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Study of vinylidene fluoride (VF_2) telomerization and cotelomerization. Part II. VF_2 and chlorotrifluoroethylene (CTFE) cotelomerization with 2-hydroxyethylmercaptan by radical initiation

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Abstract

The radical telomerization of vinylidene fluoride (VF_2) and of chlorotrifluoroethylene (CTFE) with 2-hydroxyethylmercaptan as the telogen was investigated. The corresponding homotelomers $R—S—(CF_2—CFCl)_n—H$ (C_n) and $R—S—(CH_2—CF_2)_n—H$ (V_n) with $R = —CH_2CH_2OH$ were synthesized and the 1:1 adducts identified. The VF_2/CTFE/thiol reaction gave a mixture of the expected products, homotelomers and cotelomers. By various methods, mainly by ^{19}F NMR spectroscopy, the chain length and tacticity of these telomers were determined. For example, after analysis, a fraction of the cotelomers was in good agreement with the general formula $HO—CH_2—CH_2—S—(CF_2—CFCl)_x—(CH_2—CF_2)_y—H$, with x and y close to 4. Moreover, by comparison with the spectra of homotelomers of VF_2 and CTFE, it was shown that these cotelomers exhibit an alternating structure.

Keywords: Telomerization; Cotelomerization; Vinylidene fluoride; Chlorotrifluoroethylene; 2-Hydroxyethylmercaptan; NMR spectroscopy

1. Introduction

Previous work from this laboratory [1,2] described the cotelomerization of fluorinated and vinyl monomers with thiols as telogens. Copolymers of VF_2 with CTFE have been well known for a long time and they are mainly prepared to be used as elastomers. For example, Kel-F (3M), Voltalef (Elf-Atochem) and SKF 32 (Russian product) are commercially available copolymers [3]. However little work details the cotelomerization of these two monomers. Barnhart [4] used thionyl chloride as the telogen to obtain $Cl—(VF_2—CTFE)_n—Cl$ ($n < 10$) while Hauptschein and Braid [5] prepared cotelomers with CF_3I by thermal initiation (185 °C) for 110 h. In a second patent, the same authors [6] described the use of $C_2Cl_2F_3I$ (adduct of ICl on CTFE) as the telogen and obtained $C_2Cl_2F_3—(CTFE)_m—(VF_2)_n—I$ where the $m+n$ mean value was ca. 6.5. Furakawa [7] used R_FI and $IR_F'I$ as the telogens (R_F and R_F' are perfluorinated chains of 1–8 carbons), leading to high molecular weight cotelomers without any functional group.

Recently, Brace [8] gave a complete list of work on the radical addition of ethane thiols to different kinds of monomers and Japanese work [9] describes the synthesis of cotelomers with the composition $CH_2{=}C(CH_3)CO_2CH_2—[(VF_2)_x—(TFE)_y—(CTFE)_z]_n—H$ with $\bar{M}_n$ about 1000. The main product, in this case, is prepared by cotelomerization of the fluorinated monomers with methanol as the telogen.

Our present paper describes the reaction of CTFE and VF_2 with 2-hydroxyethylmercaptan.

2. Experimental details

VF_2 cotelomerizations were carried out in a 1 l volume, high-pressure reactor, Hofer type, made of Inox with the inside layer of tantalum. Stirring was magnetic. Heating was controlled and could be programmed while the pressure could be read directly by a manometer. By double weighing, suitable quantities of gases were introduced under pressure.

One example of the reaction was conducted as follows. The different products were introduced in the order, 410 g (10 mol) acetonitrile, 7.8 g (0.1 mol) thiol, 3.03 g (10^{-2} mol) Bz_2O_2, 45 g (0.70 mol) VF_2 and 75 g (0.39 mol) CTFE (the last two products were donated by the Atochem Company. The authors thank the Elf-Atochem Company for this

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gift). After 4 h heating at 80 °C with stirring, the reaction was stopped. After evaporating the solvent and the unreacted gases, the reaction products were distilled in vacuum and analyses were made on each fraction and on the residues. Several experiments have been made in the same conditions, just changing the Bz_2O_2 quantity and the reaction time. The yields never reached more than 25%, with the same products produced each time as shown by analysis.

NMR spectra were recorded on a Bruker CW-80 or AC-250 spectrometer with TMS as reference for ^1H and $CFCl_3$ as reference for ^{19}F. Chemical shifts (δ) are downfield from TMS and upfield (negative in value) for $CFCl_3$ and are reported in ppm. Coupling constants (J) are reported in hertz (Hz). All spectra were recorded in $CDCl_3$ solutions, the data obtained being reported on Figs. 1, 3, 4 and 5 below.

Molecular weights are compared by GPC with a Waters Associate Model 5900 chromatograph, equipped with 3 μm Styrogel columns (1000, 500 and 100 Å). The detector was a Water Associates R401 differential refractometer and THF was used as the eluant. Gas chromatographic analyses have been obtained on a Delsi F30 apparatus, using OV1 columns 1 m in length.

Elementary analyses were performed by the Central Microanalysis Service of CNRS, Montpellier Division of ENSCM.

3. Results and discussion

Firstly we prepared the VF_2 telomers (V_n) and the CTFE telomers (C_n) with 2-hydroxyethylmercaptan as the telogen as models for identifying the different cotelomerization products. The general formulae of these telomers were $R—S—(CF_2—CFCl)_n—H(C_n)$ and $R—S—(CF_2—CH_2)_n—H(V_n)$ with $R = —CH_2CH_2OH$.

We have previously described the V_n telomers [1] but of the C_n products only the C_1 member has been described [10,11]. We also noted that with VF_2 similar telomers have been obtained with $C_6F_{13}C_2H_4SH$ as the telogen [12].

The cotelomerization was performed in a high-pressure reactor with benzoyl peroxide (Bz_2O_2) as initiator and acetonitrile as the solvent at 80 °C for 4 hours. The following initial conditions were employed: $[CTFE]_0 \simeq [VF_2]_0$; $R_0 = [HOC_2H_4SH]_0/([CTFE]_0 + [VF_2]_0) = 10^{-1}$ and $C_0 = [Bz_2O_2]_0/([CTFE]_0 + [VF_2]_0) = 10^{-2}$.

The crude product was distilled in order to separate the first adducts. Different fractions were weighed and analyzed (Table 1) indicating that products $P(x,y)$ were obtained with the formula $R—S—[(CTFE)_x—(VF_2)_y]—H$ in which the CTFE and VF_2 units were randomly distributed.

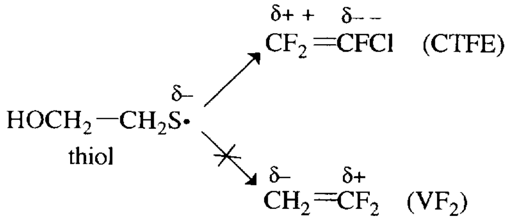
The two first products obtained by distillation were the monoadducts C_1 and V_1 of each monomer with 2-hydroxyethylmercaptan. These adducts may also be designated as P(1,0) and P(0,1).

The third product isolated [P(1,1)] was characterized by NMR spectroscopy. Elemental analysis indicated the addition of the thiol on each of both monomers. Provided such addition occurs normally, two main possibilities of structures are possible: $R—S—CF_2—CFCl—CH_2—CF_2H$ (**a**) and $R—S—CH_2—CF_2—CF_2—CFClH$ (**b**).

The ^1H NMR spectrum shows two triplets ($J = 6.2$ Hz) at δ 3.9 and 3.1 ppm characteristic of the methylene group α to the oxygen and the sulphur respectively, of the $—SCH_2CH_2OH$ group derived from the telogen. But the mode of addition is clearly demonstrated by the triple ($J = 4.3$ Hz) triplet ($J = 54.9$ Hz) at δ 6.2 ppm. This signal is characteristic of a $—CH_2—CF_2H$ end-group, and so the structure of P(1,1) is **a** depicted above.

The ^{19}F NMR confirms the above assignment. The three signals at ca. δ −86, −114 and −120 ppm correspond to the CF_2 group of CTFE, the CF_2 group of VF_2 and the CFCl group of CTFE, respectively. The AB system centred at δ −85 ppm (Fig. 1) is not split by hydrogen or fluorine atoms, so this difluoromethylene group belongs to the CTFE unit as depicted in structure **a**. All the NMR characteristics are summarized in Table 2.

This conclusion is in good agreement with the electronic effects. CTFE and VF_2 are two monomers with a poor electrophilic character, especially CTFE.



So the thiol radical (RS•) is added mainly to a CTFE unit which is the more nucleophilic. In contrast, with another

Table 1
Molar and weight compositions of the crude product arising from the cotelomerization of VF_2 and CTFE with 2-hydroxyethylmercaptan

Product designation	Molecular formula of product ($R = HOCH_2CH_2—$)	Weight composition W_i (g)	Weight composition (%)	Molar composition, N_i (%)
P(0,1)	$R—S—CH_2CF_2H$	1.42	4.6	13.8
P(1,0)	$R—S—CF_2CFClH$	3.7	12	26.2
P(1,1)	$R—S—(CTFE)—(VF_2)—H$	3.55	11.5	18.6
P(x,y)	$R—S—[(CTFE)_x—(VF_2)_y]—H$	22.15	71.9	41.4 [a]

[a] Calculated using $\bar{M}_n = 750$.

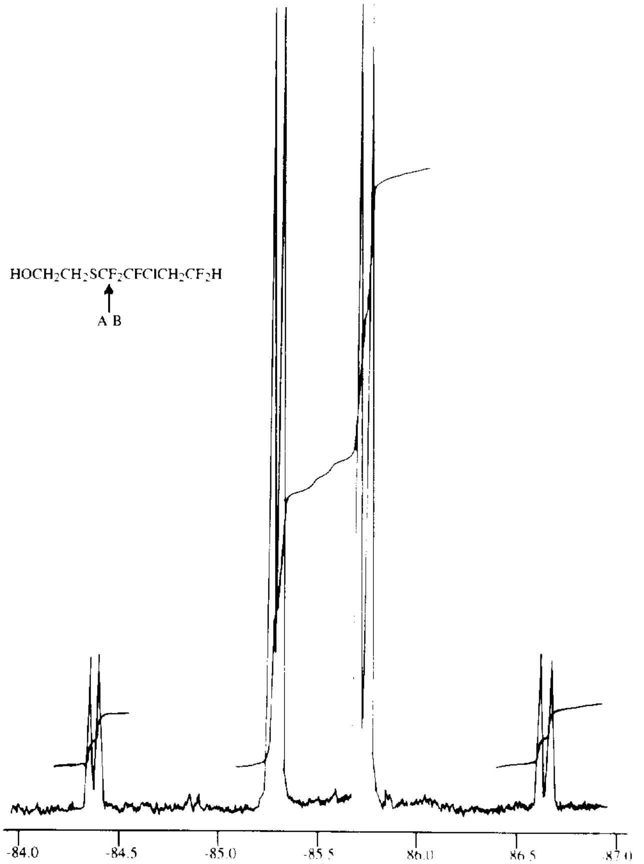


Fig. 1. ^{19}F NMR spectrum of cotelomer P(1,1) (expansion of the AB part of the CTFE unit).

electrophilic radical ($C_4F_9\cdot$), Balague [13] showed that this radical reacts only with VF_2 units and not with CTFE during the telomerizations of these two monomers. From the electronic effects of the thiol radical and the two monomers, we can explain the result of the first addition of the thiol on to CTFE which leads to structure **a**.

The residue of distillation was carefully analysed. The titration of OH groups led to an M_n value of 750. Using GPC methods, we have compared the chromatogram of the $P(x,y)$ $(x,y > 1)$ residue to that of the previously identified P(1,1) product (Fig. 2). The two chromatograms are in good agreement with the expected increase in weight of the residue. Elemental analysis shows: C, 27.67; H, 1.85; F, 47.93; Cl, 17.46%.

From these values and from the expected structure of $P(x,y)$, it can be written:

$$\frac{57x+38y}{78+116.5x+64y}=0.4793$$

and

$$\frac{35.5x}{78+116.5x+64y}=0.1746$$

Solution of these equations gives $x=4.2$ and $y=4.45$. So, by elemental analysis $M_n=840$ is obtained, which is close to the value from the OH titration methods.

Concerning the reactivity parameters of (r^a, r^b) relating to the copolymerization, few examples are quoted in the literature. Moggi et al. [14] gave the two values $r^a_{VF_2}=0.73$ and $r^a_{CTFE}=0.75$ and in the *Encyclopedia of Polymer Science and Technology* [15] the values $r^b_{VF_2}=0.17$ and $r^b_{CTFE}=0.52$ are given.

The monomer reactivity ratios could be used to calculate the molar fractions of the various monomer diads. Thus:

$$f(1,1)=\frac{p(1,1)\times p(2,1)}{p(1,2)+p(2,1)} \quad \text{and} \quad f(2,2)=\frac{p(2,2)\times p(1,2)}{p(1,2)+p(2,1)}$$

from which

$$f(1,2)=f(2,1)=\frac{p(1,2)\times p(2,1)}{p(1,2)+p(2,1)}$$

where $p(i,j)$ is the probability of addition of the radical i to the monomer unit j with the $p(i,j)$ values being related to the r_1 and r_2 ratios by the equations:

$$p(1,2)=\frac{1}{1+r_1\cdot\dfrac{[M_1]}{[M_2]}} \quad \text{and} \quad p(2,1)=\frac{1}{1+r_2\cdot\dfrac{[M_2]}{[M_1]}}$$

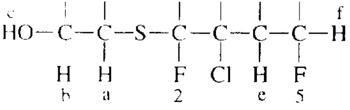
from which $p(1,2)=1-p(1,1)$ and $p(2,1)=1-p(2,2)$.

Using the literature values we obtained the different reactivity ratios noted in Table 3. As expected, it is observed that the addition is close to alternating when the r^b values [15] are employed because in that case the product $r_1 \times r_2$ is smallest (0.09).

Evidence for such an alternating structure can be confirmed by ^{19}F NMR spectroscopy.

In Fig. 3, the ^{19}F NMR spectrum of the $P(x,y)$ product exhibits five signals for the different CF_2 and CFCl groups. They are impossible to resolve, but when looking at the chemical shifts we noted two very important points regarding the extent of alternation.

Table 2
NMR data of the P(1,1) cotelomer



$$HO-CH_2-CH_2-S-CF_2-CFCl-CH_2-CF_2-H$$

H atoms	c	b	a	e–d	f
^1H NMR δ (ppm)	various	3.9	3.1	2.8–2.9	6.2
F atoms		1–2	3		4–5
^{19}F NMR δ (ppm)/$CFCl_3$		−85.6	−113.8		−119.3
Coupling constants (H_3)		$J_{ab}=6.2$	$J_{4f}=J_{5f}==54.9$		$J_{df}=J_{ef}=4.3$

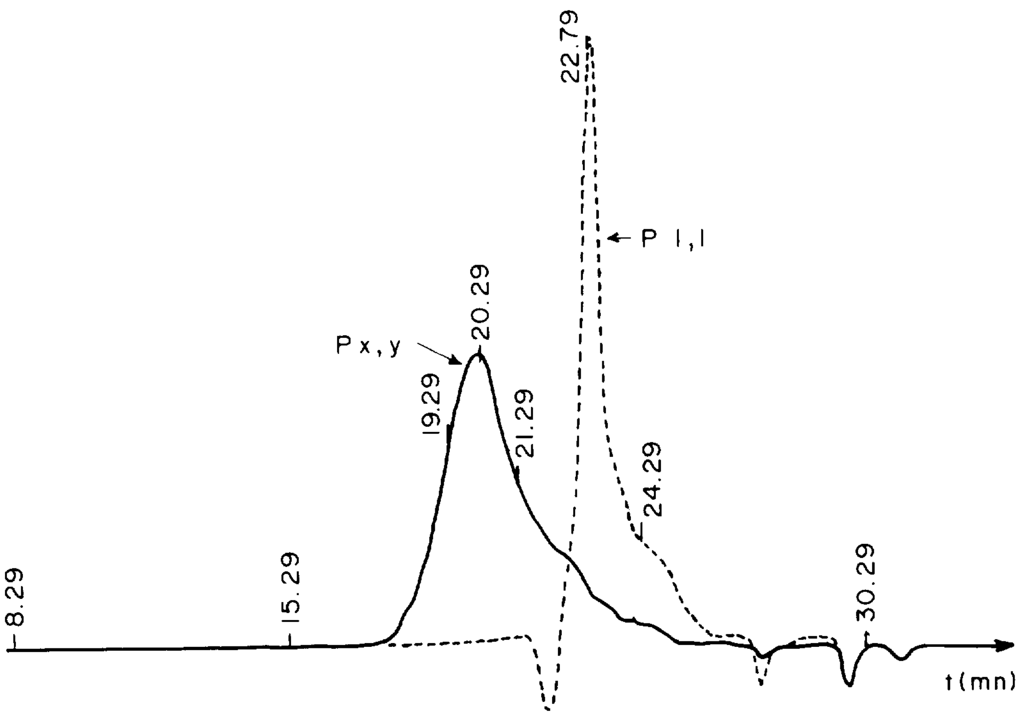


Fig. 2. GPC spectra of the P(1,1) cotelomer and of the P(x,y) residue.

Table 3
Molar fractions of VF_2 and CTFE in various diads

Mole fraction, $f(i,j)$	As obtained using quoted r^a values [14]	As obtained using quoted r^b values [15]
$f(VF_2, VF_2)$	0.210	0.063
f(VDF, CTFE)	0.287	0.372
f(CTFE, CTFE)	0.216	0.193

1. Firstly, the NMR spectrum of P(x,y) was compared to those of the CTFE/CCl_4 telomers (Fig. 4). These telomers have been synthesized and analyzed in our laboratory [16], and Fig. 4 represents the spectrum of $CCl_3(CF_2$—$CFCl)_n$—Cl (T_n) with $n = 5$. In the P(x,y) spectrum, the absence of signals between δ −124 and −130 ppm proves that there is no CFCl group between two CF_2 groups. The same observation can be made between δ −95 and −113 ppm, and it

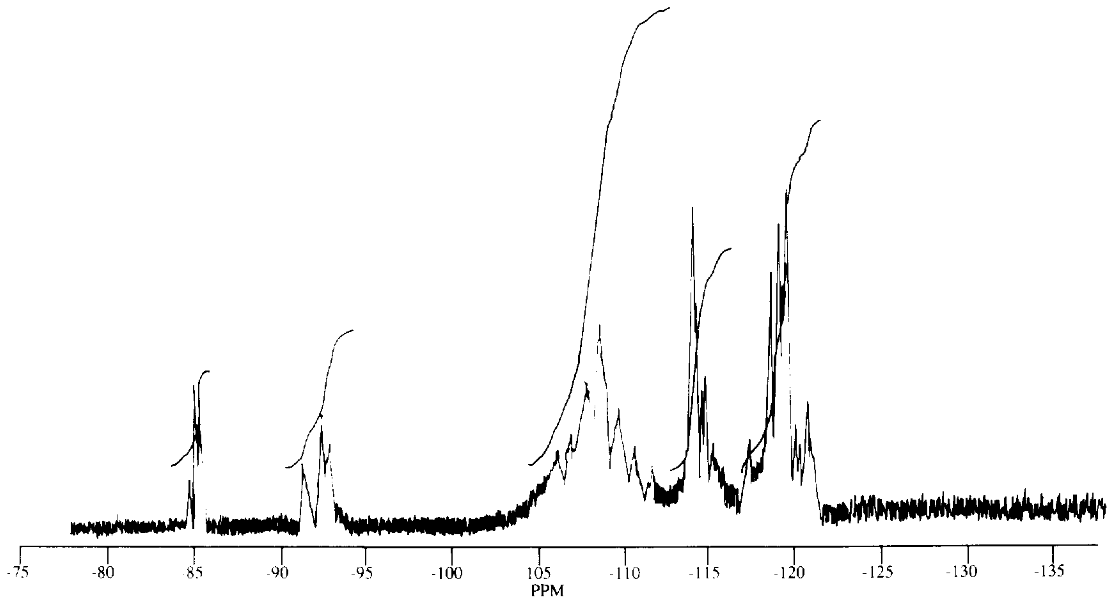


Fig. 3. ^{19}F NMR spectrum of the P(x,y) residue.

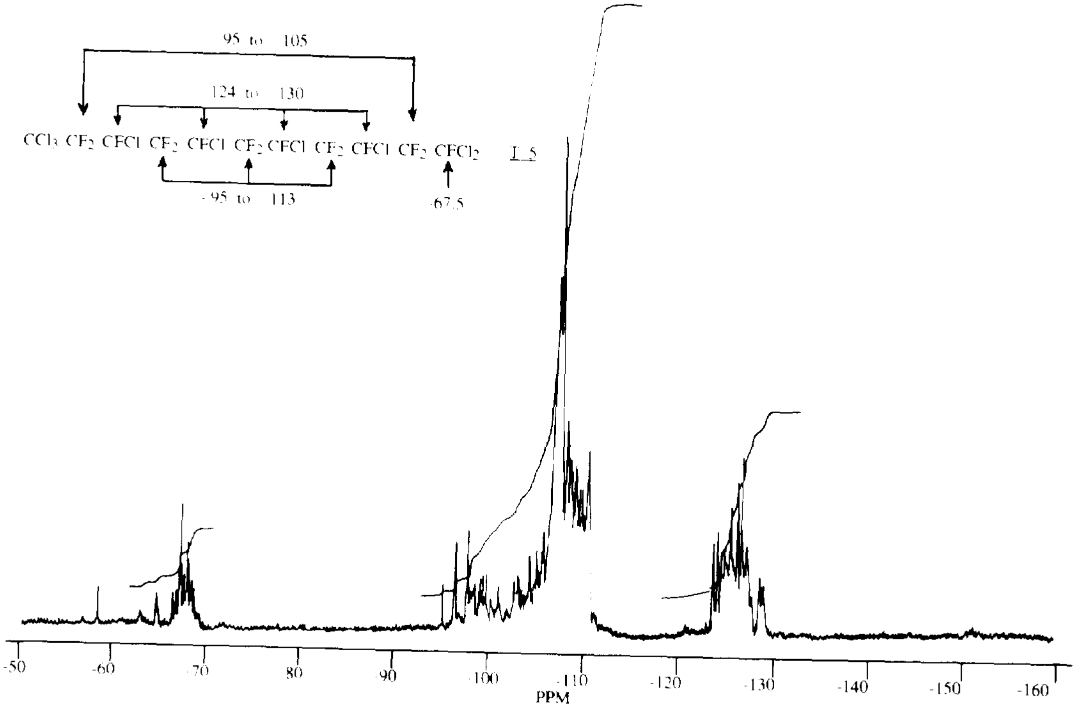


Fig. 4. ^{19}F NMR spectrum of the telomer T_5 (δ/$CFCl_3$).

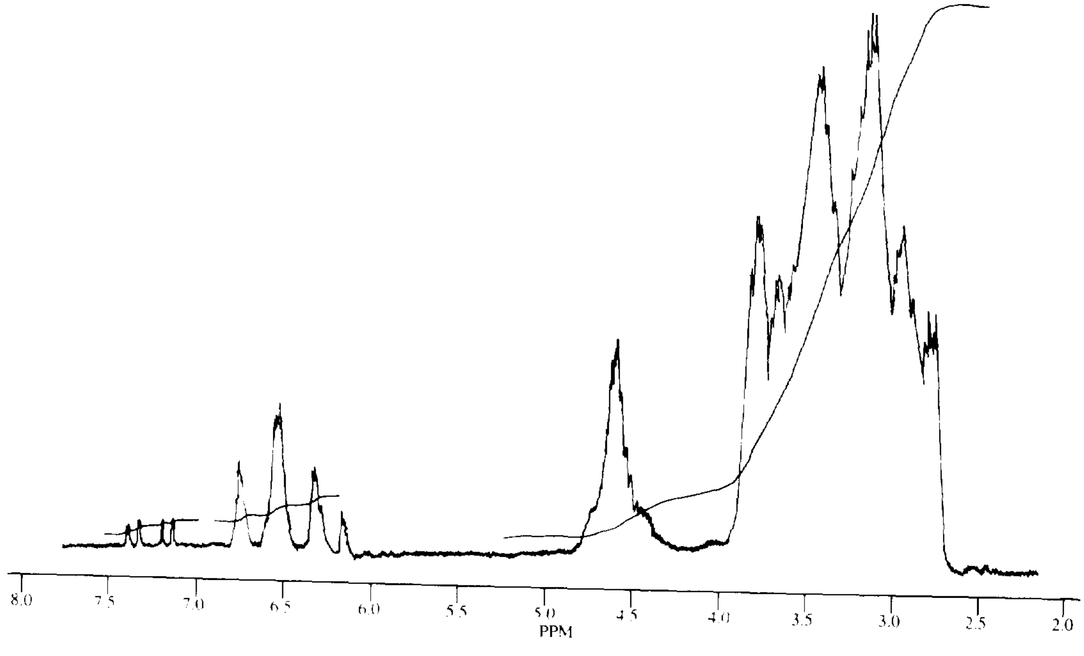


Fig. 5. ^{1}H NMR spectrum of the P(x,y) residue.

can be concluded that no CF_2 group can be found between two CFCl groups. Murasheva et al. [17] gave values of − 127.8 and (− 125 to − 131) ppm for the CF_2 and CFCl groups of CTFE thermopolymers in good agreement with our results.

2. Secondly, between −91 and −92 ppm, Fig. 3 shows a small signal corresponding to ca. 3% of all the F atoms. According to Murasheva et al. [17], this signal may be assigned to a CF_2 group in a microblock such as —CF_2—CFCl—CH_2—CF_2—CH_2—CF_2—, which corresponds to the location of a vinylidene fluoride unit between a VF_2 and a CTFE unit. So this kind of addition (i.e. two successive VF_2 units) probably occurs in our cotelomers but in small proportions.

In conclusion, these two observations suggest that the P(x,y) cotelomers formed in our reactions are most probably alternating.

Finally, ^{1}H NMR spectroscopy (Fig. 5) gave us many interesting results. The first concerns the nature of the chain end. The triplet for CF_2H is observed at δ 6.5 ppm ($J=56$ Hz is a characteristic value) and at δ 7.2 ppm a type of double quartet ($J=48$ Hz) (similar to the X part of an ABX system doubled by a geminal F atom) occurs due to the asymmetrical carbon of the —CF_2—CFClH end-groups. From integration it can be calculated that 70% of the cotelomers exhibit CF_2H end-groups, i.e. derived from VF_2 units.

Secondly, the spectrum depicted in Fig. 5 also provides information of the average number of VF_2 units y. If the peak heights corresponding to the hydrogen atoms of CF_2H, CFClH and of all the other groups in the molecules are designated h_1, h_2 and h_3 respectively, it can be deduced that:

$$\frac{h_1+h_2}{h_1+h_2+h_3}=\frac{1}{2y+6}$$

We have found $y=4.72$. This value is in good agreement with that obtained from elemental analysis.

From all the results discussed above, the most probable structure of the residue is therefore HO—CH_2—CH_2—S—(CF_2—CFCl)$_{4.1}$—(CH_2—CF_2)$_{4.4}$—H, with 70% of the VF_2 units situated at the end (CF_2H) of the molecule. Knowing this structure, other calculations can be made. Firstly, the molar and weight yields may be calculated from the formulae:

$$y_w=\frac{\sum W_i}{90^{(VF_2)}+150^{(CTFE)}+16^{(thiol)}}=12\%$$

$$y_w=\frac{\sum iN_i}{1.406^{(VF_2)}+1.288^{(CTFE)}}=12\%$$

and, secondly, the $\overline{DP}_n$ of the cotelomerization may be expressed as:

$$\overline{DP}_n=\frac{\sum iN_i}{\sum N_i}=\frac{31.1\times10^{-2}}{7.25\times10^{-2}}=4.3\ .$$

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