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ORIGINAL ARTICLE

Vinylidene fluoride telomers for piezoelectric devices

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Original telomers based on vinylidene fluoride (VDF), $C_nF_{2n+1}(VDF)_m(CH_2CH_2)_pI$, where $n=4$ or 6, $m=5$–23 and $p=0$ or 1, were synthesized, and the piezoelectric properties of the materials were investigated. Low-molecular-weight polyvinylidene fluorides (PVDFs) were prepared in good yields by iodine transfer polymerization of VDF. The polymerization of VDF was conducted in the presence of 1-iodoperfluoroalkanes (C_4F_9I or $C_6F_{13}I$) and bis(4-*tert*-butylcyclohexyl) peroxydicarbonate, which were used as a chain transfer agent and initiator, respectively. The microstructures of VDF telomers were carefully characterized by ^1H and ^{19}F nuclear magnetic resonance (NMR) spectroscopy to assess the average molecular weights and the percentage of CH_2CF_2I functionality (that ranged from 47 to 86%). X-ray diffraction patterns of these telomers indicated that PVDFs with <7 VDF units displayed the α-form. Alternatively, telomers containing a higher amount of VDF possessed both α- and β-forms. Ethylene endcapping of $C_nF_{2n+1}(VDF)_mI$ was also successfully achieved in high yield, and the telomeric precursors were converted quantitatively. Moreover, three VDF telomers were vaporized into films, and the piezoelectric properties of the materials were assessed. The results revealed that $C_6F_{13}(VDF)_{23}I$ and $C_4F_9(VDF)_{21}I$ telomer films displayed piezoelectric responses ($d_{33}=268\,pC\,N^{-1}$) and high remanent polarizations (Pr=98.2 and 93.4 mC m^{-2}, respectively). In addition, $C_4F_9(VDF)_{21}C_2H_4I$ exhibited interesting ferroelectric properties (Pr=89.9 mC m^{-2}).
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INTRODUCTION

Polyvinylidene fluoride (PVDF) is an interesting polymer that exhibits remarkable properties. Thus, PVDF has been used in high-tech applications, such as[1–3] paints and coatings, medical suture wires, mechanical substrates for fuel cell membranes, liners for containers used to carry corrosive substances (for example, bromine), separators for lithium ion batteries and backsheets for photovoltaic cells. In addition, PVDF is a piezoelectric polymer,[4,5] and pressure or mechanical stress can induce an electrical response.

Several poly(VDF-co-TrFE) copolymers (where TrFE represents trifluoroethylene) possess piezoelectric and ferroelectric properties similar to those of $CF_3(VDF)_{13.4}C_2H_5$[6,7], $CF_3(CH_2CF_2)_{12}I$[8] or $CF_3(VDF)_{17}I$[9] telomers, which have been prepared by radical telomerization of VDF with CF_3I. However, data on the synthesis and nature of the end group ($-CH_2CF_2I$, $-CF_2CH_2I$, $-CH_2CH_2I$, $-CF_2CH_3$ or $-CH_2CH_3$) are relatively scarce. Nevertheless, in previous investigations, the radical telomerization of VDF with CF_3I has been conducted, and the products were characterized by ^{19}F nuclear magnetic resonance (NMR) and matrix-assisted laser desorption/ionization–time of flight.[10] The results revealed that $CF_3(VDF)_{11}I$ and $CF_3(VDF)_{20}I$ structures were produced, and the number of VDF units and the identity of the end groups were unambiguously determined. The radical telomerization of VDF with various chain transfer agents (CTAs) has been recently summarized.[11] Moreover, studies on the iodide transfer polymerization[12] of VDF in the presence of perfluoroalkyl iodides (R_FI)[13–16] revealed that controlled polymerization could be achieved when R_FI (CTA) possessed a CF_2I end group.

Alternatively, due to their low molecular weights and satisfactory thermal stability, VDF telomers can be evaporated without thermal decomposition. Thus, a thin film can be prepared by vacuum evaporation,[6] which is an effective method for controlling the crystalline phases and the molecular orientation of VDF telomers. Among organic ferroelectrics, $CF_3(VDF)_{17}I$ possesses a relatively high remanent polarization.[9] Furthermore, previous experiments on $CF_3(VDF)_{13.4}C_2H_5$ revealed that the piezoelectric coefficient of VDF telomers was greater than that of oligo(VDF-co-TrFE) copolymers, and a thinner and more uniform film could be obtained.[6,7]

The objective of this study was to design various VDF-based telomers, such as $C_nF_{2n+1}(VDF)_p$-$(C_2H_4)_x$-X (where $n=4$ or 6; $p=6$–23; $x=0$, 1 and $X=H$ or I), and to alter the crystallinity, ferroelectric and piezoelectrical properties by controlling the number of VDF units and end groups.

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EXPERIMENTAL PROCEDURE

Materials
Perfluorohexyl iodide and perfluorobutyl iodide (purity 99%) were kindly supplied by Atofina, France, and were treated with sodium thiosulfate, dried, and distilled before use. Bis(4-*tert*-butylcyclohexyl) peroxydicarbonate (Perkadox 16S, purity 99%) and vinylidene fluoride (VDF) were provided by Akzo Nobel, Chalons sur Marne, France and Solvay S.A., Tavaux, France, respectively, and were used as received. Acetonitrile (99%) was obtained from Aldrich Chimie, Saint Quentin-Fallavier, France, and was used without further purification.

Characterizations
Structural analyses. The composition and structure of the telomers produced by iodine transfer polymerization of VDF were determined by ^{19}F (400 MHz) and ^{1}H NMR (400 MHz) spectroscopy. NMR spectra were recorded on a Bruker AC 400 Instrument (Bruker, Wissembourg, France), and deuterated acetone and tetramethylsilane were used as the solvent and the reference, respectively. Coupling constants and chemical shifts are provided in hertz (Hz) and part per million (p.p.m.), respectively. The following experimental conditions were used to obtain the ^{1}H (or ^{19}F) NMR spectra: flip angle=90° (or 30°); acquisition time=4.5 s (or 0.7 s); pulse delay=2 s (or 2 s); number of scans=128 (or 512); pulse width=5 μs (^{19}F NMR). Infrared spectra were obtained with a Nexus-Nicolet spectrophotometer (Nexus Nicolet, Nicolet, WI, USA) between 600 and 1000 cm^{-1}, and the samples were prepared as KBr pellets. The accuracy of the measurement was ± 2 cm^{-1}. Size exclusion chromatography was performed with a Varian ProStar equipped with a refractive index detector (Varian, Oxford UK). Samples (20 mg) were dissolved in *N,N*-dimethylformamide and filtered before measurement. *N,N*-dimethylformamide at a flow of 0.8 ml min^{-1} and 25 °C was used as the eluent, and a calibration curve with five polymethyl-methacrylate standards was produced. X-ray powder diffraction patterns of the products were recorded on a X'PERT PHILIPPS II diffractometer (X'PERT PHILIPPS II, Charlotte, NC, USA) equipped with Cu Kα radiation (λ=1.540 Å) at 30 kV and Braggs angles of 10–50°.

Assessment of ferroelectric properties. Electric displacement–electric field (*D–E*) hysteresis loops of the VDF telomer films were obtained with a system used to evaluate the ferroelectrics of a material. The apparatus consisted of a current/charge-to-voltage converter (Toyo Corporation, Tokyo, Japan, Model 6252), an arbitrary waveform generator (Biomation, San Diego, CA, USA, 2414B) and an analog-to-digital converter (WaveBook 516, IOtech, Cleveland, OH, USA). All measurements were carried out under a nitrogen atmosphere at room temperature.

Determination of piezoelectric effect. The experimental apparatus used to evaluate the piezoelectricity of the samples is illustrated in Figure 1, and is identical to the device used in previous studies.[6,7] The sample was clamped between the upper and lower plates of the sample holder by four screws and an O-ring. To determine the piezoelectric coefficient along the thickness of the film, the sample was supported by the lower plate, which was made of rigid metal. A cavity was positioned between the upper plate and the sample, and a pressure sensor (Keyence Corp., Osaka, Japan, AP-43, AP-C40) and an inflator were coupled to the apparatus through the upper plate. Using an inflator, the pressure of the air in the cavity was manually varied, and the stress on the sample film was uniform. The electrodes were connected to a preamplifier (gain: 40 dB; NF Corp., Yokohama, Japan, LI-75A), and the output voltages and pressure of the sample were acquired with an oscilloscope and a pressure sensor, respectively. All measurements were carried out under air at room temperature.

Autoclave
Iodine transfer polymerizations were performed in a 160-ml Hastelloy Parr autoclave system (HC-276, Molines, IL, USA) equipped with a manometer, mechanical Hastelloy anchor, rupture disk (3000 psi), and inlet and outlet valves. An electronic device was used to regulate the stirring rate and temperature of the autoclave. Before the reaction, the autoclave was pressurized with 30 bars (430 psi) of nitrogen to identify leaks. The autoclave was conditioned for the reaction by conducting several nitrogen/vacuum cycles

(10^{-2} mbar) to remove oxygen. The liquid and dissolved solid phases were introduced via a funnel, and the gas (VDF or ethylene) was introduced by double weighing (that is, the difference between the weight of the system before and after the autoclave was filled with gas).

Iodine transfer polymerization of VDF and ethylene endcapping
Example of iodine transfer polymerization of VDF in the presence of perfluorobutyl iodide at 55 °C. To the aforementioned 160-ml Hastelloy (HC-276) autoclave, 1.24 g (3×10^{-3} mol) of bis(4-*tert*-butylcyclohexyl) peroxydicarbonate, 10.82 g (3×10^{-2} mol) of perfluorobutyl iodide and 50 ml of dried acetonitrile were added. Next, 21 g (3×10^{-1} mol) of VDF was inserted into the reaction mixture. The autoclave was progressively heated to 55 °C, and an exotherm of ~10 °C was observed, followed by an increase in pressure from 5 to 12 bars. Subsequently, a sharp decrease in pressure to 1 bar was observed. When the reaction was complete, the autoclave was placed in an ice bath for 60 min, and unreacted VDF was progressively released (VDF conversion was ~100%). When the autoclave was opened, ~62 g of a brown liquid was obtained. The crude mixture was evaporated to remove acetonitrile and was redissolved in acetone. Finally, the telomers were precipitated from pentane. A yellow powder (crude sample, 30 g) was obtained, and ^{19}F NMR (Figure 2) spectroscopy indicated that the number-average degree of polymerization (DPn) value was 12. The sample was further characterized by ^{1}H NMR and Fourier transform infrared (FT-IR) (Figure 5) spectroscopy. Next, the crude sample was dissolved in a minimal amount of acetone and was precipitated from methanol. The precipitated powder (high molecular weight) was dried under vacuum for 4 h, and a yellow powder (12 g, 96% yield) was obtained. The methanol filtrate was evaporated, and 18 g of a brown wax (low molecular
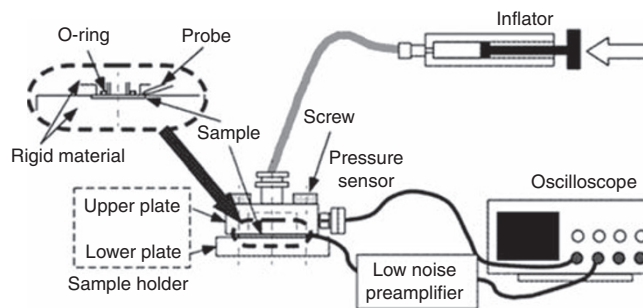

Figure 1 Schematic depiction of the experimental apparatus used to determine the piezoelectricity of the vinylidene fluoride telomers.
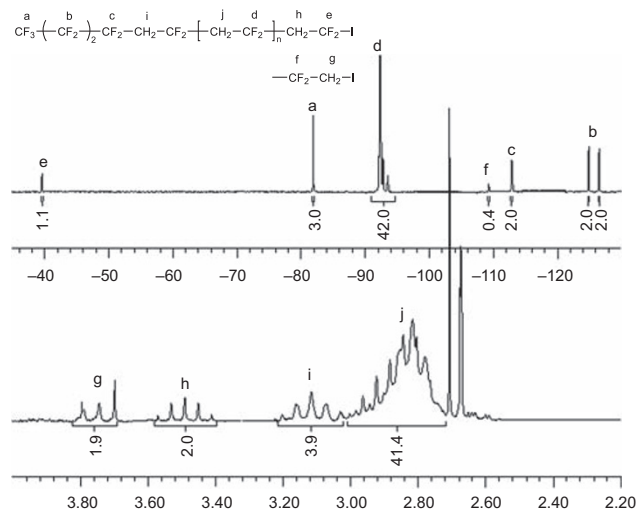

Figure 2 ^{19}F nuclear magnetic resonance (NMR) (upper spectrum) and ^{1}H (lower spectrum) NMR spectra of $C_4F_9(VDF)_{21}$-I (obtained in deuterated acetone, 400 MHz, 298K) (T1-H in Table 6).

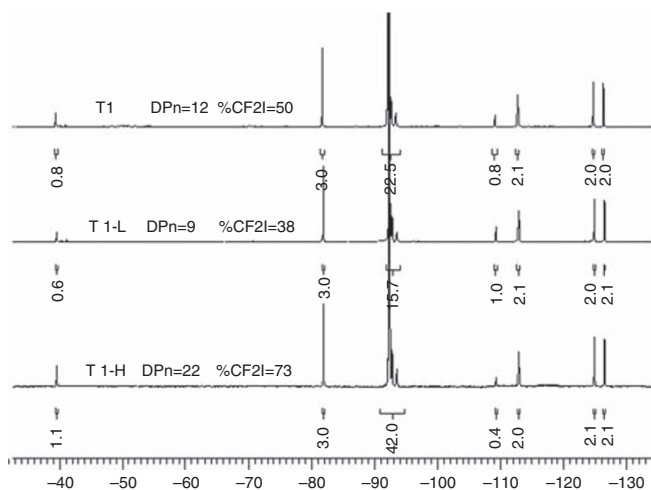**Figure 3** ^{19}F nuclear magnetic resonance (NMR) spectra of $C_4F_9(VDF)_n$-I (obtained in deuterated acetone, 400 MHz, 298 K) from T1 in Table 6 (upper spectrum, $C_4F_9(VDF)_{12}$-I), T1-L in Table 6 (middle spectrum, $C_4F_9(VDF)_9$-I), and T1-H in Table 6 (lower spectrum, $C_4F_9(VDF)_{21}$-I).
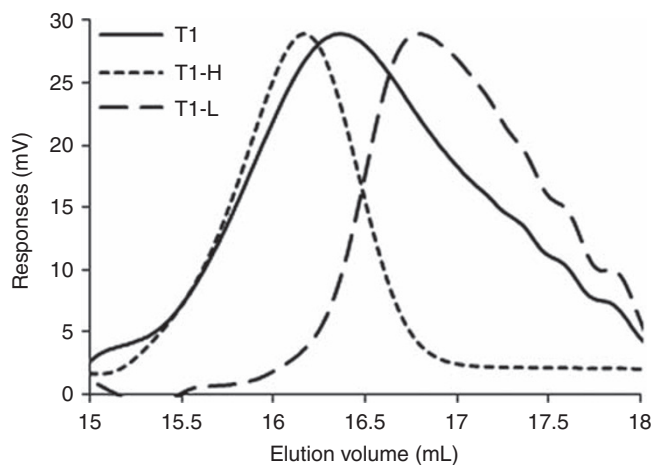

Figure 4 Size exclusion chromatograms of $C_4F_9(VDF)_n$-I (obtained in N,N-dimethylformamide (DMF), 298 K) from T1 (——, $C_4F_9(VDF)_{12}$-I), T1-H (– –, $C_4F_9(VDF)_{21}$-I) and T1-L (— —, $C_4F_9(VDF)_9$-I) in Table 6.

weight, Supplementary Figure S1) was isolated. Both fractions were characterized by ^{19}F NMR spectroscopy (Figure 3) and size exclusion chromatography, and the results revealed that the fractions displayed different DPn values (Figure 4): low-molecular-weight (L) DPn=9; high-molecular-weight (H) DPn=22.

Size exclusion chromatography was conducted in N,N-dimethylformamide, and the results confirmed that the two populations were completely separated. As a result, the polydispersity index of the material decreased (Figure 4). The same synthetic procedure was used for the iodine transfer polymerization of VDF with perfluorohexyl iodide. The NMR characteristics of the samples in deuterated acetone are reported in Tables 1 and 2.

The FT-IR characteristics of the samples (as KBr pellets) are reported in Table 3.

Example of ethylenation of PVDF-I at 55 °C. The same autoclave used in the iodine transfer polymerization of VDF was used to ethylenate the telomers. Under vacuum, 1.220 g (3×10^{-3} mol) of bis(4-*tert*-butylcyclohexyl) peroxydicarbonate, 6.12 g (4×10^{-3} mol) of C_4F_9-(VDF)$_{21}$-I and 50 ml of dried acetonitrile were transferred into the autoclave. Next, 1 g (3×10^{-2} mol) of CH_2=CH_2 was introduced into the reaction mixture, and the pressure was decreased from

Table 1 Assignments of ^{19}F NMR chemical shifts in poly(VDF)-I obtained by iodine transfer polymerization of VDF in the presence of C_4F_9I ([VDF]$_0$/[C_4F_9I]$_0$/[initiator]$_0$=100/10/1), T=55 °C; t=4 h; initiator: bis(4-*tert*-butylcyclohexyl) peroxydicarbonate

δ (p.p.m.)	Assignment
−39.0	$-CH_2-CF_2I$
−82.0	CF_3-CF_2-
−92.0	$-CH_2-CF_2-CH_2-CF_2-$
−109.0	$-CF_2-CF_2-CH_2-I$
−112.0	$-CF_2-CF_2-CH_2-CF_2-$
−124.0	$CF_3-CF_2-CF_2-CF_2$
−126.0	CF_3-CF_2-

Abbreviations: NMR, nuclear magnetic resonance; VDF, vinylidene fluoride.

Table 2 Assignments of ^{1}H NMR chemical shifts in poly(VDF)-I obtained by iodine transfer polymerization of VDF in the presence of C_4F_9I ([VDF]$_0$/[C_4F_9I]$_0$/[initiator]$_0$=100/10/1), T=55 °C; t=4 h; initiator: bis(4-*tert*-butylcyclohexyl) peroxydicarbonate

δ (p.p.m.)	Assignment
3.75	$-CF_2-CF_2-CH_2-I$
3.50	$-CH_2-CF_2I$
3.30	$-CF_2-CF_2-CH_2-CF_2-CH_2-CF_2-$
2.80	$-CH_2-CF_2-CH_2-CF_2-$
2.3–2.4 (absent)	$-CF_2-CH_2-CH_2-CF_2-$

Abbreviations: NMR, nuclear magnetic resonance; VDF, vinylidene fluoride.

Table 3 Assignments of FT-IR frequencies in $R_F(VDF)_m$-I obtained by iodine transfer polymerization of VDF in the presence of C_4F_9I ([VDF]$_0$/[C_4F_9I]$_0$/[initiator]$_0$=100/10/1), T=55 °C; t=4 h; initiator: bis(4-*tert*-butylcyclohexyl) peroxydicarbonate

v (cm^{-1})	Assignment
2900	C–H stretching
1400	C–H bending
1180–1140	C–H rocking/C–F stretching
870	C–H wagging
830	C–F bending
770	α-form
810	α-form
830	β-form
920	α-form

Abbreviations: FT-IR, Fourier transform infrared; NMR, nuclear magnetic resonance; VDF, vinylidene fluoride.

10 to 4 bars. Subsequently, the pressure remained constant over time, and the mixture was stirred at 55 °C for 14 h. Upon completion, the sample was evaporated to remove acetonitrile and was dissolved in acetone. The crude mixture was precipitated from cold pentane to obtain a yellow powder in 81% yield (6.05 g). Quantitative conversion of C_4F_9-(VDF)$_{21}$-I was achieved, as evidenced by ^{1}H and ^{19}F NMR spectroscopy (Supplementary Figures S2 and S3). The NMR characteristics of the samples in deuterated acetone are reported in Tables 4 and 5.

Preparation of thin films. VDF telomers and the top and bottom aluminum (Al) electrodes were evaporated through a shadow mask onto a quartz substrate to determine the ferroelectric and piezoelectric properties of the materials. The shape of the sample was identical to that described in previous studies.[6,7] During the deposition process, the temperature of the substrate was maintained

Table 4 Assignments of ^{19}F NMR chemical shifts in $R_F(VDF)_m$–CH_2CH_2–I obtained by ethylene endcapping of $C_4F_9(VDF)_{21}$I ([ethylene]$_0$/[$C_4F_9(VDF)_{21}$I]$_0$/[initiator]$_0$=10/1.33/1), T=55 °C; t=24 h

δ (p.p.m.)	Assignment
−82.0	CF_3–CF_2–
−92.0	–CH_2–CF_2–CH_2–CF_2– and –CH_2–CF_2–CH_2–CH_2I
−109.0	–CF_2–CF_2–CH_2–I
−112.0	–CF_2–CF_2–$(CH_2$–$CF_2)_n$–
−124.0	CF_3–CF_2–CF_2–CF_2
−126.0	CF_3–CF_2–

Abbreviations: NMR, nuclear magnetic resonance; VDF, vinylidene fluoride.

Table 5 Assignments of ^{1}H NMR chemical shifts in $R_F(VDF)_m$–CH_2CH_2–I obtained by ethylene endcapping of $C_4F_9(VDF)_{21}$I ([ethylene]$_0$/[$C_4F_9(VDF)_{21}$I]$_0$/[initiator]$_0$=10/1.33/1), T=55 °C; t=24 h

δ (p.p.m.)	Assignment
3.9	–CF_2–CH_2–I
3.3–3.5	–CH_2–CF_2–CH_2–CH_2–I
3.3	–CF_2–CF_2–CH_2–CF_2–
2.9–3.0	–CH_2–CF_2–CH_2–CF_2–
2.3	–CH_2–CF_2–CH_2–CH_2–I

Abbreviations: NMR, nuclear magnetic resonance; VDF, vinylidene fluoride.

at 123 K under a vacuum of 10^{-5} Pa to ensure that the VDF telomers were in a ferroelectric state (form I) and that the axis of the molecular chain was oriented parallel to the substrate.[8,9] The thickness of the VDF telomer and the Al electrodes was controlled at 300 and 50 nm, respectively. Stacks of Al/VDF telomer/Al acted as the capacitor, and the charge was proportional to the stress applied to the film.

RESULTS AND DISCUSSION

Mechanism of iodine transfer polymerization

Iodine transfer polymerization[12] of VDF is a degenerative transfer process[13–16] that requires an alkyl iodide as the CTA. In this study, 1-iodoperfluoroalkane (perfluorobutyl or perfluorohexyl iodide) was used as the CTA. As shown in previous investigations, macromolecular chains that undergo a transfer reaction can participate in further reactions because –CF_2I bonds are rather weak (its dissociation energy is about 45 kJ mol^{-1}). The overall reaction sequence is shown in Scheme 1.

Scheme 2 depicts the iodine transfer polymerization of the monomer (M) with a 1-iodoperfluoroalkane and bis(4-tert-butylcyclohexyl) peroxydicarbonate, which was used as an initiator. To our knowledge, bis(4-tert-butylcyclohexyl) peroxydicarbonate has not been previously used as an initiator in the iodine transfer polymerization of VDF.

In the initiation step, radicals are generated by the thermal decomposition[17–19] of a conventional initiator, such as bis(4-tert-butylcyclohexyl) peroxydicarbonate (step a). For a temperature below 90 °C (in this article), the carbonyloxy intermediate radical does not undergo any decarboxylation.[17–19] Next, the generated radicals react with the CTA to form $R_F^{°}$+ Am-I (step b), which can undergo propagation, as shown in step b. The exchange of iodine from the transfer agent (R_FI) to the propagating radical ($P_n^{°}$) results in the formation of polymeric alkyl iodides with an oligo(VDF) chain (P_n-I)

$$C_nF_{2n+1}I + {}_m H_2C = CF_2 \xrightarrow{\text{Rad.}} C_nF_{2n+1}\left[\!\!\left[CH_2CF_2\right]\!\!\right]_m I$$
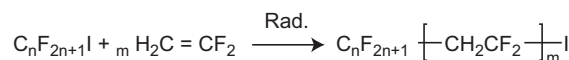
Scheme 1 Iodine transfer polymerization of vinylidene fluoride (VDF) with C_nF_{2n+1}I (n=4 or 6).

and a new initiating radical (R$^{°}$, step c). Significant differences in the stability of the reactants and products involved in step d can shift the equilibrium to the right or the left. Therefore, when the structure of R_F closely resembles the structure of the propagating radical, the transfer step is thermodynamically neutral. Thus, the exchange process described in step d is thermodynamically neutral because propagating P_n and P_m chains are identical. In step d, dormant and living species are in equilibrium. As a result, the reaction may display a *pseudo*living behavior.[12–16] As in any radical-based process, termination occurs through the coupling of VDF macroradicals (step e), as reported by Timmerman and Greyson.[20] However, to preserve living or controlled behavior, termination must be negligible compared with chain transfer. Thus, two key parameters must be considered:

- The concentration of the initiator must be minimized to avoid the accumulation of dormant (or dead) chains (by direct oligomerization of the radical initiator onto VDF). However, a sufficient amount of initiator must be present to initiate the polymerization.
- The concentration of CTA can be used to control the molar mass of the polymers. If complete conversion of the CTA is achieved, the theoretical DPn can be determined from Equation (1):
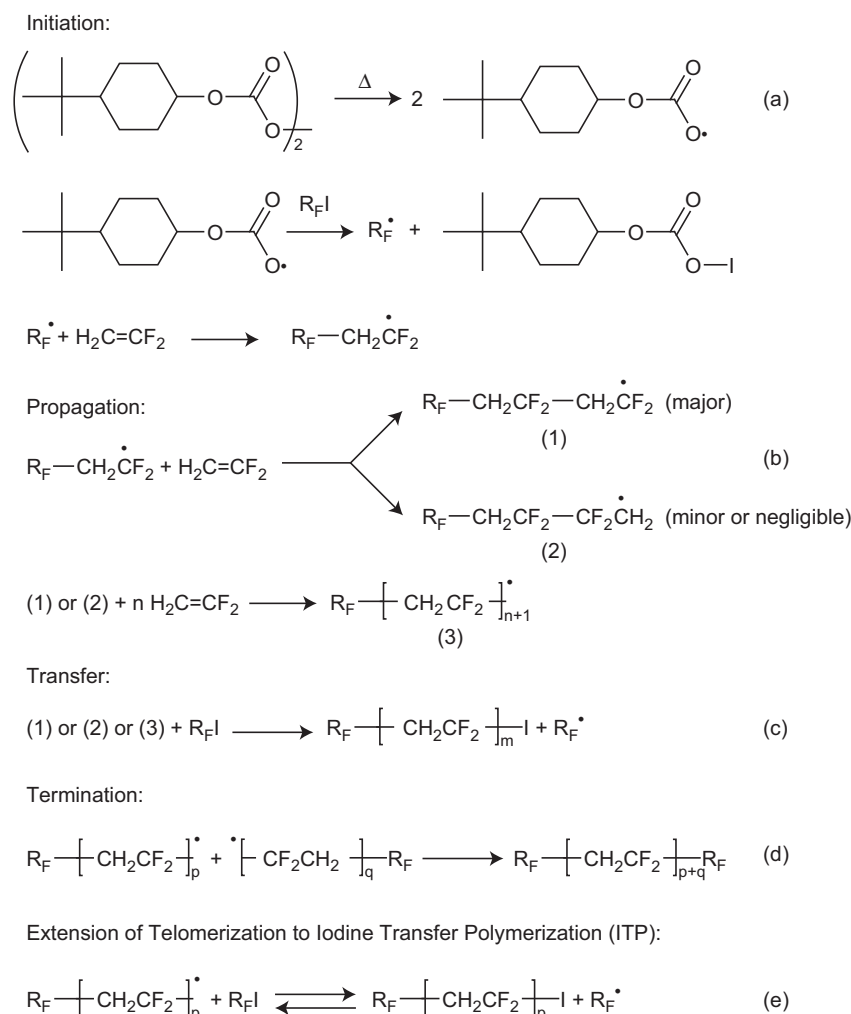
$$DPn = \frac{\alpha_{VDF}[VDF]_0}{[CTA]_0} \tag{1}$$

where $[VDF]_0$, $[CTA]_0$ and α_{VDF} are the monomer and CTA concentration in the feed, and the conversion of VDF, respectively. However, if the transfer constant to C_nF_{2n+1}I is high (C_T=7 at 74 °C),[14] the direct initiation of radicals onto VDF (oligomerization of VDF) does not occur. For instance, the transfer constant to methanol in the telomerization of VDF with methanol was 8×10^{-3} at 140 °C,[21] and thus direct initiation onto VDF was observed.

Results

Iodine transfer polymerization of VDF and ethylenation were initiated by bis(4-tert-butylcyclohexyl) peroxydicarbonate at 55 °C for 4 and 24 h, respectively. The purified telomers were characterized by ^{19}F, ^{1}H NMR and FT-IR spectroscopy.

Characterization of telomers produced by iodine transfer polymerization of VDF with C_4F_9I or C_6F_{13}I. As expected, a multiplet centered at −60.0 p.p.m. was not observed in the ^{19}F NMR spectrum (Figure 2, upper spectrum) of the telomer, indicating that the −CF_2CF_2I group of R_FI underwent a high field shift to −112.0 p.p.m. Moreover, the characteristic signals of C_3F_7 (or C_5F_{11}) end groups[13–16,22] were observed in the spectra. Namely, the peaks centered at −82.0, −124.0, −126.0 (and −128.0 p.p.m.) were assigned to CF_3 and CF_2 groups, respectively. Alternatively, the major signal centered at −92.0 p.p.m. was attributed to difluoromethylene groups –CH_2**CF_2**–CH_2CF_2–, which were formed via normal head-to-tail VDF linkages.[10,13–16,21–23]

The multiplet centered at −38 p.p.m. was indicative of –CH_2CF_2I end groups,[10,13–16,22] and the signal at −108.0 p.p.m. was attributed to difluoromethylene in –CH_2CF_2–C**F_2**CH_2I, which arise from reverse addition followed by a chain transfer.

Initiation:

(a)

(b)

(1) or (2) + n H$_2$C=CF$_2$ $\longrightarrow$ R$_F$$-\left[\text{CH}_2\text{CF}_2\right]_{n+1}^{\bullet}$

(3)

Transfer:

(1) or (2) or (3) + R$_F$I $\longrightarrow$ R$_F$$-\left[\text{CH}_2\text{CF}_2\right]_m$$-$I + R$_F^{\bullet}$ (c)

Termination:

R$_F$$-\left[\text{CH}_2\text{CF}_2\right]_p^{\bullet}$ + $^{\bullet}\left[\text{CF}_2\text{CH}_2\right]_q$$-R_F$ $\longrightarrow$ R$_F$$-\left[\text{CH}_2\text{CF}_2\right]_{p+q}R_F$ (d)

Extension of Telomerization to Iodine Transfer Polymerization (ITP):

R$_F$$-\left[\text{CH}_2\text{CF}_2\right]_p^{\bullet}$ + R$_F$I $\rightleftarrows$ R$_F$$-\left[\text{CH}_2\text{CF}_2\right]_p$$-$I + R$_F^{\bullet}$ (e)

Scheme 2 Elementary steps in the iodine transfer polymerization of vinylidene fluoride. R$_F$I and *t*-butylcyclohexylperoxydicarbonate were used as the chain transfer agent and initiator, respectively.

Surprisingly, multiplets centered at -113.0 and -116.0 p.p.m., which correspond to the difluoromethylene groups in $-$CH$_2$**CF$_2$**$-$**CF$_2$**CH$_2$$-CH_2CF_2$$-$ and are derived from reverse head-to-head addition, were not observed in the ^{19}F NMR spectrum. However, peaks derived from reverse head-to-head linkages are usually observed in VDF-based telomers,[21] oligomers[23] and copolymers.[2,3,24] Nevertheless, in the iodine transfer polymerization of VDF in the presence of C$_6$F$_{13}$I or C$_6$F$_{13}$CH$_2$CF$_2$I, reverse head-to-head additions were not observed.[13,14]

The ^{1}H NMR spectrum of the telomer (Figure 2, lower spectrum) was in agreement with the results of ^{19}F NMR spectroscopy. For instance, the methylene groups located between the difluoromethylenes produced a quintet centered at 2.80 p.p.m.,[10,13,14,21–23] and the signals centered at 3.20, 3.50 and 3.80 p.p.m. were attributed to the methylene groups in R$_F$CH$_2$$-$, $-$(VDF)$_n$$-CH_2CF_2$I and $-$CF$_2$CH$_2$I, respectively.[13] The absence of signals centered at 2.3–2.4 p.p.m. (which can be attributed to $-$CF$_2$**CH$_2$**$-$**CH$_2$**CF$_2$$-$ reverse tail-to-tail additions) suggested that the iodine transfer polymerization of VDF was a well-controlled process.[13–16]

DPn values can be determined from the ^{19}F NMR spectrum (Figure 2) by calculating the ratio of the integrals of the CF$_2$ signals of PVDF, which are centered at -91.0, -38.0 and -109.0 p.p.m., to the integral of the CF$_3$ end group, which is centered at -82.0 p.p.m. (Equation 2).

$$\text{DPn} = \frac{\frac{\text{CF}_2^{-92.0\,\text{p.p.m.}}}{2} + \frac{\text{CF}_2^{-38.0\,\text{p.p.m.}}}{2} + \frac{\text{CF}_2^{-108.0\,\text{p.p.m.}}}{2}}{\frac{\text{CF}_3^{-82.0\,\text{p.p.m.}}}{3}} \quad (2)$$

According to Equation (3), the percentage of $-$CF$_2$I and $-$CF$_2$CH$_2$I end groups can be determined via NMR from the integrals of the characteristic signals in NMR spectra:

$$\text{Percentage of} -\text{CH}_2\text{CF}_2\text{I funtionality} = \frac{\text{CF}_2^{-38.0\,\text{p.p.m.}}}{\text{CF}_2^{-38.0\,\text{p.p.m.}} + \text{CF}_2^{-108.0\,\text{p.p.m.}}} \times 100 \quad (3)$$

The DPn values and polydispersity indices were deduced by size exclusion chromatography (Figure 4). The chromatograms were assigned to the entire product mixture and the separation of the crude sample into two fractions with high and low molecular weights. Narrow polydispersity indices (approximately 1.5–1.7) were obtained, indicating that the reaction was a controlled process.

The telomers were characterized by NMR, and the results indicated that the CTA (R$_F$I) did not have an effect on the DPn. Moreover,

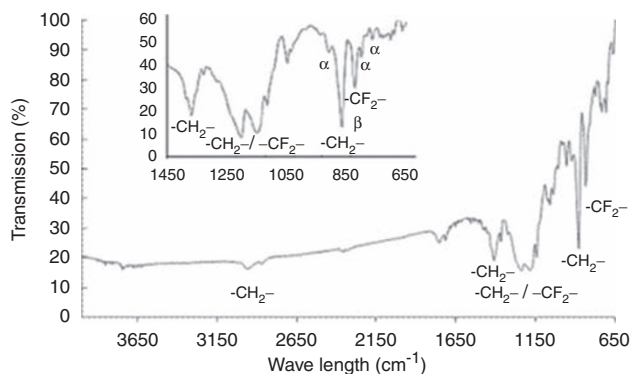**Figure 5** Fourier transform infrared (FT-IR) spectrum (between 4000 and 650 cm^{-1}) of C_4F_9-(VDF)$_{21}$-I, which was obtained by the iodine transfer polymerization of vinylidene fluoride (VDF) with C_4F_9I (from T1-H in Table 6).
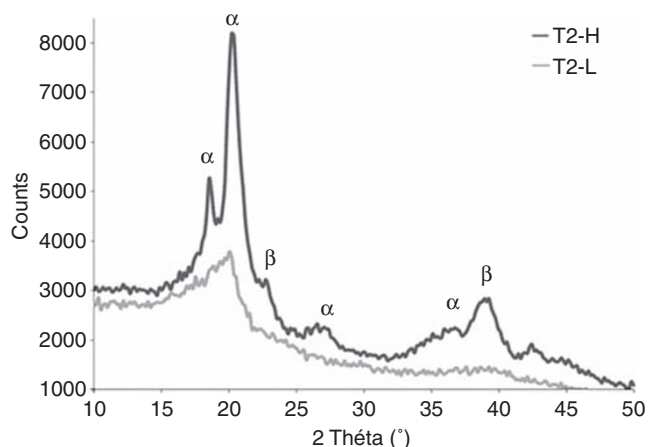

Figure 6 X-ray diffraction patterns of C_6F_{13}(VDF)$_{23}I$ (T2-H in Table 6, upper spectrum) and C_6F_{13}(VDF)$_6$-I (T2-L in Table 6, lower spectrum).

satisfactory agreement between the experimental and theoretical DPn values was obtained. However, in this study, the percentage of –CH$_2$CF$_2$I functional groups was lower than those obtained in previous studies,[13–16] which suggested that superior control can be achieved by applying tertiobutylperoxy pivalate as an initiator. Moreover, the cyclohexyl ring of bis(4-*tert*-butylcyclohexyl) peroxydicarbonate was not altered during the reaction; thus, the decomposition of the initiator may affect the polymerization results.

The results of FT-IR spectroscopy confirmed that C–C (2900 cm^{-1}), C–F (830 cm^{-1}) and C–H (1400 cm^{-1}) bonds (Figure 5) were the main functional groups present in the telomer. However, C–I bonds could not be observed in the spectra because the wavelength of the C–I bond is located at 500 cm^{-1}.

Korlacki et al.[25] characterized VDF telomers by IR at wavenumbers between 1200 and 600 cm^{-1}, and determined the crystallinity of the material by X-ray diffraction (Figure 6). Namely, two crystalline forms (α and β)[25–27] can be identified via FT-IR.

The characteristics of VDF telomers produced by iodine transfer polymerization are summarized in Table 6. The results suggest that the CTA has a minor effect on the DPn, the functional end group ratio and the crystalline form of the material. Alternatively, the chain length of the telomer has a significant effect on the crystallinity of the polymer. Namely, when the DPn ⩽7, low-molecular-weight telomers only displayed the α-form. However, when the DPn was >7, low-molecular-weight telomers displayed both the α- and β-form (Figure 6), which is in agreement with the results of Korlacki et al.[25]

*Ethylenation.* Ethylenation of 1-iodoperfluoroalkanes has been studied extensively[11] and has been achieved under a variety of conditions. For instance, ethylenation has been conducted thermally,[28–32] photochemically,[33] in the presence of copper salts or other metallic salts,[28, 32–40] and with radical initiators.[29–43] In this study, ethylenation was conducted according to a radical pathway, and a peroxide initiator was used (Scheme 3). In addition, ethylene-containing PVDF-Is were characterized by ^{19}F and ^{1}H NMR spectroscopy (Figures 7 and 8).

To achieve ethylenation, the reaction time was extended to 15 h to obtain an optimal yield, and the product was isolated by precipitation. A 10% initial (initiator)$_o$/(ethylene)$_o$ molar ratio was necessary to

Table 6 Experimental conditions of iodine transfer polymerization of VDF in the presence $C_6F_{13}I$ and C_4F_9I and results on DPn, microstructure, end groups and crystalline form

Run no.	R_FI	Molar ratio [VDF]$_o$/[R$_F$I]$_o$/[initiator]$_o$	Ti (°C)	Targeted DPn	Exp. DPn	PDI	–CF$_2$I end group (%)	α$_{VDF}$ (%)	Yield (%)	Crystalline forms
T1	C_4F_9I	10.0:1.0:0.5	55	10	12	1.7	50	100	96	α, β
T1-H	—	—	—	—	21	1.2	73	100	38	α, β
T1-L	—	—	—	—	9	1.1	38	100	58	α
T2	$C_6F_{13}I$	10.0:1.0:0.5	55	10	11	1.5	61	100	97	α, β
T2-H	—	—	—	—	23	1.1	61	100	29	α, β
T2-L	—	—	—	—	6	1.1	62	100	68	α

Abbreviations: Exp. DPn, experimental number-average degree of polymerization; PDI, polydispersity index measured by size exclusion chromatography with polymethylmethacrylate standards; VDF, vinylidene fluoride; yield, yield after fractionation of the telomers compared with initial reactant quantities introduced in autoclave; α$_{VDF}$, conversion based on the consumption of gaseous monomer. Initiator: *t*-butylcyclohexylperoxydicarbonate.
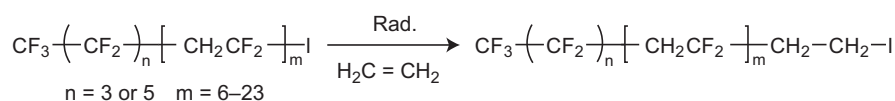
Scheme 3 Radical ethylenation of R$_F$(VDF)$_m$-I telomers.

favor the quantitative conversion of $R_F(VDF)_mI$. As a result, the conversion rate obtained in this study was higher than the rates obtained by Balague *et al.*[22] and Manseri *et al.*[28] Table 7 summarizes the experimental conditions and results of the reactions.
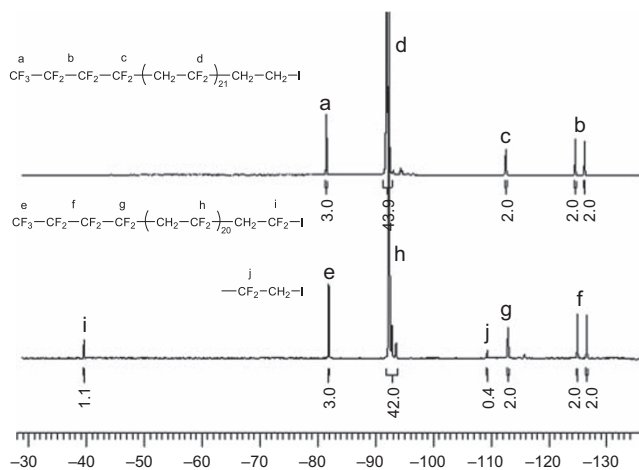

Figure 7 ^{19}F nuclear magnetic resonance spectra of $C_4F_9(VDF)_{21}I$ (T1-H in Table 6, lower spectrum) and $C_4F_9(VDF)_{21}-CH_2CH_2I$ (E1 in Table 7, upper spectrum) (recorded in deuterated acetone, 400 MHz, 298 K).
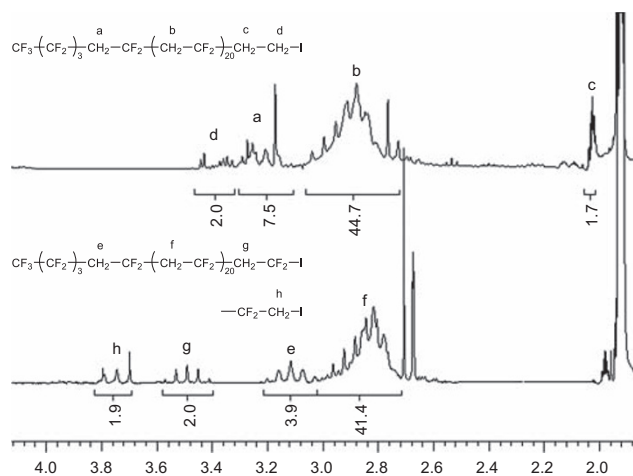
Figure 8 1H nuclear magnetic resonance spectra of $C_4F_9(VDF)_{21}I$ (T1-H in Table 6, lower spectrum) and $C_4F_9(VDF)_{21}-CH_2CH_2I$ (E1 in Table 7, upper spectrum) (recorded in deuterated acetone, 400 MHz, 298 K).

After ethylenation and purification, $R_F(VDF)_nCH_2CH_2I$ endcapped telomers were characterized by ^1H and ^{19}F NMR spectroscopy. The ^{19}F NMR spectrum of the telomers indicated that $-CF_2I$ end groups (-39 p.p.m.) were not present in the product. Moreover, the peak at -39 p.p.m., which was assigned to the difluoromethylene groups in $-CH_2\mathbf{CF_2}I$ shifted to -92.0 p.p.m., assigned to $-CH_2\mathbf{CF_2}CH_2CH_2I$. In addition, the signals centered at -92, -82 and -112 to -126 p.p.m. were attributed to VDF units and C_nF_{2n+1} end groups, respectively.

C–I bonds in $-CF_2CH_2I$ are usually less reactive than the C–I bonds in $-CH_2CF_2I$ toward alkenes or unsaturated reactants.[13] Consequently, ethylenation should occur selectively on $-CH_2CF_2I$. Interestingly, in this study, a large excess of ethylene and high initiator concentrations were used, and the successful ethylene endcapping of $R_F(VDF)_{m-1}CF_2CH_2I$ isomer was achieved. Ethylene endcapping of $R_F-(VDF)_m-I$ enables the material to be used for the synthesis of fluorinated alcohols, amines, mercaptans and carboxylic acids.[11]

Remanent polarization of evaporated films of VDF-based telomers. The ferroelectric properties of Al/VDF telomers/Al capacitors with $C_6F_{13}(VDF)_{23}I$, $C_4F_9(VDF)_{21}I$ and $C_4F_9(VDF)_{21}CH_2CH_2I$ films were determined via *D–E* hysteresis loops, which were obtained by measuring the electric displacement versus the electric field. All of the VDF telomer films showed clear hysteresis loops under a triangular electric field of 100 Hz. Figure 9 displays the *D–E* hysteresis loop of the Al/$C_6F_{13}(VDF)_{23}I$/Al capacitor, and Table 8 summarizes the remanent polarization values (P_r), which were estimated from the *D–E* hysteresis loop of the samples. The results indicated that the P_r values of all of the samples were similar (~ 100 mC m^{-2}); however, P_r values obtained in this study were lower than those observed in a previous study on $CF_3(VDF)_{17}I$ (130 mC m^{-2}).[6] The relatively low P_r values observed in the current investigation may be due to the differences in the terminal chain length of R_F (C_nF_{2n+1}) groups, which are bulkier than CF_3 and do not contribute to polarization reversal.

Piezoelectric properties of evaporated films of VDF-based telomers. The piezoelectric properties of the evaporated films of $C_6F_{13}(VDF)_{23}I$ were determined, and the piezoelectric response of the telomer film is shown in Figure 10. The data clearly indicate that the material produced in this study displays a piezoelectric response. The piezoelectric coefficient of the material determines the relationship between the mechanical input and the electrical output. Moreover, the film displays different piezoelectric coefficients, depending on the direction of the material. Thus, because the VDF telomers were glued to a glass plate, the output charge of the sample was a combination of piezoelectric coefficients along each direction of the film. However, because the sample deforms on a rigid substrate, the contribution of sample

Table 7 Experimental conditions and results of the ethylenation of $R_F(VDF)_m$-I, conversions of $R_F(VDF)_m$-I ($\alpha_{RF(VDF)m-I}$) and yields of $R_F(VDF)_m$–C_2H_4–I

Run no.	R_F of $R_F(VDF)_m$-I	*m*-value in $R_F(VDF)_m$-I	Molar ratio $[C_2H_4]_0/$ $[R_FI]_0/[initiator]_0$	T (°C)	Conversion of $R_F(VDF)_m$-I (%)	Yield (%)
E1	C_4F_9	21	10.0:1.0:1.0	55	100	81
E2	C_4F_9	9	10.0:1.0:1.0	55	100	85
E3	C_6F_{13}	23	10.0:1.0:1.0	55	100	83
E4	C_6F_{13}	11	10.0:1.0:1.0	55	100	88
E5	C_6F_{13}	6	10.0:1.0:1.0	55	100	82

Abbreviation: VDF, vinylidene fluoride.
Initiator: bis(4-*tert*-butylcyclohexyl) peroxydicarbonate.
Conversion of $R_F(VDF)_m$-I: conversion based on the consumption of solid telomers (from integral of chemical shift at -39.0 p.p.m. to that of -82.0 p.p.m. in the ^{19}F NMR spectrum).
Yield: massic yield after precipitation of the telomer compared with initial reactant quantities.
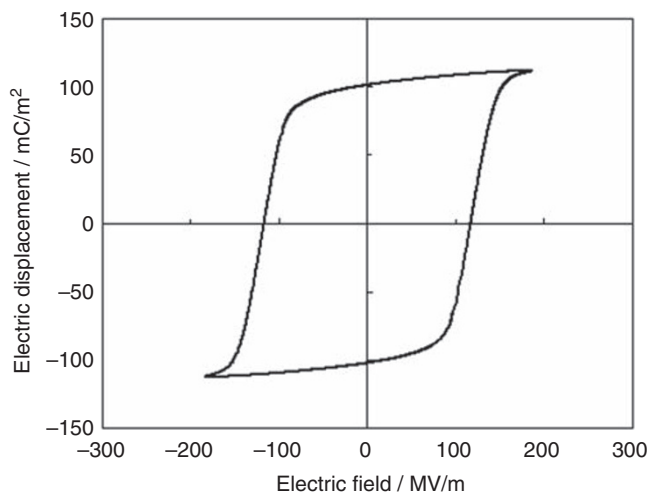
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Figure 9 D–E hysteresis curves of $C_6F_{13}(VDF)_{23}I$ telomer films with a 300 nm thickness.

Table 8 Values of the remanent polarizations (P_r) of VDF telomers calculated from electric measurements

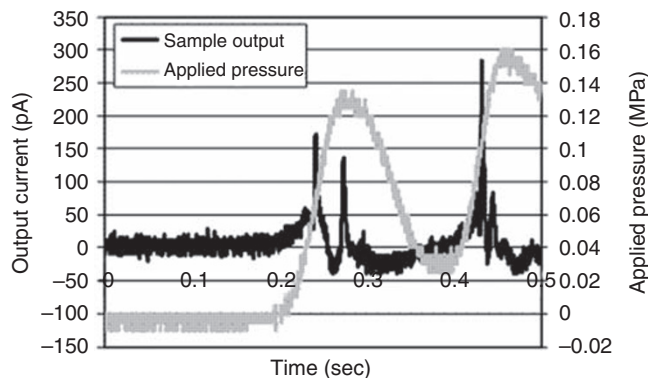| Sample	P_r (mC m^{-2})
$C_6F_{13}(VDF)_{23}I$	98.2
$C_4F_9(VDF)_{21}I$	93.4
$C_4F_9(VDF)_{21}CH_2CH_2I$	89.9

Abbreviation: VDF, vinylidene fluoride.

Figure 10 Representative sample output or piezoelectric response (black line) of $C_6F_{13}(VDF)_{23}I$ telomers when cyclic pressure was applied (gray line).

bending (namely, elongation and compression along the surface) to the piezoelectric response can be neglected. Therefore, the output current of a ferroelectric material (I) can be written as follows:[6,8]

$$I = A.d_{33}.\frac{d\sigma}{dt} \tag{4}$$

where A, d_{33} and σ are the area of overlap between the two electrodes, the piezoelectric coefficient of the material in the direction of the thickness and the applied stress, respectively. The output current is proportional to the applied stress rate ($d\sigma/dt$), and the relationship between the stress rate ($d\sigma/dt$) and the output current (I) is shown in Figure 11, along with the linear least square fit of the experimental data to Equation (4). As shown in the figure, the stress rate and output current of the samples were measured and averaged every 16 ms. The fit of Equation (4) to the experimental data formed a straight line, the
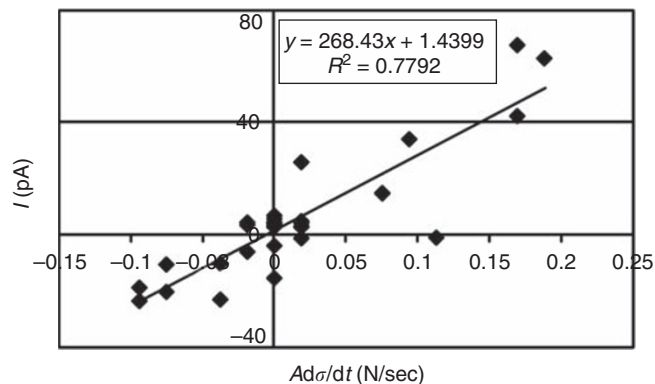

Figure 11 The current (I) versus the output stress rate ($d\sigma/dt$), which was used to calculate the piezoelectric coefficient of $C_6F_{13}(VDF)_{23}I$ telomer.

slope of which corresponds to d_{33}, and it was 268 pC.N^{-1}. The d_{33} values obtained in this study were higher than those of $CF_3(VDF)_{13.4}C_2H_5$ (181 pC.N^{-1}),[8] PVDF ($d_{33}=-30$ pC.N^{-1}) and poly(VDF-co-TrFE) ($d_{33}=-38$ pC.N^{-1}).[44] However, in this study, the piezoelectric coefficient measured by the apparatus (Figure 1) may be higher than the actual value due to the pyroelectric effect. Nevertheless, the absence of defects in the VDF chains (or the absence of reverse head-to-head or tail-to-tail dyads) should induce VDF unit poling, which improves the piezoelectric properties of the material.

CONCLUSIONS

Various telomers based on VDFs bearing an ω-iodo atom have been synthesized by iodine transfer polymerization (ITP). ITP of VDF was achieved with two different R_FI and was initiated by bis(4-*tert*-butylcyclohexyl) peroxydicarbonate. Thus, for the first time, bis(4-*tert*-butylcyclohexyl) peroxydicarbonate has been successfully used for the iodine transfer polymerization of VDF with 1-iodoperfluoroalkyl CTAs. The microstructure of the telomers did not display head-to-head or tail-to-tail VDF chains. However, a few reverse addition linkages adjacent to the iodine atom were observed. The telomers were successfully endcapped with ethylene, and the quantitative conversion of $C_nF_{2n+1}(VDF)_mI$ was attained. Although a large excess of ethylene was used, only one ethylene unit was inserted into the polymer, indicating that the transfer efficiency of $R_F(VDF)_nI$ telomers was high. Three of the proposed telomers were processed into thin films under vacuum, and their ferroelectric and piezoelectric properties were investigated. $C_4F_9(VDF)_{21}I$, $C_6F_{13}(VDF)_{23}I$ and $C_4F_9(VDF)_{21}C_2H_4I$ telomer films displayed ferroelectric responses and remanent polarization values of 110 (10 Hz), 107(10 Hz) and 101 (100 Hz) mC m^{-2}, respectively. Thus, the ferroelectric responses of the telomers were slightly lower than that of $CF_3(CH_2CF_2)_{17}I$. Preliminary piezoelectric properties of the telomeric films were successfully obtained, and the results revealed that the piezoelectric coefficient of the material was high due to an absence of defects in the microstructure of the telomers. Further investigations on the piezoelectric properties of the remaining telomers and ethylenated polymers are currently underway. In addition, recent structural thermal and crystalline characterizations have been supplied.[45]

1 Seiler, D. A. In: *Modern Fluoropolymers; PVDF in the Chemical Process Industry* (ed. Scheirs, J.) Ch. 25, 487–506 (Wiley, New York, 1997).

2 Humphrey, J. S. & Amin-Sanayeid, R Vinylidene fluoride polymers. *Encyclop. Polym. Sci. Techn.* **4,** 510–533 (2004).

3 Ameduri, B. From vinylidene fluoride (VDF) to the applications of VDF-containing copolymers: recent developments and future trends. *Chem. Rev.* **109,** 6632–6686 (2009).

4 Lovinger, A. Poly(vinylidene fluoride). *Dev. Cryst. Poly.* **1,** 195–273 (1982).

5 Bachman, M. A. & Lando, J. B. A reexamination of the crystal structure II of poly(vinylidene fluoride). *Macromolecules* **14,** 40–46 (1981).

6 Takashima, K., Horie, S., Mukai, T., Ishida, K. & Matsushige, K. Piezoelectric properties of vinylidene fluoride oligomers for use in medical tactile sensor applications. *Sens. Actuators A* **144,** 90–96 (2008).

7 Takashima, K., Horie, S., Mukai, T., Ishida, K. & Matsushige, K. Piezoelectric properties of vinylidene fluoride oligomers for use in tactile sensor. *J. Robotics Soc. Jpn.* **26,** 243–249 (2008) (in Japanese).

8 Matsumoto, A., Horie, S., Yamada, H., Matsushige, K., Kuwajima, S. & Ishida, K. Ferro- and piezoelectric properties of vinylidene fluoride oligomer thin film fabricated on flexible polymer film. *Appl. Phys. Lett.* **90,** 202906/1–202906/3 (2007).

9 Noda, K., Ishida, K., Kubono, A., Horiuchi, T., Yamada, H. & Matsushige, K. Remanent polarization of evaporated films of vinylidene fluoride oligomers. *J Appl. Phys.* **93,** 2866–2870 (2003).

10 Ameduri, B., Ladavière, C., Delolme, F. & Boutevin, B. First MALDI-TOF mass spectrometry of vinylidene fluoride telomers endowed with low defect chaining. *Macromolecules* **37,** 7602–7609 (2004).

11 Ameduri, B. & Boutevin, B. In: *Well-architectured fluoropolymers: synthesis, properties and applications* Ch.1, 1–99 (Elsevier, Amsterdam, 2004).

12 David, G., Boyer, C., Tonnar, J., Ameduri, B., Lacroix-Desmazes, P. & Boutevin, B. Use of Iodocompounds in Radical Polymerization. *Chem. Rev.* **106,** 3936–3962 (2006).

13 Boyer, C., Valade, D., Sauguet, L., Ameduri, B. & Boutevin, B. Iodine Transfer Polymerization (ITP) of Vinylidene Fluoride (VDF). Influence of the Defect of VDF on the Control of ITP. *Macromolecules* **38,** 10353–10362 (2005).

14 Boyer, C., Valade, D., Lacroix-Desmazes, P., Ameduri, B. & Boutevin, B. Kinetics of the iodine transfer polymerization of vinylidene fluoride. *J. Polym. Sci. Part A: Polym. Chem.* **44,** 5763–5777 (2006).

15 Boyer, C., Ameduri, B., Boutevin, B., Dolbier, W. R., Winter, R. & Gard, G. Radical terpolymerization of 1,1,2-Trifluoro-2-pentafluorosulfanylethylene and pentafluorosulfanylethylene in the presence of vinylidene fluoride and hexafluoropropylene by iodine transfer polymerization. *Macromolecules* **41,** 1254–1263 (2008).

16 Boyer, C., Ameduri & Hung, M. H. Telechelic diiodopoly(VDF-co-PMVE) copolymers by iodine transfer copolymerization of vinylidene fluoride (VDF) with perfluoromethyl vinyl ether (PMVE). *Macromolecules* **43,** 3652–3663 (2010).

17 Abel, B., Assmann, J., Buback, M., Grimm, C., Kling, M., Schmatz, S., Schroeder, J. & Witte, T. Ultrafast degradation of carbonyloxy radicals: influence of molecular structure. *J. Phys. Chem. A* **107,** 9499–9510 (2003).

18 Xu, W. Z., Li, X. & Charpentier, P. A. *In situ* ATR-FT-IR study of the thermal decomposition of diethyl peroxydicarbonate in supercritical carbon dioxide. *Polymer* **48,** 1219–1228 (2007).

19 Buback, M., Frauendorf, H., Janssen, O. & Vana, P. Electrospray ionization mass spectrometric study of end-groups in peroxydicarbonate-initiated radical polymerization. *J. Polym. Sci. Part A: Polym. Chem.* **46,** 6071–6081 (2008).

20 Timmerman, R. & Greyson, W. Predominant reaction of some fluorinated polymers to ionizing radiation. *J. Appl. Polym. Sci.* **6,** 456–459 (1962).

21 Duc, M., Ameduri, B., Boutevin, B., Kharroubi, M. & Sage, J. M. Telomerization of vinylidene fluoride with methanol. elucidation of the reaction process and mechanism by a structural analysis of the telomers. *Macromol. Chem. Phys.* **199,** 1271–1289 (1998).

22 Balague, J., Ameduri, B., Boutevin, B. & Caporiccio, G. Controlled step-wise telomerization of vinylidene fluoride, hexafluoropropene and trifluoroethylene with iodofluorinated transfer agent. *J. Fluorine Chem.* **102,** 253–268 (2000).

23 Guiot, J., Ameduri, B. & Boutevin, B. Radical homopolymerization of vinylidene fluoride initiated by tert-butyl peroxypivalate. Investigation of the microstructure by ^{19}F and ^{1}H NMR spectroscopies and mechanisms. *Macromolecules* **35,** 8694–8707 (2002).

24 Ameduri, B., Bauduin, G., Boutevin, B., Kostov, G. & Petrova, P. Synthesis and polymerization of fluorinated monomers bearing a reactive lateral group. 9. bulk copolymerization of vinylidene fluoride with 4,5,5-trifluoro-4-ene pentyl acetate. *Macromolecules* **32,** 4544–4550 (1999).

25 Korlacki, R., Johnson, J. T., Kim, J., Ducharme, S., Thompson, D. W., Fridkin, V. M., Ge, Z. & Takacs, J. M. Oligo(vinylidene fluoride) langmuir-blodgett films studied by spectroscopic ellipsometry and the density functional theory. *J. Chem. Phys.* **129,** 064704/1–064704/4 (2008).

26 Gregorio, R. & Ueno, E. M. Effect of crystalline phase, orientation and temperature on the dielectric properties of poly(vinylidene fluoride) (PVDF). *J. Mat. Sci.* **34,** 4489–4500 (1999).

27 Ma, W., Zhang, J. & Wang, X. Formation of poly(vinylidene fluoride) crystalline phase from tetrahydrofuran/ N,N-dimethylformamide mixed solvent. *J. Mat. Sci.* **43,** 398–401 (2008).

28 Manseri, A., Boulahia, D., Ameduri, B., Boutevin, B. & Caporiccio, G. Synthesis of telechelic dienes from fluorinated α,ω-diiodoalkanes. II. Divinyl and diallyl compounds containing tetrafluoroethylene, vinylidene fluoride and hexafluoropropene. *J. Fluorine Chem.* **81,** 103–113 (1997).

29 Brace, N. O. Addition of perfluoroalkyl iodides to aliphatic olefins. *US Patent* 3016407 (Dupont De Nemours) 9 January (1962).

30 Knunyants, I. L., Khrakyan, S. P., Zeifman, Y. Y. & Shokina, V. V. Fluorinated diiodoalkanes and diolefins. *Bull. Acad. Sci. USSR Div. Chem. Sci.* 359–361 (1964).

31 Bloechl, W. Organic fluorine compounds. *Dutch Patent*, 6506069 (Hoescht) 15 November (1965).

32 Yang, Y. Z. Process using CF_2I_2 and olefins for producing diiodofluorocompounds, and products thereof. *PCT Int. Appl.*, WO 97/44300 (Dupont De Nemours) 27 November (1997).

33 Renn, J. A., Toney, A. D., Terjeson, R. J. & Gard, G. L. A facil preparation of ICF_2CF_2I and its reaction with ethylene. *J. Fluorine Chem.* **86,** 113–114 (1997).

34 Von Werner, K. Fluoroalkyl-substituted iodoalkanes. *German Patent*, DE 3338300 A1 (Hoescht), 2 May (1985).

35 Bargigia, G., Tonelli, C. & Tortelli, V. Process for the synthesis of mono- or dihydroxy-fluoroalkanes as intermediates for textile treatment agents. *Eur. Patent Appl.*, EP 0247614 A1 (Ausimont), 27 May (1987).

36 Fuchikami, T. & Urata, H. Preparation of fluorine-containing α,ω-bifunctional compounds as starting materials for fluorine-containing polymers. *Eur. Patent Appl.*, EP 0383141 A2 (Sagami Chemical Research), 5 February (1990).

37 Urata, H., Kinoshita, Y., Asanuma, T., Kosukegawa, O. & Fuchikami, T. A facile Synthesis of α,ω-dicarboxyl acids containing perfluoroalkylene groups. *J. Org. Chem.* **56,** 4996–4999 (1991).

38 Chambers, R. D., Greenhall, M. P., Wright, A. P. & Caporiccio, G. A new telogen for telechelic oligomers of chlorotrifluoroethylene. *J. Chem. Soc. Chem. Comm.* **18,** 1323 (1991).

39 Manseri, A., Ameduri, B., Boutevin, B., Kotora, M., Hajek, M. & Caporiccio, G. Synthesis of telechelic dienes from fluorinated α,ω-diiodoalkanes. Part I. divinyl and diallyl derivatives from model $I(C_2F_4)nI$ Compounds. *J. Fluorine Chem.* **73,** 151–158 (1995).

40 Chambers, R. D., Greenhall, M. P., Wright, A. P. & Caporiccio, G. A new telogen for telechelic oligomers of chlorotrifluoroethylene. *J. Fluorine Chem.* **73,** 87–94 (1995).

41 Li, A. R. & Chen, Q. Y. One-pot synthesis of dialkyldifluoromethane and alkyldifluoromethyl iodides from the reaction of difluorodiiodomethane with alkenes in sulfinato-dehalogenation systems. *J. Fluorine Chem.* **82,** 151–155 (1997).

42 Brace, N. O. Syntheses with perfluoroalkyl iodides. A review: Part III. Addition of R_FI to norbornene esters, acids and anhydrides, alkenoic acids and esters, alkenylsuccinic anhydrides or diesters, and to vinyl monomers; lactonization and other reactions of adducts; hydroperfluoroalkylation by R_FI; synthesis and reactions of $I(CF_2)_nI$ homologues (n=1–3); perfluoroalkylation of arenes by R_FI or $[R_FCO_2]_2$; R_F-I in the synthesis of R_FSR and segmented $R_F(CH_2)_nSH$; and, useful derivatives therefrom. *J. Fluorine Chem.* **108,** 147–175 (2001).

43 Baum, K., Bedford, C. D. & Hunadi, R. J. Synthesis of fluorinated acetylenes. *J. Org Chem.* **47,** 2251–2257 (1982).

44 Omote, K., Ohigashi, K. & Koga, K. Temperature dependence of elastic, dielectric, and piezoelectric properties of 'single crystalline' films of vinylidene fluoride-trifluoroethylene copolymer. *J. Appl. Phys.* **81,** 2760–2769 (1997).

45 Durand, N., Ameduri, B. & Boutevin, B. Synthesis and characterization of functional fluorinated telomers. *J. Polym. Sci.:Part A: Polym. Chem.* (in press; doi:10.1002/pola.24420).

Supplementary Information accompanies the paper on Polymer Journal website (http://www.nature.com/pj)