Photocontrolled iodine-mediated reversible-deactivation radical polymerization with semifluorinated alternating copolymer as macroinitiator

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Supporting Information

Table S1. Visible light controlled START polymerization of monomer A with kinds of monomer B catalyzed by organocatalyst

Entry	В	Feed ratio	Time (h)	^a Yield (%)	^b M _{n,GPC} (g/mol)	${}^{b}M_{\mathrm{w}}/M_{\mathrm{n}}$
1	B_1	1:1:0.1:0.5	24	44.3	3000	1.42
2	\mathbf{B}_1	1:1:0.1:0.5	48	63.4	4600	1.71
3	\mathbf{B}_1	1.2:1:0.1:0.5	72	43.2	6400	1.75
4	B_2	1:1:0.1:0.5	24	66.4	4000	1.75
5	B_3	1:1:0.1:0.5	48	27.8	2200	1.28
6	B_4	1:1:0.1:0.5	24	51.2	9800	1.91

Polymerization conditions: $[A]_0:[B]_0:[TPP^+BF_4^-]_0:[AsAc-Na]_0; n_{(A)}= 1.0 \text{ mmol}; 25 \text{ °C}; V_{DMC}: V_{MeCN} = 3:1, V_{Total Solvent} = 8.0 \text{ mL}; under irradiation with blue LED light (<math>\lambda_{max} = 458 \text{ nm}, 0.85 \text{ mW/cm}^2$). *a*Yield of the polymerization was determined gravimetrically. *b*Molecular weights and molecular weight distributions were determined by GPC using linear PMMA as calibration standard in THF.

Table S2. Effects of various components on the photocontrolled reversible-deactivation radical polymerization of MMA

Entry	Ratio	^a Conv. (%)	^b M _{n,th} (g/mol)	^c M _{n,GPC} (g/mol)	$^{c}M_{\mathrm{w}}/M_{\mathrm{n}}$
1	500:0:0.2:1	5.7	e	96000	1.88
2	500:1:0:1	0.2	e	7000	2.77
3	500:1:0.2:0	28.1	19100	30000	1.24
^d 4	500:1:0.2:1	0.9	e	7800	1.81
5	500:1:0.2:5	54.1	32100	52900	1.33
6	500:1:0.5:5	61.5	35800	50400	1.66

Polymerization conditions: Ratio = $[MMA]_0:[(AB_1)_n]_0:[Ru(bpy)_3Cl_2]_0:[AsAc-Na]_0; V_{MMA} = V_{acetone} = 0.5 mL; 25 °C; t = 10 h; <math>M_{(AB_1)n,GPC} = 5000 \text{ g/mol}, M_w/M_n = 1.77$; under irradiation with blue LED light ($\lambda_{max} = 458 \text{ nm}, 0.85 \text{ mW/cm}^2$). ^{*a*}Conversion of the monomer was determined gravimetrically. ^{*b*}Calculated based on conversion, $M_{n,th} = M_{(AB_1)n} + [MMA]_0/[(AB_1)_n]_0 \times M_{w,MMA} \times \text{conversion}\%$. ^{*c*}Molecular weights and molecular weight distributions were determined by GPC using linear PMMA as calibration standard in THF. ^{*d*}The polymerization of MMA in the absence of visible light. ^{*e*}Not available.

Table S3. Optimization of solvent system for the polymerization strategy of MMA

Entry	Solvent	V _{Solvent} (mL)	Time (h)	<i>Conv.</i> (%)	M _{n,th} (g/mol)	M _{n,GPC} (g/mol)	$M_{ m w}/M_{ m n}$
1	Acetone	0.5	12	82.5	46300	44300	1.35
2	DMC	0.5	12	49.1	30000	84100	1.33
3	Toluene	0.5	12	42.4	26200	106800	1.32
4	DMSO	0.5	12	43.0	27000	27700	1.68
5	MeCN	0.5	12	44.4	27200	25200	1.70
6	Acetone	1.0	24	40.5	25300	35800	1.31
7	Acetone	2.0	24	32.5	21300	32200	1.40

Polymerization conditions: $[MMA]_0:[(AB_1)_n]_0:[Ru(bpy)_3Cl_2]_0:[AsAc-Na]_0 = 500:1:0.2:1; V_{MMA} = V_{acetone} = 0.5 mL; 25 °C; Ar; <math>M_{(AB1)n,GPC} = 5000 \text{ g/mol}, M_w/M_n = 1.77$; under irradiation with blue LED light ($\lambda_{max} = 458 \text{ nm}, 0.85 \text{ mW/cm}^2$). ^{*a*}Conversion of the monomer was determined gravimetrically. ^{*b*}Calculated based on conversion, $M_{n,th} = M_{(AB1)n} + [MMA]_0/[(AB_1)_n]_0 \times M_{w,MMA} \times \text{conversion}\%$. ^{*c*}Molecular weights and molecular weight distributions were determined by GPC using linear PMMA as calibration standard in THF.

1 500:1:0.2:1 CP-I Acetone 35.3 17800 21000	1.11
2 500:1:0:0 CP-I Acetone 33.9 17100 13000	1.16
3 500:1:0.2:1 EIiB Acetone 59.5 30000 13200	1.54
4 500:1:0:0 EIiB Acetone 37.2 18900 9800	1.29
5 500:1:0.2:1 EIiB Toulene 26.1 13300 69300	1.80
6 500:1:0:0 EIiB Toulene 0	
7 500:1:0:0 EIiB Bulk 0	

Table S4. Polymerization of MMA with different conditions

Polymerization conditions: $[MMA]_0$: $[Initiator]_0$: $[Ru(bpy)_3Cl_2]_0$: $[AsAc-Na]_0$; $V_{MMA} = V_{Solvent} = 0.5 \text{ mL}$; 25 °C; t = 18 h; under irradiation with blue LED light ($\lambda_{max} = 458 \text{ nm}$, 0.85 mW/cm²). ^{*a*}Determined by gravimetry. ^{*b*}Calculated based on conversion, $M_{n,th} = M_{w, \text{ Initiator}} + [Monomer]_0/[Initiator]_0 \times M_{w, MMA} \times \text{conversion}\%$. ^{*c*}Molecular weights and molecular weight distributions were determined by GPC using linear PMMA as calibration standard in THF.



Fig. S1 ¹H NMR spectrum of B₂ in CDCl₃.



Fig. S2 ¹H NMR spectrum of B₃ in CDCl₃.



Fig. S3 ¹H NMR spectrum of B₄ in CDCl₃.



Fig. S4 ¹H NMR spectrum of the alternating copolymer $(AB_2)_n$ in CDCl₃.



Fig. S5 ¹H NMR spectrum of the alternating copolymer $(AB_3)_n$ in CDCl₃.



Fig. S6 ¹H NMR spectrum of the alternating copolymer $(AB_4)_n$ in CDCl₃.



Fig. S7 UV-vis spectra of $(AB_1)_n (5.0 \times 10^{-4} \text{ M})$, AsAc-Na $(5.0 \times 10^{-4} \text{ M})$, and Ru(bpy)₃Cl₂ $(1.0 \times 10^{-4} \text{ M})$.



Fig. S8 (a) ¹⁹F NMR spectra of block copolymers $(AB_1)_n$ -*b*-PMMA, $(AB_1)_n$ -*b*-PPEGMA, $(AB_1)_n$ -*b*-PDMAEMA and $(AB_1)_n$ -*b*-PGMA in CDCl₃. (b) ¹⁹F NMR spectrum of C₆F₁₂I₂ in CDCl₃.



Fig. S9 (a) GPC traces of $(AB_1)_n$ -*b*-PS, $(AB_1)_n$ -*b*-PBA and $(AB_1)_n$ -*b*-PMA. (b) ¹H NMR spectra of block copolymers $(AB_1)_n$ -*b*-PS, $(AB_1)_n$ -*b*-PBA and $(AB_1)_n$ -*b*-PMA in CDCl₃.