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Thermal and photo RAFT Polymerization of 2,2,2-trifluoroethyl α -fluoroacrylate

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Abstract

The RAFT polymerization of 2,2,2-trifluoroethyl α -fluoroacrylate (FATRIFE) was investigated under thermal conditions and light irradiation. The performances of 4 different chain transfer agents (3,5-dimethyl-1H-pyrazole-1-carbodithioate (CTA₁), 4-cyano-4-(2-phenylethanesulfanylthiocarbonyl)sulfanylpentanoic acid (CTA₂), dibenzyl trithiocarbonate (CTA₃), and Ethyl 2-(phenylcarbonothioylthio) propionate (CTA₄)) were compared under thermal conditions. CTA₂ afforded relatively good control of the polymerization with relatively low dispersities (apparent molar mass $M_{n,SEC} \sim 37.8$ kg/mol vs. PMMA, $\mathcal{D} < 1.10$). *Pseudo*-first-order polymerization kinetics and a linear increase of the molar masses *versus* monomer conversions were observed. The RAFT polymerization of FATRIFE was further explored under photoirradiation using CTA₂ as chain transfer agent and white LED lamps (14 W \times 2) irradiation. In the absence of exogenous radical sources or catalysts, controlled polymerization was observed at room temperature. Linear increase of molar masses (up to 25.3 kg/mol) with monomer conversions and low dispersities ($\mathcal{D} < 1.10$) were successfully obtained. Temporal control of the polymerization was also observed using light ON/OFF experiments. Poly(FATRIFE) based macroCTA synthesized by photoRAFT was also extended with 1,1,1,3,3,3-hexafluoropropan-2-yl 2-fluoroacrylate and *tert*-butyl-2-trifluoromethacrylate/FATRIFE.

Introduction

The developments of reversible deactivation radical polymerization (RDRP) methods, such as nitroxide-mediated radical polymerization (NMP), reversible addition-fragmentation chain transfer (RAFT), atom transfer radical polymerization (ATRP), iodine transfer polymerization (ITP), or organometallic-mediated radical polymerization (OMRP) have revolutionized polymer science owing to the great advantages they offer for synthesizing macromolecules with well-defined functionalities and architectures.¹ Among them, RAFT is a very convenient RDRP technique which is amenable to a wide range of monomers with

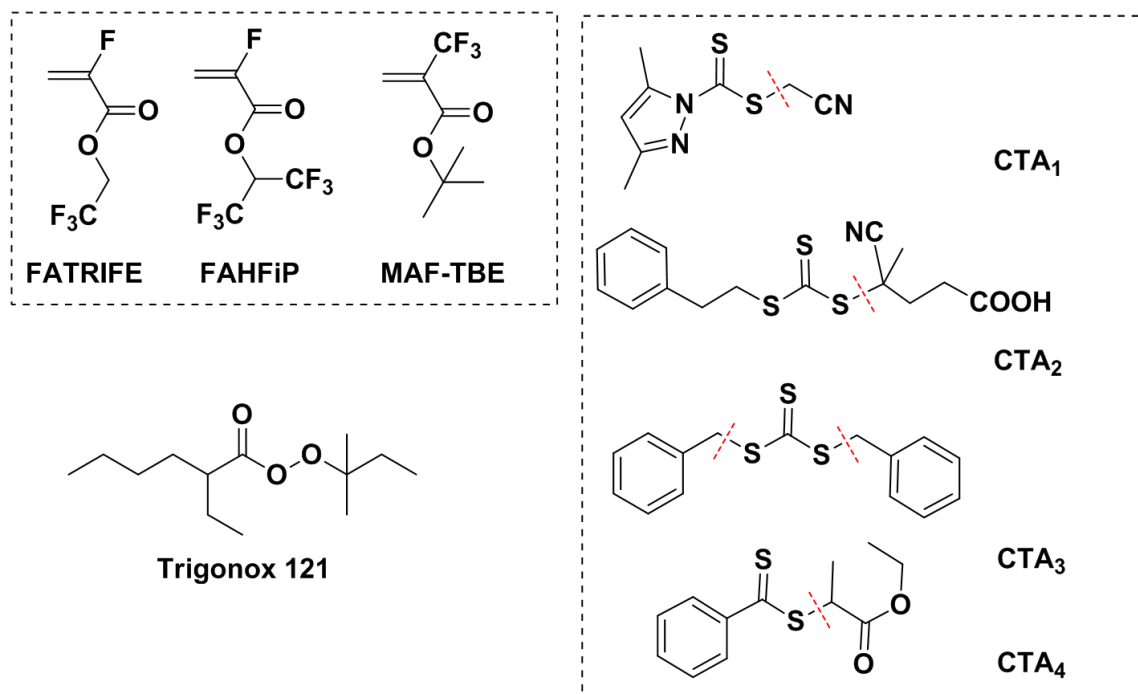
different reactivities if suitable radical initiators and chain transfer agents (CTAs) are selected.²⁻⁵ In recent years, RAFT polymerization conditions have been extended to include the traditional thermal conditions (thermal RAFT) and polymerization under light irradiation (photoRAFT).⁶⁻¹⁰ Besides lower polymerization temperature, photoRAFT may also afford better control than thermal RAFT when photoinitiators are not used.¹¹⁻²² Since the initiating species are generated from the CTAs (either by photoinduced dissociation of the CTAs themselves, or via energy transfer mediated by a photoredox catalysts),^{6,10-17,19,22} therefore, the number of polymer chains is strictly identical to the number of CTA molecules. This feature is particularly beneficial to the preparation of well-defined block copolymers. In addition, photoRAFT allows for temporal control of the polymerization by switching ON or OFF the light irradiation.

Nowadays, although RDRP methods have been used for the polymerization of fluorinated monomers such as fluorinated (meth)acrylates and styrene,^{23,24} their applications in the synthesis of polymers possessing fluorine atoms on the main chain still remain a challenge. Since these polymers have very interesting properties such as low refractive index and UV resistance, it is of great interest to implement the RAFT method into their synthesis. Recent articles have shown how thermal RAFT polymerization could be used to polymerize unconjugated fluorinated monomers such as vinylidene fluoride (VDF).²⁵⁻³⁰ However, most of the studies of photo-mediated RDRP have focused on (meth)acrylates and styrene derivatives bearing fluorinated substituents on the side chains.^{24,31-37} For example, Hawker³⁸ reported the controlled radical polymerization of semi-fluorinated polymer using copper (II) bromide/Me₆-TREN (TREN = tris(2-aminoethyl amine)) complexes as a photocatalyst. Monomers with 3 to 21 fluorine atoms were polymerized in a controlled manner. Although the amount of copper catalyst could be greatly reduced (only 2 mol% of the initiator quantity) thanks to the photo-reduction process, the residual metal salts could still be an issue for certain applications. In addition, undesired transesterification, probably due to the presence of the excess polyamine ligands, was observed in some cases. Chen et al.³⁶ reported metal-free photoRAFT under blue light of semi-fluorinated acrylates using phenothiazine as an organophotocatalyst.

On the contrary, the RDRP of α -fluorinated acrylates has only been scarcely reported.³⁹⁻⁴⁵ Boutevin's group^{39,40} reported the ATRP of *n*-butyl α -fluoroacrylate (FABu) using ethyl 2-bromoisobutyrate (EBiB) and CuX (X= Br or Cl)/ 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) as the catalyst. The dispersity of the resulting polymer was as low as 1.14. This poly(FABu) synthesized by ATRP was further used as a precursor in the preparation of the telechelic oligomers, taking advantage of brominated chain

ends.⁴¹ RDRP of FABu was also performed utilizing 2-(methoxycarbonyl)-2-propyl dithiobenzoate and 2,2'-azobis(2-methylpropionitrile) (AIBN) as chain transfer agent and radical initiator, respectively. Living chain ends were evidenced by ¹⁹F NMR spectrum and the dispersity of the resulting poly(FBu) was lower than 1.4.⁴⁰ However, the measured molar masses were quite different from the theoretical values due to the inefficient chain transfer reaction of the CTA employed. To the best of our knowledge, the RDRP of α -fluorinated monomers bearing fluorinated pendent group (1,1,1,3,3,3-hexafluoroisopropyl α -fluoroacrylate, FAHFIP) was only reported by Semchikov et al.⁴²⁻⁴⁵ using dibenzyl trithiocarbonate as chain transfer agent (CTA). After determining the reactivity ratios of FAHFIP and *N*-vinylpyrrolidone (NVP), these authors reported that an alternating copolymer was formed. However, poor information on the homopolymerization of FAHFIP and the degree of control of this polymerization were provided.

Although optical properties such as refractive index is directly related to the fluorine atom content of these polymers,^{31,46} detailed research on the RAFT homopolymerization of α -fluorinated monomer bearing semi-fluorinated side chain has not been reported yet. Thus, the RAFT polymerization of 2,2,2-trifluoroethyl α -fluoroacrylate (FATRIFE) was investigated using various chain transfer agents (CTAs) (**Scheme 1**). The RAFT polymerization of FATRIFE was tested under both thermal conditions and light irradiation using household white LED lamps (14W \times 2) as a light source.



Scheme 1 Fluorinated monomers, chain transfer agents (CTAs) and radical initiator used in this work.

Experimental Part

Materials

2,2,2-Trifluoroethyl α -fluoroacrylate (FATRIFE) and 1,1,1,3,3,3-hexafluoropropan-2-yl 2-fluoroacrylate (FAHFIP) were purchased from Scientific Industrial Application P and M (Moscow, Russia), and used as received. *Tert*-butyl-2-trifluoromethacrylate (MAF-TBE) was kindly offered by Tosoh FineChemicals Corporation (Shunan, Japan). Cyanomethyl 3,5-dimethyl-1H-pyrazole-1-carbodithioate (CTA₁),⁴⁷ 4-cyano-4-(2-phenylethanesulfanylthiocarbonyl)sulfanylpentanoic acid (CTA₂)⁴⁸ and dibenzyltrithiocarbonate (CTA₃)⁴⁹ were synthesized according to methods reported previously. Ethyl 2-(phenylcarbonothioylthio)propionate (CTA₄) was purchased from Sigma-Aldrich, and used as received. *Tert*-Amylperoxy-2-ethylhexanoate (Trigonox 121, purity 95%) was purchased from Akzo Nobel (Chalons-sur-Marne, France). Other laboratory grade reagents were used as received. Two household white LED lamps (14W, Kingfisher) were used as light source except mentioned specifically. Polymerizations using sunlight as light source were carried out on the roof of the laboratory.

Nuclear magnetic resonance (NMR) spectroscopy. The (co)polymers were characterized by ¹H and ¹⁹F NMR spectroscopies. Spectra were recorded on a Bruker AC 400 spectrometer (400 MHz for ¹H and 376 MHz for ¹⁹F) using acetone-d₆ as the solvent. Coupling constants and chemical shifts are given in hertz (Hz) and parts per million (ppm), respectively. The instrumental parameters for recording ¹H [or ¹⁹F] NMR spectra were as follows: flip angle 90° [or 30°], acquisition time 4.5 s [or 0.7 s], pulse delay 2 s [or 5 s], number of scans 32 [or 64], and a pulse width of 10.4 μ s for ¹⁹F NMR.

Size exclusion chromatography (SEC) measurement. SEC with 0.1M LiBr/DMF as eluent, calibrated with poly(methyl methacrylate) standards from Polymer Laboratories, was run with a Varian Prostar (model 210) pump at a flow rate of 0.8 mL/min using two 300 mm long, mixed-D PL-gel 5 μ m columns (molar mass range: 2×10^2 – 4×10^5 g/mol from Polymer Laboratories) thermostated at 70 °C, connected to a Shodex (model RI-101) refractometer detector.

RAFT polymerization of FATRIFE under thermal conditions: FATRIFE (3.01 g, 17.67 mmol, 200 eq.), CTA₂ (29.8 mg, 0.0878 mmol, 1.0 eq.) and *tert*-amylperoxy-2-ethylhexanoate (1.96 mg, 0.0085 mmol, 0.097 eq.) were dissolved in a Schlenk tube containing 7.00 g of acetonitrile. The solution was degassed by three freeze-pump-thaw cycles. Then, the Schlenk tube was backfilled with nitrogen, and the polymerization was started by placing the tube in an oil bath thermostated at 73 °C. The polymerization was stopped by exposing the solution to air. Several drops of solution were diluted with acetone-d₆ and

characterized by NMR spectroscopy to determine conversion (using **Equations 1** and **2**), the rest of the solution was purified by precipitation in cold methanol, resulting in a slightly yellow powder. Typical ^1H NMR and ^{19}F NMR spectra of the crude product are shown in **Figure 1** and **Figure 2**, respectively. In the kinetics experiments, sample was withdrawn from the tube at settled time through nitrogen purged springers. Instead of precipitation, the samples were directly dried under reduced pressure at room temperature.

$$\text{Conv}_{(\text{FATRIFE})} (\%) = 100 - \frac{2 \times \int_{5.61}^{5.90} \text{CH of FATRIFE}}{\left(\int_{4.24}^{4.70} \text{CH}_2 \text{ of poly(FATRIFE)} + \int_{4.70}^{4.90} \text{CH}_2 \text{ of FATRIFE} \right)} \times 100 \quad (\text{Equation 1})$$

$$\text{Conv}_{(\text{FATRIFE})} (\%) = 100 - \frac{\int_{-73.43}^{-74.76} \text{CF}_3 \text{ of FATRIFE}}{\left(\int_{-73.39}^{-73.43} \text{CF}_3 \text{ of poly(FATRIFE)} + \int_{-73.43}^{-74.76} \text{CF}_3 \text{ of FATRIFE} \right)} \times 100 \quad (\text{Equation 2})$$

PhotoRAFT polymerization of FATRIFE: FATRIFE (3.04 g, 17.68 mmol, 99 eq.) and CTA_2 (60.7 mg, 0.1787 mmol, 1 eq.) were dissolved in a Schlenk flask containing 7.64 g of acetonitrile and a magnetic stirring bar. The solution was deoxygenated by three freeze-pump-thaw cycles, then the flask was backfilled with nitrogen. Then polymerization started by placing the flask between 2 LED lamps. Aliquots were taken at settled times under nitrogen protection using a syringe. Small quantities of these samples were diluted with acetone- d_6 and analyzed by NMR spectroscopy. The rest of these samples was dried in a vacuum oven. The monomer conversion was determined according to the ^1H NMR spectrum of the crude product using **Equation 1**.

In the light “ON/OFF” experiments, a similar procedure was used except that the light source was periodically switched off at settled times, and during the “light OFF” period, the flask was wrapped in aluminum foil.

Chain extension experiment using unpurified macro chain transfer agent (in situ method): FATRIFE (4.18 g, 24.28 mmol, 103 eq.), CTA_2 (79.7 mg, 0.23mmol, 1 eq.) were added to a Schlenk tube containing 9.47 g of acetonitrile. The solution was degassed by three freeze-pump-thaw cycles, and then the tube was backfilled with nitrogen. When the temperature of the solution in the tube reached room temperature (ca. 20 °C), the polymerization was started by placing the tube between 2 white LED lamps (14W X 2). 3 mL of the solution was taken from the tube through a syringe 6 h later, and it was subsequently analyzed by NMR spectroscopy and SEC. FATRIFE conversion was determined by ^1H NMR spectroscopy using **Equation 1**. To introduce a new fraction of monomer, 5 mL of degassed acetonitrile

solution containing FATRIFE (702.0 mg, 4.08 mmol) and MAF-TBE (200.0 mg, 1.02 mmol) was added under nitrogen protection. Then, the polymerization was reinitiated by placing the tube under the irradiation, and 14 h later, the polymerization was stopped by exposing the solution to air. The FATRIFE and MAF-TBE conversions were determined by ^1H NMR spectroscopy. The crude product was purified by precipitation in a mixture of pentane/methanol (1/1 v/v) twice, then dried at 60 °C under vacuum (0.01 torr) for 5 hrs. The content of MAF-TBE was calculated using the ^{19}F NMR spectrum of the purified polymer and from **Equation S5**.

Chain extension experiment using purified macro chain transfer agent: Macro chain transfer agent, poly(FATRIFE)-TTC (300 mg, $M_{n,SEC} = 25.1$ kg/mol, $\mathcal{D} = 1.05$, synthesized by photoRAFT polymerization method), was dissolved in 10.0 g of acetonitrile. 1.50 g FAHFIP were added into the tube when poly(FATRIFE)-TTC was entirely dissolved. The mixture was deoxygenated by three freeze-pump-thaw cycles. When the temperature of the solution reached room temperature (ca. 20 °C), the Schlenk tube was charged with nitrogen and then placed between two white LED lamps. The polymerization was stopped by exposing the solution to air 5 h later when a significant increase of viscosity was observed. Several drops of the solution were diluted with acetone- d_6 to determine the monomer conversion by NMR spectroscopy. The rest of the solution was precipitated from a mixture of diethyl ether/pentane (1/1 v/v) twice. The product was collected by filtration and then dried under vacuum overnight, and 1.0 g of product was obtained. The composition and molar mass of the resulting polymer were determined by NMR and SEC, respectively.

Results and discussions

1. Thermal RAFT polymerization of FATRIFE

In RAFT polymerization, chain transfer agents (CTAs) need to be selected according to the reactivity of the monomers. Ethyl α -fluoroacrylate was reported to be more reactive ($k_p = 1120 \text{ L.M}^{-1}.\text{s}^{-1}$) than both methyl acrylate ($k_p = 720 \text{ L.M}^{-1}.\text{s}^{-1}$) and methyl methacrylate ($k_p = 450 \text{ L.M}^{-1}.\text{s}^{-1}$) judging from the propagating rates in conventional radical polymerization.⁵⁰⁻⁵² Consequently, CTAs adapted for the RAFT polymerization of acrylates or methacrylates were selected^{2, 3} for the RAFT polymerization of 2,2,2-trifluoroethyl α -fluoroacrylate (FATRIFE). The results of these preliminary experiments are listed in **Table 1**. Polymerizations were carried out in acetonitrile according to the solubility of the CTA and the resulting polymers. *Tert*-amylperoxy-2-ethylhexanoate was used as radical initiator due to it good

performance in the RAFT polymerization of fluorinated monomers, half-life time (ca. 10 h at 73 °C), and good solubility in acetonitrile.²⁶

Table 1. Experimental conditions and results of the RAFT polymerizations of FATRIFE using different chain transfer agents^a

Entry	CTA ^a	Time (h)	[M] ₀ /[CTA] ₀	Conv. ^b (¹ H/ ¹⁹ F) (%)	M _{n,SEC} ^c (kg mol ⁻¹)	Đ ^c
1 ^d	CTA ₁	0.5	50/1	30/32	-	-
2	CTA ₂	5.0	200/1	54/54	34.6	1.05
3	CTA ₃	5.0	100/1	80/78	29.2	1.52
4	CTA ₄	24.0	100/1	~0	-	-

^aPolymerization conditions: [CTA]₀:[*tert*-amylperoxy-2-ethylhexanoate]₀= 1:0.1, T = 73 °C, [M]₀ = 30 wt%.

^bMonomer conversion (α) was calculated from ¹H and ¹⁹F NMR spectroscopies, according to **Equation 1** and **Equation 2**. ^cApparent number-average molar mass (M_{n,SEC}) and dispersity (Đ), determined by SEC. ^dAs the polymer solution could not pass through the 220 μm filter, SEC analysis could not be achieved.

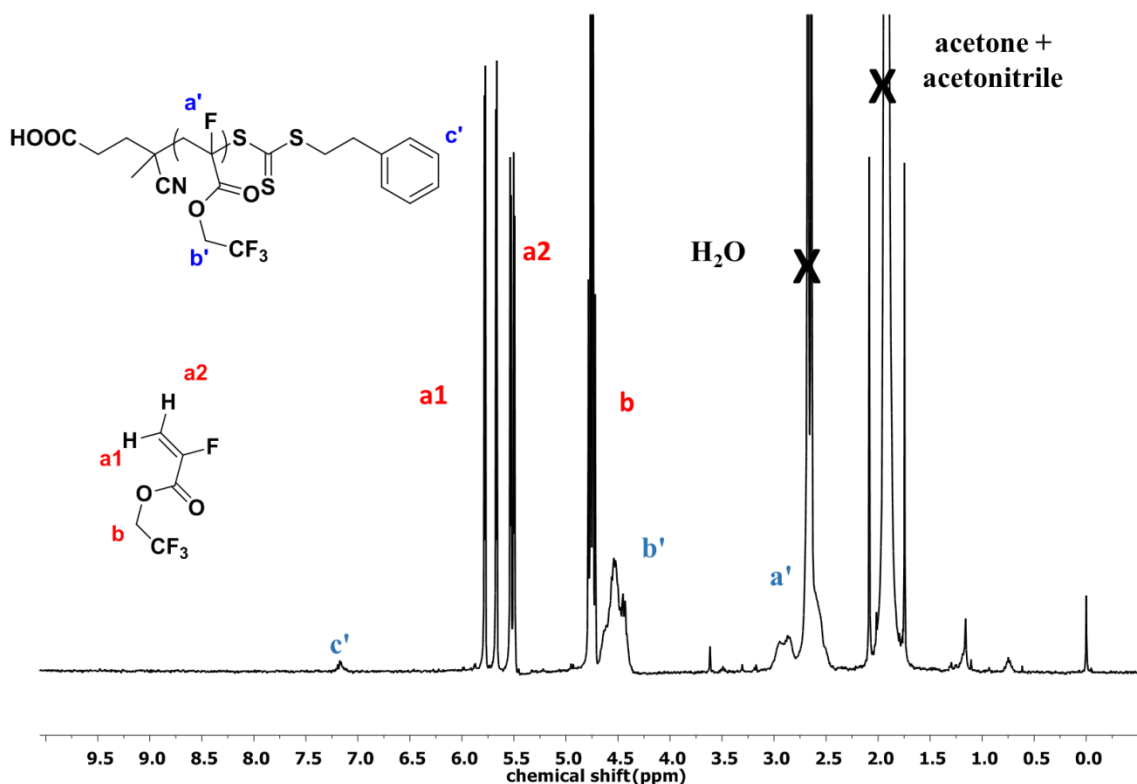


Figure 1. Typical ¹H NMR spectrum of the crude product resulting from the thermal RAFT polymerization of FATRIFE using CTA₂ and *tert*-amylperoxy-2-ethylhexanoate as chain transfer agent and radical initiator, respectively (recorded in acetone-d₆, **Table 1**, Entry 2).

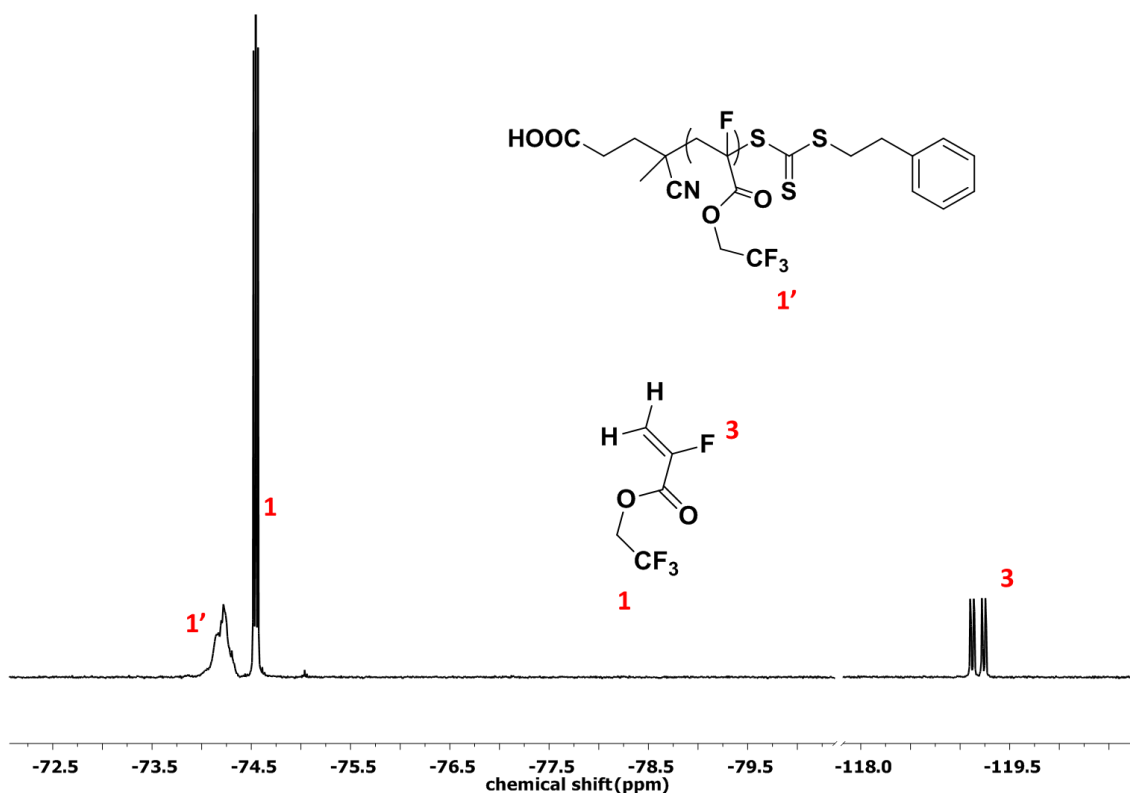


Figure 2. Expansion of the ^{19}F NMR spectrum from -72.5 ppm to -121 ppm of crude product resulting from the thermal RAFT polymerization of FATRIFE using CTA_2 and *tert*-amylperoxy-2-ethylhexanoate as chain transfer agent and radical initiator, respectively (recorded in acetone- d_6 , **Table 1**, Entry 2). The signal of the fluorine atoms in the backbone of the polymer at ca. -160~-175 ppm, is not shown.

When CTA_1 was used, the viscosity increased so rapidly that the stirring bar was stuck after 0.5 h only, although the measured monomer conversion was merely 30 % as determined by ^1H NMR spectroscopy. Meanwhile, the signal of proton assigned to the pyrazole function (**Figure S1**) was almost not observable. Moreover, the polymer solution could not pass through 220 μm PTFE filter prior to SEC analysis. Although the exact causes of this behavior (very high molar masses or presence of crosslinking) were not determined, these results indicated that CTA_1 was not suitable for the RAFT polymerization of FATRIFE.

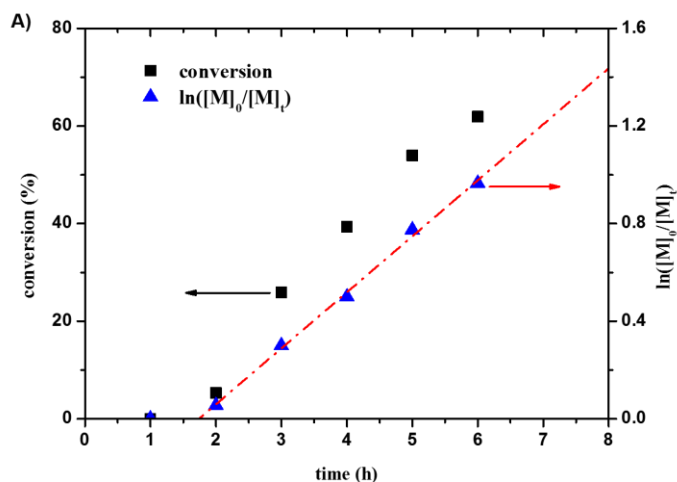
In the case of CTA_2 , a reasonable increase of viscosity was observed when the FATRIFE conversion reached 54% (according to **Equation 1** and **Equation 2**, respectively). After precipitation, the polymer (slightly yellow powder) was analyzed by NMR (**Figure S2**) and SEC. The ^1H NMR spectrum displays the

signal of the aromatic ring of CTA₂ as the end group centered at 7.35 ppm, indicating the presence of living chain ends. The dispersity of the polymer was 1.05, indicating a uniform polymer chain length.

When CTA₃ was used, the aromatic ring was observable in the ¹H NMR spectrum of the purified product (7.20 ppm, **Figure S3**), but it was not in proportion with the initial ratio (initial ratio [FATRIFE]₀/[CTA₃]₀ was 100:1, while it turned to be 325:1 in the polymer). At the same time, the dispersity reported by SEC was also relative high (*D* = 1.52). This is likely caused by a relatively low fragmentation constant of the CTA₃ with regard to the propagation rate of FATRIFE or with the fragmentation of PFATRIFE-SC(S)Z bond.

In the case of CTA₄, the polymerization was completely inhibited, with no conversion even after 24 h. Long Inhibition with dithiobenzoates CTA is well known although not always understood. It is believed to be caused by slow fragmentation or irreversible intermediate radical termination.⁵³

These preliminary reactions showed that CTA₂ is the most promising candidate.



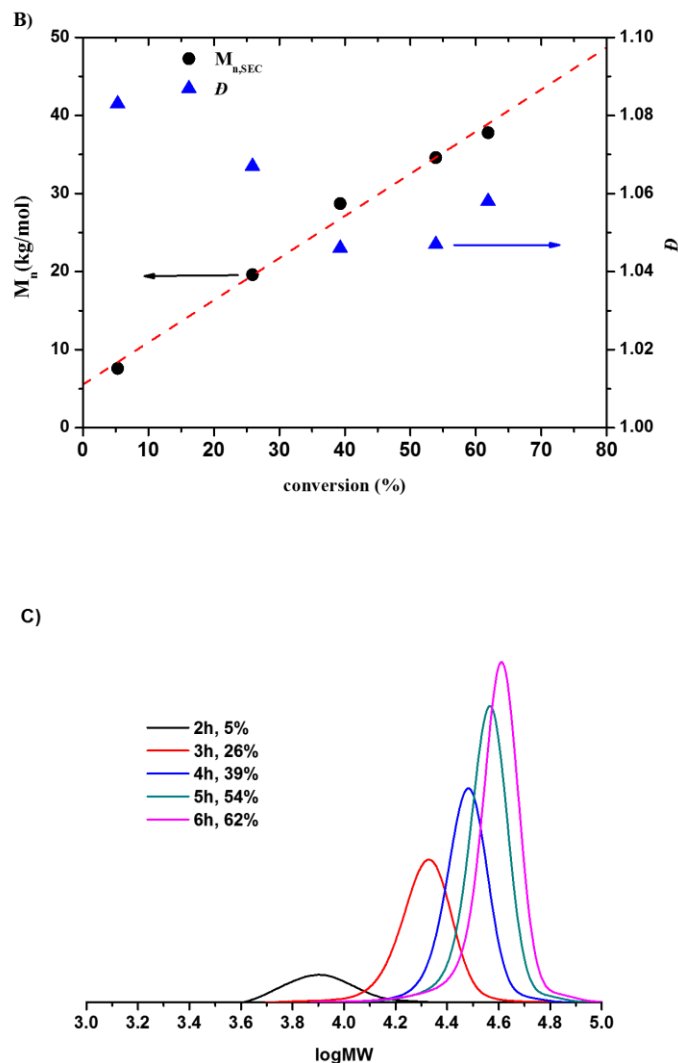


Figure 3. Kinetics of RAFT polymerization of FATRIFE using CTA_2 as the chain transfer agent and *tert*-amylperoxy-2-ethylhexanoate as radical initiator at 73 °C. $[FATRIFE]_0/[CTA_2]_0/[tert\text{-amylperoxy-2-ethylhexanoate}]_0 = 200:1:0.1$. (A) Evolution of monomer conversion with time; (B) evolution of molar mass and dispersities (D) with monomer conversion; (C) Evolution of the SEC traces with conversion. Note: The sample at $t = 1$ h could not be analyzed by SEC (molar mass and refractive index were not high enough).

To get more insight on the control of the polymerization of FATRIFE using CTA_2 as the chain transfer agent and *tert*-amylperoxy-2-ethylhexanoate as a radical initiator, the kinetics of this polymerization were studied (**Figure 3**). A short induction time (1.75 h) was observed, which is common in RAFT

polymerization.^{5, 54} It was found that the evolution of monomer conversions (determined by ¹H NMR spectroscopy using **Equation 1**) (**Figure 3A**), followed a *pseudo*-first-order kinetics, indicating a constant concentration of propagating radicals. The SEC analysis (**Figure 3B and 3C**) showed that (i) the molar mass of the polymers increased linearly *versus* monomer conversions and (ii) the dispersity (\mathcal{D}) remained below 1.10, indicating a good control of the polymerization. The satisfactory performance of CTA₂ in the RAFT polymerization of FATRIFE is likely due to a higher transfer constant, sufficiently fast reinitiation of the R-group and minimal cross-termination to the carbon-centered intermediate species. Important notes: The RI responses of PFATRIFE were negative as expected due to the fluorine atoms in the polymer.⁵⁵

2. PhotoRAFT polymerization of FATRIFE

Trithiocarbonate CTAs (such as CTA₂) are attractive reagents for photoRAFT, which in some cases do not require the use of photoredox catalysts.^{8, 13, 16, 21, 56} For example, Qiao's group¹⁶ synthesized well defined poly(acrylate)s using benzyl dodecyl trithiocarbonate as CTA without any exogenous radical sources or catalysts. According to the reports of Bai¹¹ and Qiao,¹⁷ the excellent performance of trithiocarbonate CTAs in photoRAFT are due to their reversible photo-induced homolytic cleavage and chain transfer process. In the above section, evidences of controlled polymerization of FATRIFE were shown under thermal conditions. Considering the advantages of photoRAFT over thermal RAFT,^{8, 21} such as better chain-end functionality, which was reported in literature,²¹ it was of interest to study the photoRAFT polymerization of FATRIFE using CTA₂.

To verify whether CTA₂ was a convenient candidate to conduct the photoRAFT polymerization of FATRIFE, the polymerization was first tested in the presence of Ir(ppy)₃ as a photocatalyst (**Table 2**, Entry 1). According to Boyer et al.,⁵⁴ Ir(ppy)₃ is suitable for the activation of various CTAs including trithiocarbonates via a photo-induced electron transfer process. It turned out that in the presence of Ir(ppy)₃ (9.4 ppm vs. FATRIFE), the conversion reached 78 % in 5 h using two household white LED lamps as light source. The resulting poly(FATRIFE) had a narrow molar mass distribution (\mathcal{D} = 1.06). Encouraged by this result, the polymerization was then tested in the absence of Ir(ppy)₃ (**Table 2**, Entry 2). In this case, the polymerization was slower as expected, with FATRIFE conversion reaching 53% in 5 h. Nevertheless, the dispersity of the resulting poly(FATRIFE) was still very low (\mathcal{D} = 1.05), indicating that the polymerization was also well-controlled albeit slightly slower in the absence of Ir(ppy)₃. Thus, in the following experiment, the polymerization was carried out using sunlight as a light source (**Table 2**, Entry 3). After 5 h, the FATRIFE conversion reached 78 % and the polymerization yielded poly(FATRIFE) with a

narrow dispersity ($\mathcal{D} = 1.10$). A controlled experiment without any CTA or $\text{Ir}(\text{ppy})_3$ was also carried out (**Table 2**, Entry 4). The resulting PFATRIFE could not be dissolved in SEC eluent, most likely because of high molar mass. The photoinitiation here could be similar to that observed in the case of other activated monomers such as acrylates.⁵⁷ The photoRAFT polymerization was also performed with another α -fluoroacrylate monomer, 1,1,1,3,3,3-hexafluoropropan-2-yl 2-fluoroacrylate (FAHFIP) (**Table 2**, Entry 5). In the absence of additional photocatalysts, FAHFIP conversion (determined by ^{19}F NMR spectroscopy using **Equation S2**, **Figure S4**) reached 80 % in 4 h. The resulting poly(FAHFIP) displayed very low dispersity ($\mathcal{D} = 1.09$). The photoRAFT copolymerization of FATRIFE and *tert*-butyl-2-trifluoromethacrylate (MAF-TBE) was also investigated (**Table 2**, Entry 6). Due to the lower reactivity of MAF-TBE ($r_{\text{MAF-TBE}} = 0$),^{58,59} the conversion of MAF-TBE was lower than that of FATRIFE (58 % vs. 80 %, **Figure S5**, **Equations 2** and **S4**) after 6 h. The dispersity of the resulting copolymer was as low as 1.06, also evidencing good control. These results indicated that CTA_2 is a promising candidate for the photoRAFT polymerization of α -fluoroacrylates.

Table 2 Photo polymerizations of FATRIFE and FAHFIP :^a

Entry	Light source	Time (h)	Conv. ^b (%)	$M_{n,\text{SEC}}^c$ (kg/mol)	\mathcal{D}^c
1 ^d	white LED	5	78	26.0	1.06
2	white LED	5	53	21.0	1.05
3	sunlight	5	78	27.6	1.10
4 ^e	sunlight	5	33	-	-
5 ^f	white LED	4	80	37.8	1.09
6 ^g	white LED	6	80/58	22.7	1.06

Conditions tested and characterizations: ^a $[\text{Monomer}]_0/[\text{CTA}_2]_0 = 100:1$. $[\text{Monomer}]_0 = 30$ wt%. Entries 1-4: M= FATRIFE. ^bMonomer conversion (α) determined by ^1H NMR using **Equation 1**. ^cApparent number-average molar mass ($M_{n,\text{SEC}}$) and dispersity (\mathcal{D}), determined by SEC. ^d $\text{Ir}(\text{ppy})_3$ was used as the photocatalyst $[\text{Ir}(\text{ppy})_3]_0/[\text{FATRIFE}]_0 = 9.4 \times 10^{-6}$. ^e $[\text{CTA}_2]_0 = 0$. The polymer solution could not pass through the 220 μm filter, thus SEC analysis was not attempted. ^fM= FAHFIP, conversion determined using **Equation S1**. ^gM= FATRIFE + *tert*-butyl-2-trifluoromethacrylate (MAF-TBE), $[\text{FATRIFE}]_0/[\text{MAF-TBE}]_0 = 80:20$. $\alpha_{\text{FATRIFE}} = 80\%$ and $\alpha_{\text{MAF-TBE}} = 58\%$, determined using **Equations 1** and **S4**, respectively.

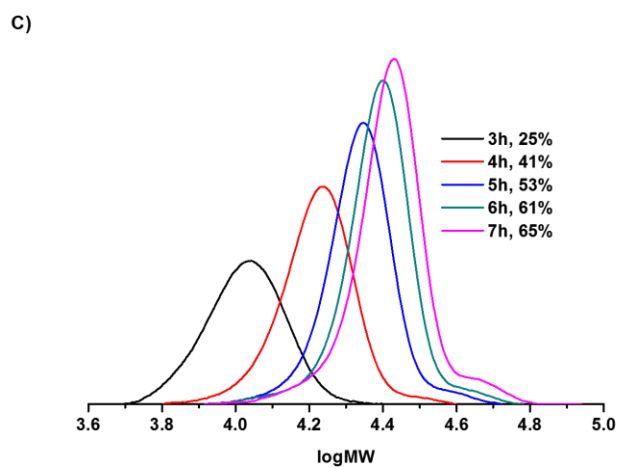
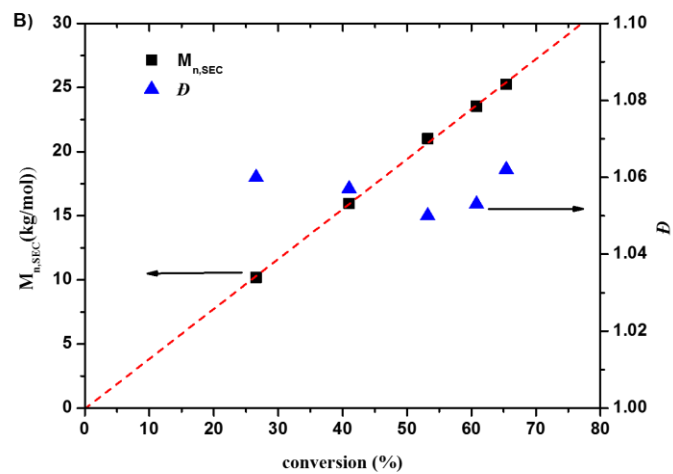
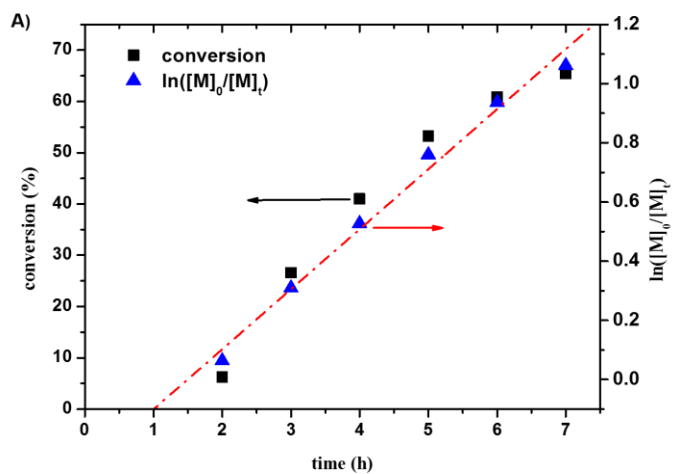


Figure 4. Kinetics of photoRAFT polymerization of FATRIFE under light irradiation (2 white LED lamps) at room temperature using CTA₂ as the chain transfer agent. [FATRIFE]₀/[CTA₂]₀ = 100/1. (A) Evolution of monomer conversions vs. time; (B) Evolution of molar masses and dispersities with monomer conversion; (C) Evolution of the SEC traces with conversion. Note: The molar mass of the sample at t=2h could not be measured by SEC.

To assess the control performance of the photoRAFT polymerization of FATRIFE, the kinetics of polymerization were studied utilising two household LED lamps as light source and without any additional exogenous radical sources or catalysts. When CTA₂ was used, the evolution of the FATRIFE conversion followed a *pseudo*-first-order kinetics (**Figure 4A**), indicating a constant concentration of propagating radicals during the polymerization. Meanwhile, a linear increase of apparent molar masses *versus* monomer conversion was also observed (**Figure 4B**). In addition, during the polymerization, the molar mass distribution of the resulting polymers remained narrow ($\mathcal{D} < 1.10$). These results indicate that CTA₂ provides very good control over the photoRAFT polymerization of FATRIFE. The molar mass of the polymer at t= 2h was too low to be suitable for SEC analysis (**Figure S6**). The minor shoulder peaks observed at higher molar masses were probably caused by irreversible chain recombination.

RDRP techniques should afford highly functional polymer chains, being able to be reactivated to produce block polymers. To further confirm the performance of CTA₂, in the photoRAFT polymerization of α -fluorinated acrylates, two different experiments were carried out: (i) light “ON/OFF” experiment and (ii) chain extension experiment using poly(FATRIFE)-TTC synthesized by photoRAFT as a macro chain transfer agent (**Scheme 2**).

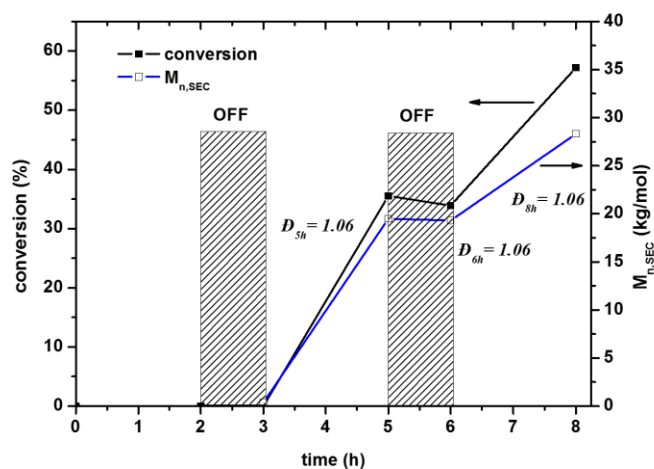
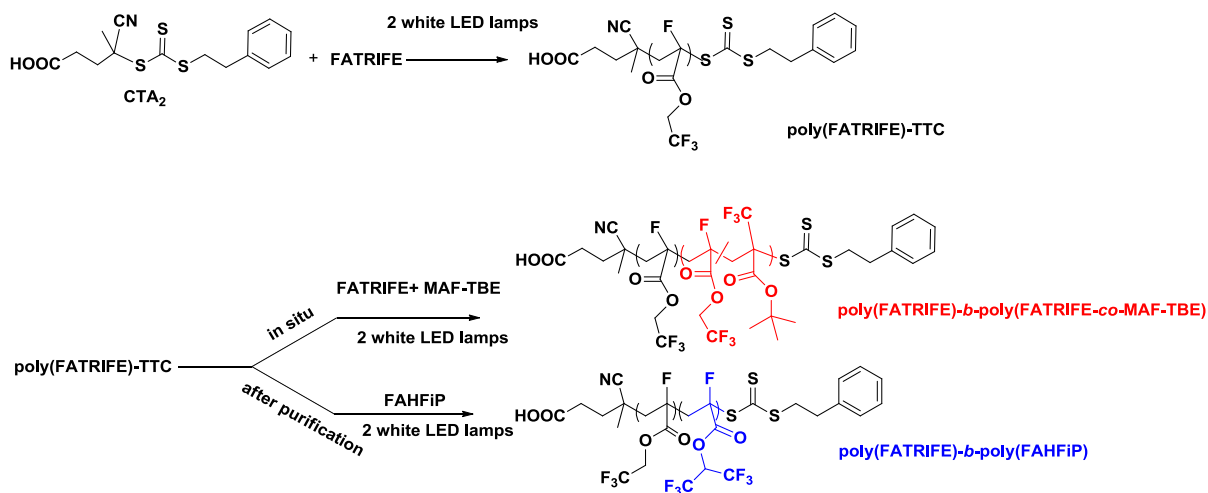


Figure 5. Evolutions of monomer conversions and molar masses during the light “ON/OFF” experiment of the photoRAFT polymerization of FATRIFE. $[FATRIFE]_0/[CTA_2]_0 = 100:1$ (Table 2, Entry 2), $T = 20\text{ }^\circ\text{C}$, light source = 2 white LED lamps. FATRIFE conversions were calculated from ^1H NMR spectroscopy, using Equation 1. Dispersity at $t = 5, 6$ and 8 were 1.06 , as reported from SEC analyses.

During the light “ON/OFF” experiment (Figure 5), the light source was switched ON/OFF purposely during the polymerization. The monomer conversion did not increase significantly during the first 2 h of irradiation, suggesting an induction time. An increase of monomer conversion (from 0 to 36 %) was observed in the second irradiation period (light ON, $t = 3 - 5$ h). In the following light OFF period ($t = 5 - 6$ h), monomer conversion did not increase at all, the decreased value of monomer conversions (less than 2%) is likely due to the error of NMR analysis. But, when the lamps were switched ON again ($t = 6 - 8$ h), the increases of both monomer conversion and molar masses were observed. During this entire light ON/OFF experiment, the dispersity of the resulting polymer remained lower than 1.10 , evidencing a uniform growth of the polymer chains. These results also indicated that the polymerization could be temporally controlled by simply switching ON and OFF the light irradiation.



Scheme 2 Chain extension using poly(FATRIFE)-TTC as macro chain transfer agent synthesized by photoRAFT polymerization. Two different block polymers, poly(FATRIFE)-*b*-poly(FATRIFE-co-MAF-TBE) and poly(FATRIFE)-*b*-poly(FAHFIP), were synthesized using crude and purified poly(FATRIFE)-TTC, respectively.

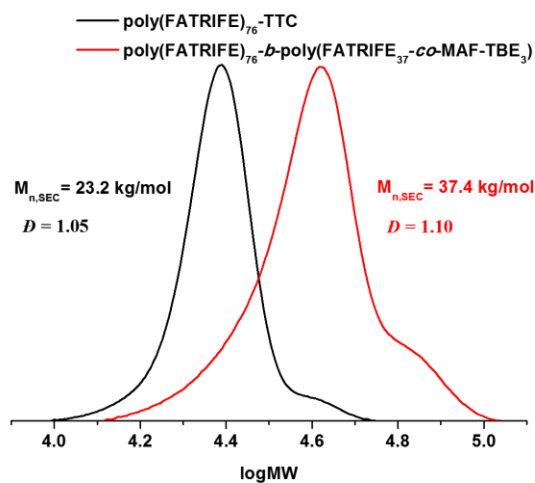


Figure 6. SEC chromatograms of the poly(FATRIFE)₇₆-TTC, macro chain transfer agent (black trace) and the resulting poly(FATRIFE)₇₆-*b*-poly(FATRIFE₃₇-co-MAF-TBE₃) block copolymer (red trace) after in situ chain extension experiment (**Scheme 2**).

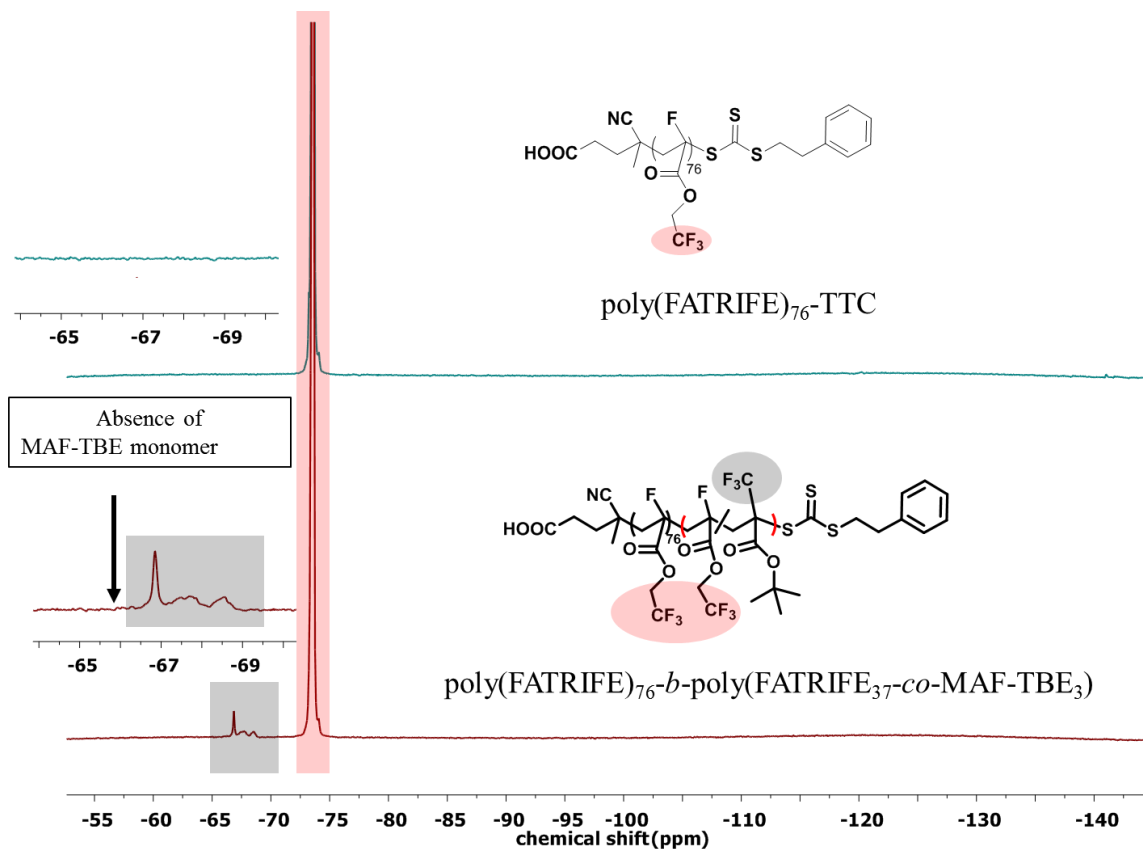


Figure 7. Comparison of the ^{19}F NMR spectra of the $\text{poly}(\text{FATRIFE})_{76}\text{-TTC}$ macroCTA (Table 2, Entry 2, blue spectrum, recorded in acetone- d_6) and $\text{poly}(\text{FATRIFE})_{76}\text{-}b\text{-poly}(\text{FATRIFE}_{37}\text{-}co\text{-MAF-TBE}_3)$ (brown spectrum, recorded in acetone- d_6) block copolymers obtained by in-situ chain extension. MAF-TBE was introduced when FATRIFE conversion was 76 %. MAF-TBE molar content in the diblock copolymer is 2.6%.

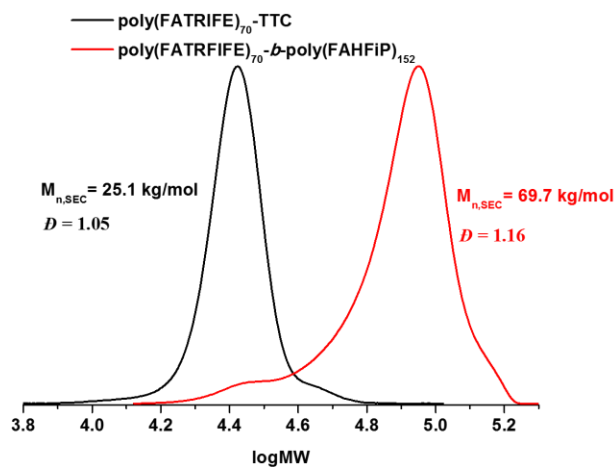
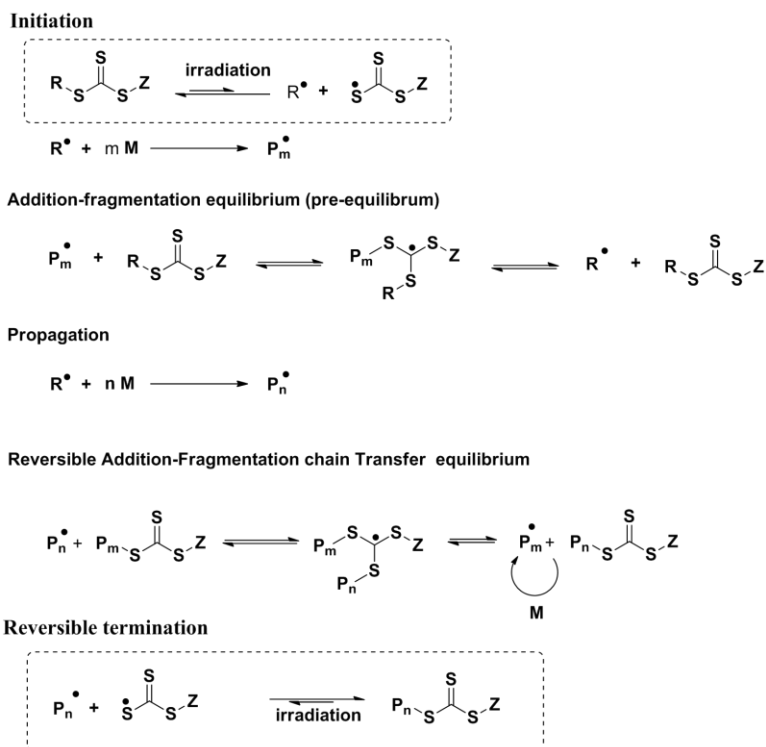


Figure 8. SEC chromatograms of the poly(FATRIFE)₇₀-TTC macroCTA (black trace) and of the poly(FATRIFE)₇₀-*b*-poly(FAHFiP)₁₅₂ diblock copolymer (red curve) obtained after photoRAFT chain extension using a purified poly(FATRIFE)₇₀-TTC macroCTA.

PhotoRAFT chain extension experiments were carried out using the poly(FATRIFE) prepared by photoRAFT as a macroCTA (poly(FATRIFE)-TTC) (**Scheme 2**). In a first experiment, poly(FATRIFE) synthesized by photoRAFT polymerization was used without any purification. A deoxygenated solution of FATRIFE and MAF-TBE ([FATRIFE]₀/[MAF-TBE]₀= 80/20) was added into the Schlenk tube containing the growing macroCTA ($\alpha_{\text{FATRIFE}} = 76\%$, determined by ¹H NMR), allowing in-situ extension of the polymer chains. This chain extension experiment yielded a well-defined block copolymer ($D = 1.10$, **Figure 6**). The minor shoulder peak observed at higher molar mass is ascribed to bimolecular chain termination. The typical signals of the MAF-TBE unit between -64.4 and -66.8 ppm in the ¹⁹F NMR spectrum and at 1.45 ppm in the ¹H NMR spectra (**Figures 7 and S7**) indicated the successful incorporation of MAF-TBE unit in the second block. While the signal at 7.35 ppm in ¹H NMR spectra (**Figure S7**) reveals the presence of functional chain ends before and after the chain extension. In a second chain extension experiment, purified poly(FATRIFE)-TTC was used in the photoRAFT homopolymerization of FAHFiP, yielding a relatively well-defined poly(FATRIFE)-*b*-poly(FAHFiP) block copolymer. **Figure 8** reveals that a small amount of macroCTA (presumably dead chains) did not take part in the chain extension reaction, probably induced by the presence of dead chain accumulated during the purification step. The ¹H NMR spectrum of the poly(FATRIFE)-*b*-poly(FAHFiP) diblock copolymer (**Figure S8**) showed the signals corresponding to the aromatic ring of the ω -chain ends (at 7.20-7.37 ppm), and to the -CH(CF₃) moieties of the FAHFiP units (at 6.0-6.5 ppm). This indicates that the diblock copolymer was still highly functional.



Scheme 3 Plausible mechanism for the photoRAFT polymerization carried out without external photocatalyst or radical initiators. The photo-induced reversible photolysis process of chain transfer agent is highlighted. Trithiocarbonate CTA was used as an example.

Several teams have investigated the mechanisms of photoRAFT polymerization in the absence of radical initiators or photocatalysts.^{13,16,17,21} The proposed mechanism is close to a hybrid process of photoiniferter polymerization and RAFT polymerization (**Scheme 3**). Under photoirradiation, the reversible photolysis of chain transfer agent contributes to the generation of the initiating radicals (photoiniferter process). Meanwhile, the CTA participates to the reversible chain transfer equilibrium of the RAFT process. In the case of trithiocarbonate, the photolysis was claimed to be due to the $n \rightarrow \pi^*$ excitation of the thiocarbonyl moiety, corresponding to the absorption band at 380–550 nm.^{16,17} According to Qiao,¹⁷ both the reversible photolysis and the RAFT process help to stabilize the trithiocarbonate moiety, thus contributing to the controlled polymerization. Herein, a similar mechanism is likely followed. As shown in **Scheme 3**, initiation species were generated *via* the reversible photolysis of trithiocarbonate. In this process, an equal molar amount of non-propagating radicals were also generated. In the propagation step, the RAFT equilibrium contributed to the controlled growth of polymer chains. In a reversible termination step, the propagating radicals were reversibly deactivated by recombination with the non-propagating trithiocarbonyl radicals, forming dormant species which could

be reactivated *via* photo-induced reversible photolysis or reaction with a propagating radical. Both the reversible photolysis process and the RAFT equilibrium contributed to the control of the photoRAFT polymerization.

Conclusions

RAFT polymerization of 2,2,2-trifluoroethyl α -fluoroacrylate (FATRIFE) using four different chain transfer agents was studied under thermal conditions. Cyanomethyl 3,5-dimethyl-1H-pyrazole-1-carbodithioate (CTA₁) and dibenzyltrithiocarbonate (CTA₃) resulted in poor or hardly controlled polymerizations, respectively, while ethyl 2-(phenylcarbonothioylthio) propionate (CTA₄) did not lead to any polymerization at all. In contrast, polymers with narrow molar mass distributions ($\bar{D} < 1.10$) were obtained when 4-cyano-4-(2-phenylethanesulfanylthiocarbonyl)sulfanylpentanoic acid (CTA₂) was used as chain transfer agent. Kinetics experiment revealed the *pseudo*-first-order evolution of monomer conversions with time and a monotonous increase of molar masses *versus* monomer conversions, while dispersity remained lower than 1.10. This trithiocarbonate CTA was then implemented in the photoRAFT polymerization of FATRIFE performed in the absence of additional exogenous radical sources or photocatalyst and using household white LED lamps (or sunlight) as light sources. Although the polymerization in the absence of photocatalyst was slower than that carried out in the presence of 9.4 ppm of Ir(ppy)₃, it still followed *pseudo*-first-order polymerization kinetics, linear molar masses *vs.* monomer conversion increase, and narrow dispersities, thus indicating a good control of the polymerization. Efficient reinitiation was observed in light ON/OFF experiment, which also indicated temporal control of such a polymerization. The poly(FATRIFE) macroCTA synthesized by photoRAFT polymerization was then used in the homopolymerization of 1,1,1,3,3,3-hexafluoropropan-2-yl 2-fluoroacrylate (FAHFIP) and in the copolymerization of FATRIFE with *tert*-butyl-2-trifluoromethacrylate (MAF-TBE). Efficient chain reinitiations were observed from both SEC and NMR analyses. The mechanism of the photoRAFT polymerization under light irradiation in that present study is likely close to the one proposed in previously published articles,^{11,13,16,21} i.e., a hybrid mechanism of photoiniferter polymerization and RAFT polymerization. Since the optical properties of fluorinated polymers are closely related to the fluorine content, controlled radical polymerization of α -fluoroacrylates is interesting for the design of novel optical materials, especially metal and catalyst-free conditions described here. In the future, polymerization of α -fluoroacrylate with higher fluorine contents will be studied. The tolerance of the system to impurities such as oxygen and inhibitors will also be further explored. The polymerization of FATRIFE by metal-free photoATRP⁶⁰ will be also of interest for future investigation.

Acknowledgments

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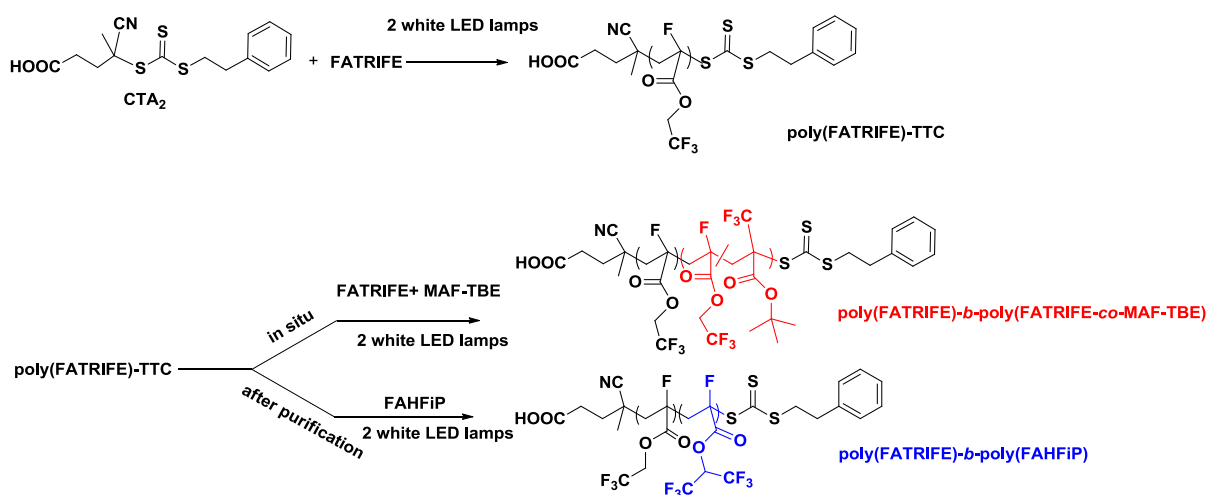
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Table of contents entry

Thermal and photo RAFT Polymerization of 2,2,2-trifluoroethyl α -fluoroacrylate

Qizhi Yang, Marc Guerre, Vincent Ladmiraal and Bruno Améduri*



RAFT polymerization of 2,2,2-trifluoroethyl α -fluoroacrylate (FATRIFE) was studied under thermal conditions and light irradiation in the presence of four chain transfer agents. Polymers with narrow dispersities were obtained in the presence of 4-cyano-4-(2-phenylethanesulfanylthiocarbonyl)sulfanylpentanoic acid and that further led to fluorinated block copolymers.

