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Ziegler–Natta Polymerization of Linear α-Olefins. Stereochemical Evidence of the Existence of Various Isotactic Sites on the $TiCl_3$ Surface

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ABSTRACT: 1-Butene and 1-hexene were polymerized in the presence of the catalytic system $TiCl_3/Al(CH_3)_2I$. The ^{13}C NMR analysis of the ^{13}C-enriched end groups shows that the first monomer addition on the Ti–CH_3 bond is only weakly enantioselective. The results are discussed in terms of a variety of isotactic active centers present on $TiCl_3$. α-Olefins bulkier than propene preferentially polymerize on some of these sites, most likely the more exposed ones.

One of the still-open problems concerning Ziegler–Natta isotactic polymerization of α-olefins deals with the existence of different types of active sites on the surface of the heterogeneous catalysts (e.g., $TiCl_3/AlR_mX_n$, where X = halogen, $m = 3 - n$, and $n = 0, 1$). A rough classification can be made by considering highly stereospecific catalytic centers producing, for example, isotactic polypropylene insoluble in boiling heptane and nonstereospecific centers producing stereoirregular polypropylene soluble in boiling pentane.

Considering only the regular polymer fraction, a relatively broad molecular weight distribution (M_w/M_n of 6–10 being quite common for isotactic polypropylene[1]) is generally[1,2] considered to be related to the presence on the catalyst surface of catalytic sites in some way different because the sites are able to produce polymer chains of very close isotactic regularity but of significantly different length. Different values of the propagation, termination, and transfer rate constants should characterize these isotactic sites.

In the absence of a direct method of determining the catalytic site structure, ^{13}C NMR analysis of the polymer microstructure is one of the most powerful tools for the indirect investigation of this question. In particular, detailed information on the stereochemistry of the first α-olefin addition on the active Mt–alkyl bond of Ziegler–Natta catalysts has been recently collected,[3-6] and an important step forward has been taken in acquiring an understanding of the steric factors controlling the enantioselective addition of the monomer.

This paper reports some new results concerning the stereochemistry of the initiation step of the polymerization in the presence of the catalytic system $TiCl_3/Al(^{13}CH_3)_2I$. The polymers of linear α-olefins bulkier than propene are considered.

Experimental Section

Reagents. δ-$TiCl_3$ (HRA Stauffer) was purified by extraction with boiling toluene.[7] $Al(CH_3)_2I$ (90% ^{13}C enriched) was prepared as described in the literature,[8] starting from 90% ^{13}C-enriched CH_3I.

Polymerizations. 1-Butene (28 g) and 1-hexene (25 g) were polymerized in an autoclave at 80 °C in 50 mL of dry heptane in the presence of 3.2 mmol of $TiCl_3$ and 2.7 mmol of $Al(CH_3)_2I$. After 24 h poly(1-butene) was precipitated in methanol while poly(1-hexene) was precipitated in ethyl acetate. The crude polymers (poly(1-butene), 13 g; poly(1-hexene), 9.4 g), 9.4 g) were then washed with methanol and dried under vacuum. Poly(1-butene) was fractionated with boiling diethyl ether; an oily fraction (0.3 g) of poly(1-hexene) was collected by evaporating the ethyl acetate solution to dryness.

^{13}C NMR Analysis. All the polymer fractions were analyzed by ^{13}C NMR by dissolving the samples in 1,2,4-trichlorobenzene and adding 1% hexamethyldisiloxane (HMDS) and $C_2D_2Cl_4$ as internal standards. Poly(1-butene) was analyzed on a Bruker HX-90 spectrometer operating at 22.63 MHz. The poly(1-hexene) analysis was carried out on an AM-270 Bruker spectrometer operating at 67.89 MHz.

Results and Discussion

Figure 1 shows the ^{13}C NMR spectra of the poly(1-butene) fractions soluble (A) and insoluble (B) in boiling diethyl ether. Figure 2 shows the ^{13}C NMR spectra of poly(1-hexene) fractions, soluble (A) and insoluble (B) in ethyl acetate at room temperature. The main resonances of the spectra of Figures 1 and 2 are related to the carbons of the inner monomeric units of the polymer chains and show that the samples are isotactic to a comparable extent. The two resonances marked by arrows in the spectra (at 17.7_6 and 18.0_8 ppm in Figure 1, parts A and B, and at 18.3_5 and 18.7_2 ppm in Figure 2, parts A and B) are due to the ^{13}C-enriched methyl carbons of the chain-end groups formed upon insertion of the first monomeric unit into the Ti–$^{13}CH_3$ bonds of the active sites.[3]

The different chemical shifts of the ^{13}C-enriched resonances can be accounted for, as previously in the case of polypropylene,[3-5] on the basis of the different configurational relationship between the $^{13}CH_3$ and the pendant alkyl group (CH_2CH_3 or $(CH_2)_3CH_3$) of the second inserted monomer unit. The intensity ratio between the higher field and the lower field ^{13}C-enriched resonances (I_e/I_t ratio) represents the isotactic regularity of the first inserted unit.[9] Actually, the insertion of the first 1-butene and 1-hexene into the Ti–$^{13}CH_3$ bond, evaluated from the ^{13}C-enriched resonances of Figures 1B and 2B, appears weakly enantioselective ($I_e/I_t = 1.4$ in poly(1-butene), $I_e/I_t = 1.6$ in poly(1-hexene)). Therefore, the isotacticity of the first addition of 1-butene and 1-hexene is noticeably low when compared with the isotacticity observed in the first addition of propene[6] in the presence of the same iodine-containing catalyst ($I_e/I_t = 3$).

The spectra of the poly(1-butene) and poly(1-hexene) fractions soluble, respectively, in boiling diethyl ether and in ethyl acetate (Figures 1A and 2A) are reported in order to show that the solubility of these fractions mainly results from their low molecular weight, as shown by the very intense resonances of the ^{13}C-enriched end groups, and is not due to their lack of stereoregularity. Indeed, only small amounts of different stereochemical configurations (not well resolved in Figure 2B) are detectable in the C1, C2, and C3 carbon resonances.

In recent papers it has been shown that the presence of the iodine atoms in the environment of the catalytically active titanium accounts for the observed isotactic control on the first propene insertion on Ti–alkyl bonds.[5,6,10]

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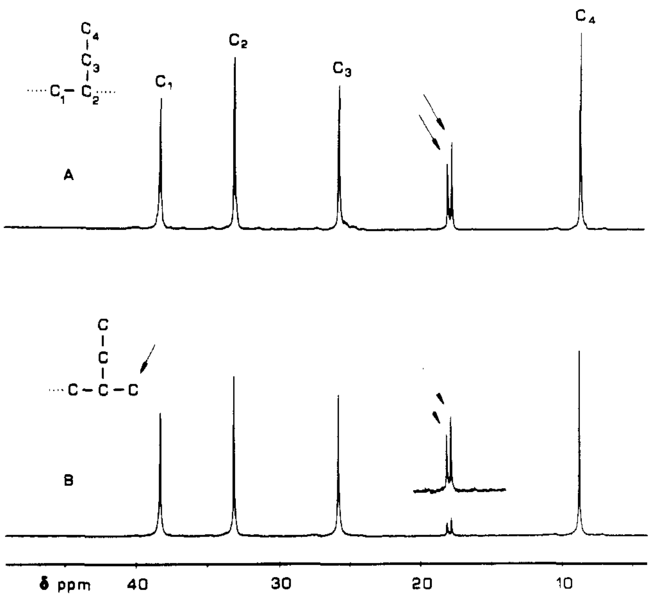

Figure 1. ^{13}C NMR spectra of the poly(1-butene) fractions soluble (A) and insoluble (B) in boiling diethyl ether. The chemical shifts are in ppm downfield from hexamethyldisiloxane (HMDS).

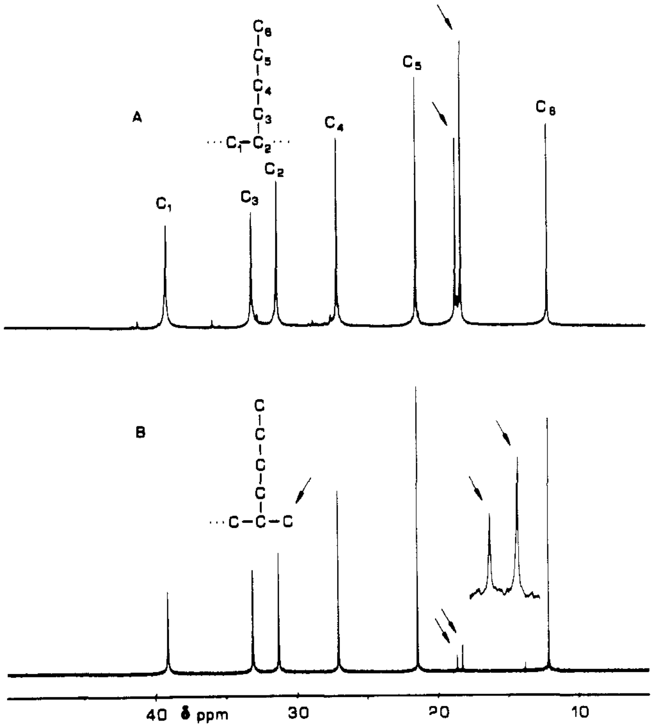

Figure 2. ^{13}C NMR spectra of the poly(1-hexene) fractions soluble (A) and insoluble (B) in ethyl acetate at room temperature. The chemical shifts are in ppm downfield from hexamethyldisiloxane (HMDS).

Actually such control is modest when all the titanium halogen ligands are iodine (catalyst: $TiI_3/Al(CH_3)_3$)[6] while it becomes remarkably strong when partial substitution of chlorine by iodine occurs (catalyst: $TiCl_3/Al(CH_3)_2I$).[5] The further increase observed when iodine and an alkyl ligand bulkier than methyl are simultaneously present on the active titanium allowed us to deduce that the iodine preferentially substitutes for one of the chlorine ligands, in a selected position.[11]

The decrease (with respect to propene) of the steric control of the first 1-butene and 1-hexene insertions in the presence of the catalyst $TiCl_3/Al(CH_3)_2I$ seems to indicate that α-olefins bulkier than propene preferentially polymerize on active sites in some ways different from those polymerizing propene. This is in keeping with the results of Jung and Schnecko.[12] These authors showed that in the presence of the catalyst $TiCl_3/Al(CH_2CH_3)_2Cl$ the number of active centers polymerizing 1-butene does not exceed $^2/_3$ of the number of active centers polymerizing propene. In addition, for polymerization times up to 30 min, a narrower molecular weight distribution ($M_w/M_n = 5$) was observed in poly(1-butene) compared to polypropylene ($M_w/M_n > 10$), indicating that this catalyst is sensitive to the individual monomer.

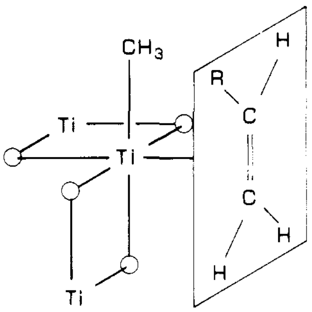

Figure 3. Schematic model of catalytic site. On more exposed sites, the Cl–I exchange could involve one or more chlorine atoms in different positions within the titanium ligands.

As far as the stereochemistry of polymerization is concerned, the hypothesized differences between active centers polymerizing propene and those polymerizing bulkier linear α-olefins cannot be investigated with regard to the isotactic steric control during chain propagation. Indeed, from the ^{13}C NMR analysis, all the above polymers prepared in the presence of the catalyst δ-$TiCl_3/Al(CH_3)_2I$ are highly isotactic ([mm] > 0.8 for polypropylene and [mm] > 0.9 for poly(1-butene) and poly(1-hexene)).[13] This means that during chain growth steric requirements for the enantioselective monomer addition are in any case satisfied. On the contrary, even small differences in the environment of the catalytically active complex noticeably affect the steric control of the first monomer addition. The observed low isotactic steric control of the first 1-butene and 1-hexene addition suggests the possibility that these monomers predominantly polymerize on isotactic sites located on more exposed points of the catalyst surface. The greater exposure of these sites should allow both an easier approach of the bulkier monomers to the active titanium and a different and/or more extensive exchange between the chlorine ligands of titanium and the iodine coming from $Al(CH_3)_2I$.

Such a possibility can reasonably explain the reported stereochemical observations. Indeed, considering the active site schematic representation of Figure 3, the Cl–I exchange on the less exposed sites polymerizing propene could involve preferentially a titanium ligand in a given position, causing different nonbonded interactions with the two prochiral monomer faces and then the higher steric control observed on the first propene addition.[10] On the contrary, the Cl–I exchange on more exposed sites could involve chlorine ligands located in more than one position around the chiral titanium, thus producing less asymmetrical nonbonded interactions between the titanium ligands and the pendant group of the monomer. A smaller isotactic steric control on the first monomer unit should result.

These last experimental findings support a hypothesis put forward in a recent paper[14] dealing with poly(1-butene) and poly(1-pentene) prepared in the presence of the catalytic system $TiCl_3/Al(^{13}CH_2CH_3)_3$. In the presence of the aforementioned catalyst, not containing iodine but having alkyl groups larger than methyl, the greater freedom of

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orientation of the ethyl group bonded to titanium in the more exposed isotactic sites should account for the lower steric control observed for the first 1-butene and 1-pentene insertion ($I_e/I_t = 2.2$ and 1.9, respectively) with respect to propene ($I_e/I_t = 3.4$).[14] Also in this case the two prochiral faces of the first 1-butene and 1-pentene units undergo quite similar nonbonded interactions despite the presence of a titanium alkyl ligand bulkier than methyl.

In conclusion, the experimental results reported in this paper, together with the previously reported results[14] concerning the stereochemistry of the first addition on Ti–alkyl bonds of linear olefins of various degrees of bulkiness in the presence of different Al–alkyl cocatalysts (i) point out once again the extreme sensitivity of the first polymerization step to small changes in the catalyst composition and toward the individual monomers, and (ii) strongly support the hypothesis that some of the active sites existing on the catalyst surface, depending on their particularly exposed location, are preferentially chosen by monomers bulkier than propene.

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Registry No. $TiCl_3$, 7705-07-9; $Al(CH_3)_2I$, 2938-72-9; 1-butene, 106-98-9; 1-hexene, 592-41-6; poly(1-butene) (homopolymer), 9003-28-5; poly(1-hexene) (homopolymer), 25067-06-5.

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Isotactic Polymerization of Styrene and Vinylcyclohexane in the Presence of a ^{13}C-Enriched Ziegler–Natta Catalyst: Regioselectivity and Enantioselectivity of the Insertion into Metal–Methyl Bonds

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ABSTRACT: Styrene and vinylcyclohexane have been polymerized in the presence of an isotactic-specific catalytic system based on δ-$TiCl_3$–$Al(^{13}CH_3)_3$. The diastereomeric composition of the end groups resulting from initiation steps has been evaluated by ^{13}C NMR analysis. It is observed that the initiation steps are highly regioselective and partially enantioselective for both these monomers.

Introduction

In previous papers[1–6] we have investigated by ^{13}C NMR the initiation step of the isotactic-specific polymerization of propene and 1-butene in the presence of heterogeneous catalytic systems consisting of TiX_3 and AlR_3, AlR_2Y, or ZnR_2 (X, Y = halide; R = hydrocarbon radical). By initiation step we mean the insertion of the monomer into the active metal–R bond of the catalytic sites resulting after the chemical interactions of the titanium halide and the organometallic compound of the basic metal.

By a proper choice of R, it is possible to determine by ^{13}C NMR the stereochemical structure of the polymer end groups resulting after the initiation, and consequently one can evaluate the regioselectivity and the enantioselectivity of this reaction.[6]

By using different catalytic combinations of titanium halides and organometallic compounds, it is also possible to observe the effect of changing the constitution of the isotactic-specific sites.

In the presence of the title catalytic systems the chain-propagation steps (i.e., the insertion steps following the initiation) are highly, and sometimes completely,[1] regiospecific (anti-Markovnikov addition) and highly enantioselective.[1–7]

The initiation steps are also highly regiospecific, but the enantioselectivity is strongly influenced by the ligands of TiX_3 and of the organometallic compounds. When X and Y are chlorine, the insertion of propene and 1-butene on Mt–CH_3 (Mt = metal atom of the catalytic sites) is negligibly enantioselective.[3]

The initiation becomes appreciably enantioselective when $R = C_2H_5$[3] and highly enantioselective when $R = i$-C_4H_9.[3] It is also observed that when X or Y is iodine the insertion on Mt–CH_3 becomes appreciably enantioselective.[2,4]

In this paper we report some results concerning initiation of styrene and vinylcyclohexane polymerization in the presence of δ-$TiCl_3$–$Al(^{13}CH_3)_3$. ^{13}C-enriched organometallic compounds have been used in order to increase the sensitivity of the ^{13}C NMR analysis in detecting the polymer end groups resulting from the initiation step. Styrene was investigated in order to compare a vinyl

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