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Some aspects on the polymerization of ethylene oxide initiated by diphenylzinc-butanone and diphenylzinc-cyclohexanone systems

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SUMMARY

The diphenylzinc-butanone and diphenylzinc-cyclohexanone systems were used as catalyst for ethylene oxide polymerization in benzene solution at 60°C. The catalytic activity of both systems is influenced by the molar ratio of ketone to diphenylzinc. Regardless of the molar ratio employed, the diphenylzinc-cyclohexanone combination was more active in the polymerization than diphenylzinc-butanone system. GPC results strongly suggest the presence of more than one active species for these systems.

INTRODUCTION

Some systems formed by the combination of dialkylzinc with various ketones have been employed as catalyst to induce the polymerization of propylene oxide (1-3) and phenyl glycidyl ether (4). However in these reports there is not any mention about the behaviour of ethylene oxide (EO) with these systems. Recently we proved that diphenylzinc (Ph_2Zn) in combination with butanone or cyclohexanone, when the molar ratio ketone/ $Ph_2Zn=1$ are effective catalysts in propylene oxide polymerization (5). The present paper reports some preliminary results for EO polymerization initiated by Ph_2Zn-butanone and Ph_2Zn-cyclohexanone at molar ratios ketone/ $Ph_2Zn=0.0$; 0.5; 1.0 and 1.5.

EXPERIMENTAL

Butanone (BDH) and cyclohexanone (BDH), were dried over anhydrous sodium sulfate for 24 hours and then fractionally distilled twice (6). Fractions b.p. 71°C and 144°C of butanone and cyclohexanone, respectively, were collected at atmospheric pressure (640torr). Then the ketones were passed through a Molecular Sieve 5Å column and stored under dry nitrogen in the absence of light. Ethylene oxide (BDH), diphenylzinc (Ventron Co.) and benzene (BDH) were purified as previously reported (7).

Polymerizations were carried out in benzene at 60°C in glass vials that were filled using a vacuum line technique and after the established polymerization time elapsed, the polymers were isolated as already described (7).

Intrinsic viscosities, $|\eta|$, were measured at 25°C in benzene. Viscosity-average molecular weights, $\overline{M}_v$, were calculated according to the equation (8):

$$|\eta| = 3.97 \times 10^{-4} (\overline{M}_v)^{0.686}$$

Gel permeation chromatography, (GPC), was performed with a Waters Associates Model 200 chromatograph, operated at 40°C and equipped with four columns connected in series and packed with "styragel" 10^3, 10^4, 10^5, 10^6 Å; chloroform was used as solvent and the instrument was calibrated to a first approximation with polystyrene of known molecular weights.

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RESULTS AND DISCUSSION

Table 1 shows the experimental results of the polymerization for EO by each system at mole ratios ketone/Ph_2Zn=0.0; 0.5; 1.0 and 1.5.

Table 1. Results of the polymerization of ethylene oxide catalyzed by Ph_2Zn-butanone and Ph_2Zn-cyclohexanone systems in benzene at 60°C for 24 hours[a].

Ketone	ketone/Ph_2Zn (mol/mol)	Yield[b] (%)	$\|\eta\|$[c] dlg^{-1}	$\bar{M}_v$ x10^{-5}	$\bar{M}_w/\bar{M}_n$[d]
none	0.0	1.21	0.55	0.38	-
butanone	0.5	5.90	1.95	2.40	19.53
butanone	1.0	55.76	2.01	2.51	35.81
butanone	1.5	53.58	1.01	0.92	29.39
cyclohexanone	0.5	27.49	13.30	39.47	1.52
cyclohexanone	1.0	80.98	2.18	2.83	59.52
cyclohexanone	1.5	77.70	1.22	1.21	41.68

a) Ph_2Zn = 0.1326 mmol; EO/Ph_2Zn = 200 (mol/mol); EO/C_6H_6 = 1 (v/v); EO = 1.3 ml.
b) Based on initial EO.
c) Measured in benzene at 25°C.
d) From GPC, measured in chloroform at 40°C.

The results obtained indicate that the diphenylzinc-butanone and diphenylzinc-cyclohexanone systems provide an efficient catalyst to induce the EO polymerization, where the conversion of monomer to polymer, the molecular weight and the molecular weight distribution (MWD) of the obtained polymers are strongly influenced by the molar ratio ketone/Ph_2Zn. It is also noted that the conversion to polymer increases as the molar ratio ketone/Ph_2Zn goes from 0.0 to 1.0, whereas for a molar ratio of 1.5, the yield decreases slightly. In general a lowering in molecular weight is observed with the increase of the molar ratios between 0.5 and 1.5. Both systems show the broadest MWD for the molar ratio equal to unity. Although for the two systems the polymerization take place in a similar way, the Ph_2Zn-cyclohexanone system in all cases produced larger yields and higher molecular weights.

Taking into account the GPC results for PEO, it is clear that there are more than one process occurring during the polymerization, which strongly suggest the formation of more than one active species. Figure 1 shows the GPC chromatograms for the obtained polymers, most of them display a multinodal pattern. A tendency to move towards the region of low molecular weight, can be observed from the chromatograms as the molar ratio ketone/Ph_2Zn goes from 0.5 to 1.5 regardless of the ketone employed. Also it was observed that in both catalytic systems the polymer resulted predominantly with a high molecular weight fraction when the molar ratio was 0.5. Conversely when Ph_2Zn alone was used, the GPC curve showed the formation of a very low molecular weight polymer.

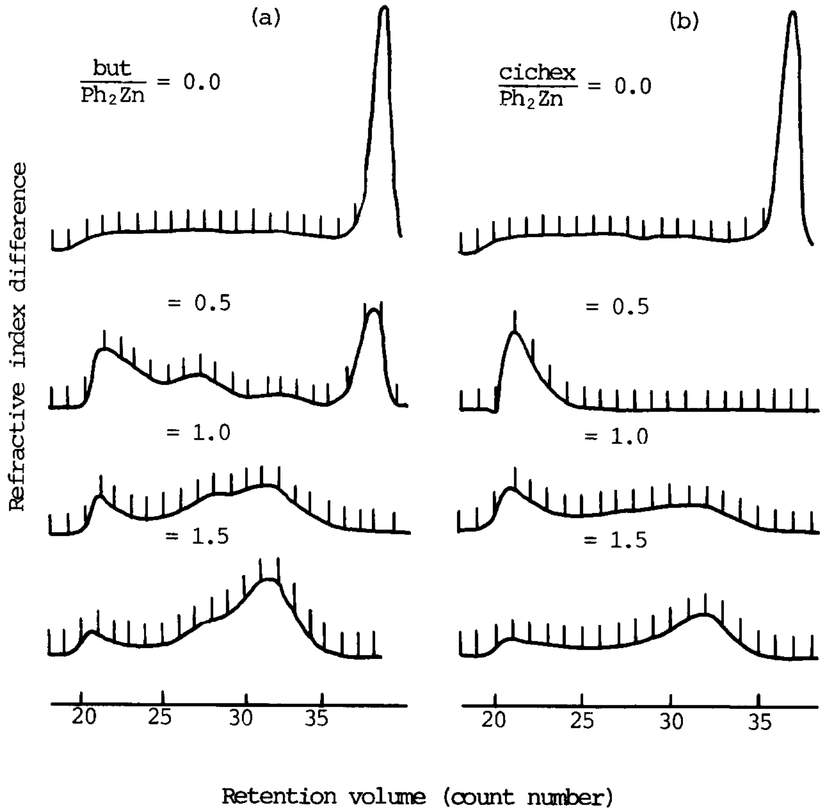

Figure 1. Gel permeation chromatograms of PEO obtained using Ph_2Zn-ketone systems at various molar ratios ketone/Ph_2Zn, in benzene solution at 60°C for 24 hours. (a) butanone as cocatalyst (b) cyclohexanone as cocatalyst. 1 count = 4.42 ml.

According to our results, we can conclude that the Ph_2Zn-ketone systems used are complex. More than one active species responsible for the OE polymerization may participate, parallel to the Ph_2Zn-H_2O system (7,9). More work is now in progress from which conclusive results are expected.

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