Ethylene Homopolymerization and Copolymerization with Functionalized 5-Norbornen-2-yl Monomers by a Novel Nickel Catalyst System

Steve J. Diamanti,[†] Prasenjit Ghosh,[†] Fumihiko Shimizu,[‡] and Guillermo C. Bazan*[,†]

Mitsubishi Chemical Center for Advanced Materials, Institute for Polymer and Organic Solids, Departments of Chemistry and Materials, University of California, Santa Barbara, California 93106, and Mitsubishi Chemical Corporation, Science and Technology Research Center, 1000 Kamoshida-cho, Aoba-ku, Yokohama 227-8502, Japan

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ABSTRACT: The homopolymerization and the copolymerization of ethylene with functionalized 5-norbornen-2-yl derivatives by the nickel catalyst system L(^{i}Pr$_2$)Ni(η^1-CH$_2$Ph)(PMe$_3$) (**1**) [L = *N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamide] and Ni(COD)$_2$ (bis(1,5-cyclooctadiene)-nickel) produces polymers with high molecular weights and narrow molecular weight distributions. A typical ethylene polymerization reaction proceeds under 100 psi of ethylene and at 20 °C, using **1** (0.34 mM) and Ni(COD)$_2$ (0.83 mM). Likewise, under similar conditions, the copolymerization of ethylene with 5-norbornen-2-yl acetate (**3**) (0.15 M) for 90 min by **1** (0.67 mM) and Ni(COD)$_2$ (1.67 mM) produced a high molecular weight functionalized polyethylene bearing ester functionalities. 5-Norbornen-2-ol (0.15 M) underwent a similar copolymerization with ethylene for 20 min to yield a hydroxy-functionalized polyethylene. Narrow molecular weight distributions, coupled with the increase of polymer molar mass with time, are consistent with a quasi-living polymerization process in the case of ethylene homopolymerization and ethylene copolymerization with **3**.

Introduction

Polyolefins are a class of materials with enormous economic impact. Tailoring of their bulk properties by synthetic control is a major focus of many industrial and academic research groups.[1] In the past 15−20 years, these efforts have produced a progression in catalyst design, from heterogeneous catalysts to “single-site” systems whose reactivity can be fine-tuned by choice of the ligand environment surrounding the active metal center.[2] Novel structures based on electrophilic early transition-metal-based catalysts, together with advances in their activation by cocatalysts and improved mechanistic understanding, have played a significant role in this development. Examples of how the metal center can tailor material properties by controlling monomer insertion include the stereospecific polymerization of propene[3] and the copolymerization of ethylene and 1-alkenes.[4]

Recently, the design of late-transition-metal initiators has received renewed interest because of their lower oxophilicity and resistance toward deactivation by polar functionalities, relative to early transition metal counterparts.[5,6] The observation that hindered *N*-aryl moieties in α-diimine complexes give rise to high molecular weight polyethylene provides an important guideline for the design of nickel-,[7,8] palladium-,[9,10] and iron-based initiators.[11] Palladium catalysts have been shown to catalyze the quasi-living polymerization of norbornene and ester-substituted norbornenes, although the polymerization of ester-substituted norbornenes is living only if a pure exo feedstock is used.[12] These structural guidelines have also produced neutral nickel initiators capable of copolymerizing ethylene with functionalized monomers.[6] Polar functionalities within the hydrophobic polyolefin backbone can change important properties, such as toughness, adhesion, surface properties (paintability, wettability, printability), solvent resistance, blend compatibility with other functional polymers, and rheological properties. Neutral nickel initiators can even be used in the production of a high molecular mass polyethylene aqueous latex via emulsion polymerization techniques.[13] There are few examples of the copolymerization of ethylene and polar monomers via coordination insertion polymerization,[6b,7,14] and to our knowledge, there are no examples of the living copolymerization of ethylene and polar monomers.

A recent review highlights the importance of living insertion polymerization of alkenes by transition-metal complexes.[15] In a living polymerization the rates of termination and chain transfer are negligible, relative to the rate of propagation.[16] When these conditions are met, it is possible to attain polymer architectures such as block copolymers,[17] star-shaped polymers,[18] and end-functionalized polymers.[19] Although reports of the living polymerization of olefins with transition metal catalysts can be traced to 1979,[20] the majority of examples have been reported only within the past 5 years.[21] That few examples exist reflects the difficulties in optimizing the reactivity at the metal center to obtain large rates of olefin insertion in the absence of any competing processes.[15] Despite these difficulties, substantial progress has been reported, such as the stereospecific living polymerization of 1-hexene.[22]

In work related to the development of initiators for the tandem polymerization[23] of ethylene to branched polyethylene, we reported that addition of 2 equiv of B(C$_6$F$_5$)$_3$ to **1** results in the formation of **2** (Scheme 1).[24] Compound **2** is an initiator for ethylene polymerization. The isopropyl groups block the two pseudoaxial sites

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[†] University of California, Santa Barbara.

[‡] Mitsubishi Chemical Corporation.

* To whom correspondence should be addressed: phone (805)-893−5538; fax (805)-893-4120; email bazan@chem.ucsb.edu.

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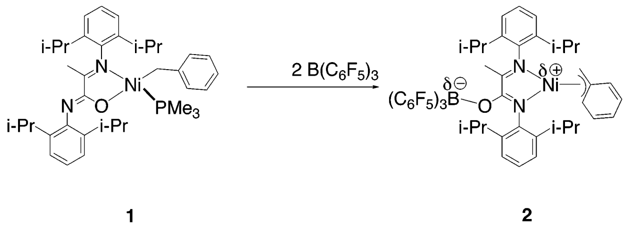
Table 1. Ethylene Homopolymerization by 1 and Ni(COD)$_2$ Complexes at 100 psi Ethylene, 20 °C, and 20 min Reaction Time

entry	**1** (mM)	Ni(COD)$_2$ (mM)	activity[a] (kg/(mol h))	M_n	M_w/M_n	T_m (°C)	Me branches per 1000 C
1	0.34	0	0	–	–	–	–
2	0.34	0.34	153	8.1×10^4	1.5	126.0	12
3	0.34	0.83	364	1.1×10^5	1.3	125.4	19
4	0.34	1.67	377	1.1×10^5	1.4	125.4	17
5	0.34	3.39	395	1.3×10^5	1.3	125.2	19
6	0	0.34	0	–	–	–	–

[a] Calculated using mass of the isolated polymer and moles of **1**.

Scheme 1



and increase the molecular weight of the product.[25,26] The η^3-benzyl fragment was selected, instead of the more frequently used methallyl ligand, because it exhibits faster rates of initiation.[27]

In this contribution we disclose that the coactivation of **1** with Ni(COD)$_2$ results in an active olefin polymerization catalyst which is capable of catalyzing not only the quasi-living[28] homopolymerization of ethylene but also the quasi-living copolymerization of ethylene with 5-norbornen-2-yl acetate (**3**).

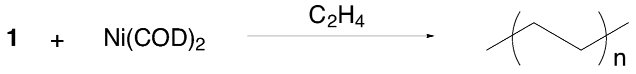
Experimental Section

General Remarks. All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk techniques. All reagents were used as received from Aldrich unless otherwise specified. Ethylene was from Matheson Tri-Gas (research grade, 99.99% pure) and was further purified by passage through an oxygen/moisture trap (Matheson model 6427-4S). Solvents like toluene, THF, hexane, and pentane were distilled from benzophenone ketyl. All polymerization reactions were carried out in a glass reactor as described below. Toluene for polymerization runs was distilled from sodium/potassium alloy. L(^{i}Pr$_2$)Ni(CH$_2$Ph)(PMe$_3$) [L = *N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamide] and Ni(COD)$_2$ were synthesized as reported previously[24] and purified by recrystallization prior to polymerization use. NMR spectra were obtained using a Varian Unity 400 or 500 spectrometer. ^{1}H NMR spectra of the polymers were obtained in mixed solvent (C$_6$D$_6$/1,2,4-trichlorobenzene 1:4 ratio in volume) at 115 °C. GPC analyses were done at Mitsubishi Chemical Corp., Japan, in *o*-dichlorobenzene at 135 °C. Polymer melting points were measured on a TA Instruments differential scanning calorimeter (model DSC 2920) at a rate of 10 °C/min for three cycles using a temperature range of 50–200 °C.

Typical Ethylene Homopolymerization. A glass reactor was loaded inside a glovebox with L(^{i}Pr$_2$)Ni(CH$_2$Ph)(PMe$_3$) (10 μmol; 1.00 g of 8.77 mM solution in toluene) and Ni(COD)$_2$ (25 μmol; 1.25 g of 17.6 mM solution in toluene) and toluene (23.7 g) such that the final volume of the toluene solution was 30 mL. The glass reactor was sealed inside the glovebox and was attached to a vacuum/nitrogen line manifold. Ethylene was fed continuously into the reactor at 100 psi, and the pressurized reaction mixture was stirred at 20 °C. Ethylene was vented after 3 min, and acetone was added to quench the polymerization. The precipitated polymer was collected by filtration and dried under high vacuum overnight.

Typical Copolymerization of Ethylene and 5-Norbornen-2-yl Monomers. A glass reactor was loaded inside a glovebox with L(^{i}Pr$_2$)Ni(CH$_2$Ph)(PMe$_3$) (20 μmol; 2.00 g of 8.77 mM solution in toluene), Ni(COD)$_2$ (50 μmol; 2.50 g of 17.6 mM solution in toluene), 5-norbornen-2-yl acetate (4.50 mmol; 3.00 g of 1.30 M solution in toluene), and toluene (18.45 g) such that the total volume of the toluene solution was 30 mL. The glass reactor was sealed inside the glovebox and was attached to a vacuum/nitrogen line manifold. Ethylene was fed continuously into the reactor at 100 psi, and the pressurized reaction mixture was stirred at 20 °C. Ethylene was vented after 90 min, and acetone was added to quench the polymerization. The precipitated polymer was collected by filtration and dried under high vacuum overnight.

Scheme 2



Results and Discussion

Ethylene Polymerization. Initial efforts involved optimizing the formation of the catalyst by varying the relative amounts of Ni(COD)$_2$ and **1** (Scheme 2). Specifically, polymerization reactions were carried out by adding varying amounts of Ni(COD)$_2$ to **1** (Table 1). Entries 1 and 6 show that no polyethylene is formed when either **1** or Ni(COD)$_2$ is used alone. Comparison of entries 2–5 shows that there is a sharp increase in reactivity when the Ni(COD)$_2$/**1** ratio increases from 1 to ca. 2.5, followed by a slower increase in activity as this ratio approaches 10 (Table 1, entry 5). NMR spectroscopy shows that the polyethylene has a relatively low branching content (10–20 Me branches per 1000 C).[29] The polymers have similar melting points and molecular weights and possess relatively narrow, monomodal molecular weight distributions (MWDs).

Efforts to identify a neutral, catalytically significant species were not successful.[30] When mixtures of **1** and Ni(COD)$_2$ are mixed in C$_6$D$_6$ at room temperature and the solution is monitored by ^{1}H NMR spectroscopy, one observes no reaction before Ni(COD)$_2$ decomposition begins to occur in ca. 1.5 h. That the catalyst does not form in the absence of ethylene is consistent with the displacement of a COD ligand by ethylene itself.[19] Once this step takes place, the resulting nickel species reacts with **1** to generate the active site. If COD displacement is slow, one would expect a slower initiation step relative to the propagation rate.

To demonstrate the quasi-living nature of the ethylene polymerization, a series of experiments were carried out in which the ethylene polymerization was quenched at specific intervals and the molecular weight of the resulting polymers was determined by GPC. As shown in Figure 1, one observes a linear dependence of M_n vs time over a period of 30 min as well as uniformly narrow MWDs; both of these observations are consistent with a quasi-living polymerization mechanism. MWDs are higher than expected for a truly living polymerization,

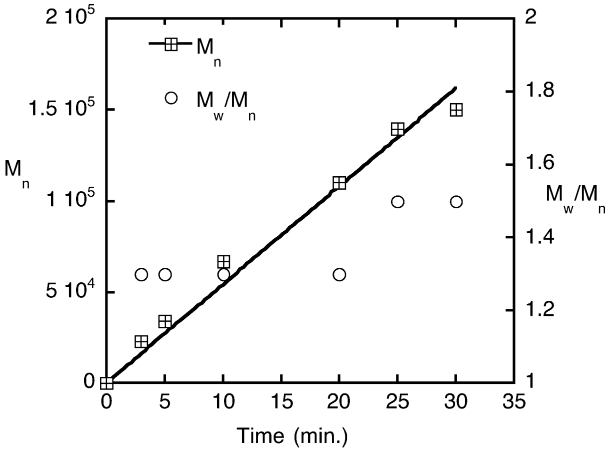


Figure 1. Plot of M_n and M_w/M_n as a function of reaction time for **1**/Ni(COD)$_2$/C$_2$H$_4$.

Scheme 3

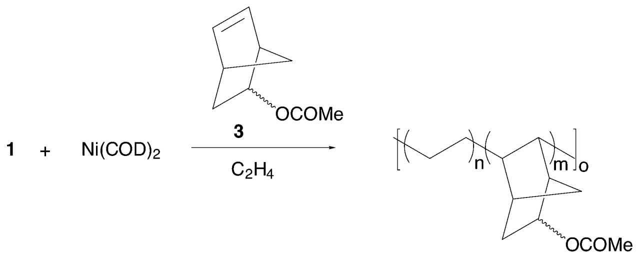


Table 2. C$_2$H$_4$/3 Copolymerization by 1/Ni(COD)$_2$ Complexes[a]

entry	**3** (M)	time (min)	M_n	M_w/M_n	incorp (mol %)	activity (kg/(mol h))
1	0.15	8	3.0×10^4	1.2	17	111
2	0.15	15	4.2×10^4	1.3	12	165
3	0.15	30	6.8×10^4	1.4	13	109
4	0.15	60	8.0×10^4	1.4	10	45
5	0.15	90	1.1×10^5	1.4	7	36
6	0.06	60	9.4×10^4	1.8	4	69

[a] [**1**] = 0.68 mM, [Ni(COD)$_2$] = 1.70 mM, 100 psi of ethylene, and 20 °C.

and this may reflect an initiation step that is slower than propagation[31] and/or that the polyethylene product precipitates during the reaction, entrapping the catalyst site within the polymer matrix.

The ability of **1**/Ni(COD)$_2$ to incorporate functionalized monomer was tested using 5-norbornen-2-yl acetate (**3**) (Scheme 3). The entries in Table 2 show the results from these experiments. Copolymers are produced that contain 5−15% molar incorporation of **3** within a polyethylene backbone, as determined by ^{1}H NMR spectroscopy.[32] Higher incorporation is observed with short reaction times because the concentration of **3** decreases as the reaction proceeds (Table 2, entries 1−5). A decrease in copolymer molecular weight occurs with increasing concentration of **3** (Table 2, entries 4 and 6), suggesting competition between the acetate functionality and ethylene for the metal active site. Significantly, the time dependence of the number-average molecular weight and the narrow molecular weight distributions (M_w/M_n = 1.2−1.4, Table 2) are consistent with a copolymerization process that is quasi-living.[33]

Addition of ethylene to a solution containing 5-norbornen-2-ol (**4**) and **1**/Ni(COD)$_2$ produces C$_2$H$_4$/**4** copolymers (Scheme 4). Table 3 summarizes the results from these polymerization experiments. The molecular weights of the **4**/C$_2$H$_4$ copolymers are lower than those observed with **3**, under similar reaction conditions, probably due to the encapsulation of the active site in the polymer precipitate and because the hydroxyl functionality competes more effectively with ethylene for the metal site, relative to the acetate counterpart.[34] Incorporation values of **4** are proportional to the initial concentration of **4** (Table 3, entries 1, 2, and 4). Entries 3−6 show a decrease in the final incorporation of **4** and a nonlinear increase in molecular weight with increasing reaction time. The incorporation of the hydroxyl functionality was verified by GPC−IR measurements (Figure 2). The constant ratio of the hydroxyl O−H stretching peak (3620 cm^{-1}) relative to the C−H stretching peak (2927 cm^{-1}) vs elution fraction shows that the C$_2$H$_4$/**4** composition of the copolymer is uniform throughout the entire molecular weight range. The data in Table 3 are consistent with a nonliving polymerization process that incorporates ethylene and **4** in a random fashion along the polymer backbone.[35]

Scheme 4

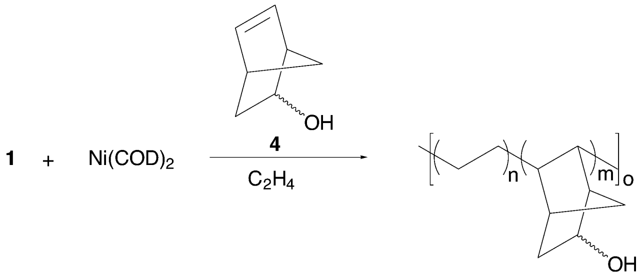


Table 3. C$_2$H$_4$/4 Copolymerization by 1/Ni(COD)$_2$[a]

entry	**4** (M)	time (min)	M_n	M_w/M_n	incorp (mol %)	activity (kg/(mol h))
1	0.03	20	1.1×10^4	1.9	5	88
2	0.13	20	4.7×10^4	1.4	13	118
3	0.15	10	3.1×10^4	1.3	18	191
4	0.15	20	4.3×10^4	1.3	16	110
5	0.15	40	5.5×10^4	1.5	12	50
6	0.15	60	5.6×10^5	1.9	10	44

[a] [**1**] = 0.68 mM, [Ni(COD)$_2$] = 1.70 mM Ni(COD)$_2$, 100 psi of ethylene, toluene, 20 °C.

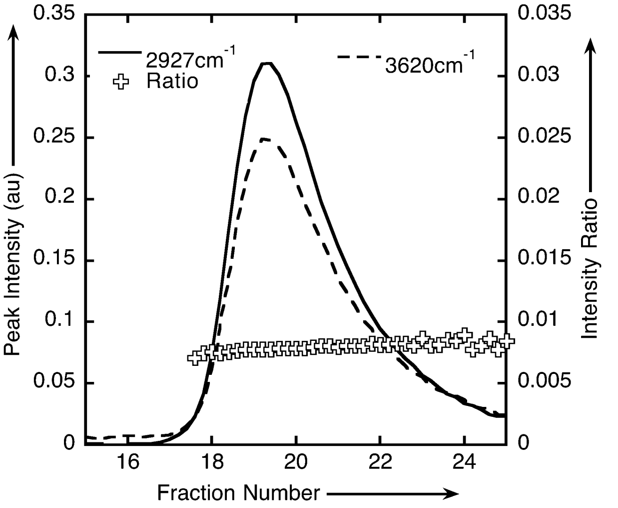


Figure 2. GPC-IR chromatogram showing the constant ratio of the hydroxyl peak (3620 cm^{-1}) to that of the C−H peak (2927 cm^{-1}) against elution fraction.

Conclusion

In conclusion, the **1**/Ni(COD)$_2$ combination provides a versatile catalyst for ethylene homopolymerization and for copolymerization of ethylene with functionalized norbornenes. The properties of the homopolymerization products are consistent with a quasi-living polymerization mechanism. The molecular weight distributions are not as narrow as would be expected from a truly living system; we propose this to be a result of an initiation step considerably slower than the propagation sequence[31] and also to the precipitation of the polymer which results in a range of environments where the catalytic centers reside. The copolymerization of ethylene with **3** also shows quasi-living behavior, even after 90 min of reaction time. Thus, the catalytic species is robust, showing little chain transfer to monomer or termination within the time scale of propagation. Copolymerization with **4** is not living; however, the products contain a homogeneous distribution of hydroxy functionalities throughout the polymer structure. Future plans include taking advantage of the quasi-living nature of this polymerization system to produce block copolymers and polymeric structures with nonlinear architectures.

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Supporting Information Available: Representative NMR spectra of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) "Quasi-living" refers to a polymerization with a long-lived active species that satisfies several, but not all, of the conditions for living polymerization. See: Masuda, T. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1736.

(29) The branching content of the polymer was determined by ^{1}H NMR spectroscopy in which the methyl protons were integrated against the methylene protons of the polyethylene backbone peak (methylene + methine) and reported as methyl branches per 1000 methylene carbons.

(30) Addition of 1 equiv $B(C_6F_5)_3$ to **1** yields a ca. 1:1 mixture of **1** and **2**, even after long reaction periods (ca. 3 h). It appears that once an equivalent of PMe_3 is removed from **1**, the resulting species is more reactive toward $B(C_6F_5)_3$.

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