Supporting Information for:

Synthesis of Well-Defined Unsaturated Polyesters by Transition-Metal-Catalyzed Polycondensation of Bis(diazoacetate)s

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Experimental Section

Materials. CH₂Cl₂ (Nacalai Tesque, 99%) and 1,1,2,2-tetrachloroethane (Nacalai Tesque, 95%) were dried over CaH₂ and used without further purification. Catalysts C₁ (Aldrich, 97%), C₂ (Aldrich, 97%), C₃ (AZmax, 99%), and C₄ (TCI, 97%) were used as received. M₅ and M₆ were prepared according to the general procedure reported by Fukuyama and co-workers.¹ The characterization data for M₅² and M₆¹ were reported in the literature. Caution! Extra care must be taken for preparation and handling of the diazoacetates because of their potential explosiveness.

Monomer Syntheses. Bis(diazocarbonyl) compounds (M₁-₄) were prepared from ethylene glycol, 1,4-butylidene, 1,4-cyclohexanediol, and bisphenol A, respectively, in a similar manner as reported by Fukuyama and co-workers except for the use of the corresponding bifunctional diols instead of monofunctional alcohols. M₁: ¹H NMR (400 MHz, CDCl₃, δ): 4.82 (s, 2H, -CH=⁻N₂), 4.37 (s, 4H, -O-CH₂-CH₂-O-). ¹³C NMR (100 MHz, CDCl₃, δ): 166.4 (C=O), 62.3 (-O-CH₂-CH₂-O-). Anal. Calcd. for C₈H₁₀N₂O₄: C, 42.48; H, 4.46; N, 24.77. Found: C, 42.54; H, 4.43; N, 24.71. M₂: ¹H NMR (400 MHz, CDCl₃, δ): 4.76 (s, 2H, -CH=⁻N₂), 4.19 (s, 4H, -O-CH₂-CH₂-CH₂-CH₂-O-), 1.73 (s, 4H, -O-CH₂-CH₂-CH₂-CH₂-O-). ¹³C NMR (100 MHz, CDCl₃, δ): 166.7 (C=O), 64.2 (-O-CH₂-CH₂-CH₂-CH₂-O-), 46.1 (-CH=N₂), 25.3 (-O-CH₂-CH₂-CH₂-CH₂-O-). Anal. Calcd. for C₈H₁₀N₂O₄: C, 36.37; H, 3.05; N, 28.28. Found: C, 36.67; H, 3.18; N, 28.32. M₃: ¹H NMR (400 MHz, CDCl₃, δ): 4.92 (m, 2H, -O-C₆H₁₀-O-), 4.74 (s, 2H, -CH=⁻N₂), 1.98-1.57 [m, 8H, -O-C₆H₁₀-O-]. ¹³C NMR (100 MHz, CDCl₃, δ): 166.3 (C=O), 71.3 (-O-C₆H₁₀-O-), 70.4 (-O-C₆H₁₀-O-), 46.3 (-CH=N₂), 28.0 (-O-C₆H₁₀-O-), 27.4 (-O-C₆H₁₀-O-). Anal. Calcd. for C₁₀H₁₄N₂O₄: C, 47.62; H, 4.80; N, 22.21. Found: C, 47.82; H, 4.62; N, 22.11. M₄: ¹H NMR (400 MHz, CDCl₃, δ): 7.22 (d, J = 8.6 Hz, 4H, Ph-⁻H), 7.02 (d, J = 8.6 Hz, 4H, Ph-⁻H), 4.94 (s, 2H, -CH=⁻N₂), 1.66 [s, 6H, -Ph-C(CH₃)₂-Ph-]. ¹³C NMR (100 MHz, CDCl₃, δ): 165.1 (C=O), 148.3 (Ph), 147.8 (Ph), 127.8 (Ph), 120.9 (Ph), 46.6 (-CH=N₂), 42.4 [-Ph-C(CH₃)₂-Ph-], 30.9 [-Ph-C(CH₃)₂-Ph-]. Anal. Calcd. for C₁₉H₁₆N₂O₄: C, 62.53; H, 4.43; N, 15.38. Found: C, 62.39; H, 4.31; N, 14.85.
Measurements. The number-average molecular weight ($M_n$) and polydispersity ratio [weight-average molecular weight/number-average molecular weight ($M_w/M_n$)] were measured by means of gel permeation chromatography (GPC) on a Jasco-Chro mNAV system equipped with a differential refractometer detector using tetrahydrofuran as eluent at a flow rate of 1.0 mL/min at 40 °C, calibrated with poly(methyl methacrylate). The column used for the GPC analyses was a combination of Styragel HR4 (Waters; 300 mm × 7.8 mm² i.d., 5 µm average particle size, exclusion molecular weight of 600K for polystyrene) and Styragel HR2 (Waters; 300 mm × 7.8 mm² i.d., 5 µm average particle size, exclusion molecular weight of 20K for polystyrene), and poly(methyl methacrylate) standards (Shodex M-75, $M_p = 212000, M_w/M_n = 1.05, M_p = 50000, M_w/M_n = 1.02, M_p = 22600, M_w/M_n = 1.02, M_p = 5720, M_w/M_n = 1.06, M_p = 2400, M_w/M_n = 1.08$) were used for the calibration. Purification by preparative recycling GPC was performed on a JAI LC-918R equipped with a combination of columns of a JAIGEL-3H (600 mm × 20 mm² i.d., exclusion molecular weight of 70K for polystyrene) and a JAIGEL-2H (600 mm × 20 mm² i.d., exclusion molecular weight of 5K for polystyrene) for polymers and a combination of columns of a JAIGEL-2H and a JAIGEL-1H (600 mm × 20 mm² i.d., exclusion molecular weight of 1K for polystyrene) for monomers, using CHCl₃ as eluent at a flow rate of 3.8 mL/min at 25 °C. The sample solution (3 mL containing ca. 0.3 g of the crude product) was injected and recycled before fractionation. $^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra were recorded on a Bruker Avance 400 spectrometer in chloroform-d (CDCl₃) at room temperature for monomers or at 50 °C for polymers. $^1$H NMR spectra were referenced with internal standard tetramethylsilane (δ = 0 ppm) and $^{13}$C NMR spectra were referenced by solvent shifts (77.16 ppm). Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) analyses were performed on a PerSeptive Biosystems Voyager RP equipped with 1.3-m linear and 2-m reflector flight tubes and a 337-nm nitrogen laser (pulse width, 3 ns). All experiments were carried out at an accelerating potential of 20 kV in both linear and reflector modes under the pressure of ca. 2~3 × 10⁻⁷ mmHg. Angiotensin I (human; MW = 1296.5) (SIGMA, 97%) and insulin (bovine pancreas, MW = 5733.50) (Nacalai, 28.0 U/mg solid) were used as internal standards to calibrate the mass scale. A 1.5 µL portion of the mixture consisting of an oligomer solution (100 µL, 10 mg/mL in THF), a
matrix, 1,8,9-trihydroxyanthracene (Alfer Aesar, 97%), solution (300 µL, 30 mg/mL in THF), and a
cationizing agent, sodium trifluoroacetate (TCI, 98%), solution (100 µL, 10 mg/mL in THF) was deposited
onto a sample target plate and allowed to dry in air at room temperature. Elemental analyses were
performed on a YANAKO CHN Corder MT-5. The thermal stability of the polymers was investigated
using thermogravimetric analysis (TGA, EXSTAR TG/DTA6200, Seiko Instruments Inc.). The samples
were heated from room temperature to 500 °C at a constant heating rate of 20 °C/min under air atmosphere.
Glass transition temperature ($T_g$) was determined by differential scanning calorimetry (DSC, EXSTAR
DSC6000, Seiko Instruments Inc.) in the range from -50 °C to 150 °C for product polymers. The heating
and cooling rates were 10 °C/min. The $T_g$ of the polymers was defined as the temperature of the midpoint
of a heat capacity change on the second heating scan.

**Polymerization Procedure.** As a typical procedure, polycondensation of M1 with C1 (entry 1 in
Table 1) was described as follows. Under a N$_2$ atmosphere, M1 (0.127 g; 0.56 mmol) and C1 (4.76 mg; 5.6
× 10$^{-3}$ mmol) were placed in a Schlenk tube. Polymerization was initiated by adding CH$_2$Cl$_2$ (3.0 mL) into
the tube using a syringe, and the solution was warmed to 30 °C. The reaction mixture was constantly stirred
during polymerization using a magnetic stirring bar. After 17 h, 1 mL of acetone was added to quench the
reaction. After the volatiles were removed under reduced pressure, 10 mL of 1 N HCl/methanol, 10 mL of
1 N HCl aqueous solution, and 20 mL of CHCl$_3$ were added to the residue. The CHCl$_3$ phase was separated
using a separatory funnel, and the aqueous phase was extracted with CHCl$_3$. The combined CHCl$_3$ phase
was washed with 1N HCl aqueous solution and water, dried over Na$_2$SO$_4$, filtered, and concentrated under
reduced pressure to afford a crude product. Purification with preparative recycling GPC gave polyM1$^\cdot$

**Procedure for Model Reactions.** As a typical procedure, dimerization of M5 with C1 (entry 1 in
Table 2) was described as follows. Under a N$_2$ atmosphere, C1 (5.56 mg; 6.5 × 10$^{-3}$ mmol) and CH$_2$Cl$_2$ (3.0
mL) were placed in a Schlenk tube and kept at 30 °C. After a CH$_2$Cl$_2$ solution of M5 (0.27 mL, 0.65 mmol)
was added using a syringe, the reaction mixture was constantly stirred for 17 h. After workup procedure for
the above polymerization was applied and purified with recycling GPC in CHCl₃.

**Isomerization Procedure.** As a typical procedure, isomerization of polyM1’ (entry 1 in Table 1) with diethylamine was described as follows. PolyM1’ (10 mg) was dissolved in CDCl₃ (1 mL) and 0.6 equivalent of diethylamine was added. The solution was allowed to stir and isomerization progress was checked by ¹H NMR spectroscopy.
Figure S1. $^1$H NMR spectrum of dimerM5' obtained with C1 (Table 2, entry 1).

Figure S2. $^1$H NMR spectra of cis-2 and trans-2dimerM6' obtained with C1 (Table 2, entry 2, isolated by recycling GPC).
Figure S3. Part of the MALDI-TOF-MS spectrum of oligoM5' obtained with C3 (Table 2, entry 5, $M_n = 940, M_w/M_n = 1.17$) in reflector mode.

Figure S4. $^1$H NMR spectrum of oligoM5' obtained with C3 (Table 2, entry 5, $M_n = 940, M_w/M_n = 1.17$).
Figure S5. TGA curves of polyM2' (solid line, entry 2 in Table 1) and polyM4' (dotted line, entry 4 in Table 1).

References
