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Stereochemical Investigation of the Initiation Step in $MgCl_2$-Supported Ziegler–Natta Catalysts. The Lewis Base Activation Effect

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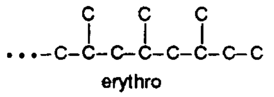
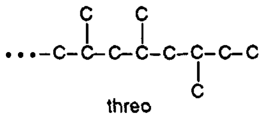
ABSTRACT: The ^{13}C NMR analysis of the initiation step is applied to the study of the effect of the Lewis bases on high-yield supported Ziegler–Natta catalysts for isotactic propene polymerization. Catalytic systems containing ethyl benzoate (EB) and bis(2-ethylhexyl) phthalate (BEHP) as internal bases are studied in the absence of external base and in the presence of 2,2,6,6-tetramethylpiperidine (TMPip) and phenyltriethoxysilane (PTS), as external bases. The fact that the increase of isotactic productivity here observed, due to the presence of either internal or the external base, is accompanied by a change of the first step stereoregularity gives evidence of the direct participation of the Lewis base on the formation of the isospecific centers.

Introduction

It is generally accepted that the stereoregulating effect of the Lewis bases in high-yield supported Ziegler–Natta catalysts cannot be reduced to a selective poisoning of the nonstereospecific centers, since the increase of isotactic productivity, observed in some cases, indicates that there is also an activation of the stereospecific centers.[1-7] However, up to now, the actual mechanism of this activation and the participation, or nonparticipation, of the Lewis base in the formation of the active centers are still open problems.

The purpose of this paper is to report our contribution to the understanding of the mechanism of the Lewis base activation and to give some evidence of the actual presence of the base in the isospecific site environment. Our approach to this problem consists in the study of the effect of the Lewis base, used both as an internal and external base, on the steric structure of isospecific centers of different catalytic systems. The method we use to obtain structural information on the active centers is the investigation, by ^{13}C NMR, of the initiation step in propene polymerization in the presence of the selectively ^{13}C-enriched cocatalyst $Al(^{13}CH_2CH_3)_3$. Taking into account only monomer insertion on the isotactic-specific centers, when polymerization starts on a metal–ethyl bond, we have two possible stereoisomers of chain end groups:


erythro


threo

Erythro (or isotactic) is the stereoisomer in which the two first monomeric units have the same configuration and threo (or syndiotactic) that one in which they have the opposite configuration. The use of ^{13}C-enriched ethyl group (coming from the cocatalyst $Al(^{13}CH_2CH_3)_3$) makes it possible to detect and distinguish the two stereoisomers by ^{13}C NMR.[8,9] If e (erythro) and t (threo) are the integrated peak areas of the enriched methylene resonances assigned, respectively, to the isotactic and syndiotactic placements of the first propene unit, the e/t ratio represents the extent of the first-step stereoregularity. A previous analysis of the stereochemistry of the ethyl chain end groups obtained in the presence of different conventional nonsupported catalytic systems has shown the following: (i) The stereospecificity of the first monomer insertion on the titanium–ethyl bond is always lower than the stereospecificity of the following propagation steps.[8,9] (ii) The extent of the first-step stereoregularity depends on the bulkiness of the halide and alkyl ligands of the catalytically active titanium and on their mutual interactions.[10,11] (iii) While the stereoregularity within the polymer chains is rather independent on the catalytic system, the extent of the first-step stereoregularity varies from one catalyst to another and is a reproducible characteristic of each catalytic system.[12]

On the basis of these findings, we applied this method to the study of the effect of the Lewis bases on the features of the active centers in supported catalysts.

Results and Discussion

We studied the effect of different internal bases in the absence of external base (see Table I).

Catalyst a is a simple catalyst without any base, catalyst b contains ethyl benzoate (EB), and catalyst c contains bis(2-ethylhexyl) phthalate (BEHP) as internal base. The addition of $ZnEt_2$ to the cocatalyst, due to its high chain-transfer ability, reduces the molecular weight of the polymers and increases the concentration of polymer chain end groups. In the presence of $ZnEt_2$, due to their lower molecular weight, some of the isotactic chains become heptane soluble. This fact, which produces a change of the fraction distribution (in particular the percent of heptane insoluble fraction, usually considered the isotacticity index, appears sensibly lower than in the absence of $ZnEt_2$) and of the chain and chain end stereoregularity of the ether and heptane soluble fractions, does not sensibly affect the e/t ratio of the heptane insoluble fractions.

Table I shows that in catalysts b and c the presence of the internal base produces a noticeable increase of the isotactic fraction with respect to sample a. We can also see that this increase of the isotactic fraction is accompanied by a noticeable enhancement of the first-step stereoregularity. It is worthwhile to remind that, while both

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Table I
Effect of Ethyl Benzoate and Bis(2-ethylhexyl) Phthalate Used as Internal Bases[a]

			isotactic fraction		
catalyst	Ti %	Y	wt %	[mm]	e/t
(a) $MgCl_2$–$TiCl_4$	2.4	55	29	0.91	2.2
(b) $MgCl_2$–EB–$TiCl_4$	1.4	44	70	0.94	2.8
(c) $MgCl_2$–BEHP–$TiCl_4$	3.0	55	66	0.94	3.4

[a] Cocatalyst, $Al(^{13}CH_2CH_3)_3$–$Zn(CH_2CH_3)_2$; EB, ethyl benzoate; BEHP, bis(2-ethylhexyl) phthalate; Y, yield in grams of polymer per grams of catalyst per hour; wt %, weight percent of heptane insoluble fraction; [mm], molar fraction of isotactic triads by NMR; e/t, intensity ratio (integrated peak area) of resonances related to the isotactic (e) and syndiotactic (t) placement of the first propene unit.

the percent of isotactic fraction and the e/t ratio are rather constant and characteristic values of the catalyst c containing a diester as an internal base, they can vary, depending on the polymerization conditions, with the catalyst b containing a monoester as an internal base. This is in agreement with the data of other authors,[13] according to which the internal base can be removed to a high extent from the catalysts, due to the effect of the cocatalyst. Therefore, even a slight change in the polymerization conditions could drastically change the amount of EB present in the catalyst. As a consequence the fraction distribution and the e/t ratio can vary either.

Figure 1 shows the methylenic chain end group region of the spectra of the three samples, where one can evaluate the variation of the e/t ratios due to the presence of the two internal bases.

In general there are two current interpretations as to the role of the internal base:

(i) The first points out that the base, $MgCl_2$, and $TiCl_4$ form a three-component complex, which is the actual active center;[14-16] thus, the base has a direct function.

(ii) The second states that the two-component complex $MgCl_2$–$TiCl_4$ is the true polymerization center;[17,19] thus, the base has an indirect function, for instance, by controlling the titanium fixation on $MgCl_2$.[20]

The fact that the two internal bases we have examined produce a change of the e/t ratio of the stereospecific fractions means that the internal base changes the steric features of the isospecific centers. This indicates that the internal base is present in the environment of at least part of the isospecific centers. Therefore, without ruling out other interpretations as to the role of the internal base, our data support the hypotheses of the direct effect of the internal base on the isospecific centers.

Next we have studied the effect of two different Lewis bases, 2,2,6,6-tetramethylpiperidine (TMPip) and phenyltriethoxysilane (PTS), used as external bases, with the same catalyst containing bis(2-ethylhexyl) phthalate as internal base. Table II shows that both bases produce a moderate reduction of the total productivity and a noticeable increase of the isotactic fraction: therefore in both cases an increase of the isotactic productivity is observed. Here also the increase of the isotactic productivity is accompanied by a variation of the e/t ratio. It is worthwhile to observe that, while with both bases the stereoregularity within the chain is nearly the same (both fractions are highly stereoregular), the e/t ratios differ to a great extent from each other.

Figure 2 shows the methylenic chain end group region of the spectra of the three samples, where one can evaluate the variation of the e/t ratios due to the addition of the two external bases.

These data allow us to state that the external base or a product of its coordination or reaction with the cocatalyst is present in the environment of at least part of the isospecific centers; only this hypothesis accounts for the increase in isotactic productivity, the remarkable variation of the first-step stereoregularity, and the fact that different external bases produce different variations of

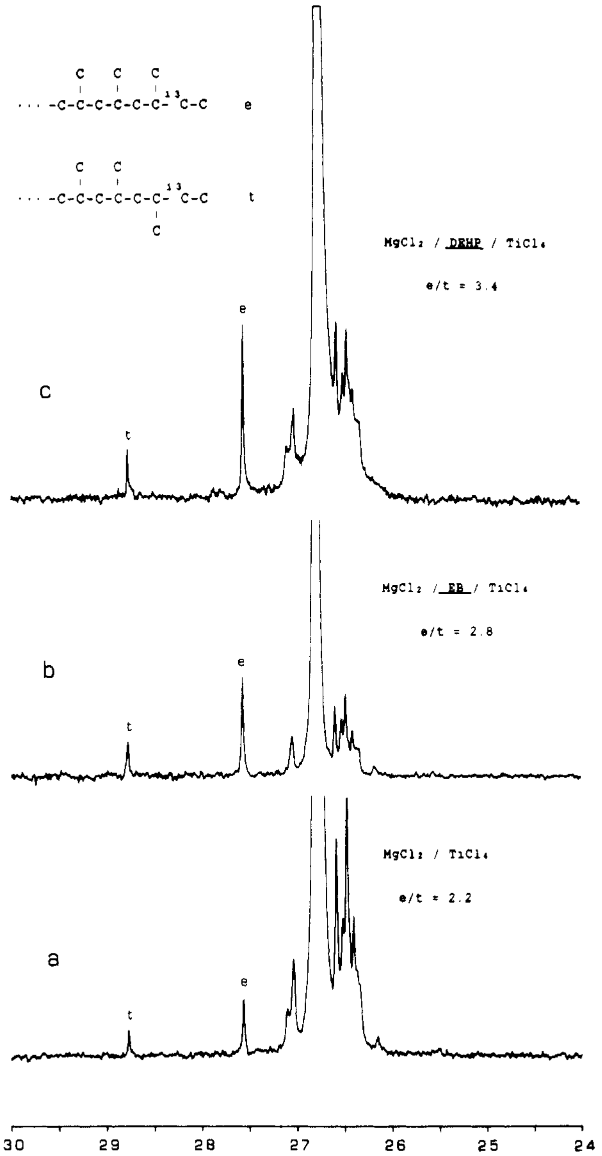

Figure 1. Methylenic chain end group region of the ^{13}C NMR spectra of the isotactic fractions of the polypropene samples obtained, respectively, with the catalytic systems a–c of Table I. The resonances labeled with e and t are assigned to the enriched methylene corresponding, respectively, to the isotactic and syndiotactic placement of the first propene unit.

Table II
Effect of Tetramethylpiperidine and Phenyltriethoxysilane Used as External Bases[a]

			isotactic fraction		
catalyst	Lewis base	Y	wt %	[mm]	e/t
$MgCl_2$–BEHP–$TiCl_4$		55	66	94	3.4
$MgCl_2$–BEHP–$TiCl_4$	TMPip	46	87	95	3.0
$MgCl_2$–BEHP–$TiCl_4$	$PhSi(OEt)_3$	47	92	97	8.1

[a] Cocatalyst, $Al(^{13}CH_2CH_3)_3$–$Zn(CH_2CH_3)_2$; BEHP, bis(2-ethylhexyl) phthalate; TMPip: 2,2,6,6-tetramethylpiperidine; Y, yield in grams of polymer per grams of catalyst per hour; wt %, weight percent of heptane insoluble fraction; [mm], molar fraction of isotactic triads by NMR; e/t, intensity ratio (integrated peak area) of resonances related to the isotactic (e) and syndiotactic (t) placement of the first propene unit.

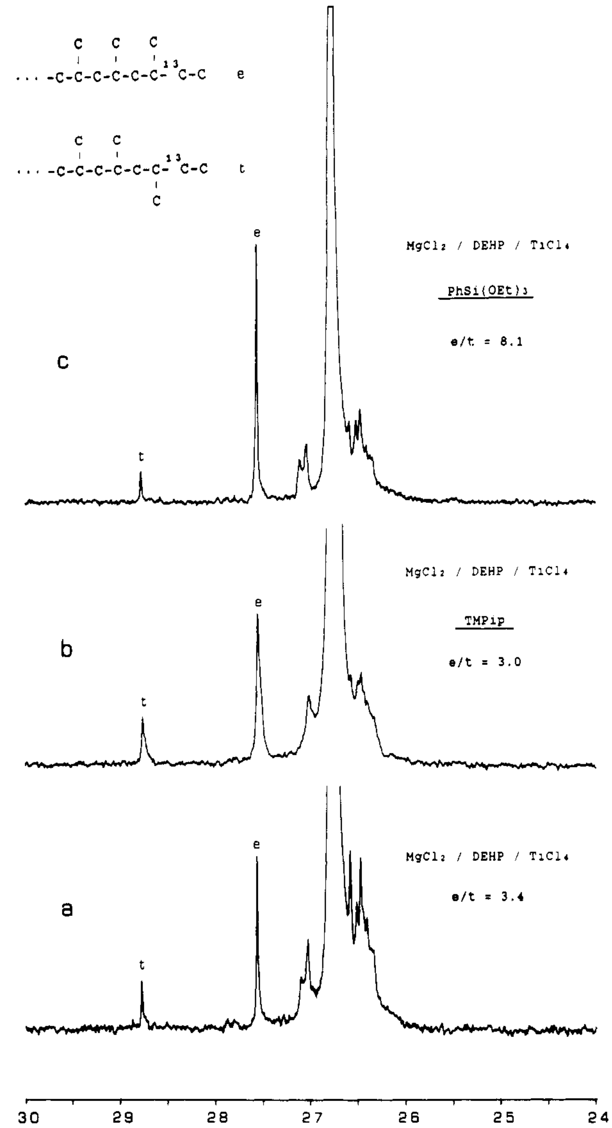

Figure 2. Methylenic chain end group region of the ^{13}C NMR spectra of the isotactic fractions of the polypropene samples obtained with the same catalytic system, containing BEHP as an internal base, in the absence of the external base (a) and, respectively, with TMPip (b) and PhSi (OEt)$_3$ (c) as an external base.

the e/t value. On the basis of the data presently available, it is not possible to distinguish whether the external base is present in the environment of the isospecific centers due to the exchange with the internal base or as a complex with the cocatalyst or both.

Conclusions

The increase of the isotactic productivity here observed, due to the presence of either the internal or the external bases, is accompanied by a change of the e/t ratios of the isotactic fractions. On the basis of these findings and of our previous data concerning conventional Ziegler–Natta catalysts, it is possible to deduce that both the internal and the external bases are present in the environment of at least some of the isospecific centers. The data presently available do not allow us to give more details as to the mechanism of the Lewis base activation and to the actual position of the base in the coordination sphere of the active titanium. However, every interpretation as to the role of both internal and external base must also take into account their direct participation on the formation of the isospecific centers.

Experimental Part

Reagents. The MgCl$_2$–TiCl$_4$ catalyst a (Ti = 2.4%) was obtained by chlorination of the Grignard compound n-C$_4$H$_9$MgCl as described in the patent literature.[21] Catalyst b, containing ethyl benzoate as an internal base (Ti = 1.4%, EB = 10.5%), was kindly supplied by Dr. Albizzati of the Istituto G. Donegani, Novara, Italy. Catalyst c, containing bis(2-ethylhexyl) phthalate as an internal base (Ti = 3.0%, PTS = 17.9%), was prepared from soluble MgCl$_2$, 2-ethylhexanol, phthalic anhydride, and TiCl$_4$ according to patent literature.[22] Al(^{13}CH$_2$CH$_3$)$_3$ was prepared by reaction of CH$_3$^{13}CH$_2$Li with AlCl$_3$ as reported in literature.[23]

Polymerizations. All the polymerizations were carried out in a glass reactor containing 50 mL of heptane as a solvent. Al(^{13}CH$_2$CH$_3$)$_3$ (Al/Ti = 20), Zn(CH$_2$CH$_3$)$_2$ (Zn/Al = 3), the Lewis base (base/Al = 0.1), and the solid catalyst (0.2 g) were added in the said order. The reactor was filled with propylene, and the polymerizations were performed under atmospheric pressure for 1 h at 20 °C. The polymers were fractionated with boiling solvents by conventional methods.

NMR Analysis. The NMR samples were prepared by dissolving ca. 100 mg of polymer in 1 mL of 1,2,4-trichlorobenzene in a 10-mm-o.d. tube. A total of 0.5 mL of C$_2$D$_2$Cl$_4$ was added as a lock solvent, and 1% of hexamethyldisiloxane was used as an internal chemical shift reference. All the spectra were obtained by using a Bruker AM-270 spectrometer operating at 67.89 MHz in PFT mode, at a temperature of 115 °C. A standard pulse sequence (INEPT) was employed:

$$\begin{array}{ll} ^{1}\mathrm{H} & \mathrm{RD{-}90{-}}\tau_1\mathrm{{-}180{-}}\tau_1\mathrm{{-}90{-}}\tau_2\mathrm{{-}180{-}}\tau_2\mathrm{{-}decouple} \\ ^{13}\mathrm{C} & \qquad\quad 180 \quad 90 \quad 180 \quad \mathrm{detect} \end{array}$$

In this sequence, the recycle time of 5 s ensures that the system is fully relaxed. A total of 16K data points were accumulated over a sweep width of 7.5 kHz. Delay times t_1 and t_2 were 1.9 and 1 ms, respectively; ^{13}C pulse widths were 8.4 s (90°) and 16.8 s (180°).

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Registry No. TMPip, 768-66-1; EB, 93-89-0; DEHP, 117-81-7; MgCl$_2$, 7786-30-3; TiCl$_4$, 7550-45-0; Al(^{13}CH$_2$CH$_3$)$_3$, 97-93-8; PhSi(OEt)$_3$, 780-69-8; Zn(CH$_2$CH$_3$)$_2$, 557-20-0; isotactic polypropylene, 25085-53-4.

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Excitation Spectroscopy of a Reactive Label for Characterization of the Cure Process in an Epoxy Network

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ABSTRACT: Fluorescence excitation spectra of a reactive label, *p,p'*-diaminoazobenzene (DAA), were investigated to characterize the cure process in an epoxy network composed of a stoichiometric mixture of diglycidyl ether of Bisphenol A and diaminodiphenyl sulfone. Under ideal conditions, the corrected excitation spectra should resemble UV–visible absorption spectra with an intensity proportional to the fluorescence quantum yield. Therefore, corrected excitation spectra of the model cure products as well as a function of various composition of cure products were simulated. Due to the sharp increase in the fluorescence quantum yields of the later cure products, such simulated excitation spectra are well separated from each other. Experimentally obtained excitation spectra of the model cure products and of the curing epoxy showed some distortions in the spectra that are probably due to instrumental factors. Nevertheless, the excitation maximum was observed near 470 nm, corresponding to the absorption maximum of the tertiary–tertiary amine product of DAA. The intensity of the experimental excitation spectra after calibration with UV–visible absorption spectra was found to show sharp increase as a function of cure time, followed by leveling off after vitrification of the epoxy network. This profile was very similar to that of the intensity of fluorescence emission, reported in our previous study. Under the assumptions that the reactions between the diamines and the epoxide are the main cure reactions and the primary amine and the secondary amine react at similar rates, the cure product composition has been estimated, on the basis of the excitation intensity. The results show a reasonable trend of the formation and the disappearance of the cure species. Therefore, this study demonstrates that excitation spectra can be used for cure characterization of epoxy network.

Introduction

Recently, we introduced the approach of reactive labeling techniques for the study of polymerization and cross-linking in polymers. In this approach, the reactive label is designed to have similar reactivities as one of the polymerizing components and to exhibit spectral changes in the region of UV–visible absorption and fluorescence spectra where the polymerizing matrix has little absorption or emission. Basically, we take advantage of the magnified effects of the substituent changes in the para and para primed positions of aromatic reactive labels on the UV–visible and fluorescence spectra. This approach has been applied to several polymers such as cross-linked epoxies,[1] polyimides,[2] polyurethanes,[3] and polyamides.[4] One particular advantage of this approach is that we can often distinguish between several cure species in some polymers while with other spectroscopic techniques such as IR or NMR we cannot. This is because the electronic spectra such as UV–visible absorption are influenced by both of the substituents at the para and para primed positions of conjugated aromatic compounds, while IR or NMR is determined only by the functional groups in each substituent. For example, we have shown that each of the several cure species in polyimide synthesis such as polydiamic acids, polyamic acid–imide, and polydiimide has its characteristic UV–vis absorption spectra and is thus clearly distinguishable.[2a,5] This advantage makes it possible to follow cure composition throughout the cure process and to analyze the kinetics and the mechanisms of several consecutive polymerization steps in some polymers.

In the characterization of epoxy cure, we found that a reactive label, *p,p'*-diaminoazobenzene (DAA), showed significant red shifts in UV–vis spectra and drastic enhancement of fluorescence emission intensity when reacted with epoxide. Thus, the deconvolution of UV–vis absorption spectra provided the estimates of the fraction of each cure species. The fluorescence intensity at the emission maxima was also used to quantify the fraction of each cure species, assuming a certain kinetic scheme. In UV–vis absorption spectra, significant spectral overlap between different cure species made the deconvolution difficult, especially at the intermediate cure extent. This overlap

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