

STRUCTURES OF THE PRODUCTS OF THE REACTIONS OF DIETHYLZINC WITH TRIHYDRIC PHENOLS

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Summary

Reactions of diethylzinc with 1,2,3-trihydroxybenzenes containing substituent X (X = H, C₂H₅, C₆H₁₁, C(CH₃)₃, Cl, Br, COCH₃) in the aromatic ring at a 2/1 molar ratio have been carried out in tetrahydrofuran and 1,4-dioxane solutions. The kinetics of the reactions have been studied and the products have been characterized by means of ¹H NMR spectroscopy and cryoscopy. The structures of the intermediates and the final products of the reactions were determined.

Introduction

The products of the reaction of diethylzinc (ZnEt₂) and pyrogallol (PG) at a molar ratio of 2/1 are known to be catalysts of the alternating copolymerization of CO₂ and propylene oxide, yielding poly(propylene carbonate) [1]. It has recently been found [2] that the yield and the molecular weight of the resulting copolymer can be increased considerably by modification of the catalytic system consisting of introducing alkyl or halogen substituents into the aromatic ring of the PG molecule. During research on the process of copolymerization of CO₂ and propylene oxide in the presence of a catalytic system modified in this way, the authors noticed the course of the consecutive degradation and depolymerization of the copolymer formed. Metal atoms of the catalyst introduced into the copolymerization system were suspected to be responsible for the copolymer destruction processes. Investigation of a simplified model system allowed the mechanism of poly(propylene carbonate) decomposition by organozinc compounds to be postulated [3]; however, it needed to be proved under real conditions of CO₂/propylene oxide copolymeriza-

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tion. Besides, for an explanation of the phenomena occurring in the copolymerization system catalysed by the compounds produced from ZnEt_2 and trihydric phenols, knowledge of the products' structures is essential.

This sequence of research was undertaken by Tsuruta et al. in investigations of propylene oxide polymerization in the presence of a catalytic system produced from ZnEt_2 and methanol. After choosing conditions of the catalyst's formation ensuring the highest catalytic activity of the product formed [4], the structure of the catalyst's molecule was described [5] and the first step of propylene oxide polymerization, i.e. inclusion of a monomer molecule into the catalyst's molecule, was studied [6].

Concerning the products of the reaction trihydric phenols and ZnEt_2 , an attempt was made to identify those obtained from PG [7], although their coordination structures were not described. Identification of the active centre of the catalyst based on PG allowed the mechanism of alternating copolymerization of CO_2 and propylene oxide to be suggested [8]. However, the copolymerization mechanism proposed gave no explanation of the catalyst's low efficiency which meant the catalyst had to be applied in a considerable amount in relation to the co-monomers.

The present paper deals with the reactions of 1,2,3-trihydroxybenzenes and ZnEt_2 conducted in cyclic ethers as solvents, the products of which showed especially high activity as catalysts of CO_2 and propylene oxide copolymerization [2]. The aim of this work was to determine the mechanism of the reaction and the structures of the products formed. According to the results of preceding investigations of the analogous reaction of monohydric phenols [9], the reaction under study is considered in terms of polycondensation.

Results and discussion

The reactions of diethylzinc (ZnEt_2) and a series of 1,2,3-trihydroxybenzenes (XPG) * in a molar ratio of 2/1 were carried out at a temperature of 0°C in a mixture of 1,4-dioxane (DOX) and tetrahydrofuran (THF) as solvent. The course of the reactions, monitored by measurement of the volume of ethane evolved within the reaction time is illustrated in Fig. 1.

As can be seen from Fig. 1., the first stage of ethane evolution is very fast, irrespective of the kind of pyrogallol substituent X. The volume of ethane evolved in the first stage corresponds to acidolysis of half the amount of ethyl groups in ZnEt_2 . Taking into account the fact that ZnEt_2 is more active in the reactions with phenols than the corresponding phenoxyethylzinc formed as an intermediate [9], it can be assumed that the fast ethane evolution is caused by the reaction of ZnEt_2 , and the

* XPG: PG, benzene-1,2,3-triol, (pyrogallol);
 4-EtPG, 4-ethylbenzene-1,2,3-triol;
 4-CHPG, 4-cyclohexylbenzene-1,2,3-triol;
 4-CIPG, 4-chlorobenzene-1,2,3-triol;
 4-BrPG, 4-bromobenzene-1,2,3-triol;
 4-AcPG, methyl 2,3,4-trihydroxyphenyl ketone;
 5-BuPG, 5-(α, α)-[dimethylethyl]benzene-1,2,3-triol;
 4,6-Bu₂PG, 4,6-bis[(α, α)-dimethylethyl]benzene-1,2,3-triol.

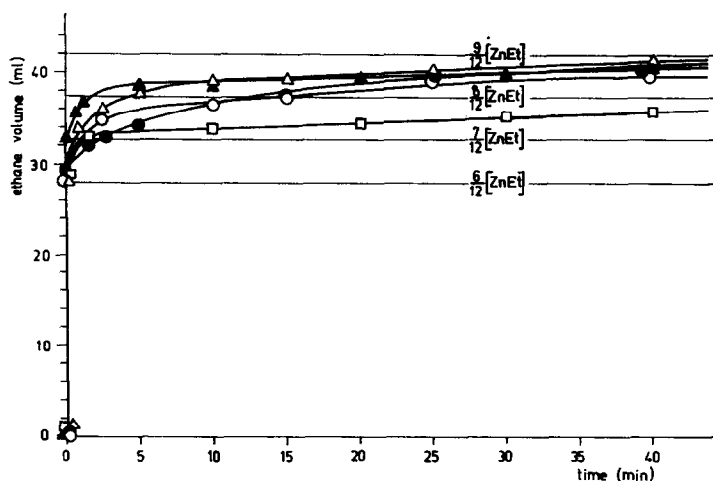
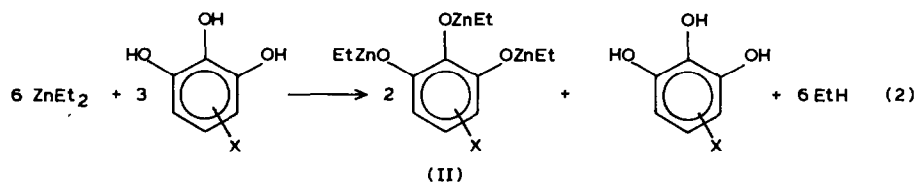
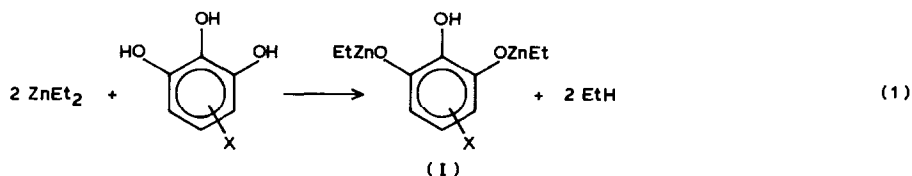


Fig. 1. Reactions of ZnEt_2 and trihydric phenols (PG Δ , 5-BuPG \blacktriangle , 4-EtPG \circ , 4-CIPG \bullet and 4-BrPG \square) in a 2/1 molar ratio in DOX/THF solution at 0°C . The volume of ethane evolved plotted as a function of the reaction time.

slower one, by the reaction of the ethylzincoxy compound already formed. Two pathways, described by eqs. 1 and 2, are possible for the first stage of the reaction:

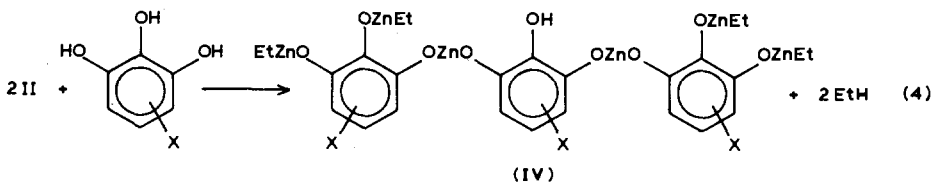
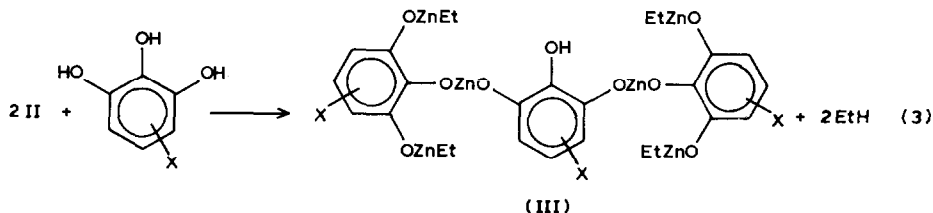


The reaction course corresponding to eq. 2 was mentioned previously [7] for the PG/ ZnEt_2 system. The probability of the course of reaction following eq. 1 or eq. 2 depends on the reactivity of the numerous hydroxyl groups in trihydric phenols against ZnEt_2 which can be different in the case of PG derivatives substituted with various substituents X. The course of the reaction can also depend on the procedure according to which the reaction was carried out. The procedure applied for preparing the organozinc catalysts for copolymerization of carbon dioxide and propylene oxide, based upon adding the trihydric phenol solution dropwise to the ZnEt_2 one [2,8], favours the course given by eq. 2, since the first stage of the reaction proceeds in an excess of ZnEt_2 . Since we are interested in the formation of

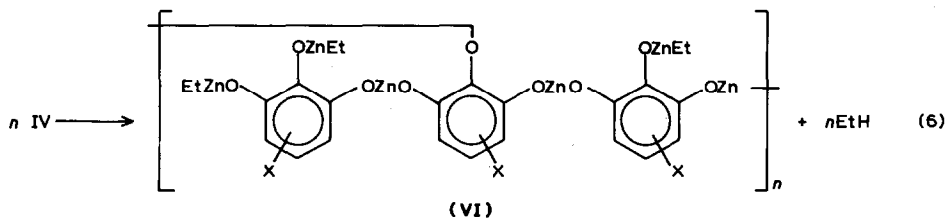
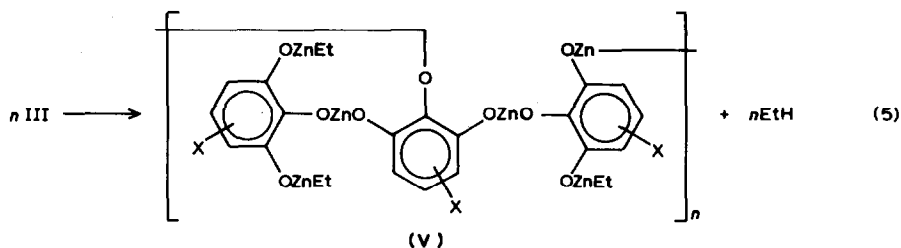
products which act as catalysts of CO_2 and propylene oxide copolymerization, the rest of this paper will deal with the reaction whose first stage is described by eq. 2, without considering the probability of the reaction proceeding according to eq. 1. Such treatment of the ZnEt_2/PG reaction course seems to be reasonable, especially when it is considered that the reaction of ZnEt_2 with dihydric phenol, like resorcinol, was previously found [10] to produce 1,3-bis(ethylzincoxy)benzene in the first stage, irrespective of the molar ratio of diethylzinc to resorcinol in the feed.

1,2,3-Tris(ethylzincoxy)benzene (II, $\text{X} = \text{H}$) was obtained in DOX solution as a product of the reaction of ZnEt_2 and PG at a 3/1 molar ratio. It was subjected to molecular weight determination by means of cryoscopy without isolation from the solution. The result obtained (molecular weight found: 410; II calcd., $\text{X} = \text{H}$: 405) indicates that II exists as a monomer in DOX solution. It is worthwhile noting that it can associate during evacuation of the solvent, resulting in a relatively stable aggregate of association degree $n = 8-12$ which cannot be destroyed by redissolving [7].

Compounds of general formula II can continue the reaction with unreacted trihydric phenol, although the reaction rate is much slower than that of the first stage. The structure of the product formed in the second stage of the reaction was determined from the reactivities of particular ethylzinc groups in II and particular hydroxyl groups in trihydric phenol. Taking into account the fact that the replacement of a phenol active proton with a Zn atom decreases the activity of the hydroxyl group in the *ortho* position but in the same reaction practically does not affect that group in the *meta* position, two paths of the second stage of the reaction under study, described by eqs. 3 and 4, should be expected:



As was established in the investigations on the reaction of ZnEt_2 and monofunctional phenols in cyclic ethers [9], the activity of phenoxyethylzinc in the reaction with phenol was increased by donor substituents and decreased by acceptor ones. The choice of the reaction pathway between those described by eqs. 3 and 4 depends on the kind of substituent X. Nevertheless, the reaction between the molecules of III or IV continues until all the hydroxyl protons are replaced by Zn atoms, according to eq. 5 or 6, respectively.



The course of the reaction described by eqs. 3 and 5 or eqs. 4 and 6 was confirmed by kinetic studies of the system 1,2,3-tris(ethylzincoxy)benzene/pyrogallol. The aim of the investigation was to measure the reactivity of PG hydroxyl groups as the rate of ethane evolution, therefore PG was treated with an excess of the organozinc reagent. As can be seen from Fig. 2, in which the ethane volume and the rate of evolution are plotted as functions of the reaction time, the reaction consisted of three stages corresponding to the conversion of particular hydroxyl groups of PG. The rate of ethane evolution decreased in successive stages, achieving a relatively low value in the third one. It should be noted that the differences in the

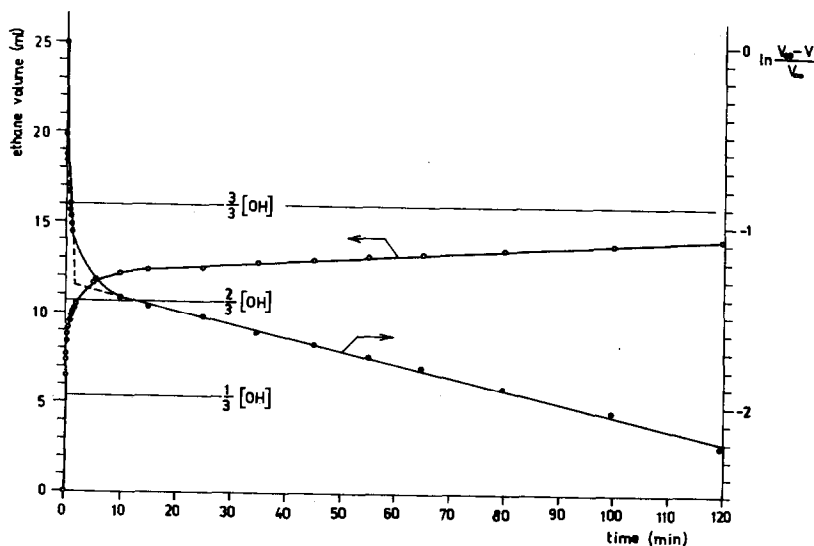


Fig. 2. Reaction of 1,2,3-tris(ethylzincoxy)benzene and pyrogallol in DOX/THF solution at 0°C. The volume of ethane evolved and the rates of the reaction stages are plotted as functions of the reaction time.

TABLE 1

¹H NMR SPECTRA^a OF THE PRODUCTS OF THE (2/1) REACTION OF ZnEt₂ AND XPG

No.	XPG	$n_{\text{ZnEt}}^b/n_{\text{Ar}}$	Chemical shift (δ ppm)				
			Aromatic ^c	Hydroxyl	Ethylzinc ^c		Substituent
					CH ₂	CH ₃	
1	PG	1.0	6.83 6.50	–	0.39	1.30	–
2	4-CHPG	1.0	6.60 6.50 6.40	–	0.34	1.12	1.78 1.37
3	5-BuPG	1.1	6.55 6.40 6.10	–	0.35	1.20	1.25
4	4-BrPG	1.2	6.97 6.72 6.37 6.12	–	0.30	1.22	–
5	4-CIPG	1.7	6.85 6.66 6.45 6.20	2.30	0.23	1.12	–
6	4-AcPG	1.6	7.10 6.50	2.32	0.04	1.17	2.60
					0.28 ^d	1.25 ^d	
					0.40 ^d		
7	4,6-Bu ₂ PG	2.0	6.52	–	0.67	1.32	1.47
					0.04 ^d	1.09 ^d	

^a 100 MHz, solvent 1,4-dioxane, temperature 25°C. ^b The molar ratio of the ethylzinc groups to the aromatic ones was calculated from the intensities of the corresponding signals. ^c Shifts of the maxima of broad signals. ^d Multiplication of signals was visible.

reaction rates of the successive stages were so high that each part of the plot illustrates each separate stage of the reaction.

The products formed in the reaction of ZnEt₂ and XPG in a 2/1 molar ratio were examined by means of ¹H NMR spectra, the details of which are collected in Table 1. The different values of the intensities of the ethylzinc signals related to those of the aromatic protons for various XPG reaction products indicate that the spectra were recorded at various stages of the reaction, the rate of which depends strongly on the kind of substituent X, and they could contain signals corresponding to the products of general formula II, III, IV, V and VI. The presence of products of general formula III or IV is demonstrated directly by the signals appearing at δ 2.3 ppm (Table 1, Nos. 5 and 6) which can be attributed to the hydroxyl groups placed in the *ortho* position to two zincoxy groups. The ¹H NMR spectra of the XPG/ZnEt₂ reaction products (data in Table 1) contain broadened and badly resolved signals of aromatic protons, shifted to higher values of δ in relation to those of the corresponding XPG (data in Table 2). This is evidence of the high coordination of the non-bonding electrons of oxygen to the zinc atoms which can change the inductive effect of oxygen on the aromatic ring. The shift and the lack of resolution of the ethylzinc signals confirms the intermolecular coordinations of the zinc atoms with the oxygen ones.

The molecular weights of the final products of the reaction of XPG and ZnEt₂ at a 1/2 molar ratio were measured by means of cryoscopy. The reactions were carried out in DOX solution until an amount of ethane corresponding to 100% conversion of the hydroxyl groups was evolved. The products were not isolated from the solution and their masses were calculated by subtracting the mass of ethane evolved from the mass of the substrates. The content of dissolved ethane determined from the ¹H NMR spectra was taken into account in the calculations since it would influence the result strongly. The mean molecular weights and the calculated contents of aromatic rings in the molecule are given in Table 3.

TABLE 2

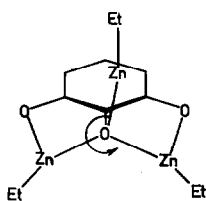
 ^1H NMR SPECTRA OF XPG ^a

No.	XPG	Chemical shift (δ ppm)						
		Hydroxyl			Aromatic			Substituent X
		OH(1)	OH(2)	OH(3)	H(4)	H(5)	H(6)	
1	PG	7.30	7.02	7.30	6.25	6.50	6.25	–
2	4-CHPG	7.16	6.90	6.97	–	6.40	6.16	2.62 1.78 1.37
3	5-BuPG	7.15	6.80	7.15	6.26	–	6.26	1.24
4	4-BrPG	7.47	7.38	7.47	–	6.73	6.23	–
5	4-CIPG	7.47	7.47	7.62	–	6.66	6.30	–
6	4-AcPG	8.12	7.65	12.60	–	7.18	6.35	2.50
7	4,6-Bu ₂ PG	6.83	6.70	6.83	–	6.52	–	1.40

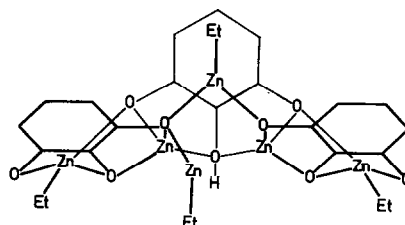
^a 100 MHz, solvent 1,4-dioxane, concentration 0.17 mol l⁻¹, temperature 25°C.

On the basis of the results obtained, the structures of the intermediates and of the end products of the XPG/ZnEt₂ reaction for various kinds of substituents X can be suggested.

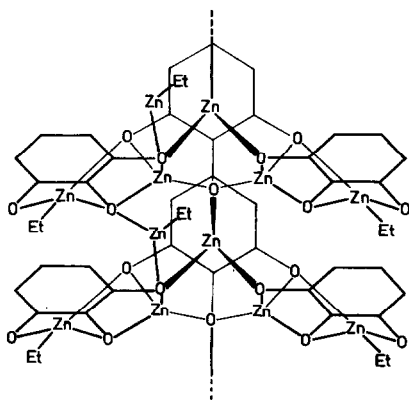
PG and its alkylated and halogenated derivatives react with ZnEt₂ according to eqs. 2, 3 and 5 describing the successive stages of the reaction. The structures of intermediates II and III and of the final products V formed in the reaction of PG and ZnEt₂ are presented.



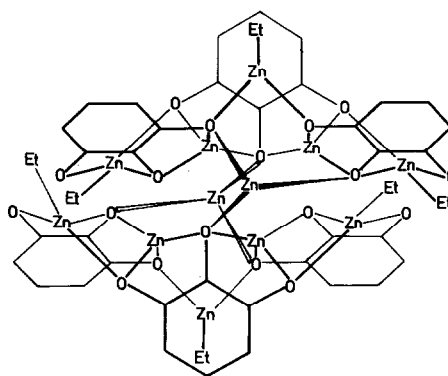
II (X = H)



III



Va



Vb

TABLE 3

MOLECULAR WEIGHTS ^a OF THE PRODUCTS OF THE REACTION OF ZnEt₂ AND XPG (2/1) IN 1,4-DIOXANE

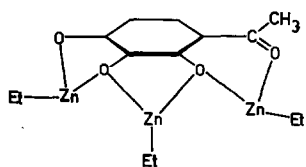
No.	XPG	Molecular weight	<i>n</i> ^b
1	PG	2900	10.28
2	4-CHPG	2150	5.91
3	5-BuPG	2020	5.94
4	4-CIPG	1920	6.08
5	4-EtPG	2610	8.42
6	4-AcPG	> 5000 ^c	> 15

^a Based on the standard freezing point depression measurement of the post-reaction mixture. ^b Degree of XPG polycondensation calculated as the content of benzene rings in the product molecule from formula V or VI. ^c Calculated from the sensitivity of the apparatus, as no depression of the freezing point was observed.

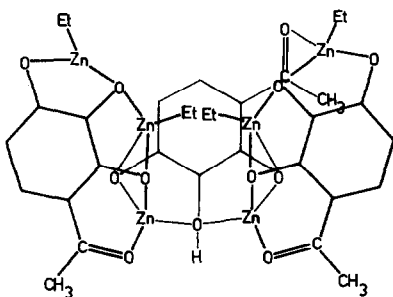
The proposed structure of II (X = H) is in agreement with the ¹H NMR spectral data already published [7]. The broadening of the signals of the methylene groups bonded to the Zn atoms is caused by the rotation of the ethylzinc groups around the central oxygen atom of the trioxybenzene group. Small differences in the shifts of the aromatic protons in relation to those of PG (Table 2, No. 1) indicate the lack of intermolecular coordinations between the molecules of II, although complexation of deficiently coordinated Zn atoms by DOX molecules is possible. The reaction of II with PG proceeds via a four-centred transition state, as in the case of monohydric phenols [9]; hence the less coordinated ethylzinc group bonded to the central oxygen atom should be the most active one since it contains the less polarized Zn–C bond. The rest of PG reacts in turn with two molecules of II. The kinetic data reported above indicate that the side hydroxyl groups of PG participate in this stage of the reaction, resulting in the formation of intermediate III. The last stage of the reaction proceeds only between molecules of III involving the rested central hydroxyl groups and the less coordinated ethylzinc ones. The final product V formed in this reaction stage can be of linear polymeric structure Va or of a cyclic one, Vb, produced from two molecules of III.

The alkylated and halogenated derivatives of PG react with ZnEt₂ in a similar way, although the effect of the substituent on the rates of the particular reaction stages and on the probability of the formation of particular products is visible. The presence of bulky substituents in the aromatic ring of trihydric phenol hinders the formation of polymeric structure Va. The molecular weights of the products of the ZnEt₂ reaction with 4-CIPG, 4-CHPG and 5-BuPG reveal that only Vb is formed, while in the case of the PG and 4-EtPG reactions with ZnEt₂ the formation of Va besides Vb occurs (Table 3). The reaction of ZnEt₂ with 4,6-Bu₂PG practically stopped after the first stage described by eq. 2. The ¹H NMR spectrum of the reaction mixture (Table 1, No. 7) shows a Zn/Ar molar ratio corresponding to a mixture of II and unreacted trihydric phenol. The resolved signal of the ZnEt methylene groups indicates that the presence of bulky *t*-butyl substituents in the *ortho* position in relation to the oxygen atoms can even hinder the rotation of the ethylzinc groups in II. The plot of ethane evolution within the time of reaction of ZnEt₂ and 4-BrPG (Fig. 1) shows the decrease of the rate of III formation involving the hydroxyl group placed in the *ortho* position in relation to the Br substituent.

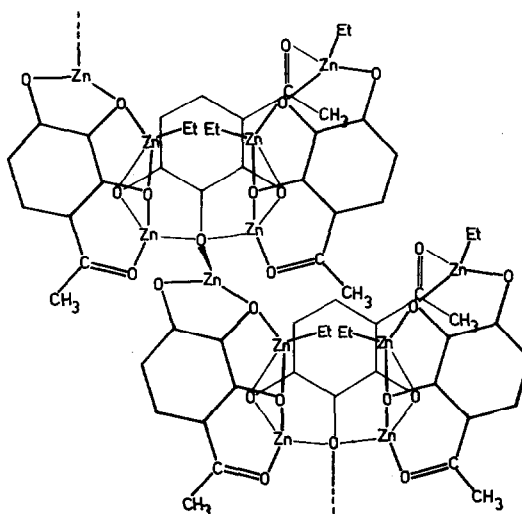
Trihydric phenols with substituents containing strongly donating electron pairs able to form a coordinate bond with a Zn atom can react with ZnEt_2 in another way, as is suggested for 4-AcPG. The reaction involves the stages described by eqs. 2, 4 and 6, yielding successive products of structures II, IV and VI.



II (X = COCH₃)



IV



VI

The presence of an internal coordinate bond between the carbonyl oxygen atom and a Zn atom in II (X = Ac) is demonstrated by the ^1H NMR spectrum (Table 1, No. 6), which contains a multiplet signal corresponding to the methylene groups of ZnEt coordinated stably to the trioxybenzene oxygen atoms and to the carbonyl ones (δ 0.40 and 0.28 ppm, respectively). As the ^1H NMR spectrum shows a higher polarization of the Zn-C bond when the metal atom is coordinated with the carbonyl oxygen, this group is suspected to be more active in the reaction with the hydroxyl groups of 4-AcPG. The product IV formed as an intermediate cannot produce a cyclic structure in the next stage of the reaction but can be subjected only to polycondensation, resulting in the formation of VI. The suggested structure of the final product of the reaction of ZnEt_2 with 4-AcPG is in agreement with the results of its molecular weight determination.

The final products of the reaction of ZnEt_2 and XPG at a 2/1 molar ratio (structures Va, Vb and VI) contain Zn atoms bonded or coordinated with three oxygen atoms of the XPG moieties. The rest of their coordination places are probably occupied by oxygen atoms of the solvent (THF, DOX) to achieve a tetrahedral bonding configuration. These Zn atoms are suspected to be the catalytic centres in CO_2 /propylene oxide alternating copolymerization. Their low amount, in comparison with the Zn atoms bonded with four oxygen atoms of the XPG moieties, explains the low efficiency of these catalysts. It is worthwhile noticing that the active centres in products of structure Vb are less hindered and more accessible

to attack by co-monomers than those in products of structure Va. This observation is in agreement with the recently published [2] results of CO₂/propylene oxide alternating copolymerization catalysed by the products of the ZnEt₂/XPG (2/1) reaction. Comparison of the poly(propylene carbonate) yields and molecular weights obtained in the presence of catalysts produced from various XPGs indicated a higher activity of catalysts showing a tendency to form structure Vb than those of structure Va.

Experimental

Materials

Diethylzinc was synthesized from zinc powder and ethyl halides and distilled under nitrogen before use. Trihydric phenols were synthesized by alkylation or halogenation of pyrogallol according to known procedures and were stored in nitrogen atmosphere. Tetrahydrofuran and 1,4-dioxane were dried and distilled under nitrogen before use.

Reaction of diethylzinc and trihydric phenols (2/1)

To a solution of ZnEt₂ (0.005 mol in 2.5 cm³ of DOX and 2.5 cm³ of THF mixture) previously saturated with ethane was added rapidly under vigorous stirring at 0°C a solution of XPG (0.0025 mol in 2.5 cm³ of DOX and 2.5 cm³ of THF mixture) which had been previously saturated with ethane and cooled down to 0°C. The volume of ethane evolved was measured in a gas burette over the reaction time.

Reaction of 1,2,3-tris(ethylzincoxy)benzene and pyrogallol

The solution of 1,2,3-tris(ethylzincoxy)benzene in THF/DOX (1/1) mixture was prepared by dropwise addition of a PG solution (0.01 mol in 20 cm³ of DOX and 20 cm³ of THF mixture) to a vigorously stirred solution of ZnEt₂ (0.03 mol in 10 cm³ of DOX and 10 cm³ of THF mixture). Stirring was continued until the evolution of ethane was complete, and 10 cm³ of the solution containing about 0.0017 mol of 1,2,3-tris(ethylzincoxy)benzene was reacted with PG (0.00024 mol in 5 cm³ of DOX and 5 cm³ of THF mixture) at 0°C according to the procedure described in the previous section. The rates of successive stages of the reaction were shown graphically as straight lines obtained by plotting $\ln[(V_{\infty} - V)/V_{\infty}]$, where V_{∞} is the ethane volume calculated for 100% conversion of the PG hydroxyl groups.

Analyses

The products of the reaction of XPG (0.0025 mol in 15 cm³ of DOX) and ZnEt₂ (0.005 mol in 5 cm³ of DOX), carried out at room temperature by dropwise addition of XPG solution to the ZnEt₂ one, were examined without isolation from the solution, by ¹H NMR spectroscopy after a reaction time of 30 min and by cryoscopy when the evolution of ethane was complete. The ¹H NMR spectra were recorded in nitrogen atmosphere at 25°C, relative to the solvent as an internal standard, using a JEOL C-100H spectrometer. The cryoscopic measurements were done using a standard freezing point depression apparatus in nitrogen atmosphere. The samples of the post-reaction mixtures were diluted with DOX to concentrations of 2–5%. Actual product concentrations were calculated from the masses of the substrates by subtracting the mass of ethane evolved and ethane diluted. The

molecular weights of the reaction products were calculated, making a correction for the content of ethane in the solution determined from the ^1H NMR spectra. The cryoscopic constant was calculated from the calibration on DOX solutions of anisole in the concentration range 0.1–0.5 mol/100 g DOX.

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References

- 1 A. Rokicki and W. Kuran, *J. Macromol. Sci. -Revs.*, C21 (1981) 135.
- 2 P. Górecki and W. Kuran, *J. Polym. Sci. -Polym. Lett. Ed.*, Vol. 23 (1985) 299.
- 3 W. Kuran and P. Górecki, *Makromol. Chem.*, 184 (1983) 907.
- 4 (a) M. Ishimori, T. Hagiwara and T. Tsuruta, *Makromol. Chem.*, 179 (1978) 2337; (b) T. Hagiwara, M. Ishimori and T. Tsuruta, *Makromol. Chem.*, 182 (1981) 501.
- 5 (a) M. Ishimori, T. Tsuruta, T. Hagiwara, Y. Kai, N. Yasuoka and N. Kasai, *Bull. Chem. Soc. Jpn.*, 49 (1976) 1165; (b) H. Kageyama, K. Miki, N. Tanaka, N. Kasai, M. Ishimori, T. Heki and T. Tsuruta, *Makromol. Chem., Rapid Commun.*, 3 (1982) 947.
- 6 H. Kageyama, Y. Kai, N. Kasai, Ch. Suzuki, N. Yoshino and T. Tsuruta, *Makromol. Chem., Rapid Commun.*, 5 (1984) 89.
- 7 W. Kuran, A. Rokicki and S. Pasynkiewicz, *J. Organomet. Chem.*, 157 (1978) 135.
- 8 A. Rokicki and W. Kuran, *Makromol. Chem.*, 180 (1979) 2153.
- 9 P. Górecki and W. Kuran, *J. Organomet. Chem.*, 265 (1984) 1.
- 10 W. Kuran, S. Pasynkiewicz and J. Skupińska, *Makromol. Chem.*, 177 (1976) 1283.