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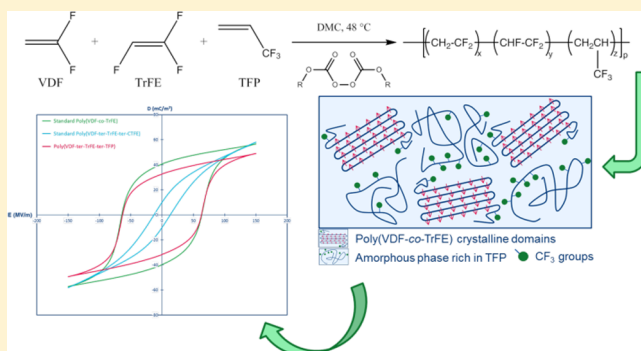
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Supporting Information

ABSTRACT: A new family of electroactive fluorinated terpolymers of vinylidene fluoride (VDF), trifluoroethylene (TrFE) and 3,3,3-trifluoropropene (TFP) is presented. Statistical poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymers with a VDF/TrFE molar ratio of ca. 65/35 and a TFP composition ranging from 0 to 10 mol % were prepared in high yields by free radical terpolymerization in dimethyl carbonate (DMC), initiated by a symmetrical peroxydicarbonate initiator. The choice of TFP as a termonomer was driven by the potential property of the CF₃ side groups to limit crystal growth and potentially favor the formation of nanodomains known to enhance electrostrictive properties. For the first time, the reactivity ratios of the TrFE/TFP ($r_{\text{TrFE}} = 0.13$ and $r_{\text{TFP}} = 3.72$ at 48 °C) couple were determined using the Kelen–Tudos linear method, and used in combination with VDF/TrFE and VDF/TFP reactivity ratios to better understand the structures of the terpolymers. Detailed ¹H and ¹⁹F solution NMR spectroscopic studies were performed and afforded the in-depth characterization of the terpolymers microstructures. The examination of the terpolymer's composition as a function of the three monomers conversions revealed a strong structural heterogeneity where a 62/33/5 VDF/TrFE/TFP initial monomer composition resulted in a 47/11/42 poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymer at low conversion. It was indeed found that TFP preferentially homopolymerizes despite its low initial concentration. The influence of the TFP units on the thermal transitions ($T_{\text{Curie}} = 65$ °C and $T_{\text{m}} = 148$ °C for a 67/28/5 poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymer), thermal stability and electroactivity ($E_{\text{c}} = 63$ MV/m at 150 MV/m) was also examined. The combination of the determination of the monomers' reactivity ratios of the terpolymer microstructures and of the assessment of the physical properties of the terpolymers provided insights on the structure–property relationship of the poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymers.



INTRODUCTION

Fluoropolymers exhibit remarkable properties such as high thermal and chemical stability and low surface tension. These attractive niche polymers are high-value added materials used in high-tech applications such as aerospace, electronics, coatings, membranes, cables, and the automotive industries.^{1–4} Understanding and establishing the structure–property relationship for these polymers is necessary to be able to prepare better materials with made to order and tunable properties.

Poly(vinylidene fluoride), PVDF, is the second most produced fluoropolymer in volume in the world after poly(tetrafluoroethylene), PTFE.⁵ In 1969, Kawai's group discovered the piezoelectric response of PVDF.⁶ Since then, ferroelectric polymers have been the subject of intense research, especially VDF-based copolymers.^{7–14} This research has been driven by the wide range of applications such fluorinated

polymers can be used for, such as energy storage (capacitors), nonvolatile memory,¹⁵ sensors,^{16,17} haptics,¹⁸ and microfluidics,¹⁹ for example. Since 1979,⁷ copolymers of VDF with trifluoroethylene (TrFE) have been well studied and are now commercially available. Interestingly, copolymers containing more than 20 mol % of TrFE display enhanced piezoelectric response compared to pristine PVDF. The presence of TrFE promotes the planar zigzag all-trans (ttt) conformation²⁰ where the strong dipoles resulting from the CF₂ units are all aligned in the same direction. Thus, poly(VDF-*co*-TrFE) copolymers crystallize directly in β -phase which facilitates the formation of ferroelectric copolymers films and avoids complex stretching

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step.^{21–23} Ferroelectricity of highly crystalline poly(VDF-*co*-TrFE) copolymers is evidenced by the existence of a Curie transition between ferroelectric and paraelectric phases. Poly(VDF-*co*-TrFE) copolymers exhibit high Curie temperatures (*ca.* 105 °C for a 70/30 poly(VDF-*co*-TrFE) copolymer), which are highly dependent on the crystal size, the polymer composition and the molecular weight.^{7,14,24,25}

Around the Curie transition, the dielectric constant of the polymer is maximum and as a consequence the polymer response to an electric field is strongly increased. Decreasing the Curie transition to lower temperatures (close to ambient temperature) is thus an essential objective in the field of electroactive polymers. E-beam irradiated poly(VDF-*co*-TrFE) copolymers display lower Curie temperature and high electrostriction.²² The lower Curie temperature may be attributed to smaller ferroelectric domains and larger interchain distances.^{12,26} E-beam treatment induces a cross-linking of the poly(VDF-*co*-TrFE) copolymers. The effects of this treatment were examined by ¹⁹F solid state NMR.²⁷ This NMR study showed that CF₃ groups, created by the irradiations, increased the interchain distance and enable easier rotational mobility (around the carbon–carbon bond axis) of CF₂ dipoles. However, this technique requires a significant amount of energy due to the chemical stability of the fluorinated copolymers and is thus ill-suited for industrial scale production of electrostrictive materials.

Chung et al.^{28,29} obtained similar results with VDF and TrFE based terpolymers containing a small amount (lower than 15 mol %) of a chlorinated monomer such as 1-chloro-1-fluoroethylene (CFE), 2-chloro-1,1-difluoroethylene (CDFE), and chlorotrifluoroethylene (CTFE) or also of vinyl fluoride (VF) and hexafluoropropene (HFP).^{30,31} These terpolymers were synthesized using a room temperature polymerization method based on the oxidation of alkyl-borane.³² This team showed that chlorine atoms act as kinks in the polymer chain and limit the crystal growth thus promoting the formation of nanometric and independent crystalline domains. These nanodomains contribute to the decrease of the Curie transition to *ca.* 20 °C. In these nanodomains, dipoles have fewer cooperative couplings and, thus acquire high mobility. Dipole mobility is directly related to the relaxor ferroelectric (RFE) behavior of poly(VDF-*ter*-TrFE-*ter*-CTFE) terpolymers indicated by polarization curves displaying narrow hysteresis.^{33,34}

In the past decade, improving the electroactive properties of VDF-based fluoropolymers has been a highly sought objective. Researchers showed that the polymer microstructure governs these properties. Establishing structure–property relationships by designing new terpolymers has thus become a crucial goal in this field.^{12,35} Though some fluorinated alkenes (CFE, CDFE, CTFE, VF and HFP) have been used in terpolymerization of VDF and TrFE, to our knowledge, no poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymers (where TFP stands for 3,3,3-trifluoropropene) have ever been reported. Hence, this article describes the syntheses of poly(VDF-*co*-TrFE) copolymers containing small amounts of TFP using free radical terpolymerization. As in e-beam-treated poly(VDF-*co*-TrFE) copolymers,²² the CF₃ groups of TFP are expected to increase the interchain distance and to decrease the size of the crystals without affecting the overall crystallinity. Moreover, the C–H bonds in the TFP units are weak dipoles and are thus expected not to disrupt the conformation of the polymer chain when the polymer is placed in an electric field. In addition, the kinetics of radical terpolymerization of these monomers had never been studied

and the TrFE/TFP monomers reactivity ratios had never been reported. This contribution presents a NMR spectroscopy study of the terpolymer microstructure. The influence of the TFP content on both the thermal properties and the electroactivity of the resulting terpolymers is also discussed.

EXPERIMENTAL SECTION

Materials. All reagents were used as received unless stated otherwise. 1,1-Difluoroethylene (vinylidene fluoride, VDF) and trifluoroethylene (TrFE) were kindly supplied by Arkema (Pierre-Benite, France). 3,3,3-Trifluoropropene (CH₂=CH(CF₃), TFP) was kindly supplied by Great Lakes Chemical Corporation, now Chemtura (West Lafayette, IN). Di(*tert*-butylcyclohexyl) peroxydicarbonate (Perkadox 16, DTBCPC) was purchased from AkzoNobel (Chalons-sur-Marne, France). ReagentPlus grade (purity >99%) dimethyl carbonate (DMC) and laboratory reagent grade pentane (purity >95%) were purchased from Sigma-Aldrich while ACS grade (purity >99%) butan-2-one (methyl ethyl ketone, MEK) from Alfa Aesar. Deuterated acetone used for NMR spectroscopy was supplied by Euriso-top (Grenoble, France) (purity >99.8%).

Characterization. Nuclear Magnetic Resonance (NMR). NMR spectra were recorded at 20 °C on a Bruker AC 400 instrument (400 MHz for ¹H and 376 MHz for ¹⁹F). Coupling constants and chemical shifts are given in hertz (Hz) and parts per million (ppm), respectively. The experimental conditions for recording ¹H [or ¹⁹F] NMR were as follows: flip angle 90° [30°], acquisition time 4.5 s [0.7 s], pulse delay 2 s, number of scans 8 [128], and a pulse width of 5 μs for ¹⁹F NMR.

Polymers Compositions. Using ¹⁹F NMR spectroscopy, the polymers compositions were calculated from eqs 1 to 3:

$$\% \text{VDF} = \frac{n_{\text{VDF}}}{n_{\text{VDF}} + n_{\text{TrFE}} + n_{\text{TFP}}} \quad (1)$$

$$\% \text{TrFE} = \frac{n_{\text{TrFE}}}{n_{\text{VDF}} + n_{\text{TrFE}} + n_{\text{TFP}}} \quad (2)$$

$$\% \text{TFP} = \frac{n_{\text{TFP}}}{n_{\text{VDF}} + n_{\text{TrFE}} + n_{\text{TFP}}} \quad (3)$$

where

$$n_{\text{VDF}} = \frac{1}{2} \int_{-89}^{-133} \text{CF}_2 - \int_{-194}^{-221} \text{CFH}$$

$$n_{\text{TrFE}} = \int_{-194}^{-221} \text{CFH}$$

$$n_{\text{TFP}} = \frac{1}{3} \int_{-65}^{-74} \text{CF}_3$$

in which $\int_i^j \text{CF}_x$ stands for the integral of the signal assigned to CF_x ranging from *i* to *j* ppm.

Polymers Molecular Weights (*M_n*). By combining the number of TrFE units calculated from the ¹H NMR spectrum (using eq 4) and the composition calculated from the ¹⁹F NMR spectrum, the molecular weights were estimated from eq 5.

$$\text{average number of TrFE units per chain} = a = \frac{\int_{5.0}^{6.1} \text{CFH}}{\int_{0.8}^{1.0} \text{tBu}/18} \quad (4)$$

$$M_n = a \times M_{\text{TrFE}} + \frac{a \times \% \text{VDF}}{\% \text{TrFE}} M_{\text{VDF}} + \frac{a \times \% \text{TFP}}{\% \text{TrFE}} M_{\text{TFP}} \quad (5)$$

where *M*_{TrFE}, *M*_{VDF}, and *M*_{TFP} are 82, 64, and 96 g/mol, respectively.

Gel Permeation Chromatography (GPC). GPC analyses were carried out on a Polymer Laboratories PL-GPC 50 Plus instrument using 2 PL gel mixed-C 5 μm columns (range of molecular weight from 200 to 2 × 10⁶ g/mol) thermostated at 35 °C equipped with a

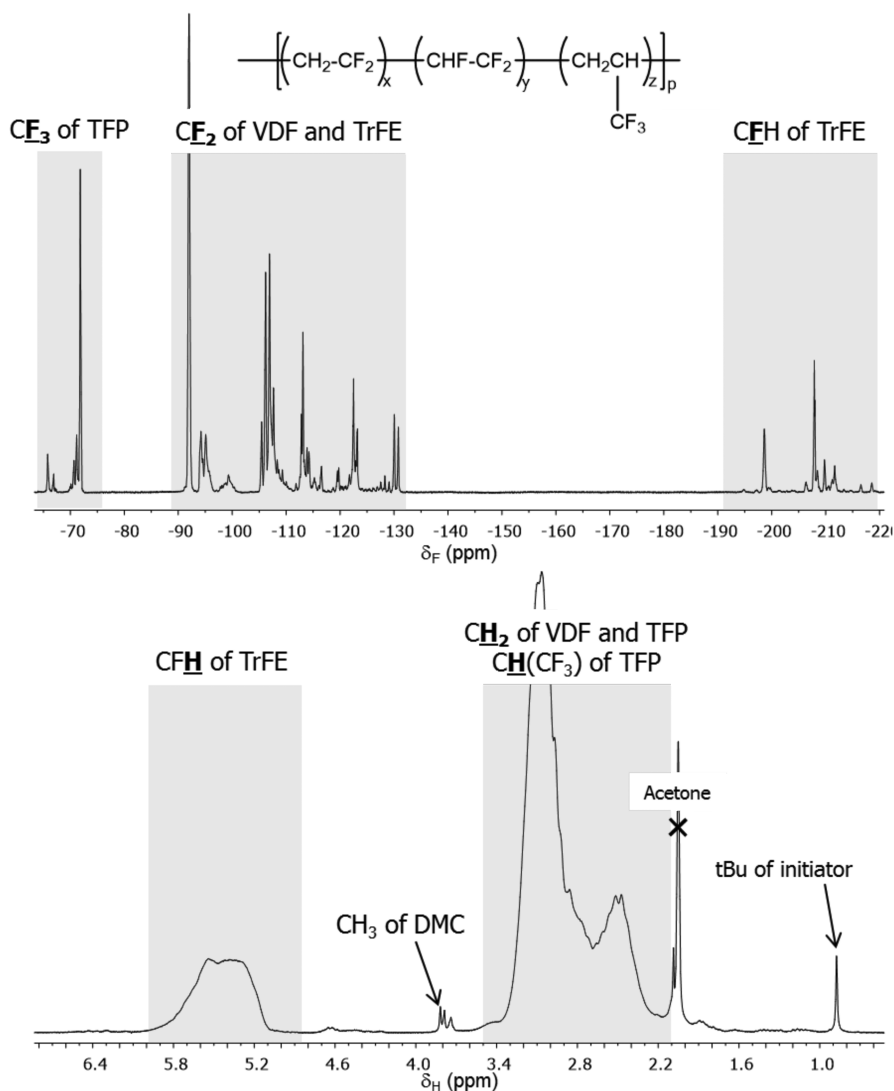


Figure 1. ^{19}F (top) and ^1H (bottom) NMR spectra recorded in deuterated acetone of a poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymer (run 10, Table 2).

refractive index detector. Tetrahydrofuran (THF) was used as eluent (1.0 mL/min). Calibration was performed using Varian polystyrene (PS) narrow standards and toluene as a flow marker.

Thermogravimetric Analysis (TGA). TGA analyses were carried out on 10–15 mg samples on a TGA Q50 apparatus from TA Instruments from 20 to 590 °C, in an aluminum pan, at a heating rate of 10 °C/min, under air.

Differential Scanning Calorimetry (DSC). DSC measurements were performed on 10–15 mg samples on a Netzsch DSC 200 F3 instrument using the following heating/cooling cycle: cooling from +20 to −50 °C at 20 °C/min, isotherm plateau at −50 °C for 5 min, first heating from −50 to +200 °C at 10 °C/min, cooling from +200 to −50 °C at 10 °C/min, isotherm plateau at −50 °C for 3 min, second heating from −50 to +200 °C at 10 °C/min and last cooling from 200 to 20 °C. Calibration of the instrument was performed with noble metals and checked before analysis with an indium sample ($T_m = 156$ °C). Curie and melting transitions were determined at the maximum of the enthalpy peaks.

Fourier Transform Infrared spectroscopy (FTIR). FTIR analyses were performed in ATR mode using a PerkinElmer Spectrum 1000, with an accuracy of ± 2 cm^{-1} .

Dielectric Measurements. The poling process was performed on 20 μm thick polymers films at 20 °C. The charging–discharging cycles were first applied at 25 MV/m and then with increasing 25 MV/m until reaching 150 MV/m at a frequency of 0.05 Hz.

Polymerization. A typical terpolymerization experiment (run 6, Table 2) requires a 100 mL Hastelloy pressure reactor equipped with inlet and outlet valves, a rupture disk, a manometer and a pressure sensor connected to a computer allowing the monitoring of the reactor pressure *versus* time. The autoclave was pressurized with 30 bar of nitrogen for 2 h to detect potential leaks. Then, the reactor was put under vacuum and pressurized three times with nitrogen to remove oxygen. In the under vacuum vessel, 60 mL of a degassed solution of di(*tert*-butylcyclohexyl) peroxydicarbonate (DTBCPC, 180 mg, 0.452 mmol) in degassed dimethylcarbonate (DMC) was introduced using a funnel. Then, the reactor was cooled to −80 °C. 3,3,3-Trifluoropropene (TFP, 1.0 g, 10 mmol), then trifluoroethylene (TrFE, 14.0 g, 171 mmol), and finally vinylidene fluoride (VDF, 20.0 g, 313 mmol) were transferred into the reactor by double weighing. The reactor was then progressively heated to 20 °C and then up to 48 °C for 20 h (Figure 2). After the reaction, the autoclave was placed in an ice bath for 30 min and degassed. The viscous and clear solution reaction was filtered on a filter paper and then diluted with 200 mL of acetone. This solution was added dropwise to 4 L of vigorously stirred cold pentane. The resulting white solid was filtered and dried at 80 °C under vacuum for 14 h. The monomer conversion was estimated to be over 95% as no weight loss was observed during the “degassing-step” after the reaction. The reaction led to a 92 wt % yield. A poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymer composition of 68/30/2 was determined by ^{19}F NMR spectroscopy. ^1H and ^{19}F NMR spectra are supplied in Figure 1 while detailed signal attributions in Table S1. ^1H NMR (376

MHz) in deuterated acetone: δ (ppm): 0.87 (s, $(\text{CH}_3)_3$ from initiator); 1.00–2.20 (m, cyclohexyl group from initiator); 2.25–3.39 (m, CH_2 of VDF and TFP, $\text{CH}(\text{CF}_3)$ in TFP); 4.68 (m, $\text{CH}-\text{O}-\text{C}(\text{O})$ from initiator); 5.10–5.95 (m, CHF of TrFE). ^{19}F NMR (400 MHz) in deuterated acetone: δ (ppm): –66.0 to –72.5 (m, CF_3 of TFP); –92.0 to –131.5 (m, CF_2 of VDF and TrFE); –198.9 to –218.9 (CFH of TrFE).

Film Preparations. A 1.00 g sample of polymer was dissolved in 5.00 g of MEK. The solution was first stirred for 30 min, then filtered on a 0.20 μm PTFE filter and finally cast on a glass slide using a 300 μm casting-knife to obtain a homogeneous thickness (Figure S1). The cast-solution was dried at 20 $^\circ\text{C}$ under air in a ventilated room equipped with a dust filtration system. After 2 h, the film was carefully taken off from the glass slide (Figure S2). Films then underwent a second drying step in an oven at 80 $^\circ\text{C}$ for 24 h. Finally, the 20 ± 1 μm films were annealed for 20 min at 10 $^\circ\text{C}$ below the onset of the melting temperature (determined by DSC).

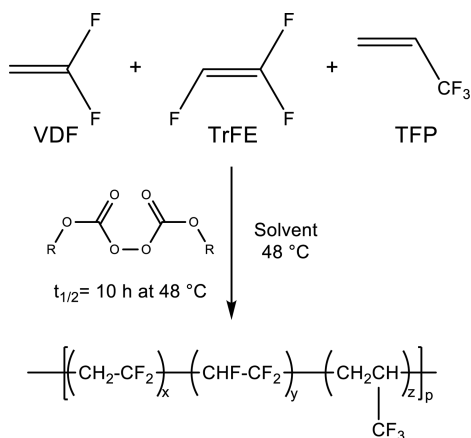
Determination of the Reactivity Ratios. Radical copolymerizations were carried out in thick 8 mL Carius tubes in which the solvent (DMC) and the initiator (DTBCPC) were added and then degassed by performing at least three freeze–pump–thaw cycles. Gaseous monomers were introduced into the Carius tube at the liquid nitrogen temperature using a custom-made manifold that enables accurate measurement of quantities of gas (using “pressure drop vs mass of monomer” calibration curves). The tube was then sealed under dynamic vacuum at the temperature of liquid nitrogen, before being placed horizontally in a shaking water bath thermostated at 48 $^\circ\text{C}$. After 30 min, the tube was placed into liquid nitrogen, opened, and then the solvent was evaporated at 60 $^\circ\text{C}$ under reduced pressure. The resulting copolymer was dissolved in deuterated acetone and its composition was determined by ^{19}F NMR spectroscopy.

RESULTS AND DISCUSSION

Introduction. The radical solution terpolymerizations of VDF with TrFE and TFP were initiated by peroxydicarbonate at 48 $^\circ\text{C}$ (Scheme 1). At that temperature, the radical initiator has a half-life of 10 h.

After reaction and purification by precipitation from cold pentane, white powders were obtained and characterized by conventional analyses (NMR and FTIR spectroscopies, DSC and TGA). The resulting transparent terpolymers films were polarized under high electric field. Before discussing the

Scheme 1. Conventional Radical Solution Terpolymerization of VDF, TrFE, and TFP with R = *tert*-Butyl(cyclohexyl) or ethyl^a



^aThe *tert*-butyl group of the symmetrical initiator provides a convenient ^1H NMR label to assess the terpolymers average molecular weights.

characterizations of such terpolymers, it is worth investigating the kinetics of copolymerization.

Reactivity Ratios. The determination of the reactivity ratios of each pair of comonomers was a required step for the understanding of the terpolymerization. Reactivity ratios of (VDF; TrFE)⁷ and (VDF; TFP)³⁶ couples, at 22 and 74 $^\circ\text{C}$, respectively, have already been reported. The reactivity ratios of the (TrFE; TFP) couple were, for the first time, determined using the well-established Finemann–Ross³⁷ (FR) and Kelen–Tudos³⁸ (KT) laws.

The results of these calculations of the reactivity ratios are summarized in Table 1 and the detailed FR and KT

Table 1. Reactivity Ratios of (VDF, TrFE), (VDF, TFP) and (TrFE, TFP) Monomer Couples Determined by the Kelen–Tudos Linearization Method

VDF/TrFE ⁷ (at 22 $^\circ\text{C}$)	VDF/TFP ³⁶ (at 74 $^\circ\text{C}$)	TrFE/TFP (at 48 $^\circ\text{C}$)
$r_{\text{VDF}} = 0.7$	$r_{\text{VDF}} = 0.28$	$r_{\text{TrFE}} = 0.13$
$r_{\text{TrFE}} = 0.5$	$r_{\text{TFP}} = 2.35$	$r_{\text{TFP}} = 3.72$

linearization methods are provided in Table S2, Figure S3, and Figure S4. VDF and TrFE are randomly distributed within the polymer chain. Surprisingly, homopropagation of TFP is favored compared to that of VDF or TrFE despite the bulky CF_3 group of TFP. VDF and TrFE monomers preferentially cross-propagate. These reactivity ratios suggest the formation of heterogeneous terpolymers as the homopropagation of TFP is most likely the main propagation reaction. Nevertheless, reactivity ratios do not take the initial monomer composition into account. If TFP is introduced in a very small amount (less than 10 mol %), cross-propagation may prevail and a homogeneous terpolymer may be obtained.

Radical Terpolymerization and Influence of TFP Monomer Composition. Table 2 presents the results of the radical terpolymerizations of VDF with TrFE and TFP using a peroxydicarbonate initiator and the main properties of the resulting polymers.

Before assessing the poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymers electroactive properties, a careful study of the radical terpolymerization and of the resulting terpolymers was performed. Radical solution terpolymerizations of gaseous monomers are complex systems. Each homopolymer, copolymer and terpolymer have been prepared rigorously in the same conditions. This allowed to compare the microstructure and properties of the polymers (^1H and ^{19}F NMR spectra of the homopolymers and copolymers are provided in Supporting Information, Figures S5–S10). Poly(VDF-*ter*-TrFE-*ter*-CTFE) and poly(VDF-*ter*-TrFE-*ter*-CFE) terpolymers, which are known to exhibit relaxor ferroelectric (RFE) properties were also synthesized for comparison.^{28,39,40} To understand the influence of TFP on the final properties, terpolymers with similar VDF/TrFE ratio (65/35) and TFP compositions ranging from 0 to 10 mol % were synthesized.

Surprisingly, the radical solution homopolymerization of TFP proceeded with low yield even with an initiator concentration 3 times higher than that used for the homopolymerization of TrFE. The resulting homopolymer was a low molecular weight amorphous elastomer with a glass transition of ca. 11 $^\circ\text{C}$. This low yield can be explained by the high stability of the TFP radical and the steric repulsion effect of the CF_3 pendent group.

Table 2. Experimental Conditions and Results for the Radical Solution Terpolymerizations of VDF, TrFE, and TFP^a

		composition (mol %)			n_M^c/n_{I_2}	time (h)	P_{\max} (bar)	ΔP (bar)	yield (%)	M_n^a (NMR) (kg mol ⁻¹)	M_w^a (GPC) (kg mol ⁻¹)	T_C (°C)	T_m (°C)	ΔH_m (J/g)
		VDF	TrFE	TFP										
1 ^b	monomer	100	—	—	745	26	32	31	>80	n.m. ^d	n.m.	—	176	62
	polymer	100	—	—										
2	monomer	—	100	—	1416	17	n.m.		87	83	40	—	190	21
	polymer	—	100	—										
3	monomer	—	—	100	449	20	n.m.		5	10	4	elastomer, $T_g = 11$		
	polymer	—	—	100										
4 ^b	monomer	63	37	—	1360	19	32	19	78	n.m.	70	72	150	21
	polymer	65	35	—										
5	monomer	69	31	—	3973	17	29	8	68	111	113	92	152	28
	polymer	69	31	—										
6	monomer	64	34	2	1272	20	22	19	92	109	64	65	148	16
	polymer	68	30	2										
7	monomer	63	32	5	1249	15	22	21	64	86	56	65	148	17
	polymer	67	28	5										
8	monomer	62	33	5	1175	25	22	20	>80	105	54	64	148	17
	polymer	67	28	5										
9 ^b	monomer	61	34	5	1186	16	27	18	77	n.m.	56	64	147	14
	polymer	62	32	6										
10	monomer	57	35	8	1212	40	22	19	91	88	51	65	147	11
	polymer	63	28	9										
11	monomer	58	34	8	23	6	25	15	57	9	15	64	125	7
	polymer	62	28	10										

^aPolymer molecular weights were estimated by ¹H NMR (from *tert*-butyl end groups) and GPC in THF calibrated with PS narrow standards (see Experimental Section). ^bDiethyl peroxydicarbonate was used as the initiator instead of di(*tert*-butylcyclohexyl) peroxydicarbonate. ^c n_M and n_{I_2} stand for the total molar amount of monomers (VDF, TrFE and TFP) and initiator, respectively. ^dn.m. stands for not measured.

In contrast, even with a low initiator concentration (less than 0.5 mol %), terpolymerizations reached high conversions as confirmed by the total pressure drop and high mass yields (>60%). Terpolymer compositions were close to the initial monomer mixtures. At the beginning of the terpolymerization, when $P = 20$ bar and $T = 48$ °C, VDF and TrFE are in a gaseous state whereas TFP seems to be in the liquid state. The reaction medium is a complex system where the solubilities of the monomers in DMC are crucial parameters since it is the *locus* of the polymerization reaction. As the monomer conversion increases during the terpolymerization, the pressure inside the vessel decreases, leading to variations in monomers' solubilities. In the case of this multiphase reaction mixture containing three monomers with different solubilities, the reactivity ratios are not sufficient to predict accurately the terpolymerization behavior, but they can give a trend. It is therefore essential to perform radical terpolymerization to evaluate the terpolymers microstructures and compositions.

The molecular weight assessment of fluorinated polymers is always a challenge.^{41,42} For the characterization of new terpolymers over a range of composition, GPC calibrations are ineffective and molecular weight equivalents are only useful for comparisons. The use of ¹H and ¹⁹F NMR spectra for the determination of molecular weights relies on easily identifiable chains-ends and is limited to relatively short polymers for which the chains-ends signals possess a sufficient signal/noise ratio.^{41,43} As mentioned above, the polymerizations were initiated by DTBCPC, a peroxydicarbonate initiator with a *tert*-butyl group that gives an intense singlet at 0.88 ppm in ¹H NMR spectroscopy (Figure 1). Since PVDF termination occurs by recombination exclusively,⁴⁴ the ratio of the integrals of this

singlet and of the broad signal between 5.00 and 6.00 ppm attributed to the CFH unit of TrFE, gives the number of TrFE units per terpolymer chain eq 4. Combining this number with the composition determined from ¹⁹F NMR affords the estimation of the molecular weights of the terpolymers eq 5. Increasing the TFP concentration from 2 to 8 mol % (runs 6 to 10 in Table 2) did not have a clear influence on the terpolymers' molecular weights. The terpolymers had slightly lower molecular weights than poly(VDF-*co*-TrFE) copolymers prepared in the same conditions.

To acquire a better understanding of the terpolymer's physical properties, an in depth microstructure study was achieved using ¹H and ¹⁹F NMR spectroscopy of the homopolymers, copolymers and terpolymers, and previously published studies.

Polymer Microstructure Study. ¹⁹F NMR spectroscopy is a powerful analytical technique for the determination of polymer microstructure.^{44–48} Microstructures of PVDF and PTrFE homopolymers have been well studied using ¹⁹F NMR.^{7,27,49,50} PTrFE homopolymers exhibit a complex ¹⁹F NMR spectra for two reasons: the tacticity and the reverse additions within the polymer chain.⁵¹ PTrFE homopolymers present more chain defects (*ca.* 18%) than PVDF homopolymers which usually display *ca.* 7–9% of reverse additions.^{52,53} This is likely due to a smaller difference in reactivity between both carbons of TrFE compared to those of VDF. The detailed ¹⁹F NMR characterization of PTrFE were successfully published by Cais⁵⁴ and by Harris⁵³ who used isoregic PTrFE obtained via reduction of poly(chlorotrifluoroethylene). Thus, considering the complexity of the microstructure due to chain defects and tacticity, a detailed attribution of sequences

can only be performed using advanced NMR experiments. Nevertheless, thanks to the synthesis of poly(VDF-co-TFP) and poly(TrFE-co-TFP) copolymers, a satisfactory assignment of poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymer sequences was performed and is listed in Table S1. The CF₃ groups of TFP appear at low field chemical shifts ranging between −65 and −71 ppm.³⁶ The CF₂ groups of VDF and TrFE give complex signals between −89 and −133 ppm due to adjacent TrFE CFH asymmetric carbon and the reverse additions of both VDF and TrFE (Figure 1). The poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymer microstructure is dominated by VDF–VDF head-to-tail dyads centered at −92.4 ppm⁴⁵ and VDF–TrFE dyads at *ca.* −107 ppm.⁷ Signals at *ca.* −72 ppm, assigned to the CF₃ groups of TFP, and at −95 ppm, assigned to central CF₂ groups in CH₂CF₂–CH₂CH(CF₃), indicate a majority of VDF–TFP dyads compared to TrFE–TFP dyads as expected from the initial monomer composition and their reactivity ratios. The comparison of the signals assigned to CF₂ and CFH in the ¹⁹F NMR spectra of a poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymer and a poly(VDF-co-TrFE) copolymer shows little differences (see Figure S10).

The ¹H NMR spectra (Figure 1) of the terpolymers are dominated by broad signals ranging between 5.10 and 5.95 ppm and between 2.25 and 3.39 ppm assigned to the CFH groups of the TrFE units and the CH₂ groups of the VDF units, respectively. The signals assigned to the CH₂ and CH(CF₃) of the TFP units are overlapping with the broad signal of head-to-tail VDF–VDF normal additions. Because of these broad signals and overlapping signals, an accurate microstructure study cannot be provided by ¹H NMR spectroscopy only.

In addition, the ¹H NMR spectrum (Figure 1) exhibits a signal at 3.78 ppm that was not observed in the spectra of the poly(VDF-co-TrFE) copolymers synthesized in acetonitrile, DMF or 1,1,1,3,3-pentafluorobutane (Figure S11). It was thus hypothesized that this signal centered at 3.78 ppm results from transfer reaction to DMC (Scheme 2). The syntheses of poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymers were performed in DMC regarded as a “green” solvent.⁵⁵ Asandei et al.⁵⁶ reported that the iodine transfer polymerization (ITP) of VDF

proceeded with much faster reaction rate in DMC compared to a broad range of other solvents. The authors also mentioned that DMC is prone to transfer and that the DMC radicals thus formed can reinitiate PVDF chains. It also affords good monomer and co/terpolymers solubilities leading to faster monomer diffusion into the propagating macroradical center. In the present study, the hypothesis of transfer to DMC (Scheme 2) was confirmed by HMQC and HMBC ¹H–¹³C 2D NMR experiment carried out on a PTrFE homopolymer (see Figures S13–S15) which clearly revealed a coupling between the signals at 3.78 ppm and the carbon atom of the carbonyl group of DMC. The signals at 3.78 ppm were thus assigned to the CH₃ groups of DMC molecules that have undergone hydrogen abstraction and initiated new polymer chains. The different signals observed for the CH₃ group could not be assigned to the attack of DMC radical onto VDF, TrFE or TFP as they are also observed in the ¹H NMR spectrum of PTrFE homopolymer. The CH₂ groups of the DMC that has initiated a new polymer chain (regardless of whether the initiation occurred onto a VDF, a TrFE, or a TFP monomer) could not be identified. Nevertheless, terpolymers synthesized in solution in DMC presented sufficiently high molecular weights to lead to self-standing films (Figure S2). This probable transfer to DMC was not a limitation for the present work.

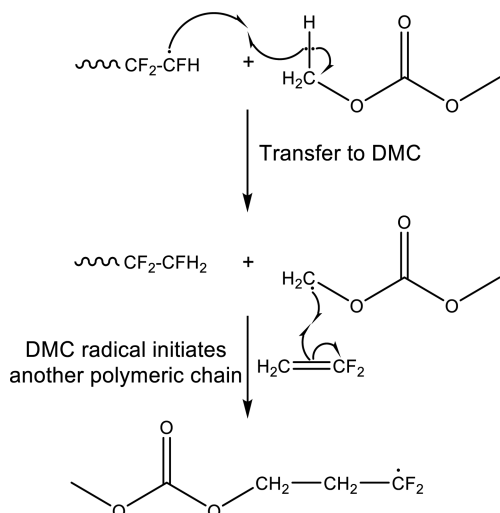
The synthesis of a short chain poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymer (run 11, Table 2) using a much higher monomer/initiator initial molar ratio, allowed the identification of the polymer chain ends. After homolytic cleavage of the peroxide bond, the peroxydicarbonate initiator can undergo a decarboxylation step. But as explained by Hirunsit and Balbuena,⁵⁷ this first radical first generated by homolytic cleavage of the peroxide bond directly initiated the polymerization and no chain ends resulting from the decarboxylation were observed (Scheme S1).^{45,58} This selectivity is reinforced by the low temperature used for the polymerization (48 °C). The presence of the carbonyl group was evidenced by the ¹H, ¹H–¹H COSY and the ¹H–¹³C HSQC 2D NMR spectra of the short chain poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymer (run 11, Table 2 and Figures S16–S21).

Heterogeneity of poly(VDF-*ter*-TrFE-*ter*-TFP) Terpolymers. The evolution of the terpolymers microstructure *versus* monomers’ conversion was examined. As VDF, TrFE, and TFP are gaseous monomers, monitoring the evolution of pressure during the reaction can bring useful information on the kinetics of the polymerization and on the terpolymer chains homogeneity.

As expected, the pressure inside the reactor decreased as the polymerization reaction proceeded. Figure 2 shows the pressure profile of three reactions with increasing TFP amounts (from 2 mol % to 8 mol %) and constant VDF/TrFE (65/35) initial molar ratio. In all cases, the pressure profile followed 3 main steps: (i) a slow pressure drop, almost negligible at the beginning of the terpolymerization, (ii) a sharp pressure drop for *ca.* 9 h, and then (iii) a stabilization at low pressure (<3 bar).

The polymerization reaction time was significantly increased from 15 to 40 h when the TFP initial amount in the monomer starting mixture was increased from 2 to 8 mol %. TFP seemed to decrease the polymerization rate in the first few hours of the polymerizations since the pressure drop was almost negligible. Moreover, the duration of this pressure plateau increased with TFP initial concentration. To understand the polymerization behavior at different sections of the pressure profile, samples of

Scheme 2. Schematic Representation of the Transfer Reaction to DMC from a Polymer Chain That Displays a TrFE Propagating Radical and of the Reinitiation from the Thereby Formed DMC Radical onto a VDF Monomer



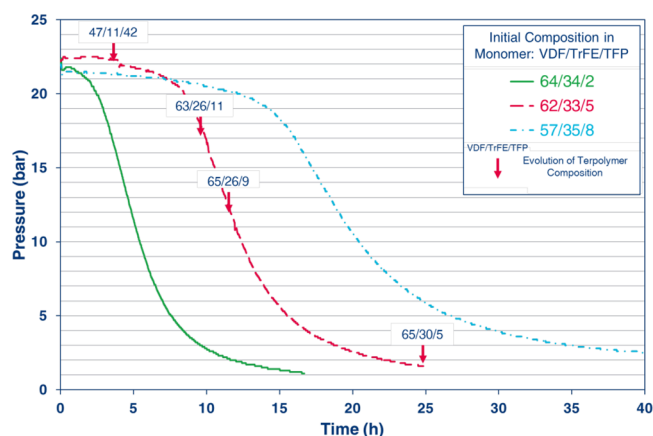


Figure 2. Pressure evolution *versus* reaction time during the radical terpolymerization of VDF, TrFE, and TFP with three different initial compositions. Arrows indicate when samples were taken off the reaction solution (at 4, 10, 12, and 25 h) to determine the terpolymer compositions by ^{19}F NMR spectroscopy.

the reaction solution (run 8, Table 2) were taken off at 4, 10, 12, and 25 h. The samples were characterized by ^{19}F NMR spectroscopy (Figure 3), and the compositions of the corresponding terpolymers were determined.

The terpolymers compositions *versus* polymerization time showed a high composition heterogeneity. Starting from a 62/33/5 VDF/TrFE/TFP initial monomer composition, the terpolymer's chains of the first sample ($t = 4$ h) contained 42

mol % of TFP and only 11 mol % of TrFE, and were totally amorphous. This is a relatively surprising result considering the low initial amount of TFP that should promote cross-propagation from TFP radical onto VDF or TrFE comonomers. Furthermore, the composition of the terpolymer chains changed dramatically in the course of the terpolymerization to reach 63/26/11 after 10 h, and a final composition of 65/30/5 when the overall monomer conversion is about 95%. TFP has thus two major effects on the terpolymerization: (i) it slows down the terpolymerization probably due to the high stability of the TFP radical, and (ii) it homopropagates preferentially even when it is only present in very small quantities (5 mol %).³⁶ This last effect is probably emphasized by a higher solubility of TFP in DMC compared to VDF and TrFE. The main consequence of these effects is that all the terpolymers synthesized in the present work exhibit pronounced composition heterogeneity.

Importantly, it is likely that this heterogeneous composition is not restricted to the case of TFP-containing terpolymers since monitoring the evolution of terpolymers' compositions with reaction time has never been reported in any other articles published so far. Indeed, such poly(VDF-*ter*-TrFE-*ter*-M) terpolymer's compositional heterogeneity has never been reported in the literature. It must also affect poly(VDF-*co*-TrFE) copolymers considering the reactivity ratios of the VDF/TrFE couple. Since the polymers' microstructure ultimately governs their electroactive properties, it is crucial to better understand and control the evolution of the composition of the polymer chains during their synthesis.

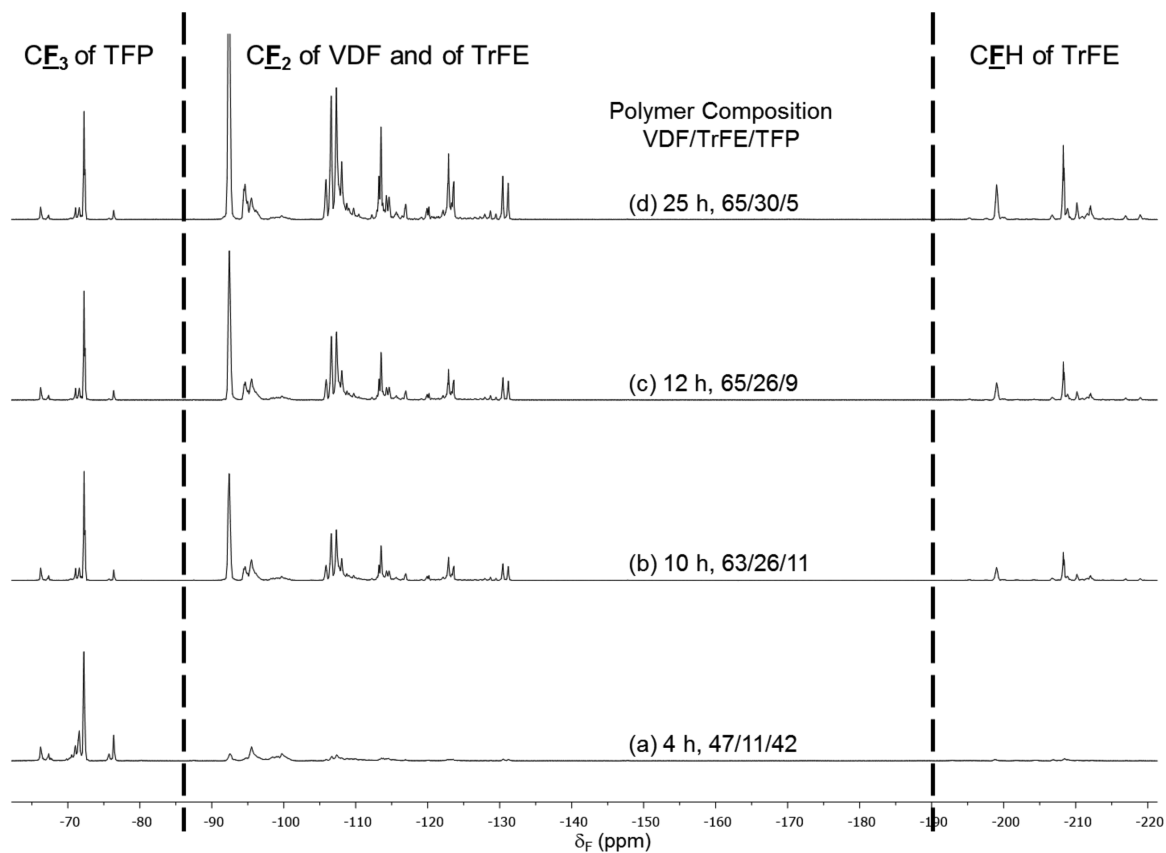


Figure 3. 376 MHz ^{19}F NMR spectra, recorded in deuterated acetone, of poly(VDF-*ter*-TrFE-*ter*-TFP) samples taken off from run 8 (Table 2) at (a) 4 h, (b) 10 h, (c) 12 h, and (d) 25 h. Initial VDF/TrFE/TFP monomer composition in mol %: 62/33/5. Terpolymer compositions in mol % of VDF/TrFE/TFP: (a) 47/11/42, (b) 63/26/11, (c) 65/26/9, and (d) 65/30/5.

The poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymers synthesized in the present study are thus in fact mixtures of terpolymers of different composition and microstructures. They most certainly contain a continuous spectrum of terpolymer composition, from terpolymers rich in TFP and VDF to terpolymers rich in TrFE and VDF but with almost no TFP. Nevertheless, the introduction of TFP units could still have an influence on the polymer crystal phase and on the crystal size, leading to modified electroactive properties compared to standard poly(VDF-*co*-TrFE) copolymers. Since previously reported terpolymers were also heterogeneous,^{29,59} the thermal and electroactive properties of the terpolymers synthesized here were also examined.

Conformation Analysis. Despite the terpolymer compositional heterogeneity, the TFP content should influence the conformation of the polymer chains in the solid state. Figure 4

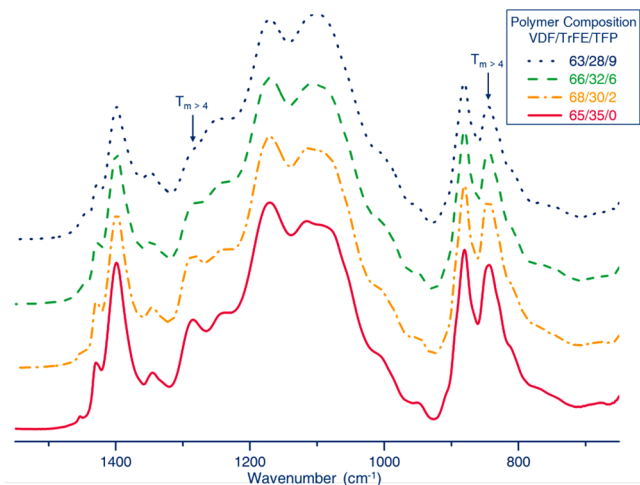


Figure 4. Expansion of the 650–1550 cm^{-1} zone of the FTIR spectra of a standard poly(VDF-*co*-TrFE) copolymer (full line) and three poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymers with increasing TFP content ranging from 2 to 9 mol % at 25 °C. Absorption bands at 1288 and 850 cm^{-1} , characteristic of the all-trans conformation of the β -phase, are highlighted with arrows.

compares the infrared spectra of several terpolymers containing a constant VDF/TrFE initial molar ratio and an increasing TFP amount. The two strong absorption bands at 1288 and 850 cm^{-1} , assigned to CF_2 vibration and CH_2 rocking modes of the all-trans conformation ($t_m > 4$) of the β -phase, decrease as the TFP content increases.^{20,29,60–62} The decrease of these absorption bands may also be related to the decrease of the overall crystallinity confirmed by DSC below (Figure 5). Thus, the change in the polymer chain conformation could not be attributed with certainty to the presence of TFP units that could create a kink along the polymer chain.³³ The presence of TFP in the blend of polymers preserved part of the all-trans conformation characteristic of the ferroelectric β -phase of poly(VDF-*co*-TrFE) copolymers. These results were consistent with the compositional heterogeneity identified above. Nevertheless, it was not possible to conclude on the influence on the chain conformation of a single TFP unit homogeneously distributed within the poly(VDF-*co*-TrFE) backbone since homogeneous poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymers could not be synthesized.

Thermal Properties of poly(VDF-*ter*-TrFE-*ter*-TFP) Terpolymers. The thermal characteristics of poly(VDF-*ter*-

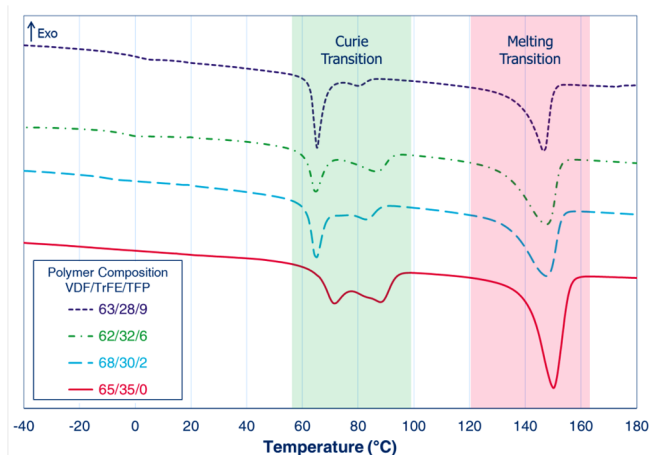


Figure 5. DSC thermograms (second heating) of a poly(VDF-*co*-TrFE) copolymer (full line) and three poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymers with increasing TFP composition ranging from 2 to 9 mol %.

TrFE-*ter*-TFP) terpolymers were studied by TGA and DSC and then compared to poly(VDF-*co*-TrFE) copolymers and poly(VDF-*ter*-TrFE-*ter*-CTFE) terpolymers.

a. Thermal Stability. The thermal stability, under air at 10 °C/min, of the fluorinated terpolymers was first studied (Figure S22). A 67/28/5 poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymer exhibited a $T_{d5\%}$ of 394 °C, compared to 414 °C for a 65/35 poly(VDF-*co*-TrFE) copolymer synthesized in similar conditions. The TFP content thus seemed to slightly decrease the thermal stability of the terpolymers due to the presence of $-\text{CH}_2\text{CH}-$ group in the polymer backbone. Increasing the TFP amount from 2 to 9 mol % did not deteriorate the thermal stability of the terpolymers. Nonetheless, these highly thermally stable terpolymers could still be easily melt-processed.⁶³

b. Thermal Transitions. Figure 5 shows the DSC thermograms of three poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymers containing similar VDF/TrFE molar ratios and increasing TFP molar amounts. All the terpolymers displayed a lower Curie temperature (*ca.* 65 °C) compared to a standard poly(VDF-*co*-TrFE) copolymer of equivalent molecular weight which exhibits a Curie temperature of *ca.* 72 °C. This might be due to the presence of smaller crystals in the terpolymers induced by defects introduced by the presence of TFP in the polymer chains.^{14,25} The double peak shape and the temperature of the Curie transition were not modified by annealing above the Curie transition (15, 45, 105, and 225 min at 125 °C) as shown in Figure S23, for films formed from the melt. As the amount of TFP increased in the polymer, the melting temperature enthalpy decreased from 21 to 11 J/g for a poly(VDF-*co*-TrFE) copolymer and a 63/28/9 poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymer, respectively (Table 2). As expected, the overall crystallinity of the polymer is thus reduced by the incorporation of bulky CF_3 side groups in the terpolymer.³¹ Besides the limited influence of TFP on the Curie temperature, the introduction of this termonomer had a significant effect on the T_g of the terpolymers. The introduction, in the amorphous phase, of polymer chains rich in TFP raised the glass transition temperature of the terpolymers from around -20 °C (for a standard poly(VDF-*co*-TrFE) copolymer) to 0 °C (for a terpolymer containing 9 mol % of TFP). As expected, the CF_3 side groups, with large van der Waals radius (2.20 Å)⁶⁴ and strong electrostatic repulsion, decreased the chain mobility. As

the T_g is characteristic of the amorphous phase of a semicrystalline polymer, TFP units thus seemed to be preferentially incorporated in the amorphous region of the terpolymer (for PTFP, $T_g = 11\text{ }^\circ\text{C}$). By extrapolating Fox's law, which was developed for polymer blends, it was possible to estimate the weight fraction of PTFP sequences in the amorphous phase. For a poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymer with a 63/28/9 molar composition, Fox's law⁶⁵ suggests that the amorphous phase contained *ca.* 65 wt % of PTFP sequences. This simple estimation method, although not strictly rigorous, appeared to be consistent with the hypothesis that terpolymers rich in TFP units were not included in the crystal phase.

The comparison of two poly(VDF-*co*-TrFE) copolymers with similar VDF/TrFE composition but with two distinct molecular weights gave unexpected results. Their melting temperatures remained identical (*ca.* 150 $^\circ\text{C}$), but their Curie temperatures increased from 72 to 92 $^\circ\text{C}$ when their molecular weights increased from 73 to 113 kg/mol (runs 4 and 5, Table 2). This molecular weight influence on the Curie transition was further confirmed in the case of a high molecular weight ($M_w = 327\text{ kg/mol}$) poly(VDF-*co*-TrFE) copolymer with equivalent VDF/TrFE ratio produced by suspension polymerization which showed a Curie temperature of *ca.* 100 $^\circ\text{C}$. Thermal and mechanical properties of polymers are often dependent on the molecular weight until they reach a plateau.⁶⁶ In the cases studied, the melting temperature had already reached its asymptotic limit, whereas the Curie transition was still strongly dependent on the polymers molecular weights.⁶⁷ This behavior might be explained by the influence of the polymer chain-ends that limit the growth of large ferroelectric domains which would require more energy to be transformed into paraelectric domains.

Polarization Curves. Figure 6 compares the D-E hysteresis curves of 20 μm films of a 65/35 poly(VDF-*co*-TrFE) copolymer and of a 61/26/13 poly(VDF-*ter*-TrFE-*ter*-CTFE) terpolymer with a 62/32/6 poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymer. The polymers were all prepared by free radical solution polymerization as detailed in the Experimental Section.

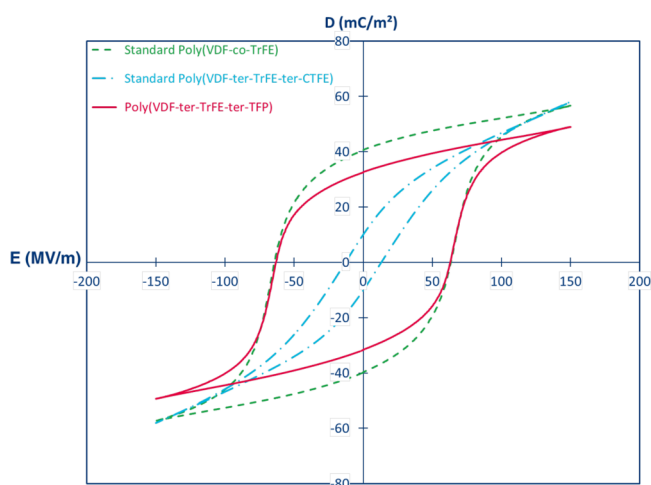


Figure 6. Comparison of continuous bipolar D-E loops for standard annealed 65/35 poly(VDF-*co*-TrFE) (dotted line) and 61/26/13 poly(VDF-*ter*-TrFE-*ter*-CTFE) (semidotted line) with a 67/38/5 poly(VDF-*ter*-TrFE-*ter*-TFP) (full line), all synthesized under the same conditions.

The poly(VDF-*ter*-TrFE-*ter*-CTFE) terpolymers exhibited the typical relaxor ferroelectric (RFE) behavior with a narrow hysteresis loop ($E_c = 13\text{ MV/m}$).⁶⁷ The poly(VDF-*co*-TrFE) and poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymers in contrast, showed wide ferroelectric (FE) hysteresis loops ($E_c = 63\text{ MV/m}$ for both polymers). The characteristic values of the polarization curves are provided in Table 3.

Table 3. Characteristic Values of Standard Poly(VDF-*co*-TrFE) Copolymer and Poly(VDF-*ter*-TrFE-*ter*-CTFE) Terpolymer Compared with a Heterogeneous Poly(VDF-*ter*-TrFE-*ter*-TFP) Terpolymer^a

	E_c (MV/m)	P_r (mC/m ²)	P_{sat} (mC/m ²)
poly(VDF- <i>co</i> -TrFE)	63	40	57
poly(VDF- <i>ter</i> -TrFE- <i>ter</i> -CTFE)	13	10	58
poly(VDF- <i>ter</i> -TrFE- <i>ter</i> -TFP)	63	33	49

^a E_c , P_r , and P_{sat} stand for coercive field, remanent polarization, and saturation polarization, respectively.

The coercive field (E_c) is characteristic of the energy required to flip the C-F dipoles of the large FE domains.^{34,35} The poly(VDF-*co*-TrFE) copolymer and the poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymer showed similar E_c . This suggests that their FE domains are similar. TFP thus seemed not to play its expected role of decreasing the crystalline domains size and limiting the cooperative effect of large FE regions. It is interesting to note that compared to the poly(VDF-*co*-TrFE) copolymer, both the remanent and saturation polarizations were decreased ($P_r = 33\text{ mC/m}^2$ and $P_{sat} = 49\text{ mC/m}^2$). This is due to the lower crystallinity of the terpolymer compared to the copolymer. D-E loops analyses thus confirmed the compositional heterogeneity of the poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymers and showed that they have the same FE behavior as poly(VDF-*co*-TrFE) copolymers.

Figure 7 compares the effect of increasing the applied electric field (E) on the D-E loops of poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymers with increasing TFP content from 2 to 9 mol %. The energy required to flip the dipoles in FE domains is indicated by the coercive field (E_c) and is related to the size of these FE domains. The saturation polarization (P_{sat}) is characteristic of the total number of dipoles that can be polarized under a given electric field whereas the remanent polarization (P_r) is related to the number of dipoles "locked" in the FE crystals.^{12,35} The all-trans conformation of the terpolymer chain in the crystals enhanced the polarization response compared to the non-organized amorphous phase. The three poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymers studied exhibited comparable high E_c (*ca.* 50–60 MV/m under 150 MV/m), which are similar to that observed for standard 65/35 poly(VDF-*co*-TrFE) copolymers (Figure 6). Both the P_{sat} (49 mC/m²) and the P_r (32 mC/m²) of 67/28/5 poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymer were higher than those observed for 63/28/9 poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymer (41 and 25 mC/m², respectively). This overall decrease of the polarization response likely originated from the lower crystallinity of 63/28/9 poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymer as seen on the DSC thermograms (Figure 5). Surprisingly, the 68/30/2 poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymer displayed an overall decreased polarization under the same electric field compared to terpolymers richer in TFP, whereas the crystallinity of this TFP-poor terpolymer remained comparable to that of 67/28/5

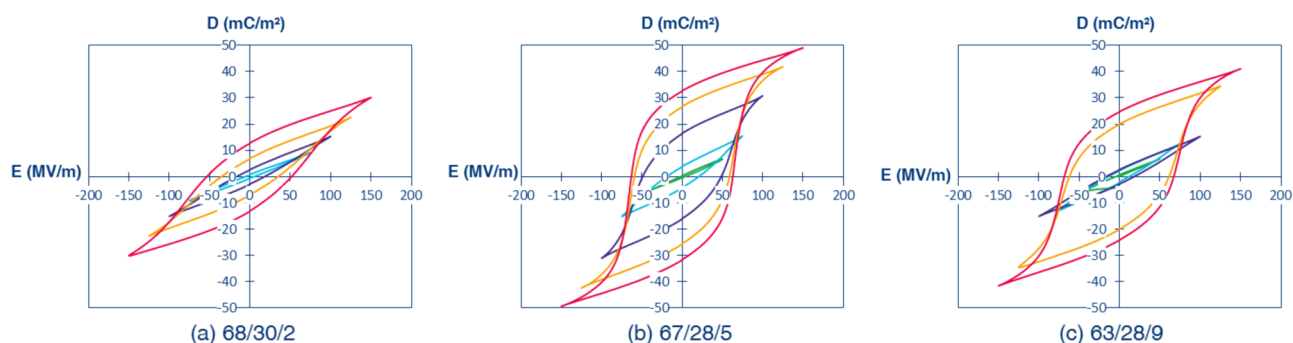


Figure 7. Comparison of continuous bipolar D–E loops for poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymers with increasing TFP content, with VDF/TrFE/TFP molar ratios of (a) 68/30/2, (b) 67/28/5, and (c) 63/28/9. The charging–discharging cycles were performed at a frequency of 0.05 Hz from gradually (step = 25 MV/m) increasing *E* from 25 to 150 MV/m.

terpolymer and higher than that of 63/28/9 terpolymer. The strong coercive field of 51 MV/m confirmed the existence of large ferroelectric domains but they did not contribute to the remanent polarization ($P_r = 12 \text{ mC/m}^2$). This surprising behavior, where only 2 mol % of TFP units completely modify the electroactivity of the terpolymer compared to poly(VDF-*co*-TrFE) copolymers, may be explained by the lower polarizability of CF_3 group of the TFP units compared to that of CFE or of CTFE units. Polarization studies at higher electric field are under investigations in our laboratory in order to understand the behavior and effect of the CF_3 groups.

CONCLUSIONS

For the first time, a new class of electroactive fluorinated poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymers was synthesized. The careful characterization of their microstructure led to the identification of a very pronounced compositional heterogeneity. 3,3,3-Trifluoropropene (TFP) was strongly incorporated in the polymer chains during the early moments of the radical terpolymerization. The resulting blend of polymers, with compositions spanning from rich TFP terpolymers to terpolymers containing almost no TFP units, has been fully characterized. These TFP units were mostly located in the amorphous phase of the terpolymer and significantly increased the T_g of the polymer synthesized. However, the presence of TFP did not modify the crystal conformations or the size of the FE domains but, surprisingly, the introduction of only 2 mol % completely modified the electroactivity of poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymer compared to poly(VDF-*co*-TrFE) copolymers. Despite the present detailed study, it is not possible to draw conclusions on the influence of TFP units homogeneously distributed along the poly(VDF-*co*-TrFE) polymer backbone. The compositional heterogeneity inherent to the monomers' reactivities has to be taken into account for the design of new fluorinated electroactive polymers and to better understand the behavior of existing terpolymers. This heterogeneity could be minimized by developing new polymerization strategies that are not yet easily accessible. Further work on the preparation of other poly(VDF-*ter*-TrFE-*ter*-M) terpolymers (where M stands for a fluorinated comonomer) is in progress in our laboratory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.5b01964.

Table of assignments of ^{19}F NMR signals for poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymers, details on the linearization methods used for the determination of the reactivity ratios in the kinetics of radical copolymerization of TrFE with TFP, photos of the solvent casting system used and poly(VDF-*ter*-TrFE-*ter*-TFP) 20 μm thick films, ^1H and ^{19}F NMR spectra of PVDF, PTrFE, PTFP, and poly(VDF-*co*-TrFE), poly(TrFE-*co*-TFP) copolymers, detailed NMR characterization of PTrFE and a low molecular weight poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymer, TGA and DSC thermograms of poly(VDF-*ter*-TrFE-*ter*-TFP) terpolymers, and a scheme showing the decomposition mechanism of peroxydicarbonate initiators. (PDF)

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Notes

The authors declare no competing financial interest.

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