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Photoorganocatalyzed Reversible-Deactivation Alternating Copolymerization of Chlorotrifluoroethylene and Vinyl Ethers under Ambient Conditions: Facile Access to Main-Chain Fluorinated Copolymers

Kunming Jiang, Shantao Han, Mingyu Ma, Lu Zhang, Yucheng Zhao and Mao Chen*

State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai, China, 200433

ABSTRACT: Fluoropolymers have found broad applications for many decades. Considerable efforts have focused on expanding accesses toward main-chain fluorinated polymers. In contrast to previous polymerizations of gaseous fluoroethylenes conducted at elevated temperatures and with high-pressure metallic vessels, we here report the development of a photoorganocatalyzed reversible-deactivation radical alternating copolymerization of chlorotrifluoroethylene (CTFE) and vinyl ethers (VEs) at room temperature and ambient pressure by exposing to LED light irradiation. This method enables the synthesis of various fluorinated alternating copolymers with low *Đ* and high chain-end fidelity, allowing iterative switch of the copolymerization between "ON" and "OFF" states, the preparation of fluorinated block alternating copolymers, as well as post-synthetic modifications.

INTRODUCTION

Fluoropolymers, endowed with outstanding properties such as thermal stability, chemical inertness, excellent weatherability and low surface energy, have found their use in many high-end applications.[1, 2] However, lots of fluorinated homopolymers possess high crystallinity, hindering their processability. Copolymerization is an effective means to regulate the crystallinity and solubility without losing the intrinsic advantages of fluoropolymers.[3, 4] Examples include commercialized products of Halar,[5] Lumiflon[6] and Tefzel,[7] all of which have been synthesized via copolymerization of fluoroethylene and other comonomers. Meanwhile, the incorporation of comonomers enables facile regulation of polymers' chemical structures and physical properties.[3, 8]

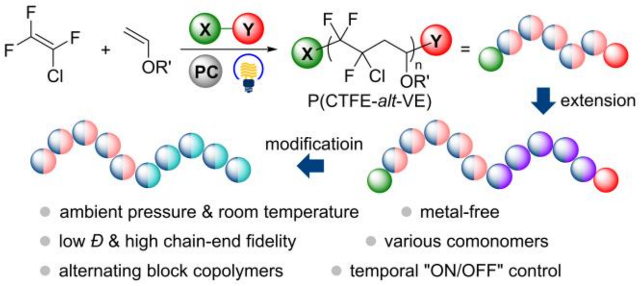
Precise polymer synthesis enables engineering of tailored materials at the molecular level for specific properties that are suitable for various applications.[9-11] While the development of reversible-deactivation radical polymerization (RDRP) has been demonstrated to be particularly effective for acrylates and styrene,[9-11] the transformation of fluoroethylene (i.e., chlorotrifluoroethylene (CTFE),[12] which constitutes the backbone of Halar and Lumiflon, to name a few) through a controlled pathway remains a significant challenge.[13, 14] Considerable research efforts have been devoted to synthesize copolymers of CTFE,[15-19] however, owing to its low boiling point,[20] the synthetic routes typically require high pressure at elevated temperatures (80 to 250 °C), which limits the broad accessibility of related products. Apart from the harsh conditions, the intrinsic characteristic of copolymerization poses challenges on regulation of the precise chain-growth since the copolymer chain-ends could connect with different comonomers during iterative initiations, and would give rise to different reactivities and unpredictable copolymer sequence. In addition, the Cl atoms on the growing copolymers could act as initiating sites or undergo chain transfer reactions under metal-catalyzed or harsh conditions.[21-23] Consequently, a number of synthetic limitations including the requirement of metal catalysts[24] or ^{60}Co γ-ray irradiation[25] in the reaction process, as well as poor chain-end fidelity, broad molecular weight distribution (MWD) at high monomer conversion, remain issues to be overcome.

Recently, the employment of photoredox catalysis in RDRPs,[26-32] cationic polymerizations[33-35] and ring-opening metathesis polymerizations[36] has enabled spatiotemporally controlled chain growth exposing to light irradiation.[37-39] However, a photo-controlled (co)polymerization of CTFE has not been achieved yet. We envision that a photoorganocatalyzed approach could provide opportunities to improve the livingness of chain-growth and decrease side reactions by implementing control through the photoredox singe-electron-transfer mechanism[31-34] under mild conditions. Meanwhile, the controlled copolymerization of CTFE under operationally simple conditions could not only facilitate the access towards a variety of fluoropolymers, but also allow the investigation of amorphous materials that would resolve the crystallinity problem of the homopolymer counterpart, which might shed light on rational design of polymeric materials (for example, solid polymer electrolytes (SPEs))[40, 41] derived from the particularly interesting performance of fluoropolymers.[42, 43]

Herein we report the development of a photoorganocatalyzed reversible-deactivation radical alternating copolymerization of CTFE and vinyl ethers (VEs) for the first time (Scheme 1). Specifically, the synthetic advances of this method include: (1) the facile transformation of CTFE and

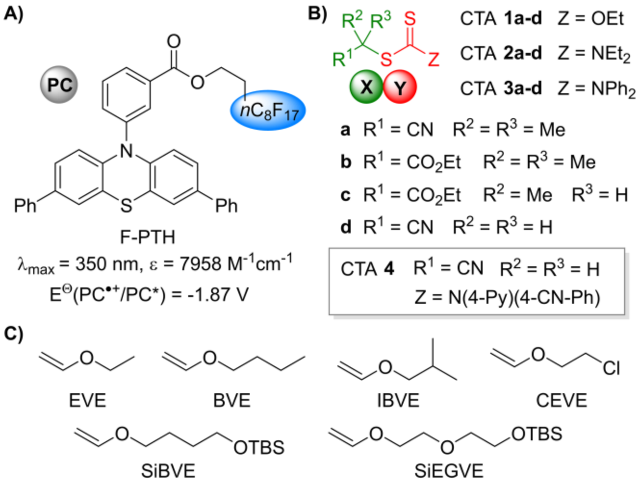
VEs in an alternating fashion achieved under ambient pressure and temperature without metal-contamination concern; (2) the controlled access to various main-chain fluorinated materials with low *Đ* and high chain-end fidelity at high VE conversions; (3) the iteratively switching of copolymerization between "ON" and "OFF" states for a gaseous monomer enabled by using light as an external trigger; (4) the unprecedented capability in expanding the synthetic scope to overall fluorinated block alternating copolymers, and in facile post-synthetic modifications. Overall, this method emerges as a simple and effective approach for the controlled synthesis of main-chain fluorinated alternating copolymers, which creates new possibilities to access functional materials.

Scheme 1. Photoorganocatalyzed reversible-deactivation radical alternating copolymerization of CTFE and VEs.



RESULTS AND DISCUSSION

Scheme 2. Chemical Structures of A) Catalyst, B) Chain-Transfer Agents and C) Comonomers used in this study.



Preliminary investigations on copolymerization conditions. At the beginning of the investigation, we employed non-fluorinated PCs [i.e., perylene and 10-phenylphenothiazine (PTH)] in the photopolymerization of CTFE and vinyl ethyl ether (EVE). However, emulsions were generated, and broad MWDs (*Đ* ~ 1.5-1.8) of the resulted copolymers were detected by size-exclusion chromatography (SEC). Instead, we synthesized fluorinated PC (F-PTH, Scheme 1A, Scheme S1 and Figures S1-S3) based on PTH.[44-46] In comparison to PTH, F-PTH possesses a redshifted absorption (λ_{max} = 350 *vs* 320 nm, Figures S4-S5) and increased molar absorptivity (*ε* = 7958 *vs* 3200 $M^{-1}cm^{-1}$). Although the reductive potential at the excited state of F-PTH is more positive than PTH ($E^{\ominus}(PC^{\bullet+}/PC^*)$ = -1.87 V *vs* -2.03 V) as caused by the electron-withdrawing substituent, F-PTH is reductive enough to react with thiocarbonylthio CTAs mostly employed in photoinduced electron transfer-reversible addition-fragmentation chain transfer (PET-RAFT) polymerization.[47] Additionally, F-PTH exhibits reversible voltammetric cycles at different scan rates (Figure S6), indicating that the oxidation is highly reversible and the resulting $PC^{\bullet+}$ is stable.

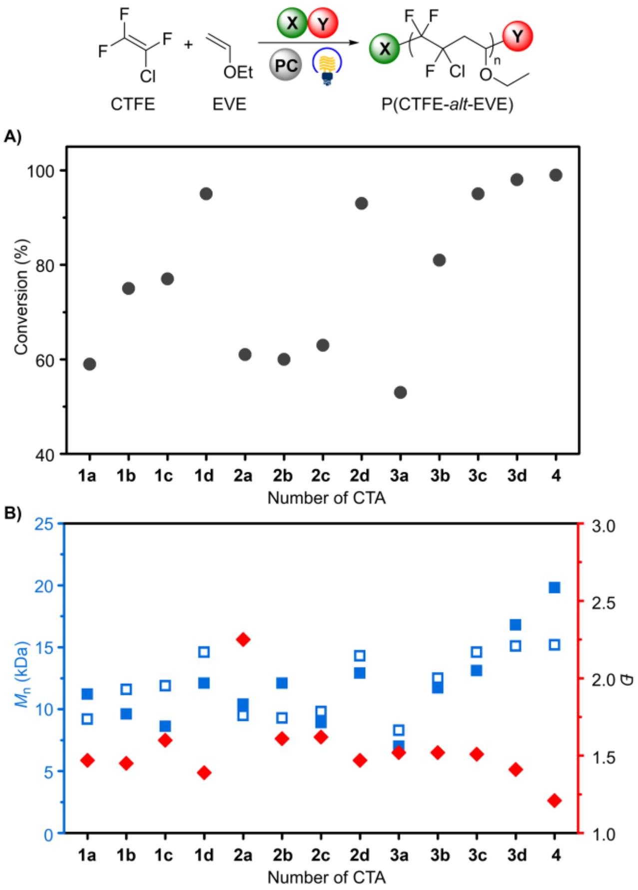


Figure 1. Optimization for the photoorganocatalyzed copolymerization of CTFE and EVE with CTA **1**-**4**. [CTFE]/[EVE]/[CTA]/[F-PTH] = 60/40/1/0.05, 410 nm purple LED, 25 °C, ambient pressure. A) EVE conversions. B) molecular weights (M_n) and *Đ* results of copolymers, filled blue squares represent M_n by SEC, empty blue squares represent M_n calculated based on monomer conversions.

Using F-PTH as a PC, we investigated the copolymerization of CTFE and EVE in the presence of a series of xanthates (CTA **1a** to **1d**, Scheme 1B & 1C) in diethyl carbonate solvent using a 13 W purple LED bulb as a light source (emission at 410 nm, Figure S7). While xanthates have shown good control in RAFT copolymerization of CTFE and VEs under thermal conditions as reported by Kamigaito, Ladmiral and co-workers,[19] as well as ^{60}Co γ-ray irradiated copolymerization by the Bai group,[25] the employment of xanthates under photoredox conditions generated copolymers of unsatisfactory control (*Đ* = 1.42-1.60, Figure 1B, Table S1); though, moderate to high conversions (59-95%, Figure 1A) were obtained. Then, we focused on tuning the structure of CTAs in order to modulate its reactivity. We observed that a better leaving group, which gives a more stable alkyl radical, affords lower monomer conversions than a poorer leaving group. For example, in comparison to CTA **1a**, **2a** and **3a** (alkyl radical = $\bullet CCN(CH_3)_2$), improved conversions (93-98% *vs* 53-61%) were obtained with CTA **1d**, **2d** and **3d** (alkyl radical = $\bullet CH_2CN$). From CTAs **1** to **3**, the employment of CTA **3d** provided the lowest MWD ($Đ$ = 1.39), others gave MWDs in a range of $Đ$ = 1.42-2.25.

When CTA **1d**, **2d** and **3d** were analyzed by cyclic voltammetry (CV) (Figure S8), CTA **3d** exhibits the most positive onset potential of reduction, suggesting that the NPh_2 group could best facilitate accepting electron from PC* during the PET process.[39] Then, we turned our attention to CTA **4**,[48] which simultaneously possesses a more positive reductive potential than CTA **3d** (-1.21 *vs* -1.54 V) and a $-CH_2CN$ leaving group. The employment of CTA **4** generated P(CTFE-*alt*-EVE) at a complete EVE conversion and high control over MWD ($Đ$ = 1.21, $M_{n,SEC}$ = 19.8 kDa). Further modifications from the optimized reaction conditions including solvents and light sources resulted in lower monomer conversions and broad MWDs (Tables S2-S3).

To further validate the importance of a fluorinated PC, we employed non-fluorinated PCs instead of F-PTH with CTA **4**, and found that broad MWDs ($Đ$ = 1.49-1.77) at 88-97% monomer conversions were obtained (Table S4). The copolymerization mixture of CTFE and EVE was characterized with dynamic light scattering (DLS). The observation of nanoparticles (343 nm) (Figures S9 and S10) indicated that the main-chain fluorinated copolymers would be prone to self-assembly during copolymerization. The *n*-C_8F_{17} substituent on F-PTH could promote the interaction between PC and the growing polymer chain by transferring into nanoparticles driven by the fluorine-fluorine interaction, thus implementing the good control over chain growth.

Reaction kinetics for the alternating copolymerization. Next, we investigated the copolymerization process of CTFE and different VEs under optimized reaction conditions. As shown in Figure 2A, for VEs including EVE, *t*-butyldimethyl(4-(vinyloxy)butoxy)silane (SiBVE), *i*-butyl vinyl ether (IBVE), *n*-butyl vinyl ether (BVE) and 2-chloroethyl vinyl ether (CEVE), the degrees of polymerization (DPs, Equations S1 and S2, Tables S5 to S9) increase with exposure times. Importantly, DPs of both CTFE and VEs are very close to each other throughout the copolymerization processes, confirming the alternating chemical structures of the copolymer backbones. Plots of $\ln([M]_0/[M]_t)$ as a function of time (Figure 2B) exhibit first order kinetics for reactions of different VEs, further demonstrating the high degree of control obtained in the alternating copolymerization process. During the propagation, molar masses of copolymers increase with monomer conversions (Figure 2C). The MWDs of all copolymers maintained within a narrow range of $Đ$ =1.12-1.29 (Figures S11 to S15), which are particularly good for main-chain fluorinated copolymers. Although the molar masses provided by SEC are higher than theoretical results at high VE conversions ($M_{n,calc}$), when measured with a multiangle laser light scattering (MALLS) detector (Figure S16), obtained molecular weights ($M_{n,MALLS}$) are in a good agreement with the predetermined values. For example, during the synthesis of P(CTFE-*alt*-BVE), when BVE reached 90% conversion, $M_{n,SEC}$ = 21.1 kDa, $M_{n,calc}$ = 15.9 kDa and $M_{n,MALLS}$ = 14.8 kDa, respectively.

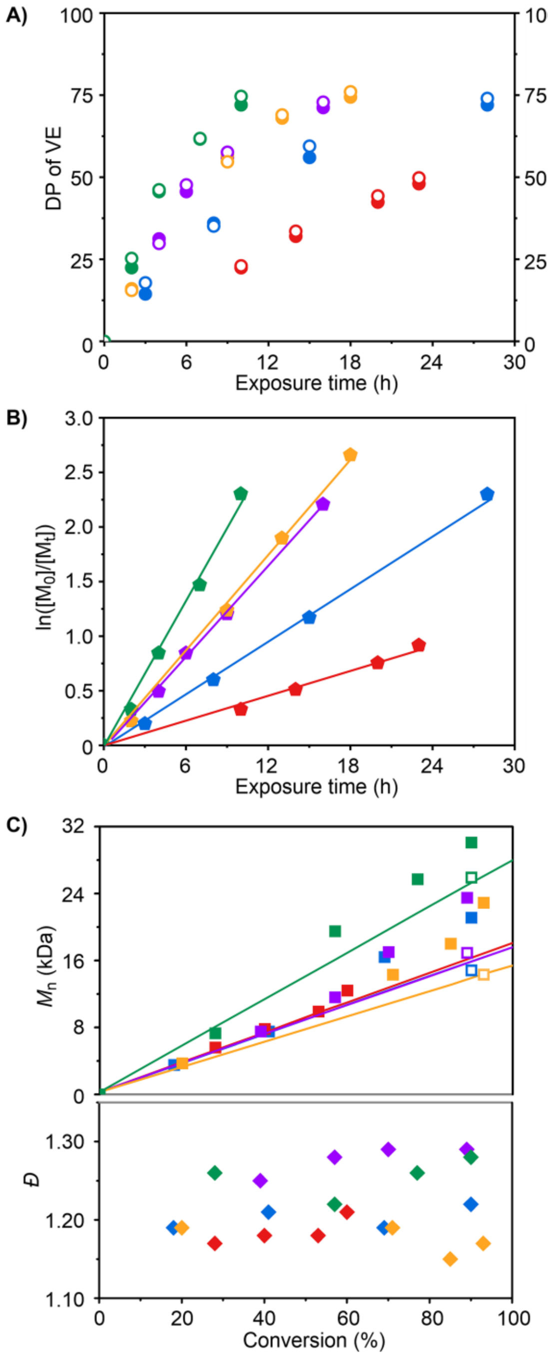


Figure 2. Alternating copolymerization of CTFE and VEs enabled by the photoredox catalysis. Points of different colors represent results obtained with different VEs: SiBVE (green), EVE (yellow), IBVE (purple), BVE (blue) and CEVE (red). [CTFE]/[VE]/[CTA **4**]/[F-PTH] = 120/80/1/0.05, 25 °C, ambient pressure. A) Degrees of polymerization (DPs) of CTFE (filled circle) and VEs (empty circle) *versus* exposure time. See the supporting information (Equations S1 and S2) for details of calculation. B) $\ln([M]_0/[M]_t)$ *versus* exposure time. $[M]_0$ and $[M]_t$ are the concentrations of VEs at time points 0 and t, respectively. C) M_n and $Đ$ *versus* % VE conversion, filled squares represent M_n obtained by SEC, empty squares represent M_n obtained using a MALLS detector.

Expanding the copolymerization scope and characterization results. With the established copolymerization method, we turned our attention to the synthesis of a variety of P(CTFE-*alt*-VE)s with different molecular weights. As shown in Table 1, good to excellent VE conversions were achieved for different combinations of CTFE and VEs upon visible-light irradiation at low organocatalyst loadings (0.01-0.05 mol% of monomer). Since ambient temperature and pressure were employed, conventional low-pressure glass tubes could be employed as reaction containers in this method, further facilitating handling gaseous CTFE without high-pressure metallic devices. For examples described in Table 1, P(CTFE-*alt*-VE)s of molecular weights ranging from 2.0 to 31.1 kDa and narrow MWDs of $Đ$ = 1.13-1.32 were obtained at up to >99% VE conversions. SEC profiles of obtained fluoropolymers (Figure S17) were symmetrical and unimodal without the detection of any shoulder peak, further manifesting the well-controlled propagation realized for each comonomer. When CTA **4** was replaced with CTA **3d** under otherwise identical conditions, the photoorganocatalyzed copolymerizations of CTFE and different VEs generated copolymers with decreased control over MWDs ($Đ$ = 1.33-1.51, Table S10).

Table 1. Photoorganocatalyzed alternating copolymerization of CTFE and VEs.[a]

entry	VE	[M]/[CTA **4**]	conv. (%)	$M_{n,calc.}$ (kDa)	M_n (kDa) SEC[b]/MALLS[c]	$Đ$[b]
1	EVE	20/1	92	1.7	2.0 / 1.8[d]	1.25
2	EVE	100/1	>99	7.8	8.5 / 7.6	1.13
3	EVE	200/1	96	14.8	26.4 / 15.0	1.21
4	EVE	400/1	95	29.0	45.3 / 31.1	1.32
5	BVE	100/1	>99	9.0	11.2 / 9.8	1.22
6	BVE	200/1	95	16.8	29.9 / 17.3	1.26
7	IBVE	40/1	90	3.4	3.4 / 3.2[d]	1.24
8	IBVE	100/1	>99	9.0	9.8 / 10.1	1.23
9	IBVE	200/1	96	16.9	29.6 / 18.7	1.28
10	CEVE	100/1	86	8.0	8.8 / 8.6	1.12
11	CEVE	200/1	83	15.1	19.1 / 15.9	1.14
12	SiBVE	100/1	>99	14.2	16.7 / 15.1	1.28
13	SiBVE	200/1	95	26.6	31.9 / 24.4	1.23
14	SiEGVE	30/1	83	3.9	4.0 / 4.3[d]	1.22
15	SiEGVE	125/1	85	15.7	19.7 / 15.8	1.19
16	SiEGVE	200/1	82	24.1	29.2 / 23.9	1.28

[a] [M] = [CTFE]+[VE], [CTFE]/[VE] = 60/40, [CTA **4**]/[F-PTH] = 1/0.05, 25 °C, ambient pressure, conducted with Schlenk glass tube, 410 nm light irradiation. Conversions are based on the ^{1}H NMR analysis of remaining VEs after reactions. [b] $M_{n,SEC}$ and $Đ$ measured by SEC. [c] $M_{n,MALLS}$ measured by MALLS instrument. [d] M_n determined by ^{1}H NMR analysis.

P(CTFE-*alt*-CEVE) synthesized with this method was characterized with proton nuclear magnetic resonance spectroscopy (^{1}H NMR) to analyze the chemical structure of the chain-end group. As shown in Figure 3, resonances corresponding to protons from H_a to H_e were clearly observed, and their integration areas are in a good agreement with the target structure, revealing that the final repeating unit of copolymer is vinyl ether, which is substituted by the dithiocarbamate group (Z(CS)S-). The molecular weight calculated based on the ^{1}H NMR spectrum is close to the $M_{n,MALLS}$ value ($M_{n,NMR}$ = 24.8 kDa, $M_{n,MALLS}$ = 24.2 kDa, , $M_{n,calc}$ = 23.9 kDa). Termination of copolymer with proton will reduce the chain-end fidelity, giving overestimated molar mass as determined by UV-vis adsorption ($M_{n,UV\text{-}vis}$).[49] When P(CTFE-*alt*-CEVE) was characterized by UV-vis instrument, $M_{n,UV\text{-}vis}$ = 25.1 kDa was obtained, suggesting that the degree of end group functionality is above 95% (Figures S18 and S19, Equations S3). The dithiocarbamate terminal groups in other alternating copolymers have also been observed in corresponding ^{1}H NMR spectra (Figures S20-S24), indicating that high chain-end fidelity was achieved with this method.

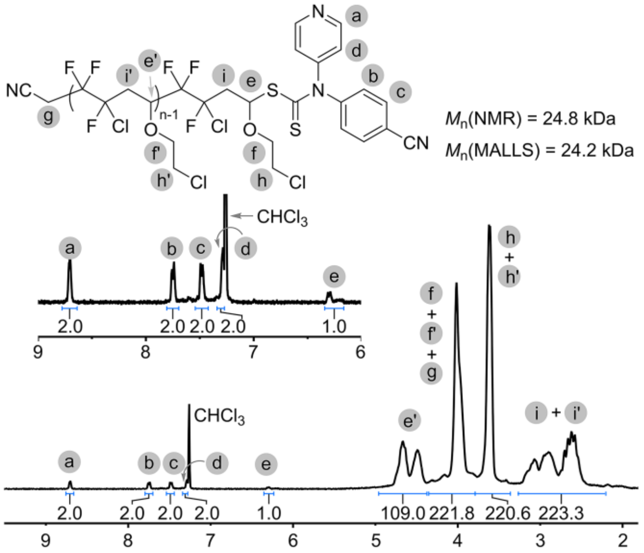


Figure 3. ^{1}H NMR spectrum of P(CTFE-*alt*-CEVE) synthesized via the photoorganocatalyzed copolymerization.

"ON/OFF" switch for the copolymerization of gaseous CTFE. An attractive advantage of photo-controlled polymerization is the capability to temporally regulate chain growth by switching light irradiation between "ON" and "OFF" states, providing a facile access to tune materials' properties.[38, 39] The ease of handling gaseous monomer enabled by this photoredox catalytic method allowed us to realize unprecedently temporal control of copolymerization based on CTFE, which operation we believe could be further expanded to other low-boiling-point monomers. During experiments, the reaction displayed good switchability as demonstrated by three cycles of "ON/OFF" chain growth (Figure 4), the molecular weights continuously increased with conversions (Table S11, and the MWDs of copolymers were kept in a range of $Đ$ = 1.22-1.26).

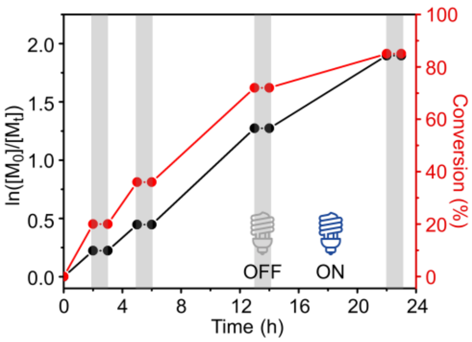


Figure 4. Photoredox catalysis enabled external control of copolymerization of CTFE and IBVE by switching light between "ON" and "OFF" states.

When the light irradiation was turned "OFF", the chain growth could keep proceeding, which might not be clear to observe with short "OFF" periods. For example, to shed light on the fidelity of temporal control in different photo-mediated RDRPs, Hawker, Anastasaki and coworkers demonstrated that there was no monomer conversion during the "dark" periods in metal-free atom transfer radical polymerization (ATRP) and PET-RAFT polymerization in comparison with Cu-mediated processes recently.[50] Then, a longer "dark" time was employed in our investigation. As shown in Figure 5, when the light irradiation was switched "OFF" during chain growth, the polymerization was immediately ceased without the observation of any monomer conversion in the following 10 h. The polymerization could be successfully turned "ON" by further exposing the reaction mixture to light irradiation. During the chain-growth process, the molecular weights of fluoropolymers improved with monomer conversions. The good temporal control observed in this metal-free system is consistent with results demonstrated by others.[31, 44, 50]

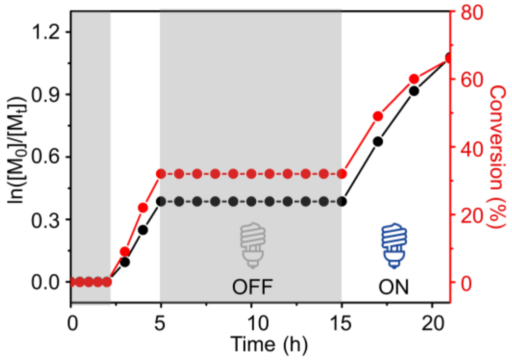


Figure 5. "ON/OFF" temporal control of copolymerization of CTFE and IBVE with long "OFF" periods.

Chain-extension via the photoorganocatalyzed alternating copolymerization and post-synthetic modifications. To illustrate the synthetic advantage of this method, we synthesized a main-chain fluorinated block alternating copolymer[51] by a two-step photoorganocatalyzed copolymerization process. As shown in Figure 6A, P(CTFE-*alt*-EVE) (M_n = 6.1 kDa, $Đ$ = 1.22) was first prepared in the presence of F-PTH and CTA **4** exposing to 410 nm light irradiation, and subsequently employed as a macroinitiator in the chain-extension reaction with CTFE and CEVE under the same photopolymerization conditions without additional photocatalyst. This process generated P(CTFE-*alt*-EVE)-*b*-P(CTFE-*alt*-CEVE) with satisfactory control over the molar mass distribution (M_n = 13.6 kDa, $Đ$ = 1.29), and the SEC profile of the copolymer revealed a clear shift of P(CTFE-*alt*-EVE) to lower retention time (Figure 6B, black *vs* blue line), indicating the good chain-end fidelity of the fluorinated macroinitiator. The incorporation of a second block and the terminal dithiocarbamate substituent of P(CTFE-*alt*-EVE)-*b*-P(CTFE-*alt*-CEVE were confirmed by the ^{1}H NMR analysis (Figures S25).

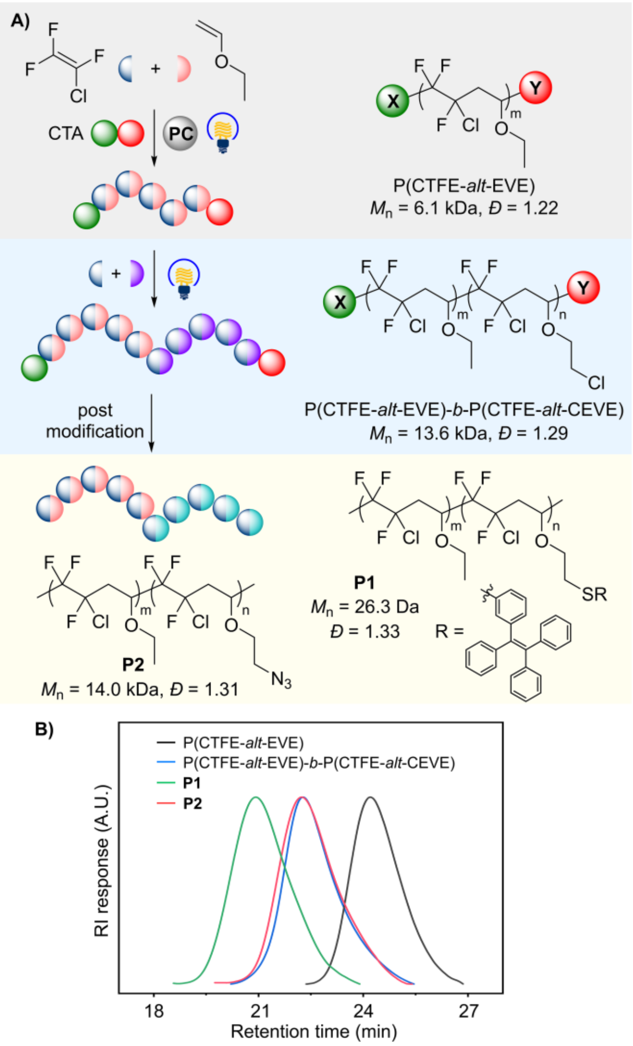


Figure 6. Synthesis and characterization of block alternating copolymers. A) Synthetic schemes of the two-step photopolymerization and post modification. B) SEC profiles of the fluorinated block alternating copolymers.

The fluorinated block copolymers with all alternating segments have provided versatile and unprecedented accesses to various fluorinated materials via post-synthetic modifications. For example, by modifying the chloride group on the side chain of the P(CTFE-*alt*-CEVE) block, different functionalities could be incorporated, including the tetraphenylethylene (TPE) (**P1**, M_n = 26.3 kDa, $Đ$ = 1.33) and azide groups (**P2**, M_n = 14.0 kDa, $Đ$ = 1.31). While the TPE group could embed the corresponding materials with aggregation-induced emission (AIE) behavior (Figures S27),[52] the tailoring of azide group provides opportunities to further connect with desirable functionalities via the copper-catalyzed "click" chemistry.[53] The successful conversions of the chloride substituent into TPE and azide groups were confirmed by ^{1}H NMR and FT-IR measurements (Figures S28-S30).

CONCLUSION

We have developed a photoorganocatalyzed reversible-deactivation alternating copolymerization of CTFE and VEs with a fluorinated photoredox catalyst, enabling the controlled synthesis of various main-chain fluorinated alternating copolymers with low $Đ$ and high chain-end fidelity at high monomer conversions. The synthetic advances of this method allow smooth transformation of gaseous CTFE at ambient pressure and room temperature by exposing to LED light irradiation, and facilitate iteratively switching the chain growth between "ON" and "OFF" states. Main-chain fluorinated block alternating copolymers have been successfully synthesized via a tandem photoorganocatalyzed alternating copolymerization, promoting the synthesis of fluoropolymers with diverse functional side groups. Given the broad applications of fluoropolymers and photopolymerization, as well as tunable physical/chemical properties of copolymers by selecting appropriate comonomers, we expect this method to be useful for creating improved opportunities to tailored fluorinated copolymers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

General experimental considerations, experimental procedures, NMR spectra, SEC profiles, and additional supporting data

AUTHOR INFORMATION

Corresponding Author

*chenmao@fudan.edu.cn

Notes

The authors declare no competing financial interest.

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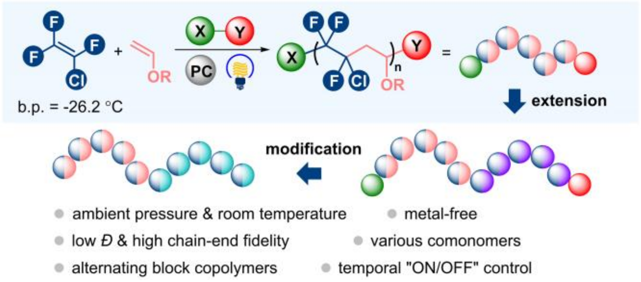
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