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Innovative Trifluoromethyl Radical from Persistent Radical as Efficient Initiator for the Radical Copolymerization of Vinylidene Fluoride with *tert*-Butyl α-Trifluoromethacrylate

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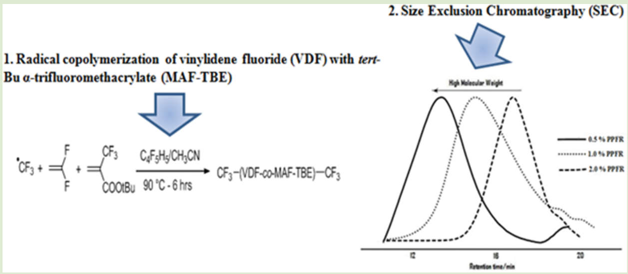
Supporting Information

ABSTRACT: A persistent perfluoroalkyl branched radical (PPFR), perfluoro-3-ethyl-2,4-dimethyl-3-pentyl, was shown to be a good source of $^{\bullet}CF_3$ radicals able to initiate the radical copolymerization of vinylidene fluoride (VDF) with *tert*-butyl α-trifluoromethacrylate (MAF-TBE). NMR characterizations of the resulting poly(VDF-*co*-MAF-TBE) copolymers showed that copolymerization was exclusively initiated by $^{\bullet}CF_3$ radicals, as evidenced by the thermal decomposition of PPFR above 80 °C. The addition of $^{\bullet}CF_3$ radical onto VDF/MAF-TBE system was regioselective leading to $CF_3\text{-}CH_2\text{-}CF_2^{\bullet}$ radical that further cross propagated onto MAF-TBE unit and the α,ω-trifluoromethyl group acted as an efficient label to assess the molecular weights of the resulting copolymers by ^{19}F NMR spectroscopy. Three $[PPFR]_0/([VDF]_0 + [MAF\text{-}TBE]_0)$ initial molar ratios (2.0, 1.0, and 0.5%) led to various molecular weights ranging from 21300 to about 105000 g·mol^{-1}. When that ratio decreased, both the molecular weights and the thermostability of these original poly(VDF-*co*-MAF-TBE) copolymers increased.



Fluoropolymers are very interesting niche specialty polymers because of their outstanding properties such as a satisfactory thermal stability, the chemical inertness (to solvents, oils, water, acids, and bases), the low refractive index values, permittivity, dissipation factor, and water absorption as well as the excellent weather durability and resistance to oxidation. Hence, they can be involved in many applications in the high technology fields such as aeronautics and aerospace (use of elastomers as seals, gaskets, and O-rings for use in extreme temperatures for tanks of liquid hydrogen or hydrazine in boosters of space shuttles), building industries (paints and coating resistant to UV and graffiti), petrochemicals (pipes and coatings as liners), automotive industries (fluids for transmission), chemical engineering (high performance membranes), optics (cores and claddings of optical fibers), textile treatment, wiring insulation, and microelectronics.[1−5] More than 95% of the fluoropolymers are prepared by radical polymerization[6] and they can be either thermoplastic,[2,4] elastomers,[2,5,7−9] or thermoplastic elastomers.[2,5,8] However, fluorohomopolymers are dealing with some drawbacks: they are highly crystalline (impossible to use as rubber), poorly soluble in common organic solvents (preventing from the complete characterization), and they are not easily cured or cross-linked.[6−10] One way to overcome these drawbacks is to incorporate comonomers (fluorinated or nonhalogenated) that enhance their properties and tuned the adhesion, solubility, cross-linking ability, ion exchange, and so on.[11−14] Among these comonomers, α-trifluoromethacrylic acid (MAF) and *tert*-butyl α-trifluoromethacrylate (MAF-TBE) are relevant comonomers and their copolymers draw a lot of interest in the area of 157 nm lithographic material,[12,15] molecularly imprinted polymers,[16−18] polymer electrolyte membranes for a fuel cell,[18] Li-ion battery,[19] micelles,[20] and stone protective coating for the preservation of old monuments.[21] Usually, these functional monomers are copolymerized with different types of commercially available radical initiators. However, a potentially useful persistent perfluoroalkyl radical has never been used in the radical copolymerization of fluorinated monomers. Usually, the radical brings the polymer end groups that may play a role on its properties. Actually, $^{\bullet}CF_3$ is an interesting radical that can be generated from various precursors: CF_3X (X = I,[22−25] Br[26]), bis(trifluoroacetyl) peroxide $(CF_3CO_2)_2$,[27,28] CF_3-*paracyclophane*,[29] and alkyl (or aryl) trifluoromethanethiosulfonates (CF_3SO_2SR;[30] Scheme 1). Scherer[31] and Ono et al.[32] synthesized an original persistent perfluoroalkyl radical (PPFR) and also reported that the thermal degradation of PPFR occurred via a β-scission to yield a trifluoromethyl radical and perfluoro-4-methyl-3-ethyl-2-pentene (*E*/*Z* forms in 8:3 ratio; Scheme 2). More recently, we proved the concept that

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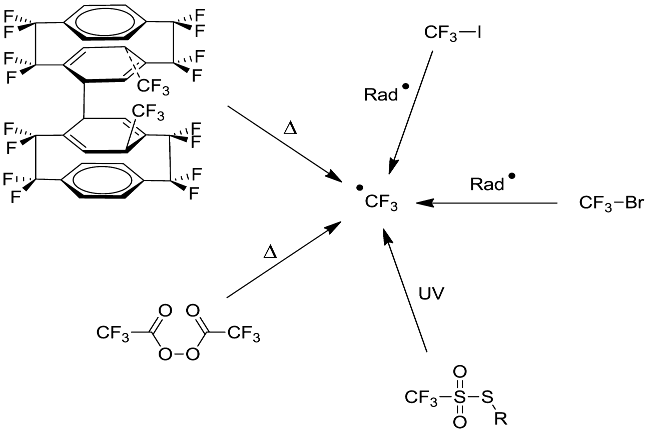
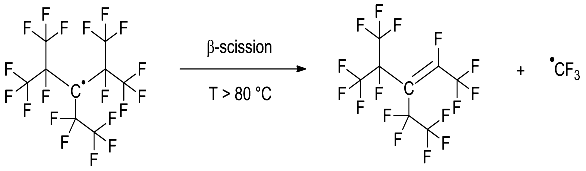
Scheme 1. Fluorinated Precursors Able to Generate a Trifluoromethyl Radical under Radical, Photochemical, Or Thermal Conditions



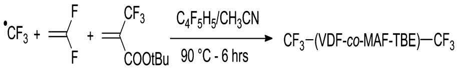
Scheme 2. Generation of a Trifluoromethyl Radical from Perfluoro-3-ethyl-2,4-dimethyl-3-pentyl Persistant Radical (PPFR)



PPFR decomposed with temperature (90 °C), releasing a $^{\bullet}CF_3$ radical that was effective for the polymerization of VDF.[33] Then, it is more interesting to apply the same strategy to investigate the radical copolymerization of VDF with MAF-TBE. The PPFR is easy to handle and to prepare, very stable, and safe. To the best of our knowledge, no radical copolymerization of VDF with MAF-TBE has been reported, whereas that of MAF with VDF was successfully achieved under conventional and controlled radical conditions.[11] Hence, it can be anticipated that MAF-TBE behaves similarly as MAF does. The objective of this present article is to evidence the presence of the $^{\bullet}CF_3$ radical, generated from a fluorinated hyperbranched radical, capable of initiating the radical copolymerization of VDF with MAF-TBE. The spectroscopic data (that should make it possible to assess the molecular weights and the defects of PVDF chaining), gel permeation chromatography, surface property, and thermal stability of the resulting poly(VDF-*co*-MAF-TBE) copolymers are also investigated.

Three copolymerizations of VDF with MAF-TBE were performed at 90 °C under different concentrations of PPFR (Scheme 3) to examine the effect on molecular weights, end groups, degrees of polymerization, yields, chains defects, and degradation temperatures of the resulting copolymers (Table 1).

Scheme 3. Radical Copolymerization of Vinylidene Fluoride (VDF) with *tert*-Butyl α-Trifluoromethacrylate (MAF-TBE) Initiated by the Trifluoromethyl Radical Generated from Perfluoro-3-ethyl-2,4-dimethyl-3-pentyl Persistent Radical



These original copolymers were characterized by NMR to assess the number of VDF and MAF-TBE units. Figure 1 displays three ^{19}F NMR spectra of purified poly(VDF-*co*-MAF-TBE) copolymers achieved from the same $[VDF]_o/[MAF\text{-}TBE]_o$ feed (80/20) but from different $[Initiator]_o/([VDF]_o + [MAF\text{-}TBE]_o)$ initial molar ratios of 0.5 (lowest), 1.0 (middle), and 2.0% (top spectrum). These spectra exhibit the characteristic signals centered at −68.5, −92, −95, −113, and −116 ppm, assigned to CF_3 group of MAF-TBE in the copolymers, PVDF block (VDF-VDF normal dyad), VDF-MAF-TBE alternating dyads, and reverse (head to head, in the case of 2.0% of initiator only) VDF-VDF addition, respectively.[11] In addition, all these ^{19}F NMR spectra showed a quintet ($^{3}J_{FH} = {}^{4}J_{FF} = 10$ Hz) centered at −61 ppm, attributed to CF_3 (arising from the persistent radical) adjacent to CH_2 of VDF, as previously observed for VDF telomers obtained from the radical telomerization of VDF with CF_3I[25] or from the photopolymerization of VDF in the presence of $CF_3SO_2SC_6H_{11}$ or $CF_3SO_2SC_6H_5$ (both of them released a $^{\bullet}CF_3$ radical under UV radiation, Scheme 1).[30] Actually, the absence of any signal at about −83 ppm characteristic of CF_3 in CF_3CF_2-R end group confirms the regioselectivity of the addition of $^{\bullet}CF_3$ radical onto CH_2 site of VDF. This proves that perfluoro-3-ethyl-2,4-dimethyl-3-pentyl decomposed at 90 °C, yielding a $^{\bullet}CF_3$ radical able to initiate the copolymerization of VDF with MAF-TBE. Moreover, none of the signals characteristic of the persistent radical derived adducts were found in the ^{19}F NMR spectra of all the produced poly(VDF-*co*-MAF-TBE) copolymers. This indicates that not only such a hindered branched radical was unable to initiate the polymerization but was never involved in the termination step of the copolymerization. Interestingly, at higher initiator concentration, the content of VDF in the copolymer increased and, as expected, produced chain defects in VDF−VDF addition of head to head or tail to tail dyads (Run 3 in Table 1).[34]

The ^{1}H NMR spectrum (Figure 2) confirms the successful copolymerization of MAF-TBE by the absences of signals at 6.5 and 6.7 ppm assigned to the methylene group (CH_2=) of MAF-TBE monomer. The spectrum also displays different signals centered at 1.5 and 2.8 ppm, which are attributed to *tert*-butyl group of MAF-TBE and methylene of VDF and MAF-TBE overlapping on each other, respectively.[11] In agreement with ^{19}F NMR, the signal centered at 2.5 ppm shows the presence of a tail to tail addition of VDF for 2.0% of initiator only. The absence of the triplet of triplets centered at 6.3 ppm, assigned to HCF_2CH_2, evidenced that there is no noticeable transfer to solvent, to the monomers, or to the copolymer.[11]

The molecular weights of the copolymers can be tuned by varying the PPFR concentration. The increase of molecular weights of copolymers at low concentrations of PPFR can be highlighted in Figure 3 that displays the size exclusion chromatograms (SEC) of copolymers achieved from three different PPFR concentrations. A strong shift from 17.4 to 13.5 min toward high molecular weights of poly(VDF-*co*-MAF-TBE) copolymers synthesized from 2.0 to 0.5% of PPFR was noted in the SEC chromatograms (Figure 3). This indicates that the higher molecular weight of copolymer occurred successfully at lower concentration of PPFR. Though a discrepancy is noted between the values assessed by SEC (with polystyrene standards) and NMR, that latter technique is more accurate than the former one. Actually, poly(VDF-*co*-MAF-TBE) copolymeric standards are not available. Moreover, no Mark−Houwink parameters have been supplied for such

Table 1. Experimental Conditions and Results for the Radical Copolymerization of Vinylidene Fluoride (VDF) and *tert*-Butyl α-Trifluoromethacrylate (MAF-TBE) in the Presence of Persistent Perfluoroalkyl Radical (PPFR)[a]

PPFR (mol %)	P_{max} (bar)	ΔP (bar)	yield (%)	VDF	MAF-TBE	VDF	MAF-TBE	M_n ^{19}F NMR[d]	M_n SEC[e]	PDI[e]	$T_{d,10\%}$ (°C)[f]	T_g (°C)[g]
				in copolymer (mol %)[b]		# of units in copolymer[c]						
0.5	47	6	42	48	52	374	410	104400	16800	1.7	186	10
1.0	48	7	48	49	51	177	196	49900	11200	1.6	177	7
2.0	49	8	63	66	34	125	66	21300	9800	1.6	169	5

[a] Reaction conditions: VDF/MAF-TBE in feed = 80:20 mol %; solvent used, $C_4F_5H_5 + CH_3CN$ = 60 mL; reaction temperature, 90 °C; reaction time, 6 h; ΔP, pressure drop observed in the autoclave during the reaction. [b] Copolymer compositions were assessed by ^{19}F NMR spectroscopy using formula:[12] mol % VDF in copolymer = $[(\int CF_2^{\text{at-92 to}-95} + \int CF_2^{\text{at }-113\text{ to }-115})/2\ ]/[(\int CF_2^{\text{at }-92\text{ to }-95} + \int CF_2^{\text{at }-113\text{ to }-115})/2) + (\int CF_3^{\text{at }-68.5}/3)]$ (where $\int CF_i^{\text{at }-i}$ stands for the integral of the signal assigned to CF_i group centered at $-i$ ppm in the ^{19}F NMR spectra). Mol % MAF-TBE in copolymer = $(\int CF_3^{\text{at }-68.5}/3)/[(\int CF_2^{\text{at }-92\text{ to }-95} + (\int CF_2^{\text{at }-113\text{ to }-115})/2) + (\int CF_3^{\text{at }-68.5}/3)]$. [c] DP_n, VDF = $(\int CF_2^{\text{at }-92\text{ to }-95}/2 + \int CF_2^{\text{at }-113\text{ to }-115})/2)/(\int CF_3^{\text{at }-61}/3)$ and DP_n, MAF-TBE = $(\int CF_3^{\text{at }-68.5}/3)/(\int CF_3^{\text{at }-61}/3)]$. [d] In g·mol^{-1}, determined from ^{19}F NMR spectroscopy using previous formula:[12] $M_n = 2M_{CF_3} + M_{VDF} \times (DP_n \text{ of VDF}) + M_{MAF\text{-}TBE} \times (DP_n \text{ of MAF-TBE})$ (where, $M_{CF_3} = 69$, $M_{VDF} = 64$, and $M_{MAF\text{-}TBE} = 196$). [e] Characterized by SEC calibrated with PS standards. [f] Assessed by thermogravimetric analysis (TGA), under air; 10 °C/min. [g] Determined by differential scanning calorimetry (DSC).

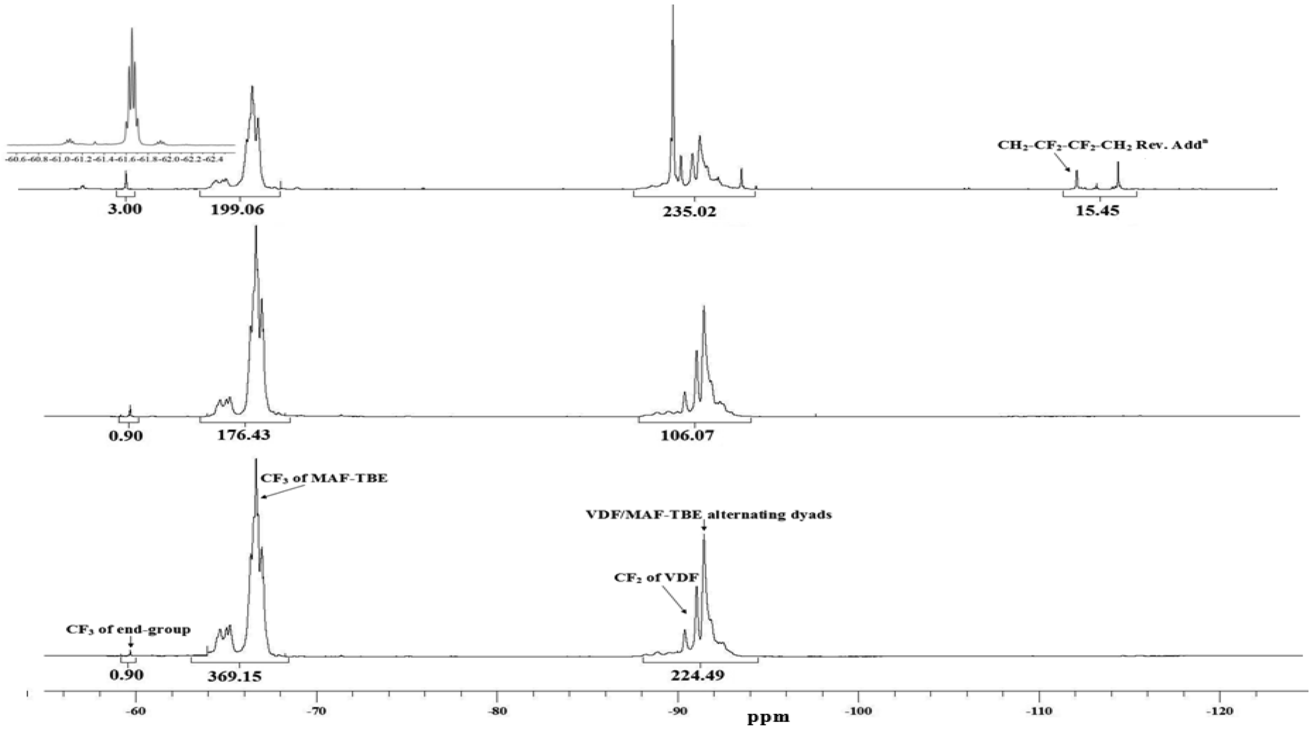


Figure 1. ^{19}F NMR spectra of CF_3-poly(VDF-*co*-MAF-TBE)-CF_3 copolymers at 2.0 (top), 1.0 (middle), and 0.5% (lower spectra); runs 1−3 in Table 1; recorded in acetone-d_6.

new copolymers. This observation is consistent with the molecular weights calculated by ^{19}F NMR (Table 1).

The T_g of poly(VDF-*co*-MAF-TBE) copolymers was found to vary with their units and from the initiator concentrations (Table 1). A slight decrease of T_g from 10 to 5 °C as the units of MAF-TBE increased (from 66 to 410) in the copolymer and decrease of initiator concentration from 2.0 to 0.5% were noted. This may be due to the bulky MAF-TBE *tert*-butyl group, which could have a plasticizing effect on the copolymers, as noted in a previous study.[14] This T_g is higher than that of VDF homopolymer (T_g = −40 °C)[33] and lower than that of MAF-TBE homopolymers (T_g = 35 °C), which confirmed the incorporation of MAF-TBE units in VDF.

The thermal stabilities of these poly(VDF-*co*-MAF-TBE) copolymers were investigated by thermogravimetric analysis (TGA) under an oxygen atmosphere (Figure 4). However, a first plateau was noted before the degradation of a polymeric chain that usually occurs from 150 °C. Several studies[12,14] reported that when copolymers containing MAF-TBE were heated above 150 °C, the *tert*-butyl ester group decomposed into a carboxylic acid group and released isobutene, which can explain the first plateau. As the temperature increased, a second weight loss was observed from 335 °C.

The thermostability slightly increases when the percentage of persistent radical decreases (Figure 4). This is consistent with the increase of molecular weights due to lower initiator content.

The surface properties of these copolymers were assessed by means of water contact angle measurements and produced hydrophobic surfaces. A slightly more hydrophobic material was obtained for the higher content of VDF in the copolymer (Figure 5).

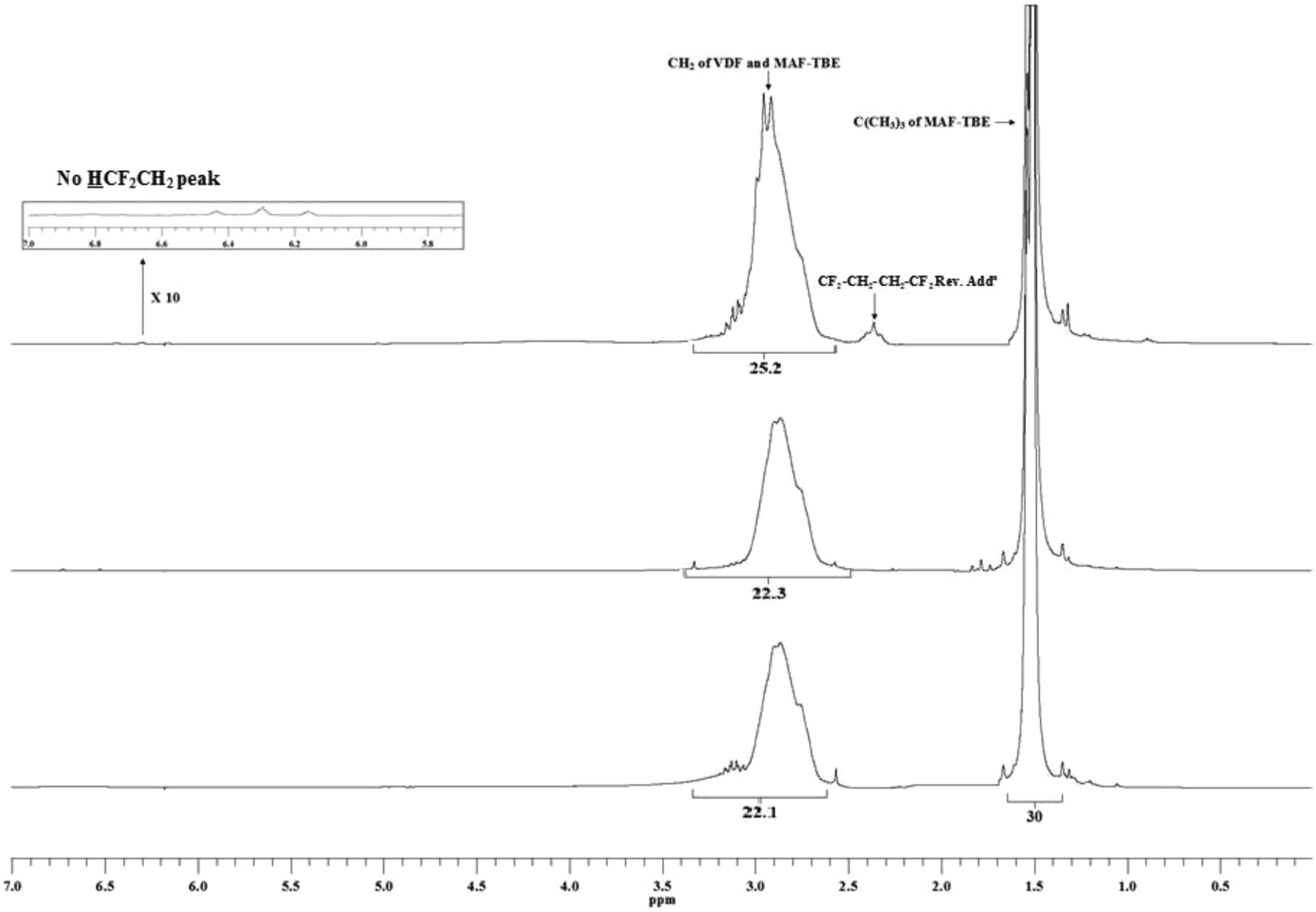


Figure 2. ^{1}H NMR spectra of CF_3-poly(VDF-*co*-MAF-TBE)-CF_3 copolymers at 2.0 (top), 1.0 (middle), and 0.5% (lower spectra); runs 1−3 in Table 1; recorded in acetone-d_6.

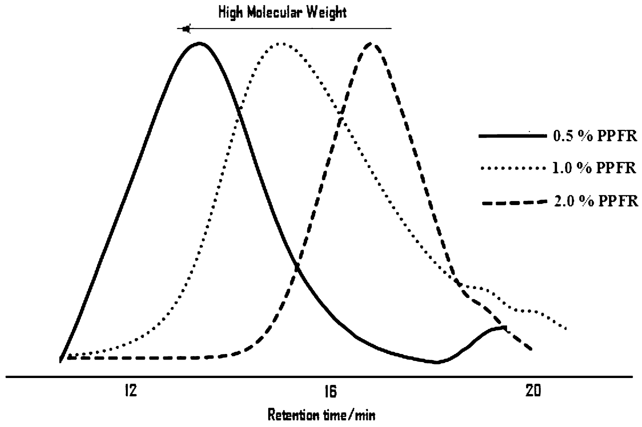


Figure 3. Size exclusion chromatograms (SEC) of CF_3-poly(VDF-*co*-MAF-TBE)-CF_3 copolymers at 0.5 (full line), 1.0 (dotted line), and 2.0% (dashed line); runs 1−3 in Table 1; in polystyrene standards.

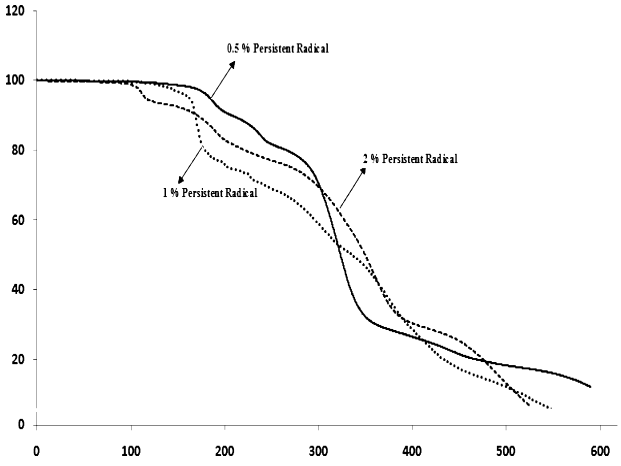


Figure 4. TGA thermograms of CF_3 poly(VDF-*co*-MAF-TBE)-CF_3 copolymers at 0.5 (full line), 1.0 (dotted line), and 2.0% (dashed line); runs 1−3 in Table 1; heated at 10 °C min^{-1} under air.

In conclusion, the use of a perfluorinated hyperbranched persistent radical, perfluoro-3-ethyl-2,4-dimethyl-3-pentyl, made it possible to generate a $^\bullet CF_3$ radical efficient in the radical copolymerization of VDF with MAF-TBE for the first time. The thermally released $^\bullet CF_3$ initiates the copolymerization by a regioselective addition onto the methylene group of VDF. Such a CF_3 end group of these copolymers acted as an original label to assess the numbers of VDF and MAF-TBE units, leading to original standards in SEC of poly(VDF-*co*-MAF-TBE) copolymers. Thermal properties showed that the lower the initiator content, the higher the molecular weights and the better the thermostability up to at least 300 °C. It was then concluded that persistent radical PPFR does not influence the termination step. Further work is under progress to apply this technique for the radical (*co*)polymerization of fluoroolefins and, thus, the molecular weight assessments of the resulting (*co*)polymers.

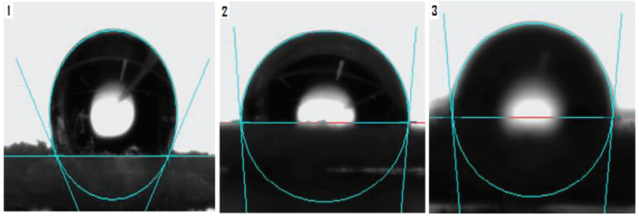


Figure 5. Water contact angle measurements of CF_3-poly(VDF-*co*-MAF-TBE)-CF_3 copolymers (1) 2.0 (98°), (2) 1.0 (89°), and (3) 0.5% (88°) of initiator.

EXPERIMENTAL METHODS

The following general procedure was applied. The 100 mL Hastelloy autoclave was filled under vacuum with persistent radical (4.0 g, 8.5 mmol) and MAF-TBE (20.10 g, 0.1 mol) and both were dissolved in a solvent mixture of 1,1,1,3,3-pentafluorobutane (30 mL) and acetonitrile (30 mL). The reactor was cooled in an acetone/liquid nitrogen bath, and three thaw−freeze pump cycles were applied before the fluorinated VDF gas (27 g, 0.4 mol) was condensed into the autoclave under weight control. Then, the reactor was stirred and gradually heated up to 90 °C, and the evolutions of pressure and temperature were recorded. An increase in the pressure to 48 bar and a decrease in pressure to 34 bar in 4 h were observed. The reaction was stopped after 6 h, and the autoclave was cooled to room temperature and then placed in an ice bath. After purging the nonreacted monomer, the conversion of gaseous monomers was determined by double weighing (65%). A light yellow liquid was obtained. The solvent was completely removed by distillation. The product was precipitated in chilled pentane, filtered off, and then dried under vacuum (10^{-2} bar, 40 °C) for 12 h. The poly(VDF-*co*-MAF-TBE) copolymer, as a light yellowish powder, was characterized by ^1H and ^{19}F NMR spectroscopy. The calculated yield was 63 wt %.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures, materials, and characterizations techniques are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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