^{13}C-Enriched End Groups of Poly(3-methyl-1-pentene) Prepared in the Presence of Metallocene Catalysts

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ABSTRACT: Polymerization of both (*S*)-3-methyl-1-pentene and (*R,S*)-3-methyl-1-pentene in the presence of two metallocene catalysts prepared from metallocene precursors of different symmetry (C_2 and C_s) and ^{13}C-enriched MAO shows that the insertion of the monomer in the initiation step is diastereoselective to an extent similar to that previously observed in the presence of the heterogeneous isotactic specific catalyst δ-TiCl$_3$−Al(^{13}CH$_3$)$_3$. Surprisingly, the catalyst prepared with the metallocene precursor of C_s symmetry promotes coisotactic polymerization of the two enantiomers of 3-methyl-1-pentene but only dimerization of (*S*)-3-methyl-1-pentene.

In the presence of heterogeneous Ziegler−Natta catalytic systems, e.g., δ-TiCl$_3$−Al(CH$_3$)$_2$Cl, (*S*)-3-methyl-1-pentene ((*S*)-3MP1) polymerizes giving isotactic homopolymers while (*R,S*)-3-methyl-1-pentene ((*R,S*)-3MP1) produces a coisotactic copolymer of the two enantiomers that can be separated into optically active fractions of opposite rotation.[1] By promoting polymerization by using ^{13}C-enriched Al(CH$_3$)$_3$ as cocatalyst and determining by ^{13}C NMR the stereochemical structure of the enriched groups arising from primary insertion of the monomer on Ti−^{13}CH$_3$, it was possible to observe that the “like” face[2] of 3MP1 is more reactive than the “unlike” one (diastereoselectivity[3]), leading to a higher amount of erythro ^{13}C-enriched end groups (see Figure 1).[4]

Polymerization of (*R,S*)-3MP1 to a crystalline isotactic material in the presence of homogeneous catalysts containing C_2-symmetric precursors, e.g., dimethylsilylbis(1-indenyl)zirconium dichloride−methylaluminoxane (MAO), has been described by Brintzinger.[5] Kashiwa[6] reported polymerization of 3-methyl-1-butene in the presence of a homogeneous catalyst, (isopropylidene)(1-cyclopentadienyl)(9-fluorenyl)zirconium dichloride−MAO, which, due the C_s symmetry of the precursor, promotes syndiotactic polymerization of propene.[7] Surprisingly, the latter catalyst promotes coisotactic copolymerization of (*R,S*)-3MP1 but only promotes oligomerization of (*S*)-3MP1.

In order to evaluate the reactivities of the diastereotopic faces of 3MP1 in the insertion into the Zr−CH$_3$ bonds (initiation) of the active species present in the homogeneous catalysts with C_2 and C_s symmetry, we performed polymerization of (*R,S*)-3MP1 in the presence of either (ethylene)bis(1-indenyl)zirconium dichloride/^{13}C-enriched MAO (catalyst **1**) or (isopropylidene)(1-cyclopentadienyl)(9-fluorenyl)zirconium dichloride/^{13}C-enriched MAO (catalyst **2**) and polymerization of (*S*)-3MP1 in the presence of ^{13}C-enriched catalyst **1**. The diffractometric spectra of two samples of poly[(*R,S*)-3MP1] prepared with the just-mentioned homogeneous metallocene catalysts (see Figure 2) are almost identical to the spectrum of an authentic sample of a crystalline coisotactic sample of poly[(*R,S*)-3MP1] prepared according to ref 1 (Figure 3a). Figure 4 shows that also the diffractometric spectrum of poly[(*S*)-3MP1] is identical to that of an authentic sample of isotactic polymer prepared with TiCl$_3$−Al(CH$_3$)$_3$[4] (Figure 3b).

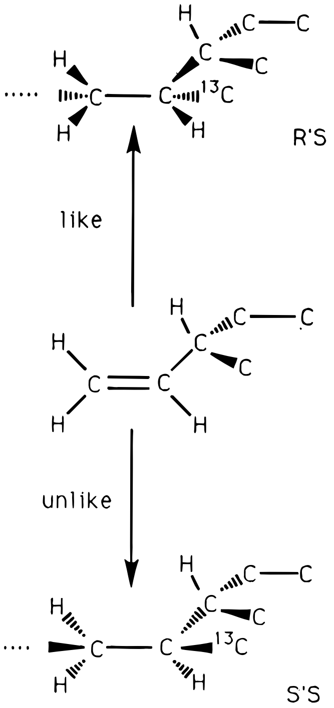

Figure 1. End groups arising from attack of the “like” face (up) and of the “unlike” face (down) of (*S*)-3MP1. The configuration of the chain methine carbon is primed.

The ^{13}C NMR spectra of poly[(*R,S*)-3MP1] prepared with catalysts **1** and **2** reported in Figure 5 are consistent with the results previously reported,[4] that the polymers of (*R,S*)-3MP1 actually are copolymers of the two enantiomers. The differences between spectra 5a and 5b are probably due to a different comonomer sequence distribution. The resonances of the ^{13}C-enriched methyls of the end groups, starred on the spectra, can be interpreted by comparison with the chemical shifts reported in the literature for polymers prepared in the presence of heterogeneous catalysts.[4]

The main result is that the intensity of the resonances at 15.0 ppm (erythro end groups) is higher than that of the resonances around 13 ppm (threo end groups), showing that the “like” faces of the monomers are more reactive than the “unlike” ones, at least in the initiation step. In comparison with the polymers obtained in the presence of the heterogeneous isospecific catalyst,[4] one can observe that the intensities of the resonances at 13.11 and 13.27 ppm are uneven (see Figure 5). The

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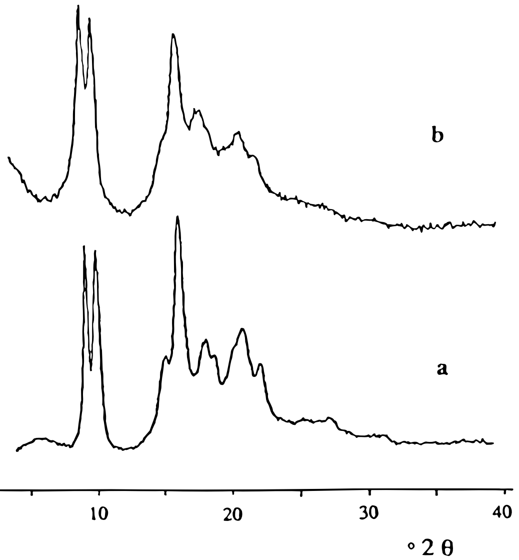

Figure 2. X-ray powder diffraction diagrams of the poly[(*R*,*S*)-3methyl-1-pentene] obtained with catalyst **1** (a) and with catalyst **2** (b). Cu Kα radiation.

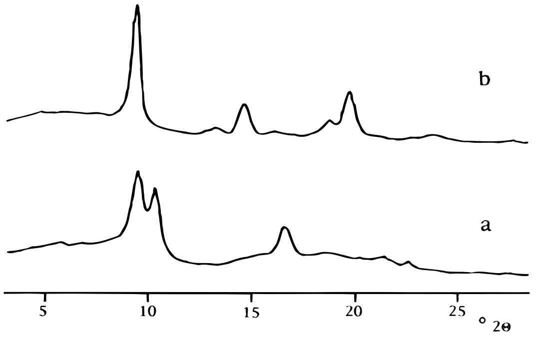

Figure 3. X-ray powder diffraction diagrams of the poly[(*R*,*S*)-3-methyl-1-pentene] (a) and poly[(*S*)-3-methyl-1-pentene] (b) obtained with δ-$TiCl_3$/$Al(CH_3)_2Cl$. Cu Kα radiation.

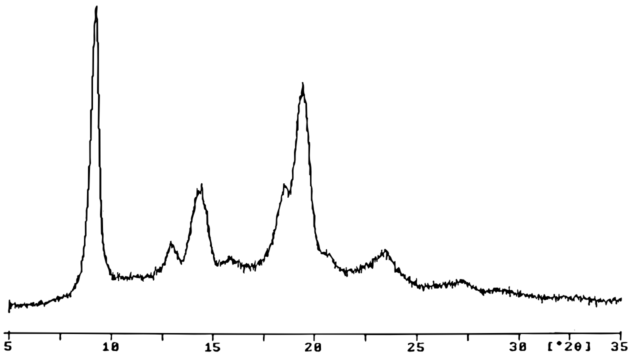

Figure 4. X-ray powder diffraction diagrams of the poly[(*S*)-3-methyl-1-pentene] obtained with catalyst **1**. Cu Kα radiation.

prominence of the signal at 13.11 ppm (...(*S′R*)(*S′S*)^{13}CH$_3$ and its antipode) with respect to that at 13.27 ppm (...(*R′S*)(*S′S*)^{13}CH$_3$ and its antipode) suggests that the insertion on the Zr−^{13}CH$_3$ bonds is at least partially stereospecific (isotactic) and not only diastereoselective as is seemingly the case in the presence of the heterogeneous catalysts.[4]

The spectrum of the poly[(*S*)-3MP1] obtained with the catalyst **1** (Figure 6) shows very sharp peaks due to the homopolymeric isotactic structure. The only enriched methyl chain end resonance detected is that of the erythro arrangement at 15.00 ppm.

As previously mentioned, the optically active monomer, (*S*)-3MP1, in the presence of catalyst **2** and under the same experimental conditions used for (*R*,*S*)-3MP1 does not produce any high polymer but at most oligomers. Actually, one can separate from the reaction mixture the dimer arising from primary insertion of the monomer into the Zr−H bond and β-hydrogen abstraction after the insertion of the second unit (see Experimental Section).

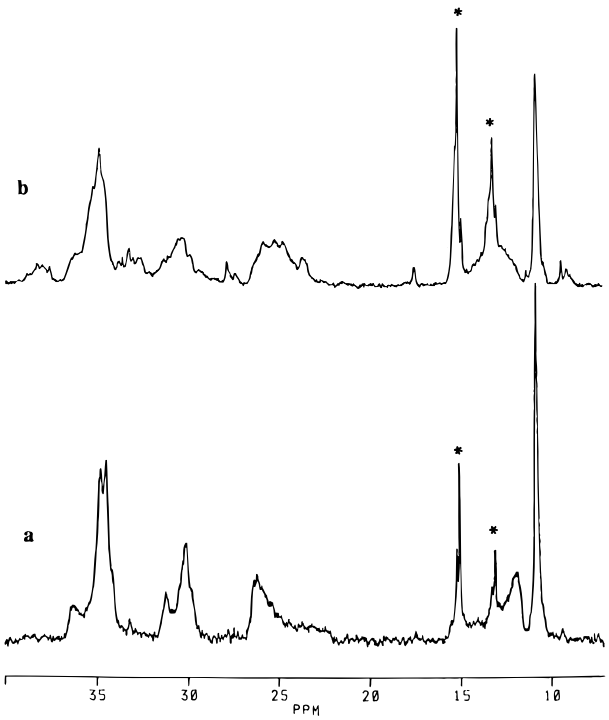

Figure 5. ^{13}C NMR spectra of isotactic poly[(*R*,*S*)-3MP1] obtained with catalyst **1** (a) and catalyst **2** (b). The starred peaks are due to ^{13}C-enriched methyl end groups (HMDS scale).

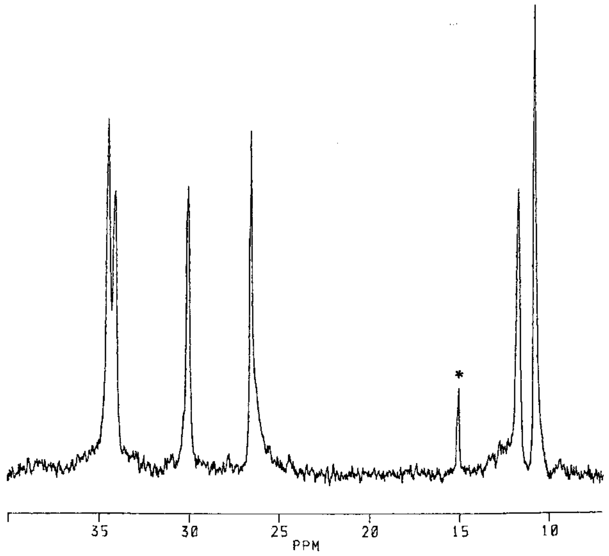

Figure 6. ^{13}C NMR spectrum of isotactic poly[(*S*)-3MP1] obtained with catalyst **1**. The starred peak is due to ^{13}C-enriched methyl end groups (HMDS scale).

The similar behavior of the two catalysts toward the insertion of (*R*,*S*)-3MP1 into the Zr−CH$_3$ bond is not surprising. On the other hand, the occurrence that in the presence of the catalyst **2** only oligomers of (*S*)-3MP1 are produced, especially dimers, suggests that in the propagation steps, catalytic sites with a C_2 symmetry preferentially react with one antipode, while sites of C_s symmetry tend to alternate the antipodes of (*R*,*S*)-

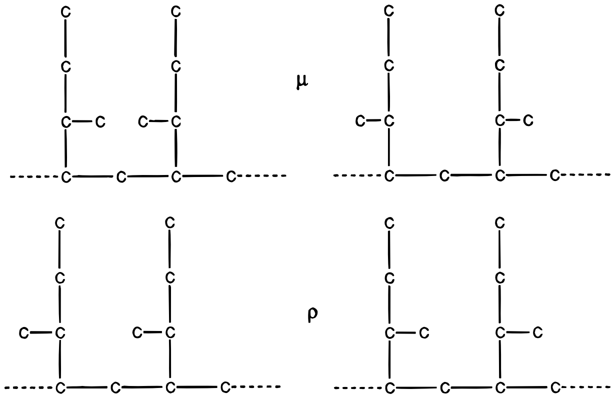

Figure 7. Fischer projections of the ρ and μ stereochemical diads.

3MP1. This hypothesis is supported by the observation that in the higher molecular weight polymer (see Experimental Section) obtained with the latter catalyst the resonances of the methylenes of the main chain bridging tertiary carbons having side substituents of opposite configuration (μ diads) prevail with respect to those of the methylene of the main chain spanning tertiary carbons having substituents of the same configuration (ρ diads)[10] (Figure 7). In accordance with this hypothesis, such a polymer should not be separable into optically active fractions of opposite rotation. Work is in progress in order to verify this fact.

Experimental Section

Reagents. Al($^{13}CH_3$)$_3$, 80% enriched, was prepared as previously described.[8] (*S*)-3MP1 was synthesized according to the literature.[9] (*R*,*S*)-3MP1 (Fluka) was distilled on Al(*i*-Bu)$_3$. Toluene was refluxed 48 h over sodium before use. (Ethylene)bis(1-indenyl)zirconium dichloride and (isopropylidene)(1-cyclopentadienyl)(9-fluorenyl)zirconium dichloride were prepared according to the literature.[7,11]

Polymerizations. Poly[(*R*,*S*)-3MP1] with the Catalyst 1. To 30 mL of toluene containing 0.87 g of MAO and 6 mL of (*R*,*S*)-3MP1 was added a solution of 0.6 mmol of Al($^{13}CH_3$)$_3$, 75% enriched, and 7 mg of (ethylene)bis(1-indenyl)zirconium dichloride. This mixture was introduced into a glass flask which was sealed, thermostated in an oil bath at 50 °C, and kept under stirring for 48 h. Then the reaction mixture was poured into acidified methanol, and the polymer was recovered by filtration, washed with fresh methanol, and dried in vacuo; yield 2.4 g. By exhaustive extraction with boiling solvents, the toluene-soluble, acetone-insoluble fraction (1.1 g), whose ^{13}C NMR spectrum is reported in Figure 4a, was separated.

Poly[(*S*)-3MP1]. The optically active monomer was polymerized with the same procedure as for the racemic one but the amounts of the reagents were as follows: toluene, 11 mL; MAO, 0.20 g; Al($^{13}CH_3$)$_3$, 0.16 mmol; (ethylene)bis(1-indenyl)zirconium dichloride, 1.5 mg; (*S*)-3MP1, 2 mL. Time, 3 days; yield 0.27 g, 28% toluene soluble.

Poly[(*R*,*S*)-3MP1] with the Catalyst 2. A solution of toluene (1.5 mL), Al($^{13}CH_3$)$_3$, 80% enriched (0.45 mmol), (isopropylidene)(1-cyclopentadienyl)(9-fluorenyl)zirconium dichloride (2.5 mg), and MAO (50 mg) was added to a solution of (*R*,*S*)-3MP1 (2.9 mL) and MAO (80 mg) in 2.5 mL of toluene. The flask containing this mixture was sealed and kept under stirring at 50 °C for a week; yield 0.12 g of a sticky material. Higher molecular weight polymer with a crystalline structure was obtained at 30 °C in the absence of the transfer agent Al(CH_3)$_3$.

Dimer of (*S*)-3MP1. The attempt to polymerize the optically active monomer was performed by mixing a solution of 1 mL of toluene containing 3 mg of (isopropylidene)(1-cyclopentadienyl)(9-fluorenyl)zirconium dichloride and 60 mg of MAO with a solution of 3 mL of toluene containing (*S*)-3MP1 (3 mL) and MAO (100 mg). The mixture was kept in a sealed flask under stirring at 30 °C for 2 weeks (under these conditions, the racemic monomer produced 0.59 g of crystalline polymer). After treatment with acidified methanol, the solution was shaken with heptane, and from the hydrocarbon phase, by distillation under reduced pressure, was isolated a product (0.1 g) whose ^{13}C NMR is in agreement with the dimer structure (2-*sec*-butyl-5-methyl-1-heptene) (resonances at δ 11.4, 11.9, 19.2, 19.7, 28.3, 29.5, 31.4, 34.4, 35.4, 41.7, 107.2, and 154.9 from TMS in CDCl$_3$); $[\alpha]_D^{25} = +35°$ (toluene).

Polymer Characterization. ^{13}C NMR Analysis. The ^{13}C NMR spectra were recorded on an AM 250 spectrometer operating in the FT mode at 62.89 MHz at 385 K for the polymers and at 293 K for the dimer. The samples were prepared by dissolving 40 mg of the toluene-soluble fraction of the polymer in 0.5 mL of tetrachlorodideuterioethane, in the presence of hexamethyldisiloxane (HMDS) as an internal chemical shift reference, or by dissolving 0.1 mL of dimer in 0.4 mL of CDCl$_3$, with tetramethylsilane (TMS) as an internal reference.

X-ray Diffraction Spectra. Wide-angle X-ray diffractograms of unoriented samples were obtained by using a PW 1050 Philips powder diffractometer (Cu Kα Ni-filtered radiation). The scan rate was 2°θ/min.

Conclusion

The results reported here were completely unexpected. Presently, we do not have any sound opinion on the possible reasons for the different stereospecificity observed in the polymerization of linear 1-alkenes and of (*R*,*S*)-3-methyl-1-pentene and for the failure of (*S*)-3-methyl-1-pentene to afford high polymers. Concerning this, it might be worth considering that the presence of a chiral substituent on the incoming monomer and the growing chain end implies 2^4 diastereoisomers of the activated state.

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References and Notes

(1) Natta, G.; Pino, P.; Mazzanti, G.; Corradini, P.; Giannini, U. *Rend. Accad. Naz. Lincei (VIII)* **1955**, *19*, 397. Pino, P.; Ciardelli, F.; Montagnoli, G. *J. Polym. Sci., Part C* **1969**, *16*, 3265.
(2) The face of the coordinated monomer having the same (opposite) configuration of the asymmetric C of the substituent is defined like (unlike).
(3) Seebach, D.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1982**, *19*, 857.
(4) Zambelli, A.; Ammendola, P.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1983**, *16*, 341. Zambelli, A.; Ammendola, P.; Longo, P.; Grassi, A. *Gazz. Chim. Ital.* **1987**, *117*, 579.
(5) Stehling, U.; Diebold, J.; Kirsten, R.; Röll, W.; Brintzinger, H. H. *Organometallics* **1994**, *13*, 964.
(6) Kashiwa, N. et al. Japanese Patent 338220, 1989 (to Mitsui Toatsu Chemical Co.).
(7) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255.
(8) Zambelli, A.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1982**, *15*, 211.
(9) Pino, P.; Lardicci, L.; Centoni, C. *J. Org. Chem.* **1959**, *24*, 1399.
(10) Zambelli, A.; Proto, A.; Longo, P. In *Ziegler Catalysts*; Fink, G., Mülhaupt, R., Brintzinger, H. H., Eds.; Springer-Verlag: Berlin, Heidelberg, 1995; p 217.
(11) Wild, F. R. W. P.; Wasincionek, M.; Hutter, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985**, *288*, 63.

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