Poly(ether-carbonate)s from Diphenolates, Cyclic Carbonates, and Dihalo Compounds

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ABSTRACT: Reactions of dipotassium diphenolates with cyclic carbonates and α,ω -dihalo compounds in the presence of 18-crown-6 ether were studied. Poly(ether-carbonate)s with various contents of carbonate linkage or polyethers were formed in these reactions depending on the kind of diphenolate and dihalo compound and the reaction temperature. The mechanism of carbonate linkage formation involving 1,3-dioxolan-2-one ring opening was discussed in terms of results of studies on the model reaction between 2-(1-phenoxy)propyl potassium carbonate and α,α' -dibromo-*p*-xylene.

KEY WORDS Dipotassium Diphenolate / Cyclic Carbonate / α,ω -Dihalo Compound / Crown Ether / Poly(ether-carbonate) / Polyether /

Although the application of carbon dioxide as a monomer for polymer syntheses has received much attention in recent years, rather convenient reactants for synthesis of linear polycarbonates seem to be cyclic alkylene carbonates. The latter compounds are easily available by addition of carbon dioxide to oxiranes.¹

As far as the present authors know cyclic carbonates have been used for synthesis of polycarbonates by transesterification reaction with aliphatic and cycloaliphatic diols.² Ethylene and propylene carbonates were also tried to be polymerized and the products appeared to contain carbonate as well as ether linkages.³

This paper is concerned with a new route for insertion of carbonate units into linear polymer chains involving the reaction system containing dipotassium diphenolates, cyclic alkylene carbonates and α,ω -dihalo compounds. The polymer produced in this system was expected to contain both the carbonate and ether linkages, formed due to the dioxolanone ring opening by the phenolate anion attack on the ring.

It is worthwhile to notice that the reaction of dipotassium diphenolate with carbon dioxide and α,ω -dihalo compound was reported previously⁴ to produce polymers containing carbonate linkages besides ether ones. The latter linkages, however, were formed by the side reaction of the dipotassium diphenolate with α,ω -dihalo compound omitting interaction with CO₂.

EXPERIMENTAL

Materials

α,α' -Dibromo-*p*-xylene was obtained from the reaction of *p*-xylene- α,α' -diol with hydrogen bromide and was purified by crystallization from carbon tetrachloride.⁵ 4,4'-Bis(bromomethyl)biphenyl was obtained from the reaction of biphenyl with paraformaldehyde in the presence of gaseous hydrogen bromide.⁶ α,α' -Dichloro-*p*-xylene was obtained from the reaction of *p*-xylene with sulfuryl chloride carried out in the presence of benzoyl peroxide; the product was crystallized from chloroform.⁷ 1,3-Dioxolan-2-one (ethylene car-

bonate), 4-methyl-1,3-dioxolan-2-one (propylene carbonate), 4-phenyl-1,3-dioxolan-2-one, 4-allyloxymethyl-1,3-dioxolan-2-one were obtained from addition of carbon dioxide to respective oxirane according to the method reported elsewhere.¹ Solvents were purified according to commonly known methods. 18-Crown-6 ether (1,4,7,10,13,16-hexaoxacyclooctadecane) was obtained according to the method described in the literature.⁸ Dipotassium 4,4'-isopropylidenediphenolate was obtained according to the following procedure. Under a nitrogen atmosphere 5.71 g (25 mmol) of 4,4'-isopropylidenediphenol, 50 cm³ of DMSO and 50 cm³ of chlorobenzene were placed into a 200 cm³ flask, equipped with a stirrer, thermometer, dropping funnel and a condenser. The system was heated under nitrogen up to 70°C with intensive stirring and the stoichiometric amount of the concentrated, aqueous solution of KOH (6.83 g of 41.0%) was added. Water from the system was removed by azeotropic distillation with chlorobenzene. Dipotassium 1,4-cyclohexanediolate was obtained from the reaction of 1,4-cyclohexanediol with potassium in THF.⁹

Polymer Synthesis

In a 50 cm³ glass reaction flask, equipped with a stirrer 5 mmol of dipotassium diphenolate or diolate, 15 cm³ of solvent, adequate amount of cyclic carbonate and 18-crown-6 ether were placed under nitrogen. The flask content was heated for 15–60 min then 5 mmol of dihalo compound was added and heated at 80–110°C for 5–6 h. The post-reaction mixture was filtered to remove potassium halide and after evaporation *in vacuo* of the part of DMSO or other solvent the isolated product was washed with water and diethyl ether and dried at room temperature *in vacuo*.

In the case of reaction carried out under carbon dioxide pressure a 50 cm³ stainless steel autoclave was used. Into the autoclave 1.52 g (5 mmol) of dipotassium 4,4'-isopropylidenediphenolate, 0.02 g (0.7 mmol) of 18-crown-6

ether, 10 cm³ of solvent and appropriate amount of cyclic carbonate were added under nitrogen. Dibromo compound (5 mmol) was placed in a sealed glass ampoule and then introduced to the autoclave. Gaseous carbon dioxide was introduced to the system under a pressure of 30 atm and the autoclave was heated at the required temperature. After 15–60 min the ampoule was broken and the reaction was carried out for another 4–6 h. After completion of the reaction, CO₂ was released from the autoclave and from that moment the procedure was as in the method without CO₂ pressure.

*The Model Reaction of 2-(1-Phenoxy)propyl Potassium Carbonate with α,α' -Dibromo-*p*-xylene*

In a 50 cm³ pressure autoclave 1.51 g (10 mmol) of potassium 2-(1-phenoxy)propanolate obtained analogously as described elsewhere⁹ was placed under nitrogen. Then, 0.04 g (1.4 mmol) of 18-crown-6 ether, 10 cm³ of THF and 1.32 g (5 mmol) of α,α' -dibromo-*p*-xylene (placed in sealed glass ampoule) were added. Gaseous carbon dioxide was introduced to the system under a pressure of 30 atm and autoclave was heated at 100°C for 20 min. Then the ampoule was broken and the reaction was carried out for additional 5 h. After the reaction completion the autoclave was cooled, CO₂ was released, precipitate of KBr was filtered off and THF was distilled off *in vacuo*.

Product Analysis

IR spectra were recorded on a Perkin-Elmer 521 spectrophotometer. ¹H NMR spectra were recorded on a 100 MHz JEOL NMR spectrometer using TMS as an internal standard. Elemental analysis was carried out by a Perkin-Elmer 240 apparatus.

RESULTS AND DISCUSSION

The product obtained from the reaction of dipotassium 4,4'-isopropylidenediphenolate,

Figure 1. IR spectrum of the product obtained from the reaction of dipotassium 4,4'-isopropylidenediphenolate, 4-methyl-1,3-dioxolan-2-one and α,α' -dibromo-*p*-xylene (Table I, No. 5).

Figure 2. ^1H NMR spectrum of the product obtained from the reaction of dipotassium 4,4'-isopropylidenediphenolate, 4-methyl-1,3-dioxolan-2-one and α,α' -dibromo-*p*-xylene (Table I, No. 5).

4-methyl-1,3-dioxolan-2-one, and α,α' -dibromo-*p*-xylene in the presence of 18-crown-6 ether were pale-yellow colored solids, soluble in polar solvents and insoluble in water. IR and ^1H NMR spectra of representative sam-

ples of the products obtained are shown in Figures 1 and 2. In the IR spectrum, strong absorption bands at 1740–1750, 1260–1275, 1100–1150 cm^{-1} , corresponding to the stretching vibration of carbonyl groups, C–O

bonds of linear carbonate and ether bonds, respectively, were observed. In the ^1H NMR spectrum, the following signals were present: aromatic protons ($\delta=7.0$ and 7.5 ppm), methine and benzyl methylene protons neighboring with the carbonate linkage ($\delta=5.1$ ppm), benzyl methylene protons neighboring with the ether linkage ($\delta=4.7$ ppm), methylene protons neighboring with the carbonate lin-

kage ($\delta=4.1$ ppm), methylene and methine protons neighboring with ether linkage ($\delta=3.6$ ppm), isopropylidene protons ($\delta=1.4$ ppm) and methyl protons ($\delta=1.1$ – 1.2 ppm).

On the basis of these results, the following reaction scheme could be considered as possible reaction route to form poly(ether-carbonate)s.

Dipotassium diphenolate I reacts with cyclic carbonate II leading to 1,3-dioxolan-2-one ring opening product according to eq 1. The product formed undergoes then reaction with the dihalo compound III yielding poly(ether-carbonate), according to eq 2. The presence of the signal of benzyl methylene protons ($\delta=4.7$ ppm) in the ^1H NMR spectrum, however, indicates the polymer chain growth not involving the cyclic carbonate contribution in 100%. Yields and some characteristic data for the poly(ether-carbonate)s formed in the reaction of I, II, and III are presented in Table I.

The halogen content in these products indicates their rather low molecular weight ($n=5$ – 8).

The carbonate linkages content in poly(ether-carbonate)s was found to be strongly dependent on the reaction temperature. At temperature in the range of 100 – 120°C the reaction with a participation of cyclic carbonate predominates due to the facile attack of phenolate anion onto 1,3-dioxolan-2-one ring which results in the relatively high content of carbonate linkages in the product (Table I, No. 4–6). Decreasing the reaction tempera-

Table I. Reaction of dipotassium 4,4'-isopropylidenediphenolate, 4-methyl-1,3-dioxolan-2-one, and α, α' -dihalo-*p*-xylene

Run no.	X	Dihalo compound g (mmol)	Propylene carbonate g (mmol)	Solvent	Temp °C	Reaction time		Product yield g	X_c^a %	Br(Cl) ^b %	η_{sp}^c dl g ⁻¹
						I step	II step				
						min	h				
1	Br	1.32 (5)	1.12 (11)	DOX	60	60	5	1.41	0	10.1	0.09
2	Br	1.32 (5)	6.00 (60)	—	70	60	6	1.32	0	7.6	0.12
3	Br	1.32 (5)	1.12 (11)	DMSO	90	60	4	1.50	43	5.3	—
4	Br	1.32 (5)	1.12 (11)	DMSO	100	30	6	1.52	73	5.0	—
5	Br	1.32 (5)	1.12 (11)	DMSO	110	60	5	1.60	80	6.8	0.10
6	Br	1.32 (5)	1.12 (11)	DMSO	120	60	6	1.48	78	—	—
7	Br	1.32 (5)	6.00 (60)	—	120	60	5	0.54	5 ^d	—	—
8	Br	1.32 (5)	6.00 (60)	DMSO	120	—	6	0.81	5	—	—
9	Cl	1.25 (5)	6.00 (60)	DMSO	120	—	6	1.10	15	6.2	—
10	Br	1.32 (5)	1.12 (11)	DMSO	170	60	5	0.83	0	5.2	—
11	Br	1.32 (5)	1.12 (11)	DMSO	160	60	5	0.90	20 ^e	6.8	0.11

^a X_c , mole fraction of carbonate linkage calculated from: $X_c = 1 - (3/2)a$, where a , the intensity ratio of methylene benzyl protons signals neighbouring with ether linkage ($\delta = 4.7$ ppm) to isopropylidene protons signals ($\delta = 1.5$ ppm) in ¹H NMR spectrum.

^b The halogen content in the product in wt%.

^c The specific viscosity of a 2% solution in DMSO at 25°C.

^d Dipotassium 4,4'-isopropylidenediphenolate contained small amount of free hydroxyl groups.

^e The reaction was carried out under a pressure of 30 atm of CO₂.

ture causes the formation of the polymer with enhanced ether linkages content and at temperature of 70°C and lower only polyether was obtained (Table I, No. 1—2). In the latter reaction no evolution of carbon dioxide was observed which indicates the cyclic carbonate is not susceptible to phenolate anion attack at relatively low temperature. It is interesting to notice that the reaction of I, II, and III run at 110°C with the reactants mixed simultaneously gave polymer with a high content of ether linkages (Table I, No. 8). Even for considerable excess of cyclic carbonate in the above

system the rate of diphenolate reaction with α, α' -dibromo-*p*-xylene is much higher than with 1,3-dioxolan-2-one ring. Replacement of the dibromo compound with less reactive α, α' -dichloro-*p*-xylene resulted in enhancement of carbonate linkages content in the product obtained (Table I, No. 9). Polyether as the only product has been found to be formed when dipotassium 4,4'-sulfonyldiphenolate instead of the salt of less acidic diphenol (4,4'-isopropylidenediphenol) was used for the reaction in the system studied, even at temperature higher than 110°C (Table II, No. 4) (eq 3).

It was found in the course of further studies that the formation of poly(ether-carbonate) depends also on the purity of dipotassium salt of diphenol. The presence of free hydroxyl

group in the salt causes the decarboxylation side reaction (eq 4) and polyether is formed as the main product (Table I, No. 7).

The decarboxylation was also observed when the reaction of I, II, and III was carried out at temperature higher than 150°C. The product of such reaction (Table I, No. 10) did not exhibit absorption bands at 1740—1750 cm⁻¹ in the IR spectrum. In the ¹H NMR spectrum of that product signals of methylene and methine protons neighboring with ether linkage were observed (Figure 3). These data indicate

the formation of polyether according to eq 5 and 6. Similar decarboxylation reaction has been reported previously¹⁰ for the copolymerization of cyclic carbonates with cyclic anhydrides catalyzed by alkali metal salts. The studied reaction of I, II, and III run at high temperature, under carbon dioxide pressure was found to yield products containing carbonate linkages, which is evidenced by

Figure 3. ¹H NMR spectrum of the product obtained from the reaction of dipotassium 4,4'-isopropylidenediphenolate, 4-methyl-1,3-dioxolan-2-one and α,α' -dibromo-*p*-xylene (Table I, No. 10).

^1H NMR and IR spectroscopic analyses (Table I, No. 11).

In order to confirm the mechanism of the reaction proceeding in the system I, II, and III the model reaction of 2-(1-phenoxy)propyl potassium carbonate with α,α' -dibromo-*p*-xylene was carried out. The reaction of 2-(1-phenoxy)propyl potassium carbonate (obtained from potassium 2-(1-phenoxy)propanolate (V) and carbon dioxide) with III was found to yield ether carbonate compound VII. The same compound VII was obtained from the reaction of potassium phenolate and 4-methyl-1,3-dioxolan-2-one (scheme). It has been

Table II. Reaction of dipotassium diphenolate (diolate), cyclic carbonate, and dibromo compound

Run. no.	Diphenolate (diolate)	Cyclic carbonate	Dibromo compound	Solvent	Temp °C	Reaction time		Product yield g	X_c^a %
						I step	II step		
						min	h		
1	IPP ^b	EC ^c	BBB ^d	DMSO	110	60	5	1.50	75
2	IPP	StC ^e	BBB	DMSO	110	60	6	1.56	65
3	IPP	AlC ^f	BBB	DMSO	110	60	5	1.47	72
4	IPP	PC ^g	BBP ^h	DMSO	100	60	5	1.30	62
5	SP ⁱ	PC	BBB	—	130	110	5	1.30	0
6	CHD ^j	PC	BBB	DOX	40	60	6	1.05	45
7	CHD	PC	BBB	—	60	60	6	1.60	78
8	CHD	PC	BBB	DOX	110	40	5	1.71	80

^a X_c , mole fraction of carbonate linkage.

^b Dipotassium 4,4'-isopropylidenediphenolate (IPP).

^c 1,3-Dioxolan-2-one (EC).

^d α,α' -Dibromo-*p*-xylene (BBB).

^e 4-Phenyl-1,3-dioxolan-2-one (StC).

^f 4-Allyloxymethyl-1,3-dioxolan-2-one (AlC).

^g 4-Methyl-1,3-dioxolan-2-one (PC).

^h 4,4'-Bis(bromomethyl)biphenyl (BBP).

ⁱ Dipotassium 4,4'-sulfonyldiphenolate (SP).

^j Dipotassium 1,4-cyclohexanediolate (CHD).

found that in the post-reaction mixture of VI (obtained from V and CO₂) with dibromo compound small amount of 4-methyl-1,3-dioxolan-2-one, besides the main product VII, was present. This result shows the possibility of the "back-biting" type reaction followed by subsequent reaction of phenolate anion with dibromo compound leading to product with ether linkage.

The formation of cyclic carbonate is influenced by the presence of phenoxy group in VI. It seems interesting to mention that an analogous compound with alkoxy group instead of the phenoxy one does not form cyclic carbonate which was found for the reaction system consisting of diethylene glycol, CO₂ and dibromo compound.¹¹

It was found that by using various cyclic carbonates for the reaction with dipotassium diphenolate and dibromo compound one may obtain poly(ether-carbonate)s with various pendant groups (Table II, No. 2 and 3).

When dipotassium 1,4-cyclohexanediolate was applied for the reaction with 4-methyl-1,3-dioxolan-2-one and α,α' -dibromo-*p*-xylene corresponding poly(ether-carbonate) was

formed at relatively low temperature in a high yield (Table II, No. 6—8).

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