Supplementary Information for

Investigation of C1 Polymerizability of Diazoacetamide: Alternating C1-cyclocopolymerization of Hetero-bis(diazocarbonyl) Compound Bearing Diazoacetate and Diazoacetamide Units

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Experimental Section

Materials

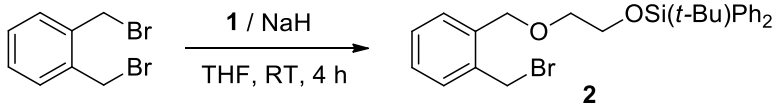
Tetrahydrofuran (THF, Kanto Chemical, >99.5%, dehydrated Super Plus grade) was used after passage through solvent purification columns (Nikko Hansen & Co., Glass Contour MINI). Diethyl ether (Kanto Chemical, >99.5%, dehydrated), *N,N*-dimethylformamide (Kanto Chemical, >99.5%, super dehydrated), chloroform (Junsei Chemical, 99%), dichloromethane (FUJIFILM Wako Pure Chemical, Guaranteed Reagent), acetonitrile (Kanto Chemical, >99.5%, super dehydrated), hexane (FUJIFILM Wako Pure Chemical, >96.0%), ethyl acetate (FUJIFILM Wako Pure Chemical, >99.5%), methanol (Yoneyama Yakuhin Kogyo, >99%), allylpalladium(II) chloride dimer (π-allylPdCl, Sigma-Aldrich, >98.0%), allyl[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]palladium(II) chloride [(NHC)Pd(nq), Sigma-Aldrich, >98.0%], sodium tetraphenylborate ($NaBPh_4$, Tokyo Chemical Industry, >99.5%), ethylene glycol (Nacalai Tesque, >99.0%), imidazole (Tokyo Chemical Industry, >98.0%), *tert*-butyldiphenylchlorosilane (*t*-$BuPh_2SiCl$, Kanto Chemical, >95.0%), *o*-xylylenedibromide (Tokyo Chemical Industry, >98.0%), 2-anilinoethanol (Tokyo Chemical Industry, >98.0%), tetrabutylammonium fluoride (TBAF, *ca.* 1 M in THF, Tokyo Chemical Industry), pyridine (Kanto Chemical, >99.5%), bromoacetyl bromide (Sigma-Aldrich, >98.0%), 1,8-diazabicyclo[5.4.0]-7-undecene (DBU, Tokyo Chemical Industry, >98%), aniline (FUJIFILM Wako Pure Chemical, >98%), salicylaldehyde (Tokyo Chemical Industry, >98%), *N*-methylaniline (Kanto Chemical, >98%), lithium aluminum hydride ($LiAlH_4$, Kanto Chemical, >92%), sodium hydride (NaH, Nacalai Tesque, with approx. 40% paraffin liquid), hydrochloric acid (Nacalai Tesque, 35–37%), Na_2SO_4 (Nacalai Tesque, > 98.5%), and CaH_2 (Nacalai Tesque, >90.0%) were used as received. *N,N*'-ditosylhydrazine was synthesized according to the literature.[1]

Synthesis of monomers and their precursors

Ethyl diazoacetate (EDA),[2] 2-diazo-*N*-methyl-*N*-phenylacetamide (**M1**),[3] *N,N*-dibenzyl-2-diazoacetamide (**M2**)[3] 2-diazo-1-(piperidin-1-yl)ethanone (**M3**),[4] and *N*-*n*-hexyl diazoacetamide (**M4**)[5] were synthesized according to the literatures. EDA was dried over CaH_2 and stored as a dichloromethane solution. The concentrations of EDA were determined with trichloroethylene (Katayama Chemical) as an internal standard by using ^1H NMR spectroscopy. ***Caution!*** Extra care must be taken for syntheses and handling of the diazocarbonyl compounds because of their potential explosiveness.

2-[(tert-Butyldiphenylsilyl)oxy]ethanol (**1**) was prepared according to the literature.[6]

*Preparation of **2**.*



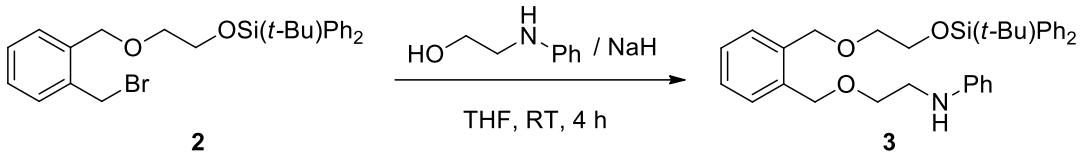
2

Under a N_2 atmosphere, a THF (30 mL) suspension of NaH (0.69 g, 29 mmol) was placed in a round bottomed flask equipped with a three-way cock, and was cooled to 0 °C. At 0 °C, a THF (34 mL) solution of **1** (7.2 g, 24 mmol) was added dropwise to the suspension, and the mixture was warmed to room temperature and stirred for 10 min. At room temperature, a THF (24 mL) solution of *o*-xylylenedibromide (6.3 g, 24 mmol) was added dropwise, and the mixture was stirred at room temperature for 4 h. H_2O (90 mL) was added to quench the remaining NaH, and THF was removed using an evaporator. After CH_2Cl_2 (90 mL) was added to the residual aqueous suspension, the mixture was transferred to a separatory funnel, with which the organic layer was separated using additional CH_2Cl_2 (90 mL × 2) and washed with

saturated aqueous NaCl solution and water. The organic layer was dried over Na_2SO_4. After the volatiles were removed under reduced pressure, the residue was subjected to purification with preparative recycling SEC using $CHCl_3$ as an eluent to afford **2** as pale yellow viscous oil (5.6 g, 12 mmol) in 49% yield.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.71–7.28 (m, 14H, Ar-*H*), 4.70 (s, 2H, PhC*H*$_2$), 4.63 (s, 2H, PhC*H*$_2$), 3.85 (t, J = 5.0 Hz, 2H, OC*H*$_2$), 3.65 (t, J = 5.0 Hz, 2H, OC*H*$_2$), 1.06 (s, 9H, *t*-Bu).

*Preparation of **3**.*

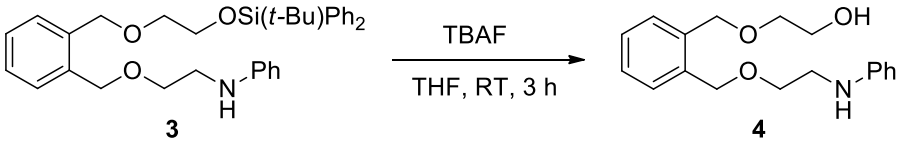


2 **3**

Under a N_2 atmosphere, a THF (10 mL) suspension of NaH (0.097 g, 4.0 mmol) was placed in a round bottomed flask equipped with a three-way cock, and was cooled to 0 °C. At 0 °C, 2-anilinoethanol (0.50 mL, 4.0 mmol) was added dropwise to the suspension, and the mixture was warmed to room temperature and stirred for 10 min. At room temperature, a THF (14 mL) solution of **2** (0.97 g, 2.0 mmol) was added dropwise, and the mixture was stirred at room temperature for 4 h. H_2O (24 mL) was added to quench the remaining NaH, and THF was removed using an evaporator. After CH_2Cl_2 (24 mL) were added to the residual aqueous suspension, the mixture was transferred to a separatory funnel, with which the organic layer was separated using additional CH_2Cl_2 (24 mL × 2) and washed with saturated aqueous NaCl solution and water. The organic layer was dried over Na_2SO_4. After the volatiles were removed under reduced pressure, the residue was subjected to purification with flash chromatography using $CHCl_3$ as an eluent to afford **3** as yellow viscous oil (1.0 g, 1.9 mmol) in 93% yield.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.71–6.60 (m, 19H, Ar-*H*), 4.62 (s, 2H, PhC*H*$_2$), 4.61 (s, 2H, PhC*H*$_2$), 4.03 (s, 1H, N*H*), 3.83 (t, J = 5.3 Hz, 2H, OC*H*$_2$), 3.66 (t, J = 5.3 Hz, 2H, OC*H*$_2$), 3.59 (t, J = 5.0 Hz, 2H, OC*H*$_2$), 3.29 (t, J = 5.3 Hz, 2H, NC*H*$_2$), 1.06 (s, 9H, *t*-Bu).

*Preparation of **4**.*

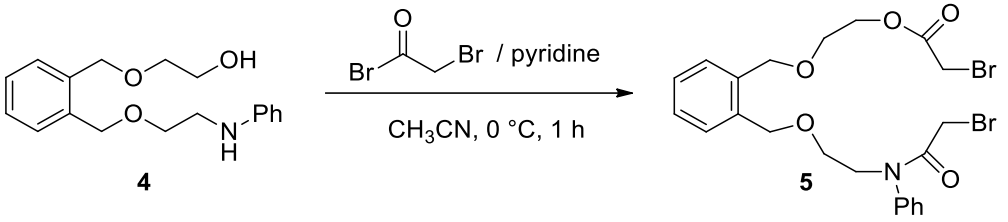


3 **4**

Under a N_2 atmosphere, a THF (10 mL) solution of **3** (0.47 g, 0.86 mmol) was placed in a round bottomed flask equipped with a three-way cock. At room temperature, TBAF (1 M THF solution, 0.3 mL, 3 mmol) was added dropwise to the solution, and the mixture was stirred for 3 h at room temperature. After H_2O (10 mL) was added, THF was removed using an evaporator. The resulting residue was transferred to a separatory funnel with $CHCl_3$ (10 mL), and the organic layer was separated using additional $CHCl_3$ (10 mL × 2) and washed with saturated aqueous NaCl solution and water. The organic layer was dried over Na_2SO_4. After the volatiles were removed under reduced pressure, the residue was subjected to purification with flash chromatography on silica gel using a gradient mixture of hexane and AcOEt (hexane/AcOEt = 1:0–3:1) as an eluent to afford **4** as yellow viscous oil (0.19 g, 0.62 mmol) in 71% yield.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.39–7.36 (m, 2H, Ar-*H*), 7.33–7.30 (m, 2H, Ar-*H*), 7.18–7.15 (m, 2H, Ar-*H*), 6.72–6.69 (m, 1H, Ar-*H*), 6.63–6.61 (m, 2H, Ar-*H*), 4.63 (s, 2H, PhC*H*$_2$), 4.63 (s, 2H, PhC*H*$_2$), 4.17 (br-s, 1H, N*H*), 3.72 (m, 2H, OC*H*$_2$), 3.72 (m, 2H, OC*H*$_2$), 3.59 (t, J = 4.5 Hz, 2H, OC*H*$_2$), 3.22 (t, J = 5.3 Hz, 2H, NC*H*$_2$), 2.49 (br-s, 1H, O*H*)

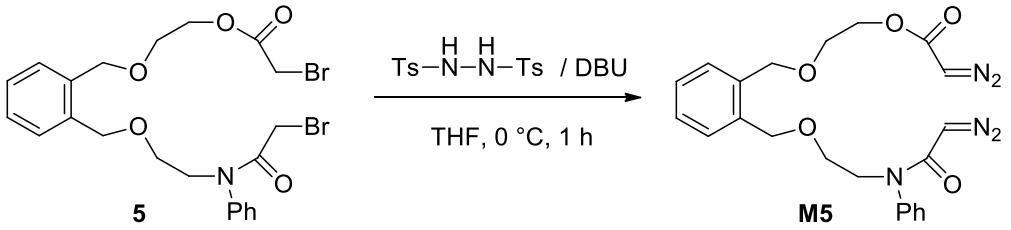
*Preparation of **5**.*



Under a N_2 atmosphere, an acetonitrile (25 mL) solution of **4** (1.0 g, 3.4 mmol) and pyridine (0.83 mL, 10 mmol) was placed in a round bottomed flask equipped with a three-way cock and was cooled to 0 °C. At 0 °C, bromoacetyl bromide (0.75 mL, 8.6 mmol) was added dropwise to the solution, and the mixture was stirred at 0 °C for 1 h. After H_2O (25 mL) was added, acetonitrile was removed using an evaporator. The residual aqueous suspension was transferred to a separatory funnel with $CHCl_3$ (25 mL), with which the organic layer was separated using additional $CHCl_3$ (25 mL × 2) and washed with saturated aqueous NaCl solution and water. The organic layer was dried over Na_2SO_4. After the volatiles were removed under reduced pressure, the residue was subjected to purification with preparative recycling SEC using $CHCl_3$ as an eluent to afford bis-bromoacetylated compound **5** as dark brown viscous oil (1.8 g, 3.3 mmol) in 96% yield.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.43–7.26 (m, 9H, Ar-*H*), 4.60 (s, 2H, PhCH_2), 4.57 (s, 2H, PhCH_2), 4.33 (t, J = 4.8 Hz, 2H, OCH_2), 3.95 (t, J = 5.8 Hz, 2H, OCH_2), 3.85 (s, 2H, COCH_2), 3.68 (t, J = 4.8 Hz, 2H, OCH_2), 3.66 (t, J = 5.8 Hz, 2H, NCH_2), 3.64 (s, 2H, COCH_2)

*Preparation of **M5**.*



Under a N_2 atmosphere, a THF (40 mL) solution of **5** (1.8 g, 3.3 mmol) and *N,N'*-ditosylhydrazine (6.7 g, 20 mmol) was placed in a round bottomed flask equipped with a three-way cock and was cooled to 0 °C. At 0 °C, DBU (7.4 mL, 49 mmol) was added dropwise to the solution, and the mixture was stirred at 0 °C for 1h. After saturated $NaHCO_3$ aqueous solution (40 mL) was added, THF was removed using an evaporator. The residual aqueous suspension was transferred to a separatory funnel with $CHCl_3$ (40 mL), with which the organic layer was separated using additional $CHCl_3$ (40 mL × 2) and washed with saturated aqueous NaCl solution and water. The organic layer was dried over Na_2SO_4. After the volatiles were removed under reduced pressure, the residue was subjected to purification with flash chromatography using a mixture of hexane and AcOEt (hexane : AcOEt = 9 : 1–0 : 1) as an eluent to afford **M5** as yellow viscous oil (1.1 g, 2.6 mmol) in 78% yield.

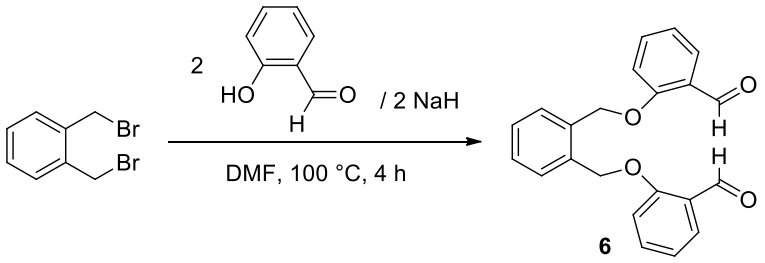
^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.39–7.20 (m, 9H, Ar-*H*), 4.81 (br-s, 1H, N_2-C*H*-CO_2), 4.58 (s, 2H, PhCH_2), 4.57 (s, 2H, PhCH_2), 4.43 (s, 1H, N_2-C*H*-CON), 4.31 (t, J = 4.8 Hz, 2H, OCH_2), 3.97 (t, J = 5.8 Hz, 2H, OCH_2), 3.67 (t, J = 5.8 Hz, 2H, NCH_2), 3.65 (t, J = 4.8 Hz, 2H, OCH_2).

^{13}C NMR (126 MHz, $CDCl_3$, δ): 167.0 (br, N_2-CH-*C*O_2), 166.0 (N_2-CH-*C*ON), 142.0 [Ar-*C*, quaternary (q.)], 136.6 (Ar-*C*, q.), 135.9 (Ar-*C*, q.), 129.8 (Ar-*C*), 128.8 (Ar-*C*), 128.8 (Ar-*C*), 128.6 (Ar-*C*), 128.2 (Ar-*C*), 128.0 (Ar-*C*), 127.9 (Ar-*C*), 70.9 (*C*H_2), 70.5 (*C*H_2), 68.3 (*C*H_2), 67.9 (*C*H_2), 64.1 (*C*H_2), 49.1 (*C*H_2), 47.6 (N_2-*C*H-CON), 46.5 (br, N_2-*C*H-

CO_2).

Elemental analyses: Anal. Calcd for $C_{22}H_{23}N_5O_5 + 1/2\ H_2O$: C, 59.32; H, 5.43; N, 15.72. Found: C, 59.32; H, 5.37; N, 14.76.

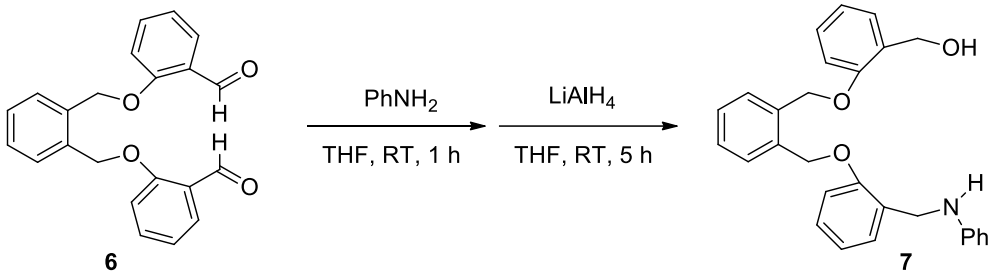
Preparation of ***6***.



Under a N_2 atmosphere, a DMF (40 mL) suspension of NaH (0.34 g, 14 mmol) and *o*-xylylenedibromide (1.5 g, 5.7 mmol) was placed in a round bottomed flask equipped with a three-way cock and was cooled to 0 °C. At 0 °C, salicylaldehyde (1.5 mL, 14 mmol) was added dropwise to the suspension, and the mixture was stirred at 100 °C for 4 h. After H_2O (20 mL) and CH_2Cl_2 (60 mL) were added, the mixture was transferred to a separatory funnel, with which the organic layer was separated using additional CH_2Cl_2 (60 mL × 2) and washed with saturated aqueous NaCl solution and water. The organic layer was dried over Na_2SO_4. After the volatiles were removed under reduced pressure, the residue was subjected to purification with preparative recycling SEC using $CHCl_3$ as an eluent to afford **6** as a colorless solid (2.0 g, 5.7 mmol) in quantitative yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 10.5 (s, 2H, CO*H*), 7.84–7.82 (m, 2H, Ar-*H*), 7.57–7.50 (m, 4H, Ar-*H*), 7.46–7.42 (m, 2H, Ar-*H*), 7.07–7.03 (m, 4H, Ar-*H*), 5.32 (s, 4H, PhCH_2).

Preparation of ***7***.



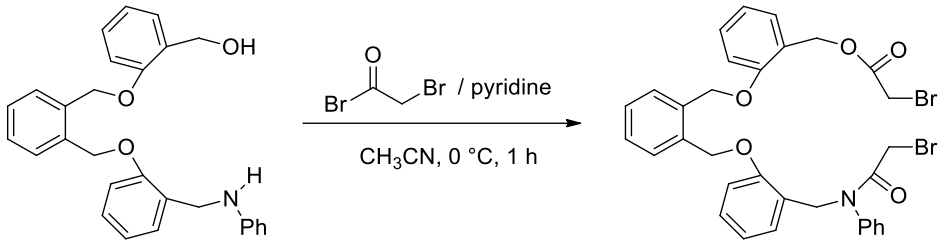
Under a N_2 atmosphere, a THF (35 mL) solution of **6** (2.0 g, 5.7 mmol) was placed in a round bottomed flask equipped with a three-way cock. At room temperature, aniline (0.52 mL, 5.7 mmol) was added dropwise to the solution, and the mixture was stirred at room temperature for 1 h. After H_2O (35 mL) was added, THF was removed using an evaporator. The residual aqueous suspension was transferred to a separatory funnel with $CHCl_3$ (35 mL), with which the organic layer was separated using additional $CHCl_3$ (35 mL × 2) and washed with saturated aqueous NaCl solution and water. The organic layer was dried over Na_2SO_4. After the volatiles were removed under reduced pressure to afford a crude mixture containing the desired mono-imine, which was subjected to the reduction with $LiAlH_4$.

Under a N_2 atmosphere, a THF (35 mL) suspension of $LiAlH_4$ (0.65 g, 17 mmol) was placed in a round bottomed flask equipped with a three-way cock and was cooled to 0 °C. At 0 °C, a THF solution (24 mL) of the above-obtained crude mixture was added dropwise to the suspension, and the mixture was stirred at room temperature for 5 h. The mixture was cooled to 0 °C, and H_2O (30 mL) was carefully added very slowly to quench the remaining $LiAlH_4$. The resulting mixture was filtered through Celite, and THF was removed using an evaporator from the filtrate. The residual

aqueous suspension was transferred to a separatory funnel with CH_2Cl_2 (30 mL), with which the organic layer was separated using additional CH_2Cl_2 (30 mL × 2). The organic layer was dried over Na_2SO_4. After Na_2SO_4 was removed by filtration, volatiles were removed under reduced pressure. The residue was subjected to purification with flash chromatography using a mixture of hexane and AcOEt (hexane : AcOEt = 1:0–0:1) as an eluent to afford **7** as a yellow solid (1.1 g, 2.5 mol) in 44% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.53–7.49 (m, 2H, Ar-*H*), 7.41–7.38 (m, 2H, Ar-*H*), 7.36–7.30 (m, 2H, Ar-*H*), 7.25–7.20 (m, 2H, Ar-*H*), 7.15–7.11 (m, 2H, Ar-*H*), 7.00–6.90 (m, 4H, Ar-*H*), 6.70–6.66 (m, 1H, Ar-*H*), 6.59–6.57 (m, 2H, Ar-*H*), 5.23 (s, 2H, PhCH_2), 5.22 (s, 2H, PhCH_2), 4.68 (s, 2H, OCH_2), 4.34 (s, 2H, NCH_2), 4.11 (br-s, 1H, N*H*), 2.17 (br-s, 1H, O*H*).

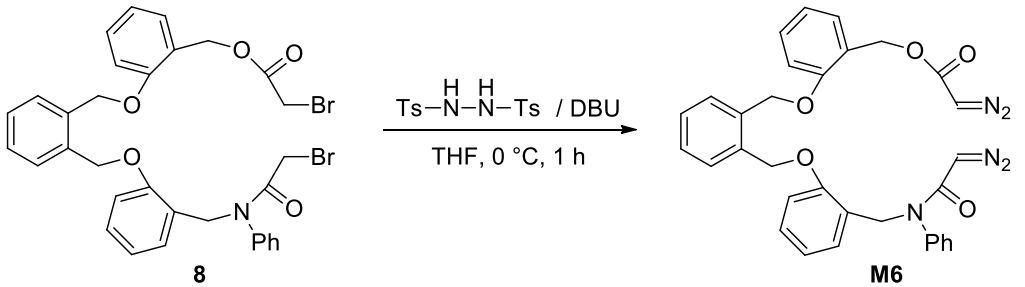
*Preparation of **8**.*



Under a N_2 atmosphere, an acetonitrile (15 mL) solution of **7** (0.52 g, 1.2 mmol) and pyridine (0.30 mL, 3.7 mmol) was placed in a round bottomed flask equipped with a three-way cock and was cooled to 0 °C. At 0 °C, bromoacetyl bromide (0.27 mL, 3.1 mmol) was added dropwise to the solution, and the mixture was stirred at 0 °C for 1 h. After H_2O (15 mL), acetonitrile was removed using an evaporator. The residual aqueous suspension was transferred to a separatory funnel with $CHCl_3$ (15 mL), with which the organic layer was separated using additional $CHCl_3$ (15 mL × 2) and washed with saturated aqueous NaCl solution and water. The organic layer was dried over Na_2SO_4. After the volatiles were removed under reduced pressure, the residue was subjected to purification with preparative recycling SEC using $CHCl_3$ as an eluent to afford bis-bromoacetylated compound **8** as a dark brown solid (0.78 g, 1.2 mmol) in 95% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.47–7.45 (m, 1H, Ar-*H*), 7.40–7.17 (m, 10H, Ar-*H*), 7.08–7.06 (m, 2H, Ar-*H*), 7.00–6.91 (m, 3H, Ar-*H*), 6.83–6.81 (m, 1H, Ar-*H*), 5.25 (s, 2H, CH_2), 5.08 (s, 2H, CH_2), 5.01 (s, 2H, CH_2), 4.98 s, 2H, CH_2), 3.75 (s, 2H, CO-CH_2), 3.63 (s, 2H, CO-CH_2).

*Preparation of **8**.*



Under a N_2 atmosphere, a THF (20 mL) solution of **8** (0.78 g, 1.2 mmol) and *N,N'*-ditosylhydrazine (2.4 g, 7.0 mmol) was placed in a round bottomed flask equipped with a three-way cock and was cooled to 0 °C. At 0 °C, DBU (2.6 mL, 18 mmol) was added dropwise to the solution, and the mixture was stirred at 0 °C for 1 h. After saturated $NaHCO_3$ aqueous solution (20 mL) was added, THF was removed using an evaporator. The residual aqueous suspension was

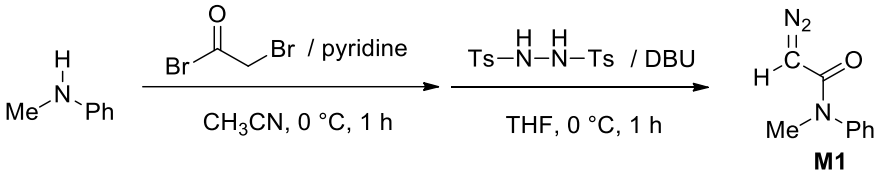
transferred to a separatory funnel with $CHCl_3$ (20 mL), with which the organic layer was separated using additional $CHCl_3$ (20 mL × 2) and washed with saturated aqueous NaCl solution and water. The organic layer was dried over Na_2SO_4. After the volatiles were removed under reduced pressure, the residue was subjected to purification with flash chromatography using a mixture of hexane and AcOEt (hexane : AcOEt = 1:9–4:6) as an eluent to afford **M6** as a yellow solid (0.50 g, 0.90 mmol) in 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.47–7.45 (m, 1H, Ar-*H*), 7.42–7.40 (m, 1H, Ar-*H*), 7.34–7.16 (m, 9H, Ar-*H*), 7.05–7.03 (m, 2H, Ar-*H*), 6.99–6.93 (m, 2H, Ar-*H*), 6.91–6.89 (m, 1H, Ar-*H*), 6.84–6.82 (m, 1H, Ar-*H*), 5.25 (s, 2H, C*H*$_2$), 5.07 (s, 2H, C*H*$_2$), 5.03 (s, 2H, C*H*$_2$), 5.00 (s, 2H, C*H*$_2$), 4.69 (s, 1H, N_2-C*H*-CO_2), 4.46 (s, 1H, N_2-C*H*-CON).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 166.9 (br, N_2-CH-*C*O_2), 166.1 (N_2-CH-*C*ON), 156.6 (Ar-*C*, q.), 156.4 (Ar-*C*, q.), 142.0 (Ar-*C*, q.), 135.2 (Ar-*C*, q.), 134.6 (Ar-*C*, q.), 130.1 (Ar-*C*), 130.1 (Ar-*C*), 129.9 (Ar-*C*), 129.5 (Ar-*C*), 128.7 (Ar-*C*), 128.6 (Ar-*C*), 128.5 (Ar-*C*), 128.3 (Ar-*C*), 128.0 (Ar-*C*), 126.2 (Ar-*C*, q.), 124.6 (Ar-*C*, q.), 121.3 (Ar-*C*), 121.1 (Ar-*C*), 111.9 (Ar-*C*), 111.8 (Ar-*C*), 68.1 (*C*H$_2$), 67.9 (*C*H$_2$), 62.2 (*C*H$_2$), 47.6 (*C*H$_2$), 47.6 (N_2-*C*H-CON), 46.4 (N_2-*C*H-CO_2).

Elemental analyses: Anal. Calcd for $C_{32}H_{27}N_5O_5$ + 4 H_2O: C, 60.66; H, 5.57; N, 11.05. Found: C, 58.94; H, 4.54; N, 10.19.

*Preparation of 2-diazo-N-methyl-N-phenylacetamide (**M1**) from N-methylaniline with bromoacetylation followed by treatment with N,N'-ditosylhydrazine and DBU.*



M1

Under a N_2 atmosphere, a CH_2Cl_2 (40 mL) solution of *N*-methylaniline (1.0 mL, 10 mmol) was placed in a round bottomed flask equipped with a three-way cock and was cooled to 0 °C. At 0 °C, bromoacetyl bromide (1.0 mL, 11 mmol) was added dropwise to the solution, and the mixture was warmed to room temperature and stirred at room temperature for 1 h. After saturated aqueous solution of $NaHCO_3$ (40 mL), the mixture was transferred to a separatory funnel, with which the organic layer was separated using additional CH_2Cl_2 (40 mL × 2) and washed with saturated aqueous NaCl solution and water. The organic layer was dried over Na_2SO_4. After the volatiles were removed under reduced pressure, *N,N'*-ditosylhydrazine (6.8 g 20 mmol) and THF (40 mL) was added to the residue under a N_2 atmosphere to form a suspension, which was cooled to 0 °C. At 0 °C, DBU (7.5 mL, 50 mmol) was added dropwise to the suspension, and the mixture was stirred at 0 °C for 1h. After saturated $NaHCO_3$ aqueous solution (20 mL), THF was removed using an evaporator. The aqueous suspension was transferred to a separatory funnel with $CHCl_3$ (20 mL), with which the organic layer was separated using additional $CHCl_3$ (20 mL × 2) and washed with saturated aqueous NaCl solution and water. The organic layer was dried over Na_2SO_4. After the volatiles were removed under reduced pressure, the residue was subjected to purification with flash chromatography using a mixture of hexane and AcOEt (hexane : AcOEt = 1:9–4:6) as an eluent to afford **M1** as yellow viscous oil (1.7 g, 0.95 mmol) in 95% yield.

Polymerization

*Copolymerization of EDA and **M1**.*

As a typical example, a copolymerization procedure for run 5 in Table 1 is described as follows.

Under a N_2 atmosphere, a THF (5 mL) solution of (NHC)Pd(nq) (4.55 mg, 0.00800 mmol) was placed in a Schlenk tube, and was cooled to −78 °C. $NaBPh_4$ (3.29 mg, 0.00960 mmol) was added to the solution and the mixture was stirred for 15 min at −78 °C. At −78 °C, a THF (3 mL) solution of **M1** (46.0 mg, 0.285 mmol) and EDA (0.26 mL of 2.02 M solution of CH_2Cl_2, 0.53 mmol) was added, and the mixture was warmed to 50 °C and stirred at 50 °C for 15 h. After volatiles were removed under reduced pressure, 1N NCl/MeOH solution (10 mL), 1H HCl aq. (10 mL), and $CHCl_3$ (20 mL) were added and the mixture was transferred to a separatory funnel, with which the organic layer was separated and washed with saturated aqueous NaCl solution wand water. The organic layer was dried over Na_2SO_4. After Na_2SO_4 was removed by filtration and the volatiles were removed under reduced pressure, the residue was subjected to purification with preparative recycling SEC using $CHCl_3$ as an eluent to afford a copolymer in 41% yield (31.5 mg).

Polymerization of hetero-bis(diazocarbonyl) compound.

As a typical example, a polymerization procedure for run 9 in Table 2 is described as follows.

Under a N_2 atmosphere, a THF (2.0 mL) solution of (π-allylPdCl)$_2$ (1.36 mg, 0.00372 mmol) was placed in a Schlenk tube, and was cooled to −78 °C. $NaBPh_4$ (4.4 mg, 0.0129 mmol) was added to the solution and the mixture was stirred for 10 min at −78 °C. At −78 °C, a THF (4.2 mL) solution of **M5** (81.9 mg, 0.187 mmol) was added, and the mixture was warmed to 50 °C and stirred at 50 °C for 15 h. After volatiles were removed under reduced pressure, 1N NCl/MeOH solution (10 mL), 1 N HCl aq. (10 mL), and $CHCl_3$ (20 mL) were added and the mixture was transferred to a separatory funnel, with which the organic layer was separated and washed with saturated aqueous NaCl solution wand water. The organic layer was dried over Na_2SO_4. After Na_2SO_4 was removed by filtration and the volatiles were removed under reduced pressure, the residue was subjected to purification with preparative recycling SEC using $CHCl_3$ as an eluent to afford a copolymer in 26% yield (18.6 mg).

Measurements

The molar mass distributions of polymers were measured via SEC in THF (flow rate = 1.0 mL/min) at 40 °C on polystyrene gel columns [Styragel HR4 and Styragel HR2 (Waters, molar-mass exclusion limit = 600 kDa and 20 kDa for polystyrene, respectively)] connected to a pump (JASCO, PU-4180), a column oven (JASCO, CO-2065 Plus), an ultraviolet detector (JASCO, UV-4075), and a refractive index detector (JASCO, RI-2031 Plus). The number-average molar mass (M_n) and dispersity [$Đ$; weight-average molar mass/number-average molar mass (M_w/M_n)] were calculated from the chromatographs on the basis of six poly(methyl methacrylate) (PMMA) standards (Shodex M-75; M_p = 2400–212000, $Đ$ < 1.1) and dibutyl sebacate (molar mass = 314.5). The absolute molecular weight of the polymers was determined by SEC coupled with multiangle light scattering (SEC-MALS) on a Dawn HELEOS II 8+ (Wyatt Technology; λ = 661.5 nm). The refractive index increment (dn/dc) values were measured assuming 100% mass recovery.

NMR spectra were recorded on a Bruker Avance 400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) or Avance 500 (500 MHz for ^{1}H and 126 MHz for ^{13}C) spectrometer at room temperature (monomers and their precursors) or at 50 °C (polymers).

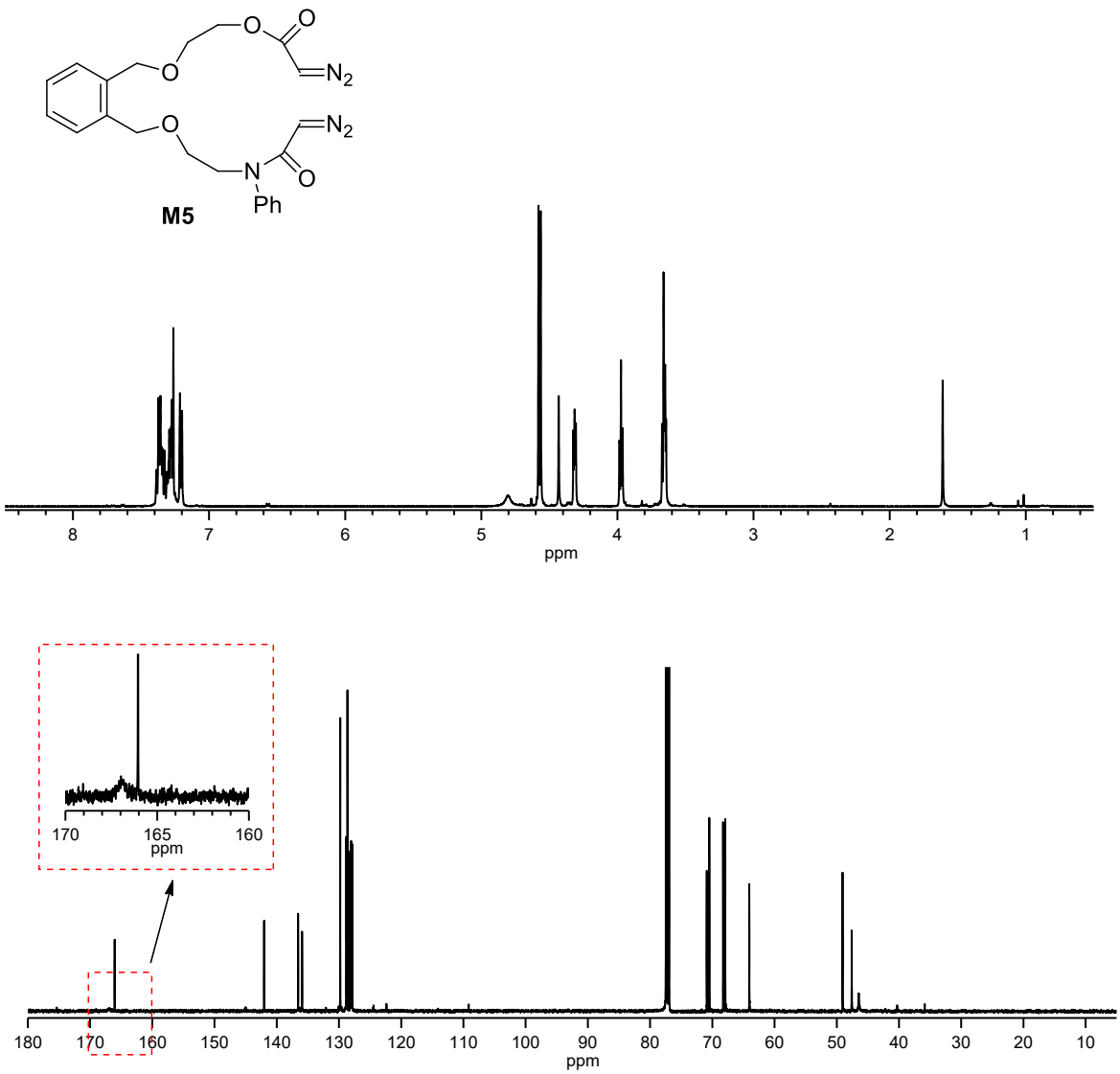
MALDI-TOF-MS (matrix-assisted laser desorption/ionization time-of-flight mass spectrometry) data were recorded on a JMS-S3000 (JEOL, spiral mode) using super-DHB (Merck, a mixture of 2,5-dihydroxybenzoic acid and 2-hydroxy-5-methoxybenzoic acid) as a matrix and sodium trifluoroacetate as an ion source. The calibration was carried out using poly(ethylene glycol) (M_n = 2700−3500).

Glass transition temperature (T_g) of polymers were determined by differential scanning calorimetry (DSC; Seiko

Instruments Inc., EXSTAR DSC6000). The heating and cooling rates were 10 °C/min. The T_g was defined as the temperature of the midpoint of a heat capacity change on the second heating scan.

Fourier transform infrared (FTIR) spectra of the samples (in the form of KBr pellets) were recorded using a Spectrum Two (PerkinElmer) at room temperature.

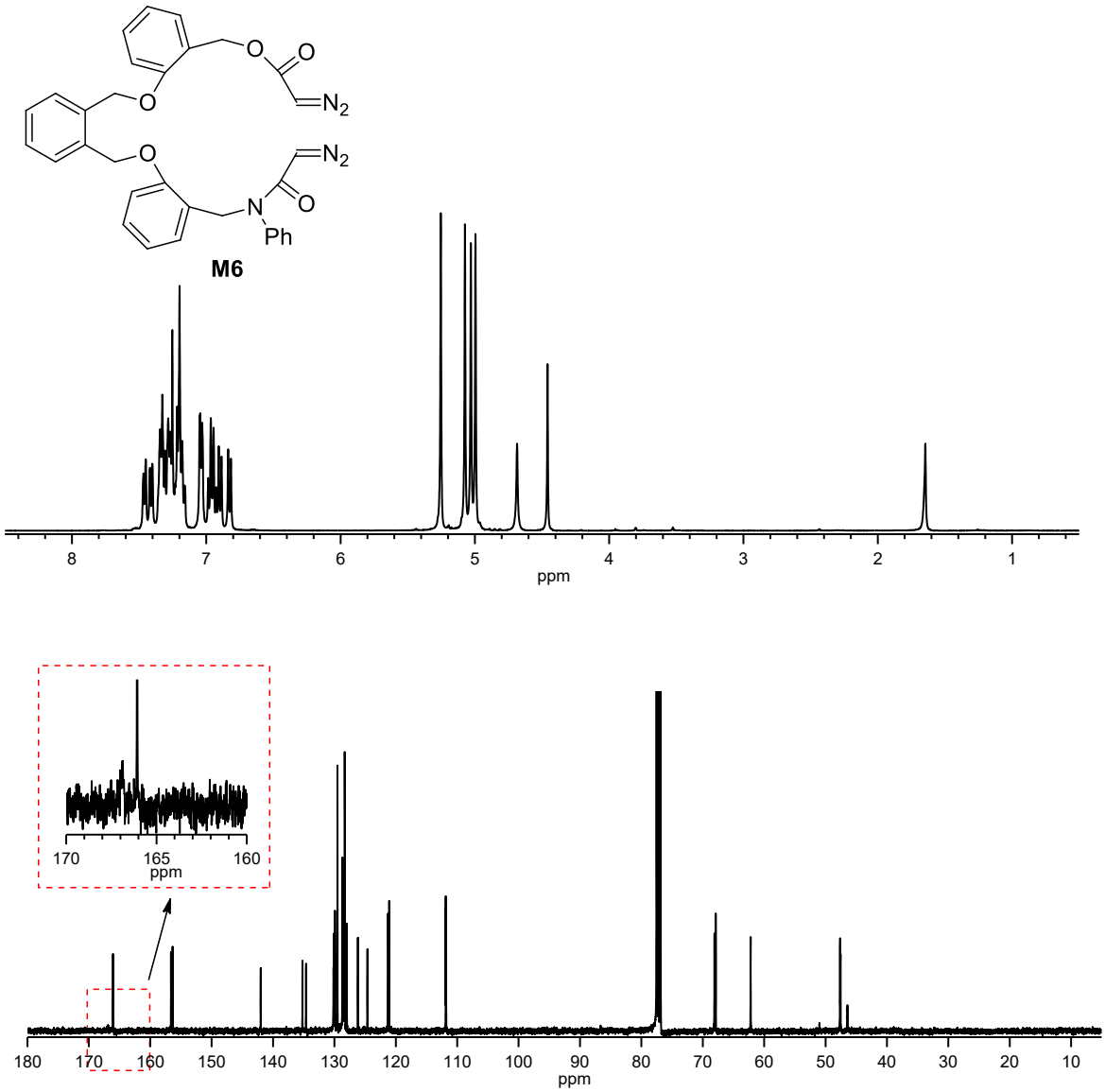
Elemental analyses were performed on a YANAKO CHN Corder MT-5.



^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.39–7.20 (m, 9H, Ar-*H*), 4.81 (br-s, 1H, N_2-C*H*-CO_2), 4.58 (s, 2H, PhCH_2), 4.57 (s, 2H, PhCH_2), 4.43 (s, 1H, N_2-C*H*-CON), 4.31 (t, J = 4.8 Hz, 2H, OCH_2), 3.97 (t, J = 5.8 Hz, 2H, OCH_2), 3.67 (t, J = 5.8 Hz, 2H, NCH_2), 3.65 (t, J = 4.8 Hz, 2H, OCH_2).

^{13}C NMR (126 MHz, $CDCl_3$, δ): 167.0 (br, N_2-CH-*C*O_2), 166.0 (N_2-CH-*C*ON), 142.0 [Ar-*C*, quaternary (q.)], 136.6 (Ar-*C*, q.), 135.9 (Ar-*C*, q.), 129.8 (Ar-*C*), 128.8 (Ar-*C*), 128.8 (Ar-*C*), 128.6 (Ar-*C*), 128.2 (Ar-*C*), 128.0 (Ar-*C*), 127.9 (Ar-*C*), 70.9 (*C*H_2), 70.5 (*C*H_2), 68.3 (*C*H_2), 67.9 (*C*H_2), 64.1 (*C*H_2), 49.1 (*C*H_2), 47.6 (N_2-*C*H-CON), 46.5 (br, N_2-*C*H-CO_2).

Figure S1. ^{1}H (upper) and ^{13}C (lower) NMR spectra of **M5**.



^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.47–7.45 (m, 1H, Ar-*H*), 7.42–7.40 (m, 1H, Ar-*H*), 7.34–7.16 (m, 9H, Ar-*H*), 7.05–7.03 (m, 2H, Ar-*H*), 6.99–6.93 (m, 2H, Ar-*H*), 6.91–6.89 (m, 1H, Ar-*H*), 6.84–6.82 (m, 1H, Ar-*H*), 5.25 (s, 2H, C*H*$_2$), 5.07 (s, 2H, C*H*$_2$), 5.03 (s, 2H, C*H*$_2$), 5.00 (s, 2H, C*H*$_2$), 4.69 (s, 1H, N_2-C*H*-CO_2), 4.46 (s, 1H, N_2-C*H*-CON).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 166.9 (br, N_2-CH-*C*O_2), 166.1 (N_2-CH-*C*ON), 156.6 (Ar-*C*, q.), 156.4 (Ar-*C*, q.), 142.0 (Ar-*C*, q.), 135.2 (Ar-*C*, q.), 134.6 (Ar-*C*, q.), 130.1 (Ar-*C*), 130.1 (Ar-*C*), 129.9 (Ar-*C*), 129.5 (Ar-*C*), 128.7 (Ar-*C*), 128.6 (Ar-*C*), 128.5 (Ar-*C*), 128.3 (Ar-*C*), 128.0 (Ar-*C*), 126.2 (Ar-*C*, q.), 124.6 (Ar-*C*, q.), 121.3 (Ar-*C*), 121.1 (Ar-*C*), 111.9 (Ar-*C*), 111.8 (Ar-*C*), 68.1 (*C*H$_2$), 67.9 (*C*H$_2$), 62.2 (*C*H$_2$), 47.6 (*C*H$_2$), 47.6 (N_2-*C*H-CON), 46.4 (N_2-*C*H-CO_2).

Figure S2. ^{1}H (upper) and ^{13}C (lower) NMR spectra of **M6**.

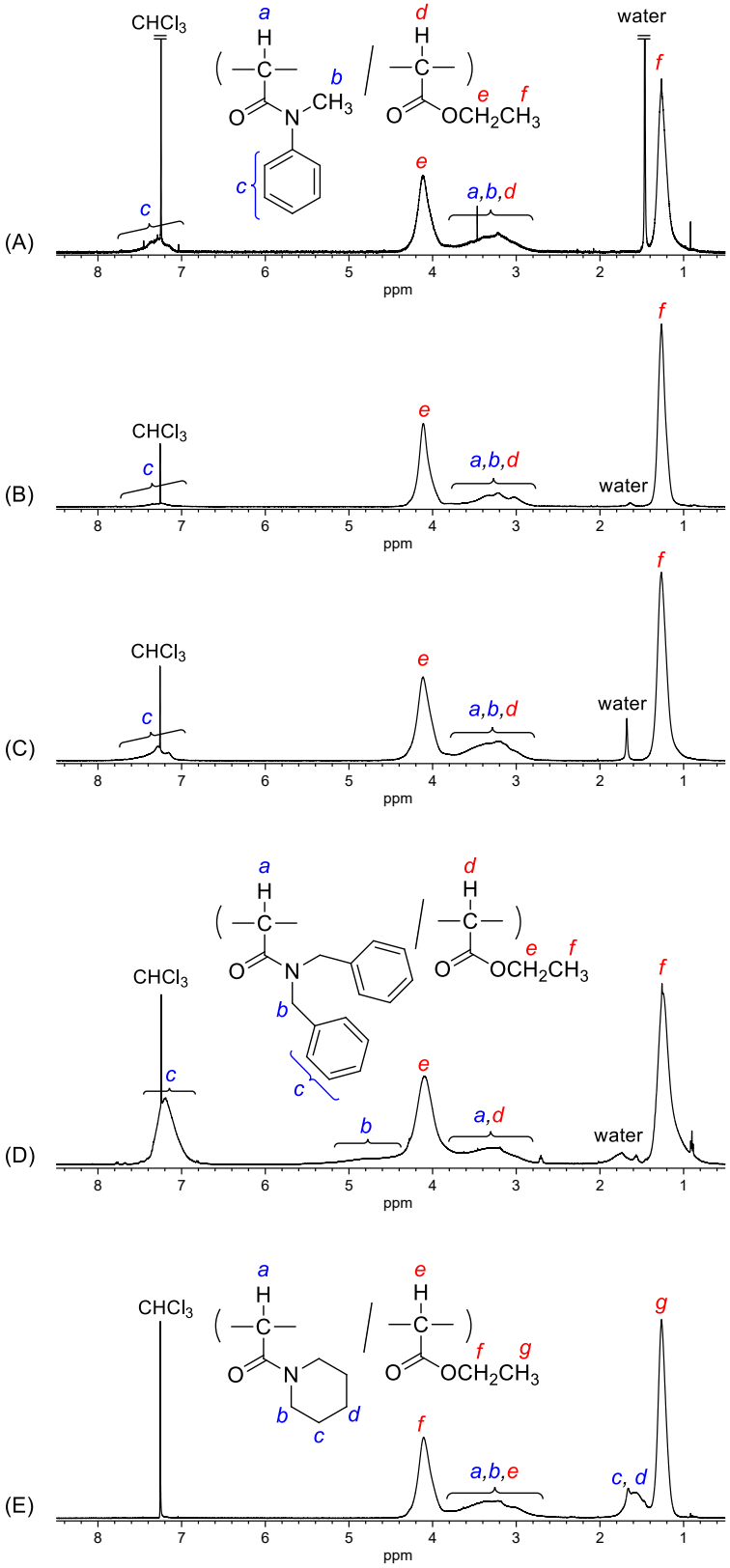
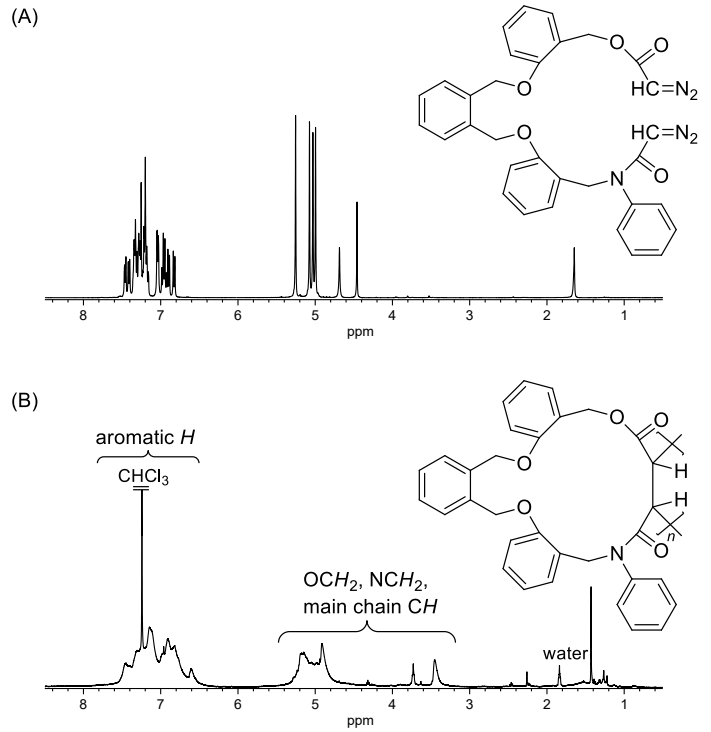


Figure S3. ^{1}H NMR spectra of (A) poly(**M1'**-*co*-EDA') obtained in run 2 in Table 1, (B) poly(**M1'**-*co*-EDA') obtained in run 3 in Table 1, (C) poly(**M1'**-*co*-EDA') obtained in run 6 in Table 1, (D) poly(**M2'**-*co*-EDA') obtained in run 7 in Table 1, and (E) poly(**M3'**-*co*-EDA') obtained in run 8 in Table 1.



Elemental analyses: Anal. Calcd for $[C_{32}H_{27}NO_5]_n + 4.5n\ H_2O$: C, 65.52; H, 6.19; N,2.39. Found: C, 65.24; H, 5.12; N, 2.79.

Figure S4. ^{1}H NMR of (A) **M6** and (B) **pM6'**.

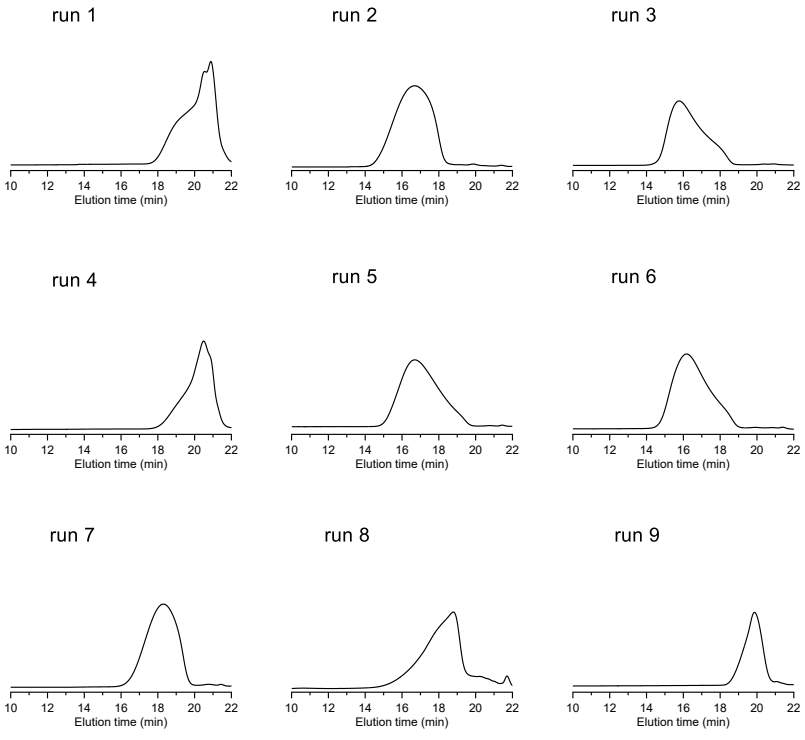


Figure S5. SEC traces of the polymeric products listed in Table 1.

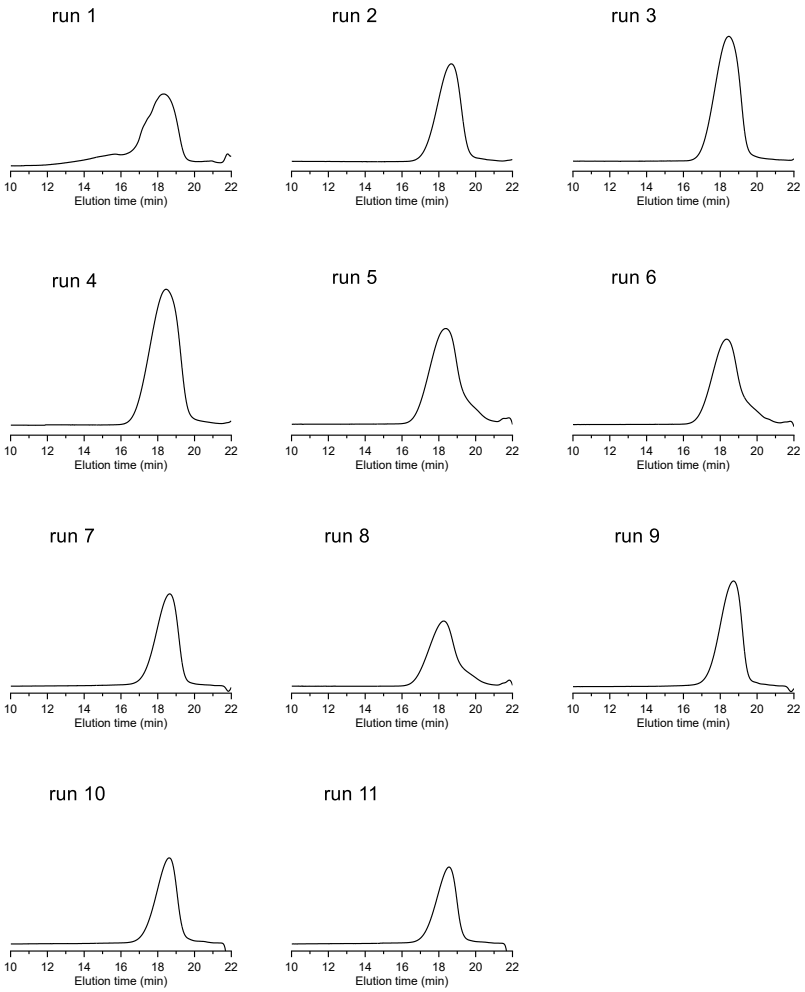


Figure S6. SEC traces of the polymeric products listed in Table 2.

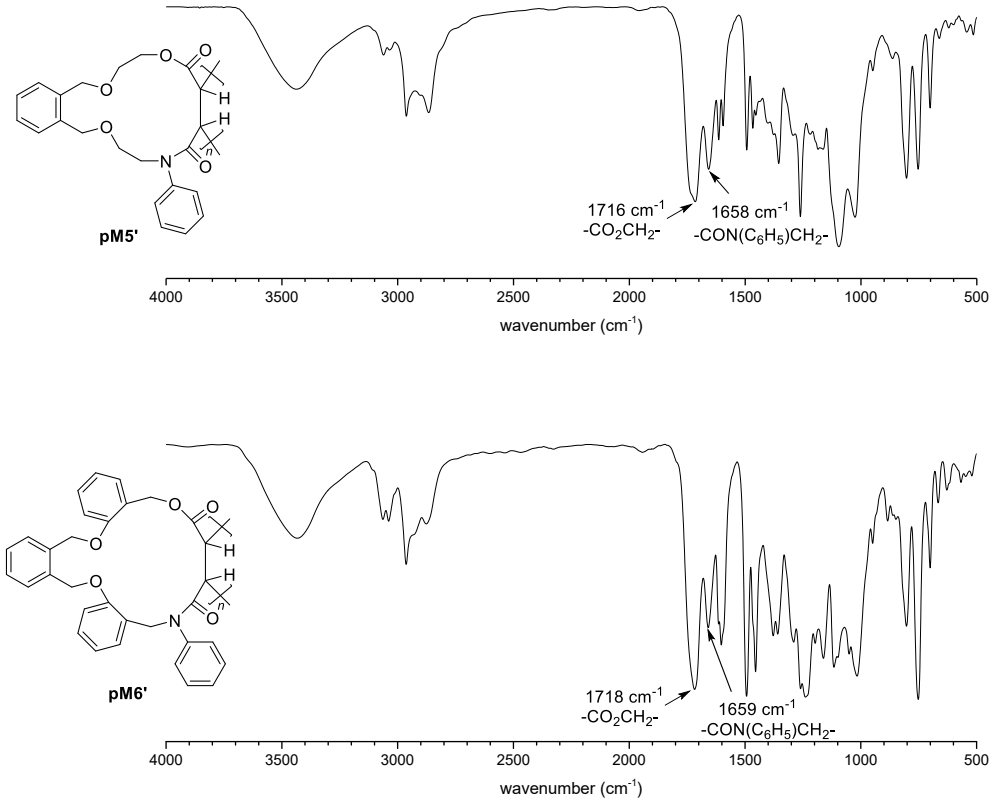


Figure S7. FTIR spectra of **pM5'** (upper, run 7 in Table 2) and **pM6'** (lower, run 11 in Table 2).

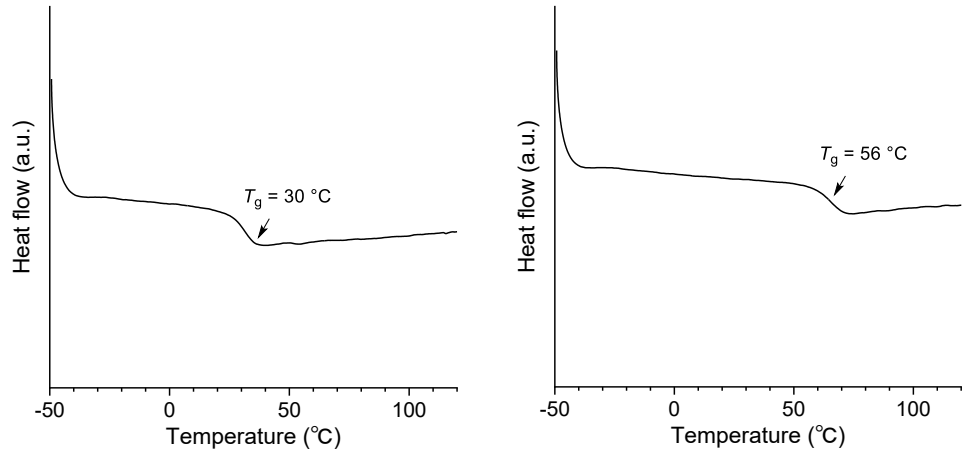


Figure S8. DSC thermograms of **pM5'** (left, run 7 in Table 2) and **pM6'** (right, run 11 in Table 2).

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