Synthesis and Polymerization of Fluorinated Monomers Bearing a Reactive Lateral Group—Part 7. Copolymerization of Tetrafluoroethylene with ω-Hydroxy Trifluorovinyl Monomers

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ABSTRACT: The radical copolymerization of tetrafluoroethylene (TFE) and trifluorovinyl ω-hydroxy comonomers [$F_2C{=}CF(CH_2)_mOH$ with $m = 1$ (FA1) and $m = 3$ (FA3)] for the synthesis of fluorinated polymers bearing hydroxy side groups is presented. FA1 was prepared by dehydrofluorination of 2,2,3,3-tetrafluoropropanol, whereas FA3 was obtained in a three-step scheme starting from the radical addition of 1,2-dichloroiodotrifluoroethane to allyl alcohol. The copolymerization conditions (in bulk or in solution in di n-butyl ether) and the polymer compositions considerably influenced the molecular weights, the molecular weight distributions, and the thermal properties of these copolymers. The kinetics of copolymerization of both couples enabled to determine the reaction order to the initiator (being 0.9) and the close values of apparent activation energies for [TFE/FA1 ($E_a = 52.4$ kJ · mol^{-1}) and for TFE/FA3 ($E_a = 46.8$ kJ · mol^{-1})] couples. From the Tidwell and Mortimer method, the relative reactivity ratios were calculated by elemental analysis or by ^{19}F-NMR spectroscopy, showing a higher reactivity of the TFE to incorporate the copolymer ($r_{TFE} = 2.47$ and $r_{FA1} = 0.41$; $r_{TFE} = 1.57$ and $r_{FA3} = 0.45$). The high values of the reaction order to the initiator and low molecular weights of copolymers were associated to the allylic chain transfer of the hydroxy comonomers and a mechanism of copolymerization was proposed. The comonomer diad and triad distribution was determined by the statistic theory and allowed one to calculate the average length of the comonomer sequences. Finally, the thermal decomposition of these cooligomers showed that those containing FA3 units are more thermostable than those synthesized from FA1, and that the higher the fluorinated alcohol content, the faster the thermal decomposition. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 189–202, 1999

Key words: tetrafluoroethylene; copolymerization; reactivity ratios; functional trifluorovinyl monomers; thermal properties

INTRODUCTION

Functional fluorinated copolymers have attracted considerable interest in the past decades, ranging

from perfluorinated ionomers and thermosetting coatings to fluoroelastomers.[1-3] Functional copolymers of fluoroolefins can be prepared by copolymerization with a comonomer containing either the functional group readily or a group able to produce the functional group by chemical modification.[4-6] The functional group, which is subsequently introduced in a lateral position about the backbone of the copolymer, brings specific and complementary properties: adhesion for a carbox-

ylic function,[7] solubility from a cyclohexyl group,[8] curability thanks to hydroxy or epoxide functions,[9–12] surface properties from a perfluorinated group,[13] and good hydrophilicity or heat and chemical resistances from phosphonated function.[14] Various functional monomers that exhibit an ω-trifluorovinyl group have already been synthesized. The Daikin Company[10–12] achieved the preparation of a series of various monomers having the formulae $F_2C=CF(CF_2)_n(CH_2)_m$ Ⓖ, where $n = 0, 1, 2$; $m = 1, 2$, and Ⓖ represents —OH or epoxy functions. Although Chvatal et al.[15] prepared $F_2C=CFC_2H_4OH$, Hu et al.[16] isolated in high yields perfluorovinyl monomers terminated with ester, amide, nitrile, or ketone groups, whereas Yang et al.[17] obtained ω-acetoxy, epoxide, furane, trimethyl silyl, or phosphonate fluoromonomers. The copolymers of vinylidene fluoride (VDF) with other fluoromonomers and nonfluorinated monomers including at least one hydroxy or other functional groups was recently outlined by Tournut.[18,19]

But, in that latter case, the functional monomers introduced hydrogenated carbon atoms in the polymeric backbone and affected the properties of the final product.[19]

Similar copolymers with a high content of tetrafluoroethylene (TFE)[4,20–24] or chlorotrifluoroethylene (CTFE)[5] have already been described. The radiation-induced copolymerization of methyl trifluoropropionate (containing an easily hydrolyzable ester group) with fluoroolefins, mainly with TFE and other olefins (ethylene, propylene), have also been discussed for other applications.[25,26]

Our present studies have two main goals: first, the synthesis of functional fluorinated comonomers and then their copolymerizations with fluoroolefins and/or other monomers. Previous investigations focussed our research on the synthesis of novel monomers bearing a reactive lateral group.[27–30] The strategy of synthesis of these trifluorovinyl functional monomers is based on the photochemical-induced addition of iodine monochloride to CTFE to give $ClCF_2CFClI$ isomer in high yields.[27] This compound reacted easily to allyl alcohol and in further steps led to 4,5,5-trifluoro-4-ene pentanol or other original trifluorovinyl ω-functional monomers[29] able to copolymerize with fluoroolefins.[30]

Copolymerization of different monomers (and especially fluoroolefins) with allylic compounds have found a little attention compared to that of vinyl derivatives because of the difficulties in free radical initiation and because the end products exhibit low molecular weights.[31]

Bartlett and Altschul,[32] Gaylord and Eirich,[33] and then Sakurada and Takahashi[34] investigated the radical homopolymerization of allyl compounds, and these last authors suggested a kinetic mechanism of this polymerization, analyzing the main peculiarities of an "allyl polymerization." Bartlett and Tate[35] demonstrated that the polymerization can be explained by "destructive chain transfer reactions." But Sakurada[34] and Gaylord[36] underlined that allyl radicals are able to add monomers as an "effective chain transfer" and allowed the propagation reaction. Further, allylic compounds (e.g., sulfides) have shown their effective radical chain transfer activity via an addition-fragmentation mechanism.[37,38] In addition, the radiation-induced copolymerization of allyl alcohol with N-vinylpyrrolidone was successful.[39]

One of the most important methods developed is radical initiation to obtain prepolymer, which, after molding, can be transfered into insoluble and infusible products with good physical properties and chemical resistance.[40]

Thus, it may be expected that copolymerization of TFE (or other fluoro-olefins) with ω-hydroxy trifluorovinyl monomers can offer new copolymers with interesting properties (better adhesion, compatibility, and crosslinking). On the other hand, these functional comonomers can be used as cure-site monomers (CSM), which should improve the curability of fluorocarbon elastomers (and in our case, TFE/propylene elastomers[41]) as a continuation of our previous investigations.[42–44]

Hence, the objective of this present work concerns the copolymerization of TFE with $F_2C=CF(CH_2)_m$—OH ($m = 1, 3$) and the thermal properties of the products obtained are discussed.

EXPERIMENTAL

Materials

TFE was synthesized by debromination of 1,2-dibromotetrafluoroethane (F-114 b2)[45] and distilled to 99.8% prior to use. The ω-hydroxy trifluorovinyl monomers were synthesized as described below. 2,2'-azobisisobutyronitrile (AIBN) and other reactants used were supplied by Aldrich.

Synthesis of Trifluorovinyl Alcohols

Preparation of 2,3,3-Trifluoroallyl alcohol (FA1)

In a three-necked round-bottom flask equipped with a condensor, a thermometer and a dropping

funnel, dried under vacuum, and flushed with argon to get rid off moisture, were placed 12.4 g (94 mmol) of 2,2,3,3-tetrafluoropropanol, 62.5 mL (367 mmol) of anhydrous dibutyl ether, and 9.5 g (94 mmol) of diisopropyl amine. The mixture was cooled to about 0°C. Then, 100 mL (200 mmol) of a 2 M butyl lithium solution in pentane was dropwise added for 30 min to prevent the temperature from exceeding 5°C. After stirring for 1 h, the medium was cooled down to an acetone/liquid nitrogen bath (-50°C). The excess of butyl lithium was decomposed with a solution of concentrated sulfuric acid (9.4 mL in 30 mL of water), and then the mixture was left to be warmed up to room temperature. The organic phase was separated by successive washings with a saturated solution of sodium hydrogen carbonate and water, then dried over anhydrous $MgSO_4$. Afterwards, the products were rectified under atmospheric pressure to separate pentane (b.p., 35°C), 32 mmol of 2,3,3-trifluoroallylic alcohol (b.p., 98°C), and dibutyl ether (134°C). Even by a second rectification, dibutyl ether was still present in the fraction of fluoroalcohol, and the yield being determined by ^{1}H- and ^{19}F-NMR was 34%.

^{1}H-NMR (CDCl$_3$) δ: 2.8 (broad signal, shifted with dilution, OH); 4.3 (d, $J_{HF} = 22.8$Hz, CH$_2$).

^{19}F-NMR (CDCl$_3$) δ: -103.4 (dd, $^2J_{FF} = 80.7$Hz, $^3J_{FFc} = 32.3$ Hz, 1F); -120.7 (dd, $^3J_{FFt} = 114.2$ Hz, $^2J_{FF} = 80.7$Hz, 1F); -181.4 (dd, $^3J_{FFc} = 32.3$ Hz, $^3J_{FFt} = 114.3$ Hz, 1F).

^{13}C-NMR (CDCl$_3$) δ: 54.88 (dt, $^2J_{CF} = 23.1$ Hz, $^3J_{CFt} = ^3J_{CFc} = 2.5$ Hz, CH$_2$); 127.76 (ddd, $^1J_{CF} = 236.1$ Hz, $^2J_{CF} = 51.7$ Hz, $^2J_{CF} = 14.5$ Hz, =CF); 153.26 (ddd, $^1J_{CF} = 290.3$ Hz, $^1J_{CF} = 277.1$ Hz, $^2J_{CF} = 45.2$ Hz, F$_2$C=).

Synthesis of 4,5,5-Trifluoro-4-ene pentanol (FA3)

Its preparation was similar to that recently described,[29] starting from the photochemical addition of iodine monochloride to CTFE, leading almost selectively to ClCF$_2$CFClI.[27] This latter reacted to allyl alcohol in the presence of AIBN, and then a selective reduction of the iodine atom occurred in the presence of tributyl stannane yielding ClCF$_2$CFClC$_3$H$_6$OH in 89% yield. Its dechlorination in the presence of zinc gave FA3 with 55% overall yield from 1,2-dichloroiodotrifluoroethane.[29]

Polymerization Procedure

Bulk and solution (in 34 wt % of butyl ether for FA1) copolymerizations of TFE with fluorinated alcohols (FA3 and FA1, respectively) were carried out by batch process in 30- and 50-cm^3 stainless steel autoclaves, equipped with a magnetic stirrer, a safety valve, a precise manometer (±0.01 MPa), and a thermometer (±0.2°C).

The autoclaves were charged by liquid monomer and initiator (AIBN), then cooled to liquid nitrogen and purged several times by evacuating and flushing with nitrogen in a stainless steel high-pressure vacuum line. The thaw–freeze cycling technique was applied to get rid off oxygen from the liquid phase. Then, the required amount of TFE was condensed in the autoclave. Polymerization reactions were carried out at different temperatures (60–75°C) at autogenious TFE pressure up to 10–12% monomer conversion.

After polymerization, the unreacted TFE was purged and FA1 and FA3 comonomers were first recovered by distillation and then evacuated under vacuum (10^{-2} mmHg at 50–60°C) until constant weight.

Analyses

The synthesis of the monomers was monitored by gas chromatography.

After reaction, the products were worked up with an alkaline sodium bisulfite solution and analyzed by gas chromatography (GC) using a Delsi apparatus (model 330) equipped with an SE-30 column, 3 m × 1/8 in (diam.). The nitrogen pressure at the entrance to the column was maintained at 0.6 bar, and the detector and injector temperatures were 260 and 255°C, respectively. The temperature programme 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) that automatically calculated the area of each peak on the chromatogram.

Molecular weight (MW) and molecular weight distribution (MWD) of the copolymers were determined by gel permeation chromatography (GPC) with a Waters II apparatus equipped with an integrator M730, a differential refraction detector R401 × 2 and 4 ultrastyragel columns, the diameters of the pores of which were: 500, 10^3, 10^4, and 10^5 Å. THF was used as the eluent at a rate of 1 mL/min at 45°C, using polystyrene and PMMA standards.

The products were characterized by ^{1}H- and ^{19}F-NMR spectroscopy at room temperature. They were recorded on a Bruker AC-200 or AC-250 instrument, using deuterated chloroform, acetone or DMF as solvents, and TMS or CFCl$_3$ as reference, for ^{1}H- and ^{19}F-NMR, respectively.

The IR spectra of the copolymer obtained were scanned by Specord M-80 (Germany) as a thin film layer on KBr cells.

The carbon, fluorine, and hydrogen contents in the copolymers were determined by elemental analysis (EA) by using an Erba Science 1108 analyser (C,H) and Dionex Serie 2001 ion-exchange chromatograph (USA) for fluorine contents.

Thermogravimetric analyses of the copolymers were monitored on a Du Pont 200 TG-1 analyses from 25 to 600°C at a heating rates of $10°C \cdot min^{-1}$.

RESULTS AND DISCUSSION

The radical copolymerizations of tetrafluoroethylene (TFE) with trifluorovinyl alcohols (FA3 or FA1) were performed in bulk or in solution, respectively, yielding random copolymers, as follows:

In the synthesis of functional fluorine-containing copolymers, one of the most difficult stage is based on obtaining the fluorinated comonomer bearing a reactive lateral group. Hence, this first topic is described below, followed by the synthesis of the copolymers and their properties.

Preparation of Trifluorovinyl Alcohols (FA1 and FA3)

Scheme 1 represents the routes for the syntheses of FA1 and FA3 fluoroalcohols.

The 2,3,3-trifluoroallyl alcohol (FA1) was prepared by reacting anhydrous *n*-butyl lithium to 2,2,3,3-tetrafluoro propanol according to the method described by Nguyen and Wakselman,[46,47] and recently optimized.[48]

Hence, we obtained comonomers containing perfluorovinyl group and ω-hydroxy or acetoxy end groups. The corresponding monomers containing acetoxy group have been successfully involved in copolymerization with vinylidene fluoride,[30] but are not used in this present study.

An advantage of such type of comonomers is the retaining of high fluorine content in the polymeric backbone, which determines the good thermal, chemical, and oil resistance of the copolymer

Scheme 1 General routes for the synthesis of 2,3,3-trifluoroallyl alcohol (FA1) and of 4,5,5-trifluoro-4-ene pentanol (FA3).

obtained. Several different fluoroolefins such as TFE, VDF, CTFE, trifluoroethylene, or vinyl fluoride can be utilized as principal monomers. In the present work, TFE was chosen.

Copolymerization of TFE with Trifluorovinyl Alcohols

Synthesis of the Copolymers and Their Characterizations

The radical copolymerization of TFE with FA1 was carried out in dibutyl ether, whereas that involving FA3 was done in bulk. As a suitable initiator for radical copolymerization, was selected AIBN in a high concentration range (from 0.5 to 2.5 mol % vs. the monomer mixture), which is preferable for allyl polymerizations due to the "allyl chain-transfer reactions."[34,35] It has a decomposition rate that can be assumed to be independent of the solvent, and its relatively low decomposition energy[49] allows one to perform reactions in the temperature range of 60–80°C (its half-life at 80°C equals 1 h). The TFE/fluoroalcohol initial molar ratios varied in a wide range, from 90/10 to 10/90 (Table I). To increase the polymerization rate and to keep the autogeneous pressure of monomer mixture higher than the critical one (it is worth 3.95 MPa at 33.4°C for

Table I **Monomer/Copolymer Compositions of TFE/F$_2$C=CF(CH$_2$)$_m$—OH Copolymers Determined by Elemental Analysis (EA, Mean of Two Analyses) and ^{19}F-NMR Spectroscopy (m = 1 (FA1), runs 1–7 and m = 3 (FA3), runs 8–14)**

| Run No. | Monomer Composition, mol % | | Polymer Yield (%) | Elemental Analysis | | | Copolymer Composition, mol % | | | |
| | TFE | FA | | % C | % F | % H | TFE | | FA | |
							EA	^{19}F-NMR	EA	^{19}F-NMR
1	91.3	8.7	13.8	24.36	74.88	0.12	96.0	95.5	4.0	4.5
2	80.1	19.9	12.2	24.79	73.55	0.26	91.2	88.1	8.8	11.9
3	65.6	34.4	11.5	25.58	71.13	0.52	82.3	81.7	17.7	18.3
4	49.7	50.3	10.0	26.46	68.43	0.81	72.2	71.5	27.8	28.5
5	30.5	69.5	7.4	28.10	63.35	1.35	52.5	51.3	47.5	48.7
6	19.8	80.2	5.4	29.48	59.09	1.80	35.2	33.9	64.8	66.1
7	10.1	89.9	3.2	30.48	56.00	2.13	22.2	21.7	77.8	78.3
8	85.6	14.4	14.2	26.22	71.85	0.59	91.3	90.4	8.7	9.6
9	79.2	20.8	13.7	27.45	69.55	0.91	86.2	84.4	13.8	15.6
10	62.6	37.4	12.0	29.98	64.81	1.59	75.1	74.1	24.9	25.9
11	49.1	50.9	8.4	32.68	59.76	2.30	62.1	61.8	37.9	38.2
12	30.2	69.8	5.6	35.36	54.75	3.01	48.0	46.7	52.0	53.3
13	21.3	78.7	5.4	38.02	49.77	3.72	32.6	33.4	67.4	66.6
14	9.6	90.4	4.1	40.58	44.97	4.40	16.1	14.9	83.9	85.1

TFE), the initial TFE content was 80 mol % in most experiments.

In this case, the copolymerization proceeded in the liquid phase of the fluorinated alcohol, in which AIBN was soluble. The TFE monomer from the gas phase diffused through the interphase boundary to enter in the reaction medium. The copolymerization of TFE with fluoroalcohols proceeded, and the end products were not soluble in the reaction medium-typical characteristic of heterophase polymerization.

Different types of products were produced under the various reaction conditions: from light-yellow oils to waxy substances. Hence, they were cooligomers with relatively low molecular weights (in the range from 500 to 2000 for TFE/FA1 products). Gel permeation chromatography (GPC) analysis was illustrated for one of these products (TFE/FA1 = 80/20 mol %), and has the following molecular characteristics: $\overline{M}_w$ = 1100, $\overline{M}_n$ = 964, $\overline{M}_z$ = 1150, and the polydispersity index (PDI) was 1.14 (Fig. 1). The higher the fluoroalcohol content, the lower the molecular weight of the copolymer and the greater the polydispersity index. This PDI reached 2.0 for an initial TFE/FA1 molar ratio of 10/90, and such a value corresponds to a statistical distribution of molecular weight (M_w). The peaks assigned to the low M_w fraction showed a tendency of increasing.

For the waxy-like TFE/FA3 products, the $\overline{M}_w$ was higher (up to 7 × 10^3 in PMMA standards) and the PDI was also increased (1.5 < PDI < 4.5).

The TFE/FA cooligomers were completely soluble in organic polar solvents such as THF, acetone, and DMF. This means that the homopolymerization of TFE did not occur. Because of the extremely low aptitude of FA for radical polymerization, homopolymerization of FA can be neglected, and such a statement was experimentally evidenced by NMR. However, two consecutive FA units can be observed in the copolymer.

Hence, a cooligomerization of TFE with FA is expected. This was shown for all the products

Figure 1 GPC curve of TFE/CF$_2$=CFCH$_2$OH oligomers, obtained at [AIBN] = 1.5 mol %, P = 4.5 MPa, T = 70°C, and TFE/FA1 = 80/20 mol % in the feed.

Figure 2 ^{1}H-NMR spectrum of TFE/CF$_2$CFCH$_2$OH cooligomer. Polymerization conditions: [AIBN] = 1.5 mol %, P = 4.5 MPa, T = 70°C, and TFE/FA1 = 80/20 mol % in the feed.

synthesized and evidenced by IR and NMR spectroscopy. For example, the IR spectrum of TFE/FA1 oligomer (from the initial TFE/FA1 molar ratio of 80/20) exhibits the characteristic absorptions of TFE base units and were observed in all IR spectra: the absorption at 660 and 550 cm^{-1} were attributed to the deformation vibrations δ_{CF2} of TFE moities. Complex absorptions at 1160–1300 cm^{-1} were assigned to very strong valence vibrations of difluoromethylene groups ν_{CF2}. On the other hand, the absorption at 1350 cm^{-1} can be assigned to the δ_{CH2}, whereas at 2970 cm^{-1} the valence vibrations of the methylene group appeared in the FA. In addition, the broad absorptions at 3100–3700 cm^{-1} were related to the hydroxy group in the FA base units.

Figure 2 represents the ^{1}H-NMR spectrum of the copolymer synthesized in bulk copolymerization of TFE with FA1 (from an initial TFE/FA1 molar ratio of 80/20). It is observed that the expected low field shifted HOCH$_2$— end groups of the pendant chain centred at 4.35 ppm. Adding a drop of trichloromethyl isocyanate in the NMR tube solution brought about a chemical shift of 1

ppm (at about 5.2 ppm) giving the evidence of such end group as previously observed for HOCH$_2$(VDF)$_n$—H telomers.[50] The broad signals centered at about 1.95 and 1.55 ppm are assigned to the methylene groups adjacent to the fluorinated backbone and to the central methylene group, respectively.

Surprisingly, the triplet (^{2}J$_{HF}$ = 54.8 Hz) of triplet (^{3}J$_{HF}$ = 4.3 Hz) centrered at 6.10 ppm was noted, and provides one with the occurrence that a CF$_2$H end group was produced. This group could come from either the allylic transfer of proton of the fluorinated alcohol or from the transfer of one proton of the methylene group adjacent to the oxygen atom in the dibutyl ether.

The ^{19}F-NMR spectra (Fig. 3) of TFE/FA1 cooligomers exhibit the expected signals at −176, −185, and −213 ppm assigned to the fluorine atoms of the fluoroalcohol unit —CF$_2$—C$\underline{F}$(CH$_2$OH)—. These assignements were deduced from those observed in the model telomers R$_F$CF$_2$CFIC$_3$H$_6$OAc recently prepared by the radical telomerization of FA3 with perfluoroalkyl iodides (R$_F$I).[51]

Figure 3 ^{19}F-NMR spectrum of TFE/CF$_2$=CFCH$_2$OH oligomer. Polymerization conditions as in Fig. 2.

The CF$_2$H end group was noted as a doublet (^{2}J$_{FH}$ = 55.0 Hz) of multiplet centred at -115.2 ppm.

The difluoromethylene groups of TFE and FA base units are observed in the -110 to -140 ppm range, for which the integration is I_1. Taking into account the integration I_2 of the fluorine atom from -175 to -215 ppm and its contributions in the -110 to -140 ppm zone, the proportion α of TFE units in the TFE/FA copolymer is given by the following ratio:

$$\alpha = \frac{I_1 - 2I_2}{4I_2}$$

Table I listed the TFE/FA molar ratios in the copolymer vs. initial TFE/FA molar ratios. It can be noted that these results are in good agreement with those calculated from elemental analysis (Table I). These compositions, determined from both techniques above, enabled us to calculate the relative reactivity ratios of both monomers in their radical copolymerization.

Kinetics of the TFE/FA Copolymerization

The kinetic study of the copolymerization of TFE with trifluorovinyl ω-hydroxy monomers (FA) was considered from two different topics. First, the polymerization rate and the apparent activation energy of the TFE/FA cooligomerization were studied, and then the determination of the reactivity ratios of the comonomers.

Determination of the Reaction Orders and of the Activation Energies

Figures 4 and 5 represent the kinetic curves of TFE monomer consumption in both reactions involving FA1 and FA3 as the comonomers, at different concentrations of AIBN initiator. The copolymerization rate R (mol $\cdot$ l^{-1} $\cdot$ h^{-1}) was determined by the initial slope of the kinetic curves.

The reaction order to AIBN was found to be 0.9 for both fluoroalcohols from the linear dependence of R vs. initiator concentration in logarithmic coordinates. This value is higher than that observed for a homogeneous free radical polymer-

Figure 4 Kinetic curves of TFE consumption (mol/L) during the copolymerization with FA1 at different AIBN concenrations (mol %): ◆—1.00; ■—1.50; ▲—2.00; ●—2.50.

ization (0.5). This may probably come from either the chain-transfer reaction to FAs or the heterophase character of the reaction studied or both.

The apparent activation energies (E_a) of the cooligomerizations were determined from the slopes of the linear R/T dependance in Arrhenius coordinates for the 60–75°C temperature range (Fig. 6). They worth 46.3 and 52.4 kJ · mol^{-1} for TFE/FA3 and TFE/FA1, respectively.

These values are rather low compared to that of heterophase reactions of TFE with α-olefins,[52] for which $E_a > 80$ kJ · mol^{-1}.

Consequently, the higher value of the reaction order to AIBN (0.9) is mainly attributed to the

Figure 5 Kinetic curves of TFE consumption (mol/L) during the copolymerization with FA3 at different AIBN concentrations (mol %): ◆—1.00; ■—1.50; ▲—2.00; ●—2.50.

Figure 6 Dependence of polymerization rate R vs. temperature (T) in Arrhenius coordinates for the copolymerization of TFE with FA1 (■) and FA3 (◆). Polymerization conditions: [AIBN] −1.5 mol %, 4.5 MPa, initial molar ratio of TFE/FA = 80/20.

allyl chain-transfer reaction that took place in the termination step. Such a statement correlates well with the low degree of polymerization ($\overline{DP_n}$ = 5–7 for TFE/FA1 products) determined by GPC.

Calculation of the Reactivity Ratios

The second part of the kinetic study concerns the determination of the reactivity ratios of both comonomers involved in the copolymerizations of each couples TFE/FA1 and TFE/FA3. In a first step, it was necessary for the monomer/polymer compositions to be investigated.

From the elemental analyses (EA) data, and especially from the carbon and fluorine contents and from the integrations of the characteristic signals in the ^{19}F-NMR spectra as shown above, the average compositions were calculated.

The results are mentioned in Table I and in Figure 7 and are in rather good agreement. For both copolymerizations and at each initial TFE/FA molar ratio, a higher reactivity of TFE than that of the fluoroalcohols was observed and that of TFE and FA1 obey of the "ideal copolymerization" (Fig. 7).

From the Tidwell and Mortimer method[53] the relative reactivity ratios (r_i) were calculated and were found to be as follows:

i) For the couple TFE/FA1

$$r_{\text{TFE}} = 2.64 \text{ and } r_{\text{FA1}} = 0.41 \text{ (from EA)}$$

Figure 7 Monomer/copolymer composition curves of TFE/FA1 solution and TFE/FA3 bulk copolymerizations. For TFE/FA1: from elemental analysis (■) and from NMR (□). For TFE/FA3: from elemental analysis (▲), and from NMR (△).

Figure 8 Joint confidential surfaces (95% probability) and most probable values: full line and cross ($r_1 = 2.64$, $r_2 = 0.41$) from elemental analysis; dotted line and circle ($r_1 = 2.30$, $r_2 = 0.40$) from NMR analysis for TFE/FA1 copolymerization.

$$r_{TFE} = 2.30 \text{ and } r_{FA1} = 0.40 \text{ (from NMR)}$$

ii) For the couple TFE/FA3

$$r_{TFE} = 1.62 \text{ and } r_{FA3} = 0.44 \text{ (from EA)}$$

$$r_{TFE} = 1.52 \text{ and } r_{FA3} = 0.46 \text{ (from NMR)}$$

The results obtained from EA and ^{19}F-NMR analyses led to rather close values of r_{TFE} and r_{FA}. Taking into account that $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, where subscripts 1 are 2 are for TFE and for FA, respectively, it can be concluded that FA3 exhibits ca. 1.5 times higher reactivity to TFE than FA1. The product $r_1 \cdot r_2$ for FA1 is almost unity (meaning an "ideal copolymerization"), and for FA3, $r_1 \cdot r_2 = 0.72$, a value typical for random copolymerization.

Figures 8 and 9 represent the joint confidential areas of 95% probability for the determination of reactivity ratios of TFE/FA1 and TFE/FA3 comonomers. In each figure, two confidential curves are observed, corresponding to both EA and NMR analyses. In the case of TFE/FA1 couple, the data from EA are more precise than those from NMR, but the most probable r_1 and r_2 values are similar; a slight difference (Fig. 8) is shown only for r_1 (less than 10%). For the TFE/FA3 couple, the intervals of confidence deduced from

EA and NMR are the same (Fig. 9), and led to very close values of r_1 and r_2 (the difference is less than 8.3 and 1.4%, respectively).

On the basis of r_1 and r_2 ratios, the Q-e values of both alcohols were determined according to Alfrey and Price equation[54] using Greenley's Q-e values[55] for TFE (0.032 and 1.63, respectively):

Figure 9 Joint confidential surfaces (95% probability) and most probable values: full line and cross ($r_1 = 1.62$, $r_2 = 0.44$) from elemental analysis; dotted line and circle ($r_1 = 1.52$, $r_2 = 0.46$) from NMR analysis for TFE/FA3 copolymerization.

Figure 10   Normalized fractions of monomer F_{AA} ($\bigcirc$), F_{BB} ($\times$), and $F_{\overleftrightarrow{AB}}$ ($\triangle$) diads vs. the TFE/FA1 copolymer composition. $F_{\overleftrightarrow{AB}}$ means $F_{AB} + F_{BA}$.

FA1: $Q = 0.011$; $e = 1.52$ and

FA3: $Q = 0.008$; $e = 1.04$

Copolymer Composition

Determination of Diads and Triads

Ito and Yamashita[56] developed a theory to characterize the copolymer composition and its microstructure by applying the statistical stationary process given by Coleman and Fox.[57]

In contrast to Ito and Yamashita,[56] who treated three models, we have selected the simplest one (i.e., the terminal model). This theory was successfully applied by Yagi and Tatemoto[58] for the copolymerization of vinylidene fluoride with trifluoroethylene. Two independant conditions of probability can be kinetically written as follows:

$$P_{AB} = 1/(1 + r_A F) \text{ and } P_{AA} = 1 - P_{AB}$$

$$P_{BA} = 1/(1 + r_B/F) \text{ and } P_{BB} = 1 - P_{BA}$$

with $r_A = r_{TFE}$, $r_B = r_{FA}$, and $F = [A]/[B]$ in the feed.

The fractions of monomer diads F_{AA}, F_{AB}, F_{BA}, and F_{BB} can be calculated by the following equations:

$$F_{AA} = P_{BA}P_{AA}/(P_{AB} + P_{BA})$$

$$F_{AB} = F_{BA} = P_{BB}P_{BA}/(P_{AB} + P_{BA})$$

Figure 11   Normalized fractions of monomer F_{AAA} ($\bigcirc$), F_{BBB} ($\times$), $F_{\overleftrightarrow{AAB}}$ ($\triangle$), and $F_{\overleftrightarrow{BBA}}$ ($*$) triads vs. the TFE/FA1 copolymer composition. $F_{\overleftrightarrow{AAB}}$ and $F_{\overleftrightarrow{BBA}}$ mean $F_{AAB} + F_{BAA}$ and $F_{BBA} + F_{ABB}$, respectively.

$$F_{BB} = P_{AB}P_{BB}/(P_{AB} + P_{BA})$$

$$F_{AA} + F_{AB} + F_{BA} + F_{BB} = 1$$

The results for the normalized fractions of monomer diads and triads vs. polymer composition are represented in Figures 10 and 11 and in Figures 12 and 13 for TFE/FA1 and TFE/FA3,

Figure 12   Normalized fractions of monomer F_{AA} ($\bigcirc$), F_{BB} ($\times$), and $F_{\overleftrightarrow{AB}}$ ($\triangle$) diads vs. the TFE/FA3 copolymer composition. $F_{\overleftrightarrow{AB}}$ stands for $F_{AB} + F_{BA}$.

Figure 13 Normalized fractions of monomer F_{AAA} ($\diamond$), F_{BBB} (*), $F_{\overleftrightarrow{AAB}}$ ($\square$), F_{ABA} ($\triangle$), $F_{\overleftrightarrow{BBA}}$ ($\bigcirc$), and F_{BAB} ($\times$) triads vs. the TFE/FA3 copolymer composition. $F_{\overleftrightarrow{AAB}}$ and $F_{\overleftrightarrow{BBA}}$ mean $F_{AAB} + F_{BAA}$ and F_{BBA} and F_{ABB}, respectively.

respectively. In these Figures, $F_{\overleftrightarrow{AB}}$, $F_{\overleftrightarrow{AAB}}$, and $F_{\overleftrightarrow{BBA}}$ stand for $F_{AB} + F_{BA}$, $F_{AAB} + F_{BAA}$, and $F_{BBA} + F_{ABB}$, respectively. Considering TFE/FA1 system, it is observed, as expected, that the crossing point for homodiad distribution corresponds to a maximum point of heterodiad (Fig. 10). In the triad distribution curve (Fig. 11), F_{ABA} is shown to overlap with F_{AAB}, and the same tendency happened for F_{BAB} and F_{BBA} triads. Obviously, fractions F_{AAB} or F_{ABA} triads are shifted toward low FA1 contents, whereas F_{BBA} and F_{BAB} fractions are moved toward higher FA1 amounts.

The same tendencies are observed for TFE/FA3 system (Figs. 12 and 13).

Average Length Distribution

To calculate the average length distribution of both units in each TFE/FA system, the following formula was applied:[59]

$$\bar{N}(A) = 1 + r_A \cdot F \quad \text{and} \quad \bar{N}(B) = 1 + r_B/F$$

where r_A and r_B represent the reactivity ratios of TFE and fluoroalcohol, respectively. The results are listed in Table III.

For both TFE/FA systems, it is noted that the higher the TFE content in the copolymer, the longer the TFE block. Further, FA3 confirms its higher reactivity because for the same initial

Table II Thermal Stabilities of TFE/F$_2$C=CF(CH$_2$)$_m$—OH Cooligomers ($m = 1$ and 3 for Samples 1–7 and 8–14, respectively)

Sample No.	TFE Content[a] in Cooligomer (mol %)	T_d, °C 2% wt loss	T_d, °C 50% wt loss
1	95.8	240	348
2	89.7	165	260
3	82.0	140	237
4	71.8	123	215
5	51.9	96	191
6	34.6	88	180
7	21.9	85	175
8	90.9	275	365
9	85.3	216	320
10	74.6	175	280
11	62.0	152	263
12	47.4	125	227
13	33.0	120	215
14	15.5	110	205

[a] Mean of EA and ^{19}F-NMR data.

TFE/FA (e.g., 80/20 in runs 2 and 9), the average chain lengths of the TFE block were equal to 10 and 6 monomeric units for 1 FA unit in the TFE/FA1 and TFE/FA3 systems, respectively.

Hence, in the copolymerization of TFE with FA, a predominant random distribution of FA

Table III Average Length Distribution of Comonomer Units in TFE/FA1 Copolymers (runs 1–7) and TFE/FA3 Copolymers (runs 8–14) from Various Feed Compositions

Run No.	TFE	FA	$\bar{N}$(TFE)	$\bar{N}$(FA)
1	91.3	8.7	26.91	1.01
2	80.1	19.9	10.95	1.10
3	65.6	34.4	5.72	1.21
4	49.7	50.3	3.45	1.41
5	30.5	69.5	2.09	1.92
6	19.8	80.2	1.62	2.62
7	10.1	89.9	1.27	4.68
8	85.6	14.4	10.33	1.08
9	79.2	20.8	6.98	1.12
10	62.6	37.4	3.62	1.27
11	49.1	50.9	2.51	1.47
12	30.2	69.8	1.68	2.05
13	21.3	78.7	1.42	2.67
14	9.6	90.4	1.17	5.09

units between TFE homodiads or homotriads, as it was observed earlier for the copolymerization of TFE with other functional fluorinated comonomers,[56] is expected.

Mechanism of Copolymerization

These results enable us to propose the following scheme for that copolymerization:

Initiation

$$NC—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—N{=}N—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—CN \xrightarrow{\Delta} 2R^\bullet \text{ with R}: NC—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{}^\bullet$$

$$R^\bullet + F_2C{=}CF_2 \rightarrow R—CF_2—CF_2^\bullet$$

Propagation

$$R—CF_2—CF_2^\bullet + F_2C{=}CF_2 \rightarrow RCF_2CF_2CF_2CF_2^\bullet$$

$$R(C_2F_4)_n—CF_2—CF_2^\bullet + F_2C{=}CF_2 \rightarrow R(C_2F_4)_{n+1}—CF_2CF_2^\bullet$$

$$R(C_2F_4)_{n+1}CF_2CF_2^\bullet + FA \rightarrow R(C_2F_4)_{n+2}—\underset{\underset{R'}{|}}{CF_2}—CF^\bullet \text{ and } R(C_2F_4)_{n+2}\underset{\underset{R'}{|}}{C}FCF_2^\bullet$$

$$\underline{A} \qquad\qquad\qquad \underline{B}$$

with R': $(CH_2)_mOH(m = 1, 3)$

and

$$\underline{A} \text{ and } \underline{B} + F_2C{=}CF_2 \rightarrow R(C_2F_4)_{n+2}CF_2—\underset{\underset{R'}{|}}{CF}—CF_2—CF_2^\bullet$$

$$+$$

$$R(C_2F_4)_{n+2}\underset{\underset{R'}{|}}{CF}—CF_2—CF_2CF_2^\bullet$$

Termination

The recombination occured in few amount compared to the allyl chain transfer.

 i) recombination

$$R—(C_2F_4)_q(FA)(C_2F_4)_r^\bullet \rightarrow R(C_2F_4)_q(FA)(C_2F_4)_{2r}(FA)(C_2F_4)_qR$$
$$\text{with } 2r + 2q < 6\text{–}8 \text{ for FA1}$$
$$\text{and } 2r + 2q < 30\text{–}40 \text{ for FA3}$$

ii) allyl chain tranfer

$$P_n^\bullet + FA \rightarrow P_nH + F_2C{=}CF\dot{C}HOH$$
$$\text{(macroradical)} \qquad\qquad \updownarrow$$
$$F_2\dot{C}—CF{=}CHOH$$

It can, thus, be observed that the higher the FA content in the monomer mixture (up to 80–90 mol %), the greater the amount of heterodiads, and at the same time, the lower the polymerization rate, the yield, and the molecular weight.

Thermal Properties

All these cooligomers obtained were studied by thermogravimetric analysis between 20 and 600°C, at a scanning rate of $10°C \cdot min^{-1}$. They exhibit relatively good thermal stability at higher TFE content in the cooligomers (Table II). The starting decomposition temperature (2 wt % loss, $T_{d,2}$) decreases from 240°C (for the TFE/FA1 initial molar ratio of 91.3/8.7) to 85°C (for the TFE/FA1 of 10/90)). Obviously, these decomposition temperatures are considerably lower than those of the fluorocarbon resins (for PTFE[61] $T_{d,2}$ = 450°C $T_{d,50}$ = 535°C), but the oligomeric character of the products has to be taken into account.

The temperature of half decomposition ($T_{d,50}$) also decreases with the FA content in the copolymer (from 348 to 175°C at FA1 content in the copolymer from 4.2 to 78.1 mol %). A similar tendency was observed for TFE/FA3 cooligomers; yet their thermal stability is higher (275–110°C) for $T_{d,2}$ and 365–205°C for $T_{d,50}$ with an increase of the FA3 content in the oligomer from 9.1 to 84.5 mol %.

CONCLUSION

The synthesis of fluorinated functional cooligomers was achieved from the radical copolymerization of TFE with trifluorovinyl ω-hydroxyl comonomers (FA1 or FA3) initiated by AIBN. The kinetics of copolymerization of TFE with FA1 or FA3 led to a reaction order to AIBN of 0.9 and to low values (for heterophase polymerization) of apparent activation energies (46.8 and 52.4 $kJ \cdot mol^{-1}$ for TFE/FA3 and TFE/FA1 copolymerizations, respectively). From this kinetics, it was supposed that the chain-transfer reaction to fluorinated alcohols involved the main contribution to the termination step. That could explain the obtaining of cooligomers instead of copolymers.

TFE was more reactive in all proportions whatever its copolymerization with FA1 or FA3, as evidenced its high reactivity ratio (r_{TFE} = 2.47 with FA1 and 1.57 with FA3) about those of the fluoroalcohols (ca. 0.4). That suggests a random distribution of FA units between TFE homodiads and triads. In addition, the FA3 comonomer was shown to be more reactive than FA1, and this was also evidenced by the average chain lengths of monomer units in each copolymer.

Such novel functional fluorinated cooligomers appear interesting precursors for the preparation of the curing system under investigation.

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