Conventional and RAFT Copolymerization of Tetrafluoroethylene with Isobutyl Vinyl Ether

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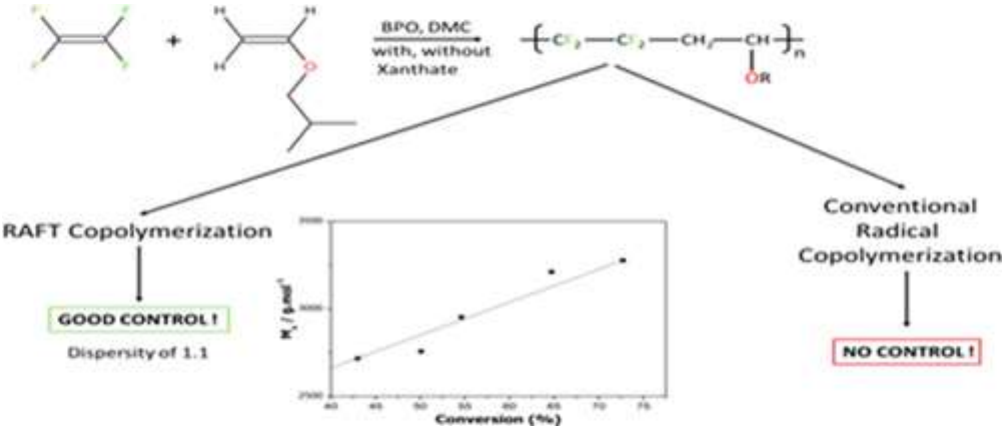
ABSTRACT:



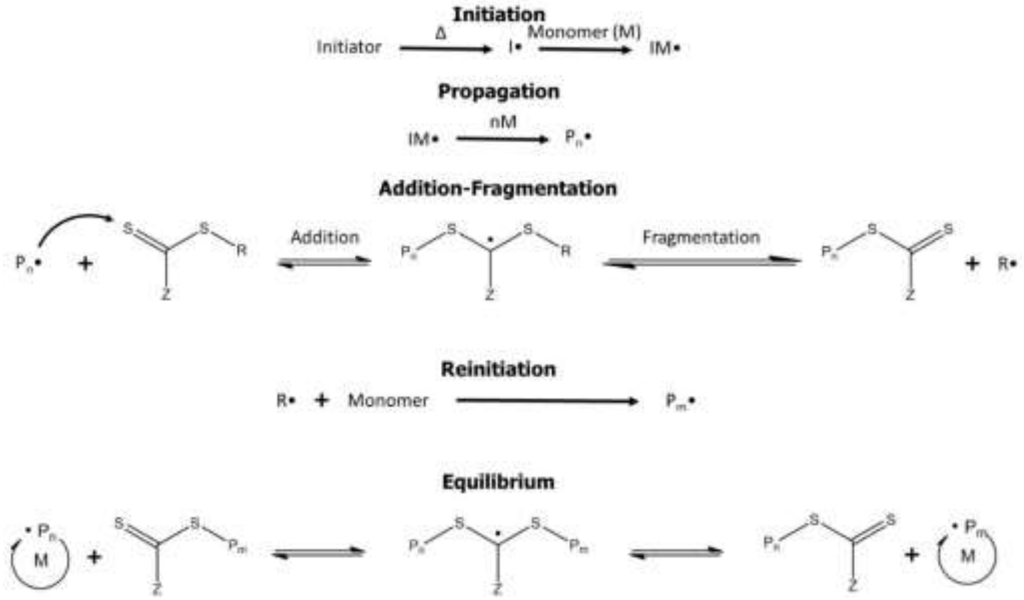
The solution copolymerizations of tetrafluoroethylene (TFE) with isobutyl vinyl ether (iBuVE), using both conventional radical and RAFT/MADIX methods are presented. O-Ethyl-S-(1-methyloxycarbonyl)ethyl xanthate and benzoyl peroxide (BPO) were used as RAFT chain transfer agent and initiator, respectively, in dimethyl carbonate. Degrees of polymerization *ca.* 20 were targeted. In all cases, alternating copolymers were obtained. Poly(TFE-*alt*-iBuVE) copolymers synthesized *via* conventional radical copolymerization using from 1 to 30 mol % BPO exhibited molar masses varying between 11000 and 4400 g·mol^{-1}, respectively, and broad dispersities (Đ = 2). Poly(TFE-*alt*-iBuVE) copolymers synthesized by RAFT/MADIX had molar masses ranging from 1200 to 2000 g·mol^{-1} at 15 min to 24 hrs, respectively, and more narrow Đs (1.08 and 1.11, respectively). The ratio of chain ends is nearly time invariant, with a slight tendency to accumulate TFE chain ends over time. Proton transfer from the solvent to the macroradicals was observed in both the conventional and RAFT polymerizations. This work is the first study of the RAFT/MADIX solution copolymerization of TFE with a vinyl ether.

INTRODUCTION

Fluorinated polymers are niche macromolecules that play an essential role in modern life[1], and due to the properties of fluorine (including among others, large electronegativity, low polarizability, and small van der Waals radius (1.32 Å)) and the strong C−F bonds (485 kJ·mol^{-1}), they exhibit unique and remarkable properties. Their applications span engineering thermoplastics and elastomers for the chemical process, automotive and aeronautics industries, weather-proof coatings, biomedical materials, separators, electrolytes, and binders for Li-batteries, exchange membranes in fuel cells, and many more. [1-11] Numerous companies, such as 3F, 3M/Dyneon, Asahi Glass (now AGC), Gore, Daikin, Chemours (formerly DuPont de Nemours), Juhua, Solvay Specialty Polymers, and Zeus, etc., produce tetrafluoroethylene (TFE) homo- and copolymers tailored for specific applications.

The practical applications of PTFE with a tailored dispersity (Đ) ranges from fluorocarbon lubricants with specific viscosities to extrudable PTFE with a custom temperature-melt viscosity relationship. Therefore, there is a purely technological, as well as a commercial interest in more effectively controlling the Đ values of TFE polymers.

TFE (co)polymers are usually synthesized *via* radical (co)polymerization [12, 13], and a number of methods are available to conduct controlled radical polymerization (also known as reversible-deactivation radical polymerization, RDRP)[14-16]. Significant studies have been reported in the last couple of decades on the controlled homo- and copolymerization of fluoroolefins using iodine transfer polymerization (ITP)[17-21] and Reversible addition-fragmentation chain transfer (RAFT/MADIX) methods[22-29]. RAFT/MADIX polymerization proceeds *via* a degenerative chain transfer (DT) mechanism in which a double equilibrium favors the control of the polymerization with high efficiency (Scheme 1)[22-38]. Recently, O-ethyl-S-(1-methyloxycarbonyl)ethyl xanthate as chain transfer agent (CTA) has been successfully applied in the RDRP of vinylidene fluoride (VDF)[22, 23, 27-29, 38] , and the limits to which VDF lends itself to controlled polymerization has been explored. Furthermore, Bai *et al.*[24, 25] reported the RAFT/MADIX copolymerizations of chlorotrifluoroethylene (CTFE) and hexafluoropropylene with n-butyl vinyl ether initiated by ^{60}Co γ-rays using S-benzyl O-ethyl dithiocarbonate as CTA.



Scheme 1: *Mechanism of reversible addition-fragmentation chain transfer polymerization (RAFT) / macromolecular design via the interchange of xanthates (MADIX).*

Telomerization of TFE, and to a certain extent, controlled radical polymerization (or RDRP) of TFE by ITP (pioneered by Tatemoto[17, 18, 39]) with various iodinated CTAs has been reviewed in a book chapter[40]. However, the control of the molar mass distribution of TFE homopolymer has heretofore not been studied significantly beyond the oligomeric stage. CTAs such as H_2 and methanol are already used in industry to cap unterminated, immobilized fluorinated macroradicals[41, 42], while numerous others have been applied to the telomerization of TFE[40], but according to the chain transfer constant value, these CTAs tend to broaden the dispersity and their effect on the dispersity is not strictly controllable. Hence, synthesis of a low molar mass PTFE with a tailored dispersity requires the use of a suitable CTA.

So far, no study has been reported on the RAFT (co)polymerization of TFE, and the application of RAFT/MADIX agents to TFE is a logical next step in the RDRP of fluoroolefins. However, homopolymers of TFE are completely insoluble in any solvent and thus cannot be subjected to any analysis for the determination of molar mass and dispersity, such as size exclusion chromatography (SEC), viscometry, light scattering, or vapor-pressure osmometry. Before attempting to apply a xanthate CTA to the TFE homopolymerization process, it was of interest to determine if such a CTA can indeed be used to control the polymerization in a soluble polymer system where TFE is present. Actually, the RDRP of TFE, that can alternate with a non-fluorinated monomer, has never been reported in the literature. As isobutyl vinyl ether (iBuVE) was previously employed with CTFE[43] and its chemistry is known (this product is marketed by Asahi Glass Co. under the Lumiflon® trade name[44]), this monomer was selected for use with TFE to render the polymer soluble and thus subjectable to liquid state NMR spectroscopy and SEC analysis. Copolymers based on TFE and vinyl ethers are produced commercially by the Daikin Company under the Zeffle® trademark.

The goal of this study aims at examining the behavior of the RAFT/MADIX copolymerization of TFE with isobutyl vinyl ether in the presence of a xanthate CTA, with the emphasis on determining if control of both the molar masses and the end groups are possible.

EXPERIMENTAL SECTION

TFE Safety. Safety is paramount when considering working with tetrafluoroethylene (TFE) as it can deflagrate, releasing approximately the same energy as blackpowder[45], potentially causing serious infrastructural damage, or even result in death . Thrasher group at Clemson University has spent years developing academic barricades to permit the safe use of large quantities of TFE in their facilities. [45] Extreme caution is advised when handling and storing TFE and the safety precautions detailed by Hercules et al.[45] should be adhered to. All work done with TFE should first be carried out in sub-gram quantities before being scaled up to any size.

Materials. TFE was produced by an in house generation unit *via* the pyrolysis of pure PTFE. [46] The PTFE (PTFE 807NX) was supplied by E.I. Du Pont de Nemours & Co and used as received.

Dimethyl carbonate (99%), acetone (99%), benzoyl peroxide (~75%, remainder water), isobutyl vinyl ether (iBuVE) (99%), K_2CO_3 (99%), and $CDCl_3$ (99%) were purchased from Sigma Aldrich. The benzoyl peroxide was dried under high vacuum at 30 °C for 24 hours before use and all other chemicals were used as received. O-Ethyl-S-(1-methyloxycarbonyl)ethyl xanthate was synthesized according to the method of

Liu *et al.* [47]. All the chemicals were stored in a fridge at 4 °C, except for the benzoyl peroxide (stored in a freezer at -25 °C).

Characterization. *Nuclear magnetic resonance spectroscopy.* Proton decoupled ^{19}F and ^{1}H NMR spectra were collected using a Bruker Avance III 400-NMR spectrometer equipped with a 5-mm broadband observe (BBO) probe. The experimental conditions for recording ^{1}H, (or ^{19}F) spectra were: flip angle 90° (or 30°); acquisition time of 4.5 s (or 0.7 s), pulse delay of 2 s, 512 scans (or 1024 scans); and a pulse width of 10.4 μs for ^{19}F NMR spectroscopy. Samples for NMR spectroscopy were prepared by dissolving 20 to 50 mg of copolymer in 1 mL of $CDCl_3$.

COSY NMR spectra of the polymers were collected at 25 °C on a Bruker Avance III 400-MHz spectrometer equipped with two independent broadband (^{15}Ne ^{31}P and ^{15}Ne ^{19}F, 300 W) and a high band (^{1}H, 100W) rf channels. A 5 mm ^{1}H/^{19}F/^{13}C TXO triple resonance pulsed field gradient probe for which ^{13}C and ^{19}F are on the inner coil and ^{1}H on the outer coil is used for three channels experiments. This probe has a lower background ^{19}F signals compared to standard dual-channel probes. This triple resonance ^{1}H/^{19}F/^{13}C probe is capable of producing short 90 °C pulses 6.5ms widths on ^{19}F, 9.5ms for ^{13}C and 9.2ms for ^{1}H channels. In all experiments, ^{1}H decoupling is realized with waltz16. ^{19}F decoupling is performed with nested loops using 0.5 ms and 1 ms chirped adiabatic pulses with 80 kHz band with in order to desynchronize and minimize decoupling artifacts.*Thermogravimetric analysis.* Thermogravimentric analysis was performed with a Hitachi STA7300 TGA-DTA instrument using α-alumina crucibles. Approximately 10 mg of sample was used for each run. Each sample was heated from 30 °C to 1000 °C at a rate of 10 °C·min^{-1} under a nitrogen atmosphere flowing at 200 mL·min^{-1}.*Size exclusion chromatography.* SEC was conducted in DMF using a Varian Prostar HPLC system coupled to a Kontron Instruments model 430 UV detector and a Shodex RI-101 refractive index detector, equipped with 2 columns in series having a total separation range of 200 to 400k g·mol^{-1} kept at 70 °C. The solvent was supplied at 0.8 mL.min^{-1}, and analyses were achieved by injection of 20 μL filtered solution (5 mg·mL^{-1}).Particle size analysis. Particle size analysis and zeta potential determination were carried out using a Malvern Zetasizer instrument fitted with a zeta potential cuvette.

Maldi-TOF spectrometry. Full scan MALDI-TOF mass spectra were recorded at Laboratoire de Mesures Physiques (Montpellier University) with a Bruker RapifleX time-of-flight mass spectrometer using a nitrogen laser for MALDI (λ 337 nm). The measurements in positive ion mode were performed with voltage and reflector lens potentials of 2 and 20 kV, respectively. For negative ion mode, the measurements were conducted with ion source and reflector lens potential of 20 and 21.5 kV, respectively. Mixtures of peptides were used for external calibration. The matrix and cationizing agent were trans-2-[3-(4-tertbutylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) (10 mg/mL in $CHCl_3$) and NaI (10 mg/mL in methanol), respectively. The polymer concentration was 30 mg/mL in acetone. The polymer and matrix were mixed in a 4:10 volume ratio, and NaI was first deposited on the target. After evaporation of the solvent, the mixture (composed of polymer, matrix and cationizing agent) was placed on the matrix-assisted laser desorption ionization (MALDI) target. The dry droplet sample preparation method was used. Number average molar masses were determined directly from the m/z domain according to the following equations[48]:

$$M_n = \frac{\sum M_i \cdot N_i}{\sum N_i} \quad \textbf{(1)}$$

$$M_w = \frac{\sum M_i^2 \cdot N_i}{\sum M_i N_i} \quad \textbf{(2)}$$

where M_i is the molar mass for a particular chain and N_i is the number of molecules of that particular chain. N_i is assumed to be directly proportional to the detector intensity.*Conventional-radical copolymerization of tetrafluoroethylene with isobutyl vinyl ether.* The experimental conditions are summarized in Table 1. For a typical reaction, TFE was copolymerized with iBuVE in a 1:1 molar ratio in thick Carius tubes at 85 °C using benzoyl peroxide (BPO) as initiator and dimethyl carbonate (DMC) as solvent. The reaction temperature of 85 °C was chosen as this is as close to the 3 hour half-life of the initiator. In all experiments, K_2CO_3 was added to the Carius tubes as an acid scavenger to prevent any cationic homopolymerization of iBuVE[49].

The Carius tubes were loaded with K_2CO_3 (0.13 g, 0.94 mmol) along with iBuVE (0.5 g, 0.5 mmol) and BPO dissolved in 5 mL of DMC. The tubes were subjected to three cycles of degassing *via* the freeze thaw method. Then, TFE (ΔP = 0.7 bar, 0.5 g) was frozen into the tube using liquid N_2, and the tubes were flame sealed under vacuum. After this, the Carius tubes were permitted to warm slowly to ambient, installed in their blast tubes within the shaking oven. After the reaction time was completed, the tubes were cooled to ambient, frozen in liquid nitrogen, and cut open. The resulting copolymer was dried, redissolved in the minimum of acetone, and precipitated into cold water, dried, precipitated once more, dried again, and subjected to vacuum (~0.1 Torr) at 80 °C to remove any remaining volatiles. Interestingly, and contrary to the behavior of poly(CTFE-*alt*-iBuVE) copolymers, the TFE-based copolymers all produced clumpy material during the first precipitation, but formed a cloudy, white suspension during the second precipitation. This suspension did not settle out over time (~8 hours observation at 22 °C) and did not settle out during centrifugation.

Furthermore, all copolymers as viscous yellow oils exhibited strong adhesive behavior, sticking to glass, metal, gloves, and skin alike.

RAFT/MADIX copolymerization of TFE with iBuVE. TFE was copolymerized with iBuVE in thick Carius tubes with the same method as above, using O-ethyl-S-(1-methyloxycarbonyl)ethyl xanthate as a CTA. The reaction temperature of 85 °C was chosen as this is close to the 3 hour-half-life of the initiator. In all experiments, and fro the same reason as above, K_2CO_3 was added to the Carius tubes as an acid scavenger. The reactions and their conditions are summarized in Table 2. A detailed procedure is given in the supporting information.

DP and Mn(NMR) Calculations Using End-Group Analysis.

DP_n and $M_{n(NMR)}$ calculations using benzoyl end-group analysis

The average number degree of polymerization (DP_n) can be calculated from ^1H NMR spectroscopy using the integrals for the signals corresponding to the methyl groups in iBuVE (doublet centered at ca. 0.81 ppm) and the ortho position hydrogens on the benzene ring of the benzoyl end-group (centered at ca. 8.02 ppm) according to equation (3), with the molar mass being calculated according to equation (4), where M_n(BPO) = 242.23 g.mol^{-1}, M_n(TFE) = 100.02 g.mol^{-1}, and M_n(iBuVE) = 100.16 g.mol^{-1}.

$$DP_n\ (BPO) = \frac{\frac{1}{6} \times \int_{0.6}^{0.95} CH_3(VE)}{\frac{1}{2} \times \int_{7.9}^{8.2} H(Ortho)} \qquad \textbf{(3)}$$

$$M_{n,NMR}(BPO) = M_n(BPO) + DP(BPO) \times M_n(TFE + iBuVE) \tag{4}$$

DP_n and $M_{n(NMR)}$ calculations using R *and* Z *end-group analysis.* Alternatively, the DP_n can be calculated from ^{1}H NMR spectroscopy using the integrals for the signals corresponding to the methyl groups of the vinyl ether (centered at ca. 0.81 ppm) and the methyl group on the CTA R-group (centered at ca. 1.15 ppm) according to equations (5) and (6), where M_n (CTA R) = 208.3 g.mol^{-1}. Similarly, the DP_n and M_n can be calculated from the CTA Z-group *via* the integral of the methyl group centered at 1.36 ppm and the six methyl protons of the vinyl ether (equations (7) and (8)),

$$DP\ (from\ CTA\ R) = \frac{\frac{1}{6} \times \int_{0.6}^{0.95} CH_3(VE)}{\frac{1}{2} \times \int_{1.05}^{1.25} CH_3(CTA\ R)} \tag{5}$$

$$M_{n,NMR}(from\ CTA\ R) = M_n CTA + DP(from\ CTA\ R) \times M_n(TFE + iBuVE) \tag{6}$$

$$DP\ (from\ CTA\ Z) = \frac{\frac{1}{6} \times \int_{0.6}^{0.95} CH_3(VE)}{\frac{1}{2} \times \int_{1.25}^{1.45} CH_3(CTA\ Z)} \tag{7}$$

$$M_{n,NMR}(from\ CTA\ Z) = M_n CTA + DP(from\ CTA\ Z) \times M_n(TFE + iBuVE) \tag{8}$$

Where M_n(TFE+iBuVE) = 200 g·mol^{-1}.

Theoretical molar mass. The theoretical molar mass for the RAFT copolymerization was calculated using equation (9) using the yields listed in Table 2.

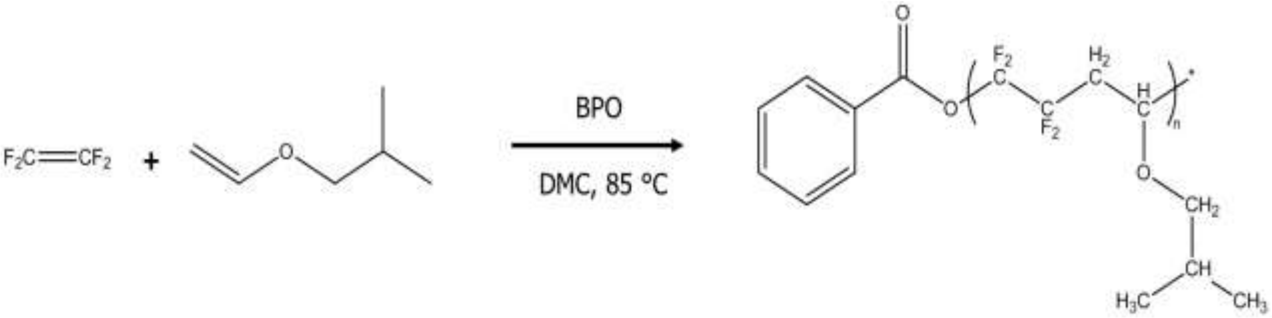
$$M_{n,theo} = M_n CTA + \frac{[TFE + iBuVE]_0}{[CTA]_0} \times yield \times M_n(TFE + iBuVE) \tag{9}$$

RESULTS AND DISCUSSION

Conventional-radical copolymerization of tetrafluoroethylene with isobutyl vinyl ether

The experimental conditions for the conventional radical copolymerization of tetrafluoroethylene (TFE) with isobutyl vinyl ether (iBuVE) using BPO as initiator, along with the characterization results, are summarized in Table 1. The expected structure of the product is shown in Scheme 2.

Benzoyl peroxide has a half-life of ca. 3 hours at 85 °C in benzene[50], decomposing into two benzoyl radical that may initiate polymerization. The decomposition kinetics for benzoyl peroxide in dimethyl carbonate are unknown, but it is reasonable to expect the kinetics to be similar to those in benzene. A polymerization temperature of 85 °C was chosen to ensure that the reaction rates are comparable to the work reported with CTFE[7,51] and persistent perfluoro-3-ethyl-2,4-dimethyl-3-pentyl radical [43]. A 50 mol % feed of TFE to iBuVE was chosen since the maximum rate of polymerization is found at this ratio[52].



Scheme 2: *Radical copolymerization of tetrafluoroethylene with isobutyl vinyl ether initiated by benzoyl peroxide (BPO) in dimethyl carbonate (DMC) leading to a poly(TFE-alt-iBuVE) alternating copolymer.*

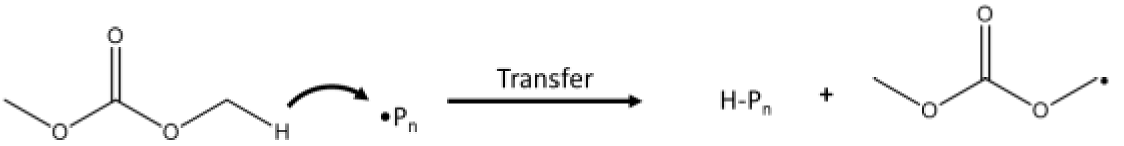
All polymers were isolated as highly viscous, yellow liquids, with the viscosity increasing as initiator concentration decreased. Precipitation into water did not alter the appearance of the final product. Attempts to precipitate in solvents besides water all met with failure. Indeed, cold pentane, n-hexane, cyclohexane, and methanol all solubilized the resulting copolymers. Likewise, the copolymer was soluble in DMSO, chloroform, acetone, THF, DMF, dimethyl acetamide, and a range of alcohols.

Measurement of the zeta potential for the polymer synthesized with 5% BPO gave a potential value of -20 mV, indicating an incipiently stable suspension[53, 54]. Particle size analysis of the polymer suspension indicated a d_{50} particle size of *ca.* 200 nm.

Nuclear magnetic resonance spectroscopy of poly(TFE-alt-iBuVE) copolymers prepared by radical polymerization.

Figure 1 and Figure S1 exhibit the ^{1}H NMR spectra for poly(TFE-*alt*-iBuVE) copolymers prepared with 1% and 30% initiator, while the ^{19}F NMR spectra are shown in Figure 2 and Figure S2. Figure 1 displays the absence of signals centered at 6.6 ppm, which is assigned to the vinyl C-H proton of iBuVE. The signals centered at ca. 4.0, 3.4, 2.43, 1.77, and 0.83 ppm are attributed to the expected groups for iBuVE in a poly(TFE-*alt*-iBuVE) copolymer. The tiny signal at -138 ppm in the ^{19}F NMR spectra (Figure 2 and Figure S2) corresponds to the CF_2-C**F**$_2$-H moiety[55, 56]. This observation is reinforced by the presence of some small signals at 6.1 ppm ($^2J_{HF}$ = 54.3 Hz) in the ^{1}H NMR spectrum, assigned to such CF_2-**H** end-groups [55, 56].

Guerre *et al.* [27] demonstrated that transfer from the solvent occurred with VDF polymerization in DMC, as shown in Scheme 3, to produce a polymer dead chain and a radical DMC fragments, which may initiate a further polymerization or terminate other macroradicals by recombination. In the ^{1}H NMR spectrum (Figure 1), where 1% BPO was used, are signals ranging between 3.5 and 3.8 ppm are assigned to **CH**$_3$-O-(C=O)-O-R moieties. These signals are quite small and indicate that proton transfer from the solvent (proton abstraction from DMC by polymer radicals) is quite negligible in such a copolymer prepared from 1% BPO.



Scheme 3: *Mechanism of proton transfer from DMC onto macroradicals to produce a polymer dead chain and DMC radical fragments.*

The ^{1}H NMR spectrum of poly(TFE-*alt*-iBuVE) copolymer achieved from 30% BPO (Figure 1) exhibits the signals of the protons in the benzene ring and several small signals ranging from 0.9 to 1.25 ppm, probably assigned to trace of solvents.

The calculated number average molar mass(calculated by equations (3) and (4)) from the NMR spectrum gives a DP_n of ~5 (~1000 g·mol^{-1}). The same calculation indicates at DP_n of ~100 (~20000 g·mol^{-1}) for the polymer initiated with 1% BPO. Table 1 lists the calculated number average molar masses of the other copolymers. The calculations assume a chain termination by recombination, as is the case for PTFE [57, 58] .

The stereochemistry of the poly(TFE-*alt*-iBuVE) copolymer backbone as viewed from a CF_2 unit is shown in Figure S1 along with an enlargement of the region from 3 to 3.5 ppm for the 1% BPO polymer showing both the normal proton and ^{19}F decoupled proton signals. The signals for the CH_2 in the polymer backbone remain unchanged with fluorine decoupling of the protons, indicating that the $^3J_{HF}$ coupling is negligible for the CH_2 protons.

The ^{19}F NMR spectra display signals at -75 ppm, assigned to the CF_2 groups adjacent to the initiator moiety (Ph-(C=O)-O-$C\mathbf{F}_2$-CF_2-). Such a chemical shift is in agreement with that of the (OCF_2CF_2) units in perfluoropolyethers (type $(OCF_2CF_2)_n(OCF_2)_m$) [59].

The region from -110 ppm to -125 ppm is shown in enlarged form in Figure S3 along with the splitting patterns and exhibits two AB systems. These systems can be explained from the stereochemistry of the chain, depicted in Figure S4. Given that each TFE-iBuVE dyad in the polymer backbone contains a stereocenter, splitting of the fluorine signals due to magnetic non-equivalence will occur. First, geminal coupling ($^2J_{FaFa'}$) between Fa and Fa' is observed at 280.4 Hz, while signals assigned to both fluorine atoms are centered at -123 and -118 ppm (Figure S3). Second, from the stereochemistry, Fa is anticipated to undergo vicinal and gauche coupling with Fb and Fb', respectively, while Fa' is expected to exhibit gauche and anti-position coupling with Fb and Fb', respectively. This is in agreement with the findings of Hikita *et al* [13].

The ^1H-^{19}F HeteroCOSY NMR spectrum for poly(TFE-*alt*-iBuVE) copolymer initiated by 1% BPO is presented in Figure S5. ^1H-^{19}F HeteroCOSY NMR confirmed the -CF_2-CF_2-CH_2-CH(OR)-CF_2-CF_2- alternating structure and the assignments made in Figure 2. Actually, that spectrum displays the expected correlation spots of i) $C\underline{\mathbf{F}}_2$-$C\underline{\mathbf{H}}_2$ at -109 to -115 ppm and 2.6-2.8 ppm and ii) those of $C\underline{\mathbf{F}}_2$-$C\underline{\mathbf{H}}$(OiBu) at -119 to -124 ppm and 4.1 ppm, respectively.

The mode of termination is of some importance and five of the six possible modes are presented in Scheme 4. The absence of the ^{19}F NMR signal at -122 ppm [60, 61] (see Figure 2) evidences the absence of central $\mathbf{CF_2}$ groups in TFE-TFE (*i.e.* -iBuVE-$CF_2\mathbf{CF_2}$-$\mathbf{CF_2}CF_2$-iBuVE-) dyads. This indicates that, in that special case of copolymerization with iBuVE, P_n-TFE• to P_m-TFE• recombination does not occur.

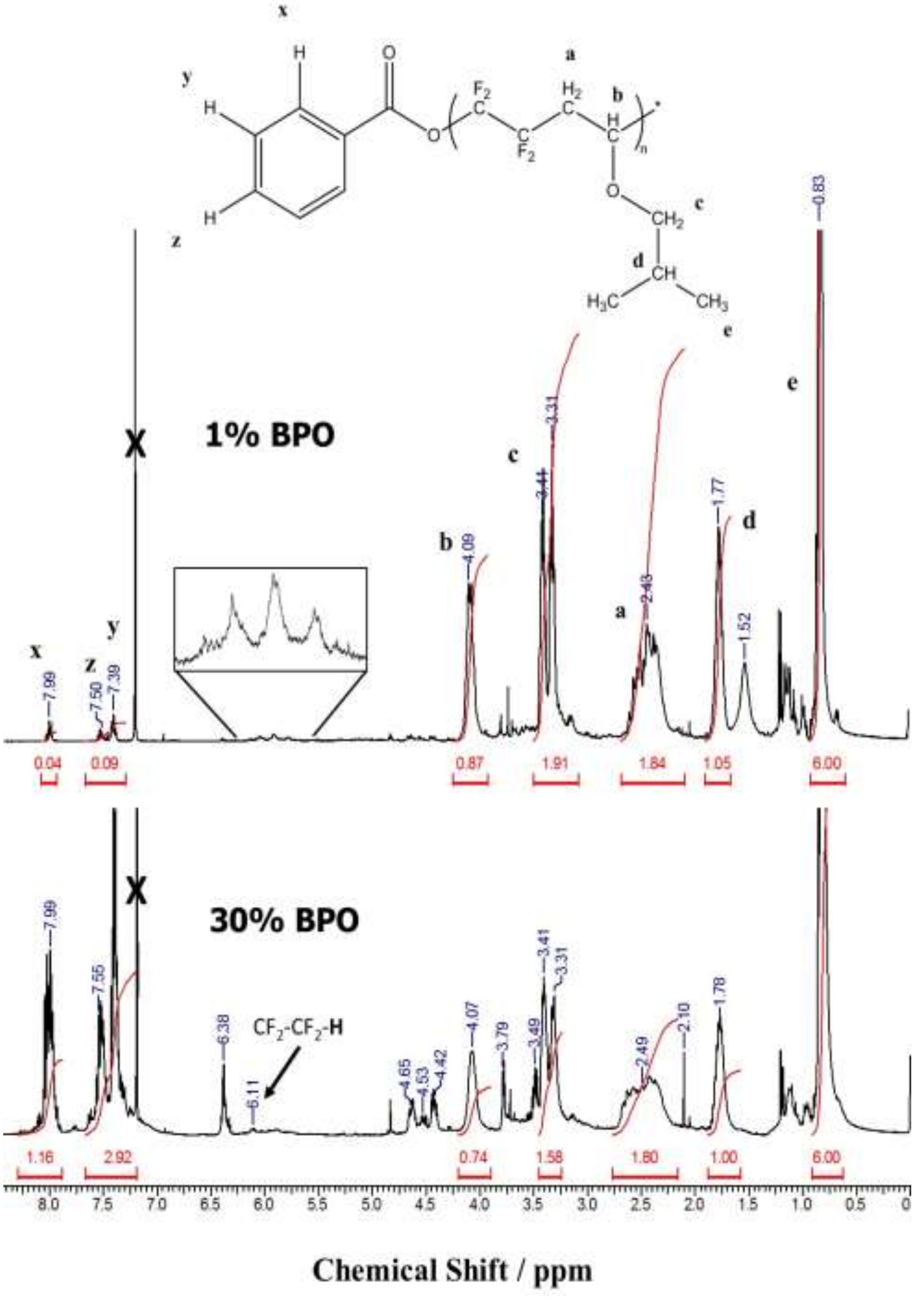


Figure 1: *^1H NMR spectra of poly(TFE-alt-iBuVE) copolymers achieved from the radical copolymerization of TFE and iBuVE initiated from 1 and 30% BPO (recorded in $CDCl_3$).*

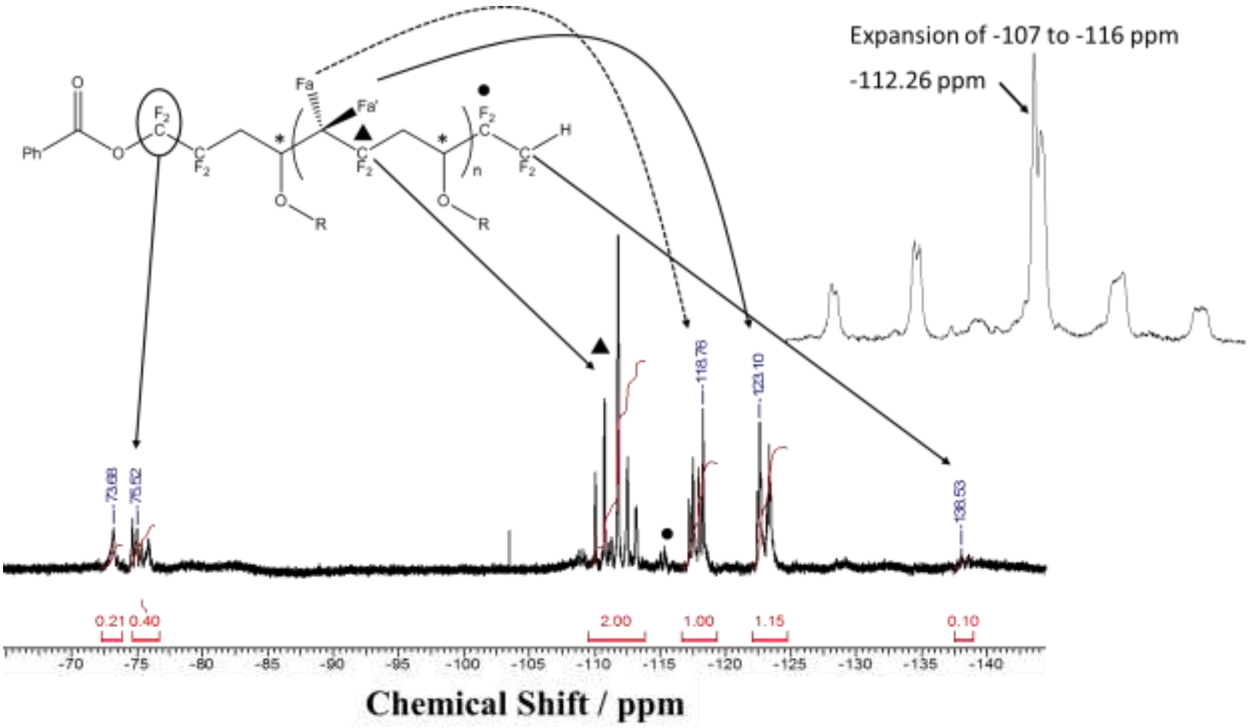
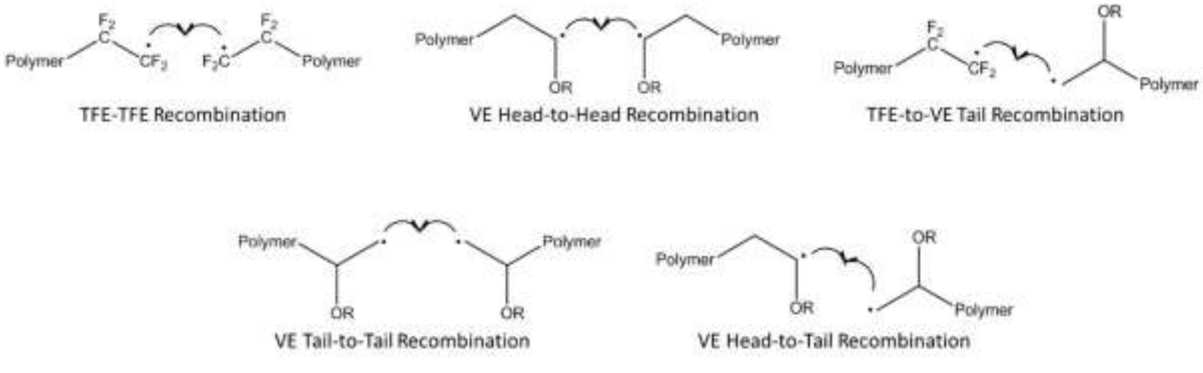


Figure 2: *^{19}F NMR spectrum of poly(TFE-alt-iBuVE) copolymers at 1% BPO (recorded in CDCl$_3$).*

Unclear assignments are for the signals at 4.65 and 4.4 ppm in the 30% BPO ^{1}H NMR spectrum (Figure 1) that may correspond to the CH-CH moieties of head-to-head termination or CH$_3$OC(O)OC**H**$_2$-CF$_2$CF$_2$, or Ph-COO-C**H**$_2$CH(OiBu)- while those at 3.79 and 3.49 ppm are assigned to CH(OR) groups. The signal centered at 1.52 ppm in the 1% BPO ^{1}H NMR spectrum may be attributed to the CH$_2$-CH$_2$ moieties of tail-to-tail termination. The preferred mode of termination in conventional radical copolymerization of TFE with iBuVE seems to be either a TFE-vinyl ether recombination (more favored) or termination *via* tail-to-tail recombination of the vinyl ether (Scheme 4).



Scheme 4: *Modes for the termination by recombination of macroradicals for poly(TFE-alt-iBuVE) copolymer.*

Moreover, regarding the possible disproportionation of $P_nCH_2C{\bullet}H(OiBu)$ into $P_nCH_2CH_2OiBu$ and $P_nCH{=}CH(OiBu)$, no expected NMR signals (3.5-3.7 ppm and 6.5-7.0 ppm, respectively) that evidence such structures have been observed.

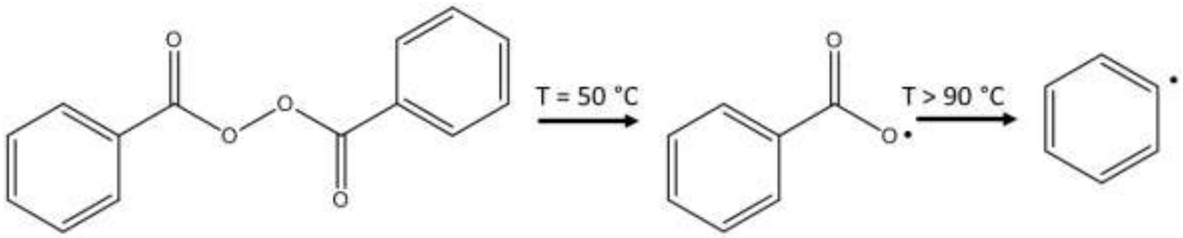
Table 1: *Experimental conditions and results obtained for the conventional radical copolymerization of TFE with iBuVE initiated by BPO at 85 °C in DMC.*

Experiment No.	**Monomer TFE + iBuVE (mmol)**	$\frac{[BPO]_0}{[TFE]_0+[iBuVE]_0}$ **(mol %)**	**Yield (%)**	**$M_n{}^a$ (g.mol^{-1})**	**$M_n{}^b$ (g.mol^{-1})**	**$T_d{}^{10\%,c}$ (°C)**	**Đ**
1	9.98	1	14	11000	20250	305	1.44
2	9.98	5	21	8000	12550	275	1.62
3	9.98	10	25	6100	3050	225	1.29
4	9.98	15	33	5100	1950	225	2.18
5	9.98	30	46	4400	1050	180	1.03

[a] M_n as determined by GPC (or SEC) [b] M_n as determined by ^1H NMR spectroscopy from equations (3) and (4) [c] Decomposition temperature at which the polymer has undergone 10% mass loss.

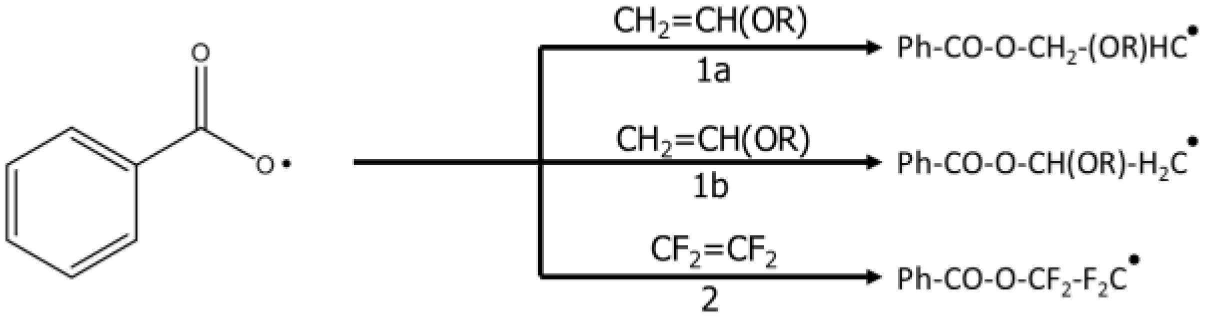
Addition preferences of the benzoyl radicals to the TFE/iBuVE monomer mixture

Benzoyl peroxide undergoes decomposition to form two kinds of radicals, as detailed in Scheme 5 [62-64]. The decarboxylation of the benzoyl radical to give a phenyl radical generally becomes significant only at high temperatures (>90 °C) [62-64], and thus, it is very slow at the reaction temperature where this work was conducted. Indeed, Bevington and Toole [65] demonstrated that when benzoyl peroxide is used as initiator at 80 °C, 93 mol% of the radicals initiating the polymerization of styrene are benzoyl radicals, not phenyl radicals. The ratio of benzoyl to phenyl radicals are a strong function of the activation energy required to add onto the double bond [65]. TFE is known to be highly reactive, much more than styrene as evidenced by the propagation constants reported in the Polymer Handbook[66] ($k_{p,\mathrm{TFE}}$ and $k_{p,\mathrm{Styrene}}$ are 7400 and 102 $L{\cdot}mol^{-1}{\cdot}s^{-1}$ at 40 °C, respectively). Hence, the possibility of attack of phenyl radicals is not considered here. Besides this, the signal for a CF_2-$\mathbf{CF_2}$-Ph moiety is expected at -111.6 ppm[67]. Furthermore, it is nearly impossible to determine the extent to which initiation by phenyl radical may have occurred since this region also contains the signals for other CF_2 groups.



Scheme 5: *Thermal decomposition process of benzoyl peroxide to release benzoyl or phenyl radicals*[62-64].

Scheme 6 details the three possible additions of benzoyl radicals onto the monomer mixture. The expected chemical shifts for the CH_2 in path 1a is *ca.* 4.5 ppm, while that for CH in path 1b is ca. 6.4 ppm. The signal assigned to CF_2 in Ph-CO-O-CF_2 moiety should appear in the region of -74 to -78 ppm in the ^{19}F NMR spectrum [59].



Scheme 6: *Possible addition reactions of benzoyl radicals onto the TFE/iBuVE mixture.*

The expected attack preference should be *via* path 1a as the benzoyl radical is electrophilic and the CH_2 of iBuVE is both slightly nucleophilic and the sterically less hindered site. Concomitantly, attack *via* TFE is not expected to occur as this monomer is an electron acceptor[40]. In contrast, the ^{1}H NMR spectrum of the copolymer obtained from 1% BPO does not exhibit any signal at 4.5 ppm nor at 6.4 ppm.

The ^{1}H and ^{19}F NMR spectra of copolymer obtained from 30% BPO seem to show attack *via* all three pathways, and this is ascribed to an excess of benzoyl radicals, stripping the DMC solution of TFE and concomitantly attacking any available double bond, as well as proton transfer from the monomer to the macroradicals.

TFE is sparingly soluble in water and slightly soluble in organic solvents such as DMC. For aqueous (co)polymerization of TFE, the main factor limiting the rate of polymerization is the diffusion of TFE into the polymerization medium. The observed concurrency of the attack pathways of BPO implies that, even in a solvent such as DMC, the limiting factor for the conventional radical copolymerization of TFE with iBuVE is the mass transfer of TFE into the solution.

MALDI-TOF mass spectrometry

The structures of poly(TFE-alt-iBuVE) copolymers synthesized via conventional radical polymerization were also characterized by matrix-assisted laser desorption/ionization coupled time-of-flight mass spectrometry (MALDI-TOF) using both positive and negative ion modes.

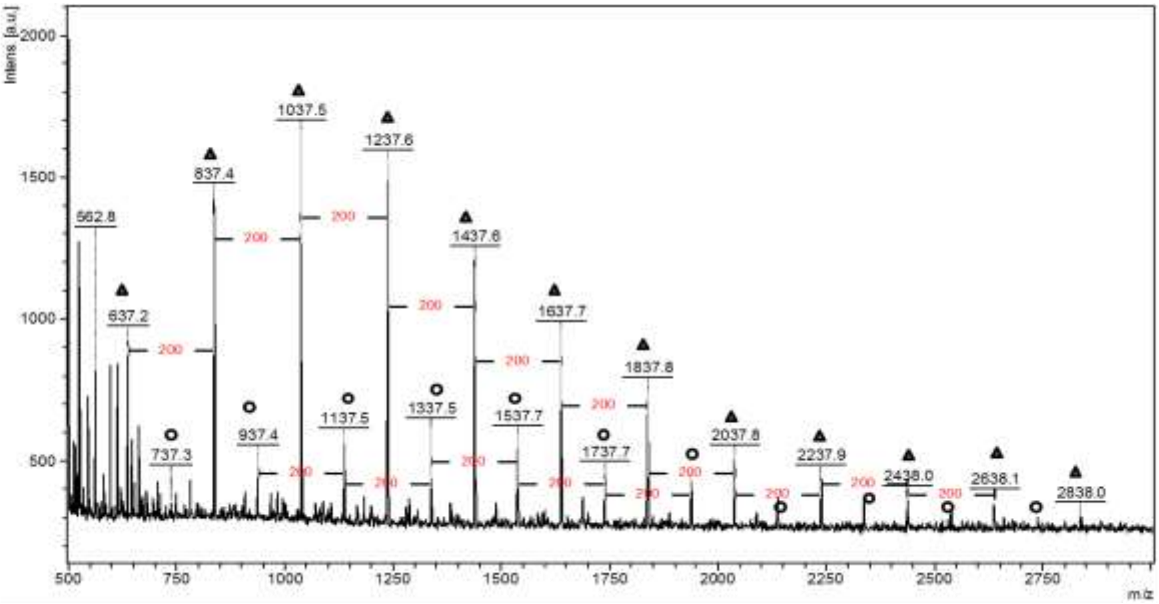


Figure 3: *Negative ion MALDI-TOF mass spectrum of poly(TFE-alt-iBuVE) copolymers synthesized by conventional radical copolymerization with 30% BPO (*Table 1*, experiment 5) with DCTB as matrix and LiCl as cationic agent. The ▲ distribution corresponds to oligomers with a CF_2-CF_2- $OCOC_6H_5$ end-group and the **o** distribution to those with a VE-$OCOC_6H_5$ end-group.*

The MALDI-TOF mass spectrum of poly(TFE-alt-iBuVE) copolymer synthesized with 30% BPO (Table 1, experiment 5) recorded in negative ion mode (Figure 3) displays two distributions in the form of deprotonated adducts (M-H)- as presented in the spectrum between 500 and 3000 m/z. The more intense distribution corresponds to oligomers of formula $HO[CF_2CF_2CH_2CH(OCH_2CH(CH_3)_2)]_mCF_2CF_2OCOC_6H_5$ (marked with a triangle, Figure 3), and the second one is attributed to formula $HO[CF_2CF_2CH_2CH(OCH_2CH(CH_3)_2)]_mOCOC_6H_5$ (marked with a circle, Figure 3). All distributions display the repeat unit mass between two consecutive peaks ($\Delta m/z = 200$ g·mol^{-1}) that confirms the presence of $[CF_2CF_2CH_2CH(OCH_2CH(CH_3)_2)]$ dyads. No oligomers were detected in the positive ion mode. Indeed, the MALDI data confirm that benzoyl radicals do preferentially attack onto TFE to initiate the copolymerization. These data also corroborate the M_n value determined by NMR spectroscopy: End group analysis by ^1H NMR spectroscopy indicates a M_n of 1050 g·mol^{-1} for experiment 5 in Table 1 while the average molar mass obtained by MALDI-TOF mass spectroscopy (equation (1)) is *ca.* 1100 g·mol^{-1}. More detailed peak assignments are given in Table S1.

Effect of [initiator] on the molar mass of poly(TFE-alt-iBuVE) copolymers

The number average molar masses, determined by both ^{1}H NMR spectroscopy (using the benzoyl end group as a label, equations (3) and (4)) and GPC (using PMMA standards), are compared in

Figure **4**. Dispersities are summarized in Table 1. According to Tobolski's law[68, 69] (equation (10)), the instantaneous degree of polymerization depends upon several parameters such as the reactant concentrations, the efficacy of the initiators (f), the propagation rate of the monomers (k_p), decomposition rate of the initiator (k_d), and the termination rate (k_t) with a = 1 when termination by recombination[57, 58] is considered.

$$Instantaneous\ DP_n = \frac{(1+a)k_p[Monomer]}{2\sqrt{(fk_d[BPO]k_t)}} \qquad \textbf{(10)}$$

As expected, for increasing BPO concentrations, the molar mass decreases, but there is little correlation between the M_n determined *via* GPC and *via* NMR spectroscopy, due to the difference between the hydrodynamic volume of the polymer and PMMA standards. However, the Đ values are rather narrower than what would be expected for a conventional radical polymerization, although considerable variance exists in Đ data, indicating that the copolymerization of TFE with iBuVE is not an inherently well behaved system with respect to abstraction and termination.

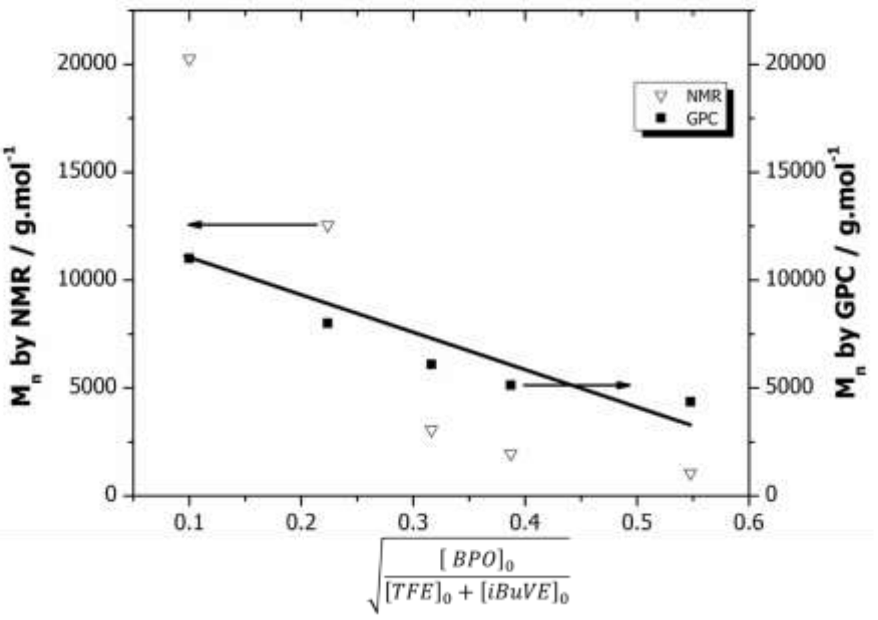


Figure 4: *Correlation of Mn decrease as BPO ratio increases, determined by both GPC (■) and ^{19}F NMR spectroscopy (∇).*

Thermal properties of poly(TFE-alt-iBuVE) copolymers terminated by benzoyl groups

TGA thermograms of poly(TFE-*alt*-iBuVE) copolymers synthesized with 1, 5, 10, 15, and 30 mol % BPO under nitrogen atmosphere are presented in Figure 5. These copolymers exhibit a satisfactory thermal stability, being thermally stable up to 200 °C, before undergoing elimination of HF and, subsequently, the scission of the polymer backbone to produce the breakdown products, as reported by Zulfiqar *et al.* [70-72]. Importantly, the effect of molar mass is strongly observed, with the evaporation of low molar mass material occurring well before proper thermal decomposition. As with the CTFE copolymers, [43] thermal decomposition temperatures remained the same whether the analyses were run in air or in nitrogen.

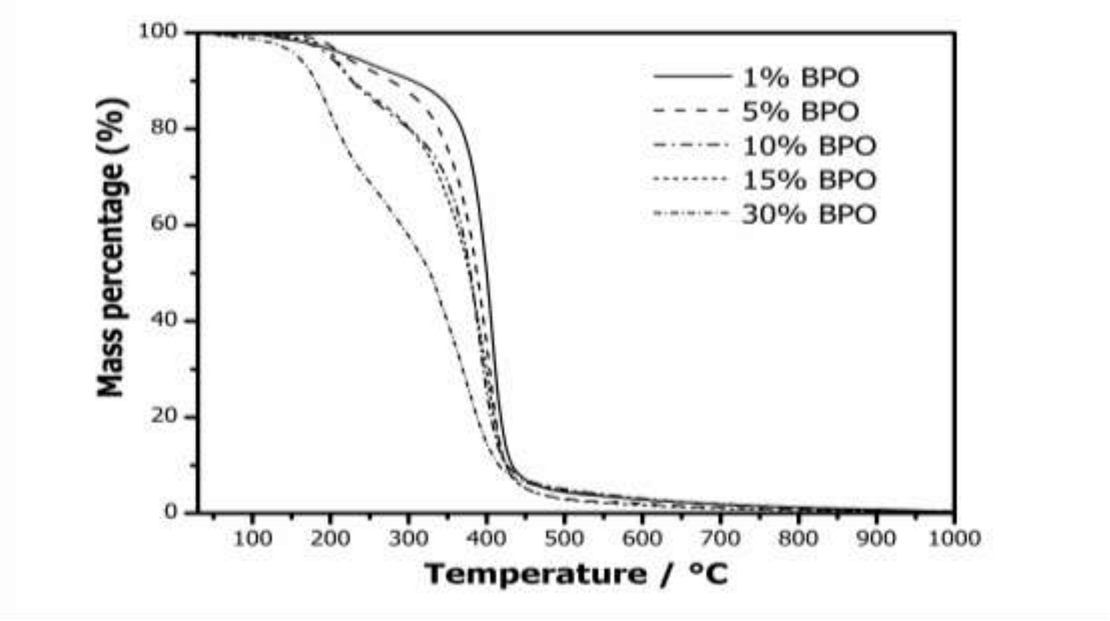


Figure 5: *TGA thermograms of poly(TFE-alt-iBuVE) copolymers synthesized with 1, 5, 10, 15, and 30 mol % BPO under an N_2 atmosphere.*

RAFT copolymerization of TFE with iBuVE

The experimental conditions for the RDRP of TFE and iBuVE using BPO as initiator and O-ethyl-S-(1-methyloxycarbonyl)ethyl xanthate as RAFT/MADIX CTA, along with the characterization results, are summarized in Table 2. The structure of the expected copolymers is shown in Figure 6. As above, the resulting copolymers were all isolated as highly viscous, yellow liquids, showing stickiness and a propensity to form an emulsion in water. Due to the nature of the xanthate, all copolymers exhibited a strong smell. The RAFT copolymerization of TFE with iBuVE is fast as 43% conversion was obtained after only 15 min.

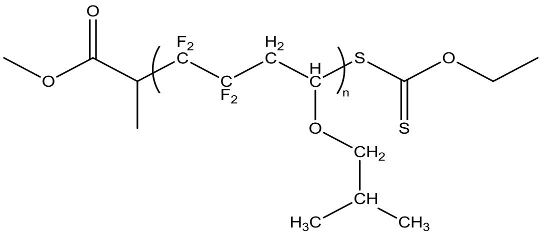


Figure 6: *Expected structure of poly(TFE-alt-iBuVE) alternating copolymer from the RAFT copolymerization of TFE and iBuVE initiated by benzoyl radical and controlled by O-ethyl-S-(1-methyloxycarbonyl)ethyl xanthate.*

Nuclear magnetic resonance spectroscopic characterization of poly(TFE-alt-iBuVE) copolymers synthesized via RAFT/MADIX

The ^{1}H and ^{19}F NMR spectra for poly(TFE-*alt*-iBuVE) copolymer controlled by xanthate taken at 15 minutes are presented in

Figure **7** and Figure 8, respectively, and enlargements of various regions of interest are given in Figure S6 along with the coupling constants and structural assignments. The structural assignments for the xanthate end groups are based on the assignments reported by Guerre *et al.* [27, 28, 38, 73]

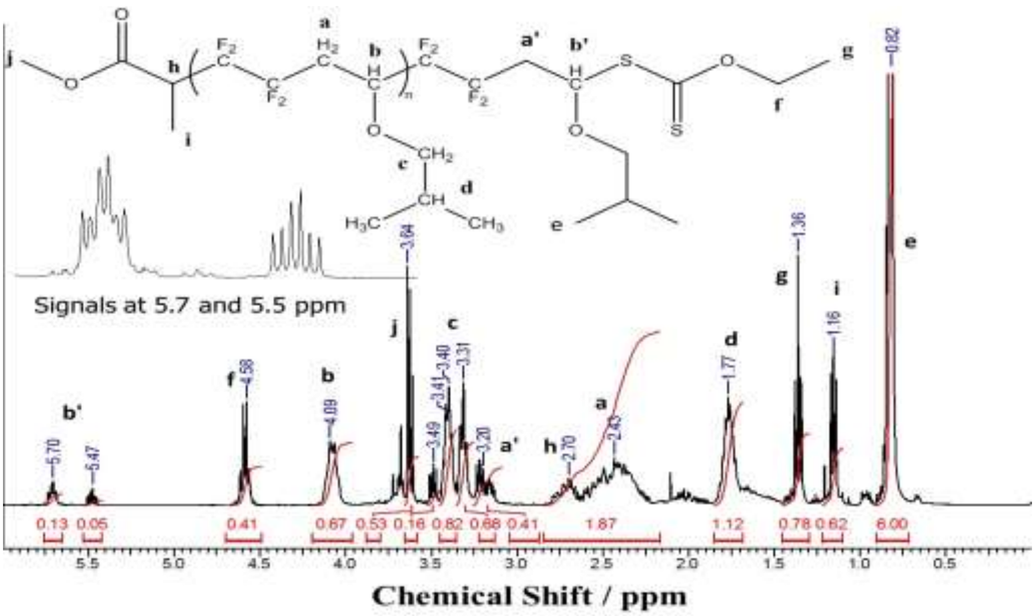


Figure 7: *^{1}H NMR spectrum of RAFT copolymerization of TFE with iBuVE controlled by xanthate, sampled at 15 min (recorded in CDCl$_3$).*

The nature of the moiety to which the Z-group of the xanthate binds is of significant interest as this functionality determines the long term reactivity of the macroradical[27]. For the RAFT/MADIX polymerization of VDF, it is possible to switch the end moiety from CF_2 to CH_2 if the VDF adds to the macroradical in a manner that produces head-to-head chain defects (and thus allows CH_2-xanthate to accumulate in the medium). Depending on the manner in which the chain initiates and the nature of the addition of the monomers to the chain end, a poly(TFE-*alt*-iBuVE) copolymer may have either CF_2 or CH end moieties adjacent to the Z-group. The evolution of the end moieties with time is of interest, as it will reveal if the monomers add to the chain in a concerted manner, or if only one monomer at a time adds to the chain end.

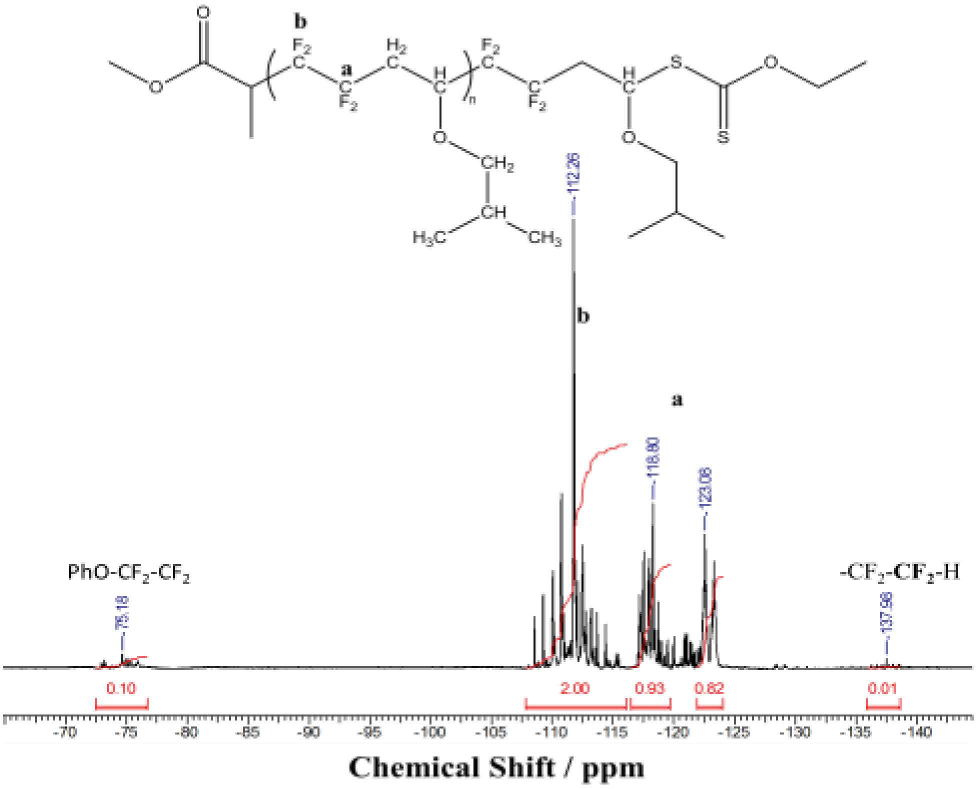


Figure 8: *^{19}F NMR spectrum of the total product mixture of the radical copolymerization of TFE with iBuVE initiated by BPO and controlled by xanthate, taken at 15 min (recorded in $CDCl_3$).*

The signal at 1.15 ppm (

Figure **7** and Figure S6) appears to be comprised of two doublets (which belong to the CO-CH(**CH_3**)- R group) that almost overlap. This indicates that the CH moiety is attached to two different groups, which arises from a mixed initiation mode by the R group. The relative intensities of these doublets are nearly equal and do not change with time, indicating a binary initiation regime, with R group attack onto TFE and iBuVE to be equally likely.

The low field shifted signals centered at -75 ppm, pose an assignment problem. Actually, Dear and Gilbert [74] reported that the ^{19}F NMR signal for central CF_2 groups in CF_3-S-C**F_2**-C**F_2**-S-CF_3 appears at -85 ppm, a signal which is absent in Figure **8**. However, Haran and Sharp [75] noted a CF_2 signal that shifts down to ca. -75 ppm when linked to a CFH group and the CF_2 adjacent to the first then exhibits a signal in the region of *ca.* -118 to -123 ppm (as in CFH-**CF_2**-CF_2-S). Assuming the electron-withdrawing CH(O-R) group in vinyl ether approximates the CFH group, the signals assigned to the difluoromethylene groups in –CH_2-

CH(OiBu)-C**F**$_2$-**CF$_2$**-S-(C=S) will be nearly identical to that of Ph-(C=O)-O-**CF$_2$**-CF$_2$ and of the main chain CF$_2$ units. In addition, the AB system at *ca.* -112 ppm is more complex by the presence of the asymmetric carbon atom of R-group in the xanthate. This makes the identification of CF$_2$-S-(C=S) very difficult from the ^{19}F NMR spectra alone (Figures S12-S16). In addition, compared to its absence in Figure 1, Figure 7 exhibits the presence of a complex systems at 5.5 to 5.6 ppm range assigned to C**H**(OiBu)SC(S)OEt end-group.

The signal at 3.21 ppm, absent in Figure 1, indicates that the CH$_2$ group of a vinyl ether unit is attached to the Z group. Furthermore, the signal at ca. 4.6 ppm corresponds to CH$_3$-**CH$_2$**-O-(C=S)-S- in Z group. This signal shows two overlapping quartets: (i) the lower field and more intense of these quartets is assigned to CH$_3$-**CH$_2$**-O-(C=S)-S-CF$_2$-CF$_2$-, whereas, (ii) the less intense and more upfield one is attributed to CH$_3$-**CH$_2$**-O-(C=S)-S-CH$_2$-CH(OCH$_2$-CH(CH$_3$)$_2$)-.

Figure 9 details the evolution of these signals with conversion. There is almost no change in the ratio of these signals with time, implying a mixed termination mode. The S-CF$_2$ and the S-CH$_2$ are cleavable with equal ease and the S-CH$_2$ does not result in a dead chain (unlike in the case for PVDF[27]). Despite the near time invariance of these signals, there is still a noticeable difference in the ratio between them, indicating that the TFE end group is preferred.

The complex signals centered at 3.64 ppm, assigned to CH$_3$ in CH$_3$-O-C(O)-O-CH$_2$-R, arises from DMC radical that initiates a chain. The observation of such a transfer is reinforced by the presence of the signals at -138 and -115 ppm in the ^{19}F NMR spectra assigned to CF$_2$-C**F**$_2$-H[56] and C**F**$_2$-CF$_2$-H end group. This indicates that transfer from the solvent (Scheme 3) occurs during RAFT/MADIX copolymerization, as observed in the RAFT polymerization of VDF[27].

Three mechanisms have been proposed for acceptor-donor copolymerization: the first one involves the formation of a charge transfer complex (CTC) which adds onto the growing macroradical [76, 77]. The second mechanism suggests that electrostatic interactions and polarity differences between the radical chain end and the inserting monomer result in vastly different activation energies that energetically favor alternating monomer addition[78], while the third mechanism proposes that both free monomers and a charge transfer complex take part in the copolymerization.

The TFE/iBuVE system has not been shown to induce a CTC formation, but does exhibit an acceptor-donor (AD) behavior[40] . The second AD mechanism is only practical if both monomers are difficult to homopolymerize, but since TFE readily propagates,[4-6] the second mechanism seems not to be applicable. Taking into account that there is a mixed initiation mode and a mixed termination mode, it appears that, once the chain has been initiated, a concerted insertion of iBuVE and TFE should occur onto the macroradical. This seems to indicate that TFE copolymerizes with iBuVE *via* the CTC addition mechanism to produce an alternating copolymer.

MALDI-TOF mass spectrometry

Characterization of the structures of poly(TFE-*alt*-iBuVE) copolymers produced from MADIX copolymerization was also performed by MALDI-TOF using both positive and negative ion modes. The MALDI-TOF mass spectrum recorded in negative ion mode of poly(TFE-*alt*-iBuVE) recovered after 15 minutes (Table 2, experiment 1, Figure 10) displays four distributions. All distributions exhibit the repeat unit mass between two consecutive peaks ($\Delta m/z = 200\ g{\cdot}mol^{-1}$) that confirms the presence of alternating $[CF_2CF_2CH_2CH(OCH_2CH(CH_3)_2)]_m$ dyads. The most intense distribution corresponds to oligomers of formula $CH_3OOC(CH_3)CH[CF_2CF_2CH_2CH(OCH_2(CH_3)_2)]_nCF_2CF_2SH$ (marked with a star) that might have decomposed in the MALDI process while the second distribution is assigned to $CH_3OOC(CH_3)CH[CF_2CF_2CH_2CH(OCH_2(CH_3)_2)]_nS(C{=}S)OCH_2CH_3$ oligomers (marked with a triangle). The oligomer of formula $CH_3OOC(CH_3)CH[CF_2CF_2CH_2CH(OCH_2(CH_3)_2)]_nSH$ (marked with a circle) and the $CH_3OOC(CH_3)CH[CF_2CF_2CH_2CH(OCH_2(CH_3)_2)]_nCF_2CF_2S(C{=}S)OCH_2CH_3$ oligomers, are the least intense. More detailed peak assignments are given in Table S2.

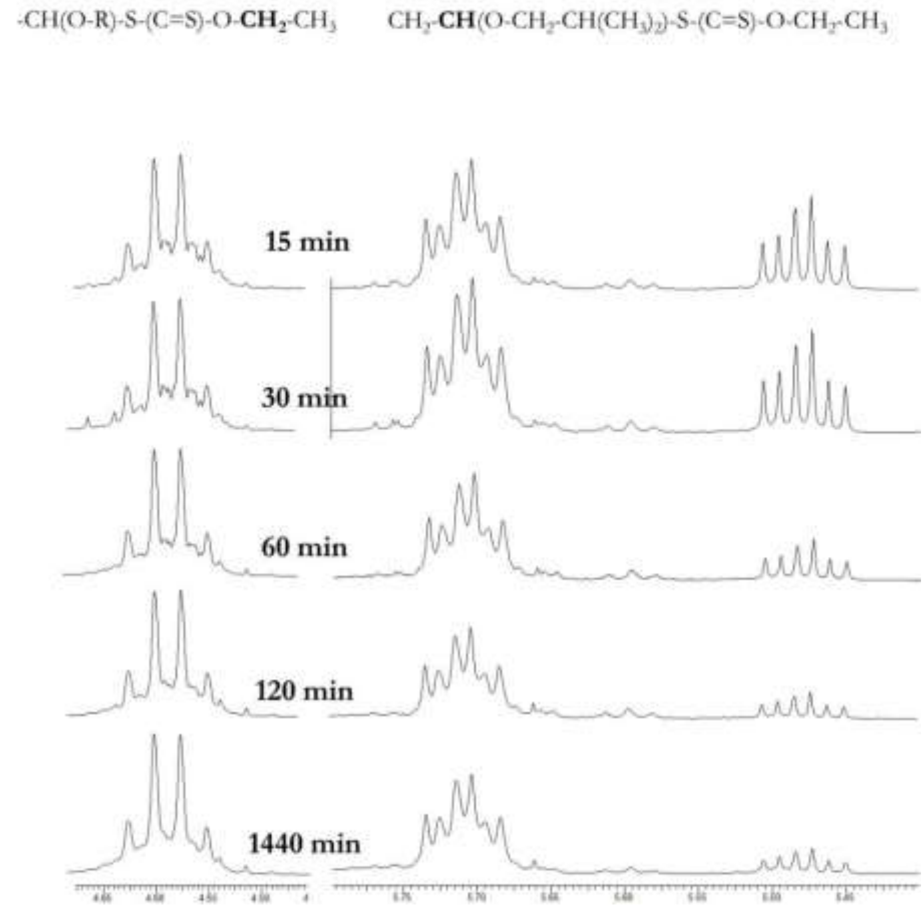


Figure 9: *Evolution of selected ^{1}H NMR spectroscopic signals with time of poly(TFE-alt-iBuVE) copolymers synthesized via MADIX polymerization using a 1:1 ratio of comonomers and a [Monomers]$_0$:[CTA]$_0$:[BPO]$_0$ initial molar ratio of 20:1:0.1, with O-ethyl-S-(1-methoxycarbonyl)-ethyldithiocarbonate as CTA.*

Table 2:

Experimental		
$M_n{}^a$	**$M_n{}^b$**	**Đ**
2700	1200	1.08
2760	1400	1.08
2950	1600	1.09
3200	1800	1.10
3300	2000	1.11

$^a M_n$ as determined by GPC $^b M_n$ as

Experiment No.	**Monomer TFE + iBuVE (mmol)**	$\frac{[\boldsymbol{BPO}]_0}{[\boldsymbol{TFE}]_0 + [\boldsymbol{iBuVE}]_0}$ **(mol %)**	**Xanthate (mmol)**	**Reaction time (minutes)**	**Yield (%)**
1	9.98	0.5	0.499	15	43
2	9.98	0.5	0.499	30	50
3	9.98	0.5	0.499	60	55
4	9.98	0.5	0.499	120	65
5	9.98	0.5	0.499	1440	73

Evolution of the molar masses of poly(TFE-alt-iBuVE) copolymers produced via RAFT/MADIX

The SEC chromatograms (Figure S17) display a shift towards higher molar masses with increasing reaction time. The evolutions of M_n and Đ as a function of conversion for the MADIX copolymerization of TFE and iBuVE are shown in Figure 11. The theoretical molar mass was calculated according to equation (9). The molar masses determined *via* NMR spectroscopy were calculated from R group (equations (5) and (6)) and from Z group (equations (7) and (8)) and are listed in Table 3. The M_n (assessed by SEC) increases linearly with conversion (Figure 11) and the Đ values are surprisingly low, possibly because of low M_n values, indicating that the TFE/iBuVE system well behaves in RAFT/MADIX copolymerization, evidencing a control of the molar masses can be achieved. The data in Table 2 starts out at 40 % that is surprisingly fast for RAFT (compared to the slow reaction rate of VDF [27]) probably due to the 50:50 TFE:VE initial molar ratio.[13]

The experimental M_n values agree well with each other, but differ substantially from the theoretical ones and those determined by GPC due to the PMMA standards.

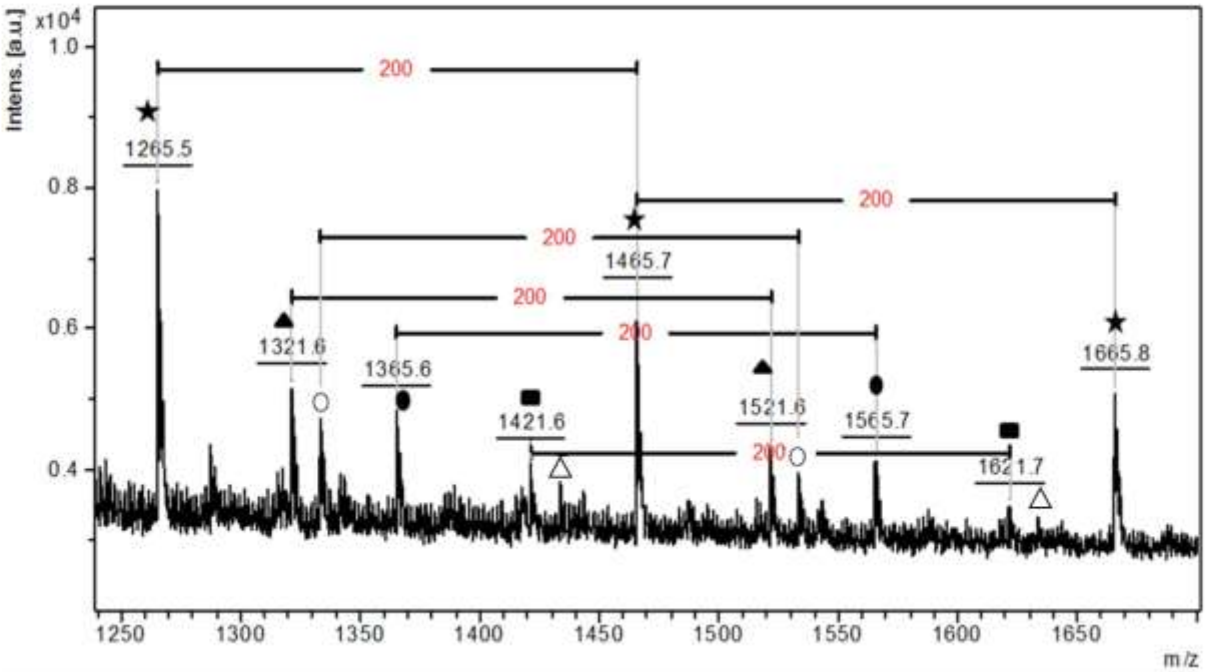


Figure 10: *Expansion of the negative ion MALDI-TOF mass spectrum of poly(TFE-alt-iBuVE) synthesized by MADIX polymerization after 15 min-reaction time (Table 2, experiment 1) with DCTB as matrix and LiCl as cationic agent.*

In the RAFT polymerization of VDF [27, 28, 79], the propagation proceeds from the PVDF macroradical especially generated from the CF_2-xanthate end group of dormant species. Due to head-to-head addition, the chain terminates in a CH_2-xanthate moiety in which the CH_2-S bond is sufficiently strong to not be easily cleaved and fragmenting again to form an active macroradical. This has been confirmed by a recent study[80] that determined the bond dissociation energies (BDEs) in CH_3CF_2-S(C=S)OR and CF_3CH_2-S(C=S)OR model species to be 59 kcal·mol^{-1} and 64 kcal·mol^{-1}, respectively. Hence, it accumulates in the medium, over time, thus leading to a broadening of Đ values. However, in RAFT copolymerization of TFE with iBuVE, electron-withdrawing CF_2 and CH(OiBu) groups adjacent to xanthate end-group induce a weak BDE to favor a fragmentation and a fast reversible equilibrium between dormant and "living" chains (Scheme 1).[80] The slight increase in dispersity is due to the generation of new polymer chains generated by the initiator. This may also account for the discrepancy between the theoretical- and the actual molar masses.

Furthermore, such low Đ values are compared to higher ones achieved by RAFT copolymerization of CTFE [24] (or HFP [25]) with VEs, initiated by ^{60}Co irradiation.

Table 3: *Molar masses of poly(TFE-alt-iBuVE) copolymers controlled by xanthate, determined by NMR spectroscopy and by GPC, versus the targeted molar masses.*

Time (min)	**Conversion (%)**	**M_n Theoretical (g.mol^{-1})**	**M_n by GPC (g.mol^{-1})**	**M_n by Z group analysis $^{a)}$ (g.mol^{-1})**	**M_n by R group analysis $^{b)}$ (g.mol^{-1})**
15	43	1900	2700	1000	1200
30	50	2200	2760	1200	1400
60	54	2400	2950	1400	1600
120	65	2800	3200	1600	1800
1440	73	3100	3300	1800	2000

$^{a)}$Calculated from equations (7) and (8) $^{b)}$Calculated from equations (5) and (6)

Tobolsky's law, relating conversion to reaction time, is supplied in equation (11)

$$\ln(1-x) = -2k_p\sqrt{\frac{f[BPO]_0}{k_t k_d}}(1-e^{-k_d t}) \qquad \textbf{(11)}$$

where x, k_p, f, k_t, k_d and t stand for the conversion, the propagation constant, the initiator efficiency, the termination constant, the initiator decomposition constant, and the reaction time (in seconds), respectively. Kinetic regression gives lumped best-fit values of 2.05×10^{-4} and 1.04×10^{-3} l·mol^{-1}·s^{-1} for k_p and k_t, respectively. A plot of $\ln\frac{[M]_0}{[M]}$ *versus* time is presented in Figure S18. The best fit was obtained for f = 1. Xu *et al.* [61] obtained rate constants for conventional free-radical polymerization in sc-CO_2 and they found $\frac{k_p}{k_t^{0.5}}$

to be 0.38. This value is *ca.* 0.0064 for the copolymerization of TFE with iBuVE using RAFT techniques. The low value is another indication of the controlled nature of the copolymerization.

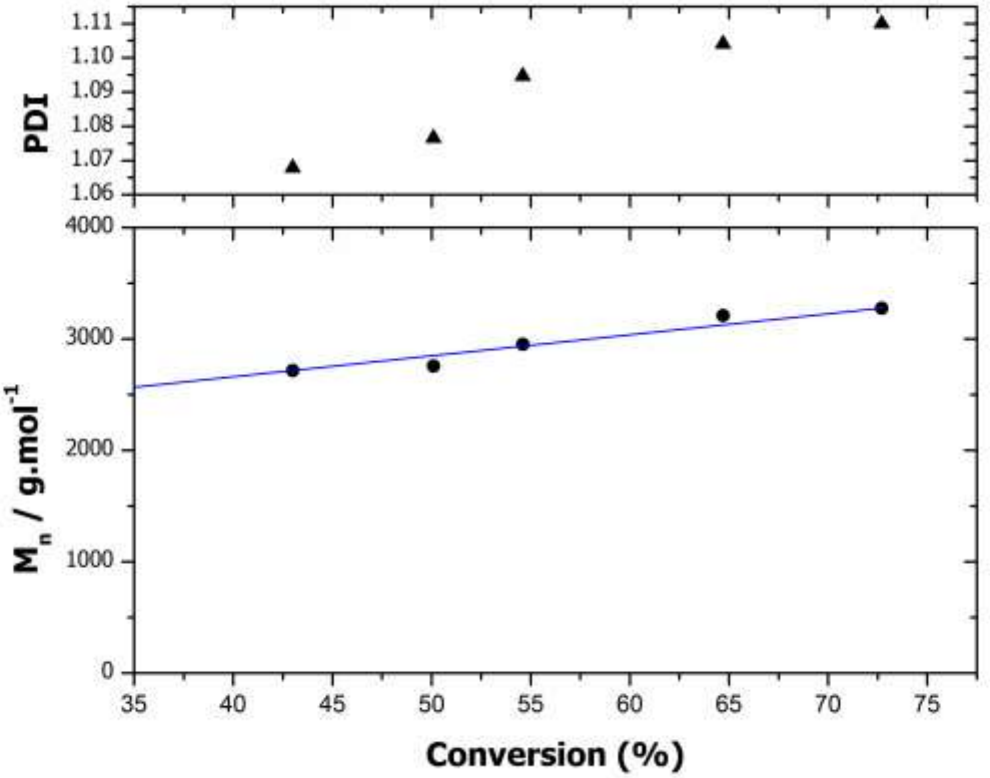


Figure 11: *Evolution of M_n (from GPC) and Đ as a function of monomer conversion for the MADIX copolymerization of TFE and iBuVE using a 1:1 ratio of monomers and a $[Monomers]_0:[CTA]_0:[BPO]_0$ initial molar ratio of 20:1:0.1, with O-ethyl-S-(1-methoxycarbonyl)-ethyldithiocarbonate as CTA.*

Thermal properties of poly(TFE-alt-iBuVE) copolymers controlled by xanthate

The TGA thermograms of poly(TFE-*alt*-iBuVE) copolymers prepared *via* RAFT/MADIX using O-ethyl-S-(1-methoxycarbonyl)-ethyldithiocarbonate are presented in Figure 12. The initial mass loss is more pronounced, as compared to that of the copolymers prepared by conventional radical synthesis, due to lower molar masses produced, the greater contribution of the xanthate end group to the low temperature elimination, as evidenced by the decrease in low temperature mass loss with increasing conversion. This behavior is comparable to that found for PVDF synthesized *via* RAFT/MADIX as the 10% weight loss ($T_d^{10\%}$) values approach a maximum (ca. 170 °C for PVDF and ca. 230 °C for poly(TFE-*alt*-iBuVE)) with increasing DP_n, but do not exceed this value regardless of how much the molar mass increases beyond the one where the elimination of xanthate becomes the determining factor in thermal stability[27] .

All the TGA thermograms exhibit nearly the same shape, which is due to the almost monodispersed nature of the copolymer chains. This implies that, even at a relatively low DP_n, the thermal stability of poly(TFE-*alt*-iBuVE) copolymer is improved by narrowing the dispersity. The TGA thermograms obtained under N_2 atmosphere do not differ substantially from those obtained under air.

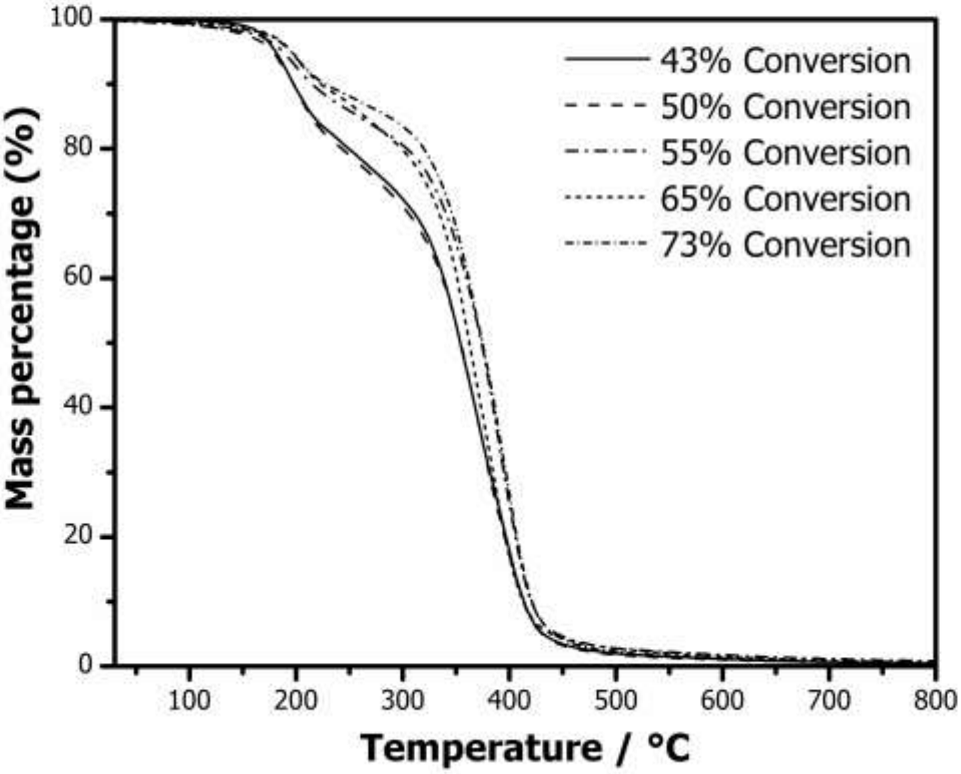


Figure 12: *TGA thermograms of poly(TFE-alt-iBuVE) copolymers prepared via RAFT/MADIX using O-ethyl-S-(1-methoxycarbonyl)-ethyldithiocarbonate at 15, 30, 60, 120 and 1440 minutes reaction times under* N_2 *atmosphere.*

CONCLUSIONS

The main goal of this study was to demonstrate the unprecedented RAFT/MADIX copolymerization of TFE with isobutyl vinyl ether using O-ethyl-S-(1-methoxycarbonyl)-ethyldithiocarbonate (as CTA) in

DMC. This includes an in-depth NMR spectroscopic study and the end group functionality of the resulting poly(TFE-*alt*-iBuVE) copolymers, both in uncontrolled and in RAFT/MADIX copolymerizations. In all cases, alternating copolymers soluble in common organic solvents, were obtained. Additionally, it was shown that benzoyl radicals preferentially attack onto TFE to initiate conventional radical copolymerization and that a transfer of xanthate exists in the controlled copolymerization, with attack onto TFE or iBuVE being equally present. Furthermore, a concerted addition of the monomers to the growing macroradical seemed to produce a mixed end group functionality. The ability of the CTA to control the copolymerization of TFE with iBuVE for producing nearly monodispersed, low-molar mass copolymers with a linear evolution of the molar masses *versus* conversions, was demonstrated evidencing the controlled nature of such a copolymerization. Proton transfer from DMC or the vinyl ether monomer onto the macroradical was observed in uncontrolled copolymerization, whereas much less proton transfer from DMC was noted in RAFT copolymerization. This is comparable to the results obtained for the RAFT polymerization of VDF. The end group functionality was invariant with monomer conversion which implies that, unlike with VDF, termination by the non-fluorinated monomer does not inhibit the ability of the RAFT agent to control the polymerization. Compared to those of PVDF, produced with the same CTA, and ranging from 1.05 to 1.34, the Đ values for poly(TFE-*alt*-iBuVE) copolymers obtained *via* RAFT copolymerization are exceptionally narrow, varying from 1.08 to 1.11. These Đs are also narrower compared to those for poly(CTFE-*alt*-iBuVE) produced from RAFT initiated by ^{60}Co irradiation, which range from 1.17 to 1.39. Further works on the limits of this RAFT copolymerization (to achieve higher molar masses) and chain extension of these poly(TFE-*alt*-iBuVE) macroRAFT agent for chain extension of hydrophilic monomers (to yield amphiphilic block copolymers), as well as the application of the O-ethyl-S-(1-methoxycarbonyl)-ethyldithiocarbonate to the homopolymerization of TFE present interesting avenues of research.

ASSOCIATED CONTENT

Additional analyses including SEC, NMR (including expansion of the ^{1}H and ^{19}F NMR spectra of poly(TFE-alt-iBuVE) copolymers), TGA thermograms, and kinetic plots (experimental monomer (TFE + iBuVE) conversion as a function of time and the conversion with time predicted from Tobolsky's law), and MALDI-TOF peak assignments for the poly(TFE-*alt*-iBuVE) copolymers. Supporting information is available free of charge on the ACS Publications website.

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