Supporting Information

Insight into the Polymerization Mechanism of Photoinduced Step Transfer-Addition & Radical-Termination (START) Polymerizations

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Table S1. Investigation of reducing agents (RAs) for our polymerization strategy[a]

Entry	Reducing agent	Time (h)	Yield (%)	$M_{n,GPC}$ (g/mol)	M_w/M_n
1	*i*Pr_2NEt	24	0	[b]--	[b]--
2	NEt_3	36	0	[b]--	[b]--
3	Fe(0)	24	83.0	10600	1.55
4	Cu(0)	24	56.8	6100	1.62
5	AsAc	48	0	[b]--	[b]--
6	Glucose	48	0	[b]--	[b]--

[a]Polymerization conditions: $[A2]_0:[B3]_0:[Ru(bpy)_3Cl_2]_0:[RA]_0$ = 1:1:0.02:0.3, $n_{(B3)}$ = 0.5 mmol, $V_{(DMC)}:V_{(MeCN)}$ = 3:1, $V_{Total\ solvent}$ = 4.0 mL, under irradiation of blue LED light (λ_{max} = 464 nm) at room temperature. [b]Not determined.

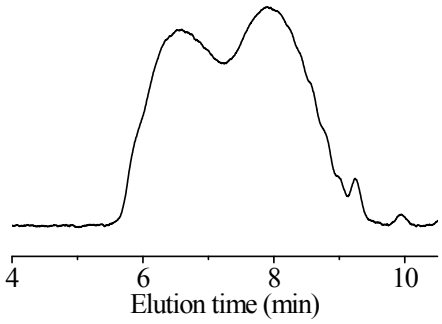

Figure S1. The corresponding GPC curve for the polymer sample of Entry 6 in Table 2. Polymerization conditions: $[A2]_0:[B3]_0:[Ru(bpy)_3Cl_2]_0:[AsAc\text{-}Na]_0$ = 1:1:0.02:0.5,

$n_{(B3)}$ = 0.5 mmol, V_{DMC}:V_{MeCN} = 3:1, $V_{Total\ solvent}$ = 4.0 mL, Time = 72 h, under irradiation of blue LED light (λ_{max} = 464 nm) at room temperature.

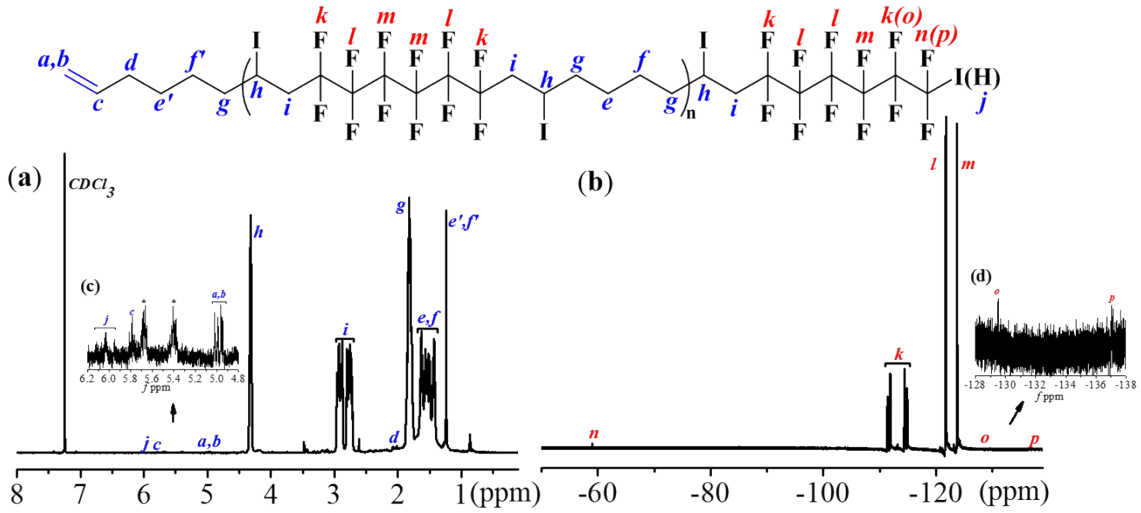

Figure S2. ^{1}H NMR spectrum (**a**) and ^{19}F NMR spectrum (**b**) of the resultant alternating copolymer (**A2B3**)$_n$ in $CDCl_3$. Magnification of ^{1}H NMR spectrum from 4.70 ppm to 6.40 ppm (**c**) and magnification of ^{19}F NMR spectrum from -138 ppm to -128 ppm (**d**). *Structure defection caused by elimination of HF. Sample (**A2B3**)$_n$: $M_{n,GPC}$ = 16400 g/mol, M_w/M_n = 1.71, $M_{n,NMR}$ = 16000 g/mol; Polymerization conditions: $[A2]_0$:$[B3]_0$:$[Ru(bpy)_3Cl_2]_0$:$[AsAc\text{-}Na]_0$ = 1:1:0.02:0.5, $n_{(B3)}$ = 0.5 mmol, $V_{(DMC)}$:$V_{(MeCN)}$ = 5:3, $V_{Total\ solvent}$ = 0.80 mL, Time = 24 h, yield% = 85.7, irradiation under blue LED light (λ_{max} = 464 nm) at room temperature.

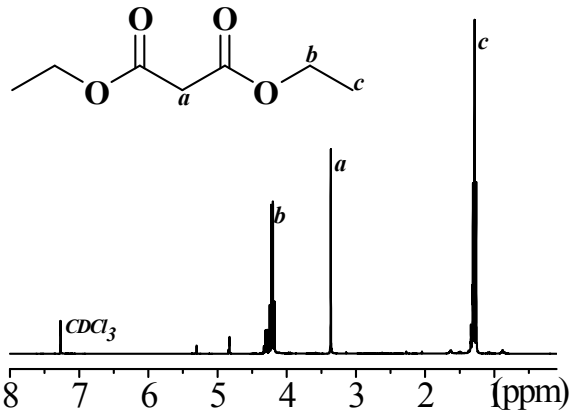

Figure S3. ^{1}H NMR spectrum of dehalogenation product. The detailed synthesis conditions are described in Scheme 3(b).

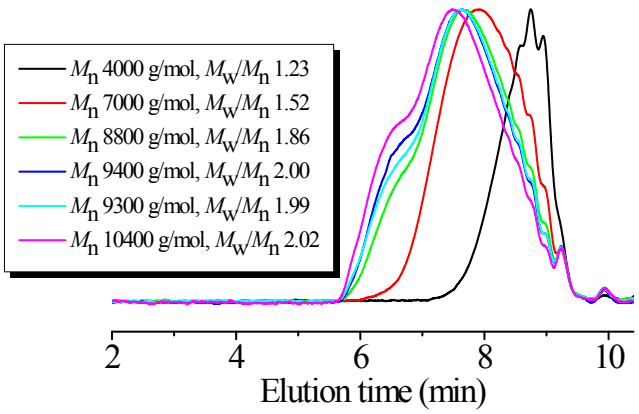

Figure S4. Corresponding gel permeation chromatogram (GPC) curves for Figure 3. Polymerization conditions: $[A2]_0$:$[B3]_0$:$[Ru(bpy)_3Cl_2]_0$:$[AsAc\text{-}Na]_0$ = 1:1:0.02:0.3, $n_{(B3)}$ = 0.5 mmol, $V_{(DMC)}$:$V_{(MeCN)}$ = 3:1, $V_{Total\ solvent}$ = 4.0 mL, under irradiation of blue LED light (λ_{max} = 464 nm) at room temperature.

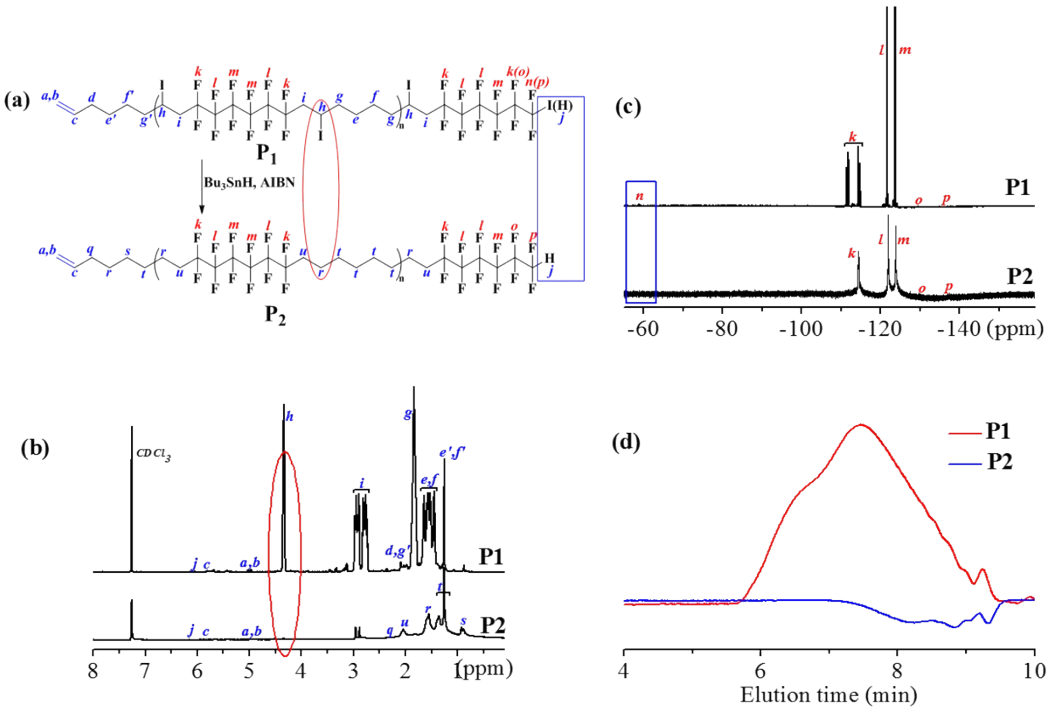

Figure S5. Post-polymerization modification for the alternating copolymer $(\mathbf{A2B3})_n$. (**a**) General post-modification process of the alternating copolymer $(\mathbf{A2B3})_n$. (**b**) Comparison of ^1H NMR spectra for **P1** and **P2** in $CDCl_3$. (**c**) Comparison of ^{19}F NMR spectra for **P1** and **P2** in $CDCl_3$. (**d**) The corresponding GPC curves for **P1** and **P2**. **P1** stands for the original $(\mathbf{A2B3})_n$ ($M_{n,GPC}$ = 10300 g/mol, M_w/M_n = 2.01, $M_{n,NMR}$ = 10400 g/mol) and **P2** stands for the semifluorinated polyethylenes $(\mathbf{F_6H_8})_n$ ($M_{n,GPC}$ = 4000 g/mol, M_w/M_n = 1.48, $M_{n,NMR}$ = 5900 g/mol).