VIP Polycarbonate Synthesis

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Stereocomplex of Poly(propylene carbonate): Synthesis of Stereogradient Poly(propylene carbonate) by Regio- and Enantioselective Copolymerization of Propylene Oxide with Carbon Dioxide**

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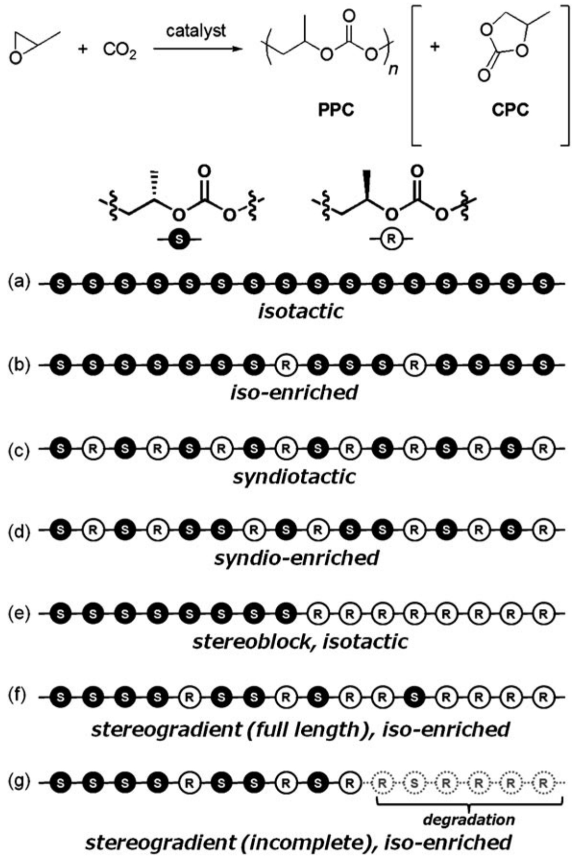
Stereocontrol has been one of the major challenges in polymer synthesis for half a century, ever since the synthesis of isotactic polypropylene by Natta et al.[1a] Not only does tacticity arise from the relative stereochemistry of the neighboring asymmetric carbon centers, but the absolute configuration of the asymmetric centers can be controlled by modern techniques.[1b,c] Thus, asymmetric polymerization of chiral polymers has been accomplished by either asymmetric synthesis polymerization starting from achiral monomers or enantiomer selective polymerization from a racemic mixture of chiral monomers.

Gradient copolymers are a new class of polymers, in which the decrement of one component and the increment of the other component occur sequentially from one chain end to the other end, unlike traditional block or random copolymers. The gradient can be realized by using two kinds of monomers as well as by the stereoregularity of the same monomer unit. Examples of such a stereogradient polymer are atactic–syndiotactic poly(methacrylic acid)[2] and D-L poly(lactic acid).[3] Herein, we report the first synthesis of a iso-enriched stereogradient poly(propylene carbonate) (PPC) which starts from an *S*-rich PPC block and ends with an *R*-rich PPC block. Higher thermal decomposition temperatures were observed relative to those of typical poly(propylene carbonate)s (PPCs) for the stereogradient and the stereoblock PPCs obtained.

Since the first report in the 1960s, copolymerization of epoxides with carbon dioxide (CO_2) has been intensively studied as one of the most promising processes for CO_2 utilization.[4–7] When using propylene oxide (PO), three diad structures (head-to-tail, head-to-head, and tail-to-tail) would form depending on whether the ring-opening reaction occurs at the methylene or methine carbon atom.[8] Because PO possesses a chiral center, stereoregular PPCs such as isotactic and syndiotactic PPCs are possibly produced from *rac*-PO by stereocontrolled copolymerization (Schemes 1 a and c). Indeed, the regio- and stereocontrolled *rac*-PO/CO_2 copolymerizations have been reported, and gave iso-enriched PPC (Scheme 1 b) and syndio-enriched PPC (Scheme 1, d).[5g, 6a–f, 9]

On the other hand, the synthesis of an isotactic stereoblock PPC (Scheme 1 e) or an iso-enriched stereogradient PPC (Scheme 1 f) has never been reported. Synthesis of stereoblock or stereogradient polymers can be realized by the regio- and enantiomer-selective copolymerization of *rac*-PO and CO_2 with complete conversion of *rac*-PO; that is, the more reactive enantiomer of PO is preferably consumed at



Scheme 1. Stereoregularities of PPCs.

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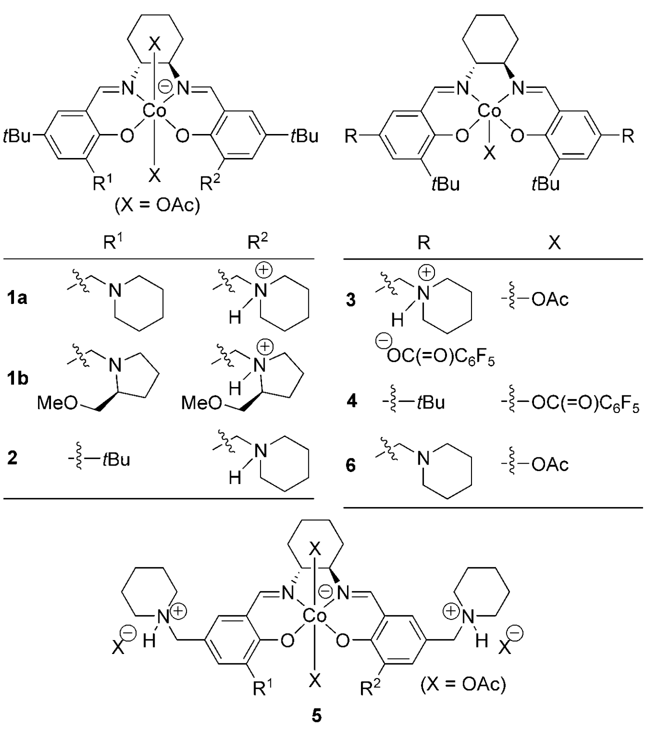
$< 50\,\%$ conversion, thus giving an isotactic (or iso-enriched) PPC with the preferable absolute configuration at the chiral centers and then the less reactive enantiomer of PO becomes incorporated into PPC chain at $> 50\,\%$ conversion. However, the reported catalysts for regio- and enantiomer-selective PO/CO_2 copolymerization cannot be applied to such a strategy because degradation occurs at $> 50\,\%$ conversion of PO (Scheme 1 g), thus giving cyclic propylene carbonate (CPC) as a by-product.[6d]

Recently, our research group has reported the first example of selective PPC production at almost complete PO conversion by using cobalt complex **1a**.[10] The key feature of the catalyst design is an ammonium arm in the salen-type ligand. Taking advantage of the complete conversion achieved by our catalyst, we started to investigate the synthesis of a stereogradient iso-enriched PPC using **1a** and its analogues.

The cobalt complexes employed here and the polymerization results are summarized in Scheme 2, and Table 1, respectively. First, we evaluated the regio- and enantioselective outcomes with complex **1a**. The PO/CO_2 copolymerization with complex **1a** (PO/**1a** = 2,000) at 25 °C for 2 hours selectively produced PPC [PPC/CPC = 98/2, yield of (PPC + PC) = 23 %] (Table 1, entry 1). However, the regioselectivity was moderate [head-to-tail linkage (HT) = 72 %] and almost no enantioselectivity ($k_{rel} = 1.1$) was observed in spite of its enantiomerically pure cyclohexanediamine unit (k_{rel} is defined as the relative rate constant of (S)-PO vs. (R)-PO or (R)-PO vs. (S)-PO. The value is estimated by means of the general equation, $k_{rel} = \ln[(1-c)(1-ee)]/\ln[(1-c)(1+ee)]$, where c is a conversion of PO and the ee value is of unreacted PO). The ee value are much lower than the reference values (Table 1, entry 10) obtained with the typical Co–salen complex **4**, with which the PO conversion cannot reach $> 50\,\%$.

To improve the selectivities, we next investigated the effects of amino/ammonium groups on the salen ligand. Complex **1b**, having amino/ammonium groups derived from (S)-prolinol moiety, demonstrated higher regio- (HT = 85 %) and enantioselectivities ($k_{rel} = 1.8$) than complex **1a** (Table 1, entry 2). Complex **1b** effectively suppressed CPC formation even at a high PO conversion of 84 % under neat condition and gave PPC selectively (> 99 %; Table 1, entry 3). In addition, when using 1,2-dimethoxyethane (DME) as a solvent, complete PO consumption was accomplished without a concomitant production of CPC (> 99 % conversion, > 99 % PPC selectivity; Table 1, entry 4). After complete PO conversion, the obtained PPC consisted of 83 % HT linkage, which is slightly lower than that at 22 % PO conversion. The decrease in regioselectivity at higher PO conversion corresponds to the fact that the more reactive (S)-PO underwent ring-opening with higher regioselectively than the less reactive (R)-PO.[6d]

Steric bulk near the cobalt center was found to be crucial for both regio- and enantioselectivities. Cobalt complex **2** with a *tert*-butyl group at the 3-position of one of the benzene



Scheme 2. Structures of cobalt complexes.

Table 1: Copolymerization of propylene oxide with CO_2 using cobalt complexes[a]

Entry	Complex	t [h]	Yield of PPC + CPC [%][b]	PPC/CPC[b]	HT [%][c]	k_{rel}	M_n [g mol^{-1}][d]	M_w/M_n[d]	T_g [°C][e]	T_d [°C][f]	T_{d5} [°C][f]
1	**1a**	2	23	98:2	72	1.1 (R)	10800	1.13	34	239	229
2	**1b**	5	22	> 99:1	85	1.8 (S)	10600	1.13	–	–	–
3	**1b**	78	84	> 99:1	86	–	39800	1.16	–	–	–
4	**1b**	48	> 99	99:1	83	–	21400	1.13	35	228	224
5	**2**	7	26	99:1	86	2.1 (S)	13600	1.12	–	–	–
6	**2**	120	83	98:2	–	–	40500	1.15	–	–	–
7	**2**	98	98	99:1	81	–	22900	1.16	33	243	237
8	**3**	9	26	98:2	92	3.5 (S)	8200	1.13	–	–	–
9	**3**	96	96	98:2	89	–	13800	1.15	35	273	236
10[g]	**4**	1	23	98:2	95	4.3 (S)	21300	1.13	35	224	222

[a] Reaction conditions: PO (2.0 mL, 28.6 mmol), cobalt complex (0.014 mmol), [PO]/[Co] = 2,000, CO_2 (1.4 MPa) at 25 °C (entries 1–3, 5, 6, 8, and 10); PO (1.0 mL, 14.3 mmol), cobalt complex (0.014 mmol), [PO]/[Co] = 1,000, CO_2 (1.4 MPa), DME (1.0 mL) at 25 °C (entries 4, 7, and 9). [b] Determined on the basis of ^1H NMR spectroscopy of the crude product by using phenanthrene as an internal standard. [c] Head-to-tail linkage determined on the basis of ^{13}C NMR spectroscopy. [d] Determined by size-exclusion chromatography using a polystyrene standard. The molecular weight is strongly affected by an amount of concomitant water since it works as a chain-transfer reagent.[10,11] Accordingly, the M_n values were not consistent with those estimated from the yields. [e] T_g values were determined from the second heating scan in DSC. [f] T_d = onset temperature of TG curve. T_{d5} = temperature of 5 % weight loss in TG. [g] $[Ph_3P{=}N{=}PPh_3]Cl$ (0.014 mmol) was added.

rings exclusively gave PPC with 86 % HT linkage at 26 % PO conversion. In addition, (*S*)-PO was consumed preferentially over (*R*)-PO with $k_{rel} = 2.1$ (Table 1, entry 5). Accordingly, complex **2** demonstrated higher regio- and enantioselectivities than complexes **1**. Complex **2** can also produce PPC selectively even at high PO conversion under neat and dilute conditions (Table 1, entries 6 and 7), thus showing that only one ammonium group is effective for suppressing CPC formation.

Further improvement in regio- and enantioselectivities was achieved by introducing *tert*-butyl group at each of the 3-positions. Because the results with complex **2** indicated that introduction of sterically hindered *tert*-butyl group(s) at the 3-position(s) should be promising for higher selectivities, we next designed complex **5** (Scheme 2). Attempt to synthesize complex **5** by the same procedure as for complexes **1** and **2**, however, did not give the desired complex but gave complex **6** without a piperidinium acetate moiety.[11,12] Such easy dissociation of acetic acid from complex **5** may be attributed to the larger separation between the cobalt center and the piperidinyl group. By changing the acid from acetic acid to a nonvolatile pentafluorobenzoic acid, we obtained complex **3** (Scheme 2). With complex **3**, the highest regio- and enantioselectivities were achieved among the complexes we investigated in this study (Table 1, entry 8). Furthermore, high selectivity for PPC was also accomplished even at complete conversion of PO (Table 1, entry 9). Thus, we finally obtained the iso-enriched stereogradient PPC (Scheme 1, f).

Stereogradient and stereoblock PPCs were found to possess high thermal decomposition temperature. Thermal properties of the obtained PPCs (reprecipitated from CH_2Cl_2/MeOH) in Table 1 were analyzed by differential scanning calorimetry (DSC) and thermogravimetry (TG). Glass-transition temperatures (T_g) determined by DSC were almost independent on regio- and stereoregularities. On the other hand, decomposition (T_d) and 5 % weight loss (T_{d5}) temperatures of stereogradient PPC (Table 1, entry 9) were higher than those of PPCs with lower regio- and stereoselectivities (Table 1, entries 1, 4, and 7) and even iso-enriched PPC (Table 1, entry 10 and Figure 1 a).

To investigate the relationship between the stereosequence and thermal decomposition property, we synthesized isotactic (*R*)-PPC and (*S*)-PPC (Scheme 1, a) with (*R*)-PO and (*S*)-PO as a monomer, respectively, using **4**/[$Ph_3P{=}N{=}PPh_3$]Cl as the catalyst system.[6d,13] In addition, isotactic stereoblock PPC (Scheme 1, e) was synthesized by stepwise (*S*)-PO/CO_2 and (*R*)-PO/CO_2 copolymerization using complex **3** according to our previously reported procedure.[10] These PPCs and stereogradient polymers (Table 2, entry 9) were purified by reprecipitation from CH_2Cl_2/MeOH and subsequent column chromatography on silica gel (AcOEt as an eluent). Among the PPC samples obtained after concentration from AcOEt (Table 2), iso-enriched stereogradient PPC (Table 2, entry 1) and isotactic stereoblock PPC (Table 2, entry 3) demonstrated higher T_d and T_{d5} values than enantiopure isotactic PPCs ((*S*)-PPC and (*R*)-PPC; Table 2, entries 5 and 7) and their equimolar mixture (Table 2, entry 9). Interestingly, further increase of the T_d and T_{d5} values for the stereogradient PPC and the stereoblock PPC was achieved through reprecipitation from AcOEt/MeOH; Table 2, entries 2 and 4).[14] The T_d values approached 280 °C and were remarkably high compared to those of the typical PPCs. No increase in thermal decomposition temperature was observed for enantiopure isotactic PPCs ((*S*)-PPC and (*R*)-PPC; Table 2, entries 6 and 8) and their equimolar mixture (Table 2, entry 10). One possible explanation for such high thermal decomposition temperature of the stereogradient PPC and the stereoblock PPC is the stereocomplex formation between a (*S*)-PPC block and a (*R*)-PPC block in the same chain.[3] Reprecipitation from MeOH (poor solvent) may accelerate the stereocomplex formation, thus resulting in higher thermal decomposition temperatures. No increase in T_d values of an equimolar mixture of (*S*)-PPC and (*R*)-PPC indicate that the stereocomplex formation was facilitated by proximity between a (*S*)-PPC block and a (*R*)-PPC block.

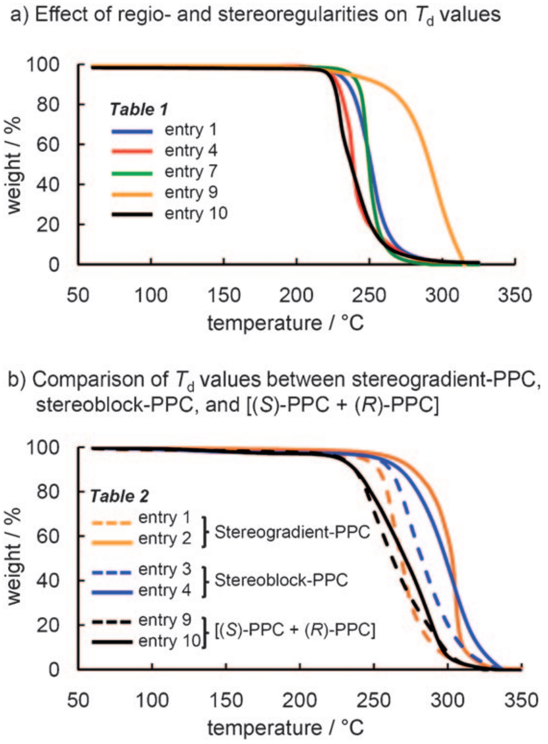


Figure 1. Thermogravimetric curves of PPCs in a) Table 1 and b) Table 2. Broken lines: concentrated from AcOEt; solid lines: reprecipitated from AcOEt/MeOH (see the Supporting Information for the solvent ratios).

In conclusion, we have demonstrated the first synthesis of stereogradient PPC that consists of two enantiomeric structures on each end by using optically active cobalt–salen complexes with ammonium arm(s). Substituents at the 3-positions of the salicylidene units had great influence on regio- and enantioselectivities. The obtained stereogradient PPC as well as stereoblock PPC were found to possess higher thermal decomposition temperature than the typical PPCs. The present report has demonstrated the possibility of stereocomplex formation of PPC and indicated a promising method for increasing thermal properties of PPC. Further investigations on the stereocomplex formation of PPCs are underway.

Table 2: Relationship between the stereosequence and thermal properties of PPCs.

Entry	PPC[a]	Preparation method	M_n [g mol^{-1}][b]	M_w/M_n[b]	T_g [°C][c]	T_d [°C][d]	T_{d5} [°C][d]
1	stereogradient PPC (iso-enriched)	AcOEt	18300	1.14	23	254	242
2		AcOEt/MeOH	17900	1.16	33	281	264
3	stereoblock PPC (isotactic)	AcOEt	11320	1.29	25	260	251
4		AcOEt/MeOH	10900	1.34	24	277	253
5	(*S*)-PPC (isotactic)	AcOEt	13900	1.15	33	245	237
6		AcOEt/MeOH	13900	1.16	25	233	219
7	(*R*)-PPC (isotactic)	AcOEt	13500	1.14	28	248	236
8		AcOEt/MeOH	13200	1.15	28	245	227
9	(*S*)-PPC + (*R*)-PPC (isotactic)	AcOEt	12800	1.20	20	235	228
10		AcOEt/MeOH	13100	1.19	22	238	226

[a] All PPCs were purified before use by reprecipitation from CH_2Cl_2/MeOH (see the Supporting Information for the solvent ratios) and the subsequent column chromatography on silica gel with AcOEt as the eluent. Stereogradient PPC: entry 9 in Table 1. (*S*)-PPC + (*R*)-PPC: a mixture of equal amounts of (*S*)-PPC and (*R*)-PPC. [b] Determined by size-exclusion chromatography analysis using a polystyrene standard. [c] T_g values were determined from the second heating scan in DSC. [d] T_d = onset temperature of TG curve. T_{d5} = temperature of 5% weight loss in TG.

Experimental Section

Propylene oxide (2.0 mL, 29 mmol) and cobalt complex (1.4×10^{-2} mmol) were added to a 50-mL autoclave under argon that contained a magnetic stirring bar. After CO_2 (1.4 MPa) was introduced, the reaction mixture was stirred at 25 °C for the required time. The CO_2 pressure was released, and the polymerization mixture was transferred into a round-bottom Schlenk flask. The flask was connected to a trap, which was cooled with liquid nitrogen, and the unchanged propylene oxide monomer was collected in the trap under reduced pressure. The remaining polymerization mixture was diluted with dichloromethane, and phenanthrene was added as an internal standard. A small aliquot of the mixture was removed and concentrated. Analysis of the residue by ^{1}H NMR spectroscopy and gel permeation chromatography gave the yield of the copolymer and cyclic propylene carbonate, molecular weight, and molecular-weight distribution.

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[11] During our investigation, the cobalt–salen complex with the same salen ligand as complex **6** was reported for PO/CO_2 copolymerization, see: B. Y. Liu, Y. H. Gao, X. Zhao, W. D. Yan, X. H. Wang, *J. Polym. Sci. Part A* **2010**, *48*, 359.

[12] The reaction scheme is described in the Supporting Information.

[13] For the synthesis of (*R*)-PPC, the enantiomer of **4** was used as a catalyst.

[14] The M_n values before and after reprecipitation were almost the same. Accordingly, the increase of thermal decomposition temperature after reprecipitation was not attributed to exclusion of lower-molecular-weight PPCs.