tected in the spectra of low molecular weight fractions, and $\bar{M}_n$ and pentad tacticity of the whole polymer are independent of polymerization time in the presence of hydrogen (not published), eq 2 is simplified to

$$\bar{P}_n = R_p/R_{tr} \tag{3}$$

where $R_p = k_p[M][C]$ and $R_{tr} = [C](k_M[M] + k_H[H_2]^n)$. [M], [C], and [$H_2$] are the concentrations of propylene, catalytic sites, and molecular hydrogen; k_p is the rate constant of the propagation reaction; k_M and k_H are the rate constants of chain transfer reactions with propylene monomer and hydrogen.

The ratio $\bar{M}_n(I)/\bar{M}_n(A)$ is given by

$$\frac{\bar{M}_n(I)}{\bar{M}_n(A)} = \frac{\bar{P}_n(I)}{\bar{P}_n(A)} = \frac{R_p(IS)R_{tr}(AS)}{R_{tr}(IS)R_p(AS)} \tag{4}$$

where IS and AS represent the IPP and APP sites, respectively.

Since $\bar{M}_n(I)/\bar{M}_n(A)$ is 7.3 (32000/4400), the ratio rate of the propagation reaction/rate of the chain transfer reaction at the IPP site is seven times as large as that at the APP site.

Conclusions

According to the two-site model for the mechanism of propylene polymerization, isotactic polypropylene is a mixture of the isotactic and atactic polymers produced at two different sites. In the successive extraction of isotactic polypropylene with boiling *n*-alkane solvents, tacticity and molecular weight fractionations occur for the isotactic polymer, while the molecular weight fractionation mainly occurs for the atactic polymer. The number-average molecular weight of the isotactic polymer is much larger than that of the atactic polymer. This suggests that the ratio rate of the propagation reaction/rate of the chain transfer reaction at the IPP site is much larger than that at the APP site.

Registry No. IPP, 25085-53-4; propylene, 115-07-1.

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Isotactic Polymerization of Propene: Homogeneous Catalysts Based on Group 4 Metallocenes without Methylalumoxane

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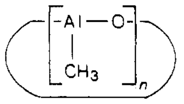
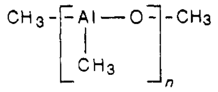
ABSTRACT: Propylene has been polymerized in the presence of stereospecific homogeneous catalytic systems consisting of group 4 metallocenes and mixtures of trimethylaluminum and dimethylaluminum fluoride. The polymers obtained are isotactic with a molecular structure very much like that of the polymers prepared in the presence of the same group 4 metallocenes and methylalumoxane.

Methylalumoxane (MAO), the reaction product of Al(CH_3)$_3$ with the appropriate amount of water, having the general formula[1]





$$CH_3-\left[-\underset{\substack{|\\CH_3}}{Al}-O-\right]_n-CH_3$$

is a key ingredient of homogeneous catalysts that promote isotactic polymerization of propene. As reported by Ewen[2] and Kaminsky,[3] this organometallic compound activates group 4[4] metallocenes, which become able to promote polymerization of propene to (a) classical isotactic polypropylene, consisting essentially of blocks of isotactic diads *m* separated by pairs of syndiotactic diads *r*, i.e., ... *mmmrrmmm...mmmrrmmm...* (hereinafter called type I polypropylene as proposed by Ewen[2]), to (b) type II isotactic polypropylene, consisting of blocks of *m* diads sep-

Table I
Polymerization of Propene in the Presence of (Dicyclopentadienyl)diphenyltitanium

sample[a,b]	DMF, mmol	TMA, mmol	MAO, mmol of Al	yield, g
1	4.8			traces
2	3.7	0.4		0.11
3	3.7	1.2		1.79
4	3.7	2.4		0.85
5	3.7	3.7		0.14
6		1.2		traces
7	1.2	1.2		0.34
8	2.4	1.2		0.50
9	4.8	1.2		0.85
10	6.0	1.2		0.20
11[c]			4.0	3.70

[a] Polymerizations have been performed in the presence of 1.2 × 10^{-5} mol of CPTP in 30 mL of toluene with 30 mL of liquid propene and were run at −60 °C for 20 h. [b] Melting points of all these polymers are ≈62 °C. [c] This polymerization has been performed in the same experimental conditions reported in *a*, but it was run for 1 h.

arated by lone *r* diads, i.e., ...*mmmrmmm*...*mmmrmmm*..., or to (c) stereoirregular polypropylene. The stereochemical structure of the polymer depends primarily on the structure of the group 4 metallocene, as previously reported in the literature.[2]

It is also worth mentioning that homogeneous catalysts consisting of very simple soluble compounds of group 4 metals, such as $Ti(CH_2C_6H_5)_4$, $Ti(OC_4H_9)_4$, and $Zr(CH_2C_6H_5)_4$, and also methylalumoxane, promote syndiotactic polymerization of styrene[5,6] and partially isotactic (type I) polymerization of propene.[7] Other organometallic compounds of aluminum, such as $Al(CH_3)_3$ or $Al(CH_3)_2X$ (where X = halide), in the presence of group 4 metallocenes, do not appreciably promote polymerization of propene.

We have now observed that a mixture of $Al(CH_3)_3$ (TMA) and $Al(CH_3)_2F$ (DMF) can be used instead of methylalumoxane for preparing an isotactic specific homogeneous catalyst based on group 4 metallocenes. In Tables I and II are reported the results of a series of polymerizations of propene performed in the presence of different metallocenes and mixtures of TMA and DMF. For comparison, we also report polymerization runs performed in the presence of MAO, TMA, and DMF alone. Under the same reaction conditions, the polymerization yields obtained in the presence of TMA-DMF mixtures are substantially lower than those obtained in the presence of MAO. The polymerization yield reaches a maximum for ≅3/1 molar ratio DMF/TMA although neither DMF nor TMA alone is an active cocatalyst. The structure of the polymers depends on the structure of the metallocene in the same manner as for the catalysts based on MAO.[2] More precisely, the polymers prepared in the presence of one particular group 4 metallocene and either MAO or DMF–TMA have very similar stereochemical structures. For example, in Figure 1 one can observe from the methyl region of the ^{13}C NMR spectra of samples 3 and 12, prepared in the presence of (dicyclopentadienyl)diphenyltitanium (achiral) and ethylenediindenyldichlorotitanium (chiral), respectively, by using DMF–TMA, that the two samples have type II and type I isotactic structures. In fact, in the spectrum of Figure 1A one observes the resonances of the *mmmr* and *mmrm* stereochemical pentads at 19.4_6 and 18.7_3 ppm, respectively, with the same intensity, diagnostic of a type II structure; in the spectrum of Figure 1B one observes the resonances of the *mmmr*, *mmrr*, and *mrrm* pentads at 19.4_6, 18.9_5, and 17.7_9 ppm, respectively, with 2:2:1 intensity ratio, diagnostic of a type I structure. The same behavior was previously observed by Ewen in the presence of MAO cocatalyst.[2] In Figure 2 are reported for comparison the ^{13}C NMR spectra of samples 13 and 14 prepared in the presence of the same metallocene, ethylenediindenyldichlorozirconium, at the

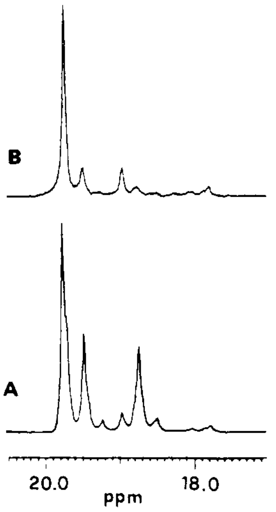


Figure 1. Methyl region of the ^{13}C NMR spectra of sample 3 (A) and of the heptane-insoluble fraction of sample 12 (B). One can observe the resonances at 19.4_6, 18.9_5, and 17.7_9 ppm with 2:2:1 intensity ratio in the spectrum of sample 12 (type I isotactic structure) and the resonances at 19.4_6 and 18.7_3 ppm with 1:1 intensity ratio (type II isotactic structure) in the spectrum of sample 3 (HMDS scale).

Table II
Polymerization Performed in the Presence of Stereorigid Chiral Group 4 Metallocenes

sample	catalyst	Al cocatalyst	temp, °C	time, h	yield, g	mp,[a] °C	% *mmmm* pentads	% regioirregularly arranged units	% 1–3 inserted units
12[b]	EBITC	DMF–TMA	−60	19	1.65[e]	133[f]	70	nd[g]	nd
13[c]	EBIZC	DMF–TMA	0	5	0.20	153	87	0.7	nd
14[d]	EBIZC	MAO	0	4	2.50	137	83	1.0	nd
15[c]	EBTHIZC	DMF–TMA	25	17	1.80	135	80	nd	0.5
16[d]	EBTHIZC	MAO	25	2	6.00	125	75	nd	1.8
17[c]	EBIZC	DMF–TMA	25	17	2.93	134	80	0.4	0.1

[a] Melting point. [b] Polymerization was performed in the presence of 1.2 × 10^{-5} mol of EBITC, 3.75 × 10^{-3} mol of DMF, and 1.2 × 10^{-3} mol of TMA, in 30 mL of toluene with 30 mL of liquid propene. [c] Polymerization were performed in the presence of 1.2 × 10^{-5} mol of zirconocenes, 3.75 × 10^{-3} mol of DMF, 1.2 × 10^{-3} of TMA, and 30 mL of toluene and under a constant pressure of 3.5 atm of propene. [d] These samples were prepared according to ref 8. [e] In the presence of EBITC, which is a mixture of rac-meso modification, a mixture of isotactic and stereoirregular polymer is obtained. The isotactic fraction is 6%. [f] Melting point of isotactic fraction. [g] Not determined.

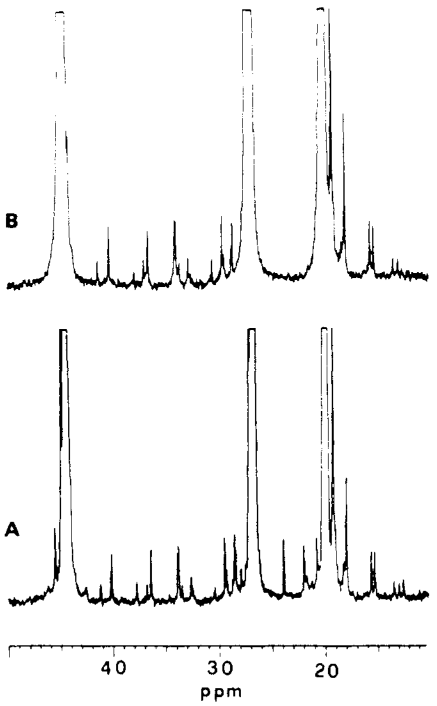


Figure 2. ^{13}C NMR spectra of sample 13 (A) and sample 14 (B). Both samples have been prepared in the presence of EBIZC and DMF–TMA (sample 13) and MAO (sample 14). The main resonances are overexpanded to observe the peaks due to regioirregular arranged units (HMDS scale).

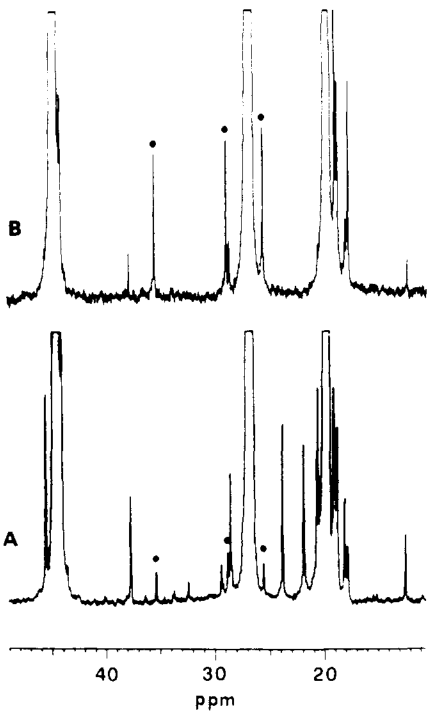


Figure 3. ^{13}C NMR spectra of sample 15 (A) and sample 16 (B). Both samples have been prepared in the presence of EBTHIZC and DMF–TMA (sample 15) and MAO (sample 16). The main resonances are overexpanded to observe the peaks of lower intensity. The labeled peaks have been assigned to 1–3 inserted propene units.[8] The resonances at 20.5_5 and 21.8_0 are due to isobutyl end groups and those at 12.3_8, 17.9_9, 18.7_1, 28.3_3, and 37.5_1 are due to *n*-propyl end groups[8] (HMDS scale).

same temperature, but with different cocatalyst, DMF–TMA for sample 13 (Figure 2A) and MAO for sample 14 (Figure 2B). One can observe that the two spectra are almost identical, not only with respect to the main resonances typical of the isotactic structure, at 19.7_6 ppm for *mmmm* methyl pentad, 26.7_4 ppm for the methines, and 44.3_5 ppm for the methylenes, but also for the presence, in both spectra, of lower intensity resonances at 15.1_2, 15.4_6, 19.5_8, 28.3_8, 29.3_3, 33.6_8, 33.7_8, 36.3_5, and 40.1_1 ppm, which are diagnostic, as reported in a previous paper,[8] of occasional regioirregular monomer units. In Figure 3 are shown the spectra of samples 15 and 16 prepared in the presence of the same chiral stereorigid metallocene, ethylenebis(4,5,6,7-tetrahydro-1-indenyl)dichlorozirconium, under similar conditions but with different aluminum cocatalysts, DMF–TMA for sample 15 (Figure 3A) and MAO for sample 16 (Figure 3B). Even in this case the spectra look very similar, including the lower intensity resonances at 25.3_6, 28.7_3, and 35.1_6 ppm, which have been attributed in a previous paper[8] to occasional 1–3 inserted propylene units. The only appreciable difference between the two spectra is the much higher intensity in sample 15 of the resonances at 20.5_5 and 21.8_0 ppm diagnostic of isobutyl end groups, and of the resonances at 12.3_8, 17.9_9, 18.7_1, 28.3_3, and 37.5_1 diagnostic of *n*-propyl end groups. The higher intensity of the isobutyl end groups in sample 15 comes from chain-transfer processes with TMA which, of course, occur more often in the presence of TMA–DMF than in the presence of MAO alone. The *n*-propyl end groups arise from initiation of chain propagation on Mt–H (Mt = group 4 metal) bonds.[8]

DMF is reported to be tetrameric in benzene solution[9] and, due to the strength of the fluoride bridge, is definitely less acidic than TMA and the other dimethylaluminum halides.[10] For example, DMF, unlike TMA, forms no complex with ethyl ether.[10]

The ability of MAO to activate group 4 metallocenes toward propene polymerization has been tentatively attributed[11-13] to the formation, in the presence of MAO, of cationic complexes, e.g., $[Mt^{IV}L_2R]^+$ where L = η^5 ligand and R = alkyl ligand (CH_3 or growing polymer chain), which would be the actual active species. Following this idea, one might speculate that in the presence of proper amounts of TMA and DMF, alkylmetallocenes fluoride is formed according to the equilibria

$$L_2MtX_2 + Al(CH_3)_3 + Al(CH_3)_2F \rightleftharpoons L_2Mt(CH_3)F + 2Al(CH_3)_2X$$

$$L_2Mt(CH_3)F + Al(CH_3)_3 \rightleftharpoons L_2Mt(CH_3)_2 + Al(CH_3)_2F$$

Due to the high ionicity of the Mt–F bond, dissociation of Cp_2MtFCH_3, assisted by TMA, may occur, e.g., according to the equilibrium

$$L_2Mt(CH_3)F + 2Al(CH_3)_3 \rightleftharpoons [L_2MtCH_3]^+ + [Al_2(CH_3)_6F]^-$$

leading to the same cationic active species proposed in the case of methylalumoxane. In this connection it is worth mentioning that the cationic complex $Cp_2Zr(CH_3)(THF)^+$, isolated by Jordan,[13] promotes polymerization of ethylene. On the other hand, the formation of dialuminate anions occurs only with fluorides.[14]

Experimental Section

Polymerization grade C_3H_6 was purchased from Societá Ossigeno Napoli and used without further purification. Toluene was dried by refluxing over metallic sodium and distilling under nitrogen atmosphere. (Dicyclopentadienyl)diphenyltitanium (CPTP), *rac*-*meso*-ethylenediindenyldichlorotitanium (EBITC), ethylenediindenyldichlorozirconium (EBIZC), ethylenebis(4,5,6,7-tetrahydro-1-indenyl)dichlorozirconium (EBTHIZC), dimethylaluminum fluoride (DMF), and methylalumoxane (MAO) were prepared as reported in the literature.[15,16,3,17,1]

Polymerization runs at −60 °C were performed in a stirred 100-mL flask under nitrogen atmosphere. Toluene (30 mL),

$Al(CH_3)_3$, and $Al(CH_3)_2F$ were introduced into the reaction flask and thermostated. Gaseous propene (30 mL) was condensed into the reactor while stirring, and finally the titanium compound was introduced, dissolved in 1 mL of toluene.

Polymerization runs at 0 and 25 °C were performed in a 100-mL glass autoclave equipped with magnetic stirrer and gas inlet. The metallocene compounds, $Al(CH_3)_2F$ and $Al(CH_3)_3$, were dissolved in toluene (30 mL) and introduced into the thermostated reactor. The system was evacuated and charged with propene at a constant pressure of 3.5 atm. Polymerization were stopped by introducing methanol, and the polymers were coagulated in acidified methanol, washed with fresh methanol, and dried in vacuo at 60 °C.

The stereoirregular fraction of sample 12 was separated from isotactic fraction by extraction with heptane at room temperature. Melting points were measured on previously melted and recrystallized samples by using a Du Pont 9000 DSC calorimeter with a rate of temperature increase of 5 °C/min. NMR spectra were recorded on an AM 250 Bruker spectrometer operating at 62.89 MHz in the Fourier transform mode and at a temperature of 393 K. The NMR samples were prepared by dissolving 80 mg of polymer in 0.4 mL of tetrachloro-1,2-dideuterioethane in a 5-mm-o.d. tube. Hexamethyldisiloxane (HMDS) was used as internal reference.

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Registry No. CPTP, 1273-09-2; EBITC, 112531-76-7; EBIZC, 112243-78-4; EBTHIZC, 112243-79-5; TMA, 75-24-1; DMF, 753-55-9; polypropylene, 25085-53-4.

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Surface Interaction in Solvent-Cast Polystyrene/Poly(methyl methacrylate) Diblock Copolymers

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ABSTRACT: The relative surface coverage of components of a series of symmetric polystyrene/poly(methyl methacrylate) (PS/PMMA) diblock copolymers solution cast from toluene was studied by X-ray photoelectron spectroscopy. The copolymers, which ranged in total molecular weight from 27 000 to 535 000, are microphase separated into domains of pure PS and pure PMMA. The surface energy of PS is a fraction of a dyne per centimeter less than that of PMMA. The surface composition of PS, Φ_{PS}, was in excess of its bulk value of 50% and increased as the total molecular weight of the copolymer, N, increased. This dependence could be described by an equation of the form $\Phi_{PS} = a - bN^{-1/2}$ where a and b are constants.

Introduction

Block copolymers have received considerable attention in recent years.[1–6] Most of this work, however, has concentrated on the bulk morphology. These studies have shown that in a microphase-separated copolymer, under near equilibrium conditions, the volume fraction of each component dictates the morphology. If the average volume fraction of one of the blocks in the copolymer is between 0.4 and 0.6, then the structure is comprised of alternating lamellae of each component. When the volume fraction of one component is 0.2 or less, then this minor component forms spherical domains whose spatial arrangement exhibits a body-centered cubic symmetry in a matrix of the major component. At volume fractions between 0.2 and 0.4, cylindrical microdomains of the minor component are arranged in a hexagonally close-packed structure in a host of the major component. There is now strong evidence[6] that the cylindrically shaped microdomains arrange themselves in a structure which exhibits diamondlike symmetry at volume fractions which lie in the narrow regime between those which dictate the formation of the cylindrical and lamellar microdomains.

The equilibrium conformation of the chains located at a free surface should be different from that in the bulk

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