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Ethylene Oligomerization and Chain Growth Mechanisms with Ziegler–Natta Catalysts

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ABSTRACT: This article presents GC data on oligomers formed in ethylene homopolymerization and copolymerization reactions with several α-olefins (1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene) using Ti- and V-based catalysts. Structural analysis of the oligomers provided a detailed confirmation of the chemical mechanism of chain formation in olefin polymerization with Ziegler–Natta catalysts. The mechanism includes chain initiation (monomer insertion into M–C or M–H bonds), chain growth (predominantly head-to-tail olefin insertion), and chain termination with hydrogen, monomer, and an organoaluminum compound. The oligomer analysis affords information on chain structures of individual molecules and complements earlier spectroscopic data on the chemical structures of olefin copolymers. A previously unknown deviation from the standard chain growth mechanism was discovered in the case of ethylene homopolymerization with a V-based catalyst: chain isomerization with predominant formation of 5-methyl-branched isoalkanes. A mechanism of the chain isomerization involving σ-bond metathesis at an active center is proposed.

The molecular mass distributions of olefin polymers produced with heterogeneous Ziegler–Natta catalysts vary from relatively narrow to quite broad: the $\bar{M}_w/\bar{M}_n$ ratios range from 3–5 for the polymers prepared with Ti-based catalysts to 8–10 for the polymers prepared with V-based catalysts. When such polymers have a medium-to-low molecular mass ($\bar{M}_w < 100\,000$), they should have measurable fractions of low molecular mass components with $\bar{M}_n$ in the 300–600 range. These polymer fractions are soluble in aliphatic hydrocarbons and can be classified as oligomers.

This article describes the structures of the low molecular mass fractions (soluble in the reaction medium) of several ethylene homopolymers and ethylene/α-olefin copolymers prepared with V- and Ti-based catalysts. GC analysis showed that these fractions contain olefin oligomers in the C_4–C_{40+} range. Absolute oligomer yields are quite low, usually 0.1–0.5% of the total polymer yields, and rarely exceed 1.0%.

The analysis of the oligomer structures gives some insights into the chemical mechanisms of the chain initiation, growth, and termination reactions with heterogeneous Ziegler–Natta catalysts. Previously, such analysis was based exclusively on IR and NMR spectroscopic studies of polyolefins and olefin copolymers.[1–4] Due to the nature of the spectroscopic methods, they provide averaged information on the chemical structure of polyolefin chains and their end groups. In contrast, the GC technique allows examination of the chemical structures of individual polymer molecules, albeit only of those with the lowest molecular mass. GPC analysis of ethylene polymers indicates that several populations of active centers are present in transition-metal catalysts.[5] The centers differ in the ratio of chain termination and chain propagation reactions. We assume that the centers that produce polymer chains with the lowest molecular mass are also responsible for the formation of oligomers. The only difference between oligomer and polymer molecules is that the former are generated when a termination reaction occurs very early in the process of polymer chain growth.

This article consists of two sections. In the first section, the data are presented which can be explained by the current chemical mechanism of polymer chain formation with Ziegler–Natta catalysts. The second section describes chain isomerization reactions which occur in ethylene homopolymerization with a V-based catalyst. These reactions cannot be reduced to the standard chain growth scheme, and a special mechanism is proposed to account for them.

Experimental Section

The polymerization reactions were carried out at 80–90 °C in hexane slurry. Experimental details were given earlier.[5,6] Both ethylene homopolymerization reactions and ethylene copolymerizations with 1-butene, 1-pentene, 1-hexene, and 4-methyl-1-pentene were examined, as well as homopolymerization reactions of 1-pentene and 1-hexene.

Two supported catalysts were used. The Ti-based catalyst[7] was prepared by dissolving a mixture of dry $MgCl_2$ and $TiCl_3\cdot 0.33AlCl_3$ (Mg:Ti = 3) in THF, contacting the solution with silica, and removing the solvent. The catalyst contains ca. 1.0 wt % of Ti. The V-based catalyst[8] was prepared by reacting silica slurry in heptane sequentially with $AlEt_3$, a mixture of $VOCl_3$ and $TiCl_4$ ([V]:[Ti] = 5.0), and, finally, THF. The catalyst contains ca. 4.0 wt % of V and ca. 2.0 wt % of Al. $AlMe_3$, $AlEt_3$, $Al(n\text{-}Pr)_3$, and $Al(i\text{-}Bu)_3$ were used as cocatalysts. The V-based catalyst requires the use of a chloro-containing activator, chloroform or trichloroethane.

Liquid samples which contained solvent, a comonomer, and dissolved oligomers were taken at room temperature from a reactor. The samples were analyzed by a GC method on a Hewlett-Packard 5880A gas chromatograph equipped with a flame ionization detector. The chromatograph operated in the splitless mode, with a 0.75-mm, 60-m SPB-1 glass capillary column and used He as a carrier gas. The temperature program was 0 °C for 15 min with a subsequent temperature increase at a rate of 2 °C/min. Peak assignments were carried out using previously published data on the GC analysis of ethylene/α-olefin cooligomers prepared with a Ni-based catalyst.[9–11]

Results and Discussion

Standard Polymerization Mechanism. The V-based catalyst produces ethylene polymers with a relatively broad MMD: the $\bar{M}_w/\bar{M}_n$ ratios are in the 8–10 range. As a result, significant quantities of oligomers, from 0.3 to 1.0% with respect to the polymer yield, are formed in the polymerization reactions even at relatively low hydrogen/ethylene partial pressure ratios (P_H/P_E = 0.3–0.5). This catalyst was used in most experiments.

Ethylene Homopolymerization. A series of ethylene homopolymers was produced with the V-based catalyst in combination with $AlMe_3$, $AlEt_3$, $Al(n\text{-}Pr)_3$, and $Al(i\text{-}Bu)_3$

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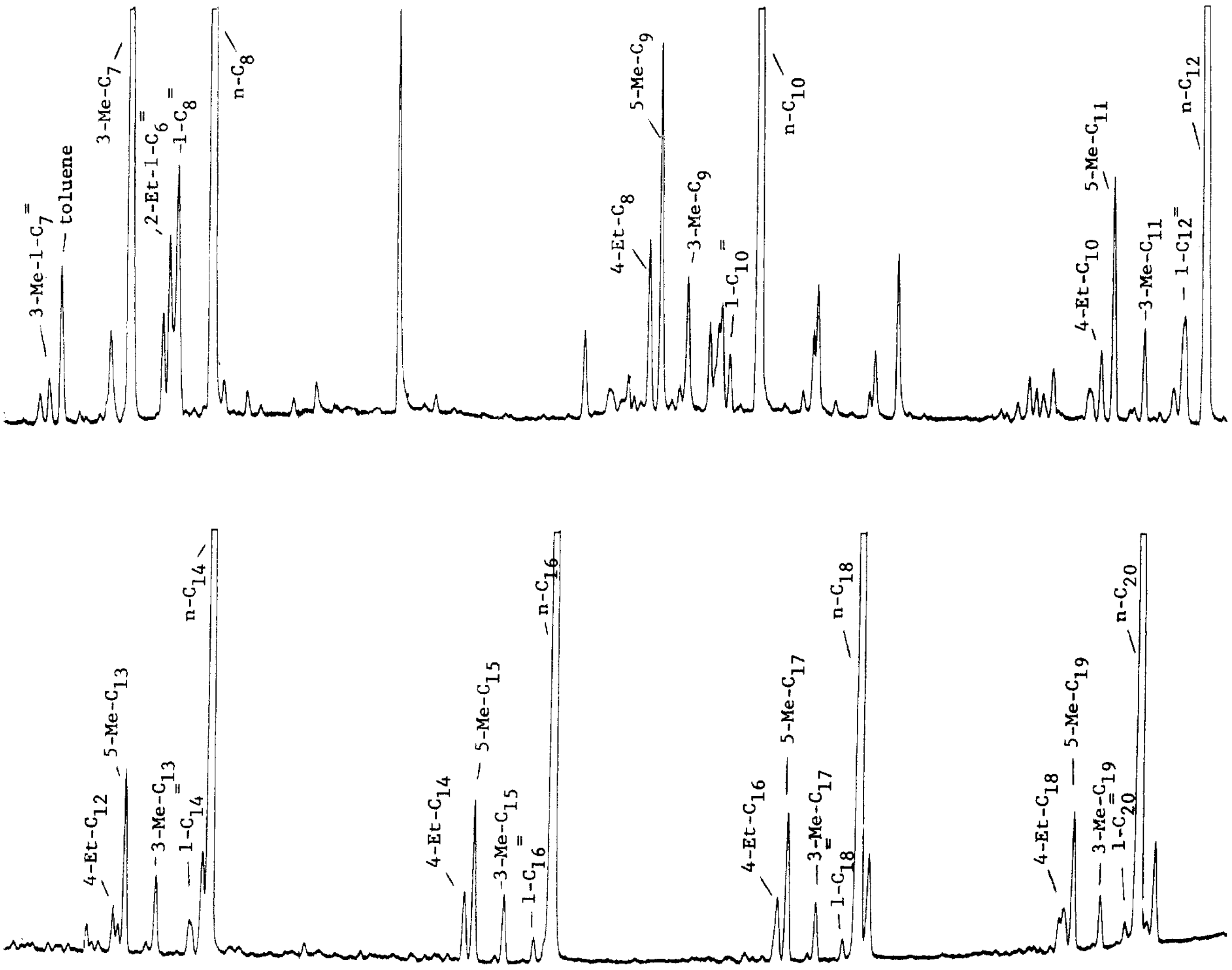


Figure 1. Gas chromatogram of ethylene hompolymer prepared with V-based catalyst activated with $AlEt_3$.

at 90 °C at a P_H/P_E ratio of 0.4. Figure 1 shows the gas chromatogram of the lightest oligomeric products (the C_8–C_{20} range) formed with $AlEt_3$. The major components in this fraction, as well as in the oligomers prepared with all other cocatalysts, are n-alkanes and α-olefins with even carbon numbers. Formation of all these compounds can be readily attributed to the simple set of chain initiation, growth, and propagation reactions shown in Scheme I. This mechanism of olefin polymerization reactions was proposed by Natta soon after the discovery of coordination polymerization catalysts (reviewed in ref 12), and it has held extremely well over nearly 40 years. Our data show that, with the exception of several deviations discussed in the last section of the paper, this mechanism correctly predicts the structural features of individual polyolefin molecules. In particular, the presence of n-alkanes with even carbon numbers irrespective of the cocatalyst type indicates that most oligomer molecules are formed via M–H species which are generated in a chain termination reaction with H_2 (reaction 7). Another argument supporting this conclusion is the fact that ethylene homooligomers are formed in measurable amounts only in the presence of H_2.

Several additional compounds are present in the oligomers generated with $AlMe_3$, $Al(n\text{-}Pr)_3$, and $Al(i\text{-}Bu)_3$ instead of $AlEt_3$. Formation of these products can be explained by the reaction with an organoaluminum compound (reaction 8). Ethylene insertion into the M–R groups formed in reaction 8 should produce alkanes $R\text{–}(CH_2CH_2)_m\text{–}H$ with R = CH_3 in the case of $AlMe_3$, R = $n\text{-}C_3H_7$ in the case of $Al(n\text{-}Pr)_3$, and R = $i\text{-}C_4H_9$ in the case of $Al(i\text{-}Bu)_3$. Indeed, these compounds are present among the respective oligomeric products, although their relative yields are quite low. For example, the relative molar yields of the $R\text{–}(CH_2CH_2)_m\text{–}H$ alkanes generated in the presence of $Al(n\text{-}Pr)_3$, normalized to the yields of the respective $H\text{–}(CH_2CH_2)_m\text{–}H$ alkanes formed in reaction 7, are $[n\text{-}C_{13}]/[n\text{-}C_{10}]_{mol} = 0.033$ and $[n\text{-}C_{15}]/[n\text{-}C_{12}]_{mol} \approx 0.015$. These low ratios confirm that chain termination with H_2 occurs much more frequently compared to the reaction with an organoaluminum compound. When $Al(i\text{-}Bu)_3$ is used as a cocatalyst, the $R\text{–}(CH_2CH_2)_m\text{–}H$ products are 2-methyl-substituted alkanes. They are also formed in relatively low amounts: the $[2\text{-}Me\text{-}C_{11}]/[n\text{-}C_8]_{mol}$ ratio is 0.057 and the $[2\text{-}Me\text{-}C_{13}]/[n\text{-}C_{10}]_{mol}$ ratio is ca. 0.02.

In addition to the molecular structures which can be explained by the standard mechanism in Scheme I, a number of branched alkanes were identified among the ethylene homooligomers prepared with the V-based catalyst, the most important among them being 5-methyl-substituted isoalkanes (Figure 1). The formation mechanism of these products is discussed in the second section of this article.

Ethylene/α-Olefin Copolymerization Reactions. Ethylene copolymerization reactions with 1-butene, 1-pentene, 1-hexene, and 4-methyl-1-pentene were carried out with the V-based catalyst activated by $AlEt_3$. These reactions produced a large variety of cooligomers. Analysis of their structures as a function of the α-olefin type provided a detailed picture of the chain growth mechanism.

Scheme I
Standard Scheme for Ethylene Homopolymerization

Active Center Formation (Ligand Exchange between Transition-Metal Halides and Organoaluminum Compounds):

$$\text{M–Cl} + \text{AlR}_3 \rightarrow \text{M–R} + \text{AlR}_2\text{Cl} \quad (1)$$

(M–R species form complexes with organoaluminum compounds)

Chain Initiation Reactions:

Initiation after reaction 1 and after chain transfer with AlR_3 (reaction 8):

$$\text{M–R} + \text{CH}_2\text{=CH}_2 \rightarrow \text{M–CH}_2\text{CH}_2\text{–R} \quad (2)$$

Initiation after chain transfer with H_2 (reaction 7) and spontaneous chain termination (reaction 5):

$$\text{M–H} + \text{CH}_2\text{=CH}_2 \rightarrow \text{M–CH}_2\text{CH}_3 \quad (3)$$

Chain Growth Reactions:

$$\text{M–R}' + m\text{CH}_2\text{=CH}_2 \rightarrow \text{M–(CH}_2\text{CH}_2)_m\text{–R}' \quad (4)$$

Chain Termination Reactions:

Spontaneous chain termination (β-hydride elimination reaction):

$$\text{M–(CH}_2\text{CH}_2)_m\text{–R}' \rightarrow \text{M–H} + \text{CH}_2\text{=CH(CH}_2\text{CH}_2)_{m-1}\text{–R}' \quad (5)$$

Chain transfer with monomer:

$$\text{M–(CH}_2\text{CH}_2)_m\text{–R}' + \text{CH}_2\text{=CH}_2 \rightarrow \text{M–CH}_2\text{CH}_3 + \text{CH}_2\text{=CH(CH}_2\text{CH}_2)_{m-1}\text{–R}' \quad (6)$$

Chain transfer with H_2:

$$\text{M–(CH}_2\text{CH}_2)_m\text{–R}' + \text{H}_2 \rightarrow \text{M–H} + \text{CH}_3\text{CH}_2\text{–(CH}_2\text{CH}_2)_{m-1}\text{–R}' \quad (7)$$

Chain transfer with AlR_3:

$$\text{M–(CH}_2\text{CH}_2)_m\text{–R}' + \text{AlR}_3 \rightarrow \text{M–R} + \text{AlR}_2\text{–(CH}_2\text{CH}_2)_m\text{–R}' \quad (8)$$

Studies of ethylene/1-pentene and ethylene/4-methyl-1-pentene copolymerization reactions were especially illuminating.

The light products of ethylene/1-pentene copolymerization (Figure 2) can be separated into two groups: oligomers with odd carbon numbers (these products most likely contain one 1-pentene fragment); oligomers with even carbon numbers (these products are mixtures of ethylene homooligomers and molecules containing two 1-pentene fragments).

Formation of all oligomers with odd carbon numbers can be explained by the standard chain growth mechanism in the copolymerization reactions shown in Scheme II.

1. The most abundant compounds are 4-methyl-substituted alkanes. Their relative yields increase with an increase in 1-pentene concentration in the reaction (Table I). These alkanes can in principle, be produced in either of two alternative reaction sequences: (a) 1-pentene insertion into the V–C bond of the V–$(C_2H_4)_m$–H growing chain followed by termination with H_2 (reactions 13–15) or (b) secondary 1-pentene insertion reaction into the V–H bond followed by several ethylene insertions (reactions 11 and 12). The same sequence of reactions generates 3-methyl-branched alkanes in ethylene/1-butene copolymerization and 5-methyl-branched alkanes in ethylene/1-hexene copolymerization. The relative contents of these products decrease slightly for oligomers with increasing carbon numbers (Table II).

2. Presence of linear α-olefins with odd carbon numbers in ethylene/1-pentene oligomers (1-undecane, 1-tridecane, etc., in Figure 2) can only be explained from primary 1-pentene insertion into the V–H bond (reaction 9) followed by several ethylene insertions (reaction 10) and spontaneous chain termination or chain transfer to a monomer (reactions 5 and 6).

3. The formation of 4-ethyl-substituted alkanes with odd carbon numbers in ethylene/1-pentene cooligomers most likely occurs as a result of the primary α-olefin insertion into the V–C_2H_5 bond. The latter is produced either in reaction 1 (formation of the catalyst center) or, more probably, as a result of a single ethylene insertion into the V–H bond (reaction 3).

Oligomers with even carbon numbers in ethylene/1-pentene copolymers belong to two different sets. The two most abundant products, *n*-alkanes and linear α-olefins, are obviously produced in ethylene homooligomerization reactions (Scheme I). The second set contains branched alkanes, mostly with the 4-methyl-substituted chains, such as 4-methylundecane, 4-methyltridecane, etc. (Figure 2). The formation mechanism of these compounds involves participation of two α-olefin fragments (see Scheme III): primary insertion of the first 1-pentene molecule into a V–H bond, several ethylene insertions, primary insertion of the second 1-pentene molecule, and, finally, reaction with hydrogen.

Figure 3 shows the gas chromatogram of the light products generated in an ethylene/4-methyl-1-pentene copolymerization reaction with the V-based catalyst. Most

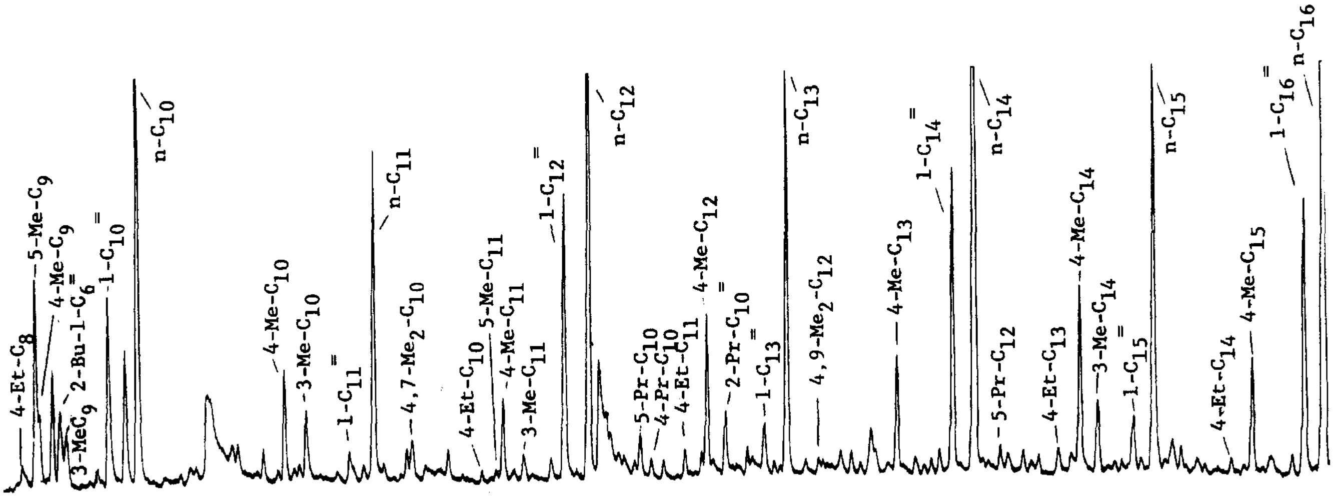


Figure 2. Gas chromatogram of ethylene/1-pentene copolymer prepared with V-based catalyst.

Scheme II
Standard Scheme for Ethylene–α-Olefin Copolymerization (One α-Olefin Molecule)

Chain initiation reaction with α-olefin (primary insertion into the M–H bond):

$$M\text{-}H + CH_2{=}CHR \rightarrow M\text{-}CH_2CH_2R \qquad (9)$$

Subsequent chain growth reactions with ethylene and chain termination with H_2:

$$M\text{-}CH_2CH_2R + mCH_2{=}CH_2 \rightarrow M\text{-}(CH_2CH_2)_m\text{-}CH_2CH_2R \xrightarrow{H_2} M\text{-}H + H\text{-}(CH_2CH_2)_m\text{-}CH_2CH_2R \qquad (10)$$

Chain initiation reaction with α-olefin (secondary insertion into the M–H bond):

$$M\text{-}H + CHR{=}CH_2 \rightarrow M\text{-}CHRCH_3 \qquad (11)$$

Subsequent chain growth reactions with ethylene and chain termination with H_2:

$$M\text{-}CHRCH_3 + mCH_2{=}CH_2 \rightarrow M\text{-}(CH_2CH_2)_m\text{-}CHRCH_3 \xrightarrow{H_2} M\text{-}H + H\text{-}(CH_2CH_2)_m\text{-}CHRCH_3 \qquad (12)$$

Chain initiation reaction and growth with ethylene:

$$M\text{-}H + CH_2{=}CH_2 \rightarrow M\text{-}CH_2CH_3 + mCH_2{=}CH_2 \rightarrow M\text{-}(CH_2CH_2)_{m+1}\text{-}H \qquad (13)$$

Chain growth step with α-olefin (primary insertion):

$$M\text{-}(CH_2CH_2)_{m+1}\text{-}H + CH_2{=}CHR \rightarrow M\text{-}CH_2CHR\text{-}(CH_2CH_2)_{m+1}\text{-}H \qquad (14)$$

Chain termination reactions after the α-olefin insertion:

$$M\text{-}CH_2CHR\text{-}(CH_2CH_2)_{m+1}\text{-}H \xrightarrow{H_2} CH_3CHR\text{-}(CH_2CH_2)_{m+1}\text{-}H + M\text{-}H \qquad (15)$$

$$M\text{-}CH_2CHR\text{-}(CH_2CH_2)_{m+1}\text{-}H \xrightarrow{\beta\text{-hydride elimination}} CH_2{=}CR\text{-}(CH_2CH_2)_{m+1}\text{-}H + M\text{-}H \qquad (16)$$

Continued chain growth after α-olefin insertion followed by chain transfer with H_2:

$$M\text{-}CH_2CHR\text{-}(CH_2CH_2)_{m+1}\text{-}H + pCH_2{=}CH_2 \xrightarrow{H_2} H\text{-}(CH_2CH_2)_p\text{-}CH_2CHR\text{-}(CH_2CH_2)_{m+1}\text{-}H + M\text{-}H \qquad (17)$$

Table I
Effect of 1-Pentene Concentration in Solution on Relative Yields of 4-Methyl-Branched Alkanes in Ethylene–1-Pentene Cooligomers Produced with V-Based Catalyst at 85 °C

[1-pentene] (wt %)	[4-Me-C_9]/[n-C_{10}]	[4-Me-C_{11}]/[n-C_{12}]	[4-Me-C_{13}]/[n-C_{14}]
9	~0.1	0.10	0.04
30	0.16	0.14	0.14
50	0.73	0.54	0.55

Table II
Relative Contents of Single-Branched Isoalkanes and Vinylidene Olefins in Ethylene–1-Hexene Cooligomers Produced with V-Based Catalyst at 85 °C[a]

C_m	([5-Me-C_{m-1}] + [vinylidene[b]])/[n-C_m]	[4-Et-C_{m-1}]/[n-C_m]
10	0.36	0.05
12	0.41	0.03
14	0.32	0.03
16	0.30	0.03
18	0.25	

[a] 1-Hexene concentration in solution 27 wt %, ethylene partial pressure 0.75 MPa. [b] $CH_2{=}C(Bu)C_{m-6}$.

Scheme III
Ethylene–α-Olefin Copolymerization (Two α-Olefin Molecules)

Chain initiation reaction with α-olefin (primary insertion):

$$M\text{-}H + CH_2{=}CHR \rightarrow M\text{-}CH_2CH_2R$$

Chain growth reactions with ethylene:

$$M\text{-}CH_2CH_2R + mCH_2{=}CH_2 \rightarrow M\text{-}(CH_2CH_2)_m\text{-}CH_2CH_2R$$

Chain growth with α-olefin (primary insertion) and chain termination:

$$M\text{-}(CH_2CH_2)_m\text{-}CH_2CH_2R + CH_2{=}CHR \rightarrow M\text{-}CH_2CHR\text{-}(CH_2CH_2)_m\text{-}CH_2CH_2R \xrightarrow{H_2} CH_3CHR\text{-}(CH_2CH_2)_m\text{-}CH_2CH_2R$$

Ethylene/1-pentene copolymerization: 4-methylnonane ($m = 0$), 4-methylundecane ($m = 1$), 4-methyltridecane ($m = 2$), etc.

Ethylene/4-methyl-1-pentene copolymerization: 2,4,8-trimethylnonane ($m = 0$), 2,4,10-trimethylundecane ($m = 1$), 2,4,12-trimethyltridecane ($m = 2$)

Chain growth with α-olefin (secondary insertion) and chain termination:

$$M\text{-}(CH_2CH_2)_m\text{-}CH_2CH_2R + CHR{=}CH_2 \rightarrow M\text{-}CHRCH_2R\text{-}(CH_2CH_2)_m\text{-}CH_2CH_2R \xrightarrow{H_2} CH_2RCH_2\text{-}(CH_2CH_2)_m\text{-}CH_2CH_2R$$

Ethylene/4-methyl-1-pentene copolymerization: 2,9-dimethyldecane ($m = 0$), 2,11-dimethyldodecane ($m = 1$), 2,13-dimethyltetradecane ($m = 2$)

of the products in the mixture are also easily identified:

1. n-Alkanes and linear α-olefins are formed in an ethylene homooligomerization reaction.

2. 2-Methyl-substituted alkanes (2-methylnonane, 2-methylundecane, 2-methyltridecane, etc.) are produced as a result of the primary 4-methyl-1-pentene insertion into the V–H bond (reaction 9) followed by several ethylene insertions and a chain termination with H_2.

3. A number of minor peaks in the chromatogram can be assigned[9,10] to cooligomer molecules containing one 4-methyl-1-pentene fragment in different positions in the chains, such as 2-methyl-4-ethylheptane in the C_{10} range, 2-methyl-4-ethylnonane and 2-methyl-4-propyloctane in the C_{12} range, 2-methyl-4-ethylundecane in the C_{14} range, etc. All these compounds are formed in the reaction sequence 13–17 in Scheme II and have the general formula $H\text{-}(CH_2CH_2)_x\text{-}CH_2CHR\text{-}(CH_2CH_2)_y\text{-}H$ with R = $CH_2CH(CH_3)_2$. The same reactions describe the formation of propyl-branched alkanes with odd carbon numbers in the ethylene/1-pentene copolymerization reaction (Figure 2).

4. Several other products in Figure 3 can only be explained if one assumes that they contain two 4-methyl-1-pentene fragments, similar to the ethylene/1-pentene copolymers. Scheme III explains the formation of these molecules and gives their structures.

Regioselectivity of α-Olefin Insertion into M–H and M–C Bonds. Although α-olefins insert into the M–C

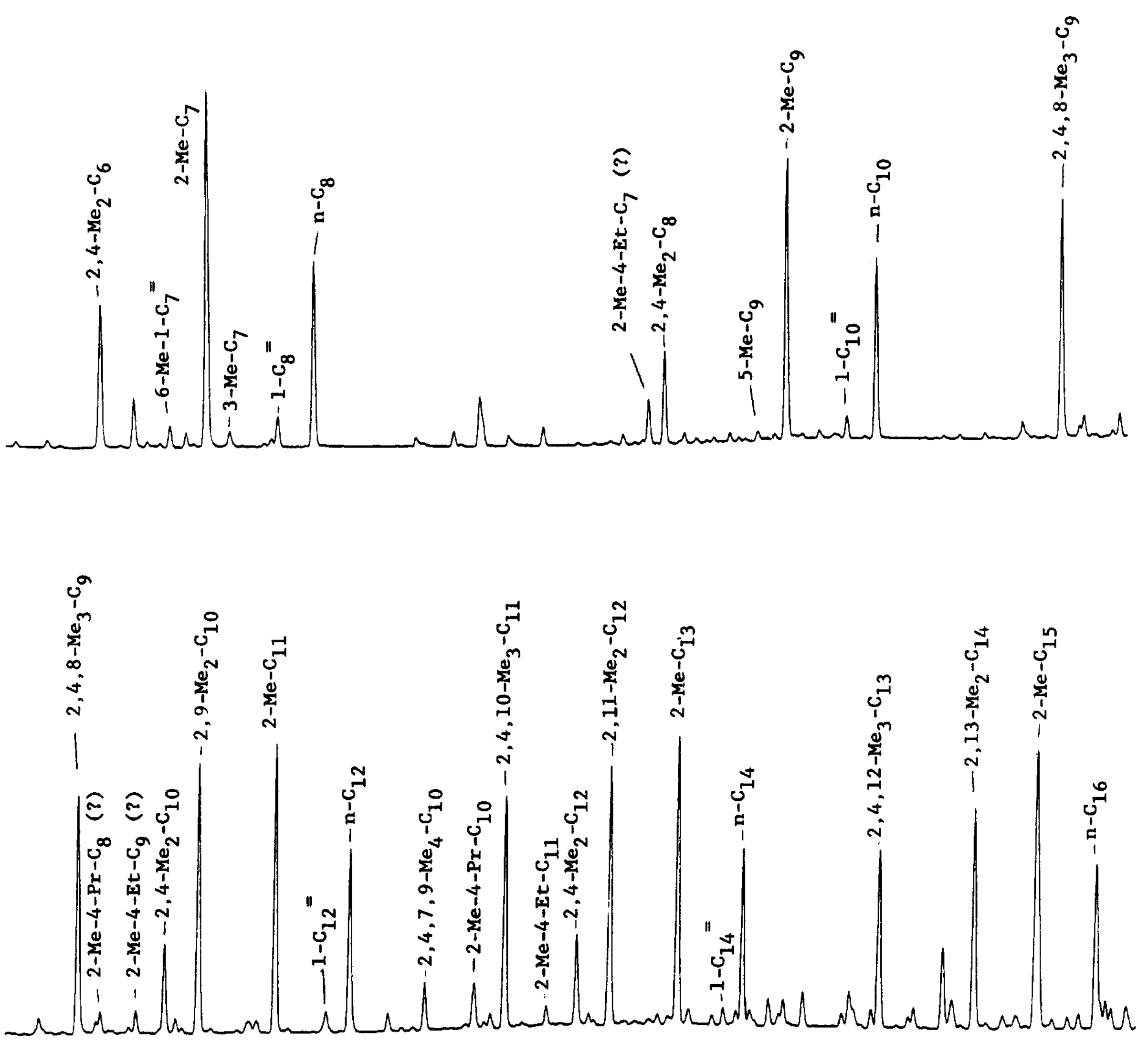


Figure 3. Gas chromatogram of ethylene/4-methyl-1-pentene copolymer prepared with V-based catalyst.

bonds mostly in a primary fashion (Scheme II), regioselectivity of this reaction depends on the nature of the transition metal in the catalyst. A literature survey of propylene polymerization reactions[12] shows that the content of head-to-head linked units varies: with Ti-based catalysts it seldom exceeds 1%, whereas with V-based catalysts it can be as high as 5–8%. One can expect that regioselectivity of the α-olefin insertion into the less sterically demanding V–H bond or into the V–CH_2R bond with a small R group can be even lower. Analysis of ethylene/α-olefin cooligomers provides some qualitative information on this subject. In the case of olefin insertion

$$\text{V–H}\begin{cases} \xrightarrow{CH_2{=}CHR} \text{V–}CH_2CH_2R \text{ (primary insertion)} & (18) \\ \xrightarrow{CHR{=}CH_2} \text{V–}CHRCH_3 \text{ (secondary insertion)} & (19) \end{cases}$$

into the V–H bond, identification of products resulting from a secondary insertion can be achieved if two α-olefin fragments are present in oligomer molecules. For example, if reaction 19 is followed by several ethylene insertions and subsequently by reactions 14 and 15, oligomer molecules containing two α-olefin moieties in this configuration, $CH_3CHR–(CH_2CH_2)_m–CHRCH_3$, can be formed. Small amounts of two such products, 3,6-dimethyloctane and 3,8-dimethyldecane, were indeed identified among ethylene/1-butene cooligomers. Their presence shows that a secondary α-olefin insertion into a V–H bond is at least feasible.

Homooligomerization reactions of 1-pentene and 1-hexene with the V-based catalyst provide information about the regioselectivity of α-olefin insertion into the V–CH_2R bond. These reactions were carried out at 85 °C in the presence of H_2 (0.56 MPa) and produced mixtures of highly branched oligomers. If a single primary α-olefin insertion into the V–H bnd (reaction 9 or 18) is followed by another primary insertion,

$$\text{V-}CH_2CH_2R + CH_2{=}CHR \rightarrow \text{V-}CH_2CHRCH_2CH_2R \tag{20}$$

a series of branched oligomers is eventually produced. If, however, the primary insertion is followed by the secondary insertion,

$$\text{V-}CH_2CH_2R + RCH{=}CH_2 \rightarrow \text{V-}CHRCH_2CH_2CH_2R \tag{21}$$

a branched V–CH(R)R′ moiety is formed which apparently cannot insert another α-olefin molecule. It reacts with H_2 to produce *n*-alkane $RCH_2CH_2CH_2CH_2R$: *n*-decane in the case of 1-pentene, and *n*-dodecane in the case of 1-hexene. These linear products are indeed present in the homooligomer mixtures. Their relative yields provide information about probabilities of a primary vs secondary α-olefin insertion (reaction 20 vs 21) into the V–CH_2R bonds with small linear R groups. These ratios are ca. 5.5 in the case of 1-pentene (R = *n*-C_3H_7) and ca. 7.5 in the case of 1-hexene (R = *n*-C_4H_9).

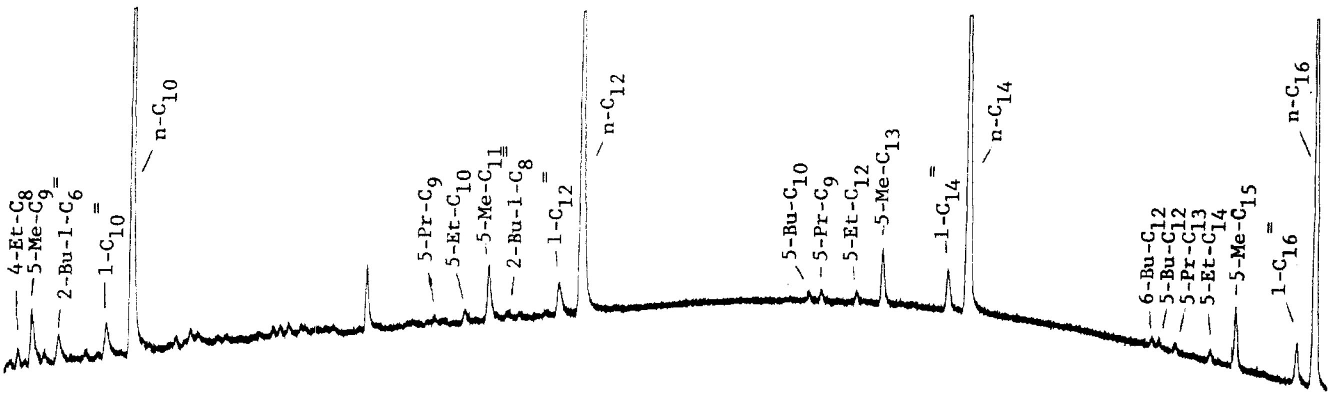


Figure 4. Gas chromatogram of ethylene/1-hexene copolymer prepared with Ti-based catalyst activated with $AlEt_3$.

Polymerization Reactions with Ti-Based Catalyst. Ethylene homooligomers are produced with the Ti-based catalyst system in measurable quantities only at high temperatures (>90 °C) and at very high P_H/P_E ratios, 2.0–2.5. The chromatograms of such oligomers are very simple and show only the peaks of n-alkanes and α-olefins with even carbon numbers. Formation of all these peaks can be readily attributed to the simple set of reactions in Scheme I. Judging by the ratios between the yields of α-olefins and the corresponding n-alkanes, chain termination with H_2 (reaction 7) proceeds at a much higher rate (because of the high H_2 concentration) than the β-hydrogen elimination reaction (reaction 5) and the chain transfer reaction with a monomer (reaction 6).

Figure 4 shows the gas chromatogram of the oligomers formed in the ethylene/1-hexene copolymerization reaction with the Ti-based catalyst at 90 °C and at $P_H/P_E = 2.5$. Only a few vinylidene molecules survive under such high H_2 concentration (reaction 16) and most products are attributed to hydrogenated cooligomers formed according to Scheme II. All these alkanes have a general formula $H\text{-}(CH_2CH_2)_xCH_2CH(C_4H_9)(CH_2CH_2)_y\text{-}H$. The most prominent cooligomer molecules correspond to $x = 0$. They are 5-methyl-substituted alkanes, except for the C_8 range, which contains 3-methylheptane. These products were formed after the primary insertion of the 1-hexene molecule into the Ti–C bond followed by the reaction with H_2 (reactions 14 and 15). The predominance of these alkanes in the reaction products indicates that the reaction rate constant for ethylene insertion into the Ti–C bond in a branched $Ti\text{-}CH_2CH(C_4H_9)R'$ group (reaction 17) is relatively low compared to the chain termination rate with H_2 (reaction 15).

Nonstandard Products in Ethylene Homopolymers Produced with V-Based Catalyst. The structures of all previously discussed oligomer molecules agree with the standard reaction mechanism presented by Schemes I–III. However, ethylene homooligomerization reaction with the V-based catalyst also produces a series of isoalkanes that cannot be explained by this mechanism, as is evident from Figure 1. These compounds include 3-methylheptane, 5-methylnonane, 5-methylundecane, and higher 5-methyl-substituted alkanes, as well as smaller quantities of 4-ethyl- and 3-methyl-substituted isoalkanes. Chain branching is not restricted to the oligomers. Solid homopolymers (which constitute over 99% of all reaction products) also contain such branches. Figure 5 shows the ^{13}C NMR spectrum of polyethylene produced with the V-based catalyst. The oligomer fraction was removed from the polymer with several successive extractions in hot hexane. The polymer, in addition to linear end groups, also contains end groups with methyl branches in the fifth position of the chain. They account for ca. 15% of all chain ends.

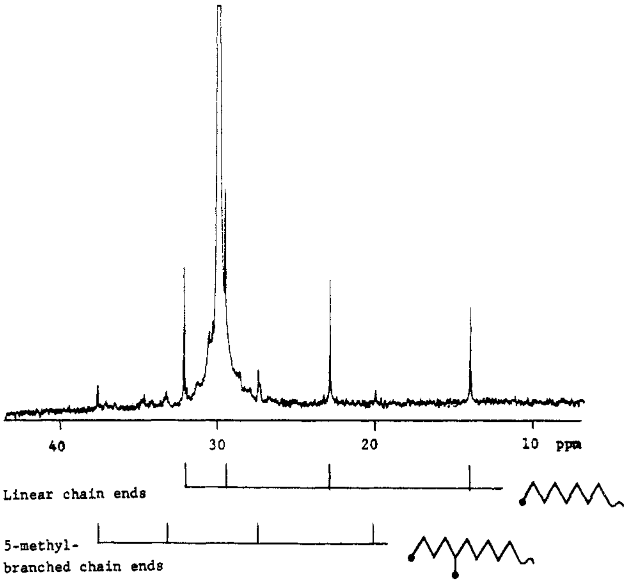


Figure 5. ^{13}C NMR spectrum of ethylene hompolymer prepared with V-based catalyst.

Table III
Contents of Nonstandard Branched Alkanes in Ethylene Homooligomers and Ethylene–α-Olefin Cooligomers Produced with the V-Based Catalyst at 85 °C

	homooligomer		cooligomers	
			E/1-B[a]	E/1-P[b]
C_m	$[5\text{-Me-}C_{m-1}]/[n\text{-}C_m]$	$[4\text{-Et-}C_{m-1}]/[n\text{-}C_m]$	$[5\text{-Me-}C_{m-1}]/[n\text{-}C_m]$	$[5\text{-Me-}C_{m-1}]/[n\text{-}C_m]$
8	1.01[c]			0.066[c]
10	0.55	0.25	0.027	0.081
12	0.019	~0.1	~0.02	0.030
14	0.07	~0.03	~0.02	~0.02
16	0.04		~0.01	~0
18	0.03		~0	~0

[a] Ethylene/1-butene. [b] Ethylene/1-pentene. [c] [3-Methylheptane]/[n-octane] ratio.

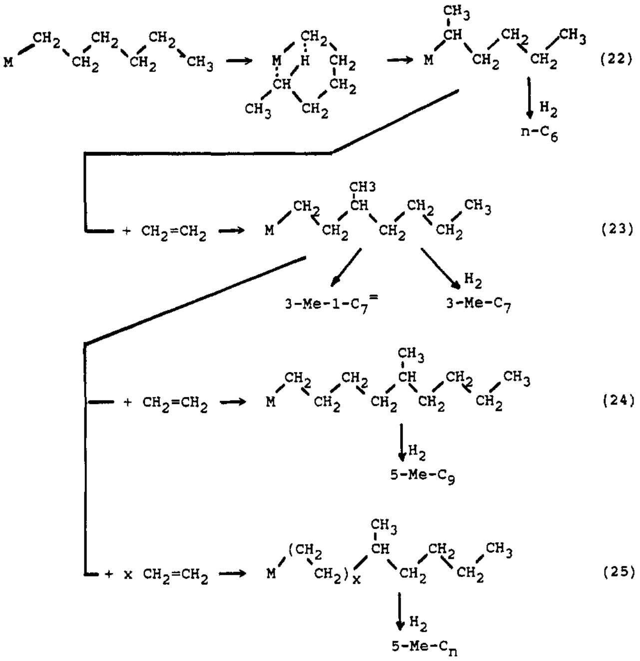
The nonstandard oligomeric products exhibit several specific features:

1. They are formed with relatively high yields only in ethylene homopolymerization reactions and virtually disappear if any α-olefin is present in the reaction medium (Table III).

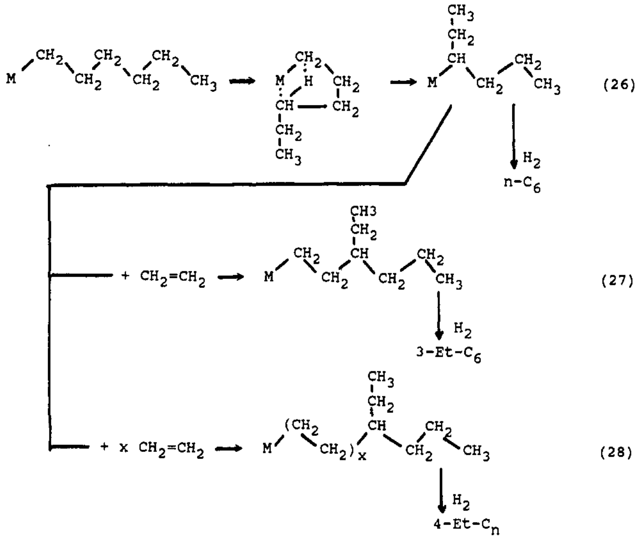
2. Relative yields of the branched alkanes with respect to those of linear alkanes with the same carbon number rapidly decrease with increasing molecular mass (columns 2 and 3 in Table III).

3. These nonstandard products cannot be attributed to conventional autocooligomers (formed in reactions between ethylene and in situ produced α-olefins such as

Scheme IV
Isomerization of Growing Chain
(Methyl Group Formation)



Scheme V
Isomerization of Growing Chain
(Ethyl Group Formation)



1-butene, 1-hexene, etc.) because these light olefins are formed with very low yields at a high hydrogen pressure.

We attribute the formation of the branched products in the ethylene homopolymerization reactions to intramolecular chain isomerization processes via a σ-bond metathesis reaction.[13,14] A possible mechanism is shown in Schemes IV and V. It involves the chain isomerization step accompanied by hydrogen transfer. The following arguments support this mechanism:

1. Scheme IV explains, in a straightforward way, the formation of 5-methyl-branched alkanes in ethylene homopolymerization. The 1→5 shift proceeds through an energetically favorable, six-atom cyclic intermediate (reaction 22). Immediate chain termination (e.g., in reaction with H_2) after this step produces n-hexane, which is indistinguishable from the normal hydrogenated ethylene trimer. However, if the 1→5 shift is followed by additional ethylene insertion steps, a series of methyl-substituted alkanes should be produced. One ethylene insertion step should give 3-methylheptane (reaction 22), two ethylene insertion steps should give 5-methylnonane (reaction 23), and further ethylene insertion steps should result in the formation of other 5-methyl-substituted alkanes (reaction 25).

2. If the isomerized chain formed in reaction 23 separates from the active center in a β-elimination reaction (a step with a relatively low probability under high hydrogen pressure), it will produce 3-methyl-1-heptene. This olefin was indeed identified among the ethylene homooligomereization products (Figure 1).

3. Scheme V explains the formation of ethyl-branched alkanes. They are formed if, instead of a 1→5 shift, a 1→4 shift via a five-membered transition state occurs (reaction 26). When the shift is followed by one or several more ethylene insertion steps and the chain is terminated with H_2, ethyl branches should appear in the fourth positions of the polymer chains (reactions 27 and 28).

4. When an α-olefin is present in the reaction medium in a significant concentration, it interferes with the metathesis reaction, e.g., by coordinating with the active center. Because of this, the yields of such branched alkanes decrease in the products of ethylene/α-olefin copolymerization reactions (Table III).

The chain isomerization reactions shown in Schemes IV and V occur only when relatively short growing chains are attached to the transition-metal atoms. This may be caused by a high mobility of short chains and explains why branched chain ends concentrate in the low molecular mass fractions of the homopolymers (Figure 5). Ethylene homooligomerization with the Ti-based catalyst also generates some chain isomerization products. However, their relative yields are 2 orders of magnitude lower than those in the reactions catalyzed by the V-based catalyst.

Conclusions

1. Structural analysis of the oligomers formed in ethylene homopolymerization reactions and in its copolymerization reactions with several α-olefins provides the most detailed confirmation of the standard chemical mechanism (proposed by Natta) of chain growth in olefin polymerization reactions with coordination catalysts. The oligomer analysis affords information on the chain structures of individual molecules. It complements earlier spectroscopic data which, by their nature, could account only for averaged structural features of the polymer molecules.

2. A previously unknown deviation from the standard chain growth mechanism was discovered in the case of ethylene homopolymerization with a V-based catalyst: chain isomerization with a predominant formation of 5-methyl-branched isoalkanes. A mechanism of the chain isomerization involving σ-bond metathesis at an active center is proposed.

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References and Notes

(1) Kissin, Y. V. *Adv. Polym. Sci.* **1974**, *15*, 91–155.
(2) Sacchi, M. C.; Locatelli, P.; Tritto, I. *Makromol. Chem.* **1989**, *190*, 139–148.
(3) Hayashi, T.; Inoue, Y.; Chujo, R. *Macromolecules* **1988**, *21*, 2675–2779.
(4) Cheng, H. N.; Smith, D. A. *Macromolecules* **1986**, *19*, 2065–2072.
(5) Kissin, Y. V. *Makromol. Chem. Symp.*, in press.

(6) Nowlin, T. E.; Kissin, Y. V.; Wagner, K. P. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 755–764.

(7) Karol, F. J. *Abstracts of Papers*, 201st National Meeting of the American Chemical Society, Atlanta, GA; American Chemical Society: Washington, DC, 1991; PMSE 67.

(8) Miro, N. D. U.S. Patent 4,912,074, 1990.

(9) Kissin, Y. V.; Feulmer, G. P. *J. Chromatogr. Sci.* **1986**, *24*, 53–59.

(10) Kissin, Y. V. *J. Chromatogr. Sci.* **1986**, *24*, 278–284.

(11) Kissin, Y. V. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 605–621.

(12) Kissin, Y. V. *Isospecific Polymerization of Olefins with Heterogeneous Ziegler–Natta Catalysts*; Springer-Verlag: New York, 1985; Chapter 1.

(13) Thompson, M. E.; Baxter, S. M.; Bulls, A. R. J.; Burger, B. J.; Nolah, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203–209.

(14) Huang, Y.; Hill, Y. D.; Freiser, B. C. *J. Am. Chem. Soc.* **1991**, *113*, 840–848.