Copolymerization of Ethene with Norbornene Derivatives Using Neutral Nickel Catalysts

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ABSTRACT: The copolymerization of ethene with norbornene derivatives, as well as their terpolymerization with 1-alkenes, using a series of neutral, square-planar nickel complexes containing anionic P∼O chelates is described. In copolymerizations, up to 50 mol % incorporation of norbornene, leading to an essentially alternating copolymer, is obtained. With norbornene derivatives bearing oxygen functionalities, the level of incorporation is lower, as are the reaction rates and polymer molecular weights. In the case of terpolymerization of ethene and norbornene with 1-alkenes, the polymer molecular weights tend to be low because of slower monomer insertion and additional chain-transfer pathways that are available following 1-alkene insertion. For the ethene/norbornene polymers synthesized, the glass transition temperature (T_g) increases smoothly with increasing norbornene content. Solution-cast films of the polymers show good optical clarity.

Introduction

Early transition metal catalysts such as vanadium complexes and zirconocenes effectively copolymerize ethene with norbornene.[4] This capability eventually led to the commercial development of the APEL and TOPAS line of cyclic olefins copolymers by Mitsui and Ticona (formerly Hoechst), respectively.[5] Interest in this class of polymers is due to its high glass transition temperatures and transparency that is imparted by the norbornene component.

Unlike early transition metals, late transition metals are more tolerant of oxygen functionalities in the monomer and the polymer. This behavior stems from the preference of late transition metals for soft ligands due to their higher electronegativity and lower oxidation states.[6] A number of nickel and palladium compounds have been shown to catalyze the addition polymerization of norbornene.[7] However, most of them are ineffective for the copolymerization of ethene/1-alkenes with norbornene because the former act as chain transfer agents through β-hydrogen abstraction. Therefore, to achieve the copolymerization of ethene and 1-alkenes with functionalized norbornene, it is necessary for the catalyst to be both tolerant of functional groups and resistant to β-hydrogen abstraction.

In the early 1970s, patents issued detailing discoveries by Keim and co-workers at Shell regarding polymerization/oligomerization of ethene with neutral, square-planar nickel complexes containing appropriate anionic, bidentate ligands, such as P∼O chelates.[8] This innovation led others to broaden the scope of nickel compounds as oligomerization/polymerization catalysts.[9] It was found that catalysts of this type are not inhibited by the presence of solvents containing functional groups and that they polymerize acyclic functional olefins.[10] Recently, there has been renewed interest in polymerization and copolymerization of ethene using nickel catalysts with chelating, anionic ligands.[11]

As an extension of the above work, methods for preparing ethene−norbornene copolymers using neutral nickel catalysts containing chelating anionic ligands have been patented.[12] Herein, we report the copolymerization of norbornene-type monomers (both nonfunctional and functionalized in the 5-position, R−NB) and ethene using the neutral nickel catalysts shown in Figure 1.

Experimental Section

General. All manipulations of organometallic complexes were carried out under an atmosphere of purified argon or nitrogen using standard Schlenk or drybox techniques. Toluene was dried by refluxing over sodium benzophenone ketyl, distilled under nitrogen, and stored over 4 Å molecular sieves. THF was dried over sodium benzophenone ketyl under nitrogen, vacuum-transferred, and stored over 4 Å molecular sieves. Cyclohexane was dried by refluxing over sodium under nitrogen, distilled, and stored over 4 Å molecular sieves.

Ni(COD)$_2$ was purchased from Strem. $Ph_3P{=}CHC(O)Ph$ was purchased from SPECS. The syntheses of $[(PPh_2CH{=}C(O)Ph)Ni(Ph)]_2$ (**2**) and $(PPh_2CH{=}C(O)Ph)Ni(Ph)(PPh_3)$ (**4**) have been described before.[13] The phosphorus ylide, $Ph_3P{=}CH_2$, was prepared according to Schmidbauer.[14] NB-CO2Et, NB-CH$_2$OC(O)Me, NB-COOMe, and *n*-butyl-NB were obtained from the BFGoodrich Co. NB-CH$_2$OH was obtained from Aldrich.

Instrumental Analysis. The ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on a Bruker AMX-500 NMR spectrometer operating at 500.14, 202.47, and 125.77 MHz, respectively. The high-field ^{13}C NMR spectra were obtained using a Varian UnityPlus 750 MHz NMR spectrometer equipped with three broad RF channels. These carbon spectra were obtained at 188 MHz in 1,1,2,2-tetrachloroethane-d_2, at 105 °C, in a 5 mm NMR tube, using inverse gated proton decoupling, with a 4 s delay between the pulses. Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced using either internal solvent resonances and are reported relative to tetramethylsilane or

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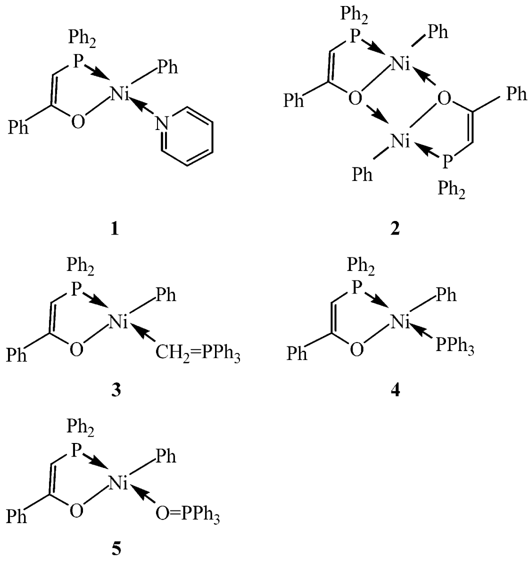


Figure 1. Structure of catalysts used for copolymerization of norbornene and ethene.

referenced to internal tetramethylsilane. The ^{31}P NMR spectra were referenced to external 85% H_3PO_4.

The amount of incorporation of various monomers in the co- and terpolymers was determined by ^1H NMR spectrometry in chloroform-d_1, *o*-dichlorobenzene-d_4, or tetrachloroethane-d_4. As an example, the methylene protons next to the oxygen in NB-CO_2Et and NB-$CH_2OC(O)Me$ appear as downfield signals separate from the main-chain signals. The integration of these protons is then compared to the integration of the total hydrogens. The composition of ethene-*co*-norbornene-*co*-propene terpolymers was determined by a combination of ^1H and ^{13}C NMR spectra. By ^{13}C NMR spectrometry, the signal of the methyl group of incorporated propene appears further downfield (20 ppm) than the end groups of ethene-*co*-norbornene copolymers (14 ppm). The integration of these methyl carbons can be made and compared to determine the propene content vs the norbornene/ethene content. The norbornene and ethene content can then be determined separately by ^1H NMR spectrometry. For ethene-*co*-hexene-*co*-norbornene terpolymers, comparison of the main-chain methylene ^{13}C NMR peaks due to hexene (~43 ppm), norbornene (~33 ppm), and ethene (~30 ppm) allowed calculation of the content of each. Molecular weights were determined by GPC vs polystyrene standards using a Waters 600 controller, a Waters 486 UV detector at 254 nm, and a Waters 410 RI detector.

Samples for transparency determination were prepared by casting copolymer films from solutions in either toluene or cyclohexane, followed by drying at 60−90 °C under vacuum. Transparency was determined by taking the average transmission from 400 to 700 nm on films between 4 and 7 mil thick using a Cary 400 (Varian) UV−vis instrument.

The tensile modulus and elongation at break of polymer films (approximately 3−4 mil thick) were determined on an Instron 5500R instrument according to ASTM standard D1708 after the samples were conditioned according to ASTM D618-90. An average of five runs is reported.

Glass transition measurements were recorded as second scans at a heating rate of 40 °C/min in an aluminum DSC pan on a Perkin-Elmer DSC7 instrument.

Synthesis of ($PPh_2CH{=}C(O)Ph$)Ni(Ph)(NC_5H_5) (1). The procedure published by Klabunde et al.[9a−c] was followed for the synthesis of **1**. From 2.31 g of bis(1,5-cyclooctadiene)nickel, 2.20 (51% yield) of **1** was obtained. ^1H NMR (C_6D_6) (ppm): 8.60 (d, 2H), 8.13 (d, 2H), 7.75 (m, 4H), 7.52 (d, 2H), 7.20 (m, 9H), 7.05 (d, 3H), 6.93 (m, 1H), 6.32 (m, 2H), 5.11 (s, 1H). ^{31}P NMR (C_6D_6) (ppm): 24.10 (s).

Synthesis of ($PPh_2CH{=}C(O)Ph$)Ni(Ph)($CH_2{=}PPh_3$) (3). The synthesis of **3** was derived from a procedure reported by Starzewski.[9i] Bis(1,5-cyclooctadiene)nickel (1.00 g, 3.63 mmol) was dispersed in 40 mL of toluene. A toluene mixture (75 mL) of $Ph_3P{=}CHC(O)Ph$ (1.38 g, 3.63 mmol) was added to the nickel compound followed by a toluene solution (30 mL) of $Ph_3P{=}CH_2$ (1.00 g, 3.63 mmol). The toluene mixture turned from yellow to brown. After heating the mixture at 50 °C for 2 h the mixture was filtered and reduced in volume in vacuo by one-half. The flask was cooled to −20 °C overnight. A yellow solid formed which was filtered cold and washed with heptane (3 × 10 mL). Yield 0.77 g (30%). ^1H NMR (C_6D_6) (ppm): 7.65 (m, 10H), 7.47 (d, 2H), 7.28 (d, 2H), 7.10 (m, 8H), 7.00 (m, 5H), 6.91 (m, 5H), 6.76 (m, 3H), 5.05 (s, 1H), 1.86 (d of d, $J_{PH} = 12$ Hz, $J_{PH} = 5$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6) (ppm): 34.59 (1 P), 19.22 (1 P).

Polymerization Procedure. Two polymerization procedures were followed and are noted separately in all data and tables.

Procedure A. A 0.5 L stainless steel reactor was heated to 70 °C under vacuum overnight and then cooled to room temperature. Norbornene (40.0 g, 425 mmol) in 150 mL of dry, oxygen-free toluene was added to the reactor under nitrogen. The solution was saturated with ethene. The catalyst was dissolved in about 10 mL of toluene and added to the reactor. The reactor was pressurized with ethene. Under a continuous feed of ethene, the reaction was allowed to proceed for 2 h. The ethene pressure was relieved at the end of the reaction, and the reactor contents were drained. Polymer was precipitated by addition of the reaction mixture to 1.5 L of methanol. The polymer was isolated by filtration and dried in a vacuum oven at 80 °C overnight.

Procedure B. Under an inert atmosphere, a solution of 0.05 mmol of $Ph_3P{=}CH{-}C(O)Ph$, norbornene(s), and 10 mL of toluene was stirred. In reactions involving $Ph_3P{=}O$, the ligand was also added to the solution at this time generating **5** in situ. To this solution 0.05 mmol of $Ni(COD)_2$ was added and stirred. This solution was charged into a 125 mL pressure reactor. This reactor was then charged once with 200 psi of ethene and stirred magnetically in a temperature-controlled oil bath. Upon completion of the reaction, the remaining ethene was vented, and the reaction mixture added to approximately 500 mL of methanol. The polymer was then isolated by filtration and dried in a vacuum overnight.

Results and Discussion

Figure 1 shows the structures of the nickel compounds employed in this study. They all contain a Ni−Ph moiety and the same P~O chelate ligand. They only differ in terms of their donor ligand, L. Compounds **1**, **3**, **4**, and **5** are bonded to L = pyridine, $Ph_3P{=}CH_2$, PPh_3, and $O{=}PPh_3$, respectively. Compound **2** is different entirely in that it is dimeric and is held together by virtue of donor interactions with the oxygen atom of the P~O chelate. Thus, in this case the donor ligand is an oxygen atom.

The study reported here focused, in the first instance, on the effect of the catalyst and the reaction conditions on the copolymerization of ethene with norbornene. The ability to incorporate functional norbornene monomers was then investigated. The copolymer microstructure and end groups were elucidated. Finally, some thermal, mechanical, and optical properties were determined.

Effect of Catalyst. Under identical reactions conditions, the effect of different catalysts was explored for the copolymerization of norbornene and ethene. The results of this study are presented in Table 1. Catalysts **1**−**3** are very similar in that they produce copolymers of norbornene and ethene with relatively high molecular weights and whose composition does not vary significantly from about 45% norbornene and 55% ethene. The catalyst activity however varies, with **3** showing significantly lower activity than **1** or **2**. The lower activity of **3** is surprising since ylid derivatives have been

Table 1. Effect of Catalyst on Copolymerization of Norbornene and Ethene[a]

entry	catalyst	conv based on NB (%)	yield (g)	NB:Et	M_w	M_w/M_n	TON[b]
1	**1**	25	6.8	44:56	60 800	2.02	1146
2	**2**	51	10.1	45:55	59 600	2.07	1683
3	**3**	11	2.1	41:59	44 300	1.97	367
4	**4**	35	7.0	46:54	2 500	1.73	1153

[a] All copolymerizations were carried out in toluene at 25 °C, at 0.65 mM [catalyst], at 1.2 M [norbornene], under 100 psi ethene, for 2 h. Polymerization procedure A was followed. [b] Turnover number = number of moles of monomers converted to polymer per mole of catalyst employed.

reported to be extremely high activity catalysts for ethene oligomerization and polymerization.[9i]

Catalyst **4**, while showing similar activity to that of **1** and **2**, produces a material that is lower in molecular weight by at least an order of magnitude. Klabunde and co-workers showed that for ethene polymerization the molecular weights could be increased by addition of ligand scavenging complexes.[9a−c] The formation of low molecular weight copolymers in the presence of a strong donor ligand like PPh_3 is entirely consistent and complementary to the observation by Klabunde et al.

Effect of Catalyst Concentration. Table 2 lists results obtained for the copolymerization of ethene and norbornene using compound **1** as a function of the catalyst concentration. All experiments were run at 25 °C, 1.2 M norbornene concentration, and under 100 psig ethene pressure for 2 h.

As the catalyst concentration is increased from 0.31 to 2.5 mM, the percentage of norbornene converted to polymer increases dramatically (from 12 to 85%). However, the catalyst turnover number or TON (number of moles of monomers converted to polymer per mole of catalyst employed) does not really change significantly, remaining between about 1100 and 1400. There is little change in composition; the norbornene content in the copolymer remains about 45%. The copolymer M_w drops somewhat from 66 500 to 50 500 as the catalyst concentration is raised.

Effect of Norbornene Concentration. Table 3 collects information regarding the copolymerization of norbornene and ethene using compound **1** as a function of norbornene concentration at 25 °C under 100 psig ethene pressure.

Within the experimental space explored thus far, the most dramatic change observed is in the copolymer molecular weight. As the norbornene concentration is increased, the M_w goes from 60 800 to 85 800. The amount of norbornene in the copolymer increases only slightly (ca. 5%) over the same range.

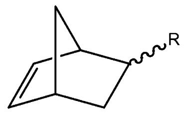
Effect of Ethene Pressure. Table 4 shows the effect of ethene pressure on ethene−norbornene copolymerization using compound **1** carried out at 25 °C, 0.65 mM catalyst concentration, and 1.2 M norbornene concentration.

The increase in ethene pressure (and thereby concentration) has a significant influence on the polymerization reaction. As the ethene pressure is raised from 50 to 300 psig, the conversion of norbornene increases until nearly complete consumption is achieved. Accordingly, the catalyst activity also increases by more than an order of magnitude. Increasing the ethene pressure also significantly raises the incorporation of ethene in the copolymer, with the molar ratio of norbornene to ethene in the copolymer going from 1:1 to 1:3. At the same time, the molecular weight is cut almost in half, from 74 000 to 40 000.

Effect of Temperature. Table 5 contains results obtained for the copolymerization of norbornene and ethene using catalyst **1** as a function of temperature. Copolymerizations were carried out at 5, 15, 25, and 45 °C at a catalyst concentration of 0.65 mM, 1.2 M norbornene concentration, and under 100 psig ethene pressure.

Conversion of norbornene increases significantly as the temperature is raised from 5 to 15 °C but then decreases as the temperature is raised further. This is reflected in the catalyst turnover. The highest catalyst turnover is observed at 15 °C. The molecular weight of the copolymer also reaches a maximum ($M_w = 70\ 000$) at 15 °C. Throughout the temperature regime explored, the norbornene-to-ethene ratio in the copolymer does not vary greatly (mole percent of norbornene = 43−49%).

Functionalized Norbornenes. Functionalized norbornenes can be incorporated into the copolymer with ethene at various rates and is dependent on the functionality on the norbornene. Table 6 illustrates the copolymerization of ethene with several norbornene derivatives functionalized at the remote 5-position using two different nickel compounds, **2** and **5**.



R = n-Butyl, CO_2Et, $CH_2OC(O)Me$, CH_2OH

Compound **2**, formed in the absence of any added ligand, is generally more active and yields copolymers with a higher level of norbornene incorporation. The higher activity of **2** relative to the other nickel compounds tested is also evident for the copolymerization of the parent norbornene with ethene (see Table 1). Therefore, compound **2** was chosen for further studies on the copolymerization and terpolymerization of functionalized norbornenes with acyclic alkenes.

Table 7 summarizes the results of the copolymerization of several different norbornene derivatives using compound **2**. In every case, compared to the copolymerization of the parent norbornene, the level of norbornene incorporation is substantially lower, as is the reaction rate and the copolymer molecular weight. Note that a substantially higher amount of catalyst relative to functionalized norbornene is necessary to achieve these results compared to that used for the parent norbornene.

Table 8 summarizes the results of a study aimed at ascertaining how the copolymer composition and molecular weight of the ethene/5-*n*-butylnorbornene copolymer vary with reaction time. While the catalytic activity clearly diminishes with time, there is no effect on copolymer composition and molecular weight. This suggests that while some of the nickel centers are deactivating over time, neither the ratio of propagation to termination rates nor the relative preference for monomer uptake is changing for the remaining active nickel species.

For all the functionalized norbornenes tested, the level of incorporation in the copolymer with ethene was

Table 2. Effect of Catalyst Concentration on Copolymerization of Norbornene and Ethene Using Catalyst 1[a]

entry	NB:Ni	[Ni] (mM)	conv based on NB (%)	yield (g)	NB:Et	M_w	M_w/M_n	TON[b]
1	3900:1	0.31	12	3.3	46:53	66 500	1.98	1134
2	1900:1	0.65	25	6.8	44:56	60 800	2.02	1146
3	1000:1	1.2	58	16.7	43:57			1424
4	480:1	2.5	85	23.4	44:56	50 500	2.00	1020

[a] All copolymerizations were carried out in toluene at 25 °C, at 1.2 M [norbornene], under 100 psig ethene for 2 h. Polymerization procedure A was followed. [b] Turnover number = number of moles of monomers converted to polymer per mole of catalyst employed.

Table 3. Effect of Norbornene Concentration on Copolymerization of Norbornene and Ethene Using Catalyst 1[a]

entry	[Ni] (mM)	[NB] (M)	conv based on NB (%)	yield (g)	NB:Et	M_w	M_w/M_n	TON[b]
1	0.65	1.2	25	6.8	44:56	60 800	2.02	1146
2	1.10	2.1	30	15.7	48:52	74 800	2.58	1241
3	1.40	2.9	26	20.2	49:51	85 800	2.20	1049

[a] All copolymerizations were carried out in toluene at 25 °C, under 100 psig ethene, for 2 h. Polymerization procedure A was followed. [b] Turnover number = number of moles of monomers converted to polymer per mole of catalyst employed.

Table 4. Effect of Ethene Pressure on Copolymerization of Norbornene and Ethene Using Catalyst 1[a]

entry	ethene (psi)	[Et] (M)	conv based on NB (%)	yield (g)	NB:Et	M_w	M_w/M_n	TON[b]
1	50	0.56	12	3.1	51:49	74 300	2.55	483
2	100	1.2	25	6.8	44:56	60 800	2.02	1146
3	150	1.85	69	20.0	40:60	55 100	2.01	3535
4	200	2.44	89	28.4	33:67	44 700	2.09	5486
5	300	3.70	93	34.0	26:74	40 000	1.90	7239

[a] All copolymerizations were carried out in toluene at 25 °C, at 0.65 mM [catalyst], at 1.2 M [norbornene], for 2 h. Polymerization procedure A was followed. [b] Turnover number = number of moles of monomers converted to polymer per mole of catalyst employed.

Table 5. Effect of Temperature on Copolymerization of Norbornene and Ethene Using Catalyst 1[a]

entry	temp (°C)	conv based on NB (%)	yield (g)	NB:Et	M_w	M_w/M_n	TON[b]
1	5	6.2	1.7	46:54	55 900	1.70	281
2	15	35	9.7	43:57	70 200	2.19	1654
3	25	25	6.8	44:56	60 800	2.02	1146
4	45	4.5	1.2	49:51	48 800	2.77	191

[a] All copolymerizations were carried out in toluene at 1.2 M [norbornene], 0.65 mM [catalyst], under 100 psi ethene, for 2 h. Polymerization procedure A was followed. [b] Turnover number = number of moles of monomers converted to polymer per mole of catalyst employed.

substantially lower than that for the parent norbornene under similar conditions. The catalytic activity was also sharply attenuated with functional norbornenes. The reason for these differences is not entirely clear. Transition-metal-catalyzed addition polymerization of functional norbornenes, particularly those containing oxygen functionalities, has proved to be difficult. This is especially true for the *endo*-functionalized isomer which predominates in the vast majority of available norbornene derivatives. We, and others, have shown that the preferred stereochemistry for insertion of norbornene into metal−carbon bonds is *exo, exo*,[15] and for isomeric mixtures of functionalized norbornenes, the *exo* isomer is preferentially incorporated into the growing polymer chain.[16] However, for norbornenes with functionalities capable of coordinating to the metal center, chelated metal species can form both upon the coordination of the *endo*-functionalized norbornene and in the *endo*-inserted product. Indeed, by using a model platinum-based system, we have demonstrated the *endo, endo* insertion of the *endo* isomer of an ester-functionalized norbornene forming a chelated platinum complex.[16a] Thus, chelate formation by the *endo*-functionalized norbornene appears to be responsible, at least in part, for the observed decrease in polymerization rate for functionalized norbornene derivatives.

Clearly, however, the above explanation cannot be valid for 5-*n*-butylnorbornene since no chelating functionality is present. Note also that the ground-state electronic effect of the remote functionality on the C═C bond of norbornene is minimal. For example, the alkene carbons of norbornene resonate at 135.5 ppm, while those of 5-norbornene-2-carboxylic acid ethyl ester appear at 137.7 and 132.5 ppm (*endo*) and 138.1 and 135.9 ppm (*exo*).

A steric argument can be made for the decreased reactivity and incorporation of butylnorbornene. The stereoselectivity of reactions involving norbornene derivatives has been studied extensively.[17] As shown in Figure 2, there are unfavorable interactions involving both *exo* and *endo* isomers. For the *endo* isomer, the rehybridization of the vinylic hydrogen upon metal coordination and insertion from sp^2 to sp^3 pushes it toward the butyl group. With the *exo* isomer, there is unfavorable interaction of the substituent with one of the apical hydrogens on the bridge causing the bridge to tilt toward the metal.

Terpolymerizations. The ability for nickel-based compounds with P∼O ligands to copolymerize ethene with norbornene led to attempts to terpolymerize norbornene and ethene with 1-alkenes. Table 9 summarizes the results from these experiments. Using compound **2**, both propene and 1-hexene were successfully terpolymerized with ethene and norbornene/5-*n*-butylnorbornene. The composition of the terpolymers was determined by a combination of ^{1}H NMR and ^{13}C NMR spectroscopy. As in copolymerizations with ethene, the level of incorporation of 5-*n*-butylnorbornene in the terpolymers was lower than that of norbornene. Additionally, the molecular weights obtained were lower, suggesting that the incorporation of the 1-alkene facilitates chain termination (see below).

Copolymer Microstructure. The microstructure of norbornene−ethene copolymers produced by metallocene catalysts has been investigated using NMR techniques by a number of researchers.[18] Based on these

Table 6. Effect of Added $Ph_3P{=}O$ (i.e., Catalyst 2 vs 5) on Copolymerization of Functional Norbornenes and Ethene[a]

entry	catalyst	monomer (M)	reaction time (h)	yield (g)	NB:Et	M_w	M_w/M_n	TON[c]
1	**5**	NB-CO_2Et (0.3)	1.25	0.25	12:88	18 500	2.31	139
2	**2**	NB-CO_2Et (0.3)	1.25	1.16	18:82	22 900	1.69	438
3	**5**	NB-$CH_2OC(O)Me$ (0.3)	4.5	1.21	8:92	N.D.[b]		617
4	**2**	NB-$CH_2OC(O)Me$ (0.3)	4.5	1.25	11:89	N.D.[b]		576

[a] All copolymerizations were carried out in toluene at 60 to 80 °C, at 5.0 mM [catalyst] (NB:Ni = 60), under a single 200 psi charge of ethene. Polymerization procedure B followed. [b] Insoluble in common GPC solvents at ambient temperature. [c] Turnover number = number of moles of monomers converted to polymer per mole of catalyst employed.

Table 7. Copolymerization of Norbornene Derivatives and Ethene Using Catalyst 2[a]

entry	NB monomer (M, NB:Ni)	reaction time (h)	yield (g)	composition (RNB:Et)	M_w	M_w/M_n	TON[b]
1	butyl-NB (0.33, 66)	1.5	1.03	20:80	7800	1.61	390
2	NB-CO_2Et (0.3, 60),	1.25	1.16	18:82	22 900	1.69	438
3	NB-$CH_2OC(O)Me$ (0.3, 60)	4.5	1.25	11:89	N.D.[b]		618
4	NB-$CH_2OC(O)Me$ (0.6, 120)	1	1.11	19:81	18 000	1.72	408
5	NB-CH_2OH (0.4, 80)	5.75	0.23	6:94	4400	1.28	129

[a] All copolymerizations were carried out in toluene at 70 °C, at 5.0 mM [catalyst 2], under a single charge 200 psi ethene. Polymerization procedure B followed. [b] Insoluble in common GPC solvents at ambient temperature. [c] Turnover number = number of moles of monomers converted to polymer per mole of catalyst employed.

Table 8. Effect of Reaction Time on Polymer Composition in the Copolymerization of Butylnorbornene and Ethene Using Catalyst 2[a]

entry	reaction time (h)	yield (g)	composition (Bu-NB:Et)	M_w	M_w/M_n
1	0.5	0.77	21:79	13 400	1.65
2	2	0.98	20:80	12 100	1.60
3	14	1.69	16:84	11 200	1.71
4	26	1.86	19:81	13 900	1.63

[a] All copolymerizations were carried out in toluene at 70 °C, at 5.0 mM [catalyst 2], under a single 200 psi ethene charge and 0.66 M butyl-NB (butyl-NB:Ni = 130). Polymerization procedure B followed.

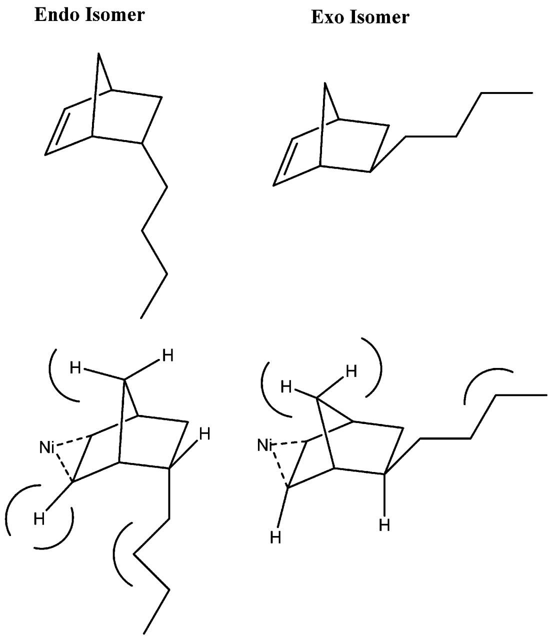


Figure 2. Isomers of *n*-butylnorbornene and steric interactions with nickel.

studies, the assignments of the ^{13}C NMR resonances have been made with some degree of confidence. We sought to reveal similarities and/or differences between the microstructure of the copolymers synthesized using nickel compounds and that made with metallocenes.

Based on the above reports, there is currently a good understanding of the rather complex nature of the ^{13}C NMR spectra. This includes the assignments and quantitation of isolated, alternating and blocky norbornene sequences including the more recently recognized tacticity effects due to the presence of two prochiral centers in the norbornene molecule.[18d,g]

Catalyst selection plays a crucial role in the outcome of the copolymerization process allowing for the design of copolymers with defined degrees of microstructure, from alternating to highly blocky for the same level of norbornene content. While the ^{13}C NMR resonances of the short NN (N = norbornene) and NNN blocks are markedly affected by the relative stereochemistry of the norbornenes in *m* and *r* diads, as well as in *mm*, *mr*, and *rr* triad configurations, the stereochemistry of the alternating sequences is only described in the ^{13}C NMR spectra as being in *m* or *r* configuration. Appropriate catalyst systems are known that can produce in the case of highly alternating E−N copolymers, a specific tacticity, such as *erythrodiisotactic*, where N−E−N sequences are placed in a *meso* configuration.[18d,l,n]

A representative 188 MHz ^{13}C NMR spectrum, obtained on a 750 MHz NMR spectrometer in tetrachloroethane-d_2 at 105 °C, of a norbornene−ethene copolymer made using catalyst **1**, is shown in Figure 3. The norbornene content of this polymer is 45.6%. The spectrum appears very close to the one for a copolymer made using $Me_2Si(Me_4Cp)(N^tBu)TiCl_2$ and methaluminoxane reported by Tritto.[18d] It corresponds, for the most part, to alternating norbornene/ethene blocks. In addition, there are some isolated norbornene units present in polyethene sequences. There are only traces of norbornene diads/triads.[19] The norbornene is clearly *exo*−*exo* enchained as *endo*−*endo* or *endo*−*exo* enchainment would have produced resonances at ~22 ppm for the C_5/C_6 methylenes and 36−37 ppm for C_7.[20]

The chemical shift assignments for this nickel catalyst-based polymer can be compared with the assignments extracted from the published data for the titanium-based polymer, corrected for the different referencing in the published data by Tritto: C_2/C_3 47.69 ppm vs 47.72 ppm in the isotactic (*m*) and 47.11 ppm vs 47.11 ppm in the syndiotactic (*r*) configuration alternating copolymer and C_1/C_4 41.90 ppm vs 41.91 ppm for the *m* and 41.40 ppm vs 41.43 ppm for the *r* configuration. The above syndiotactic (*r*) carbon resonances are broadened by an additional fine structure at this high field, which is attributed to sequencing effects in pentads like NENEN and NENEE. A possible higher order tacticity

Table 9. Results of Terpolymerization Reactions Using Catalyst 2[a]

entry	NB monomer (M, NB:Ni)	1-alkene (g)	reaction time (h)	yield (g)	composition (Et:NB:1-alkene)	M_w	M_w/M_n
1	NB (1.1, 213)	propene (8.8)	19	2.60	1:0.3:0.08	4400	1.83
2	butyl-NB (0.66, 132)	propene (8.1)	19	3.14	1:0.2:0.03	3700	1.35
3	NB (1.1, 213)	1-hexene (1.0)	13	2.66	1:0.1:0.07	10600	1.80
4	NB (1.1, 213)	1-hexene (3.0)	13	3.41	1:0.2:0.09	6800	1.84

[a] All copolymerizations were carried out in toluene at 70 °C, at 5.0 mM [catalyst 2], under a single 200 psi charge ethene. Polymerization procedure B followed.

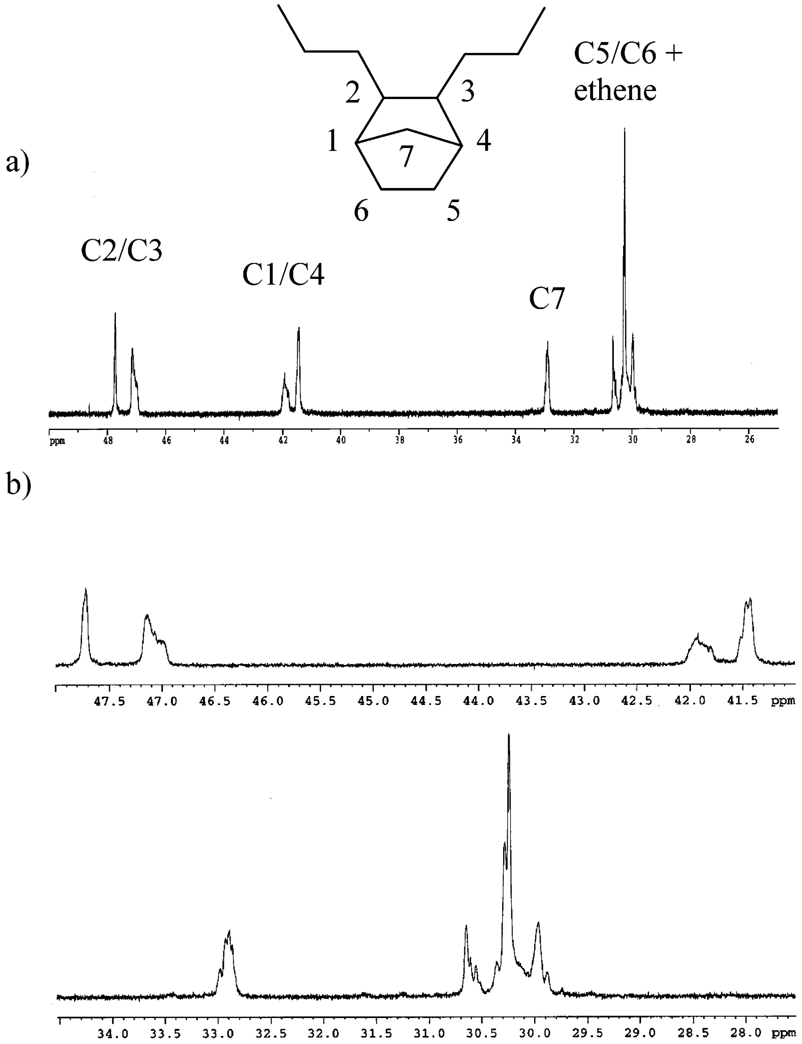


Figure 3. ^{13}C NMR spectra of norbornene/ethene copolymer: (a) complete spectrum, (b) expansion.

effect in the alternating sequence NENEN (*rr*, *mm*, and *mr* configurations) was not considered in explaining the additional fine structure observed. The C_7 carbon appears at 33.02 and 32.88 ppm in the nickel-based copolymer vs 33.17 and 32.88 ppm in the titanium-based copolymer, the difference being attributed to sequencing effects just as above. The most interesting feature we observe is in the region of the spectrum due to carbons C_5/C_6. Previously, these carbons were found to resonate as one sharp peak at 30.23 ppm. We find several resonances: one at 30.33 ppm, a more intense one at 30.26 ppm, and an even more intense one at 30.22 ppm. These peaks may show the expected sequencing effects mentioned above, but on the basis of the signal intensities, we believe that the main reason for the observed splitting is tacticity, with the isotactic configuration being responsible for the strongest peak and the syndiotactic for the next one. At this point we cannot further assign the peaks due to the overlap of the alternating and isolated norbornene sequences.

The ethene CH_2 groups due to isotactic and syndiotactic alternating sequences appear at 30.77 and 29.94 ppm in the nickel-based copolymer and 30.64 and 29.94 ppm in the titanium-based copolymer, respectively. Additional peaks are also noticed at 30.63 and 30.54 ppm as well as at 30.05, 29.95, 29.87, and 29.73 ppm, and they are mostly due to additional sequencing effects, as the ethene is more removed from norbornenes.

At higher ethene content (i.e., those made at higher ethene pressure), the fraction of NENEN sequences decrease. For a 26:74 norbornene:ethene copolymer, entry 5 in Table 4, the peaks due to the EENEE, or isolated norbornene, fraction grows considerably.

For copolymers with nearly 50:50 norbornene:ethene content, it becomes more difficult to detect the presence of the EENEE pentad as the copolymer approaches

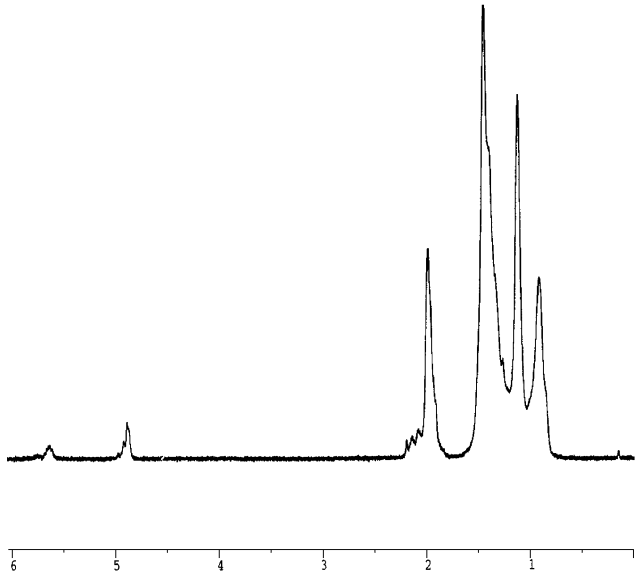


Figure 4. ^{1}H NMR spectrum of low molecular weight norbornene/ethene copolymer.

complete alternation. Integration of carbons 1 and 2 due to the NENEN sequences reveals that these copolymers contain approximately 50:50 syndiotactic:isotactic units, i.e., a truly random, alternating copolymer of ethene and norbornene is produced. Small peaks are observed above 46 ppm in these spectra that indicate a very low concentration of NN diads present. However, even at very low pressures of ethene, copolymer containing significant quantities of successive norbornene enchainment could not be attained.

Copolymer End Groups. Formation of low molecular weight polymers, primarily from catalyst **4**, facilitated investigation of the nature of the chain end of the ethene−norbornene copolymer by NMR methods. Low molecular weight (M_w = 2500) ethene−norbornene copolymers exhibited signals between 5.5−5.8 and 4.8−5.1 ppm in a 1:2 ratio, respectively, in the ^{1}H NMR experiment (see Figure 4). This is indicative of a vinyl end group formed by β-hydrogen abstraction from a Ni−CH_2CH_2−polymer intermediate; the mechanism of this termination is illustrated in Figure 5a. The same end group was also observed for ethene-5-*n*-butylnorbornene copolymer; Figure 6a shows a ^{1}H NMR spectrum of the end group. Figure 6c shows the same part of the NMR spectrum for the ethene−norbornene−propene terpolymer. In addition to the peaks due to the vinyl end groups seen in Figure 6a, there are resonances corresponding to vinylidene (~4.7 ppm) and internal vinylene groups (~5.4 ppm). Figure 5b illustrates the two different insertion (1,2 and 2,1) and termination mechanisms involving 1-alkenes. Thus, unlike ethene, the insertion of 1-alkenes allow additional termination pathways.

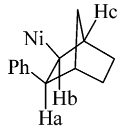
^{13}C NMR analysis of the low molecular weight ethene−norbornene copolymer stemming from catalyst **4**, in addition to exhibiting resonances at about 140 and 113 ppm consistent with vinyl end groups, also shows resonances at about 14 and 22 ppm consistent with ethyl end groups. The relative concentrations of these peaks are essentially equal based on integration.

As Table 9 shows, the level of incorporation of 1-hexene and propene relative to ethene and norbornene is similar for all four terpolymers. However, the molecular weights of the ethene−norbornene−1-hexene terpolymers are higher than those of the corresponding ethene−norbornene−propene terpolymers. This suggests that the β-hydrogen abstraction following insertion of 1-hexene is slower than that following propene insertion. Further support of this hypothesis comes from the NMR integration data for the end groups. Comparison of the relative integrations for the vinyl end group resonances (~4.9 ppm) vs those for the vinylidene (~4.6 ppm) and internal vinylene end groups (~5.5 ppm) in the ethene−norbornene−1-hexene terpolymer (Figure 6b) show that termination following 1-hexene insertion occurs twice as often as termination following ethene insertion. In the case of the ethene−norbornene−propene, the corresponding ratio is 3:1.

The differences in terpolymer molecular weights could also be due to differences in relative insertion rates. If the rates of β-hydrogen elimination following the insertions of propene and 1-hexene are similar but the propene insertion is more facile than 1-hexene, then there would also be a decrease in the molecular weight for the propene-terminated polymers. At this time it is not possible to distinguish between these two possible scenarios.

Copolymerization Mechanism. Polymerization mechanisms consist of initiation, propagation, and termination or chain-transfer steps. A proposed mechanism for norbornene/ethene copolymerization including these steps is presented in Figure 7.

With regard to initiation, it seems reasonable that ethene−norbornene copolymerization would begin in a manner identical to that proposed for ethene oligomerization/polymerization. Substitution of the donor ligand L by ethene followed by insertion of ethene into the Ni−Ph bond of the catalyst forms an intermediate that undergoes β-hydrogen elimination to form a Ni−H species and, presumably, styrene.[21] Keim and co-workers have gathered evidence for the intermediacy of a Ni−H species in the ethene oligomerization reaction.[22] Additionally, it is unlikely that norbornene initiates the polymerization since the nickel compounds do not homopolymerize norbornene. This is expected behavior since after the purported insertion of norbornene into the Ni−Ph bond, there is no β-hydrogen suitably positioned for elimination (see structure below). H_a is anti to the Ni center and therefore inaccessible; elimination of H_c would result in a bridgehead C=C, violating Bredt's rule.[23] Thus, no Ni−H species can be created to initiate the polymerization.



After formation of the Ni−H species, propagation occurs by insertion of norbornene or, more likely, ethene.[24] From the microstructure analysis of the ethene−norbornene copolymers, it is clear that insertion of norbornene occurs only after insertion of ethene; the vast majority of norbornene units are sandwiched between ethene units. Enchainment of two (or more) successive norbornene monomers would require the formation of an intermediate that may be too sterically crowded and therefore inaccessible (see Figure 7). This may explain why even when the percentage of norbornene in the copolymer approaches 50%, the appearance of norbornene diad sequences is minimal, to say nothing of triad sequences.

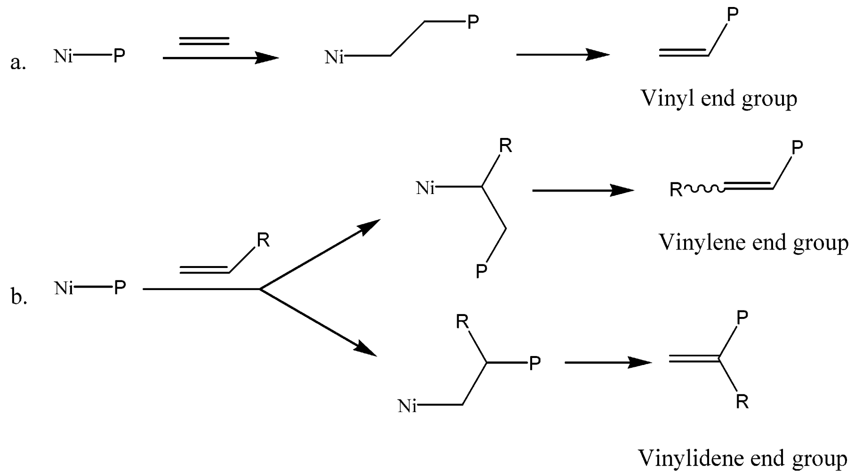


Figure 5. Mechanisms of 1-alkene termination.

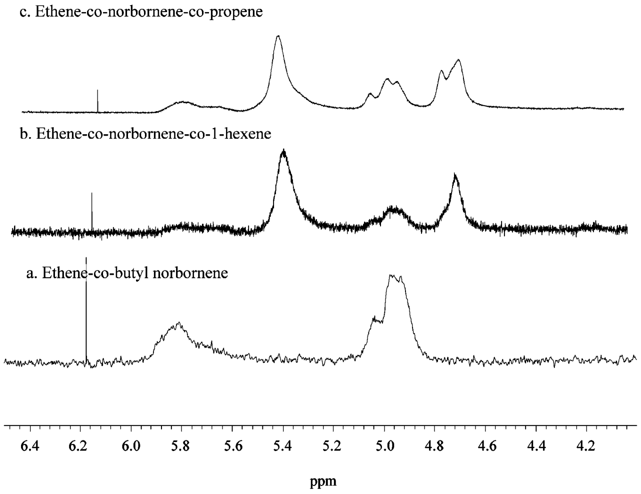


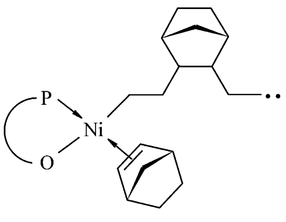
Figure 6. ^{1}H NMR spectrum of polymer end groups.

Termination and chain transfer in ethene–norbornene copolymerization occur via β-hydrogen elimination from the last inserted ethene unit to form, presumably, a Ni–H species coordinated by a vinyl-terminated polymer. Ethene competes with this coordinated polymer expelling the vinyl-terminated copolymer product and regenerating the purported Ni–H catalyst species. In the 1-alkene terpolymers, β-hydrogen elimination following 1-alkene insertion is even more favorable leading to lower molecular weight materials.

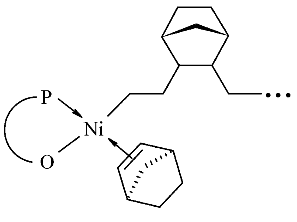
When L is a strong donor ligand such as phosphine, we find that the molecular weight of the copolymers are substantially lower. This observation strongly suggests that the phosphine effectively competes with the vinyl-terminated copolymer for a coordination site on the metal and expels the copolymer from the coordination sphere before it can reinsert into the Ni–H bond and continue growing the polymer chain.

The nickel catalysts used in this study only differ in terms of their donor ligand L. The proposed catalyst species, (P~O)NiH(C_2H_4), is devoid of L, and therefore it is anticipated that the microstructure could only be affected by the remaining P~O ligand. Since the P~O ligand is the same in every nickel complex employed here, it is not surprising that the copolymer microstructure is essentially equivalent at equivalent levels of norbornene incorporation.

With high levels of norbornene incorporation, the polymer adopts a NENEN sequence with random tacticity. Thus, there is no significant energetic difference between A and B. This would be expected since the (P~O)Ni fragment contains a plane of symmetry containing Ni, P, and O and therefore does not distinguish between coordination of norbornene with the bridging methylene group up or down.



A



B

Thermal, Mechanical, and Optical Properties of Copolymers. The glass transition temperature of selected norbornene/ethene copolymers made using catalysts **1**, **2**, and **3** were determined using DSC techniques. The T_g data are presented in Table 10 along with the molecular weight data of the copolymers. The T_g data are also plotted as a function of both mole percent norbornene (determined by NMR spectroscopy) and catalyst type in Figure 8.

As expected, the T_g of the copolymer increases as the content of norbornene increases. The plot shows a smooth, linear increase in T_g with norbornene content with no significant deviations, irrespective of the catalyst used. This behavior reflects the fact that the copolymers produced by the nickel catalysts investigated are all very similar in terms of microstructure. There are no significant runs of norbornene blocks which are known to result in higher glass transition temperatures, all else being equal.[25]

Since catalyst **3** typically yields low molecular weight copolymers relative to catalyst **1** or **2**, the data in Table 10 allow us to investigate the effect of molecular weight on glass transition temperature. For example, the T_g of the copolymer from entry 8 is 115 °C, and the M_w (30 000) is rather low. The T_g of this copolymer falls between the two other copolymers that have twice the M_w but contain slightly lower and slightly higher norbornene content (see entries 7 and 9). This behavior suggests that at M_w's as low as 30 000 the chains experience sufficient entanglement such that no significant deviation in T_g is apparent when compared to copolymers with M_w's that are 2-fold higher. The T_g vs

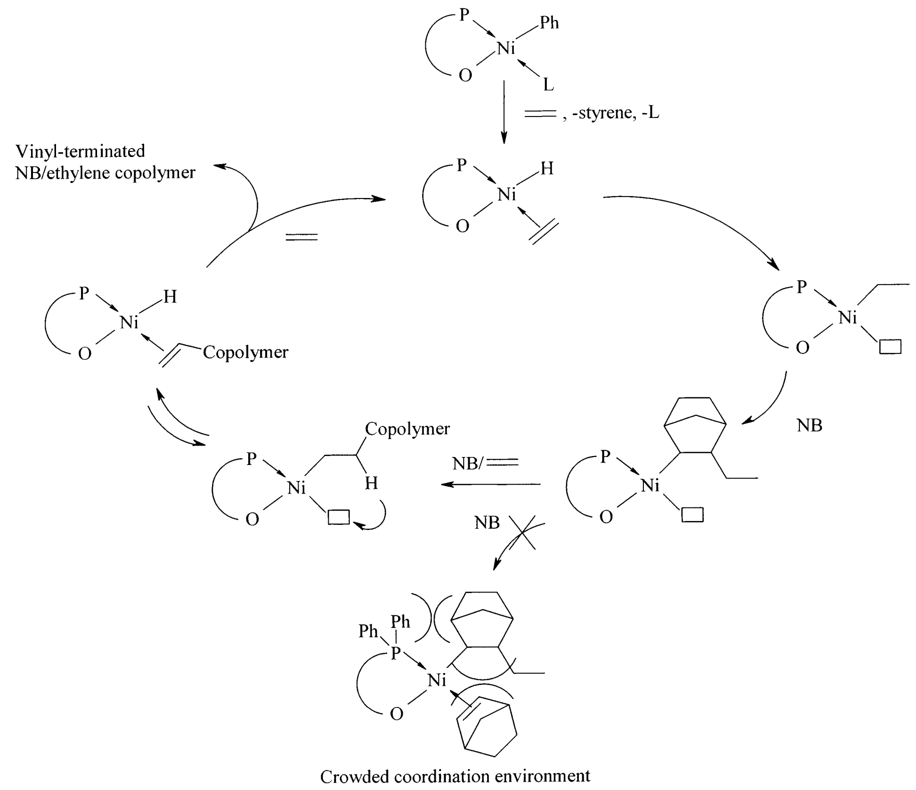


Figure 7. Mechanism of norbornene/ethene copolymerization.

Table 10. Effect of Catalyst Type and Mole Percent Norbornene on T_g

entry	catalyst	% NB	T_g (°C)	M_w	modulus (GPa)	elongation at break (%)	transmission (%) (400−700 nm)
1	**1**	26	32	42 300			
2	**1**	33	57	44 700			
3	**1**	39	78	55 100			90.3
4[a]	**1**	41	109	64 000	1.9	8.5 ± 1.4	
5	**2**	42	109	67 700	1.8	7.3 ± 2.2	
6	**1**	43	105	75 900			
7	**1**	44	110	60 900			
8	**3**	46	115	30 000			
9	**1**	47	126	66 700			90.5
10	**1**	47	123	76 000			90.1
11	**1**	48	123	85 600			
12	**3**	49	123	32 500			
13	**1**	50	133	78 700			90.6

[a] Contains 2 mol % NB-COOMe.

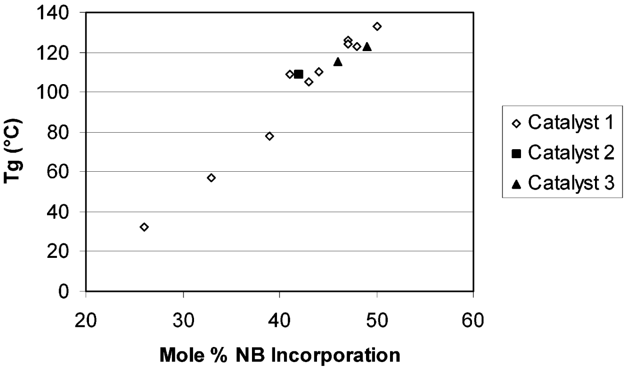


Figure 8. Plot of mole percent norbornene vs T_g of copolymer using catalysts **1**, **2**, and **3**.

M_w behavior at higher norbornene content seems to be more complicated since the T_g of entry 12 seems to be somewhat depressed compared to the T_g's of the higher M_w samples presented in entries 9, 10, 11, and 13.

Given the interest in the optical properties of norbornene/ethene copolymers made using metallocene catalysts, we investigated the transmission in the visible region of a selected number of copolymers made with nickel catalyst **1**. The transmission data, an average from 400 to 700 nm, were determined from solvent-cast thin films of the copolymers. The results are given in Table 10. Note that within the range of norbornene content investigated, 39−50%, the transmission is very high at over 90%. There is no indication of haze in the copolymers investigated. By way of comparison, metallocene-based norbornene/ethylene copolymers are reported to exhibit around 92% transparency.[26]

Pereña and co-workers have found that the tensile modulus of norbornene/ethene copolymers made using metallocene catalysts increases as the content of norbornene in the copolymer increases.[27] They investigated a range of copolymers from 31 to about 63% norbornene. For a copolymer with norbornene content of 43%, a tensile modulus of 1.97 GPa was reported. A copolymer containing 42% norbornene made with catalyst **2** exhibited a comparable tensile modulus of 1.8 GPa (see entry 5, Table 10). The elongation at break was 8.5% and is in the range reported for TOPAS.[28]

Our ability to incorporate functionalized norbornenes using nickel catalysts offered us the opportunity to investigate the effect of these monomers on the thermal and mechanical properties. A polymer of norbornene and ethene with 2 mol % of the methyl ester of norbornene carboxylic acid (NB-CO_2Me) incorporated was made using catalyst **1** (see entry 4 in Table 10). This material was very similar to the norbornene/ethene copolymer in entry 5 of Table 10 in terms of molecular weight and total norbornene content. The T_g of the terpolymer containing NB-CO_2Me was indistinguishable from the copolymer; both exhibited a transition at 109 °C. In addition, the tensile modulus and elongation at break were very similar to the copolymer material. Evidently, such low levels of incorporation of this functional monomer are insufficient to change markedly the thermal or mechanical properties evaluated herein.

Conclusions

Several conclusions can be drawn from the work described. First, the neutral nickel compounds are efficient catalysts for the copolymerization of norbornene derivatives with ethene. Up to 50 mol % incorporation of norbornene, leading to an essentially alternating copolymer, is obtained. Higher incorporation does not occur because of steric congestion resulting from the coordination of norbornene to the catalyst center with a nickel−norbornyl linkage (see Figure 7).

The distinct advantage of the nickel catalysts, when compared to the corresponding early transition metal-based analogues, is their ability to copolymerize norbornene derivatives bearing oxygen functionalities. However, the level of incorporation is lower, as are the reaction rates and polymer molecular weights. Based on work by us and others,[16] chelate formation by coordination of the *endo*-functionalized norbornene and the corresponding *endo*-inserted product is at least partially responsible for the attenuation in rate. The slower chain growth allows β-hydrogen abstraction from the last inserted ethene to compete effectively, leading to lower molecular weight polymers. The nickel catalysts also allow the terpolymerization of ethene and norbornene with an 1-alkene, such as propene. The terpolymer molecular weights tend to be low because of slower monomer insertion and additional chain-transfer pathways that are available following 1-alkene insertion.

Finally, the ethene/norbornene copolymers obtained using the nickel catalysts are essentially indistinguishable from those obtained using metallocene-based early transition metal catalysts, in terms of both the microstructure and such physical properties as T_g and tensile modulus. For the ethene/norbornene polymers synthesized, the glass transition temperature (T_g) increases smoothly with increasing norbornene content.

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(19) A reviewer pointed out that only when both comonomer reactivity ratios are close to 0 can a truly alternating copolymer be obtained. In our study the reactivity ratios of ethene and norbornene were not measured; however, it is reasonable to assume that the reactivity of ethene is much greater than that of norbornene. As such, it is conceivable to find reaction conditions in which the instantaneous copolymer composition is 50:50 by starving the comonomer feed of the more reactive monomer (ethene). Under these conditions, ethene homopolymerization should not occur. In reality, however, some ethene homo-enchainment occurs, and dimers, trimers, and higher blocks of norbornene are barely detectable. For those cases where the molar copolymer composition is 50:50 and where no NMR signals due to norbornene blocks are observed, it is assumed that the copolymer has a (quasi)-alternating structure.

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