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Comprehensive Characterization of Chain End Groups of Vinylidene Fluoride Based Polymers

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Summary: In this work an investigation of the chain end groups produced in the free radical copolymerization of vinilydene fluoride (VDF) and hexafluoropropylene (HFP) is performed. Type and amount of chain end groups are evaluated by a meticulous analytical characterization of VDF/HFP copolymer. At first pulsed gradient spin-echo nuclear magnetic resonance (spin-echo NMR) is used to identify all the chain end groups also at very low concentration (equal to $0.1\,\mathrm{mmol}\cdot\mathrm{Kg}^{-1}$). The instrument sensitivity is increased of an order of magnitude in comparison with the traditional NMR. Moreover potentiometric titration and ion chromatography (IC) are also used to study the chain end groups and, as a consequence, the nature and the amount of the acidity showed by the polymer chains. In details two intensity of acidity are detected by potentiometric titration, namely strong and weak. The strong acidity is associated to the presence of residual surfactant and can be removed washing the polymer, while the weak acidity is due to free molecules of fluoride acid (HF). The standard ion chromatography facility is properly modified to quantify the fluoride in the polymer matrix without any pre extraction in water. Thanks to this the HF concentration in the polymer is evaluated with high accuracy. A detailed kinetic scheme for the VDF/HFP polymerization is also proposed taking into account all the findings obtained studying the chain end groups.

Keywords: chain end group; chromatography; fluoropolymers; kinetics; NMR

Introduction

Type and amount of chain end groups determines several key properties of polymer chains. Chemical and thermal resistance, as well as processing behavior and mechanical properties, are strongly affected by nature of chain end groups. This consideration is particularly true for fluorine based polymers such as fluoroelastomers. These materials are designed for demanding service applications thanks to their resistance to flame, chemical compounds and oxidative attack. The special properties own of fluoroelastomers are mainly related to the polymer backbone structure and in particular to the high carbon-fluorine bond dissociation energy (up to $130\,\mathrm{kcal}\cdot\mathrm{mol}^{-1}$). In this scenario chain end groups can play an important role.

The fluorinated polymers used to produce fluoroelastomers are usually synthesized via free radical emulsion polymerization at high pressure condition.[1] A well understanding of the reaction involved in the polymerization and of the related kinetics is important to control and adjust the molecular weight, the molecular weight distribution and the polymer chain structure also in terms of chain end groups.

One of the most common fluoroelastomers is based on the vinilydene fluoride/hexafluoropropylene (VDF/HFP) copolymer.[2]

The aim of this work was to develop an accurate characterization of chain end groups generated in the VDF/HFP copolymerization initiated by ammonium

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persulfate (APS).[3,4] Different analytical techniques, i.e. spin-echo nuclear magnetic resonance (spin-echo NMR), potentiometric titration and ion chromatography (IC), were used. Qualitative and quantitative characterization of both polar and non-polar chain end groups was done to provide a convincing validation of the initiation mechanism proposed in Figure 1.[5]

From a theoretical viewpoint the sulfate anion-radical coming from the thermal dissociation of APS can react with both VDF and HFP.[6] In particular two different additions, i.e. head-tail and head-head, are possible in the case of VDF. These addition reactions are followed by hydrolysis to form alcoholic or carboxylic chain end groups according to the scheme proposed in Figure 2.

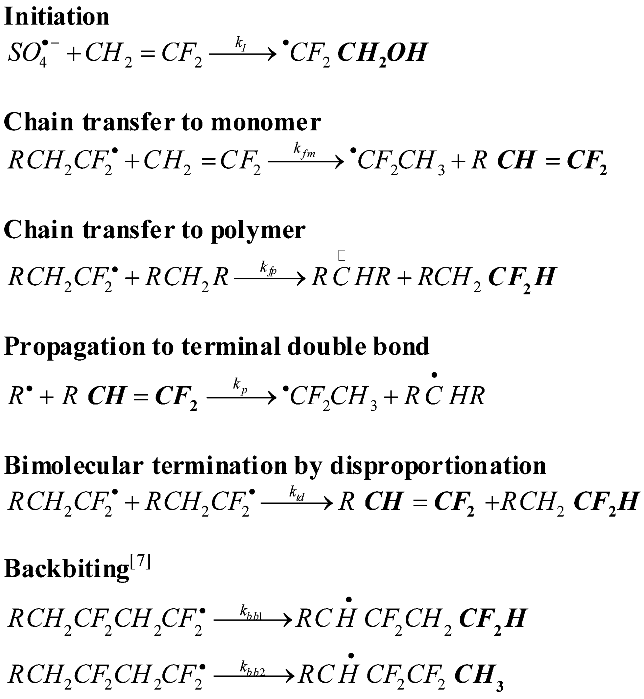
However the event probability is different between the three addition reactions. The HFP addition is the less favorite one due to the low solubility of HFP in water. In fact APS is a popular water soluble initiator and the initiation reaction takes place in water. In the case of VDF, the head-head addition represents only the 4–7% of the addition reactions, while the head-tail addition is the most favorite.[5]

According to the proposed mechanistic considerations, the initiation step is mainly described by the reaction proposed in Figure 1, while the alcoholic group is the only polar chain end groups presents in the system in a considerable and measurable amount.

In order to support these statements, the concentration of polar and non-polar chain end groups was determined by spin-echo NMR. Moreover a combination of potentiometric titration and IC was used to check the presence of possible unexpected carboxylic chain end groups.

Experimental Part

All NMR experiments were recorded on an Agilent System 500 operating at 499.86 MHz for ^{1}H and 470.30 MHz for



Initiation

$$SO_4^{\bullet -} + CH_2 = CF_2 \xrightarrow{k_I} {}^{\bullet}CF_2\,\mathbf{CH_2OH}$$

Chain transfer to monomer

$$RCH_2CF_2^{\bullet} + CH_2 = CF_2 \xrightarrow{k_{fm}} {}^{\bullet}CF_2CH_3 + R\,\mathbf{CH = CF_2}$$

Chain transfer to polymer

$$RCH_2CF_2^{\bullet} + RCH_2R \xrightarrow{k_{fp}} R\overset{\square}{C}HR + RCH_2\,\mathbf{CF_2H}$$

Propagation to terminal double bond

$$R^{\bullet} + R\,\mathbf{CH = CF_2} \xrightarrow{k_p} {}^{\bullet}CF_2CH_3 + R\dot{C}HR$$

Bimolecular termination by disproportionation

$$RCH_2CF_2^{\bullet} + RCH_2CF_2^{\bullet} \xrightarrow{k_{td}} R\,\mathbf{CH = CF_2} + RCH_2\,\mathbf{CF_2H}$$

Backbiting[7]

$$RCH_2CF_2CH_2CF_2^{\bullet} \xrightarrow{k_{bb1}} RC\dot{H}\,CF_2CH_2\,\mathbf{CF_2H}$$

$$RCH_2CF_2CH_2CF_2^{\bullet} \xrightarrow{k_{bb2}} RC\dot{H}\,CF_2CF_2\,\mathbf{CH_3}$$

Figure 1.
Reaction scheme for the VDF/HFP copolymerization. The produced polymer chain end groups are in bold.

VDF head-tail addition

$$SO_4^{\bullet -} + CH_2 = CF_2 \longrightarrow {}^{\bullet}CF_2CH_2SO_4^- \xrightarrow{H_2O} {}^{\bullet}CF_2CH_2OH + HSO_4^-$$

VDF head-head addition

$$SO_4^{\bullet -} + CF_2 = CH_2 \longrightarrow {}^{\bullet}CH_2CF_2SO_4^- \xrightarrow{2H_2O} {}^{\bullet}CH_2COOH + HSO_4^- + 2HF$$

HFP addition

$$SO_4^{\bullet -} + CF_2 = CF\left(CF_3\right) \longrightarrow \left(CF_3\right)\dot{C}\,FCF_2SO_4^-$$

Figure 2.

Possible addition reactions between the sulfate anion-radical ($SO_4^{\bullet -}$) and monomers in the VDF/HFP copolymerization initiated by APS.

^{19}F and equipped with a 5-mm triple resonance ^{1}H, ^{19}F, ^{13}C, ^{31}P PFG Agilent probe with a single axis (Z) gradient coil. Samples were dissolved in acetone-d$_6$ at about 10% $w_{polymer}/w_{acetone}$ and spectra were referenced against external $CFCl_3$. The following fluorine acquisition parameters were applied: sample temperature of 25 °C, sample spinning rate of 20 Hz, relaxation delay of 6.0 s, 90° flip angle corresponding to a pulse duration of 9.2 μs, 512 transients, and 65536 complex free induction decay (FID) data points acquired over a spectral width of 108696 Hz (acquisition time 0.6 s). The following proton acquisition parameters were applied: sample temperature of 25 °C, sample spinning rate of 20 Hz, relaxation delay of 5.0 s, 45° flip angle corresponding to a pulse duration of 4.5 μs, 1800 transients, and 16384 complex FID data points acquired over a spectral width of 8013 Hz (acquisition time 2.05 s). A distinct experiment fluorine decoupled were also recorded by applying a broadband WURST-40 decoupling scheme over a 20 KHz range during acquisition. Prior to Fourier transformation, all time domain data was processed with an exponential window function using a line broadening factor of 0.5. The spin-echo experiment was acquired with the Agilent built-in CPMGT2 sequence with the following acquisition parameters: sample temperature of 25 °C, no-sample spinning to avoid artifact, T_2 delay (τ) of 1 ms, and the pulse train repeated 350 times (n) yielding a total pulse train ($2\tau n$) of 700 ms, 2048 transients, and 7812 complex FID data points acquired over a spectral width of 5208 Hz (acquisition time 1.5 s). A broadband WURST-40 decoupling scheme over a 20 KHz range was also applied during acquisition. Prior to Fourier transformation, all time domain data was processed with an exponential window function using a line broadening factor of 0.5. Hz. In order to calculate the T_2 of repeating units and end-groups, the same CPMGT2 experiment were performed with an array of the total pulse train ($2\tau n$) from 64 ms to 4.096 s. Prior to Fourier transformation, all time domain data was processed with an exponential window function using a line broadening factor of 0.5 Hz and data were processed with a exponential curve fitting to determine the T_2 values of each requisite peak.

Titration was performed with a Metrohm titrator (model Titrando 904) equipped with a glass electrode. About 5 grams of polymer were first dissolved in acetone, than methanol was added to obtain a final solution 5% w/w concentrate. Solvent ratio was maintained 1:4. Solution obtained was then titrated with alcoholic TMAI 0,02N. Titration was also performed on washed polymer: polymer was dissolved in acetone, then coagulated in water and dried in oven at 40 °C under vacuum for 24 hours. Recovery of polymer was complete and it was dissolved once again in acetone and methanol solution.

Ionic Chromatography was also used to support titrimetric analysis. The selected column was a Dionex ion exchange column model AS14A. The instrument was modified with two pumps working together on the same circuit and with the aid of an additional pre column so as to inject in the column a solution of the VDF/HFP copolymer in an organic solvent. The instrument used was a Dionex ion chromatography ICS3000, detection is on conductibility with chemical suppression. Standardization was done in the same solvent mixture of the sample and fluoride standard solution was prepared at about 1000 ppm in isopropyl alcohol.

Results and Discussion

NMR Analysis

At first ^{19}F NMR was used to determine the VDF/HFP copolymer composition.[7] A fluorine spectrum characteristic of the VDF/HFP copolymer is shown in Figure 3a.

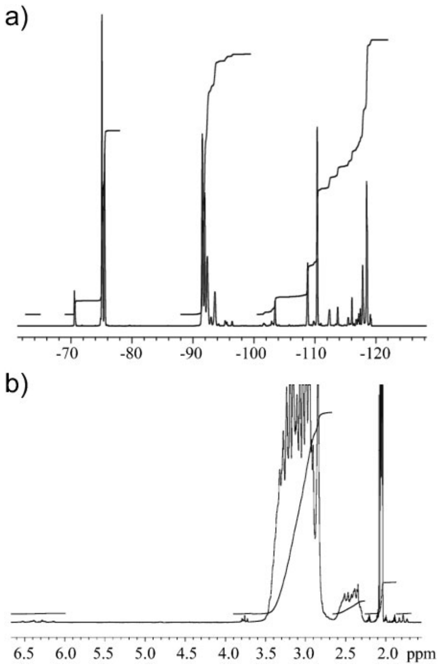


Figure 3.
NMR spectra characteristic of VDF/HFP copolymer: a) ^{19}F NMR, b) ^{1}H NMR.

Although the ^{19}F NMR technique is useful to study the polymer structure, the evaluation of chain end groups can not be quantitative in this system due to the presence of an overcrowded region in the fluorine copolymer spectrum. Fortunately as shown in Figure 1, the chain end groups under investigation contain hydrogenated moieties that can be detected with standard ^{1}H NMR technique. A proton spectrum characteristic of the VDF/HFP copolymer is shown in Figure 3b.

As expected, two complex systems were observed in the ^{1}H NMR spectrum.[8–12] The first is centered at 3.1 ppm and it belongs to the methylene groups of the VDF head-tail addition, while the second one is centered at 2.45 ppm and it is related to the VDF head-head addition. Moreover the spectrum in Figure 3b shows other peaks belonging to the different chain end groups, e.g. CF_2H, CH_2OH and CF_2CH_3.

A fluorine-decoupled proton spectrum was acquired to better understand the spectrum. In this way all the signals and their chemical shift were detected with higher accuracy.

As showed in Figure 4, it was found that the CF_2H end group is composed by three different systems, centered at 6.26, 6.30 and 6.36 ppm respectively. The splitting patterns of these signals are triplets ($^{2}J_{HF} = 54.8$ Hz) of triplets ($^{3}J_{HH} = 4.5$ Hz), , confirming the connection of the terminal proton in the CF_2H coupled with a methylene group in β-position. With regard to the CF_2CH_3 chain end group, ^{1}H NMR showed a methyl group coupled with a difluoromethylene one with a resonance at 1.79 ppm and characterized by a triplet ($^{3}J_{HF} = 19.0$Hz). Instead no signal was found at the expected chemical shifts of 5.2 ppm, i.e. $CF_2CH=CF_2$ group,[13] or 4.3 ppm, i.e. $CF_2CF(CF_3)CH=CF_2$ group.[14] Moving to the alcoholic polar end group CH_2OH, it was detected as triplet ($^{3}J_{HF} = 13.3$Hz) centered at 3.78 ppm. This finding confirms the proximity between the CH_2OH group and the difluoromethylene ones. No other signals belonging to polar or non-polar end-groups

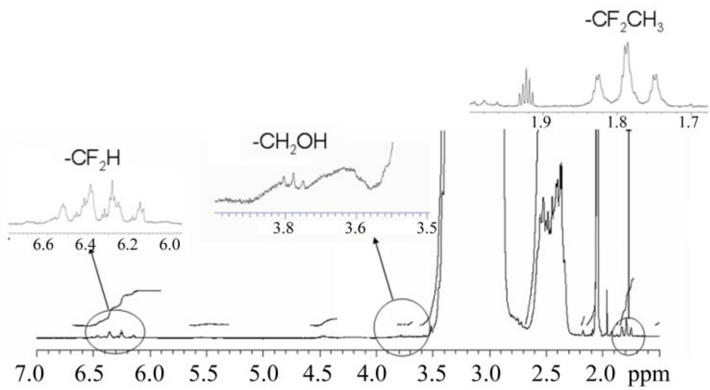


Figure 4.
^{1}H NMR spectrum characteristic of VDF/HFP copolymer. Highlight on sections related to the CF$_2$H, CH$_2$OH and CF$_2$CH$_3$ end groups.

were observed in this analytical investigation.

Focusing on the CF$_2$CH$_2$OH chain end moiety, relevant limits to its quantification were found: the low intensity of the connected signal and the overlap of this signal with the ones of the VDF monomer unit. The spin-echo technique was used in order to overcome these drawbacks.[15] The analysis was performed with the aim to reduce the fast relaxing signals belonging to the polymer backbone more than the ones of the terminal protons.[18,19] A fluorine decoupling scheme was applied simultaneously to maximize the chain end groups intensity and to reduce the overlap with other signals.

The complete assignment of the VDF/HFP copolymer proton spectrum is collected in Table 1 together with the relative T$_2$ determined by CPMGT2 experiments.[16,17] A comparison between NMR spectra determined without and with the fluorine-decoupled spin-echo technique is showed in Figure 5a and 5b respectively.

A well defined spectrum was obtained as a result, making possible an accurate peak integration. In the spin-echo experiment the signal intensity of each peak was reduced by a factor T$_2$-dependent. This intensity was predicted solving the Bloch equation[20] and it was used to calculate the concentration of the chain end group i (C_i) as a function of the polymer amount (Equation 1).

$$C_{(i)} = 10^6 \cdot \frac{\chi_{VDF} \cdot I_i}{I_{VDF} \cdot Av.P.U.} \tag{1}$$

In Equation 1, C_i is expressed in $\mathrm{mmol} \cdot \mathrm{Kg}^{-1}$, χ_{VDF} is the VDF molar fraction determined by the fluorine spectrum, I_i is the normalized integrated intensity of the chain end group i, I_{VDF} is the normalized integrated intensity of the VDF head-tail and head-head additions, $Av.P.U.$ is the Averaged Polymeric Unit

Table 1.
Assignment of ^{1}H-NMR peaks in ppm and related T$_2$ values in s. Signal expressed in Hz.

^{1}H-NMR	Signal	Attribution	T$_2$
1.79	t, $^3J_{HF} = 19$	$-CF_2\mathbf{CH_3}$	1.75
3.78	t, $^3J_{HF} = 13.3$	$-CF_2\mathbf{CH_2OH}$	1.74
6.26/6.30	tt, $^2J_{HF} = 54{,}8$	$-\mathbf{CF_2H}$	n.d.
6.36	$^3J_{HF} = 4{,}5$		
2.7–3.5	b.s.	VDF head-tail addition	0.51
2.3–2.6	b.s.	VDF head-head addition	0.30

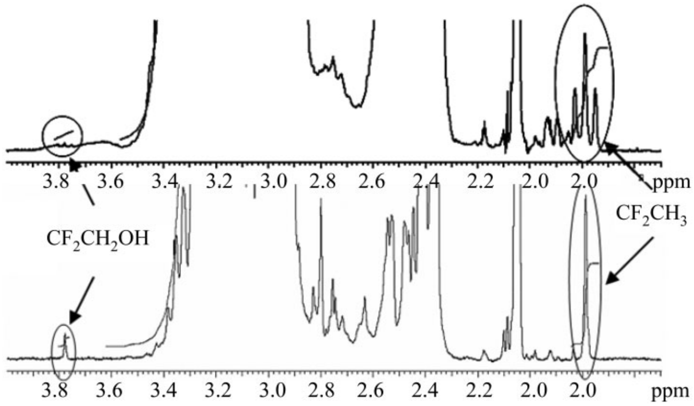


Figure 5.
Section of the VDF/HFP copolymer ^1H NMR spectra obtained with standard condition (a) and by the use of fluorine-decoupled spin-echo.

expressed as in Equation 2.

$$Av.P.U. = \sum \chi_i \cdot MW_i \qquad (2)$$

where χ_i and MW_i are respectively the molar fraction and the molecular weight of the monomer i estimated by the fluorine spectrum.

Thanks to this analytical approach superimposed signals were detected making possible the quantification of chain end groups present in the system at very low concentration (C_i equal to 0.1 $mmol \cdot Kg^{-1}$).

Potentiometric Titration

According to the consideration proposed in the Introduction, only the alcoholic group is present in the system as polar chain end group, while carboxylic chain end groups can not be present in relevant concentration due to mechanistic reasons.

A titrimetric analysis was performed with the aim to validate and to support this thesis. The result of the study on VDF/HFP copolymer based on potentiometric titration is reported in Figure 6. The analysis shows some structures characterized by a strong acidity (i.e., EP1 at 230 mV) and other different structures with a weaker acidity (i.e., EP2 at −50 mV).[21,22] The reproducibility of the measure was also investigated. Data are reported in Table 2. The weak acidity value was calculated by subtracting from EP2 value both EP1 and the solvent blank. An average value of 7.97 $meq \cdot kg^{-1}$ with a standard deviation of 0.6 was found in the repeated measurement.

To study the nature of the detected acidity, the polymer matrix was washed with water and the titration was repeated after each wash cycle. It was observed that the strong acidity completely disappears after a couple of washes, while the weak one decreases up to an asymptotic value (Figure 7). According to these findings it is reasonable to conclude that both the acidities are due to free acid molecules inside the polymer matrix and not to acid group bonded to the polymer chains. In particular the residual acidity showed in Figure 7 can be related to the presence of

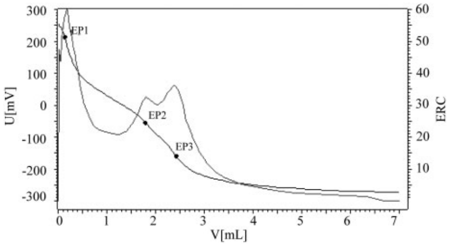


Figure 6.
Potentiometric titration of VDF/HFP copolymer with alcoholic TMAI 0.02 N.

Table 2.
Potentiometric titration data Titration method reproducibility.

polymer solution g	polymer g	EP1(230mv) mL	EP2 (-150mv) mL	weak acids $meq \cdot kg^{-1}$
50.041	5.0041	0.1487	2.4591	8.04
50.014	5.0014	0.1446	2.4266	7.93
50.0016	5.0016	0.1396	2.425	7.94

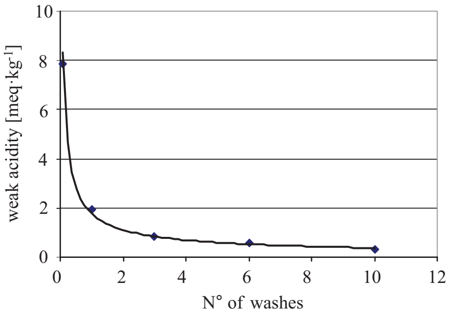


Figure 7.
Weak acidity amount as a function of wash cycles.

fluoride acid (HF) only partially removed thorough washes with water. A ionic chromatography analysis was performed to support this conclusion.

Ionic Chromatography

HF quantification in the polymer matrix was done by ionic chromatography.[23] This technique is commonly known as a separation technique able to determine the concentration of ions dissolved in water. As described in the Experimental section an appropriate method oriented to the HF quantification was developed in this work. In particular the proposed approach allows to quantify fluoride in the polymer directly without any pre-extraction with water.

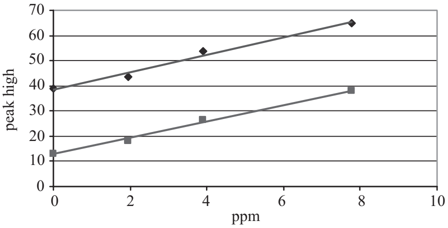


Figure 8.
Fluoride concentration calibration curves in the solvent mixture (■) and in the polymer matrix (◆).

The instrument calibration was performed to validate the analytical procedure. The calibration curves produced both in the solvent and in presence of the polymer matrix are showed in Figure 8. R^2 index around 0.99 was obtained in both cases. Moreover the fluoride response factor was the same in the two conditions. On the base of this calibration, the VDF/HFP polymer matrix was consistently analyzed. Data are collected in Table 3, while a representative fluoride chromatogram is showed in Figure 9.

Data collected in Table 3 show a good reproducibility of the measurement. An average value of $7.81\,meq \cdot kg^{-1}$ with a standard deviation of 0.37 was found.

Comparing the weak acidity average value determined by potentiometric titra-

Table 3.
Fluoride concentration in the polymer matrix, determined by ionic chromatography.

peak high	peak high-blank	fluoride concentration		
		$\mu g \cdot mL^{-1}$	$\mu g \cdot g^{-1}$	$meq \cdot kg^{-1}$
41.4347	26.6489	7.907685	154.5798	8.14
44.8795	26.7342	7.929938	155.0148	8.16
42.9497	25.905	7.683979	150.2068	7.91
39.9906	24.6103	7.299944	142.6997	7.51
39.622	24.0642	7.137959	139.5332	7.34

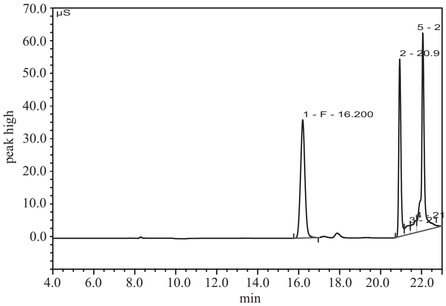


Figure 9.
Representative chromatogram of fluoride in the polymer matrix.

tion (i.e., 7.97 $\text{meq} \cdot \text{kg}^{-1}$) with the fluoride concentration average value determined by ionic chromatography, it is reasonable to conclude that the whole contribution to the residual weak acidity detected by potentiometric analysis is due to the inclusion of HF within the polymer matrix. This finding confirms that the acidity measured in the VDF/HFP copolymer is due to free acid molecules. Moreover it validates the initiation mechanism proposed in the Introduction and the statement about the absence of carboxylic chain end group in the system.

Conclusion

A detailed investigation of the chain end groups produced in the VDF/HFP free radical copolymerization was performed in this work. Chain end groups were detected at very low concentration (equal to 0.1 $\text{mmol} \cdot \text{Kg}^{-1}$) thanks to spin-echo NMR technique. The nature of the acidity showed by the polymer matrix was investigated combining potentiometric titration with ionic chromatography measurement. The findings obtained in this analytical work permit to conclude that the CH_2OH alcoholic group is the only polar chain end groups in the VDF/HFP copolymer, while the CH_2COOH carboxylic chain end group is virtually absent and in any case not detectable. Moreover an initiation mechanism based on the VDF head-tail addition to sulfate anion-radical was convincing validated.

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