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Stereoregular End Groups of Isotactic Polypropylene: A Challenging Test for the Reaction Mechanism

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ABSTRACT: Isotactic polypropylene, prepared in the presence of organometallic cocatalysts bearing ^{13}C-enriched methyl substituents, is observed by ^{13}C NMR. The enriched methyl carbon is detected, in stereoregular placement, on the end groups and never undergoes transformation to methylene. Therefore it is unlikely that metallacyclobutane intermediates are involved in the polymerization mechanism. In addition, since neither a chiral carbon nor a spiralized chain participates in the first two addition steps, the steric control arises, unequivocally, from the chirality of the catalytic center.

The mechanism of steric control in isotactic-specific polymerization of α olefins has been experimentally investigated by several independent approaches.

Pino and co-workers discovered that isotactic polymerization of racemic α olefins is stereoselective[1,2] and were able to achieve stereoelective polymerization by using optically active catalytic systems.[3] They suggested that stereoselectivity and stereoelectivity were due to intrinsic asymmetry of the catalytic centers.[4] Consequently, the inference that the isotactic steric control of the configuration of the backbone-substituted carbons was also due to intrinsic asymmetry of the catalytic centers seemed highly reasonable.[4-7]

Corradini and co-workers showed asymmetric coordination of propene on Pt complexes bearing a chiral ligand.[8]

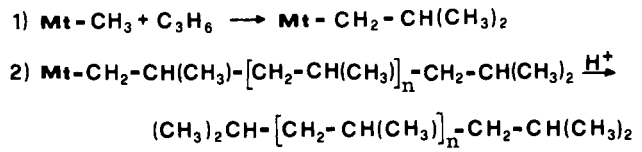
We investigated the chemical and configurational sequences of the substituted atoms in stereoregular polypropylene and ethylene–propene copolymers[9-12] and supported the suggestion that isotactic control is due to the asymmetry of the catalytic center.[5,7,9]

The results concerning Pt–olefin complexes[8] show that asymmetric coordination of prochiral olefins to transtion-metal atoms is possible but bear little direct evidence on the actual reasons of steric control in stereospecific polymerization.

Stereoselective and stereoelective polymerizations of racemic olefins[1-3] and analysis of the chemical and configurational sequences in homopolymers and copolymers of propene[9-12] converge, pointing out the role of the asymmetric environment of the catalytic center in determining isotactic chain propagation. However, the conclusions resulting from both these approaches rely somewhat on preliminary hypotheses. The arguments based upon stereoselective and stereoelective polymerizations rely on the assumptions that stereoselection of the racemic monomer and stereoregulation of the backbone-substituted carbons are due to the same cause and that the mechanism of the steric control is not dramatically affected by the presence of chiral substituents on the monomer.

The argument arising from analysis of the stereochemical sequence in isotactic homopolymers of propene relies on the hypothesis that stereochemically irregular placements are simply due to occasional failing of the catalyst. The argument concerning ethylene–propene copolymers

Scheme I[28]



relies on the hypothesis that ethylene does not dramatically affect the reaction mechanism.

All the arguments assume, in addition, that the key step in isotactic polymerization of α olefins is the insertion of the monomer on a reactive σ metal–carbon bond[5,17,18] and discard[19] chain spiralization as a possible cause of steric control.[20-23] The aim of this work is to show how isotopic substitution and ^{13}C NMR analysis of the polymer end groups can provide some additional evidence on the entire matter and help to reduce the number of preliminary hypotheses.

Experimental Section

All solvents were purified by treatment with $LiAlH_4$ and distillation, and the reactions were performed in an inert atmosphere (nitrogen or helium).

δ-$TiCl_3$ (HRA Stauffer) was purified by extraction with boiling toluene in a Kumagawa extractor.

50% enriched $Al(^{13}CH_3)_2I$ was prepared by reaction between Al scales and $^{13}CH_3I$ and subsequent distillation of the product as described in the literature.[24]

Enriched $^{13}CH_3I$ was prepared as described[25] starting from $Ba^{13}CO_3$.

The polymerization run was carried out in an autoclave at 75 °C and $p(C_3H_6)$ = 2.5 atm with the catalytic system $Al(^{13}CH_3)_2I$ (9×10^{-3} mol)–$TiCl_3$ (6.5×10^{-3} mol) suspended in toluene (250 mL). The polymerization time was 2 h and the polymer yield was 7.5 g.

The molecular weight of the isotactic polymer fraction insoluble in boiling *n*-heptane[26] (95%) was determined from the intrinsic viscosity in tetralin at 135 °C ($[\eta]$ = 2.39 100 cm^3/g; $\bar{M}_v$ = 375 000).[27] The $[\eta]$ of the fraction soluble in boiling *n*-heptane was not determined.

^{13}C NMR analysis of the polymers dissolved in 1,2,4-trichlorobenzene containing hexamethyldisiloxane (1%) as an internal standard[28] was carried out at 140 °C in the FT mode on a Bruker HX-90 spectrometer operating at 22.63 MHz.

The number average molecular weight, $\bar{M}_n$, of both fractions was evaluated from the intensity ratio between the resonances of the inner methyls and of ^{a}C, assuming the same Overhauser[34]

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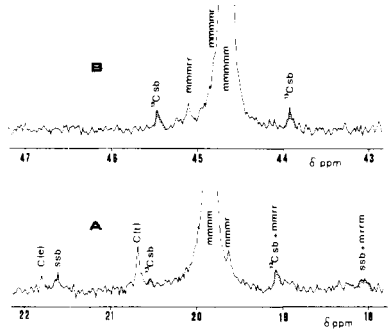
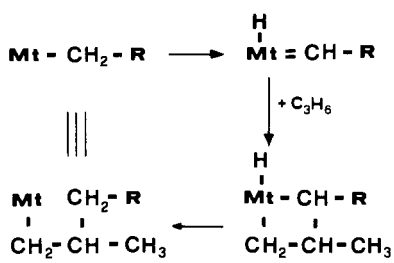


Figure 1. Expanded ^{13}C NMR spectra of the methyl (A) and methylene (B) regions of the fraction insoluble in boiling *n*-heptane of highly isotactic polypropylene. The polymerization is started on metal-$^{13}CH_3$ enriched bonds (see Experimental Section).[35] Chemical shifts are in parts per million downfield from hexamethyldisiloxane.

Scheme II[a]



[a] Mt = metal atom of the catalytic complex; R = polymer chain. H migrates to the more substituted α carbon of the metallacyclobutane intermediate.

enhancement and the presence of one ^{a}C/chain. M_n values of 230 000 and 6500 were found for the insoluble and soluble fractions, respectively.

Results and Discussion

1. Insertion of the Monomer. In a previous paper[15] we have demonstrated the presence of isopropyl end groups at both ends of isotactic polypropylene chains obtained by using suitable methyl derivatives or organometallic cocatalysts. Such end groups arise from the primary insertion of the first molecule of monomer on the reactive metal–methyl bond of the catalytic complex (right end group) and from the quenching of the polymerization by hydrolysis of the metal–methylene bond (left end group). The formation of the isopropyl end groups is shown in Scheme I; they are called right and left, respectively since, by convention, the metal atom (Mt) is always at the left end of the macromolecule.

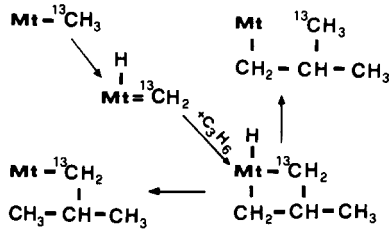
As a result of this observation and the absence of irregular chemical arrangements in the chains, we established that isotactic polymerization is fully regiospecific for primary insertion.[15,29]

Figure 1 shows the ^{13}C NMR spectrum of a heptane-insoluble sample of polypropylene obtained with the catalytic system α-$TiCl_3$ (HRA Stauffer)-$Al(^{13}CH_3)_2I$. Five sharp resonances are observed due to the inner methylene (δ 44.62), methine (δ 27.05), and methyl (δ 19.80) carbons in an isotactic stereochemical environment and the enriched methyl carbons of the right end groups (δ 20.67 and 21.78).[15,30]

The result is obvious where the addition of the monomer is a simple[15,17,18] insertion reaction. However, a different catalytic cycle involving reversible migration of α hydrogen and metallacarbene–metallacyclobutane interconversion was recently suggested for the addition of the monomer,[31,32] as shown in Scheme II.

The catalytic cycle accounts for the linearity of the polymer chain, assuming that H always migrates to the more substituted α carbon (CHR), and the stereospecificity could result from minimizing the nonbonded interaction between R and CH_3 in the metallacyclobutane.

Scheme III[a]



[a] Because of the symmetry of the metallacyclobutane intermediate, H migration is equally likely to either α carbon.

Scheme IV

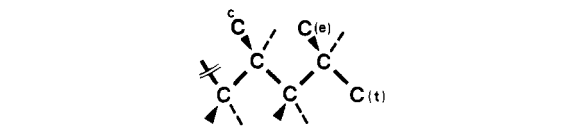


Figure 2. Zigzag planar projection of the right chain end. e is erythro, t is threo, and H atoms have been omitted.

When, in the first polymerization step, R = H, the H migration should occur, randomly to either α carbon and, even more obviously, the monomer should not experience steric control at all. Therefore the methyl and the isobutyl methylene carbons of the right end groups of the title polypropylene should share ^{13}C as shown in Scheme III. On the contrary, no resonance is detected for the enriched methylene carbons at δ 46–47 (Figure 1), as expected from previous study of model compounds.[33,34] This is evidence against the proposed[31] mechanism.

The stereospecific placement of the enriched methyls of the right end groups is further evidence, as in the following section.

2. Origin of Isotactic Steric Control. Insertion of propene into a Mt–CH_3 bond produces an isobutyl group. A chiral group (2,4-dimethylpentyl) appears at the growing chain end only after insertion of a further monomer, as shown in Scheme IV, where the methyl carbons are labeled in such a way that ^{a}C is always the one arising from the catalyst. ^{a}C and ^{b}C are diastereotopic atoms due to different configurational relationships with ^{c}C,[33] and their stereochemical placement on the polymer end groups can be readily determined by ^{13}C NMR, provided that either ^{a}C or ^{b}C is enriched (or isotopically substituted).[15,34]

Figure 1 shows that most of the (enriched) ^{a}C's are threo (and ^{b}C's are erythro) with respect to ^{c}C, since a more intense resonance is detected at 20.6_7 ppm relative to that at 21.7_8 ppm.

As shown in previous papers[15,34] the erythro and the threo methyls on the end groups considered resonate at δ 21.7_6 and 21.5_4 and δ 20.6_9 and 20.8_7, respectively.[15,34] The erythro and the threo placements have been defined in previous papers[15,34] and are shown in Figure 2. (Note that erythro is equivalent to isotactic and threo to syndiotactic.)

The stereoregular arrangement of methyls ^{a}C and ^{b}C relative to ^{c}C reveals that both the first and the second added monomer molecules have experienced the same steric control (isotactic). Since both methyl and isobutyl are achiral groups and spiralization of the chain cannot be invoked for steric control, the stereoregularity can only

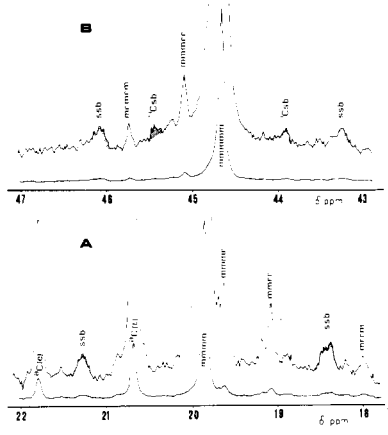


Figure 3. Expanded ^{13}C NMR spectra of the methyl (A) and methylene (B) regions of the fraction soluble in boiling *n*-heptane of the same polymer as in Figure 1 (see Experimental Section).

result from the asymmetric spatial arrangement around the metal atom of the catalytic complexes. Actually, according to the carbenic mechanism discussed in section 1, only the second added monomer unit could experience steric control and, consequently, the steric relationship between ^{a}C and ^{c}C will be randomly erythro or threo. This outcome is even more evident from the spectrum of the fraction of the same polymer soluble in boiling *n*-heptane (Figure 3), due to the higher concentration of right end groups, despite the lower stereoregularity.

Conclusion

The stereochemical structure of the selectively enriched end groups of the isotactic polypropylene examined in this paper shows that (i) metallacyclobutanes are unlikely reaction intermediates, (ii) insertion of the monomer on σ metal–carbon bonds accounts fairly well for the experimental results, and (iii) steric control by chiral catalytic centers seem to be a keystone feature of the reaction mechanism. Of course, chiral centers could be present from the beginning[6] on the surface of the solid catalyst or perhaps result from some interaction between the surface and the organometallic cocatalyst, e.g., Cl–alkyl exchange on one enantiotopic position.

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