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Active sites, nature and mechanism of carbon dioxide–propylene oxide copolymerization and cyclization reactions employing organozinc–oxygen catalysts

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Reaction of carbon dioxide with propylene oxide in the presence of catalysts with condensed zinc species (derived from diethylzinc and dihydric phenols, e.g. catechol $o-C_6H_4(OH)_2$ and saligenin $o-HOC_6H_4CH_2OH$) yields poly(propylene carbonate) as well as propylene carbonate. The above reaction in the presence of catalysts with noncondensed zinc species (derived from diethylzinc and phenol) yields propylene carbonate as the main product, but in relatively low yield. The mechanism of the linear and cyclic carbonate formation is discussed in terms of the nature of the catalyst's active sites for both types.

Keywords: Carbon dioxide, propylene oxide, organozinc–oxygen compounds, poly(propylene carbonate), propylene carbonate, copolymerization, cyclization, organozinc catalyst

INTRODUCTION

New synthetic methods which convert small molecules like carbon dioxide into products of greater complexity, especially into high-molecular-weight polymers, are of growing interest from both the theoretical and industrial points of view. The copolymerization of carbon dioxide and propylene oxide leading to poly(propylene carbonate) has, for the past 20 years, been among such methods.[1] Catalysts for this copolymerization have been usually derived from reactions of diethylzinc with di- or tri-protic compounds such as water, polyhydric phenols or aromatic hydroxycarboxylic acids as well as from reactions of inorganic zinc compounds such as zinc oxide or zinc hydroxide with dicarboxylic acids.[2,3] A common feature of all these catalysts is the appearance of condensed zinc species in their structure. The carbon dioxide–propylene oxide copolymerization in the presence of the above catalysts is usually accompanied by the formation of the cyclic carbonate, propylene carbonate, as a by-product. This has been referred to as the subsequent depolymerization of poly(propylene carbonate)[4] and the side reaction of the cyclization of comonomers.[5]

Employing novel organozinc–oxygen catalysts based on diethylzinc and catechol[6] led the author recently[7] to suggest a proposal explaining the nature of the catalyst's active sites and the mechanism of the linear and cyclic carbonate formation in the carbon dioxide–propylene oxide copolymerization system with catalysts containing condensed zinc species. The present work has been undertaken to compare the behaviour of organozinc–oxygen compounds, containing condensed and noncondensed zinc species, as the linear and cyclic carbonate formation promoters. It deals with reactions of carbon dioxide and propylene oxide in the presence of catalysts derived from systems such as diethylzinc–dihydric phenol and/or phenol.

EXPERIMENTAL

All the reactions were performed under an inert atmosphere of de-oxygenated and dried nitrogen. Catalyst components, i.e. diethylzinc, catechol, saligenin and phenol, propylene oxide and 1,4-dioxane were purified by distillation or sublimation before use by means of procedures described previously.[4,6]

Catalysts were prepared by dropping the appropriate phenol solution into the diethylzinc (or respective ethylzinc phenolate) solution in 1,4-dioxane at room temperature under vigorous stirring. When ethane evolution was complete the post-reaction solution (or suspension) was diluted with 1,4-dioxane to a concentration of $[Zn] = 0.25 \times 10^{-3}$ g-atom cm^{-3} (mol cm^{-3} Zn^{2+}).

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Table 1 Linear and cyclic carbonate formation in reactions of carbon dioxide with propylene oxide in the presence of catalysts containing noncondensed (**1–4**) and condensed (**5–11**) zinc species[a]

Catalyst			CO_2-propylene oxide copolymer			Propylene carbonate
	Components (molar ratio)	Soluble	(g)	X_c[c]	$10^{-2}[\eta]$[d]$(cm^3\,g^{-1})$	(g)
1 EtZnOPh	$ZnEt_2/PhOH$ (1:1)	Yes	0.00			0.00
2 EtZnOArOZnEt	$ZnEt_2/HOArOH$ (2:1)	Yes	0.00			0.00
3 PhOZnOPh	$ZnEt_2/PhOH$ (1:2)	No	Traces			0.27
4 PhOZnOPh·EtZnOPh	$ZnEt_2/PhOH$ (2:3)	Yes	Traces			0.19
5 $Et(ZnOArO)_7ZnEt$	$ZnEt_2/HOArOH$ (8:7)	Yes	0.34	0.95	0.35	0.21
6 EtZnOArOZnOPh	$ZnEt_2/HOArOH/PhOH$ (2:1:1)	Yes	0.85	0.96	0.55	0.54[e]
7 PhOZnOArOZnOPh	$ZnEt_2/HOArOH/PhOH$ (2:1:2)	No	0.15			0.14
8 $Et(ZnOArO)_2ZnEt$	$ZnEt_2/HOArOH$ (3:2)	Yes	2.20	0.96	1.08	1.07[e]
9 $Et(ZnOArCH_2O)_2H$[f]	$ZnEt_2/HOArCH_2OH$ (1:1)	No	0.41	0.94	1.01	0.27
10 $EtZnOArCH_2OZnOPh$	$ZnEt_2/HOArCH_2OH/PhOH$ (2:1:1)	No	0.25	0.94	0.95	0.17
11 $(EtZnOArCH_2O)_2Zn$	$ZnEt_2/HOArCH_2OH$ (3:2)	Yes	1.80	0.95	0.69	0.64

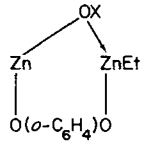
[a] For reaction conditions, see Experimental section. Pressure in the autoclave of ca. $6\times10^6\,Nm^{-2}$. Ar = o-C_6H_4. [b] Methanol-insoluble high-molecular-weight fraction. [c] Carbonate linkage mole fraction. [d] In benzene at 35°C. [e] See Ref. 7. [f] Obtained at 50°C.

Reactions of carbon dioxide with propylene oxide were run in a 95 cm^3 stainless-steel autoclave at 35 °C for 44 h using 16 cm^3 of the catalyst solution (or suspension) (4×10^{-3} g-atom Zn), 5.8 g (0.10 mol) of propylene oxide and *ca* 11 g (0.25 mol) of carbon dioxide. The reaction was stopped by decompression of the autoclave and the product was dissolved in methylene dichloride. The solution obtained was sampled by IR analysis (Spekord 71) and was then washed with 10% hydrochloric acid and then with water. A high-molecular-weight copolymer fraction was isolated from the solution by pouring it into a large quantity of methanol under stirring and it was purified by dissolving in methylene dichloride and reprecipitation from methanol; it was then dried at 50°C *in vacuo*.

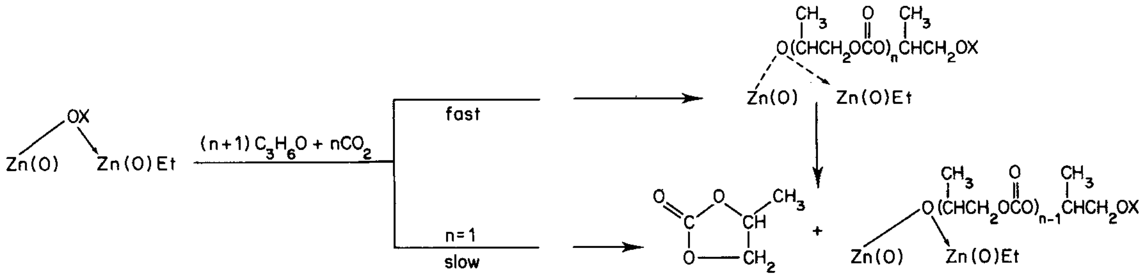
The copolymer was characterized by means of elemental analysis (Perkin–Elmer 240 microanalyser) and viscosity measurement in benzene at 35°C using an Ubbelohde viscometer. The content of propylene carbonate in the post-reaction mixture was determined from the proportion of absorption peaks at 1750 cm^{-1} and 1800 cm^{-1} in the IR spectrum.

RESULTS AND DISCUSSION

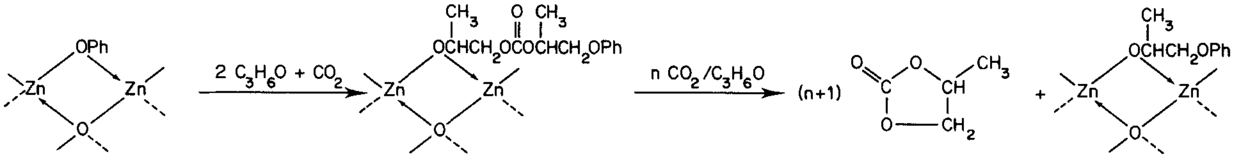
Reactions of carbon dioxide with propylene oxide were carried out in the presence of the catalysts listed in Table 1. Zinc monophenoxide type derivatives, i.e. those containing the ZnO unit as in ethylzinc phenoxide (**1**) and bis(ethylzinc) catecholate (**2**), hardly catalyse any carbon dioxide–propylene oxide reactions. Zinc derivatives with the OZnO unit such as zinc diphenoxide (**3**) and its equimolar complex with **1** (**4**) exhibit some catalytic activity in the carbon dioxide–propylene oxide reaction system, and the cyclic carbonate, propylene carbonate, is practically the sole reaction product. Only zinc derivatives containing both the ZnO and OZnO or other such units present in their structure, i.e. the zinc catecholate–diethylzinc derivative (**5**), ethylzinc phenolatozinc catecholate (**6**), bis(phenolatozinc) catecholate (**7**), zinc bis(2-ethylzincoxyphenoxide) (**8**), 2-hydroxymethylphenolatozinc 2-ethylzincoxyphenylmethoxide (**9**), phenolatozinc 2-ethylzincoxyphenylmethoxide (**10**), zinc bis(2-ethylzincoxyphenylmethoxide) (**11**), catalyse the carbon dioxide–propylene oxide reaction yielding the linear carbonate (the copolymer with predominating carbonate linkages which is proved by the elemental analysis) as well as the cyclic carbonate (Table 1).



Scheme 1 Coordination involving the X group in **8** and complexation with 1,4-dioxane are omitted from the formula.



Scheme 2 Eventual coordination involving X group and complexation with 1,4-dioxane are omitted from the formulae. In the case of saligenin-based catalysts containing alcoholatozinc species, carbon dioxide should initiate the copolymerization.



Scheme 3 The cyclisation mechanism. Complexation with 1,4-dioxane is omitted from the formulae.

Considering the above, this would suggest that carbon dioxide–propylene oxide copolymerization catalysts have active sites of similar nature to that postulated recently[7] for catalysts **6** and **8** (see Scheme 1).

The origin of the catalytic activity of catalysts **5–11** seems to lie in the presence of two sp^3-hybridized zinc atoms, linked with each other via an oxygen bridging atom. It seems clear that heterogeneous catalysts can accommodate active sites of this type involving also the respective intermolecular coordination of the OX group onto the zinc atom at the surface edge. The linear carbonate is formed via alternative comonomer insertions into a Zn–OX bond according to the mechanism postulated recently.[7] The formation of the cyclic carbonate is probably due to an internal depolymerization reaction according to the mechanism also postulated recently.[7] Thus the carbon dioxide–propylene oxide reaction pathway in the presence of catalysts containing condensed zinc species may be represented by Scheme 2.

The competition between the growth of linear carbonate and the internal reaction leading to cyclic carbonate is biased towards the former reaction in the early stages of the reaction catalysed by catalysts containing condensed zinc species. On the other hand, the cyclization reaction predominates when catalysts containing noncondensed zinc species like **3** and **4** are used for the carbon dioxide–propylene oxide reaction. Active sites of such catalysts having four-membered Zn_2O_2 rings in their structure, formed by intermolecular complexation of zinc atoms via oxygen bridging atoms, hardly catalyse the insertion of the next carbon dioxide molecule into a chain already containing the carbonate unit. The competition between the carbon dioxide monomer and the carbonate unit for interaction with the active site is biased in the case of catalysts with noncondensed zinc species towards the latter unit, and the cyclization can take place according to Scheme 3.

For the carbon dioxide–propylene oxide reaction according to Scheme 3 one can argue that the presence of 1-phenoxy-2-propanol as well as phenol found in the hydrolysed residue of catalyst **3** in the post-reaction mixture suggests that scheme 3 is the correct route.[8]

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