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Syndiotactic Polymerization of Propene: Regiospecificity of the Initiation Step

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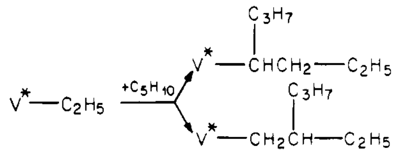
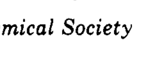
ABSTRACT: The results of the ^{13}C NMR analysis of the end groups of syndiotactic polypropylene, prepared in the presence of different aluminum alkyl cocatalysts, confirm that the regiospecificity of the insertion is a first-order Markov process. The bulkiness of the alkyl group strongly affects the relative rate of primary vs. secondary insertion of the monomer in the initiation step.

The problem of determining the regiospecificity of α-olefin insertion during Ziegler–Natta polymerization in the presence of both isotactic-specific and syndiotactic-specific catalytic systems was first tackled by Takegami and Suzuki.[1-3] In a group of elegant papers[2,3] concerning syndiotactic-specific catalysts (e.g., VCl_4 and $Al(C_2H_5)_2Cl$), these authors confirmed that propene is the only α-olefin which can afford syndiotactic polymers of high molecular weight[4] and observed that higher α-olefins (e.g., 1-pentene) react with the quoted catalytic system to give organometallic vanadium compounds that, after hydrolysis, give both *n*-heptane and 3-methylhexane. The reaction with 1-pentene was performed at low temperature (e.g., −78 °C) since these conditions are typical for syndiotactic polymerization of propene. *n*-Heptane was the major reaction product in comparison with 3-methylhexane. By considering that the catalyst system contains ethyl derivatives of vanadium, probably as $VCl_2(C_2H_5)$ formed in an exchange reaction[5] between VCl_4 and $Al(C_2H_5)_2Cl$, Takegami and Suzuki explained their experimental findings by assuming that 1-pentene can be incorporated in the vanadium–ethyl bonds with either primary or secondary regiospecificity:



The incorporation of further monomer units should be very slow because of the increased bulkiness of the alkyl groups bonded to V in comparison with C_2H_5. As a consequence the molar ratio between the *n*-heptane and 3-methylhexane resulting after hydrolysis of the organometallic complexes



$$V^*\text{—}\overset{C_3H_7}{\overset{|}{C}}HCH_2\text{—}C_2H_5 \xrightarrow{H_2O} n\text{-heptane}$$

$$V^*\text{—}CH_2\overset{C_3H_7}{\overset{|}{C}}HC_2H_5 \xrightarrow{H_2O} \text{3-methylhexane}$$

should correspond to the ratio between the rates of the incorporation of the monomer into the $V–C_2H_5$ bond, according to the possible regiospecificities. Since *n*-heptane accounted for ~70% of the total C_7H_{16}, Takegami and Suzuki concluded that insertion of propene during syndiotactic polymerization in the presence of the quoted homogeneous catalytic systems should be secondary.[2,3]

Very similar results were recently obtained by Doi et al. with a closely related catalytic system, $V(acac)_3–Al(C_2H_5)_2Cl$.[6]

We investigated the structure of syndiotactic polypropylene as well as that of ethylene–propene copolymers obtained with the same catalytic systems by IR and ^{13}C NMR spectroscopy.[7-13] Particular attention was devoted to the irregularly arranged monomer units. Our conclusions on the matter were that the insertion of propene is a first-order Markov process; i.e., incorporation of propene into growing chains ending with a secondary propylene unit is mostly secondary

$$V^*\text{–}CH(CH_3)CH_2\cdots \xrightarrow{+C_3H_6} V^*\text{–}CH(CH_3)CH_2CH(CH_3)CH_2\cdots$$

while incorporation into growing chains ending with a primary propylene unit (or eventually an ethylene unit) is mostly primary. Only a secondary propene insertion process would experience syndiotactic control. These views were corroborated by observing (1) $^{13}CH_3$-enriched *n*-propyl end groups when polymerization of 3-^{13}C-enriched

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Table I
^{13}C Chemical Shifts for Primary, Tertiary, and Secondary Carbons in Syndiotactic Polypropylene

species[a]	^{13}C NMR shift,[b] ppm
$P_{\alpha\beta}$	12.8–15.6
$P_{\beta\beta}$	18.1–19.7
$T_{\beta\beta}$	26.4
$T_{\beta\gamma}$	29.1
$S_{\alpha\beta}$	32.9–33.4
$S_{\alpha\alpha}$	44.5–45.4

[a] Each carbon is denoted according to the nomenclature scheme suggested by Carman et al.[16] [b] Downfield from internal HMDS.

propene was stopped by hydrolysis of the Mt–carbon bonds[14] ("left" end group according to a previous definition reported in the literature[15]) and (2) $^{13}CH_3$-enriched isobutyl end groups when polymerization of 3-^{13}C-enriched propene was initiated on V*–CH_3 bonds[14] ("right" end groups[15]). The results of Takegami and Suzuki can be reconciled with the statistical nature of the insertion process if it is assumed that insertion of one molecule of 1-pentene can occur not only on the syndiotactic-specific active complexes but also on other vanadium–ethyl bonds present on the catalytic system which can incorporate one monomer unit (prevailingly with secondary insertion) but which do not produce high molecular weight syndiotactic polypropylene.

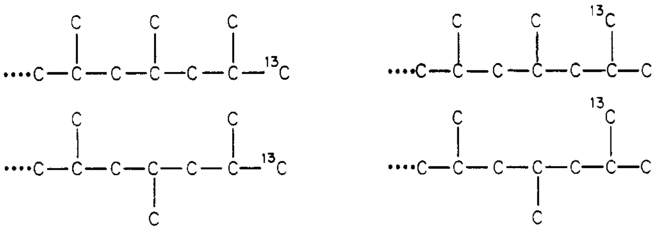
Alternatively it can be assumed that insertion of 1-pentene is not a satisfactory model of propene insertion, e.g., because of the very presence of a bulkier substituent on the monomer.

In order to settle the question we have examined the ^{13}C NMR spectra of two samples of prevailingly syndiotactic polypropylene prepared in the presence of the catalytic systems VCl_4–$Al(^{13}CH_3)_2Cl$ (sample a) and VCl_4–$Al(^{13}CH_2CH_3)_2Cl$ (sample b). Both samples were prepared at −78 °C as described in the Experimental Section.

In the spectrum of sample a (Figure 1a) one can observe, together with the typical resonances of syndiotactic polypropylene (see Table I), the presence of four resonances at 20.6_0, 20.7_9, 21.4_6, and 21.6_9 ppm due to the enriched CH_3's of the isobutyl end groups in the stereoirregular environment. Such end groups are those expected for primary stereoirregular insertion of propene into V*–$^{13}CH_3$ bonds

$$V^*\text{–}^{13}CH_3 \xrightarrow{+C_3H_6} V^*\text{–}CH_2CH(CH_3)\text{–}^{13}CH_3$$

followed by a further couple of stereoirregular primary insertions. Hence four different chain ends are formed:



No resonance is observed at 9.1_3 and 9.2_7 ppm as expected for the enriched methyl of the *sec*-butyl end groups that would arise from secondary insertion of propene into V–$^{13}CH_3$ bonds:

$$V^*\text{–}^{13}CH_3 \xrightarrow{+C_3H_6} V^*\text{–}CH(CH_3)CH_2\text{–}^{13}CH_3$$

The assignments of the resonances observed for the isobutyl groups and of that expected for the *sec*-butyl group have been achieved, as reported in previous papers,[14,17] on the grounds of suitable model compounds and by comparison with polymers prepared with unenriched $Al(CH_3)_2Cl$. It may be unequivocally concluded that (1) the insertion of propene into the V*–CH_3 bonds of the catalytic complexes is always primary, (2) primary insertion of the first monomer unit entered on the chain, as well as that of the following few, is stereoirregular, and (3), syndiotactic steric control requires that insertion turns to secondary as a consequence of the occurrence of the irregular arrangement of one unit.

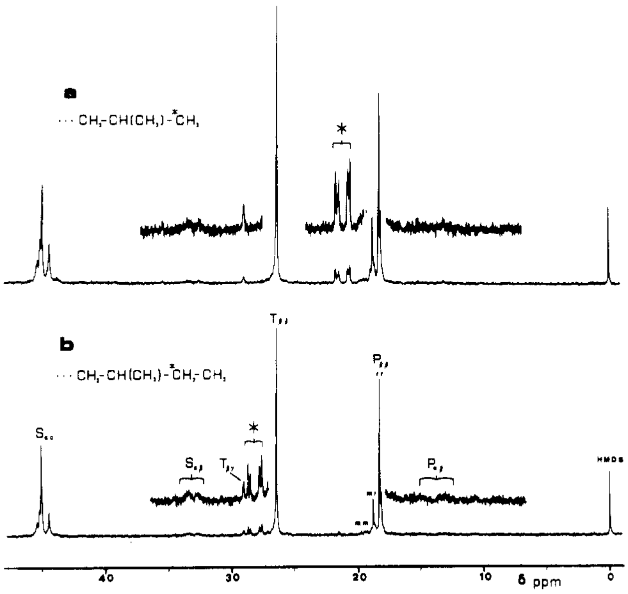
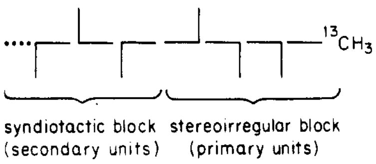


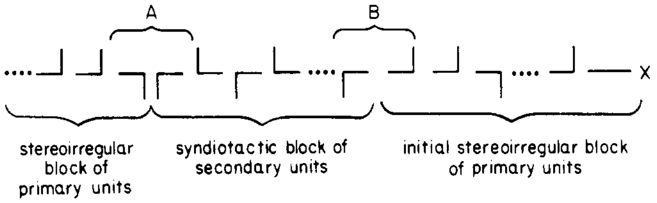
Figure 1. ^{13}C NMR spectra of syndiotactic polypropylene prepared in the presence of $VCl_4/Al(^{13}CH_3)_3$ (sample a) and $VCl_4/Al(^{13}CH_2CH_3)_3$ (sample b) at −78 °C. The chemical shifts of all peaks of syndiotactic polypropylene are reported in Table I. The resonances of ^{13}C-enriched end groups are marked by stars.



The number-average molecular weight of sample a was determined by GPC[18] ($\bar{M}_n$ = 12 700). A very close $\bar{M}_n$ (12 100) is calculated from the intensity of the resonances of the methyl end groups in comparison with the intensity of the resonances of the CH_3's of the inner monomer units of the chains (see Experimental Section). In Figure 1b is reported the spectrum of sample b. In comparison with Figure 1a one can observe the presence of four resonances at 27.6_4, 27.8_2, 28.5_5, and 28.7_6 ppm (starred in Figure 1b) due to the enriched methylene of ···$CH_2CH(CH_3)$–$^{13}CH_2CH_3$ end groups. Even in this case the assignment has been achieved, previously, by comparison with model compounds.[17] Of course, the resonances at 20.6_0, 20.7_9, 21.4_6, and 21.6_9 ppm of Figure 1a are absent.

Nothing can be said for sure concerning the presence of enriched methylene of the end groups which would arise from secondary monomer insertion (···$CH(CH_3)CH_2$–$^{13}CH_2CH_3$) since the resonances of such methylene carbons (expected at 18.3–18.4 ppm[13]) could be obscured by the CH_3 resonances of the inner monomer units. However, comparing the value of the number-average molecular weight of sample b determined by GPC ($\bar{M}_n$ = 13 800) with the value determined from the ratio between the intensity of the resonances of the enriched $^{13}CH_2$ and of the CH_2's of the inner monomer units (18 700), it seems that only $^3/_4$ of the chains bear the enriched methylene of the

$\cdots CH_2CH(CH_3)-{}^{13}CH_2CH_3$ end groups. The other chains could possibly initiate via secondary insertion. If this is true the relative rate of primary vs. secondary insertion of propene should decrease when the bulkiness of the primary alkyl group bonded to the vanadium atom of the catalytic complexes is increased.[23] On the other hand, such a decrease is also required in order to justify the prevailingly syndiotactic structure of the polymers. Actually (as reported in previous papers) the polymer consists of long blocks of secondary units in prevailingly syndiotactic arrangement and of very short blocks of primary units in stereoirregular arrangement. The different blocks are spanned by irregularly arranged (head to head or tail to tail) units:



where A represents a tail-to-tail arrangement, B a head-to-head arrangement, and X an alkyl group on which chain propagation initiates. Such structure and particularly the relative length of the blocks cannot be accounted for unless it is assumed that the ratio between the rate of the primary insertion of the monomer on primary growing chain ends and the rate of secondary insertion on the same growing chain ends is much lower than that observed for insertion into the $V^*-{}^{13}CH_3$ bonds. Actually, in a previous paper,[19] it was observed that the stereochemical sequence of the configurations of syndiotactic polypropylene is almost completely accounted for by the symmetric Bernoullian model proposed by Bovey.[20] This fact shows that the stereoirregular blocks, coming from primary insertion, cannot be longer than just a few monomer units.

From the experimental data reported in this paper concerning the initiation step of syndiotactic polymerization of propene on different primary alkyl groups and from those reported in previous papers concerning the stereochemical structure of syndiotactic polypropylene and ethylene–propene copolymers,[10,19,21] it can be confirmed that the regiospecificity of insertion is a first-order Markov process as outlined in the introductory part of the present paper. In addition, it can be observed that the relative rate of primary vs. secondary insertion of the monomer in the initiation step is strongly affected by the bulkiness of the primary alkyl group initially bonded to the V atom of the catalytic complexes.

Experimental Section

All solvents were purified by treatment with $LiAlH_4$ and distillation, and the reactions were performed in an inert atmosphere. VCl_4 was a commercial product. $Al(^{13}CH_3)_2Cl$ (60% enriched) and $Al(^{13}CH_2CH_3)_2Cl$ (90% enriched) were prepared by exchange of $Al(^{13}CH_3)_3$ and $Al(^{13}CH_2CH_3)_3$ with $AlCl_3$. $Al(^{13}CH_3)_3$ (60% enriched) and $Al(^{13}CH_2CH_3)_3$ (90% enriched) were prepared as previously described according to the literature.[19]

Polymerization runs were carried out as described in the literature[4] in 50 mL of heptane at −78 °C, in the presence of 1 L of propene, 0.5×10^{-3} mol of VCl_4, and 2.5×10^{-3} mol of $Al(^{13}CH_3)_2Cl$ or $Al(^{13}CH_2CH_3)_2Cl$ as catalyst system. After 24 h the polymers were precipitated with HCl-acidified methanol. The yield of samples a and b was 1.1 and 1.2 g, respectively. Number-average molecular weight ($\bar{M}_n$) determination was performed by GPC in *o*-dichlorobenzene at 135 °C, using a Anaprep (Waters Associates) gel permeation chromatograph equipped with a Styragel column (10^6-, 10^5-, 10^4-, and 10^3-Å pore size).

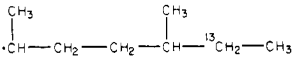
^{13}C NMR analysis of the polymers dissolved in 1,2,4-trichlorobenzene containing 1% hexamethyldisiloxane (HMDS) as an internal standard was carried out at 140 °C in the PFT mode on a Bruker HX-90 spectrometer operating at 22.63 MHz, with a pulse interval of 5 s.

The ^{13}C NMR number-average molecular weight of the polymers was evaluated from the intensity ratio between the resonances of the CH_3's of the inner monomer units of the chains and the ^{13}C-enriched methyl end groups (sample a) and from the intensity ratio between the resonances of the CH_2's of the inner monomer units and the ^{13}C-enriched methylene end groups (sample b). For the ^{13}C NMR $\bar{M}_n$ evalulations, the enrichment of the $Al(^{13}CH_3)_2Cl$ and $Al(^{13}CH_2CH_3)_2Cl$ was taken into account and the presence of one ^{13}C-enriched end group per chain was assumed. The reliability of the ^{13}C NMR $\bar{M}_n$ determination was checked by recording the spectra with different pulse interval values, in order to eliminate any possible error due to different spin–lattice relaxation times (T_1) between internal and terminal methyl and methylene groups. The results establish that a pulse interval of 5 s is sufficient to obtain accurate quantitative data from these carbons.

Registry No. Propene, 115-07-1; chlorodimethylaluminum, 1184-58-3; chlorodiethylaluminum, 96-10-6.

References and Notes

(1) Takegami, Y.; Suzuki, T.; Okazaki, T. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1060.
(2) Takegami, Y.; Suzuki, T. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 848.
(3) Takegami, Y.; Suzuki, T. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1484.
(4) Zambelli, A.; Natta, G.; Pasquon, I. *J. Polym. Sci., Part C* **1963**, *4*, 411.
(5) Natta, G.; Zambelli, A.; Lanzi, G.; Pasquon, I.; Mognaschi, E. R.; Segre, A. L.; Centola, P. *Makromol. Chem.* **1965**, *81*, 161.
(6) Doi, Y.; Ueki, S.; Tamura, S.; Nagahara, S.; Keii, T. *Polymer* **1982**, *23*, 258.
(7) Zambelli, A.; Lêty, A.; Tosi, C.; Pasquon, I. *Makromol. Chem.* **1968**, *115*, 73.
(8) Crain, W. O.; Zambelli, A.; Roberts, J. D. *Macromolecules* **1971**, *3*, 330.
(9) Zambelli, A.; Gatti, G.; Sacchi, M. C.; Crain, W. O., Jr.; Roberts, J. D. *Macromolecules* **1971**, *4*, 475.
(10) Zambelli, A.; Tosi, C.; Sacchi, M. C. *Macromolecules* **1972**, *5*, 649.
(11) Bovey, F. A.; Sacchi, M. C.; Zambelli, A. *Macromolecules* **1974**, *7*, 752.
(12) Sacchi, M. C.; Rigamonti, E.; Locatelli, P. *Makromol. Chem.* **1981**, *182*, 2881.
(13) Zambelli, A.; Allegra, G. *Macromolecules* **1980**, *13*, 42.
(14) Zambelli, A.; Locatelli, P.; Rigamonti, E. *Macromolecules* **1979**, *12*, 156.
(15) Zambelli, A.; Ammendola, P.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1983**, *16*, 341.
(16) Carman, C. J.; Harrington, R. A.; Wilkes, C. E. *Macromolecules* **1977**, *10*, 536.
(17) Zambelli, A.; Locatelli, P.; Bajo, G. *Macromolecules* **1979**, *12*, 154.
(18) GPC analyses were kindly performed by Dr. Giannotti, Montedison.
(19) Zambelli, A.; Locatelli, P.; Provasoli, A.; Ferro, D. R. *Macromolecules* **1980**, *13*, 267.
(20) Bovey, F. A.; Tiers, G. V. D. *J. Polym. Sci.* **1960**, *44*, 173.
(21) Zambelli, A.; Bajo, G.; Rigamonti, E. *Makromol. Chem.* **1978**, *179*, 1249.
(22) Zambelli, A.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1982**, *15*, 831.
(23) Further evidence supporting this hypothesis can be derived from a more careful inspection of the resonances from the enriched methylene of the end groups (Figure 1b). The resonance couple at 28.5_5 and 28.7_6 ppm appears slightly more intense than that at 27.6_4 and 27.8_2 ppm. This could be accounted for by the fact that, when a secondary inserted unit follows a first primary inserted one, the enriched methylene of the



$$\cdots\underset{}{\overset{CH_3}{\overset{|}{C}H}}-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}H}-{}^{13}CH_2-CH_3$$

end group is expected at ca. 28.5–28.6 ppm. A similar conclusion can be obtained for the enriched methyls of the end groups (Figure 1a).