

Supporting Information

Synthesis and versatile postpolymerization modification of couplable A(BC)_mD heterografted comblike block quaterpolymers

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Experimental section

Materials

All solvents, monomers, and other chemicals were purchased from Sigma-Aldrich unless otherwise stated. ϵ -Caprolactone (CL, 99%) was distilled from calcium hydride under reduced pressure. Styrene (St, 99%), 4-vinylbenzyl chloride (VBC, 90%), *N,N*-dimethylaminoethyl methacrylate (DMA, 99%), methyl acrylate (MA, 99%) and *tert*-butyl acrylate (*t*BA, 98%) were passed through a basic alumina column to remove the inhibitor. *N*-Isopropylacrylamide (NIPAM, 97%) was recrystallized twice from mixtures of hexane and toluene. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from ethanol. Monomethoxy poly(ethylene glycol) with $M_n = 750$ g/mol (MPEG, Fluka) was dried by azeotropic distillation in the presence of toluene. Propargyl alcohol (99%), propargyl bromide (99%), 3-bromopropanol (99%), and benzyl bromide (99%) were distilled under reduced pressure. *N,N'*-Dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received. Dichloromethane (DCM) and dioxane were dried and distilled over CaH₂. Tetrahydrofuran (THF) and toluene were distilled over sodium and benzophenone and stored under nitrogen. Bromide-functionalized polymers PSt-Br ($M_{n,NMR} = 2480$ g/mol, PDI = 1.10), PNIPAM-Br ($M_{n,NMR} = 3030$ g/mol, PDI = 1.06) and P*t*BA-Br ($M_{n,NMR} = 5050$ g/mol, PDI = 1.15), and PDMA grafted silica particles (SiO₂-*g*-PDMA) were samples as previously described.¹ Vinylbenzyl-terminated PEG (St-PEG),² maleimidic poly(ϵ -caprolactone) (MI-PCL, $M_{n,GPC} = 4200$ g/mol, PDI = 1.12, and $DP_{NMR} = 26.5$),³ prop-2-ynyl 4-(benzodithiioyl)-4-cyanopentanoate (PBCP),⁴ 4-cyanopentanoic acid dithiobenzoate (4-CPDB),⁵ *N*-(2-hydroxyethyl) maleimide,⁶ and 3-azido-1-propanol⁷ were synthesized and purified according to literature procedures.

Synthesis of A(BC)_mD copolymers

PBCP (0.159 g, 0.50 mmol), DMA (2.36 g, 15 mmol), and AIBN (16.4 mg, 0.10 mmol) were added to a Schlenk tube, and dry dioxane was added until the total volume was 7.5 mL. The contents were degassed with bubbled nitrogen for 15 min, and then the polymerization was performed at 70 °C for 20 h. The mixture was concentrated and precipitated into cold hexane, and 2.17 g (85.2% conversion) of PDMA was obtained. $M_{n, GPC} = 3120$ g/mol, PDI = 1.06, and $M_{n, NMR} = 4260$ g/mol. ¹H NMR (CDCl₃): δ 7.86, 7.52, 7.36 (PhH), 4.71 (terminal CH₂O), 4.06 (CH₂O of PDMA), 2.56 (CH₂N of PDMA and terminal CH), 2.28 ((CH₃)₂N of PDMA and terminal CH₂CO), 0.6-2.2 (other CH₂ and CH₃ resulting from CTA and PDMA backbone). FT-IR (KBr): 3432, 2947, 2861, 2822, 2770, 1728, 1459, 1386, 1365, 1272, 1241, 1150, 1099, 1059, 1043, 1017, 963, 851, 780, 748, 692 cm⁻¹.

PDMA (0.85 g, 0.20 mmol), St-PEG (1.74 g, 2.0 mmol), MI-PCL (6.32 g, 2.0 mmol), and AIBN (6.6 mg, 0.04 mmol) were added to a Schlenk tube, and dry dioxane was added until the total volume was 13.3 mL. The contents were degassed with bubbled nitrogen for 30 min, and the polymerization was performed at 70 °C for 18 h. The mixture was concentrated and precipitated into cold hexane, and 6.51 g (70.2% conversion) of PDMA(PEG-*alt*-PCL)_m (B1) was isolated. $M_{n, LS} = 30600$ g/mol, PDI = 1.14, and $M_{n, NMR} = 31800$ g/mol. ¹H NMR (CDCl₃): δ 6.5-8.0 (ArH of St-PEG unit and terminal PhH), 4.71 (terminal CH₂O), 4.51 (ArCH₂O of St-PEG unit), 4.06 (CH₂O of PDMA and MI-PCL unit), 3.65 (CH₂CH₂O of St-PEG unit, and CH and CH₂N of MI-PCL unit), 3.38 (CH₃O of St-PEG unit), 2.57 (CH₂N of PDMA and terminal CH), 2.31 ((CH₃)₂N of PDMA, terminal CH₂CO, and CH₂CO of MI-PCL unit), 0.6-2.2 (other CH, CH₂ and CH₃ resulting from CTA and polymer backbone). FT-IR (KBr): 3439, 2945, 2866, 2772, 1724, 1638, 1471, 1420, 1398, 1368, 1296, 1245, 1193, 1108, 1046, 962, 934, 841, 732, 710 cm⁻¹.

Last, B1 was used as a macro CTA to mediate chain extension polymerization of vinyl monomers. In a typical polymerization (run 3 of Table 1), B1 (0.636 g, 0.020 mmol), NIPAM (0.340 g, 3.0 mmol), and AIBN (0.7 mg, 0.004 mmol) were added to a Schlenk tube, and dry dioxane was added until the total volume was 3.0 mL. The contents were stirred for 2 min, degassed with bubbled nitrogen for 10 min, and subjected to polymerization at 80 °C for 20 h. The polymerization solution was precipitated into cold hexane thrice, and 0.829 g (56.9% conversion) of PDMA(PEG-*alt*-PCL)_mPNIPAM copolymer (B2) was obtained after vacuum drying. $M_{n, LS} = 41800$ g/mol, PDI = 1.20, and $M_{n, NMR} = 41300$ g/mol. Other A(BC)_mD quaterpolymers B3-B6 were synthesized and purified according to similar procedures.

PDMA(PEG-*alt*-PCL)_mPNIPAM (B2): ¹H NMR (CDCl₃): δ 5.7-8.0 (terminal PhH, ArH of St-PEG unit, and NH of PNIPAM), 4.71 (terminal CH₂O), 4.51 (ArCH₂O of St-PEG unit), 4.06 (CH₂O of PDMA and MI-PCL unit, and CH of PNIPAM), 3.65 (CH₂CH₂O of St-PEG unit, and CH and CH₂N of MI-PCL unit), 3.38 (CH₃O of St-PEG unit), 2.57 (CH₂N of PDMA and terminal CH), 0.6-2.4 ((CH₃)₂N

of PDMA, terminal CH_2CO , CH_2CO of MI-PCL unit, $CHCO$ of PNIPAM and other CH , CH_2 and CH_3 originating from CTA and polymer backbone). FT-IR (KBr): 3440, 3066, 2943, 2867, 2822, 2733, 1725, 1649, 1545, 1460, 1385, 1367, 1295, 1244, 1192, 1107, 1046, 961, 933, 841, 732, 710 cm^{-1} .

PDMA(PEG-*alt*-PCL)_mPtBA (B3-B5): 1H NMR ($CDCl_3$): δ 5.7-8.0 (terminal PhH, and ArH of St-PEG unit), 4.71 (terminal CH_2O), 4.51 (Ar CH_2O of St-PEG unit), 4.06 (CH_2O of PDMA and MI-PCL unit), 3.65 (CH_2CH_2O of St-PEG unit, and CH and CH_2N of MI-PCL unit), 3.38 (CH_3O of St-PEG unit), 2.57 (CH_2N of PDMA and terminal CH), 0.6-2.4 ($(CH_3)_2N$ of PDMA, terminal CH_2CO , CH_2CO of MI-PCL unit, and other CH , CH_2 and CH_3 originating from CTA, polymer backbone and PtBA). FT-IR (KBr): 3438, 2945, 2895, 2866, 2822, 2772, 1725, 1471, 1420, 1397, 1368, 1296, 1245, 1193, 1152, 1108, 1046, 962, 934, 845, 732, 709 cm^{-1} .

PDMA(PEG-*alt*-PCL)_mPMA (B6): 1H NMR ($CDCl_3$): δ 5.7-8.0 (terminal PhH, and ArH of St-PEG unit), 4.71 (terminal CH_2O), 4.51 (Ar CH_2O of St-PEG unit), 4.06 (CH_2O of PDMA and MI-PCL unit), 3.65 (CH_2CH_2O of St-PEG unit, CH and CH_2N of MI-PCL unit, and CH_3O of PMA), 3.38 (CH_3O of St-PEG unit), 2.57 (CH_2N of PDMA and terminal CH), 0.6-2.4 ($(CH_3)_2N$ of PDMA, terminal CH_2CO , CH_2CO of MI-PCL unit, and other CH , CH_2 and CH_3 originating from CTA, polymer backbone and PMA). FT-IR (KBr): 3437, 2946, 2895, 2866, 2824, 2772, 1725, 1459, 1420, 1398, 1369, 1296, 1245, 1193, 1166, 1108, 1047, 962, 841, 732, 710 cm^{-1} .

Synthesis of di(3-azidopropyl) 4,4'-azobis(4-cyanovalerate)

To a round flask were added 3-azido-1-propanol (2.53 g, 25 mmol), 4,4'-azobis(4-cyanovaleric acid) (2.78 g, 10 mmol), DMAP (0.122 g, 1.0 mmol) and 100 mL of DCM under nitrogen. The solution was stirred for 10 min, cooled with an ice-water bath, and then 50 mL of DCM solution containing 5.15 g (25.0 mmol) of DCC was added dropwise into the flask. After that, the reaction mixture was further stirred at room temperature for 24 h. The crude product was filtered, concentrated and subjected to purification by flash column chromatography eluting with hexane/ethyl acetate (20:1), and DAAC was obtained in 87.1% yield (3.89 g).

1H NMR ($CDCl_3$): δ 4.21 (t, $J_{2,4}$, 4H, CH_2O), 3.41 (t, $J_{2,4}$, 4H, CH_2N_3), 2.3-2.7 (m, 8H, CH_2CH_2COO), 1.93 (m, 4H, $OCH_2CH_2CH_2N_3$), 1.74 and 1.69 (each s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 171.0 (C=O), 117.4 (CN), 71.7 (CH_2O), 61.8 (CH_2N_3), 47.9 (C-CN), 32.9 (OCH_2CH_2), 28.9 (CH_2CH_2COO), 27.8 (CH_2CH_2COO), 23.7 (CH_3). FT-IR (KBr): 2962, 2941, 2882, 2100, 1737, 1454, 1384, 1298, 1261, 1181, 1118, 1032, 885, 795 cm^{-1} .

Synthesis of azido and alkyne functionalized A(BC)_mD copolymers by end group transformation

To a Schlenk tube were added B2 (0.62 g, 15 μ mol), DAAC (0.34 g, 0.76 mmol), and 5.0 mL of dioxane under nitrogen, and the mixture was reacted at 90 °C for 10 h. The polymer solution was

concentrated and precipitated into mixture of hexane and diethyl ether, and 0.54 g (87% yield) of α -azido- ω -alkyne-functionalized A(BC)_mD1 copolymer was isolated.

To a round flask were added B2 (0.73 g, 0.12 mmol OH), triethylamine (0.61 g, 0.60 mmol), and 30 mL of THF under nitrogen, and then followed by slow addition of TsCl (1.14 g, 0.60 mmol) in 15 mL of THF. After stirring at ambient temperature for 30 h, the mixture was concentrated and precipitated into hexane. The resultant *p*-toluenesulfonyl-functionalized A(BC)_mD copolymer was dissolved into 5.0 mL of DMF, and followed by addition of NaN₃ (0.10 g, 1.5 mmol) to react at 50 °C for 30 h. The mixture was subjected to filtration, concentration and precipitation into hexane, and 0.56 g (77% yield) of A(BC)_mD2 with multiple azido moieties and one alkyne functionality was isolated.

Synthesis of (A(BC)_mD)_n comblike-linear multiblock copolymer and (A(BC)_mD)_x dendritic graft copolymer by CuAAC

In a typical run, A(BC)_mD1 (0.42 g, 10 μ mol), Cu(PPh₃)₃Br (19 mg, 20 μ mol), and DMF (4.0 mL) were added to a Schlenk tube. After degassing by three freeze–pump–thaw cycles, the reaction was conducted at 60 °C for 30 h. The mixture was concentrated, diluted with 30 mL of THF, and passed through alumina column. The polymer solution was concentrated under reduced pressure and precipitated into hexane. After vacuum drying, 0.36 g (86% yield) of (A(BC)_mD)_n was isolated. (A(BC)_mD)_x was synthesized and purified according to a similar procedure using A(BC)_mD2 as a raw material.

Synthesis of A'(BC)_mD copolymers

PDMA(PEG-*alt*-PCL)_mPMA copolymers grafted with propargyl bromide (G1), 3-bromopropanol (G2), and benzyl bromide (G3) were synthesized by quaternization process. In a typical run, B6 (50 mg) and propargyl bromide (100 mg) were dissolved in 1.0 mL of DMF under nitrogen, and the mixture was reacted at 60 °C overnight. After concentration and precipitation into hexane, alkyne-functionalized G1 was obtained.

Synthesis of AB_mC_nD-graft-E toothbrushlike copolymers

In a typical experiment (run 1 of Table 2), B6 (0.42 g, 0.26 mmol of DMA unit), PSt-Br (0.25 g, 0.10 mmol), and 3.3 mL of DMF were added to a Schlenk tube under nitrogen. The mixture was reacted at 60 °C for 30 h, and then 0.50 g of SiO₂-*g*-PDMA was added and further stirred for 18 h. After filtration, the filtrate was concentrated and precipitated into hexane, and 0.55 g (52% yield) of PDMA(PEG-*alt*-PCL)_mPMA-*graft*-PSt (G4) was isolated. $M_{n,LS} = 53600$ g/mol, PDI = 1.08, and $M_{n,NMR} = 54700$ g/mol. Other graft copolymers G5 (E = PNIPAM) and G6 (E = PtBA) were prepared and isolated according to similar procedures.

Characterization

The apparent number-average molecular weight ($M_{n,GPC}$) and polydispersity index (PDI) of macromonomers, PDMA and PM-Br were measured on a Waters 150-C gel permeation

chromatography (GPC) using three Ultrastyrigel columns (pore size 50, 100, and 1000 nm, with molecular weight ranges of 100–10000, 500–30000, and 5000–600000 g/mol, respectively) with 10 μm bead size at 35 °C. THF was used as an eluent at a flow rate of 1.0 mL/min, polystyrene samples were calibrated with PSt standard samples, and other samples were calibrated using PMMA standard samples. Gel permeation chromatography with multiple angle laser scattering detection (GPC-MALLS) systems was used to determine absolute number-average molecular weight ($M_{n,LS}$), polydispersity and solution viscosity of various copolymers. GPC was conducted in THF at 35 °C with a flow rate of 1.0 mL/min. Three TSK-GEL H-type columns (pore size 15, 30 and 200 Å, with molecular weight range of 100–1000, 300–20000 and 5000–400000 g/mol, respectively) with 5 μm bead size were used. Detection consisted of a RI detector (Optilab rEX), a multi-angle (14–145°) laser light scattering (MALLS) detector (DAWN HELEOS) with the He-Ne light wave length at 658.0 nm, and on-line viscosity detector (ViscoStar). The refractive index increment dn/dc for samples were measured off-line by Optilab rEX refractive index detector ($\lambda = 658 \text{ nm}$) at 25 °C using a series of different concentration solutions. Data were collected and processed by use of ASTRA software from Wyatt Technology, and molecular weights were determined by the triple detection method. The intrinsic viscosity of copolymer solutions in THF was measured using a viscosimetric detector connected to GPC system at 35 °C. ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Varian spectrometer at 25 °C using CDCl_3 as a solvent. Fourier Transform Infrared (FT-IR) spectra were recorded on a Perkin-Elmer 2000 spectrometer using KBr discs. Differential scanning calorimetry (DSC) analysis was performed under nitrogen atmosphere using a SDT 2960 Simultaneous DSC–TGA of TA Instruments, and the heating rate was 10 °C/min. Water contact angles of various films were measured on a SL200C contact angle measuring machine.

References

- 1 M. J. Zhang, H. H. Liu, W. Shao, C. N. Ye and Y. L. Zhao, *Macromolecules*, 2012, **45**, 9312–9325.
- 2 H. Zhu, G. H. Deng and Y. M. Chen, *Polymer*, 2008, **49**, 405–411.
- 3 M. J. Zhang, H. H. Liu, W. Shao, K. Miao and Y. L. Zhao, *Macromolecules*, 2013, **46**, 1325–1336.
- 4 M. Müllner, A. Schallon, A. Walther, R. Freitag and A. H. E. Müller, *Biomacromolecules*, 2010, **11**, 390–396.
- 5 Y. Mitsukami, M. S. Donovan, A. B. Lowe and C. L. McCormick, *Macromolecules*, 2001, **34**, 2248–2256.
- 6 G. Mantovani, F. Lecolley, L. Tao, D. M. Haddleton, J. Clerx, J. J. L. M. Cornelissen and K. Velonia, *J. Am. Chem. Soc.*, 2005, **127**, 2966–2973.
- 7 V. Ladmiral, T. M. Legge, Y. L. Zhao and S. Perrier, *Macromolecules*, 2008, **41**, 6728–6732.

Table S1. Solubility of PDMA(PEG-*alt*-PCL)_mPMA (B6), A'(BC)_mD (G1-G3) and PDMA(PEG-*alt*-PCL)_mPMA-*graft*-PM (G4-G6) copolymers in various solvents

Sample	methanol	acetone	water	toluene	hexane	diethyl ether	DCM	THF	DMF
B6	–	+	–	+	–	–	+	+	+
G1	–	+	±	+	–	–	+	+	+
G2	–	+	±	+	–	–	+	+	+
G3	±	+	±	+	–	–	+	±	+
G4	–	+	–	+	–	–	+	+	+
G5	±	+	±	–	–	–	+	+	+
G6	±	+	–	+	–	±	+	+	+

Solubility: + (soluble), ± (partly soluble, with solubility lower than 0.2 mg/mL) and – (insoluble).

Table S2. DSC results of various brushlike copolymer and their precursors

sample	T_m (°C)	T_g (°C)
MI-PCL	45.9	–
PDMA	–	17.0
B1	41.7	19.6
B2	38.7	19.2, 110.4
B3	40.5	9.2, 22.5
B4	38.0, 44.2	13.2
B5	40.0, 44.9	15.5, 27.1
B6	39.6, 44.0	19.7, 24.1
G4	39.3	8.0, 13.6
G5	39.4	4.1, 10.4
G6	42.3	9.6, 17.0

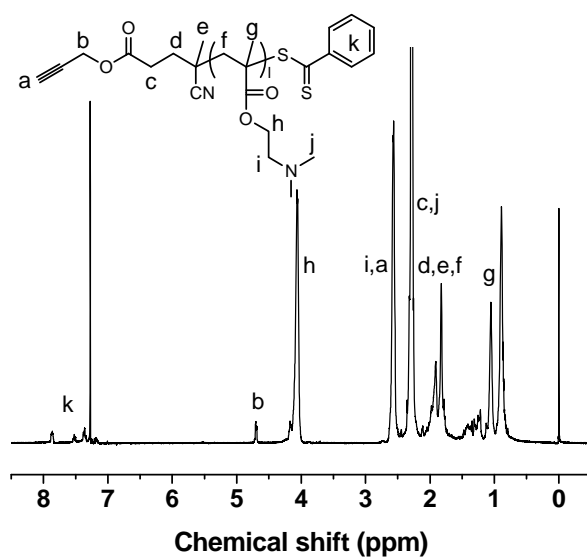


Fig. S1 ^1H NMR spectrum of PDMA ($l = 25.1$).

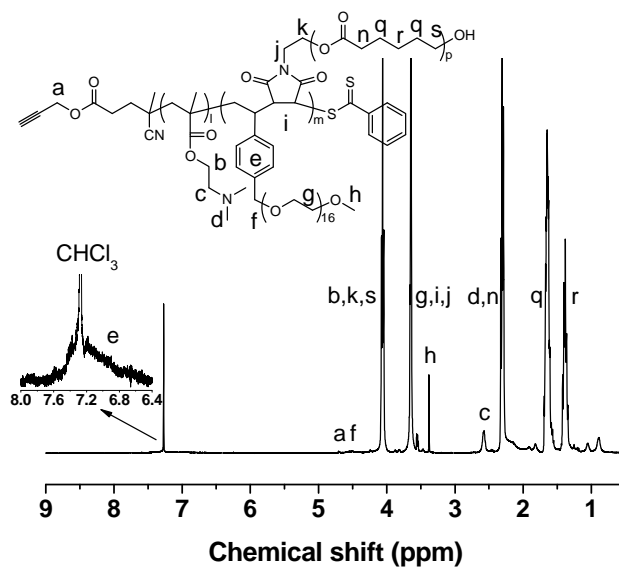


Fig. S2 ^1H NMR spectrum of PDMA(PEG-*alt*-PCL) $_m$ ($l = 25.1$, $m \approx 7.0$, $p = 26.5$) copolymer.

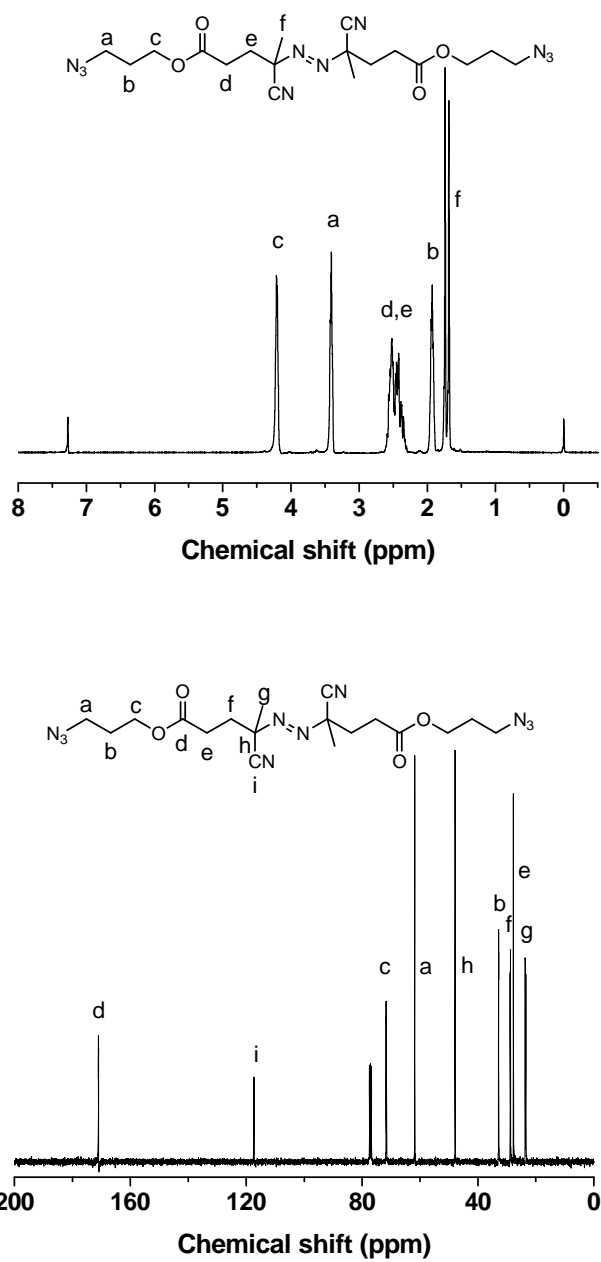


Fig. S3 ^1H (top) and ^{13}C (bottom) NMR spectra of DAAC.

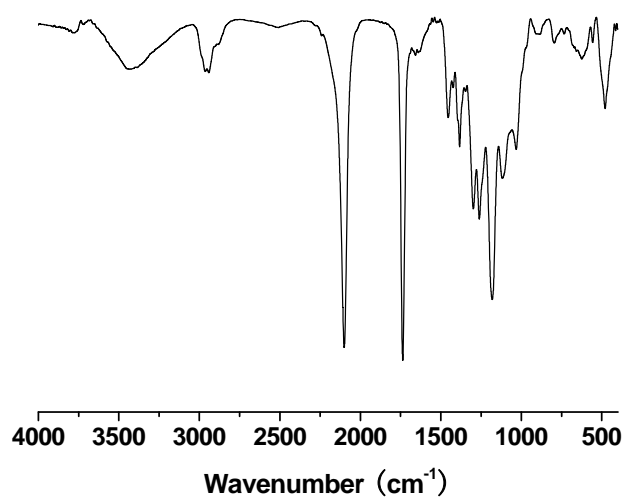


Fig. S4 IR spectrum of DAAC.

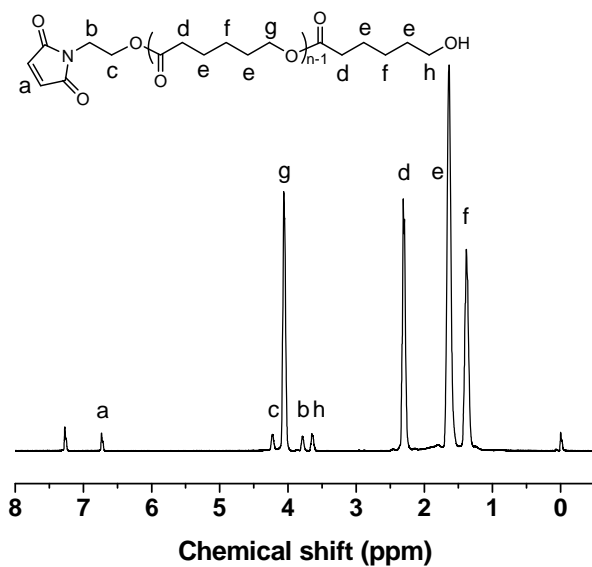


Fig. S5 ¹H NMR spectrum of MI-PCL.

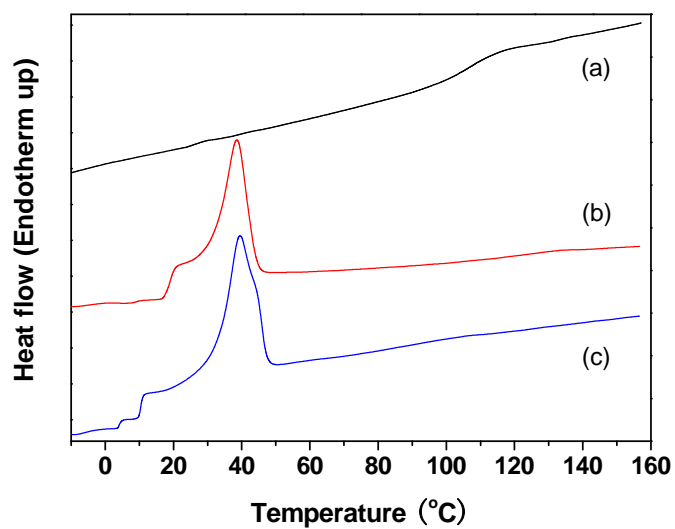


Fig. S6 DSC curves of PNIPAM-Br (a), PDMA(PEG-*alt*-PCL)_mPNIPAM (B2, b) and PDMA(PEG-*alt*-PCL)_mPMA-*graft*-PNIPAM (G5, c).

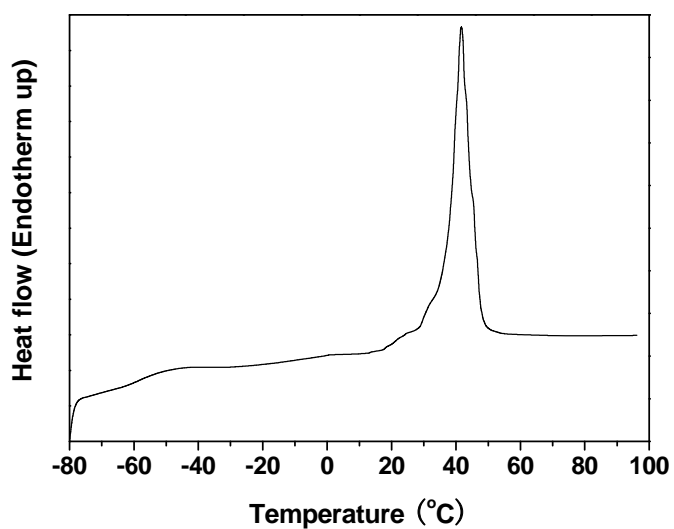


Fig. S7 DSC curve of PDMA(PEG-*alt*-PCL)_m copolymer (B1).

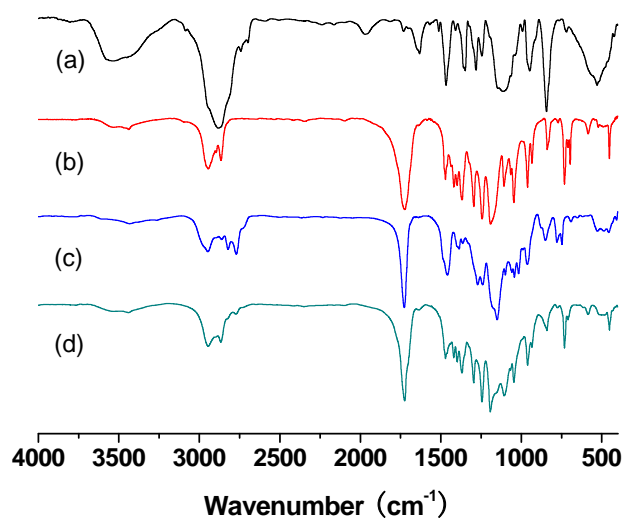


Fig. S8 IR spectra of St-PEG (a), MI-PCL (b), PDMA (c), and PDMA(PEG-*alt*-PCL)_m (B1, d).

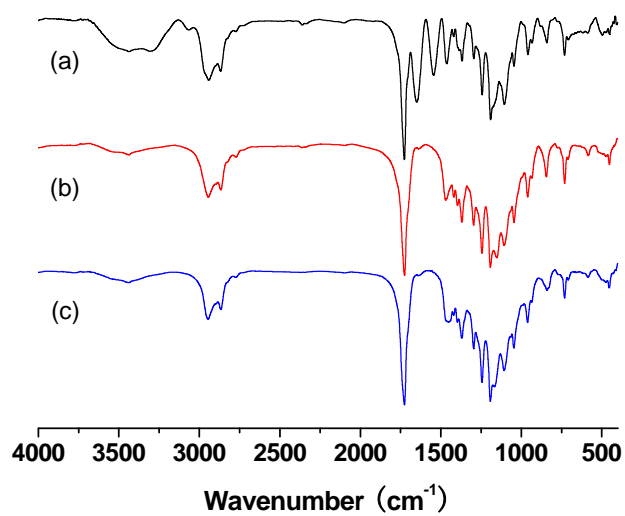


Fig. S9 IR spectra of PDMA(PEG-*alt*-PCL)_mPM copolymers (PM = PNIPAM (a), PtBA (b) and PMA (c)).

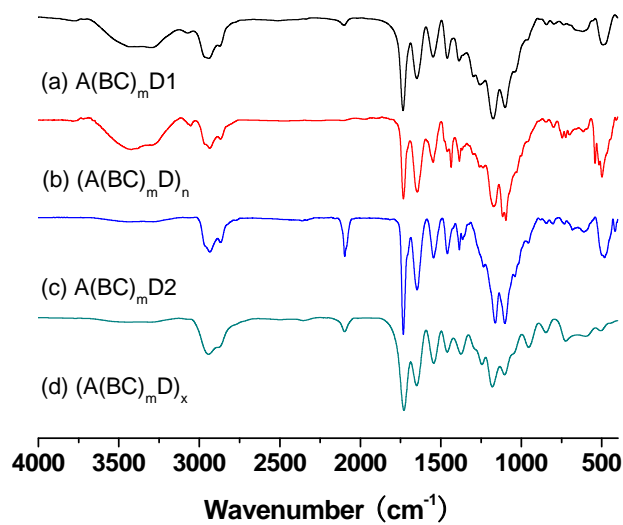


Fig. S10 IR spectra azido-modified $A(BC)_mD$ copolymers (a and c) and $(A(BC)_mD)_n$ (b) and $(A(BC)_mD)_x$ (d) copolymers obtained by click polymerization (A = PDMA, B = PEG, C = PCL, D = PNIPAM).

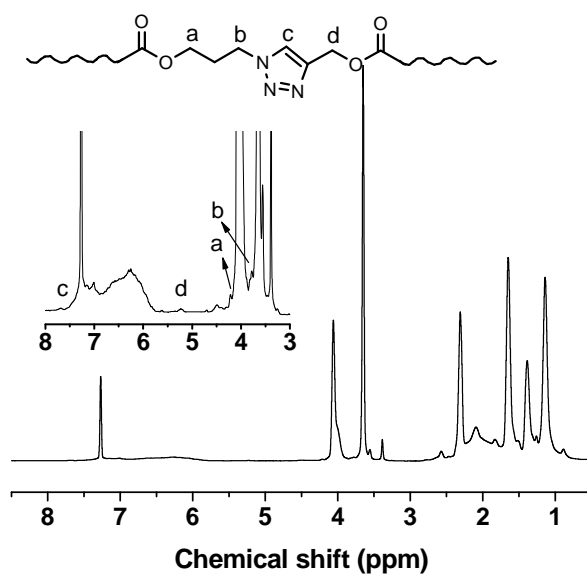


Fig. S11 ¹H NMR spectrum of $(A(BC)_mD)_n$ copolymer.

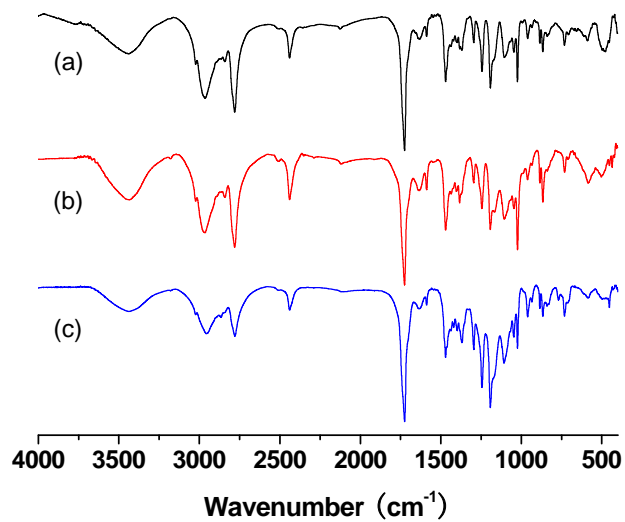


Fig. S12 IR spectra of PDMA(PEG-*alt*-PCL)_mPMA grafted with propargyl bromide (a), 3-bromopropanol (b) and benzyl bromide (c).

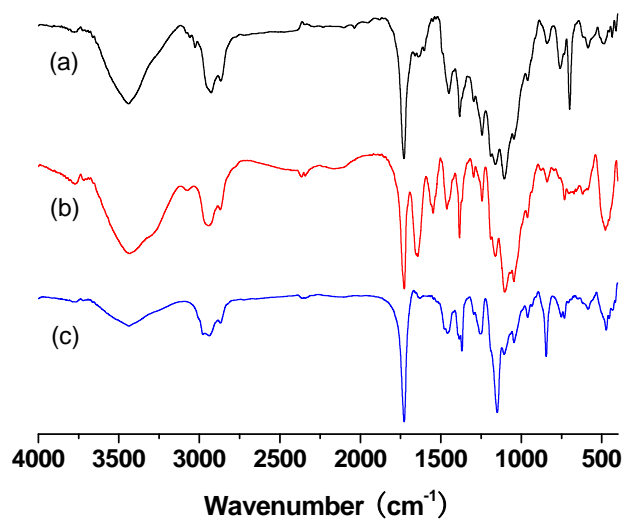


Fig. S13 IR spectra of PDMA(PEG-*alt*-PCL)_mPMA grafted with PSt-Br (a), PNIPAM-Br (b) and PtBA-Br (c).

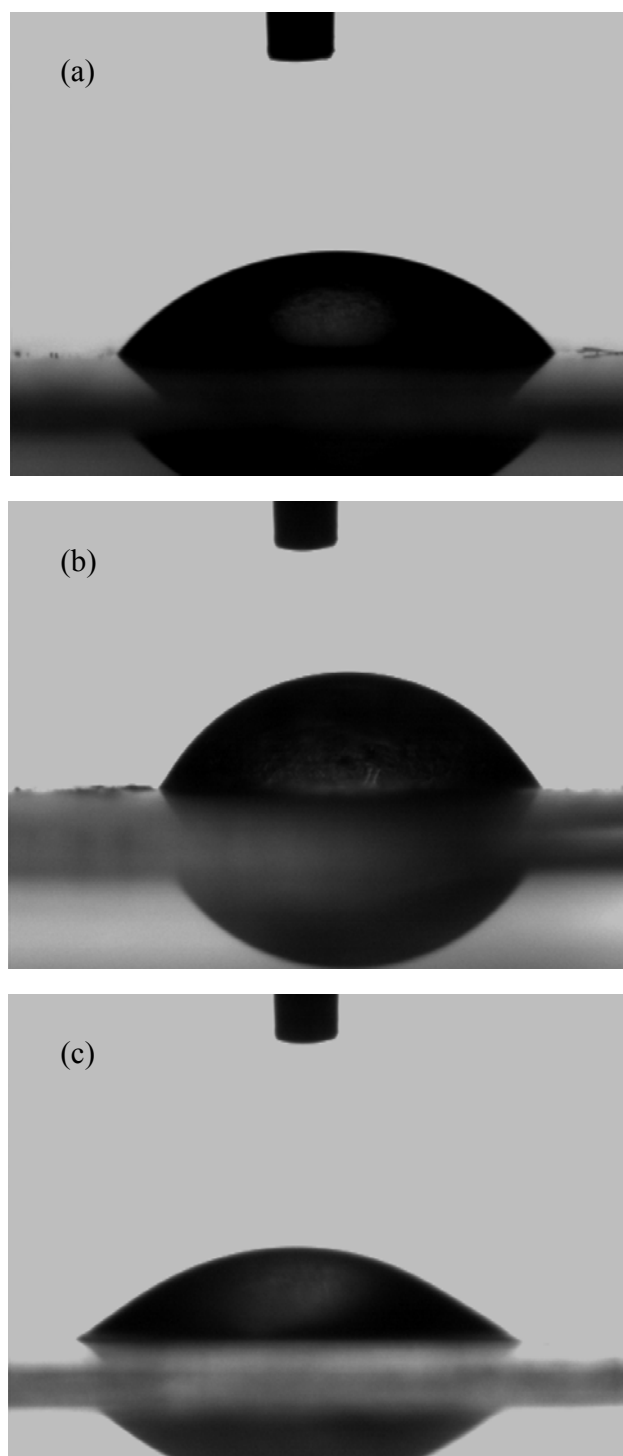


Fig. S14 Water contact angle photographs of copolymer films made from PDMA(PEG-*alt*-PCL)_mPMA grafted with propargyl bromide (G1, a), 3-bromopropanol (G2, b) and benzyl bromide (G3, c).