Supporting Information

Multicomponent Combinatorial Polymerization via the Biginelli Reaction

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Experiment Section

1. Materials and Methods

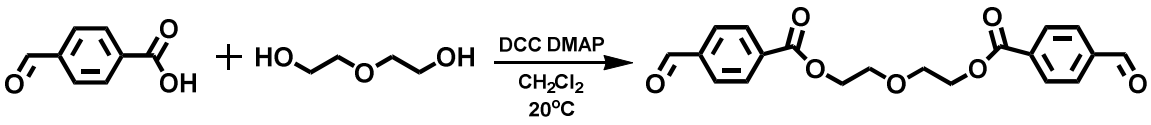
All chemicals, reagents, and solvents were purchased from commercial sources and used without further purification. 4-Formylbenzoic acid (Aladdin, 98%), 2,2'-oxybis(ethan-1-ol) (Aladdin, 99%), 2,2'-(ethane-1,2-diylbis(oxy))bis(ethan-1-ol) (Heowns, 97%), 2,2'-((oxybis(ethane-2,1-diyl))bis(oxy))bis(ethan-1-ol) (Heowns, 99%), 3,6,9,12-tetraoxatetradecane-1,14-diol (J&K, 97%), 3,6,9,12,15-pentaoxaheptadecane-1,17-diol (Alfa Aesar, 96%), 4-methyleneoxetan-2-one (Heowns, 98%), propane-1,3-diol (TCI, 98%), butane-1,4-diol (J&K, 98%), pentane-1,5-diol (J&K, 99%), hexane-1,6-diol (J&K, 98%), heptane-1,7-diol (J&K, 99%), octane-1,8-diol (J&K, 98%), nonane-1,9-diol (J&K, 97%), decane-1,10-diol (J&K, 97%) were used as purchased.

2. Instrumental Analysis

Gel permeation chromatography (GPC) analyses of polymers were performed using N, N-dimethyl formamide (DMF) containing 50 mM LiBr as the eluent. The GPC system was a Shimadzu LC-20AD pump system consisting of an auto injector, a MZ-Gel SDplus 10.0 μm guard column (50 × 8.0 mm, 10^2 Å) followed by a MZ-Gel SDplus 5.0 μm bead-size column (50 – 10^6 Å, linear), a Shimadzu RID-10A refractive index detector and a Shimadzu SPD-10A UV detector. The system was calibrated with narrow molecular weight distribution polystyrene standards ranging from 200 to 10^6 g mol^{-1}. ^{1}H NMR and ^{13}C NMR spectra were obtained using a JEOL JNM-ECA400 (400 MHz) spectrometer for all samples. The ESI-MS data were collected using a Micro TOF-QII Bruker. The *dn/dc* and $M_{n,\ LLS}$ of the model polymers were collected through a Wyatt DAWN HELEOS-II detector (658 nm, 100 mW). The FT-IR spectra were made in a transmission mode on a Perkin-Elmer Spectrum 100 spectrometer (Waltham, MA, USA). Different scanning calorimetry (DSC) was performed using TA instruments Q2000 operated at a scanning rate of 10°C/min. Matrix-assisted laser desorption ionization time-of-flight mass (MALDI-TOF MS) spectra were recorded on an AXIMA-PerformanceMA in a linear mode.

3. Synthetic procedures

3.1 Oxybis(ethane-2,1-diyl) bis(4-formylbenzoate) (Y1)



A round-bottom flask was charged with 4-formylbenzoic acid (7.07 g, 47 mmol), 2,2'-oxydiethanol (2.00 g, 19 mmol) in tetrahydrofuran (THF, 20 mL). Dicyclohexylcarbodiimide (DCC, 11.20 g, 54 mmol) and 4-dimethylaminopyridine

(DMAP, 0.24 g, 2 mmol) were added. The mixture was stirred at 20°C for 10 h, then filtered and concentrated under reduced pressure. The residue was purified by silica chromatography (ethyl acetate/petroleum ether: 0-1/3) to afford the product as a white solid (6.20 g, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 10.08 (s, CHO, 2H), 8.16 (d, *J* = 8.1 Hz, CHCHCCHO, 4H), 7.89 (d, *J* = 8.1 Hz, CHCHCCHO, 4H), 4.59 – 4.49 (m, $COOCH_2$, 4H), 3.94 – 3.86 (m, CH_2OCH_2, 4H).

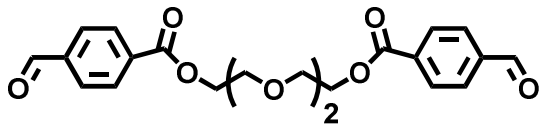
^{13}C NMR (101 MHz, $CDCl_3$, δ/ppm): 191.91, 165.79, 139.50, 135.20, 130.57, 129.79, 69.34, 64.72.

IR (v/cm^{-1}): 3298, 2929, 2852, 1694, 1648, 1547, 1339, 1234, 798, 709.

ESI-MS: observed (expected): 393.0945 (393.0942) [M+Na$^+$].

*All the Y series compounds were synthesized by the same method.

3.2 (Ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl) bis(4-formylbenzoate) (Y2)



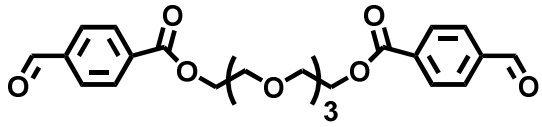
^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 10.09 (s, CHO, 2H), 8.19 (d, *J* = 8.1 Hz, CHCHCCHO, 4H), 7.93 (d, *J* = 8.1 Hz, CHCHCCHO, 4H), 4.57 – 4.44 (m, $COOCH_2$, 4H), 3.92 – 3.79 (m, $COOCH_2CH_2$, 4H), 3.73 (s, $CH_2OCH_2CH_2OCH_2$, 4H).

^{13}C NMR (101 MHz, $CDCl_3$, δ/ppm): 191.96, 165.82, 139.50, 135.32, 130.60, 129.82, 71.05, 69.47, 64.91.

IR (v/cm^{-1}): 2913, 2838, 1697, 1263, 1107, 758, 686.

ESI-MS: observed (expected): 437.1207 (437.1206) [M+Na$^+$].

3.3 ((Oxybis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl) bis(4-formylbenzoate) (**Y3**)



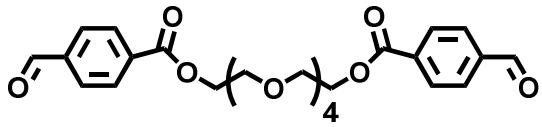
^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 10.09 (s, CHO, 2H), 8.27 – 8.13 (d, *J* = 8.1 Hz, CHC<u>H</u>CCHO, 4H), 8.01 – 7.86 (d, *J* = 8.1 Hz, C<u>H</u>CHCCHO, 4H), 4.49 (m, $COOCH_2$, 4H), 3.91 – 3.80 (m, $COOCH_2C\underline{H_2}$, 4H), 3.68 (s, $CH_2O(C\underline{H_2}C\underline{H_2}O)_2CH_2$, 8H).

^{13}C NMR (101 MHz, $CDCl_3$, δ/ppm): 191.95, 165.84, 139.53, 135.40, 130.64, 129.82, 71.05, 69.43, 64.96.

IR (v/cm^{-1}): 2910, 1713, 1373, 1263, 1107, 804, 760, 685.

ESI-MS: observed (expected): 481.1467 (481.1469) [M+Na^+].

3.4 3,6,9,12-Tetraoxatetradecane-1,14-diyl bis(4-formylbenzoate) (**Y4**)



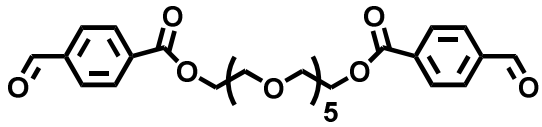
^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 10.08 (s, CHO, 2H), 8.19 (d, *J* = 8.1 Hz, CHC<u>H</u>CCHO, 4H), 7.93 (d, *J* = 8.1 Hz, C<u>H</u>CHCCHO, 4H), 4.54 – 4.43 (m, $COOCH_2$, 4H), 3.88 – 3.77 (m, $COOCH_2C\underline{H_2}$, 4H), 3.77 – 3.59 (m, $CH_2O(C\underline{H_2}C\underline{H_2}O)_3CH_2$, 12H).

^{13}C NMR (101 MHz, $CDCl_3$, δ/ppm): 191.95, 165.79, 139.44, 135.33, 130.58, 129.77, 70.95, 70.92, 69.34, 64.94.

IR (v/cm^{-1}): 2883, 1715, 1267, 1094, 729, 675.

ESI-MS: observed (expected): 525.1732 (525.1731) [M+Na^+].

3.5 3,6,9,12,15-Pentaoxaheptadecane-1,17-diyl bis(4-formylbenzoate) (Y5)



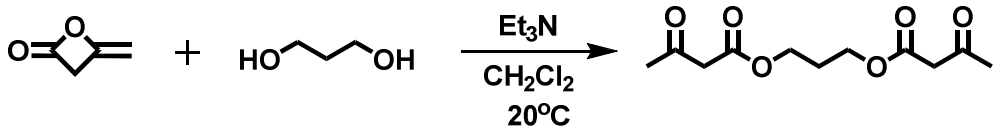
^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 10.08 (s, CHO, 2H), 8.21 – 8.17 (d, *J* = 8.1 Hz, CHC<u>H</u>CCHO, 4H), 7.95 – 7.91 (d, *J* = 8.1 Hz, C<u>H</u>CHCCHO, 4H), 4.51 – 4.47 (m, $COOCH_2$, 4H), 3.84 – 3.82 (m, $COOCH_2C\underline{H}_2$, 4H), 3.69 – 3.60 (m, $CH_2O(C\underline{H}_2C\underline{H}_2O)_4CH_2$, 16H).

^{13}C NMR (101 MHz, $CDCl_3$, δ/ppm): 192.08, 169.99, 166.00, 139.46, 130.63, 130.01, 70.91, 69.39, 64.98.

IR (v/cm^{-1}): 2918, 1720, 1274, 1200, 1088, 833, 759, 688.

ESI-MS: observed (expected): 569.1996 (569.1993) [$M+Na^+$].

3.6 Propane-1,3-diyl bis(3-oxobutanoate) (X1)



A round-bottom flask was charged with propane-1,3-diol (2.50 g, 33 mmol), dichloromethane (50 ml), triethylamine (Et_3N, 14 ml, 99 mmol). 4-Methyleneoxetan-2-one was added dropwise (6.08 g, 72 mmol) under N_2 atmosphere, and the mixture was stirred at 20°C for 10 h. The reaction mixture was washed with brine three times. The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by silica chromatography (ethyl acetate/petroleum ether: 0-1/3) to afford the product as a yellowish oil (7.1 g, 89% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 4.20 (t, *J* = 6.7 Hz, $COOCH_2$, 4H), 3.45 (s, CH_2COO, 4H), 2.24 (s, CH_3, 6H), 2.01 – 1.94 (m, $COOCH_2C\underline{H_2}$, 2H).

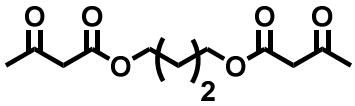
^{13}C NMR (101 MHz, $CDCl_3$, δ/ppm): 200.74, 167.27, 61.94, 50.18, 30.50, 28.13, 27.96.

IR (v/cm^{-1}): 2973, 1711, 1415, 1363, 1252, 1150, 1047, 801.

ESI-MS: observed (expected): 267.0836 (267.0839) [M+Na^{+}].

*All the X series compounds were synthesized by the same method.

3.7 Butane-1,4-diyl bis(3-oxobutanoate) (X2)



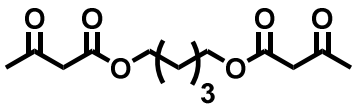
^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 4.15 – 4.11 (t, *J* = 6.7 Hz, $COOCH_2$, 4H), 3.43 (s, CH_2COO, 4H), 2.23 (s, CH_3, 6H), 1.70 – 1.67 (m, $COOCH_2(C\underline{H_2})_2$, 4H).

^{13}C NMR (101 MHz, $CDCl_3$, δ/ppm): 200.83, 167.33, 64.94, 50.24, 30.47, 25.30.

IR (v/cm^{-1}): 2968, 1709, 1415, 1363, 1318, 1251, 1145, 1034, 799.

ESI-MS: observed (expected): 281.0997 (281.0996) [M+Na^{+}].

3.8 Pentane-1,5-diyl bis(3-oxobutanoate) (X3)



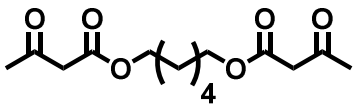
^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 4.11 (t, *J* = 6.7 Hz, $COOCH_2$, 4H), 3.43 (s, CH_2COO, 4H), 2.24 (s, CH_3, 6H), 1.65 (m, $COOCH_2(C\underline{H_2})_2$, 4H), 1.44 – 1.36 (m, $COOCH_2CH_2C\underline{H_2}$, 2H).

^{13}C NMR (101 MHz, $CDCl_3$, δ/ppm): 200.88, 167.41, 65.32, 50.32, 30.47, 28.31, 22.51.

IR (v/cm^{-1}): 2963, 1710, 1408, 1357, 1319, 1254, 1145, 1033, 798.

ESI-MS: observed (expected): 295.1149 (295.1152) [M+Na^+].

3.9 Hexane-1,6-diyl bis(3-oxobutanoate) (X4)



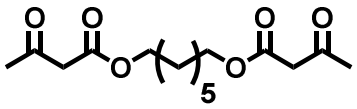
^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 4.10 (t, *J* = 6.7 Hz, $COOCH_2$, 4H), 3.42 (s, CH_2COO, 4H), 2.24 (s, CH_3, 6H), 1.65 – 1.60 (m, $COOCH_2C\underline{H}_2$, 4H), 1.37 – 1.33 (m, $COOCH_2CH_2(C\underline{H}_2)_2$, 4H).

^{13}C NMR (101 MHz, $CDCl_3$, δ/ppm): 200.93, 167.46, 65.54, 50.38, 30.49, 28.61, 25.71.

IR (v/cm^{-1}): 2957, 1710, 1415, 1358, 1311, 1248, 1145, 1037, 802.

ESI-MS: observed (expected): 309.1310 (309.1309) [M+Na^+].

3.10 Heptane-1,7-diyl bis(3-oxobutanoate) (X5)



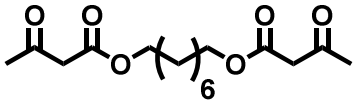
^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 4.10 (t, *J* = 6.7 Hz, $COOCH_2$, 4H), 3.42 (s, CH_2COO, 4H), 2.24 (s, CH_3, 6H), 1.64 – 1.58 (m, $COOCH_2C\underline{H}_2$, 4H), 1.35 – 1.32 (m, $COOCH_2CH_2(C\underline{H}_2)_3$, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, δ/ppm): 200.83, 167.44, 65.64, 50.37, 30.41, 28.99, 28.63, 25.93.

IR (v/cm^{-1}): 2936, 1710, 1640, 1412, 1357, 1313, 1237, 1152, 1034, 805.

ESI-MS: observed (expected): 323.1468 (323.1465) [M+Na^+].

3.11 Octane-1,8-diyl bis(3-oxobutanoate) (X6)



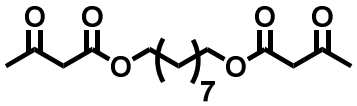
^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 4.10 (t, *J* = 6.7 Hz, $COOCH_2$, 4H), 3.43 (s, CH_2COO, 4H), 2.24 (s, CH_3, 6H), 1.64 – 1.58 (m, $COOCH_2C\underline{H}_2$, 4H), 1.31 – 1.28 (m, $COOCH_2CH_2(C\underline{H}_2)_4$, 8H).

^{13}C NMR (101 MHz, $CDCl_3$, δ/ppm): 200.94, 167.47, 65.72, 50.38, 30.45, 29.27, 28.67, 25.95.

IR (v/cm^{-1}): 2940, 1716, 1414, 1362, 1316, 1238, 1146, 1031, 802.

ESI-MS: observed (expected): 337.1619 (337.1622) [M+Na^{+}].

3.12 Nonane-1,9-diyl bis(3-oxobutanoate) (X7)



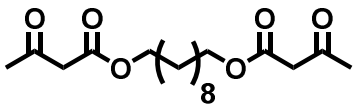
^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 4.10 (t, *J* = 6.7 Hz, $COOCH_2$, 4H), 3.42 (s, CH_2COO, 4H), 2.24 (s, CH_3, 6H), 1.63 – 1.58 (m, $COOCH_2C\underline{H}_2$, 4H), 1.32 – 1.28 (m, $COOCH_2CH_2(C\underline{H}_2)_5$, 10H).

^{13}C NMR (101 MHz, $CDCl_3$, δ/ppm): 200.85, 167.45, 65.76, 50.39, 30.40, 29.55, 29.32, 28.72, 26.02.

IR (v/cm^{-1}): 2938, 1712, 1414, 1362, 1318, 1236, 1152, 1035, 799, 722.

ESI-MS: observed (expected): 351.1779 (351.1778) [M+Na^{+}].

3.13 Decane-1,10-diyl bis(3-oxobutanoate) (X8)



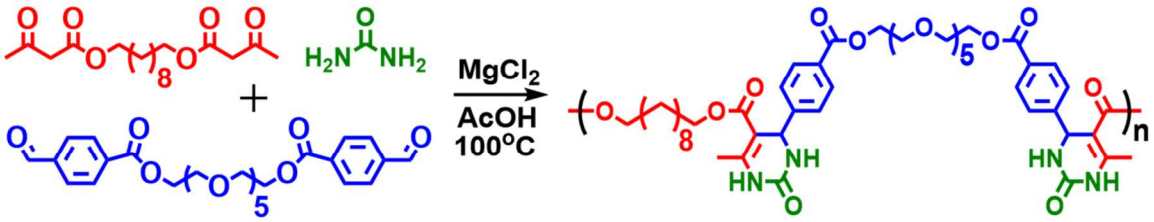
^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 4.06 (t, J = 6.7 Hz, $COOCH_2$, 4H), 3.39 (s, CH_2COO, 4H), 2.20 (s, CH_3, 6H), 1.62 – 1.54 (m, $COOCH_2C\underline{H_2}$, 4H), 1.29 – 1.22 (m, $COOCH_2CH_2(C\underline{H_2})_6$, 12H).

^{13}C NMR (101 MHz, $CDCl_3$, δ/ppm): 200.77, 167.37, 65.67, 50.29, 30.30, 29.52, 29.30, 28.64, 25.95.

IR (v/cm^{-1}): 2933, 1717, 1244, 1152, 1031, 804, 721.

ESI-MS: observed (expected): 365.1936 (365.1935) [M+Na^{+}].

3.14 Biginelli polycondensation



The Biginelli polycondensation using different combinations of monomers are performed simultaneously in a homothermal shaker. Typically, the diketoester compound B_2(5) (164 mg, 0.3 mmol), the dialdehyde compound A_2(8) (103 mg, 0.3 mmol), and urea (54 mg, 0.9 mmol) were put in a 1.5 mL centrifuge tube. Then, acetic acid (0.3 mL) and magnesium chloride (6 mg, 0.06 mmol) were added. The tube was sealed and put in a shaker (100°C) for 24 h. Samples (~ 20-40 μL, ~ 5-10% of the solution) were taken at different time points (0.5 h, 1 h, 2 h, 4 h, 10 h, 24 h), and used immediately for ^{1}H NMR and GPC analyses to test the conversion and molecular weights. The crude was simply purified by precipitation into cold water, then washed for three times by water and then diethyl ether to get the final A_2(8)B_2(5)C(1) polymer as a yellow powder (256 mg, 91% yield).

All other polymers were prepared through the same procedure.

Supporting Data

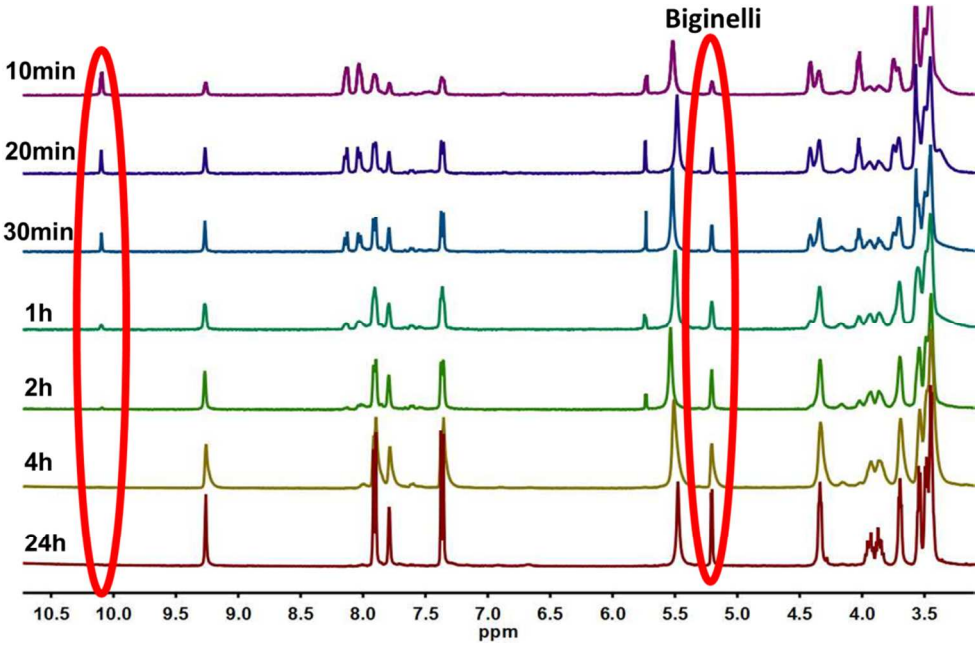


Figure S1. ^{1}H NMR spectra (DMSO-d_6, 400 MHz) during the Biginelli polycondensation (urea system).

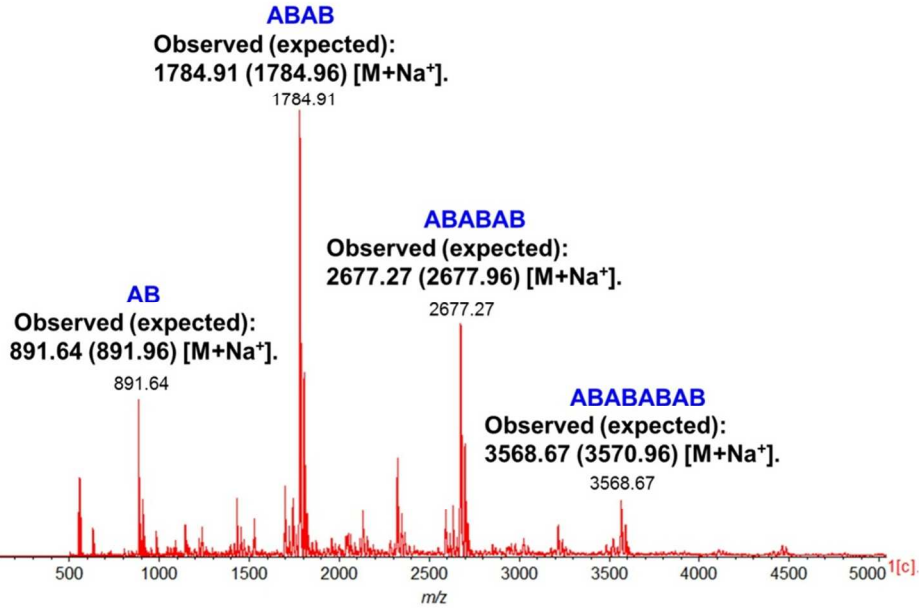


Figure S2. MALDI-TOF-MS analysis of the oligomer model ($A_2(8)B_2(4)C(1)$, $M_{n,GPC}$: 6400, 2 h polymerization under abovementioned conditions).

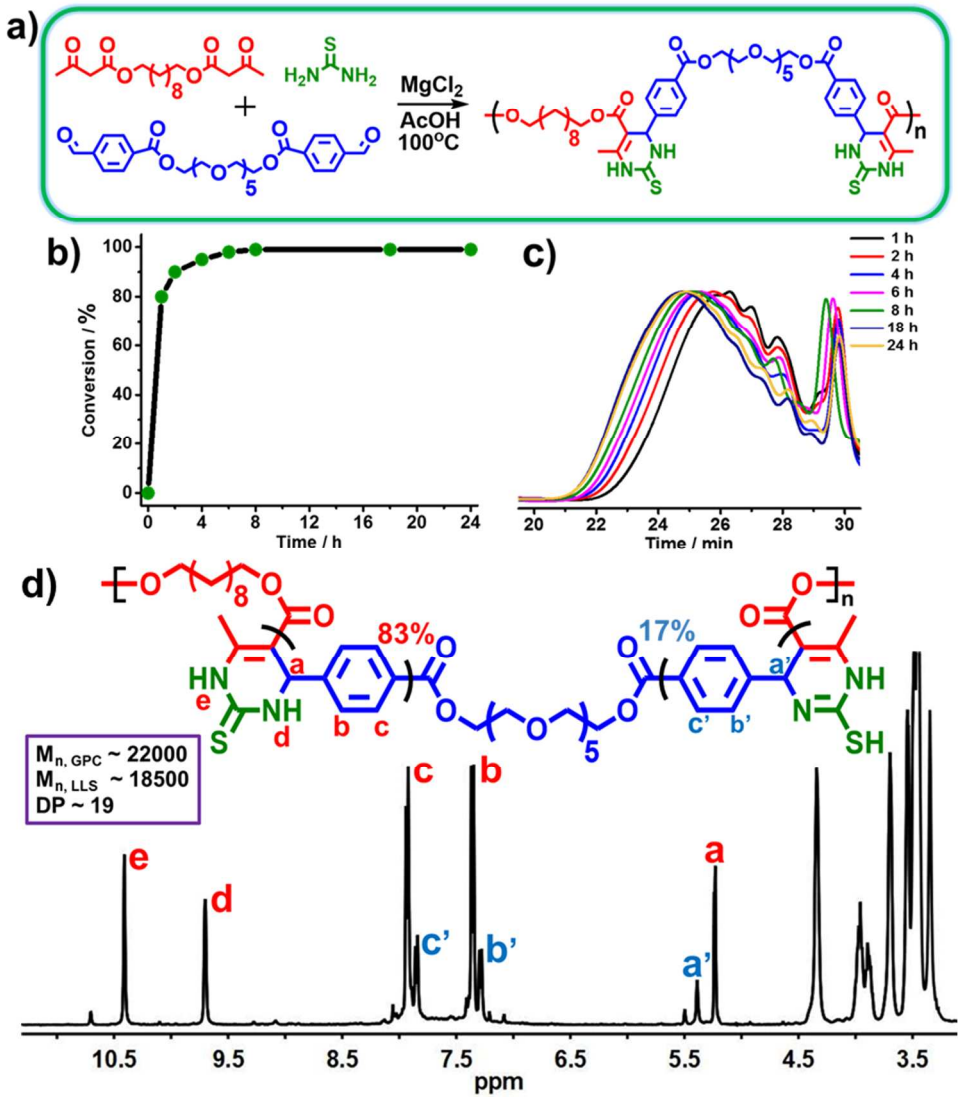


Figure S3. a) Reaction conditions: AcOH as solvent, 100°C, $[A_2(8)]/[B_2(5)]/[\text{thiolurea}]/[MgCl_2]$ = 1/1/3/0.2; b) the conversion of Biginelli reaction versus time; c) the GPC curves during Biginelli polycondensation; d) ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of the $A_2(8)B_2(5)C(2)$ polymer, $M_{n,\,LLS}$ ~ 18500 g/mol (*dn/dc* = 0.104), DP ~ 19.

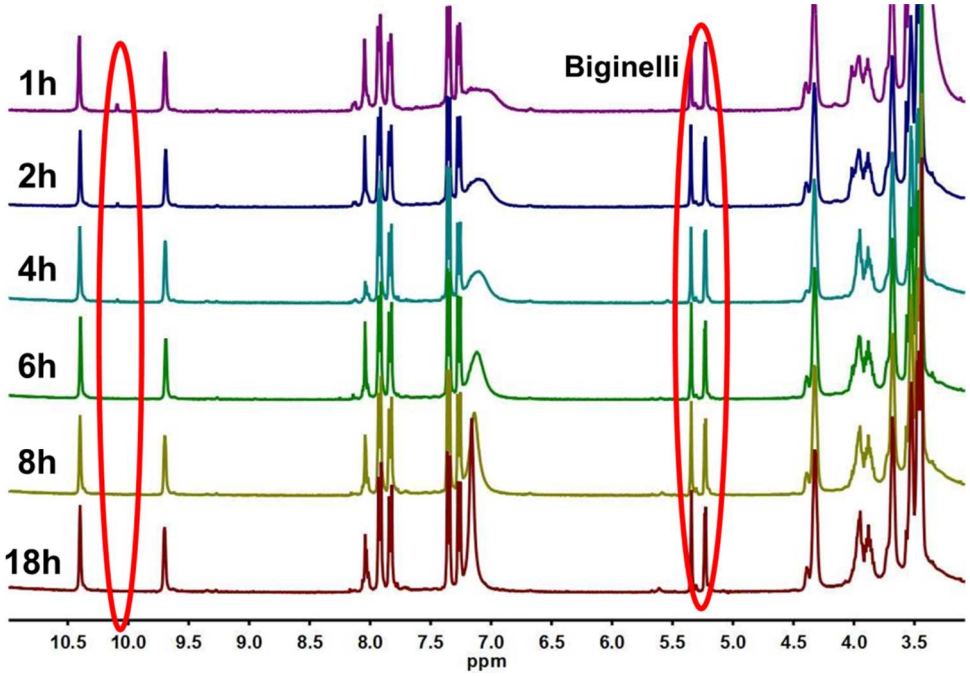


Figure S4. ^{1}H NMR spectra (DMSO-d_6, 400 MHz) during the Biginelli polycondensation (thiolurea system).

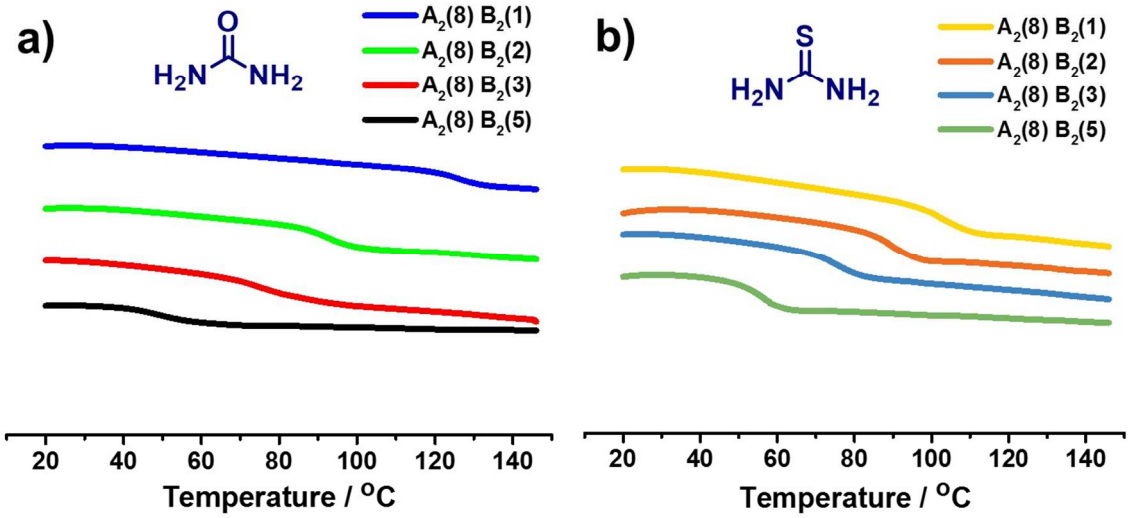


Figure S5. DSC curves of a) $A_2(8)B_2(1,2,3,5)C(1)$ and b) $A_2(8)B_2(1,2,3,5)C(2)$ polymers.

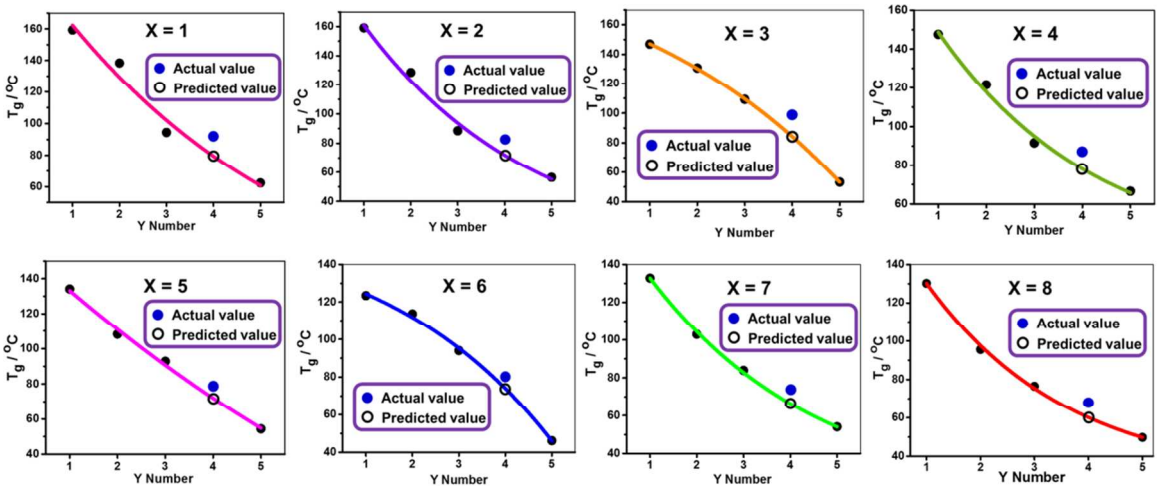


Figure S6. The eight simulation curves based on the T_g values of $A_2(X)B_2(1,2,3,5)C(1)$ polymers (black points), and the comparison between the predicted (circle point) and actual (blue point) T_g values of $A_2(X)B_2(4)C(1)$ polymers.

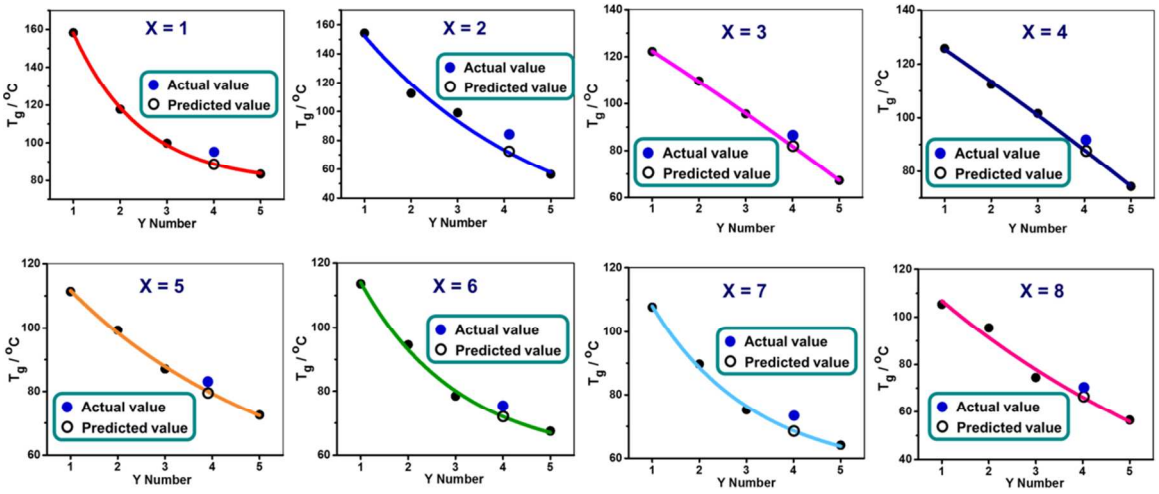


Figure S7. The eight simulation curves based on the T_g values of $A_2(X)B_2(1,2,3,5)C(2)$ polymers (black points), and the comparison between the predicted (circle point) and actual (blue point) T_g values of $A_2(X)B_2(4)C(2)$ polymers.

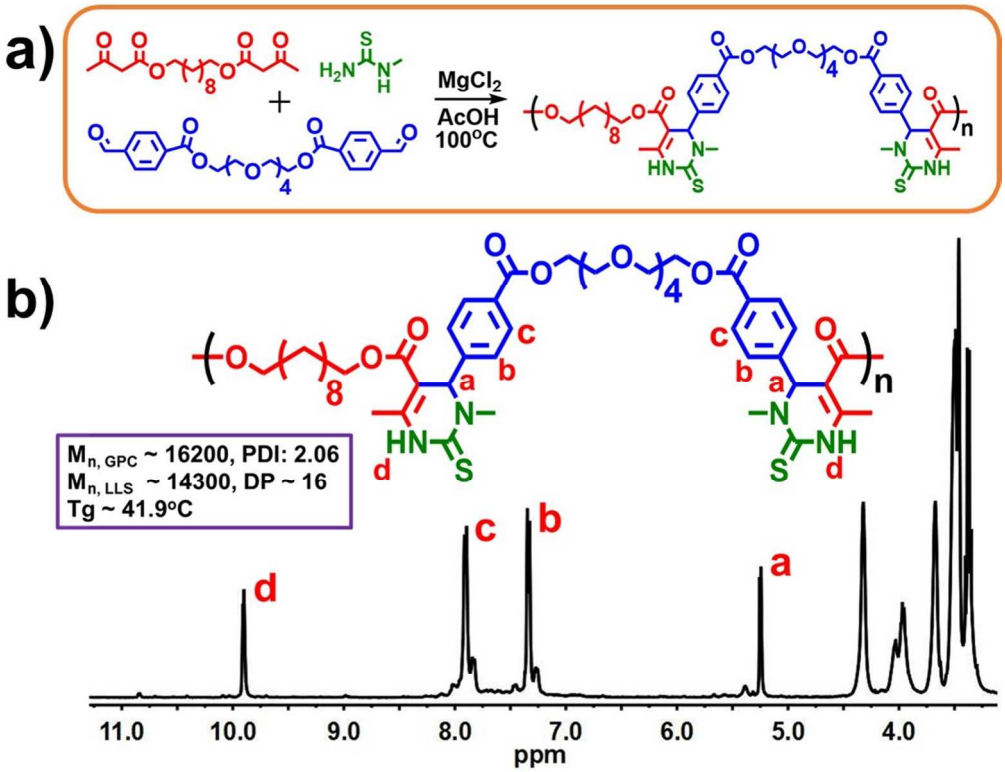


Figure S8. a) Reaction conditions: AcOH as solvent, 100°C, $[A_2(8)]/[B_2(4)]/[N\text{-methylthiolurea}]/[MgCl_2] = 1/1/3/0.2$; b) ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of the purified polymer, $M_{n,\,LLS}$ ~ 14300 g/mol (*dn/dc* = 0.146), DP ~ 16, Tg ~ 41.9°C.

Table S1. The physical parameters of the 32 $A_2(X)B_2(Y)C(1)$ polymers[a].

$B_2(Y)$	$A_2(X)$	$M_{n,\,GPC}$ (10^3 g/mol)[b]	PDI[b]	T_g (°C)[c]
1	1	7.4	1.50	159.3
	2	9.1	1.68	159.1
	3	8.9	1.65	146.9
	4	11.0	1.75	147.6
	5	10.4	1.79	134.1
	6	10.4	1.77	123.4
	7	10.5	1.74	132.8
	8	11.7	1.91	130.2
2	1	9.8	1.54	138.4
	2	10.6	1.52	128.5
	3	12.0	1.61	130.7
	4	13.3	1.67	121.5
	5	13.3	1.68	108.2
	6	11.3	1.60	113.7
	7	11.8	1.57	102.9
	8	12.0	1.60	95.6
3	1	14.2	1.65	94.4
	2	13.7	1.62	88.5
	3	23.1	1.81	109.3
	4	24.8	1.99	91.6
	5	24.3	1.79	92.8
	6	18.0	1.72	94.1
	7	18.9	1.72	83.9
	8	19.0	1.84	76.5
5	1	18.1	1.75	62.4
	2	17.5	1.73	56.5
	3	17.9	1.77	53.3
	4	28.6	2.01	66.6
	5	20.9	1.75	54.4
	6	21.6	1.87	46.2
	7	29.8	1.89	54.1
	8	27.8	2.03	49.8

a) Reaction conditions: acetic acid as solvent, 100°C, $[A_2(X)]/[B_2(Y)]/[urea]/[MgCl_2]$ = 1/1/3/0.2.

b) By gel permeation chromatography (GPC) using N, N-dimethyl formamide (DMF) as eluent (1 mL/min).

c) By different scanning calorimetry (DSC) at a scanning rate of 10ºC/min.

Table S2. The physical parameters of the 32 $A_2(X)B_2(Y)C(2)$ polymers[a].

$B_2(Y)$	$A_2(X)$	$M_{n,\,GPC}$ (10^3 g/mol)[b]	PDI[b]	T_g (^oC)[c]
1	1	14.2	1.45	158.3
	2	15.6	1.47	154.3
	3	16.5	1.55	122.3
	4	21.2	1.77	125.9
	5	18.2	1.52	111.4
	6	18.4	1.57	113.6
	7	17.6	1.53	107.7
	8	17.7	1.52	105.4
2	1	15.4	1.42	117.8
	2	15.2	1.42	112.6
	3	16.2	1.47	109.7
	4	21.5	1.50	112.5
	5	16.0	1.54	99.3
	6	17.9	1.52	94.6
	7	17.0	1.51	89.7
	8	17.4	1.52	95.5
3	1	19.6	1.53	99.8
	2	17.9	1.49	99.2
	3	20.3	1.61	95.7
	4	25.4	1.72	101.6
	5	22.8	1.65	87.1
	6	18.0	1.55	78.5
	7	19.1	1.54	75.2
	8	21.3	1.56	74.5
5	1	17.5	1.69	83.4
	2	19.9	1.61	56.5
	3	21.0	1.61	67.3
	4	22.7	1.86	74.3
	5	23.9	1.79	72.5
	6	25.0	1.94	67.5
	7	21.4	1.95	64.1
	8	22.0	1.88	56.5

a) Reaction conditions: acetic acid as solvent, 100°C, $[A_2(X)]/[B_2(Y)]/[\text{thiolurea}]/[MgCl_2]$ = 1/1/3/0.2.
b) By GPC using DMF as eluent (1 mL/min).
c) By DSC at a scanning rate of 10ºC/min.

Table S3. The physical parameters of the $A_2(X)B_2(4)C(1)$ polymers[a].

X	$M_{n,\,GPC}$ (10^3 g/mol)[b]	PDI[b]	$T_{g\,(Actual)}$ (^oC)[c]	$T_{g\,(Predicted)}$ (^oC)[d]	$\lvert \Delta T_g \rvert$ / $T_{g\,(Actual)}$
1	13.3	1.57	93.4	79.5	14.9%
2	12.5	1.51	83.5	71.9	13.9%
3	16.4	1.75	98.3	84.3	14.2%
4	14.1	1.61	88.6	78.2	11.7%
5	16.8	1.81	77.8	72.1	7.3%
6	13.3	1.57	77.5	74.1	4.4%
7	14.2	1.64	74.5	66.5	10.7%
8	12.1	1.62	64.3	60.2	6.4%

a) Reaction conditions: acetic acid as solvent, 100°C, $[A_2(X)]/[B_2(4)]/[urea]/[MgCl_2]$ = 1/1/3/0.2.
b) By GPC using DMF as eluent (1 mL/min).
c) By DSC at a scanning rate of 10ºC/min.
d) Calculated according to the fitting curves (Fig. S6).

Table S4. The physical parameters of the $A_2(X)B_2(4)C(2)$ polymers[a].

X	$M_{n,\,GPC}$ (10^3 g/mol)[b]	PDI[b]	$T_{g\,(Actual)}$ (^oC)[c]	$T_{g\,(Predicted)}$ (^oC)[d]	$\lvert \Delta T_g \rvert$ / $T_{g\,(Actual)}$
1	16.9	1.50	95.1	88.8	6.6%
2	17.2	1.47	86.1	73.4	14.8%
3	17.9	1.54	84.5	81.9	3.1%
4	18.2	1.56	89.6	87.9	1.9%
5	17.9	1.56	82.8	79.3	4.2%
6	15.2	1.47	73.3	72.1	1.6%
7	17.3	1.57	72.6	68.6	5.5%
8	15.4	1.48	67.1	66.1	1.5%

a) Reaction conditions: acetic acid as solvent, 100°C, $[A_2(X)]/[B_2(4)]/[thiolurea]/[MgCl_2]$ = 1/1/3/0.2.
b) By GPC using DMF as eluent (1 mL/min).
c) By DSC at a scanning rate of 10ºC/min.
d) Calculated according to the fitting curves (Fig. S7).