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ARTICLE

Synthesis and Microstructural Characterization of Poly(chlorotrifluoroethylene-*co*-vinylidene chloride) Copolymers

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The radical copolymerization of chlorotrifluoroethylene (CTFE) with vinylidene chloride (VDC) was investigated. A surfactant-free emulsion polymerization process was used to obtain poly(CTFE-*co*-VDC) copolymers of high molecular weight in up to 75% wt. yield. In parallel, a solution polymerization process afforded a range of poly(CTFE-*co*-VDC) copolymers of lower molecular weight and soluble enough to allow a meticulous characterization by NMR spectroscopy. Various statistical poly(CTFE-*co*-VDC) copolymers were synthesized, containing from 3 to 38 mol% of VDC. A triple resonance (¹H/¹³C/¹⁹F) 2D-NMR ¹H{¹³C}-HSQC (heteronuclear single quantum coherence) experiment was used to aid with resonance assignments and provided crucial information about monomer sequences. Quantitative ¹⁹F and ¹H 1D-NMR enabled the determination of the composition of the copolymers. In all cases, CTFE is the less reactive of both comonomers. Decomposition temperature at 10 % weight loss ($T_d^{10\%}$ values), ranged from 333 up to 400 °C under air, and a decreasing trend of the thermal stability was observed when increasing the VDC amount in the copolymer. These variations of the thermal properties were attributed to an increase in the number of C-H bonds broken in polymers with higher VDC molar percentages in the copolymer. Moreover, glass transition (T_g) and melting (T_m) temperatures ranged from 12 to 47 °C, and 162 to 220 °C, respectively.

1. Introduction

The synthesis of polychlorotrifluoroethylene (PCTFE) was pioneered in 1934 and the corresponding patent was published in 1939.¹ PCTFE is mostly commercialized as Aclar[®] and Neoflon[®] tradenames by Honeywell and Daikin companies, respectively. PCTFE is a nonflammable polymer² endowed with remarkable chemical resistance and excellent gas barrier properties³ although three major disadvantages remain: i) the high melting temperature (*ca.* 220 °C) that leads up to a high energetic cost to process this polymer, ii) the high crystallinity resulting in a poor solubility in common organic solvents (e.g. PCTFE is only soluble in 2,5-dichloro-trifluoromethyl benzene at 150 °C),^{4,5} and iii) the inherent troubles encountered when cross-linking. To overcome the aforementioned limitations, CTFE has been extensively copolymerized with monomers such as vinyl ethers,^{6,7} ethylene (poly(CTFE-*alt*-E), ECTFE, Halar[®] commercially available by Solvay Specialty Polymers),^{8,9} and propylene (poly(CTFE-*alt*-P)).¹⁰ In these three cases, the resulting copolymers are alternating in contrast to those based on vinylidene chloride,¹¹ vinyl chloride,¹¹ styrene,¹² MMA,¹² N-vinyl pyrrolidone,¹³ vinyl acetate,¹⁴ vinyl triethoxysilane,¹⁵ diallyldimethylammonium chloride (DADMAC),¹⁶ or fluorinated dioxolane,¹⁷ that lead to statistical copolymers with low CTFE contents.

On the other hand, poly(vinylidene chloride), PVDC, has interesting properties including a good resistance to a wide variety of solvents and an extremely low permeability to water, oxygen¹⁸ and aroma¹⁹ originating from its high degree of crystallinity.^{20,21} These characteristics makes it a good candidate for use as high-barrier packaging films for industry. However, PVDC homopolymer undergoes a fast degradation when heated a few degrees over its melting temperature ($T_m = 203$ °C),²² resulting in a gradual discoloration and a loss of its superior properties. PVDC starts to degrade at about 120 °C, when hydrochloric acid is the only gas product until the temperature exceeds 190 °C. The dehydrochlorination mechanism consists in an unzipping process,²³⁻²⁶ starting from defect structures identified as unsaturation randomly introduced in the polymer backbone during polymerization or processing.^{24,25,27} As PCTFE is an expensive material, it was worth synthesizing a poly(CTFE-*co*-VDC) copolymer to check whether a synergistic effect from both comonomers could be obtained. The radical copolymerization of CTFE with VDC was pioneered in 1959¹¹ while further studies were patented by various companies, especially when both comonomers were involved in terpolymerization.²⁸⁻³² However, to the best of our knowledge, the microstructure of poly(CTFE-*co*-VDC) copolymers has scarcely been investigated.³³ Hence, it was of

interest to revisit their synthesis and to carefully analyze their microstructure, as the objective of this present article.

2. Experimental

2.1 Materials. All reagents were used as received unless stated otherwise. *Tert*-butylperoxyvalerate (*tert*-butyl 2,2-dimethylperoxypropanoate) in isododecane (Trigonox® 25-C75, *t*BuOOC(O)*t*Bu, TBPPi) (purity 75%) was kindly provided by Akzo Nobel (Compiègne, France). Chlorotrifluoroethylene (CTFE, F₂C=CFCl) was kindly provided by Honeywell. Sodium persulfate, iron sulphate, chloroform, methanol, water (HPLC grade), as well as VDC were of analytical grade, purchased from Sigma-Aldrich (Saint Quentin-Fallavier, France). 1,1,1,3,3-Pentafluorobutane (C₄H₅F₅) was provided by Solvay chemicals. Deuterated solvents (CDCl₃ and toluene-d₈) for routine NMR characterizations were purchased from Euriso-top (Grenoble, France) (purity >99.8%). For more advanced experiments (performed at The University of Akron) trichlorofluoromethane (CFCl₃, 99.5%, Sigma-Aldrich Chemical Co.) was used as an internal chemical shift standard for ¹⁹F NMR. Because poly(CTFE-*co*-VDC) copolymers have a low solubility in most organic solvents, three different solvents were tested: chloroform-d (99.8%, Cambridge Isotope Laboratories Inc.), toluene-d₈ (99.6%, Matheson Co.) and 1,4-dichloro-2-(trifluoromethyl)benzene (98%, Sigma-Aldrich Chemical Co.); 20 vol% 1,4-dichlorobenzene-d₈ (98%, Cambridge Isotope Laboratories Inc.) was added to the third solvent to provide a deuterium lock signal.

2.2 Procedures for the radical copolymerization of CTFE with VDC. Example 1 (Run #7, Table 1): The copolymer was prepared in a 600 mL Hastelloy Parr Autoclave equipped with a manometer, a rupture disk, and inlet and outlet valves. The autoclave was purged with 20 bar of nitrogen pressure to prevent leakage, followed by maintenance of a 20 mm Hg vacuum for 15 minutes. The reactants including TBPPi initiator (2.13 g, 9.20 mmol, 2 mol%), VDC comonomer (3.10 g, 32 mmol, 6 mol% in the feed), and the solvent mixture (C₄H₅F₅: 200 mL, deionized water: 200 mL) were transferred into the autoclave through a funnel. After cooling in a bath containing a liquid nitrogen/acetone mixture, CTFE comonomer (66 g, 567 mmol, 94 mol%) was introduced by double weighing (i.e., the difference of weight before and after feeding the autoclave with CTFE). The reactor was heated gradually to 74 °C (P_{max} = 8 bar). The reaction was stopped after 10–20 hours (ΔP = 2 bar) and the autoclave was cooled to room temperature and then in an ice bath. After purging the unreacted CTFE, the conversion of CTFE was determined to be 90%. The reaction mixture was filtered to remove the solvent; the resulting crude product was solubilized in chloroform, and finally the product was precipitated from cold methanol. The polymer was dried to a constant weight under high vacuum at 60 °C to produce 23.0 grams of poly(CTFE-*co*-VDC) copolymer (33% yield) as a white powder. The product was analyzed by NMR spectroscopy. The molar percentage of VDC in the copolymer was determined to be 23 mol% by use of 2,5-dichlorotrifluorobenzene as an internal standard for quantitation. Differential scanning calorimetric (DSC) analysis of the copolymer revealed a glass transition temperature (T_g) value of 12 °C and a melting temperature (T_m) of 180 °C. The thermogravimetric (TGA) analysis revealed a decomposition temperature at 10% weight loss (T_d^{10%}) value of 344 °C, under air. **Example 2 (Run #9, Table 1):** The copolymer was prepared in a 600 mL Hastelloy Parr autoclave equipped with a manometer, a rupture disk, and inlet and outlet valves. The autoclave was purged with 30 bars of nitrogen pressure to prevent leakage. A 20 mm Hg vacuum was then maintained for 15

minutes. The following reactants were transferred into the autoclave through a funnel: VDC (1.26 g, 13.3 mmol, 3 mol%), (NH₄)₂S₂O₈ (2.1 grams in 10 mL of deionized water), Na₂S₂O₅ (1.7 grams in 10 mL of deionized water), FeSO₄·7H₂O (1.5 grams in 10 mL of deionized water), H₂SO₄ (1.5 grams in 10 mL of deionized water), and deionized water (460 mL). After cooling the autoclave in liquid nitrogen, CTFE (49 g, 420 mmol, 97 mol%) was transferred by double weighing (i.e., the difference of weight before and after feeding the autoclave with CTFE). The reactor was heated to 40 °C (P_{max} = 10 bar). The reaction was stopped after 20 hours (ΔP = 2 bar) and then the autoclave was cooled to room temperature. After purging the unreacted CTFE (5 g), the product mixture was filtered from the mixture, and the resulting solid was dried to a constant weight under high vacuum at 80 °C for 24 hours to produce 37.7 grams of a white powder (75% yield). The NMR spectrum for this copolymer was not obtained due to lack of solubility of the polymer in most organic solvents. DSC analysis of the copolymer revealed a glass transition temperature (T_g) of 30 °C and a melting temperature (T_m) of 220 °C. Elemental analysis indicated that the copolymer consisted of 44.74% F, 30.01% Cl, and 19.86% C, the weight ratio of F/Cl being 1.49 (ca. 4 mol% VDC). TGA analysis revealed a decomposition temperature at 10% weight loss value of 400 °C, under air.

2.3 Measurements.

NMR analysis. With the exceptions noted below, all NMR spectra were collected on a Varian Direct-Drive 500 MHz spectrometer equipped with VnmrJ 3.2A software, five broad-band rf channels and a 5mm ¹H/¹⁹F/X (X=¹⁵N-³¹P) triple resonances pulse field gradient (PFG) probe. This probe is specially designed for ¹⁹F NMR. First, there is no interference from the background signal, because the probe components are made with non-fluorine containing materials. Second, a duplexer used to combine the mixed ¹H and ¹⁹F signals from console to a single high frequency channel on the probe; and to separate the two returning signals, and send the signal of interest (¹H or ¹⁹F) to the receiver. A detailed description of this instrument has already been published.³⁴ Two samples were prepared for extensive 1D- and 2D-NMR analyses. One sample was prepared by dissolving 35 mg of the poly(CTFE-*co*-VDC) copolymer in about 700 μL of the CDCl₃ and heating in a Kugelrohr at 50 °C to help disperse/solubilize the polymer. The other sample was prepared by dissolving 35 mg of the poly(CTFE-*co*-VDC) copolymer in about 700 μL of toluene-d₈ and heating in a Kugelrohr at 90 °C to help dissolve the copolymer. To both samples, 5 μL of 1,4-dichloro-2-trifluoromethyl benzene were added as the internal standard for quantitative analysis. NMR samples appeared to be transparent and homogeneous under the conditions used to obtain the NMR spectra. Some of the ¹³C NMR data were recorded at room temperature on a Bruker 600 MHz Avance III instrument with deuterated chloroform and tetramethylsilane (or CFCl₃) as the reference for ¹H, ¹³C and ¹⁹F chemical shifts. The coupling constants and chemical shifts are given in Hz and ppm, respectively.

¹⁹F, ¹H, and ¹³C 1D-NMR: The quantitative ¹⁹F 1D-NMR spectra of poly(CTFE-*co*-VDC) copolymers were collected with 43.1 kHz spectral window using ¹H decoupling with Waltz-16 modulation (γ_HB_H = 2.7 kHz),^{35,36} during the acquisition time to suppress the nuclear Overhauser effect (NOE) from ¹H. The spectrum was collected with a 0.7 s acquisition time, 20 s relaxation delay (ca. 5 times the longest T₁, that of the low MW reference), 128 transients, and a 3.1 μs (30 °) pulse width. The data were zero-filled to 256 k points, exponentially weighted with a line broadening of 0.5 Hz and Fourier transformed. The quantitative ¹H NMR spectra were

collected using ^{19}F decoupling with CHIRP^{37,38} modulation ($\gamma_{\text{F}}B_{\text{F}} = 17.9$ kHz), during the acquisition period to suppress the NOE from ^{19}F . The spectra were collected with 0.8 s acquisition time, 75 s relaxation delay (ca. 5 times the longest T_1 , that of the low MW reference), 4.5 kHz spectral window, 16 transients, 14.5 μs (90°) pulse width. The data were zero-filled to 64 k points, exponentially weighted with a line broadening of 0.5 Hz, and Fourier transformed. The ^{13}C NMR spectrum was collected using simultaneous ^1H and ^{19}F decoupling with Waltz-16 ($\gamma_{\text{H}}B_{\text{H}} = 2.7$ kHz) and CHIRP ($\gamma_{\text{F}}B_{\text{F}} = 17.9$ kHz) modulation, respectively. The spectrum was collected with a 0.5 s acquisition time, 2 s relaxation delay, 32.2 kHz spectral window 16384 transients and 6.5 μs (45°) pulse width. The data were zero-filled to 128 k points, exponentially weighted with a line broadening of 5 Hz, and Fourier transformed.

^{19}F and ^1H T_1 -NMR Experiments: Both ^{19}F and ^1H T_1 NMR experiments were performed with the inversion recovery experiment (relaxation delay -180° - τ - 90° -acquire). The ^{19}F T_1 experiment was performed with 46.3 kHz spectral width with ^1H gated decoupling. The spectra were collected with 0.7 s acquisition time, 7 s relaxation delay, 16 transients and 90° pulse width of 9.5 μs . The relaxation times of the fluorines were measured with 14 values of τ arrayed from 0.005 s to 14 s. Data were analyzed using the standard 3-parameter exponential fitting program in Varian's VnmrJ 3.2D software. The ^1H T_1 experiment was performed with 4.5 kHz spectral widths, using ^{19}F gated decoupling. The spectra were collected with 0.8 s acquisition time, 7 s relaxation delay, 32 transients and 90° pulse width of 14.5 μs . The relaxation times of the protons were measured with 14 values of τ arrayed from 0.005 s to 14 s. Data were analyzed with the same method mentioned above.

$^1\text{H}\{^{13}\text{C}\}$ gHSQC 2D-NMR: The standard Varian $^1\text{H}\{^{13}\text{C}\}$ gHSQC sequence was modified to provide efficient ^{19}F decoupling; as well as ^1H and ^{13}C decoupling normally used during the t_1 and t_2 periods, respectively (A copy of the pulse program is included in the Supplementary Material). A composite 180° inversion pulse on the ^{19}F channel was added in the middle of ^{13}C evolution period to remove ^{19}F couplings in the f_1 dimension. Simultaneous WURST and CHIRP decoupler modulation ($\gamma_{\text{C}}B_{\text{C}} = 12.8$ kHz and $\gamma_{\text{F}}B_{\text{F}} = 17.9$ kHz) was employed to decouple ^{13}C and ^{19}F , respectively, during the acquisition time. The experiment was run with a 3 kHz spectral width in the ^1H (f_2) dimension and a 3.8 kHz spectral width (f_1) in the ^{13}C dimension, a 0.1 s acquisition time, 1 s relaxation delay and 90° pulse widths of 14.3, 11.0 and 13.4 μs for ^1H , ^{19}F and ^{13}C , respectively; 64 transients were averaged for each 2×256 increments using the States³⁹ method of phase sensitive detection. Two 45° pulses, phase shifted by 90° from one another were incorporated at the beginning of the relaxation delay to eliminate residual magnetization from the previous execution of the pulse sequence. Homospoil pulses were inserted between the last two 90° pulses in the INEPT (insensitive nuclei enhanced by polarization transfer) and reverse INEPT parts of the HSQC sequences. The gradient times/strengths for these homospoil gradient pulses were 4.0 ms/0.17 T/m and 2.4 ms/0.070 T/m, respectively. At the end of the evolution delay, a sequence $\square/2-180^\circ_{\text{H}}/180^\circ_{\text{C}}-\square/2$ was added to accommodate a ^{13}C coherence selection pulse of 2 ms and 0.097 T/m. The gradient time and strength for ^1H coherence selection pulse, inserted during the last refocusing delay in the sequence, was 1 ms with alternation ± 0.048 T/m to provide preservation of equivalent coherence pathways.⁴⁰ The data were zero-filled to 4096×4096 and weighted with sinebell and shifted sinebell functions before Fourier transformation.

TGA. Thermogravimetric analyses were performed with a TGA 51 apparatus from TA Instruments, under air, at the heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ from room temperature up to a maximum of 480°C . The sample size varied between 10 and 15 mg.

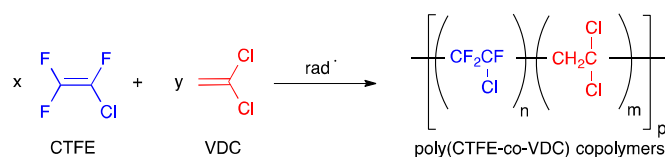
DSC. Differential scanning calorimetry measurements were conducted using a TA instruments Q100 connected to a computer. A nitrogen flow rate was used. After its insertion into the DSC apparatus, the sample was initially stabilized at -100°C for 10 min. The first scan was carried out at a heating rate of $20^\circ\text{C}\cdot\text{min}^{-1}$ up to 230°C . It was then cooled to -100°C . A second scan was performed at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ up to 230°C giving the values of T_g reported, taken at the half-height of the heat capacity jump of the glass transition.

Elemental analysis. Weight percentages of carbon, hydrogen, chlorine, and fluorine atoms were assessed by elemental analysis (EA) at the CNRS–Service Central d'Analyses (Solaize, France) on a CH elemental analyzer equipped with a $\text{CO}_2/\text{H}_2\text{O}$ infrared detector.

3. Results and Discussion

3.1 Synthesis of poly(CTFE-co-VDC) copolymers

The radical copolymerizations of CTFE with VDC were initiated either by *tert*-butylperoxyvalate (TBPPi) at 74°C or by sodium persulfate at 40°C for ca. 15 hours in 1,1,1,3,3-pentafluorobutane or in water in a 600 mL-autoclave (Scheme 1). 1,1,1,3,3-Pentafluorobutane is known as a good solvent for halogenated monomers, yet it prevents transfer from reactions in the course of radical copolymerizations.^{16,17,41-44}



Scheme 1. Radical copolymerization of chlorotrifluoroethylene (CTFE) with vinylidene chloride (VDC).

The polymerization reactions were carried out under different experimental conditions (nature of initiator, process, medium, initial molar percentages of CTFE and VDC) which are supplied in Table 1). After purification (precipitation and drying), the resulting poly(CTFE-co-VDC) copolymers were characterized by NMR spectroscopy and elemental analysis. As a matter of fact, the surfactant-free emulsion polymerization process (run #9) allowed us to obtain a poly(CTFE-co-VDC) copolymer in up to 75% wt. yield, which exhibits very good thermal properties (e.g. $T_d^{10\%} \approx 400^\circ\text{C}$ and $T_m \approx 220^\circ\text{C}$), very close to that of PCTFE. However, such a copolymer was totally insoluble in common organic solvents. This prompted us to use a solution polymerization process (runs #1 to #8) to synthesize a range of poly(CTFE-co-VDC) copolymers of lower molecular weights and soluble enough to allow a meticulous characterization by means of NMR spectroscopy.

It is worth mentioning that the spontaneous polymerization of VDC, so often observed when the monomer is stored at room temperature, is caused by peroxides formed from the reaction of VDC with oxygen.

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Table 1. Radical copolymerizations of chlorotrifluoroethylene (CTFE) with vinylidene chloride (VDC) at different initial monomer ratios in a 600 mL autoclave.

| Run # | mol% VDC (feed) | C ₄ H ₅ F ₅ /H ₂ O (mL/mL) | mol% TBPPi | mol% VDC (copolymer) NMR ^a , EA ^b | Yield (wt%) | T _d ^{10%} (°C) ^c | T _g , T _m (°C, °C) ^d |
|-------|-----------------|--|--------------|---|-------------|---|---|
| 1 | 1 | 200/200 | 2.0 | 3, 5 | 51 | 363 | 37, 166 |
| 2 | 1 | 200/200 | 1.0 | 5, 8 | 36 | 370 | 26, 176 |
| 3 | 1 | 100/300 | 2.0 | 7, 4 | 57 | 359 | 37, 162 |
| 4 | 1 | 50/350 | 2.0 | 8, 4 | 52 | 338 | 26, 167 |
| 5 | 2 | 100/300 | 2.0 | 16, 10 | 56 | 357 | 47, 166 |
| 6 | 3 | 200/200 | 2.0 | 16, 11 | 44 | 354 | 28, 171 |
| 7 | 6 | 200/200 | 0.8 | 23, 16 | 33 | 344 | 12, 180 |
| 8 | 10 | 200/200 | 2.0 | 38, 26 | 27 | 333 | 34, 179 |
| 9 | 3 | 0/500 | ^e | ^f , 4 | 75 | 400 | 30, 220 |

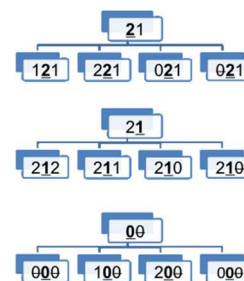
^amolar composition calculated by ¹⁹F NMR; ^bmolar compositions assessed by elemental analysis; ^cdetermined by TGA under air at 10 °C.min⁻¹; ^dassessed by DSC; ^einitiator was sodium persulfate in combination with redox systems (see experimental part, example 2); ^fNMR spectrum for the copolymer was not recorded due to lack of solubility of the polymer in most organic solvents.

That is why commercial grades of VDC contain 200 ppm of the monomethyl ether of hydroquinone (MEHQ) as an inhibitor. For many polymerizations, MEHQ needs not be removed; instead, polymerization initiators are added (peroxides in our case). In fact, VDC from which the inhibitor has been removed should be refrigerated in the dark at -10 °C, under a nitrogen atmosphere, and in a nickel-lined or a baked phenolic-lined storage tank. If it is not used within one day, it should be reinhibited.

3.2 Nomenclature and Structures

Poly(CTFE-*co*-VDC) copolymers are composed of two monomer units, chlorotrifluoroethylene (-CF₂CFCl-) and vinylidene chloride (-CH₂CCl₂-). Shorthand is used, where a number 0, 1 or 2 represents the number of fluorine atoms bound to carbon in a -CXY- group. In this article, 0, 1, 2 and θ are used to signify CH₂, CFCl, CF₂ and CCl₂, respectively. Both CTFE and VDC units have two orientations in the polymer chain: 1) normal addition units 21 and θθ, respectively, and 2) inverse addition units 12 and θθ, respectively. According to this system, there are four different groups of odd numbered carbon sequences: 2-centered, 1-centered, 0-centered and θ-centered. Two NMR active isotopes of chlorine, ³⁵Cl and ³⁷Cl, provide broad peaks, and do not have suitable NMR properties for the high-resolution NMR experiments described in this manuscript. However, both ¹⁹F and ¹H have nuclear spin I = ½ and high abundance. Therefore, the 2-centered and 1-centered sequences can be studied by ¹⁹F NMR;

the 0-centered sequences can be studied by ¹H NMR. There are four possibilities for each 0-centered, 1-centered and 2-centered three-carbon sequence. They are listed in Scheme 2.



Scheme 12. Three-carbon sequences in poly(CTFE-*co*-VDC) copolymers.

Although ¹³C NMR spectroscopy might be used to study θ-centered sequences, the low abundance and low γ of this nucleus, combined with the low solubility of these polymers makes collection of ¹³C NMR spectra time consuming. Relatively poor signal-to-noise levels are obtained in 1D-NMR spectra of the polymers studied here, even after overnight data collection times. Thus, quantitative analyses of these data are not easy to perform. The 2- and 1-centered sequences might be studied by ¹⁹F NMR experiments, including ¹⁹F {¹³C}-HSQC type NMR experiments.

However, the nature of the diastereotopic fluorine atoms in CF_2 groups requires specially modified versions of these experiments. Results from these experiments will be reported in a later article.

3.3 1D NMR Characterization of poly(CTFE-co-VDC) copolymers

Due to the fact that poly(CTFE-co-VDC) copolymer has extremely low solubility in most organic solvent, attempts were made to obtain NMR spectra in two solvents at high temperature, including chloroform-d at 50 °C and toluene-d₈ at 90 °C.

A representative ^1H NMR spectrum of poly(CTFE-co-VDC) copolymer in toluene-d₈ is shown in Figure 1. Various signals in the 0.5 to 1.4 ppm range are attributed to the end-groups that arise from TBPPi initiator.

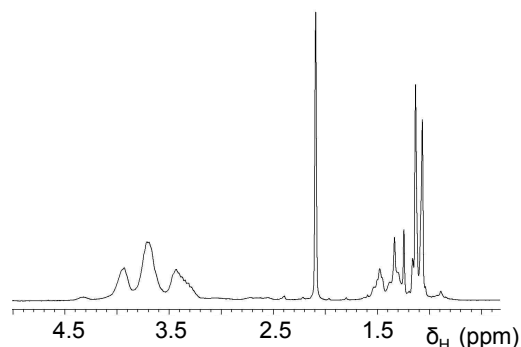
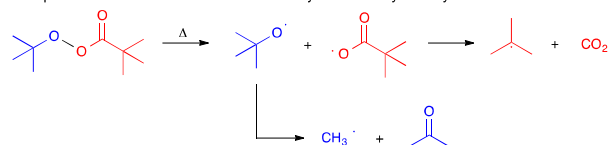


Figure 1. Aliphatic region from the 500 MHz $^1\text{H}\{^{19}\text{F}\}$ 1D-NMR spectrum of poly(CTFE-co-VDC) copolymer in toluene-d₈ obtained at 90 °C.

Indeed, it has been previously reported that when heated at 74°C, *tert*-butyl peroxyvalate undergoes a homolytic scission that generates two radicals (Scheme 3).^{45,46} One is able to rearrange into a methyl radical and acetone while the other can go through a decarboxylation to give rise to a *tert*-butyl radical.⁴⁶⁻⁴⁹

1. Decomposition of TBPPi initiator to form *tert*-butoxyl and *tert*-butylcarboxyl radicals



2. Radical Disproportionation



Scheme 3. *tert*-butoxyl and *tert*-butylcarboxyl radicals generated from *tert*-butyl peroxyvalate (TBPPi).

Hence, these four radicals may potentially react onto both dissymmetric reactive sites of both comonomers to form as many as 16 different chain-end structures. Similar spectra in CDCl_3 are obtained (Supporting Information), but with far more details in the 3.0-4.5 ppm region. However, the signal from residual water, present in the NMR sample, interferes with resolution of all the *t*-butyl resonances. The signals in the 3.0 to 4.5 ppm clearly show

three groups of peaks that might mistakenly be attributed to monomer sequence effects of VDC CH_2 groups centered in three types of triads. However, this assumption does not fit structures derived from the monomer sequences produced on this copolymer. The correct assignments will be discussed in light of the $^1\text{H}\{^{13}\text{C}\}$ gHSQC 2D NMR spectra (*vide infra*).

Figure 2 displays the ^{13}C 1D NMR spectra of poly(CTFE-co-VDC) copolymer collected in CDCl_3 at 50 °C (Figure 2a) and toluene-d₈ at 90 °C (Figure 2b). Due to the low solubility of this copolymer under these conditions, it takes a long time to obtain the ^{13}C spectra with high signal to noise level. These spectra were obtained with both ^1H and ^{19}F decoupling. Simultaneous decoupling of both nuclei produces spectral simplification, better resolution of peaks, and improved signal to noise levels. The sharp peaks between 20 and 30 ppm are attributed to the end groups of TBPPi initiator. Four groups of carbon resonances can be clearly observed in both spectra, which correspond to the four different -CXY- carbons (X and Y = H, F or Cl) in this copolymer. The various resonances at highest field between 45-65 ppm are attributed to CH_2 groups, in which the proton atom has the lowest electronegativity. The other three types of carbon resonances are assigned based on the electronegativity: CCl_2 (80-85 ppm), CFCl (102-110 ppm) and CF_2 (110-120 ppm). Data from the attached proton test (APT) support the assignments to C (CF_2 , CFCl , and CCl_2), CH_2 and CH_3 resonances.⁵⁰

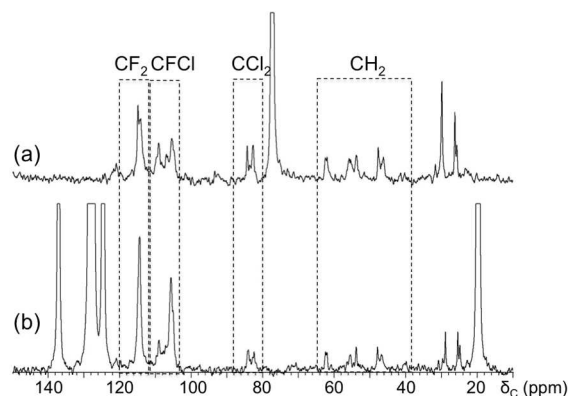


Figure 2. 125 MHz $^{13}\text{C}\{^1\text{H},^{19}\text{F}\}$ 1D-NMR spectra of poly(CTFE-co-VDC) obtained: (a) in CDCl_3 at 50 °C, and (b) in toluene-d₈ at 90 °C.

An example of determining the monomer composition by NMR is shown using the quantitative $^{19}\text{F}\{^1\text{H}\}$ and $^1\text{H}\{^{19}\text{F}\}$ NMR spectra shown in Figure 3. These spectra were both collected at 90 °C in toluene-d₈ with 5 μL 1,4-dichloro-2-(trifluoromethyl) benzene as internal standard. All the polymer fluorine resonances are from CTFE units, whereas all the polymer proton resonances are from VDC units. In the $^{19}\text{F}\{^1\text{H}\}$ spectrum, the peak at -62.5 ppm is attributed to three fluorine atoms from 1,4-dichloro-2-(trifluoromethyl) benzene. The resonances between -110 and -140 ppm are attributed to fluorine atoms from CF_2 in CTFE units. First, the number of CF_2 groups in CTFE units (Eq. 1) and CH_2 groups in VDC units (Eq. 2) are calculated based on comparison with area of the ^{19}F and ^1H signals of the internal standard. Second, the mol% of VDC is determined by the relative number of CH_2 and CF_2 groups (Eq. 3).

$$\text{Eq. 1: } N_{\text{CTFE}}/N_{\text{std}} = (A_{\text{CTFE}}/3)/(A_{\text{std}}/3) = (55.9/3)/(44.1/3) = 1.27$$

$$\text{Eq. 2: } N_{\text{VDC}}/N_{\text{std}} = (A_{\text{VDC}}/2)/(A_{\text{std}}/1) = (48.18/2)/(51.82/1) = 0.46$$

$$\text{Eq. 3: } P_{\text{VDC}} = [(N_{\text{VDC}})/(N_{\text{VDC}}+N_{\text{CTFE}})] * 100 = 27\%$$

As observed from these results, the molar percentage of VDC in the poly(CTFE-*co*-VDC) copolymers is always much higher than in the feed, thus indicating that CTFE is less reactive than VDC. This statement matches well with the kinetics of radical copolymerization reported by Kliman and Kosinar.¹¹ These authors determined the following reactivity ratios of both comonomers: $r_{\text{CTFE}} = 0.02$ and $r_{\text{VDC}} = 17.14$ at 60 °C. Indeed, except in the case of the radical copolymerization of CTFE with vinyl ethers (which leads to alternating copolymers^{6,51-53}) such a trend seems similar to those of all other radical copolymerizations of CTFE with various comonomers⁵¹ such as styrene,¹² MMA,¹² vinyl chloride,¹¹ N-vinyl pyrrolidone,¹³ vinyl acetate,¹⁴ vinyl triethoxysilane,¹⁵ diallyldimethylammonium chloride (DADMAC),¹⁶ or 4-bromo-3,3,4,4-tetrafluorobut-1-ene (BTFB)⁵⁴ although VDC seems more reactive than these above monomers.

It is noteworthy that a similar analysis of the spectra taken from the same sample in CDCl₃ at 50 °C yielded 46 mole% VDC, despite the fact that both samples appear to be clear and homogeneous solutions. Apparently, in CDCl₃, CTFE-rich polymer segments do not dissolve well and agglomerate to induce solid state-like NMR characteristics whose signals are not detected in the solution NMR experiments.

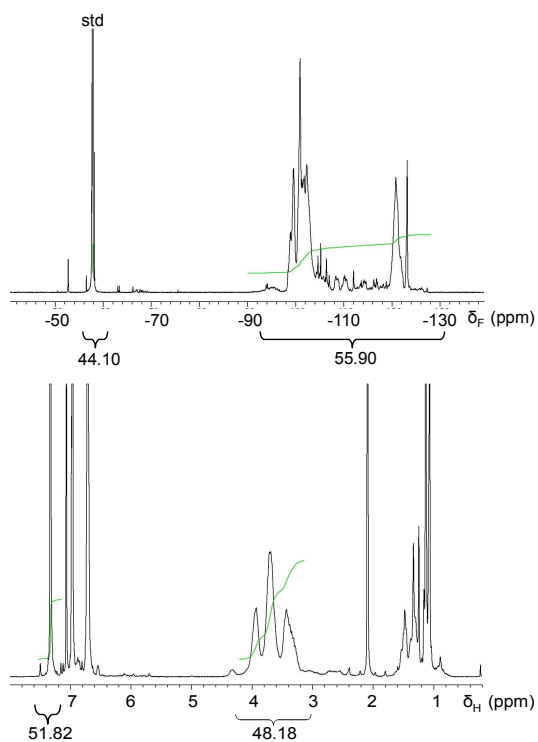


Figure 3. Quantitative NMR spectra obtained in toluene-*d*₈ at 90 °C: (a) 470 MHz ¹⁹F{¹H} spectrum of poly(CTFE-*co*-VDC) copolymer with internal standard; and (b) 500 MHz ¹H{¹⁹F} spectrum of poly(CTFE-*co*-VDC) copolymer with internal standard.

3.4 Analyses of 2D NMR Data

Figure 4 shows the CH₂ region from the ¹H{¹³C}gHSQC 2D-NMR spectrum obtained from poly(CTFE-*co*-VDC) copolymer in CDCl₃ at 50 °C. To obtain the simplification in this spectrum and to obtain better signal-to-noise levels, the data were collected with ¹⁹F decoupling in both the *f*₁ and *f*₂ dimensions. A composite 180° ¹⁹F inversion pulse was incorporated in the middle of the *t*₁ evolution to accomplish the former while continuous ¹⁹F decoupling was applied during the *t*₂ acquisition period to accomplish the latter.

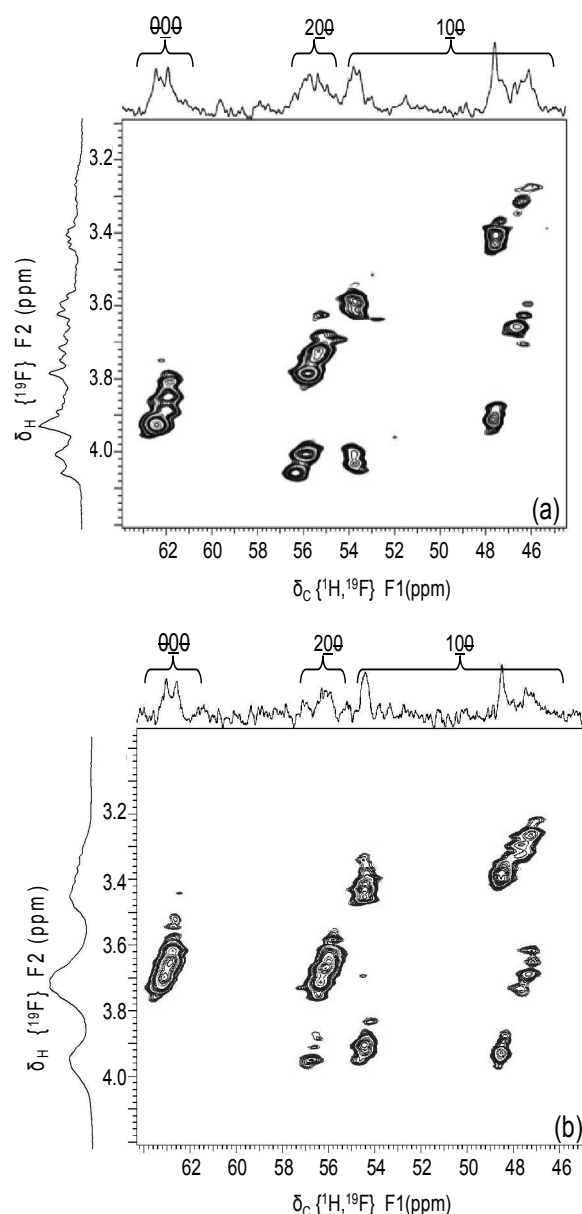


Figure 4. Selected regions from the 500 MHz ¹H{¹³C}gHSQC 2D-NMR spectra obtained from poly(CTFE-*co*-VDC) copolymer obtained: (a) in CDCl₃ at 50 °C; and (b) in toluene-*d*₈ at 90 °C.

The ¹H resonances between 3-4 ppm are attributed to CH₂ groups of VDC units based on the previous ¹H 1D NMR spectrum. As mentioned above, three proton shifts with an approximate ratio of

1:2:1 is reminiscent of patterns from triad sequences in statistical ethylene/ α -olefin copolymers. However, this pattern does not fit the possible structures derived from the comonomers in this copolymer. Four groups of peaks are expected, as there are four possible of CH₂-centered three carbon sequences, including **000**, **200**, **000** and **100**. The numbers in bold indicate the assigned CH₂ groups. Although **000** sequences are a possible permutation (from inverse addition of VDC units), they are much less probable due to unfavorable steric interactions during monomer addition. These sequences are shown in Scheme 2. The two protons in the CH₂ groups are approximately equivalent in **000** and **200** three-carbon sequences, showing a similar chemical shift. On the other hand, the two methylene protons in **100** sequences are diastereotopic, and will have different ¹H chemical shifts, because adjacent to the CFCl stereogenic centers.

In Figure 4, although the ¹H 1D-NMR spectra plotted along the left vertical axes of the 2D-NMR spectra appear very different in CDCl₃ and toluene-d₈, these differences are due to small aromatic solvent induced shifts. In the ¹H{¹³C}gHSQC spectrum very similar cross peak pattern are observed. The middle part of proton pattern in the methylene region (near 3.7 ppm) is attributed to the overlapping resonances of **000** and **200** methylene groups. These resonances are well resolved in the *f₁* dimension of the 2D NMR spectrum. In fact, the dispersion is large enough to resolve resonances of five carbon sequences (not yet assignable based on the current NMR data). The outer peaks in this pattern, near 3.4 and 3.9 ppm, are from diastereotopic methylene protons of **100** three-carbon sequences. Two types of these resonances from methylene groups are resolved near 48.5 and 54.8 ppm in the *f₁* dimension. These are tentatively attributed to **21000** (of CVV triads) and **21002** (of CVC triads) five-carbon sequences, based simply on the possible carbon sequences (once 2 is confirmed on the left edge of the central 3-carbon sequence) and the possibility of adding either V (00) or C (21) to the right of the central 3-carbon sequence. Complete and definitive assignments of resonances to various 3- and 5-carbon sequences await improvements being made in the NMR experiments that will yield F-C one- and two-bond correlations in ¹H/¹⁹F/¹³C triple resonance ¹⁹F{¹³C}HSQC-type 2D-NMR experiments.

3.5 Thermal properties of poly(CTFE-co-VDC) copolymers

The thermal characterizations of these copolymers were accomplished by means of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The stabilities of all poly(CTFE-co-VDC) copolymers were studied by thermogravimetric analysis under air (Figure 5). The results are summarized in Table 1. The degradation was attributed to the cleavage of C-H bonds present in the copolymer, and probably accompanied by HCl release, from VDC units. Therefore, it is expected that an increase in the molar percentage of VDC would result in a faster degradation rate that arises from the increase in the amount of C-H weak bonds.²³⁻²⁷ The obtained analyses have supported this assumption, as they had shown an increased rate of degradation for higher VDC molar percentages in the copolymers (Figure 6, e.g. for runs #1, #6, and #8, Table 1). In contrast to the poly(CTFE-co-VDC) copolymers, PCTFE thermal decomposition products at 400 °C consist of perhalogenated carboxylic acid and chlorofluoroalkanes,⁵⁵⁻⁵⁷ while at 800 °C, polycyclic aromatic hydrocarbon are the major non-polar products identified.⁵⁸

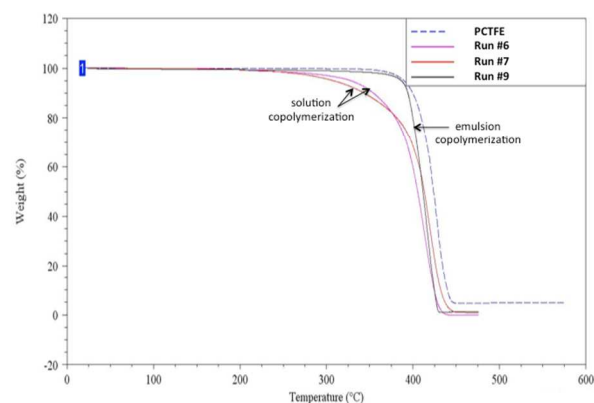


Figure 5. TGA thermograms of poly(CTFE-co-VDC) copolymers obtained under air for runs #6, #7, and #9 (Table 1) compared to that of PCTFE.

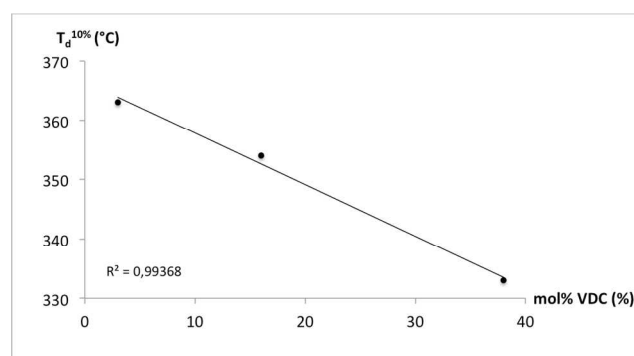


Figure 6. Plot of the $T_d^{10\%}$ values (determined by TGA under air) vs that of the molar percentage of VDC (calculated by NMR) for poly(CTFE-co-VDC) copolymers obtained at runs #1, #6, and #8 (Table 1).

Differential scanning calorimetry measurements were conducted on all poly(CTFE-co-VDC) copolymers to obtain their glass transition (T_g) and melting (T_m) temperatures (Figure 7). The results are summarized in Table 1. As reported in the literature, T_g and T_m values of PCTFE are ca. 75 °C and 211-216 °C, respectively.^{51,59} As expected, high molecular weight poly(CTFE-co-VDC) copolymers (e.g. run #9) exhibited a high T_m value close to that of PCTFE. This decrease of the melting temperature as the molar mass drops has been discussed elsewhere.⁶⁰

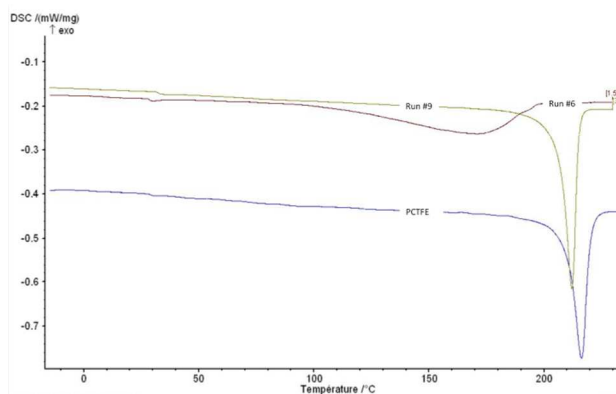


Figure 7. DSC thermograms of poly(CTFE-co-VDC) copolymers obtained for runs #6 and #9 (Table 1) compared to that of PCTFE.

It is worth mentioning that all the copolymers containing a high CTFE amount were insoluble in common organic solvents. As a result, molecular weights of these poly(CTFE-*co*-VDC) copolymers were not assessed by size exclusion chromatography.

Conclusions

Novel poly(CTFE-*co*-VDC) copolymers were synthesized in solution and in an aqueous process by radical copolymerization initiated by two different systems. A surfactant-free emulsion polymerization process allowed us to obtain poly(CTFE-*co*-VDC) copolymers in up to 75% wt. yield and exhibiting very good thermal properties. In parallel, a solution polymerization process was used to obtain a range of poly(CTFE-*co*-VDC) copolymers of lower molecular weight and soluble enough to allow a meticulous characterization by means of NMR spectroscopy. The copolymers obtained were analyzed by ^{19}F and ^1H NMR spectroscopy, and by elemental analysis. These analyses allowed us to demonstrate that poly(CTFE-*co*-VDC) copolymers exhibit a statistical microstructure with the amount of VDC in the copolymer much higher than that in the feed. The poly(CTFE-*co*-VDC) copolymers present satisfactory thermal stability. A triple resonance ($^1\text{H}/^{13}\text{C}/^{19}\text{F}$) 2D-NMR $^1\text{H}\{^{13}\text{C}\}$ -HSQC permitted the correct identification of two sets of methylene ^1H resonances: one from CH_2 groups of CTFE and VDC sequences, and a second set of resonances from the diastereotopic CH_2 protons of VDC sequences. Simplified spectra with good signal-to-noise level were provided as a result of simultaneous ^{19}F decoupling in the f_1 and f_2 dimensions. Quantitative analysis using comparison of the ^1H and ^{19}F signal intensities of the polymer with those of an internal standard containing both ^1H and ^{19}F permitted the measurement of the relative number of CTFE and VDC monomers from high sensitivity ^1H and ^{19}F 1D-NMR methods, even though neither monomer contains both protons and fluorines. These original copolymers are good candidates for barrier packaging applications.⁶¹ This matter is currently under investigation in our group and the results will be reported in due course.

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Notes and references

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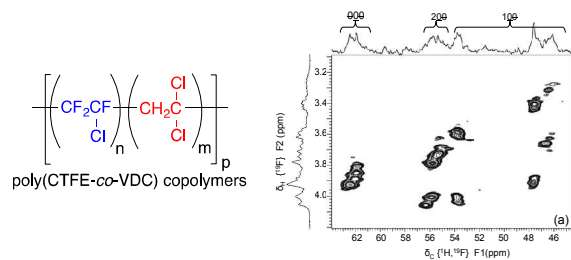
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Electronic Supplementary Information (ESI) available: Copies of the pulse program used to collect the 2D-NMR data, additional high-resolution 1D- and 2D-NMR spectra are provided. See DOI: 10.1039/b000000x/

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Graphical abstract



The synthesis of poly(chlorotrifluoroethylene-*co*-vinylidene chloride) copolymers was revisited and thorough analyses performed by NMR helped to reveal resonance assignments.