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Analysis

Epoxide Polymerization

8. Spectroscopic Studies of Poly(Propylene Oxide) Prepared with Diphenylzinc-Water as Initiating System

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SUMMARY

Poly(propylene oxide), PPO, obtained using diphenylzinc, Ph_2Zn, and using the diphenylzinc-water system at various molar ratios H_2O/Ph_2Zn, were studied through ^1H NMR and IR spectroscopy establishing that the polymerization initiates by coordition of propylene oxide (PO) to a terminal zinc atom of the active species followed by consecutive insertions of PO units at this zinc atom. The PPO obtained showed Ph- and HO-, HO- and HO- end-groups depending on the molar ratio H_2O/Ph_2Zn used, and also HO- and PhO- end-groups when oxygen was present in the polymerization system.

INTRODUCTION

In previous papers we have postulated that the system Ph_2Zn-H_2O, produced several species active in epoxide polymerization (1-5). The GPC chromatograms of poly(ethylene oxide), PEO, obtained using molar ratio $H_2O/Ph_2Zn = 1$, showed a bimodal pattern at low conversion which changes to an almost unimodal one at ca. 94% conversion (1). The benzene solution polymerization of ethylene oxide (EO) by the Ph_2Zn-H_2O system showed that the modality of the GPC chromatograms change according to the molar ratio H_2O/Ph_2Zn used (3). On the other hand, the Et_2Zn-H_2O system and the Ph_2Zn-H_2O system behave analogously in PO polymerization (4,5) indicating a catalytic system in which several active species participate. It has been reported that for the Et_2Zn-H_2O system the predominant species will depend on the actual molar ratio H_2O/Et_2Zn used (6,7) and that the polymerization will proceed by an anionic or a cationic coordinative mechanism depending on this molar ratio (7,8). Furthermore, the broad molecular weight distribution (MWD) of the PEO and of the PPO obtained also are indicative of a system in which more than one active species participate with different capacities of inducing both EO and PO polymerization.

This paper describes further evidences which corroborate our earlier considerations in the sense that several active species participate in the EO and in the PO polymerization when using the Ph_2Zn-H_2O system (2,5) and that these species initiate the PO polymerization through a coordinative process followed by anionic and/or cationic character propagation depending on the molar ratio H_2O/Ph_2Zn employed (5).

EXPERIMENTAL

Polymerization experiments were carried out in benzene solution at 60°C in vials filled using a vacuum line technique and, after the established time of polymerization has elapsed, the polymers were isolated as previously described (1,2)

For the oxygen "contaminated" experiments, the polymerization tubes were charged using a dry-box purged with dry nitrogen containing a small but undetermined amount of oxygen.

The ^1H NMR samples were prepared by dissolving 13 to 20 mg of polymer in 0.40 mL of [^2H]-chloroform or [$^2H_6$]-acetone and measured at 40°C with a Varian T-60A spectrometer using tetramethylsilane (TMS) as an internal standard.

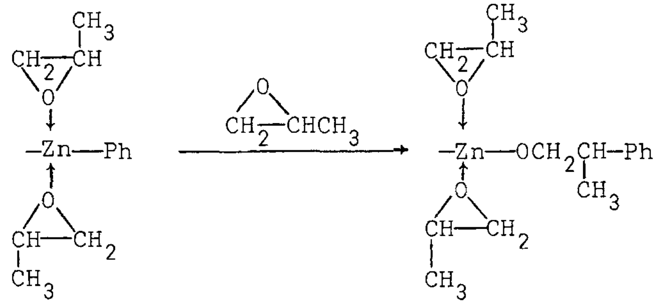
Infrared spectra were taken on a Perkin-Elmer 377 or on a Aculab-2 spectrophotometer. The polymer were normally sampled as thin films on NaCl disks.

RESULTS AND DISCUSSION

Propylene oxide polymerization using the Ph_2Zn-H_2O system is strongly influenced by the molar ratio H_2O/Ph_2Zn. For 6 hours polymerization at 60°C, high molecular weights PPO are obtained when employing molar ratios in the range $0.25 \leqslant H_2O/Ph_2Zn \leqslant 1.25$ but molar ratios equal 0 and equal or larger than 1.5 produced low yields of liquid polymers of very low molecular weights (5). These very low molecular weight PPO were studied by ^1H NMR and by IR spectroscopy.

Spectra a (Fig.1 and 2) show the ^1H NMR and the IR of PPO obtained using Ph_2Zn alone as initiator. From these spectra the presence of an aromatic group can be noted, singlet at 7.2 ppm of NMR spectrum and the 3100-3000, 1600, and 700-650 cm^{-1} IR bands. These spectra strongly support the presence of a phenyl end-group in the polymer chains. This phenyl group must arise from one of the phenyl groups of Ph_2Zn used as initiator and is incorporated to the polymer chain when the first monomer PO unit insert in the Zn-Ph bond at the initiation of the polymerization. This is in accordance with a coordination of the oxirane through its oxygen atom to the zinc atom of the Ph_2Zn, in a similar way as has been proposed by several authors (7,9,10) for the PO polymerization using alkylmetal-water systems. The polymerization process possibly will follow a sequence as is shown in scheme 1, with formation of Ph-Zn-$OCH_2CH(CH_3)Ph$ species which will be responsible for propagation through incorporation of oxirane units at the Zn-O bond after coordination of the PO monomer units to the zinc atom.

SCHEME 1



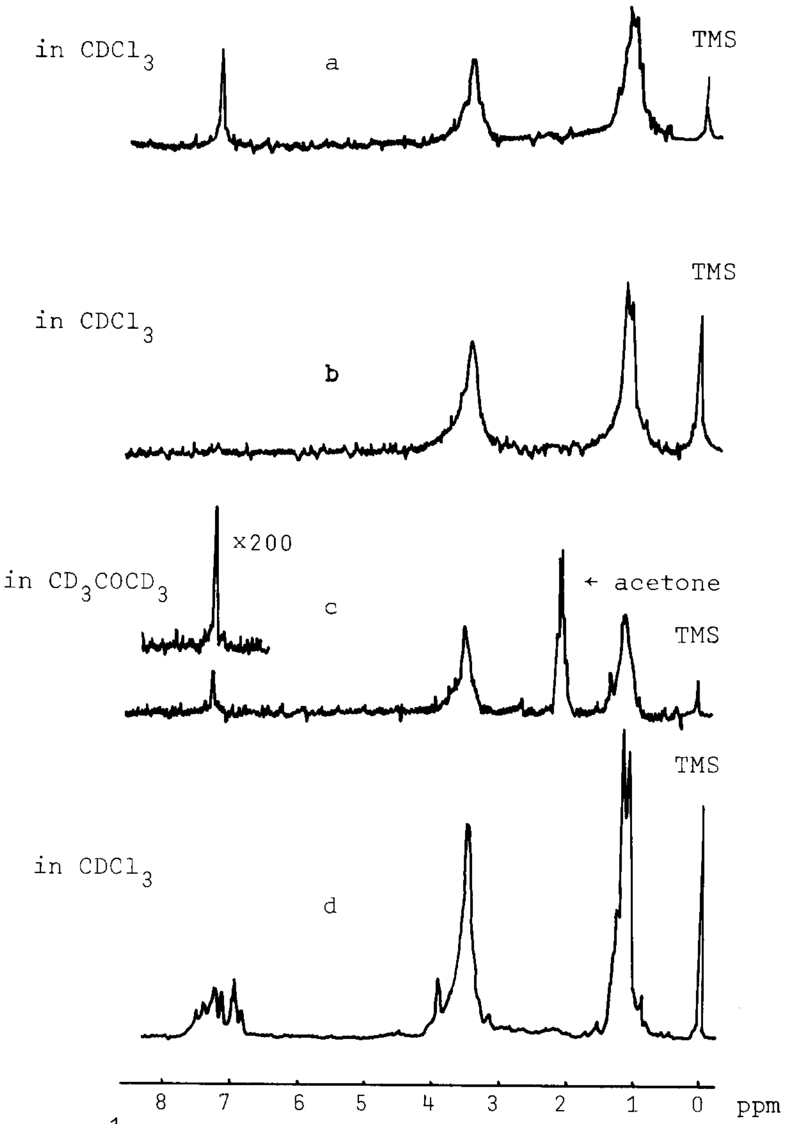


Figure 1. ^1H NMR spectra of poly(propylene oxide) samples obtained with Ph_2Zn-H_2O initiating systems. Polymerization conditions: $PO/Ph_2Zn = 200$ (mol/mol), $PO/C_6H_6 = 1$ (v/v), 60°C, a) $H_2O = 0$, 6 hours; b) $H_2O/Ph_2Zn = 1.50$, 6 hours; c) $H_2O/Ph_2Zn = 0.25$, 15 minutes; d) $H_2O/Ph_2Zn = 1.50$ "contaminated" with oxygen, 6 hours.

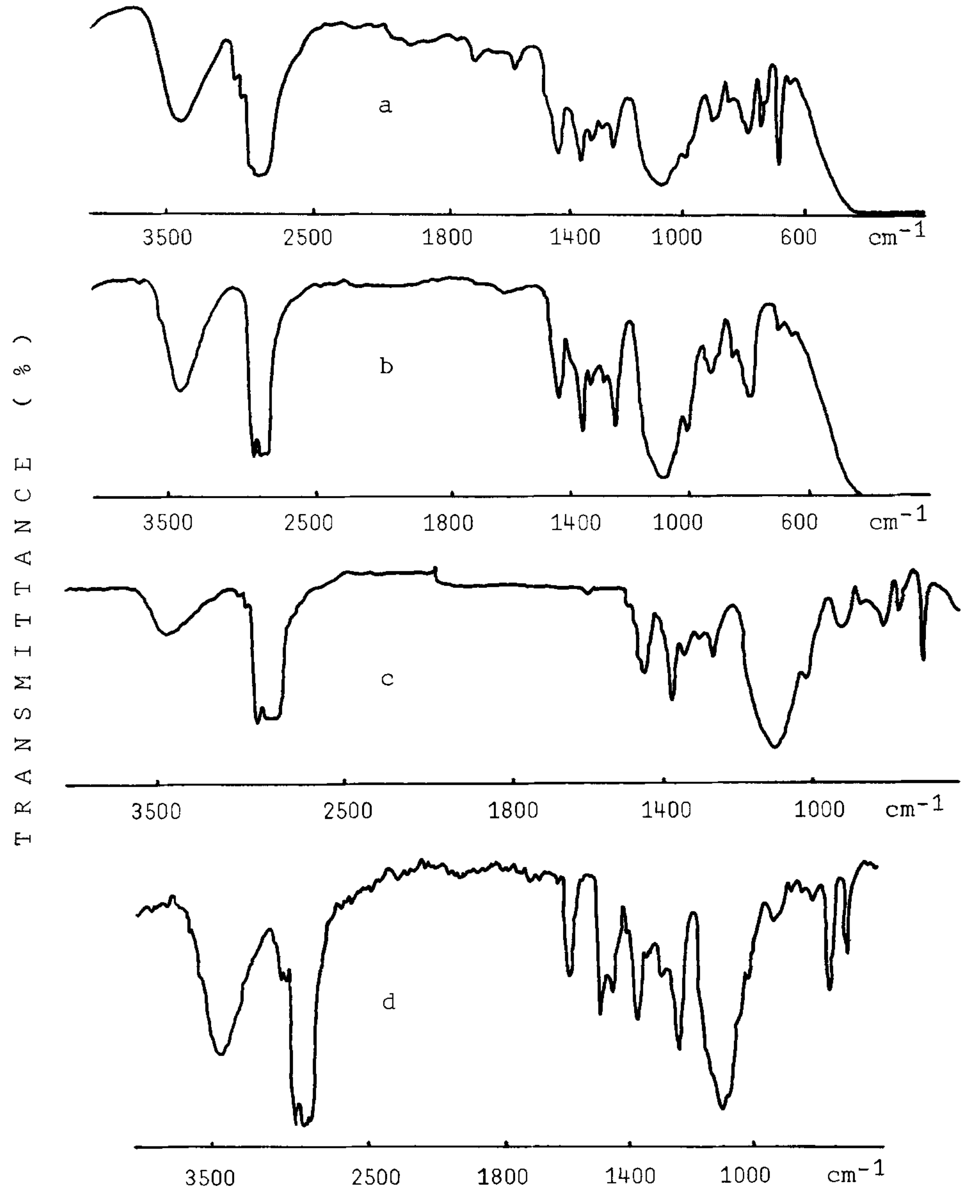
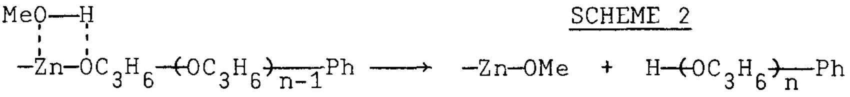


Figure 2. IR spectra of poly(propylene oxide) samples obtained with Ph_2Zn-H_2O initiating systems. Polymerization conditions, as stated in Fig. 1. a) $H_2O = 0$; b) $H_2O/Ph_2Zn = 1.50$; c) $H_2O/Ph_2Zn = 0.25$; d) $H_2O/Ph_2Zn = 1.50$ "contaminated" with oxygen.

IR spectrum (Fig. 2a) also shows the presence of an HO group, band at ca. 3400 cm^{-1}, which is the other end-group of the polymer chain. This terminal HO group is formed when quenching the polymerization with methanol. Ishimori, Hsiue and Tsuruta (11) suggested that the alcohol coordinates to the zinc atom at the growing chain causing the alcoholysis of polymer alkoxide (Scheme 2). The HO group was not detected in the NMR as its chemical shift is near to 4 ppm (12) where the signal of CH_2 and CH (3-4 ppm) appear.

SCHEME 2



$$\begin{array}{l} \mathrm{MeO{-}H} \\ \mathrm{-Zn{-}OC_3H_6{-}(OC_3H_6)_{n-1}Ph} \longrightarrow \mathrm{-Zn{-}OMe} + \mathrm{H{-}(OC_3H_6)_n{-}Ph} \end{array}$$

As is shown in spectrum b (Fig. 1) an aromatic signal was not detected in the NMR spectra of PPO obtained when using molar ratios $H_2O/Ph_2Zn \geqslant 1.50$. For these polymers, the IR spectra (Fig. 2b) show the stretching of HO group (ca. 3400 cm^{-1}) indicating that the active species will be of -Zn-OH type with the monomer units coordinating and propagating as for the case of Ph_2Zn but with an HO end-group at the growing chain. Having in mind that our conversion results are similar to the ones obtained when using the Et_2Zn-H_2O system at these molar ratios (13), we can assume that the predominant species in our system for molar ratios equal or larger than 1.50 will probably have the $HO(ZnO)_nH$ structure (6,7); the other terminal group must be an HO group due to the methanol quenching of the polymerization process.

It was not possible to detect the end-groups for the PPO obtained when using molar ratios from 0.25 to 1.25 for the 6 hours at 60°C polymerization of PO due to the high molecular weight of the polymer. However, it was possible to obtain a very low molecular weight PPO using a molar ratio of 0.25 when allowed to polymerize for only 15 minutes. From the NMR (Fig.1c) and from the IR (Fig. 2c) spectra is possible to observe the presence of an aromatic group. As already established (4,5), the molar ratio 0.25 is more effective than the Ph_2Zn alone as initiator of PO polymerization and, according to other authors (6,7) and our previous considerations (2,5), species such as $Ph(ZnO)_nZnPh$ would be present in this system. So, if the monomer coordinates to the terminal zinc atom of such species, the polymer chains would initiate as is shown in Scheme 1. The formation of these species is supported by studies of Furukawa et al (12, 14) where it is postulated that the efficiency of the catalytic species is related to the skeletal $(ZnO)_n$ and that the monomer coordinates preferentially to a terminal zinc atom. Furthermore, species such as $R(ZnO)_n$ produce α-opening of the oxirane ring of PO (7) and, as in previous works (4,5) we have shown that molar ratio of 0.25 produces β- and α-opening, we can assume that in such a system $Ph(ZnO)_n$ species are also present.

For the molar ratio of 1.0 it was not possible to obtain a PPO with a very low molecular weight capable of analysis of its end-groups by NMR and by IR spectroscopy. Despite performing experiments at very short polymerization times, high molecular weight PPO was always obtained (5).

Table 1. Polymerization of PO initiated by the Ph_2Zn-H_2O system at various H_2O/Ph_2Zn molar ratios and in presence of a small amount of oxygen, in benzene at 60°C for 6 hours[a].

$\frac{H_2O}{Ph_2Zn}$ mol/mol	Yield[b] %	$[\eta]$[c] $dL \cdot g^{-1}$	$\bar{M}_v \cdot 10^{-6}$	$\bar{M}_n$[d]	Crystalline Fraction[e] %
0.25	19.9	10.04	2.70	----	27
0.50	26.4	9.84	2.63	----	36
1.00	64.9	5.53	1.14	----	22
1.50	3.1	----	----	319	----
1.75	3.1	----	----	----	----
2.00	1.7	----	----	415	----

a) Ph_2Zn = 0.253 mmol, PO/Ph_2Zn = 198 (mol/mol), PO/C_6H_6 = 1 (v/v), PO = 3.5 mL at 20°C.
b) Based on initial PO.
c) Measured in benzene at 25°C.
d) Determined by end-group analysis through NMR spectroscopy.
e) Determined as insoluble in methanol at 0°C.

It has been demonstrated (15,16) that dialkylzinc react with oxygen forming zinc dialkoxides. Furthermore, Tsuruta et al (13) postulated the formation of $EtZnO(ZnO)_nZnOEt$ and $EtOZnO(ZnO)_nZnOEt$ species for the Et_2Zn-H_2O system in the presence of oxygen. We performed some experiments of PO polymerization with various molar ratio H_2O/Ph_2Zn in the presence of small amount of oxygen. The results are shown in Table 1. It can be noted that for molar ratios equal or larger than 1.50, low conversions were obtained. At the NMR spectrum (Fig. 1d) a multiplet signal in the aromatic region was detected, suggesting the presence of a phenoxy group. Regarding the IR spectrum (Fig. 2d), it is similar to the one shown for the Ph_2Zn case (Fig.2a), except the band at 1250 cm^{-1} which has a larger intensity. This result is in accordance with the assymetric flexion of aromatic -aliphatic ethers. According to the previous considerations, it could be possible that the terminal phenoxy group would be incorporate at the initial stage of the polymerization, after coordination of the monomer to the terminal zinc atom of $(ZnO)_nZnOPh$ species present at the polymerization system.

Finally, it can be stated that PO can be polymerized by Ph_2Zn alone and/or combined with water. The Ph_2Zn by itself is a poor catalyst producing low conversion and low molecular weight PPO with polymer chains containing a phenyl end-group, indicating that the polymerization starts by coordination of the PO to the zinc atom followed by insertion of the oxirane at the zinc-phenyl bond. The system with molar ratio of 0.25, at the initial stages of the polymerization, shows the formation of polymer chains with phenyl end-groups due to the presence of $Ph(ZnO)_nZnPh$ species which are active as initiators of PO polymerization. For molar ratios $H_2O/Ph_2Zn \geqslant 1.50$ a phenyl end-group was not detected in the obtained polymer, but only hydroxyl end -groups suggesting that $HO(ZnO)_nZnOH$ species are the active species at those molar ratios. Finally, the presence of oxygen in the system produces polymer chains with phenoxy end-groups which can be attributed to the presence of $-ZnO(ZnO)_nZnOPh$ species in the polymerization system.

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