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Insertion/Isomerization Polymerization of 1,5-Hexadiene: Synthesis of Functional Propylene Copolymers and Block Copolymers

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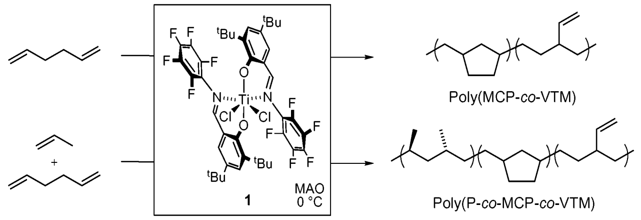
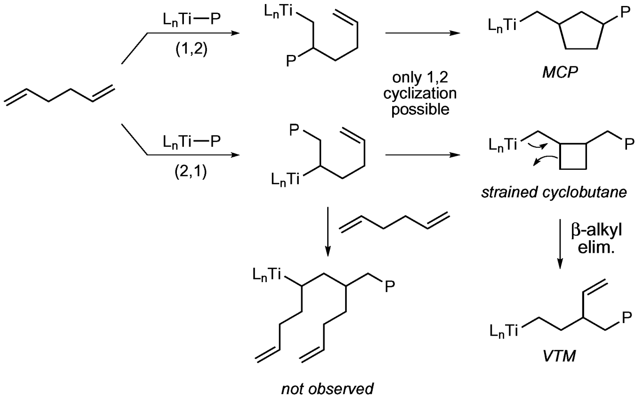
Remarkable advances in olefin polymerization have been achieved over the past two decades, largely due to the development of homogeneous catalysts. Single-site catalysts are now available that polymerize α-olefins with unprecedented degrees of control over stereochemistry and polymer architecture.[1] A number of catalysts have recently been reported to polymerize olefins in a living fashion, allowing the synthesis of new polyolefin-based materials.[2] Despite these remarkable advances, synthesis of functional polyolefins using Ziegler−Natta catalysts remains a longstanding scientific challenge. The two strategies most commonly employed toward this goal are direct copolymerization of olefins with functional monomers[3] and postpolymerization modification.[4] Direct copolymerization has been met with limited success due to catalyst poisoning and interactions of the catalyst with Lewis basic monomers. However, recent developments in late transition metal catalysts have provided improved routes to functional polyolefins.[5] Despite recent advances in alkane C−H activation, modification of preformed polyolefins is also problematic due to the inert nature of the hydrocarbon polymer and lack of control over composition and microstructure.[4,6] A third approach that has received attention in recent years involves controlled incorporation of a reactive moiety that provides easy access to a wide range of functionality through chemical modification.[7,8] Along these lines, we present here a methodology for the synthesis of vinyl-functional polyolefin copolymers and block copolymers with narrow polydispersities through the insertion/isomerization polymerization of 1,5-hexadiene.

Our group, as well as researchers at Mitsui, has recently reported bis(phenoxyimine) titanium catalysts for the syndiospecific and, in some cases, living polymerization of propylene (P).[9,10] Subsequent reports by Fujita,[11] Pellecchia,[12] as well as our group[13] revealed that an unusual secondary (2,1) insertion mechanism was operating in the polymerization. In our studies, we found that cyclopolymerization of 1,6-heptadiene was a useful method for determining the regiochemistry of propagation.[13] We were interested in studying the effect of this unusual mechanism regarding the polymerization of other nonconjugated diolefins. As part of this investigation, we polymerized 1,5-hexadiene (HD) with the fluorinated bis(phenoxyimine) catalyst system **1**/methylaluminoxane (MAO). Addition of **1** to a toluene solution of HD and MAO at 0 °C resulted in rapid polymerization, giving a soluble polymer with $M_n = 268\,000$ g/mol and narrow polydispersity ($M_w/M_n = 1.27$) (Table 1). Analysis of the ^{1}H and ^{13}C NMR spectra of the polymer revealed a high level of unsaturation; however, the shifts were consistent with vinyl substituents instead of the expected 3-butenyl groups of poly(1,2-hexadiene). Further analysis revealed that the polymer microstructure contained methylene-1,3-cyclopentane[14] (MCP) units (63%) as well as 3-vinyl tetramethylene (VTM) units (37%) (Scheme 1).[15] Doi and co-workers reported that vanadium-based catalysts produce nearly identical poly(1,5-hexadiene) with MCP units; however, different unsaturated 1-vinyl tetramethylene units were claimed to be present, and a 1,4-enchainment of hexadiene was proposed.[16]

Scheme 1



Scheme 2



The MCP units in the polymer are easily explained by the standard primary (1,2) insertion/cyclization mechanism (Scheme 2). However, conventional insertion or chain-walking[5] mechanisms cannot account for the VTM sequences. One plausible pathway invokes a methylenecyclobutane/pentenyl rearrangement, observed in many organometallic systems (Scheme 2).[17] Although β-alkyl elimination is typically negligible for alkyl groups larger than methyl,[1d] ring strain of a cycloalkane can be used to facilitate an internal β-alkyl migration, producing a polyolefin containing exo-methylene groups.[18] In our case, if cyclization occurs following a 2,1-insertion, the resulting complex possesses a methylenecyclobutane moiety capable of a similar rearrangement (Scheme 2). Ring strain is alleviated by an internal β-alkyl shift, giving rise to a VTM unit and a primary titanium alkyl. Because insertions into primary titanium alkyls (other than methyls) are regioirregular in this system,[11−13] the observed polymer contains both MCP and VTM repeat units. The MCP/VTM ratio is indicative of a slight preference for 1,2-insertion into the primary titanium alkyl generated following either cyclization or ring-opening. Furthermore, the steric protection

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Table 1. Polymerization of 1,5-Hexadiene (HD) and Copolymerization with Propylene (P) Using the **1**/MAO Catalyst System[a]

entry	feedstock HD (g)	feedstock P (psi)	time (min)	yield (g)	activity (kg P/mol$_{Ti}$ h)	M_n[c] (g/mol)	M_w/M_n[c]	composition (mol %)[d] P	composition (mol %)[d] MCP	composition (mol %)[d] VTM
1[b]	11.0	0	20	0.67	201	268 000	1.27	0	63	37
2	0	10	240	0.55	6.9	64 100	1.12	100	0	0
3	11.0	10	240	1.17	14.6	119 000	1.16	87	8.3	4.7
4	11.0	20	240	1.39	17.4	145 000	1.09	96	1.5	2.5
5[e]	0/11.0	10	240/120	0.98	7.9	51 500/93 300[f]	1.11/1.11[f]	100/93[f]	0/4.3[f]	0/2.7[f]

[a] Polymerizations performed in toluene at 0 °C, total volume 100 mL, 20 μmol **1**, Al/Ti = 150. [b] 10 μmol **1**. [c] Determined by GPC (1,2,4-trichlorobenzene, 140 °C) relative to polystyrene standards. [d] Calculated from the ^{1}H NMR spectra. [e] After reaction with P for 4 h, HD was added, and the reaction was conducted for another 2 h. [f] Data for the initial *syndio*-PP block and the final *syndio*-PP-*block*-P(P-*co*-HD) diblock copolymer.

provided by the bulky polymer chain prohibits subsequent insertions of the pendant vinyl substituent, thus preventing cross-linking.

Although the mechanistic implications of this reaction are intriguing, the real benefit of this reaction lies in its ability to generate functional polyolefins and block copolymers. In this manner, propylene/1,5-hexadiene copolymers were prepared with **1**/MAO (Scheme 1, Table 1). ^{1}H and ^{13}C NMR spectra were consistent with a P/HD copolymer and revealed the highly syndiotactic nature of the polypropylene (PP) domains.[15] A preference for MCP formation was still observed at lower propylene content, while high propylene composition favored the formation of VTM units. These trends are consistent with more insertions into the bulky secondary titanium alkyl generated upon enchainment of propylene. Furthermore, the narrow polydispersities ($M_w/M_n < 1.2$) of the copolymers were consistent with a living polymerization, which was further demonstrated by the synthesis of a *syndio*-PP-*block*-P(P-*co*-HD) copolymer. Addition of HD to a monodisperse *syndio*-PP ($M_n = 51\,500$ g/mol, $M_w/M_n = 1.11$) resulted in rapid formation of a higher molecular weight polymer ($M_n = 93\,300$ g/mol, $M_w/M_n = 1.11$) containing a reactive functional domain.

In summary, we report the synthesis of polyolefins containing reactive vinyl substituents utilizing a simple, volatile, and inexpensive diene. We believe the propensity for secondary insertion using **1**/MAO results in the insertion/isomerization polymerization of 1,5-hexadiene, giving a material composed of 3-vinyl tetramethylene and methylene-1,3-cyclopentane repeat units. Propylene/hexadiene copolymerizations give *syndio*-polypropylenes containing vinyl substituents, which are notably incapable of cross-linking yet amenable to a broad range of functionalization chemistry. The controlled nature of the polymerization also provides a route to new polyolefin-based block copolymers containing functional domains. Further studies, including a more detailed mechanistic investigation of this reaction and its application to the synthesis of new functional polyolefins, are underway.

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Supporting Information Available: Experimental procedures, ^{1}H and ^{13}C NMR, and DSC characterization of the polymers (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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