

Chemistry of Olefin Polymerization Reactions with Chromium-Based Catalysts

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ABSTRACT: Detailed GC analysis of oligomers formed in ethylene homopolymerization reactions, ethylene/1-hexene copolymerization reactions, and homo-oligomerization reactions of 1-hexene and 1-octene in the presence of a chromium oxide and an organochromium catalyst is carried out. A combination of these data with the analysis of ¹³C NMR and IR spectra of the respective high molecular weight polymerization products indicates that the standard olefin polymerization mechanism, according to which the starting chain end of each polymer molecule is saturated and the terminal chain end is a C=C bond (in the absence of hydrogen in the polymerization reactions), is also applicable to olefin polymerization reactions with both types of chromium-based catalysts. The mechanism of active center formation and polymerization is proposed for the reactions. Two additional features of the polymerization reactions, co-trimerization of olefins over chromium oxide catalysts and formation of methyl branches in polyethylene chains in the presence of organochromium catalysts, also find confirmation in the GC analysis. © 2008 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 46: 5330–5347, 2008

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INTRODUCTION

Two types of chromium-based catalysts, chromium oxide catalysts and supported organochromium catalysts, are widely used in industry for the manufacture of ethylene polymers.^{1–9} Together, these catalysts account for nearly 40% of all the polyethylene resins manufactured throughout the world. Chromium oxide catalysts also readily copolymerize ethylene with α -olefins

(1-butene, 1-hexene),^{1,4–6,10} whereas organochromium catalysts have inferior copolymerization ability.^{5,6}

In general, olefin polymerization reactions with Cr-based catalysts strongly resemble the same reactions catalyzed by Ti- and V-based Ziegler-Natta catalysts and by metallocene catalysts.⁵ However, a significant conceptual difference exists between these reactions. The principal steps in the polymerization reactions of olefins with Ziegler-Natta and metallocene catalysts are firmly established; they are listed in Scheme 1 (Reactions 1–14). The chain growth reaction (Reaction 15) is the insertion reaction of the C=C bond of an olefin molecule into the

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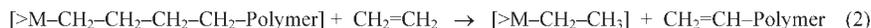
Ethylene homopolymerization reactions

Chain growth reaction (Polymer is an *n*-alkyl group of any length or a H atom)



Chain transfer reactions

Chain transfer reaction to ethylene



Chain transfer reaction to hydrogen (if H₂ is present)



Chain initiation reaction after chain transfer to hydrogen



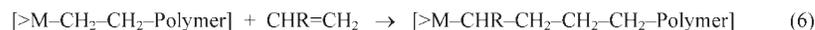
Ethylene/ α -olefin copolymerization reactions

Chain growth reactions

Chain growth reaction of α -olefin, primary insertion

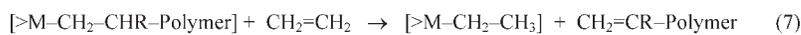


Chain growth reaction of α -olefin, secondary insertion (a relatively rare event)

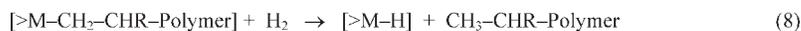


Chain transfer reactions

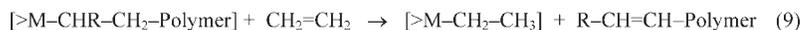
Chain transfer reaction to ethylene after Reaction 5



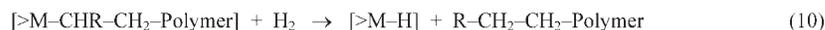
Chain transfer reaction to hydrogen after Reaction 5



Chain transfer reaction to ethylene after Reaction 6



Chain transfer reaction to hydrogen after Reaction 6



Chain transfer reaction to α -olefin (primary orientation) after Reaction 1



Chain transfer reaction to α -olefin (secondary orientation) after Reaction 1



Chain initiation reactions after chain transfer to hydrogen (Reaction 4)

Chain initiation reaction with α -olefin, primary orientation

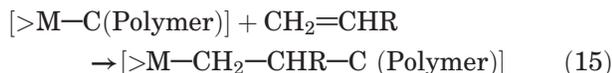


Chain initiation reaction with α -olefin, secondary orientation

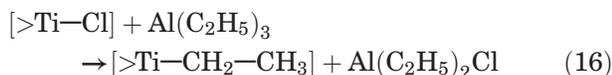


Scheme 1. Chemistry of ethylene/ α -olefin copolymerization reactions with Ziegler-Natta and metallocene catalysts.

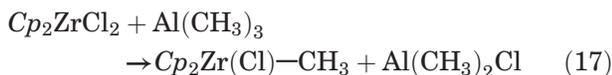
transition metal-carbon bond in an active species:



The source of the initial M—C bonds in the catalysts is also established; they are formed in exchange reactions between [$>M-\text{Cl}$] species in the catalyst precursors and Al—C bonds in cocatalysts. For example, in typical Ziegler-Natta catalysts:

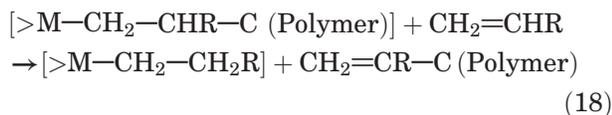


or in metallocene catalysts:

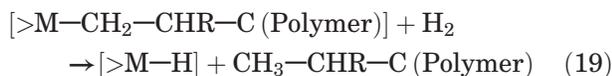


These initial alkyl groups in the active centers are converted into starting chain ends of the first polymer molecules. Their presence in the polymers (in very small quantities) has been established by various chemical and spectroscopic methods, particularly those employing $^{14}\text{CH}_3$ or $^{13}\text{CH}_3$ -labeled organoaluminum compounds and monomers.

The chemistry of chain transfer reactions in these polymerization reactions is also firmly established. Usually, a polymer molecule is separated from the active center in a chain transfer reaction to a monomer,



This reaction regenerates a new [$>M-C$] bond which is capable of further C=C bond insertion. A chain transfer reaction to hydrogen,



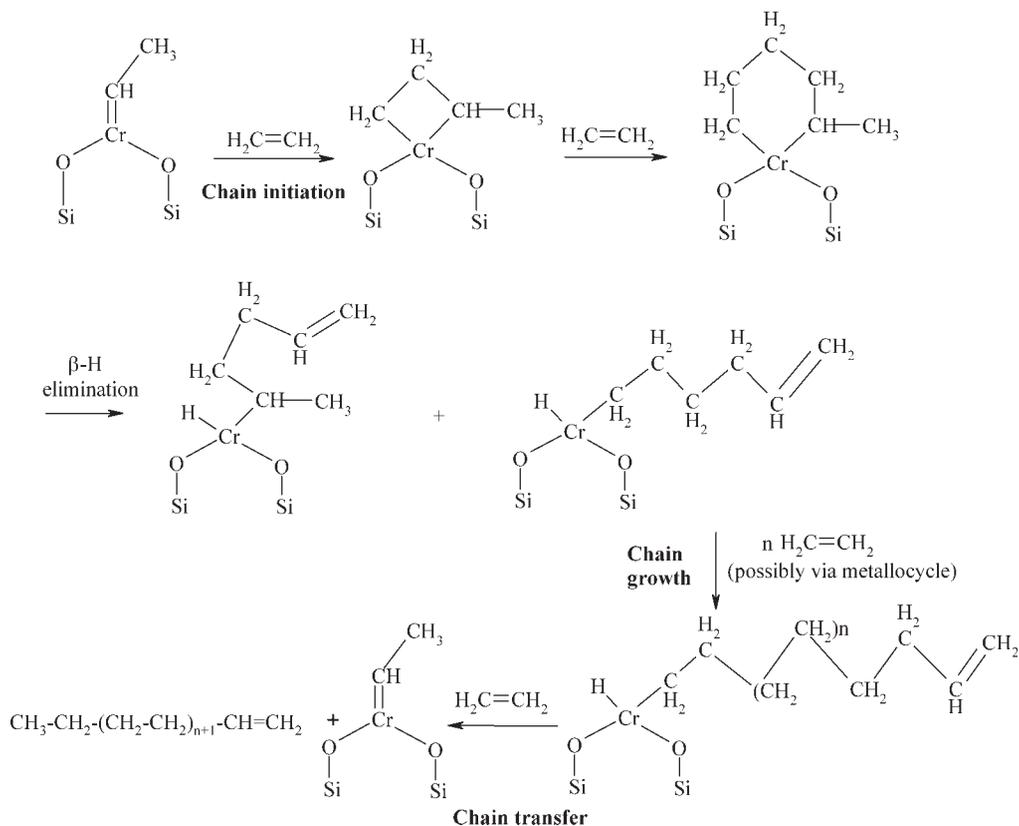
produces an [$>M-H$] bond which is also capable of C=C bond insertion.

Scheme 1 also shows the principal reaction steps of ethylene/ α -olefin copolymerization reactions with Ziegler-Natta and metallocene cata-

lysts. This scheme is applicable only to reactions that lead to copolymers with relatively low contents of α -olefins, when the formation of α -olefin diads or triads is a rare event. This scheme is adequate for the explanation of the structures of most chain ends in ethylene/ α -olefin copolymers.

Two difficulties arise when the same concept is applied to polymerization reactions with chromium-based catalysts. First, these catalysts do not usually employ organometallic cocatalysts, and the source of the initial [$>Cr-C$] bond is not certain. The second complication was discovered when ethylene polymerization reactions with chromium-based catalysts were subjected to thorough spectroscopic examination. IR studies of ethylene polymerization reactions with chromium oxide catalysts^{10,11} and with supported organochromium catalysts^{12,13} showed that the only observable reaction between freshly prepared catalysts (which contain predominantly Cr^{II} species and no [$>Cr-C$] bonds) was the formation of growing polyethylene chains, $(-\text{CH}_2-\text{CH}_2-)_n$. No saturated chain ends (methyl groups), which are expected in the "standard" scheme of olefin polymerization reactions, were observed.¹⁰⁻¹⁴ The methyl end-groups were not observed even when the polymerization reactions were carried out at a reaction time of less than one second or at very a low ethylene concentration.¹⁰

To explain these experimental data, Scott and Amor proposed a special reaction mechanism of ethylene polymerization reactions¹⁵; it is shown in Scheme 2. The precursor of the active center is a Cr^{IV} alkylidene species formed after oxidative addition of an ethylene molecule to a Cr^{II} species on the catalyst surface. The alkylidene species interacts with two molecules of ethylene and produces first a metallocyclobutane species and then a metallocyclohexane species. The scission of the Cr—C bond in the latter is accompanied by a β -H elimination step, it produces an open-chain active center with a short growing polymer chain carrying a C=C bond at its starting end. The proposed mechanism of the chain growth reaction (lengthening of the polymer chain) is the same as in polymerization reactions with Ziegler-Natta and metallocene catalysts, it involves ethylene insertion into the [$>Cr-C$] bond, possibly via a metallocycle intermediate (the modified Rooney-Green mechanism⁵). A chain termination reaction (kinetically, chain transfer to ethylene) transfers an H atom from a coordinated



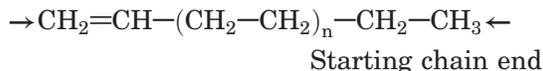
Scheme 2. Mechanism of ethylene polymerization reaction with chromium oxide catalysts proposed in ref. 15.

ethylene molecule to the growing chain end and regenerates the original Cr^{IV} alkylidene species.

In effect, this reaction mechanism proposes that the positions of chain end-groups in the polyethylene chains are opposite to those in Ziegler-Natta or metallocene catalysis.

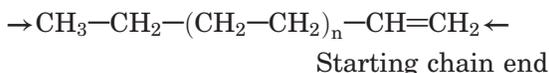
Polyethylene chain produced by a Ziegler-Natta catalyst (Reactions 1 and 2 in Scheme 1):

Terminal chain end



Polyethylene chain produced by a chromium oxide catalyst (Scheme 2):

Terminal chain end



Distinguishing between these two mechanisms is very difficult when ethylene homopolymerization reactions are examined. However, additional information about the chemistry of

the reaction steps can be produced when ethylene is copolymerized with α -olefins, or when α -olefins are homopolymerized. These homopolymerization and copolymerization reactions are the main subject of this study.

EXPERIMENTAL

Catalysts

Two chromium-based catalysts were used, a chromium oxide catalyst and an organochromium catalyst prepared from chromocene. The synthesis the chromium oxide catalyst was described in detail in patents.^{16,17} Chromium triacetate was supported on granular silica (Davison EP10X, average particle size $\sim 110 \mu$), $[\text{Cr}] = 0.24 \text{ wt } \%$. The catalyst was dehydrated at $200\text{--}210 \text{ }^\circ\text{C}$, treated with $\text{Ti}(\text{O}i\text{-Pr})_4$ in a 1:0.28 weight ratio, and calcined at $845 \text{ }^\circ\text{C}$ in air. The organochromium catalyst was prepared by reacting chromocene with silanol groups on the surface of silica.^{7,9} The support was calcined at $600 \text{ }^\circ\text{C}$, then combined with a toluene solution

Table 1. Examples of Polymerization Reactions with Chromium Oxide Catalysts; Slurry Reactions at 90 °C

Run	P_E (MPa)	P_H (MPa)	Time (min)	Productivity (g/g cat)	C_{Hex}^{copol} (mol %)	Oligomers C_{10} - C_{34} (%)	γ
Ethylene homopolymerization reactions							
1	1.33	0	60	2,400	0	0.73	0.897
2	1.33	0	60	1,960	0	0.32	0.886
3	1.27	0.19	60	1,550	0	0.41	0.884
Ethylene/1-hexene copolymerization reactions							
4	1.33	0	60	2,500	1.1 ^a	0.56	0.887
5	1.27	0.19	20	1,120	1.8 ^a	0.89	
6	1.27	0.19	60	1,700	0.8 ^a	0.93	
7	1.33	0	60	2,200	4.7 ^b	1.13	0.868

^a $(C_{Hex}/C_E)^{mon} = 0.27$.

^b $(C_{Hex}/C_E)^{mon} = 1.33$.

of chromocene at a Cr loading of 1.5 wt %, and the solvent was removed by drying the catalyst at ~50 °C.

Polymerization Reactions

Polymerization experiments were carried out in two stainless-steel autoclaves, 3.8 and 0.5 L volume, equipped with magnet-driven propeller stirrers, manometers, and external heating jackets. The reactors were dried in a nitrogen flow at 90 °C and then cooled to ~50 °C. A solvent (*n*-heptane) and, in copolymerization reactions, 1-hexene, were added to the reactors in required quantities under a nitrogen blanket followed by 0.2–0.8 mmol of MgBu₂ (as 1 M solution in heptane). As reported earlier,¹⁸ addition of a small amount of a dialkylmagnesium compound to such polymerization reactions makes the polymerization experiments highly reproducible and practically eliminates induction periods in the reactions, but it does not affect the structure of the produced polymers. The reactors were heated to the reaction temperature, ethylene was added to a total pressure ~1 atm below the final value, and, finally, 0.05 to 0.1 g of a catalyst was added with ethylene to the final reaction pressure. Table 1 lists experimental conditions of several ethylene homopolymerization reactions and ethylene/1-hexene copolymerization reactions at different ethylene partial pressures, P_E , and different [1-hexene]:[ethylene] molar ratios in solution, $(C_{Hex}/C_E)^{mon}$.

Some polymerization reactions with chromium oxide catalyst and most polymerization reactions with organochromium catalyst were carried out in the presence of hydrogen (partial pressure P_H). The molecular weight of polyethyl-

ene prepared with the latter catalyst is very sensitive to the presence of hydrogen, and a significant quantity of hydrogen is essential for the synthesis of polymers of a relatively low molecular weight. This condition is also a prerequisite for the formation of oligomers, the principal subject of this investigation. Typical reactions conditions were: temperatures from 75 to 90 °C, 1-hexene concentration from 0 to 16.0 vol %, the total reaction pressure 15 atm (kept constant throughout each run), P_E from 10 to 12.5 atm, P_H from 0 to ~2 atm, reaction time 60–120 min. To compensate for consumption of ethylene in the polymerization reactions, it was continuously added to the reactors. The kinetic features of the polymerization reactions with chromium oxide catalysts were described earlier.¹⁸

Oligomer samples (solutions in heptane) were collected immediately after the end of each reaction so that the lightest materials were not lost during sampling. Several oligomer samples were also extracted from polyethylene resins prepared in the pilot plant in gas-phase polymerization reactions catalyzed by the same chromium-based catalysts. The polymers, in 1 g amounts, were placed into 10 cm³ glass vials, 2 cm³ of *n*-heptane and 2 μ L of 7-methyltridecane (an internal GC standard) were added to the vials, which were capped with a septum and heated for 4 h at 70 °C.

Polymer Characterization

Gas chromatographic analysis of oligomers was carried out on an HP 5890 gas chromatograph equipped with a 60 m capillary column (MTX-1, Restek, coated with crosslinked silicone resin) and an FID detector. The injector and the detec-

tor temperatures were 300 °C, and the column temperature was increased from 40 to 300 °C at a rate of 5 °C/min.

¹³C-NMR analysis of polymers was carried out at 100.4 MHz on a JEOL Eclipse 400 NMR spectrometer at 130 °C using typical experimental parameters for acquiring quantitative spectra of polyolefins. The pulse angle was 90° and the pulse delay was 15 s. Continuous ¹H decoupling was applied throughout. The samples were prepared as solutions in a 3:1 mixture of 1,3,5-trichlorobenzene and *o*-dichlorobenzene-*d*₄. IR spectra of polymers (thin film) were recorded with Perkin-Elmer Paragon 1000 FTIR and 1600 FTIR spectrophotometers at 2 cm⁻¹ resolution. The 1-hexene content in ethylene/1-hexene copolymers, reported as C_{Hex}^{copol} (mol %), was measured by ¹³C-NMR¹⁹ and IR.²⁰ Molecular weights and molecular weight distributions of polyethylenes were determined by GPC, as described earlier.¹⁸ Melt indices of polyethylenes, *I*₂ and *I*₂₁, were measured at 190 °C with a Kayeness extrusion plastometer according to the ASTM method D-1238, Condition E.

RESULTS AND DISCUSSION

Principal Features of Ethylene/1-Hexene Copolymerization Reactions

¹³C-NMR analysis of the products of ethylene/1-hexene copolymerization reactions clearly shows large differences between the performance of the chromium-oxide and the organochromium catalyst. The chromium oxide catalyst readily copolymerizes α -olefins with ethylene.⁵ The *r*₁ value for the ethylene/1-hexene copolymerization reactions with the catalyst is ~30,¹⁸ which places it, in terms of efficiency of α -olefin copolymerization with ethylene, in an intermediate position between metallocene catalysts (*r*₁ ~ 20) and Ti-based Ziegler-Natta catalysts (*r*₁ ~ 80–120). Structurally, ethylene/ α -olefin copolymers with low α -olefin contents (1.0–2.0 mol %) prepared with chromium oxide catalysts strongly resemble ethylene/ α -olefin copolymers prepared with metallocene and Ti-based Ziegler-Natta catalysts.¹⁸ For example, 1-hexene units in the chains of the former ethylene/1-hexene copolymers mostly stand alone in polymer chains (in EHE triads, EHEE tetrads) whereas 1-hexene pairs (EHH triads, EHHE tetrads) are present in very small quantities (see Fig. 2 below).

In contrast, the organochromium catalyst has much lower ability to copolymerize 1-hexene with ethylene but it produces ethylene homopolymers with isolated methyl branches in the chains (see latter sections).

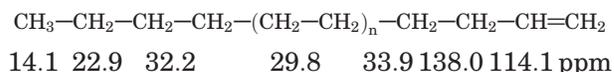
In general, two main sources of information are available for the elucidation of the copolymer structures and the polymerization mechanism:

1. Analysis of ¹³C-NMR spectra of copolymers with relatively high α -olefin contents.
2. GC analysis of the oligomers. Because of the broad molecular weight distributions of ethylene polymers prepared with chromium-based catalysts, the solvents sampled after the polymerization reactions usually contain measurable quantities of oligomers¹⁸ (significant amounts of hydrogen must be used to produce oligomers in the case of the organochromium catalyst). The studies of these oligomers are aided by two circumstances. First, GC analysis affords identification of each individual type of polymer molecules, albeit very short ones. Second, earlier research provided numerous examples of oligomer structures generated in ethylene/ α -olefin copolymerization reactions with different types of catalysts: Ziegler-Natta (both Ti-^{21–23} and V-based^{21,24,25}), metallocene,^{26–28} and non-metallocene.^{29–32} Peak assignment for branched olefins and isoalkanes in gas chromatograms of the oligomers was also based on earlier GC data.^{33,34}

Structure of Polymer Products Produced with Chromium Oxide Catalysts

Ethylene Homopolymers

¹³C-NMR and IR Data. ¹³C-NMR spectra of ethylene homopolymers prepared with chromium oxide catalyst contain, in addition to the large signal from CH₂ groups, signals from saturated chain ends and vinyl end groups:



The vinyl double bonds are also easily observable in IR spectra of the polymers: the ν (C=C) band is at 1642 cm⁻¹ and δ (CH₂=CH) bands are at 990 and 908 cm⁻¹. The polymers are strictly

linear. Their ^{13}C -NMR spectra do not exhibit a methine signal at 37.8–38.0 ppm, which is expected in the case of long-chain branching in polyethylenes.³⁵

GC Data. A series of polymerization experiments were carried out with chromium oxide catalyst under different conditions to determine the effects of reaction parameters on the distribution and structures of oligomers generated by the active centers that produce polymer components with the lowest molecular weights (Table 1).

When ethylene is homopolymerized using a chromium oxide catalyst in the absence of hydrogen, the principal oligomers are linear α -olefins with even carbon atom numbers (C_m), $\text{CH}_2=\text{CH}-(\text{E})_{n-1}-\text{H}$ with $m = 2n$. These α -olefins amount to over 95% of all oligomers in each C_m range. The structure of these products is consistent with the ^{13}C -NMR and IR data, but it is not indicative of any particular reaction mechanism by itself and, potentially, can be easily explained either by Reactions 1 and 2 in Scheme 1 or by Scheme 2.

Molar yields of the α -olefins are distributed according to a power law⁵:

$$F_{\text{number}}(n) = A \cdot \gamma^n \quad (20)$$

where A is a normalization parameter and γ is the probability of chain growth.

$$\begin{aligned} \gamma &= R_p / (R_p + \sum R_t^i) \\ &= k_p \cdot C^* \cdot C_M / [k_p \cdot C^* \cdot C_M + \sum (k_t^i \cdot C^* \cdot C_{\text{agent}}^i)] \end{aligned} \quad (21)$$

The areas under GC peaks are proportional to the weight contents of particular oligomers: peak area $\sim F_{\text{weight}}(n) = nF_{\text{number}}(n)$. The GC data for the oligomer distributions are conveniently linearized as:

$$\begin{aligned} \log[F_{\text{weight}}(n)/n] &\equiv \log[\text{peak area}/n] = \log(A) \\ &+ n \cdot \log(\gamma) \end{aligned} \quad (22)$$

with a slope of $\log(\gamma)$.

Figure 1 shows the distribution of two ethylene homo-oligomers in the coordinates of eq 22. The linear dependences hold up to a polymerization degree n of ~ 14 ; higher oligomers partially cocrystallize with the polymers and their fractions in solution decrease. The oligomers were also extracted from ethylene homopolymers pro-

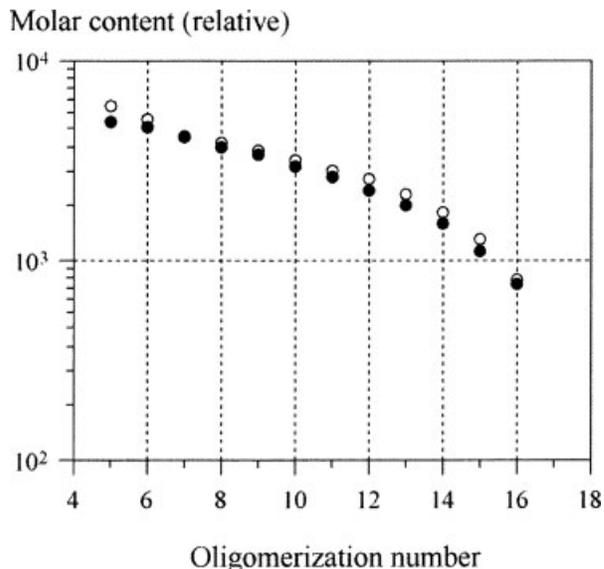


Figure 1. Distribution of oligomeric α -olefins in two ethylene homopolymers produced with chromium oxide catalyst at 90 °C and P_E of 10 atm. in coordinates of eq 22. ●, Reaction in the absence of H_2 ; ○, reaction in the presence of 2 atm of H_2 .

duced with the chromium oxide catalyst in gas-phase polymerization experiments. These oligomers have the same structure as the oligomers produced under slurry conditions, that is, they are predominantly linear α -olefins with even C_m , and their distribution is described by the same power law (eqs 20 and 22) except for the loss of the lightest oligomers, with $n = 5$ and 6, during polymer handling and storage.

When hydrogen is present during ethylene homopolymerization reactions with chromium oxide catalysts, it does not change the distribution of the olefinic oligomers (Fig. 1) but n -alkanes are also formed. The [n -alkane]:[α -olefin] ratios for the ethylene homo-oligomers prepared with chromium oxide catalyst at a P_H/P_E ratio of 0.13 are low.

Oligomerization number, n	5	6	7	8	9	10	11
[n -Alkane]: [α -olefin] ratio	0.108	0.093	0.073	0.065	0.059	0.050	0.053

However, oligomers extracted from the ethylene homopolymer produced at 95 °C in a gas-

Table 2. Results of GPC Analysis of Ethylene Homopolymers and Ethylene/1-Hexene Copolymers Prepared with Chromium Oxide Catalyst at 90 °C in Slurry Reactions at $P_E = 1.27$ MPa, 2 h Run (data from [18])

Flory Component	Homopolymer		Copolymer (C_{Hex}/C_E) ^{mon} = 0.6, C_{Hex}^{copol} = 2.3 mol %	
	M_w	Content (%)	M_w	Content (%)
I	3.2×10^3	2.6	0.9×10^3	2.9
II	1.2×10^4	9.9	3.0×10^3	8.2
III	3.8×10^4	23.5	1.3×10^4	15.8
IV	9.7×10^4	25.2	4.1×10^4	27.0
V	2.3×10^5	21.2	1.1×10^5	25.0
VI	6.0×10^5	14.5	2.8×10^5	13.8
VII	1.8×10^6	3.1	7.3×10^5	5.3

phase reaction using the same chromium oxide catalyst contained higher fractions of *n*-alkanes.

Oligomerization number <i>n</i>	7	8	9	10	11	12	13
[<i>n</i> -Alkane]: [α -olefin] ratio	0.63	0.52	0.41	0.29	0.24	0.22	0.22

In general, the formation of small quantities of *n*-alkanes indicates a slow chain transfer reaction to hydrogen, Reactions 3 and 4 in Scheme 1. This conclusion agrees with the results of the GPC analysis: molecular weights of polyethylenes prepared with chromium oxide catalysts exhibit low but measurable sensitivity to the presence of hydrogen.¹⁸ For example, weight average molecular weights of ethylene homopolymers prepared at 95 °C with the same chromium oxide catalyst in the absence of hydrogen and at $P_H/P_E = 0.13$ are, respectively, 2.79×10^5 and 2.08×10^5 (I_2 values are 0.031 and 0.077, I_{21} values are 1.22 and 3.75).

Table 1 lists relative oligomer yields as their weight fraction (C_{10} - C_{34} products) with respect to the polymer yields. The combined relative oligomer yield does not depend on the reaction duration and is only slightly affected by the presence of hydrogen or 1-hexene in the reaction medium. The table also lists γ parameters for the oligomeric α -olefins. The γ value is practically independent of the presence of hydrogen or 1-hexene. The weight-average molecular weight of the oligomer fraction (calculated from the γ values) is ~ 440 . If one compares this value and the oligomer contents in Table 1 with average

molecular weights of various Flory components constituting the polymers prepared with this catalyst (Table 2, data from¹⁸), it is clear that the oligomers constitute a subfraction (from 15 to 25%) of Flory component I, the polymer component with the lowest molecular weight.

Ethylene/1-Hexene Copolymers

¹³C-NMR and IR Data. Ethylene/1-hexene copolymers prepared with chromium oxide catalyst contain two types of double bonds at one of their chain ends, in addition to the vinyl double bonds described in the previous section. The first of them is the vinylidene double bond $CH_2=CR'$ -Polymer. It is readily observable in IR spectra, its $\delta(CH_2=CR)$ band is at 888 cm^{-1} . The second type of double bond is the *trans*-vinylene bond $R'-CH=CH$ -Polymer; its $\delta(CH=CH)$ band at 965 cm^{-1} is present in the IR spectra of ethylene/1-hexene copolymers but not in the spectra of ethylene homopolymers produced with the catalyst.

Figure 2 shows the ¹³C-NMR spectrum of an ethylene/1-hexene copolymer containing 26 mol % of 1-hexene (produced at 90 °C). The signals in the spectrum are assigned according to³⁶ either to carbon atoms in *n*-butyl branches or to carbon atoms in the main chain. In the latter case, Greek letters indicate positions of the closest CH groups (the branches) with respect to a particular carbon atom. All the features in the spectrum underline the "ordinariness" of the copolymer structure: the same NMR signals are also typical for copolymers with a relatively high 1-hexene content produced with Ti-based Ziegler-Natta catalysts and with metallocene catalysts.^{19,36} The spectrum in Figure 2 also

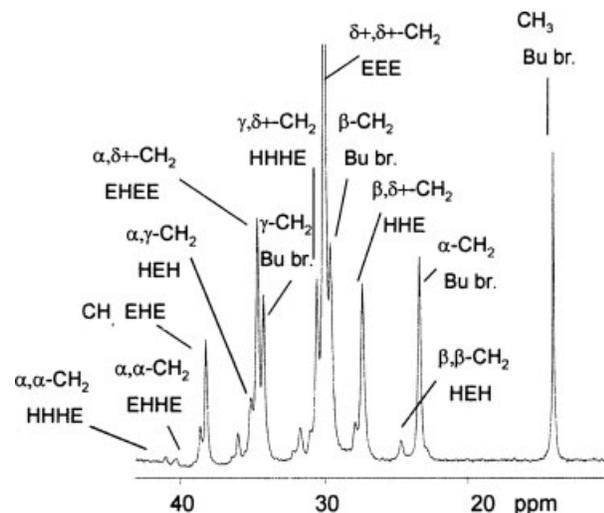


Figure 2. ^{13}C -NMR spectrum of ethylene/1-hexene copolymer produced with chromium oxide catalyst at 90°C , $C_{\text{Hex}}^{\text{copol}} = 26 \text{ mol } \%$.

contains several very small signals assigned to two types of end groups. The first type is the saturated end group $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—}$; its signals appear at 14.1, 22.9, and 32.2 ppm. The second type of chain ends is unsaturated end-groups, mostly $\text{CH}_2=\text{C}(\text{C}_4\text{H}_9)\text{—CH}_2\text{—CH}_2\text{—}$, the signals appear at 108.7 ppm for the $\text{CH}_2=\text{C}$ carbon atom (outside of the range in Fig. 2), 38.6 ppm for the $\alpha\text{-CH}_2$ -atom and at 27.8 ppm for the $\beta\text{-CH}_2$ -atom. The signal at 31.7 ppm is tentatively assigned to the $\alpha\text{-CH}_2$ -atom in the $\text{C}_4\text{H}_9\text{—CH=CH—CH}_2\text{—CH}_2\text{—}$ end group. The presence of both these types of $\text{C}=\text{C}$ bonds agrees with the IR data. There is no indication of “head-to-head” 1-hexene monomer pairs in the copolymer chains, $\sim\text{CH}_2\text{—CH}_2\text{—CH}(\text{CH}_4\text{H}_9)\text{—CH}_2\text{—CH}_2\text{—CH}(\text{CH}_4\text{H}_9)\text{—CH}_2\text{—CH}_2\sim$ sequences.

GC Data. Several ethylene/1-hexene copolymers were prepared with chromium oxide catalyst at high 1-hexene concentrations in solution. Linear α -olefins with even C_m , the same compounds that are formed in the ethylene homo-oligomerization reactions (see the previous section), remain the dominant oligomer products, and their distribution is only slightly sensitive to the presence of 1-hexene, see Figure 3.

GC analysis of heavier co-oligomers (starting with C_{16}) formed in the copolymerization reactions showed that, in addition to the linear α -olefins, two types of co-oligomers are present in sig-

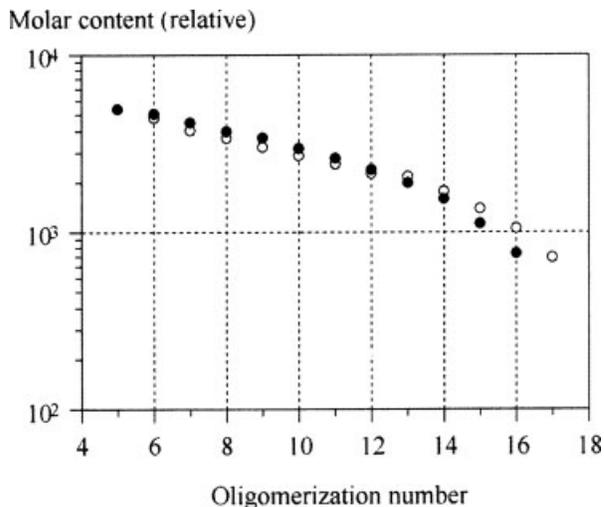


Figure 3. Distribution of oligomeric α -olefins in ethylene homopolymer (●) and in ethylene/1-hexene copolymer (○) produced with chromium oxide catalyst at 90°C and P_E of 10 atm in coordinates of eq 22.

nificant quantities (see one example of the C_{16} range in Fig. 4). The formation of these co-oligomer molecules can be readily explained by the standard scheme of ethylene/ α -olefin copolymerization reactions in Scheme 1, but it does not, by itself, represent a sufficient argument against the alkylidene mechanism in Scheme 2:

1. 2-Butyl-substituted α -olefins with vinylidene bonds, $\text{CH}_2=\text{C}(\text{C}_4\text{H}_9)\text{—R}$. According

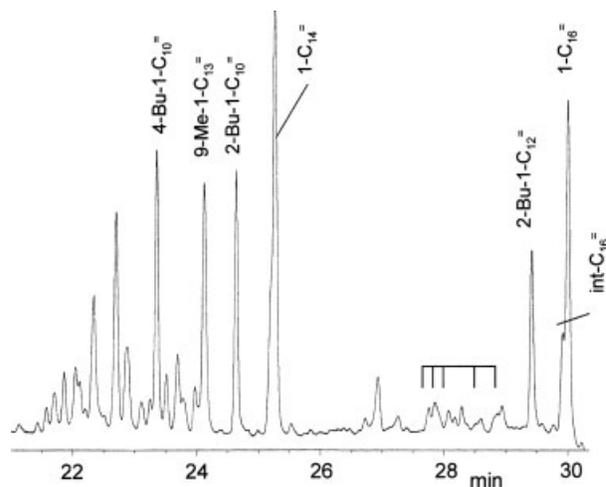


Figure 4. Gas chromatogram (C_{14} and C_{16} ranges) of ethylene/1-hexene co-oligomers produced with chromium oxide catalyst at 90°C in the absence of hydrogen. Expected co-oligomers in C_{16} range with a single 1-hexene unit are marked.

to Scheme 1, they are formed in ethylene chain growth reactions followed by Reaction 5 (primary insertion of 1-hexene) and Reaction 7 (chain transfer to ethylene).

- Linear olefins with internal double bonds, $C_4H_9-CH=CH-R$. They are formed in ethylene chain growth reactions followed by Reaction 6 (secondary insertion of 1-hexene) and Reaction 9 (chain transfer to ethylene). Judging by the relative yields of these two types of products, the probability of the secondary 1-hexene insertion into the $[>Cr-C]$ bond is less than one half of that for the primary insertion (i.e., the chromium oxide catalyst exhibits relatively poor regio-selectivity) and, apparently, all such secondary insertion steps are immediately followed by chain transfer.

Oligomer molecules with one 1-hexene unit in central positions in the chains, $CH_2=CH-(CH_2-CH_2)_x-CH_2-CH(C_4H_9)-(CH_2-CH_2)_y-H$, which are expected in standard ethylene/1-hexene copolymerization reactions in Scheme 1, are formed with relatively low yields. They are marked in Figure 4 (in the C_{16} range) and include 4-, 6-, 8-butyl-1-dodecenes and 10-ethyl-1-tetradecene. Oligomers formed in a series of steps starting with Reaction 11 followed by several ethylene insertion reactions are indistinguishable from ethylene homo-oligomers, linear α -olefins. However, if 1-hexene is inserted into $[>Cr-C]$ bond in the secondary orientation during the chain transfer (Reaction 12), subsequent ethylene insertion reactions lead to the formation of experimentally observable end-methyl-branched products, for example, 11-methyl-1-pentadecene.

Evidence for Standard Polymerization Mechanism

Conceptually, several differences between the two possible olefin polymerization mechanisms, the standard mechanism in Scheme 1 and the mechanism based on alkylidene centers in Scheme 2, can be subjected to experimental verification. Two of the differences are the most significant. First, the starting chain end according to the alkylidene mechanism in Scheme 2 is an unsaturated $C=C$ chain end, and the presence of hydrogen in the polymerization reactions cannot affect its formation. However, as the data in earlier section demonstrate, n -alkanes with even C_m , the $H-(CH_2-CH_2)_n-H$ oligomers with $m = 2n$, are

indeed formed in these reactions at significant P_H/P_E ratios, the fact that argues in favor of the standard reaction mechanism.

Second, the alkylidene mechanism does not provide a route for the formation of olefin dimers because the metallocyclobutane species in Scheme 2 is assumed to be quite stable and only the formation of a metallocyclohexane species can lead to chain separation from the active center. Consequently, the smallest possible ethylene oligomer according to this mechanism is the trimer, 1-hexene. Verification of this feature in ethylene homopolymerization reactions is difficult. GC analysis of freshly collected light reaction products indeed shows the presence of small quantities of 1-butene, a small peak immediately following the peak of dissolved ethylene. The generated 1-butene copolymerizes with ethylene. ^{13}C -NMR spectra of ethylene/1-hexene copolymers show very small resonances of isolated 1-butene units, in particular, the CH_3 signal at ~ 11.3 ppm and CH at ~ 40.4 ppm. The 1-butene content in the polymers is very low, <0.1 mol %.

The standard mechanism, in contrast to the alkylidene mechanism, also allows for dimer formation in polymerization reactions of higher α -olefins. This route was investigated in polymerization reactions of 1-hexene and 1-octene.

The oligomerization reaction of 1-hexene with chromium oxide catalyst was carried out in neat monomer at $80^\circ C$ for 5 h. GC analysis of the liquid products allowed the identification of five types of oligomers:

Oligomer Weight ratio	Dimer	Trimer	Tetramer	Pentamer	Hexamer
	1	0.48	0.34	0.22	0.14

The two most abundant dimer molecules have the structures expected from the standard reaction scheme, 2-butyl-1-octene (Reaction 11 followed by Reaction 5 and a chain transfer reaction) and a linear C_{12} olefin with an internal $C=C$ bond (Reaction 11 followed by Reaction 6 and a chain transfer reaction).

The oligomerization reaction of 1-octene with chromium oxide catalyst was also carried out in neat monomer at $90^\circ C$ for 1 h. GC analysis of the oligomer mixture clearly showed the presence of 1-octene dimers, C_{16} products. Four dimer molecules were identified, 2-hexyl-1-decene, the product of double bond isomerization in

it, and two linear hexadecenes with internal double bonds. The formation of these products is readily explained by the standard reaction scheme as well.

These observations are also in agreement with the published data on the structure of 1-decene oligomers produced with a similar chromium oxide catalyst.³⁷ After the oligomer mixture prepared in these reactions was hydrogenated and distilled into fractions, both the dimers (C₂₀ fraction) and the trimers (C₃₀ fraction) were isolated. Two hydrogenated dimers with the structures expected from the standard reaction scheme were formed in comparable amounts, 9-methylnonadecane (hydrogenation product of 2-octyl-1-dodecene, the “head-to-tail” dimer), and *n*-eicosane (hydrogenation product of eicosenes with internal double bonds, “head-to-head” dimers). The ratio between the products varied depending on the reaction temperature. The structures of the hydrogenated trimers also agreed with the reaction steps in Scheme 1.

Olefin Trimerization Reactions

Co-oligomers of ethylene and 1-hexene produced with chromium oxide catalyst contain, in addition to the expected linear α -olefins and the co-oligomers described in the previous section, several olefins in the C₁₀ and C₁₄ ranges in excessively high quantities. Differences between the C₁₀ and the C₁₂ range (Fig. 5) and between the C₁₄ and the C₁₆ range (Fig. 4) reveals the presence of these new products, which are attributed to a special type of oligomers formed in olefin trimerization reactions.

Several chromium-based homogeneous and supported catalysts selectively trimerize ethylene to 1-hexene.^{38–40} The mechanism of this reaction is principally different from the mechanism of ethylene polymerization reactions with transition metal catalysts shown in Scheme 1; it involves oxidative addition of two ethylene molecules to the Cr(II) species with the formation of a relatively stable chromacyclopentane intermediate, as shown in the first line in Scheme 3. The insertion of the third ethylene molecule into the [$>$ Cr—C] bond in this metallocycle irreversibly produces a less stable chromacycloheptane intermediate,^{41a} which expels a 1-hexene molecule either in a reductive elimination reaction^{38,39,41b} or in a concerted 3 \rightarrow 7 H-shift in the chromacycloheptane ring.^{41a}

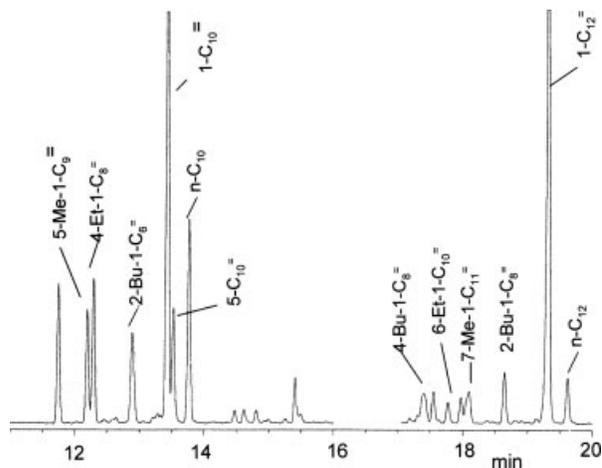
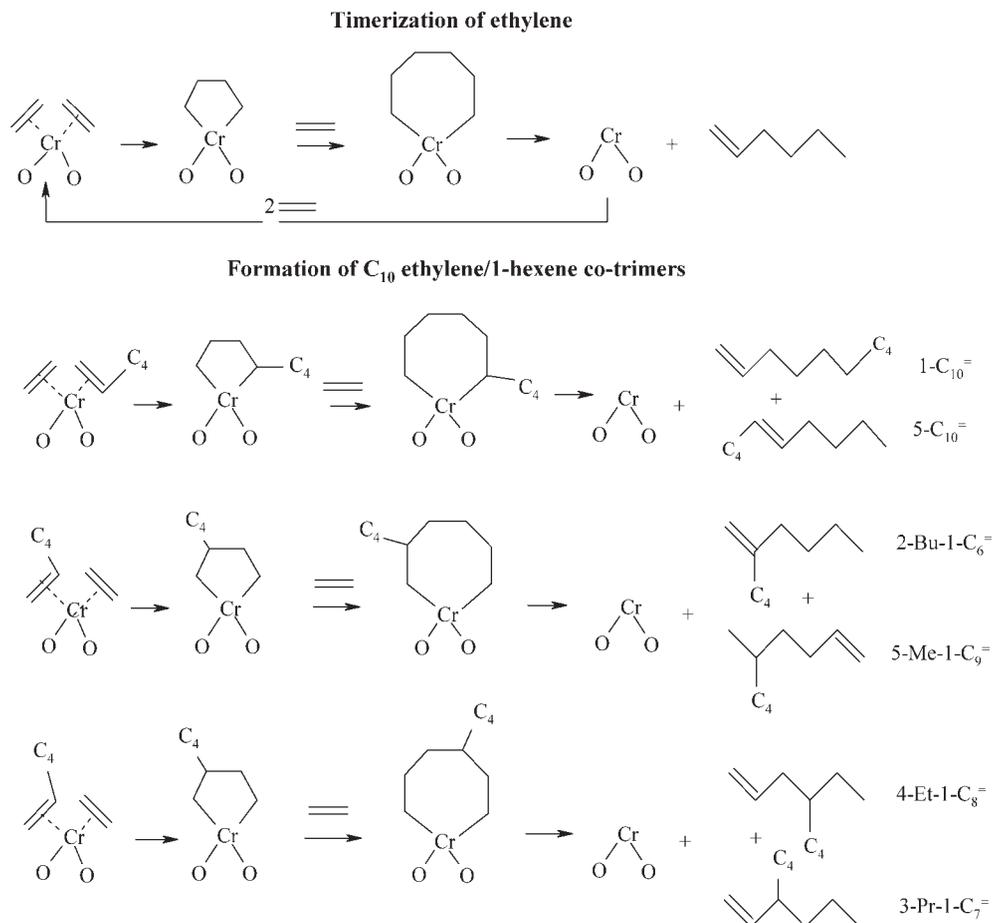


Figure 5. Gas chromatogram (C₁₀ and C₁₂ ranges) of ethylene/1-hexene co-oligomers produced with chromium oxide catalyst at 90 °C, $P_H/P_E = 0.2$.

Some active centers in freshly prepared chromium oxide polymerization catalysts also apparently contain a small number of similar trimerization centers. Ethylene trimerization with these catalysts was clearly observed at the early stages of ethylene homopolymerization reactions.⁴² Our data for the C₁₀ and C₁₄ oligomers indicate that the trimerization reaction can also involve α -olefin molecules. Scheme 3 shows the structure of possible cotrimerization products in the simplest case, one 1-hexene molecule and two ethylene molecules. Six such C₁₀ cotrimers can be expected to form, and, indeed, five C₁₀ products are present in the mixture in comparable amounts, as shown in Figure 5; whereas the sixth possible cotrimer, 1-decene, is indistinguishable from the ethylene pentamer. Four of the products can be positively assigned to the cotrimers predicted by Scheme 3. The situation is more complex for the C₁₄ products: eight types of cotrimers containing two 1-hexene molecules and one ethylene molecule can be potentially formed, three of which (*trans*-5-tetradecene, 2-butyl-1-decene, 4-butyl-1-decene) are identified. The combined yield of the ethylene/1-hexene cotrimerization products constitutes merely 0.02–0.1% of the polymer yields, depending on reaction conditions, but GC identifies these compounds with ease (Some C₁₀ and C₁₄ cotrimers were also reported in the products of ethylene trimerization with special homogeneous chromium-based catalysts⁴⁰ but their structures were not determined).

The ethylene trimerization reaction produces 1-hexene, and the latter copolymerizes with



Scheme 3. Mechanism of trimerization reactions.

ethylene. This auto-copolymerization reaction explains the formation of very small (but still clearly observable) amounts of ethylene/1-hexene co-oligomers in ethylene homopolymerization reactions with chromium oxide catalyst, such as 2-butyl-1-hexene in the C₁₀ range and 2-butyl-1-octene in the C₁₂ range.

Structure of Polymer Products Produced with Organochromium Catalyst

Organochromium catalysts are highly active in ethylene polymerization reactions. When these reactions are carried out under slurry conditions at 90–95 °C and $P_E \sim 12.5$ atm, the catalyst productivity ranges from ~ 3000 to 5500 g/g cat h. The catalyst contains several populations of active centers that differ in the molecular weights of the polymer components (Flory components) they produce. An example below gives a typical composition of an ethylene homopoly-

mer prepared with the organochromium catalyst used in these experiments in a two-hour reaction at 90 °C at $P_H/P_E = 0.15$ (average polymer parameters are as follows: $M_w^{av} = 6.65 \times 10^4$, $M_w/M_n = 8.0$, $I_2 = 13.1$, $I_{21}/I_2 = 39.1$):

Flory component	I	II	III	IV	V	VI
M_w	1.45	4.80	1.55	4.23	1.25	4.04
	$\times 10^3$	$\times 10^3$	$\times 10^4$	$\times 10^4$	$\times 10^5$	$\times 10^5$
Content (%)	1.7	8.6	32.2	34.2	16.9	6.3

Organochromium catalysts differ significantly in behavior compared to chromium oxide catalysts in two respects⁵: (a) the catalysts have very poor ability to copolymerize ethylene with α -olefins, and (b) the catalysts are quite sensitive to hydrogen; that is, the molecular weight of ethylene polymers they produce is greatly reduced in the presence of hydrogen.

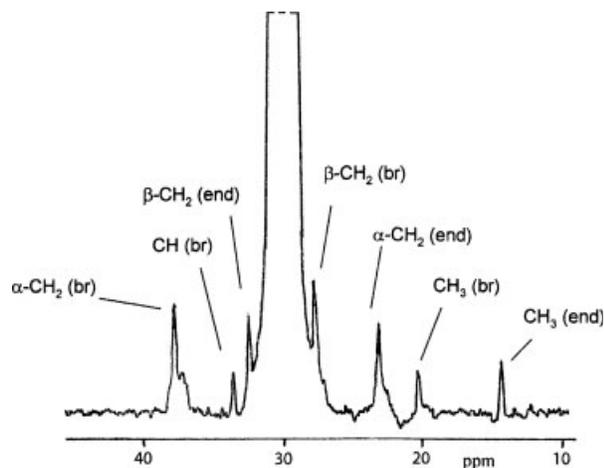


Figure 6. ^{13}C -NMR spectrum of ethylene homopolymer produced with organochromium catalyst in gas-phase reaction at 90°C in the presence of hydrogen.

Ethylene Homopolymers

^{13}C -NMR and IR Data. Figure 6 shows the ^{13}C -NMR spectrum of an ethylene homopolymer prepared with organochromium catalyst in the presence of hydrogen. The spectrum does not exhibit any evidence of double bonds. In addition to the large CH_2 resonance at ~ 30 ppm, two other groups of signals are present. They are the resonances from saturated chain ends at 14.1, 22.9, and 32.4 ppm (the same as those in the spectra of ethylene homopolymers prepared with chromium oxide catalysts, see earlier section), and the signals from isolated methyl branches in polymer chains, at 27.8, 37.7, 33.8, and 20.1 ppm.

These polymers can be viewed as ethylene/propylene copolymers with a low propylene content, ~ 0.13 mol % at 80°C and ~ 0.16 mol % at 95°C (the respective branching levels are 2.1 and 2.3 $\text{CH}_3/1000\text{C}$). The methyl branches are also observable as a band at 1376 cm^{-1} in the IR spectrum of the high molecular weight ethylene homopolymer produced in the absence of hydrogen (the polymer has very few end-methyl groups). While double bonds are practically undetected in the ^{13}C -NMR spectra, the vinyl double bond can still be observed in IR spectra of the polymers as a weak $\delta(\text{CH}_2=\text{CH})$ band at 908 cm^{-1} (this band has a very high absorption coefficient).

GC Data. Peaks from n -alkanes $\text{H}-(\text{CH}_2-\text{CH}_2)_n-\text{H}$ with even C_m ($m = 2n$) dominate the gas chromatograms of ethylene homopolymers

produced with organochromium catalyst in the presence of hydrogen. Their distribution with respect to the oligomerization number n in one of the experiments is shown in Figure 7. The γ value characterizing this distribution (see eqs 21 and 22) is ~ 0.89 , which corresponds to a weight-average molecular weight for the oligomer fraction of ~ 440 . As in the case of the oligomers prepared with chromium oxide catalysts, these oligomers constitute the low molecular weight end of Flory component I. The presence of two saturated chain-end groups in homopolymers and in oligomer molecules produced with organochromium catalyst in the presence of hydrogen is important evidence for the standard chain growth mechanism presented in Scheme 1. The starting saturated chain end is formed in Reaction 4 and the terminal saturated chain end is formed by hydrogenolysis of the $[\text{>Cr}-\text{C}]$ bond, Reaction 3. This mechanism also explains the presence of small amounts of linear oligomer molecules with vinyl double bonds in these products; they are produced in Reaction 2 in competition with Reaction 3. For example, in an experiment carried out at $P_{\text{H}}/P_{\text{E}} = 0.2$:

Oligomerization number n	5	6	7	8	9
$[\alpha\text{-Olefin}]:[n\text{-alkane}]$ ratio	0.15	0.17	0.15	0.13	0.14

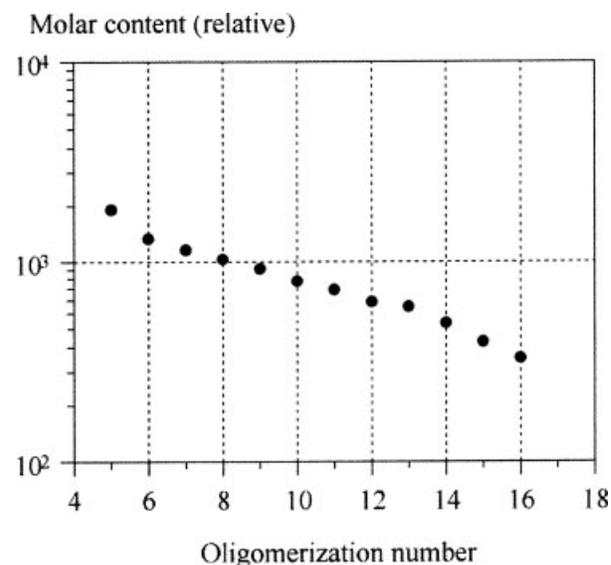


Figure 7. Distribution of oligomeric n -alkanes in ethylene homopolymer produced with organochromium catalyst at 90°C ($P_{\text{E}} = 10\text{ atm}$, $P_{\text{H}} = 2\text{ atm}$) in coordinates of eq 22.

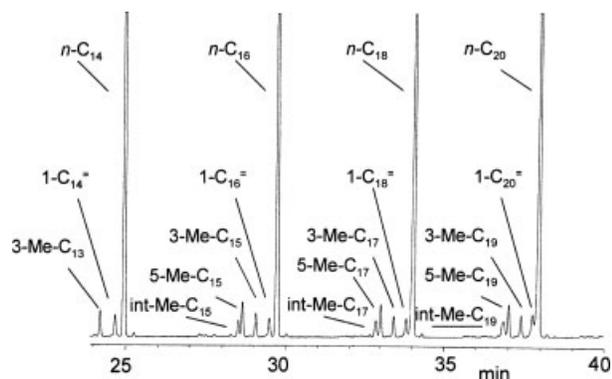


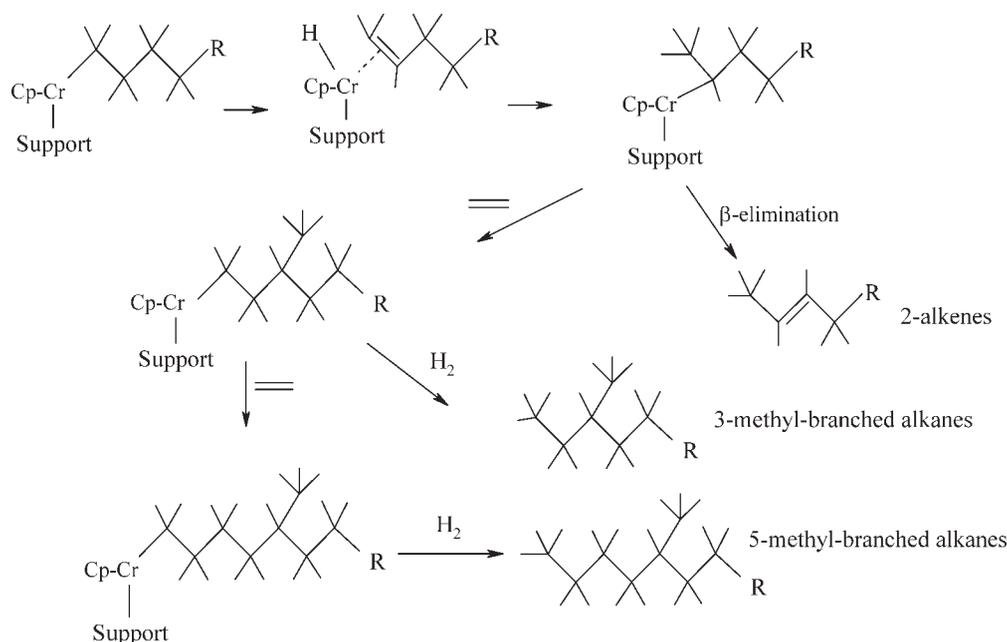
Figure 8. Gas chromatogram (C_{14} - C_{16} range) of ethylene homo-oligomers produced with organochromium catalyst in gas-phase reaction at $90\text{ }^{\circ}\text{C}$, $P_H/P_E = 0.2$.

In addition to these linear products, small amounts of mono-methyl-branched alkanes are also present in the gas chromatograms of homo-oligomers: 3- and 5-methyl-alkanes in the C_{10} and C_{12} ranges, 3-, 5-, and 7-methyl-alkanes in the C_{14} and C_{16} ranges, and 3-, 5-, and internal-methyl-substituted alkanes in the higher C_m ranges (see Fig. 8). Relative yields of the isomers in each C_m range are approximately equal. These isoalkanes are the low molecular weight analogs of polyethylene chains with isolated methyl branches produced with this catalyst, as described earlier. The same oligomers were

detected in extracts of ethylene polymers prepared in gas-phase polymerization reactions.

Scheme 4 shows the proposed mechanism of chain isomerization in ethylene homopolymerization reactions with organochromium catalyst. It is similar to the chain isomerization mechanism proposed for ethylene polymerization reactions with homogeneous metallocene catalysts^{43,44} and with homogeneous catalysts produced from α -diimine complexes of Ni and Pd.⁴⁵⁻⁴⁷ The chain isomerization starts with the transfer of a hydrogen atom from the β - CH_2 group of the growing chain to the Cr atom. The $\text{C}=\text{C}$ bond thus formed remains coordinated to the Cr atom; it rotates in the coordination sphere of the metal and re-inserts into the $[\text{>Cr}-\text{H}]$ bond in a secondary orientation. The new $[\text{>Cr}-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-]$ center either dissociates in a β -H elimination reaction (producing homo-oligomer molecules with terminal *trans*- and *cis*- $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2$ chain ends) or continues chain growth.

GC analysis of the ethylene homo-oligomers provides structural details of chain isomerization that cannot be deduced from the NMR data alone. Oligomers with methyl branches in the 3rd position, 5th position, and so forth, are formed in two different ways. Scheme 4 illustrates the first scenario, in which these types of methyl branches are produced in the final stages of



Scheme 4. Mechanism of chain isomerization in ethylene homopolymerization reaction with organochromium catalyst.

of oligomer formation. This scheme explains why particular types of methyl-branched alkanes are present in the oligomer mixtures rather than other possible branched products. The same types of methyl-substituted alkanes are formed if branching occurs early after the start of the chain growth. For example, chain isomerization after insertion of the second ethylene molecule into the [$>Cr-H$] bond produces 3-methyl-branched alkanes, isomerization after the insertion of the third ethylene into the [$>Cr-H$] bond produces 5-methyl-branched alkanes, and so forth. α -Olefins with branched alkyl chains expected from Scheme 4 (if chain transfer to ethylene occurs instead of chain transfer to hydrogen) are formed with very low yields and are virtually undetectable. The combined yield of the isomerized products (2-olefins + methyl-substituted alkanes) with respect to the corresponding linear products (n -alkanes + α -olefins) in reactions at 90 °C does not depend on the oligomerization degree:

Oligomerization number n	6	7	8	9	10
[Isomerized products]:	0.087	0.096	0.094	0.092	0.095
[linear products]					

Ethylene/1-Hexene Copolymers

¹³C-NMR and IR Data. ¹³C-NMR spectra of ethylene/1-hexene copolymers prepared with organochromium catalyst exhibit, in addition to resonances from saturated chain ends and methyl branches (the same as in the spectra of ethylene homopolymers, see Fig. 6), weak signals from butyl branches arising from 1-hexene units in the copolymer chains. These signals are most easily observed when the copolymers are prepared in the absence of hydrogen so that overlap with the signals from the end-CH₃ groups is minimal. The CH₃ resonance of the butyl branch appears at 14.1 ppm (coinciding with the end-group), that of the α -CH₂ group at ~23.5 ppm, the γ -CH₂ group at ~34.3 ppm, and the CH group at ~38.3 ppm. When such copolymers are prepared in the presence of hydrogen, only two of the signals are clearly observable, those of the α -CH₂ group in the branch and the CH group. Analysis of signal areas in the copolymer produced in a 2 h run at 90 °C at a very high

(C_{Hex}/C_E)^{mon} value of 1.45 gave a 1-hexene content in the copolymer of merely ~0.15 mol %, which corresponds to a very high reactivity ratio r_1 of ~1000. Similar estimations from the NMR spectra of other copolymers also give r_1 values in the range from ~900 to ~1100. Comparison with the r_1 value for the same monomer pair in copolymerization reactions with chromium oxide catalysts ($r_1 \sim 30^{18}$) indicates that the copolymerization ability of the organochromium catalyst is ~30–35 times lower.

GC Oligomer Data. The nature of the oligomeric products in ethylene/1-hexene copolymers produced with organochromium catalyst depends on the presence of hydrogen in the reaction. In the absence of hydrogen, the oligomers (which are formed with a very small yield, $\sum(C_{10} - C_{24}) = \sim 0.06$ wt %) are mostly linear α -olefins with even C_m , that is, the ethylene homo-oligomerization products expected according to Scheme 1 (Reactions 1 and 2). Small amounts of *cis*- and *trans*-2-olefins are also formed, as the side-products of chain-isomerization reactions (see Scheme 4). There are only two indications of a copolymerization reaction, namely, the formation of small amounts (10–12%) of 2-butyl-substituted α -olefins (2-butyl-1-hexene, 2-butyl-1-octene, etc., formed in Reaction 7) and linear alkanes with internal C=C bonds (clearly observable only in the C₁₀ range, formed in Reaction 9).

When hydrogen is present during the copolymerization reactions, the oligomer yields increase to ~0.4–0.5 wt %. The types of these oligomer molecules are practically indistinguishable from those in the ethylene homo-oligomers formed under the same conditions (see Fig. 8), they are mostly n -alkanes and linear α -olefins with even C_m and the products of chain isomerization, 3-methyl-substituted isoalkanes, 5-methyl-substituted isoalkanes, and so forth. The distributions of the n -alkanes and linear α -olefins are very similar (see Fig. 9) indicating the same mechanism of chain formation in the presence of two competing chain transfer reactions, to hydrogen (Reaction 3, the dominant reaction) and to ethylene (Reaction 2). The γ values for the n -alkane distributions in these reactions are the same as in the homopolymerization reactions, 0.87–0.90. Small quantities of 2-butyl-substituted α -olefins are also present in these oligomer mixtures. Their expected hydrogenation products, 5-methyl-substituted alkanes, are

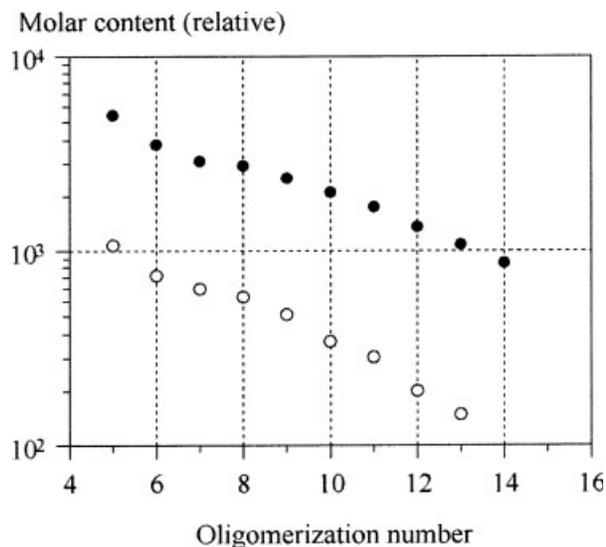


Figure 9. Distribution of oligomeric *n*-alkanes (●) and α -olefins (○) in ethylene/1-hexene copolymer produced with organochromium catalyst at 90 °C [$P_E = 10$ atm, $(C_{Hex}/C_E)^{mon} = 0.27$, $P_H = 2$ atm] in coordinates of eq 22.

indistinguishable from the isoalkanes present in the homo-oligomers, see Figure 8.

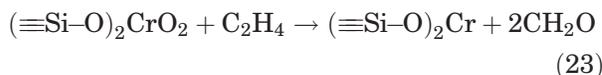
Overall, the data on the types of oligomers formed in ethylene homo- and co-oligomerization reactions are consistent with the standard mechanism of polymerization reactions outlined in Scheme 1 and cannot be reconciled with the mechanism shown in Scheme 2, which does not explain the formation of *n*-alkanes.

Olefin trimerization reactions described in earlier section are also observable in ethylene/1-hexene copolymerization reactions with organochromium catalyst (products in the C_{10} and C_{14} ranges, see Scheme 3), but the yields of these products are lower than in copolymerization reactions with chromium oxide catalyst.

Polymerization Mechanism

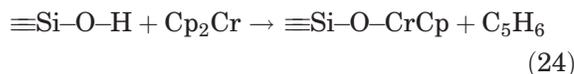
Conceptually, speculations about the mechanism of olefin polymerization reactions with chromium-based catalysts are based on more solid assumptions than in the case of heterogeneous Ziegler-Natta catalysts. Neither type of the chromium-based catalysts uses organoaluminum cocatalysts essential for the functioning of Ziegler-Natta catalysts. Additionally, and the chemistry of the initial Cr species in the catalysts is directly known from experimental studies. Chromium oxide catalysts are produced by reacting

chromium compounds (chromic acid, chromium nitrate, chromium acetate, etc.) with silanol groups on the silica surface followed by oxidation at high temperatures.^{1,4,5} The reaction produces Cr(VI) species, silyl monochromates (dominant at low Cr loadings) or bichromates.^{1,4} When these catalysts are used in ethylene polymerization reactions, the chromate species are reduced to Cr(II),¹ for example



The catalysts can be also activated with carbon monoxide^{1,4,5} which also reduces the Cr(VI) species to mixtures of Cr(II) and Cr(III).

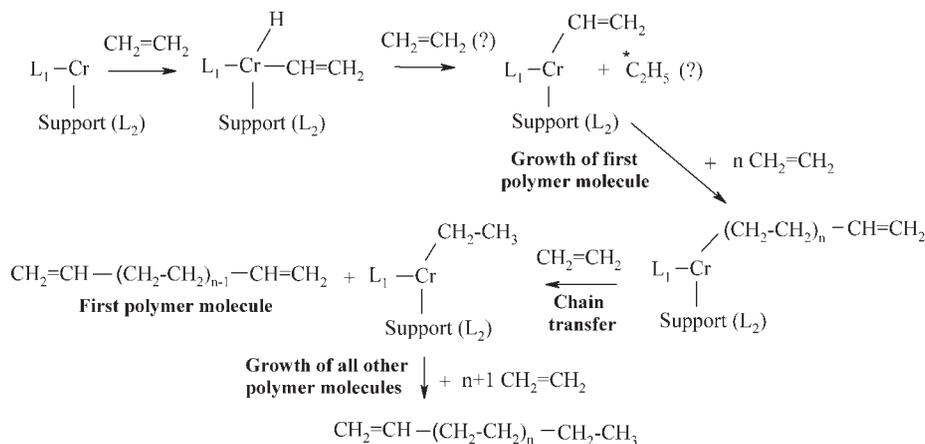
The starting Cr species in the organochromium catalyst used in this study is produced by reacting chromocene with silanol groups on the silica surface:



Scheme 5 shows the general features of the polymerization mechanism we propose based on the data discussed above. In both types of chromium-based catalysts used in the present study, the most reasonable mechanism of the first step of the active species formation involves oxidative addition of an ethylene molecule to the Cr(II) species. This reaction produces a Cr(IV) species, the common intermediate proposed both in the literature (Scheme 2) and in this study (Scheme 5). For example, the starting species in the alkylidene mechanism in Scheme 2, $(L_1)(L_2)\text{Cr}=\text{CH}-\text{CH}_3$, can be viewed as isomerization products of the starting species $(L_1)(L_2)\text{Cr}(\text{H})-\text{CH}=\text{CH}_2$ in Scheme 5.

In the present mechanism (Scheme 5), this Cr(IV) species is unstable and decomposes (possibly, via a radical route with the participation of a second ethylene molecule, the tentative second step in the scheme) into a Cr(III) intermediate, and the latter serves as the initiating species in the standard polymerization mechanism. σ -Bonded organic compounds of Cr(III) are known,⁴⁸ they are coordinatively unsaturated, a prerequisite for the coordination of the C=C bond of an α -olefin molecule prior to its insertion into the $>\text{Cr}-\text{C}$ bond.

The first polymer molecule formed by such an active center after the standard chain transfer reaction to ethylene (compare to Reaction 7 in



Scheme 5. Proposed mechanism of active center formation and polymerization reactions with chromium-based catalysts.

Scheme 1) will have vinyl bonds as both the starting and the terminal chain end. This may explain the absence (or very low intensity) of IR bands due to the methyl group at the earliest stages of ethylene polymerization reactions at low temperatures.^{10–14} However, in contrast to the literature (Scheme 2), all successive polymer chains formed according to the proposed mechanism in Scheme 5 will have saturated starting chain ends and unsaturated terminal chain ends, the same as in olefin polymerization reactions with Ziegler-Natta and metallocene catalysts. Both steps of active center formation in Scheme 5 are relatively difficult, which explains pronounced acceleration periods in ethylene polymerization reactions with chromium oxide catalysts.¹⁸

One of the L ligands in both types of chromium-based catalysts in Scheme 5 is a $\equiv\text{Si}-\text{O}-$ group. A large diversity of environment for such groups on the surface of calcined silica can account for a variety of different types of active centers. These centers are chemically similar and produce chemically similar macromolecules but they exhibit a significant variability in the probability of chain transfer to ethylene, Reaction 2, versus chain growth, Reaction 1. This variability explains the broad molecular weight distributions of polyethylenes prepared with both catalysts. The organochromium catalyst, with $L_1 = \text{Cp}$, is highly reactive in the chain transfer reaction to hydrogen (Reaction 3), as are most metallocene catalysts,⁵ whereas chromium oxide catalysts, in which both L ligands are $\equiv\text{Si}-\text{O}-$ groups, have quite low reactivity in this reaction.

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