Immortal CO_2/Propylene Oxide Copolymerization: Precise Control of Molecular Weight and Architecture of Various Block Copolymers

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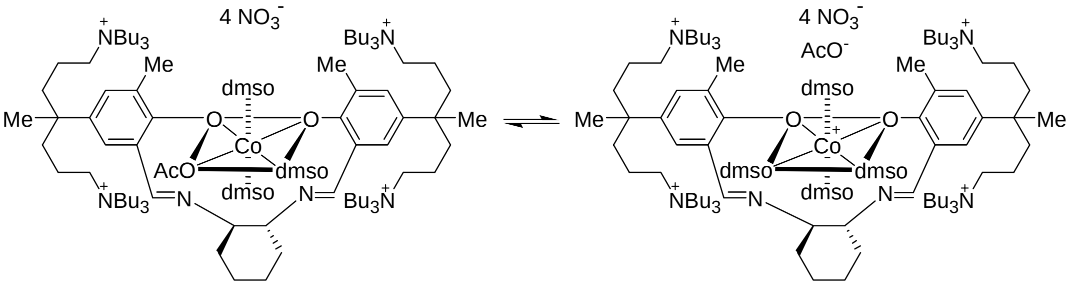
Supporting Information

General remarks. CO_2 gas (99.999% purity) was dried through storage in a column of molecular sieves 3A at a pressure of 30 bar. Propylene oxide (PO) was dried by stirring over CaH_2 and then vacuum-transferred to reservoir. The ^{1}H NMR (400 MHz) was recorded on a Varian Mercury Plus 400. The gel permeation chromatograms (GPC) were obtained in THF at 35^{o}C using a Waters Millennium apparatus with polystyrene standards. The T_g data were determined from a second heating at a heating rate of 10^{o}C/min with DSC (Differential Scanning Calorimetry). The tensile testbars (45 mm × 7.0 mm × 1.0 mm) were prepared by pressing polymer lump with screw at 120^{o}C overnight between two plates that were spaced with a spacer of 1.0 mm thickness. The tensile tests were performed according to the ASTM D 638 on UTM (WL2100). The drawing rate was 5 mm/min. All the chain transfer agents except polystyrene carboxylic acid were purchased from Aldrich. Polystyrene carboxylic acid was prepared according to the literature method (H. Zhao, S, Liu, M. Jiang, X. Yuan, Y. An, L. Liu, *Polymer* **2000**, *41*, 2705).

Synthesis of Complex 3. To a flask containing compound **2** (0.302 g, 0.166 mmol) and $AgNO_3$ (0.113 g, 0.665 mmol), ethanol (5 mL) was added rapidly with stirring inside a glove box. AgI precipitated, which was filtered off over Celite after overnight stirring. Solvent was removed under vacuum to yield a yellow residue, which was dissolved in CH_2Cl_2 (3 mL) and then filtered again to remove some residual AgI. Cobalt(II) acetate (0.029 g, 0.166 mmol) was added and the resulting solution was stirred under air for 1 day in the presence of molecular sieves (0.350 g). It was filtered over Celite and solvent was removed under reduced pressure to give a dark brown powder in quantitative yield. Two sets of signals were observed in 5:2 ratio in the ^{1}H NMR spectrum in dmso-d_6 at 38^{o}C. A major set indicated that the complex adopted a dissymetric structure which might be assignable to **3-A** shown below. The other minor set was assinable to symmetric **3-B**. The complex was paramagnetic in CD_2Cl_2 and THF-d_8, and unassignable broad signals were observed in those solvents. ^{1}H NMR (dmso-d_6, 38°C) data for the major set: δ 7.87 (s, 2H, CH=N) 7.31 and 7.29 (br s, 2H, m-H), 7.19 and 7.21 (br s, 2H, m-H), 3.83 and 3.57 (br, 2H, cyclohexyl-CH), 3.17-2.99 (br, 32H, NCH_2), 2.58 and 2.54 (s, 6H, CH_3), 2.08-1.82 (br, 4H, cyclohexyl-CH_2), 1.66-1.22 (br m, 74H), 0.88-0.84 (br, 36H, CH_3) ppm. ^{1}H NMR (dmso-d_6, 38°C) data for the minor set: δ 8.02 (s, 2H, CH=N) 7.46 (s, 2H, m-H), 7.35 (s, 2H, m-H), 3.55 (br, 2H, cyclohexyl-CH), 3.17-2.99 (br, 32H, NCH_2), 2.64 (s, 6H, CH_3), 2.08-1.82 (br, 4H, cyclohexyl-CH_2), 1.66-1.22 (br m, 74H), 0.88-0.84 (br, 36H, CH_3) ppm.



3-A **3-B**

A typical polymerization in the presence of chain transfer agent. Bomb reactor was assembled inside a glove box after **3** (3.0 mg, 1.80 μmol), PO (10 g, 170 mmol), and adipic acid (0.131 g, 900 μmol) were charged. The CO_2 gas was pressurized to 15 bar, then the reactor was immersed in an 75°C oil bath. After 50 minutes, the solution temperature reached ~73°C and the pressure started to drop. During this heating time, negligible amount of polymer was generated. Therefore, the heating time of 50 minutes was not included in the polymerization time. The polymerization was performed for 1 hour after the initiation, and a total 3-4 bar pressure drop was observed. The reactor was cooled to room temperature through immersion in an ice bath. After CO_2 gas was released, the reactor was opened. The polymer solution was filtered over a short pad of silica gel and washed with methylene chloride (10 mL) to give a colorless solution. All volatiles were removed using a rotary evaporator to give a white residue. In the ^{1}H NMR spectra, cyclic carbonate was observed with less than 5% selectivity, which was completly removed by evacuation in a vacuum oven at 150°C for several hours. The dissociated polymer chains are the ones containing -OH group at the end, from which the unzipping reaction generating cyclic carbonate is sluggish at the polymerization temperature of 70-80°C.

Polyurethane formation. To a 50 mL flask containing low molecular weight PPC-diol prepared using 900 μmol adipic acid (absolute-M_n, 2200) was added equimolar amount of 4,4'-methylenebis(phenyl isocyanate) (0.224 g, 900 μmol). Anhydrous THF (5 mL) was added to make a homogeneous solution.

After THF was completely removed using a vacuum line, the viscous residue was kept overnight at 100^{o}C under N_2 atmosphere.

Table S1. CO_2/propylene oxide copolymerization results in the presence of various chain transfer agents (AH_f).[a]

PPC	[$\mathbf{A}H_f$]/[**3**]	Measured M_n[b]	M_w/M_n	TON[c]	Absolute M_n[d]	Calculated M_n[e]	T_g[f] (°C)
15	300	5000	1.05	11500	4600	2700	31
16	300	5500	1.04	9700	3200	3000	29
17	300	5200	1.03	9300	3100	2900	28
18	300	3100	1.07	9500	3200	1600[g]	28
19	300	5300	1.05	9900	3300	2900	30
20	300	6600	1.04	10900	3600	3700	32
21	600	3800	1.06	13000	2200	2000	21
22	600	4500	1.05	16200	2700	2400	28
23	200	6200	1.04	8100	4100	3600	29
24	200	5200	1.04	9500	4700	2900	33
25	150	4200	1.03	9200	6100	2300	21

[a]Polymerization condition: PO (10 g, 170 mmol), **3** (3.0 mg, [PO]/[Cat] = 100000), CO_2 pressure (25 bar), temperature (75°C), reaction time (60 minutes). [b]Determined on GPC using polystyrene standards. [c]Turnover number calculated based on the weight of the isolated polymers. [d]Calculated from an equation of "M_n = {TON×102.13}/{[$\mathbf{A}H_f$]/[**3**] + 5}". [e]Calculated from an equation of "M_n = 0.255× [GPC-measured M_n]$^{1.09}$". [f]Glass transition temperature measured on DSC. [g]Low value may be due to water impurities present in highly hygroscopic diethylene glycol.

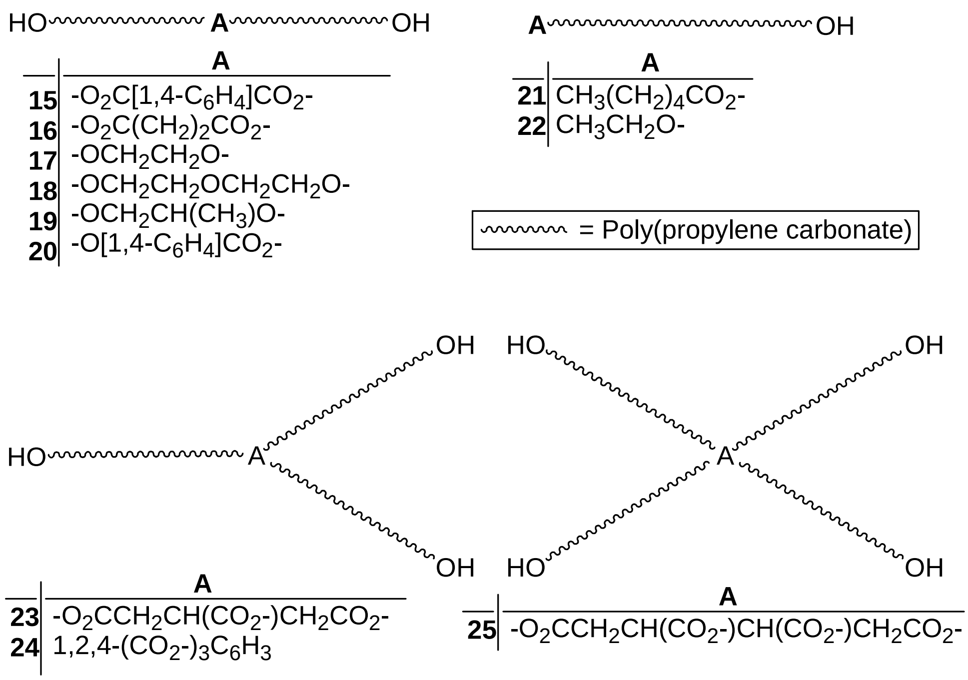
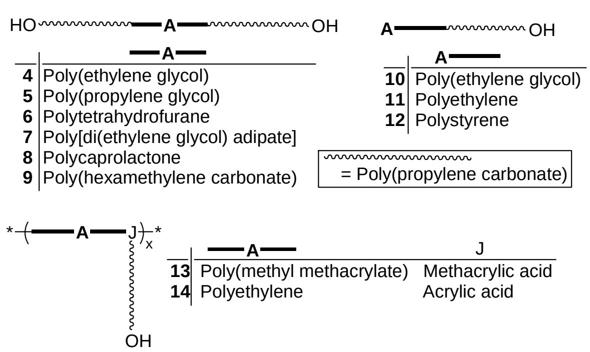


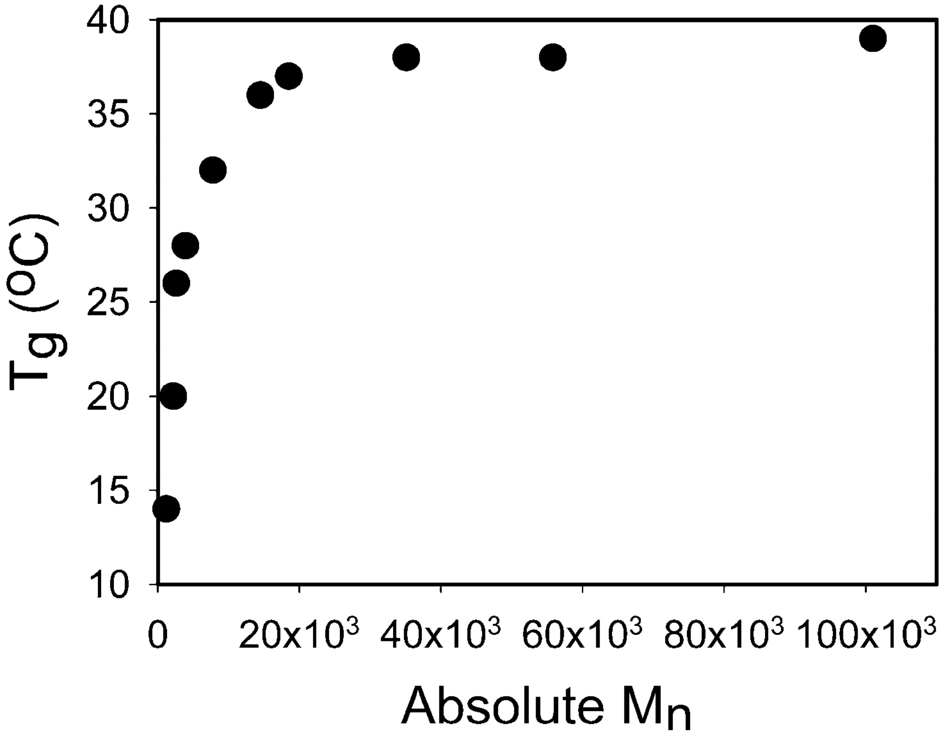
Table S2. Additional data for Table 2[a]

entry	Polymer	M_n of -**A**-	w% of -**A**-[b]	[OH or CO_2H]/[**3**]	TON[c]	M_n[d] ($\times 10^{-3}$)	M_w/M_n	T_g[e] (°C)	T_m[e] (°C)
1	**4**	2000	8.2	108	12200	19	1.30	27	
2	**4**	2000	47	542	6200	6.1	1.05	-19	
3	**4**	10000	12	22	7600	68	1.48	26	
4	**4**	10000	39	111	8600	22	1.19	-12	51
5	**5**	3500	12.4	112	13600	23	1.27	36	
6	**6**	2900	8.3	100	15700	34	1.13	37	
7	**7**	2500	9.2	90	11900	45	1.09	35	
8	**8**	2000	7.6	139	15900	32	1.07	31	
9	**9**	2000	9.2	112	11900	24	1.07	31	
10	**10**	35000	8.3	4	15100	111	1.57	39	53
11	**10**	35000	20	8	9100	54	1.19	27	55
12	**11**	700	5.5	80	9900	19	1.18	37	92
13	**11**	700	17	397	13500	7.8	1.18	34	96
14	**11**	700	39	794	8600	3.5	1.45	26	103
15	**12**	43000	11	3	11500	123	1.43	42, 102	
16	**12**	43000	22	6	9700	114	1.50	43, 108	
17	**13**	6400	9.7	18	11200	12	2.23	37	
18	**13**	6400	20.6	36	8500	71	1.93	41	
19	**14**	1400	10	78	10700	38	1.79	37	79
20	**14**	1400	22	231	11500	22	1.58	33	87

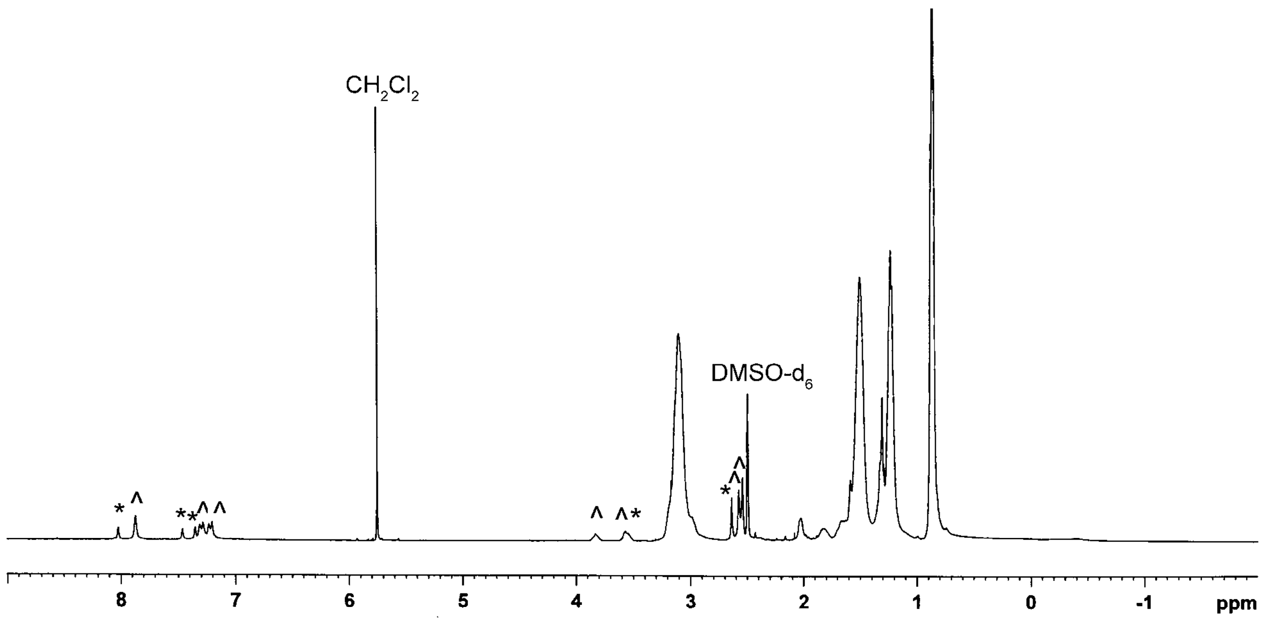
[a]Polymerization condition: PO (10 g, 170 mmol), **3** (3.0 mg, [PO]/[Cat] = 100000), CO_2 (25 bar), temperature (75°C), time (60 min). [b][added **-A-** polymer]/[obtained block copolymer]×100. [c]Turnover number calculated based on the weight of the isolated pure polymers. [d]Determined on GPC using polystyrene standards. [e]Measured on DSC.



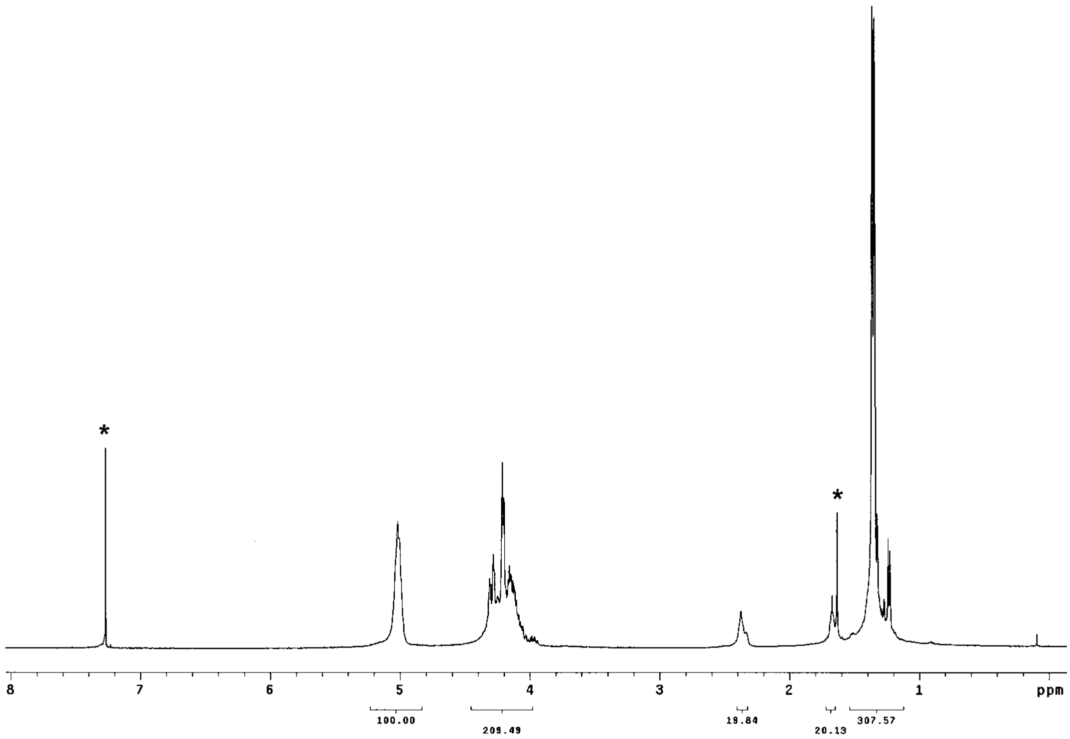
<Glass transition temperatrue (T_g) of PPC-diol prepared using adipic acid as chain tranfer agent (Table 1) *versus* the absolute-M_n>



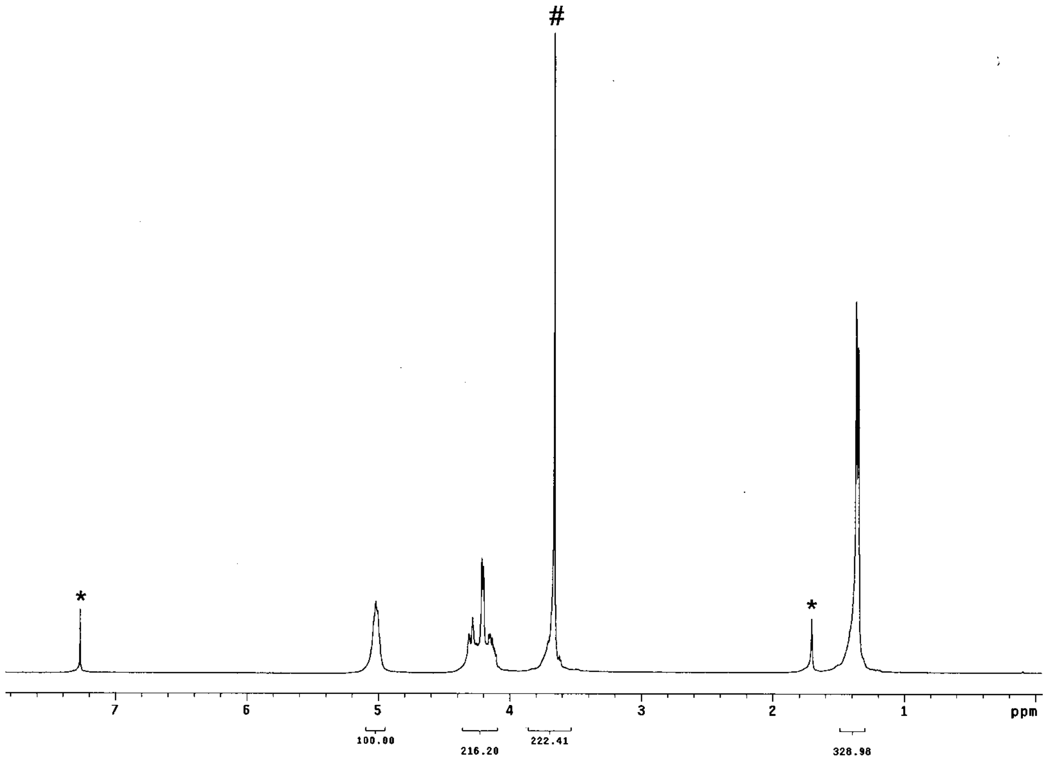
< ^{1}H-NMR spectrum of **3** in dmso-d_6 at 38°C (signals marked with "^" for the major set; signals marked with "*" for the minor set)>



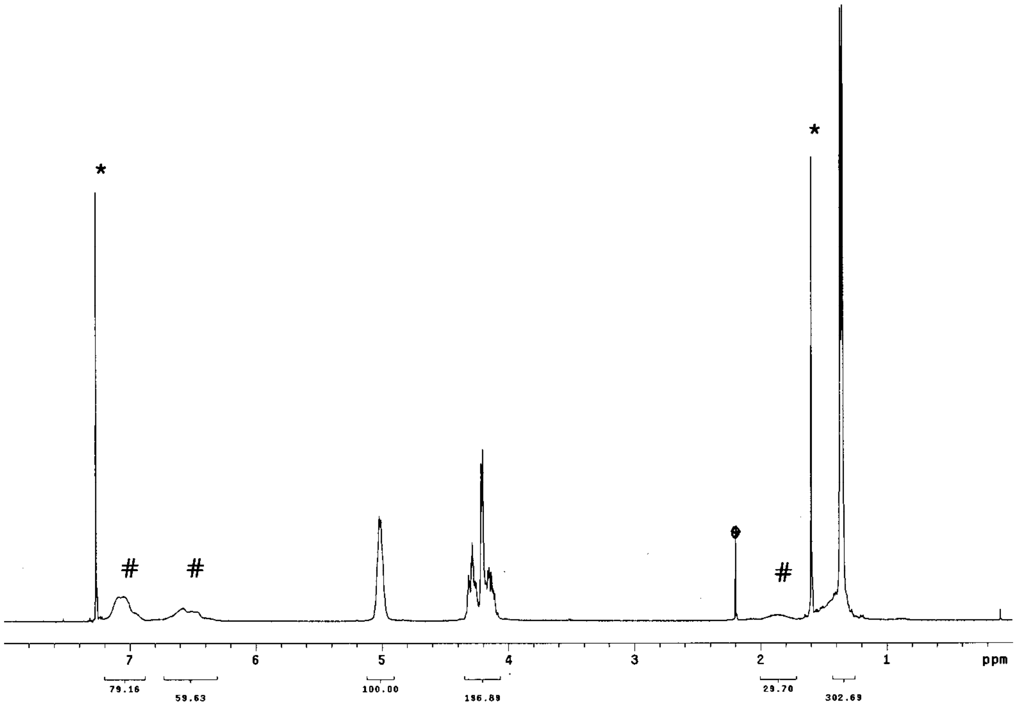
< [1]H-NMR of low molecular weight PPC-diol prepared using 500 equivalents of adipic acid (entry 9 in table 1)>



<[1]H-NMR spectrum of PPC-*block*-PEG (PEG, 20 w%) (entry 11 in table 2)>



<^{1}H-NMR spectrum of PPC-*block*-PS (PS, 22 w%) (entry 15 in table 2)>



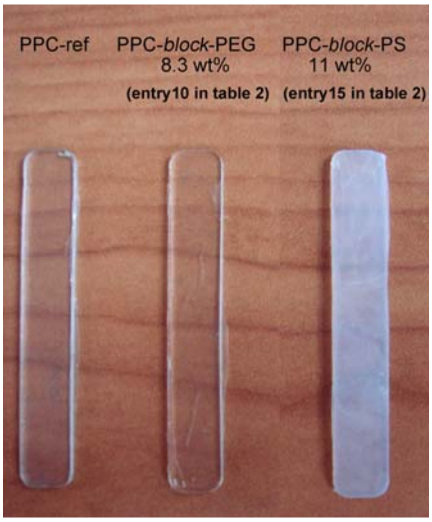
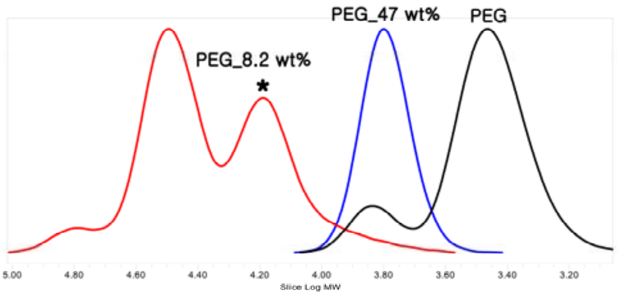


Table S3. Tensile Properties

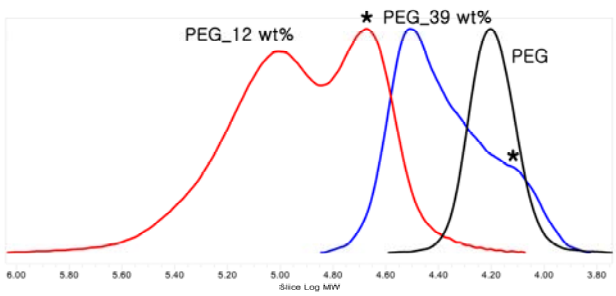
Sample	M_n ($\times 10^{-3}$)	M_w/ M_n	Tensile strength (N/mm^2)	Stress at break (N)	Strain at break (%)	Modulus (N/mm^2)
PPC-ref	133	1.28	3.0	32	7	1900
PPC-*block*-PEG (8.3 w%)	111	1.57	5.0	46	770	19
PPC-*block*-PS (11 w%)	123	1.43	5.1	55	7	400

<GPC curves of *block* copolymers (The signals marked with "*" are the chains grown from nitrate or acetate anions in **3**)>

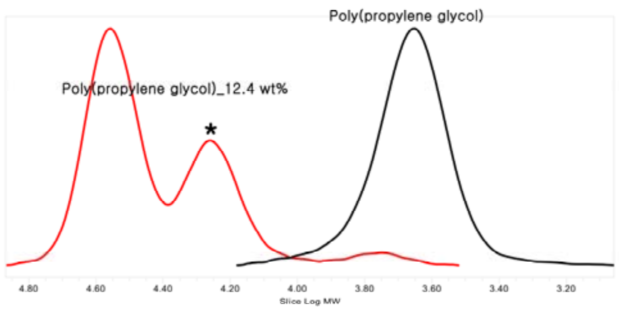
PPC-*block*-PEG-*block*-PPC
(entries 1-2 in Table 2)



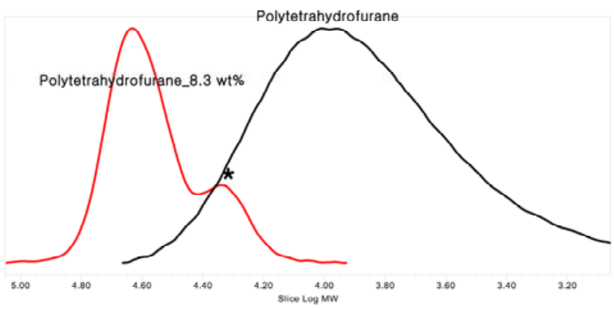
PPC-*block*-PEG-*block*-PPC
(entries 3-4 in Table 2)



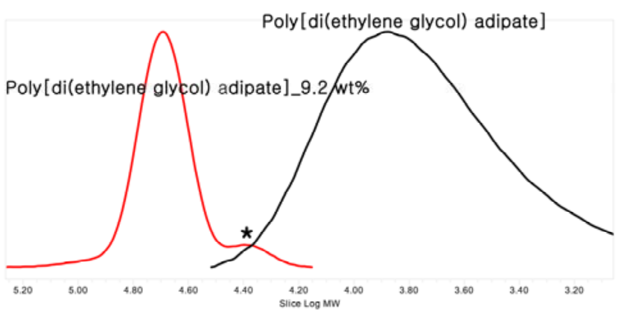
PPC-*block*-PPG-*block*-PPC
(entry 5 in Table 2)



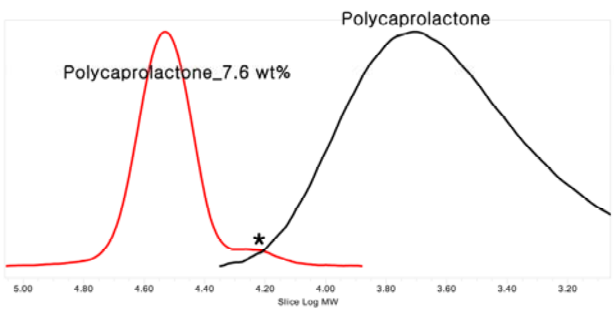
PPC-*block*-poly(THF)-*block*-PPC
(entry 6 in Table 2)



PPC-*block*-poly[di(ethylene glycol)adipate]-*block*-PPC
(entry 7 in Table 2)

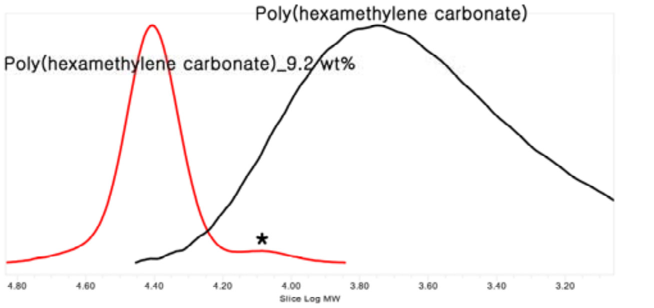


PPC-*block*-polycaprolactone-*block*-PPC
(entry 8 in Table 2)



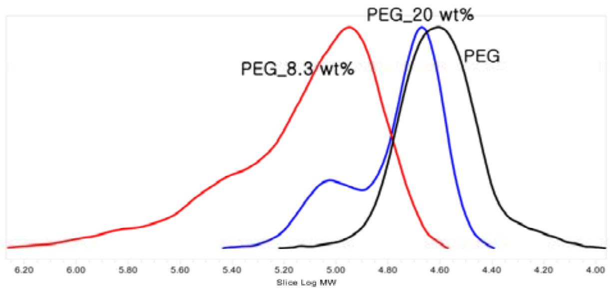
PPC-*block*-poly(hexamethylene carbonate)-*block*-PPC

(entry 9 in Table 2)



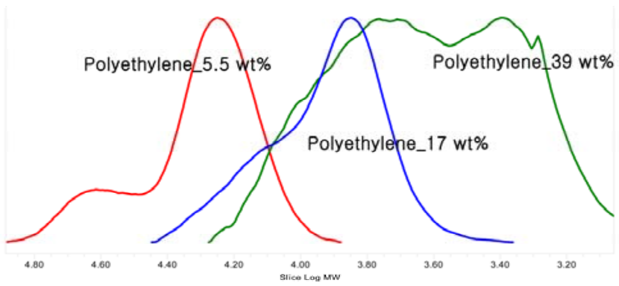
PPC-*block*-PEG

(entries 10-11 in Table 2)



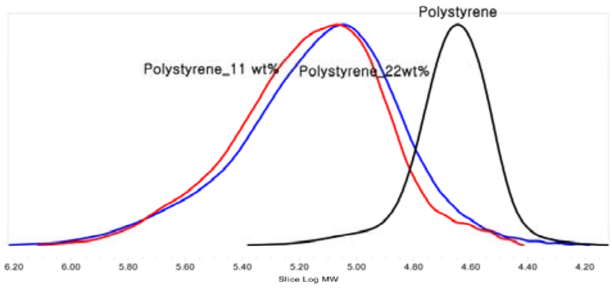
PPC-*block*-PE

(entries 12-14 in Table 2)



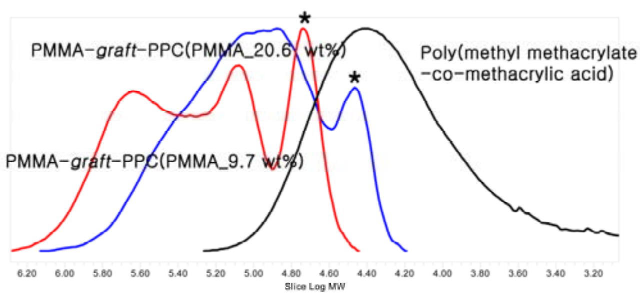
PPC-*block*-PS

(entries 15-16 in Table 2)



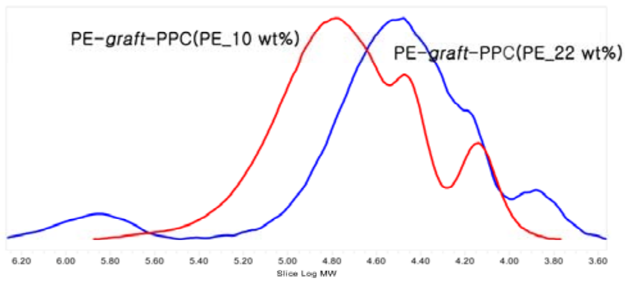
PMMA-*graft*-PPC

(entries 17-18 in Table 2)



PE-*graft*-PPC

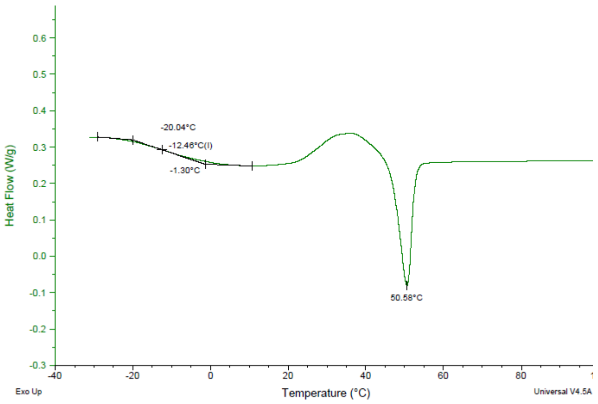
(entries 19-20 in Table 2)



<DSC thermograms of *block* copolymers>

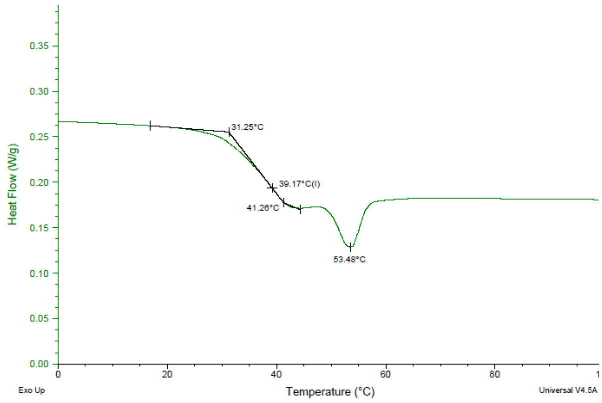
PPC-*block*-PEG-*block*-PPC

(entry 4 in Table 2)



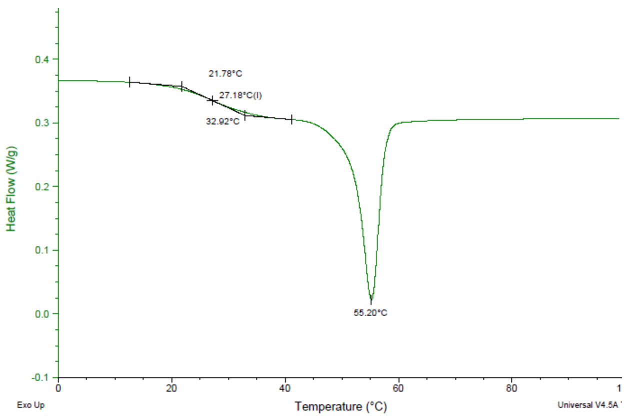
PPC-*block*-PEG

(entry 10 in Table 2)



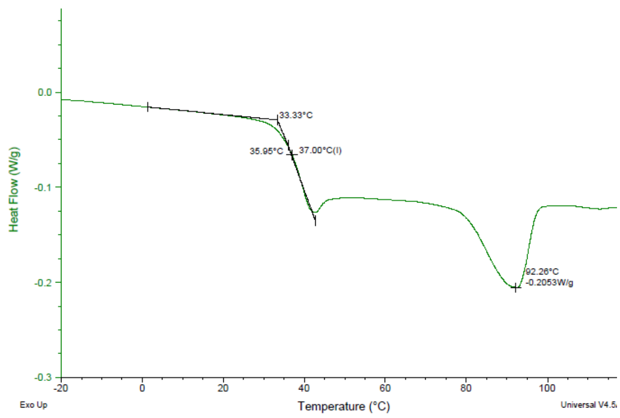
PPC-*block*-PEG

(entry 11 in Table 2)



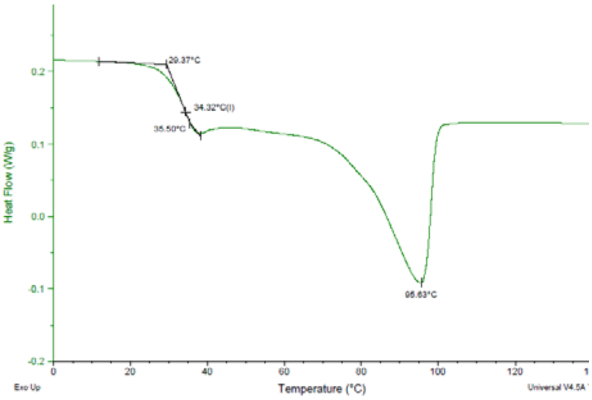
PPC-*block*-PE

(entry 12 in Table 2)



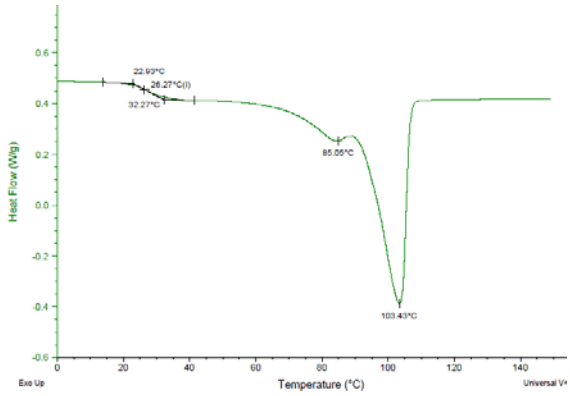
PPC-*block*-PE

(entry 13 in Table 2)



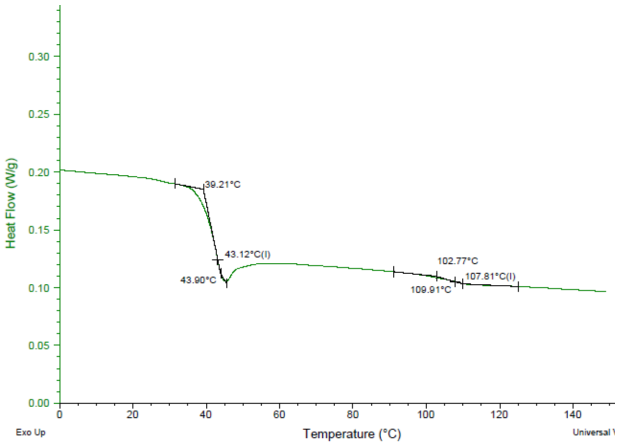
PPC-*block*-PE

(entry 14 in Table 2)



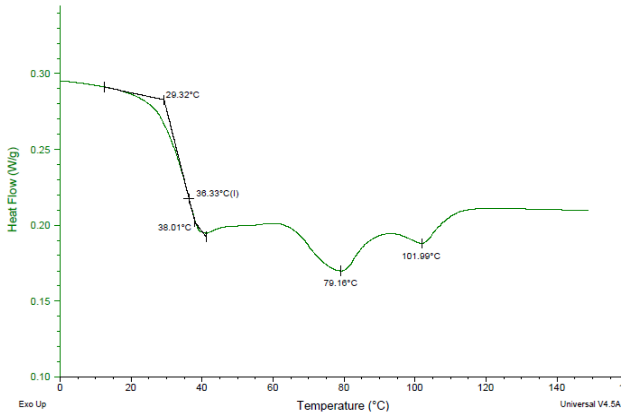
PPC-*block*-PS

(entry 16 in Table 2)



PE-*graft*-PPC

(entry 19 in Table 2)



PE-*graft*-PPC

(entry 20 in Table 2)