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NEW FLUORINATED POLYMERS BEARING PENDANT PHOSPHONIC GROUPS FOR FUEL CELL MEMBRANES. PART 1 SYNTHESIS AND CHARACTERIZATIONS OF THE FLUORINATED POLYMERIC BACKBONE

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ABSTRACT

Radical copolymerizations of chlorotrifluoroethylene (CTFE) with vinyl ethers such as 2-chloroethyl vinyl ether (CEVE) and ethyl vinyl ether (EVE) were performed at 75 °C in the presence of peroxide initiator. Three copolymers were obtained and characterized by means of both NMR and elemental analysis. Then, the chlorine atoms in the side chains were converted into iodine atoms by nucleophilic substitution, which was monitored by ^{1}H NMR spectroscopy. A series of five copolymers with different amounts of iodine atoms in the side chains were thus obtained. These copolymers exhibited molecular weight values of about 25,000 g.mol^{-1}, and the thermal analysis of the copolymers showed a starting degradation from about 220 °C. The T_g values were in the range of 34 to 41 °C and showed a linear dependance *versus* the content of iodine atoms.

INTRODUCTION

Fluorinated polymers exhibit remarkable properties such as chemical, thermal and electrical stability, inertness to acids, solvents and oils, low dielectric constant, low refractive index, low or non flammability, high resistance to ageing and oxidation, and low surface tension.[1,2] These polymers show low friction coefficient and relative permittivity, and they are strongly hydrophobic. For application in a polymer electrolyte fuel cells, they must be functionalized [3], and the choice of the protogenic group plays an important role in the proton conductivity of fuel cell separator materials. Up to now, the materials used for proton exchange membranes in fuel cell applications depend on the presence of water as proton carrier.[4] Although practicable at lower temperatures, water management at temperatures higher than 100 °C has a significant impact on the viability of the membrane electrode assembly and on overall operation of the system. Commercially available perfluorosulfonic acid (PFSA) polymers such as Nafion®, Flemion®, Hyflon® Ion, (now Aquivion®), BAM-3G®, Fumion®, Gore Select®, Dow®, 3M® or Aciplex® are references and emerging advanced membranes for proton exchange membrane fuel cells (PEMFCs), being characterized by high proton conductivity and chemical stability.[5,6] Their conductivity is dependent on the ambient relative humidity and their glass transition temperature limits their use to temperatures lower than 130 °C.[4,7] Polymers functionalized with alternative protogenic groups, including phosphonic acids[8,9] and different heterocycles[10], have been investigated with the aim to overcome the shortcomings of the Nafion® membrane.[5] Phosphonic acid derivatives in particular are considered suitable candidates as ionomers because of their efficient proton transport according to the Grotthuss mechanism.[10-16] They are both amphoteric and possess a relatively high dielectric constant. Moreover, they are able to perform even in anhydrous conditions. The combination of these properties is an important requirement for membranes operating in medium to high temperature regimes. Several phosphonic acid containing polymers have been developed for fuel cell applications, starting from polyvinylphosphonic acid (PVPA)[17] to less flexible polymers such as polysulfones.[8,18] To our knowledge, only Kotov

et al.[19] and Yamabe et al.[20] connected phosphonic acid functions to a flexible fluorinated polymeric backbone. Indeed, these authors synthesized new fluorinated monomers, bearing a phosphonic group, able to copolymerize with fluorinated olefins such as TFE. However, poor conductivity values were reached due to the low content of incorporated phosphonic group into the fluorinated backbone.

We suggest here another approach, which consists in the chemical modification of fluorinated polymers into ionomers bearing a high content of phosphonic acid groups. The objective of this article is to provide a series of fluorinated copolymers as precursors containing a controlled amount of ω-iodoalkyl pendant groups tethered to the backbone. In a second part, these iodine atoms will be modified into phosphonic groups (*via* the Arbuzov reaction) and the properties of the resulting membranes will be analyzed. This second part will be devoted to a forthcoming paper. The synthesis of fluorinated copolymers bearing iodine atoms can be achieved by radical copolymerization of fluorinated olefins, such as chlorotrifluoroethylene (CTFE), with vinyl ethers (VEs), such as 2-chloroethyl vinyl ether (CEVE) or ethyl vinyl ether (EVE). These radical copolymerizations usually result in alternated copolymers[21-25], which enable to incorporate a high amount of chlorine atoms (from CEVE). These chlorine atoms can be further modified into iodine atoms by nucleophilic substitution.[26] A series of five fluorinated copolymers based on CTFE, CEVE and EVE with a controlled amount of iodine atom is provided. These copolymers have been deeply characterized and a special attention will be paid to the determination of the halogen atom content that will govern the range of ionic exchange capacity (IEC) values.

EXPERIMENTAL SECTION

Materials.

Chlorotrifluoroethylene (CTFE) and 1,1,1,3,3-pentafluorobutane were kindly provided by Solvay S.A. Vinyl ethers such as 2-chloroethyl vinyl ether (CEVE) and ethyl vinyl ether (EVE) were purchased from Acros Organics. Diethyl ether and methanol were purchased from Aldrich, K_2CO_3

from SDS and tert-butyl peroxipivalate (TBPPI) 75% purity from Azko Nobel. All reactants were used without further purification except for 1,1,1,3,3-pentafluorobutane, which was distillated prior to use.

Characterization.

^{1}H, ^{13}C and ^{19}F nuclear magnetic resonance (NMR) spectra were recorded at room temperature on Bruker AC 400 instrument, using deuterated chloroform as the solvent. In the figures and discussion below, the letters s, d, t, q and m stand for singlet, doublet, triplet, quintet and multiplet, respectively. Coupling constants and chemical shifts are given in Hertz (Hz) and ppm. The experimental conditions to record ^{1}H, ^{13}C and ^{19}F NMR spectra were as follows: flip angle 90°, 30° and 30° ; acquisition time: 4.5 sec, 2.9 sec and 0.7 sec ; pulse delay : 2 sec, 2 sec and 5 sec ; number of scans: 16, 12000 and 64, and a pulse width of 5 μsec for ^{19}F NMR.

Thermogravimetric analyses (TGA) were performed with a TGA/SDTA 851 thermobalance from Mettler DAL 75965 and Lauda RC6 CS cryostat apparatus in static air with a heating rate of 10 °C.min^{-1} from room temperature up to a maximum of 600 °C. Differential scanning calorimetry (DSC) measurements were conducted using a TA2920 analyzer from TA Instruments DA 73085, an RCS DA cooler and Sartorius MC5 balance. Scans were recorded at a heating/cooling rate of 20 °C.min^{-1} from -100 °C to 100 °C and the T_g value was assessed from the inflexion point in the heat capacity jump.

Size exclusion chromatography (SEC) measurements were conducted on a Spectra-Physics apparatus equipped with two 5 μm Mixed-C PL-gels columns (Polymer Laboratories), a SP8430 Spectra-Physics refractive index detector using THF as the eluent at room temperature, and a flow rate of 0.6 mL.mn^{-1} min. Monodispersed polystyrene standards were used for the calibration.

Weight percentages of carbon, fluorine, chlorine, and hydrogen atoms were assessed by elemental analysis at the CNRS-Service Central d'Analyze (Solaize, France) on a CH elemental analyzer equipped with a CO_2/H_2O infrared detector. Theoretical carbon and hydrogen compositions were calculated according to the polymer compositions assessed by ^{1}H and ^{19}F NMR spectroscopy and

considering that co- or terpolymers have alternating structures (i.e., 50% of fluorinated olefins and 50% of vinyl ethers).

Radical copolymerizations

As CTFE is a gaz, the reactions were carried out in a Hastelloy (HC276) autoclave Parr system equipped with a manometer, a rupture disk (3000 psi), inlet and outlet valves, and a magnetic stirrer. Prior to reaction, the autoclave was pressurized with 30 bar (i.e., 430 psi) of nitrogen to check for eventual leaks. The autoclave was then conditioned for the reaction with several nitrogen/vacuum cycles (10^{-2} mbar) to remove any traces of oxygen. The liquid phase was first introduced via a funnel, and then the gases were inserted by double weighing (i.e., the difference of weight before and after filling the autoclave with the gas). Then, the autoclave was placed in a mantle heated with a vigorous mechanical stirring. Both heating and stirring were monitored by a controller. After an initial increase of the internal pressure due to the increasing temperature, the pressure dropped by consumption of the gaseous monomer to produce a polymer in the liquid phase. After the reaction was complete, the autoclave was cooled to room temperature and then degassed. After distillation of the solvent, the copolymers were precipitated from cold pentane. The product was dried under vacuum (10^{-2} mbar) at 70 °C until constant weight.

Synthesis of (F:Cl)

As an example, 1,1,1,3,3-pentafluorobutane (150 ml) as the solvent, tert-butylperoxypivalate 1.04 g (5.75 mmol) as the initiator, potassium carbonate 0.79 g (5.72 mmol) (to prevent the cationic homopolymerization of CEVE), CEVE 20.2 g (187.71 mmol) and CTFE 25 g (214.74 mmol) were introduced in the autoclave. The reaction was allowed to proceed at 75 °C for 12 h, showing a drop of pressure as CTFE was reacting. After purification, the copolymer, obtained as a white powder, was then dried in a vacuum oven (10^{-2} mbar) at 50 °C until constant weight. The mass yield was 75%.

Nucleophilic substitution

The copolymer was dissolved in dry acetone in a single-neck round bottom flask equipped with a magnetic stirrer and a condenser. Then, 3 equiv of sodium iodide were introduced in the flask, and the reaction was allowed to reflux for 7 days. After reaction and upon cooling to room temperature, the produced salts (sodium chloride and sodium iodide) were filtered off. Then, the polymer was precipitated from methanol and dried under vacuum at 50 °C for 4 h to produce a white powder. The product was obtained in high yield (>81%).

RESULTS AND DISCUSSION

Valade et al.[26] performed the radical copolymerizations of vinyl ethers with chlorotrifluoroethylene (CTFE) and hexafluoropropylene (HFP). HFP allowed the incorporation of a higher content of fluorine moities into the copolymers. However, the resulting terpolymers showed low molecular weights, i.e. < 8 000 g/mol, and thus polymeric membranes cannot be obtained. Hence, the radical copolymerizations of 2-chloroethyl vinyl ether (CEVE) with only CTFE were developed, the content of halogen, i.e. chlorine and then iodine, will be tuned by a controlled incorporation of ethyl vinyl ether (EVE).

Radical copolymerizations of CTFE with VE

NMR computational results of poly(CTFE-alt-VE) copolymers, and especially poly(CTFE-alt-EVE), allowed to assess the alternated structure of these copolymers.[27] Hence, alternated copolymers were synthesized by radical copolymerizations of CTFE with CEVE and EVE at 75 °C initiated with *tert*-butyl peroxypivalate (TBPPI) (Figure 1). Three copolymers were obtained. The first one did not contain any EVE units and was labelled **(F:Cl)**, the two others contained both CEVE and EVE units were labelled $\mathbf{(F:Cl)_x\text{-}co\text{-}(F:E)_y}$; where x and y represent the molar contents of oligo(CTFE-alt-CEVE) and oligo(CTFE-alt-EVE) units into the copolymers,

respectively. Indeed, these copolymers can be represented as a molar content of acceptor/donnor (A/D) couples, i.e. CTFE/CEVE and CTFE/EVE, since the mechanism of radical copolymerization proceeds via the formation of a charge transfer complex followed by its radical polymerization.[25] A series of three copolymers was obtained with x value ranging from 0.36 to 1 (Table 1) and the yields of the corresponding copolymers were up to 75% (wt. %). These copolymers were first characterized by elemental analysis. Experimental weight percentages of carbon, hydrogen, fluorine, chlorine and oxygen are in good agreement with the calculated theoretical values assuming an alternating copolymer structure (Table 2). NMR study was then conducted to determine the structure of the copolymers. The ^{1}H NMR spectrum (Figure 2) allows reaching the composition of each A/D couples, i.e. **(F:Cl)** and **(F:E)** by using intensities of signals corresponding to both CH_3 (e) and CH(OR) (b) centered at 1 and 4.5 ppm, respectively. The ^{1}H NMR analysis also affords a chain end characterization. Indeed, ^{1}H NMR spectra seem to underline some chain transfer reactions (from hydrogen radical) leading to dead polymer chains. These transfer reaction seem to occur towards the fluorinated macroradical terminated by $CF_2CFCl^{\bullet}$ and the resulting terminal chain shows a complex signal centered at about 6.5 ppm assigned to the proton in $–CF_2CFClH$. Boutevin et al.[25] already observed this termination by performing the radical transfer reaction of CTFE in the presence of a chain transfer agent. Deeper investigations are required to understand these transfer reactions, nevertheless they remain negligeable. It is also noted a series of signals centered between 1.14 and 1.58 ppm that can be attributed to methyl and t-butyl groups arising from TBPPi decomposition.

^{13}C NMR spectra (Figure 3a) also confirm the copolymer structure. As previously demonstrated by Carnevale et al.[27], two asymetrical carbon atoms (C2 and C4) are observed in the backbone inducing 4 diastereoisomers for **(F:Cl)** and 16 diastereoisomers for **$(F:Cl)_x$-co-$(F:E)_y$**. Furthermore, coupling constants of 251 and 32 Hz were obtained for $^{1}J_{CF}$ and $^{2}J_{CF}$ of CF_2 and CFCl carbons, respectively. Finally, ^{19}F NMR spectrum (Figure 3b) shows a series of complex multiplets, centered at -109.54, -115.75, -119.34 and -121.13ppm, assigned to the presences of

asymetric carbons into the backbone. No signal characteristic of bimolecular termination (e.g. CFCl-CFCl)[28] was observed on the ^{19}F NMR spectrum. Molecular weight values of the copolymers were ca. 25,000 g.mol^{-1} (Table 3). They were low but sufficient to perform membranes from the corresponding copolymers. These low M_n values are attributed to an exothermic effect observed in the course of the radical copolymerization. This exothermic effect increases the concentration of radicals which lead to initiation of new chains but also to termination reaction as well as transfer reaction (as mentioned above). This behavior results in highly polydispersed copolymers with polydispersity index (PDI) values of about 3 (Table 3).

Thermal properties of the three copolymers were determined by means of TGA and DSC (Table 3). Thermograms recorded under air of the copolymers show one main degradation step starting after 300 °C to reach a complete degradation after about 500 °C. The EVE content of the copolymers influences the thermostability: the higher the EVE content, the higher the thermostability.[29-31] This can be connected to a lower amount of CH_2-CH_2-Cl units, because the dissociation energy of C-Cl bond (from CEVE units) is about 285 KJ.mol^{-1} whereas the energy of C-H bond (from EVE units) is higher (about 370 KJ.mol^{-1}).[32] Hence, the decrease of the thermostability is certainly due to the release of HCl which might further degradate the copolymer. This degradation is however observed at high temperature (about 300 °C) and does not represent a main drawback because the operating temperatures in fuel cells are much lower (about 130 °C). Table 3 also shows that the starting degradation temperatures under nitrogen are higher than those under air of about 40 °C. In the last case, oxidation reactions occur and accelerate the thermal degradation of the copolymers. Despite, these temperatures of starting degradation remain acceptable for fuel cell application. Interestingly, glass transition temperatures of about 26 °C were obtained (Table 3), which will confer some flexibility to the resulting membranes.

Nucleophilic substitution of the copolymers

The CH_2-Cl groups in **(F:Cl)** and **$(F:Cl)_x$-co-$(F:E)_y$** copolymers were partially or totally converted into CH_2-I units by using the Finkelstein reaction, i.e. the nucleophilic substitution in the presence of NaI at 65 °C (Figure 5).[33] This chemical modification will enable these fluoroiodinated copolymers a more easily chemically grafting of the phosphonic groups, as the dissociation energy of the C-I bond is about 205 $KJ.mol^{-1}$ instead of 285 $KJ.mol^{-1}$ for C-Cl bond. This nucleophilic substitution was studied in a kinetic point of view by Valade et al.[26] to control the amount of CH_2-I units, and hence to better control the final IEC of the resulting membranes. From the three fluorochlorinated copolymers, a series of five copolymers containing iodine side atoms was obtained with different CH_2-I amounts, ranging from 30 mol.% to 97 mol.% (Table 4). These amounts were determined from ^{1}H NMR spectra (Figure 6) of the copolymers, especially by using the integrals of signals centered at 3.20 and 3.55 ppm assigned to CH_2-I and CH_2-Cl, respectively. The theoretical and experimental amounts of CH_2-I groups (Table 4) are similar except for **$(F:Cl)_{0.36}$-co-$(F:E)_{0.64}$** where the high content of EVE units may increase the steric hindrance and thus may decrease the accessibility of the CH_2-Cl groups. As expected, molecular weights of the five iodinated copolymers are in the same order as the neat copolymers (about 25,000 $g.mol^{-1}$). Figure 7 shows the thermogravimetric analyses of **$(F:Cl)_{0.03}$-co-$(F:I)_{0.97}$**, **$(F:Cl)_{0.41}$-co-$(F:I)_{0.59}$** and **$(F:Cl)_{0.05}$-co-$(F:E)_{0.64}$-co-$(F:I)_{0.31}$** copolymers recorded under air. Three main degradations can be observed. The first one occurs from about 190 °C and corresponds to the release of HI. The second one, starting from 230 °C until 430 °C, is the main degradation for all the copolymers as more than 75% of weight loss is obtained, corresponding to the degradation of the polymeric backbone. The third one begins after 430 °C and is assigned to the decomposition of alkyl groups from the different vinyl ethers. It is also observed that the higher the iodine molar content, the lower the thermal stability of the copolymers. As expected, the thermostability noted under nitrogen is higher when less oxidation reactions occurred (Table 4).

Furthermore, a slight decrease of the thermostability is obtained when the chlorine atoms were replaced by the iodine atoms due to the lower energy of C-I bond compared to that of C-Cl. This is clearly enhanced by the lowest thermostability of **$(F:Cl)_{0.03}$-co-$(F:I)_{0.97}$**, which possesses the highest content of iodine atoms. The glass transition temperatures were assessed for the five copolymers (Table 4) and ranged from 34 to 41 °C. As the molecular weight values of the five copolymers were similar (about 25,000 $g.mol^{-1}$), the evolution of the T_g values can be related to the iodine content. T_g values were plotted *versus* the molar contents of the iodine atoms, more precisely to the 2-iodoethyl vinyl ether molar content. Interestingly, a linear trend was obtained (Figure 8) from which the graphical equation may afford a theoretical determination of the T_g values, knowing both the molar contents of iodine atoms and the molecular weights of the copolymers.

CONCLUSION

Five fluorinated copolymers were synthesized by conventional radical polymerization of chlorotrifluoroethylene with vinyl ethers such as 2-chloroethyl vinyl ether and ethyl vinyl ether. The alternated behavior of this copolymerization led to a high amount of chlorine atoms in the side chains. That content was also monitored by incorporating a controlled amount of ethyl vinyl ether. Then, the chlorine atoms were quantitatively modified chemically into iodine atoms by nucleophilic substitution. These copolymers exhibit molecular weights values of ca. 25,000 $g.mol^{-1}$, which is satisfactory to process membranes. The main thermal degradation of the copolymers starts after 220 °C and is relatively dependent on the content of iodine atoms in the side chains. The T_g values ranged from 34 to 41 °C and were directly related to the content of the iodine atoms. A forthcoming paper will report the conversion of these iodine atoms into phosphonic groups, leading to original copolymers bearing fluorinated and phosphonic acid moieties, and the behaviors of the resulting membranes will be examined in term of their protonic conductivity.

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Table Captions

Table 1. Experimental conditions and compositions of poly(CTFE-alt-CEVE) and poly[(CTFE-alt-CEVE)-co-(CTFE-alt-EVE)] copolymers where CTFE, CEVE and EVE stand for chlorotrifluoroethylene, 2-chloroethyl vinyl ether and ethyl vinyl ether, respectively.

Table 2. Elemental analyses of poly(CTFE-alt-CEVE) and poly[(CTFE-alt-CEVE)-co-(CTFE-alt-EVE)] copolymers assuming alternating structures (where CTFE, CEVE and EVE stand for chlorotrifluoroethylene, 2-chloroethyl vinyl ether and ethyl vinyl ether, respectively)

Table 3: Molecular weights, polydispersity indices and thermal properties of poly(CTFE-alt-CEVE) and poly[(CTFE-alt-CEVE)-co-(CTFE-alt-EVE)] copolymers. $T_{d,\ i\%}$ stands for a thermal decomposition of i% of the copolymer at the corresponding temperature (where CTFE, CEVE and EVE stand for chlorotrifluoroethylene, 2-chloroethyl vinyl ether and ethyl vinyl ether, respectively)

Table 4: Iodine subsitution**,** molecular weights and thermal properties of poly(CTFE-alt-CEVE) and poly[(CTFE-alt-CEVE)-co-(CTFE-alt-EVE)] copolymers after nucleophilic subtitution with NaI (where CTFE, CEVE and EVE stand for chlorotrifluoroethylene, 2-chloroethyl vinyl ether and ethyl vinyl ether, respectively)

Figure Captions

Figure 1. Radical copolymerizations between chlorotrifluoroethylene and vinyl ethers (2-chloroethyl vinyl ether and ethyl vinyl ether) in 1,1,1,3,3-pentafluorobutane initiated with *tert*-butylperoxypivalate (TBPPI) (1% mol) at 75 °C.

Figure 2. ^{1}H NMR spectrum **(F:Cl)$_{0.56}$-co-(F:E)$_{0.44}$** copolymer (recorded in $CDCl_3$).

Figure 3. ^{13}C NMR spectrum of **(F:Cl)$_{0.56}$-co-(F:E)$_{0.44}$** copolymer (recorded in $CDCl_3$).

Figure 4. ^{19}F NMR spectrum of **(F:Cl)** copolymer (recorded in $CDCl_3$).

Figure 5. Nucleophilic substitution of poly(CTFE-alt-CEVE) and poly[(CTFE-alt-CEVE)-co-(CTFE-alt-EVE)] copolymers with NaI at 65 °C in acetone

Figure 6. ^{1}H NMR spectrum of **(F:Cl)$_{0.04}$-co-(F:E)$_{0.44}$-co-(F:I)$_{0.52}$** copolymer (recorded in $CDCl_3$).

Figure 7. Thermogravimetric analysis recorded under air of **(F:Cl)$_{0.03}$-co-(F:I)$_{0.97}$**, **(F:Cl)$_{0.41}$-co-(F:I)$_{0.59}$** and **(F:Cl)$_{0.05}$-co-(F:E)$_{0.64}$-co-(F:I)$_{0.31}$**

Figure 8. Tg value *vs* the iodine molar content for the poly(CTFE-co-VE) copolymers

Copolymers	Initial molar content (mol %)			Molar content in the copolymers (mol %)[a, b]			Massic yield (%)[c]
	CTFE	CEVE	EVE	CTFE	CEVE	EVE	
(F:Cl)	50	50	0	50	50	0	75
$(F:Cl)_{0.56}$-co-$(F:E)_{0.44}$	50	30	20	50	28[b]	22	70
$(F:Cl)_{0.36}$-co-$(F:E)_{0.64}$	50	20	30	50	18[b]	32	70

[a] Calculated from elemental analysis. [b] Calculated from ^{1}H NMR. [c] Experimental mass of the purified copolymer divided by the sum of the monomer masses

Table 1. Experimental conditions and compositions of poly(CTFE-alt-CEVE) and poly[(CTFE-alt-CEVE)-co-(CTFE-alt-EVE)] copolymers where CTFE, CEVE and EVE stand for chlorotrifluoroethylene, 2-chloroethyl vinyl ether and ethyl vinyl ether, respectively.

	(F:Cl)		$(F:Cl)_{0.56}$-co-$(F:E)_{0.44}$		$(F:Cl)_{0.36}$-co-$(F:E)_{0.64}$	
	cald	measd	cald	measd	cald	measd
% C	32.31	32.16	34.41	34.46	35.59	35.70
% H	3.16	3.09	3.54	3.62	3.76	3.85
% F	25.55	26.12	27.24	27.27	28.17	28.44
% Cl	31.75	30.62	27.15	26.87	24.57	24.39
% O	7.23	8.01	7.65	7.78	7.91	7.62

Table 2. Elemental analyses of poly(CTFE-alt-CEVE) and poly[(CTFE-alt-CEVE)-co-(CTFE-alt-EVE)] copolymers assuming alternating structures (where CTFE, CEVE and EVE stand for chlorotrifluoroethylene, 2-chloroethyl vinyl ether and ethyl vinyl ether, respectively)

	Mn (g/mol)	PDI	TGA under nitrogen		TGA under air		$T_{g,exp}$ (°C)
			$T_{d,5\%}$ (°C)	$T_{d,10\%}$ (°C)	$T_{d,5\%}$ (°C)	$T_{d,10\%}$ (°C)	
(F:Cl)	25 000	2.8	300	320	250	265	27
$(F:Cl)_{0.56}$-co-$(F:E)_{0.44}$	23 000	3.0	315	335	260	277	25
$(F:Cl)_{0.36}$-co-$(F:E)_{0.64}$	24 000	3.1	325	340	270	285	26

Table 3. Molecular weights, polydispersity indices and thermal properties of poly(CTFE-alt-CEVE) and poly[(CTFE-alt-CEVE)-co-(CTFE-alt-EVE)] copolymers. $T_{d,\,i\%}$ stands for a thermal decomposition of i% of the copolymer at the corresponding temperature (where CTFE, CEVE and EVE stand for chlorotrifluoroethylene, 2-chloroethyl vinyl ether and ethyl vinyl ether, respectively).

	Iodine substitution (mol %)		Mn (g.mol^{-1})	PDI	TGA under nitrogen		TGA under air		$T_{g,exp}$ (°C)
	theo	exp			$T_{d,5\%}$ (°C)	$T_{d,10\%}$ (°C)	$T_{d,5\%}$ (°C)	$T_{d,10\%}$ (°C)	
$(F:Cl)_{0.03}$-co-$(F:I)_{0.97}$	100	97	26 000	2.7	282	297	285	298	41
$(F:Cl)_{0.41}$-co-$(F:I)_{0.59}$	60	59	25 500	2.6	299	311	298	312	37
$(F:Cl)_{0.57}$-co-$(F:I)_{0.43}$	40	43	25 500	2.6	301	314	297	314	36
$(F:Cl)_{0.04}$-co-$(F:E)_{0.44}$-co-$(F:I)_{0.52}$	56	52	23 000	3.0	295	312	284	302	36
$(F:Cl)_{0.05}$-co-$(F:E)_{0.64}$-co-$(F:I)_{0.31}$	36	31	20 000	3.1	299	315	302	316	34

Table 4. Iodine subsitution**,** molecular weights and thermal properties of poly(CTFE-alt-CEVE) and poly[(CTFE-alt-CEVE)-co-(CTFE-alt-EVE)] copolymers after nucleophilic subtitution with NaI (where CTFE, CEVE and EVE stand for chlorotrifluoroéthylène, 2-chloroethyl vinyl ether, and ethyl vinyl ether, respectively)

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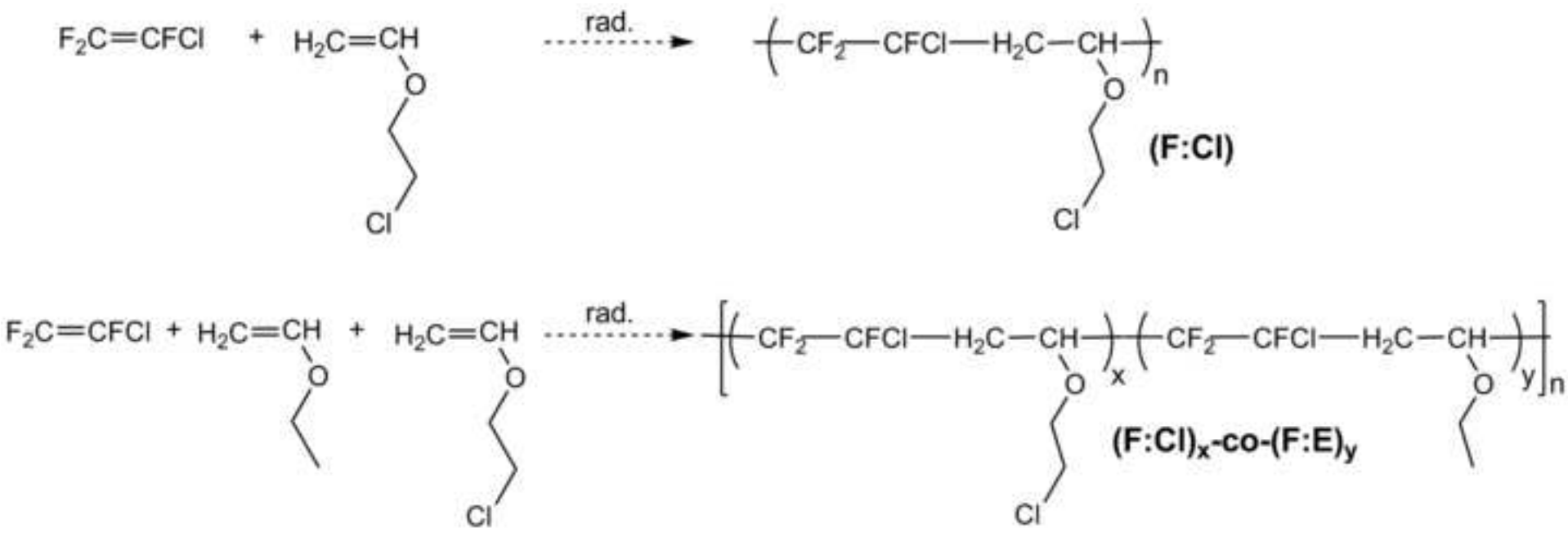

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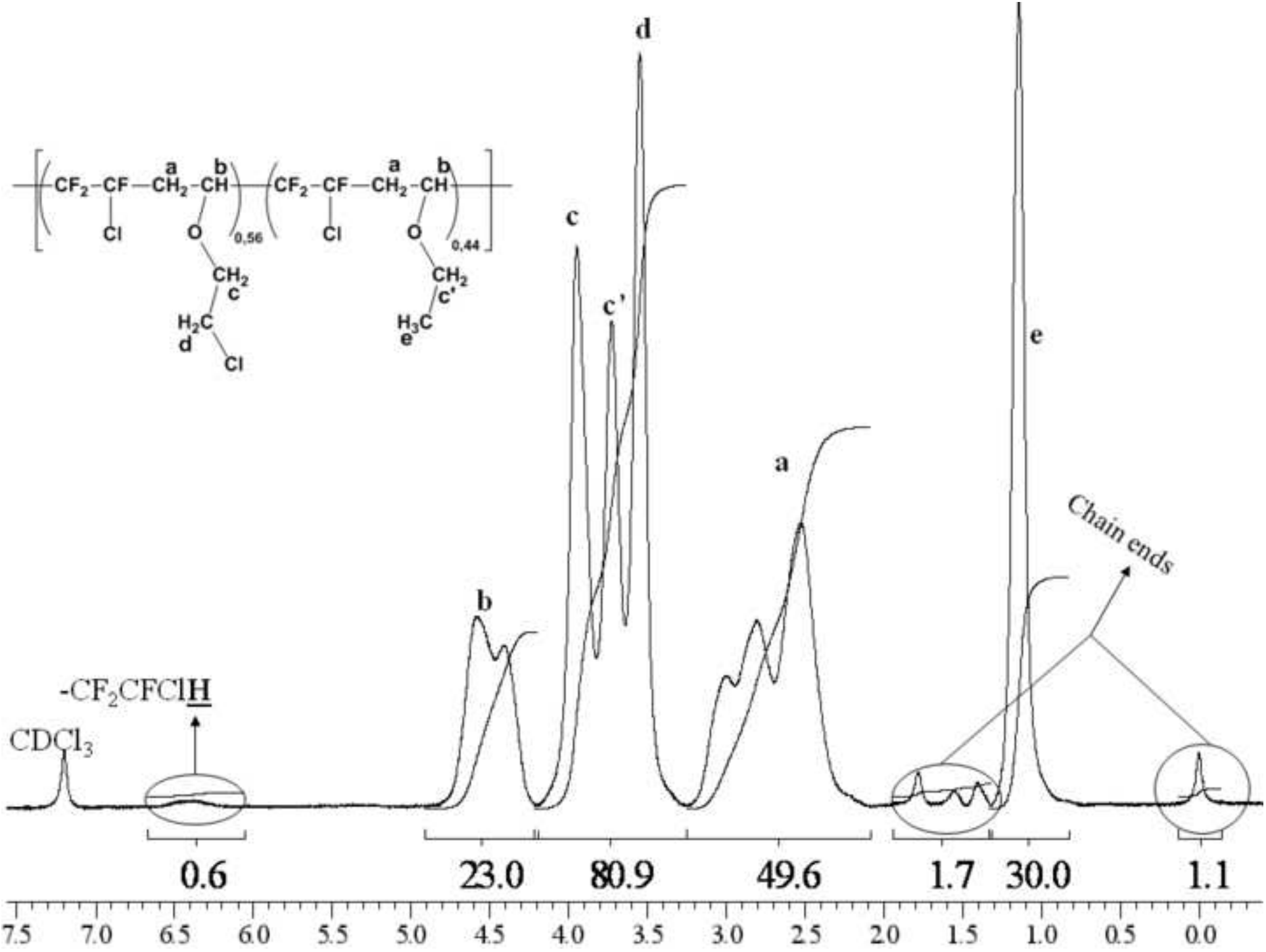

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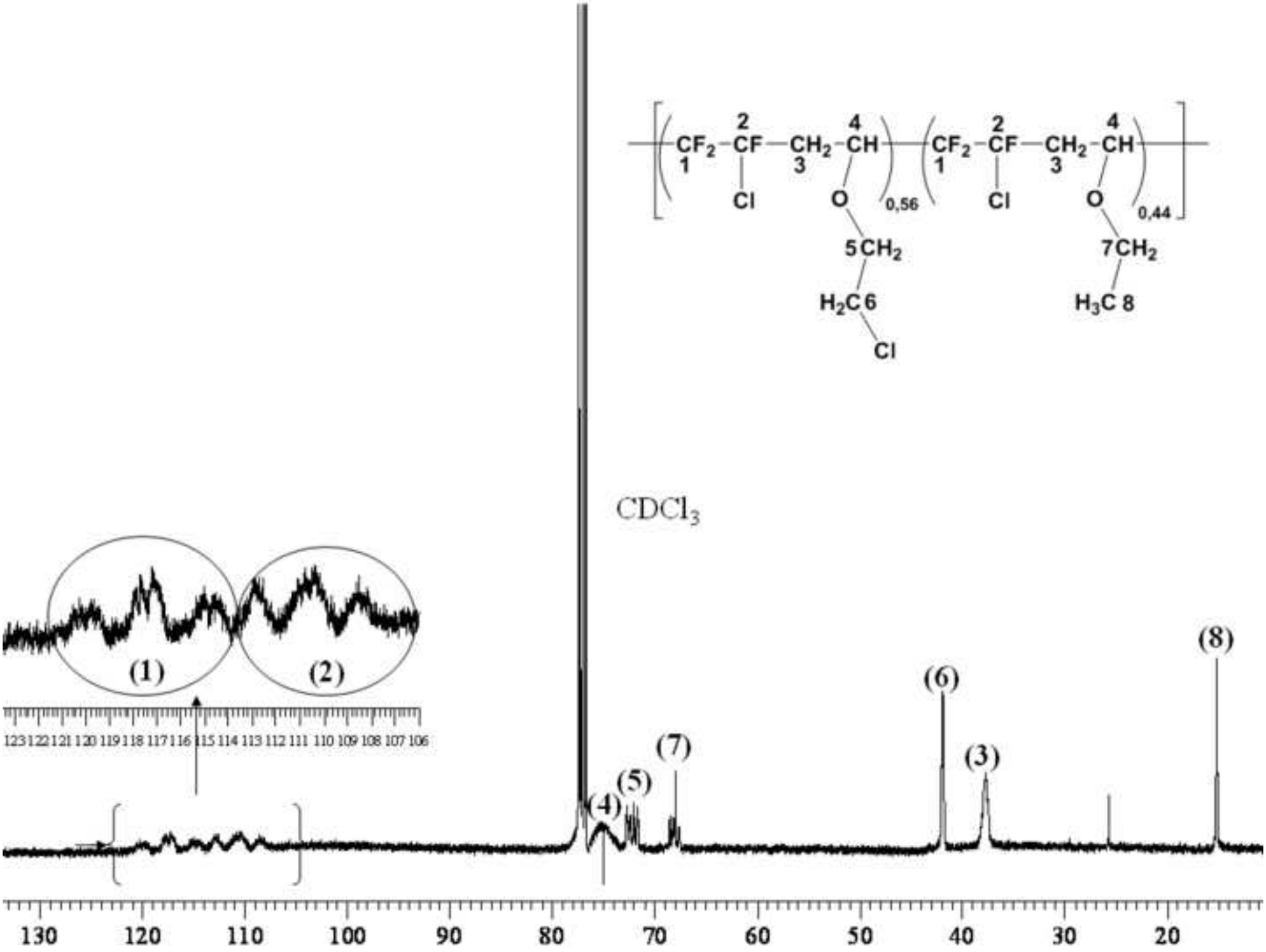

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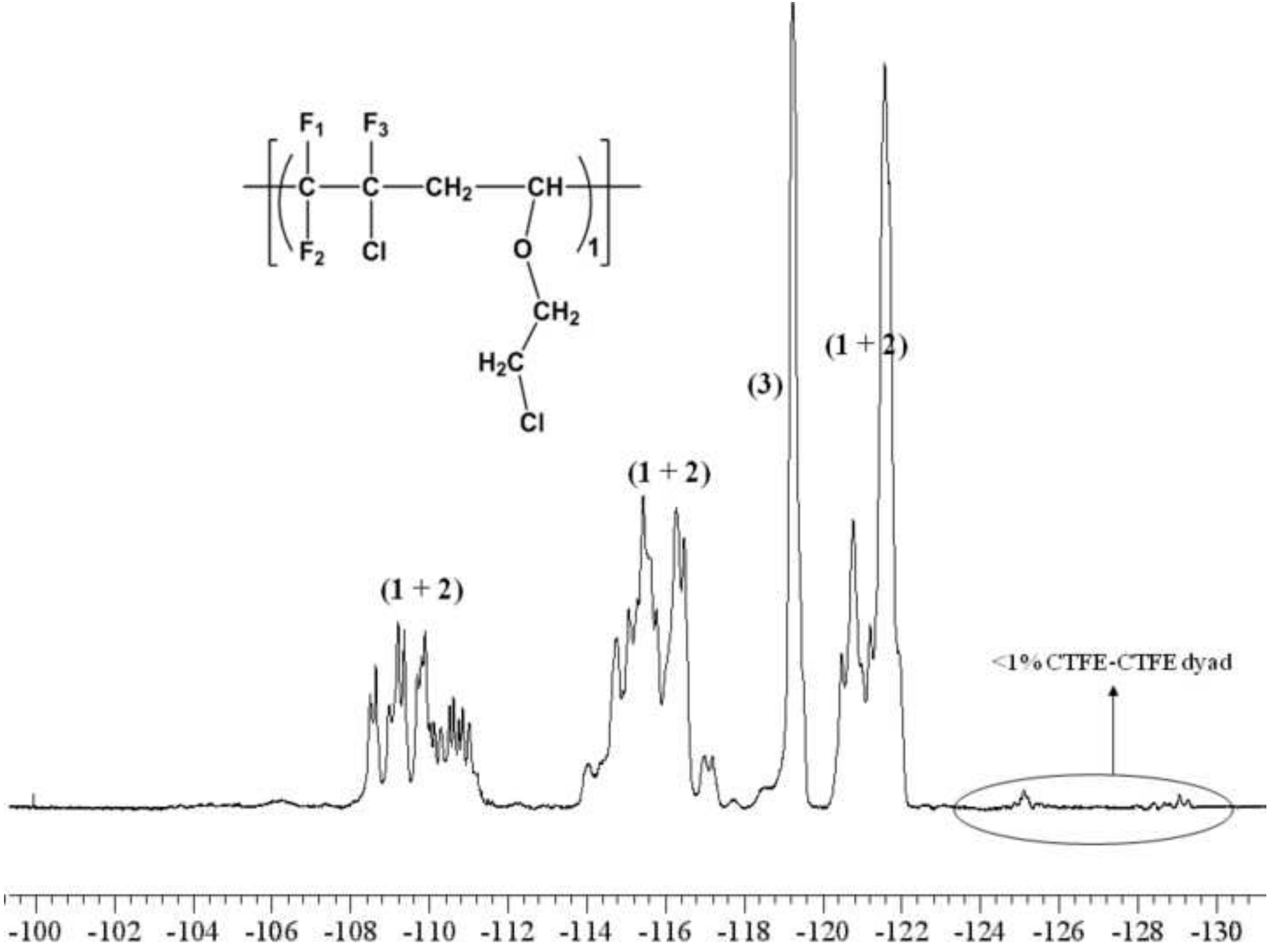

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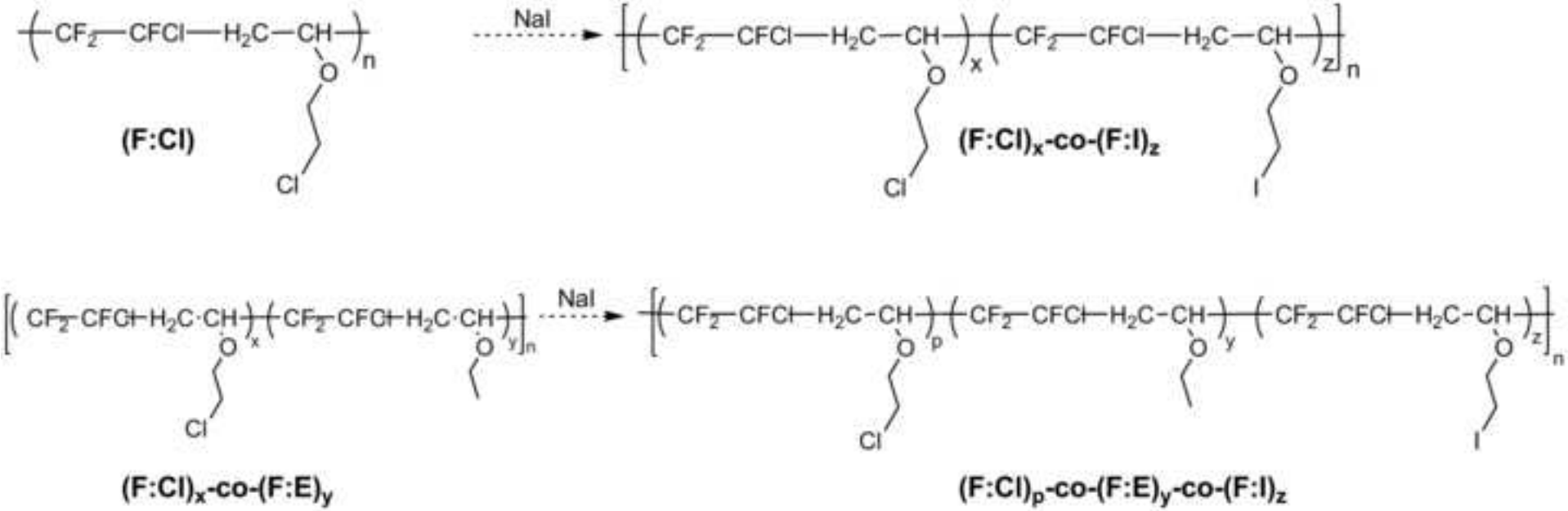

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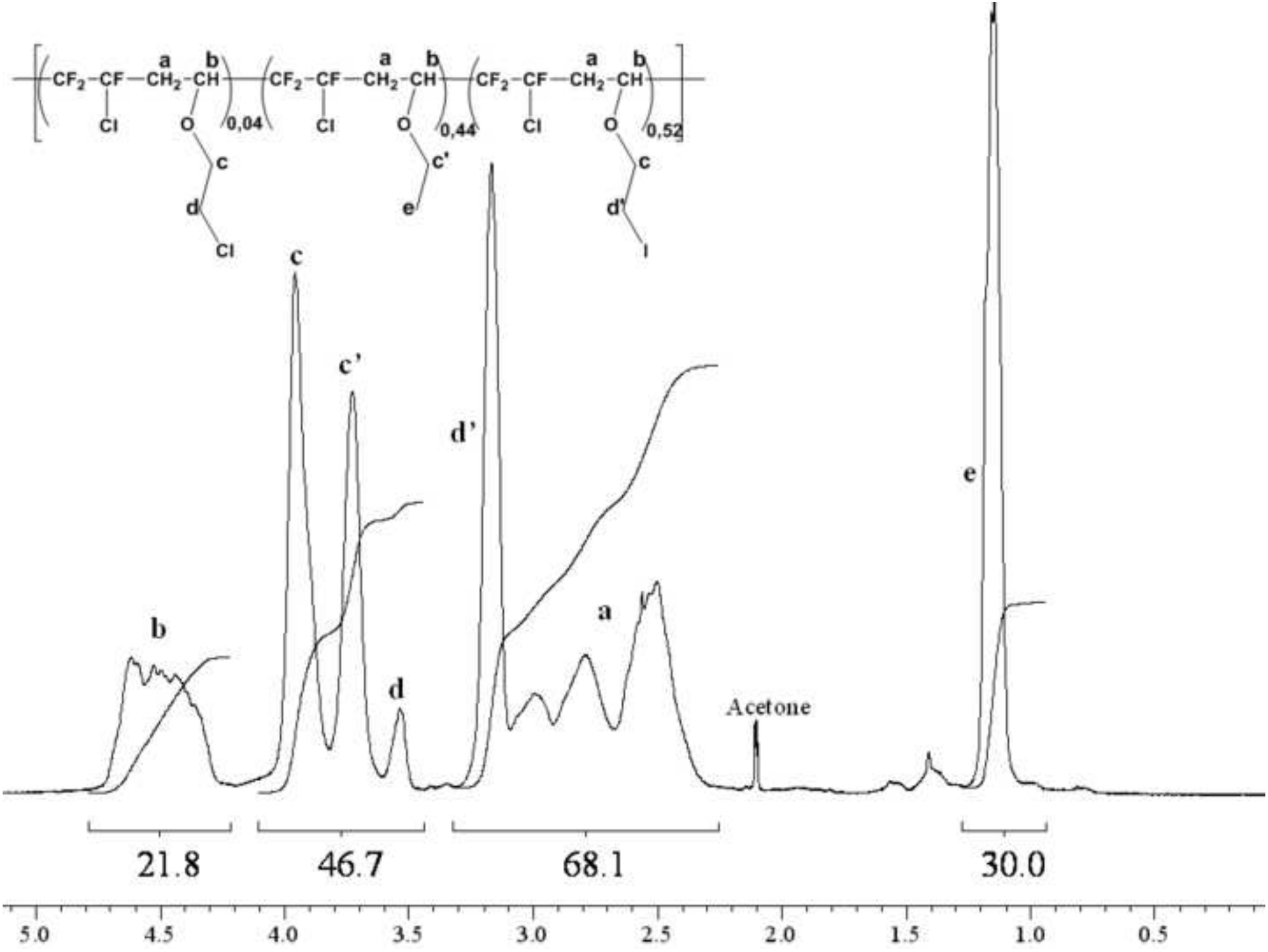

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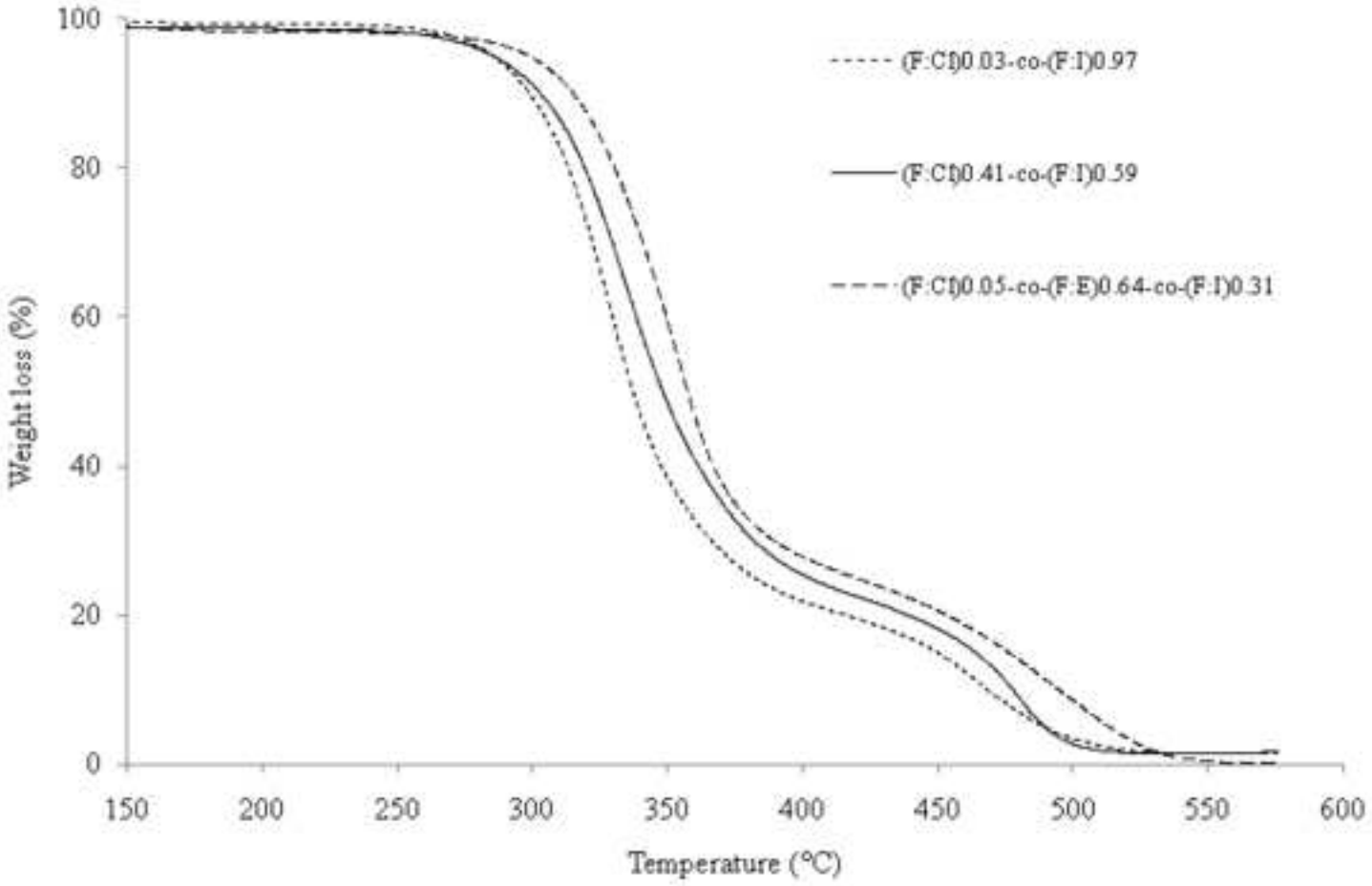
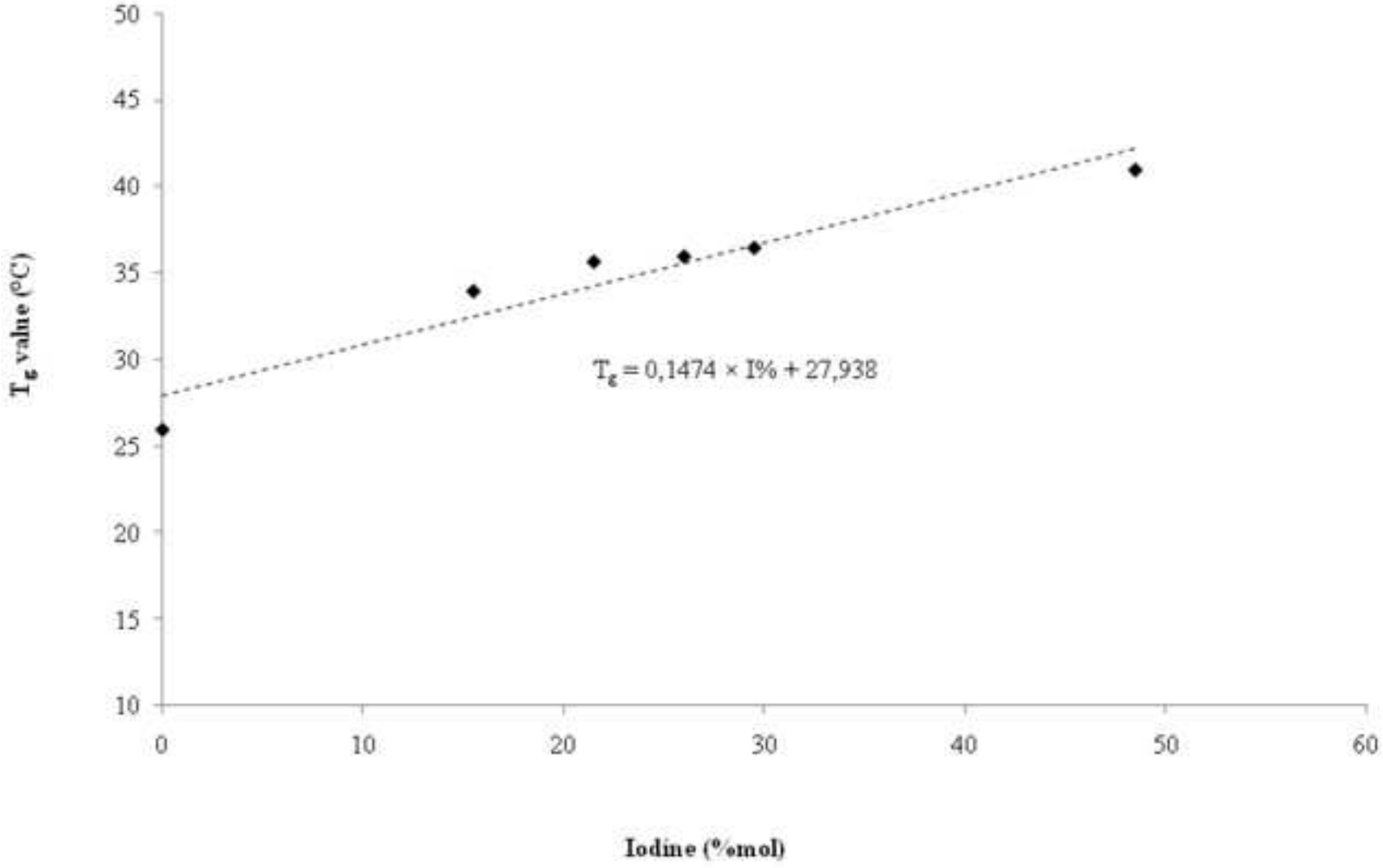
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