

Polystyrene with trifluoromethyl units: Monomer reactivity ratios, thermal behavior, flammability, and thermal degradation kinetics

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ABSTRACT: Chemical modification based on incorporation of flame retardants (FR) into the polymer backbone was used in order to reduce polystyrene flammability. 3-(trifluoromethyl)styrene (StCF₃) and 3,5-bis(trifluoromethyl)styrene (St(CF₃)₂) were applied as reactive FR. Copolymers were synthesized with different feed ratios and it gave series of copolymers with various amounts of StCF₃ and St(CF₃)₂ (5–50% mol/mol of St). Glass transition temperature (T_g) and thermal stability of obtained (co)polymers were determined from differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. Kinetic parameters such as the thermal decomposition activation energy (E) and frequency factor (A) were estimated by Ozawa and Kissinger models. Pyrolysis combustion flow calorimeter (PCFC) was applied as a tool for assessing the flammability of the synthesized (co)polymers. Relative reactivity ratios were determined by applying the conventional linearization Jaacks method ($r_{St} = 1.34$, $r_{StCF_3} = 0.54$), ($r_{St} = 0.47$, $r_{St(CF_3)_2} = 0.13$). The results suggest that incorporation of fluorinated styrenes into PSt enhance flame retardance. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42839.

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INTRODUCTION

Polymers containing halogens, especially fluorine atoms exhibit a range of outstanding properties such as chemical resistance and high-temperature stability. The incorporation of fluorine into polymers leads to enhanced thermal, chemical and oxidative stability, reduced adhesion, increased solubility, improved biocompatibility, and increased gas permeability. Additionally the introduction of fluorine provides hydrophobicity of polymers.¹ Highly halogenated polymers are hard to ignite and do not require flame-retardants (FR)s. The examples of such polymers are: polychlorotrifluoroethylene, poly(ethylenechlorotrifluoroethylene), poly(ethylenetetrafluoroethylene), polytrifluoroethylene, polytetrafluoroethyleneperefluoroether, polytetrafluoroethylene, polyvinylidene fluoride, polyvinyl fluoride.^{1–6} The ignition temperatures of these polymers are in the range of 476 to 643°C, whereas ignition of polystyrene (PSt) occurs at 356°C.⁷ Moreover, values of total heat of combustion (HR) for fluoropolymers: polyvinylidene fluoride (HR = 9.7 kJ g⁻¹), poly(ethylene-tetrafluoroethylene) (HR = 10.8 kJ g⁻¹) and polytetrafluoroethylene (HR = 3.7 kJ g⁻¹) are lower in comparison with PSt (HR = 38.3 kJ g⁻¹).⁷

Halogenated polymers are usually nonflammable and have quite high values of limiting oxygen index (LOI). The polymers with the highest values of LOI are: polyvinyl chloride (44%), polyvinylidene fluoride (43–60%), polyvinylidenechloride (60%), polytrichloroethylene (95%), polytrichlorofluoroethylene (95%), and polytetrafluoroethylene (95%).^{7,8} Apart from polymers characterized high thermal stability, there are also a lot of polymers (especially thermoplastics) that are flammable and exhibit less thermal stability. (FR)s containing halogen atoms are commonly used in order to improve these properties. The examples of additive FRs containing fluorine are: the salts of zirconium hexafluoride, potassium hexafluorotitanate, and potassium hexafluorozirconate.^{9,10} Taking into account modification of PSt, the physical modification is commonly applied in industry as well as reported in the literature. The additive FRs covalently bonded with bromine and chlorine atoms are the most often used.^{11–17} On the contrary, in the literatures there is limited number of publications reporting FRs with fluorine atoms and covalently bonded to polymer backbone. Jankova *et al.* synthesized block copolymers from 2,3,4,5,6-pentafluoro-styrene (5FSt) and styrene

(St). The obtained (co)polymers exhibited high thermal stability and low dispersity index.¹⁸ Pugh *et al.* copolymerized St with: 2,3,4,5,6-pentafluorostyrene and 4-fluorostyrene (FSt), with different feed ratios. They proved that fluorine atoms have influence on an increase of PSt thermal stability.¹⁹ Moreover, in our previous works^{20,21} such copolymers as P(St-co-5FSt) and P(St-co-FSt) were analyzed in terms of their flammability. It turned out that the values of HHR (heat release rate) and HR (total heat release) decreased with an increasing level of fluorine-containing monomers incorporation into copolymers. Teng *et al.*²² presented trifluoromethyl ($-\text{CF}_3$) substituted styrene polymers and copolymers with methacrylates. They described the kinetic of polymerization and studied optical and thermal properties of $-\text{CF}_3$ substituted polystyrenes. They concluded that such polymers may be utilized as optical materials.²² The excellent chemical and thermal stability of some polymers can be explained by C-F bond energy, which is one of the highest known (481 kJ mol^{-1}), whereas its interchain attractive forces ranks among one of the lowest ($\sim 3 \text{ kJ mol}^{-1}$).¹

In this article, attention is mainly paid to chemical modification of PSt with reactive FRs containing trifluoromethyl group. The chemical modification of PSt was carried out based on copolymerization of St with styrenic monomers containing $-\text{CF}_3$ moieties such as: 3-(trifluoromethyl)styrene (StCF_3) and 3,5-bis(trifluoromethyl)styrene ($\text{St}(\text{CF}_3)_2$). Despite the polymerization of St with these comonomers were reported in the literature,²² the relative reactivity ratios, flammability and thermal degradation kinetics of obtained (co)polymers were firstly presented in current work. Polymerizations were conducted with various amount of modified St. The purpose of research was to determine: (i) the relative reactivity ratios in order to establish how comonomers are incorporated into polymer backbone, (ii) thermal properties of obtained copolymers, (iii) thermal decomposition kinetics of selected polymers, and (iv) preliminary potential fire behavior based on the pyrolysis combustion flow calorimeter for selected (co)polymers.

EXPERIMENTAL

Materials

Styrene and azobisisobutyronitrile (AIBN) were supplied by Synthos S.A. (Oswiecim, Poland). 3-(Trifluoromethyl)styrene and 3,5-bis(trifluoromethyl)styrene, diethylene glycol dimethyl ether (diglym) were purchased from Sigma Aldrich Co. The others solvents such as methylene chloride and methanol were purchased from POCH S.A. All the reagents were used as received.

Measurements

^1H and ^{13}C NMR spectra were recorded at 25°C in deuterated chloroform (CDCl_3) on Bruker Avance UltraShield 400 MHz apparatus working at 400 and 100 MHz, respectively. Tetramethylsilane TMS was used as internal standard. Molecular weight of (co)polymers was determined by size exclusion chromatograph Waters (Milford) consists of separation modulus Alliance 2695, RI 410 refractive index detector and PDA 2996 photodiode array detector. Columns Styragel HR5E and Styragel HR4E (Waters) in series were placed in a thermostat at 30°C . Mobile phase was freshly distilled THF at flow rate

1.0 mL min^{-1} . Concentration of polymer in injected sample solution was 0.15% (in THF). Prior to injection into chromatograph the THF solution of polymer was filtrated through the 0.2 mm membrane. Calibration was done with commercial certified narrow polystyrene standards from Polymer Laboratories (part of Agilent Technologies) from 1050 to 7,000,000 g mol^{-1} . Calculation of molar mass distribution was done using RI detector signal. Differential scanning calorimeter TADSC 2010 apparatus (TA Instruments, Newcastle, DE) was applied to determine glass transition temperature (T_g) under nitrogen using aluminum sample pans, at heating/cooling rate of $20^\circ\text{C min}^{-1}$. The thermal stability of polymers was performed on TG Pyris-1, Perkin Elmer thermal analyzer with $10^\circ\text{C min}^{-1}$ in a stream of nitrogen ($20 \text{ cm}^3 \text{ min}^{-1}$) in the temperature range of 25 to 800°C . Additionally, for determination of degradation kinetics, the TGA analyses were performed at 5, 10, 20, and $30^\circ\text{C min}^{-1}$. Pyrolysis and combustion flow calorimetry (PCFC) was performed using Microscale Combustion Calorimetry (according to Standard: ASTM D7309-2007—Determining Flammability Characteristics of Plastics and Other Solid Materials). The samples (2–5 mg) were heated at a constant rate (1°C s^{-1}) from 75 to 750°C . The combustion temperature was 900°C and the gas flow was a mixture of oxygen/nitrogen in relation 20/80 $\text{cm}^3 \text{ min}^{-1}$.

Homopolymerization

Polystyrene was obtained according to the procedure described in the literature.^{23,24} The monomer St (3.6 g, 34.6 mmol) was placed into a two-necked flask. Subsequently the initiator (0.5% mol of initiator (AIBN)) and the internal standard (4% mol of diglym) were added and then content was degassed and flushed by inert gas. The homopolymerization was carried out at 60°C for 3 h and was next heated up to 90°C under argon. The mixture was kept at this temperature for a further 19 h to provide a transparent polymer and a high degree of conversion (x). The total reaction time was 22 h. The homopolymer with residual monomer was dissolved in methylene chloride and precipitated in methanol. The precipitation procedure was repeated three times. Finally the homopolymer was dried at 70°C within 24 h. The homopolymer was obtained as a white powder: PSt ($x = 99\%$)

Copolymerization

The comopolymerizations were conducted using various amounts of comonomers (5, 10, 20, 50% mol StCF_3 or $\text{St}(\text{CF}_3)_2$ /mole of St), the initiator (0.5% mol of AIBN/moles of monomer), and the internal standard (4% mol of diglym/moles of monomer). After all components were placed into the two-necked flask, the reaction mixture was degassed and flushed by argon and the polymerization was carried out at 60°C for 3 h and next heated up to 90°C . The mixture was kept at this temperature for a further 19 h to provide the transparent copolymer and high degree conversion. The precipitation procedure was the same as in case of homopolymerization with methylene chloride as a solvent. All copolymers were obtained as a white powder.

Determination of Monomer Conversion

The monomer conversion (x) was monitored by ^1H NMR spectroscopy. The samples were taken during polymerization. The

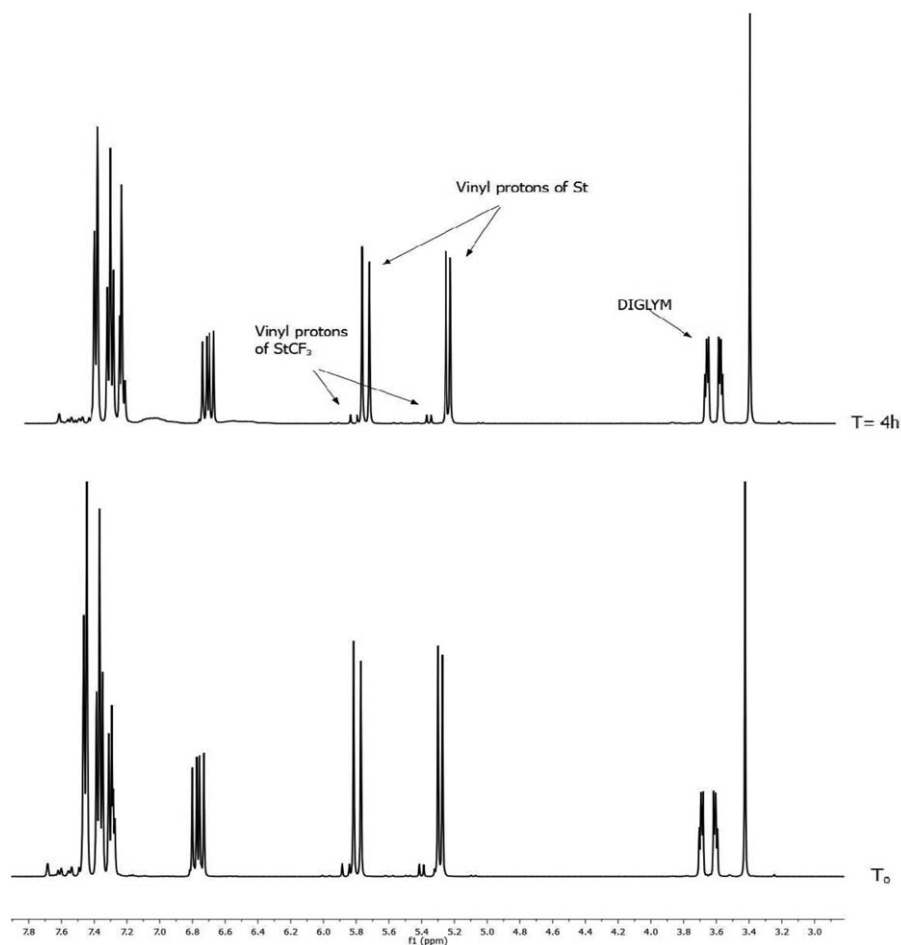


Figure 1. Polymerization kinetic by ^1H NMR in CDCl_3 for St/St CF_3 mixture (95/5).

conversions of each monomer were calculated from the peak area measurements corresponding to the vinyl protons of these monomers. In the case of the St : St CF_3 system, the vinyl protons of monomers (H_{vinyl}) were assigned to following peaks: doublet of doublet centered at 5.24 ppm for St; 5.35 ppm for

St CF_3 in CDCl_3 . Taking into account the St : St $(\text{CF}_3)_2$ system: doublet of doublet centered at 5.23 ppm for St; 5.46 ppm for St $(\text{CF}_3)_2$ in CDCl_3 . These measurements were made relative to one of the solvent peaks (H_{DIGLYM}) using following equations:²⁵

Table I. Degrees of Conversion of Comonomers, Monomer Feed, and Copolymers Composition

	Monomer feed (%)		Copolymer composition (%)		Degrees of conversion, x (%)	
	St	St CF_3	St	St CF_3	St	St CF_3
P(St-co St CF_3)						
St	100	0	100	0	99	0
P(St-co-St CF_3)-1	95	5	95	5	93	99
P(St-co-St CF_3)-2	91	9	91	9	98	99
P(St-co-St CF_3)-3	83	17	83	17	99	99
P(St-co-St CF_3)-4	67	33	66	34	95	98
P(St-co-(St CF_3) ₂)						
St		St $(\text{CF}_3)_2$	St	St $(\text{CF}_3)_2$	St	St $(\text{CF}_3)_2$
P(St-co-St $(\text{CF}_3)_2$)-1	95	5	95	5	95	99
P(St-co-St $(\text{CF}_3)_2$)-2	91	9	89	11	77	99
P(St-co-St $(\text{CF}_3)_2$)-3	83	17	82	18	88	98
P(St-co-St $(\text{CF}_3)_2$)-4	67	33	65	35	93	99

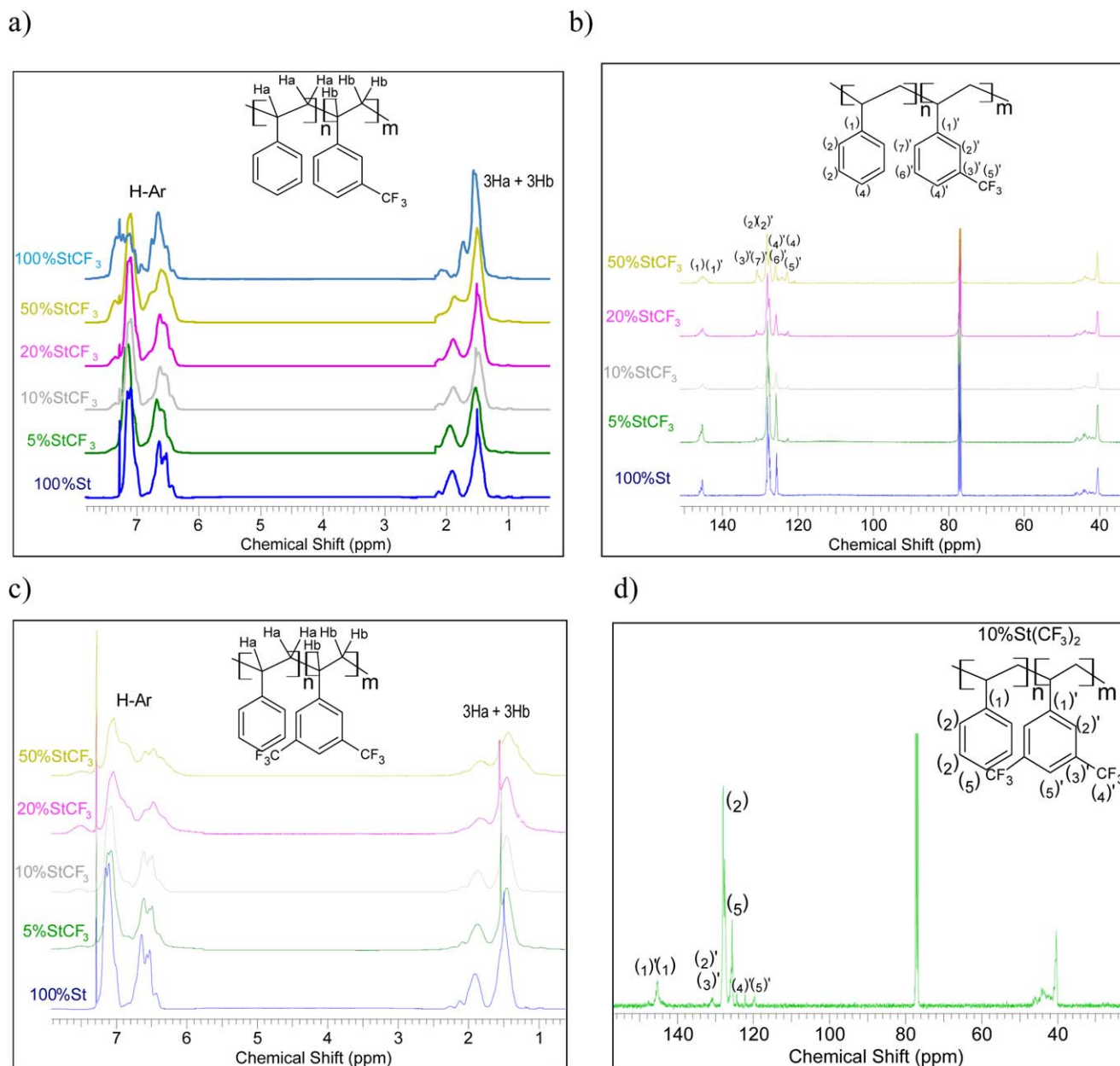


Figure 2. ^1H NMR spectra of (a) (co)polymers with various amount of StCF_3 , (c) (co)polymers with various amount of $\text{St}(\text{CF}_3)_2$ and ^{13}C NMR spectra of (b) $\text{P}(\text{St-co-StCF}_3)_s$, (d) copolymer containing 10% mol of $\text{St}(\text{CF}_3)_2$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$x = \frac{(H_{\text{vinyl}}/H_{\text{DIGLYM}})_0 - (H_{\text{vinyl}}/H_{\text{DIGLYM}})_t}{(H_{\text{vinyl}}/H_{\text{DIGLYM}})_0}$$

As can be seen in Figure 1 (for system $\text{St}:\text{StCF}_3$, 95 mol % styrene content), ^1H NMR allowed monitoring of the consumption within time of both monomers. The intensity of signals coming from vinyl protons of St and StCF_3 decreases relative to the DIGLYM peaks during time.

Determination of Reactivity Ratios by Jacks Method

This method requires the use of a large excess of one of the monomers to achieve an almost pure polymer containing only

small concentration of the second monomer.^{26,27} Consequence of this is the simplified composition equation:

$$\frac{d[M_1]}{d[M_2]} = r_1 \cdot \frac{[M_1]}{[M_2]}$$

where $r_1 = \frac{k_{11}}{k_{12}}$ is the reactivity ratios of monomer 1 (monomer which was used in excess), M_1 is the monomer 1, M_2 is the monomer 2, k_{11} and k_{12} are the rates constant of homopropagation and copropagation.

The next equation is obtained by integration of above equation:

$$\ln \frac{[M_1]_t}{[M_1]_0} = r_1 \cdot \ln \frac{[M_2]_t}{[M_2]_0}$$

The conversion degree of monomers formula is introduced into this equation. The following equations are employed:

$$[M_2]_t = [M_2]_0 - x_2 \cdot [M_2]_0 \quad [M_1]_t = [M_1]_0 - x_1 \cdot [M_1]_0$$

The finally equation is linear equation:

$$\ln \cdot (1 - x_1) = -r_1 \cdot (1 - x_2)$$

The monomer conversion was calculated as described in Experimental section (Determination of Monomer Conversion) and reactivity ratios from slope of the best fitted line.

RESULTS AND DISCUSSION

Copolymer Composition and Structural Characterization of the Copolymers

Free radical (co)polymerization reactions were carried out in bulk. The used comonomers reacted with high degrees of conversion, above 76%. It was possible to calculate the copolymer composition basing on monomers conversion. Data concerning the monomer feed mixtures, copolymers composition and degrees of conversion of used comonomers (St, StCF₃, St(CF₃)₂) were collected in Table I.

The copolymer composition was almost the same as the monomer feed for the both groups of copolymers including 5, 10, 20%, and 50% mol of fluorinated St. This indicates that the applied monomers have similar tendencies to undergo copolymerization.

The chemical structures of synthesized (co)polymers were confirmed by NMR. ¹H NMR and ¹³C NMR spectra of the (co)polymers (P(St-co-StCF₃), P(St-co-St(CF₃)₂)) are shown in Figure 2.

¹H NMR spectra of PSt and copolymers P(St-co-StCF₃) show broad peaks at 1.2 to 2.3 ppm which are assigned to -CH₂ and -CH repeated units in the main chain of these polymers. The same peaks of copolymers P(St-co-St(CF₃)₂) appear between 0.9 and 2.3 ppm. The aromatic protons of P(St-co-StCF₃)s and P(St-co-St(CF₃)₂)s are positioned between 6.3 and 7.4 ppm (as in the case of PSt), and 5.9 and 7.7 ppm, respectively. Taking into account the ¹³C NMR spectra, spectra of PSt, P(St-co-StCF₃)s and copolymer containing 10% mol of St(CF₃)₂ were presented. The peak areas at 40.5 and 41-46 ppm were assigned to carbons in the aliphatic backbone of PSt, (-CH and -CH₂ respectively), whereas in the case of obtained copolymers, aliphatic carbon peaks appear almost in the same region, at 40.5 and 41 to 47 ppm for P(St-co-StCF₃)s and 40.3 and 41 to 47 ppm for P(St-co-St(CF₃)₂). The signals corresponding to other carbons of copolymers are marked with numbers in parentheses and shown in Figure 1(b,d).

Molecular Weight of the Polymers

The molecular weight of the (co)polymers was determined by GPC with PSt and THF as the standard and solvent, respectively. The weight average (*M_w*), number average (*M_n*), molecular weight and the dispersity index (*M_w/M_n* = *D*) are presented in Table II.

The (co)polymers exhibited *M_w* in the range of 41,000 to 126,320 g mol⁻¹, *M_n* between 33,000 and 51,280 g mol⁻¹ and is dispersity from 1.4 to 2.5. The fluorinated PSts showed lower values of *M_w* than PSt, whereas the values of *M_n* are comparable values to PSt.

Table II. GPC Data of (Co)polymers PSt, P(St-co-StCF₃), P(St-co-St(CF₃)₂)

Polymer	<i>M_n</i> (g/mol)	<i>M_w</i> (g/mol)	<i>D</i>
PSt	51,280	126,320	2.5
P(St-co-StCF ₃)-1	33,000	71,000	2.2
P(St-co-StCF ₃)-2	34,000	60,000	1.8
P(St-co-StCF ₃)-3	44,800	97,000	2.2
P(St-co-StCF ₃)-4	57,000	106,000	1.9
P(St-co-St(CF ₃) ₂)-1	68,000	41,000	1.7
P(St-co-St(CF ₃) ₂)-2	85,000	47,000	1.8
P(St-co-St(CF ₃) ₂)-3	65,000	45,000	1.4
P(St-co-St(CF ₃) ₂)-4	57,000	94,000	1.7

Considering P(St-co-StCF₃)s, both *M_w* and *M_n* increase together with increasing content of StCF₃ in the copolymers. The values of *D* are slightly lower than for PSt. In the case of P(St-co-St(CF₃)₂)s differ tendencies are observed. The values of *M_w* are much lower in comparison with PSt and P(St-co-StCF₃)s, whereas the values of *M_n* are almost twice time higher relative to P(St-co-StCF₃)s.

Relative Reactivity Ratios of Comonomers in Free Radical Copolymerization

Values of reactivity ratio may be evaluated by various procedures: linear procedures, nonlinear procedures, and other copolymer composition equations.²⁸⁻³¹ In current article the monomer reactivity ratios of StCF₃, St(CF₃)₂, and St were determined by the Jaacks method described in details in Experimental section (Determination of Reactivity Ratios by Jaacks Method). For presented systems (St : StCF₃, St : St(CF₃)₂) a large excess of one monomer was used in order to simplify the determination of reactivity ratios. The feed ratios [St]₀ : [comonomer]₀ = 19 were the same for both system. The Jaacks plots for reactivity ratios calculation are presented in Figure 3.

The reactivity ratio values can be obtained from the slope. It is expected that experimental values may be affected an errors, which can be caused by inaccurate ¹H NMR spectra measurements, particularly for small monomers concentration. Clearly the greater accuracy is obtainable by taking more samples for analysis. The reactivity ratios for studied systems were found to be: (*r_{St}* = 1.34, *r_{StCF₃}* = 0.54), (*r_{St}* = 0.47, *r_{St(CF₃)₂}* = 0.13). Considering first system St : StCF₃, the product of *r_{St}* · *r_{StCF₃}* (0.72) is little less than 1, what indicates that copolymer has nearly random distribution. In this case, St reacts slightly faster with St monomeric units than with StCF₃, whereas StCF₃ is 2 times more reactive relative to St monomeric units than to itself. The product of calculated relative reactivity ratios for second system St : St(CF₃)₂ is close to 0 and equals 0.06. It means that comonomers have a tendency to form alternating copolymers. Both comonomers, St and St(CF₃)₂ react definitely faster with opposite units, St(CF₃)₂ and St, respectively. In the literature, there have been no date related to *r_{StCF₃}*, *r_{St(CF₃)₂}* calculation, but there are the relative reactivity ratios calculated for other styrene copolymers containing fluorine atoms. An example is a pair of St with 4-fluorostyrene (FSt) (*r_{St}* = 0.96, *r_{FSt}* = 0.85) and St with 2,3,4,5,6-pentafluorostyrene (5FSt) (*r_{St}* = 0.44 and *r_{5FSt}* = 0.42).¹⁹

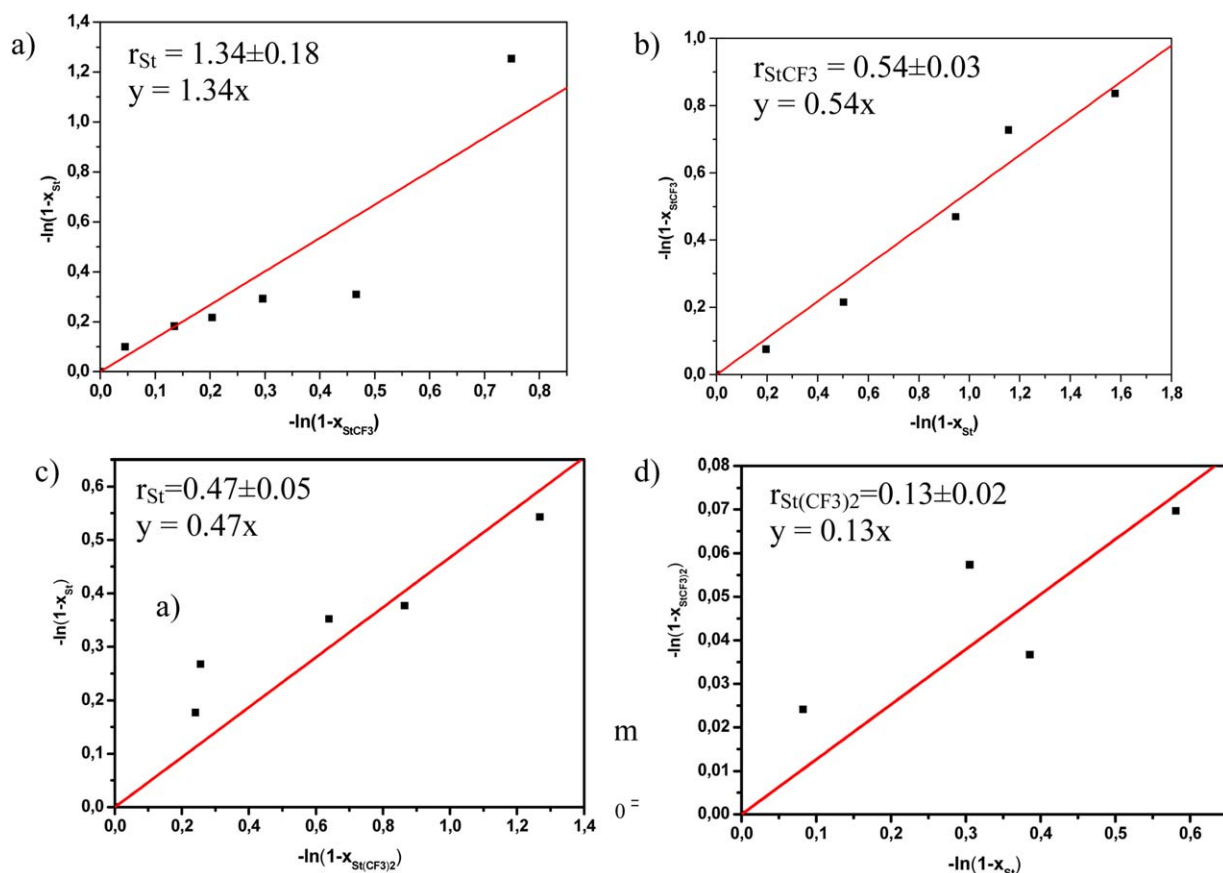


Figure 3. Jaacks plots of the free radical copolymerization at comonomers ratio (a) $[St]_0 : [StCF_3]_0 = 0.95:0.05 = 19$, (b) $[StCF_3]_0 : [St]_0 = 0.95:0.05 = 19$, (c) $[St]_0 : [St(CF_3)_2]_0 = 0.95:0.05 = 19$, (d) $[St(CF_3)_2]_0 : [St]_0 = 0.95:0.05 = 19$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

These values were confirmed and reported in our previous works.^{20,21} As can be seen, the values of relative reactive ratios of fluorinated comonomers decrease for monomers covalently bonded with fluorine atoms with an increasing fluorine atoms into macromolecule ($r_{FSt} = 0.85 > r_{StCF_3} = 0.54 > r_{5FSt} = 0.42 > r_{St(CF_3)_2} = 0.13$). Summarizing, the more fluorine atoms is bonded with used monomers, the more preferences of these monomers to react with St.

Thermal Properties

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were applied to examine the glass transition temperature (T_g) and the thermal stability of all obtained (co)polymers. The thermogravimetric data and T_g values of synthesized (co)polymers are summarized in Table III.

Introduction of fluorine atoms into polymers resulted in a decrease of the T_g values of both series of copolymers. The

Table III. Thermal Analysis Data of PSt, and Copolymers with Various StCF₃ and St(CF₃)₂ Content

Polymer	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	T_{max} (°C)	Char residue at 800°C (%)	T_g (°C)
PSt	366	382	418	0	106
P(St-co-StCF ₃)-1	372	387	418	0	101
P(St-co-StCF ₃)-2	369	384	417	0	97
P(St-co-StCF ₃)-3	375	388	417	0	95
P(St-co-StCF ₃)-4	376	389	419	0	86
P(St-co-St(CF ₃) ₂)-1	374	388	419	0	102
P(St-co-St(CF ₃) ₂)-2	383	394	418	0.1	101
P(St-co-St(CF ₃) ₂)-3	368	385	416	0.5	96
P(St-co-St(CF ₃) ₂)-4	381	391	419	0.1	95

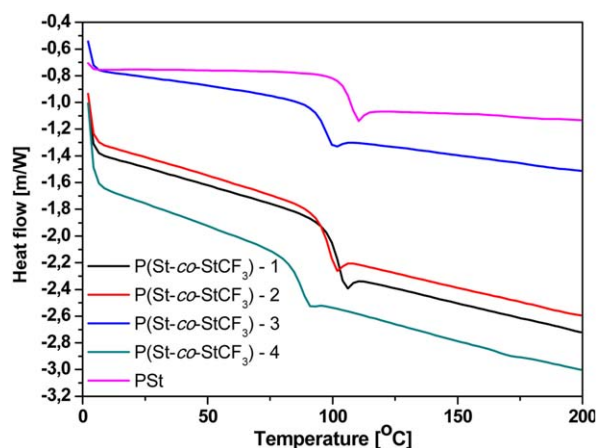


Figure 4. DSC curves of PSt and copolymers with various StCF_3 concentrations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

single T_g was detected for obtained copolymers what would indicate that the blocked copolymers were not obtained. In our previous works the negligible influence of fluorine atoms

presence in (co)polymers ($\text{P}(\text{St-co-5FSt})$ and $\text{P}(\text{St-co-FSt})$) on T_g was observed.^{20,21} Exemplary DSC thermograms of PSt and $\text{P}(\text{St-co-StCF}_3)$ s are depicted in Figure 4.

The thermal stability of obtained (co)polymers, that is, the 5 and 10% weight loss temperature ($T_{5\%}$ and $T_{10\%}$) (which is usually considered as the criterion of thermal stability of polymers), the temperature of the maximum decomposition rate (T_{max}) and char yields at 800°C were determined under nitrogen. TGA and DTG thermograms of synthesized (co)polymers are presented in Figure 5.

All polymers exhibit a similar TGA pattern in which thermal decomposition proceeded through one step. Analyzing $T_{5\%}$, $T_{10\%}$, T_{max} of $\text{P}(\text{St-co-StCF}_3)$ s, the values of these temperatures were close to each other. Moreover, almost the same tendency (slightly higher values of temperatures in comparison with $\text{P}(\text{St-co-StCF}_3)$ s) was observed in the case of $\text{P}(\text{St-co-St}(\text{CF}_3)_2)$ s, regardless the concentration of fluorinated monomers into polymers. Concluding, introduction of fluorinated monomers into polymers do not influence on thermal stability of PSt. It can be possible, that every copolymer degrades in the same way as PSt, by scissoring styrenic chain and formation low molecular weight

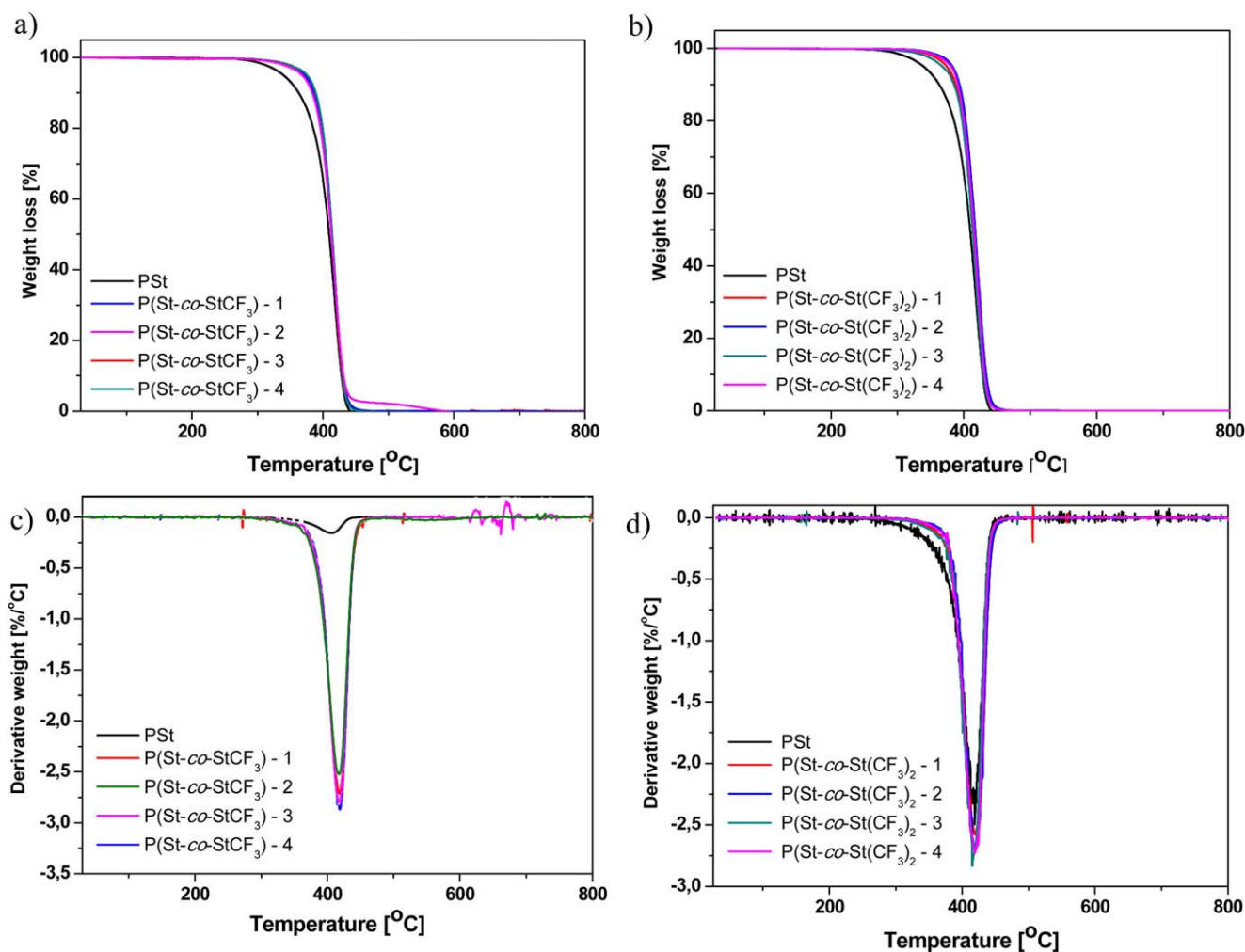


Figure 5. Thermogravimetric (a, b) and differential thermogravimetric curves (c, d) of polymers with various quantity of StCF_3 (a, c) and $\text{St}(\text{CF}_3)_2$ (b, d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

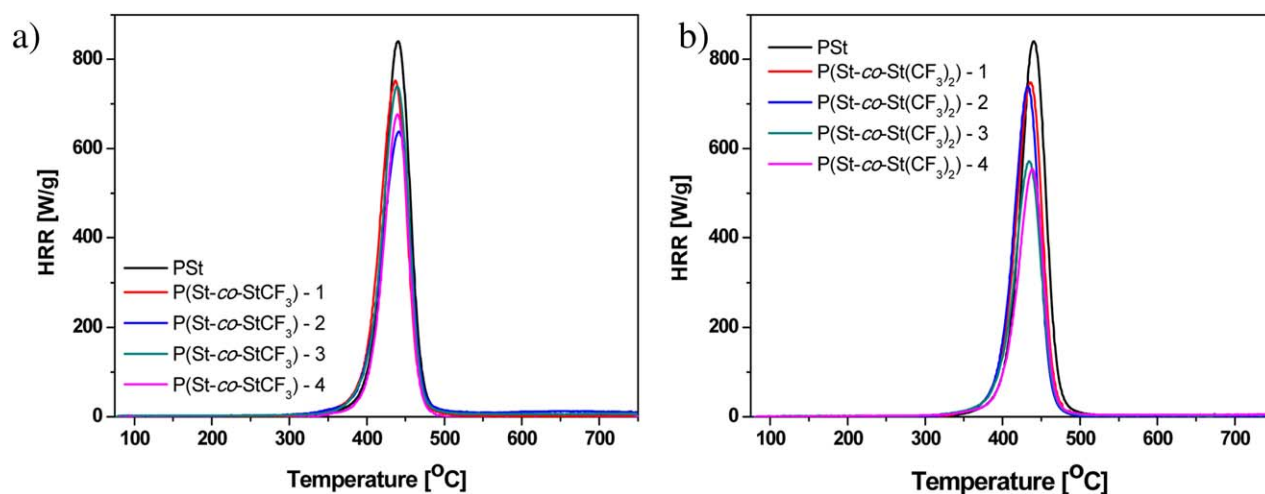


Figure 6. HRR curves for polymers with various concentrations of (a) StCF_3 and (b) $\text{St}(\text{CF}_3)_2$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chemical compounds (styrene monomers, dimers, trimers and some volatiles).³² Taking into account char residue, only copolymers containing 10%, 20%, and 50% mol of $\text{St}(\text{CF}_3)_2$ displayed insignificant quantity of residue after heating them to 800°C. Comparing our TGA data with reported in the literatures, only chemical modification by 5FSt caused improvement of PSt thermal stability.^{20,21}

Combustibility Evaluation

The pyrolysis combustion flow calorimeter (PCFC) was used to evaluate the flammability of the synthesized (co)polymers. This method is a viable method for determining combustion parameters of materials. Measured quantities include the specific heat release rate under simulated fire conditions, the heat of combustion of the fuel gases, the heat of combustion of the solid, and a derived quantity called the heat release capacity. It has been found that the heat release rate (HRR) is a reliable indicator of fire hazard.^{33–35} The heat release temperature (T_{max}), maximum specific heat release rate (HRR_{max}), time at which HRR_{max} occurs (t_{max}), and heat release (HR) were determined. The curves of heat release rate plotted versus temperature and combustibility parameters for obtained polymers are presented in Figure 6 and in Table IV.

The shape of HRR curves indicates a one-stage combustion process for PSt and the copolymer covalently bonded with StCF_3 and $\text{St}(\text{CF}_3)_2$. It was found that in most cases the greater load of fluorinated monomers resulted in the lower values of both HRR_{max} (slightly more favorable for $\text{P}(\text{St-co-St}(\text{CF}_3)_2)$) and HR. Some of discrepancies were observed and $\text{P}(\text{St-co-StCF}_3)$ -3 and $\text{P}(\text{St-co-StCF}_3)$ -4 exhibited higher values of HRR_{max} than $\text{P}(\text{St-co-StCF}_3)$ -2. However HRR_{max} of $\text{P}(\text{St-co-StCF}_3)$ -4 was lower than HRR_{max} of $\text{P}(\text{St-co-StCF}_3)$ -3. When it comes to the heat release, only in the case of $\text{P}(\text{St-co-StCF}_3)$ -2 and $\text{P}(\text{St-co-StCF}_3)$ -3 such a discrepancy was seen. Nevertheless, it should be emphasized that the incorporation of fluorinated comonomers reduced both HR and HRR_{max} comparing with pure PSt. As can be seen from Figure 6, the HRR curves of PSt containing various amount of fluorinated monomers were almost not shifted towards higher temperatures. This proves, that copolymers achieved HRR_{max} nearly in the same temperature compared with PSt. Moreover, the StCF_3 and $\text{St}(\text{CF}_3)_2$ incorporation influenced only insignificant on t_{max} values (only in the case of $\text{P}(\text{St-co-StCF}_3)$ s the time rose at about 10°C). Taking into account chemical modification of PSt basing on copolymerization of St with StCF_3 and $\text{St}(\text{CF}_3)_2$ only two combustibility parameters were improved (HRR_{max} and HR). Comparing these

Table IV. Combustibility Parameters for Polymers with Various StCF_3 and $\text{St}(\text{CF}_3)_2$ Concentrations

Polymer	t (s)	T (°C)	HRR_{max} (W/g)	HR (kJ/g)
PSt	379.5	440.8	865.4	38.3
$\text{P}(\text{St-co-StCF}_3)$ -1	374.00	436.26	752.71	34.40
$\text{P}(\text{St-co-StCF}_3)$ -2	389.01	441.72	637.84	34.40
$\text{P}(\text{St-co-StCF}_3)$ -3	388.01	439.39	739.67	35.50
$\text{P}(\text{St-co-StCF}_3)$ -4	387.50	439.62	676.57	25.19
$\text{P}(\text{St-co-St}(\text{CF}_3)_2)$ -1	383.00	435.84	748.53	32.30
$\text{P}(\text{St-co-St}(\text{CF}_3)_2)$ -2	370.01	432.78	738.74	30.92
$\text{P}(\text{St-co-St}(\text{CF}_3)_2)$ -3	372.51	433.83	571.44	27.00
$\text{P}(\text{St-co-St}(\text{CF}_3)_2)$ -4	376.50	438.15	553.49	25.50

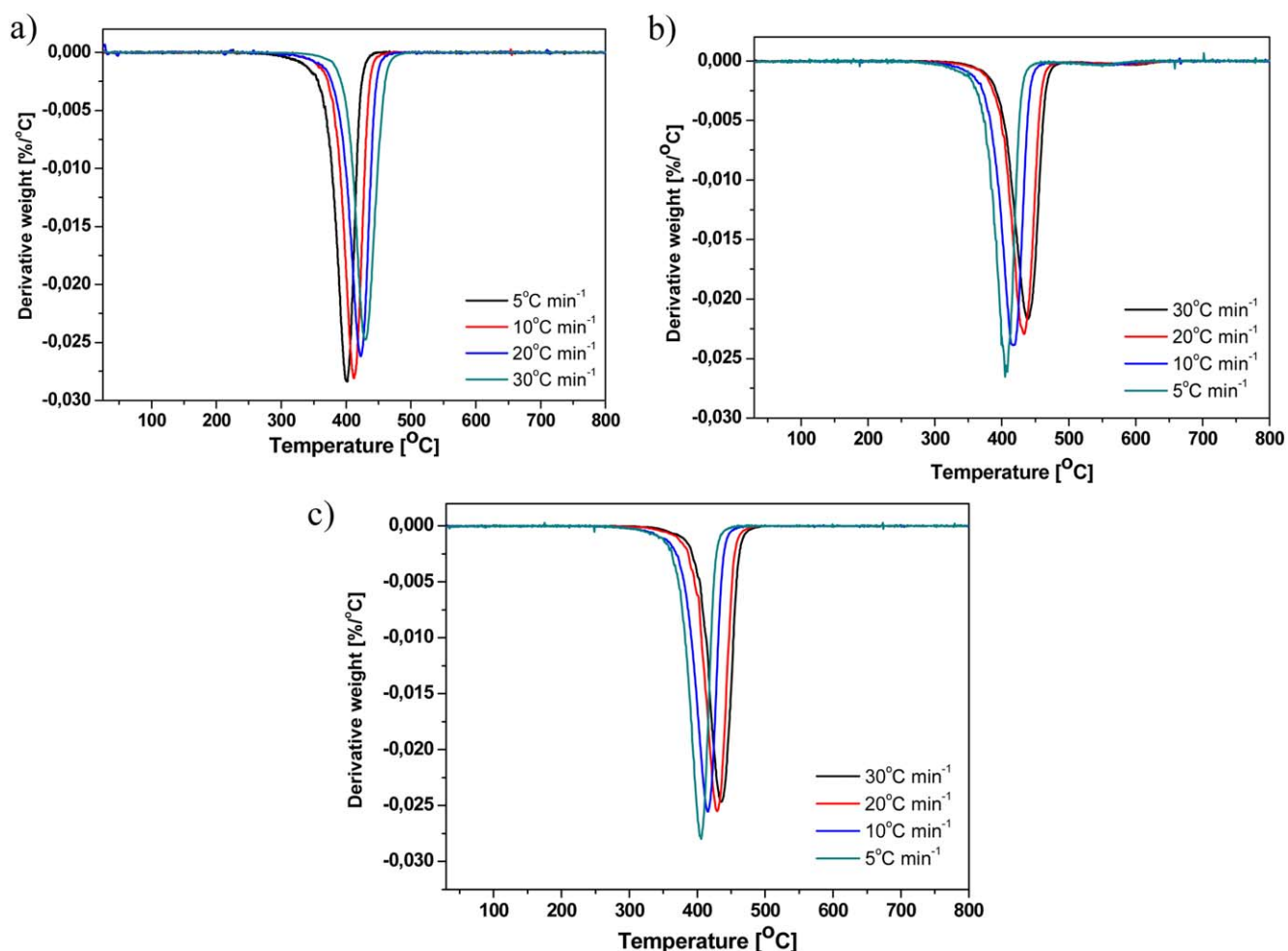


Figure 7. DTG curves at the different heating rates: $30^{\circ}\text{C min}^{-1}$, $20^{\circ}\text{C min}^{-1}$, $10^{\circ}\text{C min}^{-1}$, $5^{\circ}\text{C min}^{-1}$ of (a) PSt, (b) P(St-co-St(CF₃)₂)-2, (c) P(St-co-St(CF₃)₂)-2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

data with literatures data for reported copolymers containing 50% mol of fluorinated St (i.e. 5FSt and FSt), the best results, that is the highest values of HR and HRR_{max} were obtained for applied fluorinated monomers (StCF₃, St(CF₃)₂) and 5FSt:

- P(St-co-StCF₃)-4 (HR = 25.2 kJ g⁻¹, HRR_{max} = 676.6 W g⁻¹)
- P(St-co-St(CF₃)₂)-4 (HR = 25.5 kJ g⁻¹, HRR_{max} = 553.5 W g⁻¹)
- P(St-co-5FSt)-4 (HR = 28.9 kJ g⁻¹, HRR_{max} = 526.8 W g⁻¹)²¹
- P(St-co-FSt)-4 (HR = 35.3 kJ g⁻¹, HRR_{max} = 845.7 W g⁻¹)²⁰

However, comparing the obtained HR values with these reported for fluorinated polymers mentioned in Introduction such as polyvinylidene fluoride, poly(ethylene-tetrafluoroethylene), and polytetrafluoroethylene it can be concluded that these polymers seem to be significantly less flammable than modified with CF₃ units PSt described in this work. It will be interesting to compare our results with more similar copolymers, that is, obtained from styrenic comonomers substituted with -CF₃ groups, however, despite such (co)polymers were reported in the literature,²² their flammability has not been presented. Thus, to the best of our knowledge flammability of the (co)polystyrenes bearing CF₃ moieties is firstly presented in current work.

Thermal Degradation Kinetics

The TGA experiments with heating rates of 5, 10, 20, and 30°C/min were conducted to investigate and compare the thermal degradation kinetics of PSt and selected copolymers containing 10% mol of fluorinated monomers (P(St-co-StCF₃)-2 and P(St-co-St(CF₃)₂)-2). Common methods presented in literature and used in order to characterize the thermal degradation of polymers are: the Kissinger, Ozawa, Horowitz-Metzger, Coat-Redfen, MacCallum-Tanner and van Krevelen.³⁶⁻³⁹ In this article, two different methods i.e. Ozawa and Kissinger were chosen to analyze experimental results for the thermal degradation kinetics because of their simplicity and accuracy to estimate the activation energy (*E*) and frequency factor (*A*).^{40,41} The activation energy can be determined by Kissinger and Ozawa methods without a precise knowledge of the reaction mechanism. Both methods do not use the reaction order in the calculation of the decomposition activation energy. In this method, the relationship between the heating rates (ϕ) values and the temperature at the maximum reaction rate (*T_p*) was used to determine the reaction kinetic. According to the Ozawa method, the thermal decomposition activation energy (*E*) was determined using following equation:^{42,43}

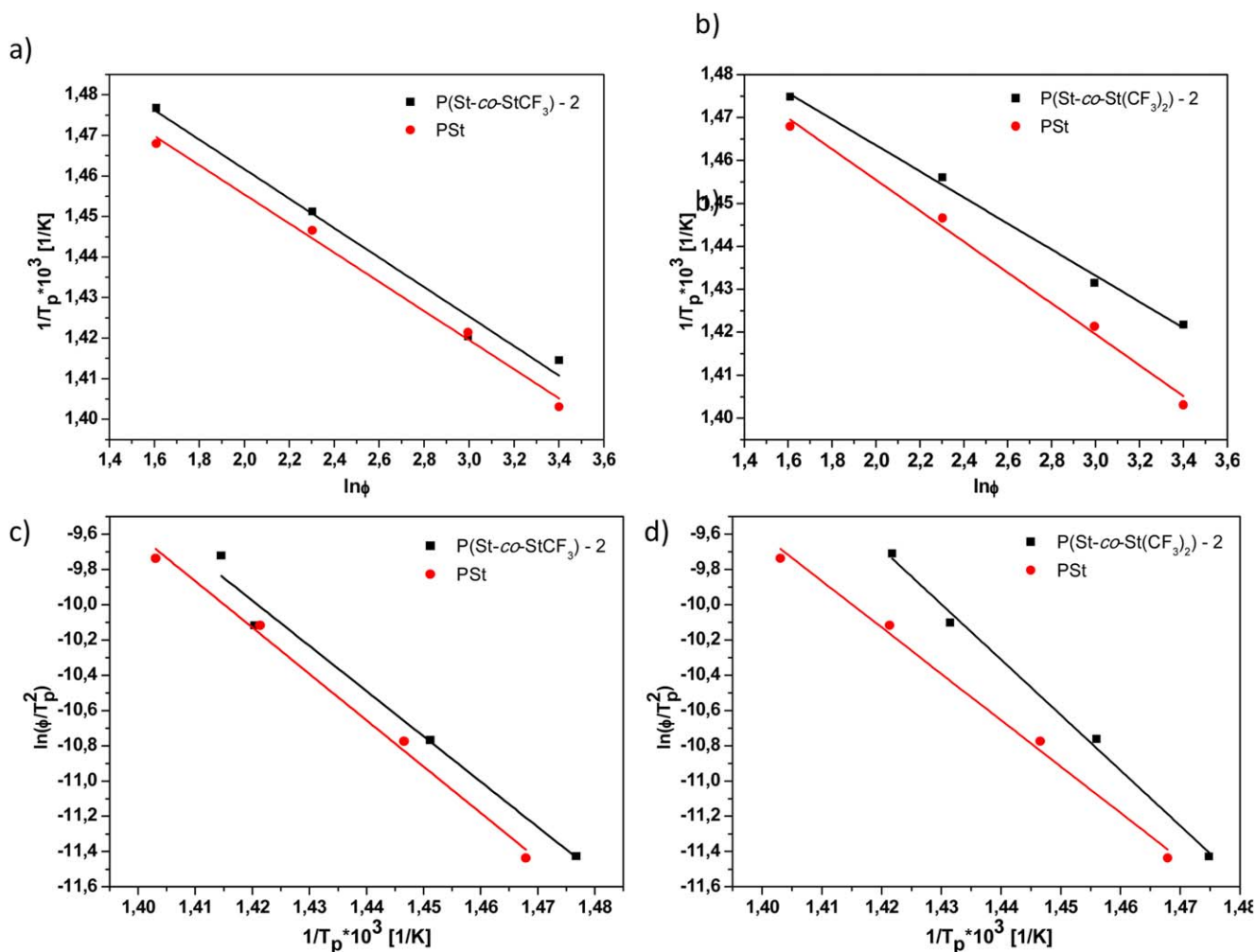


Figure 8. Plots for the determination of the thermal decomposition activation energy (E), for PSt, P(St-co-StCF₃)₂-2, (c) P(St-co-St(CF₃)₂)₂-2 by (a, b) Ozawa method, (c, d) Kissinger method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$E = -R/1.052 \cdot \Delta \ln \phi / \Delta (1/T_p) \quad (1)$$

where R is the universal gas constant. The equation derived by Kissinger for E and the frequency factor (A) is as follows:^{40,44,45}

$$-E/R = d[\ln(\phi/T_p^2)]/d(1/T_p) \quad (2)$$

For the first-order kinetic reaction, when $n = 1$, A can be calculated from equation:^{44,46}

$$A = \phi E \exp(E/RT_p) / RT_p^2 \quad (3)$$

The reaction order of degradation was assumed to be one, which is calculated from Kissinger's eq. (4):⁴⁶

$$n = 1.26\sqrt{S} \quad (4)$$

where S is shape index of the differential thermal analysis. The value of S was determined from the shape of the DTG curve. The Ozawa and Kissinger methods are independent of sample size.⁴⁷ The DTG curves at the different heating rates of PSt, P(St-co-StCF₃)₂-2 and P(St-co-St(CF₃)₂)₂-2 are shown in Figure 7.

The thermograms present one decomposition process for all (co)polymers.

A plot of $1/T_p$ versus $\ln \phi$ according to the eq. (1) (Ozawa method) for each (co)polymer is presented in Figure 8(a,b). The calculated slope for P(St-co-StCF₃)₂-2 and P(St-co-St(CF₃)₂)₂-2 is -0.036 and -0.030 , respectively and for PSt is -0.036 . Figure 8(c,d) shows the plots of $\ln(\phi/T_p^2)$ versus $1/T_p$ obtained according to the eq. (2) (Kissinger method) for each (co)polymer. In this case the slope is -25.68 for P(St-co-StCF₃)₂-2, -31.41 for P(St-co-St(CF₃)₂)₂-2, and -26.28 for PSt.

Obtained results by means of the eq. (3) are presented in Figure 9 (with the E value estimated by the Ozawa and Kissinger methods for P(St-co-StCF₃)₂-2, P(St-co-St(CF₃)₂)₂-2, and PSt).

The calculated kinetics parameters, that is, E and A for P(St-co-StCF₃)₂-2, P(St-co-St(CF₃)₂)₂-2, and PSt are estimated by the Ozawa and Kissinger models and given in Table V.

It was found that the values of activation energy and frequency factor for P(St-co-St(CF₃)₂)₂-2 are much higher, whereas for P(St-co-StCF₃)₂-2 are slightly lower than for PSt. The apparent activation energies results obtained from two models (Ozawa and Kissinger) are quite close for all obtained (co)polymers. The lower values of kinetic parameters were calculated by the

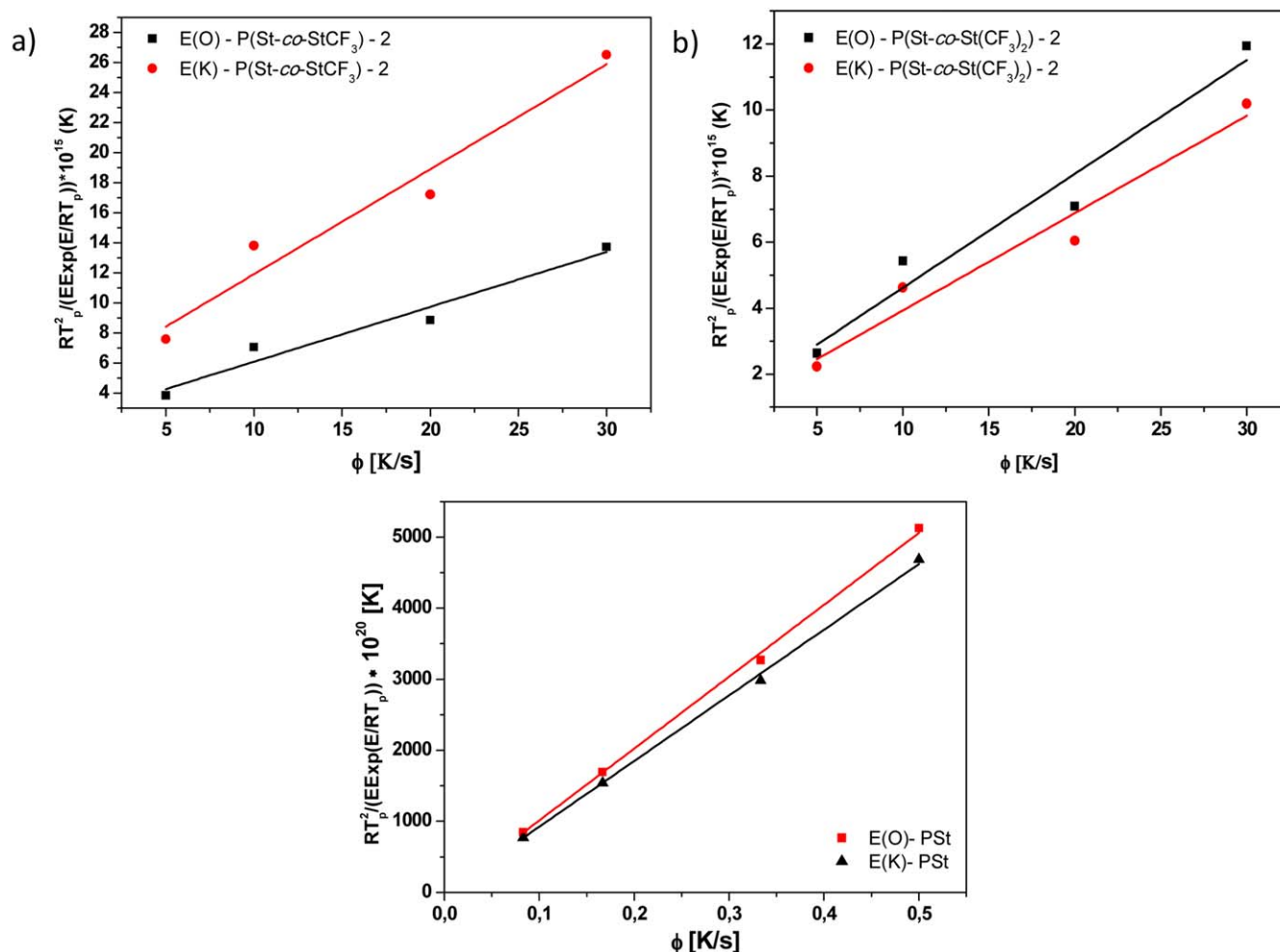


Figure 9. Plots for determination of the frequency factor (A) for thermal decomposition of (a) $P(\text{St-co-StCF}_3)_2$, (b) $P(\text{St-co-St}(\text{CF}_3)_2)_2$, (c) PSt by Kissinger method from different E : $E(O)$ from Ozawa method, and $E(K)$ from Kissinger method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Kissinger method in the case of PSt and $P(\text{St-co-StCF}_3)_2$. In literature the thermal decomposition activation energy of PSt was calculated by various models such as: the Coast-Redfern ($E = 250.3\text{--}251.5$ kJ/mol),³⁸ Friedman-Ozawa ($E = 201.2$ kJ/mol),⁴⁸ Anderson and Freeman's ($E = 193\text{--}273$ kJ/mol),⁴⁹ West-erhout *et al.*'s ($E = 204$ kJ/mol),⁵⁰ Kannan *et al.*'s ($E = 168\text{--}176$ kJ/mol) and Simard's ($E = 166.5$ kJ/mol).^{49,51} Additionally in our previous work^{20,21} the kinetic parameters (E , A) were calculated for halogeno-modified PSt i.e., poly(4-chlorostyrene)-PSt, poly(4-bromostyrene)-PSt, poly(4-fluorostyrene)-PSt, and poly(2,3,4,5,6-pentafluorostyrene)-PSt. The values of

activation energy (kJ mol^{-1}) calculated by means of Ozawa method increased in the following order: PClSt ($E(O) = 216.1$) < PSt ($E(O) = 219.9$) < PBrSt ($E(O) = 224.7$) < PFSt ($E(O) = 252.5$) < P5FSt ($E(O) = 330.9$). It should be emphasized that our calculations were not performed for homopolymers as above, but only for copolymers containing 10% mol of fluorinated monomers. Comparing values of $E(O)$ (from for example Ozawa method) for these copolymers, it is noticed that $P(\text{St-co-St}(\text{CF}_3)_2)_2$ with $E(O) = 260.2$ kJ mol^{-1} qualified between PFSt ($E(O) = 252.5$) and P5FSt ($E(O) = 330.9$). The kinetic parameters for $P(\text{St-co-StCF}_3)_2$ were nearly the same as in the case of

Table V. The Activation Energy and the Frequency Factor for PSt and Selected Copolymers

Polymer	Ozawa method		Kissinger method	
	$E(O)$ (kJ/mol)	$A(O)$ (1/s)	$E(O)$ (kJ/mol)	$A(O)$ (1/s)
PSt	219.9	3.4×10^{14}	218.5	2.7×10^{14}
$P(\text{St-co-StCF}_3)_2$	217.5	4.6×10^{13}	213.5	2.4×10^{13}
$P(\text{St-co-St}(\text{CF}_3)_2)_2$	260.2	4.8×10^{24}	261.1	5.6×10^{24}

PSt. To the best of our knowledge there is lack of data related to calculations of the activation energy and frequency factor for obtained copolymers. Moreover, thermal decomposition activation energy of PSt has not been estimated by Ozawa and Kissinger methods as so far.

CONCLUSION

Chemical modification of PSt based on copolymerization of St with styrenes containing trifluoromethyl moieties was conducted. The calculated relative reactivity ratios for the St : StCF₃ system indicate that the monomers have a tendency to form random copolymers, whereas St and St(CF₃)₂ incorporate alternating into copolymer chain. The incorporation of —CF₃ groups into PSt caused a slightly decrease in *T_g* values (from 106 to 86°C—StCF₃ and to 95°C—St(CF₃)₂). All (co)polymers exhibited one-stage thermal degradation and combustion. It was found that introduction of fluorinated St did not improve thermal stability of PSt (the temperatures: *T*_{5%}, *T*_{10%}, and *T*_{max} differed only at about few degrees of Celsius). Nevertheless, P(St-co-St(CF₃)₂)s displayed small amount of char residue after decomposition (0.1–0.5%) and only in this case the kinetic parameters the increased of activation energy values (*E*(O): from 219.9 to 260.2 kJ mol⁻¹, *E*(K): from 218.5 to 261.1 kJ mol⁻¹) and frequency factor (*A*(O): from 3.4 × 10¹⁴ s⁻¹ to 4.8 × 10²⁴ s⁻¹, *A*(K): from 2.7 × 10¹⁴ s⁻¹ to 5.6 × 10²⁴ s⁻¹) was found. Taking into account higher values of the kinetic parameters for P(St-co-St(CF₃)₂)–2 than for P(St-co-StCF₃)–2, it can be expected that P(St-co-St(CF₃)₂)s should be more thermal stable and introduction of St(CF₃)₂ should provide the better flame retardancy for PSt. The flame retardant properties of all synthesized copolymers were also confirmed by the data from pyrolysis combustion flow calorimetry. It was found that the introduction of both fluorinated comonomers improved combustibility parameters (HRR_{max} and HR) but had insignificant influence on *T*_{max} and *t*_{max}. Values of HRR_{max} were reduced from 865.4 to 676.6 W g⁻¹—StCF₃ and to 553.5 W g⁻¹—St(CF₃)₂ and HR from 38.3 to 25.2 kJ g⁻¹—StCF₃ and 25.5 kJ g⁻¹—St(CF₃)₂. Thus, it can be concluded that incorporation of trifluoromethyl groups may be perspective for flammability reduction of PSt. Furthermore, there is no limit for substitution also other polymers by trifluoromethyl groups in order to reduce their flammability. However, for confirmation of this hypothesis the LOI (limiting oxygen index) test is necessary.

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