

Supporting Information

Preparation of High-Molecular-Weight Aliphatic Polycarbonates by Condensation Polymerization of Diols and Dimethyl Carbonate

*Ji Hae Park, Jong Yeob Jeon, Jung Jae Lee, Youngeun Jang, Jobi Kodiyan Varghese, and Bun Yeoul Lee**

Department of Molecular Science and Technology, Ajou University, Suwon 443-749 Korea

Cyclohexane-1,4-dimethanol/DMC Condensation Polymerization. The first step was conducted with cyclohexane-1,4-dimethanol (10.0 g, 69 mmol, a mixture of *cis*- and *trans*-isomers in 3:7 ratio), NaH (3.3 mg, 0.14 mmol) and DMC (10.3 g, 114 mmol), using identical conditions and procedures to those used for DB/DMC condensation polymerization. In the second step, the condensation reaction was conducted at 180 °C and 380 mmHg for 1 h, at 210 °C and 0.3 mmHg for 1 h, and finally at 240 °C and 0.3 mmHg for 3 h. The catalyst was neutralized with phthaloyl dichloride using the same procedures and conditions as those used for DB/DMC condensation polymerization. ¹H NMR (CDCl₃): δ 4.04 (d, *J* = 7.2 Hz, 1.2H,

$\text{CH}_2\text{OC}(\text{O})$ in *cis*-isomer), 3.94 (d, $J = 6.4$ Hz, 2.8H, $\text{CH}_2\text{OC}(\text{O})$ in *trans*-isomer), 2.10-0.80 (m, 10H) ppm.

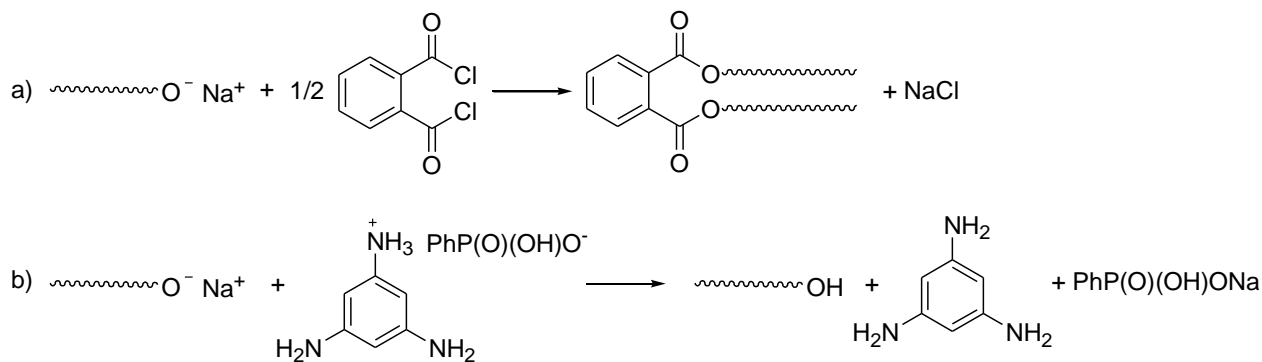
4,8-Bis(hydroxymethyl)tricyclo[5.2.1.0^{2,6}]decane/DMC Condensation Polymerization.

The polymerization was conducted using the same conditions and procedures as those used for cyclohexane-1,4-dimethanol/DMC condensation polymerization, with 4,8-bis(hydroxymethyl)tricyclo[5.2.1.0^{2,6}]decane (10.0 g, 51 mmol, a mixture of two isomers), NaH (2.4 mg, 0.10 mmol), and DMC (8.26 g, 92 mmol). ^1H NMR (CDCl_3): δ 3.89 (br, 4H, $\text{CH}_2\text{OC}(\text{O})$), 2.60-0.60 (br, 14H) ppm.

Catalyst-Quenching Studies. The catalyst residue remaining in the resin sometimes gives rise to detrimental effects during thermal processing, as well as adversely affecting the polymer durability. In the commercial development of poly(propylene carbonate), catalyst removal was one of the critical concerns. The catalyst used in our strategy was a strong base of an alkali-metal alkoxide and hence the polymer was unstable in its presence at temperatures above 200 °C. When PBC prepared using 0.20 mol% sodium alkoxide was thermally treated in an oven at 200 °C for 2 h, around 10% of the polymer was converted to THF by the reaction shown in Scheme 3e (Figure S1a). However, when the catalyst residue was thoroughly removed, THF formation was not observed, even at a temperature of 240 °C (Figure S1b), indicating that catalyst removal was critical for resin stability. In the preparation of low-molecular-weight aliphatic polycarbonate macrodiols, the catalyst residue has been removed by washing with water or precipitation in alcohol after dissolving the polymer in THF or CH_2Cl_2 . Operation of these procedures in a commercial process may be too expensive. Furthermore, catalyst removal by washing with water after dissolving the high-molecular-weight PBC in a minimum amount of

CH₂Cl₂ was unsuccessful. The CH₂Cl₂ phase became turbid by formation of a reverse emulsion of water as a result of the action of the dissolved high-molecular-weight PBC.

Scheme S1. Catalyst-Quenching Reactions



When 0.20 mol% sodium alkoxide was used, the sodium content of the resulting polymer resin was ~400 ppm. We achieved preparation of a high-molecular-weight PBC using 0.02 mol% sodium alkoxide: the sodium content of the resulting resin was just 40 ppm. The presence of such a small amount of sodium salt may be acceptable and may not seriously affect the resin properties if the alkoxide base is quenched with acid. We could not use such strong acids as hydrochloric acid, sulfuric acid, and nitric acid. These were not soluble in the resulting polymer melt and, furthermore, the polymer was degraded by the action of the strong acid during the neutralization process. The neutralizer we chose was phthaloyl dichloride, which is highly reactive toward alkoxide anions, forming an ester bond and a benign byproduct, NaCl (Scheme S1a). Phthaloyl dichloride is an inexpensive chemical used on a bulk scale in industry, and it is miscible with the polymer melt. A feed containing a half molar amount of phthaloyl dichloride improved the polymer thermal stability. No THF was formed when the quenched polymer was kept at 200 °C for 2 h (Figure S1c). However, THF was formed (~10%) at a higher temperature of 240 °C (Figure S1d); no THF was formed at this temperature for the pure PBC. When an equivalent amount of sebacoyl chloride, dibutylphosphoric acid, or phenyl phosphonic acid was

used instead of phthaloyl dichloride, the same level of thermal stability was observed; no THF was formed at 200 °C, but formation of almost the same amount (~10%) of THF was observed at 240 °C. Formation of the same amount of THF, regardless of the quencher, indicated that the formation of THF at 240 °C might be attributable to a mixing problem. When excess dibutylphosphoric acid or phenyl phosphonic acid (1.5 equiv) was added to compensate for incomplete mixing, the thermal stability deteriorated severely. The remaining acid extensively broke down the polymer chains at 200 °C. Addition of excess acryl chloride was undesirable because the remaining acyl chloride generates a strong acid, hydrochloric acid, by the action of ambient water. When the weaker acid heptanoic acid was used as a quencher, a significant amount (90%) of THF was formed at 240 °C. In this case, the action of the generated carboxylate anion might cause the weakened thermal stability. Finally, we achieved the same level of thermal stability as that of the pure PBC using melamine phenylphosphonate (Scheme S1b). The polymer was stable even at 240 °C, without formation of any THF, when it was treated with 2 equiv of melamine phenylphosphonate (Figure S1e). In this case, the byproducts were sodium phenylphosphonate and melamine. These byproducts and the remaining melamine phenylphosphonate did not react with the polymer even at 240 °C. Melamine phenylphosphonate is used as a flame-retarding additive in plastics, and can be prepared simply by mixing phenylphosphonic acid and melamine in water.

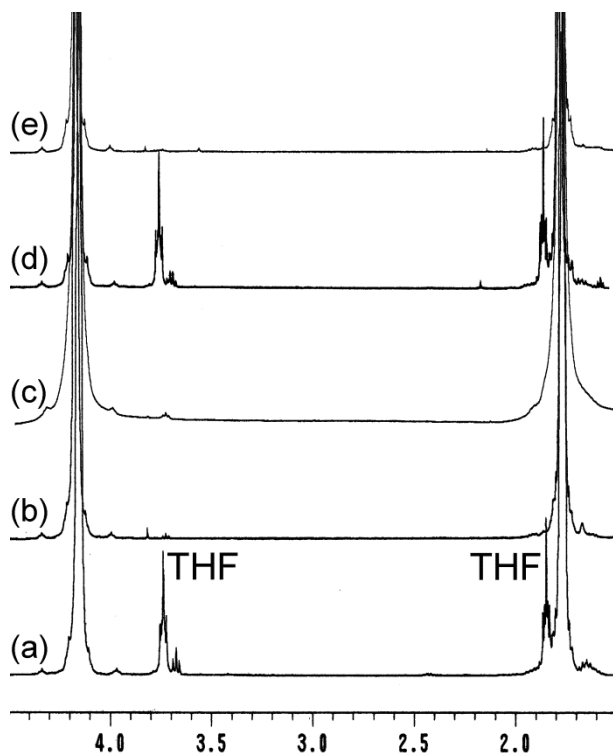


Figure S1. ^1H NMR spectra of poly(1,4-butylene carbonate)s thermally treated for 2 h at 200 °C without catalyst quenching (a); at 240 °C after catalyst removal (b); at 200 °C after quenching with phthaloyl dichloride (c); at 240 °C after quenching with phthaloyl dichloride (d); at 240 °C after quenching with melamine phenylphosphonate (e).

Using a half molar amount of phthaloyl dichloride as a quencher, we might expect the molecular weight to increase as a result of connection of two alkoxide chain-ends (Scheme S1a), but the increase in molecular weight was marginal: the molecular weight increased from M_w 120 000 to 131 000. In the GPC traces, a shift of only the low-molecular-weight portions was observed, whereas the high-molecular-weight portion was intact. The molecular-weight increase was slightly more, from 196 000 to 248 000, when phthaloyl dichloride was treated to the polymer obtained in a batch where the DP was maximized with an extended polymerization time (entry 4 in Table 1). These results can be explained by the graph of the mole fraction distribution

versus DP, simulated for general condensation polymerization. Even at a high conversion of 98%, the majority of polymer chains are low-molecular-weight oligomers. Therefore, the connection of two chains occurs mainly between low-molecular-weight oligomers, in accordance with the shift of only low-molecular-weight portion observed in the GPC curves. Even at a higher conversion of 99%, the distribution is simply flattened, decreasing monotonously with increasing DP, but with the monomer still being the most abundant species. Base on this curve, we cannot expect a substantial increase in the molecular weight through connection of the two alkoxide chain-ends using phthaloyl dichloride as a quencher.

Thermal and Tensile Properties. As the molecular weight of PBC increased, the enthalpy of melting (ΔH) decreased, but the melting temperature was constant at 68 °C (entries 1–3 in Table S1). For a high-molecular-weight PBC (M_w 248 000), the ΔH value was 38 J/g and the melting endotherm signal was unimodal with a long tail in the lower temperature region (Figure S2c). For relatively low-molecular-weight PBCs (M_w 124 000 and 61 000), two signals were observed with a shoulder signal at ~45 °C (Figure S2a and b).

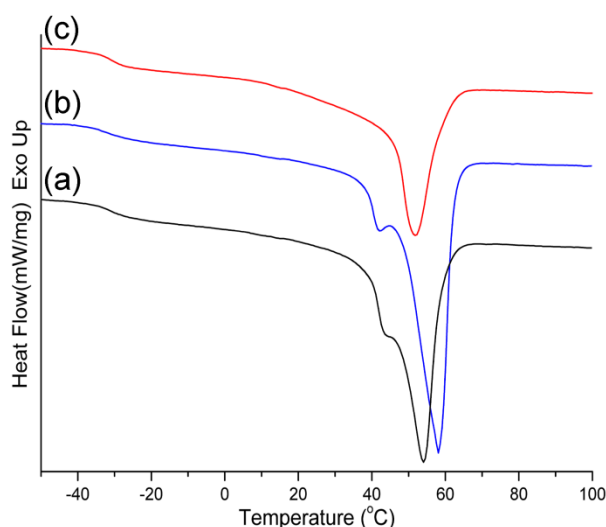


Figure S2. DSC curves for poly(1,4-butylene carbonate)s (PBCs) (M_w 61 000 (a); M_w 124 000 (b); M_w 248 000 (c))

Tensile test-bars (45 mm × 7.0 mm × 1.0 mm) were prepared by pressing a polymer lump with a screw, at 120 °C overnight, between two plates with a spacer of thickness 1.0 mm. The tensile tests were performed according to ASTM D 638 on UTM (WL2100). The drawing rate was 5 mm/min. Crystalline PBCs and a copolymer showing melting signals in the DSC curves exhibited tensile strain-stress curves of typical thermoplastics. Similar strain-stress curves were observed for the two PBCs with high-molecular-weights (M_w 124 000 and 248 000; Figure S3b and c). Both polymers were strong, exhibiting high ultimate tensile strengths (24 N/mm²). The difference between the two curves was a yield stress enhancement as a result of the increase in molecular weight. The low-molecular-weight PBC, with M_w 61000, showed a substantially different curve, exhibiting a relatively low ultimate tensile strength (11 N/mm²), indicating that it broke easily. Incorporation of a small amount (2 mol%) of **5** increased both the tensile strength and elongation at break (29 N/mm² and 1140%) compared with the values (24 N/mm² and 800%) observed for the pure PBC with the same molecular-weight (Figure S3d versus b). The PBC copolymer incorporating 10 mol% **5**, and consequently losing crystallinity, showed a totally different curve, indicating very weak mechanical strength (Figure S3e).

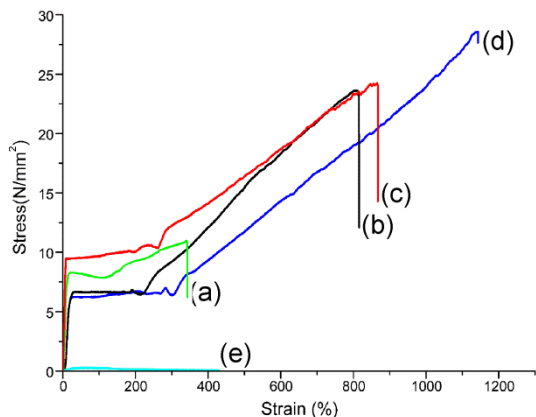


Figure S3. Tensile curves for poly(1,4-butylene carbonate)s (M_w 61 000 (a); M_w 124 000 (b); M_w 248 000 (c)) and for PBC-copolymers with M_w 120 000 incorporating **5** (2 mol% (d); 5 mol% (e))

Table S1. Thermal and Tensile Properties of Some Aliphatic Polycarbonates

Sample	M_w^a $\times 10^{-3}$	T_m^b (°C)	ΔH^b (J/g)	Tensile strength (N/mm ²)	Stress at break (N)	Strain at break (%)	Modulus (N/mm ²)
	61	68	61	11	140	340	2.0
entry 10, Table 1	124	68	49	24	230	810	2.7
entry 4, Table 1	248	68	38	24	220	870	2.2
entry 10, Table 3	125	52	19	29	250	1140	2.6
entry 11, Table 3	120	n.d.	0	0.31	1.2	430	0.25