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Radical Copolymerization of α,β-Difluoroacrylic Acid with Vinylidene Fluoride.

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ABSTRACT: The synthesis of α,β-difluoroacrylic acid (FHC═CF−CO_2H, DiFAA) and its radical copolymerization with vinylidene fluoride (CH_2═CF_2, VDF) are presented. First, DiFAA was synthesized in three steps from the radical addition of methanol onto 1,2-dichloro-1,2-difluoroethylene leading to HCFClCFClCH_2OH in 78% yield. Then, oxidation of the hydroxymethyl end-group followed by zinc-mediated dehalogenation of 2,3-dichloro-2,3-difluoropropanoic acid led to (*Z*) isomer of DiFAA in 29% overall yield. The homopolymerization of DiFAA was successfully achieved by radical polymerization initiated by *tert*-butylperoxypivalate (TBPPi) at 74 °C in 32% yield. Its radical copolymerization with VDF was carried out for the first time and at various compositions leading to functional poly(VDF). The resulting poly(VDF-*co*-DiFAA) copolymers, characterized by ^{1}H and ^{19}F NMR spectroscopies, exhibited a statistic microstructure. The kinetics of this radical copolymerization led to the assessment of the reactivity ratios (r_{DiFAA} = 0.86 and r_{VDF} = 0.34 at 74 °C), and showed that DiFAA was more reactive than VDF in copolymerization. Thermal properties of these poly(DiFAA-*co*-VDF) copolymers were also investigated. Differential scanning calorimetry analyses showed a decrease of the glass transition temperature (T_g) with increasing VDF content. Calculations using the Fox's equation led to the determination of the T_g for poly(DiFAA) homopolymer (T_g = 145 °C) in good agreement with the literature. Thermogravimetric analyses displayed increased thermostability of the resulting copolymers with increasing VDF content.

Introduction

Fluorinated polymers are high value-added materials for various applications, due to their unique properties such as thermal stability, chemical inertness (to solvents, oils, water, acids and bases), low values of the refractive index, permittivity, dissipation factor, and water absorption as well as excellent weather durability and resistance to oxidation.[1−7] Hence, they can find relevant applications in many fields of high technology like aeronautics, microelectronics, engineering, chemical industry, optics, textile finishing, automobile industry, and wiring insulation.

Among these polymers, those containing vinylidene fluoride (VDF)[8,9] are of particular importance since they can be thermoplastics,[3] elastomers[3,5,9−11] or thermoplastic elastomers.[3,5,9] They are typically prepared by radical copolymerization of VDF with other fluoroalkenes. Statistic copolymers are usually obtained although few examples of alternating VDF-containing copolymers were reported with hexafluoroisobutylene,[12−15] methyl trifluoroacrylate[16,17] and α-trifluoromethyl acrylic acid.[18] Many functional fluorinated monomers have been copolymerized with VDF, such as fluoroalkenes[9] or those bearing functional hydroxyl,[19,20] acetoxy,[19] carboxy,[18,21] thioacetoxy,[22] SF_5,[23,24] or dioxole[25,26] groups, and recently summarized.[9]

As a matter of fact, the performance of poly(VDF), especially insolubility, fusibility, thermal and mechanical properties can be improved by cross-linking. Cross-linking of poly(VDF) is still difficult and usually requires either diamines or bisphenols.[27,28] Adequate comonomers that enable an easy copolymerization and which bear functional side group are searched to insert functional groups in poly(VDF).[28] Hence, various comonomers have successfully been copolymerized with VDF. These monomers bear either a bromine atom,[29] hydroxyl,[20] thioacetate,[22] or trialkoxysilane[30,31] group.... On the other hand, some graft copolymers containing a poly(VDF) backbone have been reported,[32−36] and a functional dangling group borne by poly(VDF) should be a potential precursor of such fluoropolymers via "grafting onto" strategy. Hence, it was of interest to propose new functional monomers able to react with VDF. Poly(α,β-difluoroacrylate)s[37−42] are polymers which have been barely investigated but which present an interest because of their fluorine content (and quite few hydrogen atoms), their high transparency, and their high glass transition temperature (T_g of poly(methyl α,β-difluoroacrylate)[37] and poly(hexafluoroisopropyl α,β-difluoroacrylate)[40] = 140 and 98 °C, respectively). These fluoropolymers have been studied mainly for optical applications, as cladding materials for optical fibers.[37−39,42]

However, to our best knowledge, the literature does not mention any report regarding the ability of α,β-difluoroacrylic acid monomer to copolymerize. The objectives of this present article deal with (i) an improved synthesis of α,β-difluoroacrylic acid, (ii) its radical copolymerization with VDF to obtain materials possessing high fluorine contents and bearing carboxy side groups as potential cross-linking sites or precursors of poly(VDF)-*g*-poly(M) graft copolymers (where M stands for the comonomer), and (iii) the kinetics of the radical copolymerization. If the synthesis of α,β-difluoroacrylic acid has previously been reported from trifluoroethylene in six or seven steps,[43,44]

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we present here a facile synthesis of α,β-difluoroacrylic acid from 1,2-dichloro-1,2-difluoroethylene in three steps only.

Experimental Section

Materials. All reagents were used as received unless stated otherwise. *tert*-Butylperoxypivalate (*tert*-butyl 2,2-dimethylperoxypropanoate) in isododecane (Trigonox 25-C75, *t*BuOOC(O)*t*Bu, TBPPi) (purity 75%), and 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (Trigonox 101) were kindly provided by Akzo Nobel (Compiègne, France). Vinylidene fluoride (VDF, $CH_2{=}CF_2$), 1,2-dichloro-1,2-difluoroethylene (CFCl=CFCl), and 1,1,1,3,3-pentafluorobutane ($C_4F_5H_5$) were kindly provided by Solvay Solexis and Solvay Fluor (Bollate, Italy, and Tavaux, France). Pentane, chloroform, methanol, acetonitrile (all of analytical grade), sodium chloride (powder, 99%), calcium hydride (powder, 99%), and silica were purchased from Sigma-Aldrich (Saint Quentin-Fallavier, France). Acetonitrile was distilled over calcium hydride prior to use. Fuming nitric acid was purchased from SDS (Peypin, France). Deuterated solvents for NMR characterizations were purchased from Eurisotop (Grenoble, France) (purity > 99.8%).

Characterizations. *NMR*. The nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC 400 instrument, using either deuterated chloroform, acetone, or dimethyl sulfoxide as the solvent and tetramethylsilane (TMS) (or $CFCl_3$) as the references for ^1H (or ^{19}F) nuclei. The experimental conditions for recording ^1H (or ^{19}F) NMR spectra were as follows: flip angle 90° (or 30°), acquisition time 4.5 s (or 0.7 s), pulse delay 2 s, number of scans 128 (or 512), and a pulse width of 5 μs for ^{19}F NMR.

FTIR. Infrared spectroscopy was carried out on a Perkin-Elmer Spectrum 100 Series FTIR spectrometer fitted with an universal Diamond/ZnSe ATR accessory. Spectra were recorded between 650 and 4000 cm^{-1}, with a resolution of 4 cm^{-1} and four scans. Samples consisted of pellets that were obtained by pressing the (co)polymer powder at several tons for 5 min.

TGA. Thermogravimetric analyses (TGA) were performed with a TGA 51 apparatus from TA Instruments, under air, at the heating rate of 10 °C.min^{-1} from room temperature up to a maximum of 550 °C. The sample size varied between 10 and 15 mg.

DSC. Differential scanning calorimetry (DSC) measurements were conducted using a TA Instruments Q100 connected to a computer. A nitrogen flow rate was used. After its insertion into the DSC apparatus, the sample was initially stabilized at −80 °C for 10 min. Then, the first scan was made at a heating rate of 20 °C min^{-1} up to 180 °C. It was then cooled to −80 °C. Finally, a second scan was performed at a heating rate of 10 °C min^{-1} up to 180 °C giving the values of T_g reported, taken at the half-height of the heat capacity jump of the glass transition.

Preparation of the α,β-Difluoroacrylic Acid. *Synthesis of 2,3-Dichloro-2,3-difluoropropan-1-ol.* As 1,2-dichloro-1,2-difluoroethylene is a gas, the reaction were performed in 2 L Hastelloy Parr autoclave systems (HC 276) equipped with a manometer, a mechanical Hastelloy anchor, a rupture disk (3000 PSI), inlet and outlet valves. An electronic device regulated and controlled both the stirring and heating of the autoclave. Prior to reaction, the autoclave was pressurized with 30 bar (ca. 430 PSI) of nitrogen to check for leaks. The autoclave was then conditioned for the reaction with several nitrogen/vacuum cycles (10^{-2} mbar) to remove any trace of oxygen. The liquid and dissolved solid phases were introduced via a funnel. Then the gas was introduced by double weighing (*i.e.*, the difference of weight before and after filling the autoclave with the gas).

In the "conditioned" 2 L autoclave, 975 g (30.4 mol) of methanol, 21.8 g (0.075 mol) of 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane, and 97 g (0.726 mol) of 1,2-dichloro-1,2-difluoroethylene were introduced. The solution was stirred and heated at 134 °C for 10 h (P_{Max} = 12 bar, P_{Min} = 7 bar). The autoclave was then cooled to room temperature, put in an ice bath for 30 min, and then degassed. The total product mixture was distilled at 63−69 °C under 20 mmHg to yield two diastereoisomers (α and β) of 2,3-dichloro-2,3-difluoropropan-1-ol (colorless liquid) in 78% yield.

Diastereoisomer α or β. ^1H NMR ($CDCl_3$), δ, ppm: 3.5 (s, O**H**, 1H); 4.1 (ddd, $^3J_{H(F\text{-}2)}$ = 15 Hz, $^4J_{H(F\text{-}3)}$ = 5.5 Hz, $^4J_{HH}$ = 1.5 Hz, C**H**$_2$−OH, 2H); 6.4 (dd, $^2J_{H(F\text{-}3)}$ = 49.2 Hz, $^3J_{H(F\text{-}2)}$ = 7.2 Hz, CFCl**H**, 1H).

^{13}C NMR ($CDCl_3$), δ, ppm: 65.1 (d, $^2J_{C(F\text{-}2)}$ = 24.4 Hz, **C**H$_2$-OH) or 65.2 (d, $^2J_{C(F\text{-}2)}$ = 24.4 Hz, **C**H$_2$OH); 97.9 (dd, $^1J_{C(F\text{-}3)}$ = 248.7 Hz, $^2J_{C(F\text{-}2)}$ = 34.3 Hz, **C**FClH) or 98.3 (dd, $^1J_{C(F\text{-}3)}$ = 251.7 Hz, $^2J_{C(F\text{-}2)}$ = 31.0 Hz, **C**FClH); 110.0 (dd, $^1J_{C(F\text{-}2)}$ = 250.9 Hz, $^2J_{C(F\text{-}3)}$ = 25.9 Hz, **C**FCl) or 110.7 (dd, $^1J_{C(F\text{-}2)}$ = 251.9 Hz, $^2J_{C(F\text{-}3)}$ = 22.4 Hz, **C**FCl).

^{19}F NMR ($CDCl_3$), δ, ppm: −130.5 (ddt, $^3J_{F(F\text{-}3)}$ = 19.5 Hz, $^3J_{F(H\text{-}1)}$ = 15.5 Hz, $^3J_{F(H\text{-}3)}$ = 7.0 Hz, C**F**Cl); −153.2 (dd, $^2J_{F(H\text{-}3)}$ = 49.2 Hz, $^3J_{F(F\text{-}2)}$ = 19.5 Hz, C**F**ClH).

Diastereoisomer β or α. ^1H NMR ($CDCl_3$), δ, ppm: 3.5 (s, O**H**, 1H); 4.1 (m, C**H**$_2$−OH, 2H); 6.5 (dd, $^2J_{H(F\text{-}3)}$ = 48.2 Hz, $^3J_{H(F\text{-}2)}$ = 4.0 Hz, CFCl**H**, 1H).

^{13}C NMR ($CDCl_3$), δ, ppm: 65.2 (dd, $^2J_{C(F\text{-}2)}$ = 24.4 Hz, $^3J_{C(F\text{-}2)}$ = 2.4 Hz, **C**FClH) or 65.1 (d, $^2J_{C(F\text{-}2)}$ = 24.4 Hz, **C**H$_2$−OH) ; 98.3 (dd, $^1J_{C(F\text{-}3)}$ = 251.7 Hz, $^2J_{C(F\text{-}2)}$ = 31.0 Hz, **C**FClH) or 97.9 (dd, $^1J_{C(F\text{-}3)}$ = 248.7 Hz, $^2J_{C(F\text{-}2)}$ = 34.3 Hz, **C**FClH); 110.7 (dd, $^1J_{C(F\text{-}2)}$ = 251.9 Hz, $^2J_{C(F\text{-}3)}$ = 22.4 Hz, **C**FCl) or 110.0 (dd, $^1J_{C(F\text{-}2)}$ = 250.9 Hz, $^2J_{C(F\text{-}3)}$ = 25.9 Hz, **C**FCl).

^{19}F NMR ($CDCl_3$), δ, ppm: −130.9 (dddd, $^3J_{F(H'\text{-}1)}$ = 19.6 Hz, $^3J_{F(F\text{-}2)}$ = 19.6 Hz, $^3J_{F(H''\text{-}1)}$ = 13.5 Hz, $^3J_{F(H\text{-}3)}$ = 4.1 Hz, C**F**Cl); −148.7 (dd, $^2J_{F(H\text{-}3)}$ = 48.2 Hz, $^3J_{F(F\text{-}2)}$ = 19.6 Hz, C**F**ClH).

Synthesis of 2,3-Dichloro-2,3-difluoropropanoic acid. Into a 250 mL three-necked round-bottom flask equipped with a condenser, a dropping funnel, and a magnetic stirrer was introduced 49.86 g (0.302 mol) of 2,3-dichloro-2,3-difluoropropan-1-ol. Then, 101.09 g (1.123 mol) of fuming HNO_3 (70%) was introduced into the dropping funnel, and added dropwise to the 2,3-dichloro-2,3-difluoropropan-1-ol under stirring at 50 °C. The reaction medium was then heated at 100 °C for 24 h. After the reaction, the product (green color) was cooled down to room temperature and 10 mL of water saturated with NaCl was introduced. Three extractions were realized with 10 mL of chloroform. The organic layer was filtrated over silica, chloroform was evaporated and 35.1 g (0.196 mol) of HClFC−CFCl-COOH (colorless liquid) was obtained in 65% yield. The product was composed of two diastereoisomers (isomers α and β).

Isomer α or β. ^1H NMR ($CDCl_3$), δ, ppm: 6.8 (dd, $^2J_{H(F\text{-}3)}$ = 46.9 Hz, $^3J_{H(F\text{-}2)}$ = 13.8 Hz, CFCl**H**, 1H). ; 9.6 (s, COO**H**).

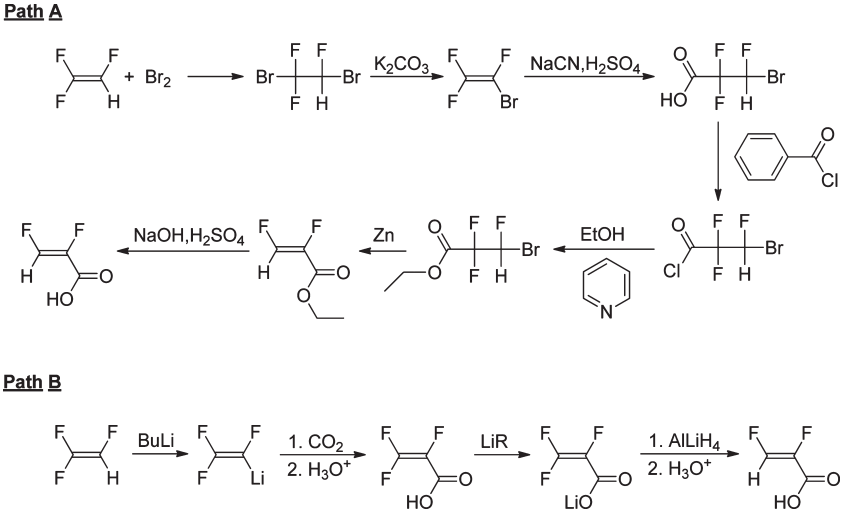
^{19}F NMR ($CDCl_3$), δ, ppm: −135.5 (dd, $^3J_{F(F\text{-}3)}$ = 19.1 Hz, $^3J_{FH}$ = 14.0 Hz, C**F**Cl); −153.1 (dd, $^2J_{F(H\text{-}3)}$ = 47.0 Hz, $^3J_{F(F\text{-}2)}$ = 19.0 Hz, C**F**ClH).

Isomer β or α. ^1H NMR ($CDCl_3$), δ, ppm: 6.7 (dd, $^2J_{H(F\text{-}3)}$ = 46.4 Hz, $^3J_{H(F\text{-}2)}$ = 13.4 Hz, CFCl**H**, 1H); 9.6 (s, COO**H**).

RMN ^{19}F ($CDCl_3$), δ, ppm: −134.6 (dd, $^3J_{F(F\text{-}3)}$ = 19.6 Hz, $^3J_{FH}$ = 13.5 Hz, C**F**Cl); −141.1 (dd, $^2J_{F(H\text{-}3)}$ = 45.8 Hz, $^3J_{F(F\text{-}2)}$ = 20.2 Hz, C**F**ClH).

Synthesis of α,β-Difluoroacrylic Acid. Into a 250 mL three-necked round-bottom flask equipped with a condenser, a dropping funnel, a magnetic stirrer, and a thermometer were introduced 24.8 g (0.38 mol) of zinc and 30 mL of methanol. A few drops of bromine (Br_2) were added dropwise under stirring to activate the zinc (an exotherm can be noted). Then, 26.6 g (0.148 mol) of 2,3-dichloro-2,3-difluoropropanoic acid was introduced slowly under stirring with a strong exotherm. The addition of the precursor was controlled to monitor the exotherm and the reaction. The synthesis of α,β-difluoroacrylic acid was instantaneous. The reaction medium was then acidified with 5 mL of HCl (33%) and α,β-difluoroacrylic acid was extracted with diethyl ether and then sublimated under a vacuum of 10^{-3} bar at 45 °C. 8.2 g (0.086 mol) of isomer (*Z*) of α,β-difluoroacrylic acid were obtained in 58% yield as a white powder.

Scheme 1. Synthesis of α,β-Difluoroacrylic Acid from Trifluoroethylene According to Yakubovich et al.[43] (Path A) and Sauvêtre et al.[44] (Path B)



RMN ^{1}H ($CDCl_3$), δ, ppm: 7.4 (dd, $^{2}J_{H(F-3)}$ = 69.6 Hz, $^{3}J_{H(F-2)}$ = 13.8 Hz, **H**FC, 1H); 9.0 (s, COO**H**).

RMN ^{13}C ($CDCl_3$), δ, ppm: 138.4 (dd, $^{1}J_{C(F-2)}$ = 255.4 Hz, $^{2}J_{C(F-3)}$ = 10.2 Hz, **C**F); 145.4 (dd, $^{1}J_{C(F-3)}$ = 280.3 Hz, $^{2}J_{C(F-2)}$ = 10.2 Hz, HF**C**); 158.0 (dd, $^{2}J_{C(F-2)}$ = 30 Hz, $^{3}J_{C(F-3)}$ = 9.5 Hz, **C**OOH).

RMN ^{19}F ($CDCl_3$), δ, ppm: −139.4 (dd, $^{3}J_{F(F-2)}$ = 6.3 Hz, $^{2}J_{F(H-3)}$ = 69.9 Hz, H**F**C); −152.4 (dd, $^{3}J_{F(H-3)}$ = 13.5 Hz, $^{3}J_{F(F-3)}$ = 6.7 Hz, C**F**).

Anal. Found: C, 33.27, H, 1.80; F, 35.24. Calcd for $C_3H_2F_2O_2$: C, 33.35; H, 1.87; F. 35.17.

Radical Copolymerizations. The radical copolymerizations of vinylidene fluoride (VDF) with α,β-difluoroacrylic acid (DiFAA) were performed in thick borosilicate Carrius tubes (length 130 mm, internal diameter 10 mm, thickness 2.5 mm, total volume 8 mL). Because of its insolubility in 1,1,1,3,3-pentafluorobutane, DiFAA was dissolved in the minimal amount of acetonitrile prior to the polymerization. In a typical copolymerization, the different reactants including the initiator (2 mol % with respect to the monomers), solvent, and α,β-difluoroacrylic acid were added in the tube. The tubes were then degassed by several thaw−freeze cycles (minimum of 4), and the required amount of VDF was introduced via a special device (see Supporting Information, Picture S1) from an intermediate cylinder from which the drop of pressure was beforehand calibrated with the amount (g) of VDF. The tubes were then sealed under dynamic vacuum at the temperature of liquid nitrogen. The tubes were then inserted in a custom design heating and shaking apparatus regulated at the desired temperature. The reaction was carried out over a 10−12 h period at constant temperature (74 °C). After cooling, the tubes were frozen and opened, and the (co)polymers were isolated by removal of the solvent. The (co)polymers were further dried under high vacuum at 70 °C until constant weight. The obtained powders were then weighed to determine the yield, and characterized by the usual techniques as explained above.

Results and Discussion

To obtain poly(VDF-*co*-DiFAA) copolymers, it was first necessary to synthesize α,β-difluoroacrylic acid (DiFAA) since this monomer is not commercially available.

Preparation of the α,β-Difluoroacrylic Acid. α,β-Difluoroacrylic acid and α,β-difluoroacrylates can be prepared from trifluoroethylene (TrFE, F_2C=CFH) either in a seven-step process described by Yakubovich et al.[43] (path A) or a six-step process described by Sauvêtre et al.[44] (path B) as indicated in Scheme 1. These processes, besides the large number of necessary steps, suffer from several drawbacks including the uses of zinc in large amounts during the dehalogenation step (path A), as well as the use of potentially flammable or explosive chemicals (F_2C=CFBr, BuLi, LiR, $AlLiH_4$ and especially TrFE[45]).

Our strategy was to decrease the risks and number of steps. Hence, α,β-Difluoroacrylic acid was prepared from 1,2-dichloro-1,2-difluoroethylene in a three-step reaction (Scheme 2). The first step consists in the radical addition of methanol (in excess) onto 1,2-dichloro-1,2-difluoroethylene,[46,47] followed by the oxidation of the alcohol into a carboxylic acid. 2,5-Bis(*tert*-butyl peroxy)-2,5-dimethylhexane (Trigonox 101) was used as the initiator as it led to the largest proportion of monoadduct in the radical telomerization of 1,2-dichloro-1,2-difluoroethylene with methanol.[46] The third and final step consists in a zinc-mediated dechlorination to obtain α,β-difluoroacrylic acid in a ca. 29% overall yield.

Only the (*Z*) isomer of α,β-difluoroacrylic acid was obtained as this isomer is the thermodynamically favored compound. Indeed, the coupling constant $^{19}F_{\alpha}-^{19}F_{\beta}$ from 60 to 70 Hz (see Supporting Information, Figure S1) is characteristic of (*Z*) isomer whereas that of (*E*) isomer is much higher (J_{F-F} = 250 Hz). The structure of (*Z*)-α,β-difluoroacrylic acid was confirmed by elemental analysis, ^{1}H and ^{19}F NMR spectroscopies (see Supporting Information, Figure S1).

Radical Copolymerization of α,β-Difluoroacrylic Acid with Vinylidene Fluoride. Several patents[37−42] report the polymerization of α,β-difluoroacrylates. Azo compounds such as azobis(isobutyronitrile) (AIBN) and organic peroxides such as dicumyl peroxide or *tert*-butyl peroxyisopropylcarbonate were used as free radical initiators. According to the literature,[40,41] poly(methyl α,β-difluoroacrylate), poly(hexafluoroisopropyl

Scheme 2. Synthesis of α,β-Difluoroacrylic Acid from 1,2-Dichloro-1,2-difluoroethylene

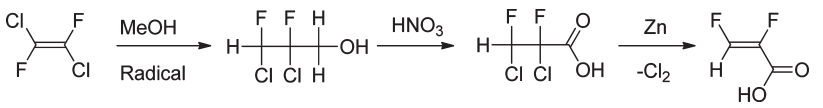
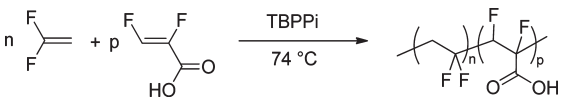


Table 1. Characteristics of the Poly(VDF-*co*-DiFAA) Copolymers and Their Thermal Properties (Where VDF and DiFAA Stand for Vinylidene Fluoride and α,*β*-Difluoroacrylic Acid, Respectively)[a]

		(co)polymer (F_{VDF})[b]		% VDF defects[c]					
run no.	feed[b] (f_{VDF})	^{19}F	^{1}H	T−T	H−H	residual[d] DiFAA (%)	yield (%)	T_g[e] (°C)	$T_{d,10\%}$[f] (°C)
1	100	100	100			0	66	−40	317
2	90	88	81	2.14	1.93	0	48	−34	238
3	80	67	65	1.47	1.34	0	63	−5	173
4	70	60	59	1.22	1.08	0	32		196
5	60	47	47	0.28	0.22	11	81	+38	149
6	50	41	42	0.34	0.23	20	74	+47	116
7	40	34	32	1.03	0.35	20	28	+58	179
8	30	26	26	0.08	0.56	10	58		156
9	20	19	24	0.85	0.27	15	44		139
10	10	13	17	2.96	1.73	8	45	+103	131
11	0	0	0	-	-	10	32		164

[a] Polymerization conditions: $[TBPPi]_0/([VDF]_0 + [TBPPi]_0) = 2$ mol %, 12 h at 74 °C in acetonitrile. [b] f_{VDF} and F_{VDF} stand for VDF mol % in the feed and in the copolymer, respectively. [c] Head-to-head (H−H) and tail-to-tail (T−T) defects of chaining were determined using ^{19}F and ^{1}H NMR. [d] Assessed by ^{19}F NMR. [e] T_g stands for glass transition temperature determined by differential scanning calorimetry. [f] Thermogravimetric analyses carried out under air ($T_{d,10\%}$ stands for the temperature at which 10 wt % of the copolymer was degraded).

Scheme 3. Radical Copolymerization of Vinylidene Fluoride with α,*β*-Difluoroacrylic Acid Initiated by *tert*-Butylperoxypivalate (TBPPi) at 74 °C



α,*β*-difluoroacrylate), poly(cyclohexyl α,*β*-difluoroacrylate) and poly(1,4,5,6,7,7-hexachlorobicycloheptenyl α,*β*-difluoroacrylate) were successfully polymerized in good yields and thermal and optical properties of these polymers were studied. Nevertheless, only polymer viscosities were determined; molecular weight and structural study of polymers are not available. The only disclosed copolymerization of α,*β*-difluoroacrylates with claimed properties deals with the copolymerization of methyl α,*β*-difluoroacrylate with hexafluoroisopropyl α,*β*-difluoroacrylate.[40] Only one experiment was realized (from 50/50 wt % in the feed) and reactivity of monomers, composition and structure of the polymer were not investigated.

For the first time, the radical copolymerization of VDF with α,*β*-difluoroacrylic acid initiated by *tert*-butylperoxypivalate (TBPPi) led to several (co)polymers (Scheme 3) according to the procedure described in the Experimental Section. They were designed to cover the whole range of composition. The results are displayed in Table 1. Copolymers are soluble in common organic solvents and in deionized water (for DiFAA content > 30%).

Both ^{19}F and ^{1}H NMR spectra enabled us to assess the composition of these copolymers, i.e. the contents in both comonomers. Figure 1 displays the ^{19}F NMR spectrum of a poly(VDF-*co*-DiFAA) copolymer (65% VDF in the copolymer, run 3, Table 1). Three characteristic multiplets were assigned to VDF: (1) normal addition ($-CH_2-CF_2-CH_2-CF_2-$) (signal centered at −92 ppm),[17−20] (2) alternated addition

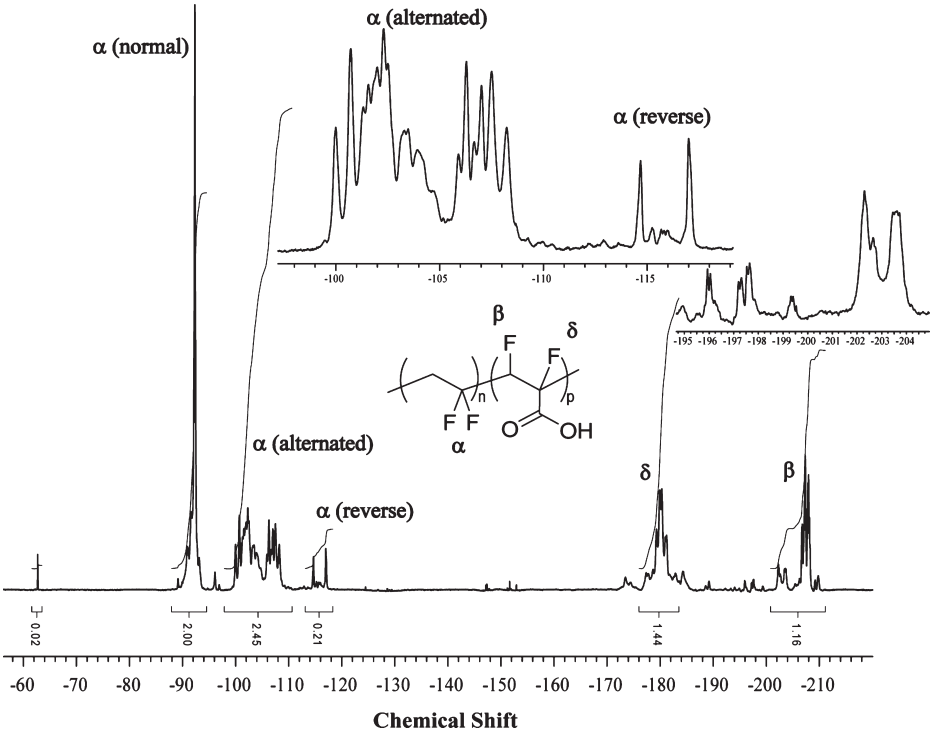


Figure 1. ^{19}F NMR spectrum of run 3 (Table 1) poly(VDF-*co*-DiFAA) copolymer (65 mol % VDF in the copolymer) in acetone-d_6 (where VDF and DiFAA stand for vinylidene fluoride and α,*β*-difluoroacrylic acid, respectively).

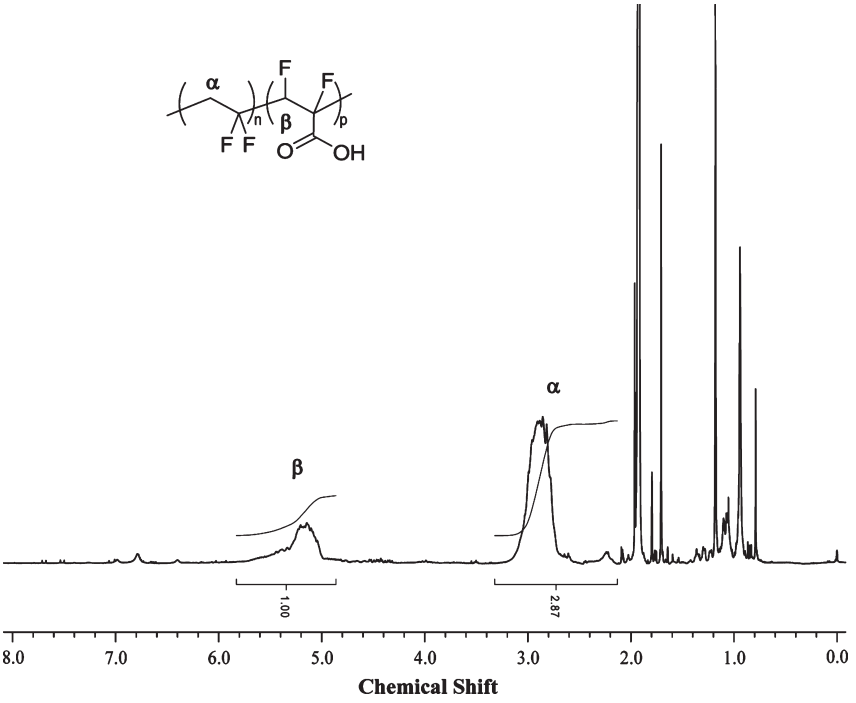


Figure 2. ^{1}H NMR spectrum of run 4 (Table 1) poly(VDF-*co*-DiFAA) copolymer (59 mol % VDF in the copolymer) recorded in acetone-d_6 (where VDF and DiFAA stand for vinylidene fluoride and α,β-difluoroacrylic acid, respectively).

in the VDF−DiFAA dyad (C**F**$_2$ of VDF adjacent to CFH of DiFAA) which is an AB system, (ranging from −100 to −109 ppm), because of the presence of an asymmetric carbon, and (3) reverse addition (−CH_2−C**F**$_2$−C**F**$_2$−CH_2−) (signals in the −113 to −117 ppm range).[17−20] Fluorine atoms in C**F**H of DiFAA unit appear clearly between −202 and −210 ppm as for C**F**H of TrFE units in poly(VDF-*co*-TrFE),[48] and fluorine atoms in C**F**(COOH) are located between −176 and −187 ppm.[17,48−50] It is expected that the macro-radical terminated by VDF (∼∼∼$CH_2CF_2^{\bullet}$) reacts selectively onto the less hindered site of DiFAA, hence leading to ∼∼∼$CH_2CF_2CFHCF(CO_2H)^{\bullet}$ radical.

In the ^{1}H NMR spectrum of poly(VDF-*co*-DiFAA) copolymer (Figure 2), the signal of VDF methylene is centered at 2.9 ppm for normal (head-to-tail) additions and 2.1−2.2 ppm for reverse (tail-to-tail) additions while that of CF**H** group of DiFAA is centered at 5.2 ppm. As the signals do not present any overlapping, the composition could be calculated from both ^{19}F and ^{1}H NMR spectra using eqs 1 and 2.

$$\%\ \mathrm{DiFAA}(^{19}\mathrm{F\ NMR}) = \frac{\int_{-202}^{-210} \mathrm{CFH}/1}{\int_{-202}^{-210} \mathrm{CFH}/1 + (\int_{-92} \mathrm{CF_2} + \int_{-100}^{-117} \mathrm{CF_2})/2} \quad (1)$$

$$\%\ \mathrm{DiFAA}(^{1}\mathrm{H\ NMR}) = \frac{\int_{5.2} \mathrm{CFH}/1}{\int_{5.2} \mathrm{CFH}/1 + \int_{2.1}^{3.1} \mathrm{CH_2}/2} \quad (2)$$

Table 1 summarizes the molar percentages of VDF in all poly(VDF-*co*-DiFAA) copolymers. Although the VDF molar percentages in copolymers are lower than those in the feed (30−100 mol % feed), it is noted that the higher the VDF feed, the higher the VDF in the copolymer which attests that statistic copolymers have been produced, in contrast to poly(VDF-*alt*-α-trifluoromethacrylic acid)[18] and poly(VDF-*alt*-methyl α,β,β-trifluoroacrylate)[17] alternating copolymers produced in similar conditions. For VDF feed lower than 30 mol %, the VDF percentage in the copolymer is slightly higher than that in the feed.

The percentage of defects (reverse addition) in the PVDF block was calculated from the integrals of the signals corresponding to the reverse units (−114 to −118 ppm and 2.1 to 2.4 ppm in ^{19}F and ^{1}H NMR spectra, respectively). It appears that the percentage of defects is low (< 5%) and that usually tail-to-tail defects (−CH_2−CH_2−) are slightly more prominent than the head-to-head defects (−CF_2−CF_2−). As expected, an increase in the defect percentage was noted with increasing VDF content in the copolymers. The percentage of defects is also null as soon as the DiFAA content is high enough to prevent from the presence of long VDF blocks.

The FTIR spectra of the copolymers gave us a good indication of the successful copolymerization of VDF with DiFAA, confirming the NMR results. From the ATR FTIR spectra of the poly(VDF-*co*-DiFAA) copolymers, poly(VDF) and poly(DiFAA) homopolymers (Figure 3), normalized at the C−F resonance at 1200 cm^{-1}, as the DiFAA content increases, an increase of intensity is observed for the O−H (3000 cm^{-1}), C−H (2500 cm^{-1}), carbonyl C=O (1750 cm^{-1}), ester C−O (1100 cm^{-1}) absorption frequencies, all related to the presence of DiFAA in the copolymers. As expected, these signals assigned to the carboxylic groups cannot be found in the poly(VDF) spectrum. It was also noted that the absorption frequency of the carbonyl is slightly higher than expected probably attributed to the hydrogen bonding.

Molecular weights could be assessed neither by NMR (due to the lack of a label) nor by size exclusion chromatography (by lack of a set of columns compatible with the carboxylic groups of DiFAA constitutive units).

Figure 4 shows the composition diagram, i.e., the copolymer composition (mol % of VDF in the copolymers calculated from the average values assessed from the ^{19}F and ^{1}H NMR) vs VDF feed composition. This figure demonstrates

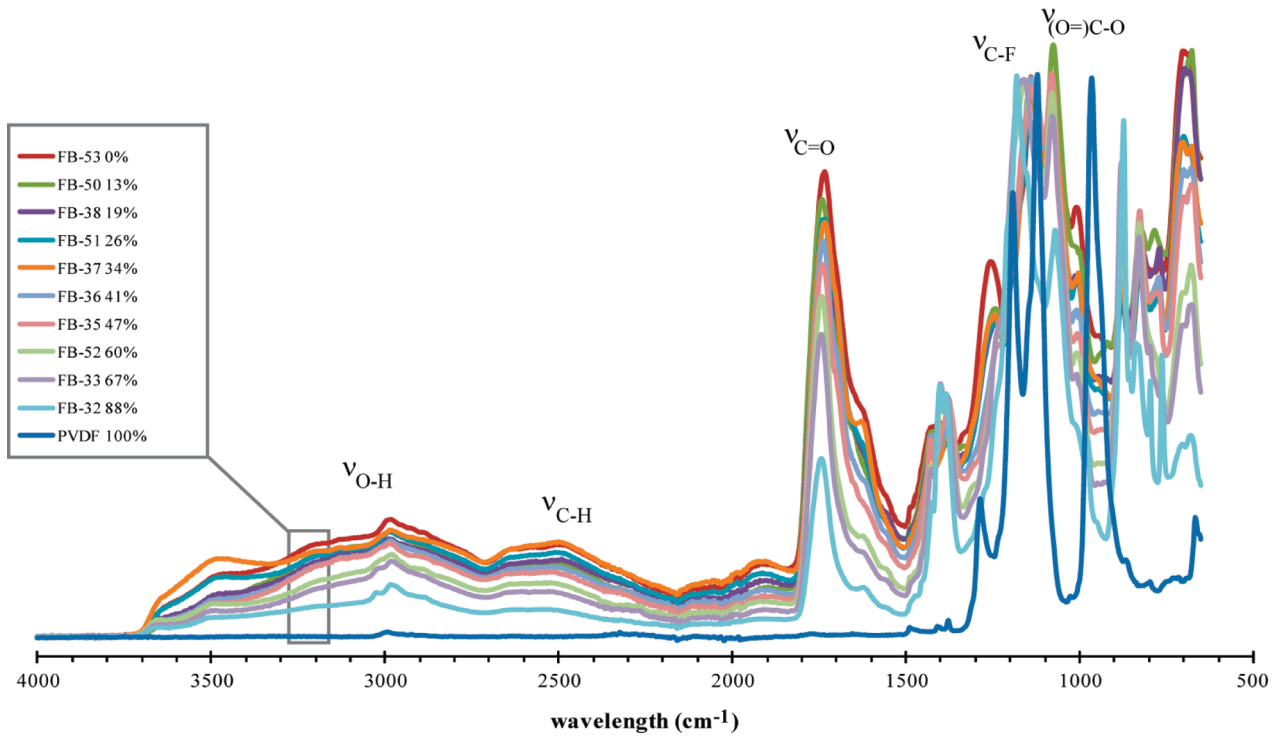


Figure 3. ATR FTIR spectra of poly(VDF-*co*-DiFAA) copolymers, poly(DiFAA) and poly(VDF) homopolymers (where VDF and DiFAA stand for vinylidene fluoride and α,*β*-difluoroacrylic acid, respectively).

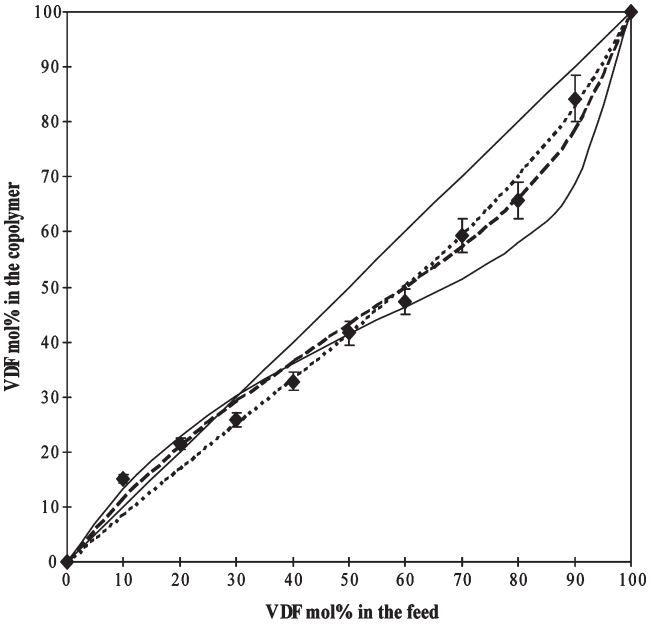


Figure 4. Polymer/monomer compositions curve for the poly(VDF-*co*-DiFAA) copolymers (experimental points represented by diamonds) (full line, dotted line, and dashed line represent the theoretical curves given by the extended Kelen−Tüdos, Fineman−Ross, and Kelen−Tüdos models, respectively) (where VDF and DiFAA stand for vinylidene fluoride and α,*β*-difluoroacrylic acid, respectively).

that DiFAA is more reactive than VDF especially for VDF feed content higher than 28 mol %. The reactivity tends to reverse toward low VDF fractions and an azeotrope was found around 25 mol % VDF (see below).

From these data, three different models were applied to assess the reactivity ratios of DiFAA and VDF comonomers: Fineman−Ross, Kelen−Tüdos, and extended Kelen−Tüdos.[51−55] The fitting curves obtained from these models are displayed

Table 2. Reactivity Ratios of VDF and DiFAA Comonomers at 74 °C Assessed by the Different Kinetic Models (Where VDF and DiFAA Stand for Vinylidene Fluoride and α,*β*-Difluoroacrylic Acid, Respectively)

	Fineman−Ross	Kelen−Tüdos	extended Kelen−Tüdos	average
r_{VDF}	0.51	0.35	0.16	0.34 ± 0.18
r_{DiFAA}	1.14	0.78	0.67	0.86 ± 0.28

in Figure 4 and the values of the reactivity ratios are listed in Table 2. Because the Fineman−Ross and Kelen−Tüdos models were designed for low conversion (< 15%), only the extended Kelen−Tüdos model should be considered as it is the only one taking into account the conversion of the copolymerization. However, although several conversions were higher than the recommended ones, both Kelen−Tüdos and Fineman−Ross models seem to be in good agreement with the experimental points. These three models indicate that DiFAA is more reactive than VDF.

The comparison of the obtained reactivity ratios with those of the literature (Table 3) shows several trends. First and as expected, acrylic acid (AA), a fully hydrogenated homologue of DiFAA, exhibits a higher reactivity than DiFAA because the fluorine atom in *β*-position decreases the polymerization rate of DiFAA. Hence, for the (AA, VDF) pair, it is observed a quite high value of $r_{AA} = 305$, compared to that of VDF ($r_{VDF} = 0.11$). It is also expected that α-fluoroacrylic acid to be even more reactive as its square of the propagation rate to the termination rate, k_p^2/k_t, is extremely high (1.6×10^{11} L mol^{-1} s^{-1})[56] compared to that of AA (0.565 L mol^{-1} s^{-1}),[57] while that of VDF is 0.019 L mol^{-1} s^{-1} in solution[58] or 0.058−1.69 L mol^{-1} s^{-1} in supercritical CO_2.[59,60] Second, it can be seen that perfluorovinyl monomers M with the general formula CF_2=CF−R, if R is an electron-withdrawing group such as CF_3 (case of HFP) or OC_nF_{2n+1} (case of PMVE or PPVE), $1/r_{VDF}$ is smaller than 1. This indicates that VDF is more reactive than the M

Table 3. Monomer Reactivity Ratios for the Radical Copolymerization of Vinylidene Fluoride with other Fluoromonomers (M), Acrylic Acid, and Vinyl Acetate

monomer M	acronym	r_{VDF}	r_M	$r_{VDF}r_M$	$1/r_{VDF}$	reference
$H_2C{=}CHCO_2H$	AA	0.11	305	33.55	9.09	61
$H_2C{=}CHOCOCH_3$	VAc	−0.40	1.67	−0.67	−2.5	62
		0.50	2.0	1.00	2.0	63
$H_2C{=}CHCF_3$	TFP	0.35	2.40	0.91	2.85	64
$H_2C{=}C(CF_3)CO_2H$	TFMA	0.33	0	0	3.03	18, 65
		1.60	0	0	0.62	21
$H_2C{=}CHF$	VF	0.17	4.2−5.5	0.71−0.94	5.88	66
		0.20−0.43	3.8−4.9	0.76−2.11	2.33−5.00	67
$H_2C{=}CFCF_2OR_F$		0.38	2.41	0.92	2.63	68
$FCH{=}CFCO_2H$	**DiFAA**	**0.34**	**0.86**	**0.29**	**2.94**	**this work**
$F_2C{=}CHCF_3$	PFP	9.0	0.06	0.54	0.11	69
$F_2C{=}CHC_6F_{13}$		12.0	0.90	10.80	0.08	70
$F_2C{=}CHBr$	BDFE	1.2	0.4	0.48	0.83	71
$F_2C{=}CFH$	TrFE	0.70	0.50	0.35	1.43	48
$F_2C{=}CFCl$	CTFE	0.73	0.75	0.55	1.37	72
		0.17	0.52	0.09	5.88	73
$F_2C{=}CFBr$	BTFE	0.43	1.46	0.63	2.33	72
$F_2C{=}CF_2$	TFE	0.23	3.73	0.86	4.35	72
		0.32	0.28	0.09	3.13	74
$F_2C{=}CF{-}CF_3$	HFP	6.70	0	0	0.15	75
		5.0	0	0	0.20	10
		2.45	0	0	0.40	76
		2.90	0.12	0.35	0.34	77
		5.13	0	0	0.19	78
		3.6−4.6	0	0	0.22−0.28	79, 80
		3.2	0	0	0.31	60
		3.3	0	0	0.86	81
$F_2C{=}CFOCF_3$	PMVE	3.40	0	0	0.29	82
		1.06	0.11	0	0.94	83
		2.5	0	0	0.4	84
$F_2C{=}CFOC_3F_7$	PPVE	1.15	0	0	0.86	82
$F_2C{=}CFCO_2CH_3$		0.30	0	0	3.33	17
$F_2C{=}CFCH_2OH$		0.83	0.11	0.09	1.02	20
$F_2C{=}CF(CH_2)_3OAc$		0.17	3.26	0.59	5.56	19
$F_2C{=}C(CF_3)COF$		7.60	0.02	0.15	0.13	85
$F_2C{=}C(CF_3)OCOC_6H_5$		0.77	0.11	0.08	1.30	86

comonomer. On the contrary, if R is an electron-donating group (CTFE, BTFE), $1/r_{VDF}$ is greater than 1 indicating a higher reactivity of M comonomer. In the present case of DiFAA, $1/r_{VDF}$ ratio is about 3, indicating that DiFAA is more reactive than VDF in the copolymerization but it is expected that its reactivity decreases when the proton on the vinyl group is replaced by a fluorine. In conclusion, DiFAA appears as a good comonomer of VDF.

The azeotropic composition was then calculated using the following equation:

$$f_{azeoptropic} = \frac{1 - r_{DiFAA}}{2 - (r_{DiFAA} + r_{VDF})} \quad (3)$$

The azeotropic composition was found to be 0.28 and 0.25 from the reactivity ratios obtained by extended Kelen−Tüdos and Kelen−Tüdos models, respectively, in good agreement with the experimental data (0.23).

Q and e are intrinsic parameters of a monomer linked to the resonance and the polarity, respectively. Q and e values for DiFAA can be determined from the reactivity ratios and the Q and e values of VDF, according to the following equations developed by Alfrey and Price:[87]

$$r_{VDF} = \frac{Q_{VDF}}{Q_{DiFAA}} \exp[-e_{VDF}(e_{VDF} - e_{DiFAA})] \quad (4)$$

$$r_{DiFAA} = \frac{Q_{DiFAA}}{Q_{VDF}} \exp[-e_{DiFAA}(e_{DiFAA} - e_{VDF})] \quad (5)$$

Several Q and e values of VDF (Table 4) have been reported in the literature: Naberezhnykh in 1974,[74] then Khodzhaev et al. in 1981,[85] followed by Greenley's database in 1999,[88] and more recently by Narita.[89] Both most recent values are in good agreement and we have averaged them for calculation of Q and e of DiFAA (Table 4).

For the first time Q_{DiFAA} and e_{DiFAA} have been assessed. The low Q value shows a poor stabilization by resonance, and a high e value is characteristic of the strong electron-withdrawing character of that monomer. From Table 4, it can be seen that the effect of the two fluorine atoms is quite strong on both Q and e values compared to acrylic acid. Also, in contrast to the electron-donating methyl group, electron-withdrawing fluorine atoms have the opposite effect on both Q and e values. It can be noted that the introduction of fluorine atoms in acrylate monomers has a strong influence on their Q and e values whether they are inserted on the double bond or in the pendant chain.

Thermal Properties. Thermal properties of these poly(VDF-*co*-DiFAA) copolymers were first investigated by differential scanning calorimetry (DSC) to determine the glass transition temperature (T_g) of the copolymers. Variation of the composition of the poly(VDF-*co*-DiFAA) copolymers led to almost a linear variation of glass transition temperatures determined by DSC (Table 1). Measured T_g increased from −40 to +103 °C as the mole percentage of DiFAA increased in the copolymers, indicating that these copolymers exhibit amorphous and elastomeric behavior, as expected. Interestingly, it is observed that the higher the VDF content, the lower the T_g, since, as expected, the presence of the acrylate side group increases the T_g values. It is well-known that polyacrylates containing fluorine atoms on the backbone of the polymer chain exhibit high T_g[1] as reported for poly(α-fluoroacrylate)s (T_g = 140 °C).[90]

Table 4. *Q* and *e* Parameters for VDF and DiFAA Calculated from Known e_{VDF} and Q_{VDF} Values and Some Values from the Literature (Where VDF and DiFAA Stand for Vinylidene Fluoride and α,*β*-Difluoroacrylic Acid, Respectively)[a]

	VDF										
					average	DiFAA	AA	MAA	AAm	AN	TFMA
Q	0.008	0.036	0.015	0.025	0.020	0.28	0.83	0.98	0.23	0.48	0.048
e	0.4	1.2	0.5	0.52	0.51	2.02	0.88	0.62	0.54	1.23	1.20
ref	74	85	88	89		this work	88	88	88	88	88

[a] Key: VDF, vinylidene fluoride; DiFAA, α,*β*-difluoroacrylic acid; AA, acrylic acid; MAA, methacrylic acid; AAm, acrylamide; AN, acrylonitrile; TFMA, trifluoromethyl acrylate.

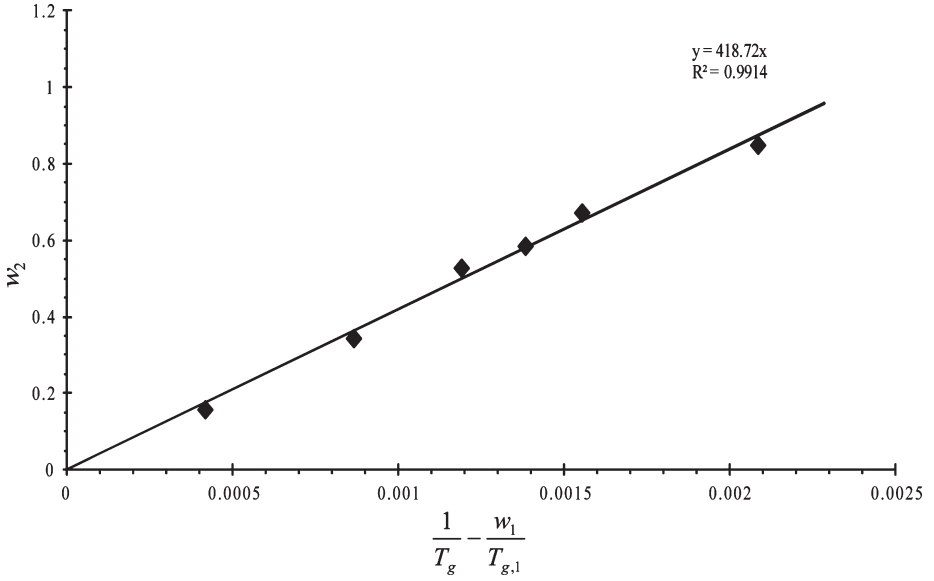


Figure 5. w_2 vs $1/T_g - w_1/T_{g,1}$ for the assessment of the glass transition temperature (T_g) of poly(DiFAA) according to Fox's relationship (where w_1, w_2, T_g, $T_{g,1}$ stand for weight percentages of vinylidene fluoride (VDF) and α,*β*-difluoroacrylic acid (DiFAA) and the glass transition temperatures of the poly(VDF-*co*-DiFAA) and poly(VDF), respectively).

Several relationships have been established to predict the T_g of polymer blends according to their composition and the T_g of the corresponding homopolymers.[91−95] We have applied Fox's[92] relationship

$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} \quad (6)$$

where T_g, $T_{g,1}$, and $T_{g,2}$ represent the glass transition temperatures (in kelvin) of the copolymer, of poly(VDF) (T_g = 233 K) and of poly(DiFAA) while w_1 and w_2 stand for the weight percentages of VDF and DiFAA, respectively.

Thus, eq 6 can be written as follows:

$$w_2 = T_{g,2}\left(\frac{1}{T_g} - \frac{w_1}{T_{g,1}}\right) \quad (7)$$

Hence, plotting w_2 vs $1/T_g - w_1/T_{g,1}$ leads to a straight line, whose slope represents the glass transition temperature of poly(DiFAA) (Figure 5). The experimental data fit well with the model, indicating a T_g of poly(DiFAA) to a value of 145 °C, in good agreement with the values reported for poly(methyl α,*β*-difluoroacrylate) (T_g = 140 °C)[37] and poly(hexafluoroisopropyl α,*β*-difluoroacrylate) (T_g = 98 °C).[40] It can be noted from these values that the bigger the acrylate substituent (H, CH_3, $CH(CF_3)_2$), the lower the glass transition temperature (145 °C, 140 °C, 98 °C, respectively). This was previously observed in the case of copolymers of 2,2,2-trifluoroethyl α-fluoroacrylate with *tert*-butyl α-trifluoromethacrylate (TBTFMA) for which an increase of the TBTFMA proportion induces a decrease of the glass transition temperature.[96]

The thermal stability of these poly(VDF-*co*-DiFAA) copolymers was also studied by thermogravimetric analysis (TGA). The decomposition temperature corresponding to 10% weight loss was evaluated from the TGA. Figure 6 shows the evolution of $T_{d,10\%}$ versus the copolymer composition. It can be noted that the decomposition temperature evolves proportionally with the composition. Indeed, the thermostability of the copolymer is decreasing with increasing DiFAA. Although the samples were carefully pumped under vacuum at 70 °C until no sublimation of DiFAA was observable, some traces of unreacted DiFAA may remain in the final copolymer (less than 20%). This residual DiFAA may affect the decomposition temperature at 10% weight loss because of its elimination ($T_{d,10\%}$ decreases). The trend lines appearing in Figure 6 clearly point out the correlation between the loss of thermostability and the proportion of residual monomer in the sample.

Conclusions

α,*β*-Difluoroacrylic acid (DiFAA) was synthesized in a simple manner via a three-step reaction from 1,2-dichloro-1,2-difluoroethylene in 30% overall yield. DiFAA and vinylidene fluoride (VDF) were copolymerized by conventional radical copolymerization over the whole range of compositions. The contents of both comonomers in the copolymer were assessed from ^{1}H and ^{19}F NMR spectroscopies. The kinetics of polymerization led to the assessment of the reactivity ratios by the classical methods ($r_{DiFAA} = 0.86 \pm 0.28$ and $r_{VDF} = 0.34 \pm 0.18$ at 74 °C), showing that DiFAA is globally more reactive than VDF. Thermal properties were also investigated, first by DSC, showing that the higher the DiFAA content in the copolymer, the higher the T_g value.

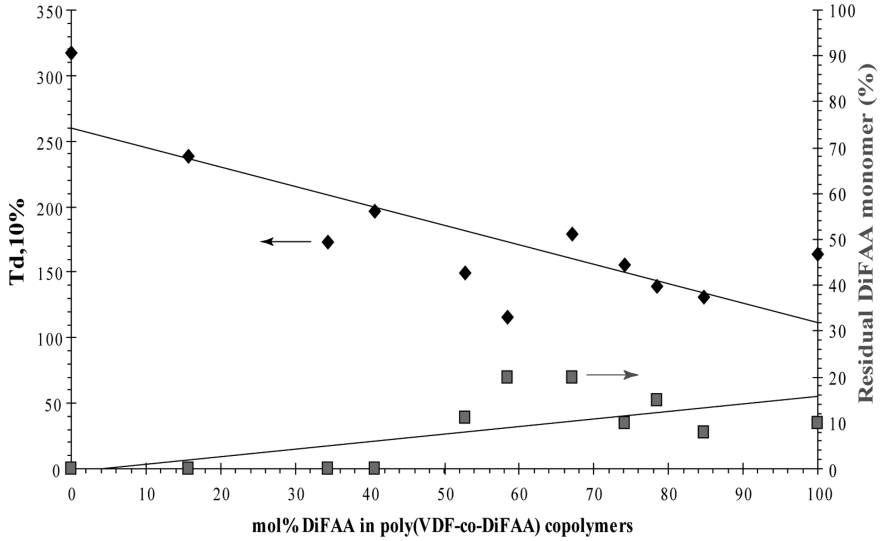


Figure 6. Evolution of the decomposition temperature at 10% weight loss as a function of mol % of DiFAA in the poly(VDF-*co*-DiFAA) copolymer compositions, and its relationship with the presence of residual unreacted DiFAA monomer in the sample (where VDF and DiFAA stand for vinylidene fluoride and α,*β*-difluoroacrylic acid, respectively).

In addition, the glass transition temperature (T_g) of poly(DiFAA) was predicted using Fox's equation leading to a value of 145 °C. Then, the decomposition temperature at 10 wt % loss decreased as the apparent result of the presence of unreacted DiFAA monomer in the sample. These poly(VDF)s bearing pendant carboxylic acid groups may be cross-linked or chemically modified, enabling cross-linked poly(VDF) by a nonconventional method (different from bisphenols or bisamines) and the synthesis of original poly(VDF)-*g*-poly(M) graft copolymers (where M stands for a monomer), which can be used for specific applications such as emulsifiers of polymer blends, fuel cell membranes, separators for lithium batteries or novel hydrophilic poly(VDF) for osmosis or water purification membranes. In addition, controlled radical copolymerization of DiFAA is under investigation, as well as the radical copolymerization of DiFAA with other fluoroolefins (such as hexafluoropropylene (HFP) or chlorotrifluoroethylene (CTFE)).

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Supporting Information Available: Picture of the device used for feeding the Carius tubes with VDF for the preparation of the copolymers, figures showing ^{1}H and ^{19}F NMR spectra of α,*β*-difluoroacrylic acid, and figures and calculations for the assessment of the reactivity ratios according to three kinetic models. This material is available free of charge via the Internet at http://pubs.acs.org.

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