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Alternating Copolymerization of Ethylene and Propylene: Evidence for Selective Chain Transfer to Ethylene

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ABSTRACT: C_1-symmetric *ansa*-metallocenes $Me_2E(Ind)(Flu)ZrCl_2$ (E = Si (**1**) and C (**2**)), upon activation with methylaluminoxane (MAO), produce atactic alternating ethylene−propylene copolymers (up to 92% EP dyads) with low molecular weight (less than 20K). Quantitative ^{13}C NMR analysis of copolymer chain ends produced with **2**/MAO indicates that the chain initiation/termination process is highly selective to generate a vinylidene as the unsaturated end group (terminating end) and an ethyl group as the saturated end group (initiating end). The high selectivity for *sec*-butyl end groups reveals a highly selective chain-initiation process where ethylene insertion is followed by propylene insertion at the initiating end. Chain transfer from a propylene-terminated polymer chain to a coordinated ethylene monomer is proposed to explain this selectivity. The facile cross-monomer chain-transfer process explains the much lower molecular weights obtained for the EP copolymers relative to the ethylene or propylene homopolymers.

Introduction

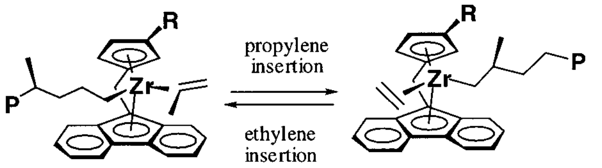
The development of well-defined polymerization catalysts has created new opportunities for the synthesis of olefin copolymers with uniform compositions and random sequence distributions.[1,2] The copolymerization of α-olefins with ethylene is a common means of tailoring the density and crystallinity of ethylene polymers: a current challenge is to tailor the copolymer sequence distribution and stereochemistry. Several groups have recently investigated strategies for controlling the sequence distribution in olefin copolymers. Galimberti has shown that, by tuning the substituents on certain *ansa*-metallocenes, ethylene−propylene copolymers with either alternating or blocky-type sequence distributions can be obtained.[1,3−6] Another approach exploits the dual coordination sites of C_1-symmetric metallocene catalysts to control the kinetic selectivities and thus the sequence specificities in olefin copolymerization. Bridged metallocenes with heterotopic coordination sites, such as $Me_2C(CpR)(9\text{-}Flu)ZrCl_2$,[7,8] $Et(Ind)(9\text{-}Flu)ZrCl_2$,[9−11] and *meso*-$Me_2Si(Ind)_2ZrCl_2$,[11] were shown to yield alternating copolymers of ethylene and α-olefins. These results were interpreted in terms of a mechanism involving the alternating insertion of olefins at the two heterotopic coordination sites (Scheme 1). The $Me_2C(CpR)(9\text{-}Flu)ZrCl_2$[8,12] and $Et(Ind)(9\text{-}Flu)ZrCl_2$[10] metallocenes were reported to yield isotactic, alternating ethylene−propylene copolymers, suggesting that it is possible to control both the sequence and stereoselectivity in olefin copolymerization.

In this paper, we report our investigations of the alternating copolymerization of ethylene and propylene with two *ansa*-indenyl/fluorenylmetallocenes $Me_2Si(Ind)(9\text{-}Flu)ZrCl_2$ (**1**) and $Me_2C(Ind)(9\text{-}Flu)ZrCl_2$ (**2**). Copolymers derived from **2** afford low molecular weight oligomers; analysis of the end groups of these alternating oligomers reveals a highly selective chain-transfer process, indicating that the sequence alternation is preserved during chain transfer.

Results

Metallocenes **1** and **2** were synthesized following procedures described in the literature.[13,14] Ethylene/propylene copolymerizations were conducted at 0 °C in liquid propylene with a constant overpressure of ethylene and kept to less than 5% conversion in propylene. Ethylene/propylene feed ratios were calculated from the fugacities and the partial pressures of ethylene and propylene.[15] The copolymerization results from metallocenes **1**−**2** activated with MAO are summarized in Tables 1 and 2. A typical productivity for the silicon-bridged metallocene **1**/MAO at 0 °C is ~ 20 000 kg/(mol of Zr h), with a tendency to increase with the increasing amount of ethylene in feed. The molecular weights of the polymers produced with metallocene **1** are modest (M_w ~ 12 000) for the 50/50 copolymer. The carbon-bridged metallocene **2** is less productive and yields oligomers with much lower molecular weights (M_w ~ 1500, ^1H NMR;Table 2) which remain constant over a range of total monomer pressures of 0.51−1.0 MPa.

Scheme 1. Proposed Two-Site Switching Insertion Mechanism (R = Me or *i*-Pr, P = Growing Polymer Chain)



The copolymer microstructure was investigated by quantitative ^{13}C NMR as described by Randall;[16] the sequence distribution at the triad level can be conveniently analyzed by the method of Kakugo.[17] A relatively narrow range of E:P feed ratios (0.02−0.26) was investigated to yield copolymers with compositions close to 50% ethylene. Representative ^{13}C NMR spectra of 50/50 EP copolymers are shown in Figure 1. Four major resonances at 20.11, 24.99, 33.35, and 38.05 ppm correspond to the four unique carbon atoms of an alternating ethylene−propylene copolymer;[18] the remaining resonances are due to resonances of carbon atoms of all possible sequence errors. In Figure 1b, a number of additional resonances are observed which we attribute to resonances corresponding to regioerrors and end groups (vide infra).

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Table 1. E/P Copolymerization Catalyzed by 1/MAO[a]

P_T (MPa)	E:P feed	%E plymr	diads[b] EE	EP	PP	r_e[b]	r_p[b]	χ[c]	prod[d]	$M_n \times 10^3$ (M_w/M_n)[e]
0.51	0.02	48.2	2.4	91.5	6.1	2.67	0.003	0.009	24 795	
0.54	0.033	49.3	4.1	90.4	5.4	2.77	0.004	0.011	20 535	12.3 (2.0)
0.57	0.049	52.4	6.6	91.5	1.9	2.95	0.002	0.006	64 000	
0.67	0.095	56.2	13.5	85.1	1.3	3.36	0.003	0.009	80 000	14.0 (2.0)

[a] Polymerization was conducted at 0 °C, with constant ethylene overpressure on liquid propylene. [b] Calculated by Kakugo's method.[17] [c] χ = EE[PP/(PE/2)^2]. [d] Prod = kg of EP/(mol of Zr h). [e] Measured by high-temperature GPC (135 °C).

Table 2. E/P Copolymerization Catalyzed by 2/MAO[a]

P_T (MPa)	E:P feed	%E[b] plymr	diads[b] EE	EP	PP	r_e[b]	r_p[b]	χ[c]	prod[d]	M_n[e]
0.51	0.02	43.1	2.8	82.5	14.7	3.44	0.006	0.024	3330	1450
0.63	0.076	50.2	6.6	85.2	8.2	2.05	0.015	0.03	13 749	1450
0.79	0.158	54.6	16.8	79.8	3.3	2.67	0.013	0.035	13 749	1430
0.91	0.21	59.2	24.3	72.7	3.0	3.18	0.017	0.055		1430
1.01	0.256	61.2	26.2	69.8	4.0	2.93	0.029	0.086	18 000	1450

[a] Polymerization was conducted at 0 °C, with constant ethylene overpressure on liquid propylene. [b] Calculated by Kakugo's method.[17] [c] χ = EE[PP/(PE/2)^2].[17] [d] Prod = kg of EP/(mol of Zr h). [e] Measured by ^{1}H NMR.

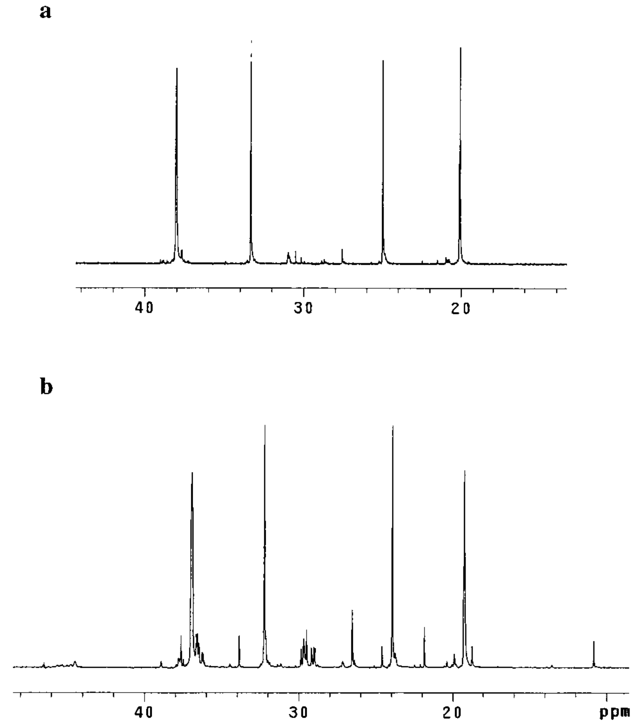


Figure 1. Spectra of EP copolymers: (a) **1**/MAO (44% E); (b) **2**/MAO (48% E).

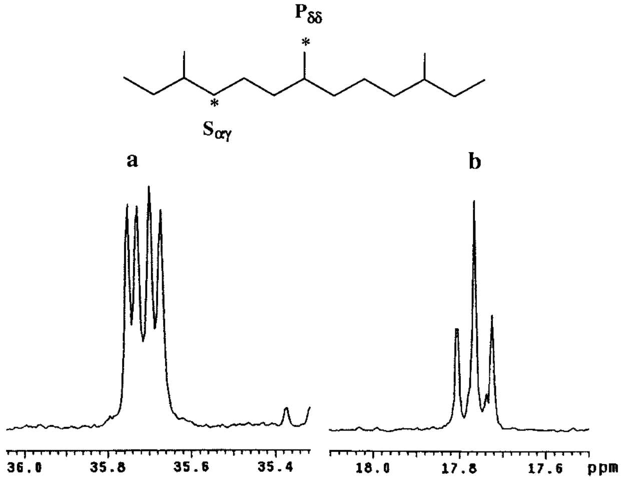


Figure 2. Atactic PEPEP by **1**−**2**/MAO: (a) $S_{\alpha\gamma}$ (mm:mr:rm:rr = 1:1:1:1); (b) $P_{\delta\delta}$ (mm:(mr + rm):rr = 1:2:1).

The diad distributions of the 50/50 copolymers made by **1**−**2**/MAO (Tables 1 and 2) reveal that the silicon-bridged metallocene **1**/MAO produces more highly alternating copolymers than the carbon-bridged metallocene **2**/MAO. The degree of alternation of the copolymers can be estimated by analysis of the sequence distributions using the parameter χ = EE[PP/(PE/2)^2].[19] This parameter is a measure of the deviation from a random sequence distribution, where values of $\chi < 1$ are indicative of an alternating sequence distribution while values of $\chi > 1$ are indicative of a blocky distribution. As shown in Table 1, the low values of χ for **1** (0.006−0.011) relative to those for **2** (0.024 to 0.086) indicate a higher degree of sequence alternation. (The sequence distributions and the calculated parameter χ did not include those resonances due to the chain end groups of the low molecular weight copolymers, which could cause some error in the measured or calculated sequence distributions.)

Copolymer Stereochemistry. Because of its highly alternating structure, the stereochemistry of the EP copolymer can be conveniently analyzed from the ^{13}C NMR spectra. The tacticity of the PE*P*EP sequences can be deduced from the multiplicity of resonances from the $S_{\alpha\gamma}$ and $P_{\delta\delta}$ carbon atoms. As shown in Figure 2, the ratio of $\mathrm{P^{m}E}P^{\mathrm{m}}\mathrm{EP}$, $\mathrm{P^{m}E}P^{\mathrm{r}}\mathrm{EP}$, and $\mathrm{P^{r}E}P^{\mathrm{r}}\mathrm{EP}$ resonances for the copolymer prepared from **1**/MAO (approximately 50% E incorporation) is 1:2:1, indicative of a stereorandom microstructure; copolymers prepared from **2**/MAO have similar microstructures.

Propylene Polymerization with 1/MAO: As previously reported,[13,20] metallocenes **1** and **2** polymerize propylene to low-tacticity isotactic polypropylenes; the ^{13}C NMR spectrum of the methyl region of polypropylene (produced under similar conditions at 0 °C in liquid propylene) reveals an isotactic pentad content of [mmmm] = 26% with a 2:2:1 ratio of pentads [mmmr]:[mmrr]:[mrrm] characteristic of isolated [rr] stereoerrors. The tacticity of the polymer depends on the monomer concentration: the isotacticity increases from 26% to 31% [mmmm] (±1.5%) as the propylene pressure is decreased from 0.80 MPa (liquid) to 0.14 MPa (in toluene) at 20 °C.

Table 3. M_w and Productivity Comparison between Copolymer and Homopolymers by 2/MAO

monomer/comonomer	[Zr] × 10^{-6} M	Al:Zr	activity (kg/(mol of Zr h))	$M_n \times 10^3$ (M_w/M_n)
E, 0.28 MPa, in toluene	1.0	2000:1	870	66.7 (4.7)[a]
P, liquid	1.0	2000:1	6750	4.2 (2.1)[a]
E(0.28 MPa) + P (liquid)	0.5	2000:1	17 400	1.4[b]

[a] Measured by gel permeation chromatography (135 °C). [b] Measured by^{1}H NMR.

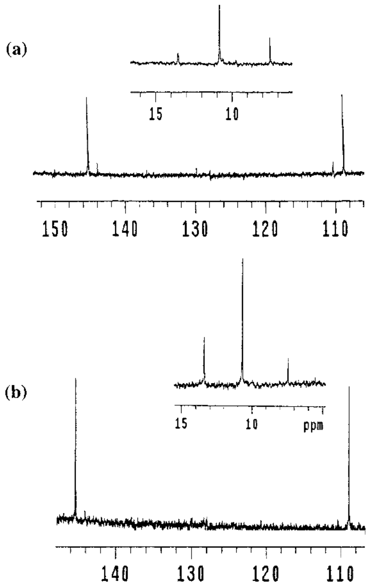


Figure 3. (a) ^{13}C NMR of chain end groups of copolymer (51% E) by **2**/MAO. (b) ^{13}C NMR of chain end groups of copolymer (64% E) by **2**/MAO.

Ethylene–Propylene Co- and Homopolymerization with 2/MAO: Ethylene and propylene polymerization reactions were carried out at 20 °C with **2**/MAO under similar conditions to those of the copolymerization reactions. Ethylene polymerization was carried out in toluene under 0.28 MPa of ethylene and propylene polymerization in liquid monomer. The productivity for the ethylene–propylene copolymerization reactions in liquid propylene with a 0.28 MPa partial pressure of ethylene is much higher than the sum of the ethylene and propylene homopolymerization productivities, but the molecular weights of the EP copolymers are much lower than either the ethylene or propylene homopolymers (Table 3).

Chain End Group Investigation with Copolymers by 2/MAO: The EP copolymers produced with **2**/MAO are of sufficiently low molecular weight that the end group structures can be conveniently analyzed by^{13}C NMR spectroscopy. Two representative end group spectra are shown in Figure 3 for copolymers containing 51 and 64 mol % ethylene, respectively. The set of resonances at 109 and 146 ppm have been assigned[21] to two olefinic carbon atoms of the vinylidene end group adjacent to an ethylene unit (polymer)–PEP$_t$ (Scheme 2, path a). A 1:2:1 triplet at 2.05 ppm in the ^{1}H NMR spectrum is indicative of allylic protons adjacent to a CH_2 group, consistent with an (EP$_t$) rather than a (PP$_t$) end group. Polymers prepared at ethylene contents above 45% E exhibit a minor set of resonances at 111 and 144 ppm corresponding to a (polymer)–EEP$_t$ end group (Scheme 2, path b). The major (polymer)–PEP$_t$ and the minor (polymer)–EEP$_t$ groups at the unsaturated chain end indicate a highly selective chain-transfer process: *chain transfer occurs selectively from propagating chain ending with a propylene unit.*

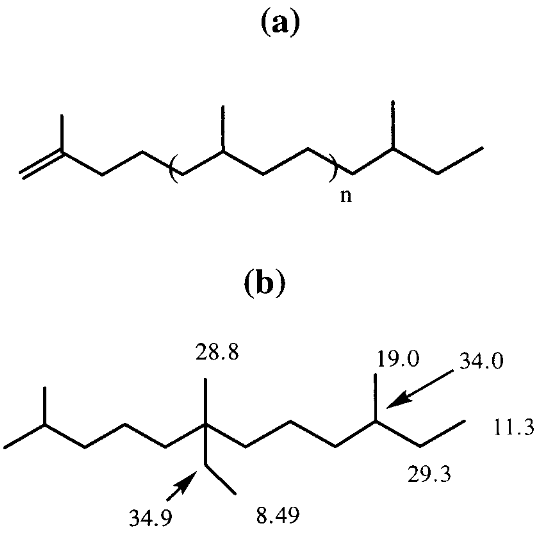
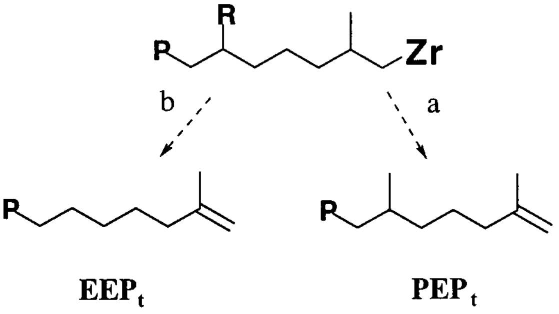


Figure 4. (a) Chain end groups of the copolymers made by **2**/MAO. (b) Proposed structure and calculated chemical shifts for quaternary branch and end group.

Scheme 2. Pathways for an EP Copolymer Chain To Undergo β-H Elimination or Transfer



The single resonance at 10.6 ppm (Figure 3a,b) is characteristic[21] of a primary carbon atom of a saturated ethyl group at the start of the chain, (polymer)–PE$_i$. For copolymers containing a higher percentage of ethylene (64%), an additional resonance appears at 13.4 ppm, corresponding to a *n*-alkyl end group (polymer)–EE$_i$. These data indicate that chain initiation is also highly selective, *initiating selectively with ethylene followed by propylene.* In summary, analysis of the end group structures reveals only two types of end groups (Figure 4a), indicating that the polymer chains selectively terminates after a propylene insertion and initiates with an ethylene, followed by a propylene.

An additional resonance at 7.4 ppm is observed in the spectra of polymers obtained from **2**/MAO (Figure 3). DEPT experiments reveal this to be a methyl group. On the basis of recent reports by Oliva[22,23] and calculated chemical shifts for a quaternary ethyl methyl branch (Figure 4b),[24] we assign this resonance to the terminal carbon atom of an ethyl group of quaternary carbon center.

Discussion

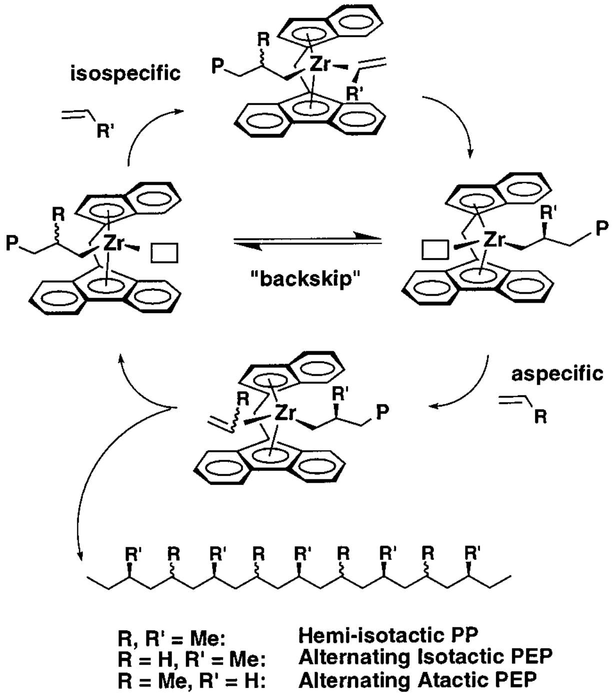
The properties of ethylene copolymers depend on the number and identities of comonomer units in the chain; incorporation of 1-butene, 1-hexene, and 1-octene comonomers is commonly used to control the density and crystallinity of polyethylene.[1,2,25] One of the advantages of metallocene and other single-site catalysts is their ability to generate random copolymers with uniform compositions. These new well-defined catalysts also present additional opportunities to develop catalyst systems for generating polymers of defined sequence distributions such as alternating[1,7−12,26,27] or blocky[1,4,5] copolymers.

Recently, several classes of metallocene catalysts have emerged which are able to generate alternating copolymers of ethylene and α-olefins such as propylene, hexene, and octene.[7−11,27] Two strategies have emerged for the synthesis of such copolymers: the first involves catalysts based on C_s-symmetric fluorenyl-ligated metallocenes. Alternating ethylene−propylene copolymers can be obtained from *ansa*-bisfluorenylmetallocenes[1,3,6,28] or $Me_2C(3,4\text{-}Me_2Cp)(fluorenyl)ZrCl_2$.[8] These metallocenes possess homotopic or enantiotopic coordination sites; the origin of the alternating tendency in these metallocenes is not known but is most reasonably attributed to a combination of low selectivity at the ethylene-terminated chain (low r_e) and high cross-propagation selectivity at the propylene-terminated chain (low r_p) according to either a first- or second-order Markov copolymerization mechanism.

The second strategy proposed for generating alternating copolymers involves the alternating insertion of the two olefin monomers at heterotopic coordination sites of C_1-symmetric metallocenes. This strategy has been reported by Soga for *meso*-$Me_2Si(indenyl)_2ZrCl_2$ and Et-(indenyl)(fluorenyl)$ZrCl_2$ metallocenes[9−11] and by Arndt, LeClerc, and Fan for $Me_2E(3\text{-}RCp)(fluorenyl)ZrCl_2$ metallocenes (E = C, R = Me (**3**), E = C, R = ^{i}Pr (**4**); E = Si, R = Me (**5**), E = Si, R = ^{i}Pr (**6**)).[7,8,12] This approach requires that the two sites exhibit different kinetic selectivities for the two monomers in order to generate an alternating structure at a given comonomer feed.

For any given catalyst system, it is difficult to establish whether the alternation is a consequence of the “single-site” mechanism or the “alternating-site” mechanism. We have argued that the stereorandom alternating copolymerization of ethylene and propylene with the $Me_2C(3,4\text{-}Me_2Cp)(fluorenyl)ZrCl_2$ metallocenes and the stereoselective alternating copolymerization with the $Me_2E(3\text{-}RCp)(fluorenyl)ZrCl_2$ is good evidence for the alternating-site mechanism for the latter catalysts.[12] In an effort to establish the structural factors that control both the sequence selectivity and stereoselectivity for the C_1-symmetric catalysts, we have investigated the *ansa*-metallocenes based on indenyl/fluorenyl ligands.[9,10] The 50:50 EP copolymers derived from **1** have a high degree of sequence alternation as shown by both the dyad distribution as well as the parameter χ[19,29] which ranges from 0.006 to 0.086 (Figure 1, Table 1). These metallocenes[9,10] yield more highly alternating copolymers than metallocenes based on 3-substituted cyclopentadienyl ligands $Me_2E(3\text{-}RCp)(fluorenyl)ZrCl_2$.[8,12] The nature of the bridge for the fluorenyl−indenyl metallocenes **1** and **2** has a significant influence on the activity and the molecular weight. The silicon-bridged metallocenes are more active and generate copolymers with higher molecular weight than those of their carbon-bridged congeners. However, to our surprise,[10,30] both metallocenes **1** and **2** generated atactic alternating EP copolymers (Figure 2) under conditions where metallocenes **3**−**6** generate isotactic alternating EP copolymers.[8,12] Thus, while the indenyl-based metallocenes **1** and **2** are more sequence selective than the cyclopentadienyl-based metallocenes **3**−**6**, they are unable to control the stereoselectivity of the copolymerization.

Scheme 3. Enantiomorphic Site Control Mechanism for 1−2/MAO-Catalyzed Polymerization



The fact that metallocenes **1** and **2** are stereorandom in EP copolymerization, in contrast to metallocenes **3**−**6**, suggests either that (1) metallocenes **1** and **2** do not possess a stereoselective coordination site or (2) these metallocenes possess a stereoselective coordination site, but propylene inserts at the nonstereoselective site during EP copolymerization or (3) stereoselective propylene insertion requires that the previously inserted unit is propylene. The fact that propylene polymerization with **1**/MAO yields poorly isotactic polypropylene ([mmmm] = 26% with isolated [mrrm] errors) and that **2**/MAO yields hemiisotactic polypropylene[20,31] argues that these metallocenes do possess a stereoselective insertion site in propylene homopolymerization. The propylene polymerization behavior of *ansa*-indenyl−fluorenyl metallocenes has been extensively investigated by Chien, Rausch, and Rieger,[32−36] who have argued that the stereoselectivity of these catalysts can be explained by the alternating insertion of propylene at a stereoselective and a nonstereoselective coordination site with frequent multiple insertions at the stereoselective site (Scheme 3).[37]

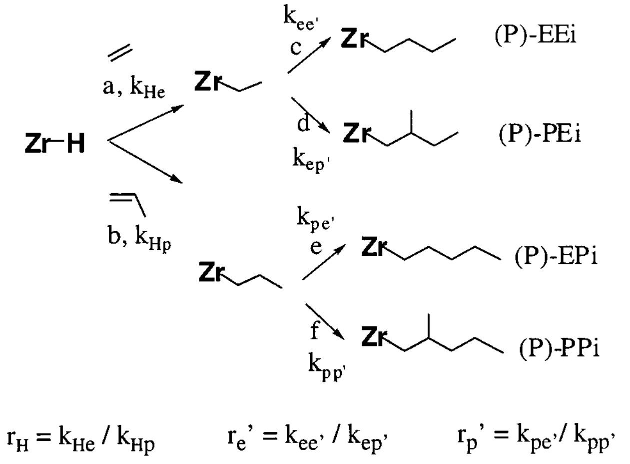
The highly alternating sequence distribution that we observe for the EP copolymers could be ascribed to an alternating-site mechanism where (in contrast to **3**−**6**) propylene inserts at the nonstereoselective site and ethylene inserts at the stereoselective site (Scheme 3). (Alternatively, it could be that the stereospecificity of these fluorenylmetallocenes requires that propylene be the last inserted monomer unit.) For an alternating-site mechanism, the higher degree of alternation for the copolymerization relative to propylene homopolymerization could be explained by less frequent “backskip” in the case of copolymerization due to the faster rate of copolymerization relative to propylene homopolymerization (Table 3).

Table 4. Comparison of Chain Structure and Chain-End Structure

entry	*f*(E:P)	E%	diads (%) EE:EP+PE:PP	diads (%) EEi:PEi
1	0.02	43.1	3:82:15	*a*
2	0.076	51.3	7:85:8	19:81
3	0.154	57.9	17:80:3	28:72
4	0.256	61.3	26:70:4	33:67
5	0.302	63.8	29:69:3	41:59

[a] NMR signal too weak to be integrated quantitatively.

Scheme 4. Pathways for a Polymer Chain Initiation via Chain Transfer to Monomer



An alternative interpretation is that these indenyl–fluorenyl metallocenes behave as single-site catalysts analogous to the bis(fluorenyl) metallocenes[1,3,6] and undergo multiple insertions at the nonstereoselective site. The similar tacticities of the EP copolymers prepared from the bis(fluorenyl)metallocenes[1,3,6] and metallocenes **1** and **2** do not allow us to distinguish between these two mechanistic interpretations. The single-site mechanism would require a higher selectivity for backskip in EP copolymerization than for propylene homopolymerization which seems unlikely at such high monomer concentrations, given what we know about the propylene polymerization behavior.[32–36,38–40] Further studies to discriminate between single-site and dual-site behavior with these metallocenes are in progress.

Chain Transfer. Analysis of the end group resonances of the low molecular weight copolymers produced with **2** reveals a highly selective chain-transfer process: the chains terminate selectively with propylene to give a vinylidene end group and initiate selectively to give an ethyl end group (Figure 4a). More significantly, the sequence alternation is preserved at the initiating end: saturated end groups derived from ethylene are followed by propylene monomer units. The degree of alternation of the end group dyads correlates well with those of the internal dyads (Table 4), indicating that the fidelity of the sequence alternation is preserved at the initiating end!

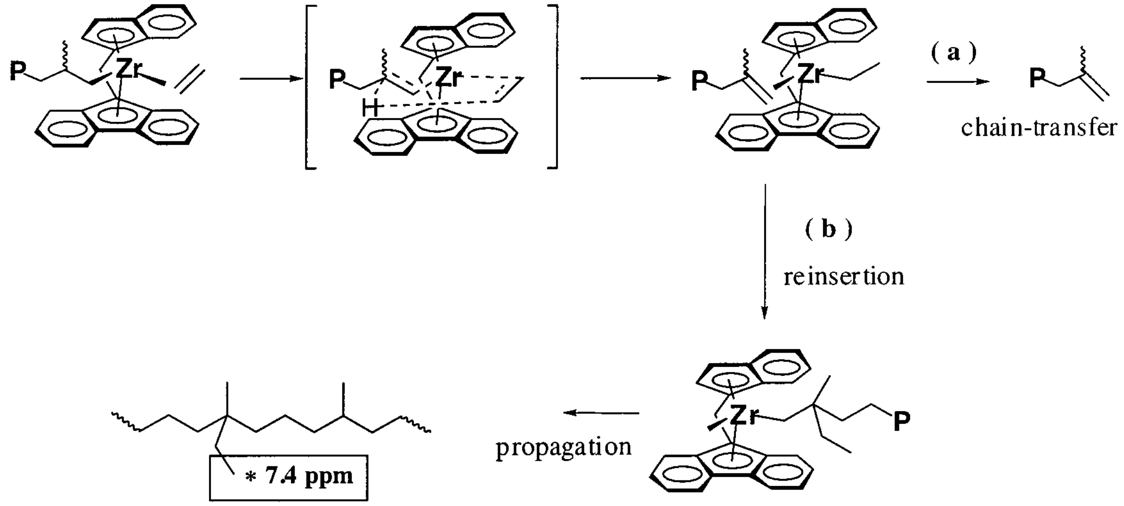
Two common chain-transfer mechanisms for metallocene-catalyzed polymerizations are β-H elimination (β-H transfer to the metal center) and β-H transfer to coordinated monomer (chain transfer to monomer).[41] The high selectivities we observe suggest that β-H elimination to generate a zirconium hydride (Zr–H) is unlikely for these catalysts (Scheme 4). If a Zr–H were formed, the selectivity for ethylene insertion into a metal hydride would have to be very large to generate exclusively an ethyl group at the start of a chain. (We do not observe any propyl or higher alkyl end groups.) For this to be true, $r_H = k_{He}/k_{Hp}$ (k_{He} and k_{Hp} are the rate constants of an ethylene and propylene to insert into Zr–H, respectively) would have to be much larger than $r_e = k_{ee}/k_{ep}$ (Scheme 4) since the feed ratios investigated are highly enriched in propylene. Furthermore, after the ethylene had inserted into the hydride, the selectivity for ethylene insertion into the Zr–Et bond (r_e') would now have to be much lower in order to selectively generate the (polymer)–PE_i end group. While we cannot rule out this possibility at this time, it does not appear reasonable to us that the selectivity for ethylene insertion into a metal hydride should be that much higher than the selectivity for ethylene insertion into a metal–polymer bond.

For these systems, we propose that chain transfer occurs by a selective β-H transfer to a coordinated ethylene (chain transfer to monomer, Scheme 5).[42] Support for this hypothesis comes from the insensitivity of the molecular weight to monomer pressure P_T (Table 2), characteristic of chain transfer to monomer.[2] The selective generation of the vinylidene end group and the ethyl initiating group would require that chain transfer occur selectively from a propylene-terminated chain to ethylene monomer (Scheme 5). The origin of this high selectivity is not clear, although a tertiary C–H would be expected to be a better H-donor than a secondary C–H bond[42,43] and ethylene is sterically a better acceptor than propylene. This facile cross-monomer chain-transfer process also explains the much lower molecular weights observed in EP copolymerization compared to either propylene or ethylene homopolymerization (Table 3).

Quaternary Branching. Oliva et al. have recently identified quaternary diethyl branches in polyethylenes produced from *meso*-EBIZrCl_2.[22,23] These diethyl branches were identified by characteristic ^{13}C NMR chemical shifts at 7.9, 23.4, 28.8, 31.0, 36.4, and 37.6 ppm and were attributed to a mechanism involving a sequence of chain-transfer events to ethylene, coupled with the insertion of the olefinic terminus into the ethyl group formed by chain transfer.[22,23] The ^{13}C spectra of ethylene–propylene copolymers derived from **2** also show a resonance at 7.4 ppm, which we assign to the terminal carbon of an ethyl branch attached to a quaternary center (Figure 4b). On the basis of the selective chain-transfer chemistry we observe and chemical shift calculations of model compounds (Figure 4b),[24] we tentatively assign this signal as arising from a quaternary ethyl–methyl branch.[44] The formation of this quaternary structure could arise by chain transfer of a propylene-terminated chain to ethylene followed by insertion of vinylidene-terminated polymer into the Zr–ethyl bond (Scheme 5b) in analogy to the mechanism proposed by Oliva.[22]

The high selectivity that we observe for chain transfer from a propylene-terminated polymer chain to a bound ethylene leads to very specific end groups on these ethylene–propylene oligomers (Figure 4a). This selectivity helps explain the formation of quaternary centers and the much lower molecular weights we observe in copolymerization relative to homopolymerizations (Table 3). The latter results in particular implies that chain transfer to ethylene might be quite common in ethylene/α-olefin copolymerization,[45–51] particularly in those cases where the molecular weights for copolymerization

Scheme 5. Proposed (a) Chain Transfer to Ethylene and (b) Formation of Quaternary Branch with 2/MAO



are lower than the corresponding ethylene homopolymerizations.[7,52,53]

Conclusions. The copolymerization of ethylene and propylene with *ansa*-(indenyl)(fluorenyl)zirconocenes yields highly alternating EP copolymers. The carbon-bridged *ansa*-metallocene $Me_2C(Ind)(Flu)ZrCl_2$ generates EP oligomers with only vinylidene and ethyl end groups. In addition, the highly alternating sequence distribution of the polymer is preserved at both the initiating and terminating ends of the chain. ^{13}C NMR analysis of polymers provided evidence for quaternary branches in these alternating EP copolymers. The selective chain transfer of a propylene-terminated polymer chain to a coordinated ethylene is proposed to explain the selective formation of end groups and the formation of quaternary branches.

Experimental Section

General Consideration. All manipulations with organometallic compounds were conducted using standard Schlenk and drybox techniques. Complexes $Me_2Si(Ind)(Flu)ZrCl_2$ (**1**) and $Me_2C(Ind)(Flu)ZrCl_2$ (**2**) were synthesized according to literature procedures.[13,14]

Toluene was passed through two purification columns packed with activated alumina and supported copper catalysts. Polymerization grade ethylene and propylene gases were purchased from Matheson. Liquid propylene was obtained either from Amoco or purchased from Scott Specialty Gases. Both monomers were further purified by passage through two columns packed with activated alumina and supported copper catalyst. Methylaluminoxane (MAO), type 3A, purchased from Akzo Nobel, was dried in vacuo prior to use.

Propylene Homopolymerization. A 300 mL stainless steel reactor (Parr) equipped with a mechanical stirrer was evacuated, purged three times with Ar and three times with propylene by pressurizing and venting, and charged with 100 mL of liquid propylene. Propylene was cooled to the 0 °C, and polymerization was started by injection of zirconocene/MAO solution. All polymerizations were run for 20 min. The reaction was quenched by injection of 5 mL of methanol solution, and the reactor was slowly vented and opened. The polymer was stirred in methanol/5% HCl, washed with methanol, and dried in vacuo at 40 °C overnight.

Ethylene–Propylene Copolymerization. A 300 mL stainess steel reactor equipped with a mechanical stirrer was evacuated, purged three times with Ar and three times with gases propylene by pressurizing and venting, and charged with 100 mL of liquid propylene. Propylene was cooled to the reaction temperature and overpressurized with ethylene to the desired total pressure. After 30 min equilibration, polymerization was started by injection of zirconocene/MAO solution and proceeded for 20 min. Temperature control was necessary due to the exothermic nature of the reaction. Subsequent polymer work up was the same as in propylene homopolymerization.

Polymer Characterization. Polymer molecular weights and molecular weight distributions were determined by high-temperature gel permeation chromatography (GPC). ^{13}C NMR measurements was carried out on a Varian UI300 spectrometer. 150–200 mg of each polypropylene or copolymer sample was dissolved in 2.5 mL of *o*-dichlorobenzene/10 vol % benzene-d_6 in a 10 mm diameter tube. The spectra was taken at 100 °C using acquisition times of 0 s (polypropylene) and 5 s for copolymers (In the copolymer case, 2–3 mg of $Cr(acac)_3$ was added to each sample to shorten the relaxation time and ensure the quantitative result.) Chain end group analysis: 100 mg of each EP copolymer sample was dissolved in 1,1,2,2-tetrachloroethane/10 vol % d_4-1,1,2,2-tetrachloroethane in a 10 mm diameter tube. The spectra were taken at room temperature (to avoid double-bond isomerization) with acquisition time 20 s.

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