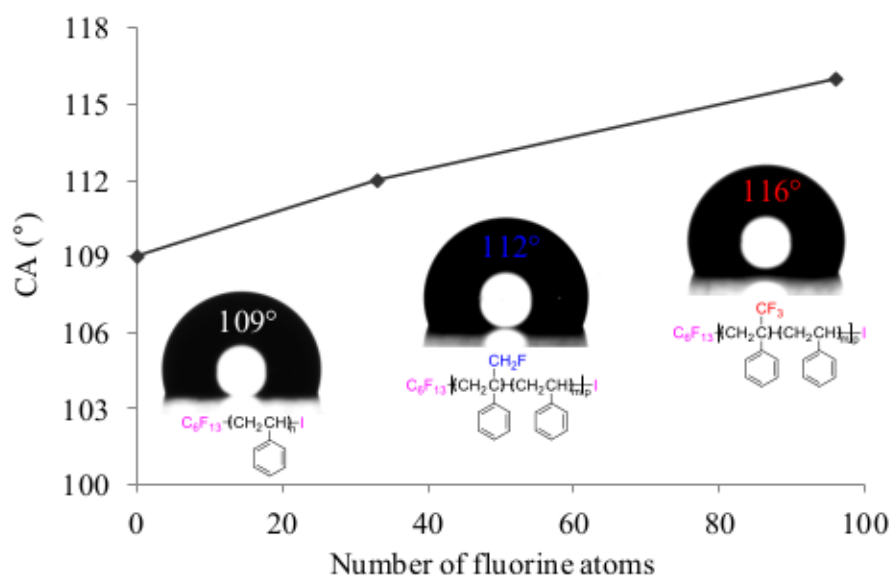
Additionally, the surface properties, i.e. the difference in the wettability of the poly(FMST-*co*-ST), poly(DFMST-*co*-ST), poly(TFMST-*co*-ST), poly(TFMST-*ter*-ST-*ter*-FMST), C_6F_{13} (TFMST-*co*-ST)I, C_6F_{13} (FMST-*co*-ST)I and C_6F_{13} (PS)I polymers were studied by water contact angle measurements. The polymer layers were deposited on (OTS)-functionalized glass wafers. Figure 12 displays the correlation of water contact angle (CA) to changes in the chemical composition of the films, i.e. content of fluorinated styrene units (mol%) incorporated in polymer structures of poly(FMST-*co*-ST) [H6], poly(DFMST-*co*-ST) [H7], poly(TFMST-*co*-ST) [H6], poly(TFMST-*ter*-ST-*ter*-FMST) [H6] and photos of water droplets placed on the surfaces of selected polymers for which the highest WCA values were obtained.



Rysunek 12. Water contact angles of functionalized glass surfaces covered with polymers: [poly(FMST-co-ST), poly(DFMST-co-ST), poly(TMST-co-ST) poly(TMST-ter-ST-ter-FMST)] versus mol% fluorinated styrene units incorporated in polymer chains [H6, H7].

Analysis of the nature of the surface showed that most of the fluoropolymers poly(FMST-co-ST), poly(DFMST-co-ST), poly (TFMST-co-ST), poly(TMST-ter-ST-ter-FMST) obtained by conventional radical polymerization method shows hydrophobic-lipophilic properties. Only the surface covered with poly(TMST-co-ST) copolymer containing over 20 mol% TFMST exhibits hydrophobic-lipophobic character. In addition, water droplets applied to the surface of the tested fluoropolymers showed a fairly high dimensional stability during measurements (10-20 s), which may indicate that in the area of contact with a droplet, the top polymer layers are homogeneous and stable.

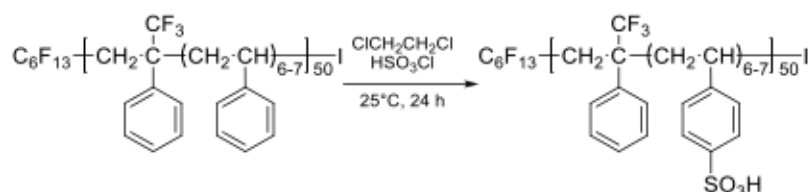
Figure 13 displays the correlation of water contact angle (CA) to changes in the chemical composition of the films, ie. the number of fluorine atoms incorporated in side-chain of polymer structures. The $C_6F_{13}(TFMST-co-ST)I$, $C_6F_{13}(FMST-co-ST)I$ and $C_6F_{13}(PS)I$ polymers were obtained by controlled polymerization ITP method. The fluorine atoms in CH_2F and CF_3 groups change the hydrophobicity of the covered surface. The $C_6F_{13}(TFMST-co-ST)I$ copolymer containing the TFMST with CF_3 groups was more suited because of the major changes in the wettability with respect to the polystyrene [H3].



Rysunek 4. Water contact angles of functionalized glass surfaces covered with polymers [$C_6F_{13}(TFMST-co-ST)I$, $C_6F_{13}(FMST-co-ST)I$, $C_6F_{13}(PS)I$] versus number of fluorine atoms incorporated into side-chain groups [H3].

MODIFICATIONS OF FLUORINATED AROMATIC POLYMERS

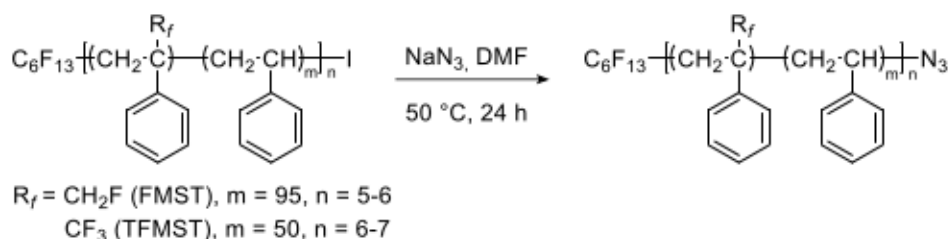
The resultant $C_6F_{13}(F-\alpha\text{-MST-co-ST})I$ copolymers structures possess functional groups (aromatic rings, ω -iodine functionalized polymer backbone) suitable for post-modifications. First attempts to modify new polymer materials focused on introduction of sulfonic group into the phenyl rings of hydrophobic fluoropolymer that enabled changing its physicochemical properties. Post-sulfonation of selected $C_6F_{13}(\text{TFMST-co-ST})I$ copolymer using chlorosulfuric acid HSO_3Cl in 1,2-dichloroethane led to the formation of desired sulfonated derivative (Scheme 12).



Scheme 12. An example of the sulfonation reaction of $C_6F_{13}(\text{TFMST-co-ST})I$ copolymer ($M_n=43000 \text{ g}\cdot\text{mol}^{-1}$).

After reaction and purification, the polysulfonated $C_6F_{13}(\text{TFMST-co-PSS})I$ copolymer was characterized by FT-IR spectroscopy. FT-IR spectrum of resultant hydrophilic sulfonated aromatic fluoropolymer exhibited frequencies attributed to the characteristic functional groups incorporated in its structure, i.e. broad band at 3432 cm^{-1} assigned to stretching vibration of the O-H bonds of sulfonic group, asymmetric ($1715, 1639 \text{ cm}^{-1}$) and symmetric ($1035, 1006 \text{ cm}^{-1}$) stretching vibrations of the S=O bonds of the sulfonic group, bands in the range of $2770\text{-}2960 \text{ cm}^{-1}$ (stretching vibration of C-H bonds) and $1550\text{-}1630 \text{ cm}^{-1}$ (stretching vibration of C=C bonds) of aromatic rings, characteristic bands of C-X bond vibrations, C-F trifluoromethyl group (1220 cm^{-1}), C-F difluoromethylene ($1127\text{-}1192 \text{ cm}^{-1}$) and strong signal of C-I bond vibrations (579 cm^{-1}). Moreover, band at 833 cm^{-1} indicated the presence of *para*-1,4- substituted phenyl rings in the structure of analyzed polymer. The observation suggested that the sulphonic acid substituents were preferably introduced to the activated aromatic rings of styrene units. Whereas, trifluoromethylstyrene units were left unsubstituted. Most probably, a strong electron-withdrawing effect of trifluoromethyl group deactivated aromatic rings of TFSMT units and thus disfavoured the electrophilic substitution reaction such as sulfonation at a neighboring rings.

In the next step of novel copolymer modifications, in order to confirm the statement that the $C_6F_{13}(\text{FMST-co-ST})I$ and $C_6F_{13}(\text{TFMST-co-ST})I$ copolymers exhibited an ω -iodine atom at the end of the chains, I performed azidation reactions [H3]. The selected $C_6F_{13}(\text{TFMST-co-ST})I$ and $C_6F_{13}(\text{FMST-co-ST})I$ copolymers were reacted with a 3-fold molar excess of sodium azide with respect to poly(F-ST-co-ST) at $50 \text{ }^\circ\text{C}$ over 24 hours (Scheme 13).



Scheme 13. Synthesis of azido-functionalized $C_6F_{13}(\text{TFMST-co-ST})N_3$ oraz $C_6F_{13}(\text{FMST-co-ST})N_3$ copolymers [H3].

After reaction and purification, the $C_6F_{13}(TFMST-co-ST)N_3$ and $C_6F_{13}(FMST-co-ST)N_3$ copolymers containing ω -azido functionality were characterized by IR spectroscopy. Figures **14b** and **14c** display the FTIR spectrum of a characteristic resulting copolymer. Besides the frequencies observed in the $1000-1200\text{ cm}^{-1}$ and $1400-1600\text{ cm}^{-1}$ ranges, attributed to C-F, C-H and C=C vibrations, respectively, two intense sharp bands at 2083 and 2128 cm^{-1} , which are characteristic of the asymmetric stretching frequency of terminal azido group, were observed. Duplication of the signal could be explained on the basis of Fermi resonance interaction of the fundamentals with the overtones or combination tones of certain low lying frequencies. Hence, IR spectroscopy confirmed the successful (quasi)quantitative) modification of iodide ω -functional poly(FMST-co-ST) and poly(TFMST-co-ST) copolymers into azido end-functionalized copolymers, with molecular weights close to $65,000\text{ g}\cdot\text{mol}^{-1}$ and $43,000\text{ g}\cdot\text{mol}^{-1}$, respectively.

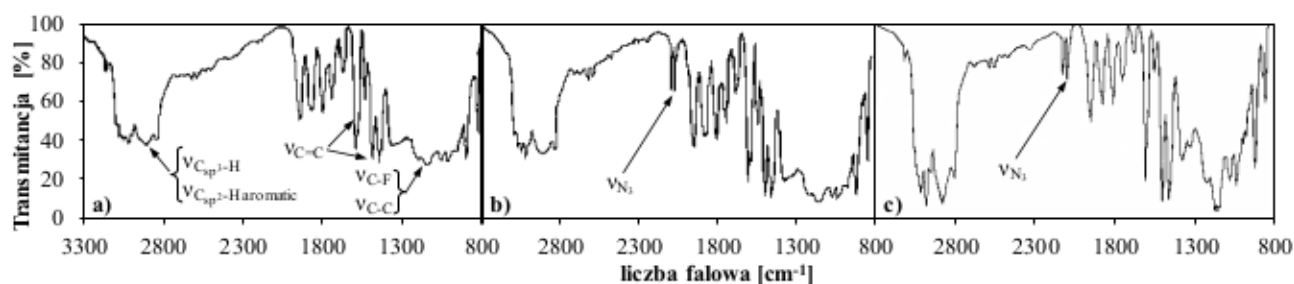


Figure 7. FT-IR spectra of: (a) $C_6F_{13}(FMST-co-ST)I$ copolymer ($M_n = 65\,000$); (b) $C_6F_{13}(FMST-co-ST)N_3$ copolymer ($M_n \approx 65\,000$) and (c) $C_6F_{13}(TFMST-co-ST)N_3$ copolymer ($M_n \approx 43\,000$), respectively.

4.3. Summary of significant results

The presented series of publications **H1-H9** includes published results of conducted researches aimed at synthesis of fluorinated styrene derivatives, investigation of its reactivity under radical polymerization conditions, preparation of new fluoropolymeric materials and studies of its structure, post-modifications, as well the influence fluorinated functional groups on its physical and chemical properties. According to the research objectives, I present the following key outcomes and achievements, and, in particular, those that contributed scientific novelty components:

1. I developed effective and cost-efficient routes suitable for synthesizing gram quantities of a range of fluoromethylstyrene derivatives with unsubstituted aromatic ring and functional groups in para positions to fluorinated propylene moieties (α -monofluoromethylstyrene, *FMST*; α -difluoromethylstyrene, *DFMST*; α -trifluoromethylstyrene, *TFMST*; 4-bromo- α -monofluoromethylstyrene, *4-BrFMST*; 4-(3-fluoroprop-1-en-2-yl)phenyl diethylphosphonate, *4-PFMST*, 4-bromo- α -trifluoromethylstyrene, *4-BrTFMST*; 4-(3,3,3-trifluoroprop-1-en-2-yl)phenyl diethylphosphonate, *4-PTFMST*).
2. I synthesized and characterized new fluorinated poly(VDF-*ter*-CTFE-*ter*-TFMST) and poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers, using conventional radical induced terpolymerization and termonomer induced copolymerization (TIC).
3. Based on the studies of conventional copolymerization reactions of fluorinated α -methylstyrene derivatives I determined the monomer reactivity ratios for each of the polymerization systems, results of the kinetics studies mentioned above allowed to propose that poly(F- α -MST-*co*-ST) polymers consisted of oligostyrenic microblocks randomly separated with single FMST and TFMST units.
4. I evidenced a *pseudo*-living character of the radical copolymerization reactions of fluorinated α -methylstyrenes with styrene in the presence of perfluorohexyliodide ($C_6F_{13}I$) that helped synthesizing well defined fluorinated aromatic polymers with predictable molar masses.
5. In the iodine transfer polymerization I synthesized series of new hydrophobic $C_6F_{13}(FMST-*co*-ST)I$ i $C_6F_{13}(TFMST-*co*-ST)I$ copolymers suitable for subsequent modification. I also converted resultant copolymers into corresponding $C_6F_{13}(FMST-*co*-ST)N_3$ i $C_6F_{13}(TFMST-*co*-ST)N_3$ copolymers due to the presence of ω -iodo functional end-groups. All the fluoropolymers were characterized by the means of available physicochemical methods.
6. I evidenced that the incorporation of a small amount of fluorinated monomeric units into polystyrenic structure with CF_3 groups in particular, improves significantly the thermal (T_d^{10} , T_g) and surface (CA) properties of the resulting polymers

4.4. References

- [1] Bae, J.-M.; Honma, I.; Murata, M.; Yamamoto, T.; Rikukawa, M.; Ogata, N. „Properties of selected sulfonated polymers as proton-conducting electrolytes for polymer electrolyte fuel cells” *Solid State Ionics* **2002**, *147*, 189-194.
- [2] Connolly, D. J.; Gresham W. F. „Fluorocarbon vinyl ether polymers” **1966**, US Patent 3,282,875.
- [3] Smith, D. W.; Iacono, S. T.; Iyer, S. S. „Handbook of Fluoropolymer Science and Technology” Wiley: Hoboken, New Jersey, **2014**.
- [4] Banerjee, S. „Handbook of Specialty Fluorinated Polymers”, 1st Edition, Preparation, Properties and Applications, Amsterdam, Elsevier, **2015**.
- [5] Ameduri, B. and Sawada, H. (Eds) „Fluorinated Polymers: Volume 1: Synthesis, Properties, Processing and Simulation”, Royal Society of Chemistry, ISBN: 978-1-78262-415-8, **2016**.
- [6] Schnabel, W. „Polymer degradation. Principles and practical applications”, Akademie-Verlag, Berlin, **1981**.
- [7] Buchi, F. N.; Gupta, B.; Haas, O.; Scherer, G. G. „Study of radiation-grafted FEP-G-polystyrene membranes as polymer electrolytes in fuel cells: *Electrochim. Acta* **1995**, *40(3)*, 345-353.
- [8] Kai, T.; Tsuru, T.; Nakao, S.; Kimura, S. „Preparation of hollow-fiber membranes by plasma-graft filling polymerization for organic-liquid separation” *J. Membr. Sci.* **2000**, *170*, 61-70.
- [9] Finsterwalder, F.; Hambitzer, G. „Proton conductive thin films prepared by plasma polymerization” *J. Membr. Sci.* **2001**, *185*, 105-124.
- [10] Bae, B.; Chun, B. H.; Ha, H. Y.; Oh, I. H.; Kim, D. „Preparation and characterization of plasma treated PP composite electrolyte membranes” *J. Membr. Sci.* **2002**, *202*, 245-252.
- [11] N. Chen, L. Hong, „Proton-conducting membrane composed of sulfonated polystyrene microspheres, poly(vinylpyrrolidone) and poly(vinylidene fluoride)” *Solid State Ionics* **2002**, *146*, 377-385.
- [12] Ostrovskii, D. I.; Torell, L. M.; Paronen, M.; Hietala, S.; Sundholm, F. „Water sorption properties of and the state of water in PVDF-based proton conducting membranes” *Solid State Ionics* **1997**, *97*, 315-321.
- [13] Hietala, S.; Koel, M.; Skou, E.; Elomaa, M.; Sundholm, F. „Thermal stability of styrene grafted and sulfonated proton conducting membranes based on poly(vinylidene fluoride)” *J. Mater. Chem.* **1998**, *5*, 1127-1132.
- [14] M. A. Hickner, H. Ghassemi, Y. S. Kim, B. R. Einsla, J. E. McGrath, „Alternative polymer systems for proton exchange membranes (PEMs)” *Chem. Rev.* **2004**, *104*, 4587-4612.
- [15] Baldwin, M. G.; Reed, Jr., S. F. „Polymerization studies on allylic compounds. III. α (substituted methyl)styrenes”, *J Polym. Sci. Part A: Polym. Chem.* **1968**, *6(9)*, 2627-2635.
- [16] Ueda, M.; Ito, H. „Radical reactivity of α -trifluoromethylstyrene”, *J. Polym. Sci. Part A Polym. Chem.* **1988**, *26*, 89-98.
- [17] Narita, T. „On the polymerization reactivity of fluorinated vinyl monomers”, *Macromol. Rapid Commun.* **2000**, *21*, 613-627.
- [18] Souzy, R.; Ameduri, B.; Boutevin, B. „Synthesis of functional polymers-Vinylidene fluoride based fluorinated copolymers and terpolymers bearing bromoaromatic side-group” *J. Polym. Sci.: Part A: Polymer Chem.*, **2004**, *42*, 5077-5097.
- [19] Kostov, G.; Tredwell, M.; Ameduri, B.; Gouverneur, V. „Kinetics of radical copolymerization of [1-(fluoromethyl)vinyl]benzene with chlorotrifluoroethylene” *J Poly Sci Part A: Polym Chem* **2007**, *45*, 3843-3850.
- [20] Klepke, T. (red.) „Nowoczesne materiały polimerowe i ich przetwórstwo. Część 3” **2017**, Politechnika Lubelska, Lublin, ISBN: 978-83-7947-300-7.
- [21] Bakshi A. K., Bhalla G. „Materials of the twenty first century” *J Sci Ind Res*, **2004**, *63*, 715-728.
- [22] Kruk T., „Wykorzystanie cienkich warstw polielektrolitowych zawierających polimery przewodzące do otrzymania ultracienkich ogniw słonecznych” *LAB Laboratoria Badania Aparatura* **2012**, *17(3)*, 6-13.
- [23] Inzelt G., „Conducting Polymers”, Springer Verlag, Heidelberg, **2008**.
- [24] Tredwell, M.; Gouverneur, V. „Electrophilic fluorination of organosilanes” *Org Biomol Chem* **2006**, *4*, 26-32.

- [25] Luo, H.-Q.; Loh, T.-P. „Synthesis of aryl allylic fluorides by direct electrophilic fluorination of alkenes” *Tetrahedron Lett.* **2009**, *50*, 1554-1556.
- [26] Hiyama, T.; Eds. *Organofluorine Compounds. Chemistry and Applications*; Springer: New York, **2000**.
- [27] Kuroboshi, M.; Hiyama, T. „Production of difluoromethylene compound” *Jpn. Kokai Tokkyo Koho* **1992**, JP,04-264041,A.
- [28] Hugenberg, V.; Haufe, G. „Oxidative Desulfurization-Difluorination of Alkyl Aryl Thioethers: Synthesis of ω -Substituted 1,1-Difluoroalkanes” *Synlett.*, **2008**, 106-108.
- [29] Miyaura, N.; Suzuki, A. „Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds” *Chem. Rev.* **1995**, *95*, 2457-2483.
- [30] Watanabe, T.; Miyaura, N.; Suzuki, A. „Synthesis of Sterically Hindered Biaryls via the Palladium-Catalyzed Cross-Coupling Reaction of Arylboronic Acids or their Esters with Haloarenes” *Synlett* **1992**, 207-210.
- [31] Sykes, A.; Tatlow, J. C.; Thomas, C. R. „A new synthesis of fluoro-ketones” *J. Chem. Soc.* **1956**, 835-839.
- [32] Tarrant, P.; Taylor, R. E. „Fluoroolefins. VI.¹ The Synthesis of Some α -Trifluoromethylstyrenes” *J. Org. Chem.* **1959**, *24*, 238-239.
- [33] Jiang, B.; Xu, Y. „Trifluoroisopropenylzinc reagent as a useful α -(trifluoromethyl)ethenyl carbanion synthetic equivalent. Preparation and palladium-catalyzed coupling with aryl halides” *J. Org. Chem.* **1991**, *56*, 7336-7340.
- [34] Jiang, B.; Wang, Q.-F.; Yang, C.-G.; Xu, M. „ α -(Trifluoromethyl)ethenyl boronic acid as a useful trifluoromethyl containing building block. Preparation and palladium-catalysed coupling with aryl halides” *Tetrahedron Lett.* **2001**, *42*, 4083-4085.
- [35] Magano, J.; Dunetz, J. R. “Large-scale applications of transition metal-catalyzed couplings for the synthesis of pharmaceuticals” *Chem. Rev.* **2011**, *111*, 2177-2250.
- [36] Tüdös, F.; Kelen, T.; Földes-Berazsrich, T.; Turcsányi, B. “Analysis of Linear Methods for Determining Copolymerization Reactivity Ratios. III. Linear Graphic Method for Evaluating Data Obtained at High Conversion Levels” *J. Macromol. Sci.-Chem.*, **1976**, *10(8)*, 1513-1540.
- [37] Chambers, R. D. “Fluorine in Organic Chemistry” Blackwell Publishing Ltd.: Oxford, UK, **2004**.
- [38] Pasto, D. J.; Krasnansky, R.; Zercher, C. “Stabilization Energies and Structures of Substituted Methyl Radicals” *J Org Chem* **1987**, *52*, 3062-3072.
- [39] Pross, A.; Radom, L. A “Theoretical Approach to Substituent Effects: Stabilities and Conformational Preferences in β -Substituted Ethyl Radicals” *Tetrahedron* **1980**, *36*, 1999-2003.
- [40] J. K. Weise, *Polym Prepr*, **1971**, *12*, 512-520.
- [41] Hawker, C. J.; Bosman, A.W.; Harth, E. „New Polymer Synthesis by Nitroxide Mediated Living Radical Polymerizations” *Chem. Rev.* **2001**, *101*, 3661-3688.
- [42] Matyjaszewski, K.; Xia, „Atom transfer radical polymerization” *Chem. Rev.* **2001**, *101*, 2921-3089.
- [43] Kamigaito, M.; Ando, T.; Sawamoto, M. „Metal-Catalyzed Living Radical Polymerization” *Chem. Rev.* **2001**, *101*, 3689-3745.
- [44] Braunecker, W. A.; Matyjaszewski, K. „Controlled/living radical polymerization: Features, developments, and perspectives” *Prog. Polym. Sci.* **2007**, *32*, 93-146.
- [45] Destarac, M.; Bzducha, W.; Taton, D.; Gauthier-Gillaizeau, I.; Zard, S. Z. „Xanthates as Chain-Transfer Agents in Controlled Radical Polymerization (MADIX): Structural Effect of the *O*-Alkyl Group” *Macromol. Rapid Commun.* **2002**, *23*, 1049-1054.
- [46] David, G.; Boyer, C.; Lacroix-Desmazes, P.; Ameduri, B.; Boutevin, B. „Use of Iodocompounds in Radical Polymerization” *Chem. Rev.* **2006**, *106*, 3936-3962.
- [47] Saugeut, L.; Boyer, C.; Ameduri, B.; Boutevin, B. „Synthesis and Characterization of Poly(vinylidene fluoride)-*g*-poly(styrene) Graft Polymers Obtained by Atom Transfer Radical Polymerization of Styrene” *Macromolecules* **2006**, *39*, 9087-9098.
- [48] Hansen, N.; Jankowa, K.; Hvilsted, S. „Fluoropolymer materials and architectures prepared by controlled radical polymerizations” *Eur. Polym. J.* **2007**, *43*, 255-293.

5. Other scientific achievements and future scientific plans

In 1997 I began master's degree studies at the Faculty of Chemistry Adam Mickiewicz University in Poznań (AMU) with graduation in 2002. From October 2000 to January 2001 I was a Socrates-Erasmus Scholarship Fellow at the Organic Chemistry Institute of Aristotle University of Thessaloniki in Greece, working in the field of application of Wittig reactions in the synthesis of vinyl quinones derivatives under the supervision of Prof. Demetrios N. Nikolaidis. In June 2002 I graduated from Faculty of Chemistry AMU upon presentation of the master thesis entitled „Synthesis and application of 1,1,3,3,3-pentafluoropropyl-*N,N*-diethylamine – a selective fluorinating agent” written under the supervision of prof. dr hab. Henryk Koroniak at Department of Synthesis and Structure of Organic Compounds.

Later the same year I started Graduate (doctoral) School at the Faculty of Chemistry and under the supervision of prof. H. Koroniak continued the research undertaken during the master's project. My studies concerned the application of 1,1,3,3,3-pentafluoropropene – secondary amine adducts as effective and selective nucleophilic fluorinating reagents in conversion of hydroxyl compounds into corresponding fluoroorganic derivatives. Since the topic was relatively new at the Department of Synthesis and Structure of Organic Compounds it was of interest to better understand the mechanism of investigated reactions as well as to study the range of application of the new fluorination reagents. Over the period of 2003-2005, due to four short-term scholarships (up to 3 months) I was a Ph. D. visiting student working under the supervision of Prof. Günter Haufe at the Organic Chemistry Institute of the University of Münster, Germany. The researches were focused on testing the fluorinating reagents efficiency in the reactions with more complex molecules containing a hydroxyl group in vicinal position to various substituents (methyl esters of fatty acids with terminal fluorohydrin moieties, methyl esters of fatty acids with vicinal diol functions, fluorinated and non-fluorinated allylic alcohols). The resulting derivatives were further investigated towards its ability to form monolayers at the water/air interface. All the results obtained during the Ph. D. studies were published in the form of 2 publications in Journals from JCR base, one monograph chapter and presented in the form of 6 communications and 3 poster presentations at the international scientific symposiums and national conferences. In June 2006 I was conferred a Ph. D. degree in chemical sciences at the Faculty of Chemistry AMU upon presentation of doctoral thesis on “Synthesis and fluorinating properties of 1,1,3,3,3-pentafluoropropene secondary amine adducts”. In October 2006 I started working at Department of Synthesis and Structure of Organic Compounds led by Prof. H. Koroniak as an assistant professor. From October to December 2006 I was a post-doctoral fellow at the Organic Chemistry Institute of the University in Münster, developing the research on synthesis and application of surface-active fluorinated derivatives.

In May 2008 I started a 2-year collaborative 7. FP Marie-Curie Post-doctoral Fellowship at renowned scientific centers Chemistry Research Laboratory, University of Oxford, United Kingdom and Institut Charles Gerhardt, Ecole Nationale Supérieure de Chimie de Montpellier, France. Working at research groups of Prof. Véronique Gouverneur (OX) and Dr. Bruno Ameduri (MPL) I conducted the interdisciplinary researches aiming at development of new proton exchange membranes for fuel cell as a final goal. The theme of project is in line with contemporary trends to search for alternative and ecological energy sources. Therefore, Project FLUPOL was highlighted

by European Commission in the article entitled *Project Success Stories - The race to cheaper fuel cells* published on the CORDIS website (<http://cordis.europa.eu/>)

The skills and knowledge gained within post-doctoral fellowship combined with previous experience in fluoroorganic synthesis have prompted me to continue the researches aiming at preparation of new functional fluoropolymers. This new topic that differed from studies undertaken so far at the Department of Synthesis and Structure of Organic Compounds or Faculty of Chemistry required creation of the lab workroom, development of new and adaptation of existing research methodologies, and most importantly building the research team. Therefore, I applied to the Ministry of Science and Higher Education for funding the research project entitled: „Synthesis of fluorinated styrene derivatives and its application to the formation of new polymeric materials”, and received it for more than 3 years (2011-2015). In 2013 I also started the collaboration with M.Sc. Joanna Wolska, master student at that time and currently graduate student at our Faculty, who is engaged in researches on reactivity of fluorinated aromatic monomers in radical polymerization conditions. Mrs Wolska has already gained a substantial experience in the field of functional fluoropolymers during one of the scholarly internships, a four-month project at the University of Massachusetts Lowell, USA in Prof. Yuyu Sun's working group (NCBiR: UDA-POKL.04.01.01-00-109/13-00), that was very fruitful for Her scientific development. Since February 2017 I am an auxiliary supervisor of the doctoral program of M. Sc. Joanna Wolska, and the results of our cooperation have been already published in the form of 3 publications in Journals from JCR base including H4 and H7, 1 publication in Journal from outside JCR base H9, a book chapter in *Polymer Engineering* and 2 monograph chapters including H8 (another under construction).

Moreover, since 2010 I have been involved in collaboration with D. Sc. Anna Szwajca, who studies the processes of organic molecules organization and binding at the solid surfaces, which has resulted in publication H3, H6, H7. In parallel, I've started the cooperation with Dr. Aleksandra Wójcik and Dr. Anna Lewandowska-Andrałojć at Department of Chemical Physics, involving the synthesis and characterization of novel nanohybrids of graphene oxide with dyes of potential use in solar cells and for photocatalytic hydrogen production. Since 2015 I've been cooperating with Dr. Bartosz Tylkowski who works at Centre Tecnològic de la Química de Catalunya, Tarragona, Spain (publication in *Physical Sciences Reviews* H9 and a book chapter in *Polymer Engineering*). I also continue the collaboration initiated during my Marie-Curie post-doc fellowship (publications H1, H3, H5, H6, H7)

My scientific achievements include the authorship and co-authorship of a total of 20 scientific papers, including 13 in JCR journals, 1 publications in non-JCR journals, 3 chapters in English-language monographs, 3 chapters in monographs in Polish, 17 conference messages. A detailed list of scientific papers covering all published works, conference talks, other scientific achievements, didactic and organizational achievements I presented in ANNEX 3 - "List of published scientific works or creative professional work and information on didactic achievements, scientific cooperation and popularization of science".

In subsequent stages of scientific work I would like to continue to develop my interests related to the development of new, efficient methods for the synthesis of fluorinated monomers, both aromatic and aliphatic having additional functional groups, studies of their properties under radical polymerization conditions and applications for the production of new functional fluoropolymer materials as well their characteristics. Fluoropolymers are durable materials with high quality and unusual interfacial properties. Due to the specific nature of carbon-fluorine bonds, they are characterized by high thermal stability and chemical resistance to acids, bases and various types of solvents. The low polarizability of the C-F bond affects the hydrophobic nature (low moisture absorption) of these materials. What's more, the low surface energy of fluorine causes that polymers of this type have oleophobic properties, and consequently increased resistance to wear and abrasion. All these features have made that fluoropolymers have found application among others as stable coating materials for exceptional resistance to adverse weather conditions.

Introduction of modifications in the form of polar functional groups into fluoropolymers gives the possibility of obtaining amphiphilic materials with unique adhesive properties and potential application for the creation of modern anti-corrosion coatings or ion-conducting materials. Such materials can be obtained by the synthesis of monomers containing appropriate functional groups and subsequent polymerization, direct modification of polymer backbone chains / groups, or chemical grafting with other comonomers, as well as combining in chemical processes with other polymers with different physicochemical properties. Hence my scientific plans concern the synthesis of new fluoromonomers containing polar functional groups in rings or side chains and the development of methods for their incorporation into polymer structures. I also intend to utilize products obtained at earlier stage of my research, eg ω -azido functionalized copolymers in cross-linking reactions and subsequent modifications, allowing to obtain fluoropolymer materials with the desired characteristics, that has been confirmed by preliminary results. In addition, the use of a "click" reaction to combine these copolymers with other organic compounds or high functional polymers seems to be a promising method for the preparation of block copolymers and materials with adhesive properties.