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Alternating Copolymerization of Propylene Oxide/Alkylene Oxide and Carbon Dioxide: Tuning Thermal Properties of Polycarbonates

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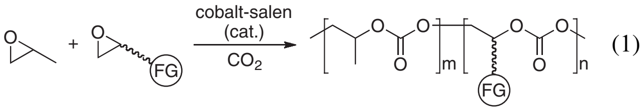
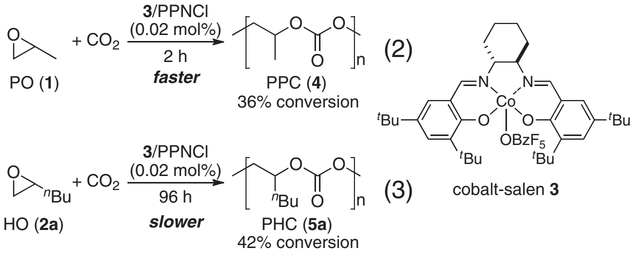
The alternating copolymerization of propylene oxide/alkylene oxide and carbon dioxide has been developed with randomly incorporated poly(propylene carbonate) and poly(alkylene carbonate) units. The ratio-controlled incorporation of the poly(alkylene carbonate) units could improve the thermal properties, such as the glass-transition temperature and thermal degradation temperature, of the obtained polycarbonates.

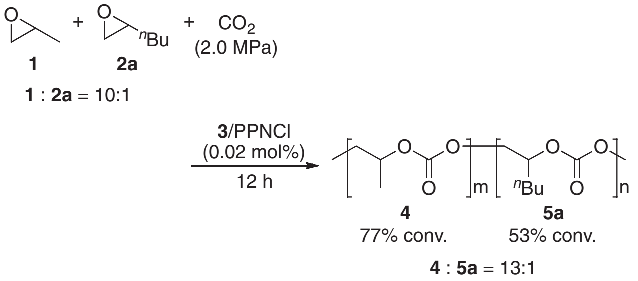
Recently, poly(propylene carbonate) (PPC) has attracted much attention because PPC can be prepared from abundant propylene oxide (PO) and "useless" carbon dioxide in the presence of transition-metal catalysts, such as cobalt Schiff-base complexes.[1] In addition, PPC exhibits several unique properties[1,2] such as a high degree of transparency, low oxygen- and moisture permeability, and biodegradability, and such an application of CO_2 for organic synthesis has been thought to be important for sustainable development.[3] Despite the potential of this polymer, drawbacks regarding its thermal properties for practical use have been pointed out, i.e., a moderate glass-transition temperature (T_g) slightly higher than room temperature ($T_g =$ ca. 40 °C)[4a] and a rather low thermal degradation temperature ($T_d =$ ca. 230 °C).[1,4b] In order to overcome these drawbacks, it is essential to functionalize the main- or side-chain of the PPC; however, neither a practical method for introducing such units into its main chain nor transformation of its side-chain methyl groups has been realized. In this report, we describe the first alternating polymerization of alkylene oxides and carbon dioxide with the random incorporation of propylene oxide and another alkylene oxide with various functionalities (eq 1). Polycarbonates with longer alkyl side chains have a lower glass-transition temperature (T_g) due to their micro-Brownian motion.[5] We have succeeded in the preparation of polycarbonates with various T_g's by controlling the length and/or content of the long side chains in the polymer. Also, the synthesis of a "networked" PPC using bifunctional monomers was accomplished.



In the preliminary study, the separate reactions of propylene oxide (PO, **1**) or 1,2-hexene oxide (HO, **2a**) with CO_2 were examined in the presence of 0.02 mol % of the *racemic trans*-1,2-cyclohexanediimine-bridged cobalt(III)–salen complex **3** with pentafluorobenzoate anion ($^{-}OBzF_5$) and bis(triphenylphosphoranylidene)ammonium chloride (PPNCl) as a cocatalyst. It was found that the reaction of PO (**1**) and CO_2 (eq 2) proceeded much faster than that with HO (**2a**) instead of PO (**1**) (eq 3).



The reaction of the mixed **1**/**2a** in a 10:1 molar ratio with CO_2 under the same reaction conditions at 30 °C for 12 h proceeded to afford a polymeric product (Scheme 1). The ^1H NMR analysis of the obtained polymer showed that the poly(propylene carbonate) (PPC, **4**) and poly(hexene carbonate) (PHC, **5a**) units were incorporated in a 13:1 ratio, which indicated that PO (**1**) was incorporated slightly more (1.3 times) than HO (**2a**). This phenomenon is rather surprising because the results of the reactions in eqs 2 and 3 suggested that PO (**1**) might be much more reactive than HO (**2**) in the copolymerization reaction with CO_2.

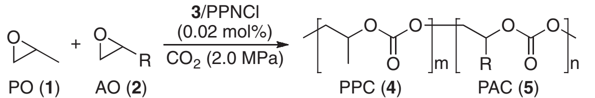


Scheme 1. Alternating copolymerization of PO/HO and CO_2.

Several reactions with varying PO/HO (**1**/**2a**) ratios were performed to examine the relationship between the ratio of PO/HO (**1**/**2a**) and that of the resulting PPC/PHC (**4**/**5a**) (Table 1, Entries 1–3). In these reactions, it was found that the ratio of the PPC/PHC (**4**/**5a**) units in the product reflected that of the starting PO/HO (**1**/**2a**). In each case, PO (**1**) was consumed around 1.5 times more than HO (**2**). It clearly showed that the ratio of the carbonate units in the product could be controlled by the ratio of starting aklylene oxides employed in the reactions. It should be also noted that the polycarbonates with more PHC (**5a**) units showed lower glass-transition temperatures. Tuning of the T_g could be achieved.

We also examined several three-component polycarbonate syntheses using PO and the alkylene oxides (AO) **2b**–**2f** with various alkyl chains to investigate their effects on the glass-transition temperature of the product as well as the generality of the relationship between the ratio of the substrates and that of the components in the products. The results shown in Table 1

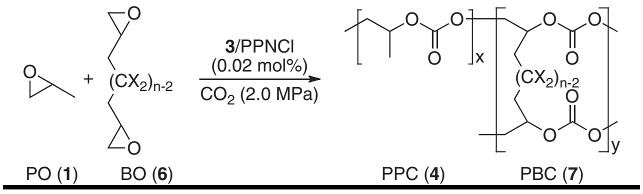
Table 1. Alternating copolymerization of PO/1,2-alkylene oxide (AO) and CO_2: relationship between substituents and T_g's[a]



Entry	Alkylene oxide **2**	**1**:**2**	Time /h	Conv. /%[b]	Yield /%[c,d]	**4**:**5**[d]	M_n /kg mol^{-1} [e]	T_g /°C[f]
1	**2a** (R = $^nC_4H_9$)	10:1	12	77/53	69/52	13:1	20.4	33.2
2	**2a** (R = $^nC_4H_9$)	5:1	12	60/32	43/27	8.0:1	9.4	25.1
3	**2a** (R = $^nC_4H_9$)	2:1	24	75/49	57/33	3.4:1	8.3	14.7
4	**2b** (R = $^nC_8H_{17}$)	10:1	12	67/38	47/33	14:1	17.7	24.0
5	**2b** (R = $^nC_8H_{17}$)	5:1	36	32/13	16/8	9.8:1	8.8	15.1
6	**2b** (R = $^nC_8H_{17}$)	2:1	24	65/34	52/31	3.4:1	14.8	3.4
7	**2c** (R = $^nC_{12}H_{25}$)	10:1	12	70/43	44/25	17:1	25.0	21.5
8	**2c** (R = $^nC_{12}H_{25}$)	5:1	24	76/49	50/23	10:1	21.9	13.2
9	**2c** (R = $^nC_{12}H_{25}$)	2:1	35	92/62	76/52	2.9:1	35.3	−8.1
10[g]	**2d** (R = $^nC_{16}H_{33}$)	10:1	12	70/34	52/34	15:1	15.2	17.8
11[g]	**2d** (R = $^nC_{16}H_{33}$)	5:1	24	72/36	61/32	9.5:1	12.0	9.5
12[g]	**2d** (R = $^nC_{16}H_{33}$)	2:1	132	77/42	28/15	3.8:1	10.3	2.5
13[g]	**2e** (R = $^nC_{18}H_{37}$)	10:1	24	73/58	76/50	15:1	52.1	17.9
14[g]	**2e** (R = $^nC_{18}H_{37}$)	5:1	48	66/34	43/21	10:1	22.7	12.5
15[g]	**2f** (R = $^nC_{20}H_{41}$)	10:1	20	78/69	85/59	14:1	59.4	29.2
16[g]	**2f** (R = $^nC_{20}H_{41}$)	5:1	20	70/39	62/32	9.7:1	38.1	20.2

[a]The reaction was performed with **1** and **2** (total 28.6 mmol) in an appropriate ratio in the presence of **3** (4.7 mg, 5.7 mmol) and PPNCl (3.3 mg, 5.7 mmol) under a 2.0 MPa CO_2 atmosphere in an autoclave (30 mL) at 30 °C.[8] [b]Consumed substrates, determined by ^{1}H NMR analysis of the crude material. [c]Isolated yield by precipitation from $CHCl_3$/MeOH. [d]Determined by ^{1}H NMR analysis of the isolated product. [e]Determined by gel permeation chromatography in tetrahydrofuran at 40 °C, calibrated with polystyrene standards. The M_w/M_n value was around 1.10. [f]Determined by DSC analysis. [g]CH_2Cl_2 (1.0 mL) was used as a solvent.

Table 2. Preparation of "networked" polycarbonates using bifunctional substrates[a]



Entry	BO **6**	*n*	X	**1**:**6**	Time /h	Conv. /%[b]	Yield /%[c]	**4**:**7**[d]	M_n /kg mol^{-1} [e]	M_w /M_n	T_d /°C[f]
1[g]	**6a**	4	H	20:1	12	n.d.	73	n.d.	n.d.	n.d.	266
2	**6a**	4	H	50:1	4	38/18	27	51:1	16.2	1.84	266
3	**6a**	4	H	100:1	4	56/30	33	69:1	36.4	2.14	269
4	**6b**	6	H	20:1	12	66/35	35	21:1	13.3	2.97	260
5	**6b**	6	H	50:1	4	40/n.d.	24	57:1	11.3	1.21	258
6	**6b**	6	H	100:1	4	65/30	36	n.d.	34.4	1.77	269
7	**6b**	6	H	500:1	24	75/n.d.	37	n.d.	36.3	1.10	235
8	**6b**	6	H	1000:1	33	90/n.d.	75	n.d.	69.9	1.27	233
9	**6c**	6	F	100:1	12	76/20	55	n.d.	22.0	2.98	276
10[h]	—	—	—	—	8	n.d.	41	—	40.1	1.10	229

[a]The reaction was performed with **1** and **6** (total 97.2 mmol) in an appropriate ratio in the presence of **3** (15.8 mg, 19.4 µmol) and PPNCl (11.1 mg, 19.4 µmol) under a 2.0 MPa CO_2 atmosphere in an autoclave (30 mL) at 30 °C. [b]Consumed substrates, determined by ^{1}H NMR analysis of the crude material. [c]Isolated yield by precipitation from $CHCl_3$/MeOH, based on the formula weight of **4**. [d]Determined by ^{1}H NMR analysis of the isolated product. [e]Determined by GPC/THF at 40 °C, calibrated with polystyrene standards. [f]Determined by TG analysis. [g]The obtained polymer was insoluble in common organic solvents. [h]PO only. n.d.: not determined.

indicated that the higher PAC ratio showed a lower T_g in each AO (Entries 1–3, 4–6, 7–9, 10–12, 13 and 14, 15 and 16). Among the polycarbonates with a PPC:PAC ratio (**4**:**5**) around 15:1, 10:1, and 3:1, those with R = $C_{16}H_{33}$, or $C_{12}H_{25}$ showed the lowest T_g's, respectively (Entries 7–12). On the other hand, those with shorter (R = C_4H_9 or C_8H_{17}) or longer (R = $C_{18}H_{37}$ or $C_{20}H_{41}$) alkyl side chains showed relatively higher T_g's (Entries 1–6 and 13–16). We considered that these observations would be attributed to the balance of the following two factors for micro-Brownian motions: while a longer alkyl side chain would be favorable for the flexibility of the polymer, an excessively crowded alkyl side chain would restrict the flexibility and/or would cause interaction between neighboring alkyl chains, resulting in a rigid side chain. Among these polymers examined in Table 2, PPC:PAC in a ca. 3:1 ratio with R = $C_{12}H_{25}$ showed the lowest T_g (−8.1 °C, Entry 9). It should be also noted that each polycarbonate shown here exhibited only a single T_g based on the DSC analysis, which obviously indicated that the polycarbonates obtained in the reactions were not block copolymers of PPC (**4**) and PAC (**5**) units, but those of these two units randomly incorporated.[6]

Thus the method for preparing polycarbonates with two carbonate units randomly and ratio-controlled could be extended into the polymerization of PO/epoxides with two or more reaction sites to form "networked polymers." If the diepoxide **6** (BO) can be incorporated into the polymer chain, the polymers with an epoxy side chain can be generated, which is also the active site for the polymerization reaction to make branched polymers.

The reaction was performed using an α,ω-diepoxide (**6**, BO) as the bridging unit. A preliminary experiment showed that in some cases, an insoluble gel was obtained (Table 2, Entry 1). This insolubility might be attributed to the structure of the obtained polymer, whose main chains were connected to each other via PBC units to make a network structure.[7] This polymer had the relatively higher thermal degradation temperature (T_d) of 266 °C (Entry 1) when compared to that of the "normal" PPC (T_d = ca. 230 °C, Entry 10). It was found that the insolubility was not necessary for a high T_d. The shorter reaction times resulted in the formation of "soluble" polymers, and their T_d's were also high at around 260 °C when the PO:BO ratios were greater than 100:1 (Entries 2–6 and 9).[8]

In summary, the preparation of polycarbonates with two carbonate units randomly and ratio-controlled was achieved. The present procedure could be used to control the thermal properties, such as T_g and T_d, using alkylene oxides which have long alkyl chains or bifunctional molecules. The polymers with a T_g lower than room temperature would make them applicable for elastomeric materials. Plastics with a higher T_d would extend their practical usefulness. A mechanistic investigation of the selectivity during this reaction is currently underway.

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8 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.