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Supporting Information

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Pd Complex-Catalyzed Polymerization of Dienes Involving Cyclization and Chain-Walking Isomerization of the Growing Polymer End. Precise Synthesis of the Polymers with Composed of Polymethylene and Five-Membered Ring Units

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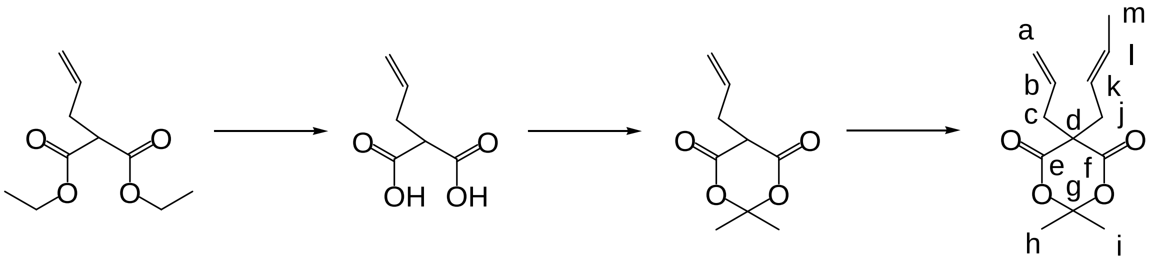
Experimental Section

General Method

Dry solvents were purchased and used as received. Diimine ligands,[1] PdCl(Me)L[2] and NaBARF[3] were prepared according to the reported procedure. NMR (^{1}H and ^{13}C) spectra were recorded on a Varian Mercury 300 or JEOL JNM-500 spectrometer. The peaks were referenced to $CHCl_3$ in the $CDCl_3$ solvent (δ 7.26) for ^{1}H and $CDCl_3$ (δ 77.0) for ^{13}C. Gel permeation chromatography (GPC) measurement was performed at 40 °C on a JASCO high-speed liquid chromatograph system equipped with a differential refractometer detector and a variable-wavelength UV-vis detector, using $CHCl_3$ as eluent at a flow rate of 1.0 mL min^{-1} with Shodex-806L column.

1. Monomer Synthesis

1) 5-Allyl-5-(2E)-2-butenyl-2,2-dimethyl-1,3-dioxan-4,6-dione (I-1)



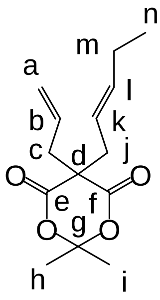
I-1

To a 100-mL two-necked round-bottomed flask containing diethyl allylmalonate (9.0 mL, 45.4 mmol) and EtOH (22.7 mL) was added NaOH aq. (6 M, 22.7 mL). After refluxed for 6 h, the reaction mixture was neutralized by HCl (6 M, 50 mL), the organic phase was extracted with ether, and washed with water and brine. The organic phase was dried over $MgSO_4$ and volatile fraction was evaporated to afford allylmalonic acid as white solid (5.68 g, 87%).

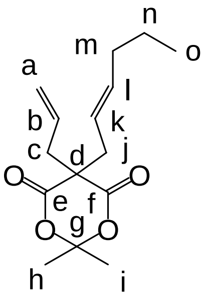
To a 100-mL Schlenk flask containing allylmalonic acid (5.19 g, 36.0 mmol) and acetic anhydride (8.64 mL, 92.2 mmol) was added conc. H_2SO_4 (150 mL) and acetone (5.76 mL, 77.8 mmol) at 0 ^{o}C. After warmed to room temperature and stirred for 15 h, the reaction mixture was extracted with chloroform, and washed with water and brine. The organic phase was dried over $MgSO_4$ and volatile fraction was evaporated to afford 5-allyl-2,2-dimethyl-1,3-dioxan-4,6-dione (3.91 g, 59%).

To a 50-mL Schlenk flask containing 5-allyl-2,2-dimethyl-1,3-dioxan-4,6-dione (3.5 g, 19.0 mmol), $Pd\{P(OC_6H_5)_3\}_4$ (130.9 mg, 97.1 mmol), and molecular sieves 4A (4.34 g) was added toluene (9.5 mL) and *trans*-crotyl alcohol (1.62 mL, 19.0 mmol) under Ar. After stirred at 80 ^{o}C for 2 h, the reaction mixture was extracted with ether, and washed with water. The organic phase was dried over $MgSO_4$ and volatile fraction was evaporated to afford 5-allyl-5-(2E)-2-butenyl-2,2-dimethyl-1,3-dioxan-4,6-dione (**I-1**) as pale yellow liquid (3.26 g, 72%).

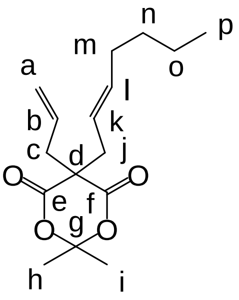
5-Allyl-5-(2E)-2-butenyl-2,2-dimethyl-1,3-dioxan-4,6-dione (**I-1**): ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.65 (m, 2H, H_b and H_l), 5.25 (m, 3H, H_a and H_k)、 2.70 (d, 2H, H_c or H_j, J = 7.5 Hz), 2.65 (d, 2H, H_c or H_j, J = 7.5 Hz), 1.66 (s, 3H, H_h or H_i or H_m), 1.65 (s, 3H, H_h or H_i or H_m), 1.64 (s, 3H, H_h or H_i or H_m). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 168.6 (C_e and C_f), 132.2 (C_k), 130.9(C_b), 123.6(C_l), 121.1(C_a), 105.8(C_g), 56.0(C_d), 42.7(C_c or C_j), 41.9(C_c or C_j), 29.9(C_h or C_i), 29.7(C_h or C_i), 17.9(C_m).



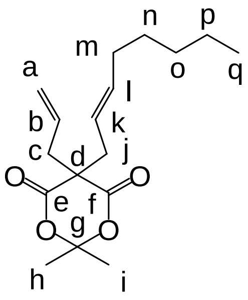
I-2



I-3



I-4



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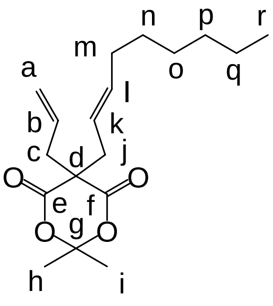
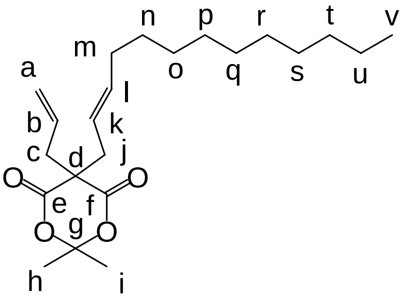


I-6



I-10

5-Allyl-5-(2E)-2-pentenyl-2,2-dimethyl-1,3-dioxan-4,6-dione (75%), 5-allyl-5-(2E)-2-hexenyl-2,2-dimethyl-1,3-dioxan-4,6-dione (74%), 5-allyl-5-(2E)-2-heptenyl-2,2-dimethyl-1,3-dioxan-4,6-dione (73%), 5-allyl-5-(2E)-2-octenyl-2,2-dimethyl-1,3-dioxan-4,6-dione (73%), 5-allyl-5-(2E)-2-nonenyl-2,2-dimethyl-1,3-dioxan-4,6-dione (63%), and 5-allyl-5-(2E)-2-tridecenyl-2,2-dimethyl-1,3-dioxan-4,6-dione (59%) were synthesized similarly.

5-Allyl-5-(2E)-2-pentenyl-2,2-dimethyl-1,3-dioxan-4,6-dione (**I-2**): ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.66 (m, 2H, H_b and H_l), 5.24 (m, 3H, H_a and H_k)、2.71 (d, 2H, H_c or H_j, J = 7.8 Hz), 2.67 (d, 2H, H_c or H_j, J = 7.5 Hz), 1.98 (dt, 2H, H_m, J = 7.2 Hz, J = 13.8 Hz), 1.66 (s, 3H, H_h or H_i), 1.65 (s, 3H, H_h or H_i), 0.93 (t, 3H, H_n, J = 7.2 Hz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ168.7 (C_e and C_f), 138.9 (C_k), 130.9(C_b), 121.1 (C_a or C_l), 121.0 (C_a or C_l), 105.6 (C_g), 55.9 (C_d), 42.6 (C_c or C_j), 41.9 (C_c or C_j), 29.9 (C_h or C_i), 29.6 (C_h or C_i), 25.3 (C_m), 13.0 (C_n).

5-Allyl-5-(2E)-2-hexenyl-2,2-dimethyl-1,3-dioxan-4,6-dione (**I-3**): ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.66 (m, 2H, H_b and H_l), 5.23 (m, 3H, H_a and H_k), 2.72 (d, 2H, H_c or H_j, J = 7.2 Hz), 2.68 (d, 2H, H_c or H_j, J = 7.2 Hz), 1.95 (dt, 2H, H_m, J = 6.9 Hz, J = 7.2 Hz), 1.67 (s, 3H, H_h or H_i), 1.66 (s, 3H, H_h or H_i), 1.34 (tq, 2H, H_n, J = 7.2 Hz, J = 7.2 Hz), 0.86 (t, 3H, H_o, J = 7.2 Hz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ168.7 (C_e and C_f), 137.6 (C_k), 131.0(C_b), 122.3 (C_a or C_l), 122.2 (C_a or C_l), 105.7 (C_g), 55.9 (C_d), 42.6 (C_c or C_j), 42.2 (C_c or C_j), 34.5 (C_m)、30.0 (C_h or C_i), 29.8 (C_h or C_i), 22.1 (C_n), 13.7 (C_o).

5-Allyl-5-(2E)-2-heptenyl-2,2-dimethyl-1,3-dioxan-4,6-dione (**I-4**): ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.66 (m, 2H, H_b and H_l), 5.24 (m, 3H, H_a and H_k), 2.71 (d, 2H, H_c or H_j, J = 7.2 Hz), 2.67 (d, 2H, H_c or H_j, J = 7.2 Hz), 1.96 (dt, 2H, H_m, J = 6.3 Hz, J =

7.2 Hz), 1.66 (s, 3H, H_h or H_i), 1.65 (s, 3H, H_h or H_i), 1.28 (m, 4H, H_n and H_o)、0.85 (t, 3H, H_p, J = 6.9 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ168.7 (C_e and C_f), 137.8 (C_k), 131.0(C_b), 122.0 (C_a or C_l), 121.1 (C_a or C_l), 105.7 (C_g)、55.9 (C_d), 42.6 (C_c or C_j), 42.2 (C_c or C_j), 32.1 (C_m)、31.1 (C_n), 30.0 (C_h or C_i), 29.8 (C_h or C_i), 22.1 (C_o), 13.9 (C_p).

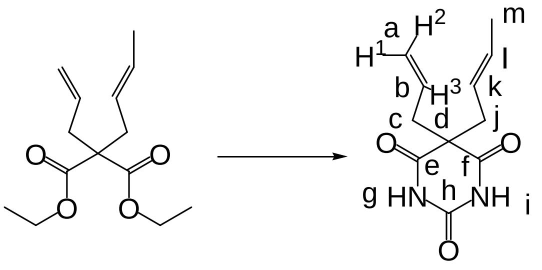
5-Allyl-5-(2E)-2-octenyl-2,2-dimethyl-1,3-dioxan-4,6-dione (**I-5**): ^1H NMR (300 MHz, $CDCl_3$): δ 5.64 (m, 2H, H_b and H_l), 5.21 (m, 3H, H_a and H_k)、2.69 (d, 2H, H_c or H_j, J = 7.2 Hz), 2.65 (d, 2H, H_c or H_j, J = 7.2 Hz), 1.93 (dt, 2H, H_m, J = 6.9 Hz, J = 6.9 Hz), 1.64 (s, 3H, H_h or H_i), 1.63 (s, 3H, H_h or H_i), 1.25 (m, 6H, H_n, H_o and H_p), 0.83 (t, 3H, H_q, J = 6.9 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ168.6 (C_e and C_f), 137.8 (C_k), 131.0(C_b), 122.0 (C_a or C_l), 121.1 (C_a or C_l), 105.7 (C_g), 55.9 (C_d), 42.6 (C_c or C_j), 42.2 (C_c or C_j), 32.4(C_m)、31.3 (C_o), 30.0 (C_h or C_i), 29.7 (C_h or C_i), 28.5 (C_n), 22.4 (C_p), 13.9 (C_q).

5-Allyl-5-(2E)-2-nonenyl-2,2-dimethyl-1,3-dioxan-4,6-dione (**I-6**): ^1H NMR (300 MHz, $CDCl_3$): δ 5.67 (m, 2H, H_b and H_l), 5.25 (m, 3H, H_a and H_k)、2.72 (d, 2H, H_c or H_j, J = 7.5 Hz), 2.67 (d, 2H, H_c or H_j, J = 7.5 Hz), 1.96 (dt, 2H, H_m, J = 6.6 Hz, J = 6.9 Hz), 1.66 (s, 3H, H_h or H_i), 1.65 (s, 3H, H_h or H_i), 1.23 (m, 8H, H_n, H_o, H_p and H_q), 0.86 (t, 3H, H_r, J = 6.9 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ168.7 (C_e and C_f), 137.9 (C_k), 131.0(C_b), 122.1 (C_a or C_l), 121.2 (C_a or C_l), 105.7 (C_g), 56.0 (C_d), 42.7 (C_c or C_j), 42.2 (C_c or C_j), 32.5(C_m), 31.6 (C_p), 30.0 (C_h or C_i), 29.7 (C_h or C_i), 28.9 (C_n), 28.8 (C_o), 22.5 (C_q), 14.0 (C_r).

5-Allyl-5-(2E)-2-tridecenyl-2,2-dimethyl-1,3-dioxan-4,6-dione (**I-10**): ^1H NMR (300 MHz, $CDCl_3$): δ 5.66 (m, 2H, H_b and H_l), 5.25 (m, 3H, H_a and H_k), 2.72 (d, 2H, H_c or H_j, J = 7.2 Hz), 2.67 (d, 2H, H_c or H_j, J = 7.2 Hz), 1.95 (dt, 2H, H_m, J = 6.9 Hz, J =

6.9 Hz), 1.66 (s, 3H, H_h or H_i), 1.65 (s, 3H, H_h or H_i), 1.23 (m, 16H, H_n, H_o, H_p, H_q, H_r, H_s, H_t and H_u), 0.87 (t, 3H, H_v, J = 6.9 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 168.7 (C_e and C_f), 137.9 (C_k), 131.0(C_b), 122.0 (C_a or C_l), 121.2 (C_a or C_l), 105.7 (C_g), 56.0 (C_d), 42.7 (C_c or C_j), 42.2 (C_c or C_j), 32.5(C_m), 31.9 (C_t), 30.0 (C_h or C_i), 29.8 (C_h or C_i), 29.6 (C_q or C_r), 29.5 (C_q or C_r), 29.4 (C_p), 29.3 (C_s), 29.2 (C_o), 28.9 (C_n), 22.7 (C_u), 14.1 (C_v).

2) 5-Allyl-5-(2E)-2-butenylbarbituric acid (II-1)

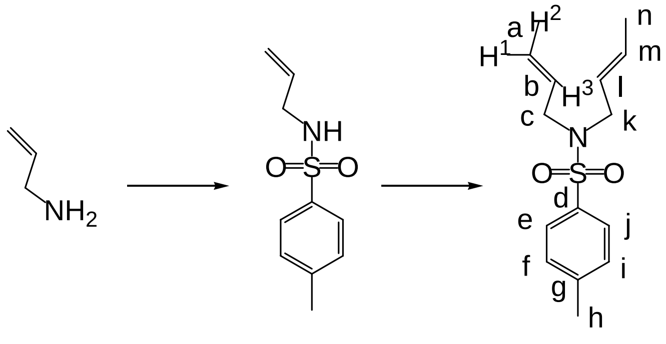


II-1

To a 500-mL Schlenk flask containing diethyl 2-allyl-2-(2E)-2-butenylmalonate (5.4 g, 22.7 mmol), urea (7.0 g, 114.4 mmol) and DMSO (261 mL) was added NaH (2.3 g, 47.4 mmol) in small portions. After stirring the reaction mixture for 3 h at room temperature, water was added and washed with ether. Aqueous phase was acidified by HCl and organic phase was extracted with ether and washed with water and brine. The organic phase was dried over $MgSO_4$ and volatile fraction was evaporated to afford 5-allyl-5-(2E)-2-butenylbarbituric acid (**II-1**) as white solid (2.34 g, 50%).

5-Allyl-5-(2E)-2-butenylbarbituric acid (**II-1**): ^1H NMR (300 MHz, $CDCl_3$): δ8.49-8.05 (br, 2H, H_g and H_i)、5.63 (m, 2H, H^3 and H_k or H_l)、5.25 (m, 1H, H_k or H_l)、5.19 (d, 1H, H^1, J = 2.4 Hz)、5.13 (ddt, 1H, H^2, J = 8.1 Hz, J = 3.0 Hz, 1.5 Hz)、2.71 (d, 2H, H_c or H_j, J = 7.8 Hz)、2.66 (d, 2H, H_c or H_j, J = 7.5 Hz)、1.62 (d, 3H, H_m, J = 5.1 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ172.0 (C_e and C_f), 149.6 (C_h), 132.3 (C_b or C_k or C_l), 130.3 (C_b or C_k or C_l), 122.4 (C_b or C_k or C_l), 121.1 (C_a), 57.3 (C_d), 42.0 (C_c or C_j), 41.6 (C_c or C_j), 18.0 (C_m).

3) 5-Allyl-5-(2E)-2-butenylbarbituric acid (III-1)



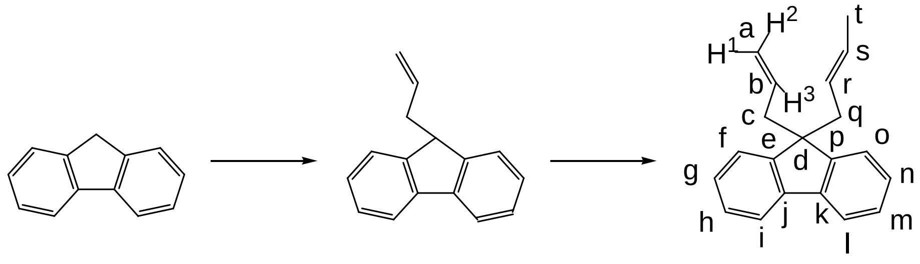
III-1

To a 200-mL Schlenk flask containing p-toluenesulfonyl chloride (2.05 g, 10.5 mmol) and dichloromethane (50 mL) was added allylamine (4.0 mL, 53 mmol) dropwise at 0 ^{o}C. After stirred for 1 h at room temperature, the reaction mixture was extracted with ethyl acetate and washed with water and brine. The organic phase was dried over $MgSO_4$ and volatile fraction was evaporated to afford N-allyl-p-toluenesulfonamide as white solid (1.62 g, 73%).

To a 200-mL two-necked round-bottomed flask containing N-allyl-p-toluenesulfonamide (1.62 g, 7.67 mmol), K_2CO_3 (4.23 g, 30.7 mmol), and acetonitrile (78.2 mL) was added trans-crotyl chloride (3.0 mL, 30.7 mmol). After refluxed for 16 h, the reaction mixture was extracted with ether and washed with water and brine. The organic phase was dried over $MgSO_4$, volatile fraction was evaporated and residue was chromatographed on silica gel (hexane:ether = 1:0.2) to afford N-allyl-N-(2E)-2-butenyl-p-toluenesulfonamide (**III-1**) as pale yellow liquid (1.29 g, 64%).

N-allyl-N-(2E)-2-butenyl-p-toluenesulfonamide (**III-1**): ^{1}H NMR (300 MHz, $CDCl_3$): δ7.69 (d, 2H, H_e and H_j, J = 8.4 Hz), 7.28 (d, 2H, H_f and H_i, J =8.4 Hz), 5.59 (m, 2H, H^3 and H_l or H_m), 5.20 (m, 3H, H^1 and H^2 and H_l or H_m), 3.78 (d, 2H, H_c or H_k, J = 6.3 Hz), 3.73 (d, 2H, H_c or H_k, J = 6.6 Hz), 2.42 (s, 3H, H_h), 1.60 (d, 2H, H_n, J = 6.9 Hz).

4) 9-Allyl-9-(2E)-2-butenylfluorene (IV-1)



IV-1

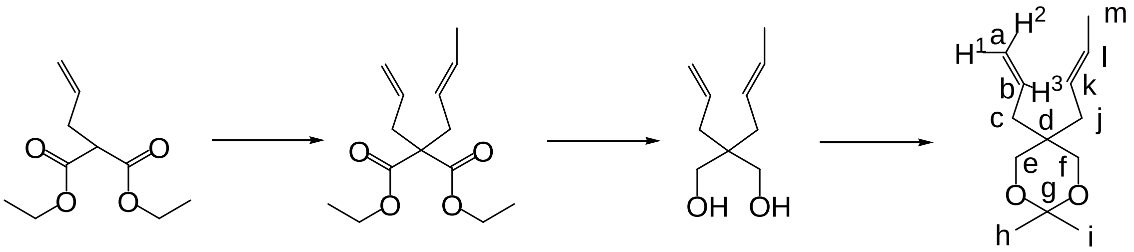
To a 200-mL three-necked round-bottomed flask containing fluorene (6.5 g, 39.1 mmol) and THF (78 mL) was added n-butyl lithium (n-hexane solution, 1.6 M, 30 mL) dropwise over a period of 30 min at -78 ^{o}C. After stirred for 10 h at room temperature, THF solution (19.5 mL) of allyl bromide (4.0 mL, 48 mmol) was added to the reaction mixture dropwise over a period of 30 min at -78 ^{o}C. The reaction mixture was slowly warmed to room temperature and was stirred for 6 h at room temperature, which was added water, extracted with ether, and washed with water and brine. The organic phase was dried over $MgSO_4$ and distilled (4 mmHg, 140 ^{o}C) to afford 9-allylfluorene as colorless oil (6.85 g, 85%).

To a 100-mL three-necked round-bottomed flask containing 9-allylfluorene (2.5 g, 12.1 mmol) and THF (31.3 mL) was added n-butyl lithium (n-hexane solution, 1.6 M, 9 mL) dropwise over a period of 30 min at -78 ^{o}C. After stirred for 2 h at room temperature, trans-crotyl chloride (1.4 mL, 14.5 mmol) was added dropwise to the reaction mixture at 0 ^{o}C. The reaction mixture was slowly warmed to room temperature and was stirred for 6 h at room temperature, which was added water, extracted with ether, and washed with water and brine. The organic phase was dried over $MgSO_4$ and distilled (4 mmHg, 155 ^{o}C) to afford 9-allyl-9-(2E)-2-butenylfluorene (**IV-1**) as colorless oil (2.43 g, 77%).

9-Allyl-9-(2E)-2-butenylfluorene (**IV-1**): ^{1}H NMR (300 MHz, $CDCl_3$): δ7.75 (d, 2H, H_i or H_k, J = 6.6 Hz), 7.74 (d, 2H, H_i or H_k, J = 6.3 Hz)、7.40 (m, 6H, H_f, H_g, H_h,

H_m, H_n and H_o)、5.30 (m, 2H, H_s and H^3)、5.07 (ddt, 1H, H_r, J = 17.7 Hz, J = 7.2 Hz , J = 1.5 Hz), 4.86 (dd, 1H, H^1, J = 17.7 Hz, J = 2.4 Hz), 4.76 (ddd, 1H, H^2, J = 10.2 Hz, J = 2.4 Hz, J = 1.5 Hz), 2.75 (d, 2H, H_c or H_q, J = 7.2 Hz), 2.63 (d, 2H, H_c or H_q, J = 7.2 Hz), 1.49 (d, 2H, H_t, J = 6.3 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ149.6 (C_e and C_p), 140.6 (C_j and C_k), 133.9 (C_b)、128.2 (C_r or C_s), 126.9 (C_g and C_n), 126.8 (C_h and C_m), 126.0 (C_r or C_s), 123.7 (C_f and C_o), 119.7 (C_i and C_l), 117.3 (C_a), 54.3 (C_d), 43.0 (C_c or C_q), 42.4 (C_c or C_q), 17.8 (C_t).

5) 5-Allyl-5-(2E)-2-butenyl-2,2-dimethyl-1,3-dioxane (V-1)



V-1

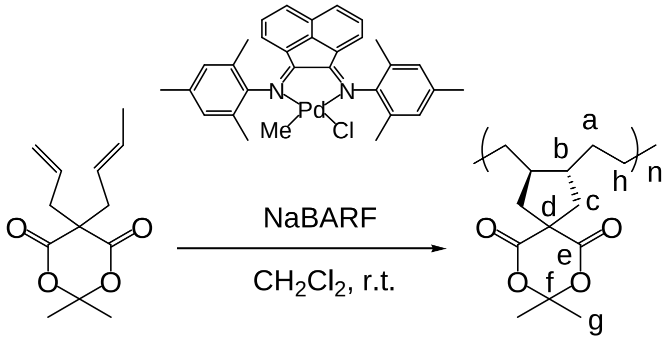
To a 200-mL two-necked round-bottomed flask containing EtOH (55 mL) was added Na (2.53 g, 110 mmol). After Na was completely consumed, diethyl allylmalonate (14.5 mL, 73.1 mmol) was added to the solution. After stirred at room temperature for 10 min, *trans*-crotyl chloride (10.5 g, 110 mmol) was added to the reaction mixture and was refluxed for 1 h. The reaction mixture was extracted with ether, and washed with water and brine. The organic phase was dried over $MgSO_4$ and volatile fraction was evaporated to afford diethyl 2-allyl-2-(2E)-2-butenylmalonate (12.1 g, 65%).

To a 100-mL two-necked round-bottomed flask containing lithium aluminumhydride (1.12 g, 29.5 mmol) and ether (17.2 mL) was added diethyl 2-allyl-2-(2E)-2-butenylmalonate (3.13 g, 12.3 mmol) at 0 ^{o}C and stirred for 30 min at 0 ^{o}C. After warmed to room temperature and the reaction mixture was stirred for 30 min at room temperature and refluxed for 12 h. The reaction mixture was cooled to 0 ^{o}C and sat. NH_4Cl aq. (1.1 mL) and NaOH aq. (1.25 M, 2.2 mL) was added dropwise to the reaction mixture, which was refluxed for 14 h. The reaction mixture was filtered, and the organic phase was dried over $MgSO_4$. Volatile fraction was evaporated to afford 2-allyl-2-(2E)-butenyl -1,3-propanediol (1.9 g, 91%).

To a 100-mL two-necked round-bottomed flask containing 2-allyl-2-(2E)-butenyl -1,3-propanediol (8.3 g, 48.7 mmol), methyl orthoformate (21.3 mL, 194.8 mmol), and acetone (30.4 mL) was added conc. H_2SO_4 (145.8 μL) and the reaction mixture was refluxed for 24 h. After $NaHCO_3$ aq. was added, the organic phase was extracted with ether and was dried over Na_2SO_4. Volatile fraction was evaporated and the residue was distilled (5 mmHg, 135 ^{o}C) over CaH_2/KOH to afford 5-allyl-5-(2E)-2-butenyl-2,2-dimethyl-1,3-dioxane (**V-1**) (5.67 g, 62%).

5-Allyl-5-(2E)-2-butenyl-2,2-dimethyl-1,3-dioxane (**V-1**): ^1H NMR (300 MHz, $CDCl_3$): δ 5.78 (ddt, 1H, H^3, J = 4.2 Hz, J = 1.2 Hz J = 7.8 Hz), 5.46 (m, 2H, H_k and H_l), 5.11 (d, 1H, H^1, J = 1.2 Hz), 5.07 (dd, 1H, H^2, J = 4.2 Hz, J = 1.2 Hz), 3.55 (s, 4H, H_e and H_f), 2.11 (d, 2H, H_c or H_j, J = 7.8 Hz), 2.05 (d, 2H, H_c or H_j, J = 8.1 Hz), 1.67 (d, 3H, H_m, J = 8.1 Hz), 1.40 (s, 6H, H_h and H_i). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 133.3 (C_b), 128.8 (C_k or C_l), 125.3 (C_k or C_l), 118.2(C_a), 97.9 (C_g), 67.3 (C_e and C_f), 36.6 (C_c or C_j), 35.6 (C_d), 35.3 (C_c or C_j), 23.8 (C_h and C_i), 18.0(C_m).

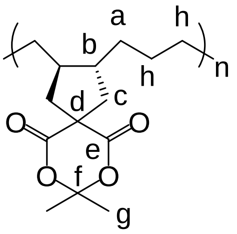
6) Polymerization of 1,6-dienes



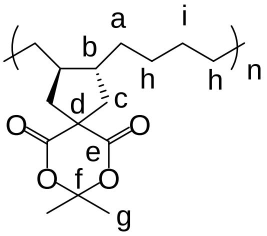
I-1 poly-**I-1**

Typically, to a 25-mL Schlenk flask containing a CH_2Cl_2 solution (0.5 mL) of Pd complex **1a** (0.01 mmol, 5.7 mg) was added NaBARF (0.012 mmol, 10.6 mg) under Ar. After stirring for several minutes, 5-allyl-5-(2E)-butenyl-2,2-dimethyl-1,3-dioxane-4,6-dione (**I-1**, 166.7 mg, 0.70 mmol) was added and the reaction mixture was stirred at room temperature. The portion of the reaction mixture was periodically taken out from the flask and subjected to ^{1}H NMR and GPC analysis to determine conversion of **I** and molecular weight of poly-**I-1** (24 h, quant. conversion). After 24-h reaction, the reaction mixture was poured into large amount of methanol (*ca.* 50 mL). A white solid formed was collected and dried in vacuo at 25 °C to give poly-**I-1** (117 mg, 76% yield, M_n = 7900, M_w/M_n = 1.68). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.42 (br, 2H, CH_2 (cyclopentane)), 1.92 (br, 2H, CH_2 (cyclopentane)), 1.83 (br, 2H, CH (cyclopentane)), 1.71 (s, 6H, CH_3), 1.62 (br, 2H, CH_2 (main chain)), 1.13 (br, 4H, CH_2 (main chain)). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 172.0 (C_e), 104.7 (C_f), 51.2(C_d), 46.9 (C_b), 45.8 (C_c), 33.0 (C_a), 28.8(C_g), 26.7(C_h).

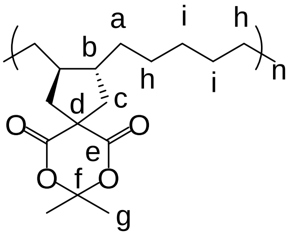
Other dienes are polymerized similarly.



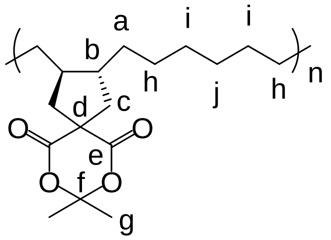
poly-**I-2**



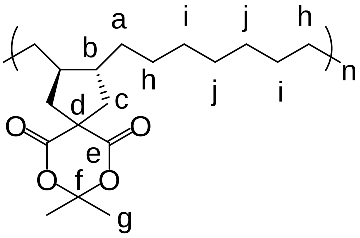
poly-**I-3**



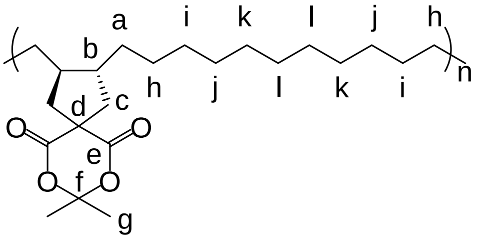
poly-**I-4**



poly-**I-5**



poly-**I-6**



poly-**I-10**

Poly-**I-2**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.41 (br, 2H, CH_2 (cyclopentane)), 1.92 (br, 2H, CH_2 (cyclopentane)), 1.83 (br, 2H, CH (cyclopentane)), 1.72 (s, 6H, CH_3), 1.60 (br, 2H, CH_2 (main chain)), 1.18 (br, 6H, CH_2 (main chain)). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 172.1 (C_e), 104.7 (C_f), 51.2(C_d), 46.4 (C_b), 45.8 (C_c), 32.8 (C_a), 28.8(C_g), 26.5(C_h).

Poly-**I-3**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.41 (br, 2H, CH_2 (cyclopentane)), 1.89 (br, 2H, CH_2 (cyclopentane)), 1.82 (br, 2H, CH (cyclopentane)), 1.70 (s, 6H, CH_3), 1.59 (br, 2H, CH_2 (main chain)), 1.13 (br, 8H, CH_2 (main chain)). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 172.1 (C_e), 104.6 (C_f), 51.2(C_d), 46.4 (C_b), 45.8 (C_c), 32.7 (C_a), 30.2 (C_i), 28.7(C_g), 28.0 (C_h).

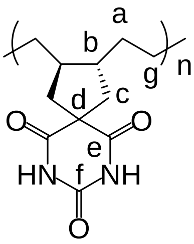
Poly-**I-4**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.44 (br, 2H, CH_2 (cyclopentane)), 1.94 (br, 2H, CH_2 (cyclopentane)), 1.85 (br, 2H, CH (cyclopentane)), 1.73 (s, 6H, CH_3),1.62 (br, 2H, CH_2 (main chain)), 1.19 (br, 10H, CH_2 (main chain)). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 172.2 (C_e), 104.7 (C_f), 51.3(C_d), 46.5 (C_b), 46.0 (C_c), 32.8 (C_a), 30.0 (C_i), 28.8(C_g), 28.1 (C_h).

Poly-**I-5**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.36 (br, 2H, CH_2 (cyclopentane)), 1.87 (br, 2H, CH_2 (cyclopentane)), 1.78 (br, 2H, CH (cyclopentane)), 1.66 (s, 6H, CH_3), 1.55 (br, 2H, CH_2 (main chain)), 1.12 (br, 12H, CH_2 (main chain)). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 171.9 (C_e), 104.4 (C_f), 51.0(C_d), 46.3 (C_b), 45.7 (C_c), 32.5 (C_a), 29.6 (C_i), 29.2 (C_j), 28.6(C_g), 27.8 (C_h).

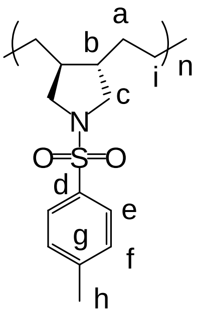
Poly-**I-6**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.43 (br, 2H, CH_2 (cyclopentane)), 1.94 (br, 2H, CH_2 (cyclopentane)), 1.84 (br, 2H, CH (cyclopentane)), 1.72 (s, 6H, CH_3), 1.61

(br, 2H, CH_2 (main chain)), 1.18 (br, 14H, CH_2 (main chain)). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 172.2 (C_e), 104.6 (C_f), 51.2(C_d), 46.5 (C_b), 46.0 (C_c), 32.7 (C_a), 29.9 (C_i), 28.8(C_g), 28.1 (C_h).

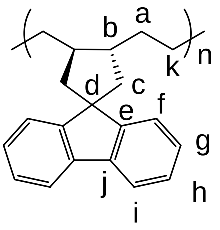
Poly-**I-10**: ^1H NMR (500 MHz, $CDCl_3$): δ 2.41 (br, 2H, CH_2 (cyclopentane)), 1.93 (br, 2H, CH_2 (cyclopentane)), 1.83 (br, 2H, CH (cyclopentane)), 1.71 (s, 6H, CH_3), 1.62 (br, 2H, CH_2 (main chain)), 1.21 (br, 22H, CH_2 (main chain)). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 172.2 (C_e), 104.6 (C_f), 51.2(C_d), 46.5 (C_b), 46.0 (C_c), 32.7 (C_a), 29.9 (C_i), 28.8(C_g), 28.1 (C_h).



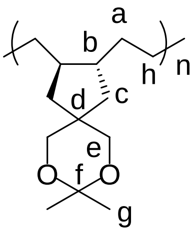
poly-**II-1**



poly-**III-1**



poly-**IV-1**



poly-**V-1**

Poly-**II-1**: ^1H NMR (500 MHz, DMF-d_7): δ 11.1 (br, 2H, NH), 2.38 (br, 2H, CH_2 (cyclopentane)), 1.80 (br, 2H, CH_2 (cyclopentane)), 1.73 (br, 2H, CH (cyclopentane)), 1.66 (br, 2H, CH_2 (main chain)), 1.31 (br, 2H, CH_2 (main chain)), 1.13 (br, 2H, CH_2 (main chain)). $^{13}C\{^1H\}$ NMR (125 MHz, DMF-d_7): δ 175.6 (C_e), 151.2 (C_f), 55.0 (C_d), 46.8 (C_b), 44.0 (C_c), 33.9 (C_a), 27.4 (C_g).

Poly-**III-1**: ^1H NMR (500 MHz, $CDCl_3$): δ 7.65 (br, 2H, H_e), 7.34 (br, 2H, H_f), 3.38 (br, 2H, CH_2 (cyclopentane)), 2.74 (br, 2H, CH_2 (cyclopentane)), 2.43 (s, 3H, H_h), 1.52 (br, 2H, CH (cyclopentane)), 1.33 (br, 2H, CH_2 (main chain)), 1.04 (br, 4H, CH_2 (main chain)). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 143.4 (C_g), 133.4 (C_d), 130.0 (C_f), 127.4 (C_e), 53.0 (C_c), 44.3 (C_b), 32.6 (C_a), 26.6 (C_i), 21.5 (C_h).

Poly-**IV-1**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (br, 2H, H_i), 7.45 (br, 2H, H_f), 7.34 (br, 4H, H_g and H_h), 2.29 (br, 2H, CH_2 (cyclopentane)), 1.90 (br, 4H, CH_2 (cyclopentane) and CH (cyclopentane)), 1.34 (br, 6H, CH_2 (main chain)). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 155.6 (C_e), 139.2 (C_j), 127.5 (C_g), 126.5 (C_h), 122.7 (C_f), 119.4 (C_i), 55.2 (C_d), 47.7 (C_b), 46.6 (C_c), 34.4(C_a), 27.3 (C_k).

Poly-**V-1**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.53 (br, 4H, OCH_2), 1.84 (br, 2H, CH_2 (cyclopentane)), 1.50 (br, 2H, CH (cyclopentane)), 1.38 (s, 6H, CH_3), 1.22 (br, 4H, CH_2 (main chain)), 0.94 (br, 4H, CH_2 (main chain) and CH_2 (cyclopentane)). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 97.5 (C_f), 70.3 (C_e), 44.9 (C_b), 40.2 (C_c), 39.6 (C_d), 34.6 (C_a), 27.1 (C_h), 23.7 (C_g).

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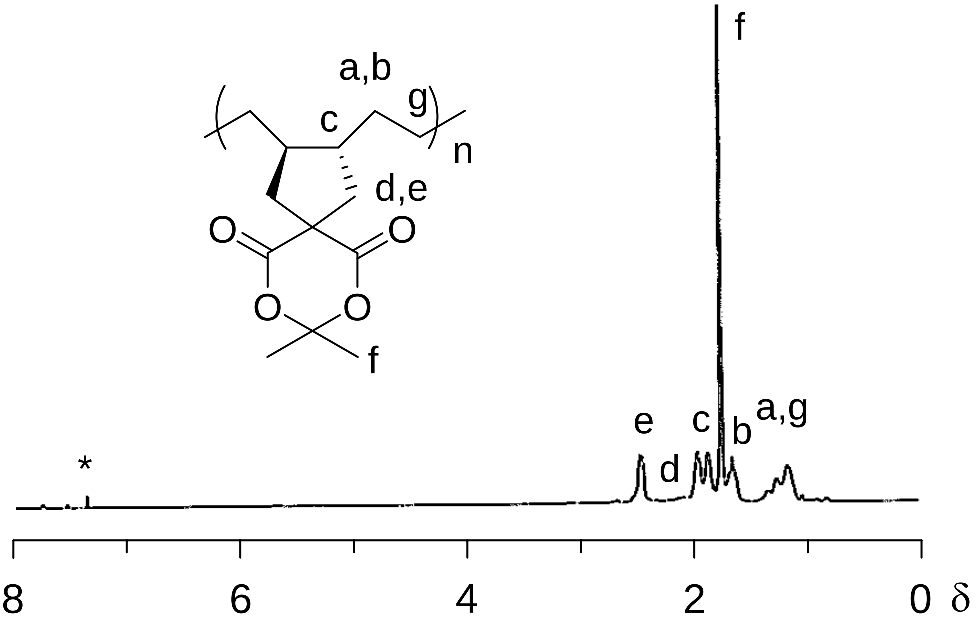

Figure S-1. ^{1}H NMR spectrum of **Poly-I-1** in $CDCl_3$ at 25 ^oC. **Poly-I-1** was prepared by polymerization of **I-1** in CH_2Cl_2 under Ar catalyzed by **1a**/NaBARF ([Pd] = 20 mM, [**Ia**]/[Pd] = 70) at room temperature. The peak with an asterisk is due to solvent.

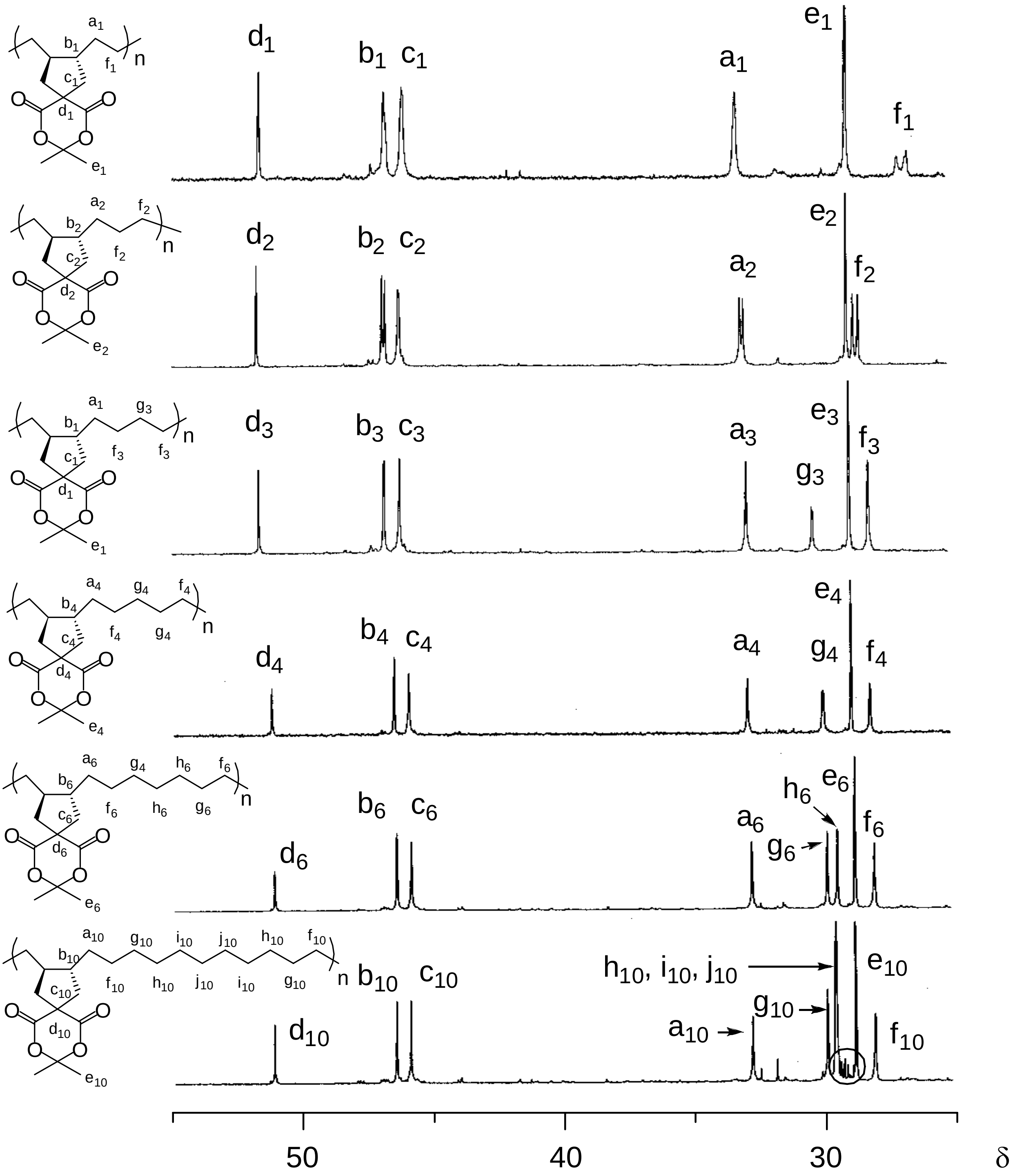

Figure S-2. $^{13}C\{^{1}H\}$ NMR spectra of poly**I**.

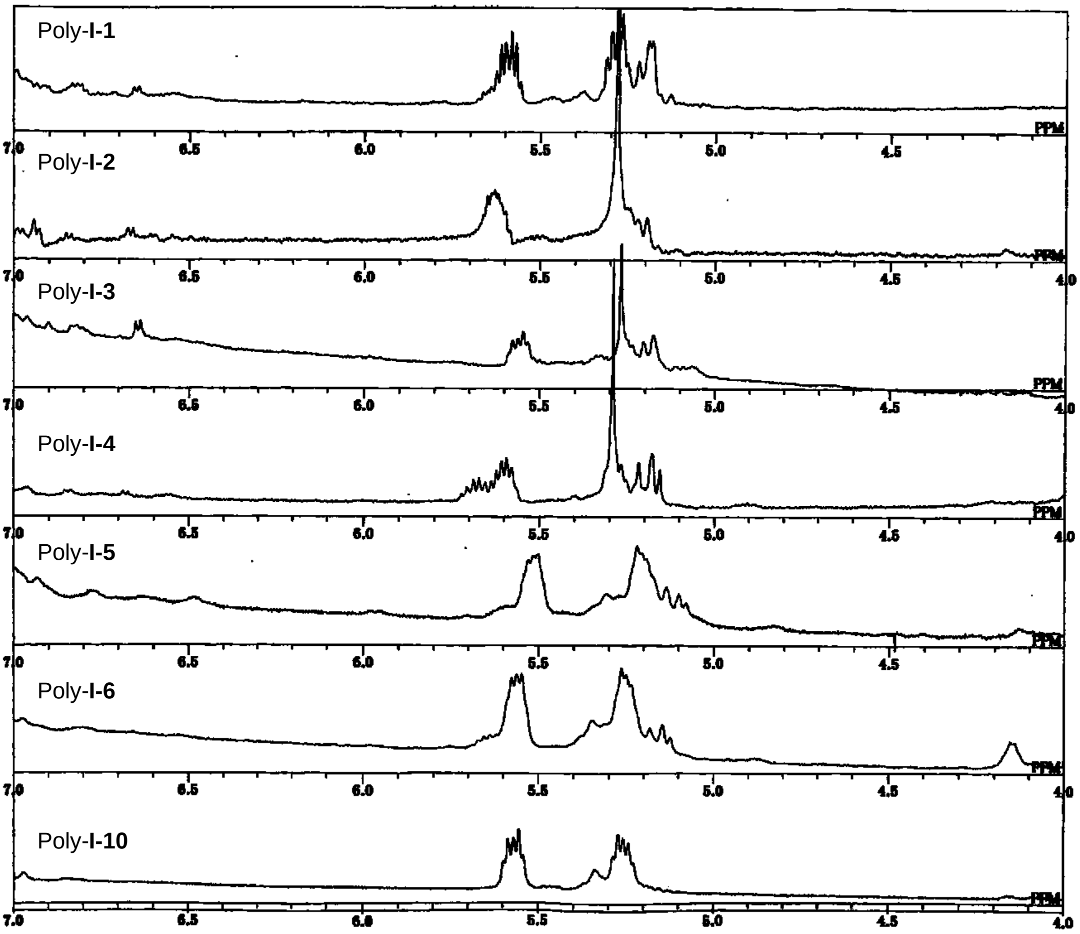

Figure S-3. Olefinic region of ^{1}H NMR spectra of poly**I**.

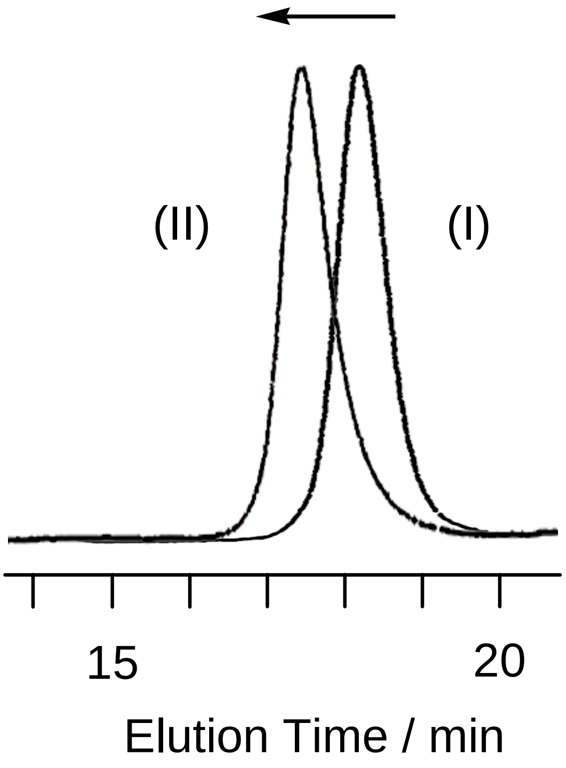

Figure S-4. GPC profiles of poly-**V-1** at (I) the first stage ([**V-1**]/[**1c**] = 40, M_n = 10800, M_w/M_n = 1.20) and (II) the second stage ([**V-1**]/[**1c**] = 40, M_n = 22400, M_w/M_n = 1.24).

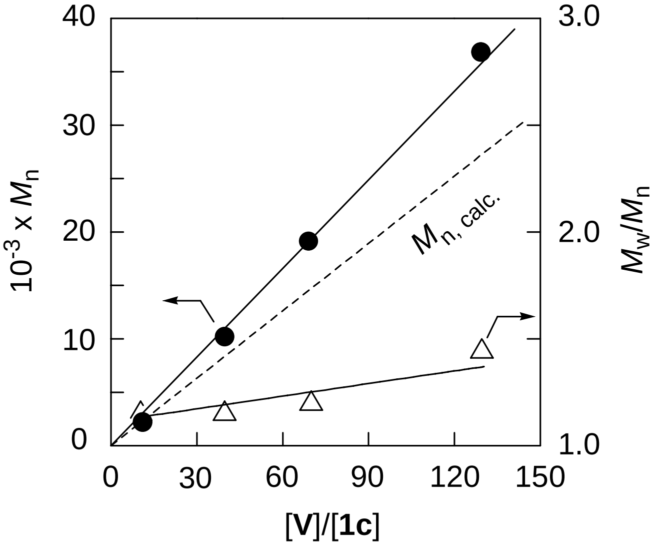

Figure S-5. Relationship between molecular weight of poly-**V-1** and **V-1**-to-**1c** molar ratio.