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

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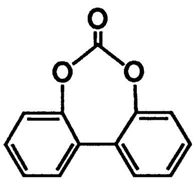
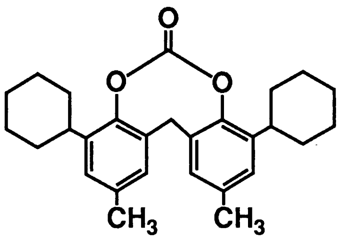
A novel aromatic cyclic carbonate (**3**) having binaphthyl structure was prepared by the reaction of 2,2'-binaphthol with 4-nitrophenyl chloroformate in the presence of a *tert*-amine. **3** polymerized very efficiently with potassium *tert*-butoxide at 20 °C to give corresponding linear polycarbonate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



1



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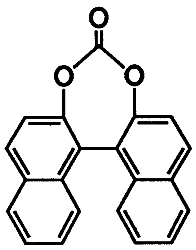
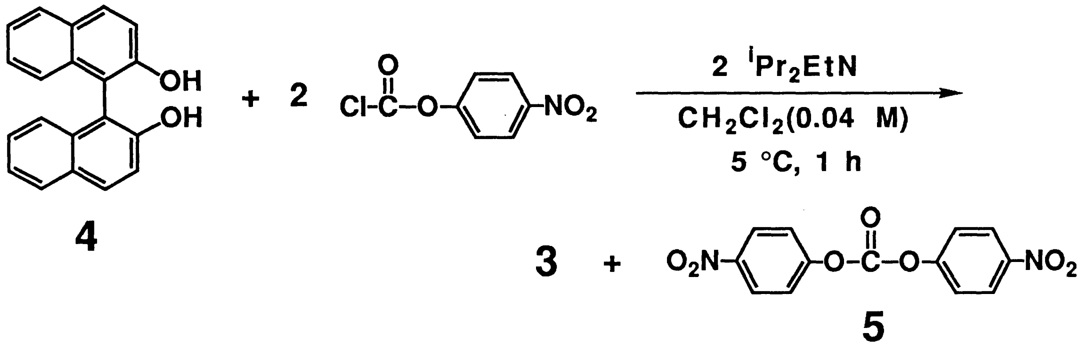


3

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)]

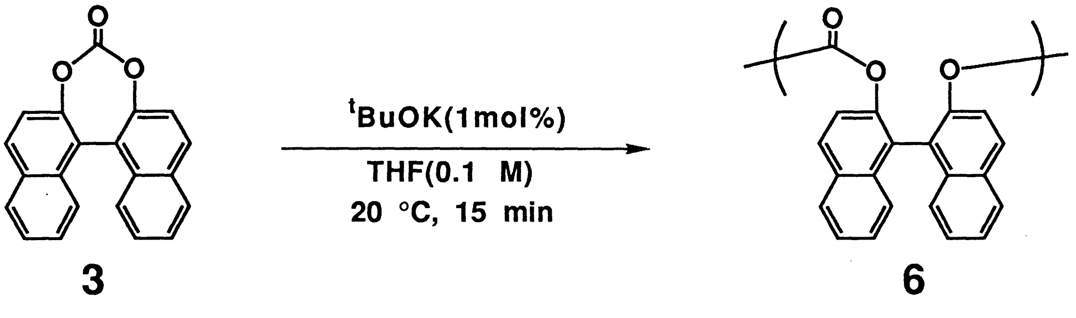
To a dichloromethane solution (40 mL) of 2,2'-binaphthol (**4**, 0.5 g, 1.75 mmol) and 4-nitrophenyl chloroformate (0.774 g, 3.84 mmol) was added dropwise ethyldiisopropylamine (0.389 g, 3.84 mmol) at 5 °C and the mixture was stirred for 1 h at 5 °C. Cyclic carbonate **3** was obtained along with bis(4-nitrophenyl)carbonate (**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.).



(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.



(2)

When **3** was treated with potassium *tert*-butoxide (ᵗBuOK,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 ᵗBuOK resulted in considerable decrease in $\overline{Mn}$ (runs 1 and 2) along with increase in molecular weight distribution ($\overline{Mw}/\overline{Mn}$). 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 $\overline{M}$n 12,800 ($\overline{M}$w 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).

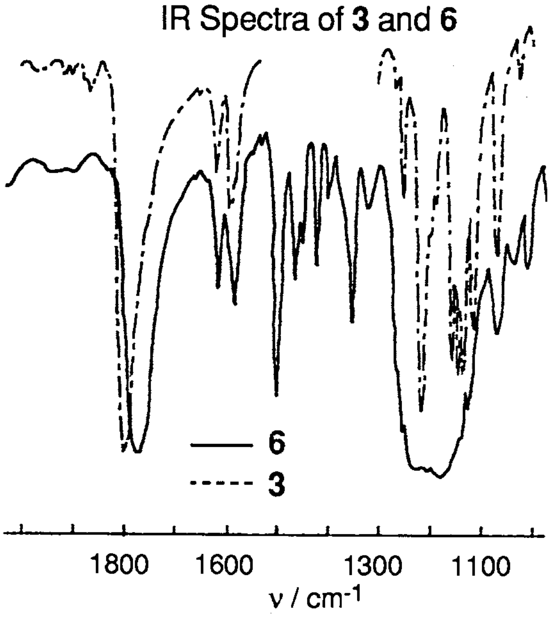
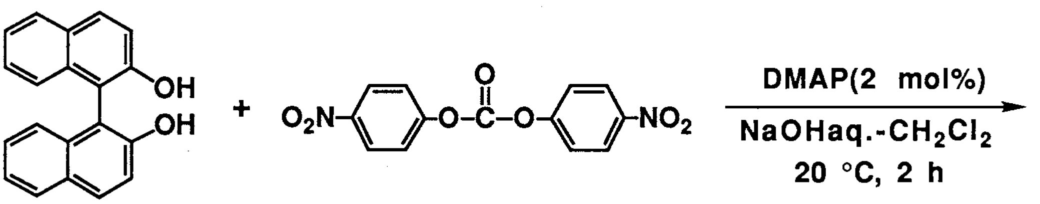


Fig. 1. IR Spectra of **3** and **6**.



4 **5** (3)

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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8) Synthesis and polymerization of several aromatic cyclic carbonates are reported in patents without details: *Japan Pat.*, 40-19709 (1965); 41-11985 (1966).
9) H.Matsuoka, T.Takata, and T.Endo, 61th National Meeting of the Chemical Society of Japan, Yokohama, March 1991, Abstr., No. 1C206: A part of the work reported in this paper has been described.
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 ^{1}H NMR spectrum of the polymer (**6**), *tert*-butyl group originated from the initiator ^{t}BuOK 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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