

Supporting Information

Synthesis of H-shaped Carbon-Dioxide-Derived Poly(Propylene Carbonate) for Topology-based Reduction of the Glass Transition Temperature

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Synthesis of (thymine-1-yl)acetyl chloride.

A two-neck flask (100 mL) containing (thymine-1-yl)acetic acid (1.84 g, 10.0 mmol) equipped with a stirring bar, a three-way stopcock, and a reflux condenser was dried in vacuo and purged with nitrogen. After CH₂Cl₂ (5 mL), thionyl chloride (5 mL), and DMF (1 drop) were added to the flask, the mixture was stirred at room temperature for 3 days. During the reaction, the yellow suspension became a homogeneous yellow solution. After the removal of volatile compounds in vacuo, a reddish orange powder was obtained. The material was used without further purification.

Synthesis of α,ω -di(thymine-1-yl) PPC (4).

A two-neck flask (50 mL) containing (thymine-1-yl)acetyl chloride (0.20 g, 1.0 mmol) and **1** (1.0 g, $M_n = 5000$, 0.40 mmol hydroxy units) equipped with a stirring bar and a three-way stopcock was dried in vacuo and purged with nitrogen. To this was added a solution of pyridine (0.50 mL, 6.2 mmol) in THF (5 mL) and the mixture was stirred at room temperature for 24 h. After the removal of volatile compounds in vacuo, the residue was dissolved with chloroform. The organic solution was washed with water, dried over Na₂SO₄, concentrated, and dried in vacuo (ca. 20 Pa) at 50 °C for 5 h to give **4a** as a slightly yellow clear solid (0.85 g, 0.34 mmol terminals, 85%). ¹H NMR (CDCl₃): δ 1.33 (d, $J = 6.4$ Hz, 3H, CH₃CH), 1.93 (s, 0.15H, CH₃C=), 4.0–4.4 (m, 2H, CHCH₂O), 4.55 (d, $J = 17.2$ Hz, 0.05H, NCH₂CO), 4.9–5.3 (m, 1H, OCHCH₂), 6.98 (s, 0.05H, NCH=C), 8.19 (br, 0.05H, NH). ¹³C NMR (CDCl₃): δ 12.39, 16.27, 48.65, 69.09, 72.48, 111.16, 140.32, 150.79, 154.32, 164.03, 167.24. $M_n(\text{GPC}_{\text{RI}}) = 5300$, $M_w(\text{GPC}_{\text{RI}}) = 5400$, $M_w/M_n(\text{GPC}_{\text{RI}}) = 1.02$. Likewise, **4b** was synthesized ($M_n(\text{GPC}_{\text{RI}}) = 17900$, $M_w(\text{GPC}_{\text{RI}}) = 20200$, $M_w/M_n(\text{GPC}_{\text{RI}}) = 1.13$) by using α,ω -bis(dicarboxy)PPC with ($M_n(\text{GPC}_{\text{RI}}) = 17600$).

Synthesis of 2,6-bis(4-carboxy-3,3-dimethylbutyrylamino)pyridine.

A two-neck flask (100 mL) containing 3,3-dimethylglutaric anhydride (2.50 g, 17.6 mmol) and 2,6-diaminopyridine (0.500 g, 4.58 mmol) equipped with a stirring bar, a three-way stopcock, and a reflux condenser was dried in vacuo and purged with nitrogen. After THF (10 mL) and triethylamine (1.0 mL, 7.2 mmol) were added to the mixture, the mixture was heated under the refluxed condition for 10 h. When cooled to room temperature, the mixture became turbid. After the removal of the volatile compounds under reduced pressure, hot water (200 mL) was added to give a white powder. The powder was purified by recrystallization with CHCl₃–methanol to afford a white crystal (0.83 g, 2.11 mmol, 46%). ¹H NMR (DMSO-*d*₆): δ 1.07 (s, 12H, CH₃), 2.32 (s, 8H, CCH₂CON), 2.45 (s, 8H, CCH₂COO), 7.67–7.78 (m, 3H, Py-*H*^{3,4}), 9.96 (s, NH), 12.04 (s, CO₂H). ¹³C NMR (DMSO-*d*₆): δ 27.26 (CH₃), 32.63

(CCH₃), 44.98 (CCH₂CON), 46.93 (CCH₂COO), 109.24 (Py-C^{3,5}), 139.85 (Py-C⁴), 150.16 (Py-C^{2,6}), 170.59 (CON), 173.14 (COO).

Synthesis of PPC having diaminopyridine group at the center of main chain (5).

A stainless steel autoclave (150 mL) containing (TPP)CoCl (35.4 mg, 0.0500 mmol), DMAP (4.6 mg, 0.0375 mmol), and 2,6-bis(4-carboxy-3,3-dimethylbutyrylamino)pyridine (197 mg, 0.500 mmol) was dried in vacuo and purged with nitrogen. DMSO (1.0 mL) and PO (7.0 mL, 100 mmol) were added with syringes and the copolymerization was started by the pressurization of the solution by CO₂ up to 50 atm (330 mmol). The mixture was stirred at 40 °C for 72 h until the average molecular weight approximately reached a predetermined value (5000). The autoclave was cooled and excess CO₂ was discharged. A small portion of the product was subjected to ¹H NMR analysis for determining the PO conversion and to GPC analysis for estimating the average molecular weight. The volatile compounds were removed in vacuo (ca. 20 Pa) at 40 °C for 3 h. To the residue was added acetic anhydride (10 mL) and the mixture was stirred at 60 °C for 24 h. The reaction mixture was poured into a large amount of water (100 mL) to precipitate a water-insoluble compound. The water-insoluble compound was collected by decantation and dried in vacuo. The compound containing three copolymers initiated from 2,6-bis(4-carboxy-3,3-dimethylbutyrylamino)pyridine, H₂O, and chloride anion derived from (TPP)CoCl was purified by acidified silica gel column chromatography by using acetone/CHCl₃ (15/100, vol/vol) as first and acetone as second eluent. The silica gel was pre-acidified with 1M HCl aq. After the neutralization with DMAP, the organic solution was poured into a large amount of methanol to afford **5a** as a slightly yellow solid (3.9 g, 38 mmol monomer units, 38%). ¹H NMR (CDCl₃): δ 1.17 (s, 0.3H, CH₃C), 1.33 (d, *J* = 6.4 Hz, 3H, CH₃), 2.05 (s, 0.15H, CH₃CO), 2.46 (s, 0.1H, CCH₂CON), 2.49 (s, 0.1H, CCH₂COO), 4.0–4.3 (m, 2H, CHCH₂O), 4.9–5.3 (m, 1H, OCHCH₂), 7.67 (t, *J* = 8.4 Hz, 0.025H, Py-H^{3,5}), 7.89 (d, *J* = 8.4 Hz, 0.05H, Py-H⁴), 8.54 (br, 0.05H, NH). ¹³C NMR (CDCl₃): δ 16.02, 20.96, 28.19, 33.44, 44.76, 47.87, 50.37, 65.58, 67.91, 68.88, 72.27, 109.15, 140.34, 149.62, 154.12, 169.73, 170.18, 172.00. *M_n*(GPC_{RI}) = 5800, *M_w*(GPC_{RI}) = 6200, *M_w*/*M_n*(GPC_{RI}) = 1.07. Likewise, **5b** was synthesized and characterized (*M_n*(GPC_{RI}) = 16800, *M_w*(GPC_{RI}) = 18100, *M_w*/*M_n*(GPC_{RI}) = 1.08).

NMR titration.

Stock solutions of **4a** (199 mg/5 mL, 7.5 mM) and **5a** (1.45 g/5 mL, 50 mM) in CDCl₃ were prepared. Each 100 μL of the solution of **4a** was placed in eight NMR tubes and predetermined volume (0, 30, 60, 90, 135, 180, 240, or 360 μL) of the solution of **5a** was added to the eight NMR tubes. Furthermore, the mixtures in the tubes were diluted with CDCl₃ until total volumes reached 500 μL. After stirring, ¹H NMR measurements were carried out.

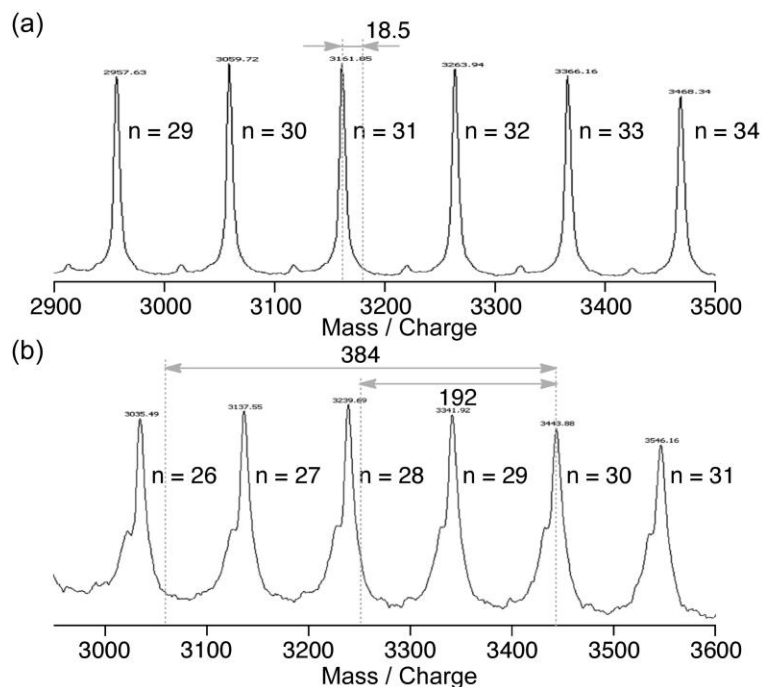


Fig. S1 Expanded MALDI-TOF mass spectra of (a) **1a** and (b) **2**.

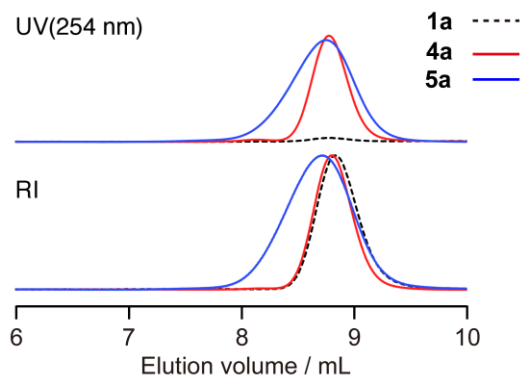


Fig. S2 GPC chromatograms of **1a** (dashed) and **4a** (red) and **5a** (blue) with UV (upper) and RI (lower) detectors.

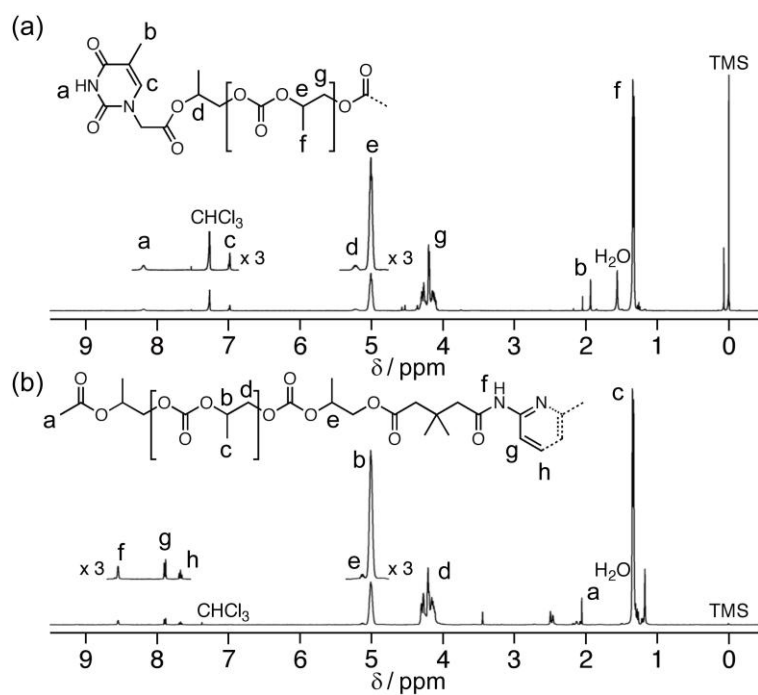


Fig. S3 ¹H NMR spectra of (a) **4a** and (b) **5a** in CDCl₃.

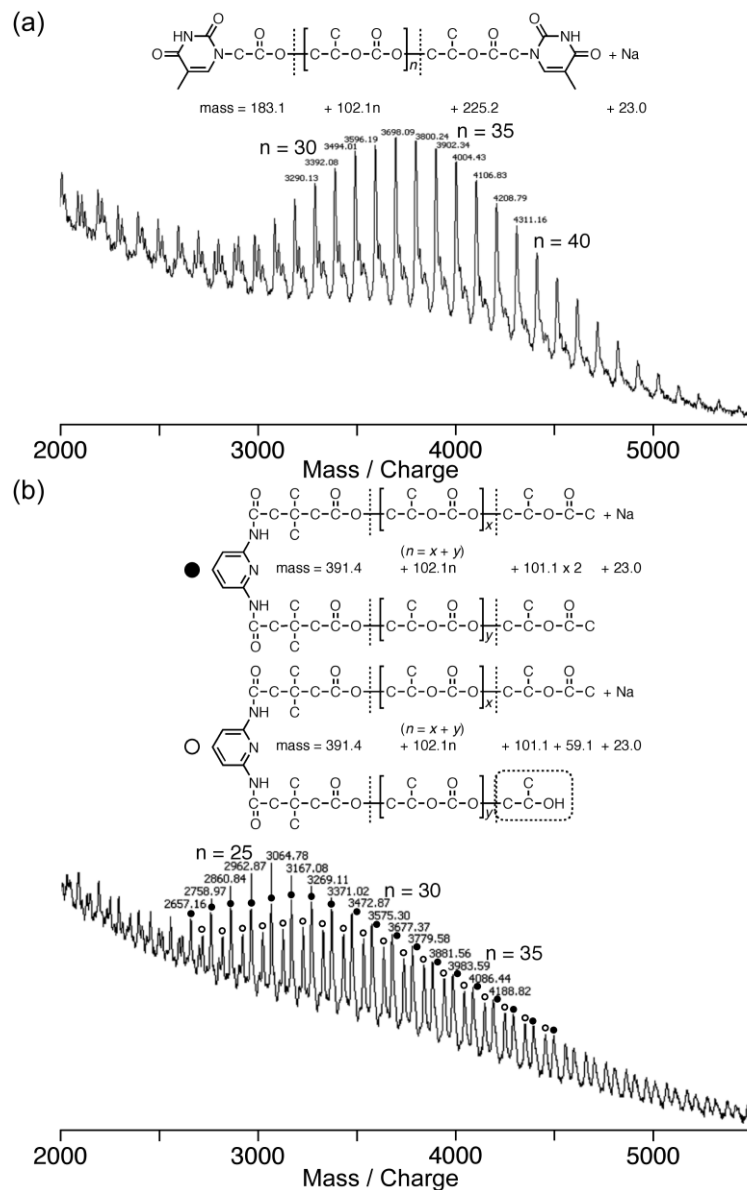


Fig. S4 MALDI-TOF mass spectra of (a) **4a** and (b) **5a**. The representative peaks are marked by open and closed circles with chemical structures of **5a**.

Table S1. T_g s of H-shaped PPCs Determined by DSC.

compound	M_w^a	M_w/M_n^a	$T_g / ^\circ\text{C}$
4a	5400	1.02	34
4b	20200	1.13	—
5a	6200	1.07	31
5b	18100	1.08	36

^a Estimated by GPC_{RI} with polystyrene standards.

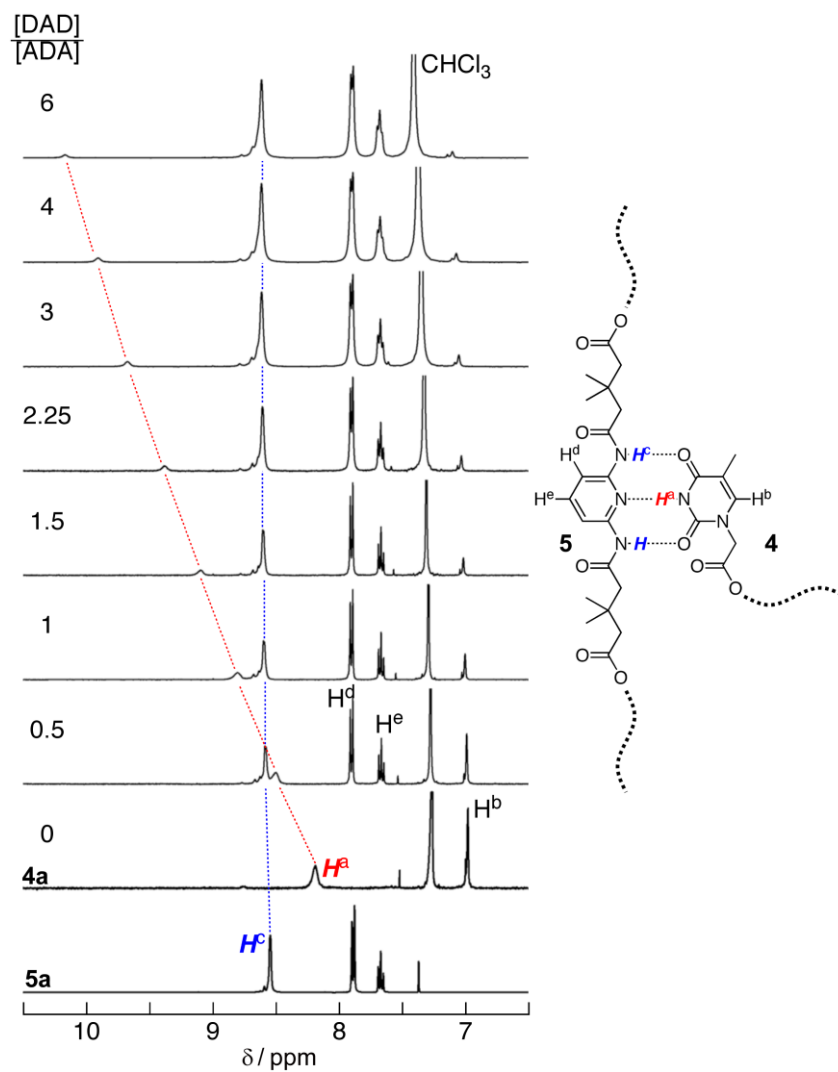


Fig. S5 Expanded ^1H NMR spectra (6.5–10.5 ppm) of **4a** in the presence of varied concentrations of **5a** in CDCl_3 at 30°C . $[\text{ADA}] = 6$ mM (constant), $[\text{DAD}] = 0, 3, 6, 9, 13.5, 18, 24,$ and 36 mM.

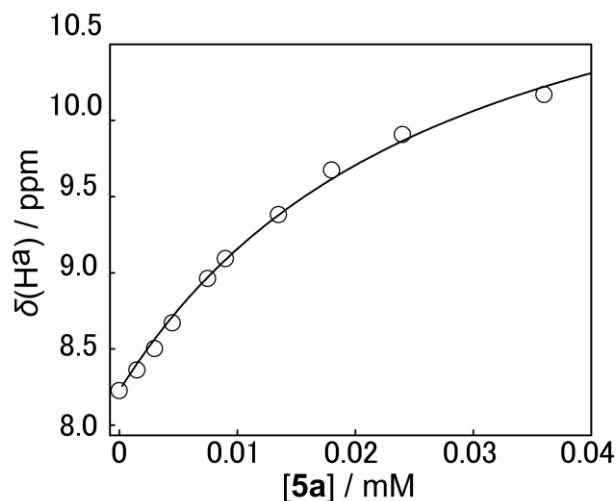


Fig. S6 Change of NH proton of **4a** with increasing amount of **5a** in CDCl_3 at 30 °C. [ADA] = 6 mM (constant), [DAD] = 0, 3, 6, 9, 13.5, 18, 24, and 36 mM.

Table S2. T_g s of H-shaped PPCs Determined by DSC.

compound	M_w of PPC units ^a		M_w^a	M_w/M_n^a	$T_g / ^\circ\text{C}$
	crossbar	side pole			
3	5200 ^b	8300 ^c	21800	1.06	21
6a	4a	5a	17800 ^d	–	24
6b	4a	5b	41600 ^d	–	28
6c	4b	5b	56400 ^d	–	24

^a Estimated by GPC_{RI} with polystyrene standards. ^b M_w of **2**. ^c Calculated with $M_{w,s}$ of **2** and **3**. ^d Calculated with $M_{w,s}$ of **4** and **5**.