

Supporting Information

Introducing the aza-Michael Addition Reaction Between Acrylate and Dihydropyrimidin-2(1H)-thione into Polymer Chemistry

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Experiment Section

1. Materials

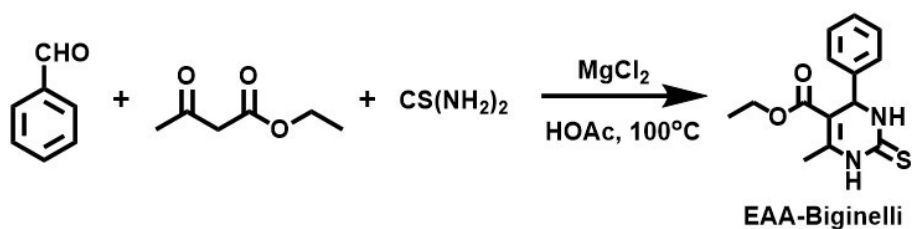
All chemicals, reagents and solvents were purchased from commercial sources. Ethyl Acetoacetate (General Reagent, 98%), benzaldehyde (Energy, 99%), thiourea (Meryer, 99%), 4-formylbenzoic acid (Bidepharm, 98%), hexane-1,6-diol (Aladdin, 98%), acryloyl chloride (Energy, 98%), 1,6-dibromohexane (Aladdin, 97%), 4-hydroxybenzaldehyde (Bidepharm, 98%), methoxypoly(ethylene glycol) acrylate (TCI, average $M_n \sim 500$ g/mol), methoxypoly(ethylene glycol) (Sigma Aldrich, average $M_n \sim 2000$ g/mol), 1-pyrenylmethanol (Meryer, 98%), chlorotrimethylsilane (Macklin, 99%), potassium carbonate (General Reagent, $\geq 99\%$), *N,N*-dimethylformamide (General Reagent, $\geq 99.5\%$) were used as purchased. Hexane-1,6-diyl diacrylate (Bidepharm, 90%) was purified by silica chromatography (petroleum ether) prior to use.

2. Instrument analysis

Gel permeation chromatography (GPC) analyses of polymers were performed using *N,N*-dimethyl formamide (DMF) containing 50 mM LiBr as the eluent. The GPC system was a Shimadzu LC-20AD pump system consisting of an auto-injector, a PLgel 5 μ m guard column (50 \times 7.5 mm) followed by three PLgel 5 μ m MIXED-D columns (300 \times 7.5 mm), a Shimadzu RID-20A refractive index detector and a Shimadzu SPD-20A UV detector. The GPC system was calibrated with narrow molecular weight distribution polystyrene standards (M_n ranging from 5200 to 672000 g/mol), and the concentration of all samples is 5 mg/mL in DMF except for specific description. The dn/dc and M_n (LLS) of the polymers were collected through a Wyatt DAWN HELEOS-II detector (GaAs linearly polarized light, 658 nm, 60 mW), and the concentration of all samples is 10 mg/mL in DMF. ^1H NMR and ^{13}C NMR spectra were obtained using a JEOL JNM-ECA400 (400 MHz) spectrometer for all samples. The ESI-MS data were collected using a Micro TOF-QII Bruker. The fluorescence spectra were collected using a Shimadzu RF-6000 spectro fluorophotometer equipped with quartz cuvettes of 1 cm path length. The UV-vis absorption spectra were obtained with a PerkinElmer Lambda 750 spectrometer. The FT-IR spectra were made in a transmission mode on a PerkinElmer Spectrum 100 spectrometer. Electron spray ionization ion trap/time-of-flight mass spectra (ESI-IT/TOF MS) were performed on a Shimadzu LCMS-IT-TOF. Matrix-assisted laser desorption ionization time-of-flight mass spectra (MALDI-TOF MS) were recorded on a Shimadzu Biotech AXIMA-Performance in a linear mode. Different scanning calorimetry (DSC) was performed using TA instruments Q2000 operated at a scanning rate of 10°C/min. Thermogravimetric analyses (TGA) were conducted on a BeiguangHongyuan WRT-121 thermalgravimetric analyzer.

3. Methods

3.1 *Ethyl 6-methyl-4-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (EAA-Biginelli)*



A round-bottom flask was charged with benzaldehyde (10.6 g, 0.10 mol), ethyl acetoacetate (13.0 g, 0.10 mol), thiourea (11.4 g, 0.15 mol) and magnesium chloride (MgCl_2 , 0.95 g, 10 mmol) in acetic acid (HOAc, 30 mL). The mixture was heated to 100°C and stirred for 2 h. The mixture was then added dropwise into stirring water when it was still hot. The sediment was collected by suction filtration and dissolved in dichloromethane (DCM, 200 mL). The solution was washed with saturated NaHCO_3 aqueous solution three times and brine once. The organic layer was dried over Na_2SO_4 and filtered followed by removal of the solvent by rotary evaporation to give a pale-yellow solid (25.5 g, 92% yield).

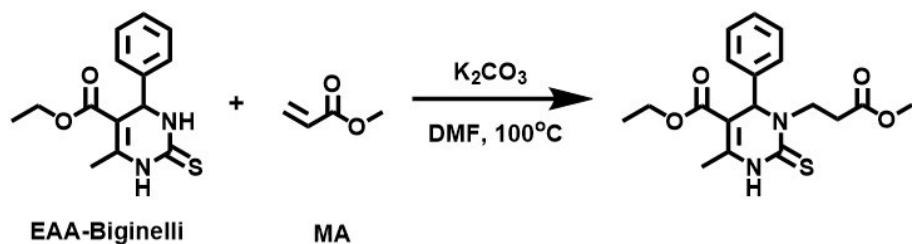
^1H NMR (400 MHz, $\text{DMSO}-d_6$, δ/PPM): 10.33 (s, $\text{C}=\text{CNHCS}$, 1H), 9.65 (d, $J = 3.8$ Hz, $\text{C}=\text{CNHCSNH}$, 1H), 7.39–7.18 (m, PhH, 5H), 5.17 (d, $J = 3.8$ Hz, PhCH, 1H), 4.01 (q, $J = 7.0$ Hz, OCH_2CH_3 , 2H), 2.29 (s, $\text{C}=\text{CCH}_3$, 3H), 1.09 (t, $J = 7.0$ Hz, OCH_2CH_3 , 3H).

^{13}C NMR (101 MHz, $\text{DMSO}-d_6$, δ/PPM): 174.33, 165.21, 145.11, 143.58, 128.64, 127.75, 126.46, 100.79, 59.66, 54.11, 17.23, 14.08.

IR (v/cm^{-1}): 3327, 1667, 1194, 1176, 1118, 759, 723, 692.

ESI-MS: observed (expected): 277.1001 (277.1005) $[\text{M}+\text{H}]^+$.

3.2 Ethyl 3-(3-methoxy-3-oxopropyl)-6-methyl-4-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (the product of the addition reaction between MA and EAA-Biginelli)



A round-bottom flask was charged with EAA-Biginelli (2.76 g, 10 mmol) and methyl acrylate (MA, 0.86 g, 10 mmol) in *N,N*-dimethylformamide (DMF, 1 mL) and heated

to 100°C. The catalyst K₂CO₃ (0.11 g, 1.0 mmol) was then added to initiate the addition reaction. After 20 min, the mixture was cooled down and dissolved by DCM (20 mL). The solution was washed with brine three times, and then the organic layer was dried over Na₂SO₄ and filtered. The solvent was removed by rotary evaporation to get the crude product which was recrystallized (DCM : petroleum ether = 1 : 2) to give a white solid as the pure product (3.30 g, 91% yield).

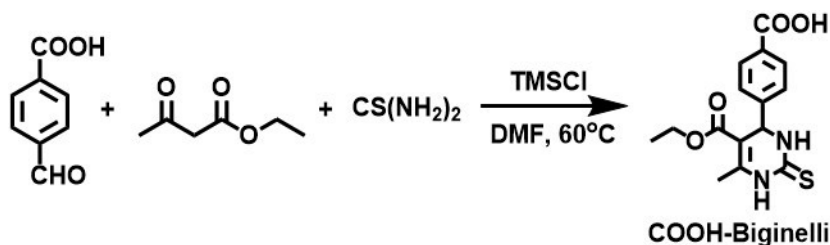
¹H NMR (400 MHz, DMSO-*d*₆, δ/PPM): 10.50 (s, C=CNHCS, 1H), 7.40–7.19 (m, PhH, 5H), 5.53 (s, PhCH, 1H), 4.21 (m, NCH₂CH₂, 1H), 4.04 (m, OCH₂CH₃, 2H), 3.59–3.48 (m, OCH₃, 3H; NCH₂CH₂, 1H), 2.83 (m, NCH₂CH₂, 1H), 2.49 (m, NCH₂CH₂, 1H), 2.24 (s, C=CCH₃, 3H), 1.16 (t, *J* = 7.1 Hz, OCH₂CH₃, 3H).

¹³C NMR (101 MHz, DMSO-*d*₆, δ/PPM): 175.03, 171.51, 164.89, 143.95, 141.95, 128.87, 128.23, 126.78, 101.55, 60.77, 59.77, 51.56, 47.56, 31.43, 16.95, 14.11.

IR (ν/cm⁻¹): 3308, 1699, 1539, 1321, 1218, 1194, 1099, 698.

ESI-MS: observed (expected): 363.1371 (363.1373) [M+H]⁺.

3.3 4-(5-(Ethoxycarbonyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidin-4-yl)benzoic acid (COOH-Biginelli)



A round-bottom flask was charged with 4-formylbenzoic acid (7.51 g, 50 mmol), ethyl acetoacetate (6.51 g, 50 mmol), thiourea (5.71 g, 75 mmol) in DMF (25 mL). Chlorotrimethylsilane (TMSCl, 10.9 g, 100 mmol) was added slowly at room temperature. The mixture was heated to 60°C and stirred for 30 min, then precipitated into cold water under stirring. After suction filtration, the light-yellow sediment was washed three times by water to get the final product as a white solid (12.5 g, 88% yield).

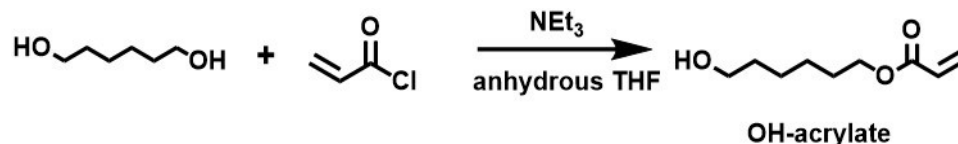
¹H NMR (400 MHz, DMSO-*d*₆, δ/PPM): 10.41 (d, *J* = 1.8 Hz, C=CNHCS, 1H), 9.71 (dd, *J*₁ = 3.7 Hz, *J*₂ = 1.8 Hz, C=CNHCSNH, 1H), 7.93 (m, CHCCOOH, 2H), 7.33 (m, CHCHCCOOH, 2H), 5.23 (d, *J* = 3.7 Hz, ArCH, 1H), 4.01 (m, OCH₂CH₃, 2H), 2.30 (s, C=CCH₃, 3H), 1.09 (t, *J* = 7.1 Hz, OCH₂CH₃, 3H).

^{13}C NMR (101 MHz, $\text{DMSO-}d_6$, δ/PPM): 174.42, 167.08, 165.08, 148.09, 146.58, 130.26, 129.82, 126.76, 100.25, 59.76, 53.99, 17.29, 14.08.

IR (v/cm^{-1}): 3174, 1318, 1182, 1096, 675.

ESI-MS: observed (expected): 319.0761 (319.0758) $[\text{M-H}]^-$.

3.4 6-Hydroxyhexyl acrylate (OH-acrylate)



A round-bottom flask was charged with hexane-1,6-diol (9.46 g, 80 mmol) and triethylamine (3.04 g, 30 mmol) in anhydrous tetrahydrofuran (THF, 30 mL) and kept in an ice-water bath. Acryloyl chloride (1.81 g, 20 mmol) in anhydrous THF (10 mL) was added dropwise into the flask under stirring. Then, the mixture was stirred at 25°C for 2 h and filtered to remove the precipitate. The organic phase was washed with saturated NaHCO_3 solution three times and brine once, then dried over MgSO_4 . After filtration, the solution was concentrated under vacuum, and the residue was purified by silica chromatography (ethyl acetate/petroleum ether = 0 – 1/8) to obtain the product as a colorless oil (2.60 g, 75% yield).

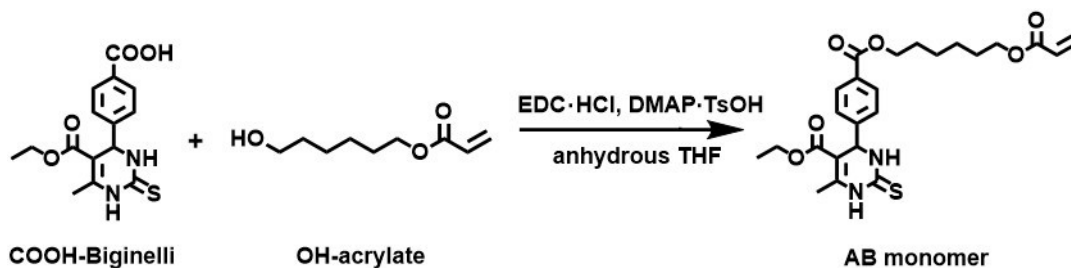
^1H NMR (400 MHz, CDCl_3 , δ/PPM): 6.37 (dd, $J_1 = 17.2$ Hz, $J_2 = 1.6$ Hz, $\text{CH}=\underline{\text{CH}}_2$, 1H), 6.09 (dd, $J_1 = 17.2$ Hz, $J_2 = 10.3$ Hz, $\underline{\text{CH}}=\text{CH}_2$, 1H), 5.79 (dd, $J_1 = 10.3$ Hz, $J_2 = 1.6$ Hz, $\text{CH}=\underline{\text{CH}}_2$, 1H), 4.13 (t, $J = 6.6$ Hz, CH_2OCO , 2H), 3.61 (t, $J = 6.6$ Hz, HOCH_2 , 2H), 1.65 (m, $\underline{\text{CH}}_2\text{CH}_2\text{OCO}$, 2H), 1.55 (m, $\text{HOCH}_2\underline{\text{CH}}_2$, 2H), 1.38 (m, $\text{HO}(\text{CH}_2)_2(\underline{\text{CH}}_2)_2(\text{CH}_2)_2\text{O}$, 4H).

^{13}C NMR (101 MHz, CDCl_3 , δ/PPM): 166.29, 130.49, 128.41, 64.42, 62.56, 32.42, 28.43, 25.59, 25.25.

IR (v/cm^{-1}): 3391, 2935, 1722, 1408, 1191, 1058, 983, 811.

ESI-MS: observed (expected): 195.0991 (195.0992) $[\text{M}+\text{Na}]^+$.

3.5 Ethyl 4-(4-(((6-(acryloyloxy)hexyl)oxy)carbonyl)phenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (AB monomer)



A round-bottom flask was charged with COOH-Biginelli (4.80 g, 15 mmol) and OH-acrylate (1.72 g, 10 mmol) in anhydrous THF (20 mL). 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (3.83 g, 20 mmol) and catalyst 4-dimethylaminopyridine (DMAP) · *p*-toluenesulfonic acid (*p*-TsOH) (0.15 g, 0.5 mmol) were then added. The mixture was stirred at 25°C for 12 h followed by precipitation in water to remove the remaining OH-acrylate. The sediment was collected by filtration and dissolved in DCM (20 mL). The solution was washed with brine three times and dried over Na₂SO₄, filtered, and concentrated under vacuum. The crude product was purified by silica chromatography (ethyl acetate/petroleum ether = 1/5 – 1/4) to obtain a white solid (1.12 g, 24% yield).

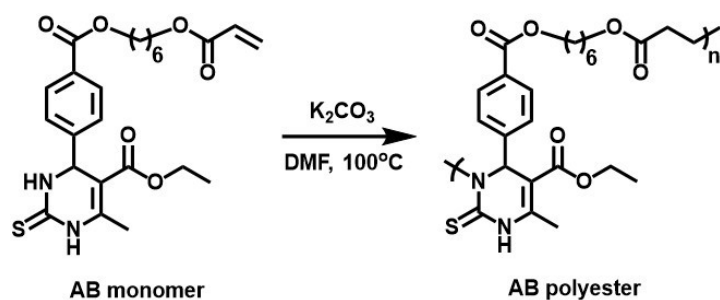
¹H NMR (400 MHz, DMSO-*d*₆, δ/PPM): 10.42 (s, C=CNHCS, 1H), 9.72 (d, *J* = 3.8 Hz, C=CNHCSNH, 1H), 7.94 (d, *J* = 8.1 Hz, CHCCO, 2H), 7.36 (d, *J* = 8.1 Hz, CHCHCCO, 2H), 6.30 (dd, *J*₁ = 17.2 Hz, *J*₂ = 1.6 Hz, CH=CH₂, 1H), 6.15 (dd, *J*₁ = 17.2 Hz, *J*₂ = 10.3 Hz, CH=CH₂, 1H), 5.91 (dd, *J*₁ = 10.3 Hz, *J*₂ = 1.6 Hz, CH=CH₂, 1H), 5.24 (d, *J* = 3.8 Hz, ArCH, 1H), 4.25 (t, *J* = 6.4 Hz, COOCH₂CH₂, 2H), 4.10 (t, *J* = 6.6 Hz, CH₂OCOCH=CH₂, 2H), 4.00 (q, *J* = 7.1 Hz, OCH₂CH₃, 2H), 2.30 (s, C=CCH₃, 3H), 1.75–1.57 (m, OCH₂CH₂(CH₂)₂CH₂CH₂O, 4H), 1.47–1.33 (m, O(CH₂)₂(CH₂)₂(CH₂)₂O, 4H), 1.09 (t, *J* = 7.1 Hz, OCH₂CH₃, 3H).

¹³C NMR (101 MHz, DMSO-*d*₆, δ/PPM): 174.45, 165.64, 165.53, 165.05, 148.50, 145.66, 131.46, 129.67, 129.33, 128.48, 126.94, 100.17, 64.67, 64.11, 59.78, 53.98, 28.15, 28.07, 25.21, 25.16, 17.28, 14.08.

IR (ν/cm⁻¹): 3318, 1720, 1662, 1272, 1195, 1177, 1110, 766, 735, 702.

ESI-MS: observed (expected): 475.1892 (475.1897) [M+H]⁺.

3.6 AB type step-growth polymerization

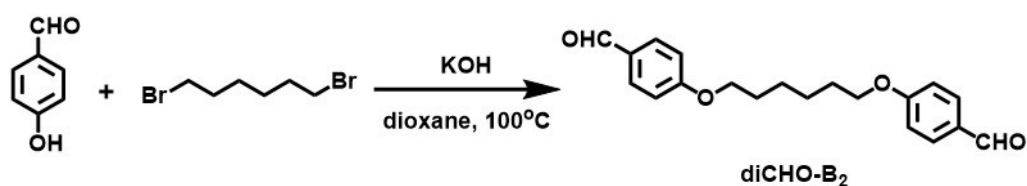


A round-bottom flask was charged with the AB monomer (0.47 g, 1.0 mmol) in DMF (1 mL) and heated to 100°C. The catalyst K_2CO_3 (0.011 g, 0.10 mmol) was then added to initiate the polymerization. Samples were taken at different time points for ^1H NMR and GPC analyses. The polymerization was stopped when the molecular weight ceased increasing. The mixture was precipitated into cold diethyl ether, then washed with cold ethanol once and brine three times. The final polymer was obtained as a light brown solid (0.35 g, 74% yield).

^1H NMR (400 MHz, $\text{DMSO-}d_6$, δ/PPM): 10.52 (b, $\text{C}=\text{CNHCS}$), 7.93 (d, CHCCO), 7.39 (d, CHCHCCO , 2H), 5.61 (s, ArCH), 4.31–4.15 (m, $\text{ArCOOCH}_2\text{CH}_2$; $\text{CH}_2\text{CH}_2\text{N}$), 4.10–3.87 (m, $\text{CH}_2\text{OCO}(\text{CH}_2)_2\text{N}$; OCH_2CH_3), 3.52 (m, $\text{CH}_2\text{CH}_2\text{N}$), 2.82 (m, $\text{CH}_2\text{CH}_2\text{N}$), 2.46 (m, $\text{CH}_2\text{CH}_2\text{N}$), 2.23 (s, $\text{C}=\text{CCH}_3$), 1.64 (m, $\text{ArCOOCH}_2\text{CH}_2(\text{CH}_2)_4\text{O}$), 1.52 (m, $\text{ArCOO}(\text{CH}_2)_4\text{CH}_2\text{CH}_2\text{O}$), 1.43–1.19 (m, $\text{ArCOO}(\text{CH}_2)_2(\text{CH}_2)_2(\text{CH}_2)_2\text{O}$), 1.11 (t, $J = 7.0$ Hz, OCH_2CH_3).

$M_n(\text{GPC}) = 2.3 \times 10^4$ g/mol, $\text{PDI} = 1.60$; $M_n(\text{LLS}) = 2.2 \times 10^4$ g/mol, $dn/dc = 0.095$.

3.7 4,4'-(Hexane-1,6-diylbis(oxy))dibenzaldehyde (diCHO-B₂)



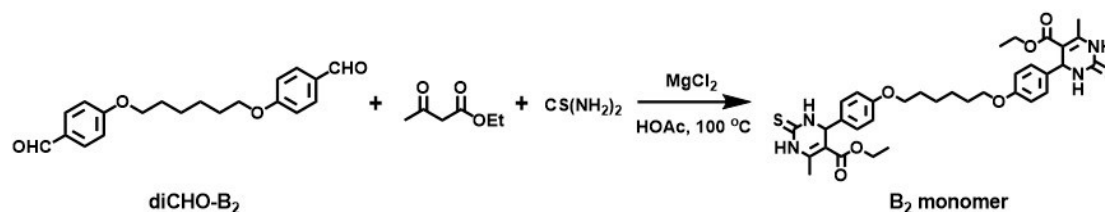
A round-bottom flask was charged with 4-hydroxybenzaldehyde (25.6 g, 0.21 mol), 1,6-dibromohexane (24.4 g, 0.10 mol), and KOH (16.8 g, 0.30 mol) in dioxane (100 mL). The mixture was kept at 100°C for 20 h. Then, the mixture was poured into a NaOH aqueous solution (~ 0.05 g/mL) under stirring. The sediment was collected by suction filtration and washed three times by water to obtain a gray solid (28.3 g, 87% yield).

^1H NMR (400 MHz, CDCl_3 , δ/PPM): 9.88 (s, CHO), 7.83 (d, $J = 8.7$ Hz, CHCCHO , 4H), 6.99 (d, $J = 8.7$ Hz, CHCHCCHO , 4H), 4.06 (t, $J = 6.4$ Hz, $\text{ArOCH}_2(\text{CH}_2)_2$, 4H), 1.87 (tt, $J_1 = 6.6$ Hz, $J_2 = 6.4$ Hz, $\text{ArOCH}_2\text{CH}_2\text{CH}_2$, 4H), 1.58 (m, $\text{ArO}(\text{CH}_2)_2\text{CH}_2$, 4H).
 ^{13}C NMR (101 MHz, CDCl_3 , δ/PPM): 190.76, 164.09, 131.95, 129.78, 114.67, 68.11, 28.93, 25.72.

IR (v/cm^{-1}): 2945, 1685, 1596, 1251, 1213, 1154, 1009, 831, 803.

ESI-MS: observed (expected): 349.1410 (349.1410) $[\text{M}+\text{Na}]^+$.

3.8 Diethyl 4,4'-((hexane-1,6-diylbis(oxy))bis(4,1-phenylene))bis(6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate) (B_2 monomer)



A round-bottom flask was charged with diCHO- B_2 (3.26 g, 10 mmol), ethyl acetoacetate (2.60 g, 20 mmol), thiourea (2.28 g, 30 mmol), and MgCl_2 (0.19 g, 2.0 mmol) in HOAc (8 mL). The mixture was stirred at 100°C for 12 h. Then, the mixture was added dropwise into stirring water when it was still hot. The sediment was collected by suction filtration and dissolved in DCM (30 mL). The solution was washed with saturated NaHCO_3 aqueous solution three times and brine once. The organic layer was dried over Na_2SO_4 and filtered followed by removal of the solvent by rotary evaporation to get a yellow solid (5.80 g, 87% yield).

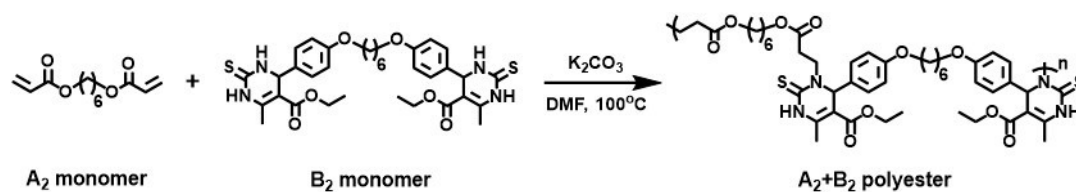
^1H NMR (400 MHz, $\text{DMSO}-d_6$, δ/PPM): 10.28 (s, $\text{C}=\text{CNHCS}$, 2H), 9.59 (d, $J = 3.6$ Hz, $\text{C}=\text{CNHCSNH}$, 2H), 7.10 (m, CHCHCO , 4H), 6.88 (m, CHCHCO , 4H), 5.10 (d, $J = 3.6$ Hz, ArCH, 2H), 4.00 (q, $J = 7.0$ Hz, OCH_2CH_3 , 4H), 3.93 (t, $J = 6.4$ Hz, ArOCH_2 , 4H), 2.28 (s, $\text{C}=\text{CCH}_3$, 3H), 1.70 (tt, $J_1 = 6.6$ Hz, $J_2 = 6.4$ Hz, $\text{ArOCH}_2\text{CH}_2$, 4H), 1.45 (m, $\text{ArO}(\text{CH}_2)_2\text{CH}_2$, 4H), 1.10 (t, $J = 7.0$ Hz, OCH_2CH_3 , 3H).

^{13}C NMR (101 MHz, $\text{DMSO}-d_6$, δ/PPM): 174.09, 165.26, 158.26, 144.81, 135.65, 127.70, 114.46, 101.04, 67.45, 60.55, 53.54, 28.71, 25.39, 17.22, 14.11.

IR (v/cm^{-1}): 1558, 1509, 1463, 1242, 1171, 1096.

ESI-MS: observed (expected): 667.2619 (667.2619) $[\text{M}+\text{H}]^+$.

3.9 A₂+B₂ type step-growth polymerization

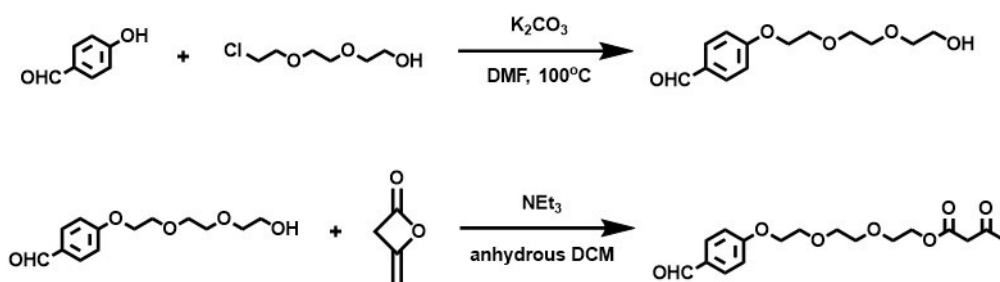


A round-bottom flask was charged with A₂ monomer (0.226 g, 1.0 mmol) and B₂ monomer (0.667 g, 1.0 mmol) in DMF (1 mL) and heated to 100°C. The catalyst K₂CO₃ (0.021 g, 0.20 mmol) was then added to initiate the polymerization. Samples were taken at different time intervals for ¹H NMR and GPC analyses. The polymerization was stopped when the molecular weight ceased increasing. The mixture was precipitated into cold diethyl ether and washed with cold ethanol once and brine three times. The final polymer was obtained as a light-yellow solid (0.61 g, 69% yield).

¹H NMR (400 MHz, DMSO-*d*₆, δ/PPM): 10.45 (b, C=CNHCS), 7.15 (d, *J* = 8.3 Hz, OCCHCH), 6.88 (d, *J* = 8.3 Hz, OCCHCH), 5.42 (s, ArCH), 4.19 (m, CH₂CH₂N), 4.06–3.82 (m, COOCH₂(CH₂)₂; OCH₂CH₃), 3.52 (m, CH₂CH₂N), 2.81 (m, CH₂CH₂N), 2.47 (m, CH₂CH₂N), 2.23 (s, C=CCH₃), 1.68 (m, ArOCH₂CH₂CH₂), 1.59–1.36 (m, COOCH₂CH₂CH₂; ArO(CH₂)₂CH₂), 1.25 (m, COO(CH₂)₂CH₂), 1.11 (t, *J* = 7.0 Hz, OCH₂CH₃).

*M*_n(GPC) = 2.3 × 10⁴ g/mol, PDI = 1.60; *M*_n(LLS) = 1.3 × 10⁴ g/mol, dn/dc = 0.100.

3.10 2-(2-(2-(4-Formylphenoxy)ethoxy)ethoxy)ethyl 3-oxobutanoate



The compound was prepared as our previous report.¹

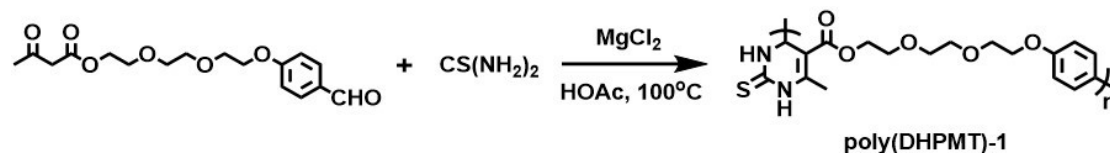
¹H NMR (400 MHz, DMSO-*d*₆, δ/PPM): 9.87 (s, CHO, 1H), 7.86 (d, *J* = 8.4 Hz, CHCCHO, 2H), 7.14 (d, *J* = 8.4 Hz, CHCHCCHO, 2H), 4.25–4.13 (m, ArOCH₂, 2H; COOCH₂, 2H), 3.77 (m, ArOCH₂CH₂, 2H), 3.46–3.53 (m, ArOCH₂CH₂O(CH₂)₂OCH₂, 8H; COCH₂CO, 2H), 2.17 (s, COCH₃, 3H).

^{13}C NMR (101 MHz, DMSO- d_6 , δ /PPM): 201.51, 191.36, 167.31, 163.55, 131.86, 129.75, 115.03, 69.96, 69.82, 68.78, 68.24, 67.74, 63.86, 49.61, 30.03.

IR (ν/cm^{-1}): 1714.37, 1599.37, 1254.21, 1158.98, 1048.04, 833.01.

ESI-MS: observed (expected): 361.1255 (361.1258) $[\text{M}+\text{H}]^+$.

3.11 Poly(DHPMT)-1

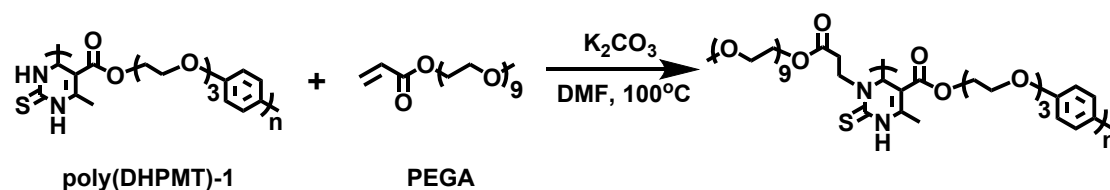


The polymer was prepared as our previous report.²

^1H NMR (400 MHz, DMSO- d_6 , δ /PPM): 10.31 (s, C=CNHCS), 9.61 (d, $J = 3.8$ Hz, C=CNHCSNH), 7.13 (d, $J = 8.4$ Hz, OCCH), 6.88 (d, $J = 8.4$ Hz, OCCHCH), 5.12 (d, $J = 3.8$ Hz, ArCH), 4.12–3.97 (m, ArOCH₂; COOCH₂), 3.69 (m, ArOCH₂CH₂), 3.60–3.43 (m, ArOCH₂CH₂O(CH₂)₂OCH₂), 2.28 (s, C=CCH₃).

M_n (GPC) = 9.9×10^3 g/mol, PDI = 1.49. M_n (LLS) = 6.7×10^3 g/mol, $dn/dc = 0.072$.

3.12 Post polymerization modification of poly(DHPMT)-1



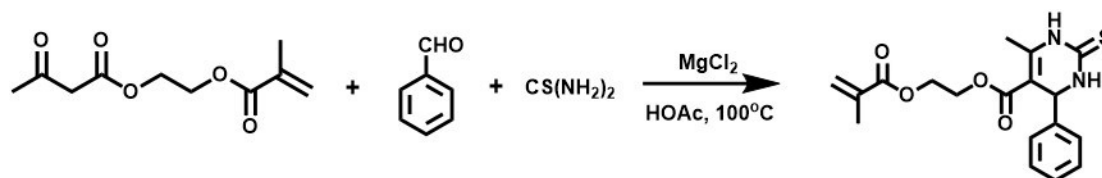
A round-bottom flask was charged with poly(DHPMT)-1 (0.38 g, DHPMT = 1.0 mmol) and methoxypoly(ethylene glycol) acrylate (PEGA, DP ~ 9, 0.60 g, 1.2 mmol) in DMF (1 mL) and heated to 100°C. The catalyst K_2CO_3 (0.011g, 0.1 mmol) was then added to initiate the reaction. Samples were taken at different time intervals for ^1H NMR analyses (Figure S13). After the modification was finished, the mixture was dialyzed against ethanol (MWCO: 3500 Da) for 24 h. The final polymer was obtained by removing the solvent as a light brown solid (0.45 g, 51% yield).

^1H NMR (400 MHz, DMSO- d_6 , δ /PPM): 10.48 (s, C=CNHCS), 7.18 (d, $J = 8.4$ Hz, OCCH), 6.89 (d, $J = 8.4$ Hz, OCCHCH), 5.44 (s, ArCH), 4.25–3.93 (m, CH₂CH₂N; ArOCH₂; CCOOCH₂CH₂O; CH₂COOCH₂CH₂O), 3.77–3.64 (m, ArOCH₂CH₂O; CH₂CH₂N), 3.62–3.38 (m, ArO(CH₂)₂O(CH₂)₂OCH₂CH₂; COOCH₂CH₂O((CH₂)₂O)₈

CH₃), 3.22 (s, COO((CH₂)₂O)₉CH₃), 2.82 (m, CH₂CH₂N), 2.47 (m, CH₂CH₂N), 2.23 (s, C=CCH₃).

$M_n(\text{GPC}) = 1.4 \times 10^4$ g/mol, PDI = 1.39; $M_n(\text{LLS}) = 1.6 \times 10^4$ g/mol, $dn/dc = 0.103$.

3.13 2-(Methacryloyloxy)ethyl 6-methyl-4-phenyl-2-thioxo-1,2,3,4-tetrahydro pyrimidine-5-carboxylate



The compound was prepared as our previous report.³

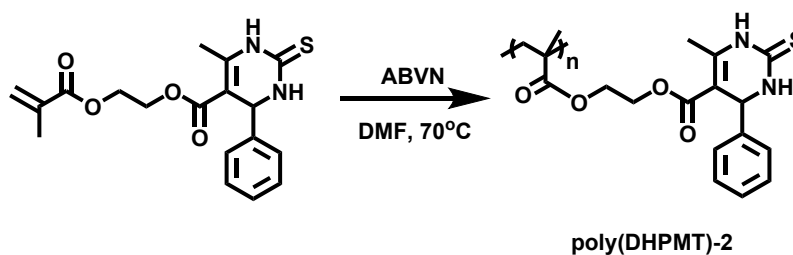
¹H NMR (400 MHz, DMSO-*d*₆, δ /PPM): 10.39 (d, $J = 1.9$ Hz, C=CNHCS, 1H), 9.69 (dd, $J_1 = 3.8$ Hz, $J_2 = 1.9$ Hz, C=CNHCSNH, 1H), 7.38–7.17 (m, PhH, 5H), 5.95 (s, CH₂=C, 1H), 5.66 (s, CH₂=C, 1H), 5.16 (d, $J = 3.7$ Hz, PhCH, 1H), 4.30–4.13 (m, O(CH₂)₂O, 4H), 2.28 (s, C=CCH₃, 3H), 1.82 (s, CH₂=CCH₃, 3H).

¹³C NMR (101 MHz, DMSO-*d*₆, δ /PPM): 174.39, 166.39, 165.00, 145.83, 143.46, 135.62, 128.63, 127.76, 126.35, 126.16, 100.37, 62.52, 61.63, 53.99, 17.98, 17.29.

IR (ν/cm^{-1}): 1715.18, 1596.58, 1183.93, 1153.93, 1090.53, 759.23, 696.68.

ESI-MS: observed (expected): 361.1211 (361.1217) [M+H]⁺.

3.14 Poly(DHPMT)-2

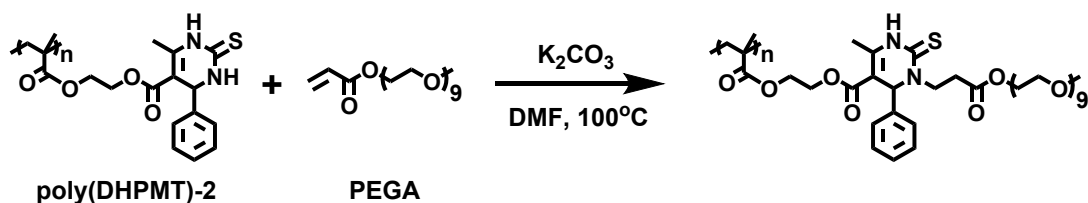


The polymer was prepared as our previous report.³

¹H NMR (400 MHz, DMSO-*d*₆, δ /PPM): 10.34 (m, C=CNHCS), 9.63 (m, C=CNHCSNH), 7.40–7.00 (m, PhH), 5.19 (m, PhCH), 4.53–3.76 (m, O(CH₂)₂O), 2.28 (m, C=CCH₃), 1.30–0.47 (m, CH₂CCH₃).

$M_n(\text{GPC}) = 4.2 \times 10^4$ g/mol, PDI = 1.98.

3.15 Post polymerization modification of poly(DHPMT)-2

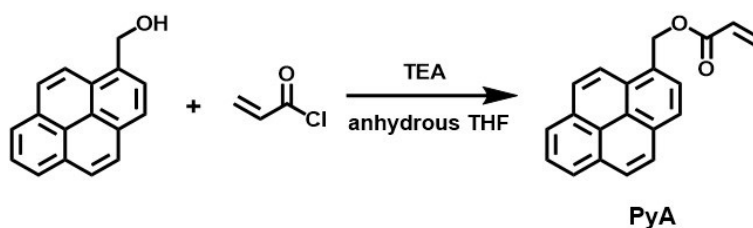


A round-bottom flask was charged with poly(DHPMT)-2 (0.36 g, DHPMT = 1.0 mmol) and methoxypoly(ethylene glycol) acrylate (PEGA, DP ~ 9, 0.60 g, 1.2 mmol) in DMF (1 mL) and heated to 100°C. The catalyst K₂CO₃ (0.011g, 0.1 mmol) was then added to initiate the reaction. Samples were taken at different time intervals for ¹H NMR analyses (Figure S14). After the modification was finished, the mixture was dialyzed against ethanol (MWCO: 3500 Da) for 24 h. The final polymer was obtained by removing the solvent as a brown sticky oil (0.50 g, 58% yield).

¹H NMR (400 MHz, DMSO-*d*₆, δ/PPM): 10.52 (s, C=CNHCS), 7.23 (m, ArH), 5.52 (s, ArCH), 4.63–3.80 (m, CCOO(CH₂)₂O; NCH₂CH₂; CH₂COOCH₂CH₂O), 3.65–3.37 (m, NCH₂CH₂; COOCH₂CH₂O((CH₂)₂O)₈CH₃), 3.21 (s, COO((CH₂)₂O)₉CH₃), 2.80 (m, NCH₂CH₂), 2.45 (m, NCH₂CH₂), 2.21 (s, C=CCH₃), 1.31–0.48 (m, CH₂CCH₃).

$M_n(\text{GPC}) = 5.0 \times 10^4$ g/mol, PDI = 2.25.

3.16 Pyren-1-ylmethyl acrylate (PyA)



A round-bottom flask was charged with 1-pyrenylmethanol (1.16 g, 5.0 mmol) and triethylamine (0.76 g, 7.5 mmol) in anhydrous THF (5 mL) and kept in an ice-water bath. Acryloyl chloride (0.54 g, 6.0 mmol) in anhydrous THF (5 mL) was carefully added dropwise into the flask. The mixture was then stirred at 25°C for 2 h. The mixture was filtered, and the liquid phase was washed with saturated NaHCO₃ solution three times and water once. The organic phase was dried over Na₂SO₄ and filtered. The product was obtained after removal of the solvent by rotary evaporation as a yellow solid (1.32 g, 92% yield).

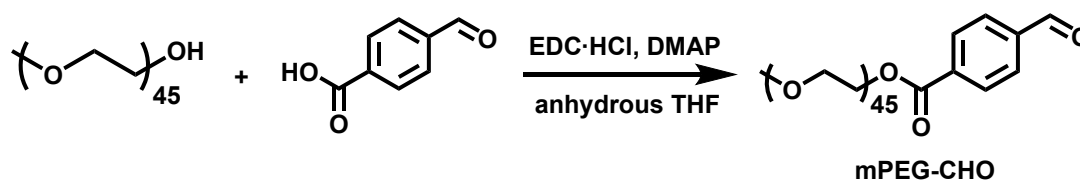
^1H NMR (400 MHz, CDCl_3 , δ/PPM): 8.31–7.94 (m, ArH, 9H), 6.48 (dd, $J_1 = 17.4$ Hz, $J_2 = 1.6$ Hz, $\text{COCH}=\underline{\text{C}}\text{H}_2$, 1H), 6.20 (dd, $J_1 = 17.4$ Hz, $J_2 = 10.3$ Hz, $\text{COCH}=\underline{\text{C}}\text{H}_2$, 1H), 5.92 (s, PyCH_2 , 2H), 5.85 (dd, $J_1 = 17.4$ Hz, $J_2 = 1.6$ Hz, $\text{COCH}=\underline{\text{C}}\text{H}_2$, 1H).

^{13}C NMR (101 MHz, CDCl_3 , δ/PPM): 166.10, 131.68, 131.19, 131.11, 130.60, 129.46, 128.63, 128.27, 128.13, 127.75, 127.63, 127.26, 125.99, 125.44, 125.37, 124.77, 124.53, 122.77, 64.74.

IR (v/cm^{-1}): 1716, 1180, 1037, 839, 811, 703.

MALDI-TOF-MS: observed (expected): 286.00 (286.10) $[\text{M}]^+$.

3.17 Benzaldehyde terminated methoxypoly(ethylene glycol) (mPEG-CHO)

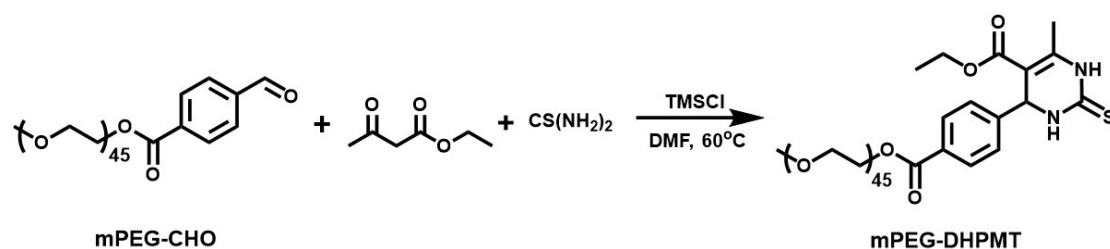


Azeotropic treatment of methoxypoly(ethylene glycol) (mPEG, $M_n \sim 2000$, 5.0 g, 2.5 mmol) with toluene was performed to remove the remaining water. Then the mPEG and 4-formylbenzoic acid (0.60 g, 4.0 mmol) were dissolved in anhydrous THF (20 mL). 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (1.0 g, 5.0 mmol) and DMAP (0.031 g, 0.25 mmol) were added in the reaction system. The mixture was stirred at 25°C for 12 h. After removing the sediment by filtration, the solution was precipitated into cold ethyl ether and the white insoluble solid was collected and washed three times with ethyl ether to give a white solid (5.0 g, 94% yield).

^1H NMR (400 MHz, $\text{DMSO}-d_6$, δ/PPM): 10.12 (s, ArCHO), 8.16 (d, $J = 8.0$ Hz, $\underline{\text{C}}\text{H}\text{CCHO}$), 8.06 (d, $J = 8.0$ Hz, $\underline{\text{C}}\text{H}\text{CHCCHO}$), 4.43 (m, COOCH_2), 3.77 (m, $\text{COOCH}_2\underline{\text{C}}\text{H}_2\text{O}$), 3.71–3.38 (m, $\text{COO}(\text{CH}_2)_2\text{O}((\underline{\text{C}}\text{H}_2)_2\text{O})_n\text{CH}_3$), 3.24 (s, OCH_3).

$M_{n, \text{GPC}} = 8.0 \times 10^3$ g/mol, PDI = 1.03.

3.18 Dihydropyrimidin-2(1H)-thione terminated methoxypoly(ethylene glycol) (mPEG-DHPMT)

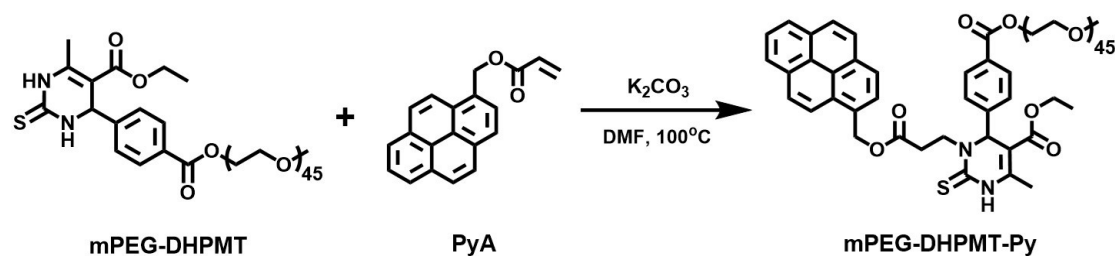


A round-bottom flask was charged with mPEG-CHO (2.13 g, 1.0 mmol), ethyl acetoacetate (0.13 g, 1.0 mmol) and thiourea (0.12 g, 3.0 mmol) in DMF (25 mL). Chlorotrimethylsilane (TMSCl, 0.22 g, 2.0 mmol) was added slowly at room temperature. The mixture was kept at 60°C for 4 h, then precipitated into cold ethyl ether and washed three times with ethyl ether. The crude product was recrystallized with isopropyl alcohol to obtain the product as a white solid (1.28 g, 54% yield).

¹H NMR (400 MHz, DMSO-*d*₆, δ/PPM): 10.41 (s, C=CNHCS), 9.59 (d, *J* = 3.7 Hz, C=CNHCSNH), 7.94 (d, *J* = 8.2 Hz, COCCHCH), 7.36 (d, *J* = 8.2 Hz, COCCHCH), 5.24 (d, *J* = 3.7 Hz, ArCH), 4.37 (m, COOCH₂), 4.00 (q, *J* = 7.0 Hz, OCH₂CH₃), 3.72 (m, COOCH₂CH₂O), 3.69–3.39 (m, COO(CH₂)₂O((CH₂)₂O)_nCH₃), 3.23 (s, OCH₃), 2.29 (s, C=CCH₃), 1.09 (t, *J* = 7.0 Hz, OCH₂CH₃).

*M*_n(GPC) = 8.8 × 10³ g/mol, PDI = 1.03.

3.19 mPEG-DHPMT-Py (chain-end modification of mPEG-DHPMT)



A round-bottom flask was charged with mPEG-DHPMT (0.48 g, 0.2 mmol) and PyA (0.068 g, 0.24 mmol) in DMF (0.5 mL). The catalyst K₂CO₃ (0.002 g, 0.02 mmol) was then added to initiate the reaction. Samples were taken at different time points for ¹H NMR analyses to monitor the reaction (Figure S15). After the modification was finished, the mixture was filtered and the liquid phase was precipitated into cold ethyl ether. The sediment was collected and washed with ethyl ether three times to get the product as a brown solid (0.38 g, 70% yield).

¹H NMR (400 MHz, DMSO-*d*₆, δ/PPM): 10.56 (s, C=CNHCS), 8.37–8.06 (m, PyH), 7.92 (d, *J* = 8.0 Hz, COCCHCH), 7.39 (d, *J* = 8.0 Hz, COCCHCH), 5.82 (m, PyCH₂),

5.66 (s, ArCH), 4.36 (m, COOCH₂), 4.27 (m, NCH₂CH₂), 3.98 (m, OCH₂CH₃), 3.75–3.39 (m, COOCH₂CH₂O; NCH₂CH₂; COO(CH₂)₂O((CH₂)₂O)_nCH₃), 3.23 (s, OCH₃), 2.93 (m, NCH₂CH₂), 2.63 (m, NCH₂CH₂), 2.21 (s, C=CCH₃), 1.09 (t, *J* = 7.1 Hz, OCH₂CH₃).

$M_n(\text{GPC}) = 8.9 \times 10^3 \text{ g/mol}$, PDI = 1.03.

Supporting data

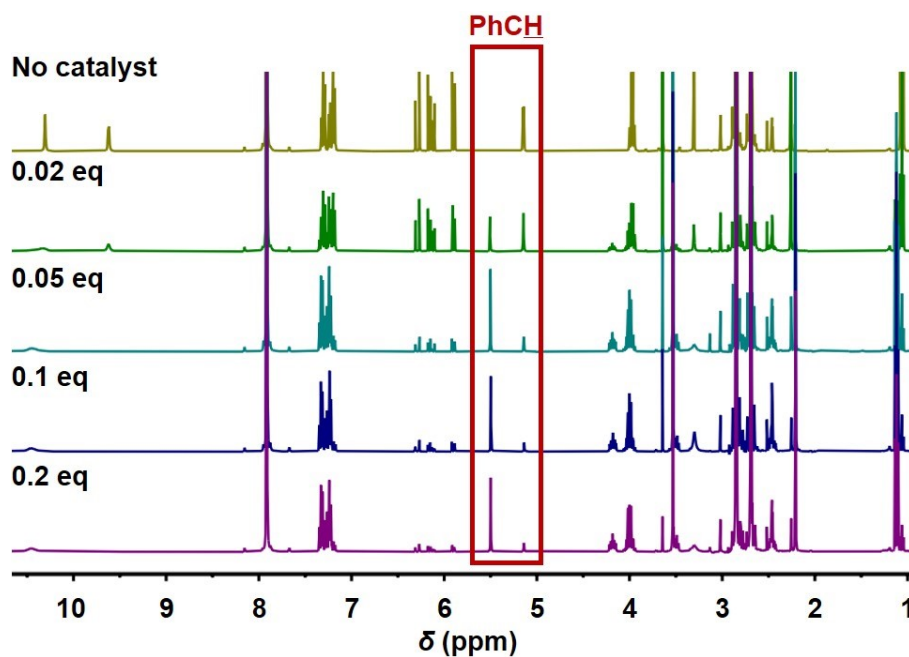


Figure S1. ¹H NMR (400 MHz, DMSO-*d*₆) spectra of the model reactions (80°C, MA/DHPMT = 1/1, 10 min) with different amount of catalyst (molar equivalent against MA).

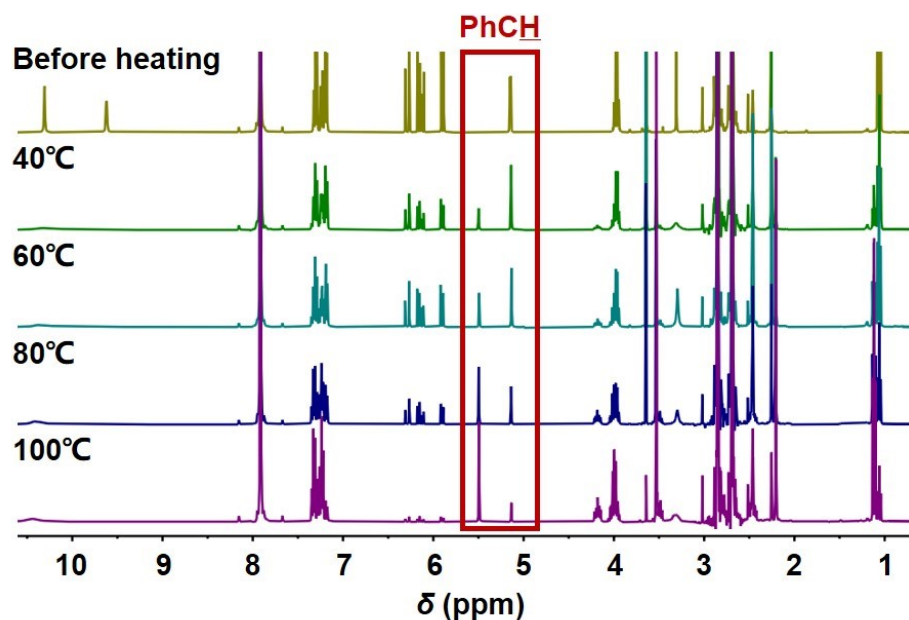


Figure S2. ¹H NMR (400 MHz, DMSO-*d*₆) spectra of the model reactions (MA/DHPMT/K₂CO₃ = 1/1/0.1, 10 min) at different temperature.

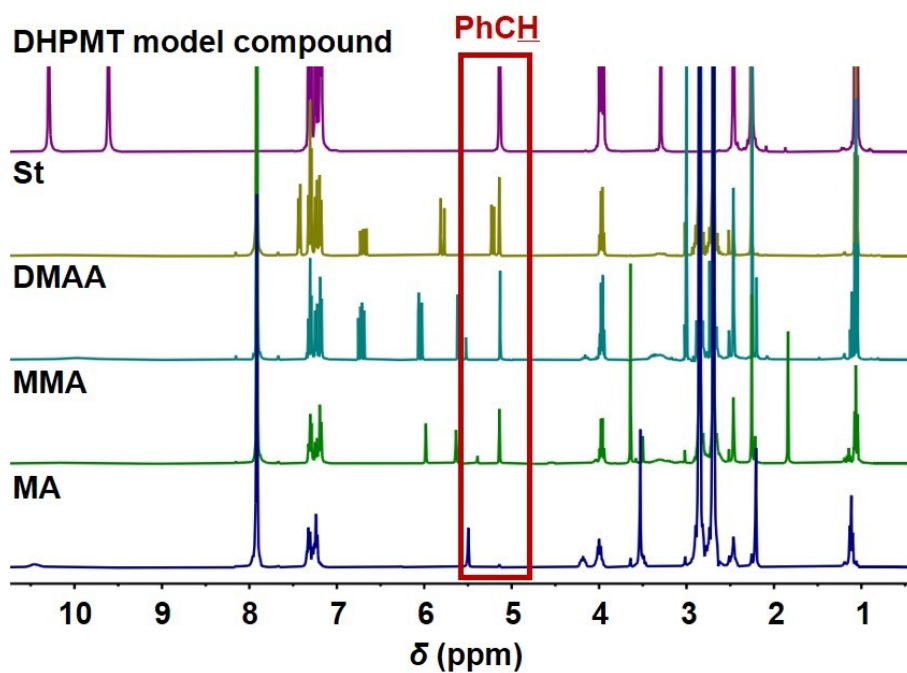


Figure S3. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) spectra of the model reactions using different substrates (100°C , monomer/DHPMT/ $\text{K}_2\text{CO}_3 = 1/1/0.1$, 15 min).

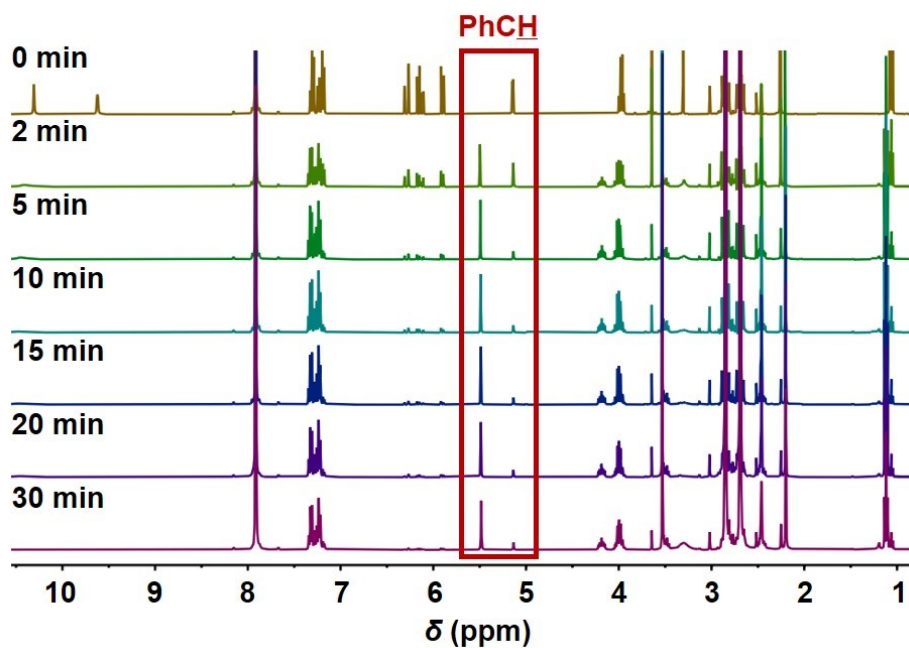


Figure S4. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) spectra of the model reaction at different time points using MA under optimized conditions (100°C , MA/DHPMT/ $\text{K}_2\text{CO}_3 = 1/1/0.1$).

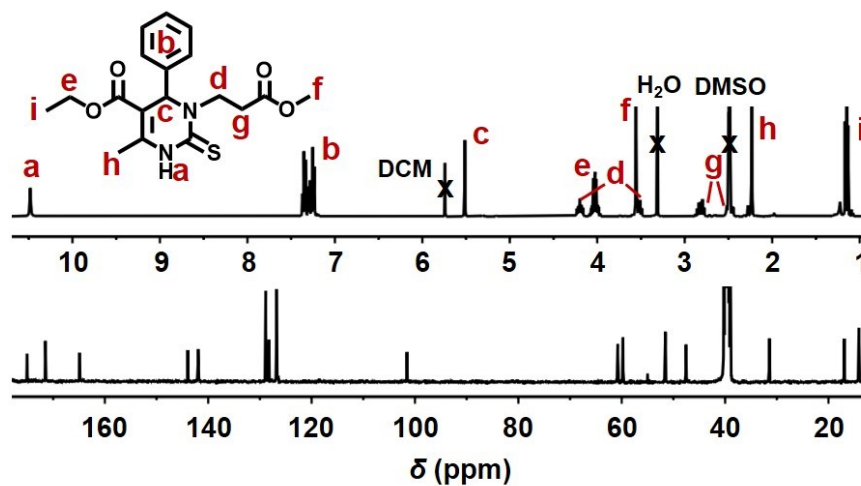


Figure S5. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) and ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) spectra of the product of the addition reaction between MA and DHPMT model compound.

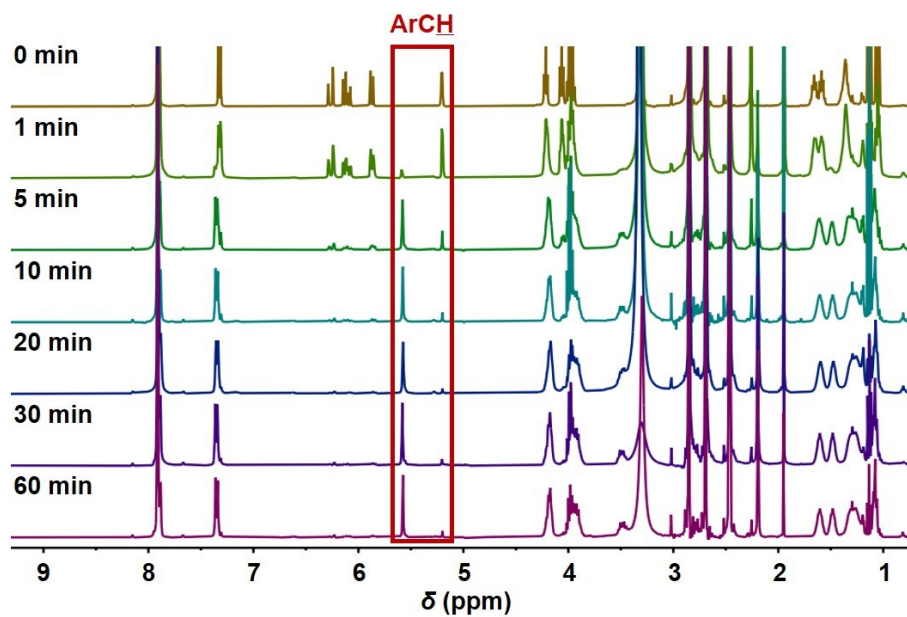


Figure S6. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) spectra of the mixture of the AB step-growth polymerization at different time points (100°C, AB monomer/ $\text{K}_2\text{CO}_3 = 1/0.1$).

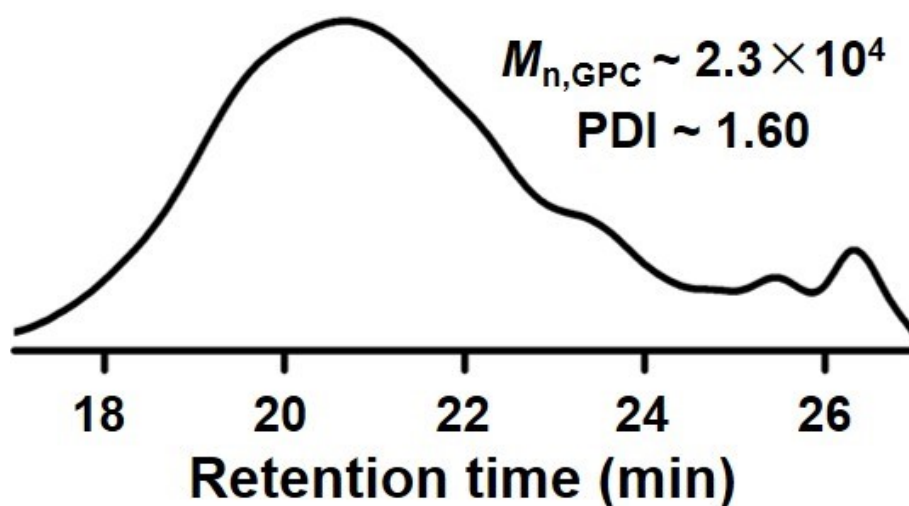


Figure S7. GPC curve of the purified AB polymer.

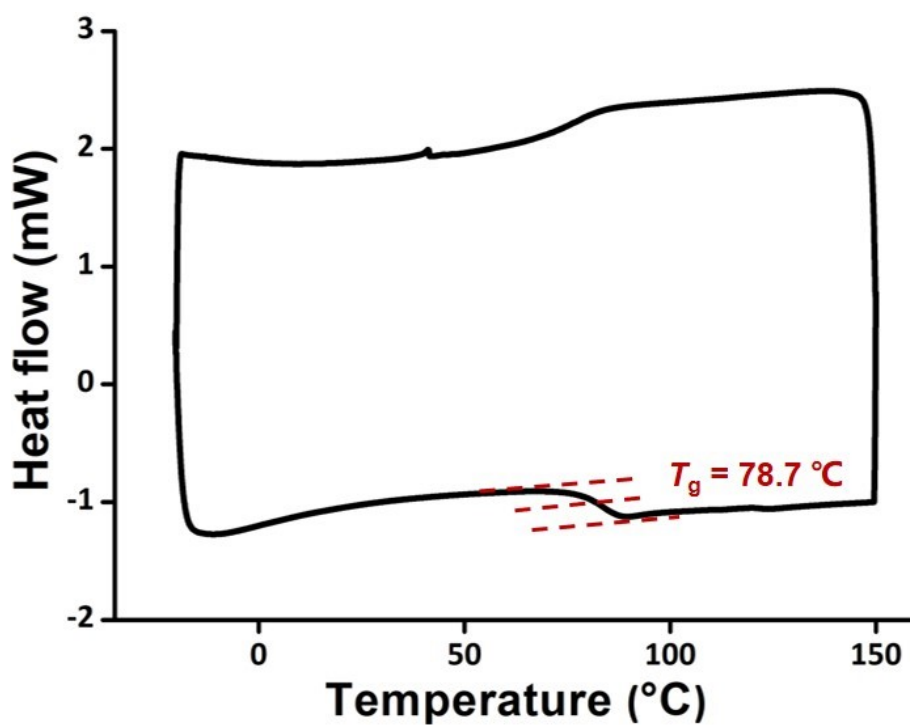


Figure S8. DCS traces for both heating/cooling (rate of $10^{\circ}\text{C}/\text{min}$) of the AB polymer.

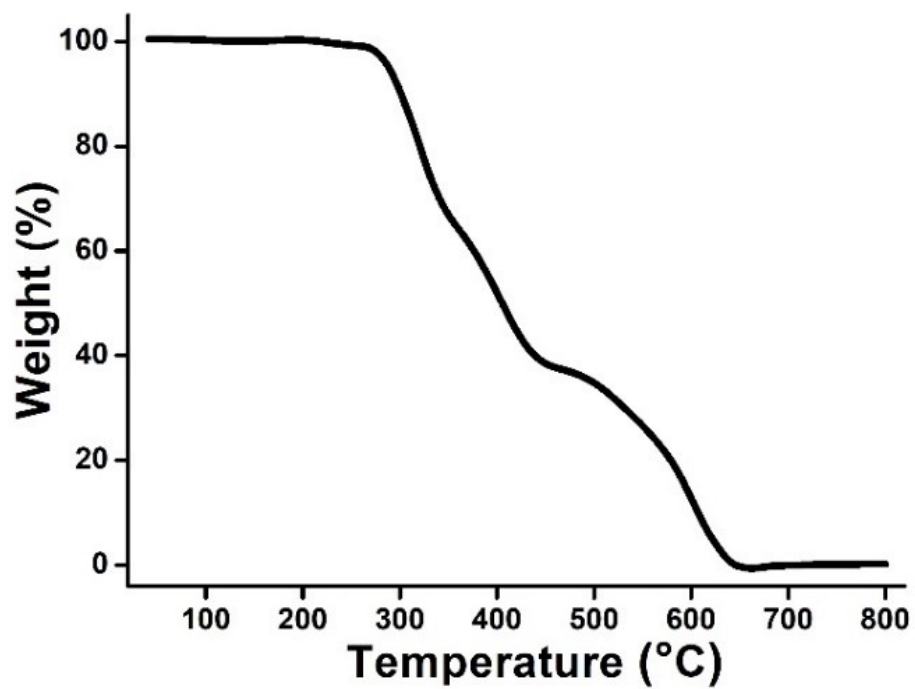


Figure S9. TGA curve of the AB polymer.

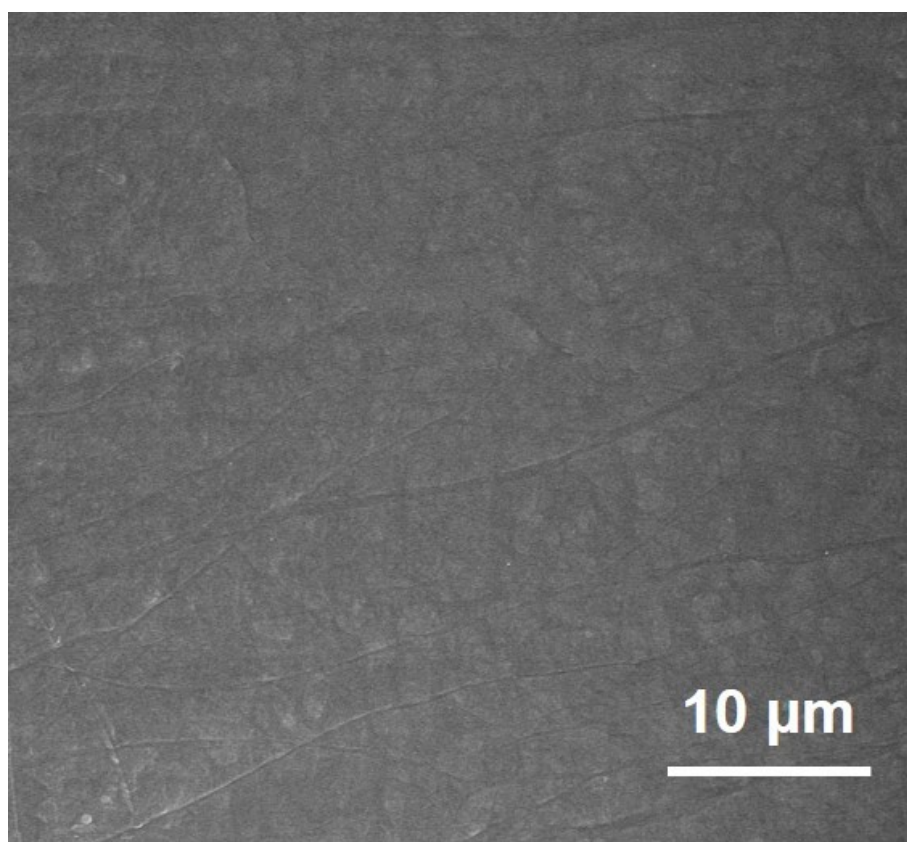


Figure S10. SEM image of AB polyester membrane.

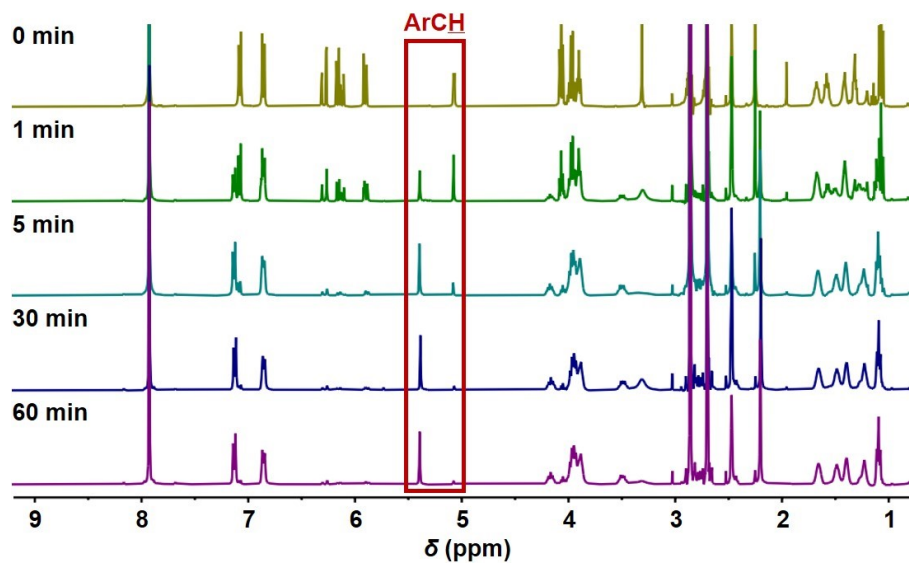


Figure S11. ¹H NMR (400 MHz, DMSO-*d*₆) spectra of the mixture of the A2+B2 step-growth polymerization at different time points (100°C, A2/B2/K₂CO₃ = 1/1/0.2).

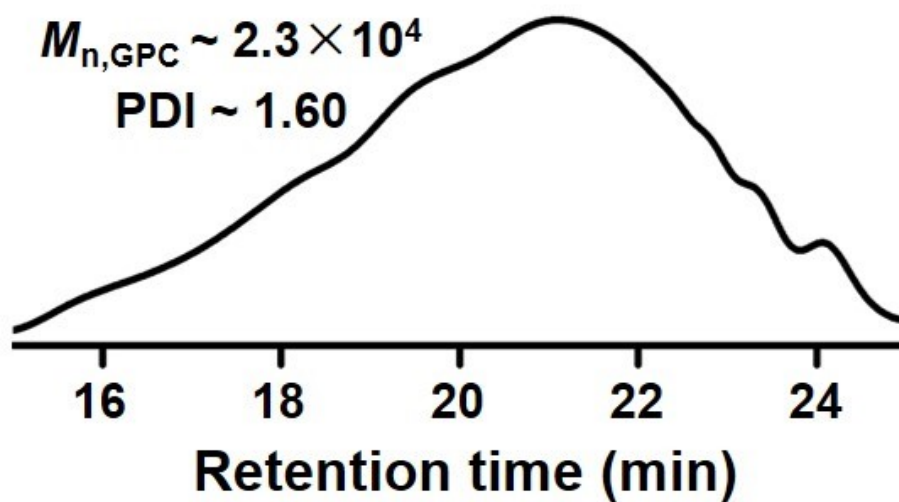


Figure S12. GPC curve of the purified A2+B2 polymer.

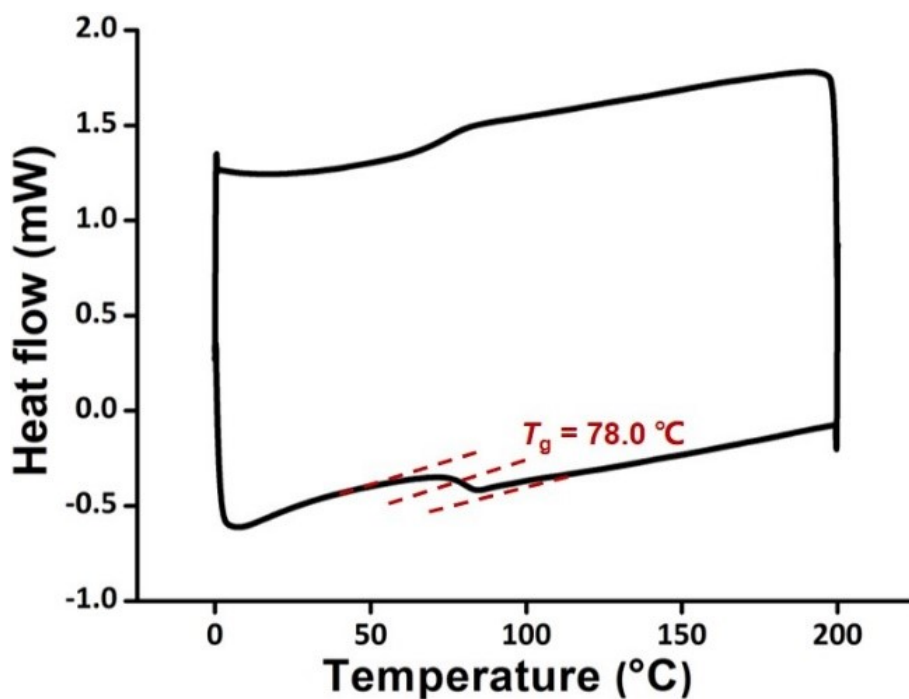


Figure S13. DCS traces for both heating/cooling (rate of $10^\circ\text{C}/\text{min}$) of the A2+B2 polymer.

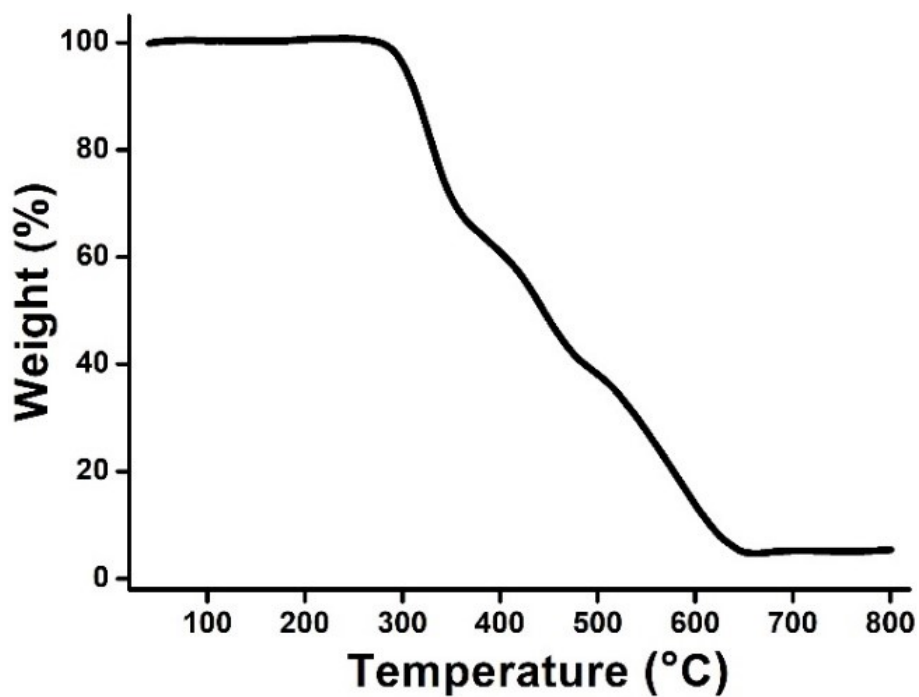


Figure S14. TGA curve of the A2+B2 polymer.

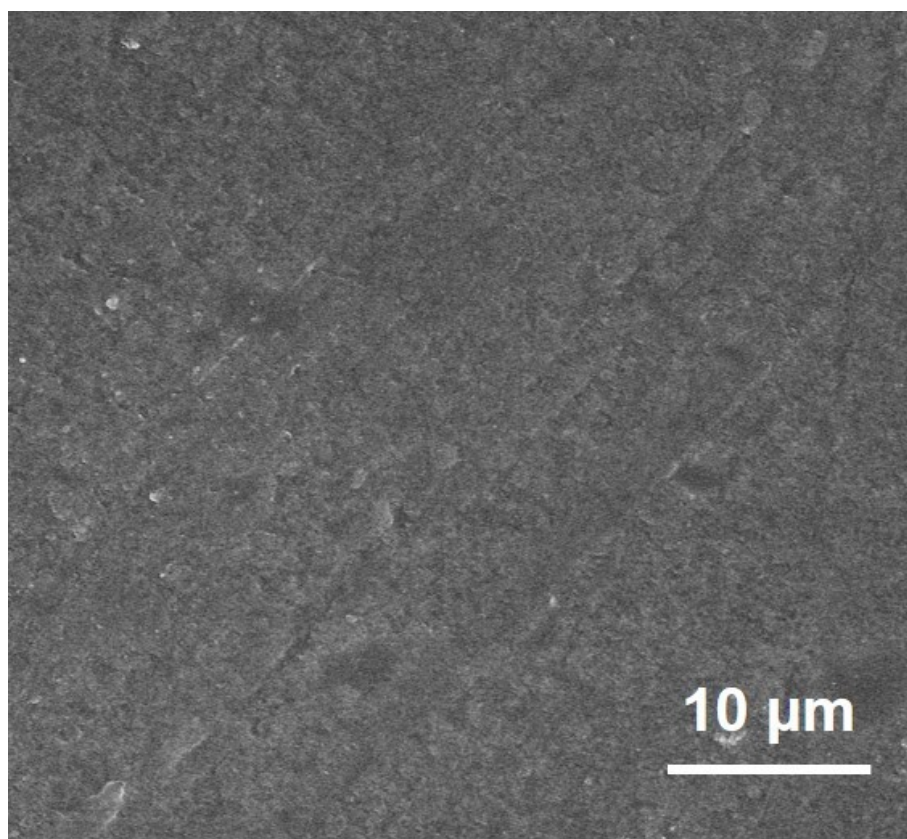


Figure S15. SEM image of A2+B2 polyester membrane.

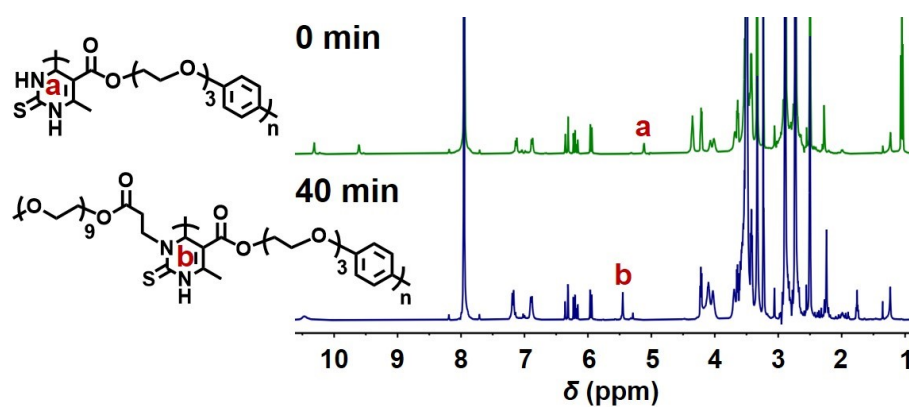


Figure S16. ¹H NMR (400 MHz, DMSO-*d*₆) spectra of the mixture of the post polymerization modification of poly(DHPMT)-1.

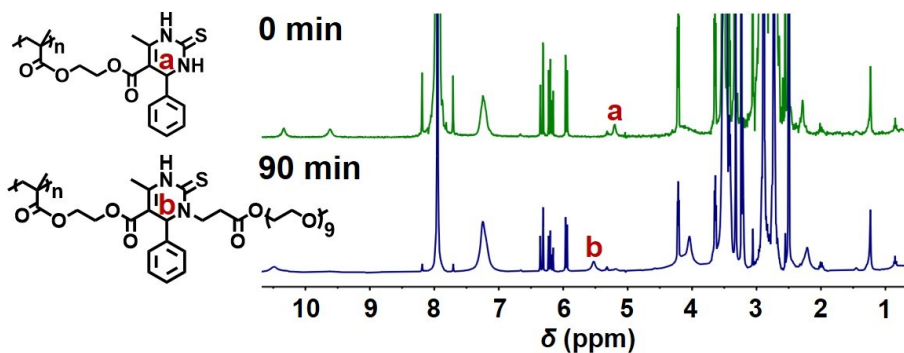


Figure S17. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) spectra of the mixture of the post polymerization modification of poly(DHPMT)-2.

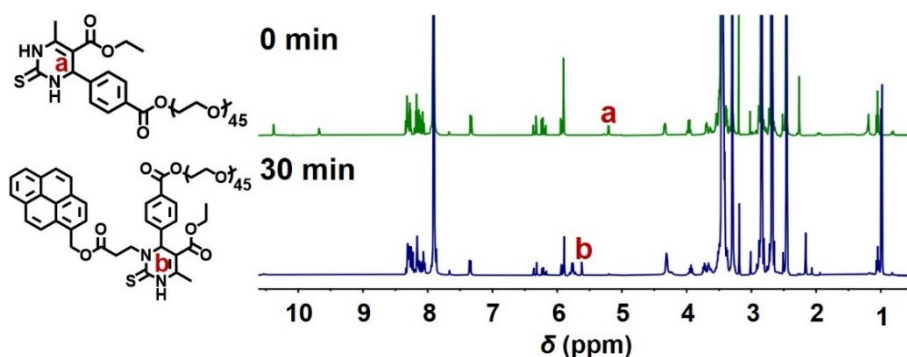


Figure S18. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) spectra of the mixture of the chain-end modification of mPEG-DHPMT.

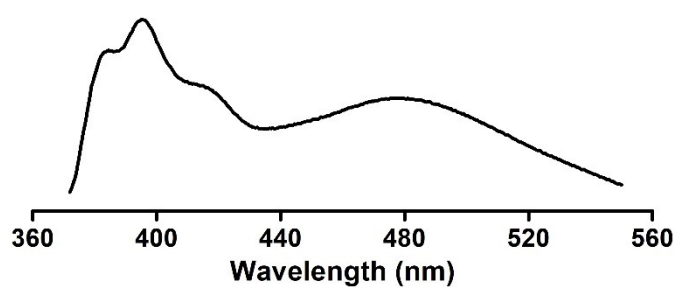


Figure S19. The emission spectrum of mPEG-DHPMT-Py in DCM (excited by 365 nm).

References:

1. Zhao, Y.; Yu, Y.; Zhang, Y.; Wang, X.; Yang, B.; Zhang, Y.; Zhang, Q.; Fu, C.; Wei, Y.; Tao, L., From Drug to Adhesive: A New Application of Poly(dihydropyrimidin-2(1H)-one)s via the Biginelli Polycondensation. *Polym. Chem.* **2015**, *6* (27), 4940-4945.
2. Zhao, Y.; Wu, H.; Zhang, Y.; Wang, X.; Yang, B.; Zhang, Q.; Ren, X.; Fu, C.; Wei, Y.; Wang, Z.; Wang, Y.; Tao, L., Postpolymerization Modification of Poly(dihydropyrimidin-2(1H)-thione)s via the Thiourea-Haloalkane Reaction to Prepare Functional Polymers. *ACS Macro Lett.* **2015**, *4* (8), 843-847.
3. Mao, T.; Liu, G.; Wu, H.; Wei, Y.; Gou, Y.; Wang, J.; Tao, L., High Throughput Preparation of UV-Protective Polymers from Essential Oil Extracts via the Biginelli Reaction. *J. Am. Chem. Soc.* **2018**, *140* (22), 6865-6872.