

Supporting Information

Facile Grafting Modification of Main-Chain-Type Semi-fluorinated Alternating Fluoropolymers *via* Simultaneous CuAAC Reaction and ATRP in One Pot at Ambient Temperature

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1. Experimental Section

1.1. Materials

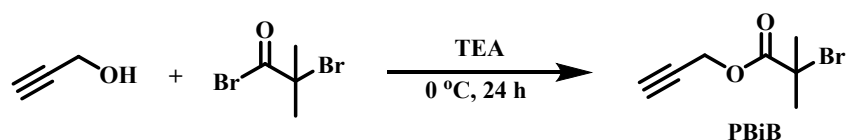
1,6-Diodoper-fluorohexane (TCI, 98%), 1,8-diodoperfluorooctane (TCI, 98%), 1,4-diodoperfluorobutane (TCI, 98%), 1,7-octadiene (Alfa Aesar, > 97%), sodium azide (NaN₃, Aldrich, 98%), 18-crown-6 (Energy Chemical, ≥ 99%), 5-hexen-1-ol (Macklin, > 97%), 6-bromo-1-hexene (J&K, 97%), pyridine (Aladdin), terephthaloyl chloride (TCI, >99%), 2-bromo-2-methylpropionyl bromide (Aldrich, 98%), propargyl alcohol (Aldrich, 99%) and Ru(bpy)₃Cl₂ (Energy Chemical, 98%) were used as received and stored in light-resistant container at 0 °C. L(+)-ascorbic acid sodium salt (AsAc-Na) (Aladdin, ≥ 99%) was used as received and stored in desiccator for a dry environment. *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, Energy Chemical, 99%) and cuprous bromide (CuBr, Macklin, 99.0%) were refined and stored in the dark environment. Methyl methacrylate (MMA) (Sigma-Aldrich, 99%), methoxypoly(ethylene glycol) methacrylate (PEGMA) (Aldrich, *M_n* = 500 g/mol, 99%), styrene (Shanghai Chemical Reagents Co. Ltd, AR), *t*-butyl acrylate (*t*-BA) (Shanghai Chemical Reagents Co. Ltd, AR) and methyl acrylate (MA) (Shanghai Chemical Reagents Co. Ltd, AR) were passed through a neutral alumina column for the removal of the inhibitor and stored in the dark environment at 0 °C. Deionized water was purchased from Hangzhou Wahaha Co. Ltd. and potassium carbonate (Shanghai Chemical Reagents Co. Ltd, AR), hydroquinone (J&K, 99%) were used as received. Toluene was obtained from an Aldrich keg system with an inline solvent drying column of activated alumina. All the regular solvents (Analytical reagent) were used directly without any further treatment unless otherwise mentioned.

1.2. Measurements

The number-average molar mass (*M_{n,GPC}*) and molar mass dispersity (*D*) values of polymers were determined with a TOSOH HLC-8320 gel permeation chromatograph (GPC) equipped with TSK gel Multi pore HZN (3) 4.6×150 mm column. Tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF) (with 0.1 wt% LiBr) were used as the eluent at a flow rate of 0.35 mL min⁻¹ at 40 °C. All the GPC samples were injected using a TOSOH HLC-8320 GPC plus autosampler and calibrated with narrow polydispersity PMMA or PS standards purchased from TOSOH. ¹H NMR spectra of monomers and polymers were recorded on a Bruker 300 MHz nuclear magnetic resonance (NMR) instrument using CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal standard at room temperature (25 °C). ¹⁹F NMR spectra of polymers were recorded on a Bruker 600 MHz Advance

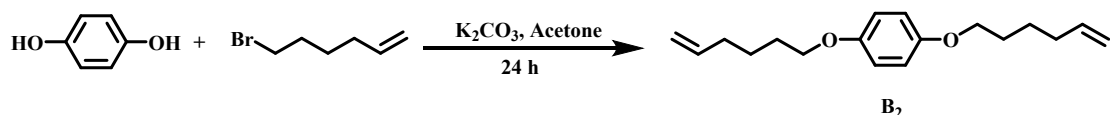
III instrument using CDCl_3 as the solvent and TMS as the internal standard at room temperature (25 °C). Fourier transform infrared spectroscopy (FT-IR) was performed on a Bruker Tensor-27 8000-350 infrared spectrometer and a potassium bromide (KBr) tablet was used as the background. The surface morphology was measured by atomic force microscopy (AFM) in tapping mode (Veeco Instruments Inc., Nanoscope IV). Samples for transmission electron microscopy (TEM) observation were prepared by placing a drop of self-assembled polymer solution onto a 300 mesh copper grid coated with a carbon film. After 30 s, excess fluid was removed using a piece of filter paper. TEM was performed on a HITACHI HT7700 transmission electron microscope with an accelerating voltage of 120 kV. Dynamic light scattering (DLS) measurements were conducted using a NanoBrook 90 Plus instrument at a scattering angle of 90°. The hydrodynamic diameter and the particle size distribution were obtained from the analysis of the autocorrelation functions using the method of cumulants. At least five measurements at 25 °C were made for each sample with an equilibrium time of 1 min before starting the measurement.

Scheme S1. Synthesis of PBiB^[1]



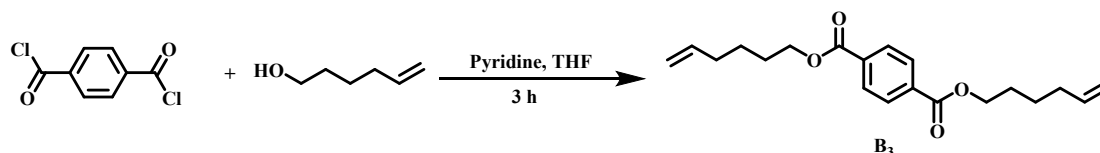
PBiB was synthesized by dropwise addition of 2-bromo-2-methylpropionyl bromide (2.04×10^{-2} mol) to propargyl alcohol (1.94×10^{-2} mol) and triethylamine (TEA) (2.04×10^{-2} mol) solution in diethylether (50 mL) at 0 °C under nitrogen atmosphere. After addition, the reaction mixture was stirred overnight at room temperature. The reaction mixture extracted with water and organic phase was dried with Na_2SO_4 . The solution was concentrated and the crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10/1) (v/v) to give the product as a colorless liquid (80 %). ^1H NMR (300 MHz, CDCl_3) δ : 4.74 (d, 2H), 3.47 (t, H), 1.93 (s, 3H).

Scheme S2. Synthesis of Monomer B₂^[2]



Under an inert atmosphere, a mixture of hydroquinone (6.61 g, 0.06 mol), 6-bromo-1-hexene (4.89 g, 0.03 mol), anhydrous potassium carbonate (4.15 g, 0.03 mol), and dried acetone (100 mL) was added to a 250 mL three-neck round flask, refluxed for 24 h and cooled down to room temperature. After filtration of potassium carbonate, the solvent was rotary evaporated. Then, the crude solid product was dissolved in ethyl acetate (150 mL), which was then washed twice with 50 mL of deionized water, and the organic layer was collected. The organic layer was dried with Na_2SO_4 and evaporated, the final crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10/1) (v/v) to obtain a colorless liquid (4.58 g, 70.0 %). ^1H NMR (CDCl_3 , 300 MHz), δ : 6.81 (s, 4H), 5.82 (ddt, 2H), 5.11-4.89 (m, 4H), 3.90 (t, 4H), 2.12 (q, 4H), 1.84-1.70 (m, 4H), 1.63-1.48 (m, 4H).

Scheme S3. Synthesis of Monomer B₃^[2]



Terephthaloyl chloride (5.08 g, 0.03 mol) was purged with argon and then dissolved in 50 mL of dry THF, followed by the dropwise addition of dry pyridine (3.90 g, 0.05 mol) *via* a syringe. 5-Hexen-1-ol (10.02 g, 0.10 mol) was added dropwise *via* a syringe, after which the mixture was heated to reflux for 3 h under argon. Then, THF was removed in vacuo. The residue was dissolved in 50 mL of H₂O and washed with 100 mL of diethyl ether. The ether fractions were combined, washed once with 10% aqueous HCl, and washed twice with 10% aqueous Na₂CO₃. The organic layer was then dried Na₂SO₄ and evaporated, the crude product was purified by column chromatography (petroleum ether/ethyl acetate = 4/1) (v/v) to obtain a colorless liquid (7.40 g, 73.3%). ¹H NMR (300 MHz, CDCl₃) δ: 8.10 (s, 4H), 5.82 (ddt, 2H), 5.12-4.92 (m, 4H), 4.35 (t, 4H), 2.14 (q, 4H), 1.81 (dt, 4H), 1.56 (ddt, 4H).

1.3. Synthesis of semi-fluorinated alternating copolymer (AB)_nA

Taking (A₂B₁)_nA₂ as the example, polymerizations of 1,6-diiodoper-fluorohexane (A₂) and 1,7-octadiene (B₁) was performed in the presence of blue LED light ($\lambda_{\text{max}} = 459 \text{ nm}$, 5.5 mW/cm²) under an argon atmosphere with a molar ratio of [A₂]₀: [B₁]₀: [Ru(bpy)₃Cl₂]₀: [AsAc-Na]₀ = 1.2 : 1 : 0.02 : 0.5 was described as follows: A mixture of 1,6-diiodoper-fluorohexane (A₂) (0.6 mmol), 1,7-octadiene (B₁), Ru(bpy)₃Cl₂ and AsAc-Na was added to a dried ampoule with a stir bar. Then 4.0 mL of the solution mixture of 1,4-dioxane and methanol (CH₃OH) with a feed ratio of 3/1 (v/v) was added for the thorough dissolution of the mixture. The reaction mixture was degassed by at least four freeze-pump-thaw cycles to totally eliminate the dissolved oxygen, and then the ampoule was flame-sealed and placed in the presence of blue LED light with stirring. The whole system was fanned for the maintenance of the temperature at 25 °C. After a predetermined period of time, the ampoule was opened and then the mixture was passed through a neutral alumina column before being precipitated into a large amount of methanol (250 mL) to remove the catalyst. The polymers obtained by filtration were dried under vacuum at 35 °C overnight until a constant weight. The yield and molecular weight of polymers were determined gravimetrically and analyzed by GPC and NMR.

1.4. Synthesis of azide semi-fluorinated alternating copolymer (AB)_nA-N₃

Taking (A₂B₁)_nA₂ as the example, (A₂B₁)_nA₂ (the theoretical moles of iodine 2 mmol), sodium azide (4 mmol) and 18-crown-6 (8 mmol) were added to a dried ampoule with a stir bar. Then 10.0 mL CHCl₃ was added and the ampoule was flame-sealed and allowed to stir at 55 °C for 36 hours. Then, the reaction mixture was purified by filtration through a short Al₂O₃ column to remove the NaN₃, followed by precipitation into a large amount of cold methanol (250 mL). The final polymer (A₂B₁)_nA₂-N₃ was gained by filtration and dried under vacuum at 0 °C for 24 h. The conversion and molecular weight of polymers were determined and analyzed by GPC and NMR.

1.5. Synthesis of fluorinated graft copolymers with semi-fluorinated alternating backbone via CuAAC and ATRP in one pot

A typical procedure of polymerization was carried out under an argon atmosphere with a molar ratio

of $[\text{PEGMA}]_0/[\text{PBiB}]_0/[(\text{AB})_n\text{A-N}_3]_0/[\text{CuBr}]_0/[\text{PMEDTA}]_0 = 50/1/1/0.2/1$ and 1/3 ratio of PEGMA/toluene (v/v), where $[(\text{AB})_n\text{A-N}_3]_0$ means moles of attached $-\text{N}_3$ groups to $(\text{AB})_n\text{A}$ main chain. The reaction mixture was weighed into the Schlenk tube and evacuated and argon-refilled at least four freeze-pump-thaw cycles to totally eliminate the dissolved oxygen. Then the polymerization was started by stirring at 25 °C. Aliquots were removed periodically and diluted into CDCl_3 for NMR analysis and calculation of conversion. The solvent from the same samples was evaporated and diluted into DMF or CHCl_3 for GPC and FT-IR characterization. After a predetermined period of time, the reaction mixture was purified by filtration through a short Al_2O_3 column to remove the catalyst, followed by precipitation into a large amount of petroleum ether (250 mL) twice to remove the unreacted monomer.

1.6. Synthesis of fluorinated graft copolymers with semi-fluorinated alternating backbone by two steps of CuAAC and ATRP

A typical procedure of polymerization was carried out under an argon atmosphere with a molar ratio of $[\text{PBiB}]_0/[(\text{AB})_n\text{A-N}_3]_0/[\text{CuBr}]_0/[\text{PMEDTA}]_0 = 1/1/0.2/1$, where $[(\text{AB})_n\text{A-N}_3]_0$ means moles of attached $-\text{N}_3$ groups to $(\text{AB})_n\text{A}$ main chain. The reaction mixture was weighed into the dried ampoule with a stir bar and argon-refilled at least four freeze-pump-thaw cycles to totally eliminate the dissolved oxygen. Then the reaction was started by stirring at 25 °C. After a predetermined period of time, the reaction mixture was purified by filtration through a short Al_2O_3 column to remove the catalyst, followed by precipitation into a large amount of petroleum ether (250 mL). The polymer $(\text{A}_2\text{B}_1)_n\text{A}_2\text{-Br}$ was gained by filtration and dried under vacuum at 35 °C overnight. The conversion and molecular weight of polymers were determined and analyzed by GPC and NMR. Then, the mixture of the ratio of $[\text{PEGMA}]_0/[(\text{A}_2\text{B}_1)_n\text{A}_2\text{-Br}]_0/[\text{CuBr}]_0/[\text{PMEDTA}]_0 = 50/1/0.2/1$ and 1/3 ratio of PEGMA/toluene (v/v) were added into the dried ampoule with a stir bar and argon-refilled at least four freeze-pump-thaw cycles to totally eliminate the dissolved oxygen, where $[(\text{AB})_n\text{A-Br}]_0$ means moles of attached initiator $-\text{Br}$ groups to $(\text{AB})_n\text{A}$ main chain. Then the reaction was started by stirring at 25 °C, 50 °C or 90 °C. After a predetermined period of time, the reaction mixture was purified by filtration through a short Al_2O_3 column to remove the catalyst, followed by precipitation into a large amount of petroleum ether (250 mL). The final graft copolymer was gained by filtration and dried under vacuum at 35 °C overnight. The conversion and molecular weight of polymers were determined and analyzed by GPC and NMR.

1.7. Self-assembly of fluorinated graft copolymers $(\text{AB})_n\text{A-g-PPEGMA}$

There are two self-assembly methods of fluorinated graft copolymers $(\text{AB})_n\text{A-g-PPEGMA}$ in the article.

1. Fluorinated graft copolymers are added directly in deionized water under vigorous stirring to obtain 0.5 mg/mL polymer aqueous solution.
2. Fluorinated graft copolymers are dissolved in the good solvent (DMF/THF) and deionized water was added slowly (about 0.1 mL/h) to the fluorinated graft copolymer solutions (DMF/THF) under vigorous stirring to obtain 0.5 mg/mL mixed solution.

2. Supporting Tables and Figures

2.1. Tables

Table S1. Synthesis of main-chain-type semi-fluorinated alternating copolymer (AB)_nA^a

Entry	A	B	time (h)	Yield ^b (%)	$M_{n,GPC}^c$ (g/mol)	\mathcal{D}^c
1	A ₁	B ₁	40	73.1	6700	2.25
2	A ₂	B ₁	48	71.0	8700	2.14
3	A ₂	B ₁	40	68.9	5600	1.64
4	A ₂	B ₁	40	69.2	5400	1.48
5	A ₃	B ₁	40	58.4	7000	1.75
6	A ₂	B ₂	36	63.0	7000	2.24
7	A ₁	B ₃	36	60.3	6400	2.47
8	A ₂	B ₃	36	64.0	4800	2.32
9	A ₂	B ₁	40	70.2	4600	1.27

^aPolymerization condition: $[A]_0/[B]_0/[Ru(bpy)_3Cl_2]_0/[AsAc-Na]_0 = 1.2/1/0.02/0.5$, $n_{(B)} = 1.0$ mmol, under irradiation with blue LED light ($\lambda_{max} = 459$ nm, 5.5 mW/cm²), T = 25 °C, $V_{1,4-dioxane}/V_{methanol} = 3/1$, $V_{total\ Solvent} = 8.0$ mL. ^bYield of the polymerization was determined gravimetrically. ^cNumber-average molar mass ($M_{n,GPC}$) and molar mass dispersity (\mathcal{D}) were determined by GPC using linear PMMA as calibration standard in THF.

Table S2. Synthesis of azide semi-fluorinated alternating copolymer (AB)_nA-N₃^a

Entry	(AB) _n A	$M_{(AB)_nA}$ (g/mol)	$\mathcal{D}_{(AB)_nA}$	Conv. ^b (%)	$M_{n,GPC}^c$ (g/mol)	\mathcal{D}^c
1	(A ₁ B ₁) _n A ₁	6700	2.25	85.2	5700	1.66
2	(A ₁ B ₃) _n A ₁	6400	2.47	72.0	8700	1.65
3	(A ₂ B ₁) _n A ₂	4600	1.27	86.5	6500	1.21
4	(A ₂ B ₁) _n A ₂	5600	1.64	88.6	11300	1.36
5	(A ₂ B ₁) _n A ₂	8700	2.14	86.0	12500	1.73
6	(A ₂ B ₂) _n A ₂	7000	2.24	84.0	11800	2.01
7	(A ₂ B ₃) _n A ₂	4800	2.32	73.6	7500	1.52
8	(A ₃ B ₁) _n A ₃	7000	1.75	87.7	9100	1.58

^aReaction conditions: $[(AB)_nA]_0/[NaN_3]_0/[18-crown-6]_0 = 1/2/4$, $[(AB)_nA]_0$ means moles of attached I atoms to (AB)_nA main chain. $m_{(AB)_nA} = 0.2$ g, $V_{CHCl_3} = 4.0$ mL, T = 55 °C, t = 40 h. ^bReaction conversion estimated by ¹H NMR spectra. ^cNumber-average molar mass ($M_{n,GPC}$) and molar mass dispersity (\mathcal{D}) were determined by GPC using linear PMMA as calibration standard in THF.

Table S3. Effects of various components on the ATRP polymerization of various monomers^a

Entry	Ratio	M	$M_{(A_2B_1)_nA_2-N_3}$ (g/mol)	$D_{(A_2B_1)_nA_2-N_3}$	time (h)	Conv. ^b (%)	$M_{n,GPC}$ ^c (g/mol)	D ^c
^d 1	100/1/0/0.2/1	MA	--	--	20	2.6	^e 100	^e 1.01
^d 2	100/1/0/0.2/1	MMA	--	--	20	6.0	^e 3300	^e 1.17
3	50/1/0/0.2/1	PEGMA	--	--	20	5.3	6600	1.11
4	50/0/1/0.2/1	PEGMA	8800	1.44	24	4.6	8500	1.01
5	50/1/1/0/0	PEGMA	8800	1.44	24	10.4	8300	1.10

^aPolymerization conditions: Ratio = [M]₀/[PBiB]₀/[(A₂B₁)_nA₂-N₃]₀/[CuBr]₀/[PMDETA]₀, [(A₂B₁)_nA₂-N₃]₀ means moles of attached -N₃ groups to (A₂B₁)_nA₂ main chain. $V_{\text{monomer}} = 1.0$ mL, $V_{\text{toluene}} = 3.0$ mL, T = 25 °C. ^bConversion of the monomer was estimated by ¹H NMR spectra. ^cNumber-average molar mass ($M_{n,GPC}$) and molar mass dispersity (D) were determined by GPC using linear PS as calibration standard in DMF (with 0.1 wt% LiBr). ^d $V_{\text{monomer}} = 0.5$ mL, $V_{\text{toluene}} = 2.0$ mL. ^eNumber-average molar mass ($M_{n,GPC}$) and molar mass dispersity (D) were determined by GPC using linear PMMA as calibration standard in THF.

Table S4. Synthesis of macroinitiator (A₂B₁)_nA₂-Br via CuAAC reaction^a

Entry	Ratio	$M_{(A_2B_1)_nA_2-N_3}$ (g/mol)	$D_{(A_2B_1)_nA_2-N_3}$	time (h)	Conv. ^b (%)	$M_{n,GPC}$ ^c (g/mol)	D ^c
1	1/1/0.2/1	6500	1.21	12	99.9	7600	1.35

^aReaction conditions: [(AB)_nA-N₃]₀/[PBiB]₀/[CuBr]₀/[PMDETA]₀, [(A₂B₁)_nA₂-N₃]₀ means moles of attached -N₃ groups to (A₂B₁)_nA₂ main chain. $m_{(AB)_nA} = 0.2$ g, $V_{\text{toluene}} = 3.0$ mL, T = 25 °C. ^bReaction conversion estimated by ¹H NMR spectra. ^cNumber-average molar mass ($M_{n,GPC}$) and molar mass dispersity (D) were determined by GPC using linear PMMA as calibration standard in THF.

Table S5. Graft polymerization of MA from macroinitiator (A₂B₁)_nA₂-Br via ATRP with different temperature^a

Entry	T (°C)	Conv. ^b (%)	$M_{n,theo}$ ^c (g/mol)	$M_{n,GPC}$ ^d (g/mol)	D ^d
1	25	--	--	--	--
2	50	--	--	--	--
3	90	74.5	62100	33600	1.72

^aPolymerization conditions: [MA]₀/[(A₂B₁)_nA₂-Br]₀/[CuBr]₀/[PMDETA]₀ = 50/1/0.2/1, [(A₂B₁)_nA₂-Br]₀ means moles of attached -Br groups to (A₂B₁)_nA₂ main chain. $V_{\text{monomer}} = 0.5$ mL, $V_{\text{toluene}} = 2.0$ mL. $M_{(A_2B_1)_nA_2-Br} = 7600$ g/mol, $D = 1.35$. ^bConversion of the monomer was estimated by ¹H NMR spectra. ^cTheoretical M_n of graft copolymers were calculated from monomer conversions. ^d $M_{n,GPC}$ and D were determined by GPC using linear PMMA as calibration standard in THF.

Table S6. The kinetics of the ATRP process of MA with different polymerization time^a

Entry	time (h)	Conv. ^b (%)	$M_{n,theo}^c$ (g/mol)	$M_{n,GPC}^d$ (g/mol)	D^d
1	0	--	--	12600	1.30
2	4	8.8	31700	17500	1.52
3	8	14.5	41500	18400	1.42
4	12	21.5	53600	20400	1.41
5	24	28.9	66300	22600	1.42
6	36	29.4	67200	24000	1.42

^aPolymerization conditions: $[MA]_0/[PBiB]_0/[(A_2B_1)_nA_2-N_3]_0/[CuBr]_0/[PMDETA]_0 = 100/1/1/0.2/1$, $[(A_2B_1)_nA_2-N_3]_0$ means moles of attached $-N_3$ groups to $(A_2B_1)_nA_2$ main chain. $V_{monomer} = 2.5$ mL, $V_{toluene} = 10.0$ mL, $T = 25$ °C. $M_{(A_2B_1)_nA_2-N_3} = 12500$ g/mol, $D = 1.73$. ^bConversion of the monomer was estimated by ¹H NMR spectra. ^cTheoretical M_n of graft copolymers were calculated from monomer conversions. ^d $M_{n,GPC}$ and D were determined by GPC using linear PMMA as calibration standard in THF.

Table S7. The kinetics of the ATRP process of PEGMA with different polymerization time^a

Entry	time (h)	Conv. ^b (%)	$M_{n,theo}^c$ (g/mol)	$M_{n,GPC}^d$ (g/mol)	D^d
1	0.0	--	--	8700	1.13
2	1.0	1.8	14400	16700	1.18
3	2.0	5.6	22400	24100	1.20
4	4.5	27.7	69400	37700	1.22
5	6.0	37.0	89200	47400	1.23
6	8.0	51.3	119500	51500	1.26
7	10.0	63.4	145300	58700	1.32
8	11.0	66.9	152700	62300	1.32
9	12.0	71.2	161800	63900	1.31
10	24.0	89.0	199700	74700	1.38

^aPolymerization conditions: $[PEGMA]_0/[PBiB]_0/[(A_2B_1)_nA_2-N_3]_0/[CuBr]_0/[PMDETA]_0 = 50/1/1/0.2/1$, $[(A_2B_1)_nA_2-N_3]_0$ means moles of attached $-N_3$ groups to $(A_2B_1)_nA_2$ main chain. $V_{monomer} = 3.0$ mL, $V_{toluene} = 9.0$ mL, $T = 25$ °C. $M_{(A_2B_1)_nA_2-N_3} = 8800$ g/mol, $D = 1.24$. ^bConversion of the monomer was estimated by ¹H NMR spectra. ^cTheoretical M_n of graft copolymers were calculated from monomer conversions. ^d $M_{n,GPC}$ and D were determined by GPC using linear PS as calibration standard in DMF (with 0.1 wt% LiBr).

Table S8. Synthesis of fluorinated graft copolymer (AB)_nA-g-PPEGMA with various fluorinated backbone^a

Entry	(AB) _n A-N ₃	$M_{(AB)_nA-N_3}$ (g/mol)	$D_{(AB)_nA-N_3}$	time (h)	Conv. ^b (%)	$M_{n,GPC}^c$ (g/mol)	D^c
1	(A ₁ B ₁) _n A ₁ -N ₃	5700	1.66	9	76.6	123000	1.62
2	(A ₃ B ₁) _n A ₃ -N ₃	9100	1.58	9	65.5	127000	1.50
3	(A ₂ B ₂) _n A ₂ -N ₃	11800	2.01	8	33.6	39600	1.72
4	(A ₁ B ₃) _n A ₁ -N ₃	8700	1.65	9	34.8	55500	1.51
5	(A ₂ B ₃) _n A ₁ -N ₃	7500	1.52	11	71.7	78300	1.49

^aPolymerization conditions: [PEGMA]₀/[PBiB]₀/[(AB)_nA-N₃]₀/[CuBr]₀/[PMDETA]₀ = 50/1/1/0.2/1, [(AB)_nA-N₃]₀ means moles of attached -N₃ groups to (AB)_nA main chain. $V_{monomer}$ = 1.0 mL, $V_{toluene}$ = 3.0 mL, T = 25 °C.

^bConversion of the monomer was estimated by ¹H NMR spectra. ^c $M_{n,GPC}$ and D were determined by GPC using linear PS as calibration standard in DMF (with 0.1 wt% LiBr).

2.2. Figures

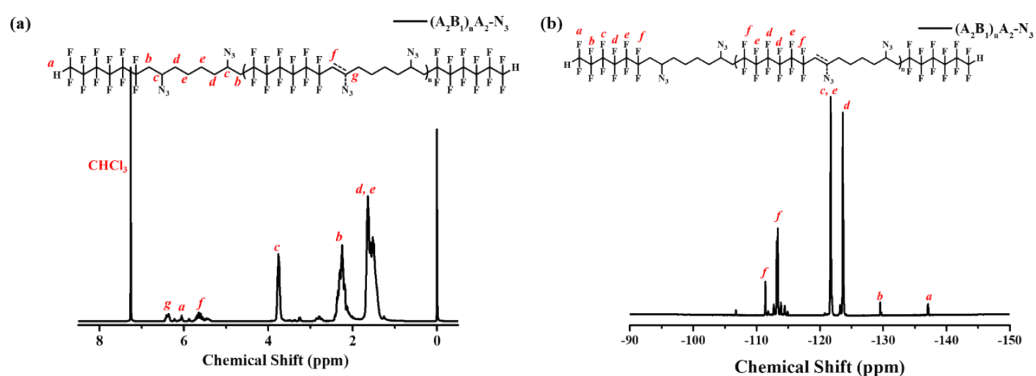


Fig. S1 (a) 1H NMR spectrum and (b) ^{19}F NMR spectrum of the semi-fluorinated alternating copolymer $(A_2B_1)_nA_2-N_3$ in $CDCl_3$.

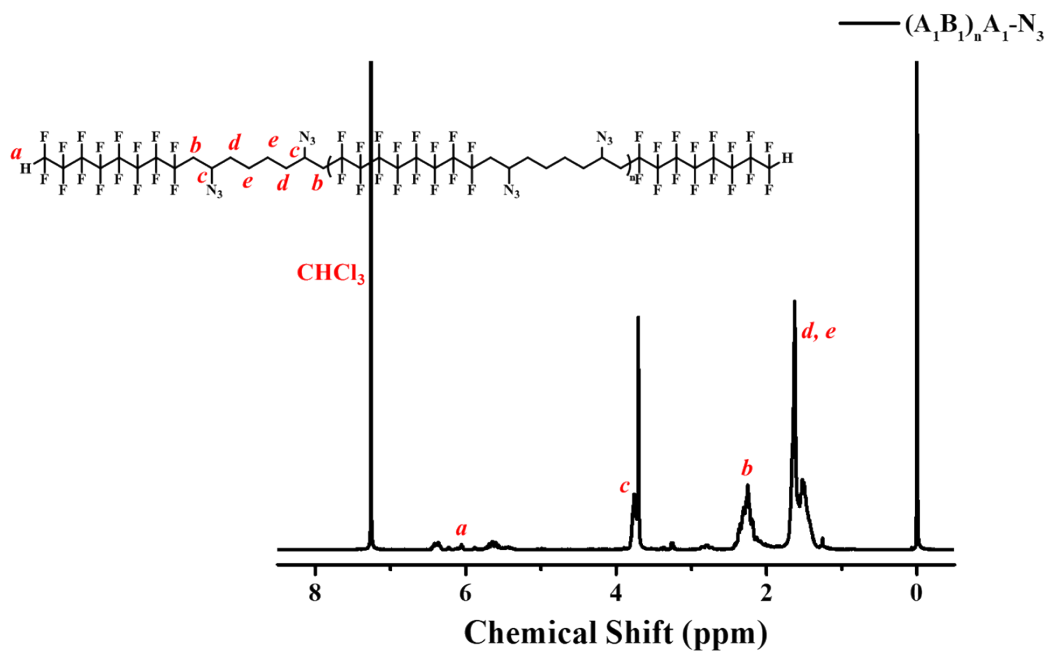


Fig. S2 1H NMR spectrum of semi-fluorinated alternating copolymer $(A_1B_1)_nA_1-N_3$ in $CDCl_3$.

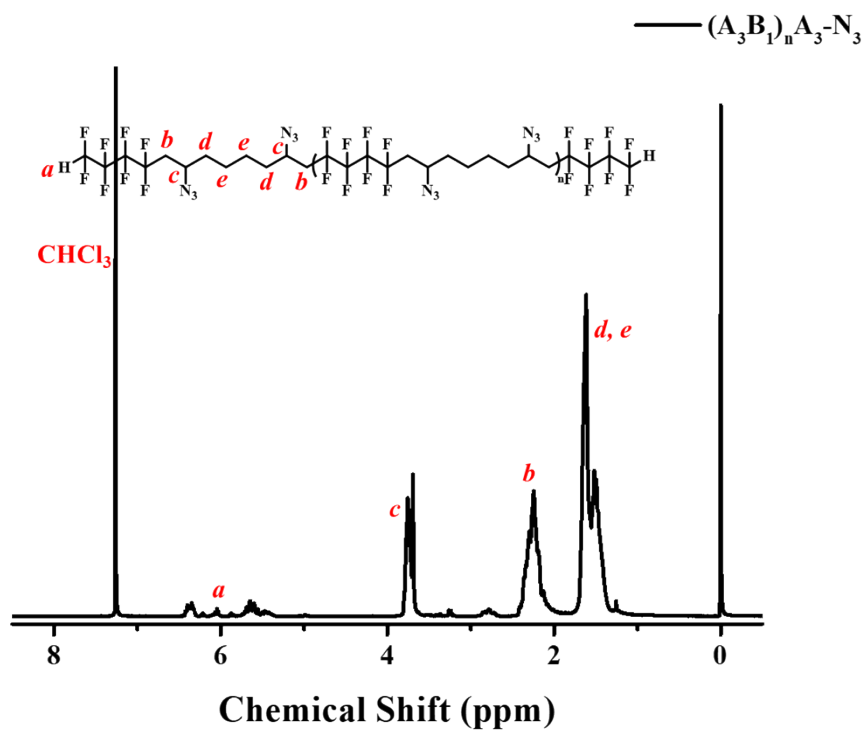


Fig. S3 ^1H NMR spectrum of semi-fluorinated alternating copolymer $(A_3B_1)_n A_3-N_3$ in CDCl_3 .

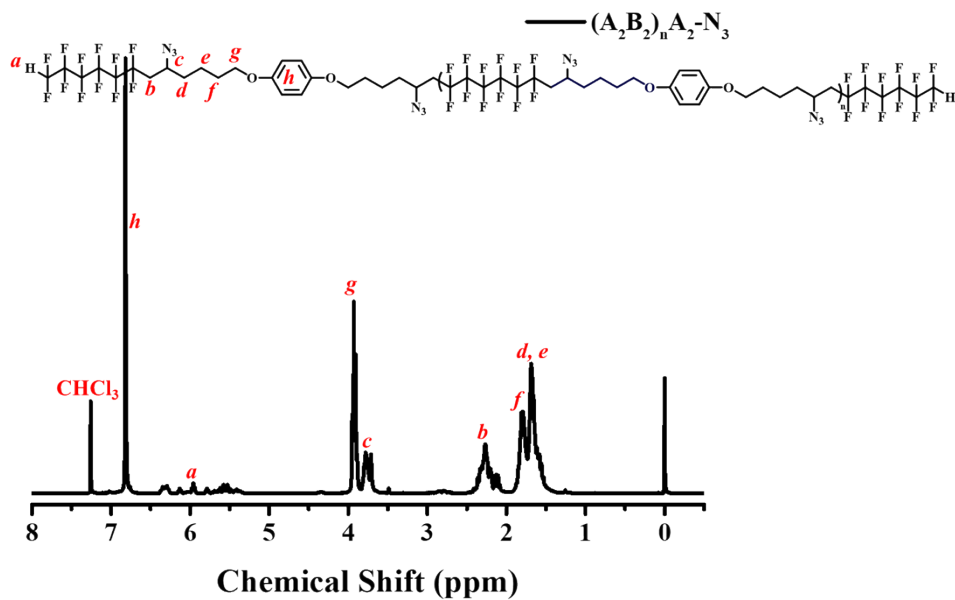


Fig. S4 ^1H NMR spectrum of semi-fluorinated alternating copolymer $(A_2B_2)_n A_2-N_3$ in CDCl_3 .

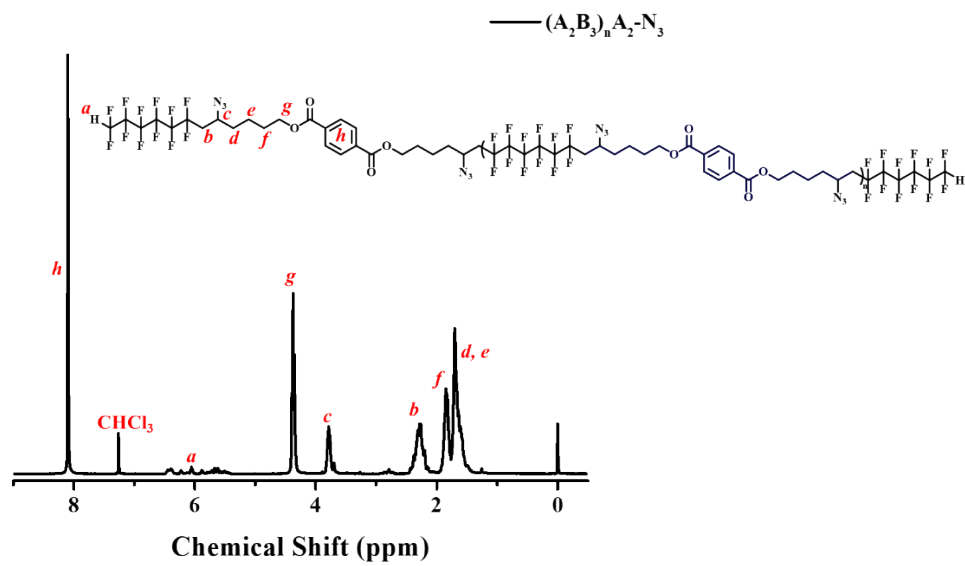


Fig. S5 ^1H NMR spectrum of semi-fluorinated alternating copolymer $(A_2B_3)_n A_2-N_3$ in CDCl_3 .

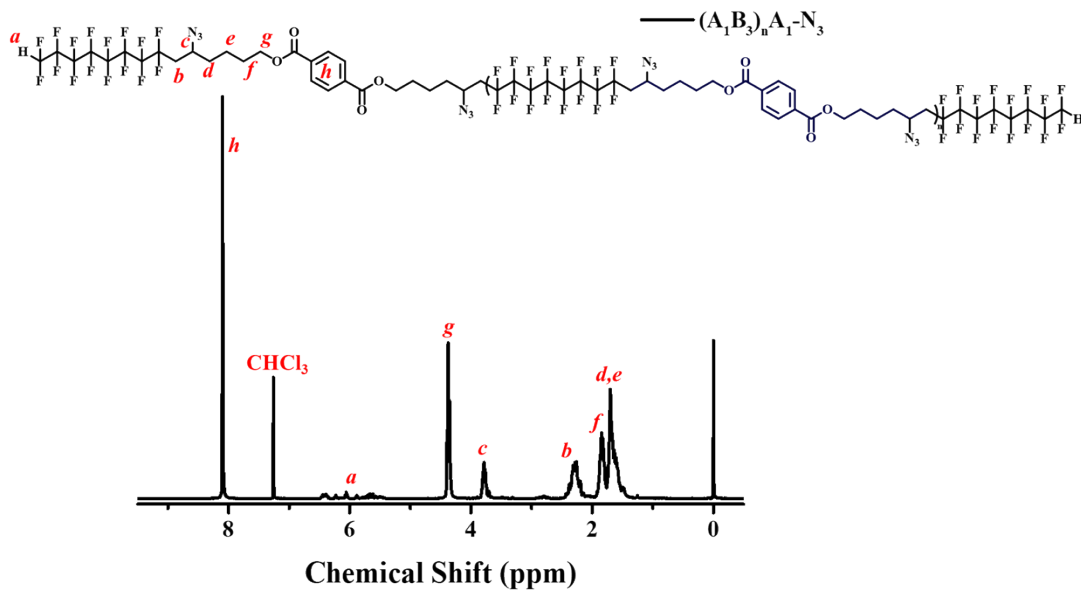


Fig. S6 ^1H NMR spectrum of semi-fluorinated alternating copolymer $(A_1B_3)_n A_1-N_3$ in CDCl_3 .

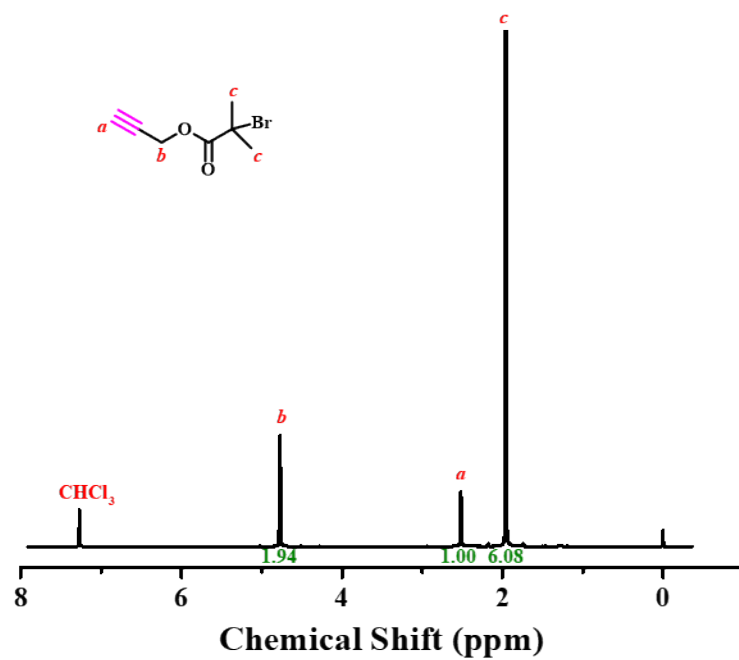


Fig. S7 ^1H NMR spectrum of PBiB in CDCl_3 .

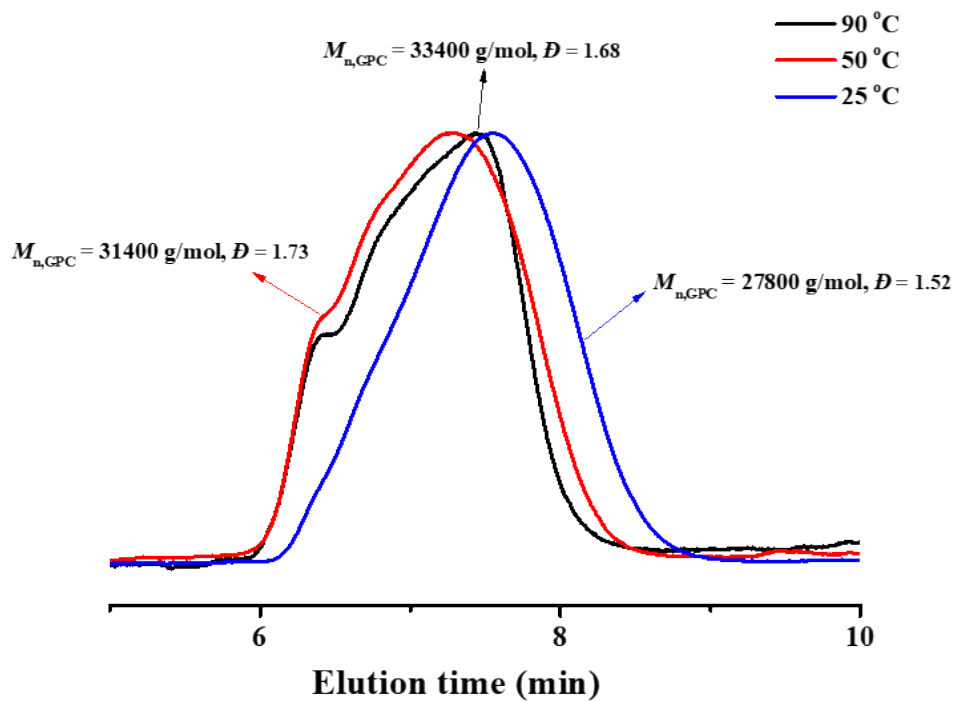


Fig. S8 GPC traces of graft copolymers $(\text{A}_2\text{B}_1)_n\text{A}_2\text{-g-PMA}$ with different reaction temperatures.

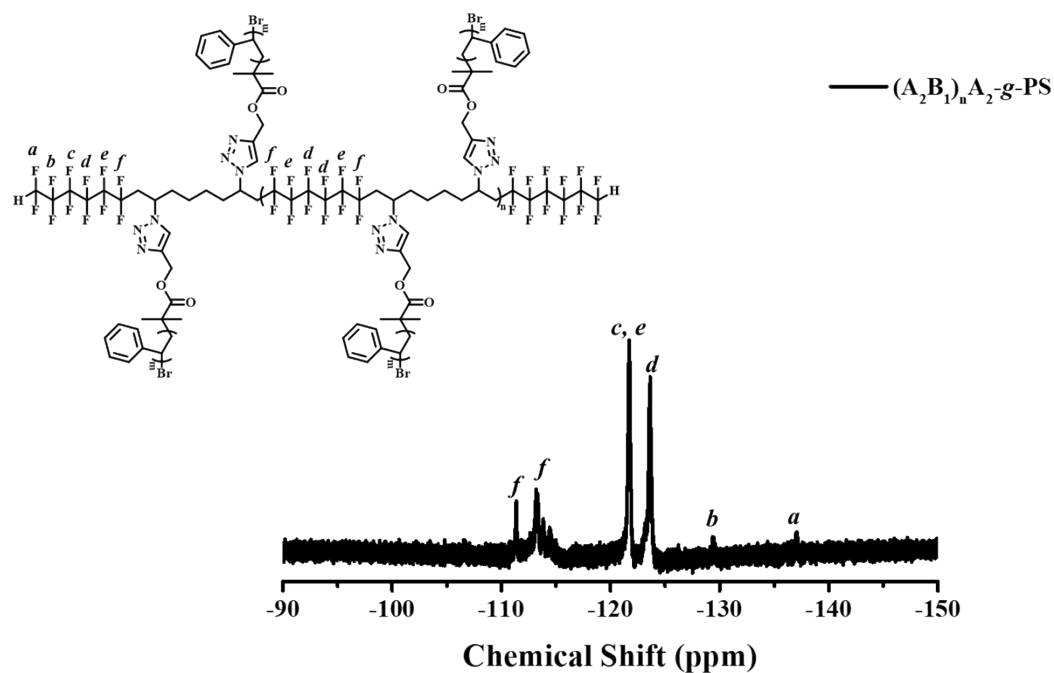


Fig. S9 ^{19}F NMR spectrum of the fluorinated graft copolymer $(A_2B_1)_nA_2$ -g-PS in CDCl_3 .

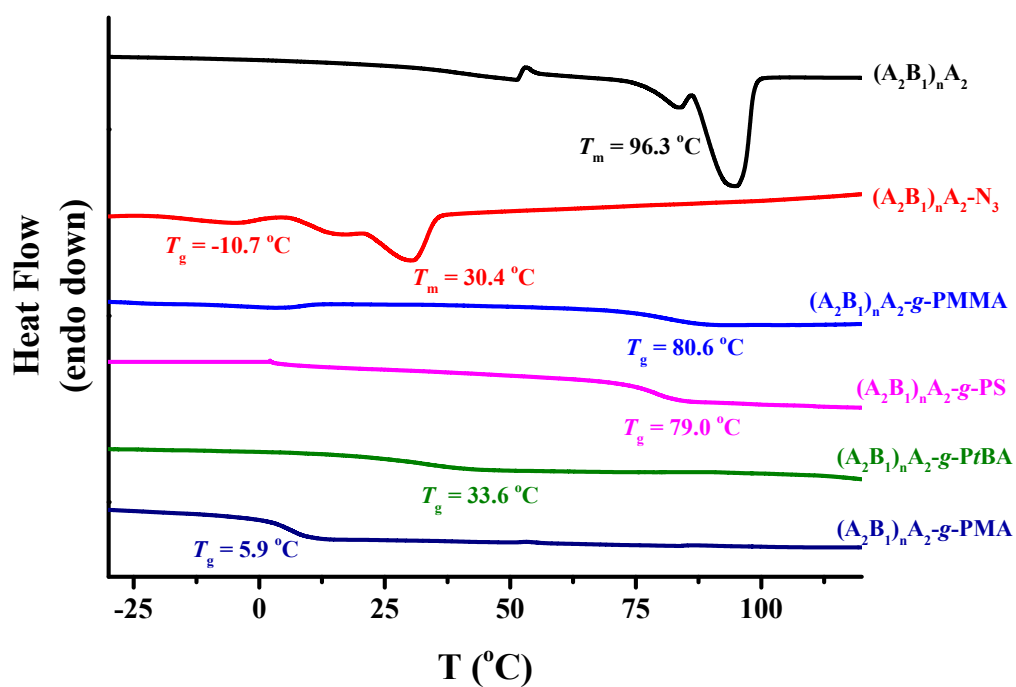


Fig. S10 DSC curves of semi-fluorinated alternating copolymers $(A_2B_1)_nA_2$, $(A_2B_1)_nA_2$ -N₃ and fluorinated graft copolymers with different monomers.

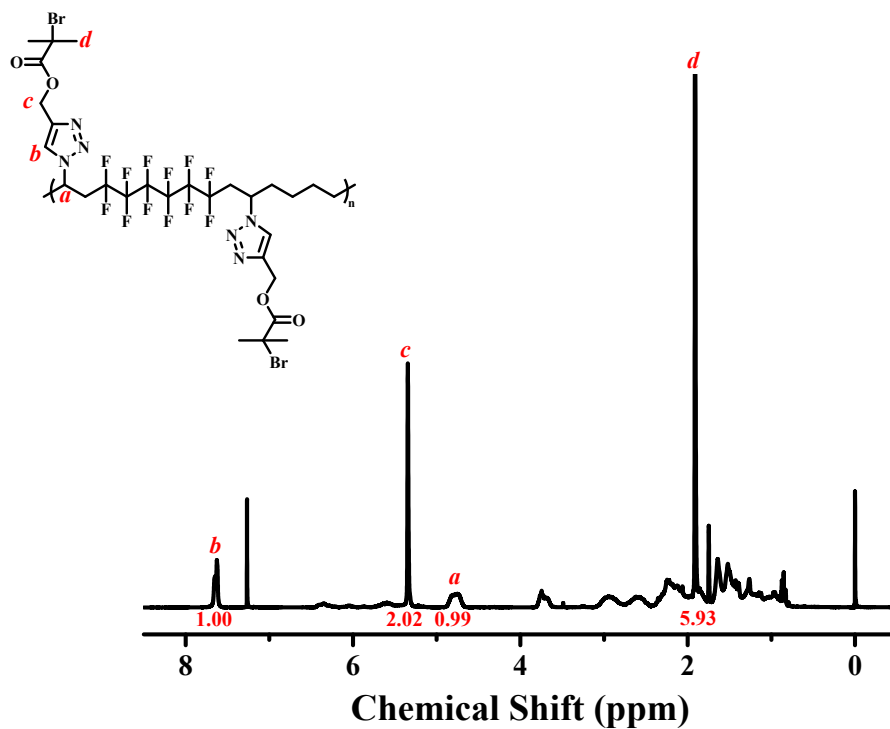


Fig. S11 1H NMR spectrum of the macroinitiator $(A_2B_1)_nA_2-Br$ in $CDCl_3$.

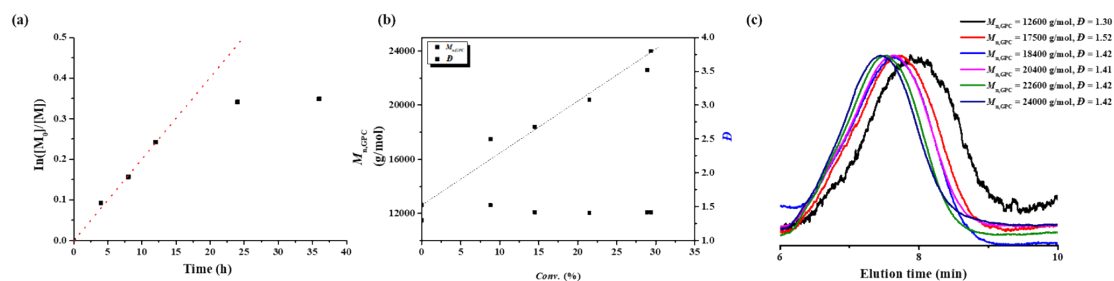


Fig. S12 (a) $\ln([M]_0/[M])$ as a function of time, (b) number-average molar mass ($M_{n,GPC}$) and molar mass dispersity (D) versus monomer conversion, (c) GPC traces for “one-pot” CuAAC reaction and ATRP of MA. Polymerization conditions: $[MA]_0/[PBiB]_0/[(A_2B_1)_nA_2-N_3]_0/[CuBr]_0/[PMDETA]_0 = 100/1/1/0.2/1$, $V_{MA} = 2.5$ mL, $V_{toluene} = 10.0$ mL, $T = 25$ °C, $M_{(A_2B_1)_nA_2-N_3} = 12500$ g/mol, $D = 1.73$.

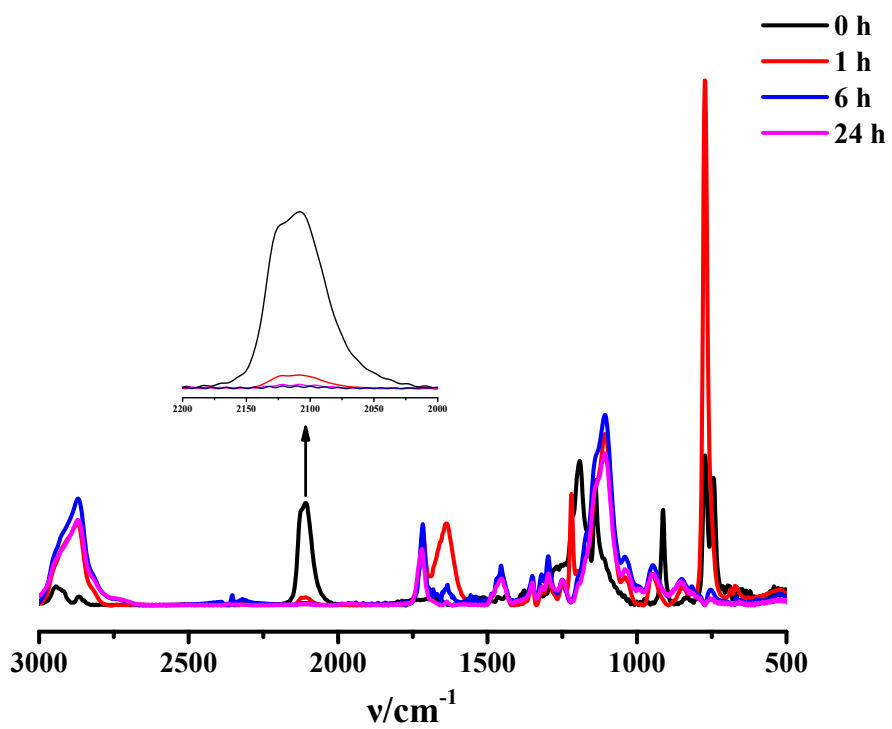


Fig. S13 The FT-IR spectra of $(A_2B_1)_nA_2$ -g-PPEGMA via “one-pot” process of CuAAC reaction and ATRP with different polymerization times.

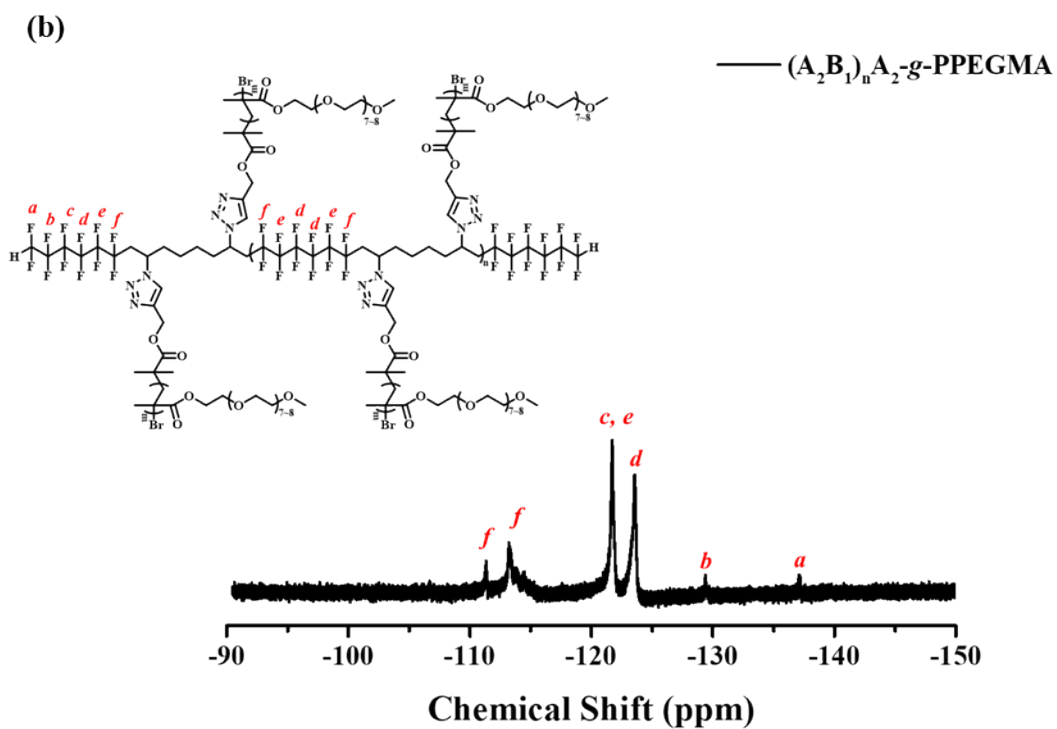
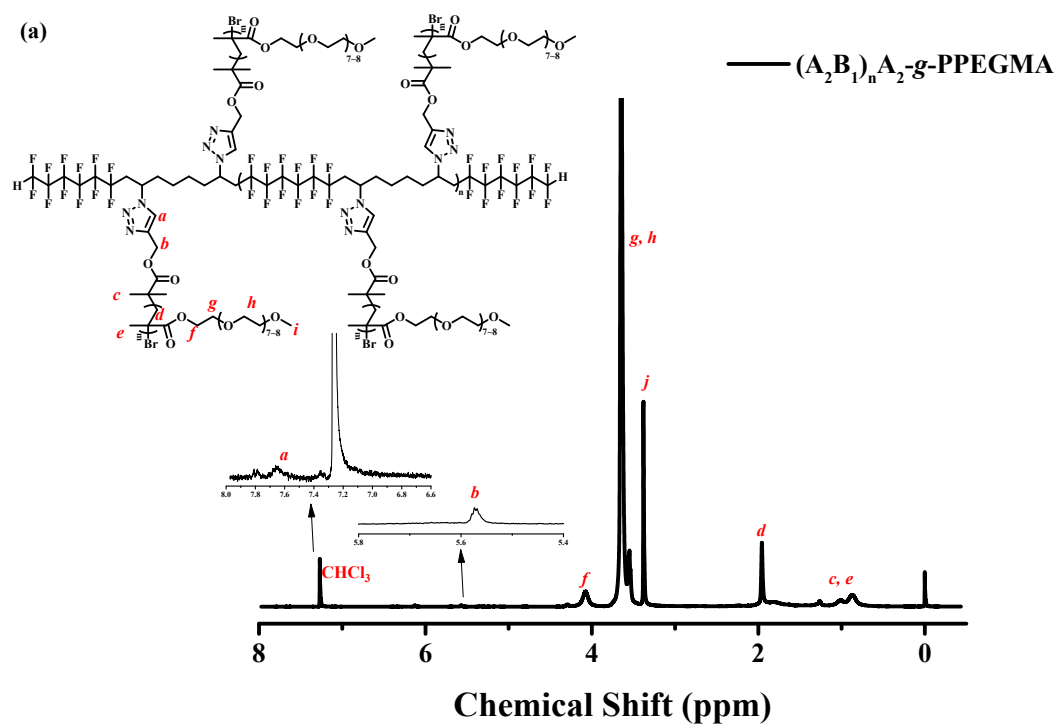


Fig. S14 (a) ^1H NMR spectra and (b) ^{19}F NMR spectrum of the fluorinated graft copolymer $(A_2B_1)_n A_2$ -g-PPEGMA in CDCl_3 .

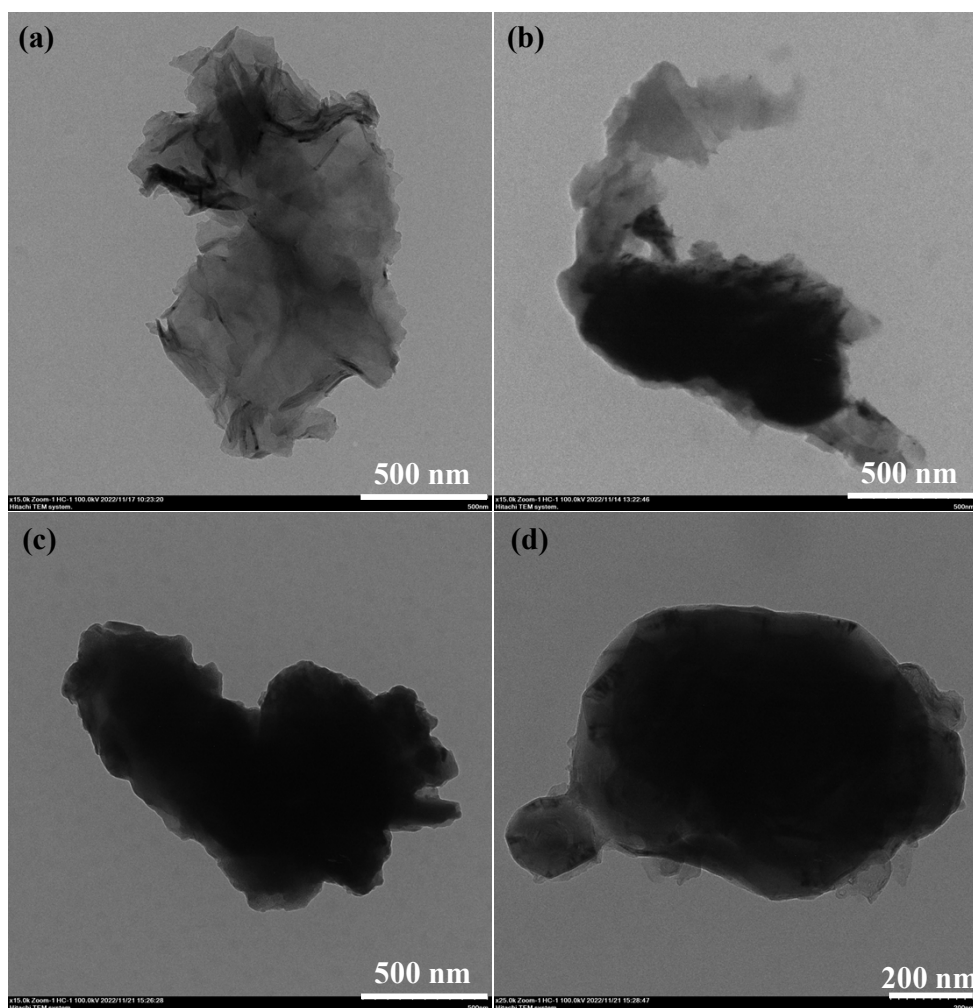


Fig. S15 TEM images of fluorinated graft copolymer $(A_1B_3)_nA_1$ -g-PPEGMA ($M_{n,GPC} = 55500$ g/mol, $D = 1.51$) and $(A_2B_3)_nA_2$ -g-PPEGMA ($M_{n,GPC} = 78300$ g/mol, $D = 1.49$) aqueous solution (0.5 mg/mL).

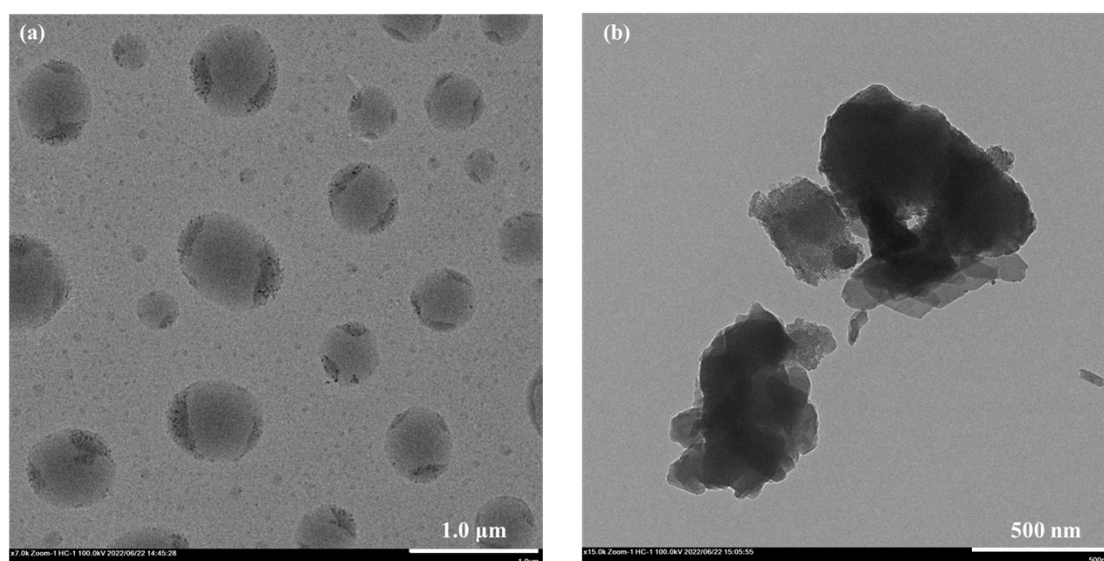


Fig. S16 TEM images of $(A_2B_1)_nA_2$ -g-PPEGMA ($M_{n,GPC} = 80000$ g/mol, $D = 1.46$) with a concentration of 0.5 mg/mL (a) THF/H₂O and (b) DMF/H₂O mixed solution.

References

1. E. Murtezi and Y. Yagci, *Macromol. Rapid Commun.*, 2014, **35**, 1782-1787.
2. J. Cheng, K. Tu, E. He, J. Wang, L. Zhang, Z. Cheng and X. Zhu, *Polym. Chem.*, 2020, **11**, 7497-7505.