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Kinetics of radical telomerization of vinylidene fluoride in the presence of CCl_3Z chain transfer agents

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Abstract

The kinetics of radical telomerization of VDF at 141 °C, initiated by ditertbutylperoxide, in the presence of three chain transfer agents (CTAs), $HCCl_3$, CCl_4 and CCl_3Br, are presented. The values of the chain transfer constants were assessed as 35, 0.25 and 0.06 at 141 °C for CCl_3Br, CCl_4 and $HCCl_3$, respectively. The values of the degree of polymerization (DP_n) were obtained for each CTA and were compared for the same CTA concentration. Hence, CCl_3Br behaved as an efficient CTA towards VDF and usually afforded the monoadduct selectively, but in certain conditions the VDF diadduct can also be produced. In contrast, $HCCl_3$ was not so efficient since a polymeric structure was identified as the major product.

Keywords: Radical telomerization; Vinylidene fluoride; Kinetics; Halogenated chain transfer agents; Chain transfer constant; NMR spectroscopy

1. Introduction

Most fluoroalkenes have been used in (co)polymerization reactions leading to fluorinated (co)polymers, regarded as high value-added materials, due to their outstanding properties which lead to various applications [1–4]. Such polymers show low intramolecular and intermolecular interactions which lead to low cohesive energy and therefore to low surface energy. They also exhibit high thermostability and chemical inertness, low refractive index and friction coefficient, good hydrophobicity and lipophobicity, valuable electrical properties, and low relative permittivity. In addition, they are non-sticky, resistant to UV, ageing, and to concentrated mineral acids and alkalis. Hence, their fields of applications are numerous [4–10]: paints and coatings, textile finishings, elastomers, membranes, surfactants and fire fighting agents [5], biomaterials, and thermostable polymers for aerospace [6–9].

The syntheses and properties of fluoropolymers were recently reviewed [9]. To perform the synthesis of fluoroelastomer oligomers, one of the most interesting strategies is that of telomerization [9–12]. This well known and easy technique requires only the use of a chain transfer agent X–Y and leads to low molar mass-polymers or telomers that possess an X group at one chain-end and a Y group at the other [9–12]. This paper focuses on specific $ZCCl_3$ chain transfer agents (CTAs) in the radical polymerization of vinylidene fluoride (VDF). Polymeric species containing a trichloromethyl end-group are of particular interest because this extremity can be functionalized by hydrolysis, dehydrochlorination, oxidation or by reduction. It can be reactivated by redox catalysis and this species may behave as a new macromolecular chain transfer agent in telomerization of various monomers [13–15]. The new macromolecular species can behave as a macroinitiator in atom transfer radical polymerization [16,17]. Both these techniques enable the synthesis of block copolymers [17–19].

Several authors have already investigated the synthesis of VDF telomers in the presence of $ZCCl_3$ as CTAs. For instance, Moore [20] reported the radical polymerization of VDF at 125 °C in the presence of $HCCl_3$. This author characterized an oligomer structure ($1 \leq$ average degree of polymerization $(DP_n) \leq 10$) with a CCl_3 chain-end. Later, Boutevin et al. [21] performed the radical polymerization of VDF with CCl_4 under different experimental conditions (135 °C or a redox system at lower temperatures). As above, an oligomeric structure was obtained ($1 \leq DP_n \leq 6$) with a CCl_3 chain-end. Finally, radical telomerization of VDF in the presence of CCl_3Br was also

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investigated [22], mainly leading to the monoadduct of VDF. These studies did not report any kinetics of telomerization, which would have enabled a better understanding of the overall mechanism.

This present paper focuses on a mechanistic understanding of such a radical process. For this purpose, three CTAs containing a CCl_3 ($HCCl_3$, CCl_4, CCl_3Br) group have been chosen for their expected different transfer efficiency towards VDF. VDF telomerization reactions have been performed with each CTA and both average degrees of polymerization and transfer constants have been determined. By gathering these data, an entire reaction pathway was finally given, especially taking into account the defects of chain extension.

2. Results and discussion

This study is devoted to the transfer efficiency of $ZCCl_3$ chain transfer agents for the radical polymerization of VDF. We will show that the transfer efficiency is related to the Z group, leading to different structures (monoadduct, telomers or polymers) of VDF. The second part of this study will be devoted to supply a complete reaction scheme of the radical transfer reaction of VDF with $ZCCl_3$ as the CTAs.

2.1. Determination of Z–CCl$_3$ transfer efficiency towards VDF

The radical reactions of vinylidene fluoride (VDF) in the presence of ω-trichloromethyled end-group chain transfer agents (chloroform, carbon tetrachloride and bromotrichloromethane) were carried out at 141 °C for 5 h, initiated by ditertbutylperoxide (DTBP), as in Eq. (1):

$$Cl_3C{-}Z + nH_2C = CF_2 \xrightarrow{\text{rad.}} Cl_3C{-}(C_2H_2F_2)_n{-}Z \quad \text{with } Z = H, Cl, Br \tag{1}$$

The initial $[DTBP]_0/[VDF]_0$ molar ratio was 0.01, whereas the initial $[ZCCl_3]_0/[VDF]_0$ molar ratio was varied. The VDF conversion and the average degree of polymerization were analyzed as first results of the transfer reactions. The results are gathered in Table 1.

Table 1
Radical telomerizations of 1,1-difluoroethylene (VDF) initiated by ditertbutylperoxide (DTBP) at 141 °C using $[DTBP]_0/[VDF]_0$ molar ratio of 1% in the presence of $ZCCl_3$ chain transfer agents

CTA	R_0 ($[CTA]_0/[VDF]_0$)	α_{VDF}	DP_n	Entry
$CHCl_3$	1.0	0.40	6.1	1
	2.0	0.73	4.4	2
	15.0	0.93	2.1	3
	20.0	0.95	2.0	4
CCl_4	1.0	0.77	3.6	5
	2.0	0.80	3.2	6
	5.0	0.81	2.3	7
CCl_3Br	0.1	0.55	1.7	8
	1.0	0.60	1.1	9
	2.0	0.62	1.0	10

CTA, α_{VDF}, R_0 and DP_n represent the chain transfer agent, the VDF conversion, the initial $[CTA]_0/[VDF]_0$ molar ratio and the average degree of telomerization, respectively. The error bar on DP_n value is ±0.1.

Table 1 shows that the DP_n values are dependent on the nature of the CTA, which indicates different transfer efficiencies for the three CTAs. This transfer efficiency can be easily characterized by comparing the DP_n values obtained for the same R_0 value of 1.0. $CHCl_3$ (entry 1) exhibits a poor transfer efficiency towards VDF as a DP_n value of only 6.1 was obtained. In contrast, CCl_3Br seems to be the most efficient CTA (value of about 1 in entry 9) whereas CCl_4 exhibits an intermediate efficiency (DP_n value of 3.6 in entry 5). These apparent transfer efficiencies are characterized by the chain transfer constant C_T.

2.2. Assessment of C_T^n values for Z–CCl$_3$ transfer agents

2.2.1. The kinetics of telomerization (the David and Gosselain's theory)

The kinetic first order-transfer constants of $Cl_3C{-}Z$ (Z = H, Cl, Br) C_T^n (Eq. (2)) with $1 < n < 8$ were determined from the molecular distributions of VDF/Cl_3CZ telomers (Fig. 1) from telomerizations using various initial $[Cl_3CZ]_0/[VDF]_0$, R_0, molar ratios:

$$C_T^n = \frac{k_{tr}^n}{k_p^n} \tag{2}$$

where k_{tr}^n and k_p^n represent the rate constants of the transfer step and of the propagation step, respectively.

2.2.2. Kinetic results

The method used is based on the David and Gosselain theory [23] that allowed us to link the C_T^n constants to the molar fraction F_n of each telomer, as in Eq. (3):

$$C_T^n = x_n\left(R' \times \sum xi\right) \tag{3}$$

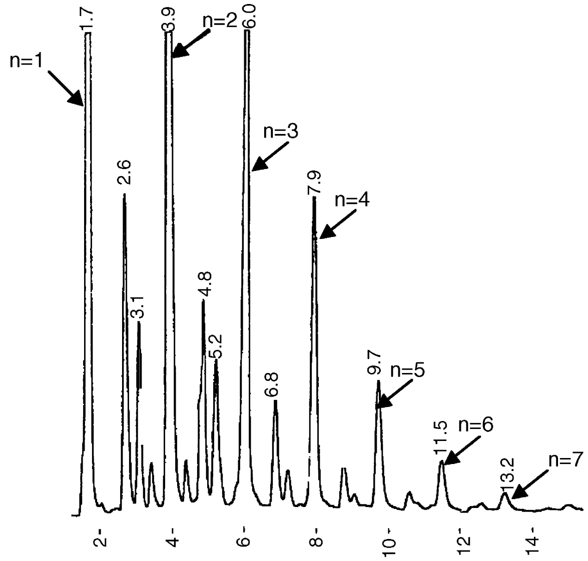

Fig. 1. Gas chromatogram of the total product mixture of the radical telomerization of VDF with chloroform (initial $[CHCl_3]_0/[VDF]_0$ molar ratio = 15).

where R' represents the ratio of the telogen concentration to that of VDF participating in the telomerization, i.e. the fraction of monomer dissolved in the liquid phase. R' can be assumed equal to R_0 by considering that the reaction occurred at low VDF and CCl_3Z conversion rates. Hence, the reaction time required for a limited VDF conversion for the three kinetics was 1 h.

From Eq. (3), the values of different C_T^n constants can be determined by plotting the $x_n/\sum xi$ ratios versus R_0, which represent straight-lines, the slopes of which led to the values of C_T^n (Fig. 2). These values are reported in Table 2, in which extrapolation to $n = \infty$ has been performed.

At 141 °C, the values of C_T^∞, characterizing the transfer efficiency are:

- for CCl_3Br/VDF, $C_T^\infty = 35 \pm 1$;
- for CCl_4/VDF, $C_T^\infty = 0.25 \pm 0.02$;
- for CCl_3H/VDF, $C_T^\infty = 0.06 \pm 0.01$.

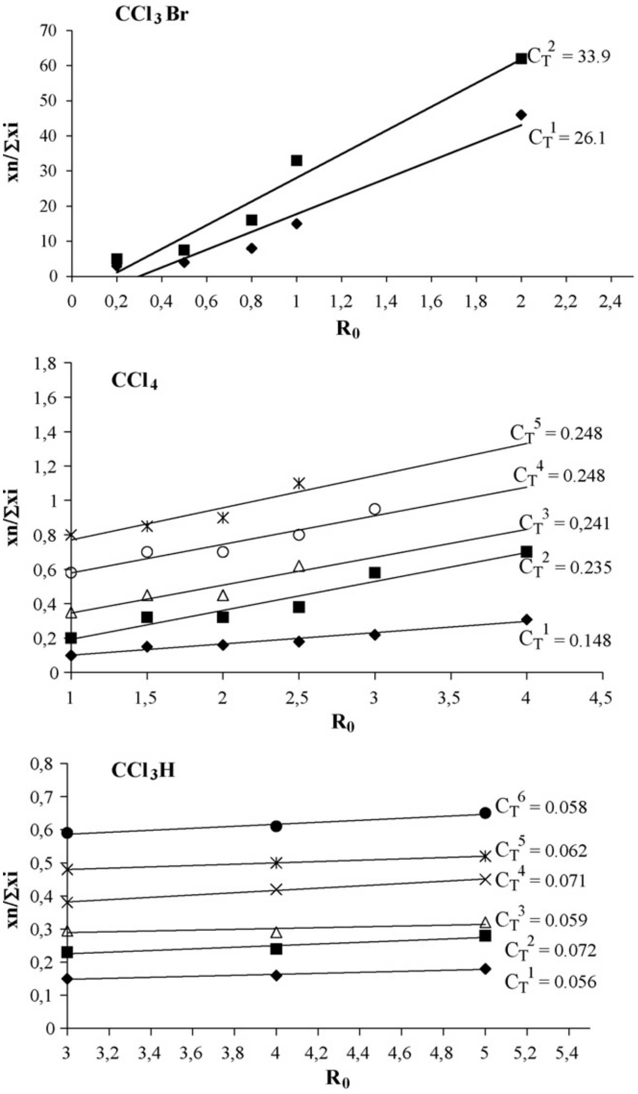

Fig. 2. Plots of $x_n/\sum xi$ ($i = n + 1$ to ∞) vs. R_0 for the radical telomerization of VDF at 141 °C initiated by DTBP in the presence of $ZCCl_3$ as the CTAs (R_0 represents the initial $[ZCCl_3]_0/[VDF]_0$ molar ratio).

Table 2

Determination of C_T^∞ values from values of kinetic transfer constants C_T^n reported from Fig. 1 (with $1 \leq n \leq 6$) for the radical telomerizations of VDF at 141 °C initiated by DTBP in the presence of $ZCCl_3$ as the CTAs

	Order I						
	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = \infty$
CCl_3Br	26.1	33.9	–	–	–	–	34.0
CCl_4	0.148	0.235	0.241	0.248	0.248	–	0.25
CCl_3H	0.056	0.072	0.059	0.071	0.062	0.058	0.06

These results indicate poor transfer efficiency for $CHCl_3$ with VDF. This low value of 0.06 was already reported with other fluorinated monomers [20]. An intermediate reactivity is indicated for CCl_4. This C_T value is in the same range as that of the CCl_4/CTFE (chlorotrifluoroethylene) system [24]. The most efficient CTA towards VDF is CCl_3Br, exhibiting a very high C_T value. This was expected as several authors reported such efficiency towards non-fluorinated monomers such as vinyl chloride [25].

These C_T values are in good agreement with DP_n values reported in Table 1. Despite a low initial CTA concentration, CCl_3Br leads to the synthesis of the $CCl_3CH_2CF_2Br$ monoadduct (major) and $CCl_3CH_2CF_2CH_2CF_2Br$ diadduct (minor).

To confirm this result both telomers, produced from the equimolar mixture of Cl_3CBr and VDF, were purified by fractionated distillation, and then characterized by ^1H, ^{19}F and ^{13}C NMR spectroscopy. The ^1H NMR spectrum of the first exhibits a triplet centred at 3.9 ppm ($^3J_{HF} = 15.4$ Hz) characteristic of the methylene group adjacent to a $–CF_2–$. Only one triplet ($^3J_{FH} = 15.4$ Hz) centred at -46.3 ppm was noted in the ^{19}F NMR spectrum, assigned to a CF_2 group adjacent to methylene. This observation enables us to eliminate the formation of $Cl_3CCF_2CH_2Br$ ($\delta_{CF2} = -100$ ppm) and $BrCCl_2CH_2CF_2Cl$ ($\delta_{CF2} = -65$ ppm), arising from the addition of $^\bullet CCl_3$ onto the fluorinated carbon atom of VDF and the formation of the monoadduct by transfer of one chloride atom of CCl_3Br, respectively. The expected $Cl_3CCH_2CF_2Br$ structure was confirmed by ^{13}C NMR, the spectrum of which shows three different triplets centered at 116.2 ppm ($^1J_{CF} = 310.5$ Hz), 90.4 ppm ($^3J_{CF} = 4$ Hz) and 64.2 ppm ($^2J_{CF} = 21.2$ Hz), assigned to CF_2, CCl_3 and to CH_2 groups, respectively.

Hence, the NMR study of this monoadduct indicates the regioselectivity of the addition of $^\bullet CCl_3$ radicals onto the less hindered (or the less fluorinated) carbon atom of VDF. Such an observation was already noted for the addition of $^\bullet C_nF_{2n+1}$ ($n = 4, 6, 8$) [26–28], $RS^\bullet$ [29,30], $(EtO)_2P^\bullet$ (= O) [31] radicals onto VDF. VDF:$HCCl_3$ and VDF:CCl_4 monoadducts were also synthesized but, unlike $BrCCl_3$, their syntheses required higher initial CTA concentrations. The NMR analyses of such monoadducts led to the same conclusion, i.e. a regioselectivity of $^\bullet CCl_3$ addition onto $\mathbf{CH_2}{=}CF_2$ of VDF.

CCl_4 exhibits a C_T^∞ value of 0.25. Ideally, C_T^∞ should be about 1 but a value of 0.25 indicates that CCl_4 can be a good CTA for reaching a telomeric VDF structure. Because of the good CTA efficiency, this telomeric structure may be telechelic, i.e. α-Cl, ω-CCl_3.

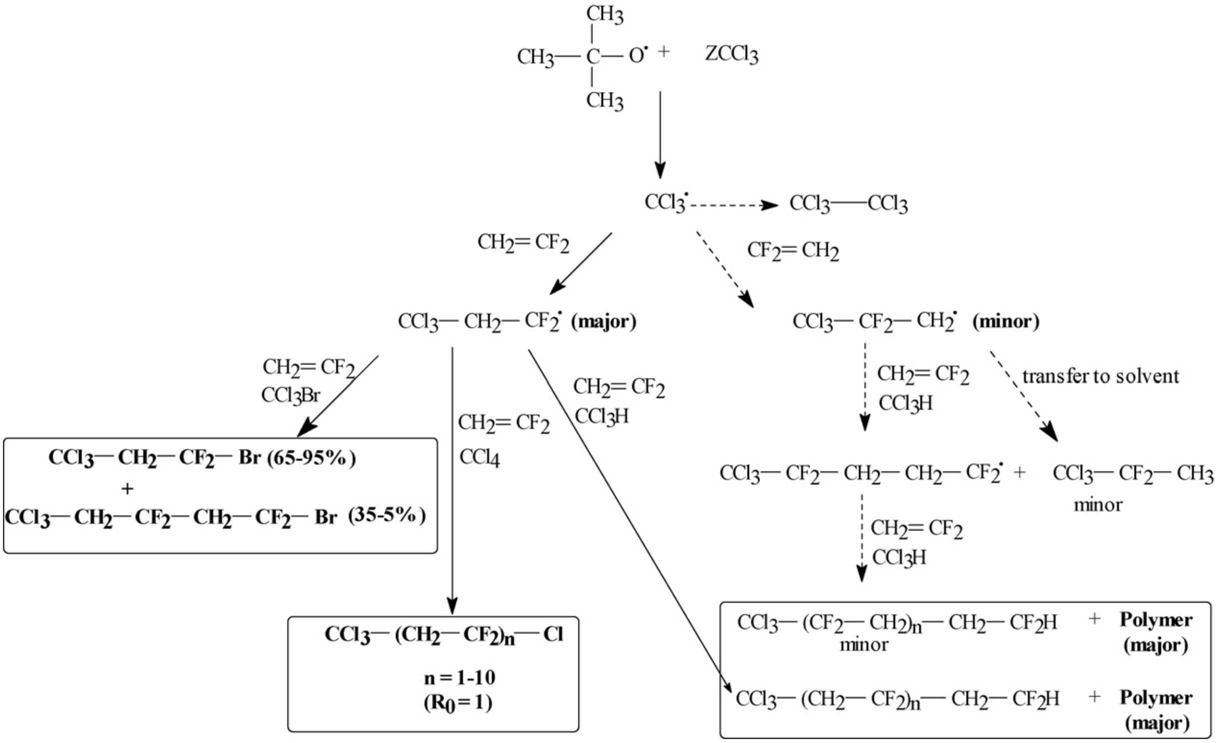

Fig. 3. Overall scheme of the radical telomerization of VDF at 141 °C initiated by DTBP in the presence of $ZCCl_3$ with Z = Br; Cl; H (acetonitrile as the solvent). The dotted arrow represents a minor reaction.

Finally, CCl_3H is shown as a poor chain transfer agent for VDF ($C_T^\infty = 0.06$). In this case, the propagation step takes place in preference to the transfer reaction. This poor efficiency was also characterized by the VDF conversions listed in Table 1. Indeed, for $CHCl_3$, the VDF conversion is unusually dependent on the initial CTA concentration. Hence, a telechelic telomeric structure will not be obtained by using $CHCl_3$ as the CTA for the VDF radical polymerization, rather, a polymeric structure will be obtained.

The decreasing order of the C_T^∞ values for the telomerization of VDF at 141 °C in the presence of CCl_3Z is as follows:

$$CCl_3Br\,(C_T^\infty = 35) > CCl_4\,(C_T^\infty = 0.25) > CCl_3H\,(C_T^\infty = 0.06)$$

Finally, taking into account the DP_n and C_T^∞, Fig. 3 shows a general pathway of the VDF radical polymerization in the presence of $ZCCl_3$ chain transfer agents.

Fig. 3 shows that CCl_3Br only leads to the two first adducts of VDF. CCl_4 affords the synthesis of VDF telomers with a molecular weight distribution depending on the initial CTA concentration. This scheme also shows that no defect (or very few) is observed in the presence of either CCl_3Br or CCl_4. Radical telomerization in the presence of $HCCl_3$ leads to different macromolecular structures. The conventional telomeric structure, obtained by the transfer to $HCCl_3$ and without any defect, can be obtained but is minor. The same telomeric structure can be obtained with defects in the chain. Due to the very low C_T^∞ value and to the very high dissociation energy of the H–Cl bond, the major structure is the VDF homopolymer obtained by conventional radical polymerization initiated by DTBP.

3. Conclusion

This paper has supplied kinetic data of the radical telomerization of VDF, initiated by ditertbutylperoxide, in the presence of three halogenated chain transfer agents (CTAs): $HCCl_3$, CCl_4 and CCl_3Br. By using the method of David and Gosselain, the chain transfer constant, C_T, has been determined at 141 °C for each CTA. The calculated values were 35, 0.25 and 0.06 for CCl_3Br, CCl_4 and $HCCl_3$, respectively. The transfer efficiency is dependent on the Z group of the $ZCCl_3$. The DP_n values were also determined for different CTA concentrations and were in agreement with the reported C_T values, i.e. mono and diadduct were obtained with CCl_3Br, while a telomeric distribution was produced from CCl_4 in contrast to a polymeric distribution obtained from $HCCl_3$. It is to be noted that CCl_3Br does not lead to any defect as only the mono and diadduct were obtained. The kinetic studies indicate that CCl_4 is the most appropriate CTA for reaching a telomeric structure. Indeed, CCl_3Br is too reactive towards VDF, almost exclusively leading to a monoadduct and a very minor percentage of VDF diadduct. On the other hand, $HCCl_3$ is not sufficiently efficient, yielding polymeric structures and also some defect at each step of the reaction path. Finally, CCl_4 affords an intermediate efficiency towards VDF. The resulting telomeric structure exhibits low defect of chain extension, enabling the synthesis of block copolymers by stepwise co-telomerization.

4. Experimental

4.1. Materials

Vinylidene fluoride (or 1,1-difluoroethylene, VDF) and tertbutylcyclohexyl peroxycarbonate were kindly supplied by Atofina and Akzo, respectively. Ditertbutylperoxide and bromotrichloromethane (Aldrich) were used as received. Chloroform and tetrachloromethane were supplied by SDS Company.

The radical telomerizations of VDF with CCl_3Z (Z = H, Cl, Br) were performed either in thick borosilicate Carius tubes (thickness 2.5 mm, internal diameter 10 mm and length 70 mm for a total volume of 8 cm^3) or in a 1 l Hastelloy C276 PARR system R495HC autoclave equipped with a digital manometer, a mechanical stirrer, two valves (for introducing VDF and for releasing unreacted gas) and a rupture disk.

After reaction, the crude reaction mixture or the products obtained after work-up were analyzed by gas chromatography (GC) using a Delsi apparatus (model 330) equipped with a SE 30 column, 3 m × 1/8 in. (i.d.). The dinitrogen pressure at the entrance to the column was maintained at 0.6 bar and the detector and injector temperatures were 260 °C and 255 °C, respectively. The temperature program started from 50 °C and reached 250 °C at a heating rate of 15 °C min^{-1}. The GC apparatus was connected to a Hewlett Packard integrator (model 3390) which automatically calculated the area of each peak on the chromatogram.

The kinetic studies were performed from reactions carried out in Carius tubes previously introduced into a preheated shaking oven, and the reaction time was 1 h. After the reaction was over, the tubes were frozen in liquid nitrogen, opened and characterized by size exclusion chromatography (SEC).

The VDF conversion was obtained from mass difference, total mixture before and after the reaction. The average degree of polymerization was calculated from the percentage of several adducts, previously determined by Gas Chromatography. The products were characterized by ^{1}H and ^{19}F NMR spectroscopy at room temperature. The ^{19}F and ^{1}H NMR spectra were recorded on Bruker AC 200, 250 or WM 360 instruments, using deuterated chloroform and $CFCl_3$ as solvent and internal reference, for ^{19}F NMR and tetramethylsilane as the reference for ^{1}H NMR. The letters d, t and qi designate doublet, triplet and quintet, respectively. Coupling constants are given in hertz.

4.2. Radical transfer reaction of VDF in the presence of CCl_3Br

A 1 l Hastelloy autoclave containing 78.1 g (0.39 mol) of Cl_3CBr, 0.6 g (4.0 mmol) of ditertbutylperoxide and 154.5 g (3.77 mol) of acetonitrile was closed and frozen into an acetone/liquid nitrogen bath. After three nitrogen-vaccum cycles, 25.0 g (0.39 mol) of VDF were transferred into the autoclave. The vessel was warmed to room temperature, placed in the mantle which was heated to 141 °C and stirred for 4 h. After reaction, the autoclave was taken off the mantle, cooled to room temperature and placed in an ice bath. Unreacted VDF was carefully released out. 9.6 g (0.147 mol) were collected as an off-gas (massic yield = 60%). The crude reaction mixture was a pale yellow liquid. After evaporation of acetonitrile, the residue was distilled.

A similar procedure was used for the radical transfer reactions of VDF in the presence of either CCl_4 or CCl_3H.

- Characterization of 1,1,1-trichloro-3,3-difluoro-3-bromopropane VDF: CCl_3Br monoadduct (Bp = 37–38 °C/10 mbar, colourless liquid):
  - ^{1}H NMR ($CDCl_3$): $\delta = 3.9$ (t, $^3J_{HF} = 15.4$, CH_2, 2H).
  - ^{19}F NMR ($CDCl_3$): $\delta = -46.3$ (t, $^3J_{FH} = 15.4$, CF_2Br, 2F).
  - ^{13}C NMR ($CDCl_3$): $\delta = 64.2$ (t, $^2J_{CF} = 21.2$, CH_2); 90.4 (t, $^4J_{CF} = 4$, Cl_3C); 116.2 (t, $^1J_{CF} = 310.5$, CF_2Br).
- Characterization of 1,1,1-trichloro-3,3,5,5-tetrafluoro-5-bromopentane VDF: CCl_3Br diadduct (Bp = 54–57 °C/2 mbar; colourless liquid):
  - ^{1}H NMR ($CDCl_3$): $\delta = 3.3$ (qi, $^3J_{HF} = 15.2$, CH_2CF_2Br, 2H); 3.5 (t, $^3J_{HF} = 15.4$, Cl_3CCH_2, 2H).
  - ^{9}F NMR ($CDCl_3$): $\delta = -43.8$ (tt, $^3J_{FH} = 15.2$, $^4J_{FF} = 10.2$, CF_2Br, 2F); -92.1 (qit, $^3J_{FH} = 15.2$, $^4J_{FF} = 10.2$, central CF_2, 2F).
  - ^{13}C NMR ($CDCl_3$): $\delta = 50.5$ (qi, $^2J_{CF} = 25.8$, CH_2CF_2Br); 58.5 (t, $^2J_{CF} = 25.4$, Cl_3CCH_2); 91.3 (t, $^3J_{CF} = 4$, Cl_3C); 116.0 (tt, $^1J_{CF} = 306.7$, $^3J_{CF} = 4.5$, CF_2Br); 117.3 (tt, $^1J_{CF} = 250.1$, $^3J_{CF} = 4$, central CF_2).

4.3. Determination of the C_T^n values

Gas chromatography (Fig. 1) of the total product mixture showed the *n*-telomeric adducts ($n = 9$ in the case of CCl_4/VDF). The area of the peaks in the chromatogram enabled the determination of $x_n/\sum xi$. Then $x_n/\sum xi$ was plotted versus R_0, the slope of which gave C_T^n.

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