

Supporting Information

Positive effect of water on photo-induced Step Transfer-Addition & Radical-Termination (START) polymerization

Tianchi Xu, Lifen Zhang,* Zhenping Cheng,* and Xiulin Zhu

Suzhou Key Laboratory of Macromolecular Design and Precision Synthesis, Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, Department of Polymer Science and Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

Contents

Supplementary Experiments for the Polymerization

Table S1. Failed trials to further enhance the polymerization efficiency

Figure S1. The actual polymerization phenomena before and after the polymerization. (a) Picture taken instantly once completion of the polymerization, and (b) picture taken after standing-still for 2 minutes

Figure S2. The total NMR (^1H and ^{19}F) spectra for one polymer sample $(\text{A2B3})_n$

Figure S3. Modification for the alternating copolymer $(\text{A2B3})_n$ and the corresponding NMR (^1H and ^{19}F) spectra.

Figure S4. ^{19}F NMR spectrum for **A2** ($\text{C}_6\text{F}_{12}\text{I}_2$) in CDCl_3 .

Table S1. Failed trials to further enhancing the polymerization efficiency

Entry	$[\text{A2}]_0:[\text{B3}]_0:[\text{Ru}(\text{bpy})_3\text{Cl}_2]_0:[\text{As Ac-Na}]_0:[\text{Additive}]_0$	Additive	Conv. (%)	$M_{n,\text{GPC}}$ (g/mol)	M_w/M_n
1	1:1:0.02:0.5:0.5	15-Crown-5	72.8	8100	1.74
2	1:1:0.02:0.5:0.2	^b TBABr	71.7	8400	1.65
3	1:1:0.02:0.5:0.08	^c SLS	74.3	8500	1.86
^a 4	1:1:0.02:0.5:0.08	^c SLS	73.8	11700	2.34

Polymerization conditions: $n_{(B3)} = 0.5$ mmol, $V_{(1,4\text{-dioxane})}:V_{(\text{MeOH})}:V_{(\text{Water})} = 3:1:3$, $V_{(\text{Total solvent})} = 7.0$ mL, Time = 12 h, irradiation under blue LED at room temperature. ^aAddition of 0.14 equiv of n-Hexadecane, ^bTBABr: tetrabutyl ammonium bromide. ^cSLS: sodium lauryl sulfate (3.5 wt%).

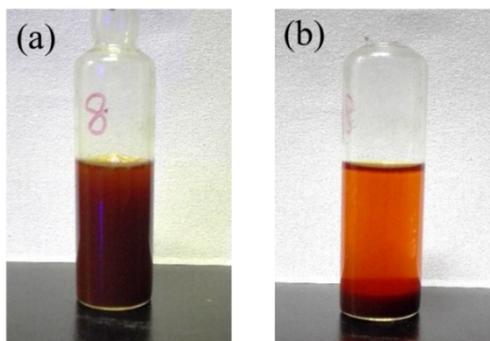


Figure S1. The actual polymerization phenomena before and after the polymerization (Polymerization conditions: $[A2]_0:[B3]_0:[Ru(bpy)_3Cl_2]_0:[AsAc-Na]_0 = 1:1:0.02:0.5$, $n_{(B)} = 0.5$ mmol, $V_{(1,4\text{-dioxane})}:V_{(\text{MeOH})}:V_{(\text{Water})} = 3:1:3$, $V_{(\text{Total solvent})} = 7.0$ mL, irradiation under blue LED at room temperature, Time = 12 h). (a) Picture taken instantly once completion of the polymerization, and (b) picture taken after standing-still for 2 minutes.

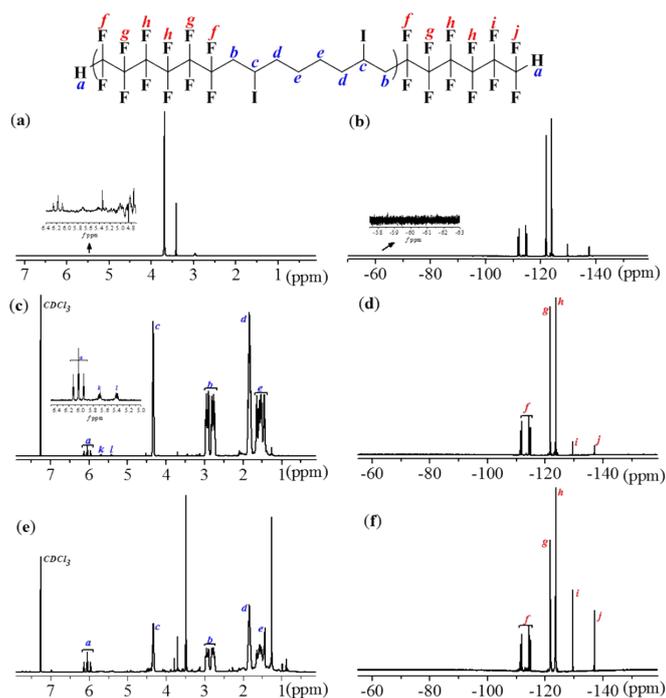


Figure S2. The total NMR (^1H and ^{19}F) spectra for one polymer sample $(\text{A2B3})_n$. (a) *in-situ* ^1H NMR spectrum of polymerization system; (b) *in-situ* ^{19}F NMR spectrum of polymerization system; (c) ^1H NMR spectrum of the perfluorocarbon-containing alternating copolymer $(\text{A2B3})_n$ (Yield% = 67.9%, $M_{n,\text{GPC}} = 6200$ g/mol, $M_w/M_n = 1.72$, $M_{n,\text{NMR}} = 5900$ g/mol); (d) ^{19}F NMR spectrum of the perfluorocarbon-containing alternating copolymer $(\text{A2B3})_n$ (Yield% = 67.9%, $M_{n,\text{GPC}} = 6200$ g/mol, $M_w/M_n = 1.72$, $M_{n,\text{NMR}} = 5900$ g/mol); (e) ^1H NMR spectrum of the residues from precipitant (MeOH), obtained through rotary evaporation; (f) ^{19}F NMR spectrum of the residues from precipitant (MeOH), obtained through rotary evaporation. All the NMR tests were carried out in CDCl_3 . The detailed sampling process for the *in-situ* NMR tests was described in the experimental part. Polymerization conditions: $[\text{A2}]_0:[\text{B3}]_0:[\text{Ru}(\text{bpy})_3\text{Cl}_2]_0:[\text{AsAc-Na}]_0 = 1:1:0.01:0.3$, $n_{(\text{B})} = 2.0$ mmol, $V_{(1,4\text{-dioxane})}:V_{(\text{MeOH})} = 3:1$, $V_{(\text{Total solvent})} = 4.0$ mL, Time = 20 h, irradiation under blue LED at room temperature.

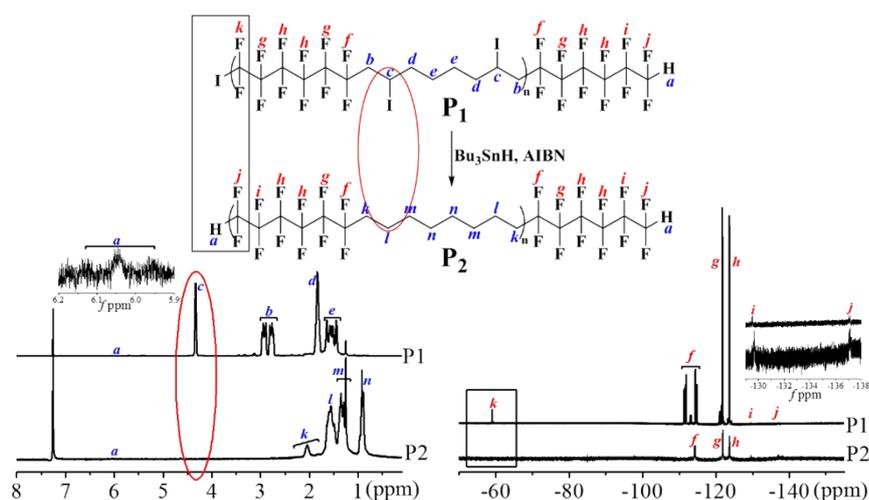


Figure S3. Modification for the alternating copolymer $(\text{A2B3})_n$ and the corresponding NMR (^1H and ^{19}F) spectra. (Polymerization conditions: $[\text{A2}]_0:[\text{B3}]_0:[\text{Ru}(\text{bpy})_3\text{Cl}_2]_0:[\text{AsAc-Na}]_0 = 1:1:0.02:0.5$, $n_{(\text{B3})} = 0.5$ mmol, $V_{(1,4\text{-dioxane})}:V_{(\text{MeOH})}:V_{(\text{Water})} = 3:1:3$, $V_{(\text{Total solvent})} = 7.0$ mL, irradiation under blue LED at room temperature, Time = 20 h). (a) General modification process of the alternating copolymer $(\text{A2B3})_n$. (**P1** stands for the original $(\text{A2B3})_n$ ($M_{n,\text{GPC}} = 8200$ g/mol, $M_w/M_n = 2.18$, $M_{n,\text{NMR}} = 6600$ g/mol); **P2** stands for $(\text{A2B3})_n$ ($M_{n,\text{GPC}} = 2700$ g/mol, $M_w/M_n = 1.07$, $M_{n,\text{NMR}} = 4200$ g/mol), which has underwent the reduction reaction.) (b) Comparison of ^1H NMR spectra of **P1** and **P2**, (c) Comparison of ^{19}F NMR spectra of **P1** and **P2**. All the NMR tests were carried out in CDCl_3 .

