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Propylene oxide polymerization using the diphenylzinc-acetone system in benzene at 60°C

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SUMMARY

The diphenylzinc-acetone system was used as catalyst for propylene oxide polymerization in benzene solution at 60°C. This system as well as the diphenylzinc-water system is greatly influenced by the molar ratio of acetone to diphenylzinc and the maximum catalyst activity was found for a ratio of unity. GPC results strongly suggest the presence of more than one active species for the system. ^{13}CNMR analysis indicates that the resulting poly(propylene oxide) has a head-to-tail arrangement. This system was not an effective catalyst for the styrene oxide polymerization.

INTRODUCTION

Ring opening polymerization of propylene oxide (PO) has been carried out employing some diethylzinc-ketone system as catalyst (1-3). The polymerization of phenyl glycidyl ether with dibutylzinc-acetone was also reported (4). However in these reports nothing was mentioned about the molecular weight distribution (MWD), nor about the microstructure of the resulting polymers.

Recently we have reported (5) that diphenylzinc (Ph_2Zn) in combination with some methyl and cyclic ketones with a molar ratio of unity was an effective catalyst for the polymerization of PO which produces high polymers with good yield. All these polymers contain a highly isotactic fraction.

This paper describes some results about PO polymerization in benzene solution initiated by the diphenylzinc-acetone system at various molar ratios ketone/Ph_2Zn.

EXPERIMENTAL

Acetone (BDH) was purified by the method of Timmermans and Gillo (6). Propylene oxide (BDH) was refluxed over potassium hydroxide, distilled, and dried over calcium oxide. Styrene oxide (Aldrich Chemical Co.), diphenylzinc (Ventron Co.) and benzene (BDH) were purified as previously reported (7, 8).

Polymerization were carried out in benzene at 60°C in glass vials using a vacuum line technique and after the established polymerization time elapsed, the polymers were isolated as previously described (8). The crude polymer was separated into a crystalline (insoluble in methanol at 0°C) and an amorphous (soluble in methanol at 0°C) fraction.

Intrinsic viscosities, $|\eta|$, were measured at 25°C in benzene. Viscosity-average molecular weights, $\bar{M}_v$, were calculated according to the equation (9):

$$|\eta| = 1.12 \times 10^{-4} (\bar{M}_v)^{0.77}$$

The ^{13}CNMR spectra were run in $|^2H_6|$ benzene on a Varian AFT-80-A spectrometer at 30°C using TMS as internal reference. Gel permeation chromatography, (GPC), was performed with a Waters Associated 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, and 10^6 Å; chloroform was used as solvent and the instrument was calibrated to a first approximation with polystyrene of known molecular weights.

RESULTS AND DISCUSSION

Table 1 shows the results for the PO polymerization catalyzed by the Ph_2Zn-acetone system at mole ratios ketone/Ph_2Zn = 0.00; 0.25; 0.50; 1.00; 1.50; 2.00 and 3.00.

Table 1. Effect of the molar ratio acetone/Ph_2Zn on the polymerization of PO catalyzed by Ph_2Zn-acetone system in benzene at 60°C for 24 hours[a].

Acetone/Ph_2Zn (mol/mol)	Yield[b] (%)	$\|\eta\|^c$ dlg^{-1}	$\bar{M}_v$ $x10^{-5}$	Crystalline[d] fraction (%)	$\bar{M}_w/\bar{M}_n$ [e]
0.00	2.32	-	-	-	-
0.25	3.87	6.29	14.72	-	4.01
0.50	9.43	9.99	26.70	-	4.21
1.00	38.27	2.96	5.50	11.79	22.24
1.50	13.77	1.12	1.56	9.57	-
2.00	9.24	0.96	1.28	-	-
3.00	4.24	0.72	0.88	-	-

a) Ph_2Zn = 0.0926 mmol; PO/Ph_2Zn = 200 (mol/mol); PO/C_6H_6 = 1 (v/v); PO = 1.3 ml.
b) Based on initial PO.
c) Measured in benzene at 25°C.
d) Determinated as insoluble in methanol at 0°C.
e) From GPC, measured in chloroform at 40°C.

The results obtained for the polymerization of PO by the Ph_2Zn-acetone system show as for Ph_2Zn-water system (10), that the conversion of monomer to polymer is strongly influenced by the molar ratio acetone/Ph_2Zn. As mentioned previously (5,10), diphenylzinc by itself possesses very little activity as catalyst for PO polymerization but by adding a small amount of acetone, the system activity increases reaching its maximum activity when acetone/Ph_2Zn = 1.00. For values larger than unity the conversion of monomer to polymer decreases progressively. On the other hand, with the increase of the molar ratio the molecular weight of the polymers diminishes and the MWD becomes broader. Fig. 1 shows the GPC chromatograms of the PPO obtained in which a general trend of the curves to move at regions of lower molecular weight as the molar ratio ketone/Ph_2Zn increases can be noted.

The change in the patterns of the GPC curves with the variation of the molar ratio and the broad MWD of some polymers strongly suggest the possibility that there are more than one species participating in the polymerization process and its proportion in the reaction mixture is influenced by the amount of acetone employed. Furthermore for the reaction of Ph_2Zn with acetone and butanone the formation of benzene has been observed (11). Taking these facts into account it may be reasonable to consider that the formation of the active species and the behaviour of the catalyst are in good agreement with previous works of Sakata (2,3).

The polymers prepared with a molar ratio of 1.00 and 1.50 were fractioned in methanol at 0°C obtaining a highly crystalline insoluble fraction. The crystallization from the melt of this fraction allowed the formation of spherulites. The amount of this fraction as shown in Table 1, is near to 10% of the total weight of the samples.

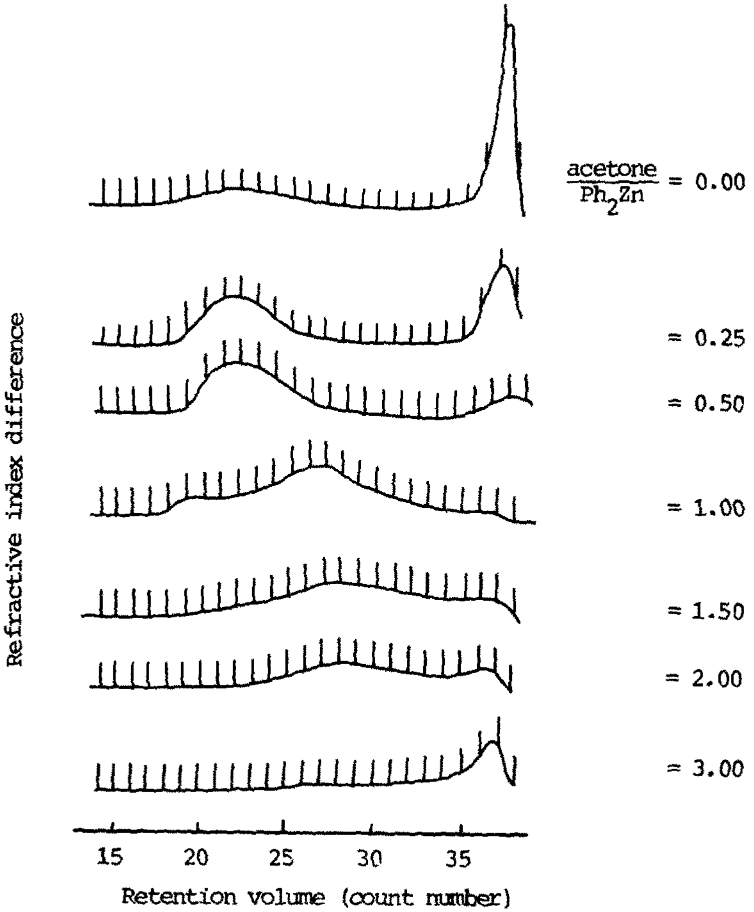

Figure 1. Gel permeation chromatograms of poly(propylene oxide) obtained using Ph$_2$Zn-acetone system at various molar ratios acetone/Ph$_2$Zn in benzene solution during 24 hours. 1 count = 4.42 ml.

The ^{13}CNMR spectra of the crude polymer and its methanol soluble fraction (a) and (b) in Fig. 2 show a CH triad (δ = 75 - 76 ppm) signal and a CH$_2$ diad (δ = 73 - 74 ppm) signal, indicating the presence of an almost pure head-to-tail polymer and suggesting a β opening of the oxirane ring (10, 12). The spectrum of the crystalline fraction of PPO (c) in Fig. 2 shows that such fraction is highly isotactic, which is clearly indicated by the single unsplit lines for CH and CH$_2$ groups that correspond to the isotactic triad and diad previously reported by Jedliński (12) and Tani (13). These results are also in concordance with our previous considerations (5). All crude PPO showed the same patterns of Fig. 2a regardless of the molar ratio used in the polymerization. The methanol soluble and crystalline fractions of the polymers prepared with a molar ratio of 1.00 and 1.50, exhibit spectra similar to those shown in Fig. 2b and 2c, respectively.

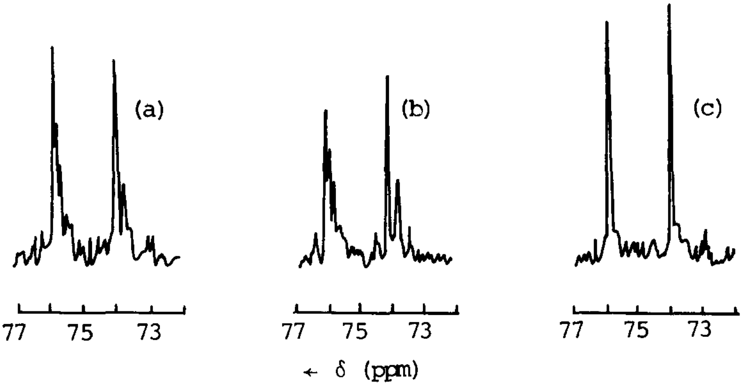

Figure 2. ^{13}CNMR spectra of PPO obtained using Ph_2Zn-acetone system with a molar ratio acetone/Ph_2Zn = 1.00. (a) Crude polymer; (b) Methanol soluble fraction; (c) Crystalline fraction. The spectra were run in $|^2H_6|$-benzene with internal TMS.

According to the ^{13}CNMR results it seems that the polymerization process for PO might follow an ionic coordinate pathway with a strong anionic character in the propagation stage.

The diphenylzinc-acetone system did not show any activity for polymerization of styrene oxide. No polymer was observed even after 744 hours under similar reaction conditions when molar ratios among 0.25 - 1.50 were used. This could possibly be attributed to inductive and steric effects due to the phenyl group attached to the oxirane ring (14).

More work is now in progress with other Ph_2Zn-ketone systems relative to the polymerization of some oxiranes which allow to establish the effects of the ketone structure and the substituent group attached to the oxirane ring on the course of the polymerization.

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