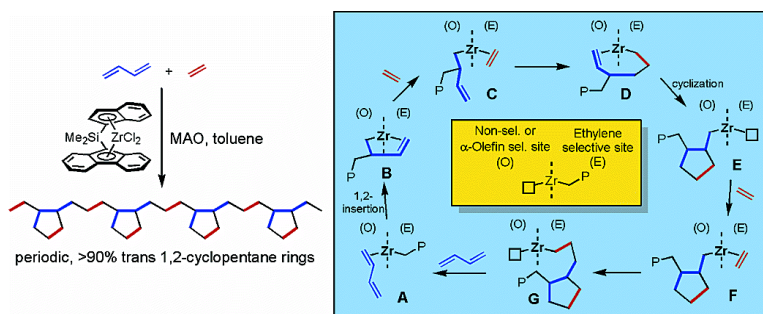


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J. Am. Chem. Soc., **2003**, 125 (30), 8970-8971 • DOI: 10.1021/ja034603x • Publication Date (Web): 03 July 2003

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The Dual-Site Alternating Cyclocopolymerization of 1,3-Butadiene with Ethylene

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The application of well-defined coordination compounds for the polymerization of olefins has created new opportunities for the preparation of novel polyolefins derived from common feedstocks.¹ The control of sequence distribution in olefin copolymerization remains a significant challenge: our ability to manipulate the sequence distribution in catalytic olefin polymerization remains rather limited.^{2,3} Metallocene catalysts possessing heterotopic insertion sites can yield highly alternating ethylene/ α -olefin copolymers when the kinetic selectivities toward the two monomers at the two sites are different.^{2,4} These dual-site catalysts provide an opportunity to generate a family of novel non-Markovian copolymers by taking advantage of multiple coordination sites with different kinetic selectivities toward two or more monomer units. In this communication, we report that the copolymerization of ethylene and butadiene^{5–9} with one of these dual-site catalysts provides a novel cyclocopolymer of ethylene and 1,3-butadiene containing 1,2-*trans*-cyclopentane units separated by three methylenes.

The copolymerization of ethylene and conjugated dienes was first reported by Natta;^{5,8} metallocene catalysts typically exhibit low activities and generate copolymers containing mixtures of unsaturated 1,4-enchained butadienes and cyclized 1,2-cyclopentane rings (Scheme 1).^{10–12} Highly alternating copolymers of ethylene and 1,4-enchained butadiene can be prepared with certain classes of Ti and V catalysts.^{5,7} Recently Longo reported the unprecedented cyclocopolymerization of butadiene and ethylene to generate 1,2-cyclopropane rings in the polymer chain. (Scheme 1).¹³

We envisioned that dual-site catalysts that generate alternating ethylene/ α -olefin copolymers might provide novel architectures for these copolymers if the selectivity of the two sites for ethylene and butadiene were different. To test this possibility, we have investigated the copolymerization of 1,3-butadiene and ethylene with *ansa*-zirconocenes Me₂Si(Cp)(Flu)ZrCl₂ (**1**), Me₂Si(1-Ind)(Flu)ZrCl₂ (**2**), and Me₂Si(Flu)₂ZrCl₂ (**3**) (where Cp = cyclopentadienyl; Ind = 1-indenyl; Flu = 9-fluorenyl) in the presence of methylaluminoxane (MAO). **1** and **3** possess two homotopic insertion sites, whereas **2** has heterotopic sites.

Copolymerizations were carried out in toluene at various ethylene and butadiene feeds at 25 °C; results are summarized in Table 1. The productivities are quite low, as is typical for most butadiene copolymerizations.^{9,11,12,14} The cyclocopolymerization of ethylene (E) and 1,3-butadiene (BD) with metallocene **2** gave rise to a completely saturated copolymer with an unusual periodic microstructure (see Scheme 2). The ¹³C NMR spectra gave no evidence for either vinyl groups derived from uncyclized 1,2-inserted butadienes or 1,4-enchained butadiene units. In the aliphatic region, resonances at 46.6, 36.3, and 24.5 ppm can be attributed to *trans*-1,2-cyclopentane units (approximately 90/10 *trans/cis*).¹¹ This high diastereoselectivity is consistent with that predicted from Stille's stoichiometric cyclizations of 4-alkyl hexenyl titanocenes.¹⁵ Resonances at 32.9 and 27.6 ppm suggest that these cyclopentane units

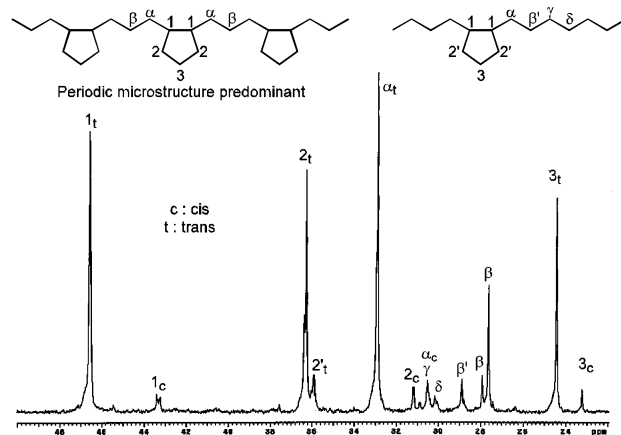
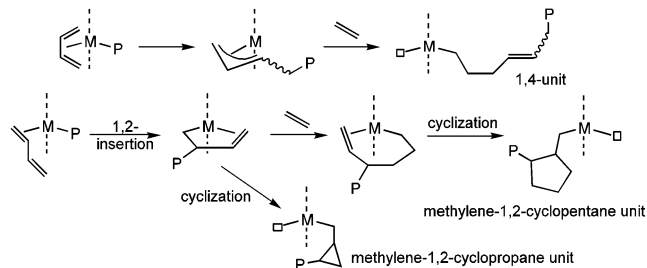
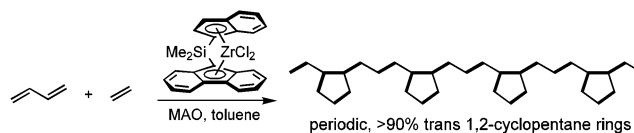


Figure 1. ¹³C{¹H} NMR spectrum of sample 2a from Table 1.

Scheme 1



Scheme 2. Cyclocopolymerization of Ethylene and 1,3-Butadiene



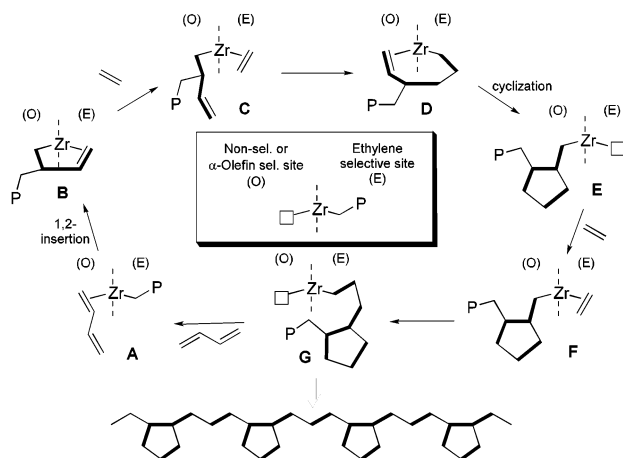
are separated predominantly by three methylenes (Figure 1). Notably, signals arising from multiple ethylene insertions were negligible, indicative of a highly regular microstructure that can be described as an alternating copolymer of ethylene and methylene-1,2-cyclopentane units where the cyclopentane units are comprised of one ethylene and one butadiene monomer. The level of butadiene incorporation approaches 33%, consistent with a 1:2 ratio of BD:E.

A comparison of the copolymers from **2** with those from the metallocenes **1** and **3** yielded striking differences. At comparable comonomer feeds (runs 1b, 2b, and 3b), **1** and **3** incorporate significantly lower amounts of butadiene. Metallocene **1** was the most active and generated both 1,2-cyclopentane units and 1,4-inserted butadiene units. For metallocene **3**, approximately 16% of the butadiene is cyclized into methylene-1,2-cyclopropane units, similar to the unusual results recently first reported by Longo.¹³

Table 1. Cyclocopolymerization of Ethylene with 1,3-Butadiene

Run No.	Metal-locene	P _E (psig)	BD in feed (mmol)	[Zr] (μM)	[Al]/[Zr]	Time (hr)	yield (g)	activity (kg/mol-Zr-hr)	BD in polym. (mol%)					
										(%) ^a	(%) ^a	(%) ^a	(%) ^a	(%) ^b
1b	1	8	93	438	240	1.25	1.34	74	12	14	trace	4	82	83
1d	1	30	35	52	1900	0.25	0.11	240	trace	trace	0	0	>99	n.d. ^c
2a	2	5	98	92	910	22	0.22	3	32	46	0	0	54	91
2b	2	8	90	150	570	5	0.33	11	31	44	0	0	56	91
2c	2	15	93	150	570	6	0.52	15	30	43	0	0	57	90
2d	2	30	35	107	920	2.25	0.33	39	22	28	0	0	72	90
3a	3	5	94	268	320	24	0.07	0.26	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c
3b	3	8	93	268	320	20	0.14	0.65	17	21	4	trace	75	90
3d	3	30	35	184	540	3	0.25	13	5	5	1	0	93	87

^a Relative abundances of various enchainment monomer units. ^b Mole fraction of cyclopentane rings trans. ^c Not determined.

Scheme 3

There seems to be a relation between the ligand steric bulk and the propensity of butadiene to cyclopropanate.¹³

The high degree of saturation of these butadiene copolymers suggests that butadiene undergoes a selective 1,2-insertion to generate a homoallylic intermediate (Schemes 1, 3);¹³ subsequent insertion of ethylene followed by cyclization generates a 1,2-cyclopentane structure.^{10–12}

The highly alternating cyclocopolymerization of butadiene and ethylene appears to be specific to the unsymmetrical metallocene **2**. At butadiene compositions approaching 33%, there is little evidence for multiple ethylene insertions (Figure 1: γ , δ peaks) or adjacent 1,2-cyclopentane units, indicating that ethylene inserts selectively after the cyclization and butadiene inserts selectively following an exocyclic ethylene insertion. We propose that this high selectivity can be explained by a dual-site mechanism where butadiene inserts and cyclizes at one coordination site and ethylene inserts at the other coordination site (Scheme 3). For the butadiene copolymerizations, selective 1,2-insertion of butadiene at the olefin-selective site (A→B), followed by an ethylene insertion at the ethylene site (B→C→D) allows the cyclization of the pendant olefin to occur at the olefin-selective site (D→E). Subsequent insertion of ethylene at the ethylene-selective (E→F→G) site generates an exocyclic ethylene unit and completes the cycle to generate intermediate A.

We have recently shown that the cyclocopolymerization of 1,5-hexadiene and ethylene with metallocene **2** generates multiple hexadiene sequences since cyclocopolymerization of α,ω -dienes require two insertion events; in this case cyclization of hexadiene competes with ethylene insertion at the ethylene site.⁴ The cyclo-

copolymerization of 1,3-butadiene with two ethylenes involves four insertion events, and leads to a new class of alternating cyclocopolymers. These results reveal that the application of multisite catalysts is a viable strategy for the synthesis of novel copolymers with non-Markovian sequence distributions.

Acknowledgment. We thank the National Science Foundation for financial support (CHE-9910240), Wendy Fan for metallocene samples and Peter Fox at Dupont Dow Elastomers for GPC and DSC analysis.

Supporting Information Available: Detailed experimental procedures, copolymer data, and ¹³C NMR spectral data and assignment (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA034603X