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Synthesis and Polymerization of Fluorinated Monomers Bearing a Reactive Lateral Group. 9.[†] Bulk Copolymerization of Vinylidene Fluoride with 4,5,5-Trifluoro-4-ene Pentyl Acetate

Bruno Ameduri,*,[‡] Gerard Bauduin,[‡] Bernard Boutevin,[‡] Georges Kostov,*,[§] and Petya Petrova[§]

Laboratory of Macromolecular Chemistry, ESA (5076) CNRS, Ecole Nationale Supérieure de Chimie de Montpellier, 8 Rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France, and Center for Electron Beam Technology and Polymers, University of Bourgas, 8010 Bourgas, Bulgaria

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ABSTRACT: Bulk copolymerization of vinylidene fluoride (or 1,1-difluoroethylene (VDF)) with 4,5,5-trifluoro-4-ene pentyl acetate (FAc) initiated by di-*tert*-butyl peroxide is presented. A series of nine copolymerization reactions was investigated from initial $[VDF]_0/[FAc]_0$ molar ratios ranging from 32/68 to 95/5. Both these comonomers copolymerized in this range of copolymerization. Moreover, these comonomers homopolymerized separately in these conditions. The copolymer compositions of these random-type copolymers were calculated by means of ^1H and ^{19}F NMR spectroscopies and allowed one to quantify the respective amount of each monomeric unit in the copolymer. From the Tidwell and Mortimer method, the reactivity ratios, r_i, of both comonomers were determined showing a higher incorporation of FAc in the copolymer ($r_{FAc} = 3.26 \pm 1.49$ and $r_{VDF} = 0.17 \pm 0.10$ at 120 °C). Alfrey−Price's Q and e values of trifluorovinyl acetoxy monomer FAc were calculated to be 0.060 (from $Q_{VDF} = 0.008$) or 0.040 (from $Q_{VDF} = 0.015$) and +1.14 (vs $e_{VDF} = 0.40$) or +1.23 (vs $e_{VDF} = 0.50$), respectively, indicating that FAc is an electron-accepting monomer. The normalized monomer-diad and -triad fractions as a function of the polymer composition were obtained from the comonomer sequence distribution theory and this was evidenced by ^{19}F NMR analysis.

Introduction

The copolymerization of fluoroalkenes with fluorinated or nonhalogenated monomers has been investigated by many authors.[1−4] Among these comonomers, perfluorovinyl functional monomers have already shown great interest to be used in copolymerization with commercially available fluorinated or nonfluorinated comonomers.[1−6] The functional group which is introduced in a lateral position about the backbone of the copolymer brings specific and complementary properties: adhesion from carboxylic functions,[7] solubility from cyclohexyl groups,[8] curability thanks to hydroxy or epoxide functions,[9−12] surface properties from perfluorinated groups,[13] or good hydrophilicity, heat and chemical resistance brought by phosphonated functions.[14] Various functional monomers exhibiting ω-trifluorovinyl groups have already been synthesized.[10−12,14] But the literature shows that no data about the reactivity ratios of these functional comonomers have been supplied. Therefore, it was of some interest to determine such parameters useful to monitor a copolymerization. Recently, we have considerably optimized the synthesis of $F_2C{=}CFC_3H_6OCOCH_3$ from a five-step scheme,[15] starting from the radical addition of iodine monochloride to chlorotrifluoroethylene.[16]

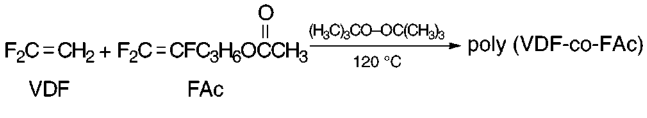
Functionalizations of polyvinylidene fluoride (PVDF), which led to various applications, have already been studied by several authors.[10−13,17−21]

The copolymers of VDF with other fluoromonomers and nonfluorinated monomers including at least one hydroxy or other functional groups were recently outlined by Tournut.[18,19] In addition, the Daikin Co.[10] achieved the preparation of $VDF/CF_2{=}CF{-}X{-}OH$ copolymers [where $X = (CH_2)_m$ or $(CF_2)_n(CH_2)_m$] and showed that the trifluorovinyl alcohols exhibited a lower reactivity.

Hence, the objective of this paper concerns the copolymerization of VDF with $F_2C{=}CF(CH_2)_3OCOCH_3$, the determination of their reactivity ratios, and the comonomer sequence distributions. Three motivations directed the choice of this trifluorovinyl acetoxy monomer about the hydroxylated one:[22,23] lower transfer behavior,[22] interesting acetoxy label group in infrared or ^1H NMR spectroscopies, and less hydrophilic character which should enable this monomer to undergo a better copolymerization with vinylidene fluoride.

Results and Discussion

The radical copolymerization of vinylidene fluoride (VDF) with 4,5,5-trifluoro-4-ene pentyl acetate (FAc) was carried out in bulk, initiated by di-*tert*-butyl peroxide as follows:



$$\underset{\text{VDF}}{F_2C{=}CH_2} + \underset{\text{FAc}}{F_2C{=}CFC_3H_6O\overset{\overset{\displaystyle O}{\|}}{C}CH_3} \xrightarrow[120\ °C]{(H_3C)_3CO{-}OC(CH_3)_3} \text{poly (VDF-co-FAc)}$$

(1) Synthesis of FAc. The fluoroacetoxy monomer (FAc) was prepared in a five-step procedure from the photochemical addition of iodine monochloride to chlorotrifluoroethylene leading to $Cl(C_2F_3Cl)I$.[16] This reaction was followed by the selective addition of the major isomer to allyl alcohol,[15] as shown in Scheme 1. The overall yield of the FAc monomer from 1-iodo-1,2-dichlorotrifluoroethane was 46%.[15]

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* To whom correspondence should be addressed.

[†] For part 8, see ref 23.

[‡] Ecole Nationale Supérieure de Chimie de Montpellier.

[§] University of Bourgas.

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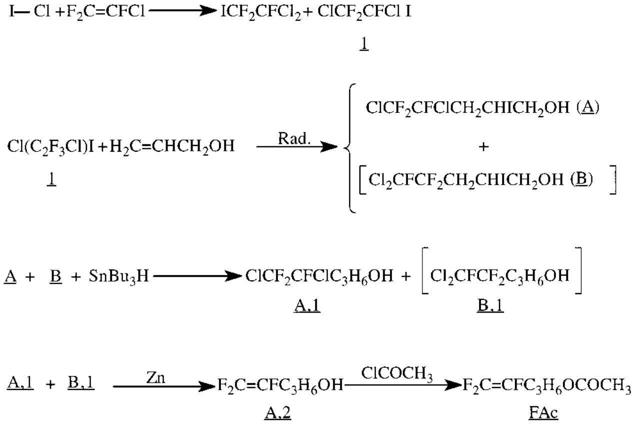
Scheme 1. Synthesis of 1,1,2-Trifluoropentene-5-ol and 4,5,5-Trifluoro-4-ene Pentyl Acetate (the Products in Brackets Have Not Been Isolated Experimentally)



(2) Copolymerization. Nine experiments of copolymerization and two homopolymerizations were performed from initial $[VDF]_0/[FAc]_0$ molar ratios ranging between 32/68 and 95/5. The experimental conditions (120 °C for 17 h) were chosen so that the conversion rates of monomers were assumed to be less than 12–15%.

The physical appearance of the copolymers obtained were from white powders (VDF-rich copolymers—from feed compositions having an initial VDF mol % higher than 94.8%) to pale yellow rubber-like sticky copolymers produced from initial VDF mol % ranging from 79.8 to 94.7%, and to very viscous liquids and waxes (FAc-rich products from initial VDF mol % of 40.4–60.1 and 0–31.9, respectively). They were soluble (or partially soluble, from VDF/FAc of 94.9/5.1) in acetone or THF (except the homopolymer of VDF) and in DMF or DMAc while FAc-rich products were partially soluble in chloroform and in methanol at room temperature.

The amounts of both comonomeric units in the copolymer were determined by means of ^1H and ^{19}F NMR. For example, Figure 1 represents the ^1H NMR spectrum of the dried poly(VDF-*co*-FAc) produced from an initial $[VDF]_0/[FAc]_0$ molar ratio of 94.7/5.3. This spectrum clearly exhibits the signals centered at 4.15, 2.93, 2.30, 2.15, 2.01, and 1.90 ppm assigned to the methylene groups adjacent to the acetoxy end group, to the head-to-tail units (or normal addition of VDF) in the oligo-VDF structure and of the $CF(C_3H_6OAc)CF_2$-CH_2CF_2- sequence, to the tail-to-tail VDF units (i.e., reversed addition of VDF), to that adjacent to the CF group, to that of the acetoxy function, and to that of the central methylene group in the side chain, respectively. In addition, the multiplet centered at 2.65 ppm overlapping with the quintet at 2.93 ppm was attributed to the methylene group of VDF in the $CF_2CF(C_3H_6OAc)CH_2$-CF_2- chaining.

Interestingly, the absence of a signal around 6.5 ppm (especially a triplet of triplets) is noted, showing evidence that no CF_2H end group was formed; for example, such a signal could have come from the allylic proton transfer as observed for the copolymerization of tetrafluoroethylene (TFE) with $F_2C{=}CFC_3H_6OH$.[22]

It is also noted the characteristic triplet ($^3J_{HH} = 6.5$ Hz) and a singlet centered at 1.05 and 1.18 ppm, assigned to $CH_3(CH_2CF_2)_n-$ and *tert*-butyl alcohol, respectively. These proofs came from the same signals observed for the direct addition of the methyl and *tert*-butoxy radicals to VDF as byproducts noted in the radical telomerization of VDF with methanol[24] (indeed, the *tert*-butoxy radicals underwent a rearrangement leading to $^{\bullet}CH_3$ radicals and acetone).

On the basis of the integrations of the signals centered at 4.15 (I_1), 2.65–2.93 (I_2) and 2.30 (I_3), the molar fraction of VDF in the copolymer was given by the following equation:

$$\%\,VDF = \frac{I_2 + I_3}{I_1 + I_2 + I_3} \times 100 \qquad (1)$$

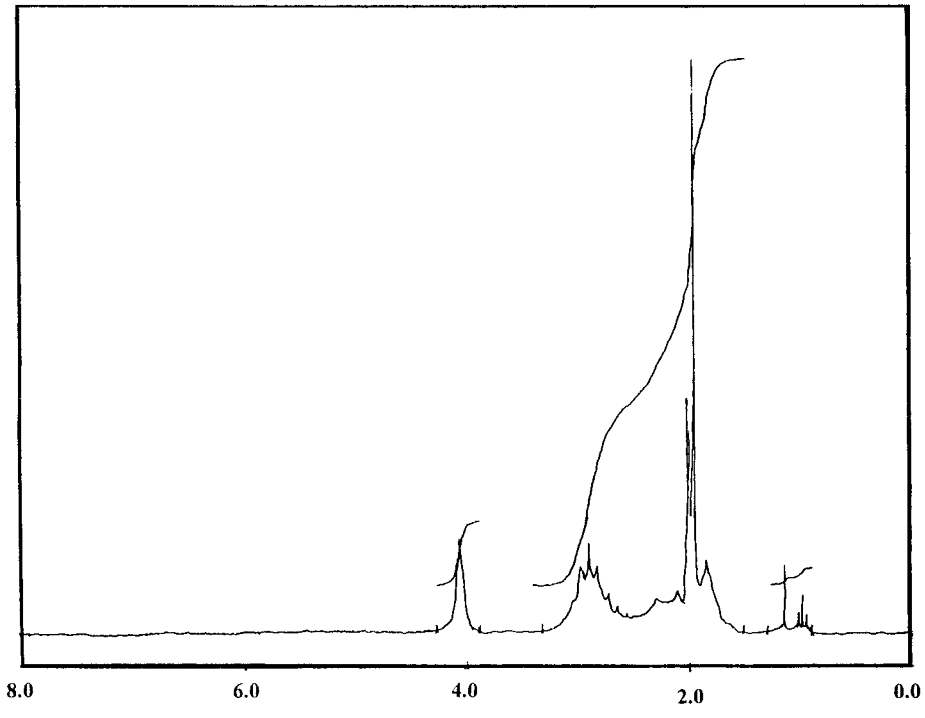


Figure 1. ^1H NMR spectrum of the VDF/FAc copolymer. Polymerization conditions: $[(t\text{-}Bu)_2O_2] = 0.05$ mol %, 120 °C, 17 h, and VDF/FAc in the feed = 94.7/5.3 mol %.

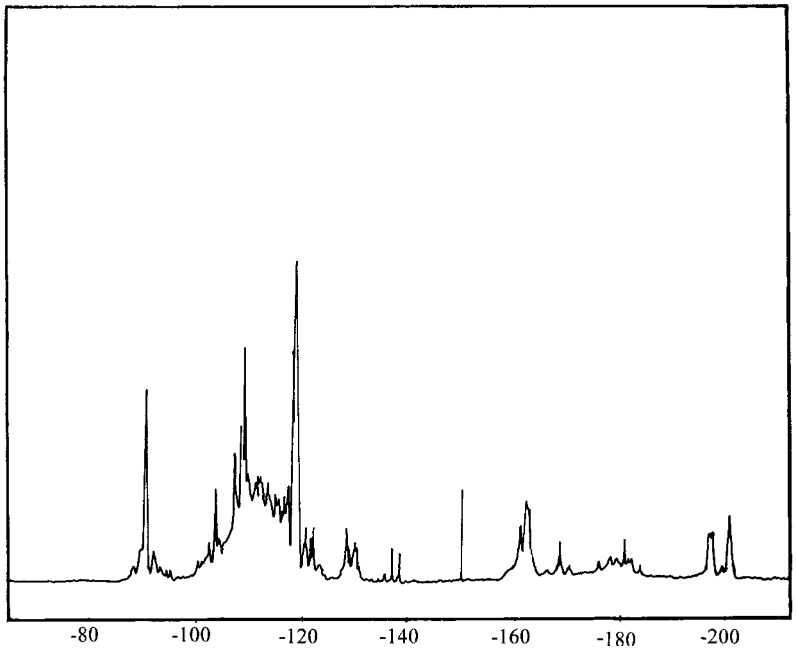
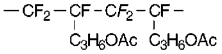
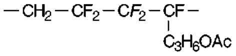
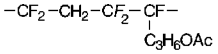
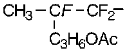
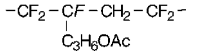
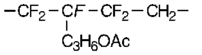


Figure 2. ^{19}F NMR spectrum of the VDF/FAc copolymer. Polymerization conditions: $[(t\text{-Bu})_2O_2] = 0.05$ mol %, 120 °C, 17 h, and VDF/FAc in the feed = 68.5/31.5.

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

no	structure	chemical shift (ppm)
1	$-\mathrm{CH_2}-\mathrm{C}F_2-\mathrm{CH_2}-\mathrm{C}F_2\mathrm{CH_2}-\mathrm{CF_2}-$	−91
2	$-\mathrm{CH_2}-\mathrm{C}F_2-\mathrm{CH_2}-\mathrm{CF_2}-\mathrm{CF_2}-\mathrm{CH_2}-$	−95
3	$-\mathrm{CF_2}-\mathrm{CH_2}-\mathrm{C}F_2-\mathrm{CF_2}-\mathrm{CH_2}-$	−108
4	$-\mathrm{CF_2}-\mathrm{CH_2}-\mathrm{CF_2}-\mathrm{C}F_2-\mathrm{CH_2}-$	−113
5	 $-\mathrm{CF_2}-\underset{\mathrm{C_3H_6OAc}}{\mathrm{CF}}-\mathrm{C}F_2-\underset{\mathrm{C_3H_6OAc}}{\mathrm{CF}}-$	−117 to −125
6	 $-\mathrm{CH_2}-\mathrm{CF_2}-\mathrm{C}F_2-\underset{\mathrm{C_3H_6OAc}}{\mathrm{CF}}-$	−120 to −130
7	 $-\mathrm{CF_2}-\mathrm{CH_2}-\mathrm{C}F_2-\underset{\mathrm{C_3H_6OAc}}{\mathrm{CF}}-$	−115 to −118
8	 $\mathrm{CH_3}-\underset{\mathrm{C_3H_6OAc}}{\mathrm{C}F}-\mathrm{CF_2}-$	−150
9	 $-\mathrm{CF_2}-\underset{\mathrm{C_3H_6OAc}}{\mathrm{C}F}-\mathrm{CH_2}-\mathrm{CF_2}-$	−160 to −165
10	 $-\mathrm{CF_2}-\underset{\mathrm{C_3H_6OAc}}{\mathrm{C}F}-\mathrm{CF_2}-\mathrm{CH_2}-$	−182 to −185
11	$-\mathrm{CF_2}-\mathrm{C}F\mathrm{H}-\mathrm{C_3H_6OAc}$	−196 to −205

On the other hand, the calculation of the copolymer compositions was also deduced from the ^{19}F NMR spectra. For example, Figure 2 represents the ^{19}F NMR spectrum of a copolymer prepared from an initial $[\mathrm{VDF}]_0/[\mathrm{FAc}]_0$ molar ratio of 68.5/31.5.

In this spectrum, three distinct zones are considered for this calculation (Table 1): (a) The signal centered at around −91 ppm is assigned to the normal PVDF chaining (i.e., head-to-tail VDF blocks). (b) The −100 to −130 ppm zone is attributed to the difluoromethylene groups of the reversed PVDF chaining (i.e., head-to-head VDF) and of those of the FAc units. (c) The signals centered at −150, −165, −183, and −200 ppm correspond to the CF group adjacent to *t*-BuO, to a methylene or to a difluoromethylene group of a VDF unit, or adjacent to a proton, respectively. This last assignment was in good agreement with those of tertiary fluorine atoms of $\mathrm{R_FC}F\mathrm{HCF_3}$[25] and $\mathrm{R_FC}F\mathrm{HCF_2H}$,[26] giving multiplets at −215 and −211 ppm, respectively.

The other assignments have been deduced from the chemical shifts corresponding to the characteristic CF group of $\mathrm{C_6F_{13}CH_2CF_2CF_2CF(C_3H_6OAc)(CH_2CF_2)}_x\mathrm{-I}$ (x = 1−3) synthesized by telomerization of VDF with $\mathrm{C_6F_{13}CH_2CF_2CF_2CFI(CH_2)_3OCOCH_3}$.[27] This latter compound was prepared by the radical addition of $\mathrm{C_6F_{13}CH_2CF_2I}$ to FAc.[27]

For the calculation of the amounts of both comonomeric units in the copolymer, the integrations of the signals in the three zones above are noted I_4, I_5 and I_6, respectively.

In addition, the ^{19}F NMR spectrum obtained from the homopolymerization of FAc exhibits signals in the −108 to −130 ppm range, at −150 ppm, in the −176 to −185 ppm range, and −192 to −202 ppm range attributed to difluoromethylene, to $\mathrm{CH_3C}F$, to $\mathrm{CF_2C}F\mathrm{(C_3H_6OAc)CF_2}$, and probably to CFCF groups (Table 1).

The formation of $\mathrm{CH_3CF}$ and CFH groups may result from the direct radical addition of $\mathrm{CH_3}^\bullet$ produced from the *tert*-butoxy radicals in the initiation step as shown above[24] and from an eventual transfer to the polymer as explained by Russo et al.[28]

From the integration of the ^{19}F NMR signals located in the three zones above, the determination of the molar fraction of VDF base units in the copolymer was as follows:

$$\%\,\mathrm{VDF} = \frac{I_4 + I_5 - 2I_6}{I_4 + I_5} \times 100 \qquad (2)$$

As expected, for initial monomeric compositions containing low FAc contents, the peak assigned to normal PVDF exhibits a greater integration than that of the reversed VDF additions. In contrast, those having a high amount of FAc (e.g., higher than 70%) led to a negligible peak of normal PVDF. For example, the former case can be explained by the structure of the copolymer in which one FAc unit is surrounded by several consecutive VDF units. They can be compared to PVDF or VDF oligomers[28] or telomers[29,30] in which the normal/reverse ratio was about 5−12%.

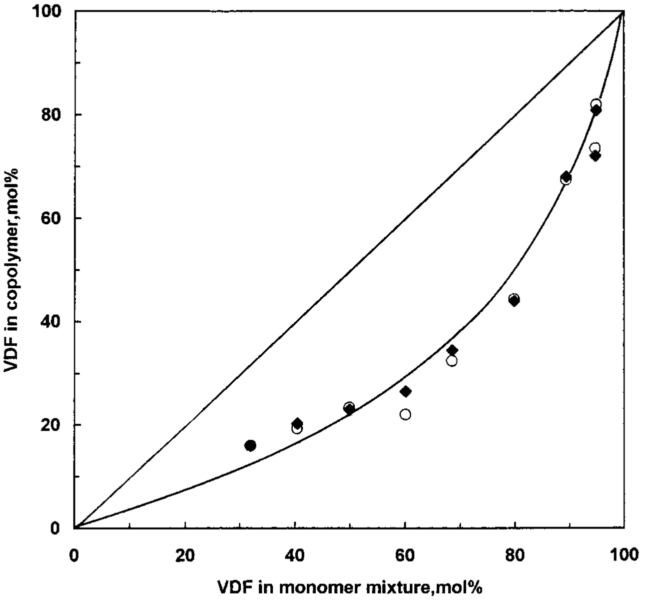


Figure 3. Monomer−polymer composition curve of vinylidene fluoride (VDF, A)/4,4,5-trifluoro-4-ene pentyl acetate (FAc, B) system, calculated from ^{1}H NMR (○) and from ^{19}F NMR (◆). The full line represents the theoretical curve.

Figure 3 represents the monomer−polymer composition curve plotted from the results calculated above.

The copolymerization of both comonomers occurred in all the ranges of compositions used, assuming that no homopolymerization happened under these conditions. However, it was observed that they were able to homopolymerize separately. On the basis of solubility, it was found that except for PVDF (soluble in DMF and in DMAc), all the copolymers were soluble in acetone. This also gives evidence that no PVDF was produced in the copolymerization. On the other hand, the homopolymer of FAc was completly soluble in methanol and in chloroform. It was also observed that the higher the FAc content in the copolymer, the better the solubility in both these solvents. But the samples prepared from initial VDF mol % ranging between 94.9 and 79.8 were soluble neither in methanol nor in chloroform. That could mean that no FAc homopolymer was produced in the copolymerization.

Monomer-Reactivity Ratios. The compositions of VDF−FAc copolymers were determined from ^{1}H and ^{19}F NMR spectra analyses. The formula for these calculations are given above (eqs 1 and 2). The composition curve (Figure 3) is a typical diagram of random structure copolymers. The results of polymer compositions, obtained from ^{1}H and ^{19}F NMR, are in very good agreement and the data of both analyses were used to calculate the reactivity ratios of the comonomers. From these values and by using the Tidwell and Mortimer method,[31] the monomer reactivity ratios were determined. It was found that r_A(VDF) = 0.17 and r_B(FAc) = 3.26 at 120 °C. The confidence area is shown in Figure 4 and it can be seen that the accuracy on the values of r_A and r_B is rather good.

Because $r_A < 1$ and $r_B > 1$, one can consider that the rate constants k can be compared as follows: $k_{AA} < k_{AB}$ and $k_{BB} > k_{BA}$, showing that both radicals ~VDF$^\bullet$ and ~FAc$^\bullet$ have a high tendency to react to the FAc monomer. In addition, the great difference between both values of reactivity ratios shows that VDF radicals are more reactive than FAc ones toward the monomer pair.

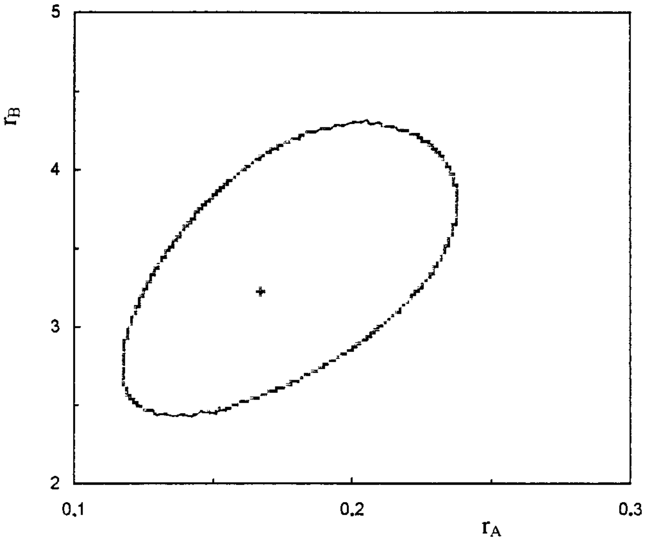


Figure 4. Joint confidential surface (95% probability) and most probable values (r_A = 0.17; r_B = 3.26) from mean composition values by ^{1}H and ^{19}F NMR.

Table 2. Monomer Reactivity Ratios for Copolymerization of VDF (A) with Other Fluoromonomers and Vinyl Acetate (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	32
$HCF{=}CF_2$ (TrFE)	0.70	0.50	0.35	1.43	33
$ClCF{=}CF_2$	0.73	0.75	0.55	1.37	34
(CTFE)	0.17	0.52	0.09	5.88	35
$BrCF{=}CF_2$ (BrTFE)	0.43	1.46	0.63	2.33	34
$F_2C{=}CF_2$	0.23	3.73	0.86	4.35	34
(TFE)	0.32	0.28	0.09	3.13	36
$CF_3{-}CF{=}CF_2$	6.70	0	0	0.15	37
(HFP)	2.45	0	0	0.41	38
$F_2C{=}CF(CH_2)_3OAc$ (FAc)	0.17	3.26	0.59	5.56	this work
$F_2C{=}CF(CH_2)_3SAc$ (FSAc)	0.60	0.41	0.25	4.07	39
$H_2C{=}CHOCOCH_3$ (VAc)	0.50	2.0	1.00	2.0	4

Compared to the reactivity ratios of other fluoromonomers able to copolymerize with VDF (Table 2), the value of FAc (r_B = 3.26) was found between that of TFE (3.73) and that of vinyl acetate (2.0). But it can also be seen that a large discrepancy may occur between r_A and r_B values for a given couple using different methods of analyses and determination. This is why we have chosen the Tidwell and Mortimer[31] method which is considered as one of the most suitable among others.[40−46]

In addition, it was worth supplying a reactivity series of fluorinated monomers about VDF. The traditional method for the determination of relative reactivity of a macroradical to several monomers was used.[47] Indeed, it is common to compare the values $1/r_A = k_{AB}/k_{AA}$ as the ratio of rate constants of crossed propagation to that of propagation (k_{AA}). Thus, the higher the $1/r$ value, the more able the radical can react with the second monomer. Table 2 allows us to suggest the following series of relative reactivities of monomers to ~VDF$^\bullet$ radicals:

$$\begin{aligned}&\text{HFP} < \text{VDF} < \text{TrFE} < \text{VAc} <\\ &\quad \text{CTFE (recent value)} \approx \text{BrTFE} < \text{TFE} <\\ &\qquad \text{FSAc} < \text{FAc} < \text{VF} \approx \text{CTFE (old value)}\end{aligned}$$

Table 3. *e* and *Q* Values of Fluorinated Monomers

monomer	*e*	*Q*	ref
$H_2C = CHCF_3$	0.42	0.130	54
$HFC = CH_2$	0.72	0.008	55
	1.28	0.012	48
	−0.05	0.016	36
$F_2C = CH_2$	0.50	0.015	55
	0.40	0.008	36
$CF_3CF = CFH$ (cis)	2.10	0.002	32
$F_2C = CFH$	1.15	0.009	36
$F_2C = CFCH_2OH$	1.52	0.011	23
$F_2C = CFC_3H_6OH$	1.04	0.008	23
$F_2C = CFC_3H_6OAc$	1.14 (1.23)	0.060 (0.040)	this work
$F_2C = CFC_3H_6SAc$	1.68	0.045	39
$F_2C = CFCl$	1.56	0.026	49, 56
	1.84	0.031	36
	1.48	0.020	48
$F_2C = CFCO_2CH_3$	1.20	0.048	49, 56
$F_2C = CFOCF_3$	1.20	0.048	37
$F_2C = CFCF_3$	4.09	0.047	36
$F_2C = CF_2$	1.24	0.049	48
	1.69	0.032	37, 49, 56
	1.84	0.031	36
$F_2C = CF{-}CF{=}CF_2$	0.58	0.820	49, 56

Much more confused is the case of the calculation of $Q-e$ values, which was already discussed by many authors.[48−54] Taking into consideration the copolymerization parameters with some reference monomers (styrene, ethylene, TFE, and VDF), the Q and e values of which are reported in the literature,[4,22,32,37,39,48,49,55−58] the $Q-e$ values of FAc were calculated from the Alfrey−Price scheme,[59] compared with those of other VDF−comonomer systems (Table 3). But we have to claim that they were determined from a set of experiments for a single copolymer system, taking into account the values of similar monomers.

The e_B (FAc) value is positive ($e_B = 1.14$) (from $e_A = 0.40$, Table 3) or $e_B = 1.23$ (from $e_A = 0.50$, Table 3) and lower than that of C_2F_4 ($e_{TFE} = 1.24-1.84$), due to the lower electron-withdrawing effect because of the $-(CH_2)_3$-$OCOCH_3$ substituent versus the fluorine atom in C_2F_4. It is interesting to mention that the e values for VDF given in the literature are rather different, and even negative[32](−0.50). Thus, in the latter case, the fluorine atom seems to act as an "electron-donating substituent". But for the FAc monomer, the e value is always positive due to the electron-withdrawing effect of three fluorine atoms and the slight donating effect of the $(CH_2)_3$ spacer. Thus, mainly random copolymerization between VDF and FAc is expected.

The Q value of VDF is very small (0.008−0.015, Table 3) which is good evidence of the poor ability of a fluorine atom for resonance stabilization of the radical on the adjacent carbon atom. Hence, the VDF radical has to be a highly unstable and reactive radical. The Q_B value of FAc was found to be 0.060 (vs $Q_A = 0.008$[36]) or 0.040 (vs $Q_A = 0.015$[55]). But as several authors[32,50−53] underlined: "the $Q-e$ concept is probably too simplified to discuss the reactivity of VDF in free radical reactions based only on separate resonance and polarity factors".[32]

Comonomer Sequence Distribution. Ito and Yamashita[60] developed a theory to characterize the copolymer composition and its microstructure by applying the statistical stationary process given by Coleman and Fox.[61] This theory was successfully used in the frame of the terminal model by Yagi and Tatemoto[33] for the VDF−trifluoroethylene system.

In this present study of the VDF−FAc binary system, this procedure was also applied to obtain the normalized fractions of monomer diads and triads as a function of polymer composition. In Figure 3, the theoretical composition curve, shown in full line, correlates rather well with the experimental one. Then, we used the equations of the conditional probabilities and the fractions of monomer diads [F_{AA}, F_{AB}, F_{BA}, and F_{BB}] and triads [F_{AAA}, F_{AAB}, F_{ABA}, F_{ABB}, F_{BAA}, F_{BAB}, F_{BBA}, and F_{BBB}] according to Yagi and Tatemoto.[33] The fractions of monomer diads are given as follows:

$$F(AA) = P_{BA}P_{AA}/(P_{AB} + P_{BA});\quad F(AB) = F(BA) = P_{BB}P_{BA}/(P_{AB} + P_{BA})$$

$$F(BB) = P_{AB}P_{BB}/(P_{AB} + P_{BA});\quad F(AA) + F(AB) + F(BA) + F(BB) = 1$$

with

$$P_{AA} = r_A/(1 + r_AF);\quad P_{AB} = 1/(1 + r_AF)$$

$$P_{BA} = 1/(1 + r_B/F);\quad P_{BB} = (r_B/F)/(1 + r_B/F)$$

where P, r_A, r_B, and F represent the condition probabilities, the reactivity ratios, and the ratio of initial monomer fractions, respectively.

As for the monomer triads, the various molar fractions are provided from the following equations:

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

$$F(AAB) = F(BAA) = P_{AB}P_{AA}P_{BA}/(P_{AB} + P_{BA})$$

$$F(ABA) = P_{BA}P_{BA}P_{AB}/(P_{AB} + P_{BA})$$

$$F(BAB) = P_{AB}P_{AB}P_{BA}/(P_{AB} + P_{BA})$$

$$F(BBA) = F(ABB) = P_{AB}P_{BA}P_{BB}/(P_{AB} + P_{BA})$$

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

$$F_{AAA} + F_{AAB} + F_{ABA} + F_{ABB} + F_{BAA} + F_{BAB} + F_{BBA} + F_{BBB} = 1$$

The results for the normalized fractions of monomer diads and triads vs polymer compositions are represented in Figures 5 and 6. In these figures, $\overline{F_{AB}}$, $\overline{F_{AAB}}$, and $\overline{F_{BBA}}$ mean $F_{AB} + F_{BA}$, $F_{AAB} + F_{BAA}$, and $F_{BBA} + F_{ABB}$, respectively. Because of the considerably higher reactivity of FAc vs VDF, the maximum of heterodiads F_{AB} (corresponding to the minimum of the homodiads F_{AA} and F_{BB}) is shifted to the lower FAc/VDF ratio in the feed. Much more complicated is the triad distribution showing mainly F_{ABA} and F_{BBA} contributions at a lower FAc/VDF ratio, and it was noted that the higher the FAc/VDF ratio, the greater the F_{BBA}. That corresponds to random copolymer structure as can be suggested by the r_1r_2 product and the $Q-e$ values.

Conclusions

The radical copolymerization of vinylidene fluoride (VDF) with 4,5,5-trifluoro-4-ene pentyl acetate (FAc) was studied in a wide range of initial monomer compositions. The ^1H and ^{19}F NMR spectroscopies allowed one to determine the copolymer compositions, and both results obtained were in good agreement. The reactivity ratios r_i of the comonomers were calculated by the Tidwell and Mortimer method, and the trifluorovinyl acetoxy monomer was found to be more reactive than VDF ($r_{VDF} = 0.17$ and $r_{FAc} = 3.26$ at 120 °C). These

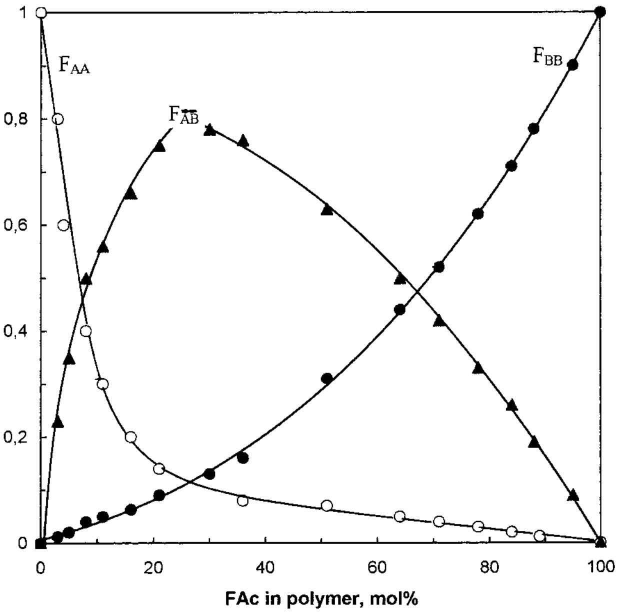


Figure 5. Normalized fractions of monomer diads as a function of polymer composition for VDF–FAc copolymers. ($F_{\overline{AB}} = F_{AB} + F_{BA}$).

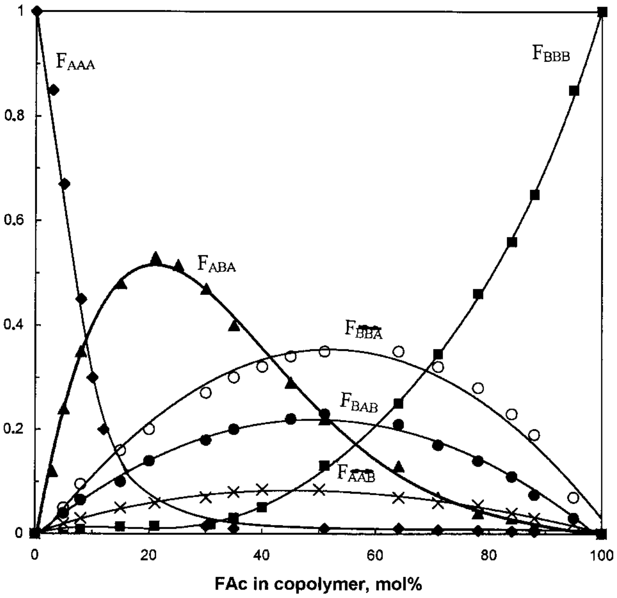


Figure 6. Normalized fractions of monomer triads as a function of polymer composition for VDF–FAc copolymers ($F_{\overline{AAB}} = F_{AAB} + F_{BBA}$; $F_{\overline{BBA}} = F_{BBA} + F_{ABB}$).

values demonstrate that a random copolymerization occurred. Taking into account the values of other fluoroalkene, the Q–e parameters of FAc were calculated as follows: $e_{FAc} = 1.14–1.23$ (from $e_{VDF} = 0.040–0.060$) and $Q_{FAc} = 0.040–0.060$ (vs $Q_{VDF} = 0.008–0.015$). In the frame of Ito and Yamashita's theory for the copolymer composition, the comonomer sequence distribution in diad and triad microstructures was determined. The main structure unit distribution was F_{AB} and F_{BBA}, depending on the FAc(B)/VDF(A) ratio. These observations are in good agreement with experimental results obtained from ^{19}F NMR. Such-PVDF containing acetoxy side groups can be easily hydrolyzed to supply novel PVDF-containing hydroxy cure sites and are under investigation.

Experimental Section

Vinylidene fluoride was kindly donated by Solvay S. A. whereas di-*tert*-butyl peroxide was supplied by Aldrich.

4,5,5-Trifluoro-4-ene pentyl acetate (FAc) was synthesized as previously[16] in a five-step route (Scheme 1). Its NMR characteristics are as follows.

^1H NMR ($CDCl_3$) δ: 1.84 (qi,$^3J_{HH} = 6.8$ Hz, $C\mathit{H}_2CH_2OAc$, 2H), 2.03 (s, $COCH_3$, 3H), 2.33 (dddt, $^3J_{HF} = 22.5$ Hz, $^4J_{HF} = 2.4$ Hz, $^4J_{HF} = 4.0$ Hz, $^3J_{HH} = 6.8$ Hz, $CFCH_2$, 2H), 4.05 (t, $^3J_{HH} = 6.6$ Hz, $C\mathit{H}_2OAc$).

^{19}F NMR ($CDCl_3$) δ: −106.0 (ddt, $^2J_{FFgem} = 88.9$ Hz, $^3J_{FF} = 32.0$ Hz, $^4J_{FH} = 2.5$ Hz,1F); −125.2 (ddt, $^2J_{FF} = 88.9$ Hz, $^3J_{FF} = 113.6$ Hz, $^4J_{FH} = 3.9$ Hz, 1F), −174.8 (ddt, $^3J_{FF} = 32.0$ Hz, $^3J_{FF} = 113.6$ Hz, $^3J_{FH} = 22.5$ Hz, 1F).

^{13}C NMR ($CDCl_3$) δ: 19.93 (s,CH_3), 21.89 (dd, $^2J_{CF} = 22.3$ Hz, $^3J_{CF} = 2.5$ Hz, $CF\mathit{C}H_2$), 24.15 (ddd, $^4J_{CF} = 2.7$ Hz, $^4J_{CF} = 1.0$ Hz, $^3J_{CF} = 2.8$ Hz, $\mathit{C}H_2CH_2OAc$), 63.02 (s,CH_2OAc), 127.52 (ddt, $^1J_{CF} = 234.41$ Hz, $^2J_{CF} = 53.4$ Hz, $^2J_{CF} = 15.7$ Hz, CF), 153.02 (ddd, $^1J_{CF} = 272.4$ Hz, $^1J_{CF} = 285.8$ Hz, $^2J_{CF} = 47.0$ Hz, $F_2C{=}$), 170.38 (s, C=O).

Bulk copolymerizations of VDF and FAc were performed in thick borosilicate Carius tubes in a batch process (length, 130 mm; internal diameter, 10 mm; thickness, 2.5 mm; for a total volume of 8 cm^3). After the initiator (0.05 mol % to the monomer mixture) and FAc were placed, the tube was connected to a vacuum line and purged several times by evacuating and flushing with helium. After 5 thaw–freeze cycles at least, to get rid of oxygen, VDF was trapped under vacuum, in the tube frozen in liquid nitrogen, after a release in an intermediate metallic container calibrated in pressure. The required amount of VDF (0.750 ± 0.008 g) introduced into the tube was assessed by the relative drop of pressure in this release container, initially fed by a cylinder of 300 g of VDF. A beforehand calibration curve—weight of trapped VDF (in g) vs drop of pressure (in bar)—was determined (for 0.75 g of VDF, a difference of pressure of 0.50 bar was required).

The tube, under vacuum and immersed in liquid nitrogen, was sealed and placed into the cavity of a shaking oven at 120 °C for 17 h.

After copolymerization, the tube was frozen in liquid nitrogen and then opened, and the total product mixture was dried at 80 °C under 10^{-2} mmHg until constant weight.

The composition of the copolymer (i.e., the content of VDF and FAc in copolymer) was determined from NMR spectroscopy, at room temperature. The ^1H and ^{19}F NMR spectra were recorded on a Bruker AC-200 or Bruker AC-250 instruments, using deuterated acetone or dimethyl formamide and tetramethylsilane (TMS) or $CFCl_3$ as solvents and internal references, respectively.

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