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^{13}C NMR Investigation of the Interactions between Amines and Ziegler–Natta Catalysts for α-Olefin Polymerization

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ABSTRACT: Propylene has been polymerized in the presence of the catalyst δ-$TiCl_3/Zn(^{13}CH_2CH_3)_2$, used as a model system, at different concentrations of Et_3N and of 2,2,6,6-tetramethylpiperidine. The ^{13}C NMR analysis of the steric structure of the chain end groups of all the fractions of the polymers indicates that there are a variety of active sites, both isotactic and atactic, with different steric features, although producing polymer chains of the same tacticity. The distribution among the different types of active sites belonging to the same class changes at different concentrations of the free and/or complexed base. Moreover at concentration corresponding to the maximum of catalyst activity, the stereospecificity of the first step in the most isotactic fractions is higher than that observed in the absence of base and depends on its steric features. This fact provides evidence for the presence of the amines in the active-center environment.

Introduction

Lewis bases are widely used in Ziegler–Natta catalysis as enhancers of the stereospecificity of $MgCl_2$-supported catalysts for the polymerization of α-olefins. In propylene polymerization the stereospecificity has always been found to increase upon addition of a base as a third component, often accompanied by a loss of productivity. On the basis of these results many authors explained the increase in polymer isotacticity by the ability of the bases to poison selectively the nonstereospecific polymerization centers.[1,2] However, increase of isotactic productivity was observed by other authors in the presence of such Lewis bases as esters of aromatic acids,[3-5] 2,2,6,6-tetramethylpiperidine,[4,5] and phenyltriethoxysilane.[5] Therefore the way by which Lewis bases affect the catalyst stereospecificity is more complex than a simple poisoning, as at least a further effect has to be considered, i.e., the activation of the isotactic centers.

In a previous paper[6] we reported a study of the effects of two amines, Et_3N and 2,2,6,6-tetramethylpiperidine (TMPip), on the catalysts $MgCl_2/TiCl_4/AlEt_3$, δ-$TiCl_3/AlEt_3$, and δ-$TiCl_3/ZnEt_2$. Our findings indicated that the poisoning and the activation act at the same time and either the former or the latter effect dominates, depending on the relative strength of the complexation equilibria between the bases and the various Lewis acids present in solution. In particular, the interaction of the uncomplexed base with the active sites was shown to be responsible for the poisoning effect, the selectivity of the process depending on the steric hindrance of the base. On the other hand, the presence in solution of sufficient base–alkylmetal complex was connected to the activating effect, the extent of the activation depending also on the structure of the base.

The purpose of this report is to obtain information on the mechanism by which the base–alkylmetal complex activates the isotactic sites. A ^{13}C NMR analysis was performed on ^{13}C-enriched chain end groups of polypropylene samples obtained in the presence of the catalyst δ-$TiCl_3/Zn(^{13}CH_2CH_3)_2$, using Et_3N and TMPip as Lewis bases. In the last few years the study of the stereochemistry of the ^{13}C-enriched chain end groups has allowed one to evaluate the steric control exerted by different alkyl and halide ligands of the catalitically active titanium and their mutual interactions.[7-9] Since such an analysis is sensitive to even small variations in the titanium coordination sphere, we expected that it could give evidence for the presence, if any, of the activating complex in the neighborhood of the active titanium and therefore of the possible direct influence of Lewis bases on the active centers.

Results

Table I summarizes the conversion and fractionation results for polypropylene samples obtained in the presence of the catalyst δ-$TiCl_3/ZnEt_2$, using Et_3N and TMPip at three significant base/$ZnEt_2$ (R) ratios. As was observed by Boor,[10] increasing the base concentration produces in dialkylzinc-based catalysts first a lowering and then an increase of activity. Therefore, this catalyst, since it allows one to partially distinguish the concurrent deactivating and activating effects, could be useful as a model system to study the mechanism of the activation and deactivation observed in many conventional and supported catalytic systems. On this basis, we have examined by ^{13}C NMR polypropylene samples prepared with the catalyst δ-$TiCl_3/Zn(^{13}CH_2CH_3)_2$, at $R = 0.032$ (minimum of catalyst activity) and 0.320 (maximum of catalyst activity). In Figure 1 are shown in the ^{13}C NMR spectra of the heptane-insoluble, octane-soluble fractions[11] of the samples obtained in the absence of base (Figure 1a) and in the presence of Et_3N (Figure 1b) and TMPip (Figure 1c), at $R = 0.032$. The labeled peaks are due to the ^{13}C-enriched

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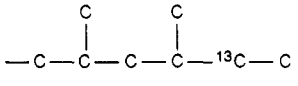
Table I
Activating and Deactivating Effects of Et_3N and TMPip in Propylene Polymerizations[a]

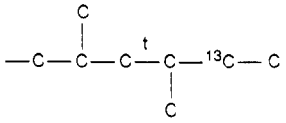
Et_3N				TMPip			
monomer conv, %	ether sol, %	heptane sol, %	heptane insol, %	monomer conv, %	ether sol, %	heptane sol, %	heptane insol, %
86	14	17	69	86	14	17	69
40	4	7	89	59	4	6	90
85	4	3	93	89	6	4	90

[a] For polymerization and fractionation conditions, see Experimental Section.

methylene chain end groups, e and t corresponding to the isotactic and syndiotactic first monomeric unit insertion:[7]



e (erythro) = isotactic first inserted unit



t (threo) = syndiotactic first inserted unit

Table II contains information concerning the stereoregularity of the end groups, expressed as the ratio between the intensities of e and t ^{13}C NMR resonances (I_e/I_t) along with R ratios. For $R = 0.032$ the I_e/I_t value is lower for both amines than that observed in the absence of base, attaining for Et_3N the lowest value we have ever observed in propylene insertion on the Ti–ethyl bond. Figure 2a reiterates the spectrum of the octane-soluble fraction of the sample obtained in the absence of base, as a reference, while parts b and c of Figure 2 show the spectra of the octane-soluble fractions of the samples obtained with Et_3N and TMPip, respectively, at $R = 0.320$. In this case, the I_e/I_t value is higher than that observed in the absence of base (cf. Table II), approaching, for TMPip, the value of the subsequent propagation steps. In order to draw a more complete picture of the effect of Lewis base on catalyst performance, all the fractions obtained from these samples have been analyzed by ^{13}C NMR. In Figure 3 the molar fraction of *mm* triads is plotted against I_e/I_t for all the fractions of the polymers obtained at the different concentrations of Et_3N and TMPip. For both amines we observe different curves at different base concentrations; i.e., the fractions having the same tacticity [*mm*] of the polymers obtained at $R = 0.032$ and 0.320 show different I_e/I_t values.

Discussion

From the above data many deductions are possible concerning both the role of the Lewis bases and the nature of the active sites.

Let us first discuss the trend of the stereoregularity of the initiation step for the most isotactic fractions at increasing base concentrations. For both amines we have observed a decreasing of I_e/I_t at low base concentrations (i.e., in the deactivation phase) with respect to I_e/I_t in the absence of base (Figure 1 and Table II). As the stereochemistry of the initiation step depends on the active-site environment, the lower stereospecificity of the initiation step indicates that the centers active at $R = 0.032$ have a different steric environment from those active without base. Taking into account that the lowering of I_e/I_t is associated with decrease of activity, the most likely hypothesis is that, among the isotactic sites initially active on the $TiCl_3$ surface (Ci), those having the higher I_e/I_t value (Ci′) are more easily poisoned, in the deactivation

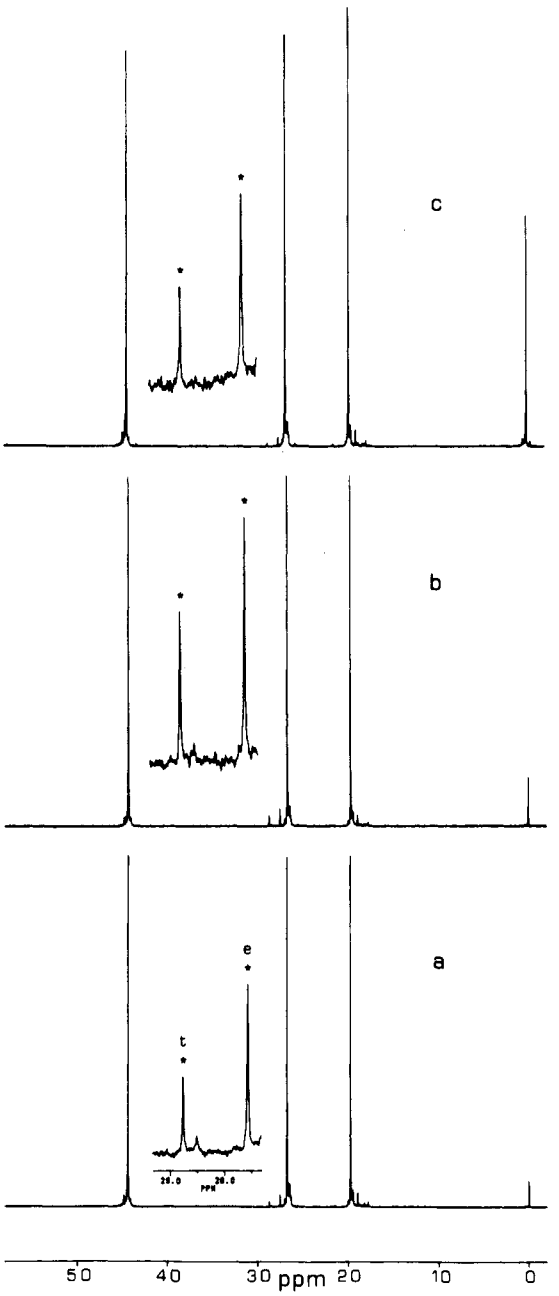


Figure 1. ^{13}C NMR spectra of the heptane-insoluble, octane-soluble fractions of polypropylene samples prepared in the absence of base (a) and at $B/ZnEt_2 = 0.032$ (deactivation phase), for B = Et_3N (b) and B = TMPip (c).

phase, compared to the others (Ci″). Therefore the use of low base concentrations gives evidence of the existence of at least two kinds of isotactic centers, Ci′ and Ci″, differing in some way in their steric environment and having respectively a higher and a lower I_e/I_t value compared to the average value observed at $R = 0$.

A further kind of isotactic active site, having the highest stereoregularity of the initiation step observed in this

Table II
Chain End Stereoregularity of the Examined Polypropylene Samples

B	$B/ZnEt_2$	ether sol fractn		heptane sol fractn		octane sol fractn	
		$[mm]^c$	$I_e/I_t{}^d$	$[mm]^c$	$I_e/I_t{}^d$	$[mm]^c$	$I_e/I_t{}^d$
	0	0.34	1.00	0.63	1.88	0.94	2.20
Et_3N	0.032[a]	0.40	0.87	0.71	1.48	0.94	1.50
Et_3N	0.320[b]	0.28	0.61	0.59	2.11	0.95	2.70
TMPip	0.032[a]	0.34	0.86	0.66	1.65	0.97	1.90
TMPip	0.320[b]	0.30	0.55	0.71	1.64	0.97	5.50

[a] $B/ZnEt_2$ corresponding to the minimum of catalyst activity. [b] $B/ZnEt_2$ corresponding to the maximum of catalyst activity. [c] Chain stereoregularity expressed as mole fraction of isotactic triads *mm*, evaluated from ^{13}C NMR spectra of the methyl groups. [d] Stereoregularity of the insertion of the first monomeric unit, expressed as the intensity ratio between the resonances at 27.72 and 28.83 ppm of the ^{13}C-enriched methylene carbons.

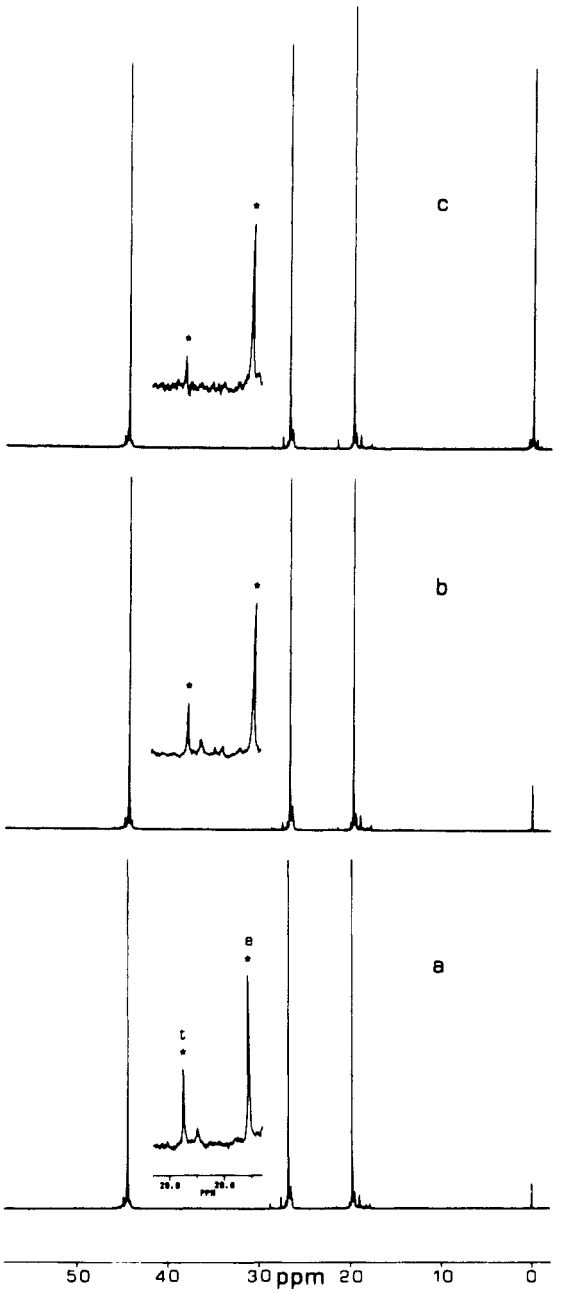


Figure 2. ^{13}C NMR spectra of the heptane-insoluble, octane-soluble fractions of polypropylene samples prepared in the absence of base (a) and at $B/ZnEt_2 = 0.320$ (activation phase), for B = Et_3N (b) and B = TMPip (c).

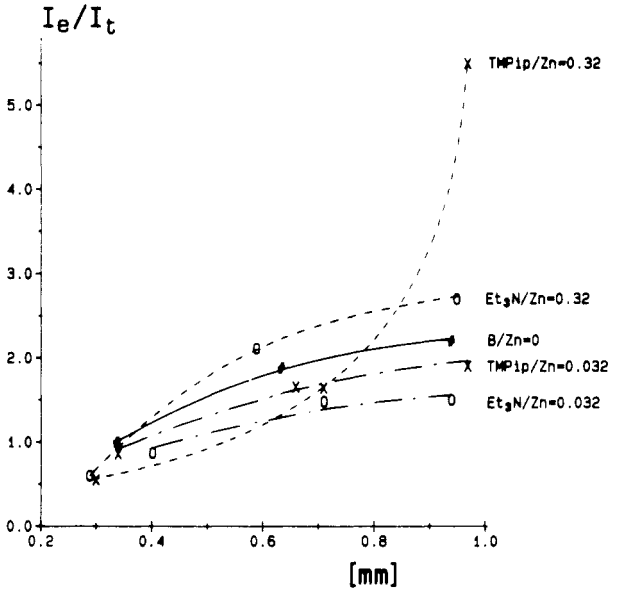


Figure 3. Stereoregularity of the insertion of the first monomeric unit (I_e/I_t) versus molar fraction of isotactic triads [*mm*] for all the fractions of polypropylene samples obtained at B/Zn = 0 (—), B/Zn = 0.032 (deactivation phase) (- · -), and B/Zn = 0.320 (activation phase) (- - -), for Et_3N (O) and TMPip (×); B/Zn = base/$ZnEt_2$.

study, is evidenced in the activation phase. Such activation was previously related[4] to the presence in solution of a sufficient base–alkylmetal complex. Concerning the mechanism by which the complex acts, two hypotheses could be in principle put forward: (i) The complex activates new centers which are actually ineffective in the absence of base or at low concentration of base, by affecting the electronic environment of potentially active titanium atoms. The function of the base would be in this case "indirect", and the higher I_e/I_t value would depend exclusively on the intrinsic steric features of these activated sites. (ii) The complex enhances the catalyst activity by direct interaction with the catalytically active titanium atoms. The higher I_e/I_t value would be due in this case to the very presence of the complex in the active-center environment, the extent of the stereospecificity of the first step depending not only on the intrinsic chirality of the active sites but also on the steric features of the complex. The coexistence of both mechanisms is possible. However, the fact that with TMPip the I_e/I_t value is remarkably high compared to that observed with Et_3N is more in keeping with the second hypothesis. Indeed, as has been pointed out,[7-9] the bulkier the titanium ligand, the higher is the control of the stereochemistry of the initiation step. Therefore it seems conceivable that centers containing a very hindered base such as TMPip may be more selective in the initiation step compared to those containing the much less hindered Et_3N.

We have observed in addition that the presence of the base induces variations in the stereochemistry of the chain

end groups in the less isotactic fractions (cf. Figure 3 and Table II). In particular, I_e/I_t in the ether-soluble fractions decreases continuously with increasing base concentration over the whole range used. These results show the existence of a variety of atactic centers with different reactivity toward Lewis bases and indicate that, like the most isotactic centers, the atactic centers having the higher I_e/I_t values are more easily poisoned by both amines.

Thus both the isotactic and the atactic centers may be described as classes of sites,[12] having different steric features, although producing polymer chains of the same tacticity. The distribution of different types of active sites belonging to the same class changes with the concentration of free and/or complexed base.

Conclusions

The ^{13}C NMR analysis of the steric structure of chain end groups of polypropylene samples obtained with the catalyst δ-$TiCl_3$/$Zn(^{13}CH_2CH_3)_2$, used as a model system, at different concentrations of Et_3N and TMPip, has allowed us to confirm the existence of a variety of catalytic centers, both isotactic and atactic, differing in steric environment and reactivity toward Lewis bases, although producing polymer chains with the same microstructure.

In addition, the comparison between the effects due to the two amines having wide differences in steric hindrance has given evidence for the presence of the bases in the active titanium environment in the activation phase. It is likely that this activation mechanism is not restricted to the catalyst used here but applies also to more complex catalytic systems.

The results of this study prompt us to explore, by the same method of analysis, the effect of Lewis bases on the high-yield supported-titanium-based catalysts.

Experimental Section

Reagents. $TiCl_3$·0.3A1Cl_3 (Stauffer) was purified by extraction with boiling toluene. Commercial Et_3N and 2,2,6,6-tetramethylpiperidine were dried by refluxing over KOH and purified by subsequent fractionation. $Zn(^{13}CH_2CH_3)_2$, 34% ^{13}C enriched, was prepared, in an inert atmosphere (N_2), by thermal disproportionation of $CH_3{}^{13}CH_2ZnBr$, the latter being obtained in situ, by direct reaction between $CH_3{}^{13}CH_2Br$ and zinc–copper couple.[13]

Polymerizations. The polymerization runs were performed in an autoclave, at 50 °C, in the presence of 30 g of C_3H_6, with the catalytic system δ-$TiCl_3$·0.3A1Cl_3 (1.5 mmol)/$Zn(^{13}CH_2CH_3)_2$ (4.5 mmol) suspended in dry toluene (100 mL). The polymerization time was 20 h. The fractionation of polymer samples with boiling hydrocarbons was carried out by a conventional method.[14] The monomer conversion and fractionation results are reported in Table I.

^{13}C NMR Analyses. ^{13}C NMR analyses of the polypropylene fractions dissolved in 1,2,4-trichlorobenzene containing 1% $C_2D_2Cl_4$ as an internal standard were carried out in the PFT mode on an AM-270 Bruker spectrometer operating at 67.89 MHz. The chemical shifts are relative to HMDS.

Registry No. $TiCl_3$, 7705-07-9; $Zn(^{13}CH_2CH_3)_2$, 87464-43-5; Et_3N, 121-44-8; TMPip, 768-66-1; $H_2C{=}CHCH_3$, 115-07-1; polypropylene, 9003-07-0.

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