Ni(II)-Catalyzed Polymerization of *trans*-2-Butene

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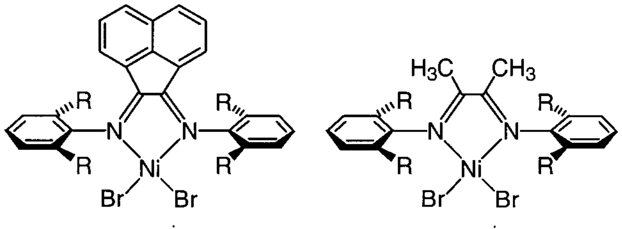
Recent interest in transition metal-catalyzed polymerization has led to the development of many versatile and highly active systems for the production of polyolefins with well-defined microstructures and interesting physical properties. Traditionally, these catalysts were based on complexes of early metals such as titanium and zirconium, which can be rationally designed to produce high molecular weight polyethylene as well as stereoregular poly(α-olefins).[1−4] Such systems are effective for the polymerization of a wide array of monomers; however, the synthesis of high molecular weight homopolymers of acyclic olefins containing an internal double bond has not been reported, presumably due to the unfavorable requirement of a polymer backbone consisting solely of tertiary carbon centers which would be produced from standard enchainment of such monomers.[5,6] The unique behavior of α-diimine Ni(II) and Pd(II) polymerization catalysts[7−10] in the presence of ethylene,[11] α-olefins,[12] and cyclopentene[13] encouraged the evaluation of these systems for the polymerization of acyclic internal olefins. Herein we report the first synthesis and characterization of high molecular weight poly(*trans*-2-butene), as well as preliminary investigations of the polymerization mechanism.

In 1995, catalyst systems based on less electrophilic late transition metals such as Ni(II) and Pd(II) complexed by aryl-substituted (α-diimine) ligands were shown to polymerize ethylene and α-olefins to high molecular weight material[7] and copolymerize ethylene and functionalized olefins such as alkyl acrylates in the case of palladium.[8,14] High polymer is obtained rather than oligomeric products due to the presence of bulky ortho alkyl groups on the orthogonal aryl rings, which inhibit chain transfer. The ethylene homopolymers produced by these systems are highly branched, due to a mechanism involving metal migration along the carbon chain via a series of *β*-hydride elimination/readdition reactions (a phenomenon termed chain walking) followed by C_2H_4 insertion into the secondary metal alkyl bonds of these isomeric complexes. A similar mechanism governs polymer microstructures observed from α-olefin polymerization. The polymers obtained contain *fewer* branches than expected from normal sequential 1,2-insertions. This chain straightening process is believed to occur similarly through metal migration along the polymer chain after monomer insertion and is crucial to the behavior of these complexes in the polymerization of internal olefins such as 2-butene.

Syntheses of the (α-diimine)nickel(II) dibromide precatalysts considered in the present study (Figure 1) have been previously published.[11,15,16] These complexes serve as precursors for active cationic Ni(II) polymerization catalysts, which are easily generated in situ by reaction of the dibromides with activators such as modified MAO.



1 (R = ^{i}Pr)   **3** (R = ^{i}Pr)
2 (R = Me)   **4** (R = Me)

Figure 1. (α-Diimine)Ni(II) precatalyst complexes.

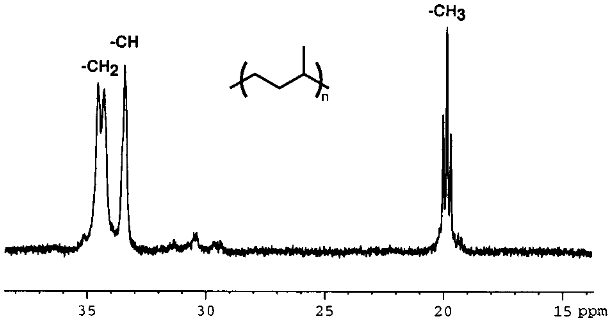


Figure 2. ^{13}C NMR spectrum of poly(*trans*-2-butene).

Initial studies with *cis*-2-butene led to isolation of no polymeric products upon reaction with precatalysts **1** and **2**. However, reaction of these systems in the presence of the *trans*-2-butene isomer allowed the synthesis of high molecular weight material under the reaction conditions described (Table 1).

The effects of ligand backbone modification on rate of reaction and polymer physical properties were studied using precatalysts **1**−**4**. For catalysts with identical aryl substituents (e.g., isopropyl groups), modification of the ligand backbone from an acenaphthyl group to methyl groups causes a significant decrease in reactivity and molecular weight of the resultant polymer (Table 1, e.g., entry 1 vs entry 8). This is thought to be due to steric factors, as the methyl backbone forces the aryl rings into a more perpendicular conformation, enhancing the steric effects of the aryl isopropyl groups and hindering coordination of the bulky disubstituted olefin. Similar steric implications of the bulk of the ortho aryl groups are also observed. For both the acenaphthyl and methyl backbone complexes, decreasing the bulk on the aryl rings from an isopropyl group to a methyl group causes a significant increase in turnover frequency, but the rate of chain transfer relative to propagation is increased, as indicated by the greater polydispersities of these polymers (entry 1 vs 6 and entry 8 vs 10). The polymerizations generally display significantly lower activity at 0 °C than at 25 °C, despite the significant increase in monomer concentration.

Spectroscopic and thermal analysis of the polymer revealed several interesting features of its microstructure. Analysis by ^{1}H NMR spectroscopy indicates that the polymers contain 250 branches per 1000 carbon atoms in all cases, exactly half that expected for a normal 2,3-monomer insertion mode. Also, as shown in Figure 2, the ^{13}C NMR spectra are fairly simple, with distinct methyl, methylene, and methine resonances, identified by ^{13}C DEPT experiments. The chemical shifts

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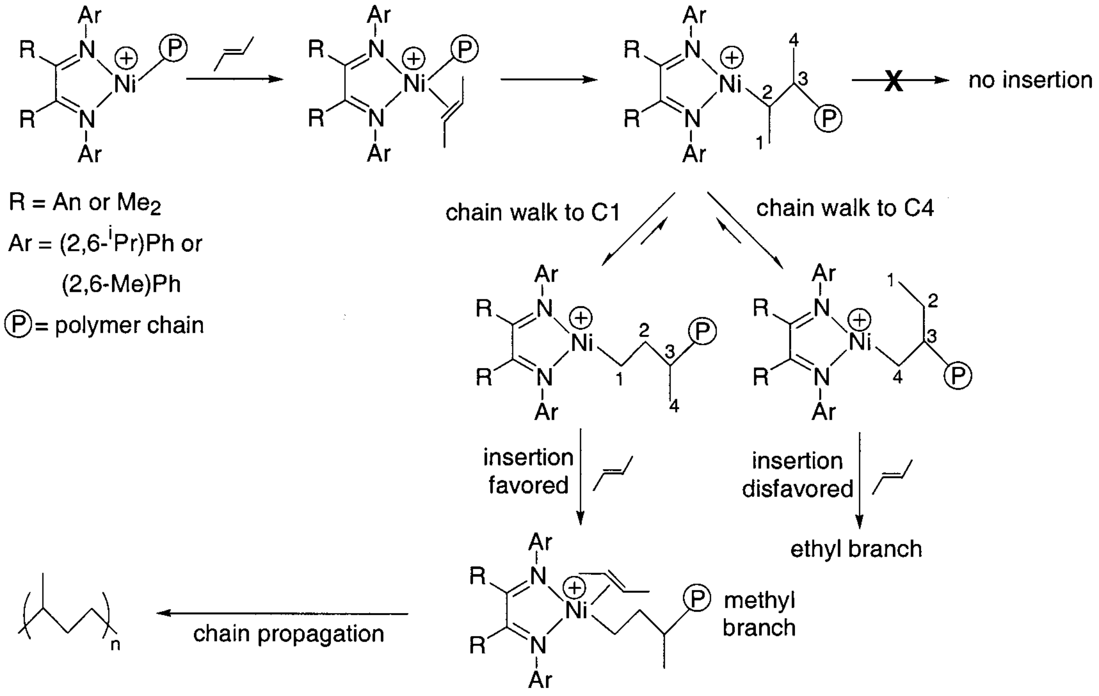
Table 1. *trans*-2-Butene Polymerization Data[a]

entry	catalyst	mol cat. ($\times10^{-6}$)	time (h)	temp (°C)	TOF (h^{-1})	M_n[b]	PDI	branches/ 1000 C[c]	T_g (°C)
1	**1**	10.1	1	25	1120	134 000	1.40	253	−52.3
2	**1**	10.3	2	25	1130	284 000	1.48	251	
3	**1**	9.9	4	25	880	496 000	1.46	255	
4	**1**	10.1	1	0	680	121 000	1.22	250	−53.1
5	**1**	9.7	4	0	430	202 000	1.24	258	
6	**2**	9.7	1	25	1700	146 000	1.98	253	−50.1
7	**2**	9.9	4	0	270	109 000	1.87	251	
8	**3**	9.9	1	25	200	33 000	1.14	251	−56.2
9	**3**	9.9	4	0	60	38 400	1.18	252	
10	**4**	10.9	1	25	1030	164 000	1.44	251	−53.8
11	**4**	10.4	1	0	550	90 700	1.15	254	

[a] Reaction conditions: 15 mL of toluene, 2 mL of MMAO/heptane solution, 15 psig of *trans*-2- butene. [b] Molecular weights determined by GPC in THF or toluene vs polystyrene standards. [c] Determined by ^1H NMR spectroscopic analysis of the polymer.

Scheme 1. Proposed Butene Polymerization Mechanism



observed are completely consistent with a highly regioregular polymer microstructure with a ($CH_2-CH_2-CH(CH_3)$) repeat unit, i.e., a linear chain with a methyl branch on every third carbon (note the similarity to polypropylene with a ($CH_2-CH(CH_3)$) repeat unit and a methyl branch on every other carbon).[17] The methyl resonances in spectra of these polymers display a consistent 1:2:1 ratio of intensities, which is best accounted for by considering the relative configuration of methyl groups along the chain. In the atactic polymer (as would be expected here[18]) the [mm]:[mr + rm]:[rr] triads occur in a 1:2:1 ratio, which matches the appearance of the methyl group resonance. Compared to polypropylene, a narrower chemical shift spread is expected since the methyl branches are separated by an additional methylene unit. The minor resonances (<10%) at δ 11.4 and 42.3 ppm in the ^{13}C spectra are attributable to the methyl and methine carbon, respectively, of ethyl branched repeat units. DSC analysis of the polymers shows a sharp glass transition at about −50 °C, and no indication of a melting transition, which, along with the observed ^{13}C methyl resonance pattern, supports the proposed atactic structure.

Analysis of the material produced from the (α-diimine)Ni(II) complex-catalyzed polymerizations of 2-butene, as well as previous studies of the behavior of these systems in the presence of ethylene and α-olefins, led to the formulation of a likely mechanism for internal olefin polymerization. This mechanistic proposal, shown in Scheme 1, involves initial 2,3-insertion of the butene monomer to give the expected disubstituted intermediate, which will not insert another monomer unit. This intermediate undergoes facile β-hydride elimination from either carbon 1 or 3, followed by reinsertion, analogous to the chain straightening behavior previously reported for these systems. Metal migration to the methyl terminus of the inserted monomer unit (C1 or C4) followed by insertion gives rise to a microstructure with one branch for every four carbon atoms, which is supported by the polymer ^1H NMR data. ^{13}C NMR analysis reveals much smaller amounts of ethyl branches as compared to methyl branches for systems with larger (e.g., isopropyl) ortho aryl groups. This observation suggests that chain walking to C4 and subsequent monomer insertion is disfavored for steric reasons, since the branch point and the growing polymer chain are situated closer to the metal center in this case than they are after the metal walks to C1.[19]

In summary, the (α-diimine)Ni(II) catalysts described are active for the polymerization of the acyclic internal olefin *trans*-2-butene to yield high molecular weight material with a well-defined, regioregular microstructure. The mechanism for this polymerization is believed to encompass facile chain walking after monomer insertion to produce a polymer chain with a methyl branch on every third backbone carbon. The apparent selectivity of these systems for the *trans*-olefin isomer is intriguing and as yet unexplained.

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Supporting Information Available: General polymerization procedures, ^{1}H and ^{13}C NMR spectra, and GPC and DSC traces of representative polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) The ligands employed are achiral; thus, no enantiomorphic site control is expected, and the disubstituted γ-carbon is sufficiently remote that chain-end control is unlikely.
(19) As noted by a reviewer, copolymerization of 1-butene would also account for the ethyl branches observed. No 1-butene is detected by GC in the monomer feed or over the course of the reaction, but due to the higher reactivity of these sytems with α-olefins, its generation and immediate incorporation into the polymer chain cannot be ruled out.

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