Polymer Bulletin 23, 483–489 (1990)

Polymer Bulletin

Epichlorohydrin polymerization using diphenylzinc-cocatalyst systems in benzene solution

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SUMMARY

Various diphenylzinc-cocatalyst systems were used as initiators of epichlorohydrin polymerization in benzene solution. Water, acetone, butanone, acetophenone and cyclopentanone were employed as cocatalyst but in the most of the cases diphenylzinc alone produced the better conversion to polymer. GPC results suggest the presence of more than one active species for the polymerization initiated by those systems. For diphenylzinc alone as initiator the reaction at 120°C is first order with respect to monomer with $k_p=1.21\times10^{-5}$ L $mol^{-1}sec^{-1}$

INTRODUCTION

Epichlorohydrin (ECH) has been polymerized by metal halides and their complexes (1,2), by organometallic complexes combined with some cocatalyst (3,4) and also through radiolitic initiation (5).

In previous papers, we have reported the polymerization of ethylene oxide (EO), and of propylene oxide (PO) using the diphenylzinc-water system (Ph_2Zn-H_2O) (6,7) and some diphenylzinc-ketone systems (8,9). Styrene oxide (SO) polymerization by diphenylzinc-water system was also carried out (10). According to those results, we postulated that the polymerization involves more than one active species capable of produce the respective polymer. At the same time, it was established that the polymerization process is greatly influenced by the molar ratio cocatalyst/Ph_2Zn. Furthermore, from ^{13}C-NMR spectroscopy, it was concluded that the crude PPO and PSO obtained had always almost only head-to-tail secuences.

The present paper describes the polymerization of ECH in benzene solution initiated by diphenylzinc-cocatalyst systems, where water, acetone, butanone, acetophenone and cyclopentanone were employed as cocatalyst.

EXPERIMENTAL

Epichlorohydrin (Merck) was dried by refluxing for six hours over calcium hydride and left stannding other 24 hours at room temperature over calcium hydride, then fractionally distilled under nitrogen atmosphere. The distillate was kept over CaH_2 under its vapour pressure.

Acetophenone (BDH) and cyclopentanone (BDH), were dried over anhydrous sodium sulfate for 24 hours and then fractionally distilled. Afterwards, the ketones were passed through a molecular sieve 5 Å column and stored under dry nitrogen in the absence of light. Acetone (BDH) and butanone (BDH) were purified as previously reported (8,9). Water was purified by passing through an ionic interchanging column, then distilled over glass. Previously to use was boiled.

Polymerizations were carried out in benzene at 60 or 120°C, in vials filled using a vacuum line technique (6). Poly(epichlorohydrin), PECH, was isolated by elimination of volatiles through vacuum distillation, dissolved in benzene and then freeze-dried.

Intrinsic viscosities, $[\eta]$, were measured at 40°C in chloroform. Gel permeation chromatography (GPC) was performed with a Waters Associates model 200 chromatograph operated at 40°C and equipped with five columns connected in series and packed with "styragel" 10^3,500, 500, 100 and 60 Å; chloroform was used as solvent and the instrument was calibrated to a first approximation with polystyrene samples of known molecular weights.

^{1}H-NMR spectra were run in [^{2}H]-chloroform or in [^{2}H$_6$]-acetone on a Varian T-60A spectrometer at 40°C, and the ^{13}C-NMR were run in [^{2}H$_6$]-benzene on a Varian AFT-80-A spectrometer at 30°C. In both cases TMS was used as internal reference .Infrared spectra were taken on a Perkin-Elmer 377 spectrophotometer. The polymers were normally sampled as thin films on NaCl disk.

RESULTS AND DISCUSSION

In earlier works we had pointed out that the epoxide polymerization by Ph_2Zn-H_2O system is much influenced by the molar ratio H_2O/Ph_2Zn. For EO (6) and for PO (7) the maximum conversion to polymers were reached for molar ratio equal to unity, while for SO (10) the largest yield was obtained for Ph_2Zn alone. We agreed with Jedlinski (11) in the sense that the course of epoxide polymerization not only depends on the initiator system being used but also on the sustituent group in the oxirane ring. The present results are in concordance with that assumption.

Table 1 shows the experimental results of the polymerization of ECH by Ph_2Zn-H_2O system at various molar ratios H_2O/Ph_2Zn at 60 and 120°C.

From these results it can be noted that the largest conversion of monomer to polymer is reached with Ph_2Zn alone as it was the case for SO polymerization, confirming the influence of the substituent group towards the course of the polymerization process. In all cases, at 120°C, largest conversions were obtained.

Table 2 shows the results for ECH polymerization when using Ph_2Zn combined with various ketones, in benzene solution at 60°C, and at molar ratios ketone/Ph_2Zn= 0.00, 0.25, 0.50, 1.00 and 1.50.

Table 1. Effect of the temperature and molar ratio water/Ph_2Zn on the polymerization of ECH catalized by the Ph_2Zn-water system in benzene at 60 and 120°C for 744 hours[a].

H_2O/Ph_2Zn (mol/mol)	744 hours at 60°C Yield[b] (%)	[η][c] dl/g	744 hours at 120°C Yield[b] (%)	[η][c] dl/g
0.00	22.64	0.03	73.70	0.04
0.25	20.78	0.03	68.90	0.04
0.50	15.49	0.06	55.20	0.05
1.00	1.46	0.08	10.84	0.05
1.50	0.00	-	1.96	0.02

a) Ph_2Zn = 0.107mmol; ECH/Ph_2Zn=200 (mol/mol); ECH/C_6H_6 = 1 (vol/vol); ECH = 1.7ml at 20°C.
b) Based on initial ECH.
c) Measured in chloroform at 40°C.

Table 2. Results of the ECH polymerization initiated by some Ph_2Zn-ketone systems in benzene at 60°C for 744 hours[a].

Ketone / Ph_2Zn mol/mol	acetone Yield[b] (%)	acetone [η][c] dl/g	butanone Yield[b] (%)	butanone [η][c] dl/g	acetoph. Yield[b] (%)	acetoph. [η][c] dl/g	cyclopent. Yield[b] (%)	cyclopent. [η][c] dl/g
0.00	22.64	0.03	22.64	0.03	22.64	0.03	22.64	0.03
0.25	17.13	0.03	25.70	0.03	-	-	9.87	0.03
0.50	18.17	0.02	16.40	0.03	25.52	0.04	11.70	0.02
1.00	11.18	0.02	11.80	0.03	20.06	0.02	7.33	0.03
1.50	9.14	0.03	9.60	0.03	20.22	0.01	5.96	0.03

a) Ph_2Zn = 0.107mmol; ECH/Ph_2Zn = 200 (mol/mol); ECH/C_6H_6 = 1 (vol/vol); ECH = 1.7ml at 20°C.
b) Based on initial ECH.
c) Measured in chloroform at 40°C.

All the obtained polymers showed a dark oily appearance and low values of intrinsic viscosity indicating very low molecular weight compounds. In all cases the molecular weight remains almost constant regardless of the system and the molar ratio employed.

Figure 1 shows the relationship between the molar ratio cocatalyst/Ph_2Zn and polymer conversion for ECH polymerization at 60°C using water, and ketones as cocatalysts. It can be appreciated that when water, acetone, butanone or cyclopentanone were used as cocatalyst for ECH polymerization the polymer yield varied accordingly with the molar ratio cocatalyst/Ph_2Zn employed. Acetophenone behaves differently and despite the molar ratio MeCOPh/Ph_2Zn used

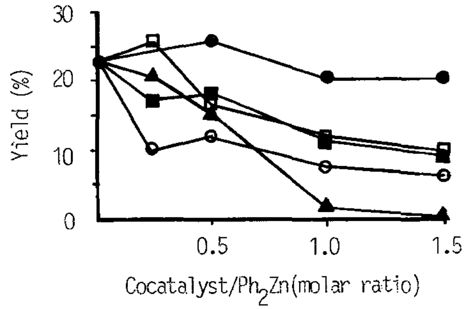

Figure 1. Polymerization of ECH by Ph_2Zn-cocatalyst systems. Relationship between molar ratio cocatalyst/Ph_2Zn and polymer yield. ECH/Ph_2Zn = 200 (mol/mol). ECH/C_6H_6 = 1 (vol/vol). 744 Hours at 60°C. Cocatalyst: ▲ water, □ acetone, ■ butanone, ○ cyclopentanone, ● acetophenone.

the conversion to polymer remained almost constant, suggesting that MeCOPh has a very low cocatalytic activity towards ECH polymerization. The course of ECH polymerization differs from the ones shown by PO (8) and EO (9) polymerizations using Ph_2Zn-ketone systems, where the maximun yield of polymer resulted for the molar ratio ketone/diphenylzinc =1 with reaction being much faster than ECH polymerization reaction.

ECH polymerization by these systems produced very low molecular weight polymers, after very long periods of time in contrast with EO and PO polymerization by these initiating systems. These results suggest that the $-CH_2Cl$ sustituent group due to its inductive effect, steric hindrance or both affected markedly the rate of polymerization and the molecular weigth of the obtained polymers. Garty (3) considered that the low catalytic activity of the dibutylzinc-water system toward ECH polymerization and the low molecular weight of the obtained polymers can be attributable to side reactions between active species and the chlorine atom of the monomer. We think that a similar situation is also possible with these Ph_2Zn-cocatalyst systems producing a very complex polymerization processes.

Figure 2 shows a typical GPC pattern of the obtained polymers. It depicts a broad nonuniform molecular weight distributions which may indicate the presence of more than one active species, as has been the case for the previous epoxide polymerization studied (6-10, 12). It is also indicative of the low molecular weight of the polymers.

^1H-NMR spectra show in all cases a signal at δ=3.3- 4.2 ppm which is in concord with those previously reported in literature (2, 13). The IR spectra, as shown in Figure 3, exhibit signals near to 3500 and 1700 cm^{-1} which correspond to the presence of hydroxyl and carbonyl groups, respectively. The first one is attributable to -OH end-group

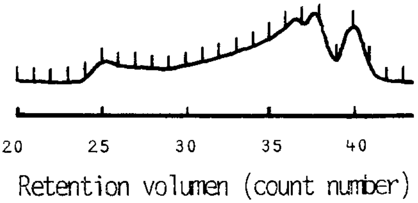

Figure 2. Typical GPC chromatogram of PECH obtained using Ph_2Zn-cocatalyst systems in benzene solution. 1 count = 4.42 ml

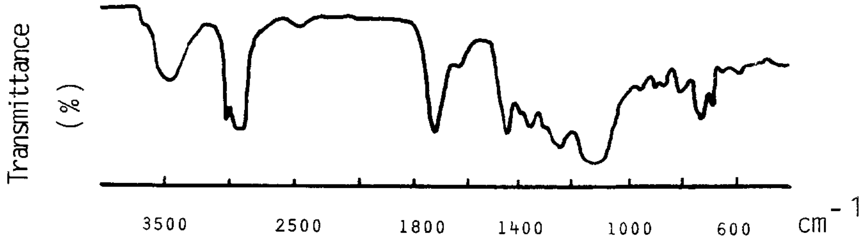

Figure 3. IR spectrum of poly(epichlorohydrin) sample obtained using Ph_2Zn-butanone system with a molar ratio butanone/Ph_2Zn = 0.25.

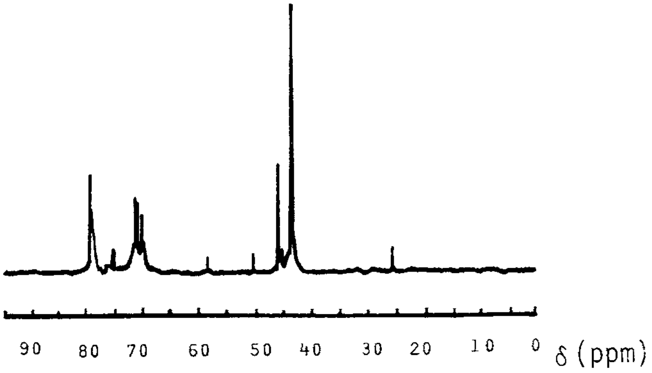

Figure 4. ^{13}C-NMR spectrum of PECH obtained using Ph_2Zn as initiator. The spectrum was run in [^{2}H]-chloroform with internal TMS.

formed when the polymerization is quenched by the addition of methanol (12). While carbonyl groups possibly can be formed due to oxidative degradation induced by the initiator system (14). Other IR signals are in good concord with those reported for poly(epichlorohydrin) (15).

All ^{13}C-NMR spectra of PECH were quite similar to the one shown in Figure 4. Comparison of the spectra with those reported in literature (4) suggested the presence of epoxy end-group which may be formed, in concord with Tsuruta (4, 16), by a mechanism where chlorine atom of monomer is abstracted by the catalyst making possible an oxonium ion propagation process. For epoxide polymerization by these initiator systems it has been proposed that the process is initiated by coordination of monomer through its oxygen atom to a zinc atom of the initiator making possible succesive incorporation of monomeric units starting from the active species (6, 7, 10).

Althogether we can point out that the ECH polymerization initiated by these systems is a complex one with several different species acting and being responsible for the low polymer formation by a very slow process.

Polymerization of ECH by Ph_2Zn at 120°C, which yield the largest conversion to PECH, was performed at various lengths of time. The results are shown in Table 3 and produced the first order plot showed in Figure 5.

Table 3. Polymerization of ECH catalyzated by Ph_2Zn in benzene at 120°C[a].

Polymerization time (hours)	Yield[b] (%)	$[\eta]$[c] dl/g
120	22.17	0.02
240	33.80	0.02
360	41.80	0.02
480	52.66	0.02
600	59.48	0.02
744	73.70	0.03

a) Ph_2Zn = 0.1077mmol; ECH/Ph_2Zn = 200 (mol/mol); ECH/C_6H_6 = 1; ECH = 1.7 ml at 20°C.
b) Based on initial ECH.
c) Measured in chloroform at 40°C.

It is clear that the polymerization is first order in monomer. A value of k_p =1.21 x 10^{-5} L $mol^{-1}sec^{-1}$was derived from this plot by dividing the slope by the initial Ph_2Zn concentration.

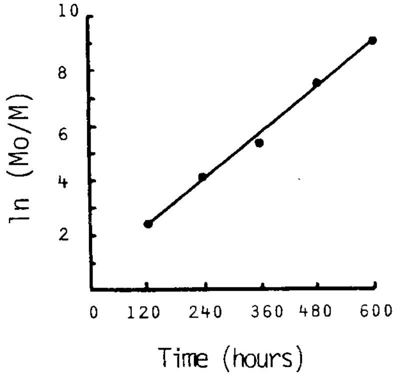

Figure 5. First order plot for ECH solution polymerization catalized by Ph_2Zn at 120°C. ECH/C_6H_6 = 1 (v/v), [Ph_2Zn] = 0.0315

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support of the Consejo de Desarrollo Científico, Humanístico y Tecnológico of the Universidad de los Andes (CDCHT-ULA) through grant N° C-247.

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Accepted February 7, 1990 K