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Cyclocopolymerization: A Mechanistic Probe for Dual-Site Alternating Copolymerization of Ethylene and α-Olefins

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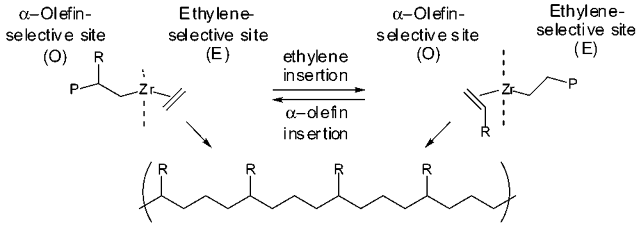
Metallocene catalysts have proven versatile for the synthesis of random ethylene/α-olefin copolymers with homogeneous and statistical sequence distributions.[1] Recently, we and others have sought to exploit the two heterotopic coordination sites of C_1-symmetric metallocenes for the copolymerization of ethylene and α-olefins to control the sequence distribution in ethylene/α-olefin copolymers (Scheme 1).[2,3] This strategy is based on the premise that the process of migratory insertion results in the movement of the polymer chain from one coordination site to the other.[4] If the kinetic selectivities of the two insertion sites are sufficiently different to discriminate the two comonomers, then alternating copolymers can be formed (Scheme 1).

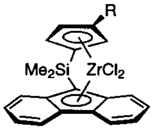
Scheme 1. Proposed Alternating-Site Mechanism



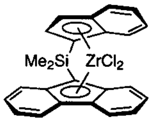
This dual-site hypothesis was recently invoked to explain the alternating copolymerization of ethylene and α-olefins with the C_1-symmetric metallocenes **2** and **3**.[2,3] This mechanism provides an appealing and potentially general strategy for the synthesis of copolymers of defined sequence distribution; nevertheless, recent reports that metallocenes **4** and **5** (possessing homo- or enantiotopic sites) can also produce alternating copolymers indicate that a dual-site mechanism is not necessary to generate alternating copolymers.[1b,2b,5]

To evaluate the viability of the two-site mechanism, we sought an independent experimental test for the involvement of both heterotopic sites in the alternating copolymerization of ethylene and α-olefins from metallocene **3.** To this end, we have investigated the copolymerization of ethylene with 1,5-hexadiene,[6] an α-olefin which, when it cyclopolymerizes, requires two insertion events to be incorporated into the chain (Scheme 2).[7−9]

The copolymerization of ethylene (E) with 1-hexene (H) or 1,5-hexadiene (HD) was carried out at 0.54 atm of ethylene at 20 °C in toluene solution at a variety of α-olefin concentrations. ^{13}C NMR analysis of the copolymer composition reveals that 1,5-hexadiene and 1-hexene are readily copolymerized with ethylene in the presence of metallocenes **1**, **3**, and **4**. Under these conditions ([HD] < 2.0 M), 1,5-hexadiene cyclopolymerizes almost exclusively to give methylene-1,3-cyclopentane units in the copolymers, with only traces of uncyclized 1,2-inserted hexadiene. The diastereoselectivity of the cyclocopolymerization favors the formation of *trans*-1,3-cyclopentane rings for metallocenes **1**, **3**, and **4** (74% trans, 81% trans, and 66% trans respectively).



1 R = H
2 R = Me



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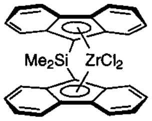

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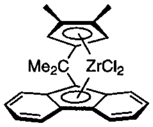

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For metallocenes **1** and **4**, the E/H and E/HD copolymerization yielded copolymers with similar comonomer compositions and sequence distributions[10] over a range of feed ratios (Table 1, entries 1−3 vs 11−13 and 8−10 vs 18−20). This result suggests that for catalysts derived from **1** and **4**, the copolymerization behavior of 1,5-hexadiene is similar to that of 1-hexene, even though the nature of the propagating polymer chain end after the insertion of the α-olefin is slightly different (i.e. a butyl branch vs a 1,3-cyclopentane unit). In contrast, the E/H and E/HD copolymers derived from metallocene **3** show very different compositions and sequence distributions over the range of feed ratios investigated. At comparable feed ratios, the E/HD copolymers obtained were enriched in the hexadiene comonomer and deficient in ethylene when compared to the corresponding E/H copolymers (Table 1, entries 4−7 vs 14−17).

Table 1. Copolymerization of Ethylene with 1-Hexene and 1,5-Hexadiene[a]

run	metallocene	olefin	[olefin] (M)	[Zr] (μM)	yield (g)	%*E*[b]
1	**1**	1-H	0.38	7.5	0.67	72
2	**1**	1-H	0.75	9.4	0.90	63
3	**1**	1-H	1.21	9.4	0.55	57
4	**3**	1-H	0.38	9.4	0.52	69
5	**3**	1-H	0.75	9.4	0.50	62
6	**3**	1-H	1.21	9.4	1.83	56
7	**3**	1-H	1.89	4.7	1.09	53
8	**4**	1-H	0.38	9.4	0.61	70
9	**4**	1-H	0.75	9.4	1.06	59
10	**4**	1-H	1.21	9.4	1.11	57
11	**1**	1,5-HD	0.38	7.5	0.22	75
12	**1**	1,5-HD	0.75	9.4	0.28	63
13	**1**	1,5-HD	1.21	9.4	0.23	60
14	**3**	1,5-HD	0.38	7.5	0.78	57
15	**3**	1,5-HD	0.75	9.4	0.56	47
16	**3**	1,5-HD	1.21	9.4	0.31	38
17	**3**	1,5-HD	1.89	7.5	1.44	21
18	**4**	1,5-HD	0.38	9.4	0.10	70
19	**4**	1,5-HD	0.75	7.1	0.10	61
20	**4**	1,5-HD	1.21	7.1	0.17	55

[a] Polymerization conditions: $T = 20$ °C, Volume $= 53$ mL, MAO $=$ 120 mg, 0.54 atm ethylene, polymerization time $= 10$ min. [b] Determined by ^{13}C NMR.

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Scheme 2. Proposed Dual-Site Alternating Mechanism in the Copolymerization of Ethylene with 1-Hexene or 1,5-Hexadiene

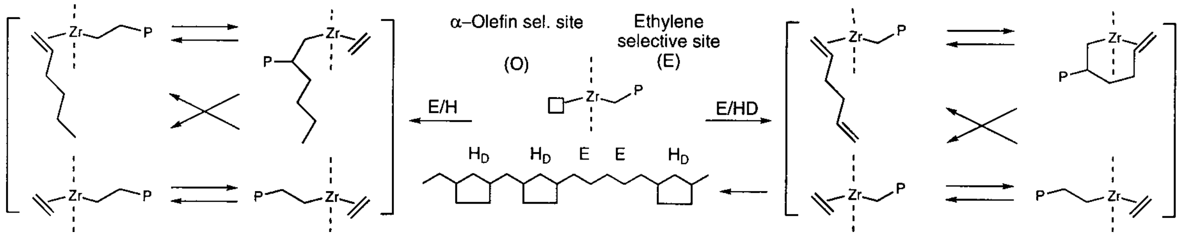

Table 2. Sequence Distribution (Dyads) and Breakdown of Ethylene Sequences for Selected Representative Copolymers

run	dyads (%)			ethylene sequences $H(E)_nH/H_D(E)_nH_D$ (%)		
E/H	HH	HE	EE	$n = 1$	$n = 2$	$n \geq 3$
1	2	50	47	39	19	42
3	9	67	24	61	22	17
4	2	58	41	54	8	38
7	4	85	11	86	4	10
8	1	58	41	43	20	37
10	3	80	17	71	19	10
E/H_D	H_DH_D	H_DE	EE	$n = 1$	$n = 2$	$n \geq 3$
11	1	46	53	31	23	45
13	4	68	29	57	21	22
14	23	40	37	8	59	33
17	65	24	11	18	72	9
18	0	58	42	43	24	33
20	2	81	17	72	19	10

The E/H copolymers from metallocene **3** exhibit highly alternating sequence distributions as previously observed for the copolymerization of ethylene with propylene,[2d] while the analysis of the ^{13}C NMR spectra of the E/HD copolymers reveals a significant fraction of HD−HD homosequences (Table 2).[6c,8] Analysis of the sequence distribution of the copolymers obtained from **3** reveals a predominance of odd-numbered ethylene sequences for the E/H copolymers (Table 2, entries 4 and 7 vs 1, 3, 8, 10) and a predominance of even-numbered ethylene sequences for the E/HD copolymers (Table 2, entries 14 and 17 vs 11, 13, 18, 20) compared to **1** and **4**.

The unique copolymerization behavior of **3** relative to that of **1** and **4** provides compelling if indirect support for a dual-site alternating copolymerization mechanism where one site is highly selective for ethylene and the other site is selective for the α-olefin (Scheme 2). For hexadiene (HD), the insertion of HD at the α-olefin site (O) followed by cyclization at the ethylene site (E) provides a mechanistic rationale for the inhibition of ethylene incorporation in E/HD copolymerization relative to E/H copolymerization with **3**. A two-step insertion−cyclization sequence returns the catalyst to the α-olefin selective site, explaining the larger number of HD−HD sequences in the E/HD copolymerizations relative to the H−H sequences observed in E/H copolymerizations with **3**. Furthermore, the strong suppression of the H_DEH_D sequences and enrichment in the H_DEEH_D sequences for **3** indicate that ethylene is preferentially incorporated in pairs (Table 2, runs 14 and 17). Even at low ethylene incorporation (run 17), we observed the paired ethylene sequence H_DEEH_D as the predominant ethylene sequence (>70%), implying that an occasional ethylene insertion at the α-olefin site is followed by a subsequent ethylene insertion at the ethylene site (Scheme 2).

The low percentage of even-numbered ethylene sequences in E/H copolymers derived from **3** (entries 4, 7 vs 8, 10) also implies a dual-site mechanism for hexene. For these copolymers, a dual-site mechanism would predict that an insertion of ethylene at the ethylene site followed by an occasional insertion of ethylene at the olefin site would be followed by another ethylene insertion, hence leading to a low probability of forming even-numbered ethylene sequences.

In summary, the cyclocopolymerization of 1,5-hexadiene and ethylene has provided an experimental test for a dual-site copolymerization mechanism as well as a new architecture for ethylene/1,5-hexadiene copolymers.

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Supporting Information Available: Representative ^{13}C NMR spectra of E/HD copolymers, peak assignments and. asequence distribution data for copolymers (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Calculated from dyads, $r_Er_H = 0.18$ and $r_Er_{HD} = 0.12$ for **1**; $r_Er_H = 0.035$ and $r_Er_{HD} = 0.020$ for **4**.

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