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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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aromatic monomer with aliphatic 1-alkenes. Vinylcyclohexane was investigated in order to check the effect of increasing the steric requirements of the monomer substitutent in comparison with propene and 1-butene. As a matter of fact monomers carrying large substituents have been previously investigated, but the resolution of the ^{13}C NMR spectra[8,9] was not sufficient to evalute the enantioselectivity of the initiation.

The $^{13}CH_3$ group was chosen because Mt–CH_3, in addition to Mt–H, is the only "active bond" not carrying a carbon β to the metal. The role of the β carbon in enhancing the enantioselectivity of the insertion has been particularly stressed[3] according to some models of the active sites.[10]

Experimental Part

Reagents. δ-$TiCl_3$, $Al(^{13}CH_3)_3$, and $Zn(^{13}CH_3)_2$ have been prepared according to the literature.[3,11,12] Toluene has been distilled under a nitrogen atmosphere after refluxing over potassium for 48 h. Styrene and vinylcyclohexane have been distilled in vacuo over CaH_2.

Polymerizations. Polymerization of styrene has been performed at 95 °C by dissolving 5 mL of styrene in 25 mL of toluene in the presence of 0.065 g of δ-$TiCl_3$ and 0.23 mL of $Al(^{13}CH_3)_3$ (90% ^{13}C enrichment). The reaction was stopped with ethanol after 30 h: yield, 0.78 g.

Polymerization of vinylcyclohexane has been performed at 50 °C by dissolving 10 mL of vinylcyclohexane in 14 mL of toluene in the presence of 1.20 g of δ-$TiCl_3$, 0.14 mL of $Al(^{13}CH_3)_3$, and 0.12 mL of $Zn(^{13}CH_3)_2$ (50% ^{13}C enrichment). The reaction was stopped with ethanol after 48 h: yield, 3.00 g.

The polymers were coagulated with acidified ethanol, washed with fresh ethanol until neutrality was attained, and dried in vacuo at 60 °C.

$Zn(^{13}CH_3)_2$ was used in the vinylcyclohexane polymerization in order to increase the chain-transfer processes and consequently the amount of ^{13}C-enriched end groups, as reported in previous papers.[8]

Fractionation. Polystyrene has been fractionated by sequential exhaustive extraction with boiling solvents (butanone, benzene, and toluene). The butanone-soluble fraction was 10%, the fraction insoluble in butanone but soluble in benzene was 75%, and the fraction insoluble in benzene but soluble in toluene was 15%. Poly(vinylcyclohexane) has been similarly fractionated. The butanone-soluble fraction was 5%, the fraction insoluble in butanone but soluble in benzene was 30%, and the fraction insoluble in benzene but soluble in toluene was 10%.

Hydrogenation of Polystyrene. The polystyrene fraction (0.3 g) soluble in benzene and insoluble in butanone, dissolved in 30 mL of decalin, was hydrogenated at 150 °C in the presence of 0.5 g of Pd on charcoal (10% Pd) under 30 atm of H_2 in an oscillating autoclave for 24 h. After filtration on silica gel at 120 °C the polymer solution was coagulated with ethanol and the polymer dried in vacuo.

^{13}C NMR Analysis. ^{13}C NMR spectra were obtained on a Bruker WM-500 spectrometer operating at 125.77 MHz in the FT mode at a temperature of 398 K. The samples were prepared by dissolving in a 5-mm-o.d. sample tube ca. 30 mg of polymer in 0.8 mL of 1,2-tetrachloroethane-d_2. Hexamethyldisiloxane was used as internal chemical shift reference. All the spectra were recorded in the inverse gated mode in order to obtain proton-decoupled ^{13}C spectra without NOE effect. On the average, the spectra are the result of 5K transients with 32K data points with an acquisition time of 0.82 s and a spectral width of 20 kHz. A pulse width of 10.7 μs, corresponding to a 90° flip angle, and a relaxation delay of 9 s were used. The resolution enhancement of the expansion of Figure 3 was obtained by Lorentzian to Gaussian transformation. All spectra were processed with a 5-Hz line-broadening function prior to transformation.

The resonances of polystyrene and poly(vinylcyclohexane) were assigned according to the literature[13-15] and by off-resonance techniques.

The resonances of the ^{13}C-enriched carbons of the end groups have been identified by comparison with the spectra of polymers prepared in the presence of nonenriched catalysts.

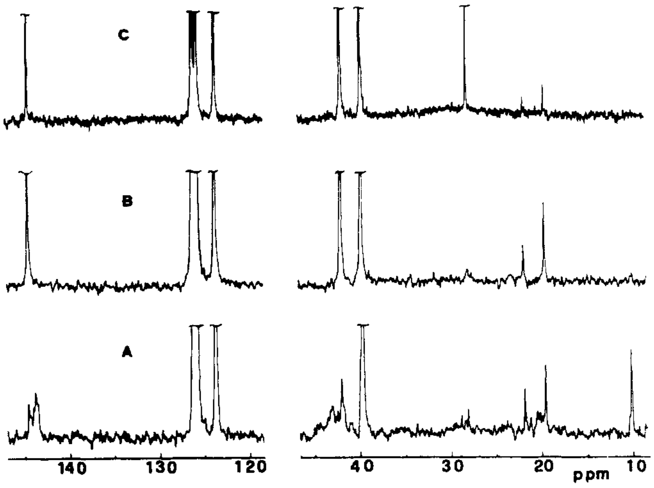
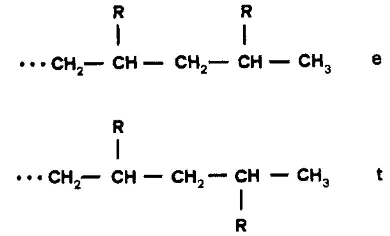


Figure 1. ^{13}C NMR spectra of fractions A (butanone soluble), B (butanone insoluble–benzene soluble), and C (benzene insoluble–toluene soluble) of polystyrene prepared in the presence of δ-$TiCl_3$–$Al(^{13}CH_3)_3$. The chemical shifts are on the HMDS scale.



$$\cdots CH_2\text{—}\overset{\displaystyle R}{\overset{|}{CH}}\text{—}CH_2\text{—}\overset{\displaystyle R}{\overset{|}{CH}}\text{—}CH_3 \qquad e$$

$$\cdots CH_2\text{—}\overset{\displaystyle R}{\overset{|}{CH}}\text{—}CH_2\text{—}\underset{\displaystyle R}{\underset{|}{CH}}\text{—}CH_3 \qquad t$$

Figure 2. Fischer projection of the [5-^{13}C]-enriched 2,4-disubstituted end groups resulting after the insertion of two monomer units on Mt–$^{13}CH_3$. R = C_6H_5 or C_6H_{11}. The end groups are labeled e and t depending on the steric relationship between the R substitutents of the two monomer units as reported in a previous paper.[6] Notice that in this paper the enriched methyls are labeled according to ref 16 by a greek letter δ, denoting the number of bonds between the enriched methyl and the R substituent of the second inserted monomer unit, and by the symbols e and t, denoting the steric relationship between the enriched methyl and R. As a consequence the enriched methyl of the e end group is δt and that of the t end group is δe.

The resonances at 19.2_2 and 21.5_2 ppm in Figure 1 are assigned respectively to the δt- and δe-enriched methyls[16] of [5-^{13}C]2,4-diphenylpentyl end groups (see Figure 2) by comparison with the chemical shifts of C-3 of the stereoisomers of 4,6,8-triphenylundecane[17] after subtraction of the contributions of C-1 and C-2 to the chemical shift of C-3.[13] The resonance at 9.8 ppm is assigned to the enriched methyls of [3-^{13}C]1-phenylpropyl end groups by comparison with the chemical shift of C-2 of 4,6,8-triphenylundecane[17] after subtracting the contribution of C-1.[13]

The resonance at 27.8_3 ppm of Figure 1, parts A and C, was assigned by comparison with the chemical shift of polyethylene and has been confirmed, as well as the previous ones, by off-resonance experiments.

The resonances at 14.8_9 ppm of poly(vinylcyclohexane) (see Figure 3A) have been assigned respectively to the δt- and δe-enriched methyls of the [5-^{13}C]2,4-dicyclohexylpentyl end groups by comparison with hydrogenated polystyrene (see Figure 3B) and by off-resonance experiments.

The evaluation of the relative amounts of the enriched methyls in diastereotopic position was measured from the intensity of the corresponding resonances.

Results

Looking at the spectrum shown in Figure 1A and considering the spectrum of highly isotactic polystyrene reported in the literature,[15] one can appreciate that the butanone-soluble fraction is only weakly stereoregular. With regard to the initiation step, one also observes weak

Table I
Enantioselectivity of the Insertion of Some 1-Alkenes on Different Active Mt–R Bonds in the Presence of Different Catalytic Systems

catalytic system	Mt–R	monomer	polymn temp, °C	enantio-selectivity	ref
δ-$TiCl_3$ + $Al(^{13}CH_3)_3$ + $Zn(^{13}CH_3)_2$	Mt–$^{13}CH_3$	C_3H_6	20	0.5[a]	3
	Mt–$CH_2CH(CH_3)^{13}CH_3$	C_3H_6	20	≅1[b]	3
	Mt–$^{13}CH_3$	C_8H_{14}	50	≅0.8[a]	this paper
	Mt–$^{13}CH_3$	C_8H_8	95	0.7[a]	this paper
δ-$TiCl_3$ + $Al(^{13}CH_3)_2I$	Mt–$^{13}CH_3$	C_3H_6	75	0.8[a]	2
	Mt–$CH_2CH(CH_3)^{13}CH_3$	C_3H_6	75	≅1[b]	2
δ-$TiCl_3$ + $Al(^{13}CH_2CH_3)_3$ + $Zn(^{13}CH_2CH_3)_2$	Mt–$^{13}CH_2CH_3$	C_3H_6	20	0.8[a]	3
δ-$TiCl_3$ + $Zn(C_6H_5)_2$	Mt–C_6H_5	C_3H_6	75	≅1[a]	5
TiI_3 + $Al(^{13}CH_3)_3$	Mt–$^{13}CH_3$	C_3H_6	75	≅0.7[a]	4
	Mt–$CH_2CH(CH_3)^{13}CH_3$	C_3H_6	75	≅1[b]	4

[a] Defined in ref 6. [b] In these cases enantioselectivity is defined as $E' = e'/(e' + t')$ where e' and t' are the amounts of the end groups resulting after the insertion of three monomer units on a Mt–$^{13}CH_3$ bond carrying the substituents of the second and the third monomer unit respectively in e and t relationship to each other.

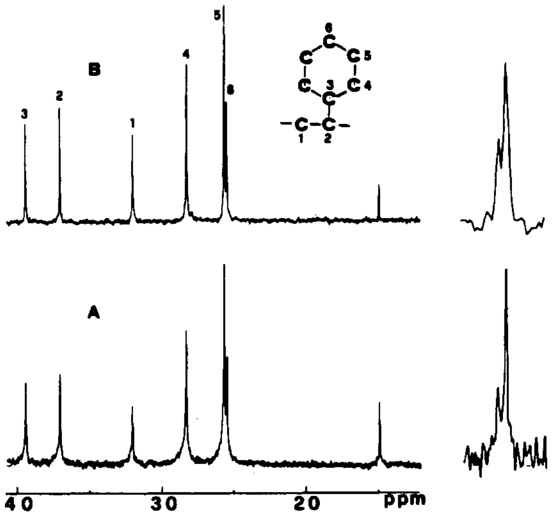


Figure 3. ^{13}C NMR spectra of (A) poly(vinylcyclohexane) (benzene insoluble–toluene soluble fraction) and (B) of hydrogenated polystyrene (butanone insoluble–benzene soluble fraction). At the right is shown a 16-fold horizontal expansion of the peak at 14.8_9 ppm (enriched methyls of the 2,4-dicyclohexylpentyl end groups). The resonances of the enriched methyls are assigned to the different diastereomeric end groups (see Experimental Part) on the ground of relative intensities, assuming that no epimerization occurred during the hydrogenation of polystyrene. The assignment of the resonances of the carbons of the inner monomer units is achieved as reported in the Experimental Part.

regioselectivity. In fact, the resonances of the enriched methyls of [5-^{13}C]2,4-diphenylpentyl end groups (anti-Markovnikov addition) at 19.2_2 and 21.5_2 ppm and that of the enriched methyls of [3-^{13}C]1-phenylpropyl end groups at 9.8 ppm (Markovnikov addition) have comparable intensities. On the other hand, the sharp resonances of the spectra of Figure 1B and 1C show that the butanone insoluble–benzene soluble and the benzene insoluble–toluene soluble fractions of polystyrene are highly isotactic.

The initiation is highly regiospecific, as suggested by Danusso[18] (the resonance at 9.8 ppm is negligible), and partially enantioselective. In fact, the resonance of the δt $^{13}CH_3$'s (at 19.2_2 ppm) is twice as intense as that of the δe $^{13}CH_3$'s (at 21.5_2 ppm).

In Figure 1, parts A and C, it is also possible to observe a resonance at 27.8_3 ppm attributed to polyethylene. In a previous paper it was reported that a small amount of [1,2-^{13}C]-enriched ethylene is formed when δ-$TiCl_3$ and $Al(^{13}CH_3)_3$[19] are mixed under the polymerization conditions. The enriched ethylene copolymerizes with 1-alkenes[19] but apparently only homopolymerizes in the presence of styrene. In fact, there is no evidence in the spectrum of isolated enriched ethylene units along the polystyrene chains but only of long polyethylene sequences.

The spectrum of Figure 3A shows that the initiation is highly regiospecific for the benzene insoluble–toluene soluble poly(vinylcyclohexane). The only resonances of the enriched methyls detected in the spectra of all the fractions of poly(vinylcyclohexane) are those of the C-5 of [5-^{13}C]2,4-dicyclohexylpentyl end groups (anti-Markovnikov addition).

The different intensities of the resonances of the $^{13}CH_3$'s δt and δe (14.8_9 and 14.9_3 ppm, respectively) in the spectrum of the butanone insoluble–benzene soluble fraction show that the insertion is appreciably enantioselective.

Discussion and Conclusion

The results of this paper in comparison with those previously reported in the literature[1–6] show that the enantioselectivity of the insertion is enhanced not only by increasing the size of the ligands of the components of the catalytic system but also by increasing the steric requirements of the monomers. In this respect, aliphatic 1-alkenes and vinylaromatic monomers seem to behave very similarly.

The enantioselective insertion of bulky monomers into Mt–CH_3 confirms the hypothesis that the stereochemistry of the addition is controlled at least in part by non-bonded interactions of the substituent of the incoming monomer with the ligands of the active site.

The enantioselectivity of a number of insertion steps concerning different monomers and different catalytic systems is reported in Table I. A particularly interesting comparison concerns insertion of propene on Mt–C_6H_5 and insertion of styrene on Mt–CH_3. In both cases the result of the insertion is a 2-phenylpropyl group, and the corresponding active states could be considered positional isomers. Insertion of propene into Mt–C_6H_5 appears to be more enantioselective than insertion of styrene on Mt–CH_3. This fact suggests that the hydrocarbon group bonded to the Mt of the active sites plays a relevant although not exclusive role in determining the stereochemistry of the addition.

Finally, the resonance at 27.8_3 ppm in Figure 1, parts A and C, due to enriched ethylene homosequences suggests that the product of the reactivity ratios in the ethylene-styrene copolymerization is very large ($r_1r_2 \cong \infty$). It is worth noting that in poly(3-methyl-1-pentene) prepared under similar conditions, the enriched ethylene units arising from the decomposition of the catalyst are mostly isolated.[19] This peculiarity of styrene implies either that one of the cross-polymerization kinetic rate constants is close to zero or that different active sites are involved in the polymerization of the two monomers.

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Registry No. C_8H_8, 100-42-5; C_8H_{14}, 695-12-5; $Al(CH_3)_3$, 75-24-1; $TiCl_3$, 7705-07-9.

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Thermoreversible Gelation and Crystallization of Homopolymers and Copolymers

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ABSTRACT: The thermodynamics, kinetics, and structural features of gels formed as a consequence of crystallization from dilute and moderately dilute solution have been investigated. Major emphasis has been on the study of homopolymers and copolymers of ethylene. The melting temperatures and enthalpies of fusion of the gels are found to be continuous with counit content and independent of the chemical type, despite the fact that the supermolecular structure and morphology undergo major changes. It was also found that for a given polymer the thermodynamic and structural properties of a crystallite formed in dilute solution and in the gels are identical. From these types of measurements some of the general principles that govern gelation by a crystallization mechanism can be established. Preliminary experiments with isotactic and atactic polystyrene fractions indicate that these polymers also follow the same general principles.

Introduction

Gels, or network structures, that involve long-chain molecules can be formed by several distinctly different molecular mechanisms. A detailed description of the different types of known gel systems has been given by Flory.[1] Among these, gelation occurring as a consequence of the crystallization of copolymers from dilute and moderately dilute solution was recognized a long time ago.[1,2] In this type of gelation a three-dimensional network is formed where primary molecules of finite molecular weight are bound together, or connected, by crystallites. It differs from the more conventional type of network, where completely disordered chains are covalently linked together. Gelation as a consequence of copolymer crystallization has been actively studied for a long time.[1,2] It has been given serious quantitative consideration in a series of papers by Takahashi and co-workers.[3-9] The observation that vinyl type polymers, properly considered as copolymers from this point of view,[10,11] also form gels has given us an interesting set of new results.[12-20] However, the concept that crystallites are involved in gel formation is not new.[21]

It has also been recently shown that gel formation is a common feature of homopolymers crystallized under quiescent conditions at comparable polymer concentrations.[22-25] It needs to be emphasized in this connection that gel formation in homopolymers does not require flow, stirring, or even any type of prestirring of the solution, as has been repeatedly implied.[21,26,27]

When gelation occurs as a consequence of crystallization from dilute or moderately dilute solution, a very fluid solution is converted to a rigid medium of infinite viscosity. The polymer system pervades the entire volume. Gels formed by this mechanism are thermally reversible. They are formed on crystallization (cooling) and disappear on melting (heating). In this respect they are completely different from gels formed by covalently cross-linking amorphous chains, wherein the networks are thermally stable. The recent observations that gels are also formed during the crystallization of vinyl polymers, such as isotactic polystyrene,[12-14,20] poly(vinyl chloride),[15,17,18] and poly(4-methylpentane),[16,19] has rekindled interest in this subject. Unfortunately, in many cases these new results were discussed in a very limited context[21,28] so that the general aspects of the problem were not recognized. Consequently, serious misconceptions developed, and some limited ideas have been espoused. One example has been the concept that the crystallites in all gels are micellar in character.[21,28] In several of these systems polymorphic

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