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SOME EVIDENCE ON THE POLYMERIZATION OF PHENYLGLYCIDYLETHER USING AIP/ZnCl$_2$ AS INITIATOR SYSTEM

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ABSTRACT

The influence of the composition of the initiator system used in the polymerization of PGE is studied. Structural studies of intermediate species by NMR and IR spectroscopies are made which allow confirmation of some characteristics on the previously proposed mechanism and clarification of the mechanism leading to the chlorinated insoluble polymer fraction. This can be explained by the formation of halogenated oligomers in the first stage of the reaction which interchange with different aluminum alkoxides to give another type of initiator system.

INTRODUCTION

The Al(OiPr)$_3$/ZnCl$_2$ system was shown by Price et al. [1, 2] to effectively initiate the polymerization of propylene oxide and phenylglycidylether. Polyethers obtained with this initiator system contained an isotactic polymer fraction, an atactic polymer fraction with a regular chain structure, and an oligomeric fraction. However, polymerization reactions conducted with Al(OiPr)$_3$ (AIP) or ZnCl$_2$ alone yielded only low molecular weight polyethers with an irregular chain microstructure. This behavior suggests a different reaction mechanism which, as has already been reported [3-5], changes from cationic for AIP or ZnCl$_2$ alone to anionic-coordinative for a mixture of them. For this initiator system there is a previously proposed two-stage mechanism [6], shown in Scheme 1, which explains most of the experimental data found in the homopolymerization of phenylglycidylether (PGE) reported by us [7]. However, the exact structure of the active species or the actual mechanism has not been fully elucidated until now.

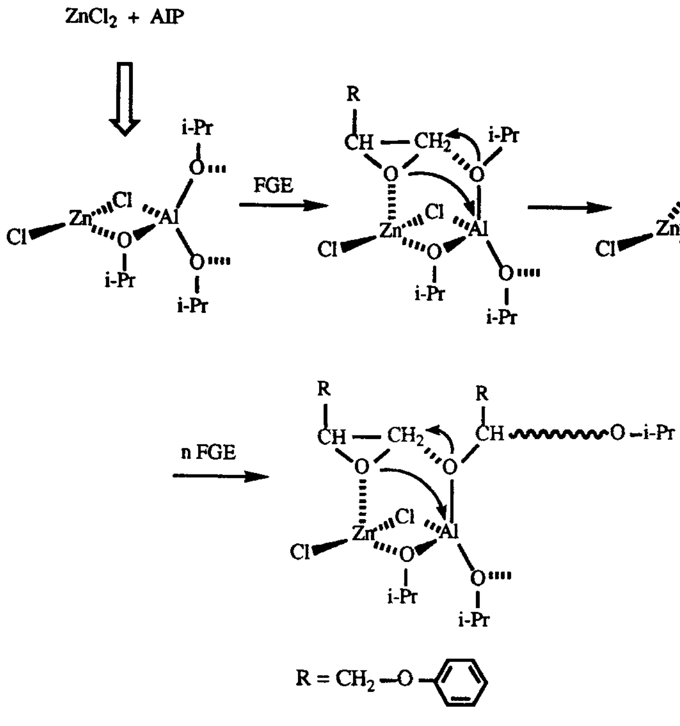
The aim of this paper is to help clarify the above subjects by means of structural studies of intermediate species using IR, ^{1}H-, ^{13}C-, and ^{27}Al-NMR spectroscopy. Moreover, the influence of the Zn/Al ratio, the zinc salt used, and the presence of water as cocatalyst were also related to this mechanism.

EXPERIMENTAL

The noteworthy influence of traces of water on the catalytic system required very accurate conditions to assure the total absence of moisture. For this reason, all preparations were carried out by the usual inert atmosphere techniques, and eventually the work was done in a dry box.

Initiators

$ZnCl_2$, $ZnBr_2$, and ZnI_2 were gold-label-grade reagents supplied by Aldrich. Alternatively the adduct $ZnCl_2$-diglyet was synthesized as a source of $ZnCl_2$, and zinc acetate was synthesized as previously reported [7].



SCHEME 1.

Commercial-grade reagent aluminum isopropoxide (AIP) (Merck) was purified by solution in dry pentane, filtered, and concentrated until dry under vacuum.

The purity of all initiators was tested by the standard titration methods for Al, Zn, and halides.

Monomer

Phenylglycidylether 99% (Aldrich) was dried prior to use by fluxing through an activated powder 4 Å molecular sieve column. Its purity was tested by HPLC. No phenol or other polar impurities were found.

Model Compounds

Aluminum alkoxides (B and C) were prepared by heating a mixture of AIP and the corresponding high boiling point alcohol [8] at 120°C until no more isopropanol was evolved. The products were used and characterized without purification.

AIP + 1-chloro-3-phenoxypropan-2-ol (B): ^{13}C-NMR spectrum ($CDCl_3$): δ 71.2 (CH), 69.8 (CH_2), and 45.8 (CH_2Cl).

AIP + 1-phenoxy-3-isopropoxypropan-2-ol (C): ^{13}C-NMR spectrum ($CDCl_3$): δ 71.8 (CH), 71.4 (CH_2), 71.2 (CH_2), 69.5 (CH), and 22.0 (CH_3).

Instrumentation

^{1}H, ^{13}C, and ^{27}Al spectra were recorded using a Varian Gemini 300 spectrometer working at 300 MHz for ^{1}H, 75.4 MHz for ^{13}C, and 78.1 MHz for ^{27}Al with different deuterated solvents. Chemical shifts are reported in ppm downfield from the internal reference $Si(CH_3)_4$ for ^{1}H, solvent signal for ^{13}C, and aluminum acetylacetonate for ^{27}Al.

IR spectra were recorded (film in a high density polyethylene cell) on a Nicolet 5ZDX FT-IR spectrometer.

Chlorine content was determined using a EUROGLASS microcoulometer with KCl solution as standard.

SEC measurements were made using WATERS 510 GPC equipment with polystyrene standards for calibration. The measurements were made using a two-serial column system (SHODEX K80M and PLGEL 3n MIXED-E lineal columns) with a HPLC WATERS 484 UV detector. The solvent was dichloromethane.

RESULTS AND DISCUSSION

Past attempts to elucidate the actual structure of this initiator system by spectroscopic techniques have been unsuccessful due to the great insolubility of $ZnCl_2$ in most common solvents. The only mechanistic studies on this type of ionic coordinative initiator system in the polymerization of epoxides were carried out by IR spectroscopy on the AIP/$ZnEt_2$ system [9], although these results are not entirely extrapolable to the AIP/$ZnCl_2$ system because of the differences which exist between the polymerization processes.

Nature of End Groups

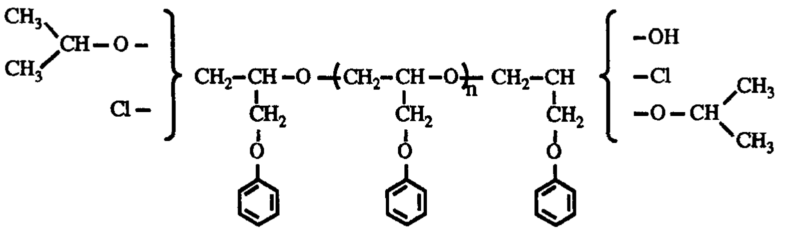
In the case of the isotactic insoluble polymer fraction, —OiPr and —OH end groups were also detected by ^{13}C-NMR in the spectra of the lowest molecular weight samples. Chlorine groups were also confirmed by microcoulometric measurements in this fraction. These latter studies demonstrate that chlorine content progressively increases as $ZnCl_2$ increases in the initiator system, indicating a clear increase in the percentage of polymer chains containing a chlorine atom.

A ^{13}C-NMR study demonstrated that hydroxylic groups are attached to a methine carbon as final groups (—CH—OH), and isopropoxide and chlorine groups are attached to a methylene carbon as initial groups. These latter groups are also attached to a methine carbon in the soluble polymer fraction, but in a very low percentage.

Scheme 2 summarizes these initial and final groups for both fractions.

According to the general anionic-coordinative mechanism, the polymer chain should have —OiPr and —OH as initial and final groups, respectively, but this mechanism does not explain the presence of other initial or final groups. The presence of the chlorine initial group cannot be attributed to a parallel mechanism initiated by $ZnCl_2$ alone since this process only leads to oligomers with very low molecular weight. This seems to be in contradiction with the presence of halogenated units in polymers with high molecular weights, mentioned above.

In the mechanism proposed by Jedlinski [6], the presence of chlorine atoms at the ends of polymer chains is attributed to participation of chlorinated oligomers formed in the first stage of the reaction in the initiator complex. This assumption is in agreement with the fast oligomerization we observed in the first stages of the polymerization which is related to the Zn/Al ratio used. This can be seen in Fig. 1 where SEC curves of the PPGE soluble fraction as a function of the Zn/Al ratio at 4 hours are plotted. On the other hand, NMR analysis shows that this initial oligomeric fraction mainly contains chlorine but no isopropoxide groups, whereas the oligomeric fraction recovered at the end of polymerization contains isopropoxide groups and only a low percentage of chlorine groups. This suggests that these halogenated oligomers with low molecular weights are built into the high molecular weight polymer. In this way, chlorine content measurements demonstrate that polymers obtained in the first polymerization stages have a much higher percentage of chlorine built into the chain.



SCHEME 2.

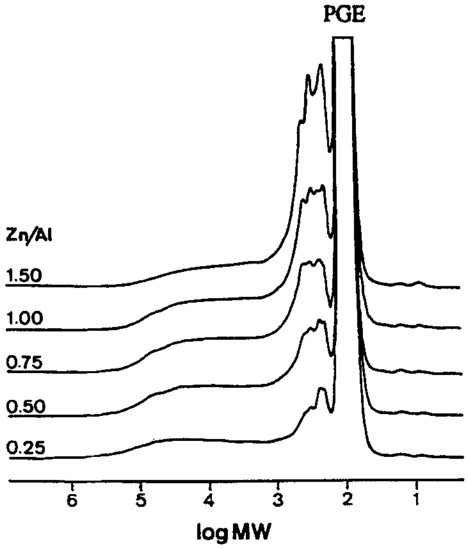


FIG. 1. SEC curves from the polymerization mixture obtained with 100/1 monomer/initiator ratio and different Zn/Al ratios at 100°C for 4 hours.

Nature of the Initiator

In order to obtain evidence about this polymerization mechanism and the nature of the initiator complex, several spectroscopic experiments were carried out with AIP, $ZnCl_2$, and monomer.

The inherent limitation due to the insolubility of $ZnCl_2$ was overcome by using the $ZnCl_2$-diglyet complex which is highly soluble in solvents such as chloroform, tetrachloroethane, and diglyme. An additional advantage of using this complex in NMR experiments is the possibility of following its evolution from changes observed in the chemical shifts of the coordinated diglyet molecule.

By means of IR spectroscopy and using high density polyethylene cells, we studied diglyet solutions of AIP, $ZnCl_2$, and their mixtures. The region between 700 and 400 cm^{-1} was studied since metal—C and metal—O vibrations [10] and torsional modes of alcoxy groups [11] appear in this zone. The results obtained are summarized in Fig. 2.

In spectrum a) the $ZnCl_2$ shows three absorptions at 552, 527, and 448 cm^{-1} (*a*, *b*, and *c*, respectively) which may be attributable to the "donor-acceptor" interaction between the $ZnCl_2$ and diglyet since in this zone neither $ZnCl_2$ nor solvent show significant signals.

In the AIP spectrum, b), 8 signals whose frequencies and relative intensities coincide with the ones reported by Bell et al. [12] are observed, and they correspond to a tetrameric molecule with a partially hexacoordinate structure which is already well established [13, 14]. In accordance with these studies, the vibrations between 750 and 600 cm^{-1} (1 and 2) are due to the terminal Al—O linkages whereas signals such as the ones that appear at 569 cm^{-1} (3) are generally assigned to the vibration of Al—O stretching in a bridge linkage [9].

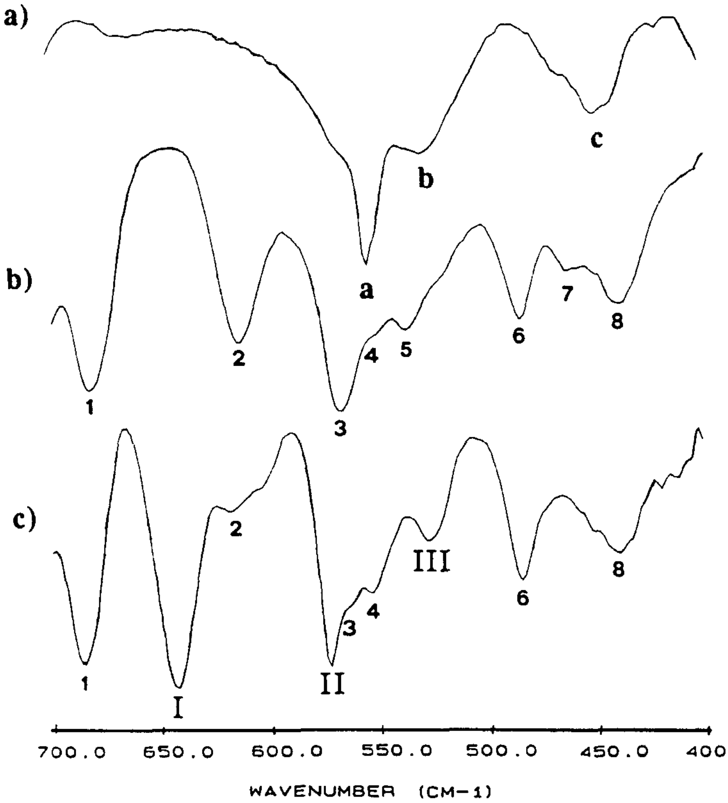


FIG. 2. Region between 700 and 400 cm^{-1} of the IR spectra of a) $ZnCl_2$, b) AIP, and c) $ZnCl_2$ + AIP (after heating at 90°C for 3 hours).

When the spectra (not shown) of both $ZnCl_2$ and AIP solutions are recorded together, the signals of both compounds are superimposed. However, after a certain time or by heating the mixture, the resulting spectrum, c), shows the appearance of new bands or the shift of others, and therefore some interaction has taken place between the species. The most important changes which can be observed are the disappearance of the band at 612 cm^{-1} (2), the appearance of a new band at 641 cm^{-1} (I), the disappearance of the band at 536 cm^{-1} (5), the appearance of a new band at 526 cm^{-1} (III) (although the latter may correspond to signal *b*, which may have increased its intensity), the shift of band *a*, corresponding to a $ZnCl_2$-diglyet interaction, from 552 to 572 cm^{-1} (II), and the partial overlapping with signal 3. All these changes took place gradually, and although they show that a reaction occurs, they do not allow us to determine if this reaction corresponds to the formation of an adduct "donor-acceptor" or implies the breaking of Zn—Cl and Al—OiPr linkages.

In this way, Zn—OR linkage formation seems to be discounted since there are neither the typical absorptions at 450 and 500 cm^{-1} nor the band at 470 cm^{-1} due to the O—Zn—O vibration [15].

All the aforesaid observations confirm that this is a coordinative process between zinc chloride and AIP which forms a new adduct in which the solvent also plays a role.

Other experiments were carried out in order to differentiate the free from the coordinated solvent molecules, so the $ZnCl_2$-diglyet adduct was characterized. Results from ^1H- and ^{13}C-NMR spectroscopy are collected in Table 1. As can be seen, when Zn increases, all chemical shifts change, which suggests that the Zn atom is able to coordinate through the three oxygens of the diglyet. The adduct formed is stable above its melting point (91-92°C).

The AIP used in all polymerization experiments was a tetramer as some authors have already reported [11, 13, 14]. This structure has isopropoxide groups attached to one or two aluminum atoms through a coordination linkage. Consequently, in the ^{13}C-NMR spectrum (a) in Fig. 3, two signals can be observed which correspond to methine carbons at 65.7 (II′) and 62.8 (I′) ppm and two pairs of signals of methyl carbons at 27.7-27.5 (I) ppm and at 26.0-24.9 (II) ppm corresponding to both environments. Thus, I and I′ correspond to the free isopropoxide groups whereas II and II′ correspond to the coordinated ones.

^{13}C-NMR spectra of several mixtures of AIP + $ZnCl_2$-diglyet for four Zn/Al ratios, previously heated at 100°C for 30 minutes, were recorded. The results are also shown in Fig. 3. Even at low Zn/Al ratios the reaction between AIP and $ZnCl_2$ (b in the figure) can be observed by the appearance of two new signals, a methyl carbon (A) and a methine carbon (A′). Moreover, the tetrameric AIP signals show a more complex pattern. On comparing all spectra, it can be seen that signal A is proportional to the $ZnCl_2$ present in the mixture and therefore must belong to the isopropoxide group directly coordinated to the $ZnCl_2$. As can be seen in the figure, in the spectra of the different mixtures, all signals are similar and only their relative

TABLE 1. ^1H- and ^{13}C-NMR Chemical Shifts of Diglyet and Its Adducts with $ZnCl_2$

$$\overset{a}{CH_3}-\overset{b}{CH_2}-O-\overset{c}{CH_2}-\overset{d}{CH_2}-O-CH_2-CH_2-O-CH_2-CH_3$$

		Chemical shifts, ppm	
NMR	Position	Diglyet	$ZnCl_2$-Diglyet
^1H	a	1.21 (t)	1.41 (t)
	b	3.53 (q)	3.86 (q)
	c and d	3.60 and 3.66 (m)	3.79 and 3.97 (m)
^{13}C	a	14.7	14.4
	b	66.1	68.5
	c	69.4	(66.7 and 69.9)
	d	70.2	

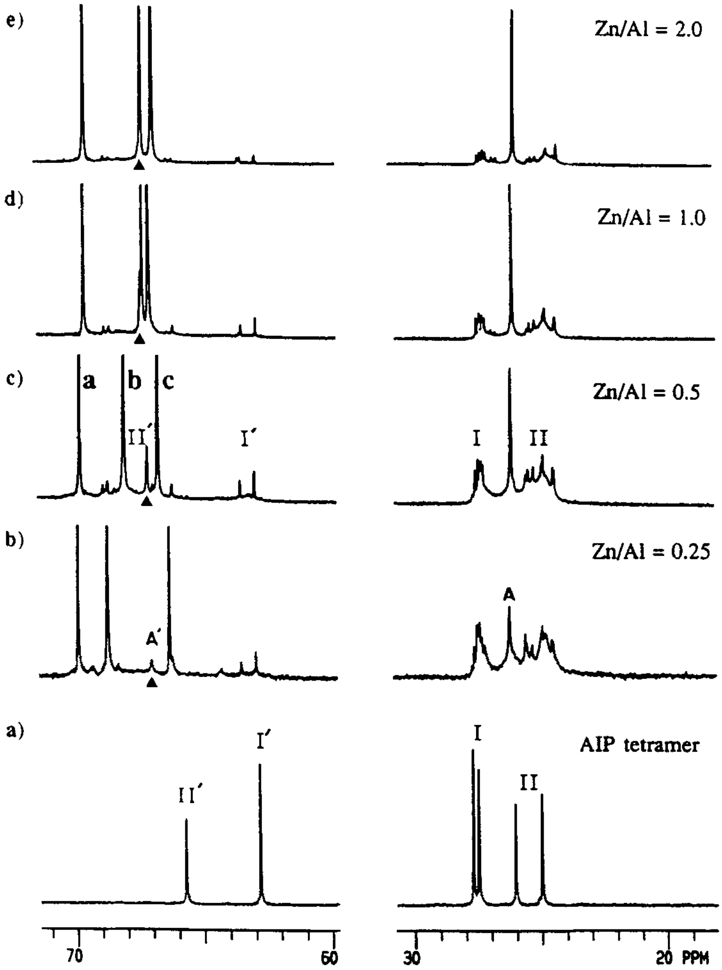


FIG. 3. Regions between 70–60 ppm and 30–20 ppm of the ^{13}C-NMR spectra of (a) AIP and (b)–(e) AIP + $ZnCl_2$-diglyet at 100°C using different Zn/Al ratios. Recorded in TCE-d_2.

intensities change, which suggests that no significant free AIP or $ZnCl_2$ is present. Therefore, the structure of this adduct must be a polymeric aggregate which becomes larger when the Zn/Al ratio increases.

Another important observation is that the signals corresponding to the diglyet (a, b, and c) change their chemical shifts but never reach the values observed for the free molecule (see Table 1), except in the case of the 0.25 Zn/Al ratio. This behavior suggests that diglyet molecules are also coordinated to the complex, and so they must be replaced by the monomer molecule in the polymerization process.

It has been shown experimentally that the diglyet does not significatively coordinate with AIP. Thus, the diglyet must be coordinated to the Zn atom in the complex and, therefore, this may be the coordinative site in the complex.

The ^{27}Al-NMR spectrum of the complex gave a signal only in the region between 2 and 6 ppm [$(Al(AcAc)_3 = 0$ ppm], characteristic of hexacoordinate Al complexes [16, 17], which indicates the high coordination of the complex.

Polymerization Mechanism

Before studying the polymerization of PGE with the AIP/$ZnCl_2$ initiator system, it seemed of interest to find out how PGE behaved with AIP and $ZnCl_2$ separately. Thus, a series of experiments were carried out (summarized in Table 2) in which assignments were made by comparison with previously synthesized model compounds [8] and previously reported data [18, 19].

Experiments 1 and 2 suggest that there is no coordination between oxiranic oxygen and Al, and that there is not considerable oligomerization.

On the other hand, Experiments 3a and 3b indicate a strong coordination between $ZnCl_2$ and PGE and a fast oligomerization process, following the typical cationic mechanism which leads to zinc chloroalkoxides (A) (see Scheme 3).

Experiments 3c and 3d suggest that the formation of an adduct between this zinc chloroalkoxide (Cl—Zn—OR) (A) and AIP is an unfavorable process whereas an interchange of alkoxide groups between this product (A) and aluminum isopropoxide occurs more easily to give the compound B. All the aforesaid results seem to discard the mechanism proposed by Jedlinski [6] as an explanation of the incorporation of halogenated groups in the initiation process, since they suggest the formation of an adduct between the zinc chloroalkoxides (A) and AIP.

The presence of aluminum chloroalkoxides (B) suggests an alternative mechanism to explain the incorporation of halogenated groups. This mechanism supposes that the new aluminum alkoxides from the interchange may also participate in the formation of the initiator. In this way, the halogenated group is incorporated into the initiator and therefore acts in the polymerization in a similar way to the isopropoxide group. This parallel process to form active species with halogenated groups is summarized in a series of equilibrium reactions shown in Scheme 4.

From Experiments 4a and 4b it can be deduced that oligomerization takes place in the first step of the reaction due to $ZnCl_2$. Once the adducts are formed, the polymerization process (the growing of chains) starts. These chains possess either chlorine or isopropoxide as the initial group (D and E, respectively).

Experiment 4c suggests that when larger amounts of monomer are present, polymerization preferentially occurs through isopropoxide initiation, indicating that incorporation of chlorinated oligomers mainly takes place in the first stage of polymerization.

Experiments 5a and 5b confirm that the chlorinated oligomers are progressively built into the growing chains through the aforesaid chloroalkoxide interchange.

Influence of the Zn/Al Ratio on the Polymerization Mechanism

As has been previously mentioned, the composition of the initiator complex varies with the Zn/Al ratio. This change does not affect the structure of active sites, and therefore the structure of soluble and insoluble PPGE polymer chains remains practically unaltered for different Zn/Al ratios. However, the conversion, the mo-

TABLE 2. Reaction Conditions and ^{13}C-NMR Results for Several Experiments Carried Out with AIP, $ZnCl_2$, and PGE

Expt.	Reagents	Ratio	Solvent	T, °C	Time	Changes in ^{13}C-NMR spectra and other observations	Assignment[d]
1	PGE + AIP	1:1	$TCEd_2$	80	1 h	No changes in the chemical shifts of PGE and AIP signals	
2 a	PGE + AIP	1:1	DGM[b]	80–100	1 to 24 h	PGE and AIP remain unaltered. Very slow oligomerization at 100°C	
3 a	PGE + $ZnCl_2$[a]	1:1	$CDCl_3$	Room	5 min	Exothermic reaction. No new products are detected but chemical shifts of PGE are slightly shifted	
b				50	1 h	PGE is consumed and diglyet becomes uncoordinated. Signals appear at 71.2 (CH), 69.9 (CH_2), and 45.8 (CH_2Cl) ppm	A
c	AIP is added to the reaction mixture 3b	1:1:1	$CDCl_3$	50	1 to 24 h	AIP remains unaltered. Signals appear at 70.2 (CH), 69.6 (CH_2), and 47.8 (CH_2Cl) ppm, in addition to those mentioned above	B
d					>24 h	Small signals similar to the ones observed for the AIP/$ZnCl_2$ complex	
4 a	AIP + $ZnCl_2$ + PGE	1:1:1	$TCEd_2$ or DGM	100	10 min	AIP remains unaltered. PGE signals decrease a lot and the same signals as in Expt. 3b appear	A

	b					10 h	PGE is consumed. In addition to the signals of A, signals appear at 72.4 (CH), 72.2 (CH_2), 72.0 (CH_2), 69.2 (CH), and 22.0 ppm (CH_3). Diglyet is not coordinated. Low intensity signals are observed[c] at 78.0 (CH), 73.5 (CH), 71.2 (CH_2), 68.9 (CH_2), 66.8 (CH_2), 43.2 (CH_2Cl), and 21.6 ppm (CH_3). AIP is consumed and new methylic signals appear	C D and E
	c	New amount of PGE			100	3 h	Intensity of signals corresponding to compound E increases.	
5	a	AIP + $ZnCl_2$; after heating at 100°C, PGE is added	1:0.5:2	$TCEd_2$	100	15 min	Adduct AIP:$ZnCl_2$ is formed. Diglyet becomes uncoordinated. Monomer is partially consumed and compounds A, B, and C are formed. Intensity of B signals is twice that of A	
	b					30 min	Monomer completely reacts. Compounds D and E are formed and signals of compound B undergo a noteworthy decrease	

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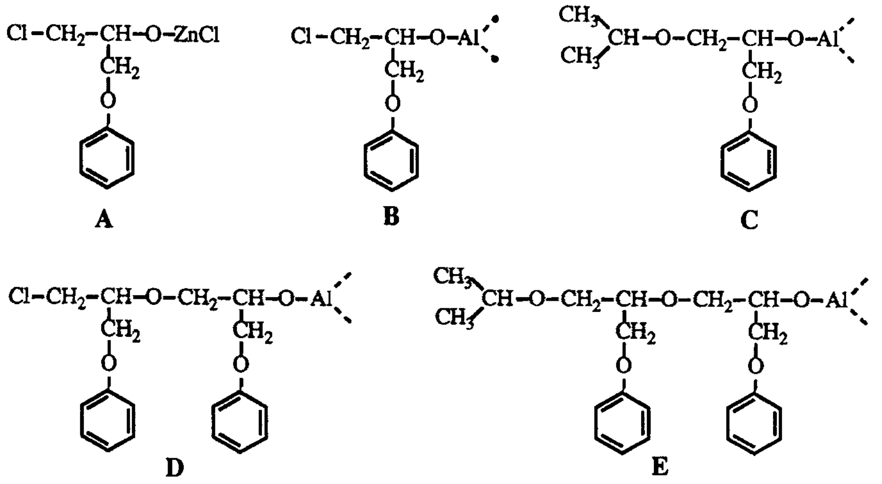
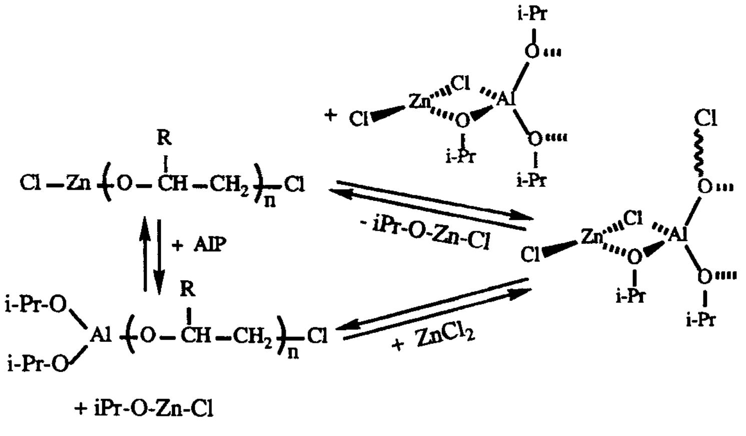
[a] $ZnCl_2$:diglyet was used in all cases.
[b] Diglyme-d_{14}.
[c] Some signals appear as a doublet.
[d] See Scheme 2.



SCHEME 3.

lecular weight, and the percentage of chain-end groups of these fractions are considerably affected.

The number of stereoselective active species appears to progressively increase with the Zn/Al ratio, as may be deduced from the great decrease in the molecular weight of the insoluble fraction when the proportion of $ZnCl_2$ increases [7]. It also seems that there is a parallel increase in the number of nonstereoselective active sites which lead to the atactic polymer. In this last fraction the relationship between propagation and termination rates is disfavored. Thus, the degree of polymerization reached is generally low (DP = 15–30), and the increase in the number of active species produces an increase in the conversion of this fraction.



SCHEME 4.

In all cases it has been proved that if the Zn/Al ratio is below 0.5, the conversion of the isotactic polymer increases with the proportion of zinc. At this point the conversion reaches a maximum value which decreases when the Zn proportion increases.

The evolution of the relative proportion between soluble and insoluble fractions above a Zn/Al ratio of 0.5 seems to be influenced by competitive mechanisms which lead to two types of polymers.

The oligomeric fraction, which is found in addition to the regular polymer, mainly originates by the action of isopropoxide groups of the initiator adduct without the participation of $ZnCl_2$. Most of the oligomers initiated by $ZnCl_2$ at the beginning of the reaction, in accordance with the results obtained, are incorporated into the soluble and insoluble fractions through a parallel initiation mechanism (Scheme 4).

The different behavior of this polymerization system as a function of the Zn/Al ratio was also proved by the nature and proportion of the different chain-ends and the content of irregular linkages [20]. In the case of isotactic PPGE, the monomeric units are regularly linked and isopropoxide and hydroxylic groups are mainly the initial and final groups, although halogenated groups are also detected as initial groups when the Zn/Al ratio used is increased. For the soluble fraction, the quantification of different end-groups as a function of the Zn/Al ratio, calculated from the average molecular weights obtained by SEC, is shown in Fig. 4.

As can be seen in this figure, addition of the percentages calculated for initial groups (Cl and O—iPr) closely coincides with the percentage of OH end-groups.

Finally, taking the results of structure and composition of initiator into account, the polymerization process could be explained according to the following assumptions: The composition of the initiator corresponds to a polymeric aggregate $(ZnCl_2)_n(AIP)_m$, in which m and n progressively change with the Zn/Al ratio used. The resulting adduct structure possesses at least two zones: one in which $ZnCl_2$ is encircled by AIP molecules and the other basically composed of AIP alone. Only

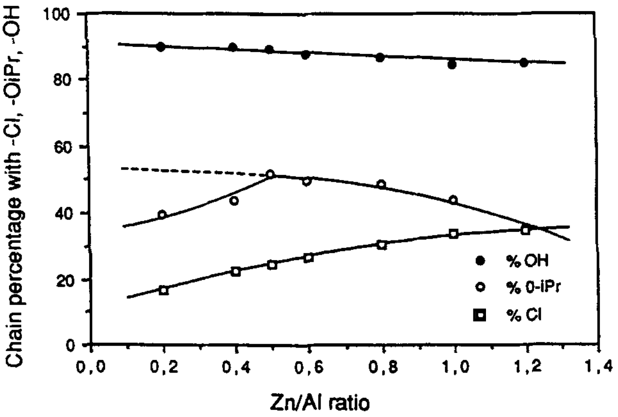


FIG. 4. Percentage of chains terminated in —Cl, —OiPr, and —OH as a function of the Zn/Al ratio for the PPGE-soluble fraction. The discontinuous line also includes iPrO—CH group percentages that are only important below the Zn/Al ratio of 0.5.

the former is able to start polymerization through a coordinative mechanism which leads to an isotactic polymer when the tridimensional arrangement makes chiral induction possible. If not, an atactic chain is created.

The latter behaves in a similar way to the tetrameric AIP complex, leading only to oligomeric products following a typical cationic mechanism.

Thus, when low Zn/Al ratios are used, extensive oligomerization is observed and the isotactic polymer conversion is low. However, molecular weights are highest due to the small number of stereoselective sites formed. When the amount of $ZnCl_2$ is increased, the m/n ratio in the $(ZnCl_2)_n(AIP)_m$ complex changes up to a certain value at which practically all zones of the initiator have the former structure and, therefore, the coordination mechanism is predominant. According to our results, this occurs at a Zn/Al ratio of 0.5. Only in the 0.5 to 1.0 range do the mechanisms leading to isotactic and atactic chains compete.

As the amount of $ZnCl_2$ becomes larger, stereoselective sites quickly decrease and the oligomerization process starts to increase again.

Influence of Zinc Salt

The Lewis acid character of the Zn salt used (ZnX_2) seems to affect the formation of the adduct and the monomer coordination process, since the ability to form a donor-acceptor complex decreases as follows: $Cl > Br > I \gg AcO$. In this sense the conversion of the isotactic polymer and the molecular weight of both fractions also diminishes, as has been reported [7].

Moreover, a noteworthy decrease in the percentage of chains initiated with isopropoxide groups was detected [8], which seems to suggest that the lower coordination ability of the zinc derivative delays the formation of the initiator complex, and therefore the cationic oligomerization increases. This could also explain the increase observed in the percentage of irregular linkages [20].

Influence of Water as Co-initiator

As previously reported [7], the presence of water leads to an increase in the molecular weight, conversion, and crystallinity of the isotactic fraction and a noteworthy decrease in the conversion of the atactic one.

The generally accepted function of water is to partially hydrolyze the alkoxide groups and to form new species which contain M—O—M linkages. The catalytic activity of these complexes is related to their stoichiometry and depends on the proportion of water added, the maximum ratio being between 1.0 and 1.5.

^{13}C-NMR experiments did not show remarkable changes in the AIP-$ZnCl_2$ adduct, with the only exception that a partial hydrolysis takes place leading to isopropanol whose chemical shifts suggest that it is also coordinated in the initiator complex. This suggests that the coordination of the isopropanol formed selectively inhibits the sites which lead to the atactic polymer, and therefore this mechanism does not compete with the sites which lead to the isotactic polymer.

At higher proportions of water the catalyst is destroyed, giving low activity oxides and hydroxides. Therefore, conversion of the insoluble polymer decreases and the predominant reaction is oligomerization.

CONCLUSIONS

All the above-mentioned experiments allow us to conclude the following about the polymerization process.

1. AIP and $ZnCl_2$ react to give an adduct of the donor-acceptor type with a complex structure that may also be polymeric. The formation of this adduct is better at higher temperatures, being considerably faster at 100°C.
2. In the presence of the AIP/$ZnCl_2$ initiator system, the monomer is attacked by $ZnCl_2$. Chlorinated oligomers are formed in which the halogen is mainly attached to a primary carbon.
3. The reaction between AIP and $ZnCl_2$ to form the initiator complex occurs after the beginning of the reaction between $ZnCl_2$ and PGE, suggesting that there is an induction period in the formation of the stereoregular active species and that a significant parallel oligomerization process takes place.
4. PGE is coordinated to the initiator complex through a Zn atom which replaces the diglyet molecule. Simultaneously to the coordination process and oxirane ring-opening, a change in the coordination initiator structure occurs due to incorporation of the new species.
5. An interchange reaction occurs between the halogenated oligomers formed in the first polymerization step and the different aluminum alkoxides, yielding another type of initiator complex which presumably is the one responsible for the presence of initial halogenated groups in a certain number of polymeric chains.
6. At a Zn/Al ratio of 0.5 the coordination mechanism is predominant and so isotactic polymer is mainly obtained due to the tridimensional arrangement of the resulting adduct that makes chiral induction possible.
7. The lower coordination ability of the zinc derivative delays the formation of the initiator complex, and therefore cationic oligomerization increases.

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