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

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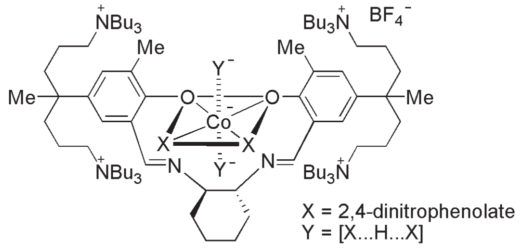
Recently, CO_2/epoxide copolymerization has drawn much attention in both academic and industrial fields.[1] A highly active catalyst for CO_2/propylene oxide (PO) copolymerization was developed which enables to construct a pilot plant of continuous commercial process.[2] It was initially designed on the concept of binding two components or two metal centers,[3] and later it was revealed that the high activity is due to an unusual binding mode of a cobalt(III) complex prepared from a Salen-type ligand tethered by four quaternary ammonium salts (**1**).[4] The imine nitrogens on the Salen-type ligand do not coordinate. Instead, the counteranions of the tethered quaternary ammonium coordinate to cobalt. Complex **1** showed a high turnover number (TON, 16 000) and a high turnover frequency (TOF, 16 000 h^{-1}) that produce a strictly alternating copolymer with a high molecular weight (M_n, 300 000).



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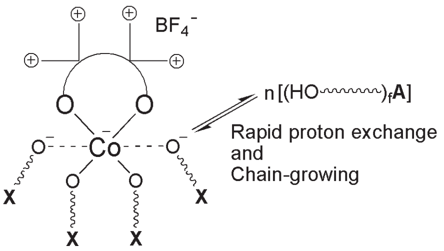
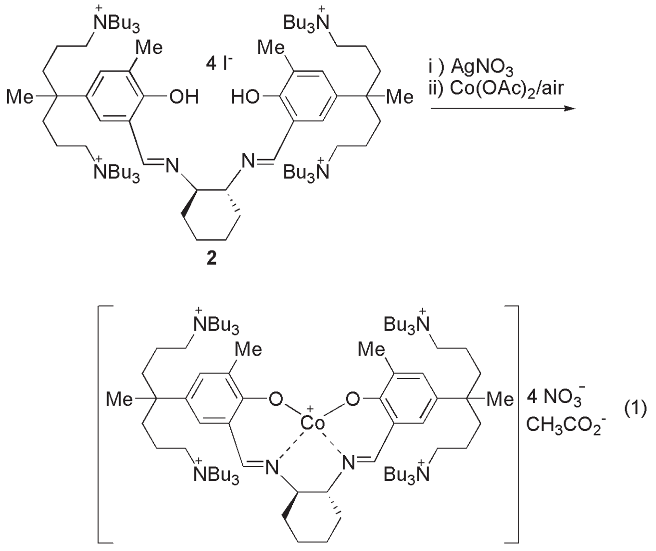


In the polymerization reaction, 2,4-nitrophenolate (DNP) anions in **1** attack PO, becoming alkoxide anions which subsequently react with CO_2 to be carbonate anions. In the presence of water impurity, the anion at a growing-chain end deprotonates water to be a neutral polymer chain, and a new polymer chain starts to grow from the generated hydroxyl anion. The neutral polymer chain is dormant, but it re-enters the chain-growing process when it is reversely deprotonated, consequently resulting in a bimodal distribution in the GPC curve. Chains grown from DNP^- adopt a low-molecular-weight modal, while a high-molecular-weight modal results from chains grown biaxially from water. The same type of chain transfer reaction to water and methanol was described in other catalytic systems of cobalt and aluminum complexes.[5] This kind of growing-chain swapping was discovered in the ring-opening polymerization of epoxide initiated by aluminum complex and was named "immortal polymerization".[6]

A drawback of **1** is that it shows some induction time (1−10 h) in the presence of water impurities.[4a] Once it is initiated after some induction time, the polymerization rate is almost invariable, which indicates that the protic compound influences only on the initiation, not on the chain growing reaction. To make matters worse, **1** cannot initiate polymerization at all when water or methanol is deliberately added at [water or methanol]/[**1**] > 20. Hydrogen bonds of water may stabilize DNP^- to hamper the nucleophilic attack onto PO.[4a] Complex **3** bearing NO_3^- instead of DNP^- is prepared (eq 1). Complex **3** exhibits almost the same performance as **1** in the CO_2/PO copolymerization (TON, 15 000; TOF 15 000 h^{-1}). A scaleable synthetic route for iodide salt **2** was developed,[7] but expensive $AgBF_4$ and hazardous NaH are used along with anhydrous THF and deaerated ethanol to convert **2** to **1**. Furthermore, DNP^- can be explosive. Complex **3** is simply obtained, allowing a large scale synthesis, through treatment of $Co(OAc)_2$ under air just after I^- in **2** is replaced with NO_3^- using inexpensive $AgNO_3$.



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Complex **3** preserves the excellent catalytic performance even in the presence of a large amount of a protic compound, adipic acid (Table 1). Almost the same level of TOF achieved in the absence of adipic acid (~15 000 h^{-1}) is attainable without any induction time at [adipic acid]/[**3**] ≤ 200 (entries 1−6). At a high ratio of 300−500, the TOF is somewhat lowered to ~11 000 h^{-1}. Catalyst residue is thoroughly removed by just filtration through a short pad of silica gel to provide a colorless resin, which is thermally stable up to 160 °C. Neither a change of the GPC curve nor formation of propylene carbonate is observed by keeping the sample at 160 °C for several hours.[8] In the ^1H NMR spectrum, adipate signals are broadly observed along with poly(propylene carbonate) (PPC) signals. Integration values indicate that all the added adipic acid participates in the chain-growing process.

In the GPC curves of the polymers obtained at low [adipic acid]/[**3**] ratios ≤50, a bimodal distribution is observed (Figure 1). Polymer chains in the main high-molecular-weight modal are the

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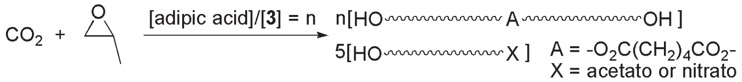
Table 1. CO_2/PO Copolymerization Results in the Presence of Variable Amount of Adipic Acid[a]



entry	[adipic acid]/[**3**]	TON	measured M_n[b]	M_w/M_n	absolute M_n[c]	T_g (°C)
1	10	14800	96800	1.15	101000	39
2	25	16400	69000	1.12	55800	38
3	50	18900	47300	1.06	35100	38
4	75	14500	27800	1.03	18500	37
5	100	14900	23600	1.04	14500	36
6	200	15700	12400	1.03	7800	32
7	300	11600	7100	1.03	3900	28
8	400	10300	4700	1.05	2600	26
9	500	10700	3700	1.05	2200	20
10	600	7300	2400	1.07	1200	14

[a] Polymerization conditions: PO (10 g, 170 mmol), **3** (3.0 mg, [PO]/[Cat.] = 100 000), CO_2 (25 bar), temperature (75 °C), time (60 min). [b] Determined on GPC using a polystyrene standard. [c] Calculated from an equation of "M_n = {TON × 102.13}/{[adipic acid]/[**3**] + 5}".

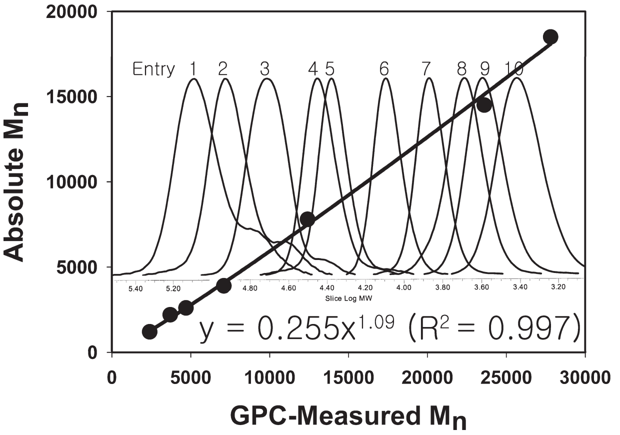


Figure 1. Plot of the absolute M_n vs the GPC-measured M_n (inside are GPC curves of PPC samples in Table 1).

ones grown biaxially from adipic acid, while those of the minor low-molecular-weight modal are the ones grown from NO_3^- or acetate anion in **3**. When the [adipic acid]/[**3**] ratio exceeds 50, polymer chains grown from adipic acid overwhelm those grown from the anions in **3**, and a narrow monomodal distribution is observed ($M_w/M_n \sim 1.05$). The measured molecular weight on GPC using polystyrene (PS) standards systematically decreases with the increase of [adipic acid]/[**3**] ratio. This feature indicates "immortal polymerization", in that polymer chains grow uniformly not only from the anions in **3** but also from all adipic acid fed as a chain transfer agent. The absolute molecular weight can be calculated by the equation of "M_n = {TON × 102.13}/{[adipic acid]/[**3**] + 5}". Some discrepancy between the GPC-measured M_n and the absolute M_n is attributed to employing PS standards on GPC measurement. The absolute molecular weight of PPC (M) has a relationship with the GPC-measured molecular weight ($M_{(PS)}$) by an equation of $KM^{\alpha+1} = K_{(PS)}M_{(PS)}^{\alpha(PS)+1}$, where "$K$", "$K_{(PS)}$" and "α", "α(PS)" are Mark−Houwink parameters of PPC and PS, respectively. This equation is simply derived from the fact that the hydrodynamic volumes (V_h) of PPC and PS standard are equal at a same elution volume. The V_h is theoretically described as $KM^{\alpha+1}/2.5A$ (A = Avogadro number). The data set of the absolute M_n (y) and the GPC-measured M_n (x) fit almost perfectly to an equation of $y = 0.255x^{1.09}$ (r^2 = 0.997, Figure 1). From this fitting and the known "$K_{(PS)}$" and "α(PS)" values (0.0070 mL/g and 0.750 in THF at 35 °C),[9] the Mark−Houwink parameters of PPC, "K" and "α", are calculated to be 0.063 mL/g and 0.61, respectively.

DSC studies show that the glass transition temperatures (T_g) stay at a plateau of 36−39 °C when the absolute M_n is above 15 000 but rapidly decrease when the absolute M_n is below 15 000 (Table 1). When the absolute M_n is 2200, the T_g is 20 °C.

Many other protic compounds such as dicarboxylic acids (terephthalic acid and succinic acid), diols (ethylene glycol, diethylene glycol, and propylene glycol), and a compound containing both −OH and $-CO_2H$ (4-hydroxybenzoic acid) also work well as a chain transfer agent with high TOFs (9300−11 500 h^{-1}) at a high feed ratio of [$-CO_2H$ or −OH]/[**3**] = 600, providing low-molecular-weight PPC-diols. Feeding monool or monocarboxylic acid such as ethanol or hexanoic acid provides a PPC-monool. All the polymer samples show a narrow molecular-weight distribution ($M_w/M_n \sim 1.05$), and the absolute M_n (y) and the GPC-measured M_n (x) fit well into the equation "$y = 0.255x^{1.09}$".

Either three-armed or four-armed star-shaped PPC is prepared by feeding tricarboxylic acid (tricarballylic acid and 1,2,4-benzenetricarboxylic acid) or tetracarboxylic acid (1,2,3,4-butanetetracarboxylic acid), respectively, with a high TOF of 8100−9500 h^{-1} at [$-CO_2H$]/[**3**] = 600. In these cases, the data sets of GPC-measured M_n and the absolute M_n deviate, a little for the three-armed ones and significantly for the four-armed one, from the equation derived for the linear PPCs. These deviations are explainable when considering that V_h of a linear chain is higher than those of three- or four-armed star-shaped chains at the same absolute M_n.One of the possible applications of a low-molecular-weight PPC-diol or -polyol is as a midsegment of polyurethane (PU).[10] Reported advantages of PU prepared using other types of poly(alkylene carbonate)-diol such as $HO-\{OCO_2-(CH_2)_a\}_n-OH$ (a = 4, 5, or 6) over those prepared using the conventional polyether-diol or polyester-diol are hydrolytic stability and antistatic property.[11] The M_n increases to 14 000 when low-molecular-weight PPC-diol (absolute M_n, 2200) is reacted with equimolar amount of 4,4′-methylenebis(phenyl isocyanate).

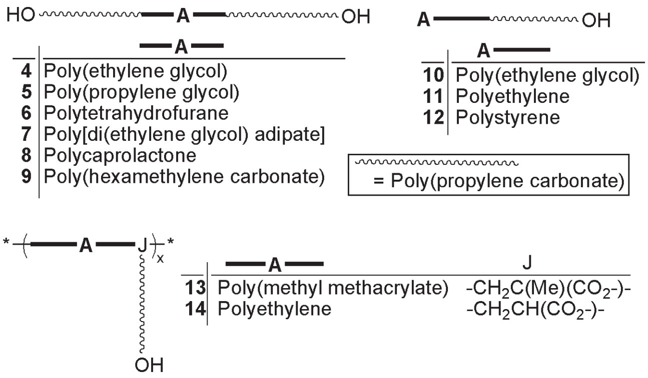
By feeding polymers bearing −OH or $-CO_2H$ at both ends, triblock copolymers of PPC-*block*-**A**-*block*-PPC are obtained, where the −**A**− block is polyether, polyester, or polycarbonate (**4**−**9** in Chart 1, Table 2). Diblock copolymers of PPC-*block*-PEG [poly(ethylene glycol)], PPC-*block*-PE (polyethylene), and PPC-*block*-PS (polystyrene) are obtained by feeding poly(ethylene glycol), polyethylene monoalcohol, and polystryrene carboxylic acid, respectively (**10**−**12**). Graft copolymers are also prepared by feeding poly[(methyl methacrylate)-*co*-(methacrylic acid)] or poly[ethylene-*co*-(acrylic acid)] (**13** and **14**). Simultaneous

Table 2. CO_2/PO Copolymerization Results by Feeding Various Polymers as a Chain Transfer Agent[a]

entry	polymer	M_n of −**A**−	TON	wt % of −**A**−	M_n ($\times 10^{-3}$)	T_g (°C)	T_m (°C)
1	**4**	2000	12200	8.2	19	27	
2	**4**	2000	6200	47	6.1	−19	
3	**4**	10000	7600	12	68	26	
4	**4**	10000	8600	39	22	−12	51
5	**5**	3500	13600	12.4	23	36	
6	**6**	2900	15700	8.3	34	37	
7	**7**	2500	11900	9.2	45	35	
8	**8**	2000	15900	7.6	32	31	
9	**9**	2000	11900	9.2	24	31	
10	**10**	35000	15100	8.3	111	39	53
11	**10**	35000	9100	20	54	27	55
12	**11**	700	9900	5.5	19	37	92
13	**11**	700	13500	17	7.8	34	96
14	**11**	700	8600	39	3.5	26	103
15	**12**	43000	11500	11	123	42, 102	
16	**12**	43000	9700	22	114	43, 108	
17	**13**	6400	11200	9.7	12	37	
18	**13**	6400	8500	20.6	71	41	
19	**14**	1400	10700	10	38	37	79
20	**14**	1400	11500	22	22	33	87

[a] Polymerization conditions: PO (10 g, 170 mmol), **3** (3.0 mg, [PO]/[Cat.] = 100 000), CO_2 (25 bar), temperature (75 °C), time (60 min).

Chart 1. Structures of Block Copolymers



formation of monoblock PPC that is grown from the anions in **3** is inevitable, and it is observed in the GPC curves especially when the [−OH or −CO_2H]/[**3**] ratio is low. Architecture by varying chain length of each block is possible by controlling the amount and M_n of the feeding polymer. The chain length (M_n) of PPC block is determined by the equation "{TON × 102.13}/{[OH or CO_2H]/[**3**] + 5}".

A PEG melting signal is observed at 53−55 °C along with a PPC T_g signal in the DSC studies of PPC-*block*-PEG copolymers that are produced by feeding high-molecular-weight PEG (entries 10 and 11). The PE melting signals are observed at 92−103 °C for PPC-*block*-PE (entries 12−14) and at 79−87 °C for PE-*gaft*-PPC (entries 19 and 20). For PPC-*block*-PS, PPC T_g signal is observed at a slightly higher temperature of 42−43 °C than that of PPC itself (40 °C), and a weak PS T_g signal is additionally observed at 102−108 °C (entries 15 and 16).

The PPC exhibits favorable properties such as clean incineration, printability, and adhesiveness. When it is processed to a film or sheet, it shows good barrier property for both oxygen and water, but mechanically it is easily breakable (brittle). A sheet prepared from PPC-*block*-PEG of 8.3 wt % PEG unit (entry 10) is not as brittle as that of PPC itself. It is flexible and stretchable as the conventional PE film. A sheet prepared from PPC-*block*-PS of 11 wt % PS unit (entry 15) is translucent and tougher than PPC itself. Figure 2 shows their tensile properties.

Precise control of molecular weight and architecture of chain blocks is a main concern in polymer synthesis. Living polymerization is the best tool to achieve this goal.[12] In this study, it is demonstrated that immortal polymerization in the presence of chain transfer agent containing −OH or −CO_2H group is also a good tool to attain this goal in the CO_2/epoxide copolymerization. A highly active catalyst that is insensitive to protic compounds is prerequisite. Low-molecular-weight PPC-diol prepared in this way may be employed in PU manufacturing. Some block copolymers containing ~10 wt % common bulk polymer units can supplement demerits of PPC itself.

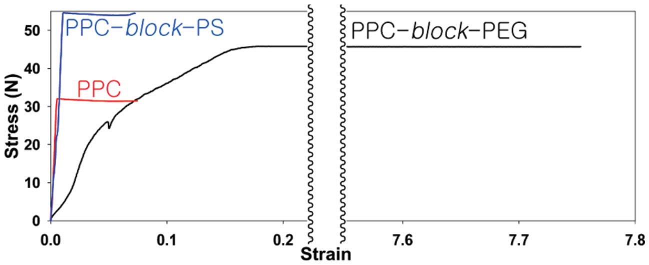


Figure 2. Tensile stress−strain curves for PPC, PPC-*block*-PEG (8.3 wt % PEG), and PPC-*block*-PS (11 wt % PS).

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Supporting Information Available: Experimental details and the characterization data of ^1H NMR, GPC, and DSC. The material is available free of charge via the Internet at http://pubs.acs.org.

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