^{13}C and 2D NMR Analysis of Propylene Polymers Made with α-Diimine Late Metal Catalysts[†]

E. F. McCord,* S. J. McLain, L. T. J. Nelson, S. D. Arthur, E. B. Coughlin, and S. D. Ittel*

DuPont Central Research & Development, Wilmington, Delaware 19880-0328

L. K. Johnson, D. Tempel, C. M. Killian, and M. Brookhart

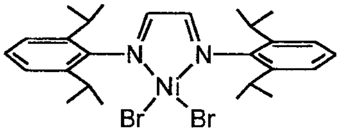
Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290

Received July 24, 2000; Revised Manuscript Received November 7, 2000

ABSTRACT: Late transition metal catalysts bearing α-diimine ligands allow ethylene and α-olefin homo- and copolymerizations to polyolefins with unprecedented structures. The polypropylenes made with these new late metal catalysts have very complex microstructures that include combinations of features not seen in any known polypropylenes. These unusual structures include long branches, branches on branches including isobutyl branches, and moderate highly variable levels of 1,3-enchainment leading to runs of methylenes in the backbone of many different well-defined lengths. These features vary with the nature of the catalyst used for polymerization and with the polymerization conditions. Many of the polypropylenes are made primarily by 1,2-insertions to give syndiotactic placements via chain end control. A mechanistic description of catalyst behavior has been developed to explain these observed microstructures.

Introduction

The discovery of α-diimine-derived late transition metal catalysts like **1** has led to a surge in interest in olefin polymerizations by catalysts other than those derived from the more traditional, early metal complexes.[1] These catalysts allow unprecedented ethylene and α-olefin homo- and copolymerizations with a variety of other monomers.[2,3] There are several unique features of these catalysts which can be discerned by NMR: (1) they give highly branched and probably hyperbranched polyethylenes with unusual branching distributions; (2) they copolymerize polar monomers such that most of the comonomer is located at the ends of branches; and (3) they can polymerize α-olefins in a “straightened” fashion resulting in α-olefin polymers that show very unusual branching distributions. In this report we describe our results and conclusions based on the characterization of propylene polymers made with these α-diimine late metal catalysts by ^{13}C and 2D NMR spectroscopy.



1

Propylene can be polymerized into three primary tactic forms—isotactic, syndiotactic, and atactic—and many combinations of the three.[4] Isotactic polypropylene was first produced and characterized in 1954 by Natta using a Ziegler−Natta catalyst.[5] Today, the preponderance of commercial polypropylene is isotactic, produced by heterogeneous titanium-based Ziegler−Natta catalysts.[6] Metallocene catalysts allow the synthesis of a variety of new structures.[7] Most of the metallocene effort is directed toward isotactic polypropylene.[8] Syndiotactic polypropylene is produced with metallocene catalysts via 1,2-insertion and enantiomorphic site control.[9] It can also be prepared with vanadium-based, homogeneous Ziegler−Natta catalysts via 2,1-addition and chain end control;[10,11] the degree of syndiotacticity increases as the temperature is lowered.[6] A variety of Ziegler−Natta catalysts and metallocene catalysts yield stereoirregular atactic polypropylene.[12] For a titanium-based metallocene catalyst that gives atactic polypropylene at ambient polymerization temperatures, the isotactic content increases dramatically as the temperature of polymerization is lowered.[6] Catalysts that yield polypropylenes having isotactic and syndiotactic blocks,[13] syndiotactic and stereoirregular blocks,[14] or isotactic and atactic blocks have also been reported.[15] Stereochemical defects can take on several different forms, depending on whether the polymerization is chain end controlled (Bernoullian)[16] or enantiomorphically controlled.[6,17] The assignment of the NMR resonances of polypropylenes to various tactic sequences and regioirregular defects has been investigated by a number of groups.[10,11,18−21] Ethylene−propylene (E/P) copolymers are known that have either isotactic, syndiotactic, or atactic stereochemistries.[22] In addition to these stereochemical defects, regioirregularities are observed with both head-to-head and tail-to-tail propylene structures in E/P polymers.[23,24]

Monomer addition in propylene polymerizations can display either 1,2- or 2,1-regiochemistry. Regioirregularities yield tail-to-tail and head-to-head monomer sequences. Heterogeneous Ziegler−Natta catalysts based on Ti(III) produce mostly isotactic polypropylene via a 1,2-addition and exhibit enantiomorphic site control.[25,26] Nonspecific homogeneous zirconium or titanium metallocene catalysts (single site catalysts) produce atactic polypropylene via 1,2-addition.[6] At lower temperatures the titanocene-based catalysts can produce isotactic polymer via a chain end control mechanism and cis-1,2-

---

[†] Contribution No 8079 from DuPont Central Research and Development.

10.1021/ma0012898 CCC: $20.00

insertion with retention of configuration at the coordinated carbon.[6] The change in tacticity with temperature indicates two different catalytic sites. If metallocene catalysts exhibit C_1 or C_2 symmetry or have chiral ligands, they may produce isotactic polypropylene via 1,2-addition with enantiomorphic site control.[6] The method of addition can sometimes be inferred by analysis of the chain end structures. However, in some cases this can be misleading, as the initial insertion can proceed by a different mode of addition than the main chain polymerization.[27] The selectivity for 1,2- or 2,1-addition can be determined by the presence of regioirregular monomer placements.[28,29] Regioirregular monomer units can exist in blocks of more than one monomer.[29] Further structural complications exist in that the regioirregular monomer or groups of monomers can have well-defined stereochemistries, which differ depending on the particular catalyst system.[6,28,29] Enchainment of propylene by an apparent 1,3-addition also indicates 2,1-addition followed by isomerization.[29] 1,3-Enchainment has been reported by several groups,[13,29−38] though several of these reports have been questioned.[33] However, those which appear sound show different regimes of 1,3-enchainments along what should be a continuum of regiospecificities: (1) the polymer contains a very low level of isolated 1,3-enchainments,[29−34] resulting in the expected 1000 Me/1000 CH_2; (2) the material is mostly (60−95%) normal 1,2-insertion with lesser straightened 1,3-enchainments, resulting in 500 or more Me/1000 CH_2;[13] or (3) the monomers are predominantly chain straightened, resulting in less than 36 Me branches/1000 CH_2 or about 90% 1,3-enchainment (comparable to an E/P copolymer with 7 mol % propylene).[33]

Polymerization of propylene with α-diimine late metal catalysts has been the subject of several publications[36−39] since our original disclosure.[3] The syndiotactic character of the resulting polypropylene increases as the temperature of polymerization is lowered.[37] Studies of ^{13}C-labeled end groups of these polypropylenes indicated that they were the result of 1,2-insertions with chain end control.[38,39] In this paper, we expand on our original report[3] with a more complete description of the wide variety of microstructures in polypropylenes made with these new α-diimine late metal catalysts. Our conclusions expand upon and are in substantial agreement with the previous studies.

Experimental Section

Catalysts. The ligands for the catalysts are prepared by the Schiff-base condensation of anilines with α-diones, all commercially available from Aldrich. The transition metal complexes are prepared by addition of the resulting α-diimine ligands to metal halide precursors. Details of the preparations of the individual catalysts have been described elsewhere.[2] The particular catalysts used for this study are shown in Figure 1.

Polymer Preparation. Polymers were prepared in general according to the methods described previously.[2] Typical examples are as follows:

Polymerization in Glassware. A 250 mL Schlenk flask was charged with 20 mg of catalyst **1** (3.2×10^{-5} mol) and 75 mL of dry, deaerated toluene. The flask was cooled to 0 °C and filled with propylene (100 kPa absolute) before addition of 1.5 mL of a 10% MAO solution in toluene. After 30 min, acetone and water were added to quench the reaction. Solid polypropylene was recovered from the flask and washed with 6 M HCl, H_2O, and acetone. The resulting polymer was dried under high vacuum overnight.

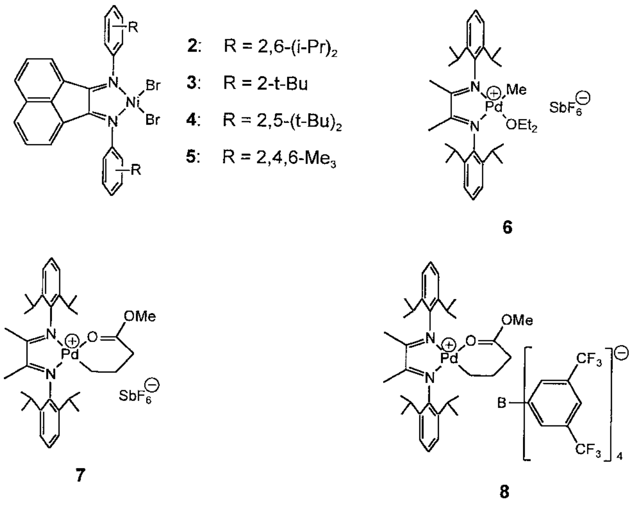


Figure 1. Structures of catalysts used to make the polypropylenes.

^{13}C NMR. The 100 MHz ^{13}C NMR spectra were obtained on a Varian Unity 400 MHz spectrometer typically on 10% (w/v) solutions of the polymers and 0.05 M $Cr(acac)_3$ in 1,2,4-trichlorobenzene (TCB) unlocked at 120−140 °C using a 90° pulse, a spectral width of 35 kHz, a relaxation delay of 5 s, an acquisition time of 0.64 s, and inverse gated decoupling. Samples were preheated for at least 15 min before acquiring data. The data acquisition time was typically 11 h per sample. The T_1 values of the carbons of a polyethylene sample were measured under these conditions to be all less than 0.9 s. The longest T_1 measured was for the Bu^+, EOC resonance at 14 ppm, which was 0.84 s. Polymer K was run at 20% (w/v) polymer under similar conditions except that a small amount of benzene-d_6 (16 vol %) was added, and the sample was run locked. One exception is sample I, which was run in chloroform-d_1 (locked) at 30 °C under similar acquisition parameters. Spectra are referenced to the solvent—either the TCB highfield resonance at 127.9 ppm (measured vs TMS under these conditions) or the chloroform-d_1 triplet at 77 ppm. Integrals of unique carbons in each branch were measured and were reported as number of branches per 1000 methylenes (including methylenes in the backbone and branches).

2D INADEQUATE. The 2D INADEQUATE experiment was run on a Varian VXR-S 400 MHz NMR spectrometer using a 10 mm probe. The sample was 2 g of polypropylene K and 0.05 M $Cr(acac)_3$ (60 mg) with TCB-d_3 in a total volume of 3.1 mL. The spectrum was run at 120 °C. To obtain the high resolution needed in a reasonable amount of time, the spectral width in the f_1 dimension was folded one time. Linear prediction was used to extend the data set in the f_1 dimension by a factor of 4. An additional factor of 4 was gained by zero-filling two times. A T_1 relaxation experiment was performed on this sample which showed that the T_1 values of the carbons were all less than 0.6 s under these conditions. A homospoil pulse was not used. A delay of 1.0 s, 4800 transients per increment, 32 increments, and an acquisition time of 0.23 s were used. The inadequate experiment took 4.4 days to complete under these conditions.

Nomenclature. The ^{13}C NMR resonances are labeled according to the following naming scheme:

1. xB_y: B_y is a branch of length y carbons; x is the carbon being discussed, and the methyl at the end of the branch is numbered 1. Thus, the second carbon from the end of a butyl branch is $2B_4$. xB_y+ refers to branches of length y and longer.

2. The methylenes in the backbone are denoted by a capital S and with Greek letters that determine how far from a branch point methine each methylene is. Thus, $S_{\beta\beta}$ denotes the central methylene in the following structure: $RRCHCH_2CH_2CH_2CHRR$. γ^+ refers to methylenes γ and further from a branch point.

3. When x in xB_y is replaced by a T, the methine carbon of that branch is denoted.

Table 1. Catalysts and Conditions Used To Prepare Polypropylenes and Characterization of the Polymer Structure

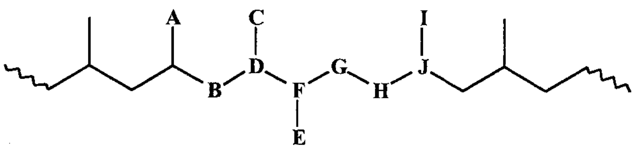
polymer	catalyst[a]	temp[b] (°C)	adj Me[c,d] (%)	1,3-ins[c,e] (%)	2,1-ins[c,f] (%)
A	2	0	17	9	22
B	1	0	8	11	7
C	1	25		16	
D	2	25		13	
E	3	25		52	
F	4	25	14	39	53
G	5	25	27	25	
H	5	0	14	55	
I	6	25		34	
J	7	22		31	
K	8	?		40	

[a] The catalyst number refers to Figure 1. [b] The temperature is the polymerization temperature. [c] The absence of a number in this table means only that we did not calculate it. [d] Adjacent methyls is the percentage of methyls in the 14−18 ppm region as a percentage of the total methyls of all kinds in the sample. [e] 1,3-Insertions is the percent of 1,2-insertions followed by isomerization to 1,3 as given by eq 1. [f] 2,1-Insertions is the % of 2,1-incorporation as calculated from the total of the % chain straightening, plus half of the % adj methyls (adjusted to total monomer units), plus the number of structures with resonance of type K per 100 monomer units (see Figure 2a). Assumes predominant insertion mode for runs of methyl-branch-containing insertions is 1,2.

4. In the polypropylene literature, a T followed by two Greek letters indicates a methine carbon and how far away the next methine is. A P followed by two Greek letters indicates a methyl branch and the distance to the two neighboring branch points. For example, the methyls and methines in a highly regioregular polypropylene would be denoted $P_{\beta\beta}$ and $T_{\beta\beta}$. We have in general not indicated stereochemistry, though it certainly plays a role in some of the observed structures.

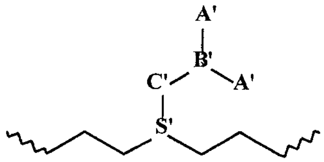
Results

^{13}C NMR Spectra. The catalysts used to make the polypropylene polymers discussed in this paper are shown in Figure 1. The conditions employed are described in Table 1. The ^{13}C NMR spectra of polypropylenes made with the α-diimine late metal catalysts are far more complex than expected and differ dramatically depending on the catalyst and polymerization conditions used. Figure 2a shows the ^{13}C NMR spectrum of polypropylene B made with a Ni version of these catalysts. Resonance assignments for the indicated carbons in the following structure (**9**) are shown in Figure 2a.

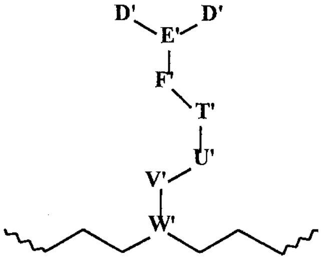


9

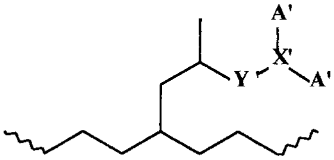
The ^{13}C NMR spectrum of a polypropylene made with a Pd version of these catalysts is shown in Figure 2b. Branch structures observed include methyl, butyl, hexyl$^+$, 2-methylhexyl$^+$, isobutyl, and 2,4-dimethylpentyl$^+$. Also observed are runs of methylenes between branches $(CH_2)_n$ where $n = 4$, runs of methylenes between branches $(CH_2)_n$ where $n = 7^+$, and isolated methyl branches. Resonance assignments for the indicated carbons in the following structures are shown in Figure 2b:



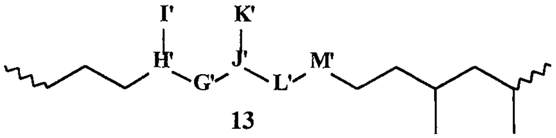
10



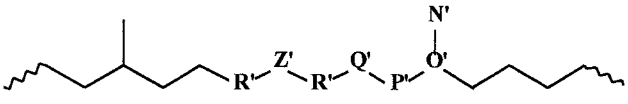
11



12



13



14

In many cases the α-diimine polypropylenes are very similar to an ethylene−propylene (E/P) copolymer with runs of adjacent methylenes. In the polymers resulting from the Pd catalysts, these runs consist of discrete numbers of methylenes (4, 7, and longer adjacent methylenes); in the Ni-catalyzed systems all different values of n in $(CH_2)_n$ runs are observed. The polymers tend to show slight syndiotacticity, though they would be more aptly described as atactic. Regioirregular placements are observed in both Ni- and Pd-derived polymers, but insertions at secondary carbon atoms are observed only in the Ni-derived polymers.

Chain Straightening. From the number of methyl groups present and the total number of carbons, one can calculate the percentage of “chain straightening” or 1,3-enchainment in these polymers. The percentage of monomer units that are “straightened” generally falls within the range of 9−55% 1,3-enchainment. For polypropylene the calculation is

$$\% \ 1,3 = (100)(1000 - B)/(1000 + 2B) \qquad (1)$$

where B is the total methyl groups per 1000 methylene groups. Some typical values are listed in Table 1.

Adjacent Backbone Methylenes. The backbone and branch structure of the polymer can also be analyzed in terms of the number of adjacent methylenes.

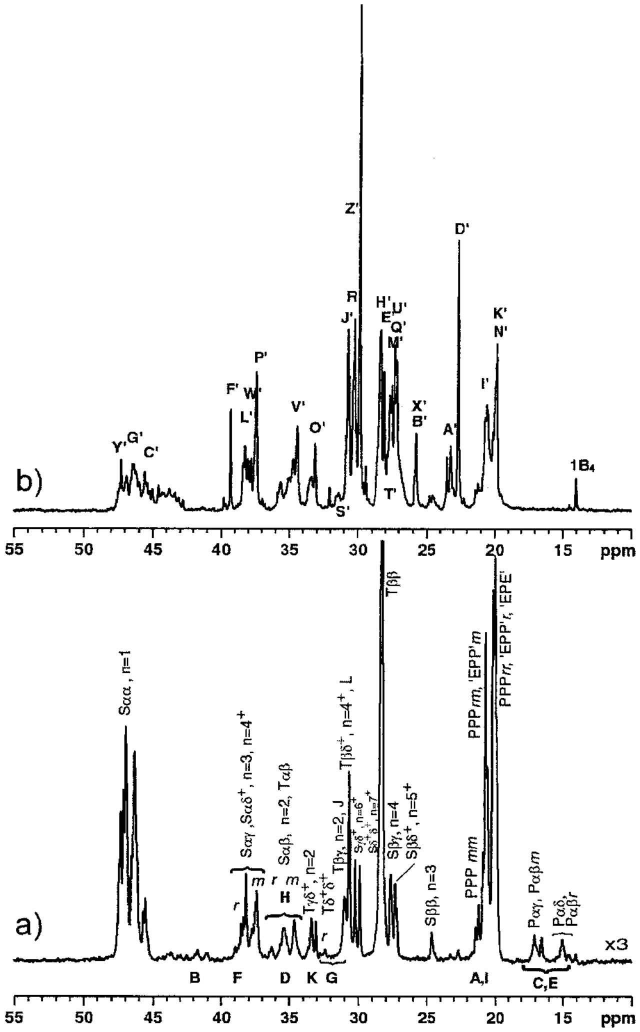
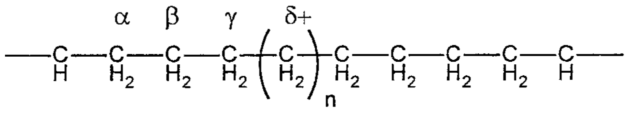


Figure 2. (a) ^{13}C NMR spectrum of a nickel-catalyzed polypropylene, B, in TCB, 120 °C, vs TMS. (b) ^{13}C NMR spectrum of palladium-catalyzed polypropylene, J, in TCB, 120 °C, vs TMS.

We can define the following, according to the resonance assignments shown in Figure 2a:

(i) δ^+: the number of methylenes that are four or more carbons removed from a branch site per 1000 methylenes (these methylenes can be in the backbone or in the side chain, as long as they are at least four carbons removed from the end of the branch). The existence of δ^+ carbons depends on having at least two adjacent monomers with 1,3 enchainment.



(n greater than or equal to 1)

(ii) δ^+/γ: the ratio of δ^+ or longer to a branch to γ to a branch methylenes. The branch can be any length. δ^+ and γ can be in the branch as well, as long as they are at least four carbon atoms removed from the end of the branch. In fact, there are a very low percentage of these long branches in the polymers. For runs of length 7 methylenes only, the theoretical minimum of δ^+/γ is 0.5. This means that as δ^+/γ approaches the minimum value of 0.5, no more than two polypropylene monomers in a row have chain straightened.

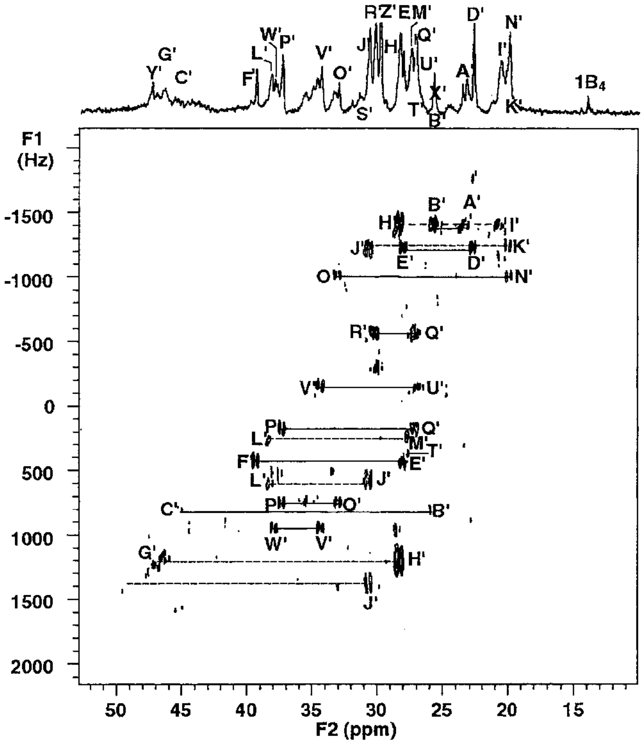


Figure 3. ^{13}C NMR INADEQUATE spectrum of polypropylene K.

Unique Branches. The existence of several unique types of branches in these polypropylenes has been determined by chemical shift calculations, comparison with literature chemical shift values, and a 2D INADEQUATE experiment on polymer K (see Figure 3), which is very similar to polymer J (shown in Figure 2b). The branches observed include methyl, ethyl, butyl, hexyl$^+$, isobutyl, and 2-methylhexyl$^+$ shown in structures **10**−**14**. The 2D INADEQUATE NMR technique allows one to directly trace the connections among adjacent carbon atoms in a molecule. This technique uses single quantum−double quantum correlations to locate the chemical shifts of adjacent ^{13}C atoms in a molecule. The INADEQUATE technique suffers from a lack of sensitivity, being 200 times less sensitive than normal ^{13}C NMR, thus taking 40 000 times as long to obtain the same signal-to-noise spectrum. However, some polymers are sufficiently soluble that this technique can be used to advantage to study microstructures. 2D INADEQUATE is especially useful in these pure hydrocarbon polymers, where the lack of chemical shift discrimination in the ^{1}H NMR spectrum makes it difficult to effectively use ^{1}H−^{13}C two-dimensional techniques to study polymer microstructure. In fact, there are several reports in the literature of 2D INADEQUATE applied to polypropylene and E/P structures.[18,31,32]

We have used the 2D INADEQUATE spectrum shown in Figure 3 to study a polypropylene made with one of the α-diimine Pd catalysts. Additional correlations are observed at lower contour levels. We can trace out isobutyl branches shown in structure **10**: A′ to B′, B′ to C′. There is a second resonance under B′, which we have labeled X′, which correlates to resonance Y′. Y′ is shifted about 2 ppm downfield from C′, which is consistent with a structure such as a 2,4-dimethylpentyl branch **12**. This

Table 2. Frequency of Various Structures per 1000 Methylene Carbon Atoms in the Polypropylenes[a,j]

polymer sample	δ+[b]	δ+/γ[c]	total Me[d]	Bu+[e]	*i*-Bu[f]	2MeH+[g]	Et[h]	Hex+[i]
Ni catalysts								
F			346	12	12	6	3	5
E	254	1.96	226	8.5	2	12	tr	4
A	~3	~0.4	782	tr	tr			
B	32	0.87	739	3	tr			
G	21	0.71	594	4	tr	tr		
H	71	1.08	216	5	9	5		8
Pd catalysts								
J	138	1.36	349	8	31	23		4
K	126	1.25	332	9	34	24		11

[a] Blank entries means the structure was not detected. [b] δ^+ is defined above, resonances at about 29.75 ppm; detection limit is about 10. [c] δ^+/γ is defined above, γ resonance at 30.15 ppm. [d] Total Me is the total methyls per 1000 CH_2. [e] Bu^+ is the butyl or longer branches and 2-EOC (end of chain) per 1000 CH_2. [f] *i*-Bu is the isobutyl type branch structures. [g] $2MeH^+$ are the branches that end in isopropyl groups and have at least 3 methylenes between methines. We believe these are predominantly 2-methylhexyl$^+$. [h] Et are the ethyl branches. [i] Hex^+ are the hexyl and longer, 3-EOC. [j] tr indicates that only trace levels were detected.

structure can arise from multiple 1,2-insertions from a methyl branch. Also observed are connected resonances that can be attributed to a 2-methylhexyl branch **11**: D′, E′, F′, T′, U′, V′, W′. The T′ to U′ correlation is absent, probably because these two resonances have very similar chemical shifts. The conditions of our 2D INADEQUATE experiment result in a distortion and weakening of the correlation as the difference between the chemical shift of the two signals approaches or becomes less than the *j* value of the carbon—carbon through bond coupling.[42] The U′, V′, W′ correlations also can arise from long amyl$^+$ branches and from four or more methylenes in the backbone adjacent to a propyl$^+$ branch, which can be terminated in either a straight chain or isopropyl end. Because there are relatively few propyl$^+$ branches in these samples, it seems most likely that these correlations are primarily from the 2-methylhexyl$^+$ branches. At lower contour levels a correlation from a $1B_4^+$ carbon is observed. The correlation to $2B_4^+$ is missing, but from the symmetry of the 2D INADEQUATE, it can be shown that this correlation would be to the chemical shift of $2B_4$ and not to $2B_5^+$. This confirms the presence of *n*-butyl branches in this polymer and also indicates that amyl groups are much less common, if they occur at all. This is further supported by the observation of a CH_2 at the $2B_4$ position in the methylene-only spectral-edited DEPT spectrum for this polymer. Also observed in the 2D INADEQUATE are correlations indicating methyl branches separated by single methylenes and also by runs of only four methylenes as in **13**. Finally, isolated methyls flanked by longer runs of methylenes, and methylene runs of at least seven carbons are observed. These structures are indicated in structure **14**.

Having assigned the spectra, it is then possible to quantify the relative abundance of the various structural features. The values for the number of these branch and backbone sequence structures per 1000 methylenes are given in Table 2.

Discussion

Mechanistic Explanation. The unusual structures we see in polypropylenes made with Pd versions of these new α-diimine catalysts can be explained by several "rules" of polymerization:

(i) Both 1,2- and 2,1-addition can occur. (The first number refers to the monomer position that the catalyst attaches to, and the second number refers to the position of attachment of the growing polymer chain.)

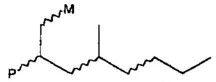
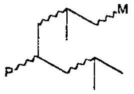
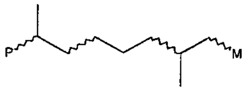
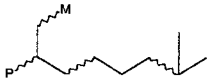
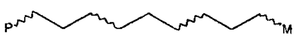
(ii) The catalyst can "walk" backward along the polymer or forward along the newly added monomer; this chain walking occurs faster than monomer addition.

(iii) Insertion of the next monomer can only occur from a primary carbon; thus, 2,1-insertions which leave the palladium at a secondary carbon atom are necessarily followed by an isomerization before the next insertion.

Thus, for example, 1,3-enchainment or "chain straightening" occurs via 2,1-addition and catalyst walking to the end of the monomer; the percentage of monomers undergoing straightening ranges from 9 to 55%. Catalyst walking occurs by repeated β-hydride elimination and addition. The catalyst can walk "past" a methine position but not past a quaternary carbon. Butyl and hexyl$^+$ branches occur if the catalyst walks backward along the polymer until it locates a primary carbon (methyl branch) from which to insert. Methyl branches are formed via 1,2-insertion and then direct addition of the next monomer. It is possible that the catalyst may walk to the other end (methyl group) of the monomer, but this isomerization is degenerate; there is no observable difference between a 1,2-insertion and a 3,2-insertion. Many of the different structures that could occur in propylene dyads or triads by following these rules are shown in Table 3. From the 2D INADEQUATE, we have identified groups of connected carbons that belong to all of these structures, with the exception of the 5-methylhexyl(+) branch, whose resonances cannot be distinguished from others in our spectra. This is not to say that this branch does not occur in the polymers—quite the contrary—we expect it to be present but are simply unable to assign unique resonances. Equally important to note is that there are no resonances present in Pd-catalyzed polymers which cannot be explained by structures generated with these rules.

Support for 1,2-Insertion as the Predominant Mode. It is reasonable that Pd catalysts polymerize polypropylene by both 1,2- and 2,1-insertion, and chain straightening occurs with each 2,1-insertion based on the following analysis. The isobutyl and 5-methylhexyl (2MeH) branches can only be explained if the terminal polypropylene unit on the branch is inserted in a 1,2-fashion from a methyl branch. An approximate analysis of the percentage of 2,1-insertions implied by the types of branches agrees very well with the percentage of chain straightening for the polypropylenes made with Pd polymers as follows. Isobutyl branches imply a single 1,2-insertion. $2MeH^+$ branches imply one 1,2- and one

Table 3. Selected Structures Possible from PP Triads in Pd-Catalyzed Polymers Starting from the Unit, P∿M

Structure	Mechanistic Sequence[a]	Observed Defining Structure
	(1,2) (1,2) (1,2)	'traditional' polypropylene
	(1,2) (1,2) (1,2) I	Isobutyl branch
	(1,2) (1,2) (1,2) I	2,4-Dimethylpentyl
	(1,2) (1,2) (2,2)	methyl branches/linear polymer junction
	(1,2) (1,2) (2,1) I	n-Butyl branch
	(1,2) (1,2) (2,1) I	5-methylhexyl
	(1,2) (1,2) I (1,2)	Isobutyl branch
	(1,2) (1,2) I (2,1)	Isobutyl branch
	(1,2) (2,1) (1,2)	4 Methylenes
	(1,2) (2,1) (1,2) I	2-Methylhexyl
	(1,2) (2,1) I (1,2)	n-Butyl branch
	(1,2) (2,1) (2,1)	7 or more methylenes
	(1,2) (2,1) I (2,1)	n-Butyl branch
	(2,1) (1,2) (1,2)	methyl branches/linear junction
	(2,1) (1,2) (1,2) I	Isobutyl branch
	(2,1) (1,2) (2,1)	Isolated methyl branch
	(2,1) (1,2) (2,1) I	n-Butyl branch
	(2,1) (2,1) (1,2)	
	(2,1) (2,1) (2,1)	7 or more methylenes

[a] P is terminal methylene of the polymer chain. M is the metal center of the catalyst. Insertions are indicated by (1,2) and (2,1), and it is assumed that there is an isomerization after each 2,1-insertion to give a chain-straightened 1,3-insertion. Other isomerizations are indicated by I.

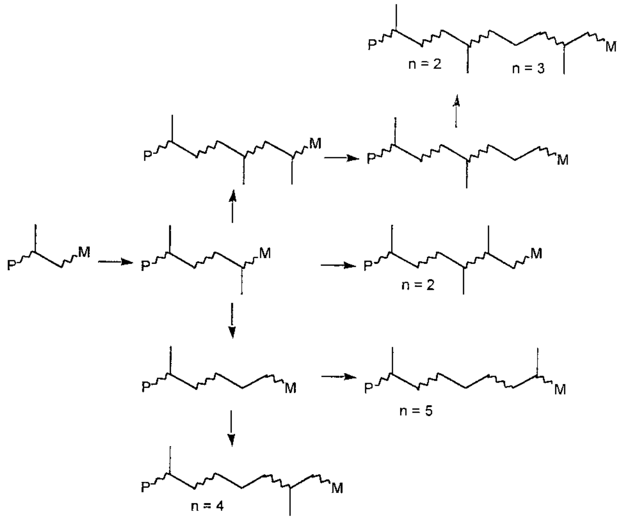


Figure 4. Route to the $-(\mathrm{CH_2})_n-$ segments available in nickel-catalyzed polymerizations.

2,1-insertion, assuming these are all 2MeH and not longer. Assuming

$$\mathrm{Bu} = \mathrm{Bu}^{+} - \mathrm{Hex}^{+} \tag{2}$$

Bu branches are from a single 2,1-insertion. Assume Hex$^+$ are mostly heptyl branches from two 2,1-insertions. Then, for polymer J (Figure 2b)

$$1{,}2 = 31\ (\text{i-Bu}) + 23\ (\text{2MeH}) = 54 \tag{3}$$

$$2{,}1 = 4 \times 2\ (\text{Heptyl}) + 4\ (\text{Bu}) + 23\ (\text{2MeH}) = 35 \tag{4}$$

$$\%\ 2{,}1 \text{ in branches: } 39\% \tag{5}$$

$$\%\ \text{overall 1,3-enchainment: } 31\% \ (\text{calculated from } \mathrm{CH_2/CH_3} \text{ ratio}) \tag{6}$$

This supports our theory that all 2,1-insertions with Pd catalysts in these polypropylene polymers lead to chain straightening. This analysis assumes that the probability of 2,1-insertion does not depend on the previous insertion/straightening.

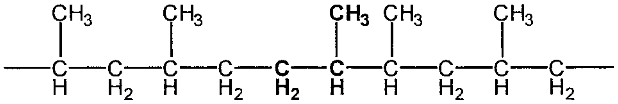
Insertion at a Secondary Carbon and 1,2- vs 2,1-Insertions with Ni Catalysts. Little, if any, insertion from secondary carbons is occurring in the polypropylenes made from Pd catalysts studied to date based on the following three observations: (a) The incidence of ethyl and propyl branches is low (almost undetectable). (b) The majority of resonances in the spectra can be readily assigned without invoking insertion from secondary carbons. (c) We see no sign of adjacent methyl branches, which would give resonances in the 14–20 ppm region. However, with Ni catalysts, insertion from secondary carbons is observed. The possibility of insertion from secondary carbons greatly increases the complexity of possible microstructures in these polypropylenes. In Ni-catalyzed polypropylenes, we observe most of the ^{13}C observable numbers of adjacent methylenes in the backbone, $(\mathrm{CH_2})_n$ where $n = 0, 1, 2, 3, 4, 5^+, 6^+$, and 7^+, as indicated in Figure 2a. When insertion from a secondary carbon is allowed, in addition to the rules 1 and 2 above (1,2- and 2,1-insertions, chain walking), all of these can be mechanistically explained. Figure 4 shows schematically the production of these different lengths of methylenes.

We can do the same branch analysis for a Ni-catalyzed polymer that we did for a Pd-catalyzed polymer (above). However, in this case, the calculation is less reliable because the number of branches is much lower, long runs of chain straightening are more common, and insertion from a secondary methylene means that the branches may not occur entirely at the end of a chain. For example, in polymer F, the branch analysis gives 56% 2,1- and the 2,1-estimate from chain straightening and inversions is 53%, which is excellent agreement considering the major assumptions that were made.

It should be mentioned that the NMR spectra of polypropylenes made with Ni catalysts can be interpreted in two opposite ways: (1) Adjacent insertions are 2,1-insertions; some 2,1-insertions give chain straightening; occasional isolated 1,2-insertions give tail to tail adjacent methyl branches. (2) Adjacent insertions are 1,2-insertions; 2,1-insertions often give chain straightening; 2,1-insertions without chain straightening are isolated. We prefer the second interpretation and proceed assuming it is correct; it is consistent with the Pd results and is in line with results obtained by others with ^{13}C-labeled end groups in these same Ni-catalyzed polypropylenes.[38]

Regioirregularity. Although resonances from adjacent methyls in tail-to-tail structures are not seen in Pd-catalyzed polymers, we do see these resonances in the 14−20 ppm region in the polypropylenes made from Ni catalysts. We assign the resonances from 14 to 16 ppm and from 16 to 18 ppm to P$\alpha\beta$, P$\alpha\gamma$ with *r* and *m* stereochemistry, respectively.[18] The percentage of these adjacent methyls vs total methyl branches for various polymers are listed in Table 1 and range from about 8−27% of the total methyls. For polymer A, the summed stereochemical relationships of these regioirregular adjacent methyls are 45% *m*, 55% *r*.

Head-to-head placements give rise to two adjacent methylenes flanked by methyl branches, RCH(CH$_3$)(CH$_2$)$_n$CH(CH$_3$)R. There are definitely resonances arising in the $n = 2$ region of the spectrum for polypropylene made from Ni-based catalysts, as shown in Figure 2a. Several detailed studies of these types of defects in polypropylene using a wide variety of model compounds have been reported.[14,18,43−45] By comparison of our spectra with the spectra of these authors, it appears that the inverted monomers are isolated inversions as shown in **15**, with no strongly preferred stereochemistry.

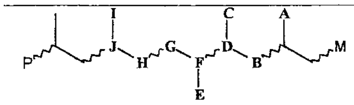
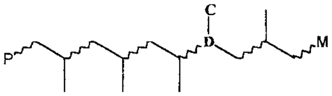
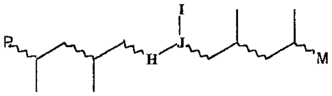
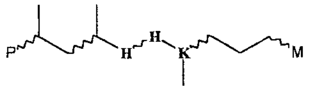


15

Table 4 shows several possible arrangements of monomers in our systems. The Arabic labels on the carbons correspond to those in Figure 2a. For this polymer, and also for polymer A, the relative amounts of peaks (D + H), K, and L are such that we can estimate the relative frequencies of the five structures as indicated in Table 4. The amount of 2,1-insertion can be estimated to be the amount of chain straightening, plus half of the amount of tail-to-tail methyls, plus the amount of the structures involving methine K. This estimate should be good as long as the 2,1-inversions without chain walking are isolated and as long as isobutyl, 2-methylhexyl$^+$, and butyl$^+$ branches are at low levels.

One can consider many of the polypropylenes made with Ni-based catalysts (especially those with lower levels of chain straightening, indicating limited chain walking) to be the copolymerization of three monomers, giving the structural units in the polymer that are indicated together with their derivation in Table 4.

Table 4. Additional Structures Possible from Nickel-Catalyzed Propylene Insertions into P$\sim$M and Their Relative Abundance and Their Spectral Assignments

Structure	Mechanistic Sequence[a]	Obs? (Relative Intensity)
	(1,2) (1,2) (2,1*) (1,2) (1,2)	Yes 2
	(2,1*) (2,1*) (2,1*) (1,2) (1,2)	No 0
	(1,2) (1,2) (2,1*) (2,1*) (2,1*)	Little to none <0.05
	(1,2) (1,2) (2,1*) (2,1)	Yes 1
	(1,2) (1,2) (2,1) (2,1)	Yes 4

[a] P is the terminal methylene of the polymer chain. M is the metal center of the catalyst. Insertions are indicated by (1,2) or (2,1). It is assumed that there is an isomerization after each 2,1-insertion to give a chain-straightened 1,3-insertion unless indicated by (2,1*) where the next insertion takes place at a secondary center.

Tacticity. If a polymerization proceeds by chain end control, the tacticity follows Bernoullian statistics.[16] The defects will be isolated, for example:

$$m\ m\ m\ m\ m\ m\ m\ m\ m\ m\ m\ \mathbf{r}\ m\ m\ m\ m\ m\ m\ m \tag{7}$$

One can test for Bernoullian statistical behavior by comparing the tacticity distribution of dyads, triads, tetrads, etc., and ascertaining whether they follow the following (and higher-order) equations:

$$mm = m^2 \tag{8}$$

$$mr = 2m(1 - m) \tag{9}$$

$$rr = (1 - m)^2 = r^2 \tag{10}$$

When a polymerization proceeds by chain end control, that means that the tacticity of the system is controlled by the stereochemistry of the terminal unit.

When a polymerization proceeds by enantiomorphic site control, the catalyst structure is controlling the stereochemistry of addition, and the statistics relating the stereochemical structures are quite different. If a polymerization proceeds by enantiomorphic site control, then the defect structures consist of pairs of dyads:

$$m\ m\ m\ m\ m\ m\ m\ m\ m\ m\ m\ \mathbf{r}\ \mathbf{r}\ m\ m\ m\ m\ m\ m\ m \tag{11}$$

The statistics that describe this case have been discussed in the literature.[6] In general, for an isotactic polymer, NMR resonances arising from sequences in-

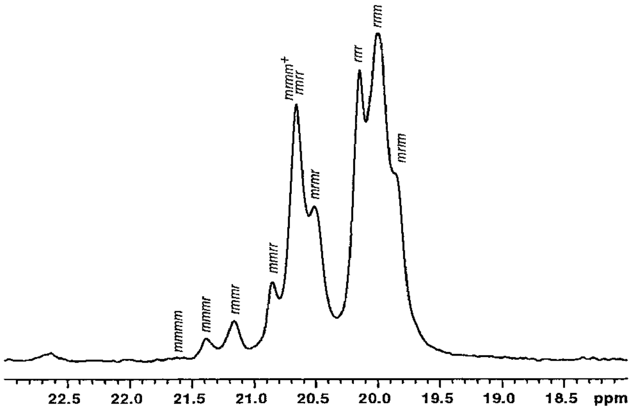


Figure 5. Expansion of the methyl region of ^{13}C spectrum of polypropylene B.

volving adjacent *r* groups, such as *mrrm* and *mmrr* will be more prevalent if the polymerization is site controlled.

It is difficult to accurately measure the tacticity in these α-diimine late metal-catalyzed systems, as the pseudo "EPE", "EPP" methyl resonances arising from a chain straightened PP adjacent to a PP dyad overlap the *mr* and *rr* methyl resonances arising from tacticity effects in PPP triads. However, a rough idea of the tacticity in a Pd-catalyzed polypropylene has been obtained by studying the methyl region of the polypropylene polymer J. We have subtracted out area in the *mr* and *rr* regions to account for the "EPP*m*" and "EPP*r*" type resonances that arise due to propylene monomer chain straightening. The amount of area subtracted in each region was adjusted until a self-consistent solution was obtained which gives the same % *r* for PPP and EPP sequences. For this Pd-catalyzed polymer, the % *r* is about 0.6 and the relative ratios of *mm*, *mr*, and *rr* are consistent with a chain end control mechanism, although, again, this is a very approximate determination.

In Ni-catalyzed polypropylenes, a better value for the tacticity can be gained by looking at a polymer with a very low level of 1,3 enchainment. From the methyl resonances for polypropylene A (Ni catalyst, 9% 1,3-enchainment, no correction applied for EPP sequences), one can identify three resonance groups which correspond to *mm*, *mr*, and *rr* PP triads (see Figure 5). This polymer is predominantly syndiotactic (*rr*: 64%; *mr*: 32%; *mm:* 3.5%). These triad intensities are consistent with a Bernoullian chain end control mechanism and not with an enantiomorphic site control mechanism,

$$r = rr + 0.5mr = 80\% \qquad (12)$$

$$(\mathrm{P}r)^2 = 0.64 \qquad (13)$$

exactly in agreement with the observed *rr* of 64%, as expected for Bernoullian statistics and chain end control.

Polypropylenes made with one of these α-diimine late metal catalysts have a higher percentage of syndiotactic arrangements, *rr* (to about 80%), when the polymerization is carried out at low temperatures.[37] Pentad analysis also indicates that the polymerization is "chain end controlled" (*rrmr*:*rrrm* is 1:1); the polymer consists mainly of blocks of *r* dyads separated by isolated (not pairs) of *m* dyads. An expansion of the methyl region of polymer B (11% chain straightening, 8% adjacent methyls) is shown in Figure 5. The *rr* triad region contains overlaps from "EPP*r*" type resonances, and the *mr* triad contains a much lower level of overlaps from the "EPP*m*"-type triads. It is clear that the polymer is predominantly syndiotactic. Triad analysis of these signals gives a very good match to Bernoullian statistics, indicating chain end control. There are some deviations at the pentad level, which may be due to the poor peak resolution, uncertainties due to "EPP"-type overlaps, or to a Markovian mechanism. It is hard to fit a pentad analysis to a site control mechanism, because in a site control mechanism for syndiotactic polymerization, an insertion error leads to the structure *rrrrrmmrrrrr* with two *meso* insertions. However, another type of error in these catalysts is the "missed insertion" whereby the metal center switches from one chirality to the other without an olefin insertion occurring.[12] This type of error gives the structure *rrrrmrrrr* with an isolated *meso* insertion. This type of error is the same error that occurs in chain-end-control, syndiotactic polymerization. Both types of errors seem to occur in site-controlled syndiotactic polypropylene polymerizations.

Effect of Catalyst Structure and Polymerization Conditions on Polymer Microstructure. The microstructures of polypropylenes made with the Pd catalysts can be entirely understood from the rules of polymerization detailed above. The Pd catalysts produce predominantly syndiotactic polymer by primarily 1,2-insertions with chain end control. 2,1-Insertions always lead to 1,3-enchainment. Chain walking occurs commonly, with insertion of monomer only into primary carbon atoms. Polymerizations with the Ni-based catalysts that exhibit a low level of chain walking appear also to occur via 1,2-insertion predominantly, giving predominantly syndiotactic placements. With a Ni catalyst, when a 2,1-insertion occurs, about 57% of the time it undergoes chain straightening; the rest of the time insertion of the next monomer occurs from the secondary carbon. If chain straightening does not occur, the following monomer after the 2,1-insertion will be 66% 1,2-insertion and 33% 2,1-chain-straightened. Adjacent 2,1-insertions without chain straightening are infrequent.

From the comparisons in Tables 1−3, we can make the following observations regarding the effect of catalyst and polymerization conditions on the polymer microstructure:

1. All of the Pd catalysts used in this study had the same α-diimine ligand but different counterions and initiating groups. All of the Pd-catalyzed polypropylenes had similar structures. Therefore, the counterion and initiating group had little effect on the polypropylene backbone structure, as expected.

2. Catalysts with more steric bulk, that is, with more or larger substituents in the ortho position of the aromatic ring, give less chain straightening. This probably supports the theory that chain straightening arises from 2,1-insertion. A monomer oriented for 2,1-insertion probably has more steric interference with the ligand. Thus, 2,1-insertion and chain straightening both decrease with increasing steric bulk.

3. Less chain straightening is observed at lower polymerization temperatures. This may arise from a variety of effects, including activation energy of chain walking, steric constraints, solution viscosity, etc.

Conclusions

The microstructures of polypropylenes are among the most varied of any polymer system. They have been studied extensively by ^{13}C NMR and give a wealth of insight into the behavior of various polypropylene catalysts. Structural variations and issues include tacticity, monomer inversion, tacticity of monomer inversion, statistical frequency of inversions (paired or isolated), type of tacticity defects indicating chain end or site control, end group structures, type of catalyst insertion, and 1,3-enchainment.

The polypropylenes made with the α-diimine late metal catalysts show all of these features. In addition, these new polypropylenes show additional features not seen in any known polypropylenes, including long branches, branches on branches, isobutyl branches, intermediate and highly variable levels of 1,3-enchainment, and runs of methylenes in the backbone of many different well-defined lengths. These features vary with the type of catalyst used and with the polymerization conditions.

We have been able to explain all of these structural variations in Pd-catalyzed polypropylenes using three rules of catalyst behavior: (a) the polymerization goes by both 1,2-and 2,1-insertion; (b) catalyst chain walking occurs faster than monomer addition; and (c) insertion occurs only from primary carbons.

The Ni-catalyzed polymers appear to be predominantly syndiotactic with chain end control, and this is most likely also for the Pd-catalyzed polymers, though the evidence is not as strong in the latter case. This combination of 1,2-insertion, syndiotactic, and chain end control has never before been observed in a polypropylene polymerization with any other catalyst and has also been observed by other workers with these late metal catalysts.[38] In Ni-catalyzed systems, insertion can occur from secondary carbons as well as from primary carbons. The polypropylenes made with Ni catalysts have widely varying structures depending on the exact polymerization conditions. There are two alternate ways in which the Ni data can be interpreted. For Ni-based systems with low levels of chain straightening (1,3-incorporation), one interpretation is that the polymerization proceeds primarily by 1,2-insertion, and inverted, or 2,1-insertions, tend to be isolated between 1,2-inserted monomers or incorporated in a 1,3-fashion. A few catalysts give more than 50% 2,1-insertion with a similarly high level of chain straightening. In cases where tacticity can be estimated, the polypropylenes made with both metals appear to have about 60−80% syndiotactic diads (*r*) with polymerization proceeding via chain end control.

Acknowledgment. The technical assistance of Carole Urbston, Michael Halfhill, Anju Parthasarathy, Keith Raffell, and Kathy Murschel is gratefully acknowledged. Thanks go to Jeff Sweetman for preparing several catalysts. Acknowledgment is made to the National Science Foundation (CHE-9710380) for partial support of this work.

References and Notes

(1) See, for instance: (a) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169−1204. (b) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 428. (c) Johnson, L. K.; Killian, C. M. In *Metallocene-Based Polyolefins, Preparation, Properties and Technology*; Scheirs, J., Kaminsky, W., Eds.; Wiley: West Sussex, England, 2000; p 233. (d) Ittel, S. D. In *Metalorganic Catalysts for Synthesis and Polymerization*; Kaminsky, W., Ed.; Springer-Verlag: Heidelberg, 1999; p 616.
(2) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414.
(3) Johnson, L. K.; Killian, C. M.; Arthur, S. D.; Feldman, J.; McCord, E. F.; McLain, S. J.; Kreutzer, K. A.; Bennett, A. M. A.; Coughlin, E. B.; Ittel, S. D.; Parathasarathy, A.; Tempel, D. J.; Brookhart, M. S. Pat. Appl. WO 9623010 to DuPont, Aug 1, 1996.
(4) See for instance: Razavi, A.; Atwood, J. L. *J. Organomet. Chem.* **1995**, *497* (1−2), 105−11, or Dolle, V.; Rohrmann, J.; Winter, A.; Antberg, M.; Klein, R. Eur. Pat. Appl., EP 399347 to Hoechst A.-G, Priority date Nov 28, 1990, for examples of isotactic/syndiotactic block polymers. See: Ewen, J. A. Eur. Pat. Appl., EP 423101 to Fina Technology, Priority date April 17, 1991, for examples of hemi-isotactic polymers.
(5) (a) Natta, G.; Pino, P.; Massanti, G.; Natta, G.; Pino, P.; Massanti, G. Ital. Pat. 535,712 to Montacatini, 1954. (b) Natta, G. *J. Am. Chem. Soc.* **1955**, *77*, 1708.
(6) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355.
(7) For a review, see: Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.
(8) See for instance: Rieger, B.; Reinmuth, A.; Roell, W.; Brintzinger, H. H. *J. Mol. Catal.* **1993**, *82*, 67−73.
(9) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255−6256.
(10) Zambelli, A.; Locatelli, P.; Provasoli, A.; Ferro, D. R. *Macromolecules* **1980**, *13*, 267.
(11) Zambelli, A.; Locatelli, P.; Zannoni, G.; Bovey, F. A. *Macromolecules* **1978**, *11*, 923.
(12) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355−64.
(13) Spaleck, W.; Anthberg, M.; Aulbach, M.; Bachmann, B.; Dolle, V.; Haftka, S.; Keuber, F.; Rohrmann, J.; Winter, A. In *Ziegler Catalysts;* Fink, G., Mulhaupt, R., Brintzinger, H. H., Eds.; Springer-Verlag: Heidelberg, 1995; pp 83−97.
(14) Zambelli, A.; Bajo, G.; Rigamonti, E. *Makromol. Chem.* **1978**, *179*, 1249.
(15) (a) Kravchenko, R.; Masood, A.; Waymouth, R. M.; Myers, C. L. *J. Am. Chem. Soc.* **1998**, *120*, 2039−2046. (b) Bruce, M. D.; Coates, G. W.; Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 11174−11182. (c) Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 11586−7.
(16) Bovey, F. A.; Tiens, G. V. D. *J. Polym. Sci.* **1960**, *44*, 173.
(17) Sheldon, R. A.; Fueno, T.; Tsunetsuga, T.; Furukawa, J. *J. Polym. Sci., Part A: Polym. Chem.* **1965**, *3*, 23.
(18) Asakura, T.; Nakayama, N.; Demura, M.; Asano, A. *Macromolecules* **1992**, *25*, 4876.
(19) Schilling, F. C.; Tonelli, A. E. *Macromolecules* **1980**, *13*, 270.
(20) Randall, J. C. *Polymer Sequence Determination: Carbon-13 NMR Method*; Academic Press: New York, 1978.
(21) Zambelli, A.; Locatelli, P.; Bajo, G.; Bovey, F. A. *Macromolecules* **1975**, *8*, 687.
(22) Tritto, I.; Fan, Z. Q.; Locatelli, P.; Sacchi, M. C.; Camurati, I.; Galimberti, M. *Macromolecules* **1995**, *28*, 3342.
(23) Cheng, H. N.; Smith, D. A. *Macromolecules* **1986**, *19*, 2065.
(24) Cheng, H. N. *Macromolecules* **1984**, *17*, 1950.
(25) Doi, Y. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 293.
(26) Wolfsgruber, C.; Zannoni, G.; Rigamonti, E.; Zambelli, A. *Makromol. Chem.* **1975**, *176*, 2765.
(27) Dahlmann, M.; Erker, G.; Nissinen, M.; Froehlich, R. *J. Am. Chem. Soc.* **1999**, *121*, 2820−2828.
(28) Zambelli, A.; Locatelli, P.; Rigamonti, E. *Macromolecules* **1979**, *12*, 156.
(29) Grassi, A.; Zambelli, A.; Resconi, L.; Albizzati, E.; Mazzocchi, R. *Macromolecules* **1988**, *21*, 617.
(30) Busico, V.; Cipullo, R. *Macromol. Symp.* **1995**, *89*, 277.
(31) Dolle, V.; Rohrmann, J.; Winter, A.; Antberg, M.; Klein, R. German Patent Appl. DE 3826075 to Hoechst Aktiengesellischraft, Feb 1, 1990.
(32) Yuguchi, S.; Iwamoto, M. *Polym. Lett.* **1964**, *2*, 1035.
(33) Ketley, A. D.; Braatz, J. A. *Polym. Lett.* **1968**, *6*, 341.
(34) Busico, V.; Cipullo, R.; Monaco, G.; Vacatello, M. S.; Anna, L. *Macromolecules* **1997**, *30*, 6251.
(35) Soga, K.; Shiono, T.; Takemura, S.; Kaminsky, W. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 305.
(36) Svejda, S. A.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1999**, *121*, 10634.
(37) Pellecchia, C.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1996**, *17*, 333.

(38) Pellecchia, C.; Zambelli, A.; Olivia, L.; Pappalardo, D. *Macromolecules* **1996**, *29*, 6990.

(39) Pellecchia, C.; Zambelli, A.; Mazzeo, M.; Pappalardo, D. *J. Mol. Catal. A: Chem.* **1998**, *128*, 229.

(40) Hayashi, T.; Inoue, Y.; Chujo, R.; Asakura, T. *Polym. J.* **1988**, *20*, 895.

(41) Hikichi, K.; Hiraoki, T.; Ikura, M.; Higuchi, K.; Eguchi, K.; Ohuchi, M. *Polym. J.* **1987**, *19*, 1317.

(42) Bax, A.; Freeman, R. *J. Magn. Reson.* **1980**, *41*, 507.

(43) Cheng, H. N.; Ewen, J. A. *Makromol. Chem.* **1989**, *190*, 1931.

(44) Asakura, T.; Nishiyama, Y.; Doi, Y. *Macromolecules* **1987**, *20*, 616.

(45) Cheng, H. N. *Polym. Bull. (Berlin)* **1985**, *14*, 347.

MA0012898