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Synthesis and Anionic Ring-Opening Polymerization of a Novel Aromatic Cyclic Carbonate Having Binaphthyl Structure

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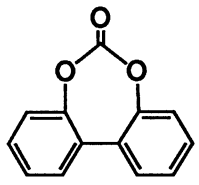
A novel aromatic cyclic carbonate (**3**) having binaphthyl structure was prepared by the reaction of 2,2'-binaphthol with 4-nitrophenyl chloroformate in the presence of a *tert*-amine. **3** polymerized very efficiently with potassium *tert*-butoxide at 20 °C to give corresponding linear polycarbonate with $\overline{M}n$ 12800 ($\overline{M}w/\overline{M}n$ 1.34) in 94% yield.

Synthesis and ring-opening polymerization of cyclic carbonates[1-5] and cyclic poly(oligo)carbonates[6,7] to linear polycarbonates are of current interest in the fields of polymer synthesis from a viewpoint of advantageous processing. Although the polymerization is fairly studied with a few aliphatic cyclic carbonates,[1-4] synthesis and polymerization of aromatic cyclic carbonate are little examined.[8] Two reports on the polymerizations of aromatic cyclic carbonates are presented with **1** and **2** so far. In contrast to **2**, **1** undergoes sluggish anionic ring-opening polymerization with zinc stearate or potassium carbonate to give moderate yield of corresponding linear polycarbonate under very drastic conditions, although **1** does not polymerize with usual anionic initiators such as alkoxide and alkyllithium.[5,9] In order to enhance the polymerizability of **1** we have designed the introduction of additional phenyl rings into **1** which can increase the ring strain leading to the expected high ring-opening sensitivity as a driving force for the polymerization. Recently, we have succeeded in synthesizing a novel aromatic cyclic carbonate (**3**) capable of easily polymerizing under mild conditions.[9] In this communication synthesis and polymerization of **3** are preliminarily described.



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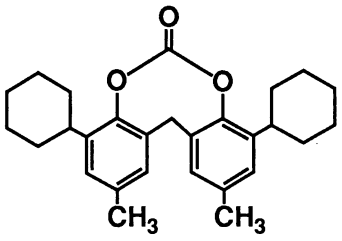

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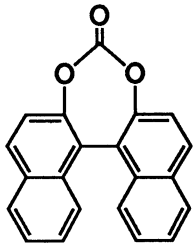
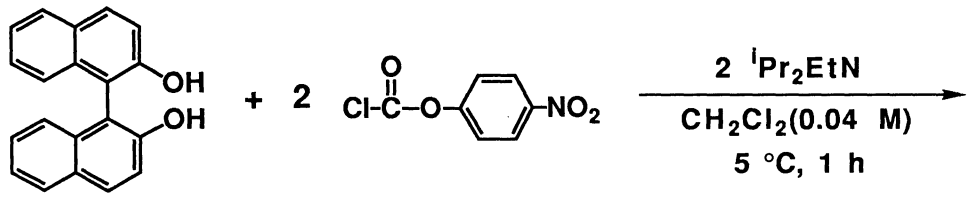


3

Synthesis of **3** was attempted by various methods, *e.g.* by treatment with phosgene, diethyl carbonate-sodium methoxide, or bis(4-nitrophenyl)carbonate-sodium methoxide system, by depolymerization of corresponding polymer, *etc.*, however, none of them afforded **3**. Successful synthesis of **3** was accomplished

by our preparative method for cyclic carbonate which has recently been developed as a new phosgene-free method.[10]

To a dichloromethane solution (40 mL) of 2,2'-binaphthol (**4**, 0.5 g, 1.75 mmol) and 4-nitrophenyl chloroformate (0.774 g, 3.84 mmol) was added dropwise ethyldiisopropylamine (0.389 g, 3.84 mmol) at 5 °C and the mixture was stirred for 1 h at 5 °C. Cyclic carbonate **3** was obtained along with bis(4-nitrophenyl)carbonate (**5**). The mixture was subjected to purification with preparative HPLC (Nippon Bunseki Kogyo (JAI) LC-408, with two JAI GEL columns H-1000 and H-2000), affording 0.47 g (78%) of **3** as white crystals, mp 170-175 °C (decomp.).



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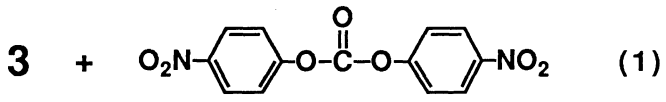
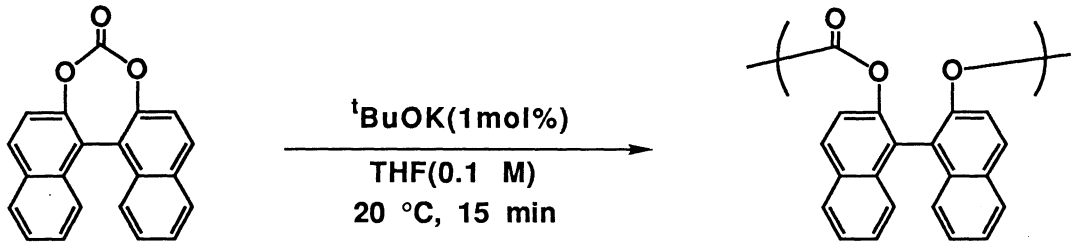


5 (1)

The structure of **2** was confirmed by its characteristic carbonate carbonyl absorption appearing around 1800 cm^{-1} in the IR,[11] eleven carbon signals corresponding to the symmetrical structure in the ^{13}C NMR, molecular ion peak and fragmentation pattern in the mass spectrum (m/z 313[M^++1, 12%], 312[M^+, 57%], and 268[M^+-CO_2, 100%]), and the satisfactory elemental analysis data (Found: C, 80.76; H, 3.87. Calcd for $C_{21}H_{12}O_3$: C, 80.55; H, 3.60).

The cyclic carbonate **3** was labile, especially toward basic conditions, whereas quite stable toward acidic conditions. For example, **3** was completely decomposed within 1 h only by treatment with triethylamine (1 mol%) in dichloromethane at room temperature but was not changed by treating with BF_3OEt_2 (5.6 mol%) (60 °C, 20 h). On dissolving in methanol, **3** decomposed within 1 h at room temperature.



3 **6** (2)

When **3** was treated with potassium *tert*-butoxide (^{t}BuOK,1 mol%) at 20 °C for 15 min in tetrahydrofuran ([C] 0.1 M), **3** was immediately consumed in accordance with its above high reactivity and the corresponding polymer was obtained as white powder in 94% yield (methanol-insoluble fraction). Increasing the amount of ^{t}BuOK resulted in considerable decrease in $\overline{M}n$ (runs 1 and 2) along with increase in molecular weight distribution ($\overline{M}w/\overline{M}n$). Prolonged reaction time caused lowering of both yield and molecular weight (runs 2 and

3, Table 1). A similar polymer was obtained only by heating **3** at 250 °C without initiator in a short time (run 4).[12] The structure of the polymer was determined to be the corresponding linear polycarbonate (**6**) by IR, ^{1}H NMR,[13] ^{13}C NMR, and gel permeation chromatography (GPC).

Table 1. Polymerization of **3**[a]

Run	Solv.	Cat.(mol%)	Temp/°C	Time/min	Methanol-insoluble polymer		
					Yield/%	$\overline{Mn}$[b]	$\overline{Mw}/\overline{Mn}$[b]
1	THF	*t*-BuOK(1)	20	15	94	12,800	1.34
2	THF	*t*-BuOK(5)	20	15	90	6,400	1.86
3	THF	*t*-BuOK(5)	20	60	80	3,200	2.45
4	none	none	250	5	80	7,100	1.52

a) Concentration of **3** was 0.1 M. b) Estimated by GPC based on polystyrene standards.

As shown in Fig. 1, by the polymerization the carbonyl absorption of the seven-membered aromatic cyclic carbonate at 1800 cm^{-1} was clearly changed to 1780 cm^{-1} attributable to that of linear aromatic carbonate. In GPC analysis a unimodal peak was observed which had $\overline{Mn}$ 12,800 ($\overline{Mw}$ 17,200). No elimination of carbon dioxide during the polymerization was observed,[14] and it was confirmed by ^{13}C NMR spectrum of the polymer in which only eleven carbon signals were observed in any case.

The polycarbonate **6** was prepared independently by the interfacial polycondensation of **4** with bis(4-nitrophenyl)carbonate (**5**) in the presence of 4-(N,N-dimethylamino)pyridine (DMAP) (Eq. 3).

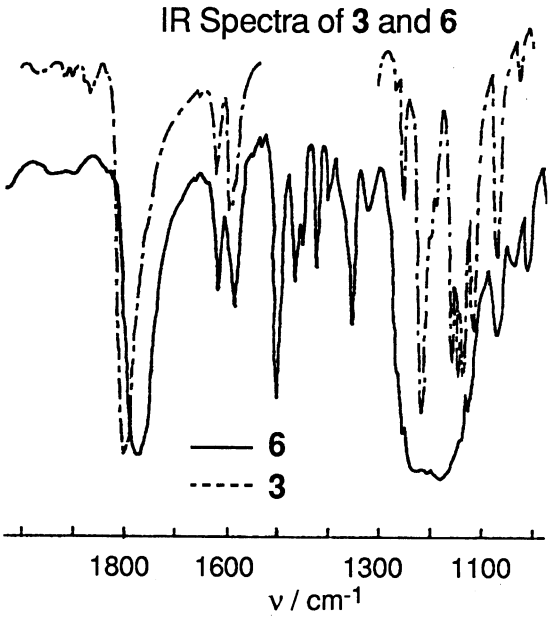
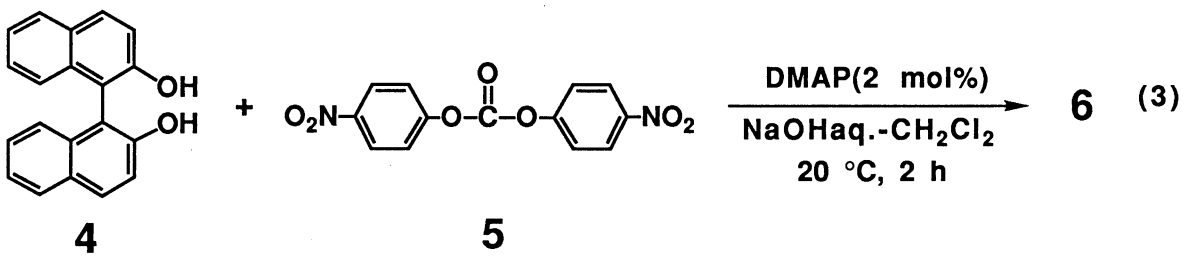


Fig. 1. IR Spectra of **3** and **6**.



The obtained polymer (**6**: yield of the methanol-insoluble polymer: 81%; $\overline{M}n$ 15300 and $\overline{M}w/\overline{M}n$ 2.19) showed the same IR spectrum as that obtained for **3**. These two polymers had similar thermal properties, *i.e.* softening point at 260 - 265 °C and 10% weight loss temperature around 295 °C (by thermogravimetric analysis).

Thus, in this paper was described synthesis of the novel aromatic cyclic carbonate (**3**) which polymerized very efficiently and rapidly to afford the corresponding linear polycarbonate (**6**) in 94% yield. The ring-opening polymerization of **3** was superior to the polycondensation of 2,2'-binaphthol (**4**) with bis(4-nitrophenyl)-carbonate (**5**) in yield of the polymer, ease of the procedure, formation of byproduct, and so on.

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10) T.Ariga, T.Takata, and T.Endo, 61th National Meeting of the Chemical Society of Japan, Yokohama, April 1991, Abstr., No. 4D138.

11) $\nu_{C=O}$ of **1** was 1810 cm^{-1}.[9)]

12) The initiation species of this polymerization is not clear: a very small amount of some anionic impurity is a possible candidate, although direct thermal anionic polymerization cannot be ruled out.

13) In the ^1H NMR spectrum of the polymer (**6**), *tert*-butyl group originated from the initiator ^tBuOK appeared at 1.53 ppm as a singlet peak, which suggested the formation of the linear polycarbonate.

14) Elemental analysis data of **6** supported it: Found: C, 79.84; H, 3.92. Calcd for $C_{21}H_{12}O_3$: C, 80.76; H, 3.87.

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