

Electronic Supplementary Information (ESI)

Synthesis of Hyperbranched Polyester via Ring-opening Alternating Copolymerisation of Epoxide and Cyclic Anhydride having a Carboxyl Group

Ryota Suzuki,^a Xiaochao Xia,^{b,c} Tianle Gao,^a Takuya Yamamoto,^b Kenji Tajima,^b Takuya Isono,^{*,b}

Toshifumi Satoh^{*,b}

^a Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo 060-8628,
Japan

^b Division of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060-8628,
Japan

^c School of Materials Science and Engineering, Chongqing University of Technology, Chongqing
400054, China

E-mail: isono.t@eng.hokudai.ac.jp

satoh@eng.hokudai.ac.jp

1. Experimental section

1.1. Chemicals

Trimellitic anhydride (TA; >98.0%, TCI) and phthalic anhydride (PA; >98.0%, TCI) were recrystallised and then purified by sublimation before use. Ethyl glycidyl ether (EGE; >98.0%, TCI), propylene oxide (PO; >99.0%, TCI), 1,2-butylene oxide (BO; >99.0%, TCI), cyclohexene oxide (CHO; >98.0%, TCI), and 5-hexen-1-ol (>97.0%, TCI), were distilled over CaH₂ under reduced pressure and stored under argon atmosphere. 6-Azido-1-hexanol was synthesised according to a previous report¹ and purified by distillation over CaH₂ under reduced pressure. *N,N*-Dibenzylglycidylamine (DBGA) was prepared according to reported methods² and purified by silica gel column chromatography followed by distillation over CaH₂ under vacuum (twice), which were then stored under an argon atmosphere. Caesium pivalate (CsOPiv; >97.0%, TCI) was dried by heating at 100 °C under high vacuum for at least 72 h prior to use. 1,4-Benzenedimethanol (BDM; >99.0%, TCI) was used as received. Poly(ethylene glycol) monomethyl ether (MeO-PEG-OH; typical $M_n = 400$, $M_{n,SEC} = 440$, $D = 1.33$, TCI) and poly(ethylene glycol) (HO-PEG-OH; typical $M_n = 2000$, $M_{n,SEC} = 4,020$, $D = 1.07$, Sigma–Aldrich) was dried by azeotropic distillation in benzene. Chloroform-*d* (CDCl₃; >99.8%), dimethyl sulfoxide-*d*₆ (DMSO-*d*₆; >99.9%), benzoic acid (BA; >98.0%, TCI), and 2-propanol (>99.7%, Kanto Chemical) were used as received.

1.2. Instruments

The polymerisation was 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. ^1H and ^{13}C NMR spectra were recorded at 25 °C on JEOL JNM-ECS400 (^1H : 400 MHz, ^{13}C : 100 MHz) or JNM-ECZ600R (^{13}C : 125 MHz) instruments .

The absolute number-averaged molecular weight ($M_{n,\text{MALS}}$), weight-averaged molecular weight ($M_{w,\text{MALS}}$) and dispersity (D) of the hyperbranched and linear polymer samples were determined by triple-detection size elution chromatography (SEC-MALS-Visco) in CHCl_3 (flow rate, 1.0 mL min^{-1}) at 40 °C using a Jasco high-performance liquid chromatography system (PU-4180 HPLC pump, AS-4550 auto sampler, and CO-4060 column oven) equipped with a Shodex K-800D guard column (8.0 mm \times 100 mm; particle size, 10 μm), K-806L column (linear, 8.0 mm \times 100 mm; particle size, 10 μm), K-804L column (linear, 8.0 mm \times 100 mm; particle size, 10 μm), a DAWN 8 multiangle laser light scattering detector (Wyatt Technology), a Viscostar viscosity detector (Wyatt Technology), and an RI-501 refractive index detector (Shodex).

Fourier-transform infrared (FT-IR) spectra were measured in an ATR mode with a PerkinElmer Frontier MIR spectrometer (PerkinElmer, Inc., Waltham, MA 02451, USA).

The preparative SEC was performed at 25 °C in CHCl_3 (flow rate, 10.0 mL min^{-1}) using a LaboACE LC-7080 liquid chromatography system (Japan Analytical Industry Co. Ltd., Tokyo, Japan) equipped with a JAIGEL-HR-P guard column (8 mm \times 40 mm, Japan Analytical Industry Co. Ltd.), a JAIGEL 2HR column (linear, 20.0 mm \times 600 mm; exclusion limit, 5.0×10^3 , Japan Analytical Industry Co.

Ltd.), and a JAIGEL 2.5HR column (linear, 20.0 mm × 600 mm; exclusion limit, 2.0×10^4 , Japan Analytical Industry Co. Ltd.).

The thermal properties of the samples were measured by a Hitachi DSC 7000X. Sample was heated from 20 °C to 100 or 120 °C at a rate of 10 °C min⁻¹ and held at 100 or 120 °C for 5 min to erase thermal history. Then, the sample was cooled to -100 °C at a rate of 10 °C min⁻¹ and held at -100 °C for 5 min. Finally, the sample was heated to 100 or 120 °C at a rate of 10 °C min⁻¹. The second heating DSC curve was used to evaluate the glass transition temperature.

Static water contact angle measurements were performed with a DropMaster (DMe-201, Kyowa Interface Science Co. Ltd., Saitama, Japan) under an ambient environment. The needle diameter was 0.47 mm, and the water droplet volume was set to ~5 μL. Each measurement was repeated 5 times for a better statistical significance. The error bars resulted from the standard deviation based on the measurement series.

1.3. The general synthesis of hyperbranched polyester via ROAC of latent A₃ type cyclic anhydride and epoxide

- Synthesis of HB-P(TA-*alt*-EGE)

A typical polymerisation procedure is given as follows: In an argon-filled glovebox, 1,4-benzenedimethanol (BDM; 2.8 mg, 20 μmol), caesium pivalate (CsOPiv; 2.3 mg, 10 μmol), trimellitic anhydride (TA; 192 mg, 1.00 mmol), and ethyl glycidyl ether (EGE; 323 μL, 3.0 mmol) were added

to the reaction vessel and stirred at 80 °C. After 5.5 h, crude aliquot was withdrawn from the system by pipette and monitored by ^1H NMR spectroscopy in CDCl_3 to determine the monomer conversions. The reaction mixture was diluted with small amount of dichloromethane to terminate the polymerisation. The crude polymer was purified by preparative SEC to completely remove the unreacted EGE and catalyst, giving hyperbranched-poly(TA-*alt*-EGE) (HB-P(TA-*alt*-EGE)) as a colorless viscous liquid (84.3 mg). Yield: 21.1%

$M_{n,\text{MALS}} = 16,900 \text{ g mol}^{-1}$ (CHCl_3), $D_{\text{MALS}} = 1.11$ (CHCl_3)

- Synthesis of HB-P(TA-*alt*-EGE) without alcohol initiator

In an argon-filled glovebox, CsOPiv (11.7 mg, 50 μmol), TA (480 mg, 2.50 mmol), and EGE (806 μL , 7.50 mmol) were added to the reaction vessel and stirred at 80 °C. After 5 h, crude aliquot was withdrawn from the system by pipette and monitored by ^1H NMR spectroscopy in $\text{DMSO-}d_6$ to determine the monomer conversions. The reaction mixture was purified by dialysis in Acetone/MeOH to completely remove the unreacted EGE and catalyst, giving HB-P(TA-*alt*-EGE) without the initiator residue as a colorless viscous liquid (680 mg). Yield: 68.6%

- Synthesis of HB-P(TA-*alt*-PO)

HB-P(TA-*alt*-PO) was synthesised in the same way, excepting the molar ratio of the reactants; BDM (5.5 mg, 40 μmol), CsOPiv (4.7 mg, 20 μmol), TA (192 mg, 1.00 mmol), and propylene oxide

(PO; 210 μL , 3.00 mmol). After 4 h, the reaction mixture was diluted with small amount of dichloromethane and purified by preparative SEC to give HB-P(TA-*alt*-PO) as a colorless viscous liquid (41.6 mg). Yield: 16.4%

$$M_{n,\text{MALS}} = 24,300 \text{ g mol}^{-1} (\text{CHCl}_3), D_{\text{MALS}} = 1.30 (\text{CHCl}_3)$$

• Synthesis of HB-P(TA-*alt*-BO)

HB-P(TA-*alt*-BO) was synthesised in the same way, excepting the molar ratio of the reactants; BDM (5.5 mg, 40 μmol), CsOPiv (4.7 mg, 20 μmol), TA (192 mg, 1.00 mmol), and butylene oxide (BO; 261 μL , 3.00 mmol). After 4 h, the reaction mixture was diluted with small amount of dichloromethane and purified by preparative SEC to give HB-P(TA-*alt*-BO) as a colorless viscous liquid (248 mg). Yield: 72.5%

$$M_{n,\text{MALS}} = 28,500 \text{ g mol}^{-1} (\text{CHCl}_3), D_{\text{MALS}} = 1.21 (\text{CHCl}_3)$$

• Synthesis of HB-P(TA-*alt*-CHO)

HB-P(TA-*alt*-CHO) was synthesised in the same way, excepting the molar ratio of the reactants; BDM (5.5 mg, 40 μmol), CsOPiv (4.7 mg, 20 μmol), TA (192 mg, 1.00 mmol), and cyclohexene oxide (CHO; 302 μL , 3.00 mmol). After 2 h, the reaction mixture was diluted with small amount of dichloromethane and purified by preparative chromatography to give HB-P(TA-*alt*-CHO) as a colorless viscous liquid (274 mg). Yield: 69.6%

$$M_{n,\text{MALS}} = 98,600 \text{ g mol}^{-1} (\text{CHCl}_3), D_{\text{MALS}} = 1.58 (\text{CHCl}_3)$$

- Synthesis of HB-P(TA-*alt*-DBGA)

HB-P(TA-*alt*-DBGA) was synthesised in the same way, excepting the molar ratio of the reactants; BDM (5.5 mg, 40 μmol), CsOPiv (4.7 mg, 20 μmol), TA (192 mg, 1.00 mmol), and dibenzyl glycidyl amine (DBGA; 261 μL , 3.00 mmol). After 5.3 h, the reaction mixture was diluted with small amount of dichloromethane and purified by preparative SEC to give HB-P(TA-*alt*-DBGA) as a colorless viscous liquid (127.5 mg). Yield: 89.8%

$$M_{n,\text{MALS}} = 134,000 \text{ g mol}^{-1} (\text{CHCl}_3), D_{\text{MALS}} = 1.68 (\text{CHCl}_3)$$

1.4. The general synthesis of linear polyester via ROAC of cyclic anhydride and epoxide

- Synthesis of L-P(PA-*alt*-EGE)

Linear-poly(PA-*alt*-EGE) (L-P(PA-*alt*-EGE)) was synthesised in the same way, excepting the molar ratio of the reactants; BDM (5.5 mg, 40 μmol), CsOPiv (4.7 mg, 20 μmol), phthalic anhydride (PA; 148 mg, 1.00 mmol), and EGE (323 μL , 3 mmol). After 5 h, the reaction mixture was diluted with small amount of dichloromethane and purified by reprecipitation from a dichloromethane solution into cold methanol to give L-P(PA-*alt*-EGE) as a colorless viscous liquid (103.6 mg). Yield: 40.5%

$$M_{n,\text{MALS}} = 8,000 \text{ g mol}^{-1} (\text{CHCl}_3), D_{\text{MALS}} = 1.06 (\text{CHCl}_3)$$

- Synthesis of L-P(PA-*alt*-PO)

L-P(PA-*alt*-PO) was synthesised in the same way, excepting the molar ratio of the reactants; BDM (6.9 mg, 50 μmol), CsOPiv (5.9 mg, 25 μmol), PA (185 mg, 1.25 mmol), and PO (525 μL , 7.50 mmol). After 2 h, the reaction mixture was diluted with small amount of dichloromethane and purified by reprecipitation from a dichloromethane solution into cold methanol to give L-P(PA-*alt*-PO) as a colorless viscous liquid (150 mg). Yield: 75.9%

$$M_{n,\text{MALS}} = 7,900 \text{ g mol}^{-1} (\text{CHCl}_3), D_{\text{MALS}} = 1.02 (\text{CHCl}_3)$$

- Synthesis of L-P(PA-*alt*-BO)

L-P(PA-*alt*-BO) was synthesised in the same way, excepting the molar ratio of the reactants;

BDM (6.9 mg, 50 μmol), CsOPiv (5.9 mg, 25 μmol), PA (185 mg, 1.25 mmol), and BO (652 μL , 7.50 mmol). After 2 h, the reaction mixture was diluted with small amount of dichloromethane and purified by reprecipitation from a dichloromethane solution into cold methanol to give L-P(PA-*alt*-BO) as a colorless viscous liquid (107 mg). Yield: 74.3%

$M_{n,\text{MALS}} = 5,700 \text{ g mol}^{-1}$ (CHCl_3), $D_{\text{MALS}} = 1.01$ (CHCl_3)

- Synthesis of L-P(PA-*alt*-CHO)

L-P(PA-*alt*-CHO) was synthesised in the same way, excepting the molar ratio of the reactants; BDM (5.5 mg, 40 μmol), CsOPiv (4.7 mg, 20 μmol), PA (148 mg, 1.00 mmol), and CHO (605 μL , 6.00 mmol). After 3 h, the reaction mixture was diluted with small amount of dichloromethane and purified by reprecipitation from a dichloromethane solution into cold methanol to give L-P(PA-*alt*-CHO) as a colorless viscous liquid (233 mg). Yield: 92.5%

$M_{n,\text{MALS}} = 8,300 \text{ g mol}^{-1}$ (CHCl_3), $D_{\text{MALS}} = 1.03$ (CHCl_3)

- Synthesis of L-P(PA-*alt*-DBGA)

L-P(PA-*alt*-DBGA) was synthesised in the same way, excepting the molar ratio of the reactants; BDM (1.4 mg, 10 μmol), CsOPiv (1.2 mg, 5.0 μmol), PA (37.0 mg, 250 μmol), and DBGA (380 mg, 1.50 mmol). After 27 h, the reaction mixture was diluted with small amount of dichloromethane and purified by reprecipitation from a dichloromethane solution into cold methanol

to give L-P(PA-*alt*-DBGA) as a colorless viscous liquid (63.0 mg). Yield: 61.9%

$M_{n,MALS} = 13,300 \text{ g mol}^{-1}$ (CHCl_3), $D_{MALS} = 1.39$ (CHCl_3)

1.5. The general synthesis of polyether via ROP of epoxide

• Synthesis of PEGE

In an argon-filled glovebox, BDM (12.0 mg, 87.0 μmol), CsOPiv (10.2 mg, 43.5 μmol) and EGE (488 mg, 4.78 mmol) were added to the reaction vessel and stirred at 100 °C. After 1.6 h, crude aliquot was withdrawn from the system by pipette and monitored by ^1H NMR spectroscopy in CDCl_3 to determine monomer conversion. The reaction mixture was diluted with small amount of dichloromethane and purified by reprecipitation from a dichloromethane solution into cold methanol to give PEGE as a colorless oil (236 mg). Yield: 48.4%

$M_{n,NMR} = 6,000 \text{ g mol}^{-1}$ (CDCl_3)

1.6. Model reactions for investigation of TA's reactivity

• Reaction of TA and 2-propanol

CsOPiv (23.4 mg, 100 μmol), TA (96.1 mg, 500 μmol), and 2-propanol (115 μL , 1.50 mmol) were added to the reaction vessel and stirred at 80 °C. After 2 h, reaction mixture was evaporated to removed unreacted 2-propanol and measured by ^1H NMR spectroscopy in $\text{DMSO-}d_6$ to check the reaction products. Yield: 99.2%

- Reaction of PA and 2-propanol

CsOPiv (11.7 mg, 50.0 μmol), PA (74.1 mg, 500 μmol), and 2-propanol (195 μL , 1.50 mmol) were added to the reaction vessel and stirred at 80 $^{\circ}\text{C}$. After 1.5 h, reaction mixture was evaporated to removed unreacted 2-propanol and measured by ^1H NMR spectroscopy in $\text{DMSO-}d_6$ to check the reaction products. Yield: 63.6%

- Reaction of BA and 2-propanol

CsOPiv (11.7 mg, 50.0 μmol), BA (61.1 mg, 500 μmol), and 2-propanol (195 μL , 1.50 mmol) were added to the reaction vessel and stirred at 80 $^{\circ}\text{C}$. After 1.5 h, reaction mixture was evaporated to removed unreacted 2-propanol and measured by ^1H NMR spectroscopy in $\text{DMSO-}d_6$ to check the reaction products. Yield: 72.0%

- Reaction of BA and EGE

CsOPiv (11.7 mg, 50.0 μmol), BA (61.1 mg, 500 μmol), and EGE (161 μL , 1.50 mmol) were added to the reaction vessel and stirred at 80 $^{\circ}\text{C}$. After 1.5 h, reaction mixture was evaporated to removed unreacted EGE and measured by ^1H NMR spectroscopy in CDCl_3 to check the reaction products. Yield: 83.6%

2. Supporting figures and tables

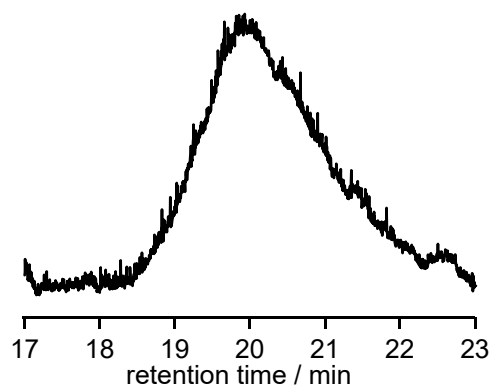


Figure S1. SEC trace of HB-P(TA-*alt*-EGE) obtained from run 1 in Table 1 (eluent, CHCl₃; flow rate, 1.0 mL min⁻¹).

Table S1. Synthesis of linear polyesters via ROAC of PA and epoxide ^a

run	epoxide	time / h	conv.TA / % ^b	$M_{n,theo.}$ ^c	$M_{n,MALS}$ ^d	$M_{w,MALS}$ ^d	\bar{D} ^d	$[\eta]$ / mL min ⁻¹ ^d	T_g / °C ^e
1	EGE	5.0	>99	6,390	8,000	8,500	1.06	4.98	7.1
2	PO	2.0	73	4,000	7,900	8,100	1.02	3.23	11.0
3	BO	2.0	50	2,870	5,700	5,800	1.01	4.61	3.2
4	CHO	3.0	>99	6,300	8,300	8,500	1.03	5.40	64.4
5	DBGA	27.0	>99	10,200	13,300	18,400	1.39	3.65	38.7

^a Polymerization conditions: [CsOPiv]/[BDM]₀/[PA]₀/[epoxide]₀ = 0.5/1/25/150; atmosphere, Ar; initiator, BDM; temp, 80 °C. ^b Determined by ¹H NMR in CDCl₃. ^c Calculated from (M.W. of BDM) + [PA]₀/[BDM]₀ × (M.W. of PA) × (conv. of PA) + [epoxide]₀/[BDM]₀ × (M.W. of epoxide) × (conv. of epoxide). ^d Determined by SEC-MALS-VISCO measurement in CHCl₃. ^e Measured by DSC.

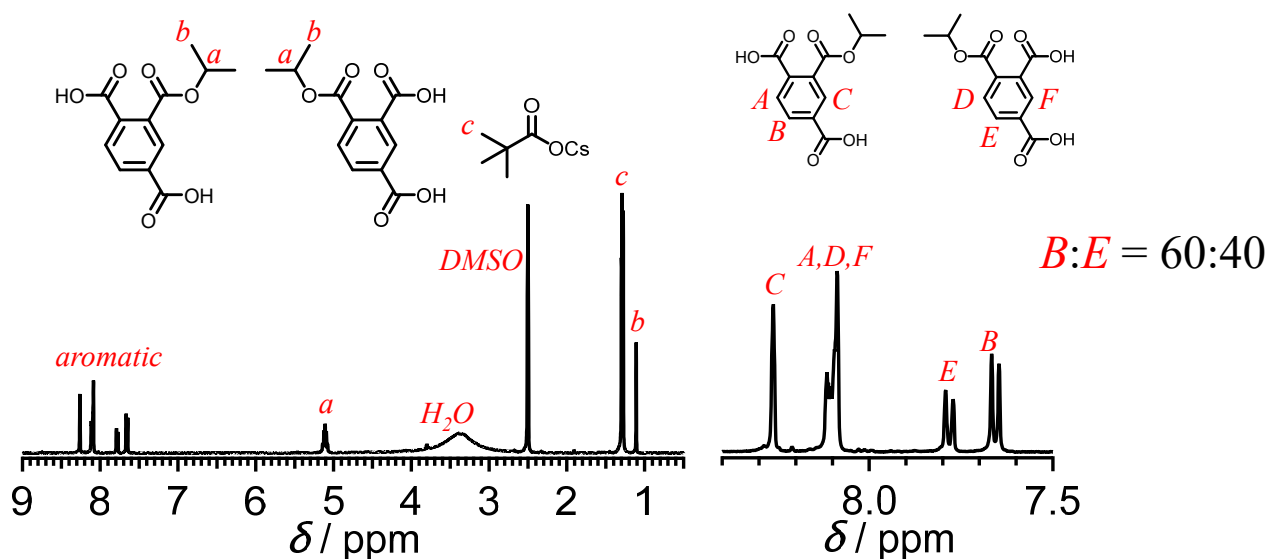


Figure S2. ^1H NMR spectrum of the products obtained from mixtures of 2-propanol, TA, and CsOPiv at 80 °C for 2 h with the feed ratio of $[\text{CsOPiv}]/[\text{TA}]_0/[\text{2-propanol}]_0$ being 1/5/15 (400 MHz, $\text{DMSO-}d_6$).

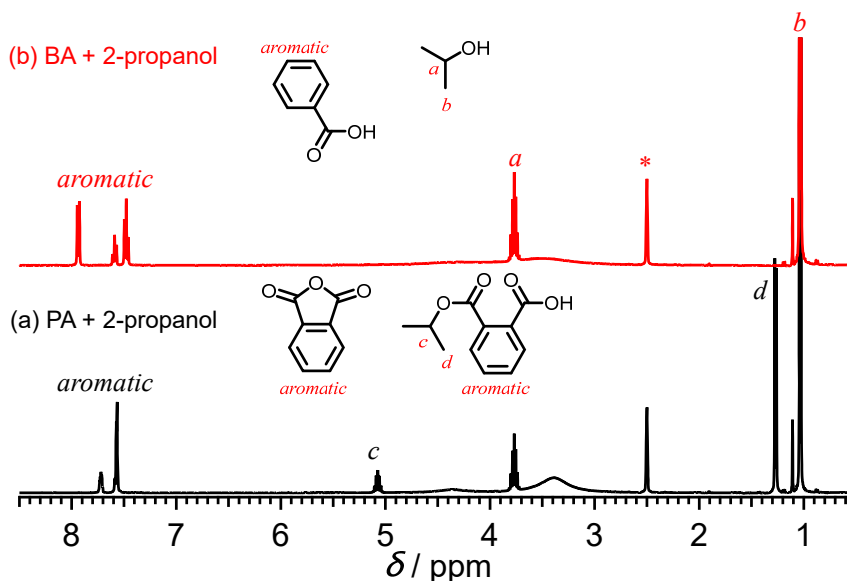


Figure S3. ^1H NMR spectra of the products obtained from mixtures of (a) 2-propanol + PA and (b) 2-propanol + BA in the presence of CsOPiv at 80 °C for 90 min with the feed ratio of $[\text{CsOPiv}]/[\text{PA or BA}]_0/[\text{2-propanol}]_0$ being 0.5/5/15 (400 MHz, $\text{DMSO-}d_6$).

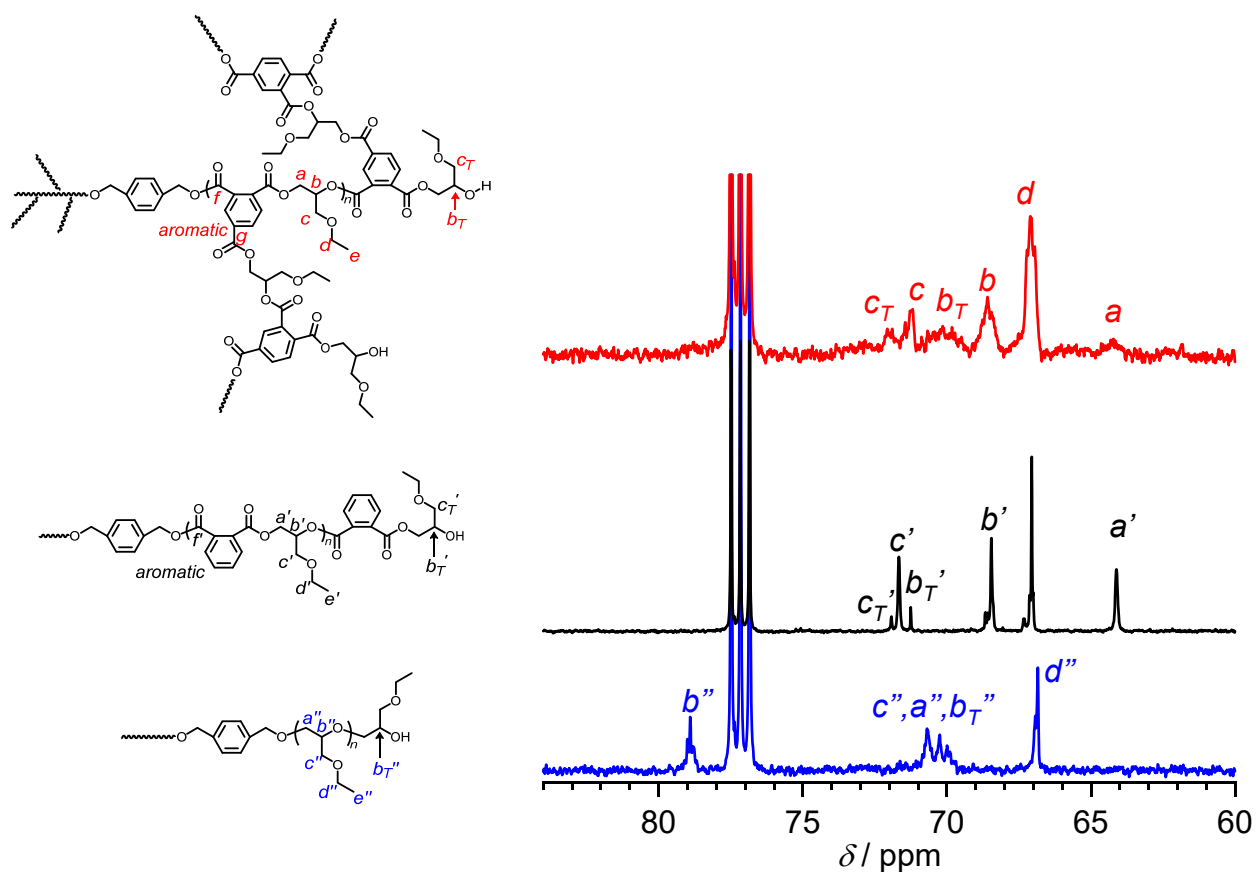


Figure S4. ^{13}C NMR spectra (100 MHz) of PEGE (blue), L-P(PA-*alt*-EGE) (run 1, Table S1; black), and HB-P(TA-*alt*-EGE) (run 1 in Table 1; red) in CDCl_3 .

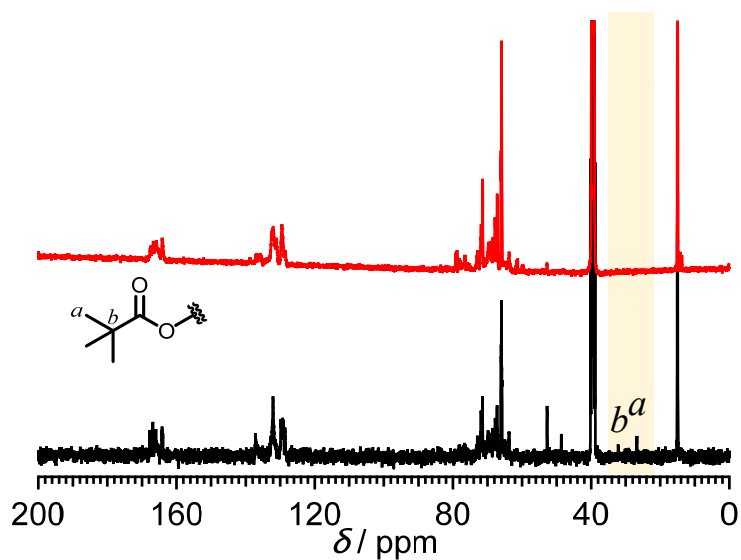


Figure S5. ^{13}C NMR spectra of HB-P(TA-*alt*-EGE) obtained from ROAC without alcohol initiator (black; 100 MHz) and with alcohol initiator (red; run 1, Table 1; 125 MHz) in $\text{DMSO-}d_6$.

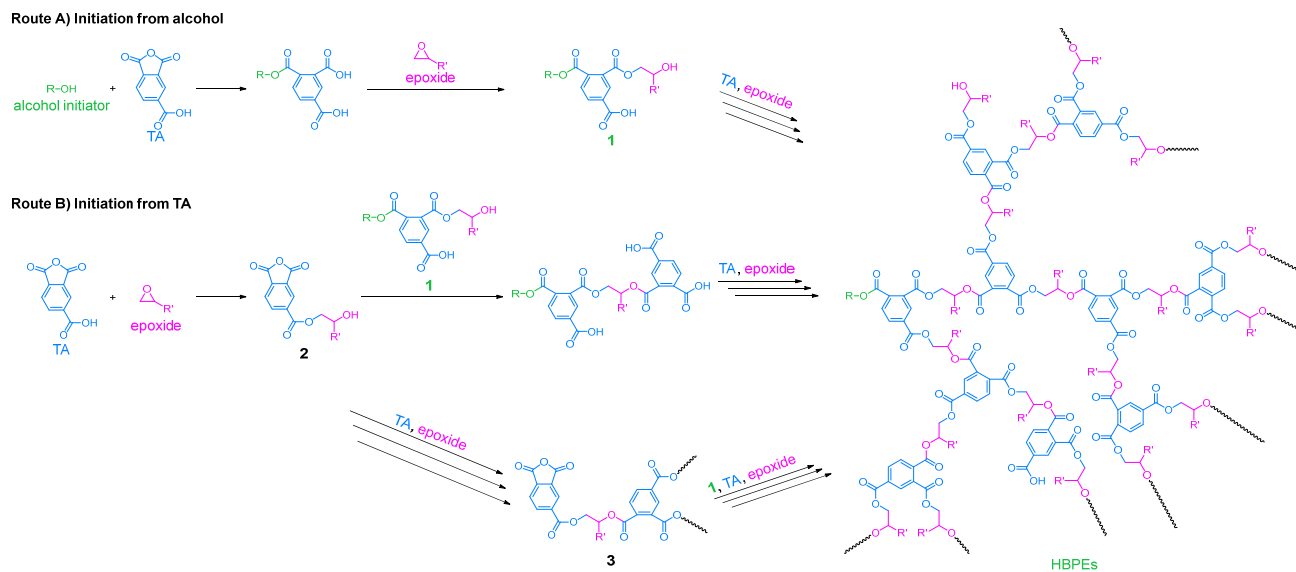


Figure S6. Reaction mechanism of ROAC of TA and epoxide.

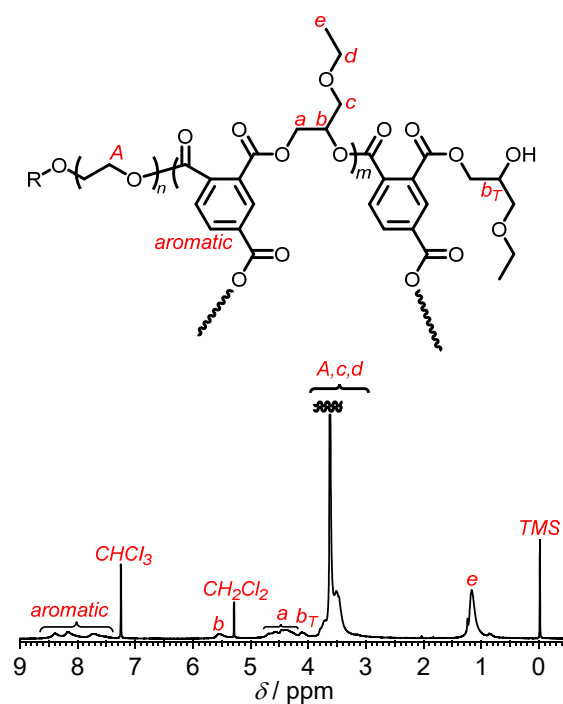


Figure S7. ^1H NMR of HB-P(TA-*alt*-EGE) initiated by HO-PEG-OH (run 2, Table 1) in CDCl_3 (400 MHz).

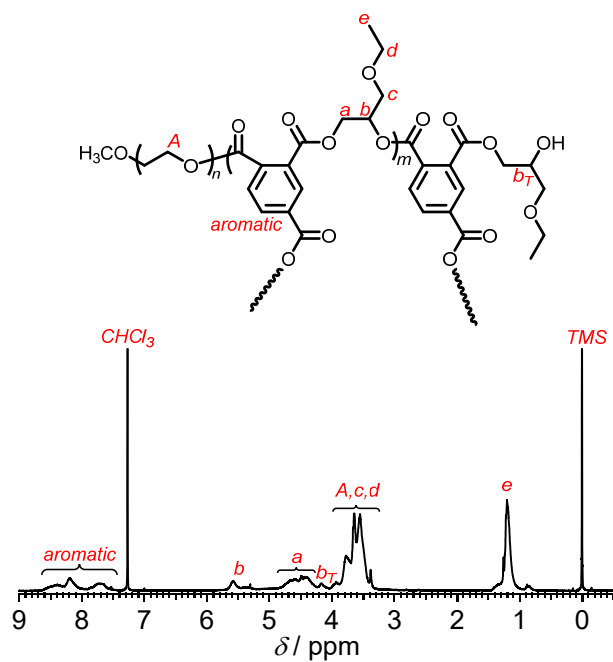


Figure S8. ^1H NMR of HB-P(TA-*alt*-EGE) initiated by MeO-PEG-OH (run 3, Table 1) in CDCl_3 (400 MHz).

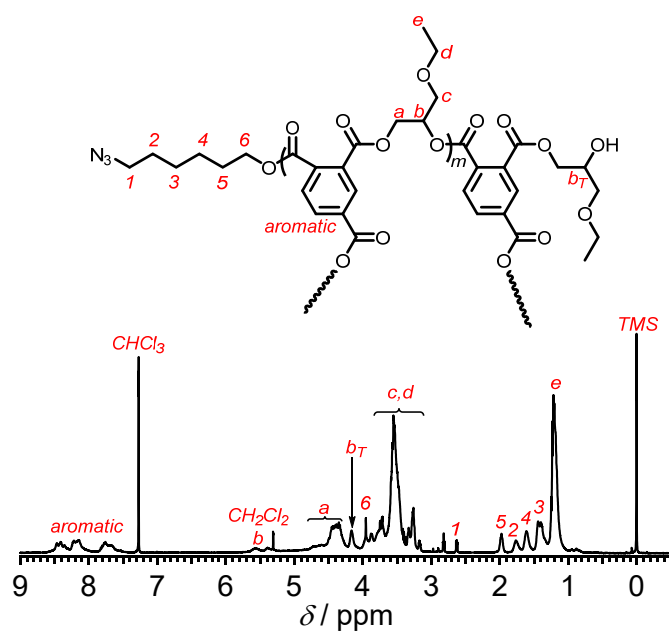


Figure S9. ^1H NMR of HB-P(TA-*alt*-EGE) initiated by 6-azidohexan-1-ol (run 4, Table 1) in CDCl_3 (400 MHz).

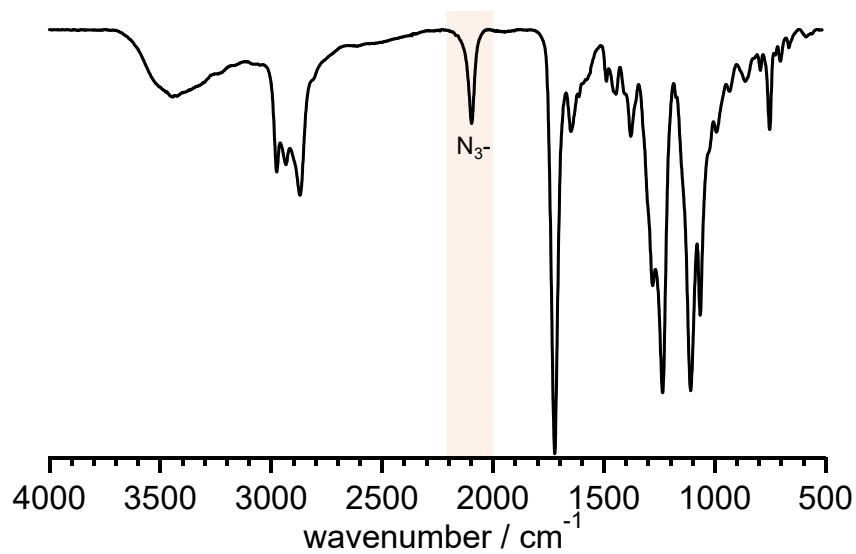


Figure S10. FT-IR spectrum of HB-P(TA-*alt*-EGE) initiated by 6-azidohexan-1-ol (run 4, Table 1).

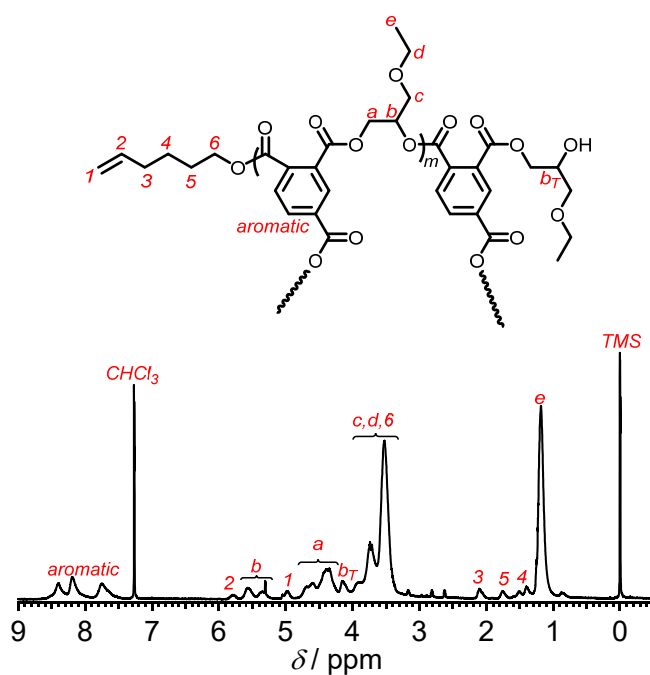


Figure S11. ^1H NMR of HB-P(TA-*alt*-EGE) initiated by 5-hexen-1-ol (run 5, Table 1) in CDCl_3 (400 MHz).

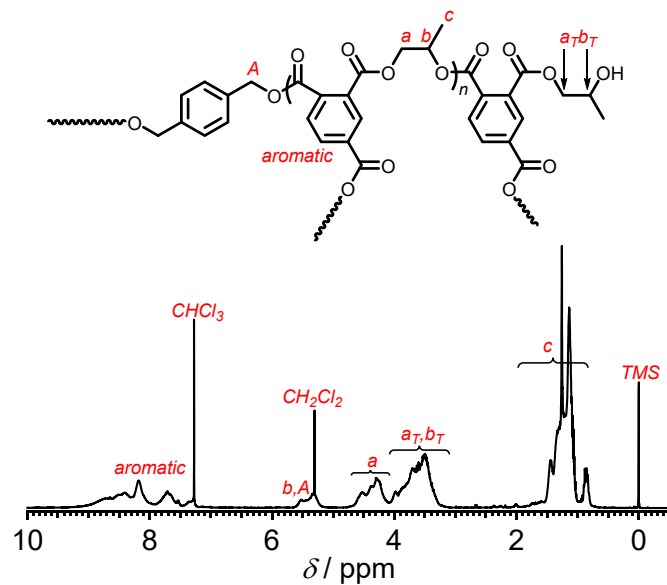


Figure S12. ¹H NMR of HB-P(TA-*alt*-PO) (run 6, Table 1) in CDCl₃ (400 MHz).

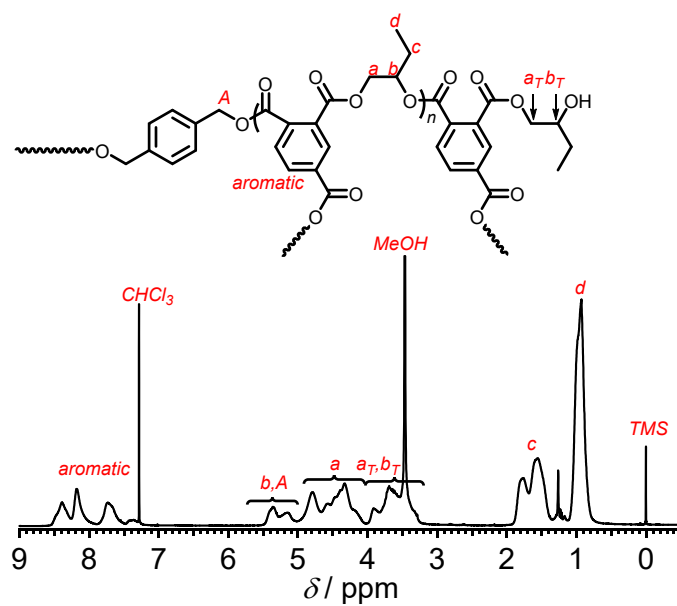


Figure S13. ¹H NMR of HB-P(TA-*alt*-BO) (run 7, Table 1) in CDCl₃ (400 MHz).

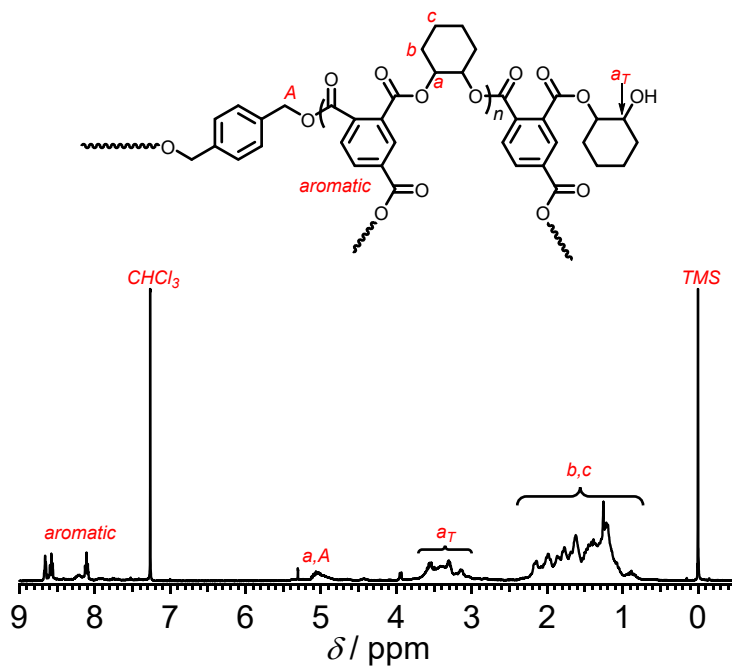


Figure S14. ^1H NMR of HB-P(TA-*alt*-CHO) (run 8, Table 1) in CDCl_3 (400 MHz).

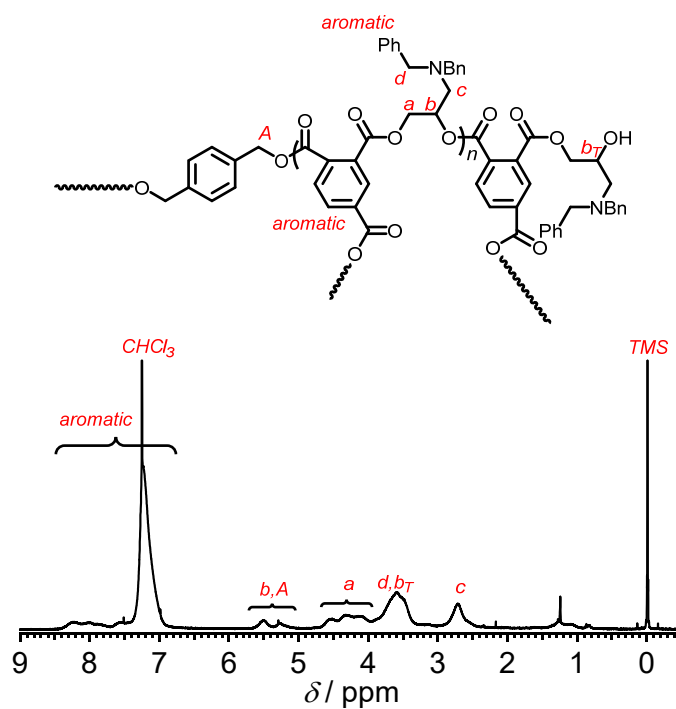


Figure S15. ^1H NMR of HB-P(TA-*alt*-DBGA) (run 9, Table 1) in CDCl_3 (400 MHz).

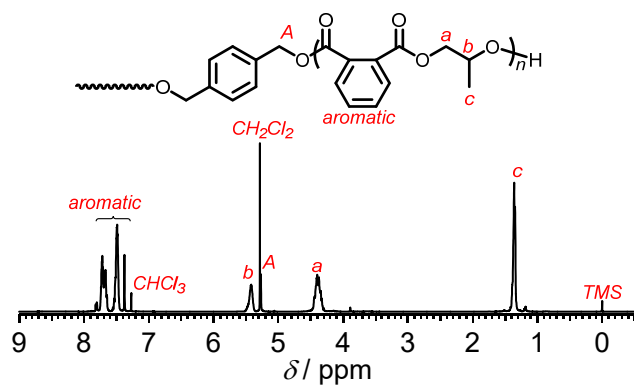


Figure S16. ¹H NMR of L-P(PA-*alt*-PO) (run 2, Table S1) in CDCl₃ (400 MHz).

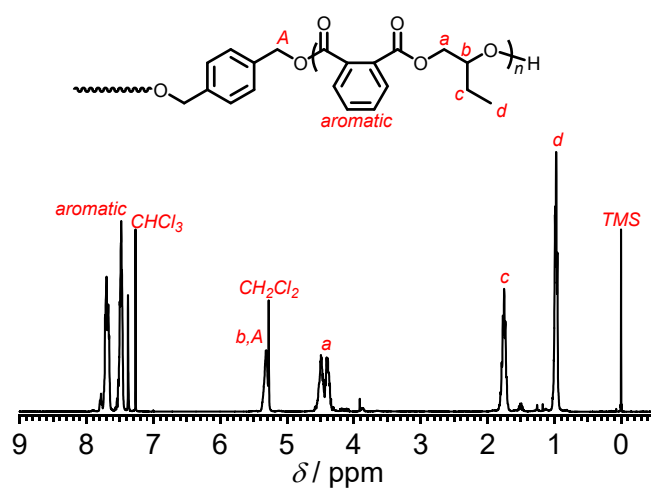


Figure S17. ¹H NMR of L-P(PA-*alt*-BO) (run 3, Table S1) in CDCl₃ (400 MHz).

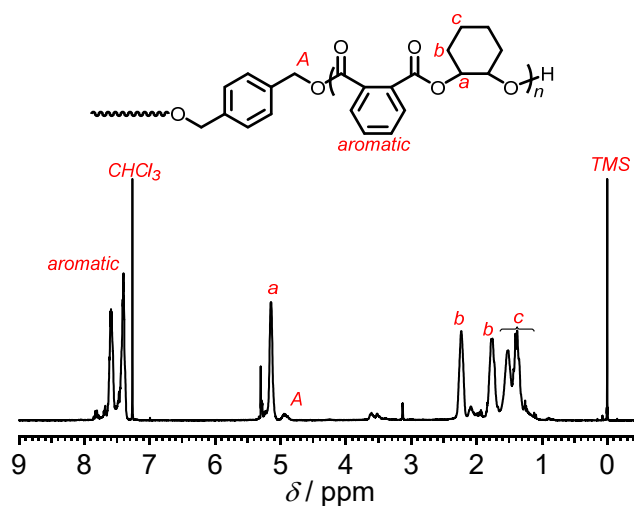


Figure S18. ¹H NMR of L-P(PA-*alt*-CHO) (run 4, Table S1) in CDCl₃ (400 MHz).

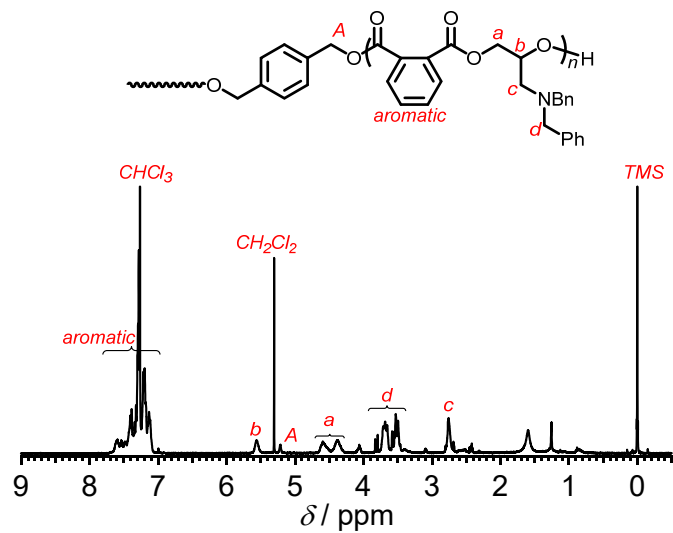


Figure S19. ¹H NMR of L-P(PA-*alt*-DBGA) (run 5, Table S1) in CDCl₃ (400 MHz).

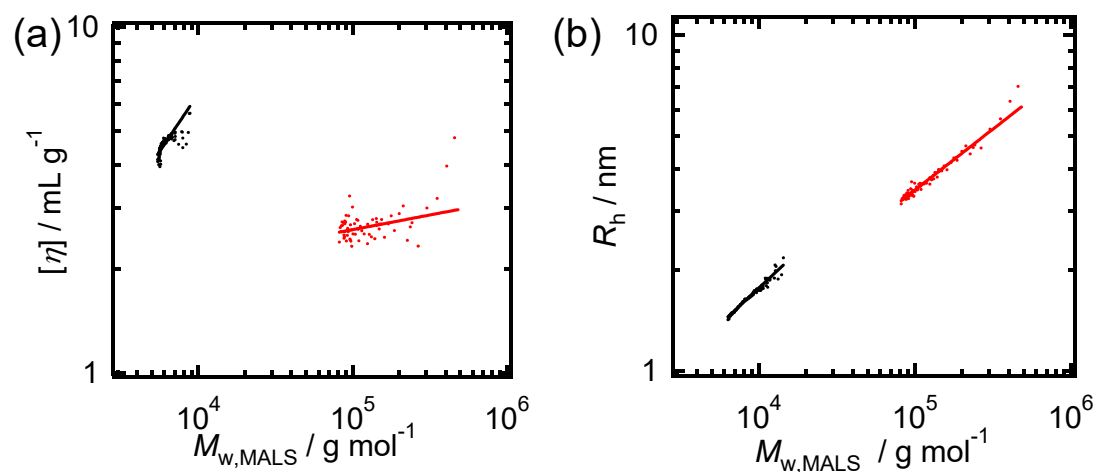


Figure S20. (a) Mark-Houwink-Sakurada plots and (b) conformation plots for HB-P(TA-*alt*-PO) ($M_{n,MALS} = 24,300 \text{ g mol}^{-1}$, red) and L-P(PA-*alt*-PO) ($M_{n,MALS} = 7,900 \text{ g mol}^{-1}$, black).

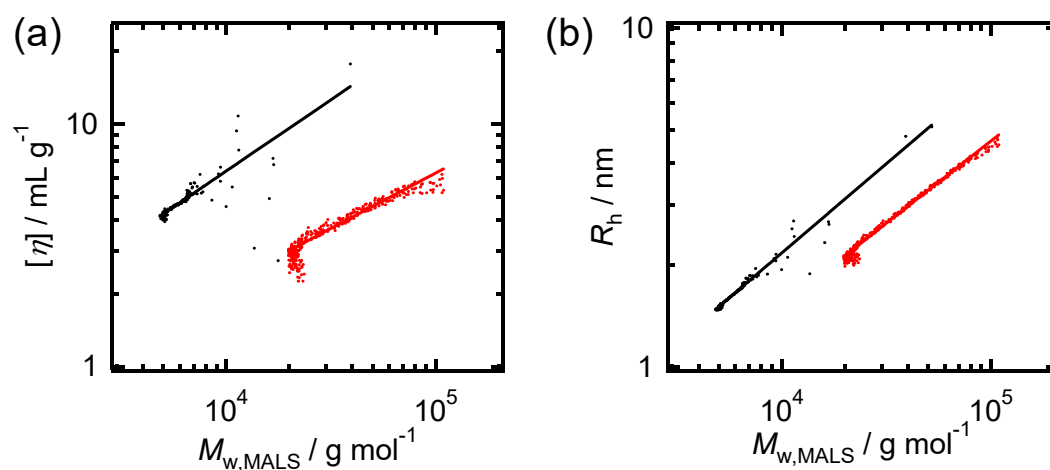


Figure S21. (a) Mark-Houwink-Sakurada plots and (b) conformation plots for HB-P(TA-*alt*-BO) ($M_{n,MALS} = 28,500 \text{ g mol}^{-1}$, red) and L-P(PA-*alt*-BO) ($M_{n,MALS} = 5,700 \text{ g mol}^{-1}$, black).

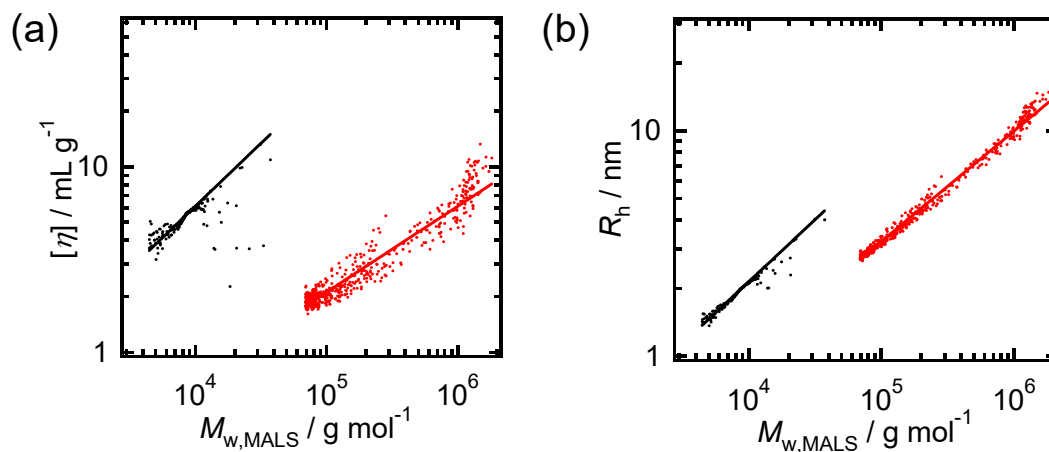


Figure S22. (a) Mark-Houwink-Sakurada plots and (b) conformation plots for HB-P(TA-*alt*-CHO) ($M_{n,MALS} = 98,600 \text{ g mol}^{-1}$, red) and L-P(PA-*alt*-CHO) ($M_{n,MALS} = 8,300 \text{ g mol}^{-1}$, black).

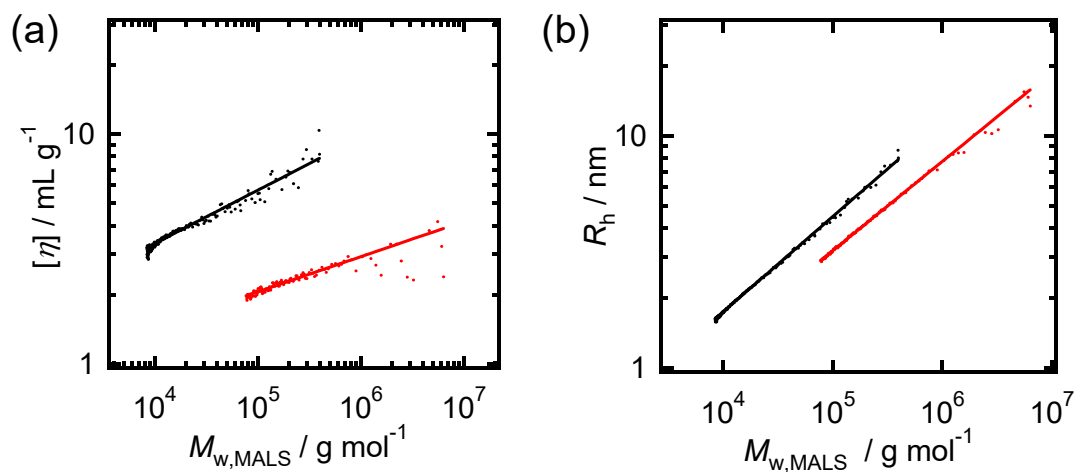


Figure S23. (a) Mark-Houwink-Sakurada plots and (b) conformation plots for HB-P(TA-*alt*-DBGA) ($M_{n,MALS} = 134,000 \text{ g mol}^{-1}$, red) and L-P(PA-*alt*-DBGA) ($M_{n,MALS} = 13,300 \text{ g mol}^{-1}$, black).

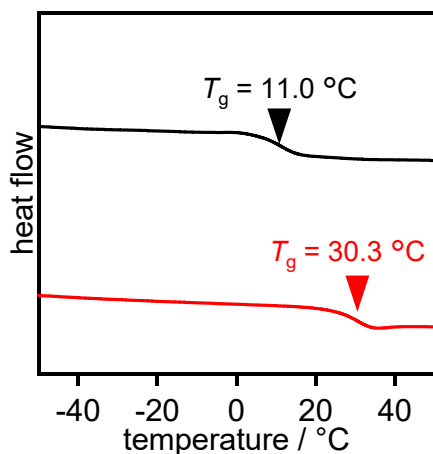


Figure S24. DSC curve of HB-P(TA-*alt*-PO) (red) and L-P(PA-*alt*-PO) (black).

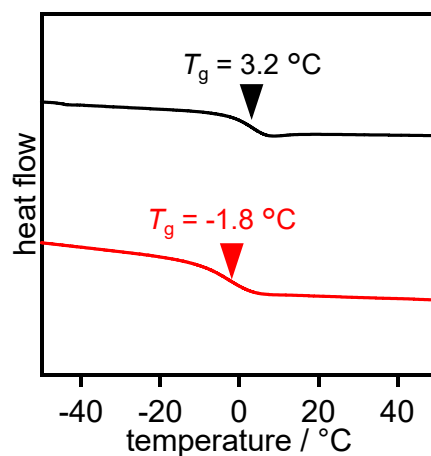


Figure S25. DSC curve of HB-P(TA-*alt*-BO) (red) and L-P(PA-*alt*-BO) (black).

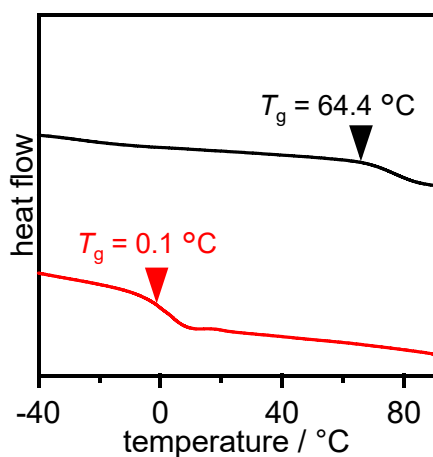


Figure S26. DSC curve of HB-P(TA-*alt*-CHO) (red) and L-P(PA-*alt*-CHO) (black).

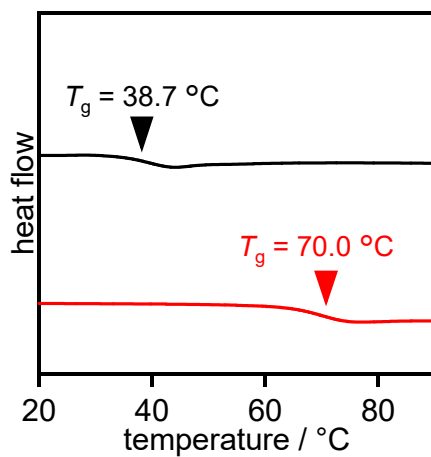


Figure S27. DSC curve of HB-P(TA-*alt*-DBGA) (red) and L-P(PA-*alt*-DBGA) (black).

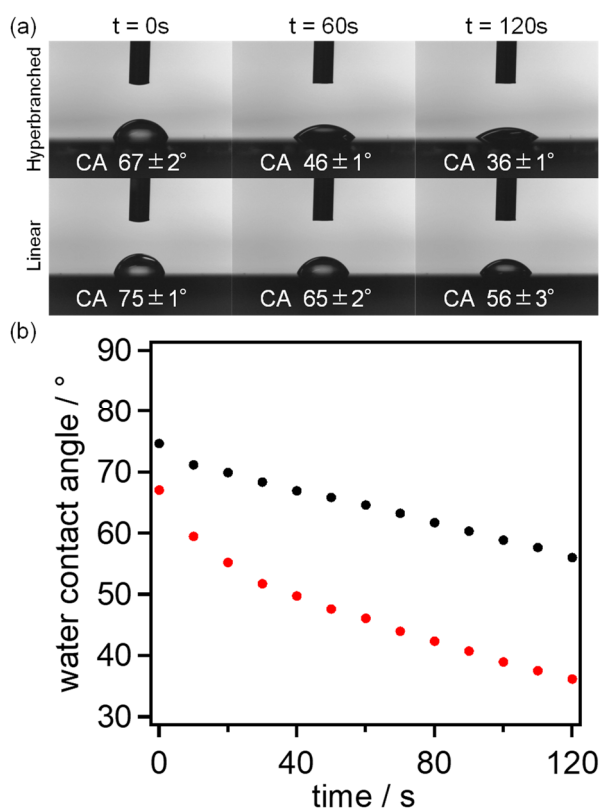


Figure S28. (a) contact angles versus time measurements of HB-P(TA-*alt*-PO) (red) and L-P(PA-*alt*-PO) (black). (b) Images used in the contact angle analysis of HB-P(TA-*alt*-PO) (upper) and L-P(PA-*alt*-PO) (lower).

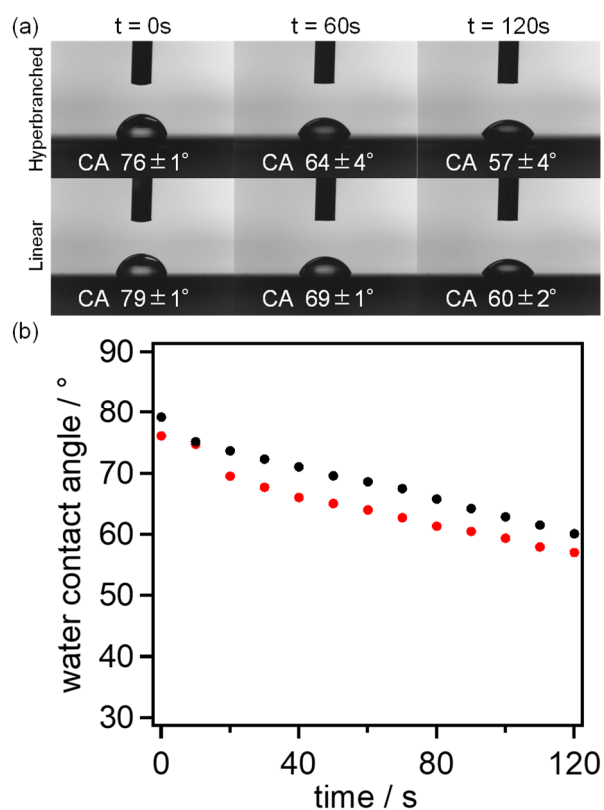


Figure S29. (a) contact angles versus time measurements of HB-P(TA-*alt*-BO) (red) and L-P(PA-*alt*-BO) (black). (b) Images used in the contact angle analysis of HB-P(TA-*alt*-BO) (upper) and L-P(PA-*alt*-BO) (lower).

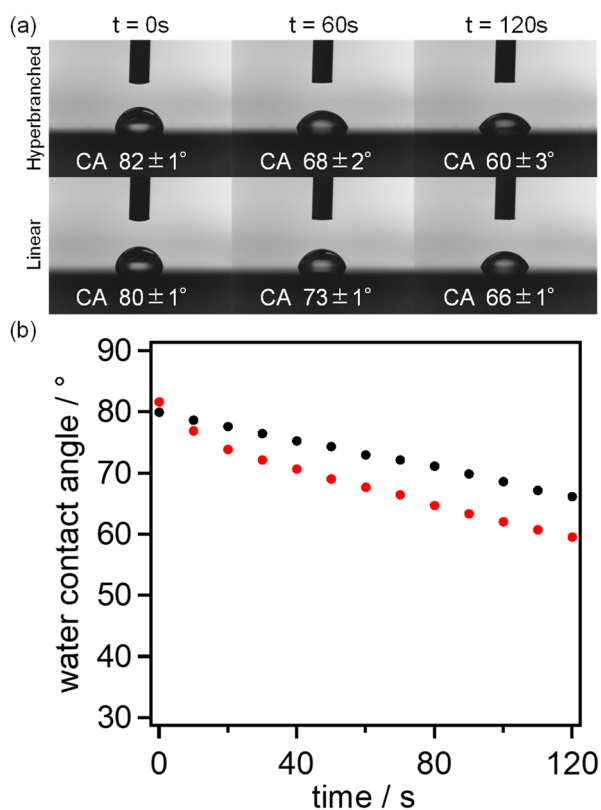


Figure S30. (a) contact angles versus time measurements of HB-P(TA-*alt*-CHO) (red) and L-P(PA-*alt*-CHO) (black). (b) Images used in the contact angle analysis of HB-P(TA-*alt*-CHO) (upper) and L-P(PA-*alt*-CHO) (lower).

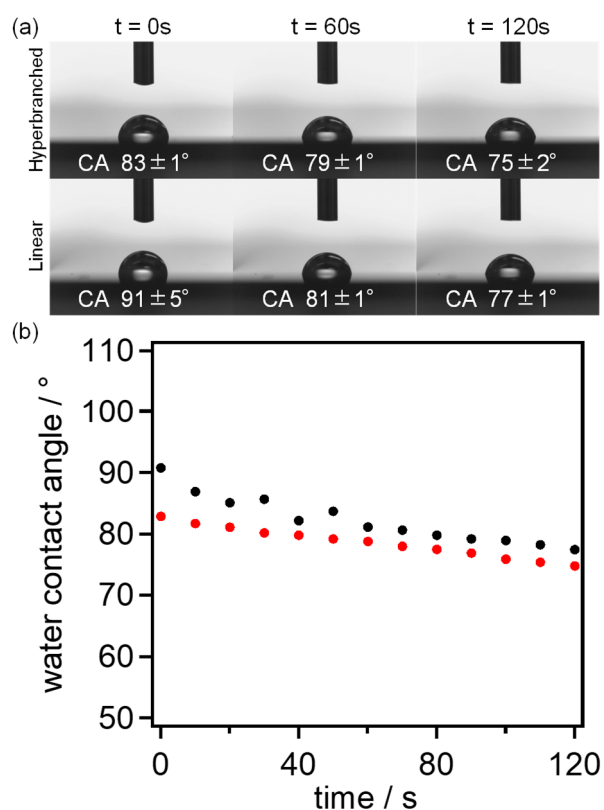


Figure S31. (a) contact angles versus time measurements of HB-P(TA-*alt*-DBGA) (red) and L-P(PA-*alt*-DBGA) (black). (b) Images used in the contact angle analysis of HB-P(TA-*alt*-DBGA) (upper) and L-P(PA-*alt*-DBGA) (lower).

3. References

- (1) A. E. Speers, G. C. Adam, B. F. Cravatt, Activity-Based Protein Profiling in Vivo Using a Copper(I)-Catalyzed Azide-Alkyne [3 + 2] Cycloaddition. *J. Am. Chem. Soc.* **2003**, *125* (16), 4686–4687.
- (2) T. Isono, S. Asai, Y. Satoh, T. Takaoka, K. Tajima, T. Kakuchi, T. Satoh, Controlled/Living Ring-Opening Polymerization of Glycidylamine Derivatives Using *t*-Bu-P₄/Alcohol Initiating System Leading to Polyethers with Pendant Primary, Secondary, and Tertiary Amino Groups. *Macromolecules* **2015**, *48* (10), 3217–3229.