Studies of the Alternating Copolymerization of Vinyl Ethers with Chlorotrifluoroethylene

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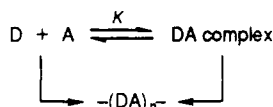
ABSTRACT: The copolymerization of chlorotrifluoroethylene (CTFE) with several vinyl ethers (VE) (hydroxyethyl vinyl ether, glycidyl vinyl ether, and chloroethyl vinyl ether) was studied. CTFE is an acceptor monomer ($e \sim +2$), whereas the VE's are highly donor ones ($e \sim -2$), so they can copolymerize and lead to alternating copolymers. Such a behavior was shown by determining the composition of the copolymer at the beginning of the reaction, and we proved by ^{19}F NMR of CTFE that the equilibrium constant of the charge-transfer complex formation (CTC) is high ($K = 1.4$). Then, the structure of the copolymer was investigated by performing the cotelomerization of CTFE and a VE with a fluorinated thiol ($C_6F_{13}C_2H_4SH$). This reaction produced both the monoadducts and the dimer structure (opposite to that expected from the CTC) which are in contradiction with the polymerization by propagation of the transfer complex. Thus a polymerization of free monomers is proposed, and the alternating behavior of the copolymer comes from the great difference in polarity between these two kinds of monomers.

I. Introduction

The synthesis of alternating copolymers from donor–acceptor monomers has been reported in many surveys[1] but has also been much debated. Most authors suggest that the propagation occurs via a "charge-transfer complex",[2] but others[3] explain the alternation from the minimization of the energy of activation of the cross-propagation with regard to homopropagation due to the presence of electrostatic interactions. Finally other authors[4,5] consider both possibilities: propagation by complex and propagation by free monomers.

The possible pathways are

$$D + A \; \overset{K}{\rightleftharpoons} \; DA \text{ complex}$$
$$\longrightarrow \; -(DA)_n- \; \longleftarrow$$

Tirrell et al.[6-8] have shown in a series of papers that, even in a good example (maleimide/vinyl ether), the maleimide consumption occurs entirely by addition of the free olefin.

Recently, Japanese workers have shown that fluorinated monomers are able to give alternating copolymers with vinyl ethers,[9] and Lumiflon paints have been available for five years. However, no basic studies have been performed on such systems because of the boiling points of these monomers.

So we started a survey with chlorotrifluoroethylene (CTFE) and various vinyl ethers: 2-chloroethyl vinyl ether (CEVE; I), ethyl vinyl ether (EVE; II), 2,3-epoxypropyl vinyl ether (GVE; III), and 2-acetoxyethyl vinyl ether (AcOVE; IV).
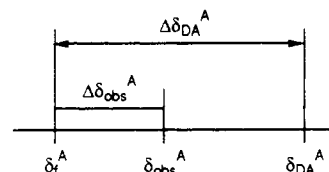
II. Results

The first important point to mention concerns the Q and e values of these monomers[10] (Table I). Alfrey and Price equations[11] permit the calculation of their reactivity ratios (Table II). The values of r_1r_2 show clearly that alternating copolymers are to be expected with CTFE/vinyl ether systems.

We have used NMR spectroscopy for the calculation of the complex constant formation, K_F. Among the different

Table I
Q and e Values of CTFE, CEVE, and EVE

monomers	Q	e
CTFE	0.026	1.56
CEVE	0.017	−1.58
EVE	0.018	−1.80

techniques the Hanna and Ashbaugh[12] method seems to be more convenient. It is well-known in the DA complexes that there is a quick exchange between the complexed and noncomplexed states and so the chemical shifts of the nuclei of one of the monomers (δ_{obs}) are each observed as a single peak, corresponding to the weighted average of the shift due to the free molecules (δ_f) and that due to the complexed monomers (δ_{DA}) as schematically shown.
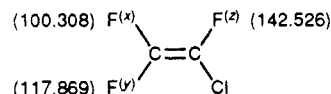
Hanna and Ashbaugh[12] obtained the following equation to determine K_F:

$$\frac{1}{\Delta\delta_{obs}} = \frac{1}{\Delta\delta_{DA}} + \frac{1}{\Delta\delta_{DA}[D]_0 K_F}$$

$[D]_0$ represents the concentration of the donor, whereas usually the acceptor concentration remains constant.

In the ethyl vinyl ether/chlorotrifluoroethylene (EVE/CTFE) system we have studied the ^{19}F NMR of the CTFE. Each fluorine atom of the free CTFE exhibits the following chemical shift:

$$\underset{(117.869)\ F^{(y)}}{\overset{(100.308)\ F^{(x)}}{\diagdown}} C = C \underset{Cl}{\overset{F^{(z)}\ (142.526)}{\diagup}}$$

For example, when the VE concentration was 1.6133 mol/L, the $\Delta\delta_{obs}$ for the fluorinated atoms $F^{(x)}$, $F^{(y)}$, and $F^{(z)}$ were 0.692, 0.631, and 0.574, respectively. We have chosen the $F^{(x)}$ atom for the determination of K_F (Table III).

Table II
Reactivity Ratios Obtained with Q and e Values

	CEVE	EVE
CTFE		
r_1	0.011	0.008
vinyl ether		
r_2	0.005	0.002
$r_1 r_2$	5×10^{-5}	2×10^{-6}

Table III
^{19}F NMR Data in a EVE/CTFE System

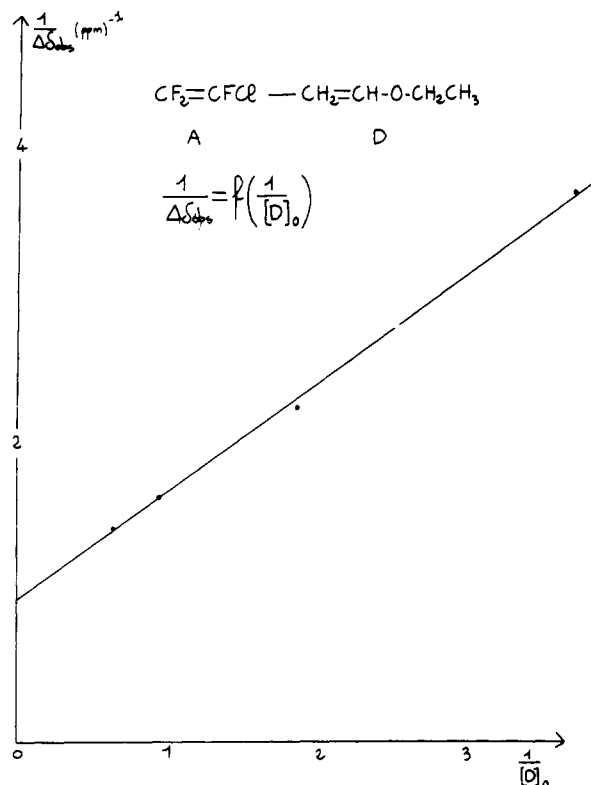| $[D]_0$, mol/L	0.2688	0.5377	1.0755	1.6133
$\Delta\delta_{obs}$, ppm	0.2715	0.4465	0.601	0.692

Figure 1. NMR determination of the equilibrium constant of complexation of the charge-transfer complex. $T = 20\,°C$, solvent $CDCl_3$.

We plotted $1/\Delta\delta_{obs}$ versus $1/[D]_0$ (Figure 1), and from the slope we have obtained $K_F = 1.4$ L·mol^{-1} at 20 °C.

This result gave rise to two main conclusions:

(1) The first one concerns the very high value of K_F obtained with these kinds of monomers. Actually we found in the literature different values of such a constant: for donor/maleic anhydride, $10^{-2} < K < 1$,[13] for C_2H_5-$OCH=CHCH=CH_2$/acrylonitrile, $K = 0.19$,[13] and for vinyl ether/maleimide, $K = 0.2$.[14]

(2) The second one is about the good distribution of the electronic charges which come from the donor monomer on the three fluorinated atoms of the acceptor one. So the polarizability of CTFE is low, although the results of Haszeldine[15] showed that CTFE, like all the other fluorinated compounds, is polarized as follows:

$$^{\delta+}CF_2{=}^{\delta-}CRF \quad \text{with } R = Cl \text{ and } CF_3$$

Then, we studied the copolymerization of CTFE with ethyl vinyl ether (EVE) and 2-chloroethyl vinyl ether (CEVE) initiated by benzoyl peroxide in acetonitrile at 70 °C (Table IV). Three feed compositions were used, 80/20, 50/50, and 20/80, in order to determine the composition

Table IV
Conditions of the Reaction of the Copolymerization of CTFE with Vinyl Ethers I and II[a]

	mole content of CTFE/EV	CTFE, g	EV, g	overall wt, g	obtained wt, g	yield, %
E	80/20	13.048	2.02	15.064	2.9	19
V	50/50	8.155	5.04	13.195	7.6	58
E	20/80	3.262	8.04	11.302	3.4	30
C	80/20	13.048	2.982	16.03	3.8	24
E	50/50	8.155	7.455	15.61	11.1	71
V	20/80	3.262	11.928	15.19	4.5	30
E						

[a] Initiator: *tert*-butyl peroxypivalate (2×10^{-2} M ratio to monomers).
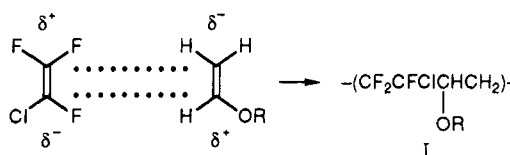
of the copolymers nearly at the beginning of the reaction. In Table V, we have listed the percentages of each atom using the alternating formula and also the experimental results.

From these results we note that the atom contents of the obtained copolymers are very close, whatever the feed composition, so these copolymers were shown to have a highly alternating sequenced structure.
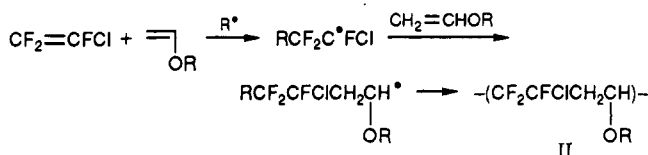
In conclusion, the studies of the copolymerization of CTFE with different vinyl ethers are in good agreement with the high value of the constant of charge transfer K_F. Consequently, we are not surprised to obtain alternating copolymers.

In order to confirm such results, we performed the NMR characterization of these copolymers. Usually in most couples of monomers, the acceptor is symmetrical (maleic anhydride, maleimide), but in our case CTFE is not symmetrical and consequently two structures may be expected: the first one comes from the propagation of the DA complex (Scheme I), and the second one comes from the propagation of the free monomers (Scheme II).

Scheme I

Scheme II

In all the ^{1}H NMR spectra, we observe a doublet at about 4.5×10^{-6}, but we cannot assign that as a coupling with the -CFCl- group (instead of a triplet with the CF_2 group) because the J value is too high for a vicinal coupling. In the same way, the ^{13}C NMR spectra also cannot provide evidence of these two structures, but this technique shows the characteristic peaks of the copolymers.

The NMR results did not permit us to conclude between both structures I and II.

So we performed the radical cotelomerization of these monomers with thiols. Actually previous works in our laboratory have shown that this technique produces oligomers which are easier to study by NMR spectroscopy.

In such cases, we used cotelomerization of $C_6F_{13}CH_2$-CH_2SH with CTFE and vinyl ether IV by *tert*-butyl

Table V
Yield and Analytical Data for the Copolymerization of CTFE with EVE, on the One Hand, and CTFE with CEVE, on the Other Hand

	C %		H %		F %		Cl %	
	calcd	found	calcd	found	calcd	found	calcd	found
CTFE/EVE								
80/20		39.4		4.4		28.6		19.3
50/50	38.2	39.1	4.2	4.7	30.2	29.3	18.8	18.0
20/80		38.9		4.8		28.8		17.4
CTFE/CEVE								
80/20		33.0		3.4		25.1		30.7
50/50	32.3	32.7	3.1	3.5	25.6	24.4	31.8	30.6
20/80		32.9		3.7		23.5		31.5

peroxypivalate:

$$R_0 = \frac{[\text{mercaptan}]}{[\text{AcOVE}] + [\text{CTFE}]} = 0.5 \quad \text{and} \quad C_0 =$$

$$\frac{[\text{I}_2]}{[\text{AcOVE}] + [\text{CTFE}]} = 10^{-2}$$
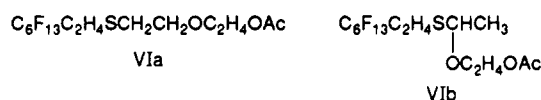
After the reaction, we obtained and isolated by distillation the three following products and their weight percentages: $C_6F_{13}CH_2CH_2S(CF_2CFCl)H$ (V), 18%; C_6F_{13}-$CH_2CH_2SCH_2CH(OCH_2CH_2OAc)H$ (VI), 50%; $C_6F_{13}CH_2$-$CH_2SCF_2CFClCH_2CH(OCH_2CHOAc)H$ (VII), 23%; residue of distillation, 8%.

In order to determine the structure of these adducts, studies by NMR have been done and are described in the Experimental Part. However, we give below the most important characteristics.

The ^{1}H NMR spectrum of product V exhibits at 6 ppm a doublet ($J^2 = 47$ Hz) which is detripled ($J^3 = 15$ Hz) characteristic of the proton of CF_2CFClH. So the adduct V has the structure $C_6F_{13}C_2H_4SCF_2CFClH$.

It is interesting to note that the sulfur radical reacts with the less hindered side of the CTFE, as expected.

For product VI the results of centesimal analysis correspond to both isomeric structures

$$C_6F_{13}C_2H_4SCH_2CH_2OC_2H_4OAc$$
$$\text{VIa}$$

$$C_6F_{13}C_2H_4SCHCH_3$$
$$\hspace{1.5cm}|$$
$$\hspace{1.5cm}OC_2H_4OAc$$
$$\text{VIb}$$

However, ^{1}H NMR gives evidence that the ketal (VIb) has not be produced. Actually, we noted the absence of a doublet in the 1–1.5 ppm range corresponding to the methyl group of VIb. On the contrary, we observed the four methylene groups of the VE at 2.75, 3.68 (twice), and 4.2 (in the α position of the ester group).

So from these NMR characterizations (also confirmed by ^{13}C and ^{19}F NMR), it is easier to describe the structure of the 1 + 1 adduct (Table VI and Figure 2). In this case we expected to get four structures by taking into account that the sulfur radical reacts exclusively on the less hindered side of both monomers:

expected structures by the AD complex

$$RSCF_2CFClCHCH_3$$
$$\hspace{1cm}|$$
$$\hspace{1cm}OR$$
$$\text{VIIa}$$

$$RSCH_2CHCFClCF_2H$$
$$\hspace{1cm}|$$
$$\hspace{1cm}OR$$
$$\text{VIIb}$$

expected structures by the free monomers

$$RSCF_2CFClCH_2CH_2$$
$$\hspace{1cm}|$$
$$\hspace{1cm}OR$$
$$\text{VIIc}$$

$$RSCH_2CHCF_2CFClH$$
$$\hspace{1cm}|$$
$$\hspace{1cm}OR$$
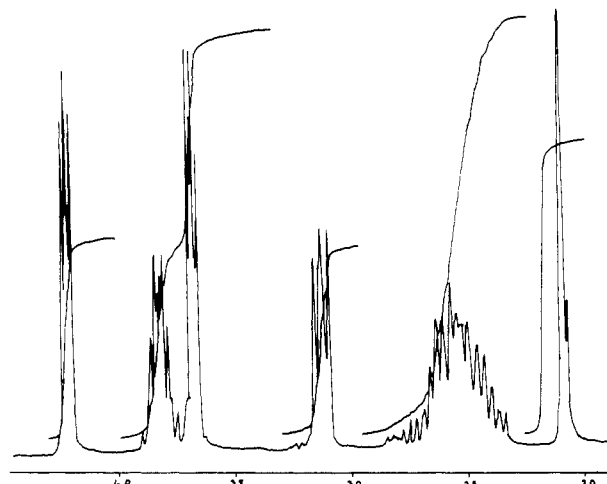$$\text{VIId}$$

with R = $CH_2CH_2OCOCH_3$.

Figure 2. ^{1}H NMR of the 1 + 1 adduct VII.

On the ^{1}H NMR spectrum of the 1 + 1 adduct (Figure 2) we do not observe the presence of a peak either at 6 ppm (this excludes structures VIIb and VIId) or at 1.5 ppm (expected for the methyl group of structure VIIa). Consequently, VIIc is obtained selectively.

In order to confirm the monoadduct of mercaptan monomers, we also performed the homotelomerization of CTFE and AcOVE with the same telogen and we obtained both the monoadducts V and VI. It was interesting to note that the addition of mercaptan onto vinyl ether is quantitative in a few minutes even at room temperature and without any initiator, whereas the reaction involving CTFE required both heat and initiator and the yield was about 70% after 5 h at 70 °C.

In the previous cotelomerization, we did not observe such a difference of reactivity between both monomers. On the contrary, the mercaptan was added onto CTFE rather than onto AcOVE.

These results have shown that the propagation occurred not only by complex addition of VII but also by simple addition of the noncomplexed olefins V and VI.

In conclusion, we can state that the high constant of charge transfer (i.e., a high amount of monomer in a complexed state) and the results obtained from the copolymerization follow a mechanism by propagation of the AD complex. On the contrary, the structure of the 1 + 1 adduct was in good agreement with a mechanism by propagation of free monomers.

III. Discussion

First, the formation of the AD complex and consequently propagation by means of this complex were often contradictory. For example Tirrell and co-workers[6] studied the reaction of N-phenylmaleimide and CEVE with Bu-
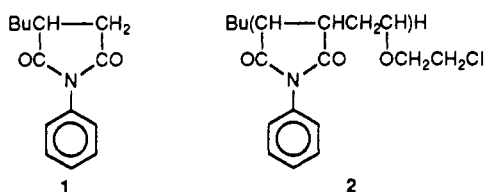
Table VI
^1H and ^{13}C NMR Characteristics of Compound VII

^1H

$|C_6F_{13} - CH_2 - CH_2 - S - CF_2 - CFCl - CH_2 - CH_2 - O - CH_2 - CH_2 - O - CO - CH_3$

signal behavior: m   t   m   m   t   t   s

chemical shift (10^{-6}):   2.55   3.15   2.55   3.85   3.65   4.25   2.1

^{13}C

$|C_6F_{13} - CH_2 - CH_2 - S - CF_2 - CFCl - CH_2 - CH_2 - O - CH_2 - CH_2 - O - CO - CH_3$

signal behavior: t   s   d   d   s   s   s   s

chemical shift (10^{-6}):   32.75   19.32   (m)   36.62   65.10   63.16   68.94   170.5   19.54

90 - 135

HgBr as initiator and $NaBH_4$ as transfer agent in order to identify the first adducts.
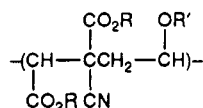
But, they obtained only product 1 and not the expected product, 2. They concluded that this result appears
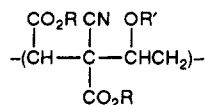

inconsistent with the concept that the concerted complex addition is the dominant pathway for maleimide consumption in copolymerization with CEVE.

Second, the steric hindrance has to be taken into account. Actually we recall that the structure of the complex described above exhibits a maximum of steric hindrance between the vicinal carbons due to both the chlorine and ether groups.

Besides, Butler et al.[14] showed that in the copolymerization of cyanoethylene dicarboxylate/CEVE, the structure obtained is

rather than the expected complex addition structure

Third, the polarizability of CTFE is not as important as the other usual monomers.

So it is well-known that, in the homopolymerization of CTFE, the inverse addition (tail to tail) is important (about 10%) and depends on the temperature,[16] 8,8%, 11,6%,

and 12,9% at -80, 0, and 80 °C, respectively. In the same way, Hauptschein et al.[17] have shown that the temperature has played an important role in the direction of the addition of ICl on CTFE monomer. Actually the only product which may be expected from the normal polarizability would be $ICFClCF_2Cl$. This latter compound was selectively obtained at 100 °C, whereas its amount was only 35% at 0 °C. The other isomer $ClCFClCF_2I$ was 65%.

Finally we noted above that the distribution of electronic charges from the donor to the three fluorine atoms of the acceptor was close together in the AD complex. Thus, because of the steric hindrance, the presence of two complexes can be suggested.

So, by taking into account all these results, we can propose two possibilities: In the first one, if we assume that the polarizability of CTFE is not so important, two kinds of complexes can be obtained and the copolymerization will occur from that which leads to the most thermodynamically stable complex from the corresponding complex.

In the second one, if we consider that the CTFE is rather polarized and only one structure of the complex is favored, the propagation occurred from free monomers only and the complex can be considered as a monomer source. Actually the equilibrium provides free monomers for the copolymerization, and the difference of polarizability explains the alternating structure given during copolymerization.

In our opinion, according to previous work[18] about the oligomerization of the CTFE, it is very difficult to explain 100% inversion of the structure of the 1 + 1 adduct by the low polarizability of the CTFE. So the second hypothesis seems better to us. Furthermore, such a statement may explain that the copolymerization occurs in a classical way (i.e., without a high exothermicity as in the case of

homotelomerization of VE). That is assigned to the low amount of free VE in the medium. Moreover, in the structure of the 1 + 1 adduct we note that addition of the nucleophilic thiol occurs selectively on the electrophilic group of the CTFE and this does not occur on the VE.

IV. Conclusion

We recall the main conclusions of this work:

First, in the products of cotelomerization we observe the formation of two monoadducts of each monomer.

Second, the structure of the 1 + 1 adduct, which is produced in the same time as the monoadducts, is opposite to that predicted by the CT complex.

Third, the equilibrium constant K_F of the AD complex is much higher ($K_F = 1.4$) than that in the other couple of AD monomers ($K \ll 1$).

Finally, elemental analysis of copolymers obtained at various feed compositions and in the beginning of the copolymerization is in good agreement with that of a high alternating structure.

The first two results demonstrate a propagation of the copolymerization by free monomers, and the last ones show a homopolymerization of the AD complex.

So we can think that the complex is a monomer reservation, that the equilibrium provides free monomers for the reaction, and that the difference of polarizability explains the alternating structure given during copolymerization.

V. Experimental Part

Starting Material. EVE and CEVE were supplied by Aldrich. CTFE and $C_6F_{13}C_2H_4SH$ were kindly supplied by ATOCHEM.

Apparatus. GPC was performed on a Spectra Physics SP 8810 chromatograph, fitted with five phenogel columns, 10^4, 10^3, 500, 100, and 50 Å. THF was used as eluant at a flow rate of 1.5 mL/min.

The viscosimeter was a Viscosimatic VSO AMTEC equipped with an Ubbelohde capillary of 0.5 mm.

^{1}H and ^{19}F NMR spectra were recorded with a Bruker WH-250 spectrometer (CDCl$_3$ as solvent) respectively with TMS and CFCl$_3$ as reference.

Glycidyl Vinyl Ether (GVE). GVE was prepared by transesterification as follows: In a 250-mL flask, fitted with a condenser and a mechanical stirrer, we introduced 48 g (0.65 mol) of glycidol, 74 g (0.97 mol) of EVE, 4.5 g of mercuric acetate, and 0.1 g of hydroquinone.

The mixture was kept at 40 °C and stirred for 48 h. After cooling, several washes by water/pentane mixtures (glycidol is hydrophilic, whereas the GVE is soluble in pentane) were performed and, in a last step, the water phase was treated with pentane.

The organic phases were gathered and dried with sodium sulfate, and the pentane was evaporated.

We obtained 22 g of GVE (yield after distillation 30%).

Synthesis of AcOVE. The preparation of AcOVE was carried out by solid–liquid phase-transfer catalysis in stoichiometric amounts of CEVE (50 g) and sodium acetate (39 g). A total of 2.2 g of TBAH was added.

The stirring rate was 450 rpm, and the reaction was kept at 109 °C for 12 h.

After cooling and filtration, the solid part (mainly NaCl) was washed by diethyl ether. The distillation of the gross led to AcOVE [bp = 72 °C (20 mm)] with 90% yield.

Determination of the Constant of the Complex CT. We prepared a primary well-known concentration [PC]$_1$ of EVE in CDCl$_3$; we also prepared a second one ([PC]$_2$ of CTFE in CDCl$_3$ (cooled to −15 °C)).

After 14 h, in order to obtain an equilibrium state, 0.2 mL of [PC]$_2$ was added carefully in each NMR tube. The [PC]$_1$ was introduced in the tubes in increasing quantities in order to obtain a known concentration (Table III). The ^{19}F chemical shifts were

also given in each case. Figure 1 shows that straight lines obtained in the constant determination.

Copolymerizations. All copolymers were prepared by such a method. The nonvolatile reactant was introduced in a Carius tube (2 mm thick, 260 mm long, 23-mm exterior diameter). After cooling with a liquid nitrogen/acetone mixture (−80 °C), CTFE was introduced by distillation until the required monomer weight was obtained. The tube was sealed and put in a shaken Prolabo oven fitted with a temperature regulator. After the reaction, the tubes were frozen in liquid nitrogen and opened.

Their contents were vacuum-distilled in order to remove solvent and monomers, and the polymers were kept under vacuum (10^{-2} Torr) until a constant weight was reached (Table IV). Elemental analysis results are listed Table V.

Cotelomerizations. Cotelomerizations were performed in a manner similar to the copolymerizations.

Thus, 11.1 g of AcOVE, 32.7 g of $C_6F_{13}C_2H_4SH$, 10.2 g of CTFE, and 0.7 g of *tert*-butyl peroxypivalate were heated to 68 °C for 4 h. The distillation gave the products V–VII.

Compound V. Anal. Calcd for $C_6F_{13}CH_2CH_2SCF_2CFClH$: C, 24.16; Cl, 7.15. Found: C, 24.46; Cl, 7.64. $Eb_{0.45mbar} = 25$ °C. ^{1}H NMR: δ 2.2–3.3 (two m, 4 H), 6.2 (t (J = 48.75 Hz), det (J = 5.25 Hz), 1 H). ^{19}F NMR: δ −80.5, −114.25, −121.5, 125.5 ($CF_3(CF_2)_5$), −85.5 (CF_2 from CF_2CFClH, 2 F), −147 ($CFClH$ from CF_2CFClH, 1 F).

Compound VI. Anal. Calcd for $C_6F_{13}CH_2CH_2SCH_2$-$CH_2OCH_2CH_2OAc$: C, 32.94; H, 2.94. Found:C, 33.41; H, 3.09. $Eb_{0.3mbar} = 95$ °C. ^{1}H NMR: δ 2.4 (m), 2.75 (m), 2.75 (t), 3.68 (t), 3.68 (t), 4.2 (t), 2.08 (s). ^{13}C NMR: δ 31.9 (t), 22.9 (s), 31.45 (s), 62.95 (s), 68.6 (s), 71.1 (s), 170.2 (s), 19.9 (s).

Compound VII. Anal. Calcd for $C_6F_{13}CH_2CH_2SCF_2$-$CFClCH_2CH_2OCH_2CH_2OAc$: C, 30.64; H, 2.39; Cl, 5.66. Found: C, 31.13; H, 2.45; Cl, 6.10. $Eb_{0.3mbar} = 130$ °C. ^{1}H and ^{13}C NMR: spectra previously described in text. ^{19}F NMR: C_6F_{13}, same peaks as in compound V; for CF_2CFCl group: CF_2, −84.5 (2 F) and $CFClH$, −116.75 (1 F).

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Registry No. I, 110-75-8; II, 109-92-2; III, 3678-15-7; IV, 6026-79-5; V, 136194-42-8; VIa, 136194-41-7; VIb, 140411-77-4; VIIa, 140411-78-5; VIIb, 140411-79-6; VIIc, 140411-80-9; VIId, 140411-81-0; (I)(CTFE) (alternating copolymer), 140411-83-2; (II)(CTFE) (alternating copolymer), 140411-82-1; CTFE, 79-38-9; glycidol, 556-52-5; sodium acetate, 127-09-3.