Electronic Supplementary Information (ESI)

Synthesis of Amino-Functionalized Polyester via Ring-Opening Alternating Copolymerization of Glycidylamines with Cyclic Anhydrides

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1. Experimental section

1.1. Chemicals

Phthalic anhydride (PA; >98.0%, Tokyo Chemical Industry Co. Ltd. (TCI)), succinic anhydride (SA; >95.0%, TCI), glutaric anhydride (GA; >98.0%, TCI), and diglycolic anhydride (DGA; >98.0%, TCI) were purified by sublimation before use. Epichlorohydrin (>99.0%, TCI), dibenzylamine (>97.0%, TCI), diallylamine (>98.0%, TCI), *N*-methylbenzylamine (>98.0%, TCI), phosphazene base P_2-*t*-Bu solution (*t*-BuP_2; 2.0 M solution in THF, Sigma-Aldrich), phosphazene base P_1-*t*-Bu (*t*-BuP_1; >97.0%, Sigma-Aldrich), phosphazene base P_4-*t*-Bu solution (*t*-BuP_4; 0.8 M solution in *n*-hexane, Sigma-Aldrich), 1,4-benzene dimethanol (BDM; >99.0%, TCI), tetra-*n*-butylammonium hydrogen sulfate (TBAHS; >98.0%, TCI), and sodium hydroxide (NaOH; >97.0%, FUJIFILM Wako Pure Chemical Corp. (WAKO)) were purchased from commercial sources and used as received. 3-phenyl-1-propanol (PPA; >98%, TCI), butanol (>99.0%, TCI), triethylamine (>99.0%, Kanto Chemical Co. Inc. (KANTO)), butylene oxide (BO; >99.0%, TCI), ethyl glycidyl ether (EGE; >98.0%, TCI), 5-hexen-1-ol (>97.0%, TCI), and propargyl alcohol (>95%) were purified by distillation over CaH_2 under vacuum, which were then stored under an argon atmosphere. Cesium pivalate (CsOPiv; >97.0%, TCI) and sodium acetate (NaOAc; >99%, Sigma-Aldrich) were dried by heating at 100 °C for 3 days. Poly(ethylene glycol) monomethyl ether (MeO-PEG-OH; typical M_n = 400, $M_{n,SEC}$ = 440, $Đ$ = 1.33, TCI) was dried by azeotropic distillation in benzene. *N*,*N*-Dibenzylglycidylamine (DBGA), *N*-benzyl-*N*-methylglycidylamine (BMGA), and *N*,*N*-diallylglycidylamine (DAGA) were prepared

according to reported methods and then purified by distillation.[1] Chloroform-*d* ($CDCl_3$; >99.8%, KANTO), acetone (>99.0%, KANTO), hexane (>95.0%, KANTO), dry-tetrahydrofuran (dry-THF; >99.5%, KANTO), methanol (>99.8%, Sigma-Aldrich), and pyridine (>99.5%, KANTO) were used as received.

1.2. Instruments

Polymerizations were carried out in an MBRAUN stainless steel glovebox equipped with a gas purification system (molecular sieves and copper catalyst) in a dry argon atmosphere (H_2O, O_2 <0.1 ppm). The moisture and oxygen contents in the glovebox were monitored by a MB-MO-SE-1 and MB-OX-SE-1, respectively.

Nuclear magnetic resonance (NMR) spectra were recorded at 25 °C on a JEOL JNM-ECS400 instrument (400 MHz) or a JEOL JNM-ECZ600R (600 MHz) using $CDCl_3$ as the solvent and chemical shifts were referenced to an internal standard (TMS). The diffusion-ordered NMR (DOSY) analyses were carried out at 30 °C using the ledbpgp2s sequence with at least 15 gradient increments.

Size exclusion chromatography (SEC) was conducted in DMF at 40 °C and a flow rate of 0.6 mL min^{-1} using a Jasco high performance liquid chromatography system (PU-980 Intelligent HPLC pump, CO-965 Column oven, RI-930 Intelligent RI detector, and Shodex DEGAS KT-16) equipped with a Shodex KD-G guard column, Shodex Asahipak GF-310-HQ (7.6 mm ID × 300 mm L), and Shodex Asahipak GF-7M-HQ (7.6 mm ID × 300 mm L). The polystyrene standard curve ranging from

2170 to 1 320 000 was used for calibration to achieve the molecular weight ($M_{n,SEC}$) and polydispersity index ($Đ$) of the polymers.

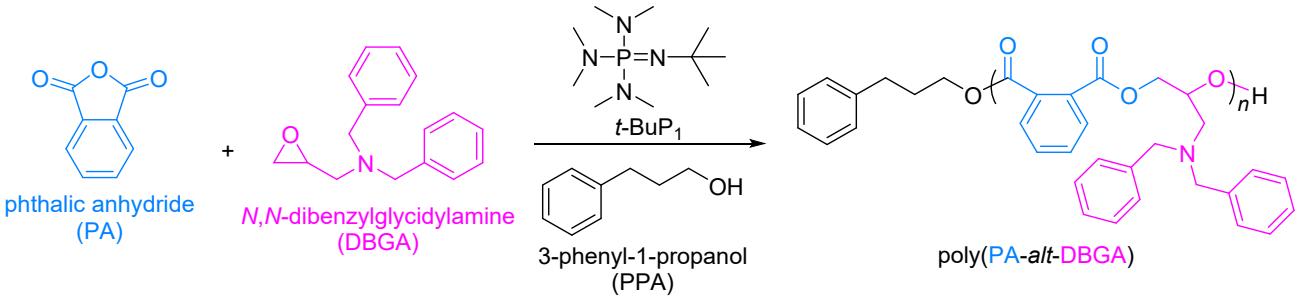
Thermogravimetric analysis (TGA) experiments were performed using a Hitachi High-Tech Science STA200RV under nitrogen atmosphere. The sample was preheated to 100 °C for 30 min to removed water. Then, the sample was cooled to room temperature and heated to 550 °C at the heating rate of 10 °C min^{-1}.

Diffrerential scanning calorimetry (DSC) was conducted using a Hitachi DSC 7000X. The sample was heated from 20 °C to 150 at a rate of 10 °C min^{-1} and held at 100 °C for 10 min to erase thermal history. Then, the sample was cooled to −100 °C at a rate of 10 °C min^{-1} and holed at −100 °C for 10 min. Finally, the sample was heated to 150 °C at a rate of 10 °C min^{-1}. The second heating DSC curve was used to evaluate the glass transition temperature (T_g).

Matrix-assisted desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) experiment of the polymer was performed in linear mode using a Bruker Daltonics (Germany) Ultraflex MALDI-TOF/TOF mass spectrometer equipped with a 355 nm Nd:YAG laser. The sample for the measurement was prepared by mixing the polymer (10 μL, 10 g L^{-1} in THF), matrix (2-(4-hydroxyphenylazo)benzoic acid; 50 μL, 100 g L^{-1} in THF).

1.3. ROAC of PA and DBGA

Scheme S1. ROAC of PA and DBGA catalyzed by *t*-BuP$_1$



A typical procedure for the ROAC is as follows (method A): In an argon-filled glovebox, *t*-BuP$_1$ (40 μmol, 9.4 μL, 1.0 equiv.), PPA (40 μmol, 5.4 μL, 1.0 equiv.), PA (1.0 mmol, 148 mg, 25 equiv.), and DBGA (3.0 mmol, 760 mg, 75 equiv.) were placed in an oven-dried reaction vessel with a magnetic stir. To keep the argon atmosphere, the vessel was sealed with a greaseless valve. After removing the vessel from the glovebox, the reaction mixture was stirred at 80 °C in an oil bath. During the polymerization, a crude aliquot was time-regularly obtained from the system by a syringe in an argon flow and monitored by ^{1}H NMR spectroscopy and SEC to determine monomer conversion and molecular weight. After the defined time, the polymerization was terminated by diluting the reaction mixture with acetone. The reaction mixture was purified by reprecipitation from an acetone solution into *n*-hexane/acetone = 4/1 (vol/vol). The purified product was dried under vacuum at 40 °C to give poly(PA-*alt*-DBGA) as a colorless solid ($M_{n,NMR}$ = 8000; $M_{n,SEC}$ = 3760, $Đ$ = 1.10; yield: 206 mg, 74.3%).

Synthesis of poly(PA-*alt*-DBGA) using Me-PEG-OH as an initiator: The method A was

used for the reaction of *t*-BuP_1 (40 μmol, 9.4 μL, 1.0 equiv.), Me-PEG-OH (40 μmol, 16 μL, 1.0 equiv.), PA (1.0 mmol, 148 mg, 25 equiv.), and DBGA (3.0 mmol, 760 mg, 75 equiv.) to give PEG-*b*-poly(PA-*alt*-DBGA) as a colorless viscous liquid ($M_{n,NMR}$ = 6700; $M_{n,SEC}$ = 4830, $Đ$ = 1.22; yield: 138 mg, 94.0%).

Synthesis of poly(PA-*alt*-DBGA) using 5-hexen-1-ol as an initiator: The method A was used for the reaction of *t*-BuP_1 (40 μmol, 9.4 μL, 1.0 equiv.), 5-hexen-1-ol (40 μmol, 4.0 μL, 1.0 equiv.), PA (1.0 mmol, 148 mg, 25 equiv.), and DBGA (3.0 mmol, 760 mg, 75 equiv.) to give poly(PA-*alt*-DBGA) as a colorless viscous liquid ($M_{n,NMR}$ = 7200; $M_{n,SEC}$ = 5240, $Đ$ = 1.16; yield: 164 mg, 79.1%).

Synthesis of poly(PA-*alt*-DBGA) using propargyl alcohol as an initiator: The method A was used for the reaction of *t*-BuP_1 (40 μmol, 9.4 μL, 1.0 equiv.), propargyl alcohol (40 μmol, 2.4 μL, 1.0 equiv.), PA (1.0 mmol, 148 mg, 25 equiv.), and DBGA (3.0 mmol, 760 mg, 75 equiv.) to give poly(PA-*alt*-DBGA) as a colorless viscous liquid ($M_{n,NMR}$ = 9000; $M_{n,SEC}$ = 5240, $Đ$ = 1.20; yield: 178 mg, 49.1%).

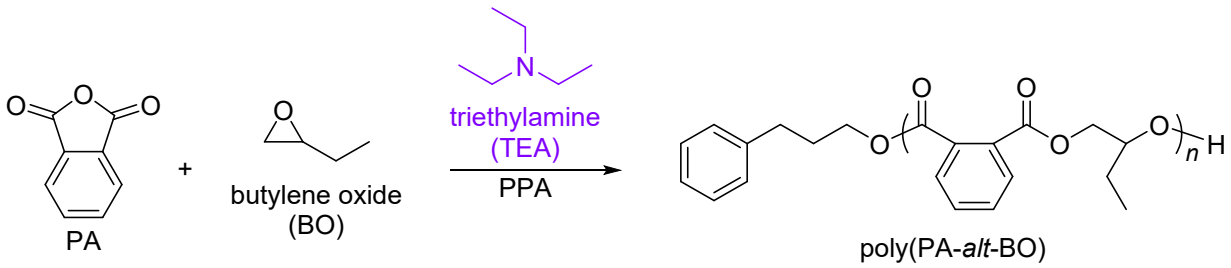
Synthesis of poly(PA-*alt*-DBGA) using BDM as an initiator: The method A was used for the reaction of *t*-BuP_1 (40 μmol, 9.4 μL, 1.0 equiv.), BDM (40 μmol, 5.5 mg, 1.0 equiv.), PA (1.0

mmol, 148 mg, 25 equiv.), and DBGA (3.0 mmol, 760 mg, 75 equiv.) to give poly(PA-*alt*-DBGA) as a colorless viscous liquid ($M_{n,NMR}$ = 7900; $M_{n,SEC}$ = 4150, $Đ$ = 1.21; yield: 255 mg, 79.1%).

Synthesis of poly(PA-*alt*-DBGA) without alcohol initiator: The method A was used for the reaction of *t*-BuP_1 (40 μmol, 9.4 μL, 1.0 equiv.), PA (1.0 mmol, 148 mg, 25 equiv.), and DBGA (3.0 mmol, 760 mg, 75 equiv.) to give poly(PA-*alt*-DBGA) as a colorless liquid ($M_{n,SEC}$ = 44 500, $Đ$ = 1.43; yield: 164 mg, 82.3%).

1.4. ROAC of PA and BO catalyzed by TEA

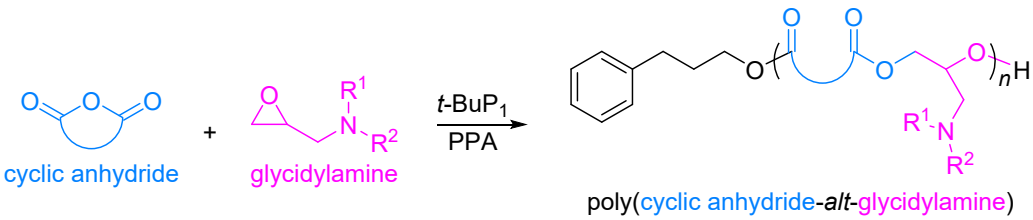
Scheme S2. ROAC of PA and BO catalyzed by TEA

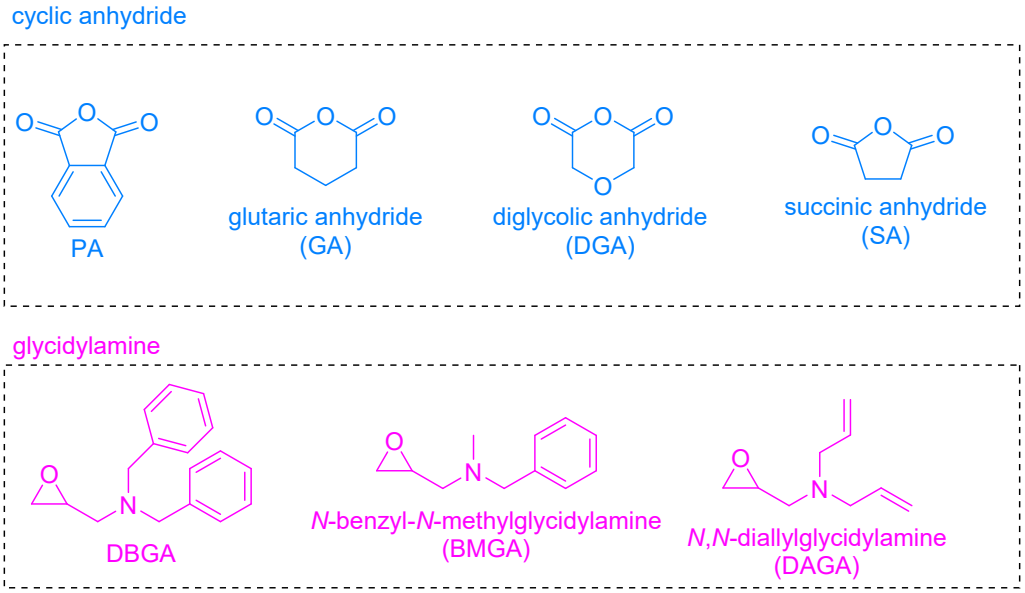


In an argon-filled glovebox, PPA (50 μmol, 6.8 μL, 1.0 equiv.), PA (1.3 mmol, 185 mg, 25 equiv.), BO (3.8 mmol, 270 mg, 75 equiv.), and TEA (3.8 mmol, 380 mg, 75 equiv.) were placed in an oven-dried reaction vessel with a magnetic stir. To keep the argon atmosphere, the vessel was sealed with a greaseless valve. After removing the vessel from the glovebox, the reaction mixture was stirred at 80 °C in an oil bath. After 6.5 h, a crude aliquot was monitored by ^{1}H NMR spectroscopy to determine monomer conversion.

1.5. Synthesis of poly(cyclic anhydride-*alt*-glycidylamine) catalyzed by *t*-BuP$_1$

Scheme S3. ROAC of cyclic anhydride and glycidylamine catalyzed by *t*-BuP$_1$





A typical procedure for the ROAC is as follows (method B): In an argon-filled glovebox, *t*-BuP$_1$ (40 μmol, 9.4 μL, 1.0 equiv.), PPA (40 μmol, 5.4 μL, 1.0 equiv.), PA (1.0 mmol, 148 mg, 25 equiv.), and BMGA (3.0 mmol, 532 mg, 75 equiv.) were placed in an oven-dried reaction vessel with a magnetic stir. To keep the argon atmosphere, the vessel was sealed with a greaseless valve. After removing the vessel from the glovebox, the reaction mixture was stirred at 80 °C under an argon atmosphere in an oil bath. During the polymerization, a crude aliquot was time-regularly obtained from the system by a syringe in an argon flow and monitored by ^{1}H NMR spectroscopy and SEC to determine monomer conversion and molar mass. After the defined time, the polymerization was

terminated by diluting the reaction mixture with acetone. The reaction mixture was purified by reprecipitation from an acetone solution into *n*-hexane/acetone = 4/1 (vol%). The purified product was dried under vacuum at 40 °C to give poly(PA-*alt*-BMGA) as a light yellow solid ($M_{n,NMR}$ = 4600; $M_{n,SEC}$ = 1790, $Đ$ = 1.23; yield: 118 mg, 48.2%).

Synthesis of poly(PA-*alt*-DAGA): The method B was used for the reaction of *t*-BuP_1 (40 μmol, 9.4 μL, 1.0 equiv.), PPA (40 μmol, 5.4 μL, 1.0 equiv.), PA (1.0 mmol, 148 mg, 25 equiv.), and DAGA (3.0 mmol, 460 mg, 75 equiv.) to give poly(PA-*alt*-DAGA) as a light yellow solid ($M_{n,NMR}$ = 5300; $M_{n,SEC}$ = 2480, $Đ$ = 1.30; yield: 216 mg, 70.5%).

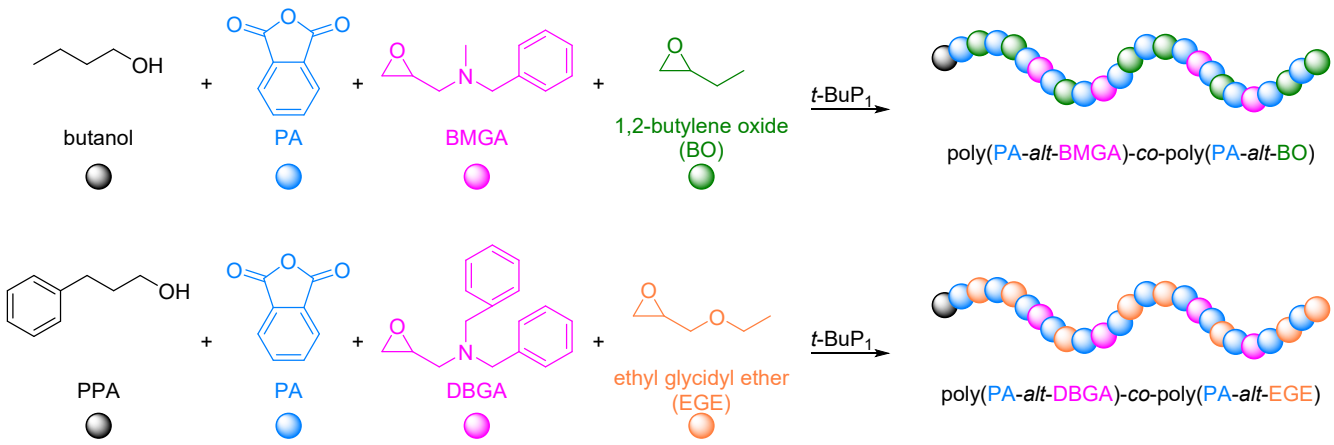
Synthesis of poly(GA-*alt*-DBGA): The method B was used for the reaction of *t*-BuP_1 (40 μmol, 9.4 μL, 1.0 equiv.), PPA (40 μmol, 5.4 μL, 1.0 equiv.), PA (1.0 mmol, 114 mg, 25 equiv.), and DBGA (3.0 mmol, 760 mg, 75 equiv.) to give poly(GA-*alt*-DBGA) as a colorless viscous solid ($M_{n,NMR}$ = 2000; $M_{n,SEC}$ = 4390, $Đ$ = 1.50; yield: 105 mg, 75.8%).

Synthesis of poly(DGA-*alt*-DBGA): The method B was used for the reaction of *t*-BuP_1 (40 μmol, 9.4 μL, 1.0 equiv.), PPA (40 μmol, 5.4 μL, 1.0 equiv.), DGA (1.0 mmol, 116 mg, 25 equiv.), and DBGA (3.0 mmol, 760 mg, 75 equiv.) to give poly(DGA-*alt*-DBGA) as a light yellow viscous solid ($M_{n,NMR}$: N.D.; $M_{n,SEC}$ = 5000, $Đ$ = 1.86; yield: 338 mg, 90.2%).

Synthesis of poly(SA-*alt*-DBGA): The method B was used for the reaction of *t*-BuP_1 (40 μmol, 9.4 μL, 1.0 equiv.), PPA (40 μmol, 5.4 μL, 1.0 equiv.), SA (1.0 mmol, 100 mg, 25 equiv.), and DBGA (3.0 mmol, 760 mg, 75 equiv.) to give poly(SA-*alt*-DBGA) as a black solid ($M_{n,NMR}$ = 4900; $M_{n,SEC}$ = 6800, $Đ$ = 2.22; yield: 150 mg, 62.1%).

1.6. Terpolymerization of cyclic anhydride, glycidylamine, and non amino-functionalized epoxide

Scheme S4. Ring-opening terpolymerization of anhydride, glycidylamine, with other epoxides



Terpolymerization of PA, BMGA, and BO: The method B was used for the reaction of *t*-BuP_1 (40 μmol, 9.4 μL, 1.0 equiv.), *n*-butanol (40 μmol, 3.7 μL, 1.0 equiv.), PA (4.0 mmol, 593 mg, 100 equiv.), BMGA (6.0 mmol, 1.06 g, 150 equiv.), and BO (6.0 mmol, 433 mg, 150 equiv.) to give poly(PA-*alt*-BMGA)-*co*-poly(PA-*alt*-BO) as a light yellow viscous solid ($M_{n,NMR}$ = 6200; $M_{n,SEC}$ = 3120, $Đ$ = 2.23; yield: 980 mg, 89.6%).

Terpolymerization of PA, DBGA, and EGE: The method B was used for the reaction of *t*-BuP_1 (40 μmol, 9.4 μL, 1.0 equiv.), PPA (40 μmol, 6.7 μL, 1.0 equiv.), PA (4.0 mmol, 593 mg, 100 equiv.), DBGA (6.0 mmol, 1.46 g, 150 equiv.), and EGE (6.0 mmol, 613 mg, 150 equiv.) to give poly(PA-*alt*-DBGA)-*co*-poly(PA-*alt*-EGE) as a light yellow viscous solid ($M_{n,NMR}$ = 14 700; $M_{n,SEC}$ = 6350, $Đ$ = 1.39; yield: 1.03 g, 79.5%).

2. Supporting figures and tables

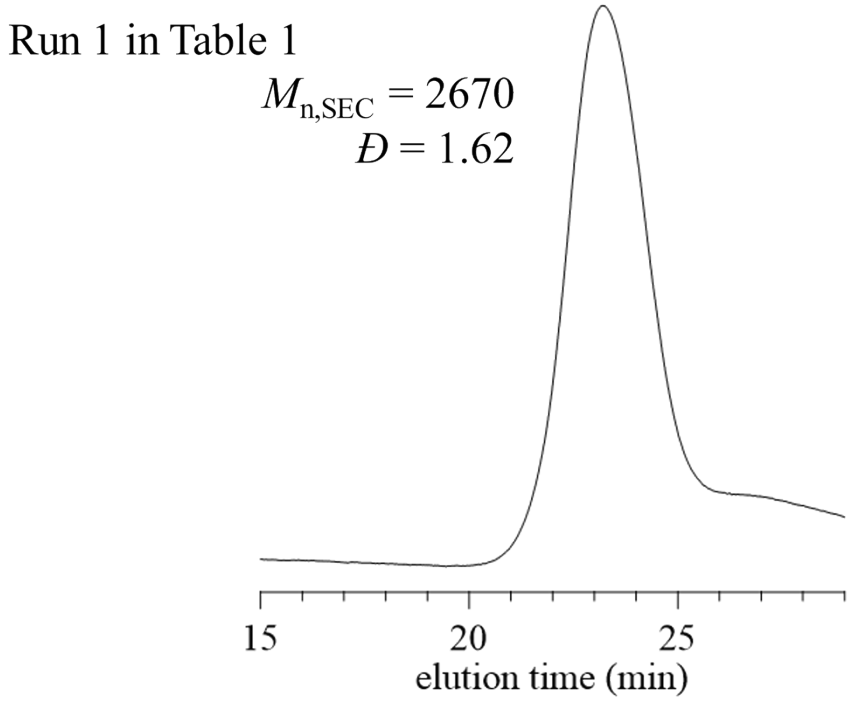


Figure S1. SEC trace of poly(PA-*alt*-DBGA) obtained via run 1 in Table 1 (eluent, DMF containing 0.01 mol L^{-1} LiCl; flow rate, 0.6 mL min^{-1}).

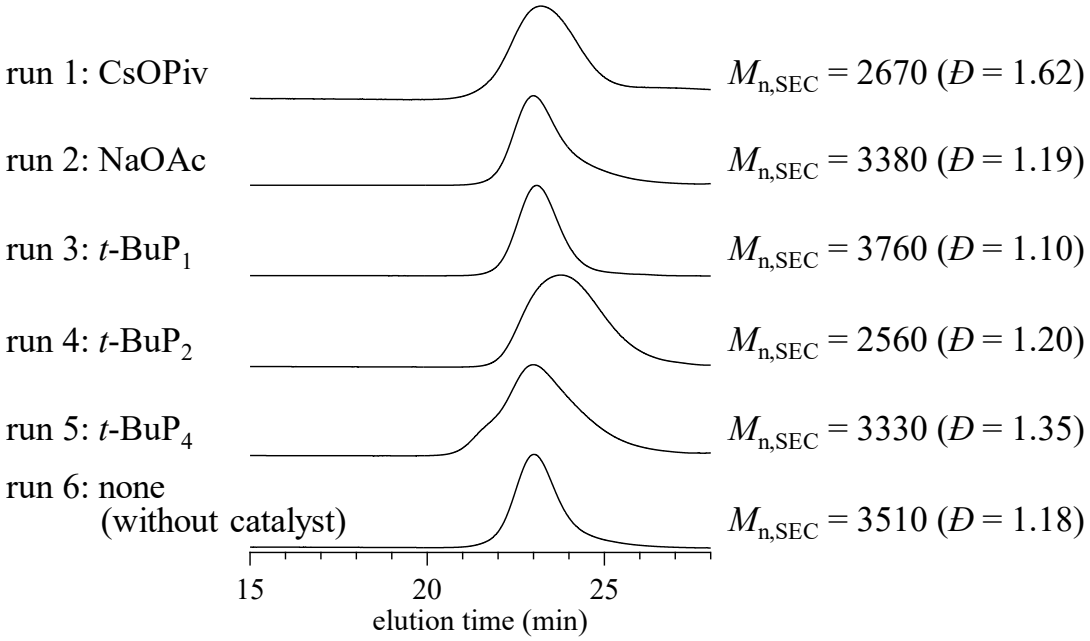


Figure S2. SEC traces of poly(PA-*alt*-DBGA) obtained via runs 1–6 in Table 1 (eluent, DMF containing 0.01 mol L^{-1} LiCl; flow rate, 0.6 mL min^{-1}).

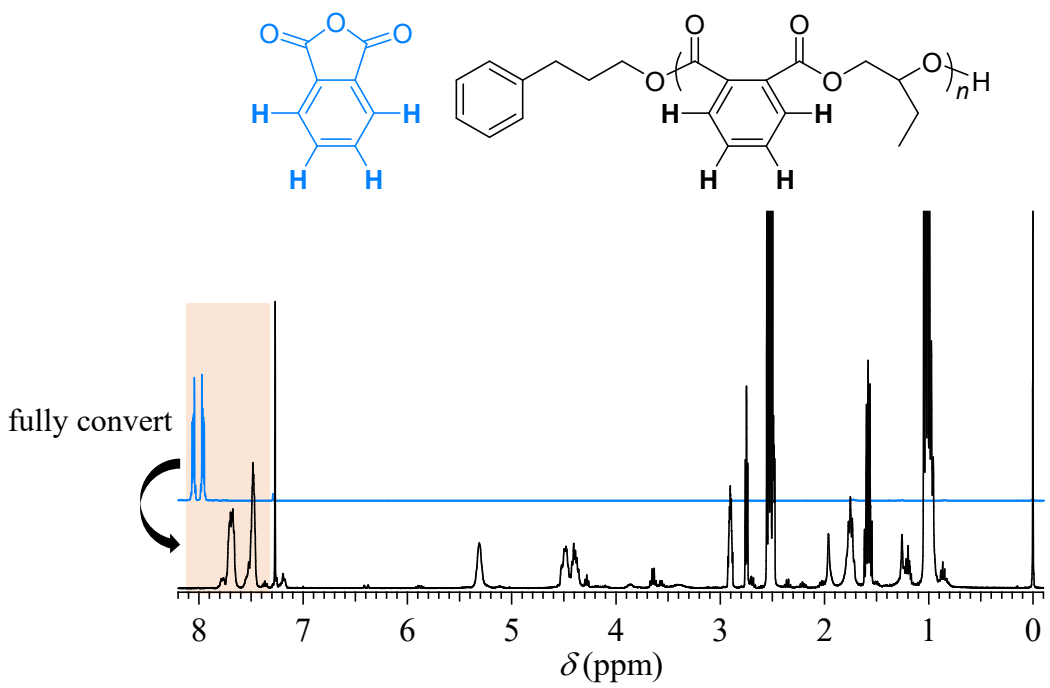
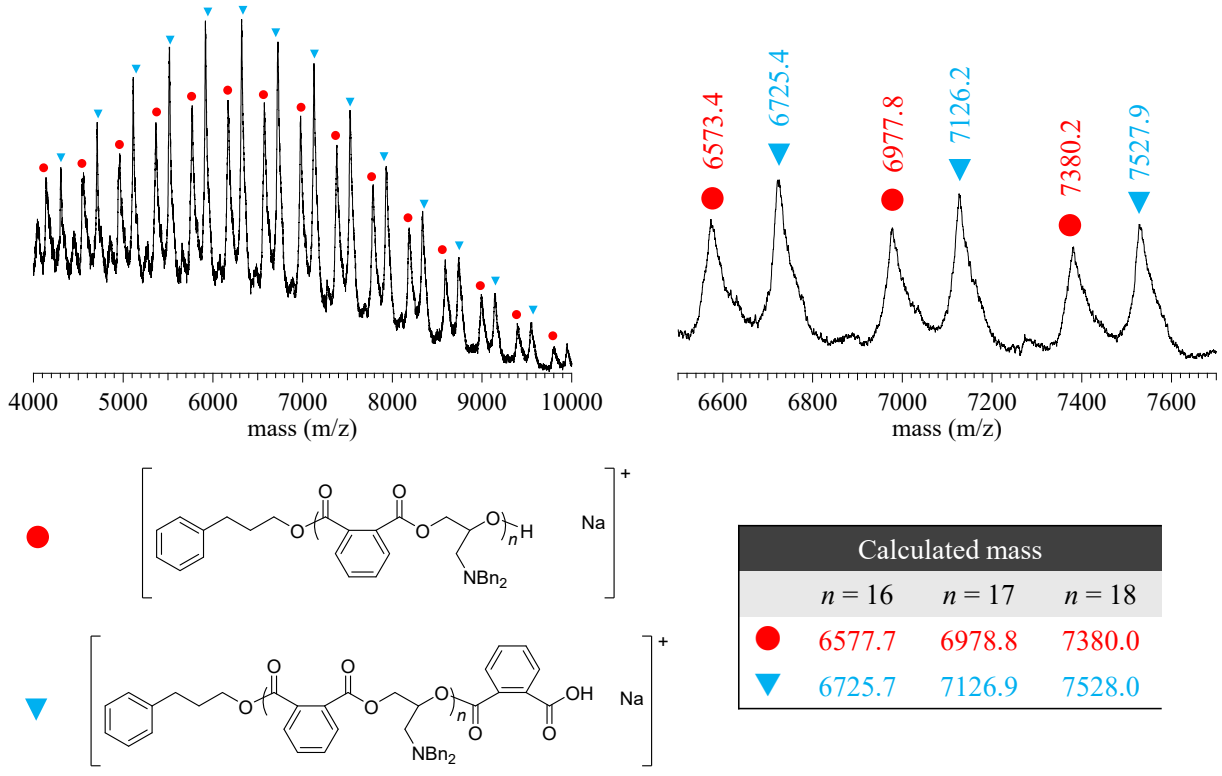


Figure S3. ^{1}H NMR spectra of PA (upper) and crude aliquot obtained via run 1 in Table 2 (in $CDCl_3$, 400 MHz).



Calculated mass			
	n = 16	n = 17	n = 18
●	6577.7	6978.8	7380.0
▼	6725.7	7126.9	7528.0

Figure S4. MALDI-TOF MS analysis of poly(PA-*alt*-DBGA) (run 3 in Table 1).

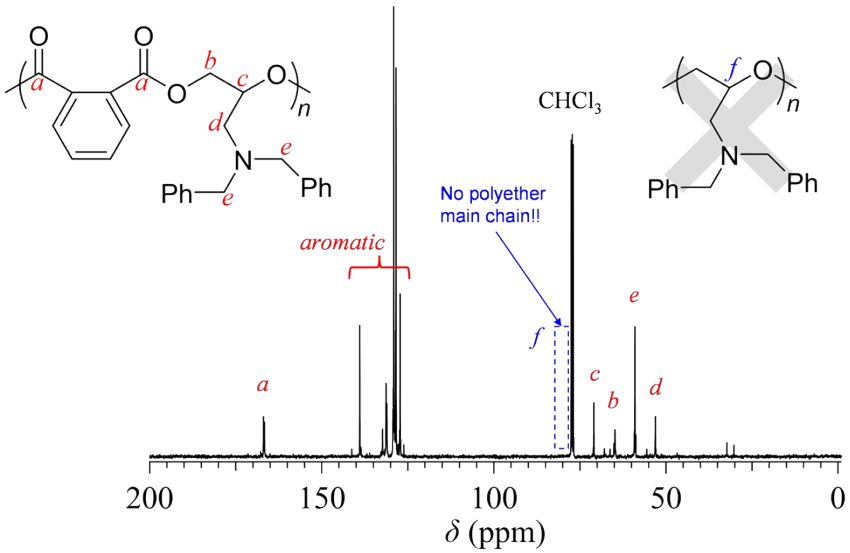


Figure S5. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of poly(PA-*alt*-DBGA) (run 3 in Table 1).

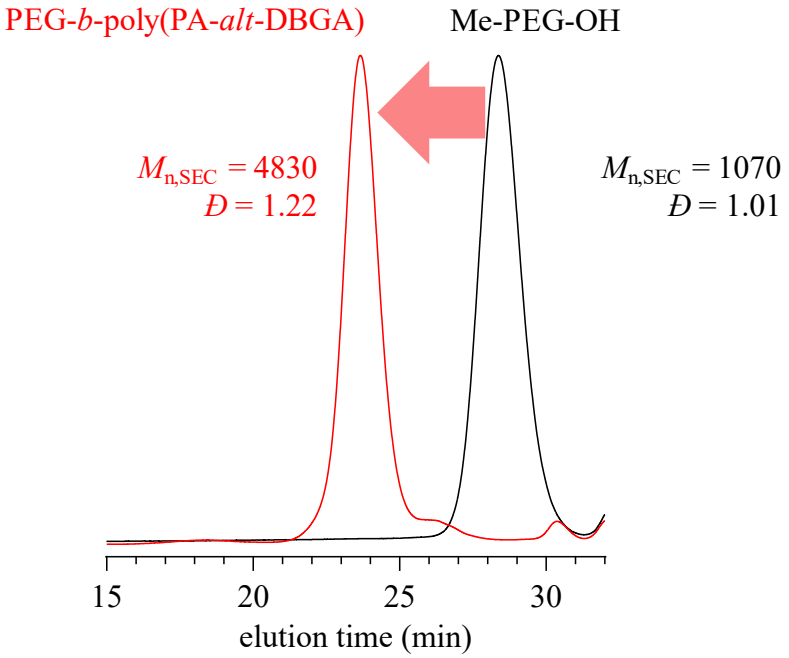


Figure S6. SEC traces of Me-PEG-OH (black line) and PEG-*b*-poly(PA-*alt*-DBGA) (red line) obtained via run 1 in Table 2 (eluent, DMF containing 0.01 mol L^{-1} LiCl; flow rate, 0.6 mL min^{-1}).

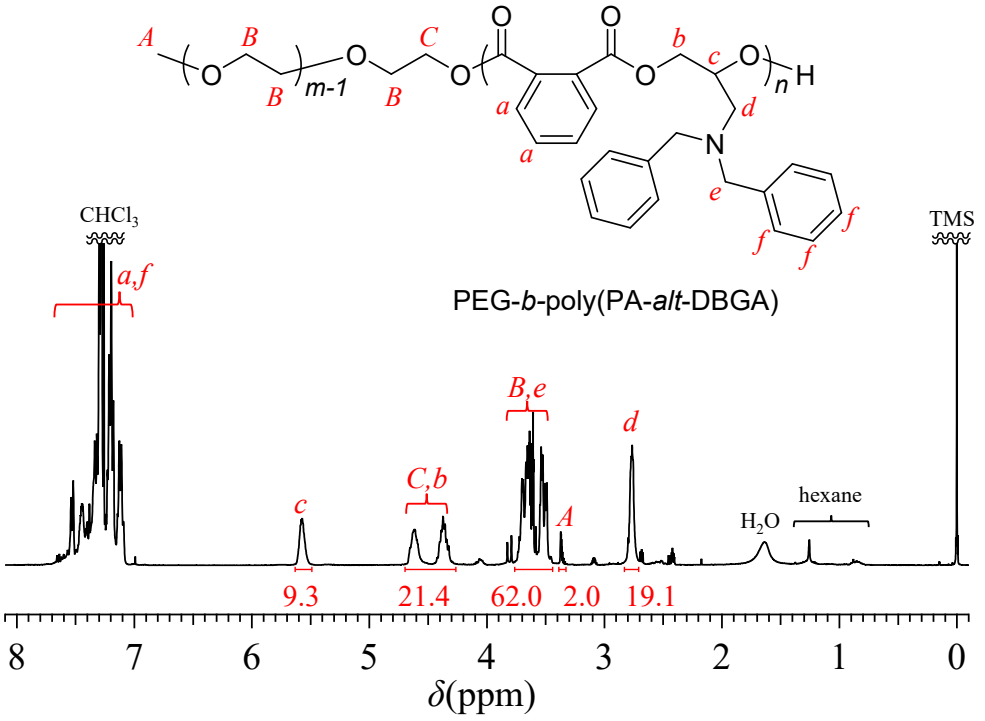


Figure S7. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of PEG-*b*-poly(PA-*alt*-DBGA) (run 1 in Table 2).

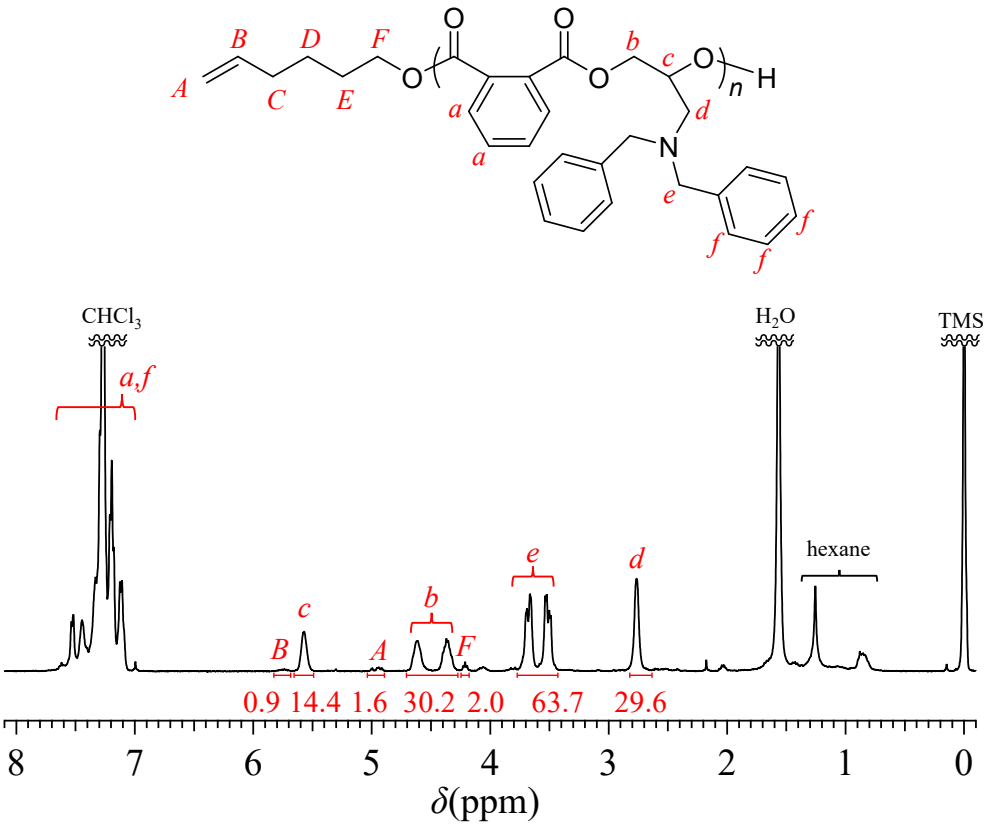


Figure S8. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of poly(PA-*alt*-DBGA) using 5-hexen-1-ol as an initiator (run 2 in Table 2).

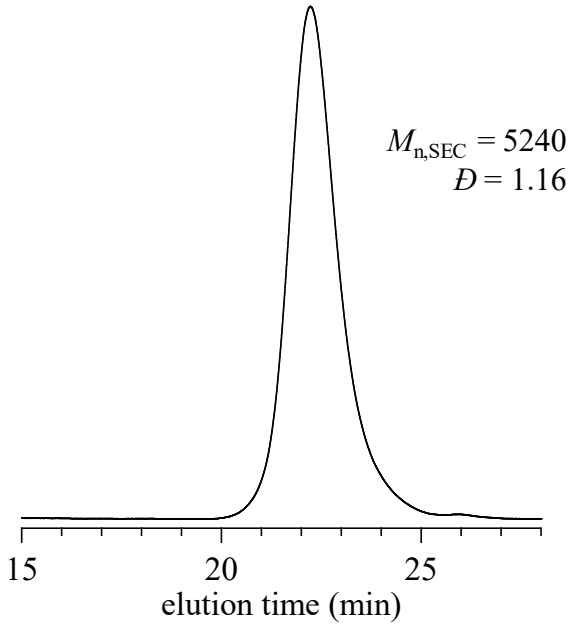


Figure S9. SEC trace (eluent, DMF containing 0.01 mol L^{-1} LiCl; flow rate, 0.6 mL min^{-1}) of poly(PA-*alt*-DBGA) using 5-hexen-1-ol as an initiator (run 2 in Table 2).

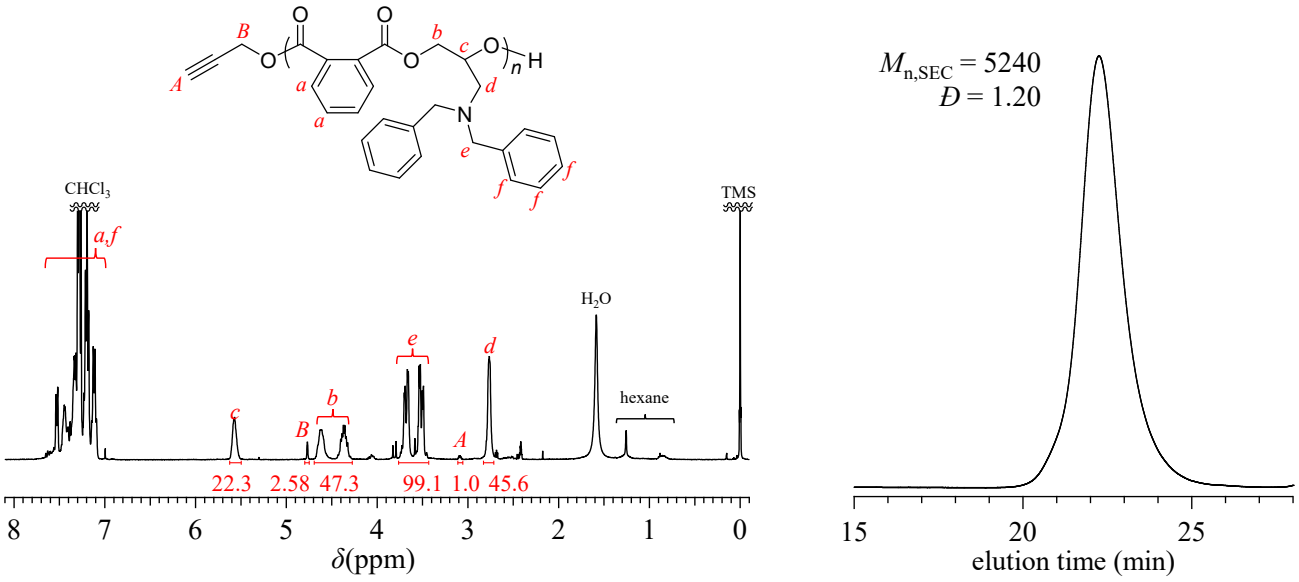


Figure S10. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz; left panel) and SEC trace (eluent, DMF containing 0.01 mol L^{-1} LiCl; flow rate, 0.6 mL min^{-1}; right panel) of poly(PA-*alt*-DBGA) using propargyl alcohol as an initiator (run 3 in Table 2).

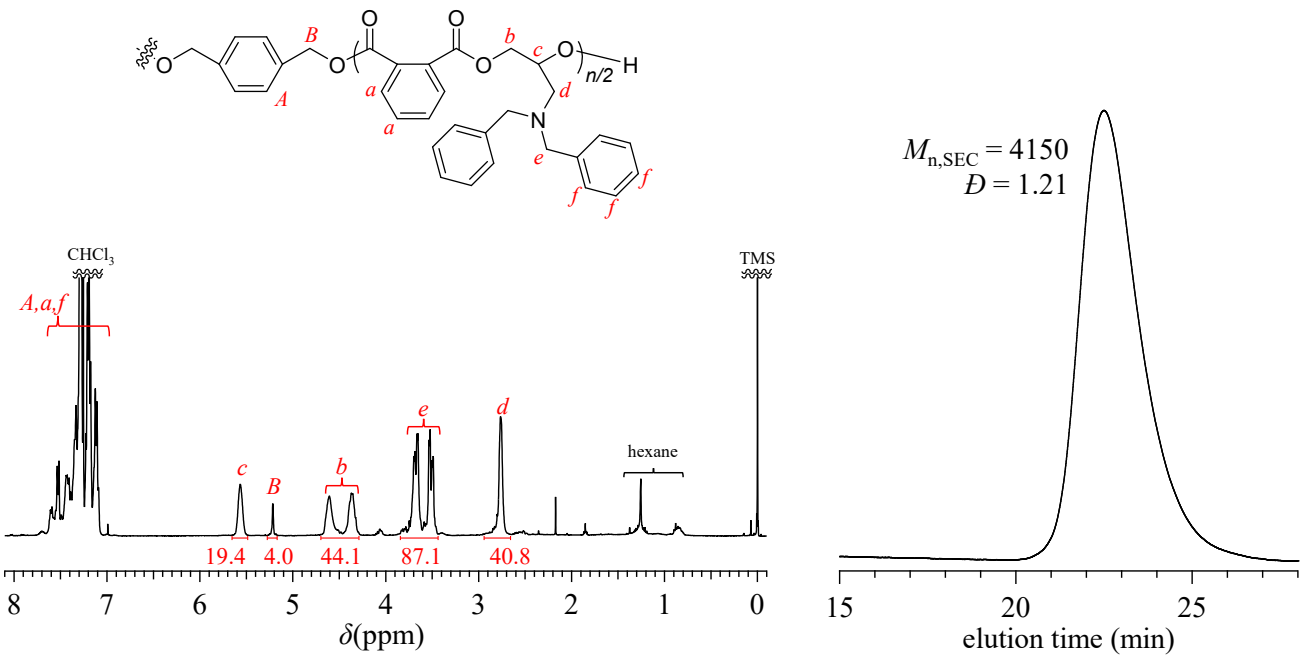


Figure S11. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz; left panel) and SEC trace (eluent, DMF containing 0.01 mol L^{-1} LiCl; flow rate, 0.6 mL min^{-1}; right panel) of poly(PA-*alt*-DBGA) using BDM as an initiator (run 4 in Table 2).

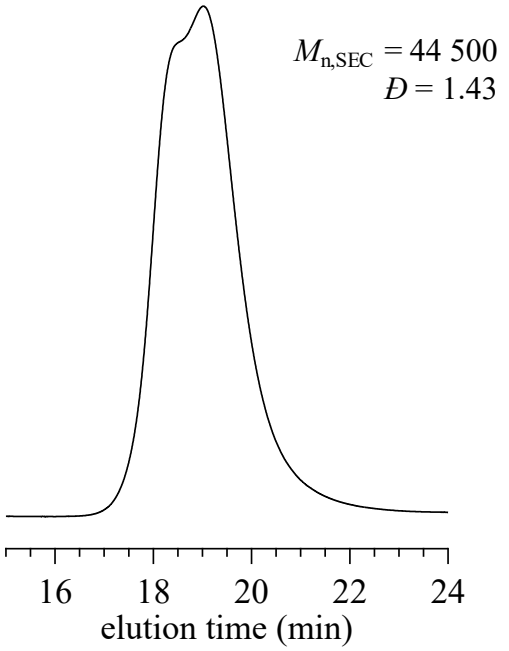


Figure S12. SEC trace (eluent, DMF containing 0.01 mol L^{-1} LiCl; flow rate, 0.6 mL min^{-1}) of poly(PA-*alt*-DBGA) synthesized without catalyst (run 5 in Table 2).

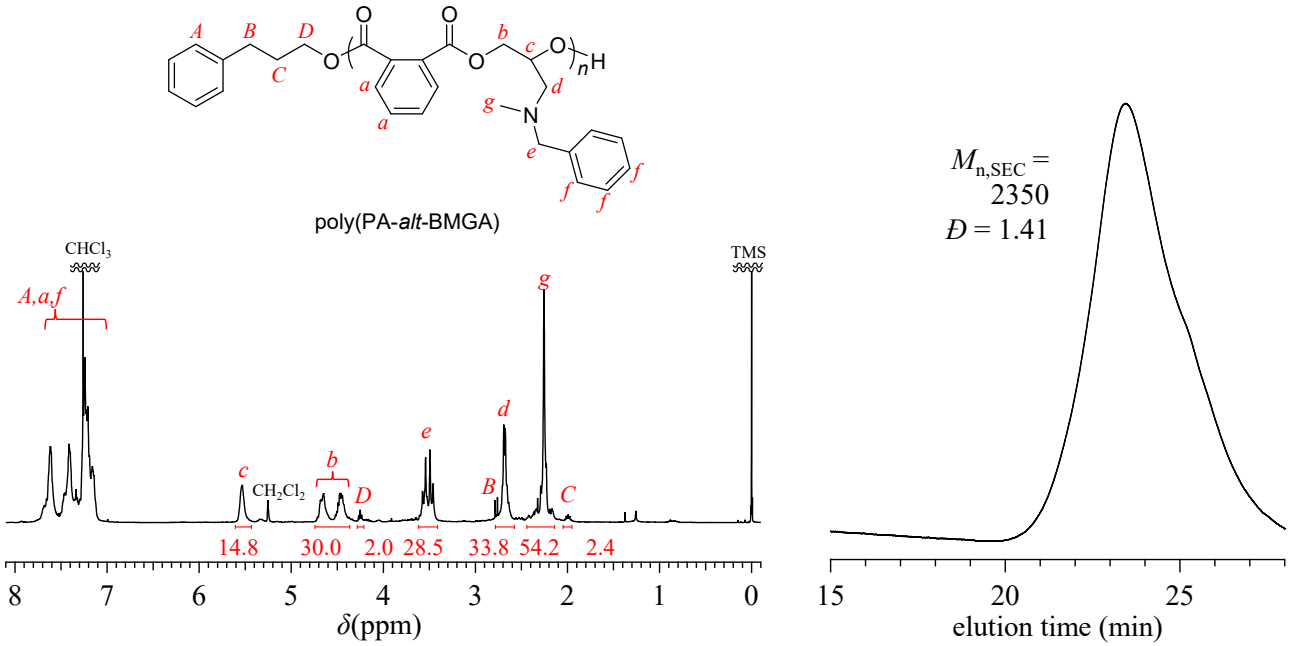


Figure S13. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz; left panel) and SEC trace (eluent, DMF containing 0.01 mol L^{-1} LiCl; flow rate, 0.6 mL min^{-1}; right panel) of poly(PA-*alt*-BMGA) obtained via run 2 in Table 3.

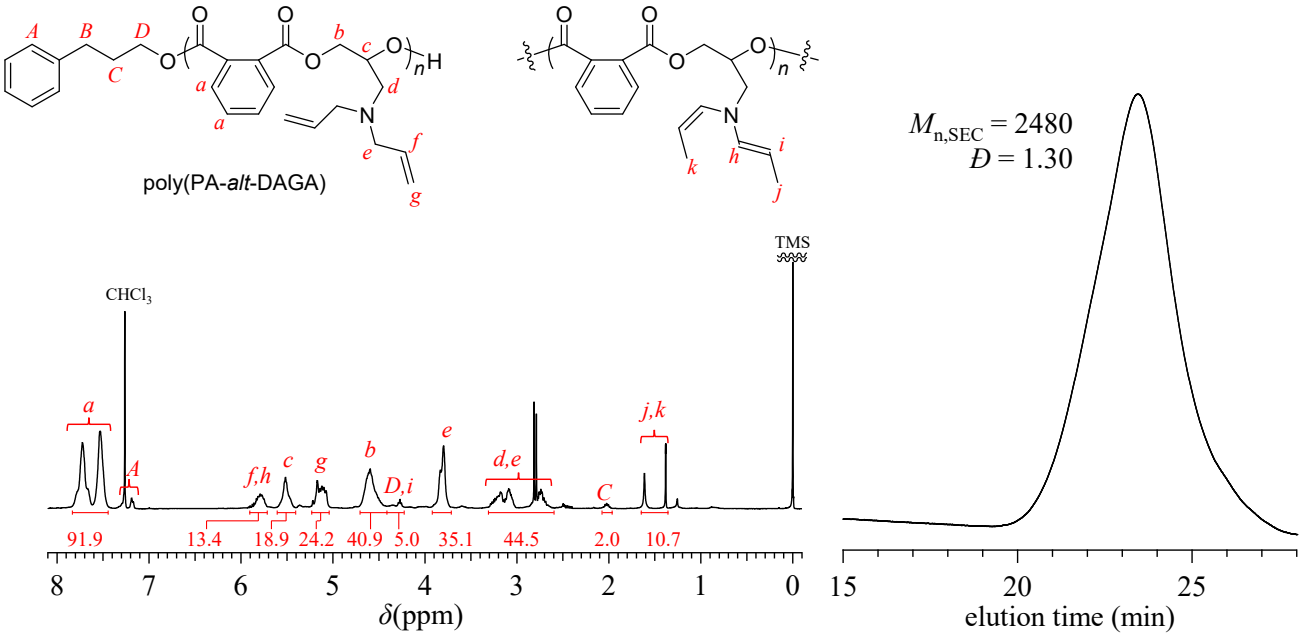


Figure S14. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz; left panel) and SEC trace (eluent, DMF containing 0.01 mol L^{-1} LiCl; flow rate, 0.6 mL min^{-1}; right panel) of poly(PA-*alt*-DAGA) obtained via run 3 in Table 3.

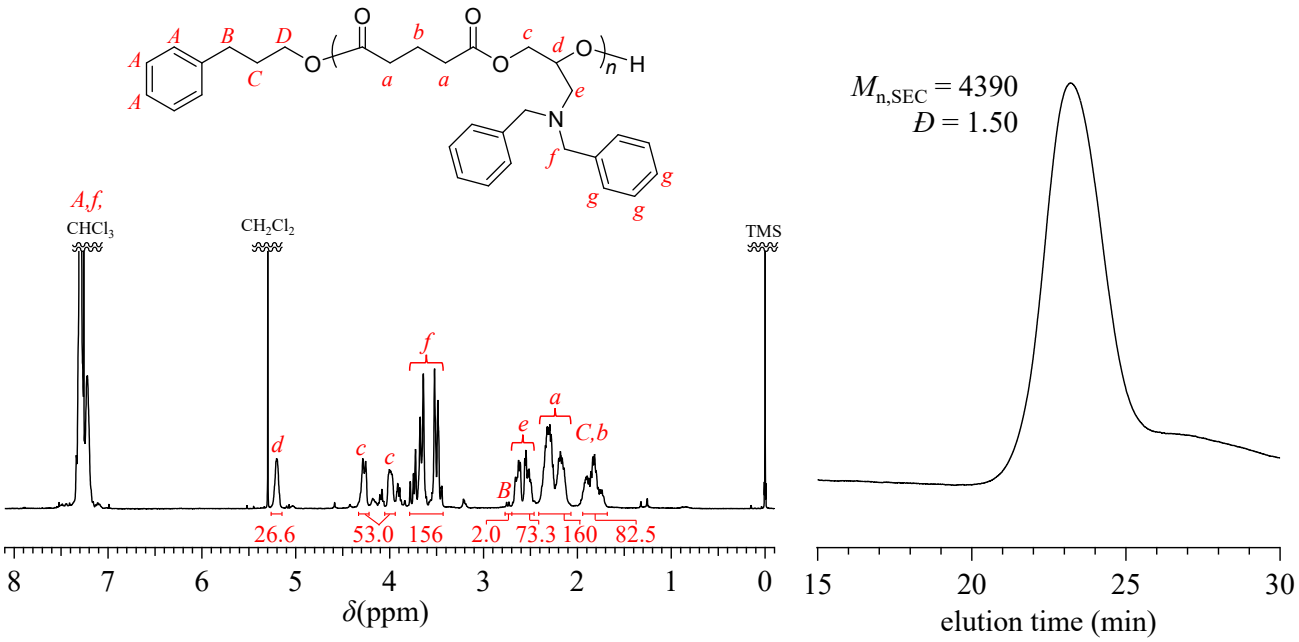


Figure S15. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz; left panel) and SEC trace (eluent, DMF containing 0.01 mol L^{-1} LiCl; flow rate, 0.6 mL min^{-1}; right panel) of poly(GA-*alt*-DBGA) obtained via run 4 in Table 3.

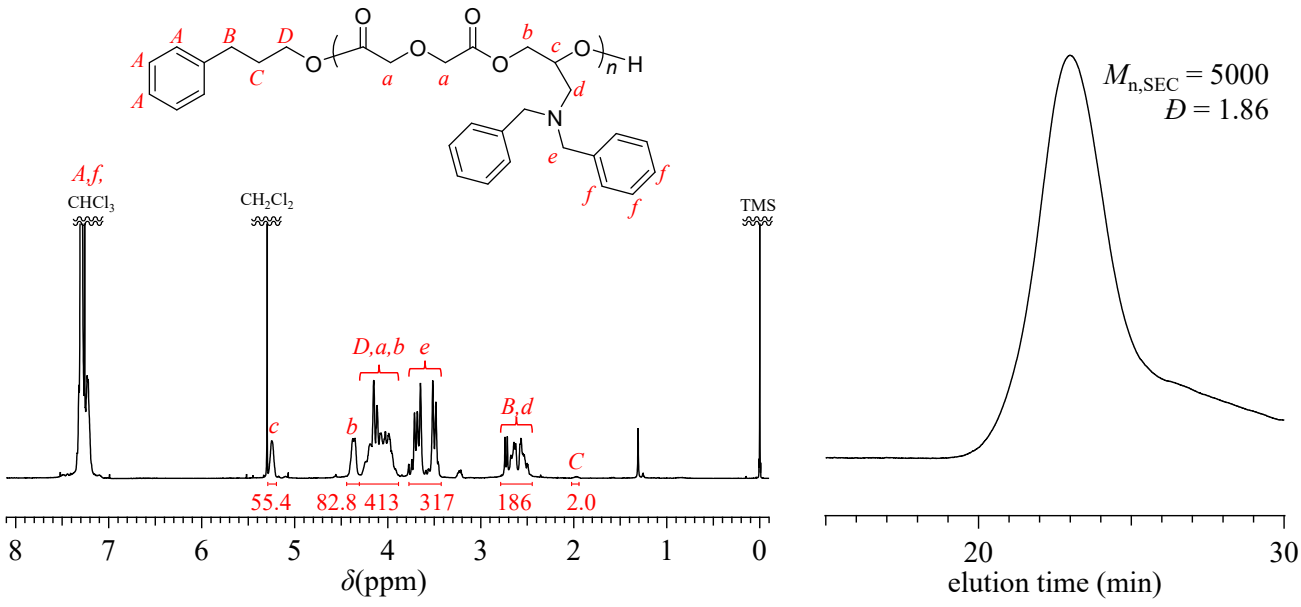


Figure S16. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz; left panel) and SEC trace (eluent, DMF containing 0.01 mol L^{-1} LiCl; flow rate, 0.6 mL min^{-1}; right panel) of poly(DGA-*alt*-DBGA) obtained via run 5 in Table 3.

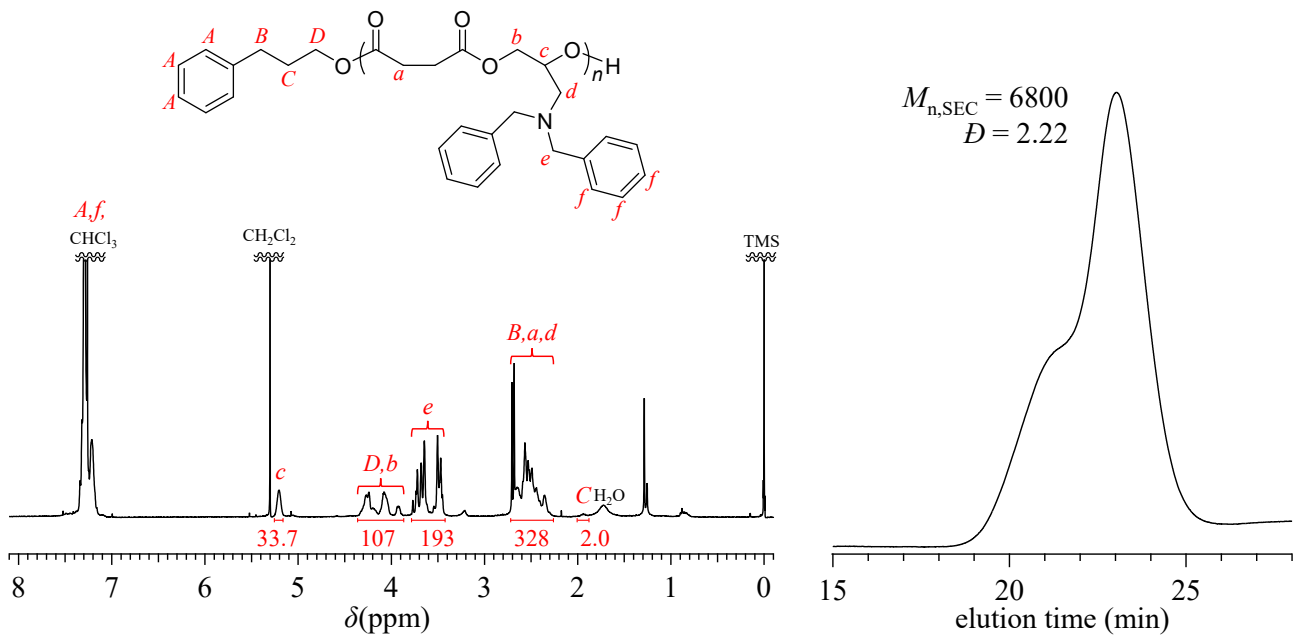


Figure S17. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz; left panel) and SEC trace (eluent, DMF containing 0.01 mol L^{-1} LiCl; flow rate, 0.6 mL min^{-1}; right panel) of poly(SA-*alt*-DBGA) obtained via run 6 in Table 3.

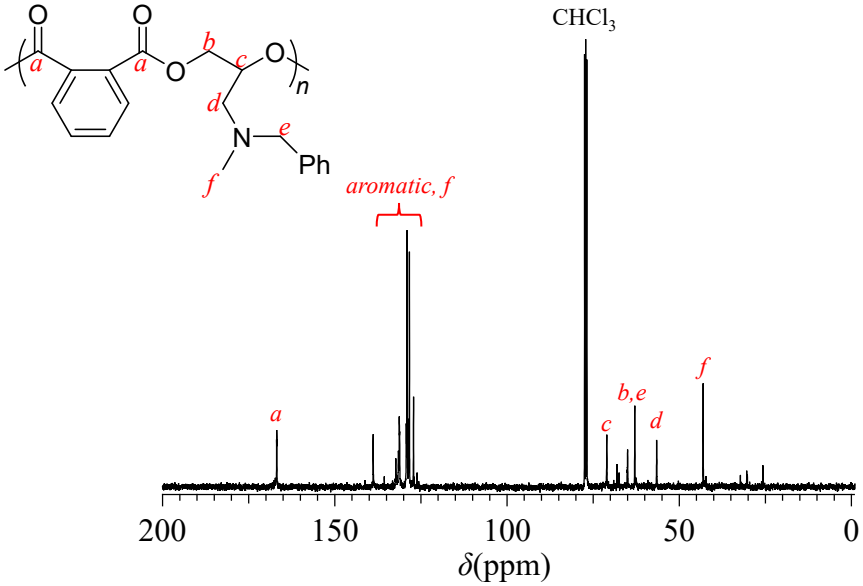


Figure S18. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of poly(PA-*alt*-BMGA) (run 1 in Table 4).

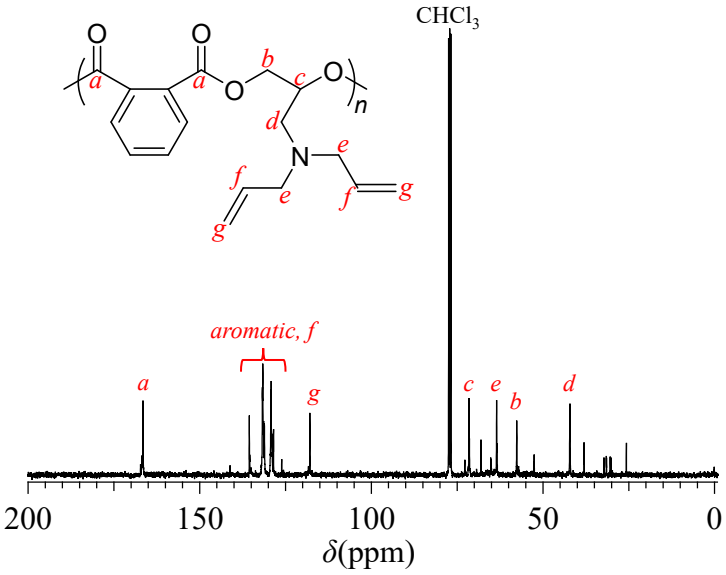


Figure S19. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of poly(PA-*alt*-DAGA) (run 2 in Table 4).

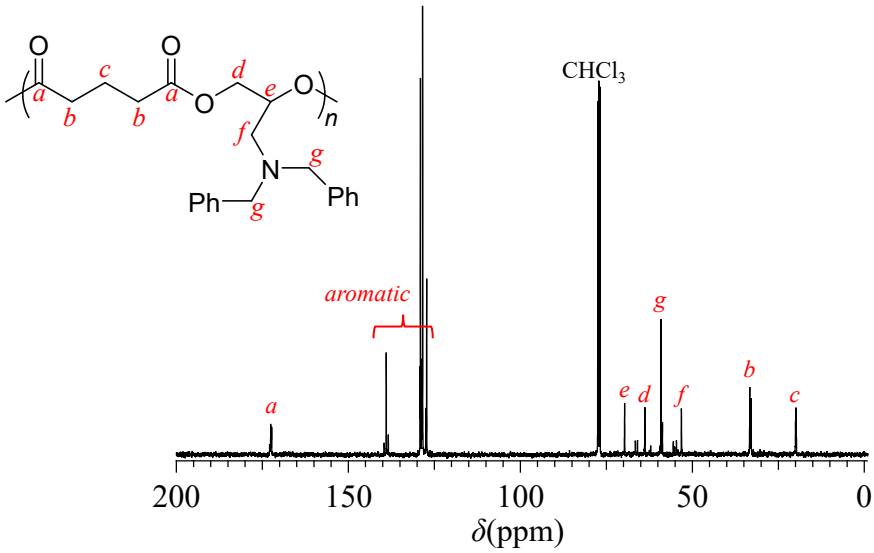


Figure S20. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of poly(GA-*alt*-DBGA) (run 3 in Table 4).

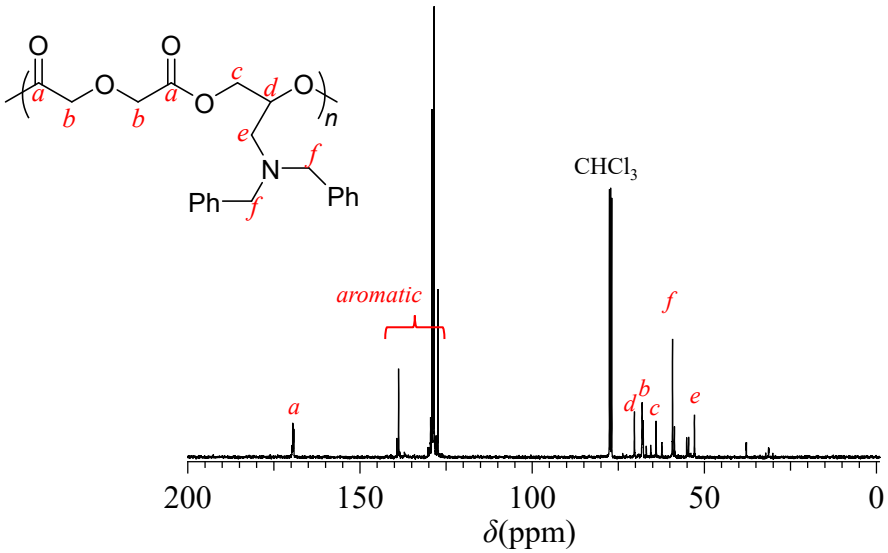


Figure S21. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of poly(DGA-*alt*-DBGA) (run 4 in Table 4).

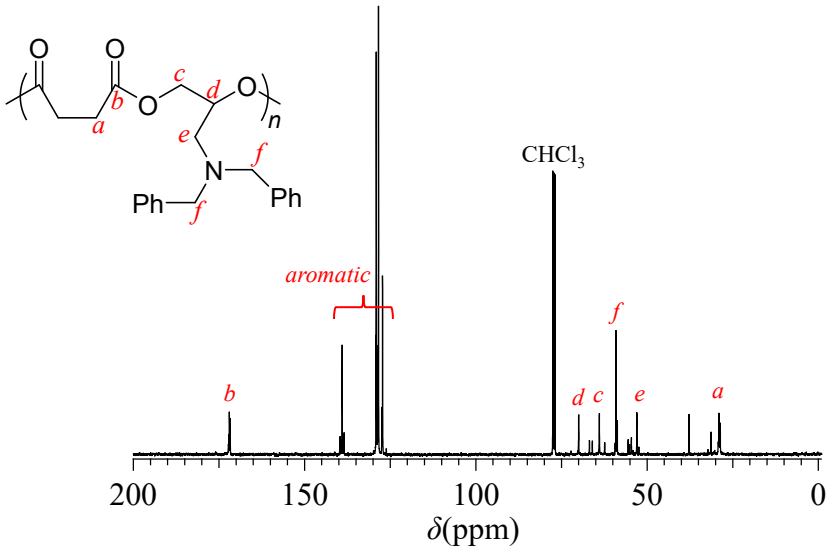


Figure S22. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of poly(SA-*alt*-DBGA) (run 5 in Table 4).

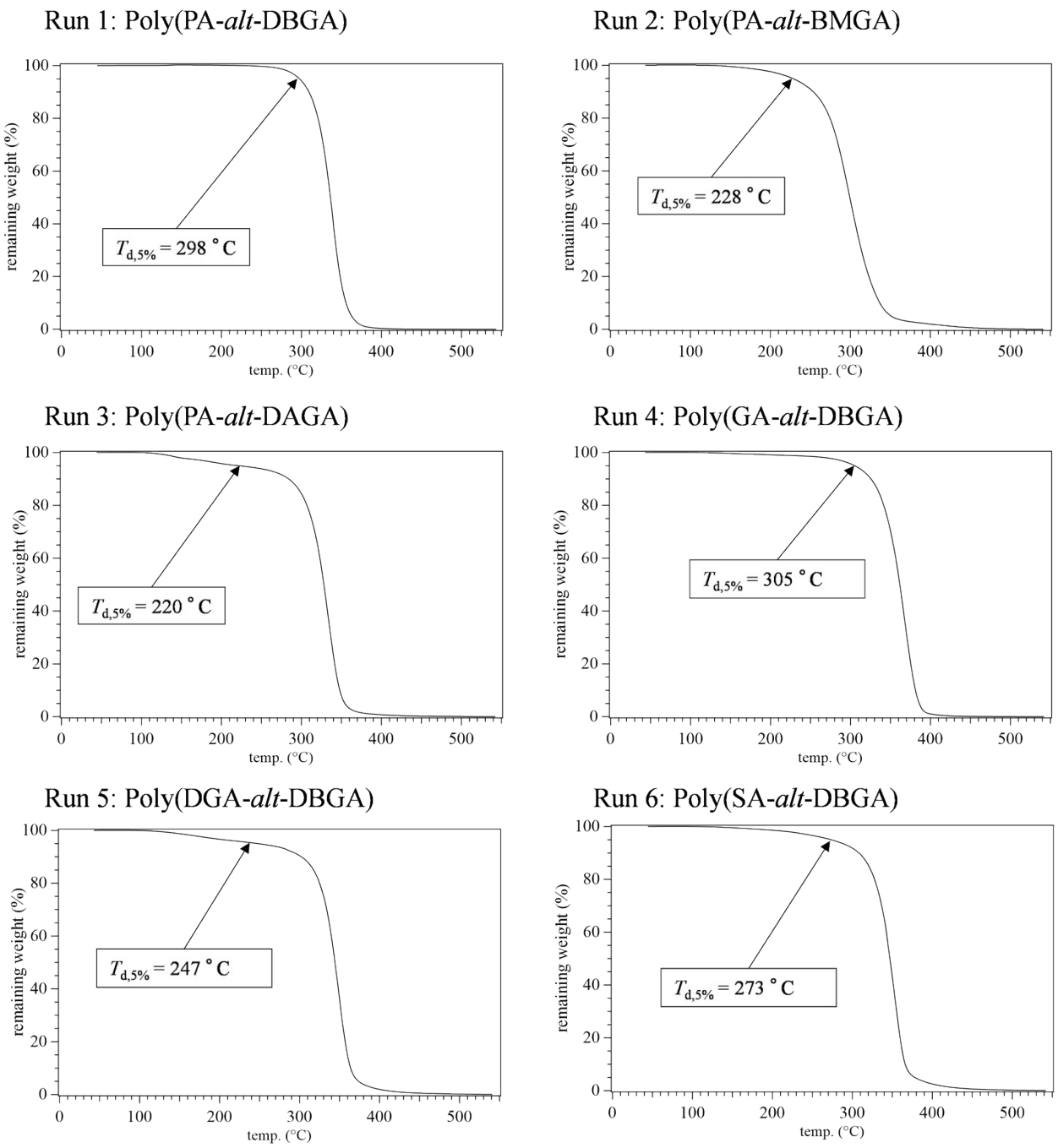


Figure S23. Thermogravimetric analysis of the poly(cyclic anhydride-*alt*-glycidylamine)s in Table 3.

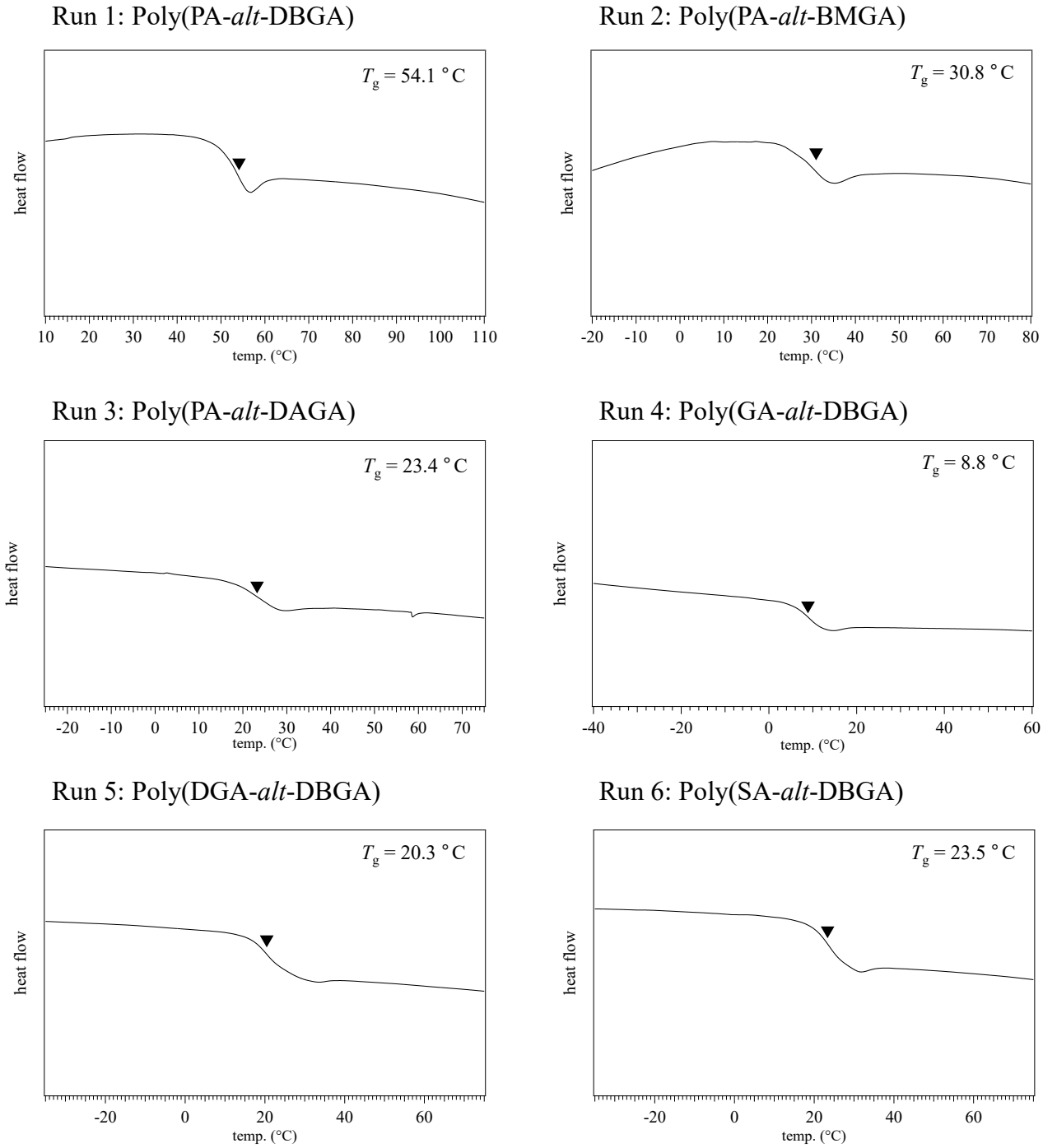


Figure S24. DSC thermograms of the poly(cyclic anhydride-*alt*-glycidylamine)s in Table 3.

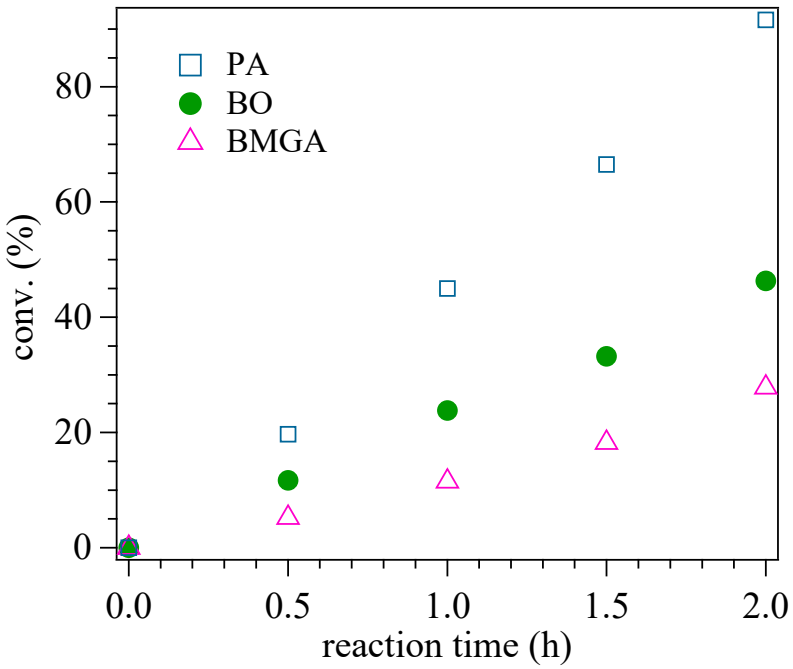
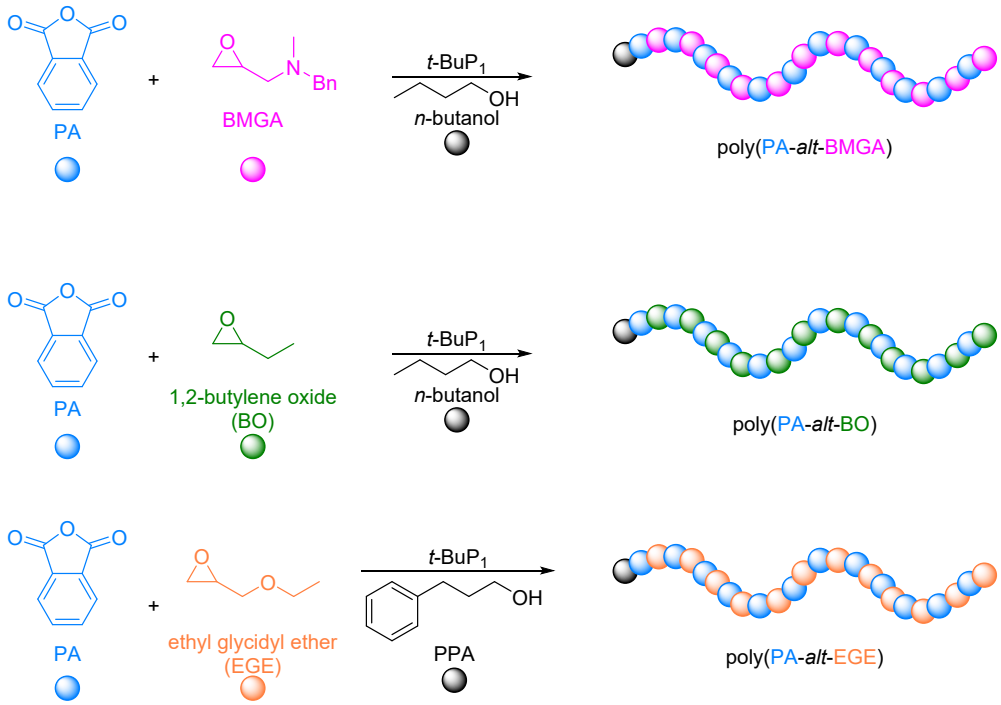


Figure S25. Time to conv. plots of PA (square), BO (filled circle), and BMGA (triangle) determined via ^{1}H NMR spectrum for run 1 in Table 4.

Table S1. ROAC of PA and cyclic ethers using *t*-BuP$_1$ as a catalyst [a]



run	monomer	initiator	time (h)	conv.$_{PA}$ (%) [b]	$M_{n,theo.}$ [c]	$M_{n,NMR}$ [b]	$M_{n,SEC}$ [d]	$Đ$ [d]
1	PA/BMGA	*n*-butanol	3.0	>99	33 000	5800	3520	2.11
2	PA/BO	*n*-butanol	1.5	>99	22 000	18 000	11 000	1.22
3	PA/EGE	PPA	2.0	98	25 000	20 000	5680	1.31

[a] Polymerization conditions: temp., 80 °C; atmosphere, Ar; catalyst, *t*-BuP$_1$; monomer; [*t*-BuP$_1$]/[initiator]$_0$/[PA]$_0$/[glycidylamine or epoxide]$_0$ = 1/1/100/300. [b] Determined via ^{1}H NMR in $CDCl_3$. [c] Calculated from (M.W. of initiator) + [PA]$_0$/[initiator]$_0$ × conv.$_{PA}$ × (M.W. of PA + M.W. of glycidylamine or epoxide). [d] Determined via SEC in DMF containing 0.01 mol L^{-1} LiCl using PSt. standard.

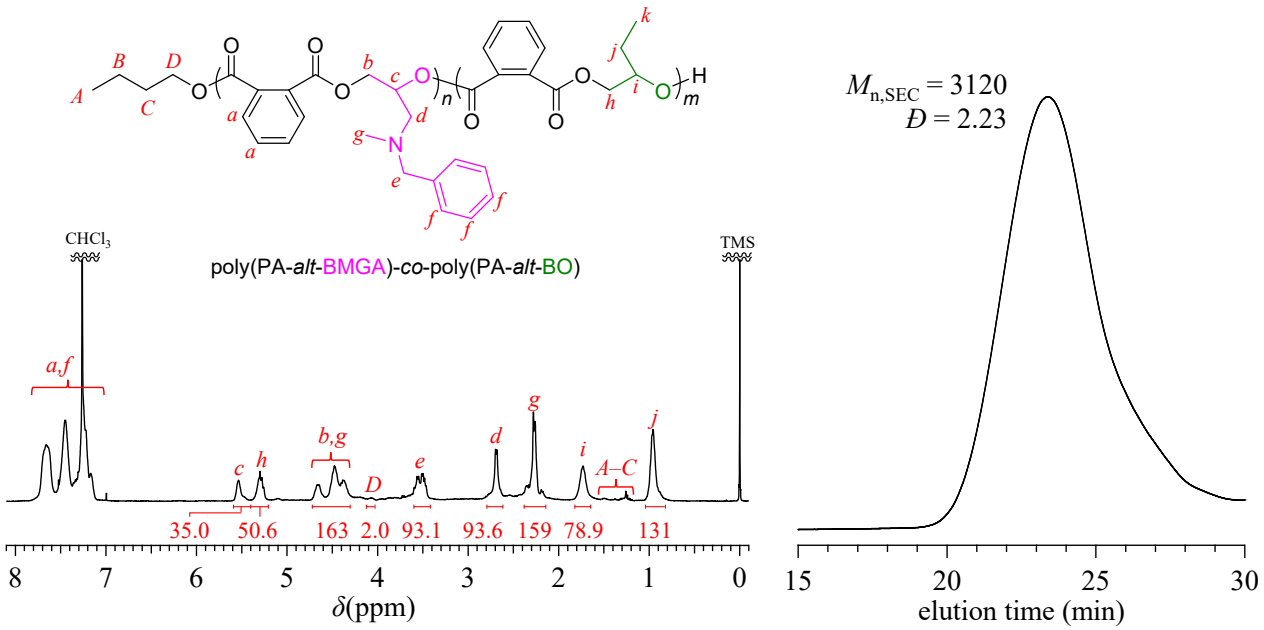


Figure S26. ^{1}H NMR ($CDCl_3$, 400 MHz; left panel) and SEC trace (eluent, DMF containing 0.01 mol L^{-1} LiCl; flow rate, 0.6 mL min^{-1}; right panel) of poly(PA-*alt*-BMGA)-*co*-poly(PA-*alt*-BO) obtained via run 1 in Table 5.

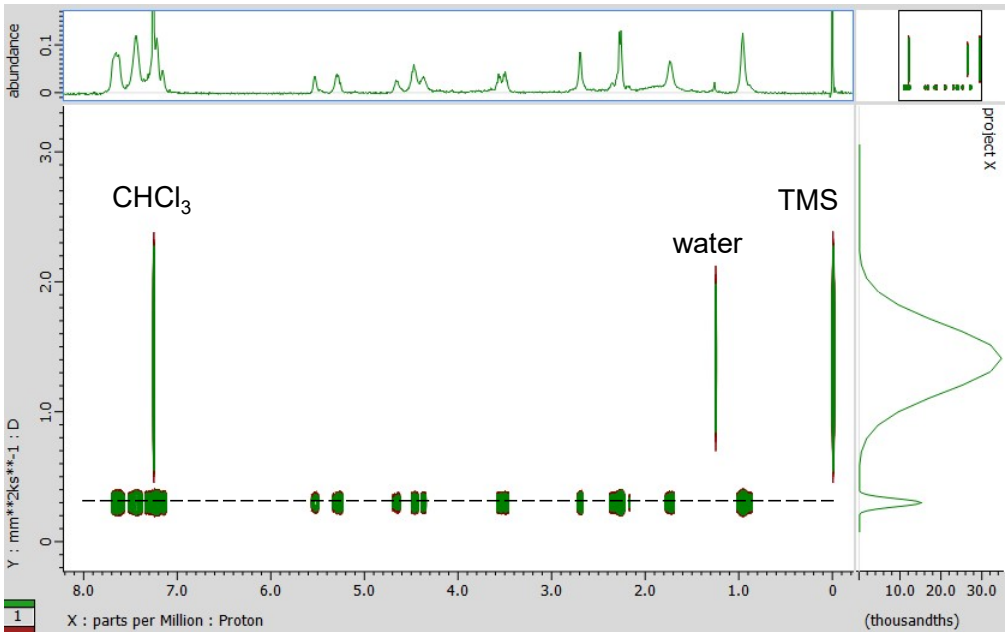


Figure S27. DOSY ($CDCl_3$, 600 MHz) spectrum of poly(PA-*alt*-BMGA)-*co*-poly(PA-*alt*-BO) obtained from run 1 in Table 5.

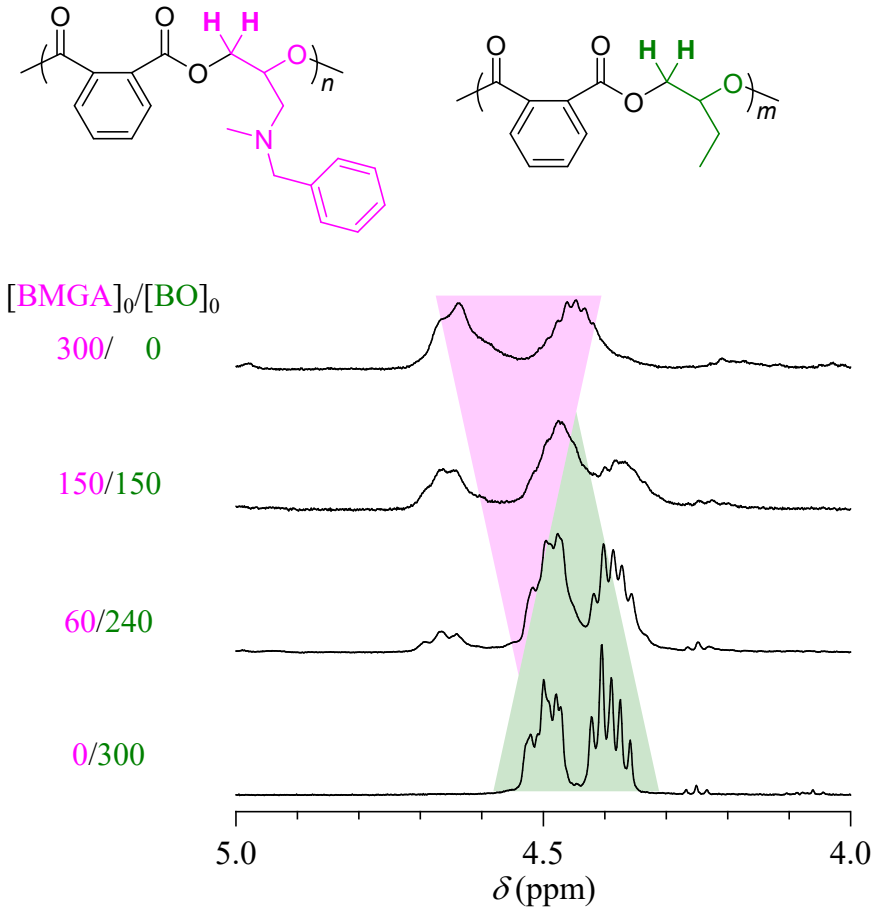


Figure S28. ^{1}H NMR spectra of poly(PA-*alt*-BMGA) (run 1 in Table S1), poly(PA-*alt*-BMGA)-*co*-poly(PA-*alt*-BO) ($[BMGA]_0/[BO]_0$ = 150/150, run 1 in Table 5; $[BMGA]_0/[BO]_0$ = 60/240, run 2 in Table 5), and poly(PA-*alt*-BO) (run 2 in Table S1) in $CDCl_3$ (400 MHz).

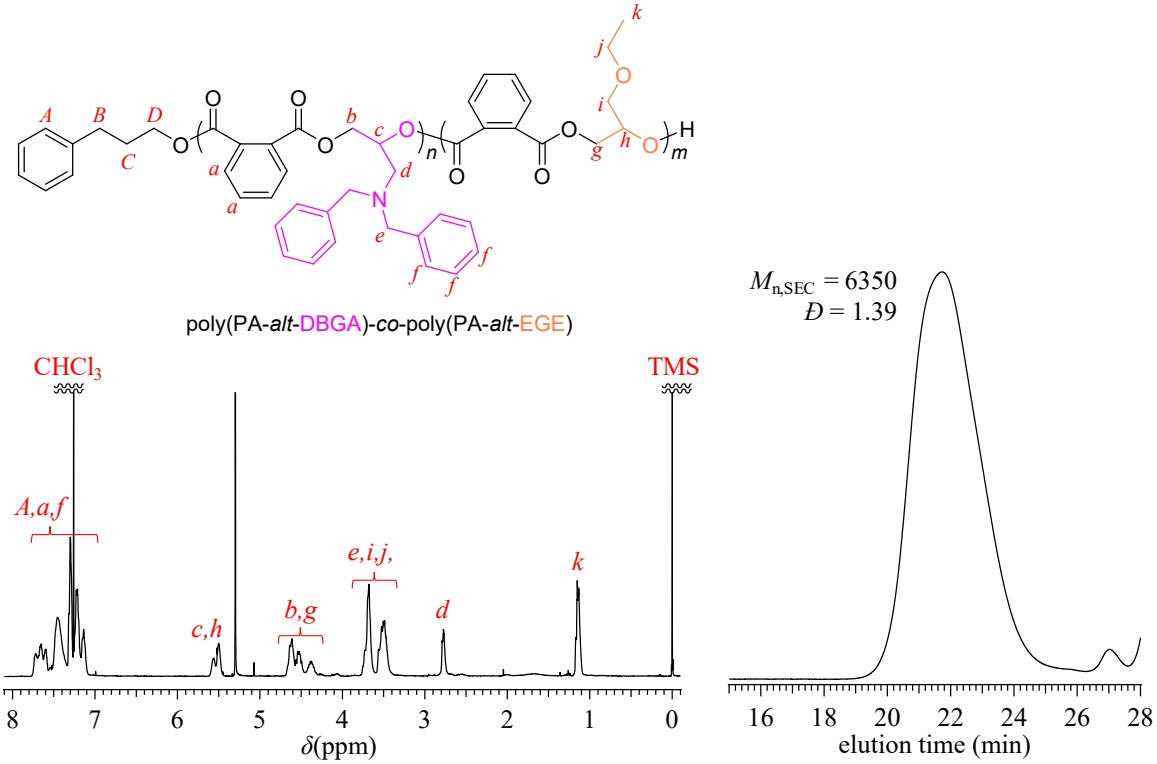


Figure S29. ^{1}H NMR ($CDCl_3$, 400 MHz; left panel) and SEC trace (eluent, DMF containing 0.01 mol L^{-1} LiCl; flow rate, 0.6 mL min^{-1}; right panel) of poly(PA-*alt*-DBGA)-*co*-poly(PA-*alt*-EGE) obtained from run 3 in Table 5.

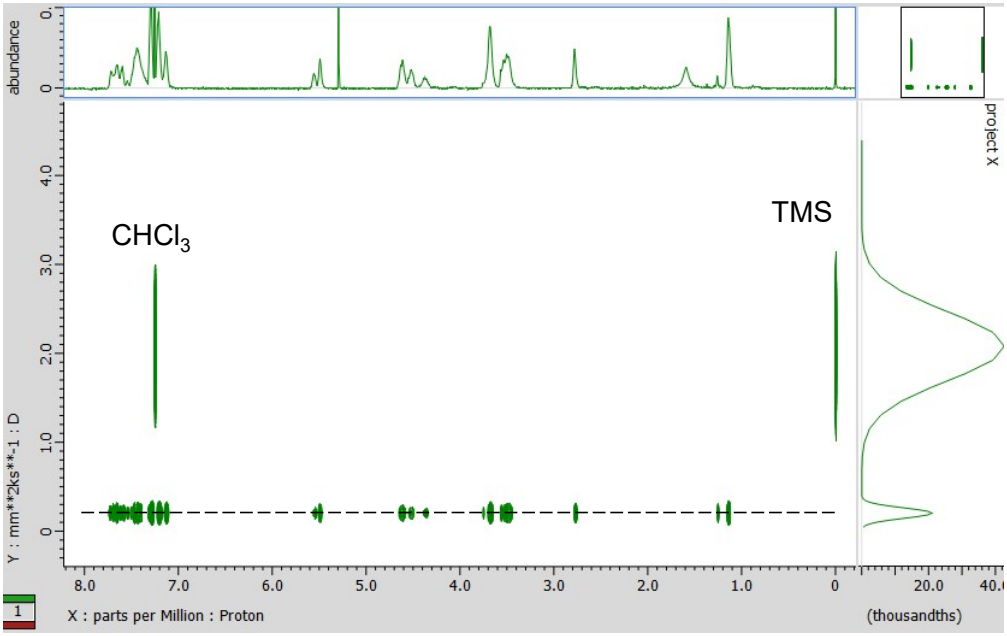


Figure S30. DOSY ($CDCl_3$, 600 MHz) spectrum of poly(PA-*alt*-DBGA)-*co*-poly(PA-*alt*-EGE) obtained from run 3 in Table 5.

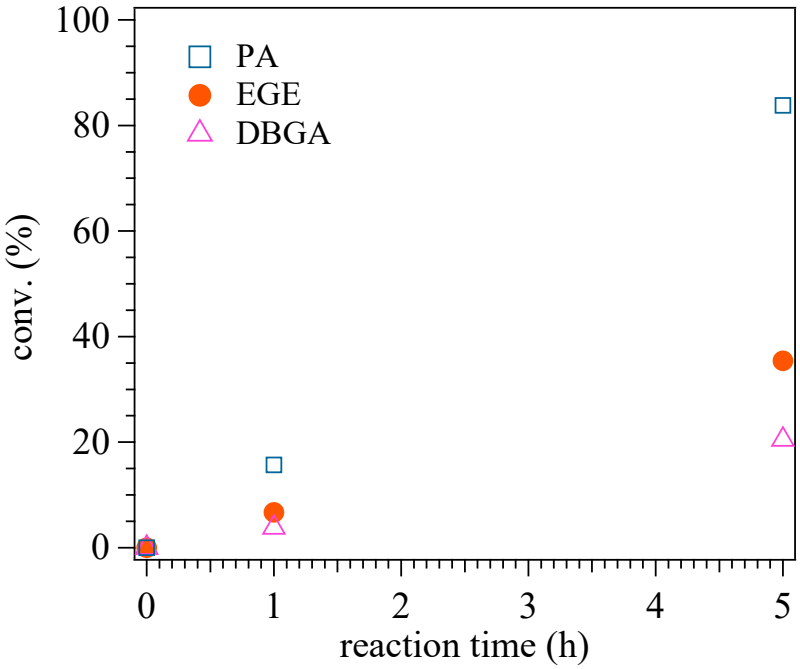


Figure S31. Time to conv. plots of PA (square), EGE (filled circle), and DBGA (triangle) determined via ^{1}H NMR spectrum for run 3 in Table 5.

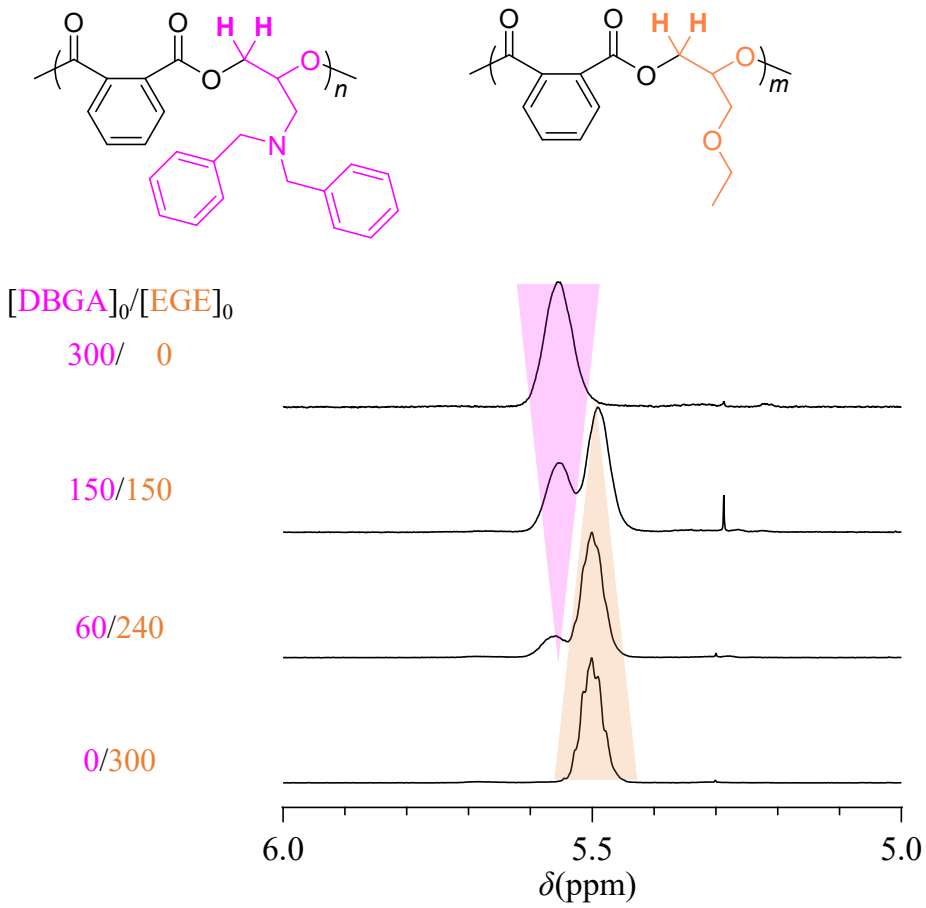


Figure S32. ^{1}H NMR spectra of poly(PA-*alt*-DBGA) (run 8 in Table 1), poly(PA-*alt*-DBGA)-*co*-poly(PA-*alt*-EGE) ($[DBGA]_0/[EGE]_0$ = 150/150, run 3 in Table 5; $[DBGA]_0/[EGE]_0$ = 60/240, run 4 in Table 5), and poly(PA-*alt*-EGE) (run 3 in Table S1) in $CDCl_3$ (400 MHz).

3. References

(1) Isono, T; Asai, S.; Satoh, Y.; Takaoka, T.; Tajima, K.; Toyoji, K.; Satoh, T. Controlled/Living Ring-Opening Polymerization of Glycidylamine Derivatives Using *t*-Bu-P_4/Alcohol Initiating System Leading to Polyethers with Pendant Primary, Secondary, and Tertiary Amino Groups. *Macromolecules* **2015**, *48*, 3217–3229.