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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.202107066

Link to VoR: https://doi.org/10.1002/anie.202107066

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# Visible-Light Enabled Organocatalyzed Controlled Alternating Terpolymerization of Perfluorinated Vinyl Ethers

Qinzhi Quan, Mingyu Ma, Zongtao Wang, Yu Gu and Mao Chen\*

**Abstract:** Polymerizations of perfluorinated vinyl ethers (PFVEs) provide an important category of fluoropolymers that have received considerable interests in applications. In this work, we report the development of an organocatalyzed controlled radical alternating terpolymerization of PFVEs and vinyl ethers (VEs) under visible-light irradiation. This method not only enables the synthesis of a broad scope of fluorinated terpolymers of low dispersities and high chainend fidelity, facilitating tuning the chemical compositions by rationally choosing the type and/or ratio of comonomers, but also allows temporal control of chain-growth, as well as the preparation of a variety of novel fluorinated block copolymers. To showcase the versatility of this method, fluorinated alternating terpolymers have been synthesized and customized to simultaneously display a variety of desirable properties for solid polymer electrolyte design, creating new opportunities in high-performance energy storage devices.

### Introduction

Fluoropolymers are finding continuously expanding applications because of outstanding thermal and chemical stability, low dielectric constant and surface energy, etc.<sup>[1]</sup> However, many high-end utilizations of fluorinated homopolymers have been limited by their high crystallinity, incompatibility with non-fluorinated composites and/or lack of functional substituents.<sup>[2]</sup> Therefore, novel synthetic methods are being actively pursued to promote the facile regulation of fluoropolymers with well-defined architectures and desirable substituents for applications such as electrolytes in lithium-ion batteries,[3] drug/gene carriers,<sup>[4]</sup> photolithography,<sup>[5]</sup> etc. Terpolymerization is an important approach to effectively extend the utility of fluoropolymers by means of covalently introducing three functional segments into the macromolecular structure, and thereby alleviating crystallinity of fluoropolymers and minimizing phase separation between fluorophilic and non-fluorophilic moieties.<sup>[2]</sup> Additionally, it enables delicate regulation of properties that are dictated jointly by multiple distinct domains on the fluoropolymers without compromising their intrinsic attributes. Commercialized products such as Viton,<sup>[6]</sup> Kalrez,<sup>[7]</sup> Lumiflon<sup>[8]</sup> and others,<sup>[1a]</sup> all include terpolymers of fluoroalkenes.

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Recent combinations of photoredox catalysis and controlled/living polymerization have stimulated advances of synthetic approaches that allow precise polymer engineering with spatiotemporal control.<sup>[9]</sup> Elegant systems include photocontrolled radical polymerization of acrylates and acrylamides,<sup>[10]</sup> photo-controlled cationic polymerization of vinyl ethers<sup>[11]</sup> and photo-controlled ring-opening metathesis polymerization of cycloalkenes,[12] and so forth. However, the vast majority of photocontrolled polymerizations developed to date are focused on nonfluorinated monomers.<sup>[9]</sup> The controlled polymerization of fluoroalkenes remains a major challenge.<sup>[13]</sup> In particular, the controlled co- and terpolymerization of perfluorinated vinyl ethers (PFVEs), which represent an important category of industrially relevant fluoroalkenes (e.g., Viton,<sup>[6]</sup> Kalrez<sup>[7]</sup>), have been rarely achieved. Conventional methods not only typically require elevated temperature and pressure, but also suffer from uncontrolled molecular weight, broad dispersity, poor chain-end fidelity and incomplete conversion,<sup>[14]</sup> restricting the broader accessibility of well-defined fluoropolymers and applications that are facilitated by mild operation conditions.[5, 9a]

In controlled terpolymerization, a growing chain would end up with three different terminal units, which lead to dormant species of varied reactivities for re-initiation and monomer addition, thus raising difficulties to realize good livingness. We envisioned that the photo-controlled polymerization conducted under mild conditions could offer opportunities to mitigate increased disturbance from propagating radicals in a complex reaction system.<sup>[9b, 15]</sup> Meanwhile, fluoropolymers have recently been discovered as a particularly interesting class of solid polymer electrolytes (SPEs) in the development of all-solid-state batteries (ASSBs).<sup>[16]</sup> Nevertheless, fluorinated SPEs of preferential properties are lacking as limited by exisiting synthetic methods to access on-demand fluoropolymers. The controlled synthesis of alternating terpolymers of PFVEs under operationally simple conditions could facilitate access towards a series of fluorinated polymeric electrolytes and allow the investigation of fluorinated materials of potential.

Herein, we report the development of an organocatalyzed controlled/living radical alternating terpolymerization of PFVEs driven by visible light for the first time (Scheme 1), enabling the facile transformation of various PFVEs (even for gaseous PFVE) and VEs under ambient conditions. The obtained alternating terpolymers exhibit low dispersity (D) and high chain-end fidelity at high conversions of VEs, allowing chain-end extension with different monomers (e.g., PFVEs, VEs, vinyl esters, styrene) to furnish a variety of unprecedented block copolymers. Furthermore, taking advantage of this method, fluorinated terpolymers that simultaneously provide a variety of desirable properties for SPEs (e.g., low glass-transition temperature ( $T_g$ ), high storage modulus (G), good ionic conductivity, non-flammability) were obtained, which resulted in outstanding

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performance compared with conventional polyethylene oxide (PEO) and mixtures of copolymers during the long-term cycling in lithium metal-based ASSBs, affording a promising bottom-up platform to access high-performance fluoropolymeric materials.



metal-free
 low D
 egood chain-end fidelity
 etemporal control

Scheme 1. Organocatalyzed controlled alternating terpolymerization of PFVEs and VEs driven by light.



### **Results and Discussion**

**Figure 1.** A) Chemical structures of PFVEs (**FM1-FM4**) and VEs (**M1-M7**). B) Chemical structures of CTAs **1-3**. C) Chemical structure of organic photocatalyst. D) Cyclic voltammetry (CV) of CTAs conducted using 0.1 M  $nBu_4NBF_4$  as electrolyte in acetonitrile at 25 °C.

#### Condition Optimization

In order to optimize the terpolymerization conditions, we vinyl employed perfluoro(propyl ether) (FM1), tertbutyldimethylsilyl (TBS) protected ethylene glycol vinyl ether (M1) and 2-(ethenyloxy)ethyl ethyl ester (M2) as comonomers (Figure 1A, Figure S1) with N-biphenylphenothiazine derivative<sup>[17]</sup> (biPh-PTZ, Figure 1B) as a photoredox catalyst (PC) and diethyl carbonate (DEC) as a low cost, non-fluorinated solvent under visible-light irradiation (13 W white LED light, Figure S2). We first with cyanomethyl attempted the reaction substituted thiocarbonylthio compounds as chain transfer agents (CTAs) (1a-1e, Figure 1C, Figures S3-S4 and Scheme S1). When CTAs from **1a** to **1d** were employed, polymers of low molecular weights  $(M_n, M_n)$ entries 1-4 in Table 1) were obtained at moderate to high conversions of M1 and M2, which could be attributed to the oligomerization of VEs.[18] Although CTA 1e has shown good control in the copolymerization of chlorotrifluoroethylene,<sup>[19]</sup> the employment of 1e in the terpolymerization of FM1 resulted in poor VE conversion (entry 5). The dithiocarbamate fragment generated by the C-S bond cleavage<sup>[9a]</sup> has precipitated in the reaction mixture upon light irradiaion (Figure S5). Additionally, PFVEs have higher steric hinderance and lower solubility in conventional solvents than many fluoroalkenes, imposing difficulties on the chain growth.

 Table
 1.
 Condition
 optimization
 of
 CTAs
 for
 the
 organocatalyzed

 terpolymerization
 under visible-light irradiation.<sup>[a]</sup>
 index
 index

Entry	СТА	Conv. of <b>M1/M2</b> (%/%) <sup>[b]</sup>	<i>M</i> n,calc. (kDa) <sup>[c]</sup>	<i>M</i> <sub>n,SEC</sub> (kDa) <sup>[d]</sup>	$\pmb{\mathcal{D}}^{[d]}$
1	1a	97/83	12.9	6.6	1.37
2	1b	96/71	12.1	3.9	1.42
3	1c	65/43	8.0	3.7	1.29
4	1d	86/71	11.3	8.9	1.35
5	1e	16/6	1.8	4.7	1.30
6	2a	76/46	8.9	4.1	1.31
7	2b	75/38	8.4	7.1	1.52
8	2c	44/17	4.8	4.6	1.37
9	2d	81/70	10.9	9.6	1.29
10	3a	79/66	10.5	8.2	1.32
11	3b	84/72	11.3	10.8	1.30
12	3c	94/81	13.0	12.3	1.23

[a] [**FM1**]/[**M2**]/[**C**TA]/[PC] = 45/15/15/1/0.025, white LED light, 25 °C, 18 h, ambient pressure. [b] Determined by GC analysis. [c] Calculated based on VE conversions. [d] Determined by SEC.

Then, we turned our attentions to benzyl substituted CTAs (**2a-2d**, entries 6-9, Scheme S2 and Figures S6-S7). We observed that CTA **2d** gave higher conversions of **M1** and **M2**, and the molecular weight detected by size-exclusion chromatography (SEC) was close to the theoretical value calculated based on monomer conversions ( $M_{n,SEC}$  = 9.6 kDa,  $M_{n,calc}$  = 10.9 kDa). When CTAs from **2a** to **2d** were characterized by cyclic voltammetry (CV), compound **2d** showed the most

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positive potential of reduction (Figure 1D), indicating that the pyrryl substituent could effectively promote the electron acceptance from photo-activated catalyst (PC\*) during the photo-induced electron transfer process.<sup>[9b]</sup>

Next, we focused on tuning the chemical structure of leaving group to regulate the reactivity of pyrryl substituted CTAs (**3a-3c**, entries 10-12, Scheme S3 and Figures S8-S9). We observed that compound **3b** with an ester group on the phenyl ring gave slightly improved conversions (84% *vs* 81% for **M1**, 72% *vs* 70% for **M2**) and molecular weight ( $M_{n,SEC} = 10.8 \text{ vs} 9.6 \text{ kDa}$ ) comparing to **2d**, while the molecular weight distribution (MWD) were kept close ( $\mathcal{D} = 1.30 \text{ vs} 1.29$ ).

Because **FM1** has limited solubility in the reaction mixture, which could influence the control in terpolymerization, a new fluorinated ester substituted CTA **3c** was synthesized (Scheme S4 and Figures S10-S12). CTA **3c** exhibited a more positive reductive potential than other CTAs, suggesting that it could be more easily reduced by PC\* to generate a benzyl radical. The employment of CTA **3c** provided further increased conversions of **M1** (94%) and **M2** (81%), and low dispersity (D = 1.23). The higher conversions of **M1** are due to its faster reaction rate with **FM1** (Figures S13-S14). Further variations of the optimal terpolymerization conditions including catalysts, solvents and light sources resulted in decreased VE conversions and broad dispersities (Tables S1-S3).

#### Investigation of the Terpolymerization Process

We next investigated the terpolymerization process of PFVE and VEs at three initial ratios of [M1]/[M2] (8/32, 20/20, 32/8) under optimized reaction conditions. As shown in Figures 2A-2C, for both VEs, the degrees of polymerization (DPs, Equations S1-S3, Tables S4-S6) increase with exposure time at different ratios. DPs of FM1 and VEs (M1 + M2) are very close to each other throughout the reaction processes, confirming the chemical structures of alternating terpolymers.<sup>[14b]</sup> Plots of ln([M]<sub>0</sub>/[M]<sub>t</sub>) as a function of exposure time display first order kinetics (Figure 2D). Increasing the ratio of [M1]/[M2] afforded higher apparent polymerization constants (e.g., [M1]/[M2] = 8/32,  $k_{\rm D}$  = 0.09 h<sup>-1</sup>; [M1]/[M2] = 32/8,  $k_p = 0.17 \text{ h}^{-1}$ ), which follows the trend that FM1 has a faster copolymerization rate with M1 (Figure S13). During the chain-growth, molecular weights of terpolymers increase with monomer conversions (Figure 2E), and MWDs keep within a narrow range (D = 1.17 - 1.28). The linear reaction kinetics and low dispersities demonstrate that the terpolymerization could provide a high degree of control for different VE ratios. Although  $M_{n,SEC}$  of terpolymers were slightly lower than  $M_{n,calc}$ , when a multiangle laser light scattering (MALLS) detector was employed, the observed absolute molar masses  $(M_{n,MALLS})$  were in good agreement with  $M_{n,calc}$  as shown by the empty squares in Figure 2E. SEC profiles measured during the kinetics studies are symmetrical and unimodal, which are in accordance with characteristics of controlled/living terpolymerization (Figure 2F and Figures S15-S16).



Figure 2. Investigations on the organocatalyzed alternating terpolymerization process at different initial ratios of [M1]/[M2]. Conditions: [FM1]/[VEs]/[CTA 3c]/[PC] = 60/40/1/0.025 ([VEs] = [M1] + [M2], [M1]/[M2] = 8/32, 20/20, 32/8),  $25 \,^{\circ}$ C, white light. A) to C) Degrees of polymerization (DPs) of M1 (blue circle), M2 (red circle), M1 + M2 (black empty rhombus) and FM1 (green circle). In D) and E), points of different colors represent results collected at different [M1]/[M2] ratios: 8/32 (blue), 20/20 (red), 32/8 (green). D) ln([M]\_0/[M]\_1) vs exposure time. [M]\_0 and [M]\_t are the concentrations of VEs at time points 0 and t, respectively. E)  $M_n$  and  $\mathcal{D} vs \%$  conversion of VEs, filled squares and triangles represent  $M_{n,SEC}$  and  $\mathcal{D}$  measured by SEC, respectively, empty squares represent  $M_{n,MALLS}$  measured by MALLS. F) SEC profiles of terpolymers obtained at [M1]/[M2] = 8/32.

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#### Tuning the Chemical Composition by Changing the VE Ratio

The controlled alternating terpolymerization could facilitate the regulation of chemical compositions at a constant [PFVE]/[VEs]/[CTA] ratio by changing the relative amounts of two VEs. As shown in Figure 3, a molar ratio of [FM1]/[VEs]/[CTA] = 30/20/1 ([VEs] = [M1] + [M2]) was maintained during the synthesis of fluoropolymers under visible-light irradiation. When five [M1]/[M2] ratios including 0/20, 4/16, 10/10, 16/4 and 20/0 were used, the polymerization yielded fluoropolymers of varied amounts of M1 and M2 as analyzed by the characteristic methyl groups (protons a and b) in proton nuclear magnetic resonance (<sup>1</sup>H NMR). Since almost quantitative VE conversions have been achieved by extending the exposure time, the ratios of M1 and M2 incorporated in five polymers are very close to the corresponding initial ratios, which are 0/20, 4.1/15.9, 9.8/10.2, 16.1/3.9 and 20/0, respectively, showcasing the capability of incorporating desirable ratios of VEs into polymers by simply adjusting their feeding amounts (Figure S17, Table S7). The obtained co- and terpolymers exhibited clearly observed terminal groups from CTA **3c** in <sup>1</sup>H NMR and narrow MWDs (D = 1.13-1.23, Figure S18). To analyze the chain-end fidelity, terpolymer was synthesized at [FM1]/[VEs]/[CTA 3c] = 24/16/1 ratio. The NMR result suggests that the chain-end group (pyrryl(CS)S-) is connected with vinyl ether in the terpolymer chain, and the molecular weight calculated based on <sup>1</sup>H NMR ( $M_{n,NMR}$ ) is close to  $M_{n,calc}$  (Figure S19), illustrating that good chain-end fidelity was achieved with this method.



**Figure 3.** <sup>1</sup>H NMR spectra of fluoropolymers synthesized via the organocatalyzed photopolymerization.

#### Expanding the Synthetic Scope and Characterization Results

With the established terpolymerization method, we turned our attention to the synthesis of fluoropolymers with a variety of PFVEs and VEs. As shown in Table 2 and Table S8, good to excellent VE conversions (up to >99%) were realized for a broad combination scope of PFVEs and VEs at low catalyst loadings (0.025-0.25 mol% of VEs) by exposing to white light irradiation. Although different comonomers were examined, the ratios of VEs in terpolymers were determined by their initial ratios and conversions as analyzed by <sup>1</sup>H NMR (Figures S20-S54), suggesting that VEs were efficiently transformed into target terpolymers. The various combinations of PFVEs and VEs yielded a series of main-chain and side-chain fluorinated terpolymers of narrow MWDs (D = 1.04-1.28), which are still difficult to access with other methods. All SEC traces were unimodal without discernible shoulder peak (Figures S55-S61).

When **FM1** was used to react with VEs of diversified substitutents including TBS protecting hydroxyl (**M1**), carbonate (**M2** and **M3**), ester (**M4**), alkyl (**M5**) and polyether (**M6** and **M7**), the terpolymerizations afforded fluoropolymers of  $\mathcal{D}$  = 1.16-1.28 (entries 1-10 in Table 2, entries S1-S2 in Table S8). For terpolymers exhibiting higher deviations of molecular weights from the calculated values, absolute molar masses were measured, providing  $M_{n,MALLS}$  similar to  $M_{n,calc}$  (e.g.,  $M_{n,MALLS}$  = 13.9 kDa,  $M_{n,calc}$  = 14.3 kDa, entry 8). The terpolymerization of perfluoro(2-propoxypropyl vinyl ether) (**FM2**) allows the incorporation of 16 fluorine atoms per PFVE molecule. As attributed to the higher boiling point of **FM2** (b.p. = 90 °C, entries 11-13, entries S3-S4 in Table S8), a declined initial ratio of [PFVE]/[VEs] = 1/1 could be employed in this method.

Because the photo-controlled termpolymerization were conducted under ambient temperature and pressure, conventional glass tubes could be adopted as reaction vessels to facilitate the operation of gaseous PFVE of perfluoro(methyl vinyl ether) (FM3, b.p. = -22 °C) without handling high-pressure metallic reactors. As shown in entries 14-17, when the [VEs]/[CTA] ratio increased from 10/1 to 100/1, the terpolymerization generated fluoropolymers of D = 1.10-1.19 and  $M_{n,SEC} = 3.6-24.1$ kDa. Although  $M_{n,SEC}$  deviates from  $M_{n,calc}$  at a high [VEs]/[CTA] ratio (entry 17), M<sub>n,MALLS</sub> (32.8 kDa) is in a good agreement with  $M_{n,calc}$  (34.9 kDa). Moreover, the facile operation with gaseous FM3 allows the preparation of terpolymers containing different fractions of VEs by simply varying the initial ratio (entries 18 and 19). When other VEs were used to react with FM3 instead of M1 and M2, the terpolymerization also delivered fluoropolymers of low dispersities (entries S5-S6 in Table S8).

Beyond linear PFVEs, perfluoro-2,2-dimethyl-1,3-dioxole (**FM4**), which has been used to synthesize materials of low index of refraction in the terahertz range and amorphous copolymers,<sup>[20]</sup> was investigated as an *O*-heterocyclic olefin to react with VEs under visible-light irradiation. As shown in entries 20-23 in Table 2 and entries S7-S8 in Table S8, when the terpolymerization partners were selected arbitrarily, reactions formed terpolymers of narrow MWDs ( $\mathcal{D} = 1.04$ -1.24) at high VE conversions, which has not been demonstrated for perfluorinated cyclic monomer yet.

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Entry	PFVE	V	Es	[PFVE]/[VEs]/[CTA]	Initial feeding ratio of VEs	Conv. of VEs (%/%) <sup>[b]</sup>	Ratio of VEs in terpolymer <sup>[c]</sup>	<i>M</i> <sub>n,calc.</sub> (kDa) <sup>[d]</sup>	<i>M</i> <sub>n,SEC</sub> (kDa) <sup>[e]</sup>	${\cal D}^{[e]}$		
1	FM1	M1	M2	45/30/1	50/50	99/99	47/53	14.6	13.5	1.26		
2	FM1	M1	М3	45/30/1	50/50	99/99	49/51	15.2	14.1	1.28		
3	FM1	M1	M4	45/30/1	50/50	99/99	53/47	15.7	14.3	1.26		
4	FM1	M1	M5	45/30/1	50/50	99/99	49/51	13.2	11.9	1.24		
5	FM1	M1	M6	45/30/1	50/50	99/96	53/47	14.2	12.1	1.25		
6	FM1	M2	M5	45/30/1	50/50	96/99	47/53	11.8	11.4	1.25		
7	FM1	M2	M6	45/30/1	50/50	94/98	53/47	12.7	12.9	1.26		
8	FM1	M2	M7	45/30/1	50/50	95/93	53/47	14.3	17.8(13.9	) <sup>[f]</sup> 1.18		
9	FM1	М3	M6	45/30/1	50/50	99/97	53/47	13.6	12.1	1.23		
10	FM1	M4	M6	45/30/1	50/50	99/96	52/48	14.1	10.1	1.16		
FM2: 16 fluorine atoms per monomer												
11 <sup>[g]</sup>	FM2	M1	M2	15/15/1	50/50	94/90	51/49	9.4	8.9	1.22		
12 <sup>[g]</sup>	FM2	M1	M6	15/15/1	50/50	92/91	52/48	9.2	7.8	1.21		
13 <sup>[g]</sup>	FM2	M2	M7	15/15/1	50/50	90/91	53/47	9.5	11.5	1.15		
•••••	•••••	••••			FM3: Gaseous	PFVE (b.p. = -22	°C)					
14	FM3	M1	M2	30/10/1	50/50	97/95	52/48	4.2	3.6	1.10		
15	FM3	M1	M2	75/25/1	50/50	99/99	49/51	9.8	9.2	1.14		
16	FM3	M1	M2	150/50/1	50/50	99/99	49/51	18.9	16.8	1.19		
17	FM3	M1	M2	300/100/1	50/50	95/90	52/48	34.9	24.1(32.8	) <sup>[f]</sup> 1.18		
18	FM3	M1	M2	120/40/1	80/20	99/98	78/22	16.2	14.6	1.21		
19	FM3	M1	M2	120/40/1	20/80	99/96	18/82	13.9	12.5	1.16		
FM4: Perfluorinated dioxole												
20	FM4	M1	M2	45/30/1	50/50	99/96	48/52	13.7	11.2	1.16		
21	FM4	M1	M4	45/30/1	50/50	99/97	51/49	14.8	12.8	1.22		
22	FM4	M2	M5	45/30/1	50/50	95/99	52/48	11.7	10.9	1.24		
23	FM4	M2	M6	45/30/1	50/50	95/98	52/48	12.1	10.6	1.04		

Table 2. Organocatalyzed controlled alternating terpolymerization of various PFVEs and VEs under visible-light irradiation.<sup>[a]</sup>

[a] [CTA **3c**]/[PC] = 1/0.025, [VEs] = 0.667 M in DEC, 13 W white LEDs, 25 °C, ambient pressure, 24 h. [b] Determined by GC analysis. [c] Calculated based on <sup>1</sup>H NMR. [d] Calculated based on VE conversions. [e] Determined by SEC. [f] Measured by a MALLS detector. [g] Conducted with a cosolvent ( $V_{DEC}/V_{n-pentane} = 2/1$ ) instead of DEC.



Figure 4. "ON/OFF" Temporal control of the terpolymerization of FM1, M1 and M3.

#### "ON/OFF" Switch of the Controlled Terpolymerization

Photo-controlled polymerizations have an attractive advantage to provide spatiotemporal control over the chaingrowth process at will, which highly relies on the reversible photoactivation. While the vast majority of the photo-controlled reported to polymerizations date are based on homopolymerization,<sup>[9a, 9b, 21]</sup> we next investigated the ability of switching the terpolymerization between "ON" and "OFF" states using a reaction mixture of FM1, M1, M3, catalyst and CTA ([FM1]/[M1]/[M3]/[CTA 3c]/[PC] = 45/15/15/1/0.025) with white LED light as an external trigger. As shown in Figure 4, when the reaction mixture was kept in dark or the light irradiation was switched "OFF", there's no monomer conversion or the polymerization was temporarily ceased. Although different lengths of dark periods were employed, the terpolymerization could be efficiently re-initiated by exposing the mixture to light.

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Similar conversions of two VEs were observed at different exposure times as caused by similar reactivities. The SEC results further demonstrate that the molecular weights grow only during periods of light irradiation (Table S9 and Figure S62), supporting that the organocatalyzed terpolymerization could provide high degree of photo-control during chain growth, which is analogous to metal-free homopolymerizations driven by light.<sup>[22]</sup>



Figure 5. Synthesis and characterization of block fluoropolymers.

#### Photo-Controlled Chain-Extension from Terpolymers

To validate the living characteristics of this method and the chain-end fidelity of fluoropolymers, we probed the synthesis of block copolymers using terpolymers as macroinitiators in chainextension reactions. Two alternating terpolymers (P1 and P2) were first prepared at complete conversions of VEs under optimized conditions. Terpolymer P1 ( $M_{n,SEC}$  = 7.2 kDa, D = 1.21, Figure 5A) is composed of FM1, M1 and M2, terpolymer P2  $(M_{n,SEC} = 7.3 \text{ kDa}, D = 1.26, \text{ Figure 5B})$  is composed of FM1, M2 and M5. After terpolymerization, comonomers for the formation of second blocks were added into the reaction mixtures, and the mixtures were directly exposed to white light irradiation without additional catalyst (e.g., P1a and P1b). When the second blocks were formed with a different PFVE (e.g., P1c) or homopolymers (e.g., P2a-P2c), reaction mixtures were concentrated under vacuum to remove excess FM1 before adding comonomers. The obtained fluoropolymers were isolated and characterized by <sup>1</sup>H and <sup>19</sup>F NMR (Figures S63-S70), which clearly manifest the incorporation of new blocks. Of note, two types of block copolymers, including using either alternating copolymers (e.g.,

P(**FM1**-*alt*-**M4**), P(**FM1**-*alt*-**M6**), P(**FM4**-*alt*-**M6**)) or homopolymers (e.g., poly(vinyl propionate) (PVP), poly(vinyl benzoate) (PVBz), polystyrene (PS)) as the second blocks, were both synthesized with narrow MWDs (D = 1.21-1.34). For all block copolymers, the SEC profiles displayed clear shifts to lower retention times in comparison to the macroinitiators (Figures 5C and 5D), and no discernible low-molecular-weight tailing. In contrast to P1 and P2, block copolymers of **P1a** and **P2a-P2c** exhibited complete inversions of the *d*RI signals, attributing to the connection of fluorinated macroinitiators (negative *dn/dc*) with second blocks of positive *dn/dc* values.<sup>[10b]</sup> Taken together, the successful chainextension with PFVEs, VEs, vinyl esters and styrene manifests the good flexibility and compatibility of this system, indicating that a large scope of fluoropolymers could be prepared via the photocontrolled polymerization.

#### Preliminary Studies on Terpolymer Electrolyte

SPEs are one of the key materials for the development of advanced lithium-ion batteries.<sup>[3, 23]</sup> Replacing traditional liquid electrolytes with polymers could overcome the safety issues (e.g., electrolyte leakage) and bring good processability.<sup>[3]</sup> Fluorinated materials are a class of emerging solid electrolytes for their chemical, physical properties as well as unique interfacial electrochemical properties as ion conducting media.<sup>[16a-c]</sup> However, many fluoropolymers can hardly be used as SPEs because it is rather difficult to achieve low  $T_g$ , good Li ions (Li<sup>+</sup>) dissolving capability, and sufficient mechanical strength at the same time, all of which are required for practical SPEs. Inspired by recent examples of fluoropolymer electrolytes<sup>[16]</sup> and innovations enabled by the bottom-up engineering of copolymers as SPEs,<sup>[24]</sup> we probed the potential of our alternating terpolymers in electrochemical energy storage devices.

Firstly, terpolymers of P(FM1-alt-M2)-co-P(FM1-alt-M7) (P3a-P3d, Mn = 16.8-19.6 kDa, D = 1.14-1.23)<sup>[25]</sup> composed of fluorinated, ether and carbonate segments on the polymer chains, which are by design responsible for different desired functionalities for SPEs (Figure 6), were synthesized with the terpolymerization (Table S10, Figure S71). Different ratios of [M2]/([M2]+[M7]) in terpolymers were employed to allow the regulation of properties. To investigate the necessity of terpolymerization, copolymers of P(FM1-alt-M2) (P4, M<sub>n</sub> = 16.1 kDa, D = 1.21) and P(FM1-alt-M7) (P5,  $M_n = 20.4$  Da, D = 1.22) with either only ether or carbonate segment besides PFVE were prepared with the same method. As shown in Figure 6A, the  $T_{\rm q}$ values of polymers increase from -39.4 to 6.3 °C as the ratios of [M2]/([M2]+[M7]) raised from zero to 1.0 based on differential scanning calorimetry (DSC). In sharp contrast, when P4 and P5 were blended together at different ratios without covalent connections as terpolymers, all blended materials gave two distinct  $T_g$  (Figure 6B, Figure S72), which are the same as  $T_g$  of P4 (6.3 °C) and P5 (-39.4 °C). Moreover, while the terpolymers exhibited transparent appearance, the physical blend rendered cloudy mixtures (e.g., P3a vs mixture of P4 and P5, Figures 6C and 6D), suggesting that the phase separation problem could not be avoided by simply mixing two alternating copolymers together. Importantly, it is evident that terpolymers (e.g., P3a, Figure 6E Figures S73-S74) delivered notably higher ionic conductivity ( $\sigma$ ) than the blended materials of P4 and P5, attributed to covalent

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connectivity between the three otherwise incompatible functional domains.



**Figure 6.** Properties of fluorinated co- and terpolymers. A)  $T_g$  plots of **P3-P5**. **[M2]**/(**[M2]+[M7]**) indicates ratios of **M2**/VEs in co- and terpolymers. B)  $T_g$  of **P4**, **P5** and mixtures of **P4** and **P5**. **[M2]**/(**[M2]+[M7]**) reveals ratios of **P4**/**P5** used to prepare copolymer mixtures. C) and D) Optical images of **P3a**, mixture of **P4** and **P5**.<sup>[26]</sup> E) lonic conductivity ( $\sigma$ ) of **P3-P5** and mixtures of **P4** and **P5** at 70 °C. **P4**/**P5** = 4/1 (a), 1/4 (b). F) Storage modulus (G', filled cycles) and loss modulus (G'', empty cycles) as functions of temperature measured by rheometer. G) Voltage profiles comparison of **P3a** vs **P5**, PEO SPEs as a function of time, whereby each half-cycle lasted for 3 h at a current density of 0.05 mA cm<sup>-2</sup>.

An important feature of SPEs is the capability to endow the energy storage devices with flexible shapes without leakage concern thanks to their dramatically improved mechanical strength comparing to liquid electrolytes.<sup>[3, 23]</sup> The storage and loss moduli (*G*' and *G*'') of **P3a** and **P5** were measured by rheometer (Figure 6F). It is worthy noting that **P3a** maintained good conductivity as **P5**, while affording much higher mechanical strength than **P5** from 25 to 100 °C, attributed to the incorporation of carbonates in terpolymer. For example, **P3a** delivered *G*' of about 70 kPa at 60 °C, but **P5** behaved like viscous liquid at elevated temperatures (Figure S75), indicating that **P5** could have the leakage problem for a high-temperature application. Besides, different from **P3a**, PEO, a conventionally employed polymer electrolyte,<sup>[27]</sup> displayed a dramatic decline of the mechanical strength above its melting point ( $T_m = 61$  °C, Figure S76), further highlighting the outstanding mechanical performance of a fluorinated terpolymer.

The combined properties improvements achieved by terpolymerization resulted in significantly enhanced interfacial stability and electrodeposition behaviors in lithium metal-based ASSBs. Investigations on galvanostatic polarization and the reversibility of Li plating and stripping were conducted for **P3a**, **P5** and PEO. Figure 6G shows the voltage profiles over time of three SPEs. It is clear that the ASSBs assembled with **P3a** displayed superior resistance to premature cell failure, and exhibited stable cycling for more than 1100 h. In sharp contrast, ASSBs with both **P5** and PEO showed quick decline in voltage as caused by the progressive penetration of dendrites,<sup>[16c, 28]</sup> and were completely short-circuited within 180 h, suggesting unstable flux of Li ions in the polymer matrix.<sup>[29]</sup>

Moreover, the fluorinated terpolymer exhibited excellent thermal stability within the operating temperature range of Li batteries (Figure S77), and exhibited nonflammable property (Figure S78). Taken together, we expect that this synthetic method furnishes a useful system to engineering highperformance SPEs by optimizing the ternary compositions of fluoropolymers that could be difficult to realize by either copolymerization of two components or physical mixing of copolymers.

### Conclusion

We have developed an organocatalyzed controlled alternating terpolymerization of PFVEs and VEs driven by visible-light irradiation, enabling the synthesis of a broad scope of fluorinated terpolymers of narrow MWDs and good chain-end fidelity at high monomer conversions. The synthetic advantages of this method allow on-demand tuning the chemical compositions of fluoropolymers via rational selection of types and/or ratios of comonomers, smooth transformation of gaseous PFVE under ambient conditions using conventional low-pressure glass tubes, as well as temporal control of the chain-growth between "ON" and "OFF" states. Based on the chain-extension from alternating terpolymers, a variety of fluorinated block copolymers, which contain either alternating copolymers or homopolymers as second blocks, have been successfully synthesized. Furthermore, as demonstrated with P(FM1-alt-M2)-co-P(FM1-alt-M7), this terpolymerization provides a versatile and promising system to effectively integrate diverse properties (e.g., compatibility of functional domains, mechanical strength, ionic conductivity, interfacial stability and non-flammability) for SPEs, which should facilitate the design of advanced lithium-ion batteries. We believe that this approach will offer new opportunities to create fluoropolymers of complex structures and compositions, facilitating the integration of desirable properties into polymers to fulfill diverse requirements in practical applications.

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### Acknowledgements

This research was financially supported by the NSFC (no. 21971044), funding from Fudan University and State Key Laboratory of Molecular Engineering of Polymers. We appreciate Prof. Xinrong Lin (Yunnan University) for suggestions of electrochemical analysis of polymers.

Keywords: fluorine • terpolymer • controlled radical polymerization • photocatalysis • synthetic methods

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# **RESEARCH ARTICLE**

### Entry for the Table of Contents



A metal-free photoredox catalyzed controlled alternating terpolymerization of perfluorinated vinyl ethers has been established, enabling the on-demand synthesis of various fluorinated terpolymers driven by light. This method offers a versatile and convenient platform to tailor fluoropolymers, which facilitates the preparation of novel block copolymers and engineering of high-performance solid terpolymer electrolytes.