Supporting information

Facile photochemical synthesis of main-chain-type semifluorinated alternating copolymers catalyzed by conventional amines or halide salts

Yuxue Wang, Kai Tu, Jiannan Cheng, Enjie He, Jinying Wang, Lifen Zhang,* and Zhenping Cheng*

1. Experimental section

1.1 Materials

1,4-Diiodoperfluorobutane (98%, TCI), 1,6-diiodoperfluorohexane (98%, TCI), diallyl adipate (98%, TCI) and diallyl 1,4-cyclohexanedicarboxylate (a mixture of *cis* and *trans*, 98%, TCI) were stored in a light-resitant container at 0°C. *N,N,N',N'*-tetramethylethylenediamine (TMEDA, 99%), tetrabutylammonium bromide (TBAB, 99%), tetrabutylammonium iodide (TBAI, 99%), methyltriphenylphosphonium iodide (MTPPI, 98%) and pyridine (99%) were purchased from Energy Chemical. NaI (99%) and triethylene glycol (>97%) were purchased from TCI. Ethylenediamine (EDA, AR), allyl bromide (98%) and 6-bromo-1-hexene (>97%) were purchased from J&K. 1,7-Octadiene (>97%, Alfa Aesar) and 1,9-decadiene (>97%, TCI) were stored in a light-resitant container at 0 °C, which require neutral alumina to remove inhibitors before use. 1-Ethyl-3-methylimidazolium iodide (EMII) was purchased from Adamas, triethylamine and sodium chloride (NaCl, AR) were purchased from Chinasun Specialty Products Co., Ltd. Diethylamine was purchased from Yonghua Chemical Co.,

Ltd. Other unspecified raw materials and reagents were purchased from Shanghai Chemical Reagent Company and used directly without treatment.

1.2 Methods

The structure of the polymer was analyzed by nuclear magnetic resonance (NMR) spectra, gel permeation chromatograph (GPC) and ultraviolet-visible (UV-*vis*) absorption spectroscopy. The ^{1}H NMR spectrum of the copolymers was measured on a Bruker 300 MHz nuclear magnetic resonance (NMR) instrument at 25 °C with CDCl$_3$ as a deuterated solvent and tetramethylsilane (TMS) as an internal standard. The ^{19}F NMR spectrum was measured on a Brucker 600 MHz Advance III instrument using CDCl$_3$ as the solvent at 25 °C. The number-average molar mass ($M_{n,GPC}$) and molar mass dispersity ($Đ$) of copolymers were determined by TOSOH HLC-8320 gel permeation chromatography (GPC) equipped with a differential refractive index detector (TOSOH). The test was carried out using THF or DMF as the eluent at a flow rate of 0.35 mL min^{-1} at 40 °C, and PMMA or PS were used as the standard for calibration. The UV-*vis* spectrum was measured on a Shimadzu UV-2600 photometer.

1.3 Synthesis of α,ω-unconjugated dienes

As shown in **Scheme 1**, the synthesis of the monomers B5 and B6 used in the polymerization system was prepared by the method reported in the literature.[1, 2]

1.4 General procedure for visible light-induced polymerization

The steps of amine-promoted polymerization under visible light irradiation were as follows: The mixture of 1,6-diiodoperfluorohexane (0.25 mmol), 1,7-octadiene (0.25 mmol) and TMEDA (0.05 mmol) was added into a clean ampoule equipped with a stir bar and dissolved in 2 mL CHCl$_3$. Then, the oxygen in the ampoule was removed by three freeze-pump-thaw cycles, and the ampoule was immediately sealed by flame. The ampoules were placed on a stirrer surrounded by purple light LED aperture (λ_{max} = 403 nm, 29.7 mW cm^{-2}), and the polymerization temperature was controlled by 14 ^{o}C circulating water cooling and electric fan at 25 ^{o}C. After the specified reaction time, the ampoule was taken out and broken, and the product was dissolved in a small amount of THF and precipitated in 200 mL of ice methanol. Then, the obtained solid product was filtered and dried to constant weight in 30 ^{o}C vacuum oven, and the yield was calculated by gravimetric analysis. The polymerization procedures of other amine promotors or solvents were the same as above.

The feed of the polymerization system promoted by NaI under the induction of visible light was [1,6-diiodoperfluorohexane]$_0$:[1,7-octadiene]$_0$:[NaI]$_0$ = 1:1:9. When the 1,6-diiodoperfluorohexane was 0.25 mmol, the mixture was dissolved in 2 mL acetone and other polymerization steps were the same as above.

Table S1. START Polymerization using various amines as the catalyst

Entry	Amine	[a]Yield (%)	[b]$M_{n,GPC}$ (Da)	[b]$Đ$
1	Et$_3$N	81.0	7200	1.78
2	Et$_2$NH	86.5	6900	1.80
3	EtNH$_2$	81.6	8200	1.80
4	TMEDA	76.3	8100	1.75
5	EDA	78.3	8200	1.78
6	Pyridine	63.9	3100	1.60
[c]7	[d]--	0	[d]--	[d]--

Polymerization conditions: R = [A1]$_0$:[B1]$_0$:[Amine]$_0$ = 1:1:0.4, n$_{(B1)}$ = 0.25 mmol, V_{CHCl_3} = 2.0 mL, time = 21 h, purple LED light (λ_{max} = 403 nm, 29.7 mW cm^{-2}), 25 °C. [a]Determined by gravimetry. [b]Determined by GPC using PMMA as the standard in THF. [c]Polymerization was performed in the absence of amine catalyst. [d]Not available.

Table S2. Effect of the amount of TMEDA on START polymerization

Entry	X	[a]Yield (%)	[b]$M_{n,GPC}$ (Da)	[b]$Đ$
1	0.2	69.8	8100	1.69
2	0.4	74.3	7700	1.67
3	0.7	88.5	7200	1.71
4	1.0	58.4	7300	1.47
5	3.0	40.4	4800	1.37

Polymerization conditions: R = [A1]$_0$:[B1]$_0$:[TMEDA]$_0$ = 1:1:X, n$_{(B1)}$ = 0.25 mmol, V_{CHCl_3} = 2.0 mL, time = 21 h, purple LED light (λ_{max} = 403 nm, 29.7 mW cm^{-2}), 25 °C. [a]Determined by gravimetry. [b]Number-average molar mass ($M_{n,GPC}$) and molar mass dispersity ($Đ$) were determined by GPC using PMMA as the standard in THF.

Table S3. Effect of solvents on START polymerization using simple amine as the catalyst

Entry	Solvent	[a]Yield (%)	[b]$M_{n,GPC}$ (Da)	[b]$Đ$
1	CHCl$_3$	79.6	12000	1.61
2	DMSO	69.2	5200	2.15
3	1,4-Dioxane	66.2	5100	1.65
4	DMAc	49.6	3200	1.42
5	DMC	68.8	9100	3.00
6	NMP	18.2	2300	1.28
7	Acetone	76.4	7300	2.03
[c]8	NMP	0	[d]--	[d]--
[c]9	DMAc	0	[d]--	[d]--

Polymerization conditions: R = [A1]$_0$:[B1]$_0$:[TMEDA]$_0$ = 1:1:0.2, n$_{(B1)}$ = 0.25 mmol, $V_{solvent}$ = 2.0 mL, Time = 21 h, purple LED light (λ_{max} = 403 nm, 29.7 mW cm^{-2}), 25 °C. [a]Determined by gravimetry. [b]Number-average molar mass ($M_{n,GPC}$) and molar mass dispersity ($Đ$) were determined by GPC using PMMA as the standard in THF. [c]Polymerization was performed in the absence of amine catalyst. [d]Not available.

For example, chloroform (CHCl$_3$), dimethyl sulfoxide (DMSO), 1,4-dioxane, *N,N*-dimethylacetamide (DMAc), dimethyl carbonate (DMC), *N*-methylpyrrolidone (NMP) and acetone are suitable for this system, but the corresponding polymerization rate and results are much different (entries 1-7, Table S3). When NMP was used as the solvent (entry 6, Table S3), its polymerization efficiency more obviously decreased than that of other organic solvent systems. Moreover, our group previously reported that DMC as a green solvent can slow down the occurrence of terminal iodine transfer significantly. However, when we used DMC in this polymerization system, only a part of the terminal iodine functional groups were effectively attached on the resultant alternating copolymer chains (as indicated in Figure S1), resulting in a bimodal distribution in the GPC curve and a broad molar mass distribution. By comparison of the polymerization results in several different organic solvents, we found that the alternating copolymer with relatively high molar mass was available when CHCl$_3$ was used as the solvent. On the other hand, as reported by our previous work, some special "carbonyl" solvents such as DMAc and NMP could also form XB with iodine to promote iodine-mediated reversible-deactivation radical polymerization (RDRP). Therefore, in order to confirm it works well in our system, we also conducted the reference experiments just in the presence of NMP (entry 8, Table S3) and DMAc (entry 9, Table S3) without adding amines mentioned above. However, no polymerization happened in these cases, which further indicating that amines are indispensable for this simple polymerization system.

Table S4. Effect of the feed ratio of polymerization component and light source on START polymerization using amine as the catalyst

Entry	R	$^a\lambda_{max}$ (nm)	^{b}E (mW cm^{-2})	Time (h)	^{c}Yield (%)	$^dM_{n,GPC}$ (Da)	$^dÐ$
^{e}1	1:1:0.2	403	29.7	21	0	^{f}--	^{f}--
2	1:0:0.2	403	29.7	21	0	^{f}--	^{f}--
3	0:1:0.2	403	29.7	21	0	^{f}--	^{f}--
4	1:1.2:0.2	403	29.7	21	63.5	3900	1.55
5	1.2:1:0.2	403	29.7	21	87.3	5600	1.64
6	1:1:0.2	373	23.9	24	80.0	7700	1.69
7	1:1:0.2	403	29.7	24	79.3	8400	1.79
8	1:1:0.2	460	4.84	24	86.2	6800	1.84
9	1:1:0.2	525	6.05	24	11.9	^{f}--	^{f}--
10	1:1:0.2	740	99.2	24	0	^{f}--	^{f}--

Polymerization conditions: R = $[A1]_0$:$[B1]_0$:$[TMEDA]_0$, $n_{(B1)}$ = 0.25 mmol, V_{CHCl_3} = 2.0 mL, 25 °C. ^{a}Wavelength of LED light. ^{b}Light intesity of LED light. ^{c}Determined by gravimetry. ^{d}Number-average molar mass ($M_{n,GPC}$) and molar mass dispersity ($Ð$) were determined by GPC using PMMA as the standard in THF. ^{e}In dark. ^{f}Not available.

Table S5. Monomer applicability for simple amine catalyzed START polymerization

Entry	Comonomer	Time (h)	^{a}Yield (%)	$^bM_{n,GPC}$ (Da)	$^bÐ$
1	A1B3	19	73.7	9300	1.59
2	A1B4	23	66.9	8600	1.68
^{c}3	A1B6	19	96.2	25600	1.59
^{c}4	A1B5	19	76.3	4300	1.73
5	A2B3	23	42.2	5600	1.38
6	A2B4	23	59.5	7500	1.78

Polymerization conditions: R = $[A]_0$:$[B]_0$:$[TMEDA]_0$ = 1:1:0.2, $n_{(A)}$ = 0.25 mmol, V_{CHCl_3} = 2.0 mL, purple LED light (λ_{max} = 403 nm, 29.7 mW cm^{-2}), 25 °C. ^{a}Determined by gravimetry. ^{b}Determined by GPC using PMMA as the standard in THF. ^{c}Determined by GPC using PS as the standard in dimethyl formamide (DMF) (with 0.1 wt.% LiBr).

It was necessary to further expand the scope of monomer suitability after screening out the optimal polymerization conditions. Even 1,4-diiodoperfluorobutane (A2, Scheme 1) with low activity can be effectively polymerized with different α,ω-unconjugated dienes under visible light at room temperature (entries 5 and 6, Table S5). Importantly, functional monomers can be designed easily by introducing functional groups into unconjugated dienes through chemical bonds or physical effects to obtain various functional main-chain-type semifluorinated alternating copolymers, such as the hydrophilic group in the α,ω-unconjugated dienes B5 (the structure shown in Scheme 1) and the rigid group in α,ω-unconjugated dienes B6 (the structure shown in Scheme 1). Therefore, we believe that the establishment of this facile polymerization method is conducive to the simple and rapid preparation of smart fluorinated materials.

Table S6. Effect of the amount of water on START polymerization

Entry	$V_{Acetone}:V_{H_2O}$ (v/v)	[a]Yield (%)	[b]$M_{n,GPC}$ (Da)	[b]$Đ$
1	0:2	83.9	1700	2.56
2	2:0	76.4	7300	2.03
3	1.75:0.25	91.9	13200	4.49
4	1.5:0.5	93.5	12300	2.37
5	1.25:0.75	91.9	16500	2.92
6	1.0:1.0	99.6	11300	2.61
7	2.0:0.5	92.2	16700	3.38
8	2.0:1.0	96.5	20700	3.75
9	2.0:2.0	95.0	8500	2.19

Polymerization conditions: R = $[A1]_0:[B1]_0:[TMEDA]_0$ = 1:1:0.2, $n_{(B1)}$ = 0.25 mmol, time = 21 h, purple LED light (λ_{max} = 403 nm, 29.7 mW cm^{-2}), 25 °C. [a]Determined by gravimetry. [b]Number-average molar mass ($M_{n,GPC}$) and molar mass dispersity ($Đ$) were determined by GPC using PMMA as the standard in THF.

Table S7. START Polymerization using various halide salts as the catalyst

Entry	Halide salt	[a]Yield (%)	[b]$M_{n,GPC}$ (Da)	[b]Đ
1	NaI	64.6	3300	1.77
2	MTPPI	66.7	3500	1.70
3	TBAI	68.5	3300	1.70
4	EMII	73.1	3300	2.13
5	NaCl	58.7	2400	1.43
6	TBAB	34.0	2100	1.42

Polymerization conditions: R = $[A1]_0$:$[B1]_0$:[halide salt]$_0$ = 1:1:1, $n_{(B1)}$ = 0.25 mmol, $V_{Acetone}$ = 2.0 mL, time = 21 h, purple LED light (λ_{max} = 403 nm, 29.7 mW cm^{-2}), 25 °C. [a]Determined by gravimetry. [b]Number-average molar mass ($M_{n,GPC}$) and molar mass dispersity (Đ) were determined by GPC using PMMA as the standard in THF.

Table S8. Effect of solvents on START polymerization using halide salt as the catalyst

Entry	Solvent	[a]Yield (%)	[b]$M_{n,GPC}$ (Da)	[b]Đ
1	CHCl$_3$	0	[c]--	[c]--
2	Acetone	65.9	5400	2.92
3	DMAc	40.3	2300	1.40
4	THF	21.1	1800	1.40
5	MeCN/DMC (1/1)	17.0	1900	1.31
6	Acetone/Methyl perfluorobutyl ether (1/1)	35.1	1900	1.53
[d]7	Acetone	0	[c]--	[c]--

Polymerization conditions: R = $[A1]_0$:$[B1]_0$:$[NaI]_0$ = 1:1:5, $n_{(B1)}$ = 0.25 mmol, $V_{solvent}$ = 2.0 mL, time = 21 h, purple LED light (λ_{max} = 403 nm, 29.7 mW cm^{-2}), 25 °C. [a]Determined by gravimetry. [b]Number-average molar mass ($M_{n,GPC}$) and molar mass dispersity (Đ) were determined by GPC using PMMA as the standard in THF. [c]Not available. [d]In dark.

Table S9. Effect of the amount of NaI on START polymerization

Entry	X	[a]Yield (%)	[b]$M_{n,GPC}$ (Da)	[b]$Đ$
1	0	0	[c]--	[c]--
2	0.5	51.8	2500	1.52
3	1.0	64.6	3300	1.77
4	3.0	64.2	3800	2.26
5	5.0	66.3	4000	2.47
6	9.0	70.9	7700	2.95
7	12.0	70.3	5400	4.11

Polymerization conditions: R = $[A1]_0$:$[B1]_0$:$[NaI]_0$ = 1:1:X, $n_{(B1)}$ = 0.25 mmol, $V_{Acetone}$ = 2.0 mL, time = 21 h, purple LED light (λ_{max} = 403 nm, 29.7 mW cm^{-2}), 25 °C. [a]Determined by gravimetry. [b]Number-average molar mass ($M_{n,GPC}$) and molar mass dispersity ($Đ$) were determined by GPC using PMMA as the standard in THF. [c]Not available.

Table S10. Effect of the amount of TBAI on START polymerization

Entry	X	[a]Yield (%)	[b]$M_{n,GPC}$ (Da)	[b]$Đ$
1	0	0	[c]--	[c]--
2	0.25	48.0	2700	1.41
3	1.0	41.4	3400	1.61
4	3.0	67.9	3700	1.57
5	4.0	74.6	4300	1.61
6	9.0	81.9	5400	1.87

Polymerization conditions: R = $[A1]_0$:$[B1]_0$:$[TBAI]_0$ = 1:1:X, $n_{(B1)}$ = 0.25 mmol, $V_{Acetone}$ = 2.0 mL, time = 21 h, purple LED light (λ_{max} = 403 nm, 29.7 mW cm^{-2}), 25 °C. [a]Determined by gravimetry. [b]Number-average molar mass ($M_{n,GPC}$) and molar mass dispersity ($Đ$) were determined by GPC using PMMA as the standard in THF. [c]Not available.

Table S11. Effect of the feed ratio of polymerization component on START polymerization using halide salt as the catalyst

Entry	Feed ratio	[a]Yield (%)	[b]$M_{n,GPC}$ (Da)	[b]Đ
[c]1	1:1:5	0	[d]--	[d]--
2	1:1.2:9	67.8	3300	2.25
3	1.2:1:9	72.1	4000	3.54
4	1:1.4:9	68.2	2700	1.75
5	1.4:1:9	90.3	3300	2.41
6	1:0:9	0	[d]--	[d]--
7	0:1:9	0	[d]--	[d]--

Polymerization conditions: R = $[A1]_0$:$[B1]_0$:$[NaI]_0$, $n_{(B1)}$ = 0.25 mmol, $V_{Acetone}$ = 2.0 mL, time = 21 h, purple LED light (λ_{max} = 403 nm, 29.7 mW cm^{-2}), 25 °C. [a]Determined by gravimetry. [b]Number-average molar mass ($M_{n,GPC}$) and molar mass dispersity (Đ) were determined by GPC using PMMA as the standard in THF. [c]In dark. [d]Not available.

Table S12. Monomer applicability for simple halide salt catalyzed START polymerization

Entry	AB	Time (h)	[a]Yield (%)	[b]$M_{n,GPC}$ (Da)	[b]Đ
1	A1B2	23	72.2	6400	2.86
2	A1B3	63	51.6	6500	1.23
3	A1B4	63	68.2	9200	1.73
[c]4	A1B6	27	94.8	14800	3.70
5	A2B1	27	32.6	2300	1.41
6	A2B2	27	38.4	3200	1.96

Polymerization conditions: R = $[A]_0$:$[B]_0$:$[NaI]_0$ = 1:1:9, n(B) = 0.25 mmol, $V_{Acetone}$ = 2.0 mL, purple LED light (λ_{max} = 403 nm, 29.7 mW cm^{-2}), 25 °C. [a]Determined by gravimetry. [b]Number-average molar mass ($M_{n,GPC}$) and molar mass dispersity (Đ) were determined by GPC using PMMA as the standard in THF. [c]Number-average molar mass ($M_{n,GPC}$) and molar mass dispersity (Đ) were determined by GPC using PS as the standard in DMF (with 0.1 wt.% LiBr).
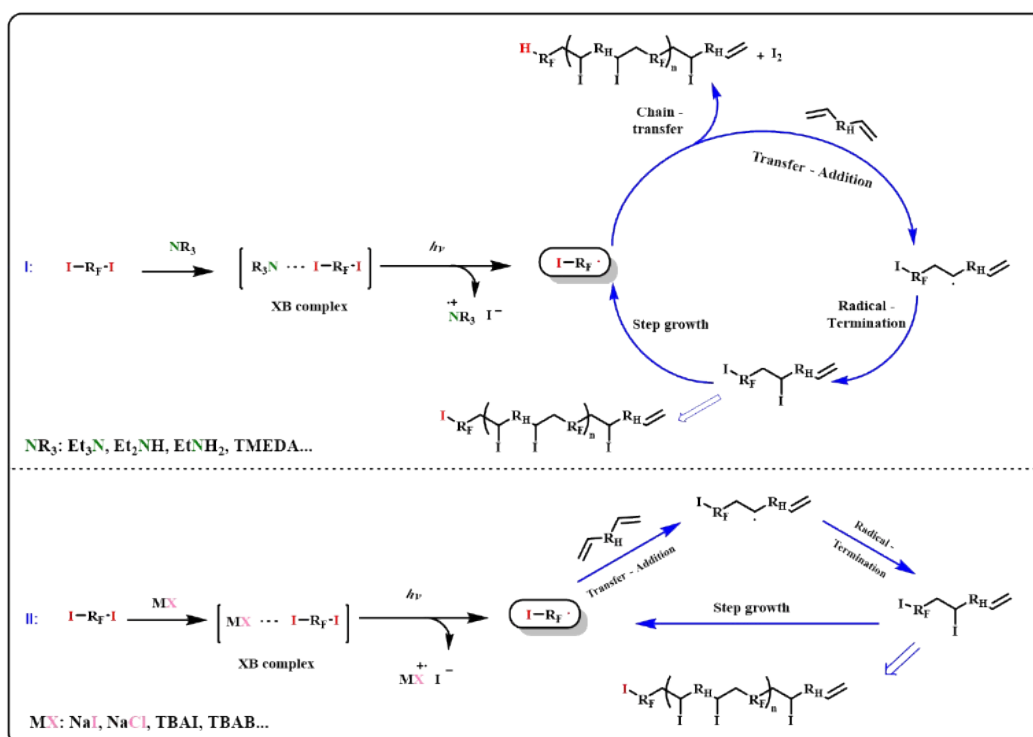
Scheme S1. Proposed possible polymerization mechanism of photocontrolled START with simple amines (I) and halide salts (II) as the catalysts.
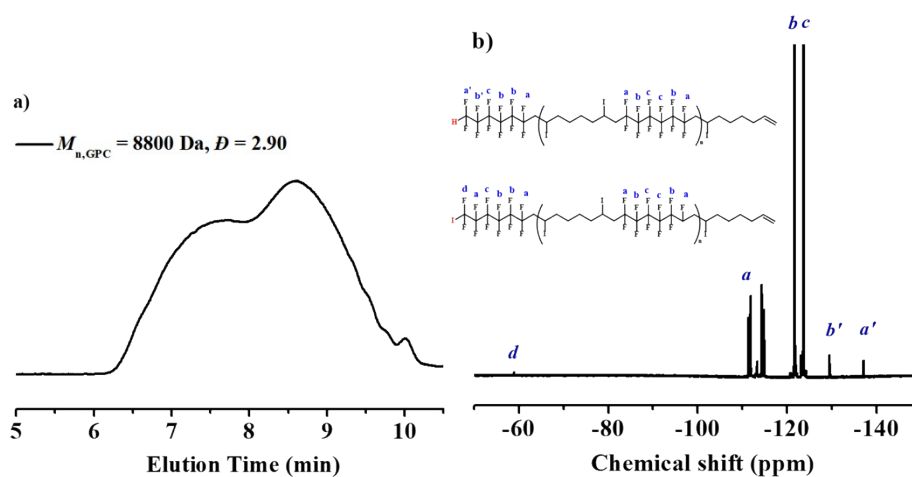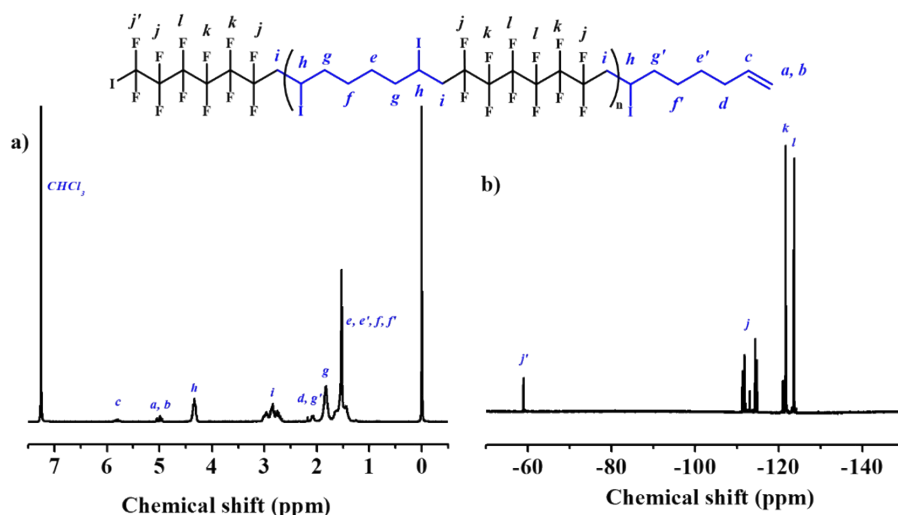

Figure S1. a) Gel permeation chromatogram (GPC) curve and b) ^{19}F NMR spectrum in CDCl$_3$ of the resultant main-chain-type semifluorinated alternating copolymer ($M_{n,GPC}$ = 8800 Da, Đ = 2.90) by using TMEDA as the catalyst in DMC. Polymerization conditions: R = [A1]$_0$:[B1]$_0$:[TMEDA]$_0$ = 1:1:0.2, n$_{(B1)}$ = 0.25 mmol, V_{DMC} = 2.0 mL, time = 21 h, purple LED light (λ_{max} = 403 nm, 29.7 mW cm^{-2}), 25 °C.

Figure S2. a) ^{1}H and b) ^{19}F NMR spectra of the resultant main-chain-type semi-fluorinated alternating copolymer ($M_{n,NMR}$ = 4000 Da, $M_{n,GPC}$ = 2300 Da, $Đ$ = 1.37, yield = 32.8%) by using TMEDA as the catalyst in CDCl$_3$. Polymerization conditions: R = [A1]$_0$:[B1]$_0$:[TMEDA]$_0$ = 1:1:0.2, n$_{(B1)}$ = 0.25 mmol, V_{CHCl_3} = 2.0 mL, time = 3 min, purple LED light (λ_{max} = 403 nm, 29.7 mW cm^{-2}), 25 ^{o}C.

Degree of polymerization based on ^{1}H NMR: $\dfrac{I_h/I_C + 1}{2}$

Degree of polymerization based on ^{19}F NMR: $\dfrac{I_k/4}{I_{j'}/2}$
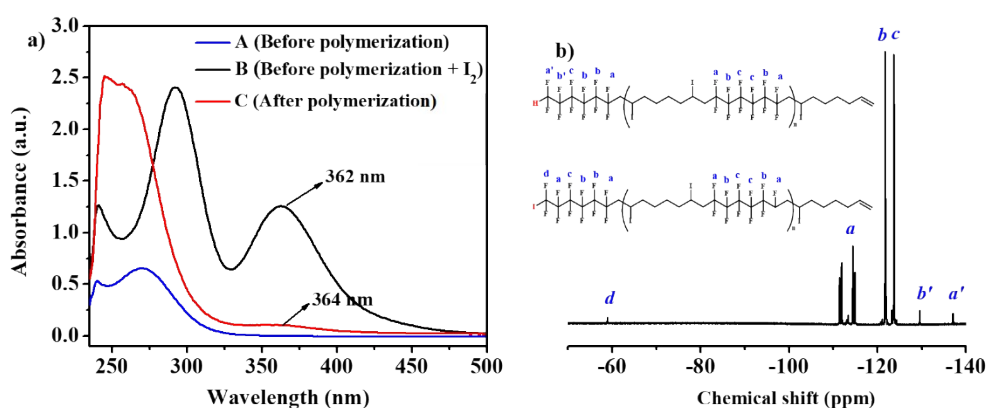
Figure S3. a) UV-*vis* absorption spectra before and after polymerization (C_A, C_B = 1.25 mmol/L, C_C = 2.5 mmol/L); b) ^{19}F NMR spectrum of the resultant main-chain-type semi-fluorinated alternating copolymer ($M_{n,GPC}$ = 8100 Da, $Đ$ = 1.69) by using TMEDA as the catalyst in CDCl$_3$. Polymerization conditions: [A1]$_0$:[B1]$_0$:[TMEDA]$_0$ = 1:1:0.2,

$n_{(B1)} = 0.25$ mmol, $V_{CHCl_3} = 2.0$ mL, purple LED light ($\lambda_{max} = 403$ nm, 29.7 mW cm^{-2}), 25 °C.
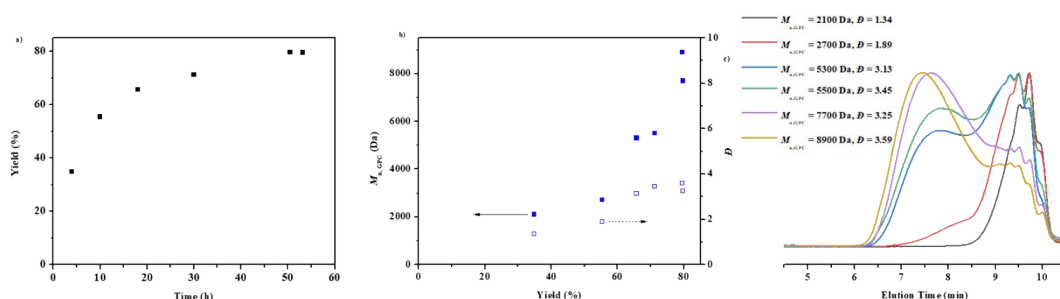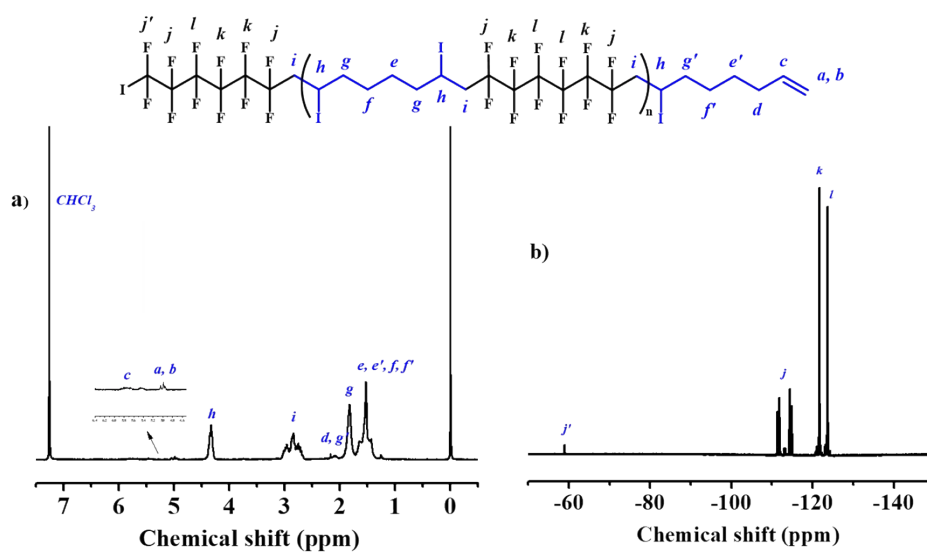

Figure S4. a) Time-yield curve, b) number-average molar mass ($M_{n,GPC}$) and molar mass dispersity (Đ) versus yield, and c) GPC curves for the START polymerization of A1 and B1 by using NaI as the catalyst. Polymerization conditions: [A1]$_0$:[B1]$_0$:[NaI]$_0$ = 1:1:9, $n_{(B1)} = 0.25$ mmol, $V_{Acetone} = 2.0$ mL, purple LED light ($\lambda_{max} = 403$ nm, 29.7 mW cm^{-2}), 25 °C.

Figure S5. a) ^{1}H and b) ^{19}F NMR spectra of the resultant main-chain-type semi-fluorinated alternating copolymer ($M_{n,GPC} = 7700$ Da, Đ=2.95, yield = 70.9%) by using NaI as the catalyst in CDCl$_3$. Polymerization conditions: [A1]$_0$:[B1]$_0$:[NaI]$_0$ = 1:1:9, $n_{(B1)} = 0.25$ mmol, $V_{Acetone} = 2.0$ mL, time = 21 h, purple LED light ($\lambda_{max} = 403$ nm, 29.7 mW cm^{-2}), 25 °C.
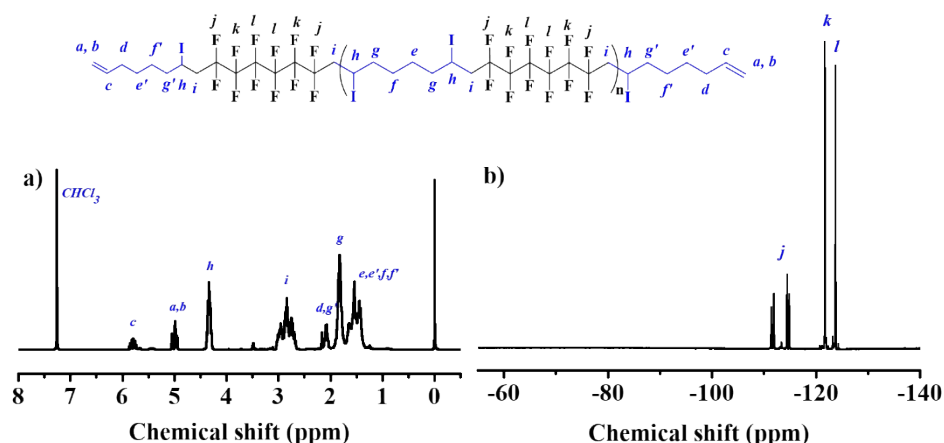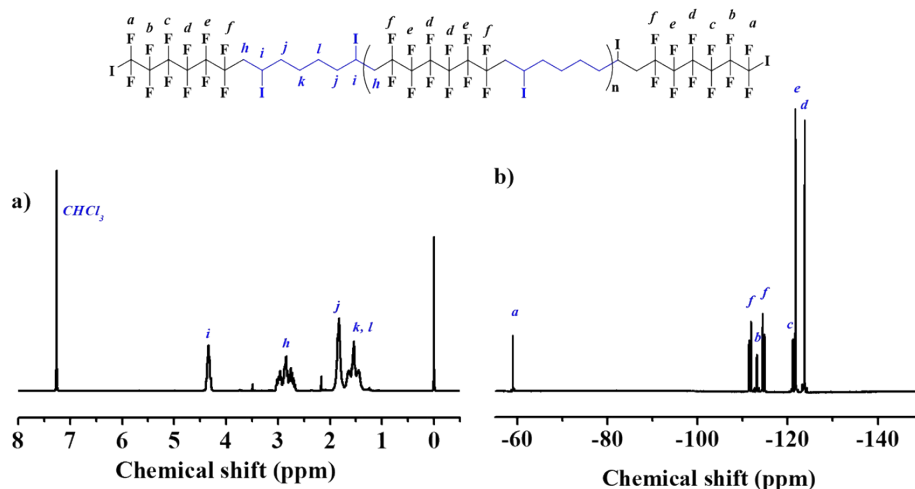
Figure S6. a) ^{1}H and b) ^{19}F NMR spectra of the resultant main-chain-type semi-fluorinated alternating copolymer ($M_{n,GPC}$ = 2700 Da, $Đ$ = 1.75, yield = 68.2%) by using NaI as the catalyst in the case of excess of monomer B1 in CDCl$_3$. Polymerization conditions: R = [A1]$_0$:[B1]$_0$:[NaI]$_0$ = 1:1.4:9, $n_{(B1)}$ = 0.25 mmol, $V_{Acetone}$ = 2.0 mL, time = 21 h, purple LED light (λ_{max} = 403 nm, 29.7 mW cm^{-2}), 25 °C.
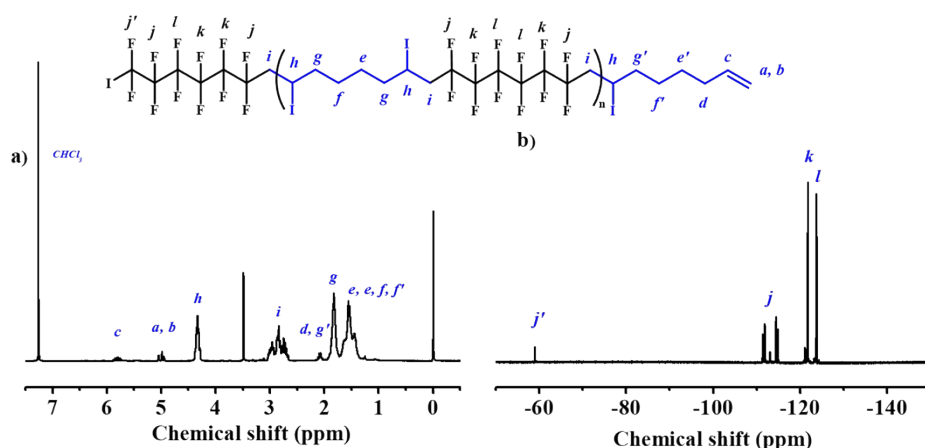

Figure S7. a) ^{1}H and b) ^{19}F NMR spectra of the resultant main-chain-type semi-fluorinated alternating copolymer ($M_{n,GPC}$ = 3300 Da, $Đ$ = 2.41, yield = 90.3%) by using NaI as the catalyst in the case of excess of monomer A1 in CDCl$_3$. Polymerization conditions: R = [A1]$_0$:[B1]$_0$:[NaI]$_0$ = 1.4:1:9 , $n_{(B1)}$ = 0.25 mmol, $V_{Acetone}$ = 2.0 mL, time = 21 h, purple LED light (λ_{max} = 403 nm, 29.7 mW cm^{-2}), 25 °C.

Figure S8. a) ^{1}H and b) ^{19}F NMR spectra of the resultant main-chain-type semi-fluorinated alternating copolymer ($M_{n,GPC}$ = 3300 Da, $Đ$ = 1.70, yield = 68.5%) by using TBAI as the catalyst in CDCl₃. Polymerization conditions: $[A1]_0:[B1]_0:[TBAI]_0$ = 1:1:1, $n_{(B1)}$ = 0.25 mmol, $V_{Acetone}$ = 2.0 mL, time = 21 h, purple LED light (λ_{max} = 403 nm, 29.7 mW cm⁻²), 25 °C.
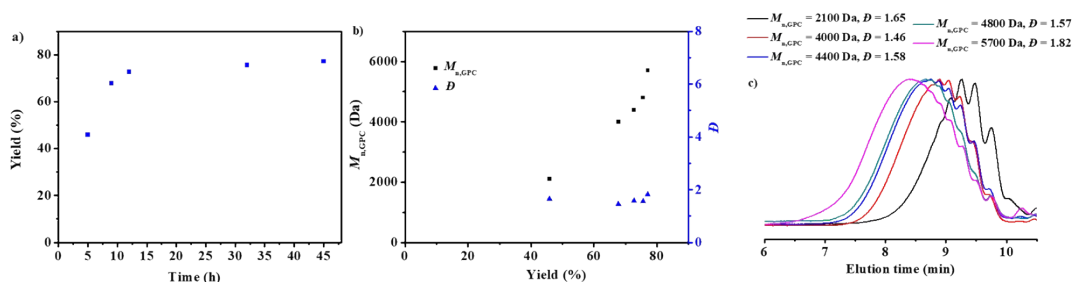

Figure S9. a) Time-yield curve, b) number-average molar mass ($M_{n,GPC}$) and molar mass dispersity ($Đ$) versus yield, and c) GPC curves for the START polymerization of A1 and B1 by using TBAI as the catalyst. Polymerization conditions: $[A1]_0:[B1]_0:[TBAI]_0$ = 1:1:9, $n_{(B1)}$ = 0.25 mmol, $V_{Acetone}$ = 2.0 mL, purple LED light (λ_{max} = 403 nm, 29.7 mW cm⁻²), 25 °C.

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[2] E. J. He, K. Tu, J. N. Cheng, H. J. Lu, L. F. Zhang, Z. P. Cheng and X. L. Zhu, *Polym. Chem.* **2021,** *12*, 736-743.