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Unexpected Alternating Copolymerization of Vinylidene Fluoride Incorporating Methyl Trifluoroacrylate

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ABSTRACT: The radical copolymerization of methyl trifluoroacrylate (MTFA) with vinylidene fluoride (or 1,1-difluoroethylene, VDF), initiated by *tert*-butyl 2,2-dimethylperoxypropanoate, is presented. The kinetics of copolymerization was investigated in a series of eight reactions for which the initial $[VDF]_0$/$[MTFA]_0$ molar ratios ranged between 14.5/85.5 and 88.7/11.3. The composition of copolymers, i.e., the molar ratios of VDF and MTFA monomeric units in the copolymers, was determined by ^{19}F NMR spectroscopy mainly. The reactivity ratios, r_i, determined according to the Tidwell and Mortimer law, were assessed to be: $r_{VDF} = 0.30 \pm 0.03$ and $r_{MTFA} = 0$ at 50 °C, which clearly shows tendency of the copolymerization system toward alternation copolymerization. Copolymerizations at high monomer conversions were also attempted and showed a good incorporation of MTFA and rather high molecular weights (up to 26000).

Introduction

Fluorinated polymers are interesting materials thanks to their outstanding properties[1−4] such as thermal stability, chemical inertness (to solvents, oils, water, acids, and bases), low values of the refractive index, permittivity, dissipation factor, and water absorptivity, excellent weather durability, and resistance to oxidation. Hence, they can find relevant applications in many fields of high technology: aeronautics, microelectronics, engineering, chemical and automobile industries, optics, textile finishing, and wiring insulation.

Among these polymers, those containing vinylidene fluoride (VDF or 1,1-difluoroethylene) monomeric units are of particular importance, since they can be thermoplastics,[5,6] elastomers,[7−10] or thermoplastic elastomers.[11] They are typically prepared by radical copolymerization of VDF with other fluoroalkenes. Statistic copolymers are usually obtained. However, VDF/hexafluoroisobutylene, commercialized by the Allied Co. under the CMX trademark, is an alternating copolymer.[12−13] Many functional fluorinated monomers have been copolymerized with VDF, mainly those bearing the following functional end groups: hydroxy,[14−16] acetoxy,[15,17] carboxy,[17] thioacetoxy,[17,18] benzoate,[19] sulfonyl fluoride,[20−24] nitrile,[25,26] bromine,[27−31] or a perfluorinated group.[25,32−39]

Another interesting fluorinated monomer is methyl trifluoroacrylate (MTFA), which does not homopolymerize.[40] However, MTFA successfully copolymerized with monomers such as tetrafluoroethylene,[41] vinyl chloride,[42] styrene,[42] vinyl acetate,[42] ethylene,[43] propene,[44] or vinyl ethers.[45] Some of the copolymers found applications as ion exchange membranes.[46] Copolymerization of VDF with MTFA has been reported by Watanabe et al.[47] and claimed in Japanese patents.[48,49] The first authors carried out the electron beam irradiation induced copolymerization (one experiment only) and showed that VDF was more incorporated into the resulting copolymer compared to MTFA (a copolymer containing 62 mol % VDF units was formed from an irradiated equimolar mixture of VDF and MTFA).

In the present paper, we report results of a more detailed study on the VDF/MTFA radical copolymerization system, in which we have used classical initiation by peroxides that provides robust results according to our previous investigations.[15−19,24,26,31,39]

Experimental Part

(a) Reactants and Methods of Analysis. Vinylidene fluoride and 1,1,1,3,3-pentafluorobutane (Solvay S.A., Tavaux, France), 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane, tech, 90% (Luperox 101) (Aldrich), and *tert*-butyl 2,2-dimethylperoxypropanoate (la Chalonnaise des Peroxydes) were used as supplied, acetonitrile of analytical grade (Aldrich Chimie, 38299 Saint Quentin-Fallavier, France) was distilled over calcium hydride prior to use. Methyl trifluoroacrylate was prepared by a procedure described previously.[50]

The compositions of the copolymer (the molar contents of VDF and MTFA monomeric units in the prepared copolymer) were determined by ^{19}F NMR spectroscopy. The NMR spectra were recorded on Bruker AC 200 and AC 250 instruments, using deuterated acetone as the solvent and TMS (or $CFCl_3$) as the reference for ^{1}H (or ^{19}F) nuclei. Coupling constants and chemical shifts are given in hertz and parts per million, respectively. The experimental conditions for ^{1}H (or ^{19}F) NMR spectra are the following: flip angle 90° (30°), acquisition time 4.5 s (0.7 s), pulse delay 2 s (5 s), number of scans 16 (64), and pulse width 5 μs for ^{19}F NMR.

(b) Copolymerization: Determination of the Reactivity Ratios. The batch copolymerizations of VDF with MTFA were performed in thick borosilicate Carius tubes (length 130 mm, internal diameter 10 mm, thickness 2.5 mm, total volume 8 cm^3). After introduction of the initiator (1.0 mol % relative to the monomer mixture), MTFA, and acetonitrile under inert atmosphere, the tube was connected to a vacuum line and purged several times by evacuating and flushing with helium. After at least five thaw−freeze cycles, VDF was trapped under vacuum in the tube cooled in liquid nitrogen, after release from the pressure-calibrated metal container. The required amount of VDF introduced into the tube was assessed from the pressure drop in the container initially fed by a cylinder of

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Table 1. ^{19}F NMR Assignments of the VDF/MTFA Copolymers

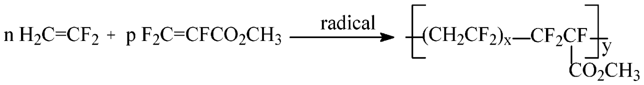
chemical shift (ppm)	structure	chemical shift (ppm)	structure
−91	$-CF_2CH_2C\mathit{F}_2CH_2CF_2-$	−115.7	$(CH_2CF_2)(C\mathit{F}_2CH_2)(CH_2CF_2)-$
−92.4	$HCF_2CH_2C\mathit{F}_2CH_2-$	−119 to −121	$-(CH_2CF_2)[C\mathit{F}_2CF(COOCH_3)]-$
−94.8	$(CH_2CF_2)(CF_2CH_2)(CH_2C\mathit{F}_2)(CH_2CF_2)$	−150	$NCCH_2CH_2C\mathit{F}_2-$ or $NCCH_2C\mathit{F}_2CH_2-$
−104 to −116	$-(CH_2C\mathit{F}_2)[CF_2CF(COOCH_3)]-$	−175 to −179	$-[CF_2C\mathit{F}(COOCH_3)]-$
−113.7	$(CH_2C\mathit{F}_2)(CF_2CH_2)(CH_2CF_2)-$	−194	$-CF_2C\mathit{F}(COOCH_3)H$
−114.5	$HC\mathit{F}_2CH_2CF_2CH_2-$		

300 g of VDF. A calibration curve, weight of trapped VDF (g) vs drop of pressure (bar), was determined (for 0.75 g of VDF, a drop difference of 0.50 bar was required). The reaction tube was sealed under vacuum and placed into a shaking oven heated to the temperature for the time required. At a given time, the tube was taken out from the oven, cooled in liquid nitrogen, and opened, and its contents were analyzed. Part of the mixture was analyzed by ^{19}F NMR spectroscopy, while the remaining part of the mixture (ranging usually from a wax to solid particles) was precipitated from 100 mL of cold pentane. The polymer formed was isolated by filtration and dried under vacuum at 80 °C for at least 4 h.

(c) Copolymer Synthesis at High Monomer Conversion Rates. A 160 mL HASTELLOY (HC 276) autoclave, equipped with a manometer, a rupture disk, and an inlet valve, was left closed for 20 min, purged with 20 bar of nitrogen pressure to prevent any leakage, and degassed afterward. Then, a 20 mmHg vacuum was applied for 15 min, and the initiator, MTFA, and 1,1,1,3,3-pentafluorobutane were introduced successively via a funnel. Next, VDF was introduced by double weighing. The autoclave was then heated to 134 °C for 10 h. After reaction, the autoclave was cooled to room temperature and then put in an ice bath followed by a release of unreacted VDF. Then, the crude product was analyzed by ^{19}F NMR spectroscopy. The solvent was evaporated, and the crude product was solubilized in DMF and then precipitated from cold water. The precipitate was filtered off and dried over P_2O_5 agent. A white powder was thus obtained.

Results and Discussion

The radical copolymerization of VDF with MTFA was carried out in acetonitrile or 1,1,1,3,3-pentafluorobutane solutions (these solvents do not induce any chain-transfer reactions), yielding random copolymers as follows:



$$n\,H_2C{=}CF_2 + p\,F_2C{=}CFCO_2CH_3 \xrightarrow{\text{radical}} \left[(CH_2CF_2)_x\!-\!CF_2\underset{\displaystyle CO_2CH_3}{CF}\right]_y$$

(a) Determination of the Copolymer Composition by Using ^{19}F NMR Spectra. Due to the very wide field of ^{19}F compared with the ^{1}H field, the amounts of both comonomeric units in the copolymers were determined by ^{19}F NMR only. All ^{1}H NMR spectra exhibit (1) signals assigned to methylene groups of VDF units adjacent to difluoromethylene groups in the 3.0−3.4 ppm range arising from normal head-to-tail additions (with high amounts of VDF units in the copolymer, the tail-to-tail addition gave rise to signals centered at about 2.4 ppm) and (2) signals of methyl ester groups at about 3.9 ppm. However, ^{19}F NMR spectroscopy was chosen to identify the corresponding MTFA and VDF units in the copolymers. Figure 1 shows the ^{19}F NMR spectrum of dry poly(VDF-*co*-MTFA) produced with an initial $[VDF]_0/[MTFA]_0$ molar ratio of 59.2/40.8. First, this spectrum shows the characteristic peak centered at about −91 ppm which is assigned to the difluoromethylene groups in the head-to-tail arrangement of VDF units (normal VDF addition), which was likely to increase for higher VDF contents. In addition, other signals are also good evidence of VDF units in the copolymers (Table 1). They are centered at −113.4, −115.7, and −94.8 ppm and assigned to the CF_2 groups of $(CH_2C\mathit{F}_2)(CF_2CH_2)(CH_2CF_2)$, $(CH_2CF_2)(C\mathit{F}_2CH_2)(CH_2CF_2)$, and $(CH_2CF_2)(CF_2CH_2)(CH_2C\mathit{F}_2)(CH_2CF_2)$ sequences, respectively, attributed to CF_2 groups corresponding to reverse VDF adducts (head-to-head addition).[15−19,51−53] Furthermore, the signals located in the −104 to −116 ppm region are assigned to the difluoromethylene groups of the VDF units adjacent to MTFA units. The values of these chemical shifts fit with those of the signal assigned to the difluoromethylene group of VDF adjacent to a hexafluoropropylene base unit in poly(VDF-*co*-HFP) copolymers These complex signals are characteristic of an AB system linked to anisochronous fluorine atoms, arising from the presence of the asymmetric carbon atom of the MTFA unit adjacent to VDF. Such an observation is in good agreement with the signal assigned to the difluoromethylene group located in the β position about the iodine atom in model molecule $C_3F_7CF_2CF_2CFICF_3$ synthesized by the thermal addition of perfluorobutyl iodide onto hexafluoropropylene.[54] The ^{19}F NMR spectrum of this product showed various AB systems attributed to different CF_2 groups and arising from the presence of the asymmetric carbon bearing the iodine atom that imposes both fluorine atoms of the difluoromethylene groups in the α and β positions to be nonequivalent.

In addition, the complex multiplet that appears in the −119 to −121 ppm region is attributed to the difluoromethylene of the MTFA unit. Finally, and as explained above, the peaks located in the −175 to −179 ppm region are assigned to the tertiary fluorine atom in the CF group of MTFA. Thus, this spectrum can be divided into three distinct zones: from −85 to −118 ppm, the peaks of CF_2 belonging to VDF units, the −119 to −121 ppm region attributed to the difluoromethylene group of MTFA, and the signals located in the −175 to

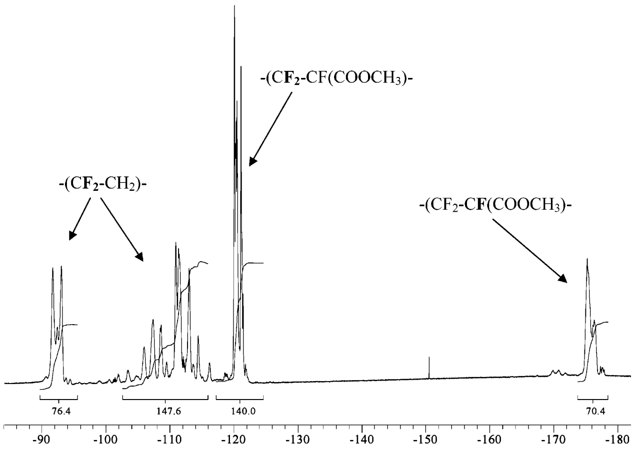


Figure 1. ^{19}F NMR spectrum of the VDF/MTFA copolymer. Copolymerization conditions: $[tBuOOCOtBu]_0/([VDF]_0 + [MTFA]_0) = 2\%$, 50 °C, 15 min, and VDF/MTFA initial molar ratio in the feed, 59.2/40.8.

Table 2. Conversion versus Reaction Conditions in the Radical Copolymerization of VDF with MTFA[a]

t, min	I_1	I_2	MTFA conversn (%)
15	7.4	92.6	7.4
30	20.5	80.0	20.0
60	38.0	62.0	38.0
120	64.0	36.0	64.0
240	75.0	25.0	75.0

[a] Copolymerization conditions: $[t\text{BuOOCO}t\text{Bu}]_0/([\text{VDF}]_0 + [\text{MTFA}]_0) = 1/100$, $[\text{VDF}]_0/[\text{MTFA}]_0 = 7/3$, 50 °C. The integrals of the signals between −175 and −179 ppm and at −186 ppm are denoted I_1 and I_2, respectively.

−179 ppm range belonging to the CF group from MTFA. To assess the amount of both comonomeric units in the copolymer, the integrals of the signals in the three regions are taken into account. They are denoted I_3, I_4, and I_5, respectively. From these ^{19}F NMR integrals, the mole fraction of VDF units in the copolymer is given by the following equation:

$$\text{mol \% VDF in the copolymer} = \frac{I_3}{I_3 + I_4} \times 100 \qquad (1)$$

(b) Characteristics of the VDF/MTFA Copolymerization System. The first step for the determination of the reactivity ratios was to determine the reaction conditions under which the monomer conversions were lower than 10%, as is required for an application of the Tidwell and Mortimer law.[55] Hence, five copolymerizations were performed (Table 2) using an initial $[\text{VDF}]_0/[\text{MTFA}]_0$ molar ratio of 70/30 and an initial C_0 ([initiator]$_0$/[total monomers]$_0$) molar ratio of 0.02. For each copolymerization, the reaction temperature was maintained at 50 °C, while the reaction times were 0.25, 0.5, 1, 2, and 4 h. After the reaction, the total product mixture was characterized by ^{19}F NMR spectroscopy. By comparison of the integrals of two peaks located in the −175 to −179 ppm region ($-\text{CF}_2C\mathit{F}(\text{CO}_2\text{CH}_3)-$ in the copolymer) and of the peak at −186 ppm ($\text{CF}_2{=}\text{C}\mathit{F}\text{CO}_2\text{CH}_3$ in the monomer), the MTFA conversion could be determined (see Figure 2). The integrals of the signals located at ca. −175 and −186 ppm being denoted I_1 and I_2, respectively, the MTFA conversion was assessed as follows:

$$\text{MTFA conversion (\%)} = \frac{I_1}{I_1 + I_2} \times 100 \qquad (2)$$

The data in Table 2 show that for a reaction time of 15 min the conversion was 7.4%, which is acceptable for a determination of copolymerization kinetics.

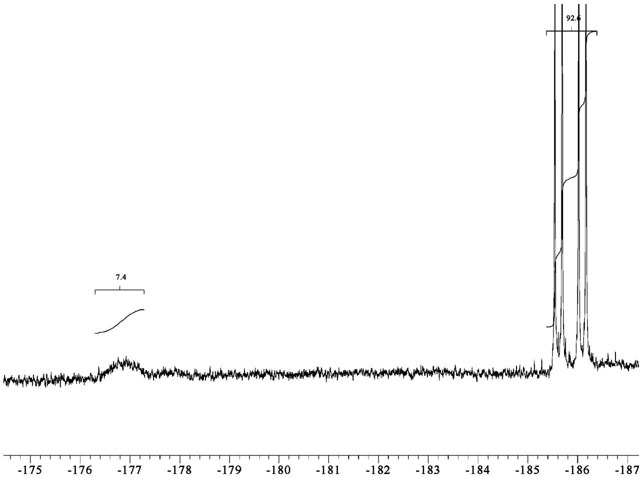
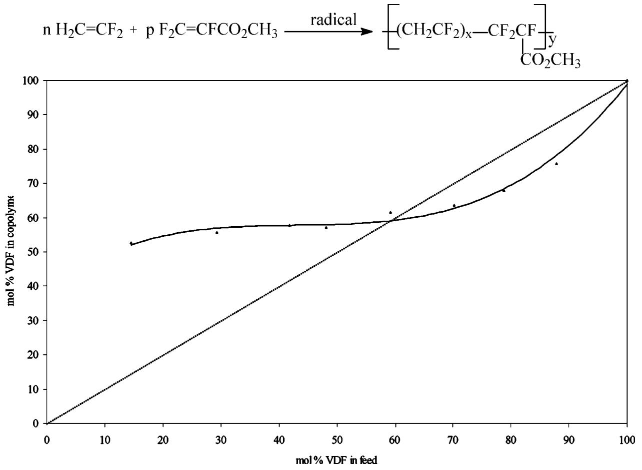


Figure 2. ^{19}F NMR spectrum of the crude VDF/MTFA copolymer in the −175 to −187 ppm range. Copolymerization conditions: $[t\text{BuOOCO}t\text{Bu}]_0/([\text{VDF}]_0 + [\text{MTFA}]_0) = 2\%$, 50 °C, 15 min, and VDF/MTFA ratio in the feed, 70/30.



$$n\,\text{H}_2\text{C}{=}\text{CF}_2 + p\,\text{F}_2\text{C}{=}\text{CFCO}_2\text{CH}_3 \xrightarrow{\text{radical}} \left[(\text{CH}_2\text{CF}_2)_x{-}\text{CF}_2\underset{\text{CO}_2\text{CH}_3}{\text{CF}}\right]_y$$

Figure 3. Monomer−polymer composition curve for the VDF/MTFA system, calculated from ^{19}F NMR. The full line represents the theoretical curve.

Therefore, eight copolymerizations with initial $[\text{VDF}]_0/[\text{MTFA}]_0$ molar ratios ranging from 14.5/85.5 to 88.7/11.3 were performed using this reaction time and were characterized by ^{19}F NMR. The results are presented in Table 3, and the composition curve (i.e., the mol % VDF units in the copolymer versus the mol % VDF in the feed) is shown in Figure 3. From these values by using the Tidwell and Mortimer method, the monomer reactivity ratios were determined. It was found that $r_{\text{VDF}} = 0.30 \pm 0.03$ and $r_{\text{MTFA}} = 0$ at 50 °C. These values can be compared with the reactivity ratios of other fluoromonomers capable of copolymerization with VDF (Table 4) and with the values arising from the copolymerization of TFE with MTFA ($r_{\text{TFE}} = 3.0$[41] or 5.0[47] and $r_{\text{MTFA}} = 0.15$[41] or 0.1[47]), confirming that MTFA does not homopolymerize and showing, as expected, that TFE is more reactive than VDF, even with regard to MTFA.

Furthermore, it was worth examining a reactivity series of fluorinated monomers with VDF. The traditional method for the determination of the reactivity of a macroradical to several monomers was used. Indeed, it is common to compare the value $1/r_{\text{A}} = k_{\text{AB}}/k_{\text{AA}}$, the ratio of the rate constant of copropagation to that of homopropagation (k_{AA}). Thus, the higher the 1/*r* value, the higher the copropagation reactivity of the radical.

Table 3. Monomer/Copolymer Composition of VDF/MTFA Determined by ^{19}F NMR Spectroscopy[a]

[VDF] in the feed (mol %)	[VDF] in the copolymer (mol %)	[VDF] in the feed (mol %)	[VDF] in the copolymer (mol %)	[VDF] in the feed (mol %)	[VDF] in the copolymer (mol %)
88.7	75.8	59.2	61.5	29.3	55.7
78.8	67.8	48.1	57.1	14.5	52.7
70.2	63.5	41.8	57.6		

[a] Copolymerization conditions: $[t\text{BuOOCO}t\text{Bu}]_0/([\text{VDF}]_0 + [\text{MTFA}]_0) = 1/100$, 50 °C, 15 min.

Table 4. Monomer Reactivity Ratios for Copolymerization of VDF (A) with Other Fluoroalkenes (B)

monomer B	r_A	r_B	r_Ar_B	$1/r_A$	ref
$HCF{=}CH_2$ (VF)	0.17	4.2−5.5	0.71−0.94	5.88	56
	0.20−0.43	3.8−4.9	0.76−2.11	2.33−5.00	57
$HCF{=}CF_2$ (TrFE)	0.70	0.50	0.35	1.43	51
$ClCF{=}CF_2$ (CTFE)	0.73	0.75	0.55	1.37	58
	0.17	0.52	0.09	5.88	59
$BrCF{=}CF_2$ (BrTFE)	0.43	1.46	0.63	2.33	58
$F_2C{=}CF_2$ (TFE)	0.23	3.73	0.86	4.35	59, 60
	0.32	0.28	0.09	3.13	61
$CF_3CF{=}CF_2$ (HFP)	6.70	0	0	0.15	62
	2.45	0	0	0.40	60
	2.90	0.12	0.35	0.34	63
$F_2C{=}CHCF_3$	9.0	0.06	0.54	0.11	64
$F_2C{=}CFCH_2OH$ (FA1)	0.83	0.11	0.09	1.20	16
$F_2C{=}CF(CH_2)_3OAc$ (FAc)	0.17	3.26	0.59	5.56	15
$F_2C{=}CF(CH_2)_3SAc$ (FSAc)	0.60	0.41	0.25	4.07	18
$H_2C{=}CFCF_2ORf$	0.38	2.41	0.92	2.63	65
$F_2C{=}CHC_6F_{13}$	12.0	0.90	10.80	0.08	66
$F_2C{=}CFOC_3F_7$ (PPVE)	1.15	0	0	0.86	67
$F_2C{=}CFO(HFP)OC_2F_4SO_2F$	0.57	0.07	0.04	1.75	24
$F_2C{=}CFOCF_3$ (PMVE)	3.40	0	0	0.29	67
$F_2C{=}C(CF_3)COF$	7.60	0.02	0.15	0.13	68
$F_2C{=}C(CF_3)OCOC_6H_5$	0.77	0.11	0.08	1.30	19
$F_2C{=}CFCO_2CH_3$ (MTFA)	0.30	0	0	3.33	this work

On the basis of the data in Table 4, the increasing order of relative reactivities of monomers to VDF• macroradicals is as follows: $F_2C{=}CHC_6F_{13} < F_2C{=}CHCF_3 <$ HFP < PMVE < PPVE < VDF < $F_2C{=}C(CF_3)OCOC_6H_5 <$ TrFE < CTFE (recent value) ≈ BrTFE < $H_2C{=}CFCF_2OR_F <$ MTFA < TFE < $F_2C{=}CFC_3H_6SCOCH_3 < F_2C{=}CFC_3H_6OAc < H_2C{=}CHF \approx$ CTFE (old value) < $H_2C{=}CH_2$, although numerous kinetics still deserve to be investigated.

Because $r_{VDF} < 1$ and $r_{MTFA} = 0$, the azeotropic composition, an indication of the same ratio of comonomers in the copolymer and in the feed, is given by the equation

$$\text{azeotropic composition} = \frac{1 - r_2}{2 - (r_1 + r_2)} \qquad (3)$$

For VDF/MTFA copolymer, the azeotropic composition calculated from determined r_i values is 58.8 mol % VDF, and is in good agreement with the experimental value (Figure 3). On the other hand, the overall shape of the polymer/monomer composition curve shows a tendency to alternation of both comonomers, although the radical copolymerization is not totally alternated. Indeed, monomer pairs such as MTFA/ethylene,[43] MTFA/propene,[44] or MTFA/vinyl ethers[45] led to alternating copolymers just like the unexpected VDF/hexafluoroisobutylene couple.[12] These two monomers have led to alternating copolymers regarded as a rare case, in contrast to random or statistic fluorocopolymers[10] arising from two fluoromonomers.

The tendency to alternation in these copolymers can be explained by the Q and e values of both comonomers. The literature reports that these pairs are (0.008, 0.40),[61] (0.015, 0.50),[69] and (0.036, 1.20)[68] for VDF while for MTFA they are (0.035, 2.37),[44] (0.048, 1.20),[69,70] (0.15, 1.7),[41] and (0.05, 2.4).[42] Besides, according to the Alfrey and Price[71] equation and considering average values of $Q_{MTFA} = 0.04$, $e_{MTFA} = 1.8$, $Q_{VDF} = 0.015$, and $e_{VDF} = 0.5$, such values should lead to $r_{VDF} = 0.7$, while $r_{MTFA} = 0$, which are rather close to the experimental values.

Table 5. *e* and *Q* Values of Fluoroalkenes

monomer	e	Q	ref
$H_2C{=}CHCF_3$	0.42	0.130	70
$HFC{=}CH_2$	0.72	0.008	70, 73
	1.28	0.012	73
	−0.05	0.016	61
$F_2C{=}CH_2$	0.40	0.008	61
	0.50	0.015	69
	1.20	0.036	68
(*z*) $CF_3CF{=}CHF$	2.10	0.002	56
$F_2C{=}CHF$	1.15	0.009	61
$F_2C{=}CFCH_2OH$	1.52	0.011	74
	2.24	0.075	16
$F_2C{=}CF(CH_2)_3OH$	1.04	0.008	74
$F_2C{=}CF(CH_2)_3OAc$	1.14 (1.23)	0.060 (0.040)	15
$F_2C{=}CF(CH_2)_3SAc$	1.68	0.045	18
$F_2C{=}CFCl$	1.56	0.026	69
	1.84	0.031	61
	1.48	0.020	70
$F_2C{=}CFCO_2CH_3$	1.20	0.048	41, 42, 70
	2.37	0.035	43, 44
	2.11	0.067	43, 44
$F_2C{=}CFOCF_3$	3.01	0.250	67
$F_2C{=}CFCF_3$	4.09	0.047	70
$F_2C{=}CF_2$	1.22	0.049	41
	1.63	0.032	70, 69
	1.84	0.031	61
$F_2C{=}CFCF{=}CF_2$	0.58	0.820	70
$F_2C{=}C(CF_3)OCOC_6H_5$	2.27	0.081	19

The determination of the Q and e values is more difficult from the Alfrey and Price equation[71] since $r_{MTFA} = 0$. However, a recent program for the assessment of the reactivity ratio values, using a nonlinear method,[72] could be useful and deserves deeper investigation. Taking into account compilation of Q and e values for fluoromonomers,[10,69] the general tendency is such that the higher the number of fluorine atoms on the double bond, the greater the e value. In most cases, Q values are very small except for those of styrenic and acrylic monomers. However, it is difficult to rationalize these values since various processes and different methods of initiation, temperatures, solvents, and ways of determining the corresponding reactivity ratios have been used. The low Q values are good evidence of the poor ability of the fluorine atom to stabilize by resonance the radical on the adjacent carbon atom (Table 5) although previous quantum chemical calculations describing π-bond orders of the double bond in MTFA are decreased.[75] This means that in MTFA monomer, the

Table 6. Monomer/Copolymer Composition of VDF/MTFA Determined by ^{19}F and ^{1}H NMR Spectroscopy[a]

experiment	[VDF] initial (%)	[VDF] final (%) from ^{1}H NMR	[VDF] final (%) from ^{19}F NMR	conversion (%) VDF	conversion (%) MTFA	yield (%)	M_n (g·mol^{-1})	M_w (g·mol^{-1})
1	96.7	96.8	97.7	92.0	75.6	91.2	25600	35600
2	93.9	91.2	92.4	50.7	70.0	53.0	19900	32000

[a] copolymerization conditions: [2,5-bis (*tertio*-butylperoxy)-2,5-dimethylhexane]$_0$/ ([VDF]$_0$+[MTFA]$_0$) = 7 mol %, 1,1,1,3,3-pentafluorobutane, 134 °C, 8 h.

double bond acquires a small electrical charge arising from the electron-withdrawing effect of three fluorine atoms and of the ester group.

Although the literature supplies various data on the copolymerizations of VDF with donating monomers, it is difficult to compare the kinetic characteristics (r, Q, e) of the copolymerization of VDF with MTFA with other copolymerizations including electrowithdrawing monomers. As a matter of fact, it was noteworthy to compare the influence of the Q values on the reactivity.

Furthermore, the Q values of hydrogenated acrylates and methacrylates are 0.97 and 1.13, respectively.[76] Interestingly, the fluorinated acrylates show lower values of Q[77] (0.43 and 0.048 for α-fluoroacrylate and α,*β*,*β*-trifluoroacrylate, respectively) which indicate that the delocalization is less favored when the ethylenic carbon atoms bear fluorine atoms.

(III) Synthesis of Poly(VDF-*co*-MTFA) with a High Monomer Conversion Rate. To prepare a PVDF bearing lateral acrylate functions, the synthesis of a poly(VDF-*co*-MTFA) with a high monomer conversion rate was investigated. Two radical copolymerizations were carried out using a high-pressure autoclave system. The initial molar percentages of VDF in the feed were 96.7 and 93.9, respectively, and as above 1,1,1,3,3-pentafluorobutane was chosen as solvent. These reactions were performed at 134 °C using 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (Luperox 101) as the radical initiator. The half-time of such an initiator was 1 h at 134 °C. By this process, two white powders were produced, and their compositions were also determined by ^{19}F and ^{1}H NMR (see Table 6). The ^{1}H NMR spectra exhibit three characteristic signals: The first one is assigned to the methylene groups of VDF units ($-CH_2$-$CF_2CH_2CF_2-$) in the 3.0−3.4 ppm range arising from normal head-to-tail additions. The second one at 2.4 ppm is assigned to methylene groups of VDF units resulting from a tail-to-tail addition. The last one is the singlet attributed to the methyl ester groups centered at about 3.9 ppm. ^{19}F NMR spectroscopy was chosen to identify the corresponding MTFA and VDF units in the copolymers (see Table 6).

However, the results listed in Table 6 showed that the presence of MTFA monomer made the mass yields decrease. In the same experimental conditions, starting from MTFA feed molar percentages of 3.3 and 6.1 mol % led to copolymers containing 91.2 and 53.0 mol %, respectively. In addition, size exclusion chromatography (or GPC) analyses (see Table 6) showed that the value of the molecular weight of the copolymer synthesized in experiment 1 (3.3 mol % in the feed of MTFA) is higher than that of experiment 2 (copolymer obtained from 6.1 mol % in the feed of MTFA). These results confirmed the last hypothesis described above regarding the low reactivity of MTFA$^•$ macroradical and the possible transfer to the methyl group of MTFA. Furthermore, the thermal analyses (see Figure 4) indicate that the copolymer prepared in experiment 1 is more thermostable than that synthesized in experiment 2, which indicated that the higher the mole percent of MTFA in the copolymer, the lower the thermal properties of the copolymer.

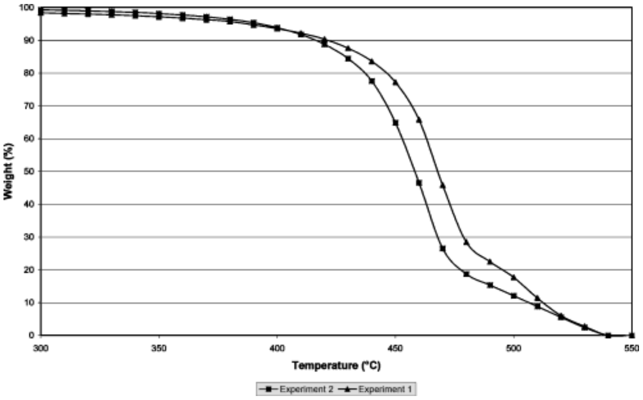


Figure 4. TGA thermogram of VDF/MTFA copolymers.

Conclusion

In this work we describe the radical copolymerization of VDF with MTFA and its kinetics and results (composition, reactivity) at high monomer conversion. The reactivity ratios of both comonomers were assessed: $r_{MTFA} = 0$ and $r_{VDF} = 0.30 \pm 0.03$ at 50 °C. Interestingly, the copolymers show alternating structures, which is quite unusual for copolymers achieved from two fluoroalkenes. Because $r_{VDF} < 1$ and $r_{MTFA} < 1$, an azeotropic composition was deduced. For VDF/MTFA copolymers, the azeotropic composition was 58.8 mol % VDF. The literature Q and e values of MTFA are consistent with the r_i values obtained experimentally. This means that, for MTFA monomer, the fluorinated double bond bears a low electric charge, and as a consequence, the ability of the fluorine atom to stabilize the radical on the adjacent carbon atom is poor. Furthermore, TGA and GPC analyses have indicated that the copolymer incorporating the lowest amount of MTFA exhibited the best thermal properties and the highest molecular weights. These synthesized PVDFs bearing ester side groups are novel materials, and their cross-linking is under investigation.

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