Synthesis of Functional Polymers—Vinylidene Fluoride Based Fluorinated Copolymers and Terpolymers Bearing Bromoaromatic Side-Group

R. SOUZY, B. AMEDURI, B. BOUTEVIN

Laboratory of Macromolecular Chemistry, UMR (CNRS) 5076, Ecole Nationale Supérieure de Chimie de Montpellier,
8 rue Ecole Normale, 34296 Montpellier Cedex 05, France

Received 7 May 2004; accepted 26 May 2004
DOI: 10.1002/pola.20324

ABSTRACT: The radical co- and terpolymerization of 4-[(α,β,β-trifluorovinyl)oxy]bromo benzene (TFVOBB) with 1,1-difluoroethylene (or vinylidene fluoride, VDF, or VF_2), hexafluoropropene (HFP), perfluoromethyl vinyl ether (PMVE), and chlorotrifluroroethylene (CTFE) is presented. Although TFVOBB could be thermocyclodimerized, it could not homopolymerize under radical initiation. TFVOBB could be copolymerized in solution under a radical initiator with VDF or CTFE comonomers, while its copolymerization with HFP or PMVE were unsuccessful. The terpolymerization of TFVOBB with VDF and HFP, or VDF and PMVE, or VDF and CTFE also led to original fluorinated terpolymers bearing bromoaromatic side-groups. The conditions of co- and terpolymerization were optimized in terms of the nature of the radical initiators, and of the nature of solvents (fluorinated or nonhalogenated). Various monomer concentrations in the co- and terpolymers were assessed by ^{19}F and ^{1}H-NMR spectroscopy. The thermal and physico chemical properties were also studied. © 2004 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 42: 5077–5097, 2004

Keywords: 4-[(α,β,β-trifluorovinyl)oxy] bromo benzene (TFVOBB); vinylidene fluoride (VDF); hexafluoropropene (HFP); chlorotrifluorethylene (CTFE); perfluoromethyl vinyl ether (PMVE); radical initiation; ^{19}F and ^{1}H-NMR spectroscopy

INTRODUCTION

Fluoropolymers are well known because of their unique combination of outstanding properties,[1–4] such as chemical inertness (to acids, bases, solvents, and petroleum), low dielectric constants and dissipation factors, low water absorptivities, excellent weatherabilities, and very interesting surface properties. Hence, these high value added products can find relevant applications in many fields of high technology: aeronautics,[5] microelectronics, engineering, chemical and automobile industries, optics,[6–10] textile finishing,[10] and military use.[11] The specific properties (adhesion, solubility, curability, surface properties, good hydrophilicity, and heat or chemical resistance) of a fluoropolymer are brought by the nature of the functional group, which is subsequently introduced in a lateral position of the copolymer backbone. The synthesis of fluoropolymers can be realized by copolymerization of fluoroalkenes with fluorinated or nonhalogenated monomers. However, fluorinated homopolymers (e.g., polyvinylidene fluoride, polytetrafluoroethylene, or polychlorotrifluoroethylene) exhibit a high crystallinity rate that induces high costs in the processing at the molten state, poor solubility in organic common solvents, and difficult crosslinking. In-

---

Correspondence to: B. Ameduri (ameduri@cit.enscm.fr).

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 42, 5077–5097 (2004)

deed, to improve the properties of those fluoropolymers, crosslinkings from polyamines,[12,13] polyphenols,[12–14] electron beam,[13,15] or peroxides[12,13,16] can be required; and several ways are possible.[12,13,17,18]

Among these fluoropolymers, those incorporating vinylidene fluoride (VDF) monomeric units are of particular interest, because they can be either thermoplastics,[19,20] elastomers,[12,13,21,22] or thermoplastic elastomers.[23–29] Such fluoropolymers can be synthesized by radical copolymerization of VDF with other fluoroalkenes leading to statistic copolymers,[13,22,30,31] except for copolymers prepared from VDF and hexafluoroisobutylene[32,33] (commercialized by the Allied Company under the trade mark of CMX®), methyl trifluoroacrylare/VDF,[34] and α-trifluoromethyl acrylic acid/VDF,[35] which are unexpected alternating copolymers. As a matter of fact, VDF was copolymerized with various fluorinated monomers and the resulting copolymers bear functions such as: hydroxy,[36–39] acetoxy,[38] carboxy,[40] thioacetoxy,[40–42] sulfonyl fluoride,[43–47] nitrile,[48,49] bromine,[18,50–53] or a perfluoro group.[47,48,54–61]

[(α,β,β-Trifluorovinyl)oxy]benzene and polymers incorporating such a monomer are very interesting materials[62,63] because of the combination of processability and performance provided by trifluorovinyl ethers, and they have received attention by various research groups[64–68] and industries,[69–73] and are currently used as materials for the preparation of ion exchange resins,[72,74] ionomer membrane and fuel cell,[75–77] microphonic,[78] optics,[79–82] liquid crystalline,[83–85] interlayer dielectrics,[86,87] circuit board laminates,[88] and coating applications.[89,90]

[(α,β,β-Trifluorovinyl)oxy]benzene ethers were initially synthesized by Beckerbauer[91] in 1968, and several routes concerning the preparation of [(α,β,β-trifluorovinyl)oxy]benzene functionalized by different chemical groups are reported in the scientific literature.[62,63,92–101] (See Table 1.)

One of the most interesting properties of perfluoroalkyl [(α,β,β-trifluorovinyl)oxy]benzene is to undergo thermal cyclopolymerization $[2\pi + 2\pi]$ (Fig. 1). The formed perfluoroalkylpolymers is a thermoplastic and thermoset perfluorocyclobutane (PFCB).[67,73,91,93,102–105]

Surprisingly, before 2004, no co- and terpolymerizations, under radical conditions, of these [(α,β,β-trifluorovinyl)oxy]benzene with fluoro or non fluoro-olefins was achieved. Hence, the present investigation wishes to reach two main goals: the first one is to find fluoro-olefins able to copolymerize with 4-[(α,β,β-trifluorovinyl)oxy] bromo benzene, and the second target is to prepare and to characterize (by NMR spectroscopy, chromatography, calorimetry, and thermal gravimetry) original terpolymers incorporating TFVOBB, VDF/HFP, VDF/PMVE, and VDF/CTFE, or mixtures of all of them.

EXPERIMENTAL PROCEDURES

Materials

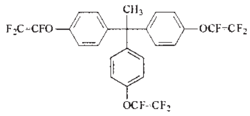
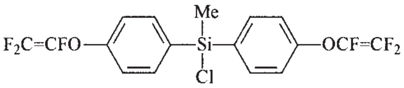
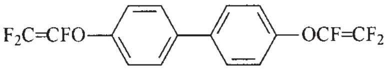
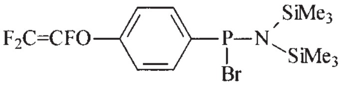
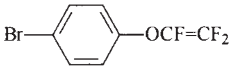
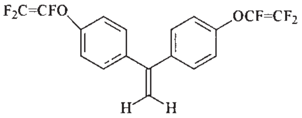
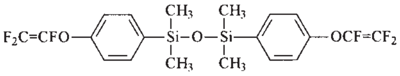
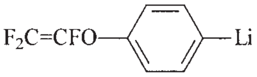
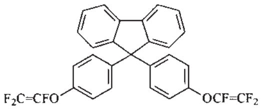
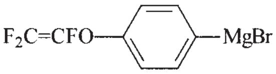
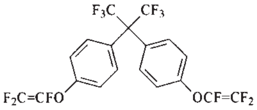
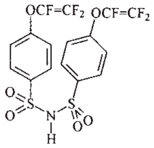
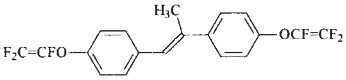
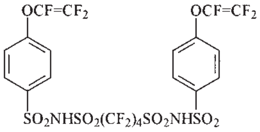
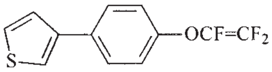
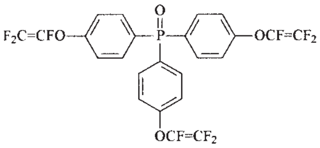
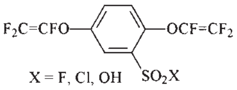
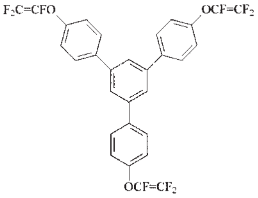
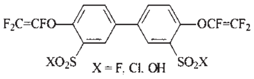
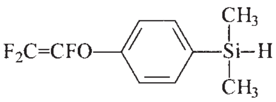
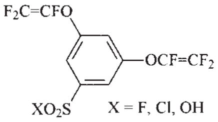
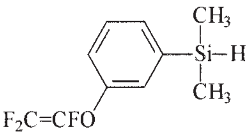
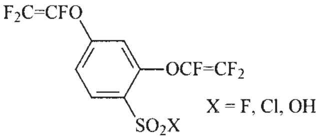
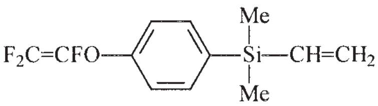
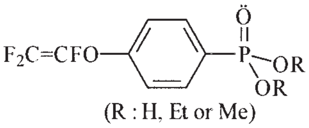
VDF, HFP, and 1,1,1,3,3-pentafluorobutane were kindly offered by Solvay Solexis S.A., Tavaux, France and Brussels, Belgium; perfluoromethylvinyl ether (PMVE, Fluorochem was a gift from CEA, Grenoble, France), 1,2-dibromotetrafluoroethane was kindly offered by Professor Oldrich Paleta (Institute of Chemical Technology, Czech Republic); 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane, tech, 90% (Luperox 101®) (Aldrich Chimie, 38,299 Saint Quentin-Fallavier, France); *tert*-Butyl 2,2-dimethylperoxypropanoate and *tert*-butylperoxypivalate were a gift from la Chalonnaise des Peroxydes, Chalons sur Marne, France. They were used as supplied. Acetonitrile and dimethylsulfoxyde of analytical grade (Aldrich Chimie, 38,299 Saint Quentin, Fallavier, France) were distilled over calcium hydride prior to use.

Analysis

The purity of 4-[(α,β,β-trifluorovinyl)oxy] bromo benzene (TFVOBB) and the compositions of the co- and terpolymers (the molar contents of VDF, HFP, CTFE, PMVE, and TFVOBB) 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 references for ^{1}H (or ^{19}F) nuclei. Coupling constants and chemical shifts are given in Hz and ppm, respectively. The experimental conditions for ^{1}H (or ^{19}F) NMR spectra were the following: flip angle 90 ° (or 30 °), acquisition time 4.5 s (or 0.7 s), pulse delay 2 s (or 5 s), number of scans 16 (or 64), and a pulse width of 5 μs for ^{19}F NMR.

Differential scanning calorimetry (DSC) measurements were conducted using a Perkin–Elmer Pyris 1 instrument connected to a micro-computer. The apparatus was calibrated with indium and n-decane. After its insertion into the DSC

Table 1. Synthesis of [(α,β,β-Trifluorovinyl)Oxy]Benzene

Monomer	Reference	Monomer	Reference
	93,94		95
	93,94		95
	67		95
	67		92,95–97
	90		98
	90		97
	90		97
	98		72
	99		72
	100		72
	101		72
	101		72
	95		62,92

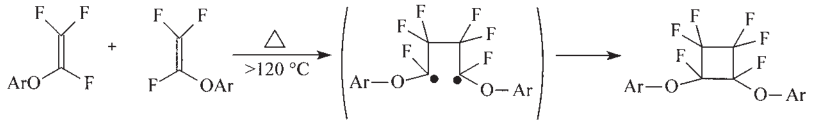


Figure 1. Formation of aromatic perfluorocyclobutane (PFCB).[67,73,91,93,102–105]

apparatus, the sample was initially cooled to –105 °C for 15 min. Then, the first scan was made at a heating rate of 40 °C min^{-1} up to 80 °C, where it remained for 2 min. It was then cooled to –105 °C at a rate of 320 °C min^{-1} and left for 10 min at that temperature before a second scan was started at a heating rate of 20 °C min^{-1}. Finally, another cycle was performed, and a third scan at a heating rate of 20 °C min^{-1} was initiated, giving the values of Tg reported herein, taken at the half-height of the heat capacity jump of the glass transition.

Thermogravimetric analyses were performed with a Texas Instrument TGA 51–133 apparatus in air at a heating rate of 10 °C min^{-1} from room temperature up to a maximum of 600 °C.

Gel Permeation Exclusion Chromatography (GPC) or Size Exclusion Chromatography (SEC) was carried out in tetrahydrofuran at 30 °C, at a flow rate of 0.8 mL/min, by means of a Spectra Physics Winner Station, a Waters Associate R 401 differential refractometer, and a set of four columns connected in series: Styragel (Waters) HR4 5μ, HR3 analyses 5μ, PL and Gel (Polymer Laboratories) 5μ 100 Å. Monodispersed poly(styrene) standards were used for calibration. Aliquots were sampled from the reaction medium, diluted with tetrahydrofuran up to a known concentration ($C_{p,t}$) ~ 4% wt. %, filtered through a 20 μm PTFE Chromafil Membrane, and finally analyzed by GPC under the conditions described above.

Synthesis of TFVOBB

TFVOBB was prepared by published method.[67] Into a two-necked round bottom flask equipped with a Dean-Stark azeotropic distillation assembly, a reflux condenser, and a magnetic stirrer were introduced, under nitrogen atmosphere, 100.1 g (0.582 mol) of 4-bromophenol, 37.4 g (0.583 mol) of KOH, 320 mL of DMSO, and 80 mL of xylene. The mixture was stirred and heated to 100 °C (~ 200 mmHg) for 48 h during which time water was removed. The solution was cooled to 30 °C, and 166.5 g (0.641 mol) of 1,2-dibromotetrafluoroethane were added in 4 h such that the temperature did not exceed 30 °C. The mixture was stirred for 16 h at 22 °, and 10 h at 35 °C. The reaction mixture was diluted with H_2O, extracted with methylene chloride, and dried with $MgSO_4$. The 4-(2-bromotetrafluoroethoxy)bromobenzene (**1**) was purified (yield 70%) from the crude oil by distillation (bp = 110–115 °C/25 mm Hg). Afterwards, 100 g (0.284 mol) of the bromo ether (**1**) was slowly added under nitrogen conditions to a stirring mixture of 18.6 g (0.284 mol) of zinc turnings in 250 mL of acetonitrile at 80 °C. The mixture was refluxed for 24 h, then evaporated. The crude product was extracted from the salts successively with hexane, concentrated, and distilled (bp 65–75 °C, 20 mmHg), giving 57 g (78%) of 4-[(trifluorovinyl)oxy]bromobenzene. ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 6.9 (2*H*, d, J = 8.8 Hz), 7.4 (2*H*, d, J = 8.8 Hz); ^{19}F NMR (250 MHz, $CDCl_3$) δ: −119.8 (dd, *cis*-CF = CF_2, F_a, J_{FaFb} = 96 Hz, J_{FaFc} = 58 Hz, 1F), −126.7 (dd, *trans*-CF = CF_2, F_b, J_{FbFa} = 96 Hz, J_{FbFc} = 110 Hz, 1F), −134.9 (dd, C*F* = CF_2, F_c, J_{FcFa} = 58 Hz, J_{FcFb} = 110 Hz, 1F).

Homopolymerization

The batch homopolymerizations of TFVOBB were performed in thick borosilicate Carius tubes (length 130 mm, internal diameter 10 mm, thickness 2.5 mm, total volume 8 cm^3). After introducing initiator (tertiobutyl peroxide, 2.0 mol % relative for the monomer mixture), TFVOBB, and acetonitrile under inert atmosphere, the tube was connected to a vacuum line and purged several times by evacuating and flushing with helium. 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 cooled in liquid nitrogen, opened, and the content was analyzed. Part of the mixture was analyzed by ^{19}F and ^{1}H-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 mixture formed was isolated by filtration and dried under vacuum at 80 °C for 4 h at least.

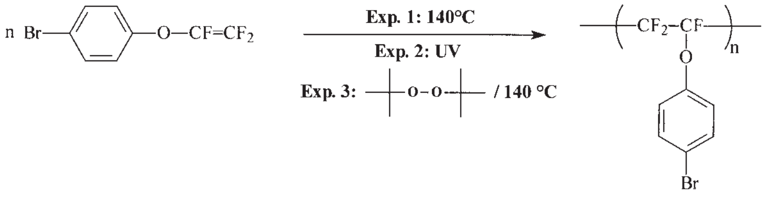


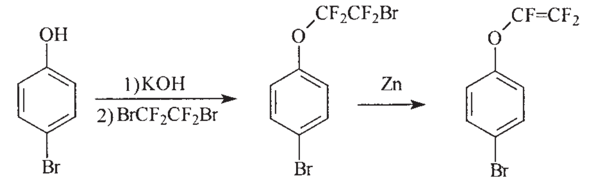
Figure 2. Radical homopolymerization of TFVOBB by different methods of initiation.

Copolymerization and Terpolymerization

The batch co- or terpolymerizations of VDF, HFP, CTFE, or PMVE with TFVOBB were performed in a 160 mL HASTELLOY (HC 276) autoclave, equipped with a manometer, a rupture disk, an inlet valve left closed for 20 min and purged with 20 bars of nitrogen pressure to prevent any leakage, and degassed afterwards. Then, a 20 mm Hg vacuum was operated for 15 min, and the initiator (2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane, tech, 90%), TFVOBB, and 1,1,1,3,3-pentafluorobutane were introduced successively via a funnel tightly connected to the introduction valve. Next, HFP, CTFE, or PMVE, and VDF were, respectively, introduced by double weighing. The autoclave was then heated up to 134 °C for 10 h. After reaction, the vessel was cooled to room temperature and then put in an ice bath. 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 at room temperature under a 20 mm Hg vacuum for 48 h.

RESULTS AND DISCUSSION

TFVOBB was prepared by published method.[67] Its synthesis is based on a nucleophilic substitution of 4-bromophenate to 1,2-dibromotetrafluoroethane, followed by a dehalogenation reaction:



TFVOBB

Yield = 78 %

Radical Homopolymerization of TFVOBB

The aim of the first step of our work was to carry out the radical homopolymerization of TFVOBB. From this monomer we tried to generate radicals, which could be able to initiate TFVOBB homopolymerization (Fig. 2), by using initiating methods such as heating (Experiment 1—Table 2), photochemical (Experiment 2—Table 2), and peroxide initiator (Experiment 3—Table 2) processes. All the experiments were carried out in a sealed ampoule containing reactants and acetonitrile as the solvent.

In the thermal and peroxide radical homopolymerization reactions (Experiments 1 and 3), a yellow color of the solution was observed. The ^{19}F NMR showed the presence of characteristic peaks (Fig. 3) of the thermocyclodimerization of TFVOBB (Fig. 1),[67,73,93,104,105] but the absence of signals that could be characteristic of the homopolymer -(C[b]F$_2$-C[b]F(O-Ph-Br))- (i.e., a signal centered at –115 ppm assigned to a –C[b]F$_2$-group located between two methylene groups).

Table 2. Homopolymerization of TFVOBB (Experimental Conditions and Results)

Experiment #	Initiation Process	F_2C = CF-O-Ph-Br in Feed (mol)	Initial mol % of Tertiobutyl Peroxide	Temperature (°C)	Time (hr)	TFVOBB Conversion Rate (%)
1	Thermal	0.0093	0	140	16	100
2	Photochemical Initiation (UV)	0.0090	0	Room temperature	16	0
3	Sealed Bulk Tube	0.0087	2	140	16	0

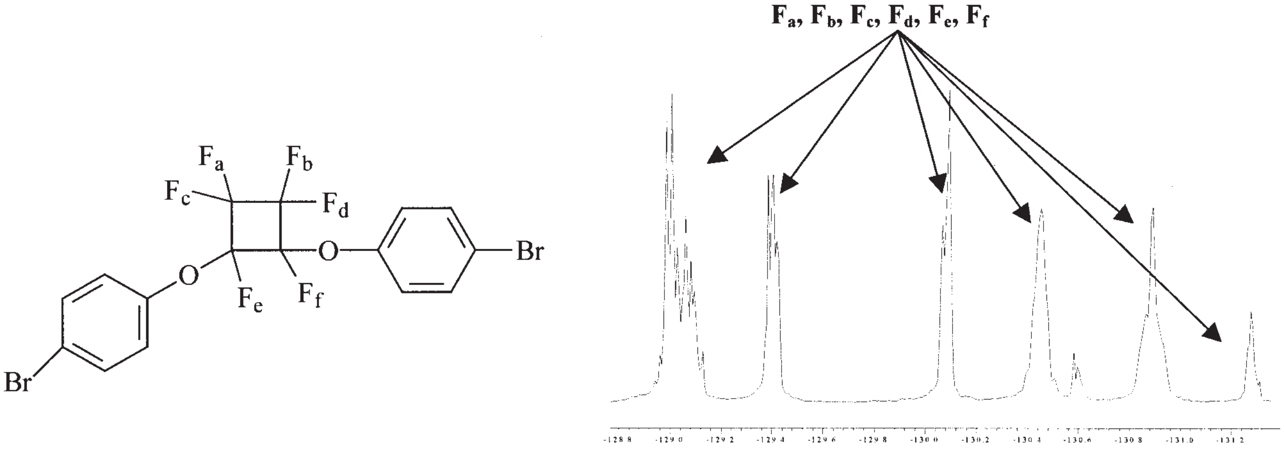


Figure 3. ^{19}F NMR spectrum of the thermocyclodimerization [2π+2π] of [(α,β,β-trifluorovinyl)oxy]bromobenzene.

This aryl α,β,β-trifluorovinyl ether [2π + 2π] thermocyclodimerization is favored thermodynamically and is due to an increase of the double bond strain,[106] a lower C = C π-bond energy,[107] and the strength of the resulting fluorinated C-C single bond. For trifluorovinyl ether (TFVE) monomers, exothermal polymerization reached a measurable rate (DSC at 10 °C/min) near 140 °C, and polymerizations were typically carried out at temperatures between 150 and 210 °C.[108]

In the photoinduced radical homopolymerization (Experiment 2), no cyclodimerization and homopolymerization have been observed.

Radical Copolymerization of TFVOBB with VDF, HFP, CTFE, or PMVE

The radical copolymerizations of TFVOBB with VDF (X,W:H and Y,Z:F, Fig. 4), CTFE (X,W,Y:F and Z:Cl, Fig. 4), PMVE (X,W,Y:F and Z:OCF_3, Fig. 4), or HFP (X,W,Y:F and Z:CF_3, Fig. 4) were carried out in acetonitrile or 1,1,1,3,3-pentafluorobutane solutions (these solvents do not induce any chain-transfer reactions), and initiated by 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane or ditertiobutyl peroxide, yielding random copolymers as shown in Figure 4.

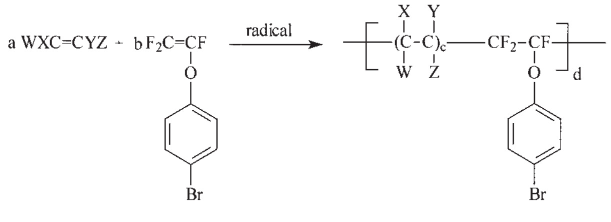


Figure 4. Radical copolymerization of TFVOBB with VDF, CTFE, HFP, or PMVE.

Influence of the Solvent and of the Initiator on the Yields of VDF/TFVOBB or CTFE/TFVOBB Copolymerizations

To find out the best reaction conditions (initiator, solvent, and temperature) for which the fluoroolefin conversion rates and the mass yields were the highest, two radical copolymerizations were carried out using a high pressure autoclave system. The initial molar percentages of CTFE in feed were 94 and 96 (Experiments 4 and 5, respectively, in Table 3). Acetonitrile (Experiment 4) and 1,1,1,3,3-pentafluorobutane (Experiment 5) were chosen as the solvents. We chose two radical initiators, ditertiobutyl peroxide (Experiment 4) and 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (Experiment 5), the half times of which, were one hour at 140 and 135 °C, respectively.

However, the results listed in Table 3 showed that the copolymerization initiated by 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane led to better mass yields. In the same experimental conditions, starting from CTFE feed molar percentages of 94 and 96 mol %, the copolymerization led to mass yields of 5 and 25% (Experiments 4 and 5), respectively. In addition, the CTFE conversion rate (the mass conversion rate was defined as the ratio of the weight of the gases that reacted in the polymerization to the total weight of the gases introduced in the autoclave) (see Table 3) is higher for Experiment 5 (initiated by 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane and performed in 1,1,1,3,3-pentafluorobutane) than for Experiment 4.

These results confirmed that 1,1,1,3,3-pentafluorobutane has a lower transfer activity on the growing macroradical than acetonitrile.[109]

Similar results were obtained with VDF/TFVOBB systems initiated by 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane and ditertiobutyl peroxide, and confirmed the results summarized in Table 3.

Because of the low yields produced from ditertiobutyl peroxide/acetonitrile system, we have decided to perform all the following experiments in solution in pentafluorobutane initiated by 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane.

Determination of the Copolymer Compositions by using ^{19}F NMR Spectra

VDF/TFVOBB copolymers. The second step of this study concerns the estimation of the copolymer compositions by using NMR method. All ^{1}H-NMR spectra exhibit: (1) the signals assigned to methylene groups of VDF units (in the VDF/TFVOBB copolymerizations) 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) the signals of aromatic groups at about 7.3 ppm (Fig. 5). However, ^{19}F NMR spectroscopy was chosen to identify the corresponding TFVOBB and VDF, HFP, CTFE, or PMVE units in the copolymers.

Figure 5 also shows the ^{19}F NMR spectrum of dry poly(VDF-*co*-TFVOBB) produced with an initial $[\text{VDF}]_0/[\text{TFVOBB}]_0$ molar ratio of 96/4. Firstly, this spectrum shows the characteristic peaks (see Table 4) centered at about −91 ppm (noted I_{-91}), which is assigned to the difluoromethylene groups in the head-to-tail arrangement of VDF units (normal VDF addition). In addition, other signals are also good evidence of VDF units in the copolymers (Table 4). They are centered at −95.1 (noted $I_{-95.1}$), −113.7 (noted $I_{-113.7}$), and −115.9 ppm (noted $I_{-115.9}$), assigned to the CF_2 groups of $(CH_2\text{-}CF_2)\text{-}(CF_2\text{-}CH_2)\text{-}(CH_2\text{-}\mathbf{CF_2})\text{-}(CH_2\text{-}CF_2)$ $(CH_2\text{-}\mathbf{CF_2})\text{-}(CF_2\text{-}CH_2)\text{-}(CH_2\text{-}CF_2)$, and $(CH_2\text{-}CF_2)\text{-}(C[b]\mathbf{F_2}\text{-}CH_2)\text{-}(CH_2\text{-}CF_2)$ sequences, respectively, attributed to CF_2 groups corresponding to reverse VDF adducts (head-to-head addition).[34,35,38–42,110,111] Furthermore, the signal located at –107.5 ppm is characteristic of -(C[b]$\mathbf{F_2}$-

Table 3. Influence of Solvent and of the Initiator in the Radical Copolymerization of CTFE with TFVOBB

Exp. #	CTFE in Feed (mol %)	(1) in Feed (mol %)	Initiator	Initiator (mol %)	Solvent	Temperature (°C)	Time of Reaction (hours)	CTFE Conversion Rate (%)	Massic Yields (%)
4	94	6	di-tertiobutyl peroxide	1.2	CH_3CN	140	8	12	5
5	96	4	2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane	1.2	$CF_3CH_2CF_2CH_3$	135	8	41	25

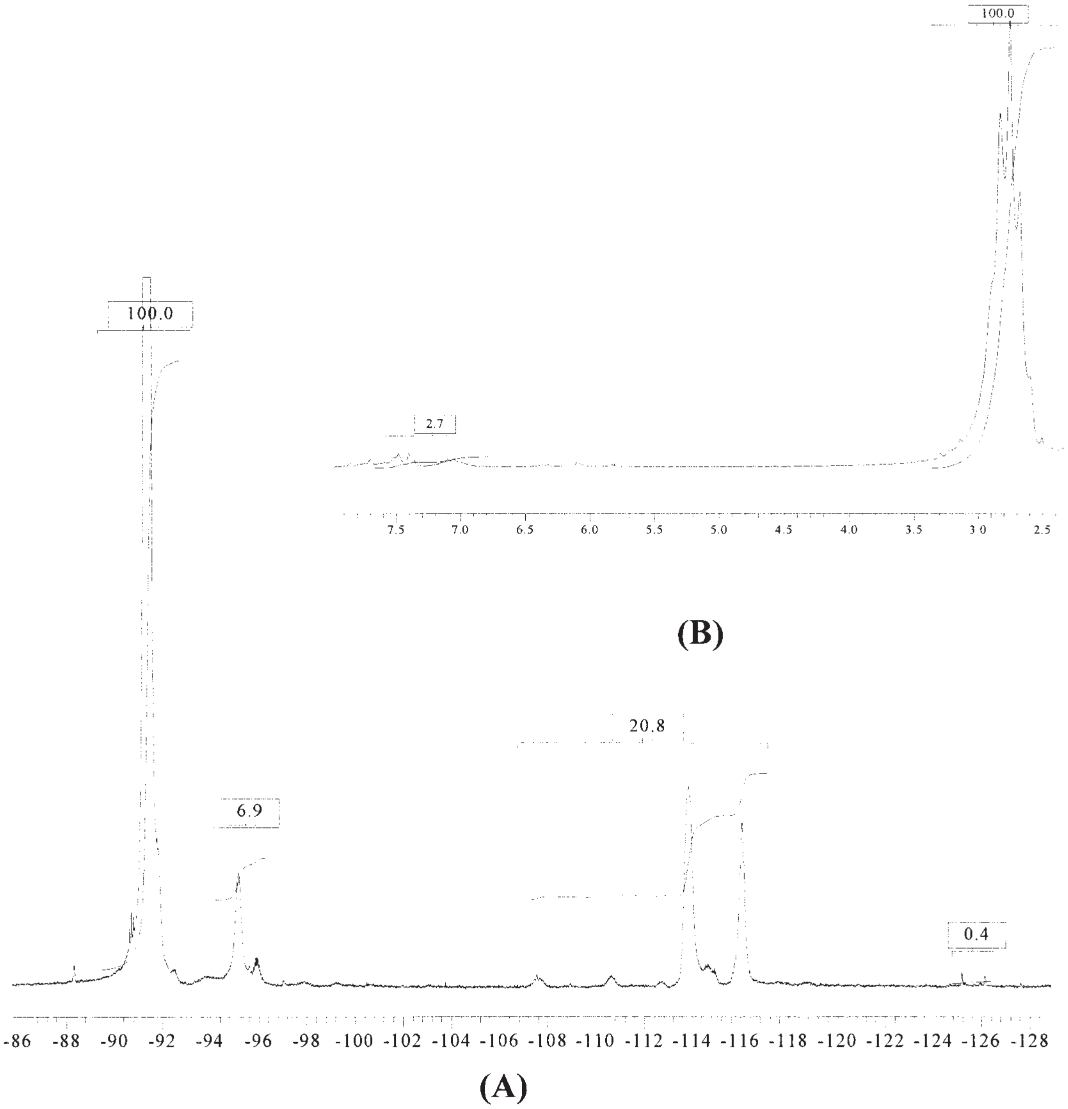


Figure 5 ^{19}F (A) and ^{1}H (B) NMR spectra of VDF/(TFVOBB) copolymer, recorded in deuterated acetone. Copolymerization conditions: [2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane /($[\mathrm{VDF}]_0$ + $[\mathrm{TFVOBB}]_0$) = 1.2%, 134 °C, 6 h, and VDF/TFVOBB initial molar ratio in the feed = 96/4.

CH_2)-CF_2-CH_3, and the peak at –110.6 ppm region is assigned to the difluoromethylene groups of the VDF units adjacent to TFVOBB units, and are noted $I_{-107.5}$ and $I_{-110.6}$, respectively. The values of these chemical shifts fit with those of the signal assigned to the difluoromethylene group of VDF adjacent to a perfluoromethyl vinyl ether base-unit in poly(VDF-*co*-PMVE) copolymers.[61] The signal $I_{-113.9}$ centered at –113.9 ppm is attributed to the difluoromethylene of TFVOBB unit. Finally, and as explained above, the peak located in the –125.7 to –130.7 ppm region, noted $I_{-125.7}$, is assigned to the tertiary fluorine atom in the CF group of (**1**). The amount of VDF units in the copolymer is assessed by using the following equation (Eq. 1):

$$\text{Mol \% VDF in the copolymer} = \frac{I_A}{I_A+I_B} \times 100 \quad (1a)$$

$$\text{Mol \% TFVOBB in the copolymer} = \frac{I_B}{I_A+I_B} \times 100 \quad (1b)$$

with:

Table 4. ^{19}F NMR Assignments of VDF/TFVOBB Copolymers Recorded in Deuterated Acetone

Chemical Shift (ppm)	Structure	Integrals in (Eq. 1)
−91	-CF$_2$-CH$_2$-CF$_2$-CH$_2$-CF$_2$-	I_{-91}
−95.1	(CH$_2$-CF$_2$)-(CF$_2$-CH$_2$)-(CH$_2$-CF$_2$)-(CH$_2$-CF$_2$)	$I_{-95.1}$
−107.5	-(CF$_2$-CH$_2$)-CF$_2$-CH$_3$	$I_{-107.5}$
−110.6	(CH$_2$-CF$_2$)-(CF$_2$-CF(O-Ph-Br))	$I_{-110.6}$
−113.7	(CH$_2$-CF$_2$)-(CF$_2$-CH$_2$)-(CH$_2$-CF$_2$)	$I_{-113.7}$
−113.9	(CH$_2$-CF$_2$)-(CF$_2$-CF(O-Ph-Br))	$I_{-113.9}$
−115.9	(CH$_2$-CF$_2$)-(CF$_2$-CH$_2$)-(CH$_2$-CF$_2$)	$I_{-115.9}$
−125.7	-CH$_2$CF$_2$-CF$_2$-CF(O-Ph-Br)-CH$_2$CF$_2$-	$I_{-125.7}$

$$I_A = I_{-91} + I_{-95.1} + I_{-107.5} + I_{-110.6} + 2 \times I_{-115.9}$$

$$I_B = I_{-113.7} - I_{-115.9}$$

CTFE/TFVOBB copolymers. Both ^{1}H and ^{19}F NMR spectroscopies enabled us to characterize the microstructure of these CTFE/TFVOBB copolymers. As explained in the former copolymerization of TFVOBB, the ^{1}H-NMR spectrum shows a multiplet centered at 7.3 ppm and attributed to the aromatic proton. Its ^{19}F NMR spectrum (recorded in the deuterated DMSO) exhibits some signals[112] between −107 (noted I_{-107}) and −110.2 ppm (noted $I_{-110.2}$), corresponding to difluoromethylene of CTFE adjacent to a TFVOBB and CTFE unit, respectively. A signal centered at −113.4 ppm(noted $I_{-113.4}$) is assigned to difluoromethylene of TFVOBB. The presence of signals centered at −125.7 (noted $I_{-125.7}$, assigned to the tertiary fluorine TFVOBB), and −128.5 (noted $I_{-128.5}$), and −130.9 ppm (noted $I_{-130.9}$) are corresponding to the tertiary fluorine of CTFE units (Table 5). Hence, the molar percentages of CTFE in the copolymers can be assessed from the following equation (Eq. 2):

Mol % of CTFE in the Copolymer

$$= \frac{I_C}{I_C + I_D} \times 100 \quad (2a)$$

Mol % of TFVOBB in the Copolymer

$$= \frac{I_D}{I_C + I_D} \times 100 \quad (2b)$$

with:

$$I_C = \frac{I_{-107} + I_{-110.2}}{2} + I_{-128.5} + I_{-130.9}$$

$$I_D = \frac{I_{-113.4}}{2}$$

Finally, radical copolymerizations using Hexafluoropropene (HFP) or Perfluoromethyl vinyl ether (PMVE) as comonomers have not been achieved.

Influence of the Molar Percentages of TFVOBB on the Physicochemical Properties of the Copolymers

The next goal of the study was the copolymerization of TFVOBB with fluoro-olefins. A series of

Table 5. ^{19}F NMR Assignments of CTFE/TFVOBB Copolymers Recorded in Deuterated DMSO

Chemical Shift (ppm)	Structure	Integrals in (Eq. 2)
−107.6	(CF$_2$-CF(O-Ph-Br))-(CF$_2$-CFCl)	I_{-107}
−110.2	(CF$_2$-CFCl)-(CF$_2$-CFCl)	$I_{-110.2}$
−113.4	(CF$_2$-CF(O-Ph-Br))-(CF$_2$-CFCl)	$I_{-113.4}$
−125.7	-CF$_2$CFCl-CF$_2$-CF(O-Ph-Br)-CF$_2$CFCl-	$I_{-125.7}$
−128.5	(CF$_2$-CFCl)-(CF$_2$-CFCl)	$I_{-128.5}$
−130.9	(CF$_2$-CFCl)-(CF$_2$-CF(O-Ph-Br))	$I_{-130.9}$

TFVOBB/fluorocomonomers (VDF or CTFE) copolymers were synthesized and characterized for average molecular weights, degradation temperature (Td), and glass transition temperature (Tg), the results of which are summarized in Table 6. All of the copolymers were soluble in common organic solvents such as acetone, DMSO, and DMF.

The initial molar percentages of VDF in feed were 79, 90, and 96 (Experiments 6, 7, and 8, respectively), and the initial molar percentages of CTFE in feed were 83, 90, and 97 (Experiments 9, 10, and 11, respectively). These reactions were carried out using a high pressure autoclave system and performed at 134 °C using 2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane as the radical initiator and 1,1,1,3,3-pentafluorobutane as solvent (see Influence of the solvent and of the initiator on the yields of VDF/TFVOBB or CTFE/TFVOBB copolymerizations, above). By this process, after precipitation in pentane, white powders were produced and their compositions were also determined by ^{19}F and ^{1}H-NMR (see Table 6). The ^{1}H and ^{19}F NMR spectra exhibit characteristic signals described in Determination of the copolymer compositions by using ^{19}F NMR spectra. above. The ^{19}F NMR spectroscopy was chosen to identify the corresponding TFVOBB and VDF or CTFE units in the copolymers (see Table 6).

However, in the VDF/TFVOBB system, the results showed that the presence of TFVOBB in feed made the massic yields decrease, while the final mol % of TFVOBB in the copolymer increases. In the same experimental conditions, starting from TFVOBB feed molar percentages of 4 and 21 mol % led to copolymers containing 2 and 5 mol %, (Experiments 8 and 6), respectively. Furthermore, SEC analyses showed that the value of the molecular weights of the copolymer synthesized in Experiment 8 (2 mol % of TFVOBB in the copolymer) is higher than that of Experiment 6 (5 mol % of TFVOBB in the copolymer); The higher the mol % of TFVOBB in the copolymer, the lower the average molecular weights. In addition, the thermal analyses indicate that copolymers prepared in Experiment 8 are more thermostable than those prepared in Experiment 6. The glass transition temperature values, measured by DSC, were in the average –33 °C and +33 °C for poly(VDF-*co*-TFVOBB) and for poly(CTFE-*co*-TFVOBB), respectively. In both copolymerization systems, Tg increased with the growing value of TFVOBB in the copolymer, which brings hardness in the copolymers.

Hence, in the CTFE/TFVOBB copolymerization, the results listed in Table 6 showed also that the molecular weights and the thermal properties go down when the final mol % of TFVOBB increases. Interestingly, if the initial mol % of CTFE is lower than 85%, the copolymerization does not occur, and homopolymer of CTFE was obtained with a low yield by mass.

These results showed that the increasing molar percentages of TFVOBB in the copolymers made the thermal stability decrease, the glass transition increase, and the molecular weights decrease. It confirmed the hypothesis of the low reactivity of ~ TFVOBB $^{\bullet}$ macroradical.

Radical Terpolymerization of TFVOBB with VDF/HFP, VDF/CTFE, or VDF/PMVE Blends

To enhance the reactivity of VDF in a VDF/TFVOBB copolymerization, and the final mol % of TFVOBB in the polymer, we decided to introduce a termonomer such as hexafluoropropene (HFP), chlorotrifluoroethylene (CTFE), or perfluoromethyl vinyl ether (PMVE). It could be a very interesting way to yield fluoroterpolymers bromo benzene side groups (Fig. 6). Furthermore, physicochemical properties of the fluoropolymers can be improved with the increase of mol % of fluorine in the polymer backbone.[2–4,113]

The different series of terpolymerizations were performed using initial C_0 ($[\text{initiator}]_0$ / ($[\text{VDF}]_0$ + $[\text{HFP}]_0$ + $[\text{TFVOBB}]_0$) molar ratio of 1%. These radical terpolymerizations were carried out using a high pressure autoclave system and performed at 134 °C for 10 h using 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane as the radical initiator and 1,1,1,3,3-pentafluorobutane as solvent. After reaction, the terpolymers were precipitated from cold pentane, and the products were characterized by ^{1}H and ^{19}F NMR spectroscopies, which enabled us to characterize the microstructure of these terpolymers.

In all cases, statistic terpolymers were obtained in which the different monomeric units were randomly distributed in the chaining, and microblocks of oligo(VDF)s were noted in the terpolymer. The amounts of termonomeric units in the terpolymers were assessed by ^{19}F NMR. In addition, all ^{1}H-NMR spectra exhibit: (1) the signals assigned to methylene groups of VDF units adjacent to difluoromethylene groups in the 3.0–3.4 ppm range (with high amounts of VDF units

Table 6. Determination of the TFVOBB/Copolymer Composition of VDF/TFVOBB and CTFE/TFVOBB vs. the Reaction Conditions in the Radical Copolymerization of VDF or CTFE with TFVOBB. Copolymerization Conditions: [2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane]$_0$/([VDF or CTFE]$_0$ + [TFVOBB]$_0$) = 0.9 mol %, 134 °C, 10 hours. Average molecular weights, M_n and M_w, assessed from SEC with poly(styrene) standards. T_g and T_d were measured by DSC and TGA (under air conditions), respectively.

Exp. #	VDF in Feed (mol %)	CTFE in Feed (mol %)	TFVOBB in Feed (mol %)	VDF in the Copolymer (mol %)	CTFE in the Copolymer (mol %)	TFVOBB in the Copolymer (mol %)	Yields by Mass (%)	M_n (g/mol)	M_w (g/mol)	PDI	T_g (°C)	T_d (°C) (Δm = 5%)	T_d (°C) (Δm = 10 %)
6	79	0	21	95	0	5	7	15,900	25,400	1.6	−32	211	305
7	90	0	10	96	0	4	22	20,400	30,600	1.5	−33	225	317
8	96	0	4	98	0	2	32	22,700	31,700	1.4	−35	240	330
9	0	83	17	0	100	0	8	16,700	28,400	1.7	34	240	280
10	0	90	10	0	95	5	17	19,600	31,300	1.6	33	280	310
11	0	97	3	0	98	2	25	22,100	33,150	1.5	32	320	350

T_g stands for glass transition temperature.
T_d stands for decomposition temperature.

in the terpolymer, the head-to-head addition gives rise to signals at about 2.4 ppm); and (2) the signals of aromatic groups at about 7.5 ppm.

Determination of the Terpolymer Compositions by using ^{19}F NMR Spectra

The radical terpolymerization of aromatic perfluorovinyl ethers has not been studied. The main goal of this part was to identify the peaks characteristics of TFVOBB in the terpolymers. Nevertheless, the determination of the different NMR signals of VDF, HFP, PMVE, or CTFE units in the (ter)polymers have been the subject of different papers.[13,34,35,42,109,112]

To attribute the monomer signals, three series of three experiments were realized (Table 7) involving an increasing molar ratio of TFVOBB. Figure 7 represents the superposition of three ^{19}F NMR spectra of a VDF/CTFE/TFVOBB terpolymerization. Comparing the increasing of the high of the signals, we concluded that the signals centered at –113.5 and –124.5 ppm were assigned to the difluoromethylene group and the tertiary fluorine of TFVOBB, respectively.

Terpolymerization of TFVOBB with VDF and CTFE

The same investigations were performed for the radical terpolymerization of VDF, CTFE, and TFVOBB initiated by 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane.

The ^{19}F NMR spectrum (Fig. 8) of the poly(VDF-*ter*-CTFE-*ter*-TFVOBB) shows the presence of characteristic head-to-tail signals (CH_2-C[b]F_2)$_n$ (“normal” additions in the VDF blocks) at −91.9 ppm (noted $I_{-91.9}$), and that of several expected signals at −95.1, −113.4, and −115.8 ppm, assigned to the “reversed” head-to-head additions and noted $I_{-95.1}$, $I_{-113.4}$, and $I_{-115.8}$, respectively. Its ^{19}F NMR spectrum exhibits also some signals between −107.6 and −110.1 ppm ($I_{-107.6}$ and $I_{-110.1}$), and −118.7 and −153.9 ppm ($I_{-118.7}$ and $I_{-153.9}$), corresponding to the peaks of the difluoromethylene and the tertiary fluorine groups of CTFE, respectively. The main feature of this spectrum comes from the signal at −113.5 ($I_{-113.5}$) and −128.5 ppm ($I_{-128.5}$), attributed to difluromethylene and tertiary fluorine groups, respectively, of TFVOBB (Table 8).

Hence, the molar percentages of VDF in the terpolymers can be assessed from Equation 3:

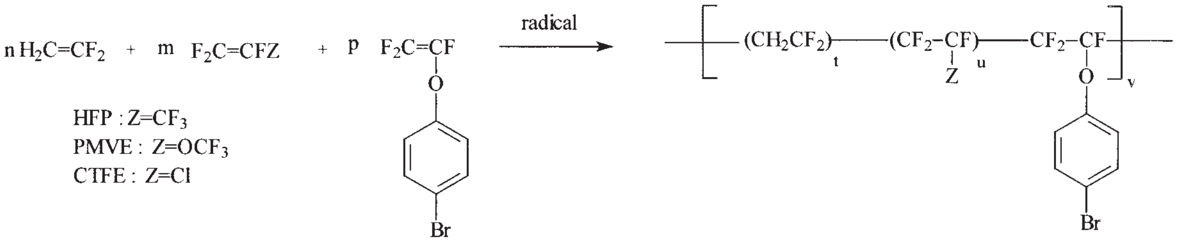


Figure 6. Terpolymerization of TFVOBB with fluoroalkenes (VDF, HFP, PMVE, and CTFE).

Mol % of VDF in the terpolymer

$$= \frac{I_E}{(I_E + I_F + I_G)} \times 100 \quad (3a)$$

Mol % of CTFE in the terpolymer

$$= \frac{I_F}{(I_E + I_F + I_G)} \times 100 \quad (3b)$$

Mol % of TFVOBB in the terpolymer

$$= \frac{I_G}{(I_E + I_F + I_G)} \times 100 \quad (3c)$$

with

$$I_E = \frac{I_{-91.9} + I_{-95.1} + 2 \times I_{-115.8}}{2}$$

$$I_F = \frac{I_{-110.1}}{2} + I_{-118.7} + I_{-153.9}$$

$$I_G = \frac{I_{-113.4} - I_{-115.8}}{2}$$

The final molar percentages of each termonomer are given in Table 7.

Terpolymerization of TFVOBB with VDF and HFP

Firstly, this ^{19}F NMR spectrum (Fig. 9) shows different signals (see Table 9). First, there is a peak centered at about −91.1 ppm (noted $I_{-91.1}$) assigned to the difluoromethylene groups located in the head-to-tail VDF chaining (i.e., normal VDF addition). Furthermore, a series of other signals centered at −95.2 (noted $I_{-95.2}$), −113.7 (noted $I_{-113.7}$), and −115.7 (noted $I_{-115.7}$) ppm assigned to the CF$_2$ groups in (CH$_2$-CF$_2$)-(CF$_2$-CH$_2$)-(CH$_2$-C***F[b]***$_2$)-(CH$_2$-CF$_2$), -(CH$_2$-CF$_2$)-(C[b]F$_2$-CH$_2$)-(CF$_2$-CH$_2$)-, and (CH$_2$-CF$_2$)-(C[b]F$_2$-CH$_2$)-(CH$_2$-CF$_2$) sequences, respectively, are also observed and are attributed to the reverse VDF addition (i.e., head-to-head addition) (Table 9). Furthermore, the signals located at −109.8 ppm (noted $I_{-109.8}$) and −110.1 (noted $I_{-110.1}$) range are assigned to the difluoromethylene groups of the VDF unit adjacent to HFP and TFVOBB unit, respectively.

In addition, the chemical shifts centered at −71.2 (noted $I_{-71.2}$) and −74.8 (noted $I_{-74.8}$) are assigned to the trifluoromethyl side group of HFP in the terpolymer -CH$_2$CF$_2$CF$_2$CF(C[b]F$_3$)- CF$_2$-CH$_2$- and -CH$_2$-CF$_2$-CF$_2$-CF(C[b]F$_3$)-CH$_2$-CF$_2$-; while those centered at −118.8 (noted $I_{-118.8}$) and −183.5 (noted $I_{-183.5}$) ppm are attributed to the difluoromethylene groups in -CH$_2$CF$_2$C[b]F$_2$-CF(CF$_3$)- sequences and to the tertiary fluorine in CF$_2$C[b]F(CF$_3$) of HFP, respectively.

Finally, the multiplet centered at −113.8 ppm (noted $I_{-113.8}$) is attributed to the difluoromethylene of TFVOBB unit in the terpolymer -(C[b]F$_2$-CF(O-Ph-Br))-. Hence, the peaks located in the −123.5 to −125.5 ppm region (noted $I_{-124.7}$) are assigned to the tertiary fluorine atom in the CF group of TFVOBB.

From the integrations in the ^{19}F NMR spectra (denoted above), the determination of the molar fractions of VDF, HFP, and TFVOBB units in the terpolymer is given by the following equations (Eq. 4):

Mol % of VDF in the terpolymer

$$= \frac{I_H}{I_H + I_I + I_J} \times 100 \quad (4a)$$

Mol % of HFP in the terpolymer

$$= \frac{I_I}{I_H + I_I + I_J} \times 100 \quad (4b)$$

Table 7. Determination of the Monomer/Terpolymer Composition of VDF/Terolefin/TFVOBB vs. the Reaction Conditions in the Radical Terpolymerization of VDF, Terolefin (HFP, PMVE, or CTFE) with TFVOBB. Terpolymerization Conditions: [2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane]$_0$/([VDF]$_0$ + [Terolefin]$_0$ + [TFVOBB]$_0$) = 0.9 mol %, 134 °C, 10 hours. Average molecular weights, M_n and M_w, assessed from SEC with poly(styrene) standards. T_g and T_d were measured by DSC and TGA (under air conditions), respectively.

Exp. #	VDF in Feed (mol %)	Terolefin in Feed (mol %)	TFVOBB in Feed (mol %)	VDF in Terpolymer (mol %)	Terolefin in Terpolymer (mol %)	TFVOBB in Terpolymer (mol %)	Yields by Mass (%)	M_n (g/mol)	M_w (g/mol)	PDI	T_d (°C) Δm (5%) (Δm (10%))	T_g (°C)
12	83	12 HFP	5	84	10 HFP	6	38	21,900	32,800	1.5	260 (330)	−39
13	79	13 HFP	8	82	8 HFP	10	20	20,700	35,200	1.7	180 (240)	−34
14	80	9 HFP	11	81	5 HFP	14	17	18,900	30,200	1.6	160 (220)	−26
15	70	25 PMVE	5	78	15 PMVE	7	41	23,100	39,300	1.7	310 (350)	−38
16	66	24 PMVE	10	72	13 PMVE	15	17	21,900	39,400	1.8	260 (290)	−35
17	64	22 PMVE	14	71	10 PMVE	19	15	19,800	37,600	1.9	250 (280)	−26
18	71	21 CTFE	8	47	49 CTFE	4	45	22,800	36,400	1.6	250 (290)	−21
19	62	24 CTFE	14	44	44 CTFE	12	31	20,200	36,300	1.8	240 (270)	−17
20	56	22 CTFE	22	41	41 CTFE	18	24	17,000	25,500	1.5	220 (260)	−15

T_g stands for glass transition (°C).
T_d stands for decomposition temperature (°C) (under air conditions).

Mol % of TFVOBB in the terpolymer

$$= \frac{I_J}{I_H + I_I + I_J} \times 100 \quad (4c)$$

with:

$$I_H = \frac{I_{-91.1} + I_{-94.9} + I_{-109.8} + I_{-110.1} + 2 \times I_{-115.7}}{2}$$

$$I_I = \frac{I_{-71.2} + I_{-74.8}}{3}$$

$$I_J = \frac{I_{-113.8} - I_{-115.7}}{2}$$

The incorporation rates of each monomer in the terpolymers are listed in Table 7.

Terpolymerization of TFVOBB with VDF and PMVE

As for the characterization of VDF/HFP/TFVOBB terpolymer, the ^{19}F NMR spectrum (Fig. 10) shows the peaks characteristic of the difluoromethylene groups of VDF addition and centered at about −91, −94.4, −113.2, and −115.9 ppm, noted I_{-91}, $I_{-94.4}$, $I_{-113.2}$, and $I_{-115.9}$, respectively. Furthermore, the signals located in the −110.1 and −110.8 ppm range are assigned to the difluoromethylene groups of the VDF unit adjacent to a PMVE (noted $I_{-110.1}$) and TFVOBB (noted $I_{-110.8}$) unit, respectively.

In addition, the chemical shifts centered at −52.2 (noted $I_{-52.2}$) are assigned to the trifluoromethyl side group of PMVE in the terpolymer and those located at −120.9 ($I_{-120.9}$) and −122.4 ($I_{-122.4}$) are attributed to the difluoromethylene groups, while those at −125.5 ($I_{-125.5}$) and −145.1 ($I_{-145.1}$) ppm are characteristic to the tertiary fluorine of PMVE.

Finally, as mentioned above, the peaks centered at −113.7 ($I_{-113.7}$) and −125.3 ($I_{-125.3}$) ppm are attributed to the difluoromethylene group and tertiary fluorine atom of the TFVOBB unit in the terpolymer, respectively (Table 10).

The determination of the molar fractions of VDF, PMVE, and TFVOBB units in the terpolymer is given by the following equations (Eq. 5):

Mol % of VDF in the terpolymer

$$= \frac{I_K}{I_K + I_L + I_M} \times 100 \quad (5a)$$

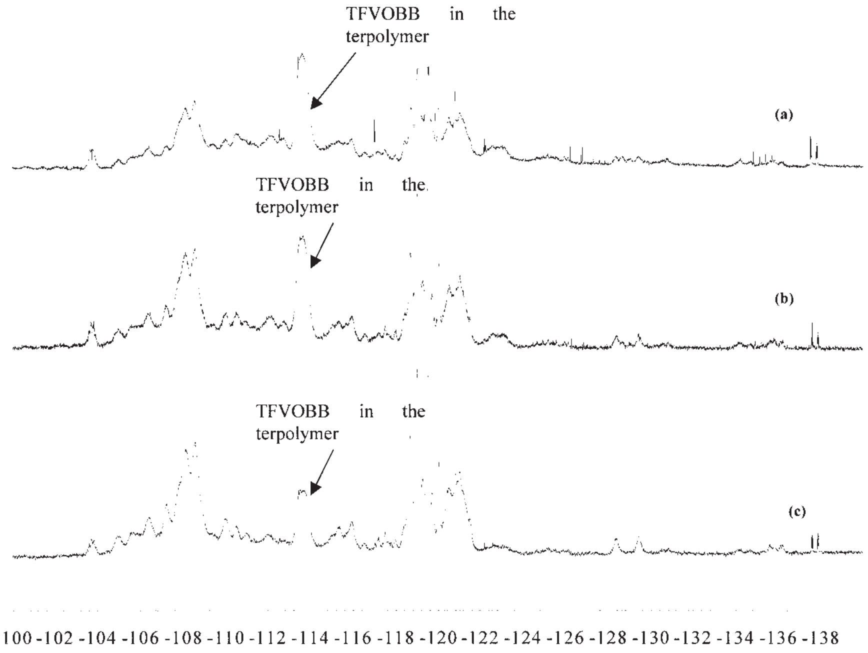


Figure 7. Assignment of the TFVOBB signals in the terpolymers. Spectra of VDF/CTFE/TFVOBB terpolymers recorded in deuterated DMSO. Terpolymerization conditions: [2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane /([VDF]$_0$ + [CTFE]$_0$ + [TFVOBB]$_0$) = 0.9%, 134 °C, 6 h. Terpolymer ratio (mol % TFVOBB) in feed: (a) 22, (b) 14, and (c) 8.

Mol % of PMVE in the terpolymer

$$= \frac{I_L}{I_K + I_L + I_M} \times 100 \quad (5b)$$

Mol % of TFVOBB in the terpolymer

$$= \frac{I_M}{I_K + I_L + I_M} \times 100 \quad (5c)$$

with:

$$I_K = \frac{I_{-91} + I_{-94.4} + I_{-110.1} + I_{-110.8} + 2 \times I_{-115.9}}{2}$$

$$I_L = \frac{I_{-52.2}}{3}$$

$$I_M = \frac{I_{-113.7} - I_{-115.9}}{2}$$

Table 7 indicates the final molar percentages of each termonomer.

Characterization of the terpolymers

Table 7 presented the final molar percentages of each termonomer and also the physicochemical properties of each terpolymer.

However, the results listed in Table 7 showed that the higher the TFVOBB molar percentage, the lower the yields by mass. In the same experimental conditions (Experiments 12, 13, and 14: terpolymer VDF/HFP/TFVOBB, starting from TFVOBB feed molar percentages of 5, 8, and 11 mol % led to copolymers containing 6, 10, and 14 mol %, respectively. The increasing mol % of TFVOBB in feed increases its mol % in the terpolymer and decreases the yields. Interestingly, the final molar percentages of VDF are higher than the molar percentages in feed (except the VDF/CTFE/TFVOBB terpolymerization). As a matter of fact, these remark is the evidence of the presence of oligo(VDF) in the terpolymer.

While the ^{19}F NMR spectroscopy shows the insertion of CTFE, VDF, and HFP base units in the terpolymers, several methods were used to characterize these fluorinated terpolymers: the molecular weights by SEC (with poly(styrene) standards, the polymers were solubilized in THF) and the thermal properties by DSC and thermogravimetric analyses (TGA).

The SEC chromatograms in all cases showed a monomodal distribution that is in good agreement with the statistic of terpolymerization (i.e., lack of two binary systems). The value of the average molecular weights, $\overline{Mn}$, of the VDF/HFP/TFVOBB (Ex-

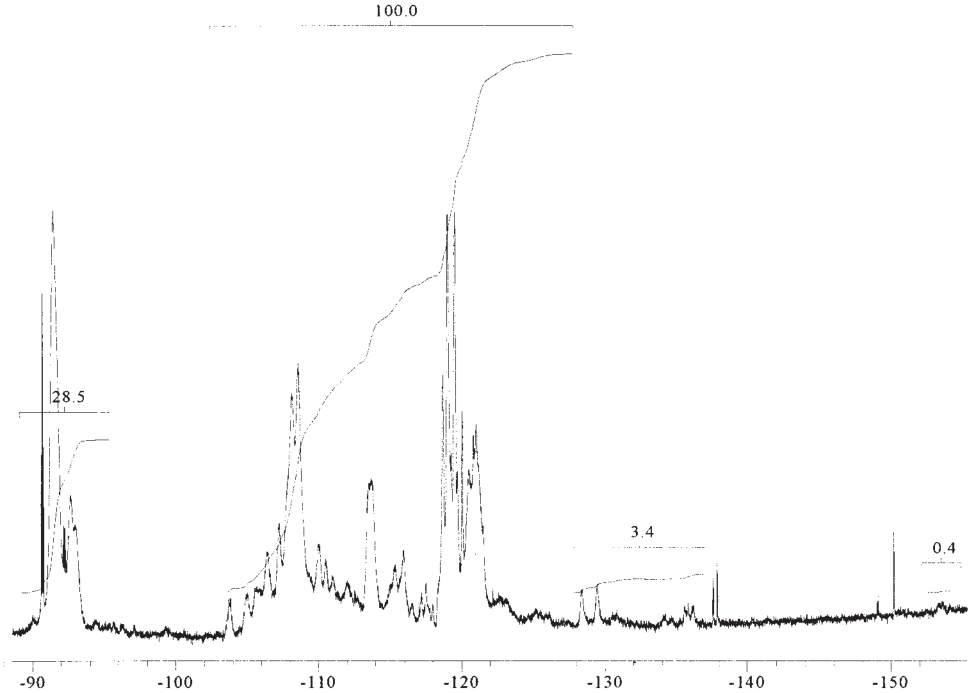


Figure 8. ^{19}F NMR spectrum of VDF/CTFE/TFVOBB terpolymer, recorded in deuterated DMSO. Terpolymerization conditions: [2,5-Bis(*tert*- butylperoxy)-2,5-dimethylhexane]$_0$/([VDF]$_0$ + [CTFE]$_0$ + [TFVOBB]$_0$) = 0.9%, 134 °C, 6 h, and VDF/CTFE/TFVOBB initial molar ratio in the feed = 71/21/8.

periments 12, 13, and 14; 5, 8, and 11 mol % in feed of TFVOBB), VDF/PMVE/TFVOBB (Experiments 15, 16, and 17; 5, 10, and 14 mol % in feed of TFVOBB), and VDF/CTFE/TFVOBB (Experiments 18, 19, and 20; 8, 14, and 22 mol % in feed of TFVOBB) terpolymers were about 21,900, 20,700, and 18,900 g.mol^{-1}, 23,100, 21,900, and 19,800 g.mol^{-1}, and 22,800, 20,200, and 17,000 g.mol^{-1}, respectively. As expected, the lower the mol % of TFVOBB in the terpolymer (or the lower mol % of TFVOBB in the feed), the higher the average $\overline{Mn}$. Regarding these results, the hypothesis of (1) the low reactivity of ~ TFVOBB $^{\bullet}$macroradical, or (2) a recombination of two oligo ~ TFVOBB $^{\bullet}$ can be proposed. The transfer reaction on the macroradical can be ruled out because of the absence of transfer

Table 8. ^{19}F-NMR Assignments of Fluorinated Groups in the Poly(VDF-Co-CTFE-Co-TFVOBB) Terpolymers Recorded in Deuterated DMSO

Chemical shift (ppm)	Structure	Integrals in (Eq. 3)
−91.9	$-CF_2-CH_2-CF_2-CH_2-CF_2-$	$I_{-91.9}$
−95.1	$-CH_2-CF_2-CH_2-CF_2-CF_2-CH_2-$	$I_{-93.6}$
−107.6	$-CH_2-CF_2-CF_2-CFCl-$	$I_{-107.6}$
−110.1	$-CF_2-CFCl-CF_2-CFCl-CH_2-CF_2-$	$I_{-110.1}$
−113.4	$-CH_2-CF_2-CH_2-CF_2-CF_2-CH_2-$	$I_{-113.4}$
−113.5	$-(CH_2-CF_2)-[CF_2-CF(O-Ph-Br)]-$	$I_{-113.5}$
−115.8	$-CH_2-CF_2-CF_2-CH_2-CH_2-CF_2-$	$I_{-115.8}$
−118.7 to 128.5	$-CH_2-CF_2-CF_2-CFCl-CH_2-CF_2$	$I_{-118.7}$
−128.5	$-(CH_2-CF_2)-[CF_2-CF(O-Ph-Br)]-$	$I_{-128.5}$
−130.1 to −153.9	$-CF_2-CFCl-CF_2-CFCl-CF_2-CFCl-$	$I_{-153.9}$

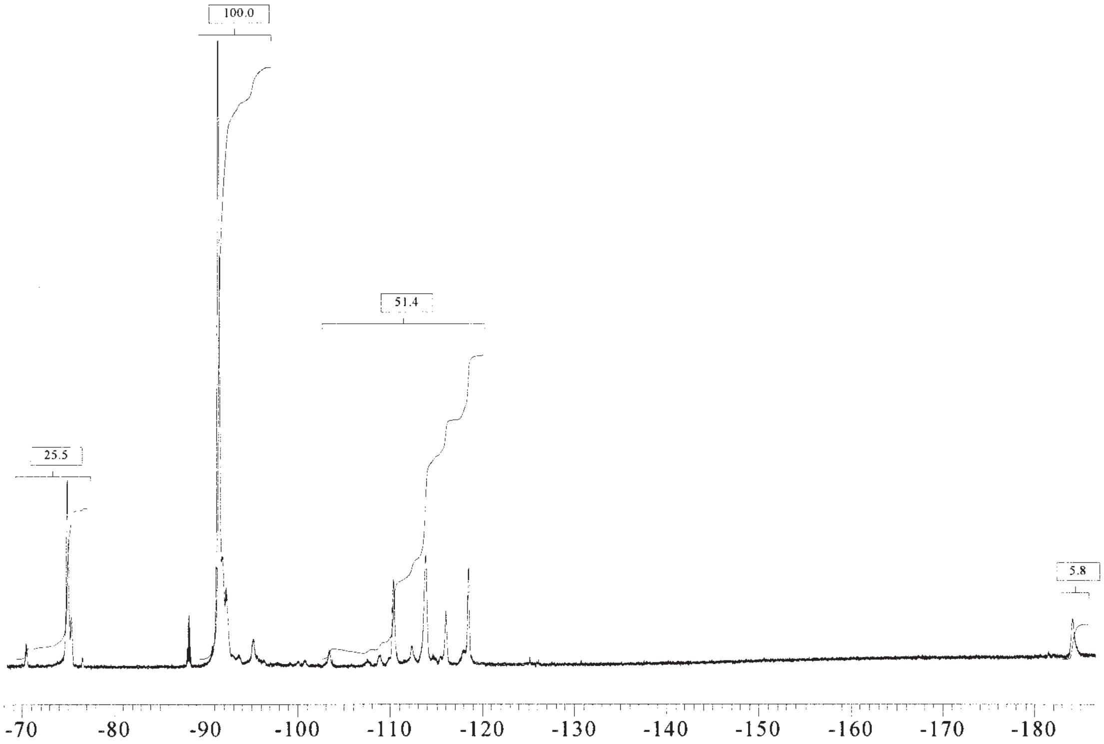


Figure 9. ^{19}F NMR spectrum of VDF/HFP/TFVOBB terpolymer, recorded in deuterated acetone. Terpolymerization conditions: [2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane]$_0$/([VDF]$_0$ + [HFP]$_0$ + [TFVOBB]$_0$) = 1%, 134 °C, 6 h, and VDF/HFP/TFVOBB initial molar ratio in the feed = 83/12/5.

signals in ^{19}F (−114.8 ppm) and ^{1}H (t.t. at 6.1 pmm) NMR spectra. However, these measurements were not quite accurate because of the lack of standards for VDF polymers.

The thermogravimetry curves show that these terpolymers exhibit a good thermal stability since their decomposition occurs from 260, 310, and 250 °C (Table 7) for VDF/HFP/TFVOBB, VDF/PMVE/TFVOBB, and VDF/CTFE/TFVOBB blends, respectively. For example, Figure 11 represents the TGA curves of VDF/PMVE/TFVOBB terpolymers. As in previous cases, the higher the mol % of

Table 9. ^{19}F-NMR Assignments of Fluorinated Groups in the Poly(VDF-Co-HFP-Co-TFVOBB) Terpolymers Recorded in Deuterated Acetone

Chemical Shift (ppm)	Structure	Integrals in (Eq. 4)
−71.2	$-CH_2CF_2CF_2CF(CF_3)-CF_2-CH_2-$	$I_{-71.2}$
−74.8	$-CH_2-CF_2-CF_2-CF(CF_3)-CH_2-CF_2-$	$I_{-74.8}$
−91.1	$-CF_2-CH_2-CF_2-CH_2-CF_2-$	$I_{-91.1}$
−94.9	$(CH_2-CF_2)-(CF_2-CH_2)-(CH_2-C\mathit{F}_2)-(CH_2-CF_2)$	$I_{-94.9}$
−109.8	$-CH_2CF_2CF_2CF(CF_3)-$	$I_{-109.8}$
−110.1	$-(CH_2-CF_2)-[CF_2-CF(O-Ph-Br)]-$	$I_{-110.1}$
−113.7	$-(CH_2-CF_2)-(CF_2-CH_2)-(CF_2-CH_2)-$	$I_{-113.7}$
−113.8	$-(CH_2-CF_2)-[CF_2-CF(O-Ph-Br)]-$	$I_{-113.8}$
−115.7	$-(CH_2-CF_2)-(CF_2-CH_2)-(CH_2-CF_2)-$	$I_{-115.7}$
−118.8	$-CH_2CF_2CF_2CF(CF_3)-$	$I_{-118.8}$
−124.5	$-(CH_2-CF_2)-[CF_2-CF(O-Ph-Br)]-$	$I_{-124.7}$
−183.5	$-CH_2CF_2CF_2CF(CF_3)-$	$I_{-183.5}$

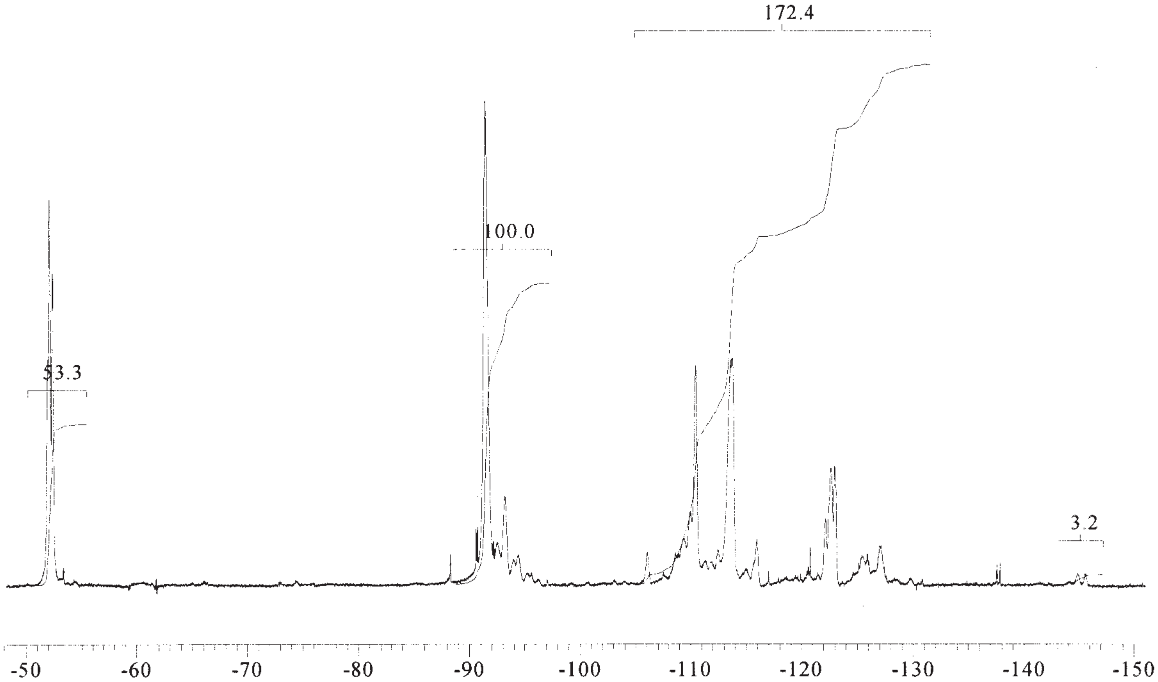


Figure 10. ^{19}F NMR spectrum of VDF/PMVE/TFVOBB terpolymer, recorded in deuterated acetone. Terpolymerization conditions: [2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane]$_0$/([VDF]$_0$ + [PMVE]$_0$ + [TFVOBB]$_0$) = 0.9%, 134 °C, 6 h, and VDF/PMVE/TFVOBB initial molar ratio in the feed = 66/24/10.

TFVOBB in the terpolymer, the lower the thermal properties of the copolymer.

Furthermore, the terpolymer thermal properties were assessed. DSC was used to determine the glass transition temperature and the results are listed in Table 7. In the VDF/HFP/TFVOBB terpolymerization, Tg increases with the $\overline{Mn}$ and decreases with the increasing molar percentages of VDF in the terpolymer, confirming former investigations.[13] In the VDF/PMVE/TFVOBB (Experiments 15, 16, and 17) and VDF/CTFE/TFVOBB systems (Experiments 18, 19, and 20),

Table 10. ^{19}F-NMR Assignments of Fluorinated Groups in the Poly(VDF-Co-PMVE-Co-TFVOBB) Terpolymers Recorded in Deuterated Acetone

Chemical Shift (ppm)	Structure	Integrals in (Eq. 5)
−52.2	$-CH_2-CF_2-CF_2-CF(OCF_3)-CH_2-CF_2-$	$I_{-52.2}$
−91	$-CF_2-CH_2-CF_2-CH_2-CF_2-$	I_{-91}
−94.4	$-CH_2-CF_2-CH_2-CF_2-CF_2-CH_2-$	$I_{-94.4}$
−110.1	$-CH_2-CF_2-CF_2-CF(OCF_3)-CH_2-CF_2-$	$I_{-110.1}$
−110.8	$-(CH_2-CF_2)-[CF_2-CF(O-Ph-Br)]-$	$I_{-110.8}$
−113.2	$-CH_2-CF_2-CH_2-CF_2-CF_2-CH_2-$	$I_{-113.2}$
−113.7	$-(CH_2-CF_2)-[CF_2-CF(O-Ph-Br)]-$	$I_{-113.7}$
−115.9	$-CH_2-CF_2-CF_2-CH_2-CH_2-CF_2-$	$I_{-115.9}$
−120.9	$-CF_2-CF(OCF_3)-CH_2-CF_2-CF_2-CF(OCF_3)-CH_2-CF_2$	$I_{-120.9}$
−122.4	$-CH_2-CF_2-CF_2-CF(OCF_3)-CH_2-CF_2-$	$I_{-122.4}$
−125.3	$-(CH_2-CF_2)-[CF_2-CF(O-Ph-Br)]-$	$I_{-125.3}$
−125.5	$-CH_2-CF_2-CF_2-CF(OCF_3)-CH_2-CF_2-$	$I_{-125.5}$
−145.1	$-CH_2-CF_2-CF_2-CF(OCF_3)-CH_2-CF_2-$	$I_{-145.1}$

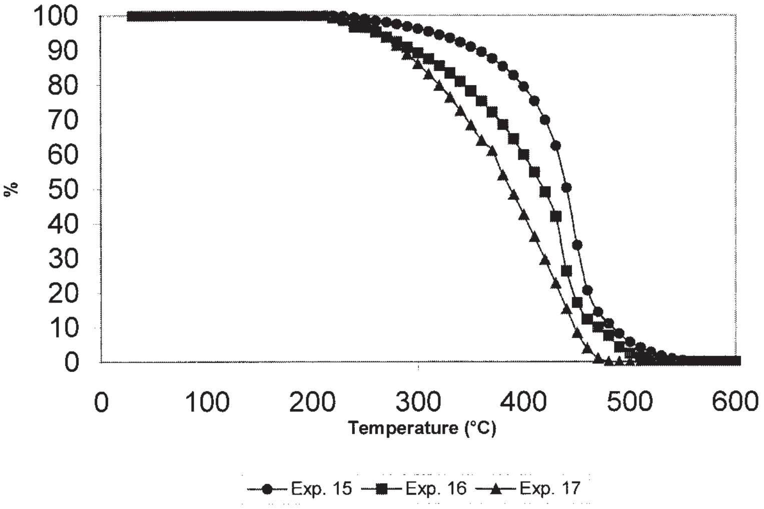


Figure 11. TGA thermogram under air of VDF/PMVE/TFVOBB terpolymers (terpolymer 78/15/7:VDF/PMVE/TFVOBB:●; terpolymer 72/13/15:VDF/PMVE/TFVOBB:■; terpolymer 71/10/19:VDF/PMVE/TFVOBB:▲).

Tg increases with the molar percentages of TFVOBB in the terpolymer. Except for the VDF/CTFE/TFOVBB terpolymers, which were semicrystalline, the terpolymers were amorphous. Moreover, the glass transition temperatures ranged between −26 and −39 °C, −26 and −38 °C, and −15 and −21 °C for VDF/HFP/TFVOBB, VDF/PMVE/TFVOBB, and VDF/CTFE/TFVOBB blends, respectively. With such T_gs, and as reported in the literature,[13] it is known that fluoropolymers containing VDF and HFP or PMVE base units only exhibit average T_g of −26 °C and are fluoroelastomers.

Finally, regarding the results gathered in Table 7, it appears that the TFVOBB incorporation is favored in the VDF/PMVE system, which is better than the VDF/HFP and VDF/CTFE.

CONCLUSION

The co- and terpolymerization of TFVOBB with VDF, HFP, PMVE, and CTFE is for the first time described. As a matter of fact, it has been shown that radical polymerization of TFVOBB is optimized in pentafluorobutane initiated by 2,5-bis-(*tert*-butylperoxy)-2,5-dimethylhexane. Furthermore, the radical copolymerizations of TFVOBB with VDF or CTFE enabled us to assess copolymers incorporating a low molar percentage of TFVOBB. To improve the final mol % of the perfluorinated bromoaromatic monomer, the terpolymerization has been investigated. Interestingly, the synthesized terpolymers show that the VDF/PMVE blend enhanced the incorporation of TFVOBB. Hence, the VDF/PMVE blend allowed us to have a better incorporation rate of TFVOBB in the terpolymer than those obtained with VDF/HFP and VDF/CTFE systems. Finally, DSC, TGA, and GPC analyses indicated that the terpolymer incorporating the lower amount of TFVOBB exhibited the better thermal properties and the higher molecular weights. This study allowed us to know the fluoroalkenes that could be polymerized with aromatic perfluorovinyl ethers. This polymerization model will be used for the polymerization of aromatic perfluorovinyl ether monomers functionalized by sulfonic or phosphonic acid groups.[114] The prepared materials may have proton exchange properties and could be used in fuel cell applications.[62]

The authors acknowledge the Centre National de la Recherche Scientifique, the GDR PACEM 2479, and the Commissariat à l'Energie Atomique for financial support of the PhD studies (to R.S.). The authors thank the Solvay Solexis S.A. (Tavaux in France and Brussels in Belgium) for the generous gifts of vinylidene fluoride, hexafluoropropene, and 1,1,1,3,3-pentafluorobutane; La Chalonnaise des peroxydes company for supplying the *tert*-butyl 2,2-dimethylperoxypropanoate; and Professor O. Paleta (Institute of Chemical Technology, Czech Republic) for the gift of 1,2-dibromotetrafluoroethane.

REFERENCES AND NOTES

1. Wall, L. A. Fluoropolymers; Wiley: New York, 1972.
2. Feiring, A. E. In Organofluorine Chemistry: Principles and Commercial Applications; Banks, R. E.; Smart, B. E.; Tatlow, J. C., Eds.; Plenum Press: New York, 1994; pp. 15, 339–372.
3. Scheirs, J. Modern Fluoropolymers; Wiley: New York, 1997.
4. Hougham, G.; Davidson, T.; Cassidy, P.; Johns, K. Fluoropolymers; Kluvert: New York, 1999.
5. Banks, B. A. The Use of Fluoropolymers in Space Applications, Modern Fluoropolymers; Wiley and Sons: New York, 1999; Chapter 4, pp. 103–114.
6. Kobayashi, T.; Munekuta, S.; Unoki, E. European Patent 239,935, 1987.
7. Yamamoto, S.; Matsumoto, M.; Shimada, T. European Patent 256,765, 1988.
8. Skutnik, K. AU Patent 569,145, 1988.
9. Yamamoto, S.; Matsumoto, M. Japanese Patent 63,430,104, 1988.
10. Boutevin, B.; Pietrasanta, Y. Les Acrylates et poly Acrylates fluorés; Erec: Paris, 1998.
11. Brady, R. Chem In Britain 1990, 26, 427.
12. Logothetis, A. C. Prog Polym Sci 1989, 14, 251.
13. Ameduri, B.; Boutevin, B.; Kostov, G. Prog Polym Sci 2001, 26, 105.
14. Venkateswarlin, P.; Guenthner, R. A.; Kolf, R. E.; Kestner, T. A. 136th ACS Rubber Division Meeting, Detroit, Michigan, Paper 123, 1999.
15. Forsythe, J. S.; Hill, D. J. T Prog Polym Sci 2000, 25, 101.
16. Apotheker, D.; Finlay, J. B.; Krusic, R. J.; Logothetis, A. C. Rubber Chem Tech 1982, 55, 1004.
17. Wlassics, I.; Navarrini, W.; Albano, M. (Ausimont). Eur Pat. Appl. EP 0,769,521 A1, 1991.
18. Arcella, V.; Barchiesi, A.; Chiodini, B. Rubber World 1993, 207, 18.
19. Tournut, C. Macromol Symp 1994, 82, 99.
20. Tournut, C. J. In Modern Fluoropolymers; Scheirs, J., Ed.; Wiley: New York, 1997; Chapter 31, pp. 577–596.
21. Cook, D.; Lynn, M. Rapra Review Reports 1995, 3, Report 32, Shrewbury, pp. 1–27.
22. Van Cleef, A. In Modern Fluoropolymers; Scheirs, J., Ed.; Wiley: New York, 1997; Chapter 32, pp. 597–614.
23. Carlson, D. P. (Du Pont de Nemours). Eur Pat. Appl. 0444700A2, 1991.
24. Yagi, T.; Tsuda, N.; Noguchi, T.; Sakaguchi, K.; Tanaka, Y.; Tatemoto, M. (Daikin). Eur Pat. Appl. 0422644A2, 1991.
25. Yutani, Y.; Tatemoto, M. (Daikin). Eur Pat. Appl. 0489370A1, 1991.
26. Arcella, V.; Brinati, G.; Albano, M.; Tortelli, V. (Ausimont S.p.A.). Eur Pat. Appl. 0661312A1, 1995.
27. Arcella, V.; Brinati, G.; Albano, M.; Tortelli, V. (Ausimont S.p.A.). Eur Pat. Appl. 0683186A1, 1995.
28. Hull, D. E.; Johnson, B. V.; Rodricks, J. P.; Staley, J. B. In Modern Fluoropolymers; Scheirs, J., Ed.; Wiley: New York, 1997; Chapter 13, pp. 257–270.
29. Gayer, U.; Schuh, T.; Arcella, V.; Albano, M. (Ausimont S.p.A). Eur Pat. Appl. EP1231239A1, 2002.
30. Arcella, V.; Ferro, R. In Modern Fluoropolymers; Scheirs, J., Ed.; Wiley: New York, 1997; Chapter 2, pp. 71–98.
31. Kostov, G.; Ameduri, B.; Bauduin, G.; Boutevin, B.; Stankova, M. J Polym Sci Part A: Polym Chem, to appear.
32. Minhas, P. S.; Petrucelli, F. Plast Eng 1977, 33, 60.
33. CMX® Technical Brochure, Allied, 1992.
34. Souzy, R.; Guiot, J.; Ameduri, B.; Boutevin, B.; Paleta, O. Macromolecules 2003, 36, 9390.
35. Souzy, R.; Ameduri, B.; Boutevin, B. Macromol Chem Phys 2004, 205, 476.
36. Ohmori, A.; Tomihashi, N.; Inukai, H.; Shimizu, Y. (Daikin Kogyo Co). Eur Pat. Appl. 0,138,091, 1984.
37. Ameduri, B.; Boutevin, B.; Kostov, G.; Petrova, P. J Fluorine Chem 1999, 93, 139.
38. Ameduri, B.; Bauduin, G.; Boutevin, B.; Kostov, G.; Petrova, P. Macromolecules 1999, 32, 4544.
39. Guiot, J; Ameduri, B.; Boutevin, B. J. Polym Sci, Part A: Polym Chem 2002, 40, 3534.
40. Petrova, P.; Ameduri, B.; Boutevin, B.; Kostov, G. (Solvay Solexis). World Patent PCT 99/09147 WO 00/31009, 1999.
41. Ameduri, B.; Boutevin, B.; Kostov, G.; Petrova, P. Designed Monomers Polym 1999, 2, 267.
42. Guiot, J; Ameduri, B.; Boutevin, B.; Lannuzel, T. Eur Polym Mater 2003, 39, 887.
43. Connolly, D. J; Gresham, W.F. (Du Pont). US Patent 3,282,875, 1966.
44. Feiring, A. E.; Doyle, C. M.; Roelofs, M. G.; Farnham, W. B.; Bekiaram, P. G.; Blair, H. A. K. (Du Pont). PCT WO 99/45048, 1999.
45. Farham, W. B.; Feiring, A. E.; Morken, P. (Du Pont). WO 99/41292A, 1999.
46. Farham, W. B.; Bekarian, P. G. (Du Pont). WO 00/52060A, 2000.
47. Ameduri, B.; Armand, M.; Boucher, M.; Manseri, A. (Hydro-Quebec). WO 01/49757, 2001.
48. Worm, A. (Dyneon). PCT WO 00/12574, 2001.
49. Ameduri, B.; Boucher, M.; Manseri, A. (Hydro-Quebec). PCT CA 01/01439, 2001.
50. Apotheker, D.; Krusic, P. J. (Du Pont). USP 4,214,060, 1976.
51. Moggi, G.; Bonardelli, P.; Monti, C.; Bart, J. C. J Polym Bull 1984, 11, 35.
52. Chiodino, G.; Lagostina, A.; Merenda, M.; Minutillo, A.; Montessoro, E. (Ausimont). Eur Pat. Appl., 0,410,351 B1, 1993.

53. Ameduri, B.; Boucher, M.; Manseri, A. (Hydro-Quebec). WO 01/96268, 2001.
54. Albin, J. R.; Gallagher, G. A. (Du Pont). USP 3,136,745, 1964.
55. Schuman, P. D. Sci Tech Aerosp Rep 1968, 6, 957.
56. Schmiegel, W. W. Angew Makromol Chem. 1979, 76/77, 39.
57. Tatemoto, M.; Amano, T. (Daikin). Eur Pat. Sp. 0,077,998, 1982.
58. Yamabe, M.; Kojima, G.; Wachi, G. H.; Kodama, S. (Asahi Glass Co Ltd). USP 4,418,186, 1983.
59. Albano, M.; Arcella, V.; Chiodini, G.; Minutillo, A. (Ausimont). EP 0,618,241 B1, 1994.
60. Kruger, R.; Piejko, K. E.; Negele, M.; Eisele, U.; Marhold, A. (Bayer). USP 5,426,165, 1995.
61. Ameduri, B.; Boutevin, B.; Armand, M.; Boucher, M. (Hydro-Quebec). WO 01/49758, 2001.
62. Pineri, M.; Marsacq, D.; Ameduri, B.; Souzy, R. (Commissariat à l'Energie Atomique) French Patent, 2,843,398, 2002.
63. Souzy, R.; Ameduri, B.; Boutevin, B. Prog Polym Sci 2004, 29, 75.
64. Watanabe, M.; Ishiuchi, H. JP 5,013,070, Japan, 1993.
65. Yang, Z. Y.; Feiring, A. E.; Smart, B. E. J Am Chem Soc 1994, 116, 4135.
66. Feiring, A. E.; Smart, B. E.; Yang, Z. Y. (DuPont de Nemours). PCT Int. Appl WO 9,414,741, 1994.
67. Smith, Jr. D. W.; Babb, D. A. Macromolecules 1996, 29, 852.
68. Pereta, K. P. U.; Krawiek, M.; Smith, Jr. D. W. Tetrahedron 2002, 58, 10197.
69. Clement, K. S.; Ezzel, B. R.; Babb, D. A.; Richey, W. F. (Dow Chem) US 5,037,919, 1991.
70. Clement, K. S.; Ezzel B. R.; Babb, D. A. (Dow Chem) US 5,021,602, 1991.
71. Bartmann, E.; Plach, H.; Eidenschink, R.; Reiffenrath, V.; Pauluth, D.; Poetsch, E.; Schoen, S.; Meyer V.; Junge, M.; Hittich, R. (Merck). US 5,403,512, 1995.
72. Desmarteau, D. D.; Martin, C. W.; Ford, L. A.; Xie, Y. (3M Innovative Properties Company). US 6,268,532, 2001.
73. Ligon, Jr. S. C.; Krawieck, M.; Kitaygorodskiy, A.; Smith, Jr, D. W. J Fluorine Chem 2003, 123, 139.
74. Grot, W. G.; Molnar, C. J.; Resnick, P. R. (DuPont de Nemours). AU 544027 1985.
75. Martin, C. W.; Nandapurkar, P. J.; Katti, S. S. In Polymeric Materials Encyclopedia; CRC Press Inc.: Boca Raton, FL, 1992.
76. Stone, C.; Steck, A. E.; Lousenberg, R. D. (Ballard Power Systems Inc.). US 5,602,185, 1997.
77. Stone, C.; Daynard, T. S.; Hu, L. Q.; Mah, C.; Steck, A. E. J New Mater Electrochem Syst 2000, 3, 43.
78. Smith, Jr. D. W.; Chen, S.; Kumar, S.; Ballato, J.; Shah, H.; Topping, C.; Foulger, S. Adv Mater 2002, 14, 1585.
79. Foulger, S. H.; Jiang, P.; Lattam, A.; Smith, Jr, D. W.; Ballato, J. Langmuir 2001, 17, 6023.
80. Foulger, S. H.; Lattam, A.; Ballato, J.; Jiang, P.; Ying, Y.; Smith, Jr. D. W. Adv Mater 2001, 13, 1898.
81. Zengin, H.; Zhou, W.; Jin, J.; Czerw, R.; Smith, Jr. D. W.; Echegoyen, L.; Caroll, D.; Foulger, S.; Ballato, J. Adv Mat 2002, 14, 1480.
82. Luo, J; Liu, S.; Haller, M.; Liu, L.; Ma, H.; Jen, A. K. Y. Adv Mater 2002, 14, 1763.
83. Smith, Jr. D. W.; Boone, H. W.; Traiphol, R.; Shah, H.; Perahia, D. Macromolecules 2000, 33, 1126.
84. Traiphol, R.; Shah, H. V.; Smith, Jr. D. W.; Perahia, D. Macromolecules 2001, 34, 3954.
85. Traiphol, R.; Smith, Jr. D. W.; Perahia, D. J Polym Sci Part A (Polym Chem) 2002, 40, 2817.
86. Townsend, P. H.; Shaffer, E. O.; Mills, M. E.; Blackson, J.; Radler, M. J. Materials Research Society Symposium Proceedings, 443 (Low-Dielectric Constant Materials II), 1997, pp. 33–40.
87. Fishbeck, G.; Moosburger, R.; Kostrzewa, C.; Achen, A.; Petermann, K. Electronics Letters 1997, 33(6), 518.
88. Perretie, D.; Bratton, L.; Bremmer, J; Babb, D. A.; Chen, Q.; Judy, J. H. In Proceedings of SPIE—The International Society for Optical Engineering 1911(Liquid Crystal Materials, Devices, and Applications II), 1993, pp. 15–20.
89. Tumolillo, Jr. T. A., Thomas, A.; Ashley, P. R. Appl Phys Lett 1993, 62, 3068.
90. Smith, Jr. D. W.; Babb, D.; Shah, H.; Hoeglund, A.; Traiphol, R.; Perahia, D.; Boone H.; Langhoff, C.; Radler, M. J Fluorine Chem 2000, 104, 109.
91. Beckerbauer, R. (DuPont de Nemours). US 3397191, 1968.
92. Souzy, R.; Ameduri, B; Boutevin, B.; Virieux, D. J Fluorine Chem, to appear.
93. Babb, D. A.; Ezzel, R. B.; Clement, K. S. Richey, W. F.; Kennedy, A. P. J Polym Sci Part A: Polym Chem 1993, 31, 3465.
94. Babb, D. A.; Clement, K. S.; Ezzel, B. R. (Dow Chem). US 5159038, 1992.
95. Ji, J.; Narayan-Sarathy, S.; Neilson, R. H.; Oxley, J. D.; Babb, D. A.; Rondan, N. G.; Smith, Jr., D. W. Organometallics 1998, 17, 783.
96. Narayan-Sarathy, S.; Neilson, R. H.; Smith, Jr., D. W. Polym Prepr (Am Chem Soc Div Polym Chem) 1998, 39, 609.
97. Ford, L. A.; Smith, Jr., D. W.; Desmarteau, D. D. Polym Mater Sci Eng (Am Chem Soc, Div PMSE) 2000, 83, 10.
98. Xu, Y.; Loveday, D. C.; Ferraris, J. P.; Smith, Jr., D. W. Polym Prepr (American Chem Society, Division of Polymer Chemistry) 1998, 39, 143.

99. Babb, D. A.; Boone, H. W.; Smith, Jr., D. W.; Rudolph, P. W. J Appl Polym Sci 1998, 69 2005.
100. Boone, H. W.; Smith, Jr., D. W.; Babb, D. A. Polym Prepr (Am Chem Soc Div Polym Chem) 1998, 39, 812.
101. Rizzo, J.; Harris, F. W. Polymer 2000, 41, 5125.
102. Babb, D. A.; Clement, K. S.; Ezzel, B. R. (Dow Chem) US 5,023,380, 1991.
103. Babb, D. A.; Clement, K. S.; Richey, W. F.; Ezzel, B. R. (Dow Chem) US 5,037,917, 1991.
104. Kennedy, A. P.; Babb, D. A.; Bremmer, J. N.; Pasztor, A. J. Jr. J Polym Sci: Part A: Polym Chem 1995, 33, 1859.
105. Babb, D. A.; Rondan, N. G.; Smith, Jr., D. W. Polym Prepr (Am Chem Soc, Div Polym Chem) 1995, 36, 721.
106. Bernett, W. A. J Org Chem 1969, 34, 1772.
107. Wang, S. Y.; Borden, W. T. J Am. Chem Soc 1989, 111, 7282.
108. Cheatman, C. M.; Lee, S. E.; Laane, J.; Babb, D. A.; Smith, Jr. D. W. Polym Int 1998, 46, 320.
109. Guiot, J.; Ameduri, B.; Boutevin, B. Macromolecules 2002, 35, 8694.
110. Russo, S.; Behari, K.; Chengji, S.; Pianca, M.; Barchiesi, E.; Moggi, G. Polymer 1993, 34, 4777.
111. Pianca, M.; Barchiesi, E.; Espoto, G.; Radice, S. J Fluorine Chem 1999, 95, 71.
112. Baradie B.; Shoichet, M. S. Macromolecules 2002, 35, 3569.
113. Ameduri, B.; Boutevin, B. Well-Architectured Fluoropolymers: Synthesis, Properties and Applications; Elsevier: Amsterdam, 2004.
114. Souzy, R.; Ameduri, B.; Boutevin, B. Fuel Cell—From Fundamentals to Systems; to appear.