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Addition Polymerization of Norbornene-Type Monomers Using Neutral Nickel Complexes Containing Fluorinated Aryl Ligands

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ABSTRACT: The strong Lewis acid $B(C_6F_5)_3$ was found to activate complexes of nickel toward the polymerization of norbornene-type monomers. The active species in this reaction is created by the transfer of C_6F_5 from boron to nickel. As a result, a class of neutral, single-component nickel complexes was developed containing two electron-withdrawing aryl ligands that polymerize norbornene and norbornenes with functional pendant groups. Active complexes include $Ni(C_6F_5)_2(PPh_2CH_2C(O)Ph)$, ($\eta^6$-toluene)Ni($C_6F_5$)$_2$, and Ni(2,4,6-tris(trifluoromethyl)phenyl)$_2$(1,2-dimethoxyethane). In the case of (η^6-toluene)Ni(C_6F_5)$_2$, isolation and characterization of low molecular weight norbornene polymers, using ethylene, indicated that each polymer chain contained a C_6F_5 headgroup. This points to the initiation step as being the insertion of norbornene into the Ni−C_6F_5 bond. The polymer microstructure as revealed by ^{1}H and ^{13}C NMR spectrometry is entirely different from that produced using the cationic nickel catalyst, [(η^3-crotyl)Ni(1,4-COD)]PF_6. This difference in microstructure led to improved mechanical properties for 80:20 copolymers of norbornene and 5-triethoxysilylnorbornene.

Introduction

The homopolymerization of bicyclic olefins such as norbornene can be effected by three commonly known routes: ring-opening metathesis polymerization (or ROMP), cationic polymerization, or vinyl addition polymerization. ROMP of norbornene yields a polymer containing unsaturation in the backbone. Cationic polymerization typically results in the formation of low molecular weight polymers with rearranged norbornene units in the backbone. Vinyl addition of norbornene yields a completely saturated polymer with no rearranged norbornene units. Reviews of routes to vinyl addition norbornene polymers have recently appeared.[5]

Addition polymers of norbornene-type monomers exhibit a combination of properties that make them ideal for many electronic and optical applications. These properties include a very high glass transition temperature, high optical transparency, and low dielectric constant.

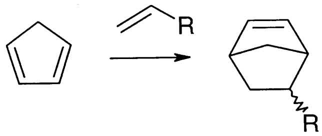
A T_g of up to 370 °C has been reported for the addition homopolymer of norbornene.[6] Such a high T_g is necessary for integration of polymers into electronic applications since electronic devices typically go through high-temperature processing.

The high optical transparency of addition poly(norbornenes) in the infrared region of the spectrum makes them viable candidates for data and telecommunication waveguide materials.[7] In the visible region (400−700 nm) transmission in excess of 90% is typical, which is a necessary attribute for any plastic display substrate material.[8] For optical applications, the amorphous nature of addition polymerized norbornenes and subsequent low birefringence are a plus. The high transparency of polynorbornenes in the deep-UV region and their good reactive ion etch resistance make them ideal as photoresist matrix materials.[9]

Low dielectric constant and high T_g are two criteria for polymers used in electronic packaging applications. These two properties and the rather low moisture absorption characteristic of addition poly(norbornene) make it a viable material for this application.[10] Addition poly(norbornene) can be made photodefinable,[11] a desirable attribute for electronics packaging when connection and redistribution of circuitry are required.

In addition, the rather sharp decomposition temperature and low char yield of certain addition poly(norbornenes) have enabled the development of sacrificial materials for the creation of micron or submicron air gaps for the creation of electrical interconnection and microfluidic devices and for creation of nanoporous glass matrices for interlayer dielectrics in semiconductors.[12]

Tailoring addition poly(norbornenes) for so many applications is possible in large part due to the accessibility of norbornene monomers with different functional pendant groups. The functional pendant group on norbornene arises from the substituent R on the dienophile in the Diels−Alder cycloaddition with cyclopentadiene.



Incorporation of functional pendant groups in the polymer can change the properties of the polymer significantly. For example, pendant silyl ethers yield addition poly(norbornenes) with increased adhesion,[13] while pendant carboxylic acid functional addition poly-

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(norbornenes) can be developed using aqueous base to give submicron features in photoresist formulations.[14]

Polymerization of norbornenes with functional pendant groups has relied on the development of cationic, late transition metal catalysts that are more tolerant of, for example, oxygen-containing substituents than early transition metals.[15] Early success in this area was enabled by the discovery that complexes such as $[(\eta^3\text{-crotyl})\mathrm{Ni}(1,4\text{-COD})]\mathrm{PF_6}$ (COD = cyclo-1,5-octadiene) were effective at polymerizing norbornene-type monomers.[6,16]

In the course of developing multicomponent catalysts of nickel, it was discovered that mixtures of nickel complexes, Lewis acids (e.g., $\mathrm{BF_3{\cdot}Et_2O}$), organometallic alkylating agents (e.g., $\mathrm{AlEt_3}$), and a Brønsted acid (e.g., $\mathrm{HSbF_6}$), behave essentially identically to cationic allyl complexes of nickel such as $[(\eta^3\text{-crotyl})\mathrm{Ni}(1,4\text{-COD})]\mathrm{PF_6}$. The activity of the single and the multicomponent systems is similar for norbornene polymerization. The ^{1}H and ^{13}C NMR spectra of the homopolymers of norbornene are identical, and the response of each catalyst system to olefinic chain transfer agents such as decene-1 is similar.[17] In an attempt to broaden the scope of this discovery, the efficacy of several other Lewis acids was explored, including $\mathrm{B(C_6F_5)_3}$. Herein, we describe the results of the activation of nickel complexes using $\mathrm{B(C_6F_5)_3}$ toward the polymerization of norbornene-type monomers, evidence that the polymerization is initiated by a $\mathrm{Ni{-}C_6F_5}$ group formed by $\mathrm{C_6F_5}$ transfer from B to Ni, the impact of catalyst on polymer microstructure, and the resulting polymer properties. During the preparation of this paper, reports appeared by Janiak and co-workers describing borane activators for norbornene polymerization using nickel complexes.[18]

Experimental Section

General Procedures and Materials. All manipulations were carried out under an atmosphere of prepurified nitrogen using standard Schlenk or drybox techniques. Solvents were dried and deoxygenated with prepurified nitrogen. The ^{1}H and ^{19}F NMR spectra were recorded on a Bruker AMX-500 NMR spectrometer operating at 500.13 and 470.53 MHz, respectively. Chemical shifts for ^{1}H NMR spectra were referenced to internal residual protio solvent resonances and are reported relative to tetramethylsilane. The ^{19}F NMR spectra were referenced to external $\mathrm{CFCl_3}$. Solid-state ^{13}C CP MAS (cross-polarization with magic angle spinning) NMR spectra were obtained on a Varian Unity Plus NMR spectrometer operating at 50 MHz. The mass spectra were recorded on a Finnigan MAT 95Q mass spectrometer.

Molecular weights were determined using a Waters 150C GPC instrument equipped with a refractive index detector. Homopolymer samples were dissolved in trichlorobenzene (80 mg/15 mL) and filtered hot through a 0.45 μ Teflon filter. Copolymer samples were dissolved in monochlorobenzene at room temperature. All molecular weights are relative to polystyrene standards.

Norbornene was purchased from Aldrich and was distilled from $\mathrm{CaH_2}$ prior to use. 5-Triethoxysilylnorbornene was obtained from Gelest. $\mathrm{B(C_6F_5)_3}$ was obtained from Akzo-Nobel as a 3.15 wt % solution in Isopar E. Triethylaluminum (1.7 M in cyclohexane) was purchased from Albemarle Corp. Nickel(2,2,6,6-tetramethyl-3,5-heptanedionate)$_2$ (Ni(dpm)$_2$, **1**)[19] and Pd(dpm)$_2$ (**2**)[20] were prepared according to a literature procedure. $\mathrm{[Ni(Ph)(PPh_2CH{=}C(O)Ph)]_2}$ (**3**), $\mathrm{Ni(C_6F_5)_2(PPh_2CH_2C(O)Ph)}$ (**4**), and $\mathrm{B(C_6F_5)_3{\cdot}3H_2O}$ were synthesized according to a published method.[21] $(\eta^6\text{-toluene})\mathrm{Ni(C_6F_5)_2}$ (**5**) has been synthesized previously.[22] Ni(2,4,6-tris(trifluoromethyl)phenyl)$_2$-(1,2-dimethoxyethane) (**6**) was prepared as reported previously.[23] Ni(ethylhexanoate)$_2$ (Ni Hexcem, 8 wt % solution in mineral spirits) was purchased from OMG.

Caution: Care must be taken when handling lithium and magnesium fluorinated aryl reagents since certain compounds may explode violently during their preparation.[24]

$[(\eta^3$-Crotyl)(cycloocta-1,5-diene)nickel]hexafluorophosphate. This preparation is adapted from the synthetic procedure for the corresponding methallyl complex.[25] A solution of crotyl bromide (1.35 g, 10.0 mmol) and butadiene (2.5 g, 46 mmol) in toluene (24 mL) was added to a flask containing bis(cycloocta-1,5-diene)nickel (2.75 g, 10.0 mmol). A deep-red solution of $(\eta^3$-crotyl)nickel bromide dimer resulted. After 2 h at ambient temperature the solvent was removed under reduced pressure. To the resulting powder was added a solution of 1,5-cyclooctadiene (3.6 mL) in THF (32 mL). The solution was cooled to 0 °C, and thallium hexafluorophosphate (3.5 g, 10 mmol) was added to the resulting mixture which was warmed to ambient temperature and stirred for 1 h. The solvent was removed in vacuo, and dichloromethane (24 mL) was added. Insoluble thallium bromide was removed by filtration. The filtrate solution was reduced in volume, and diethyl ether was added. The solution was cooled to afford 1.3 g (35% overall yield) of $[(\eta^3$-crotyl)(cycloocta-1,5-diene)nickel]hexafluorophosphate as orange crystals. Anal. Calcd for $\mathrm{C_{12}H_{19}F_6PNi}$: C, 39.28; H, 5.23. Found: C, 39.00; H, 5.30. ^{1}H NMR ($\mathrm{CDCl_3}$): 5.99 (m, 1H); 5.85 (m, 1H); 5.85 (m, 1H); 5.75 (m, 1H); 5.02 (m, 1H); 4.31 (m, 1H); 4.20 (d, 1H); 3.10 (m, 1H); 3.01 (d, 1H); 2.92 (m, 1H); 2.51 (m, 6H); 1.29 (d, 3H).

Homopolymerization of Norbornene Using $[(\eta^3$-Crotyl)(cycloocta-1,5-diene)nickel]hexafluorophosphate. To a 3 L wide-mouth glass flask equipped with a mechanical stirrer was added the following materials in the order given: norbornene (230 g, 2.44 mol), 1,2-dichloroethane (2340 mL), and $[(\eta^3$-crotyl)(cycloocta-1,5-diene)nickel]hexafluorophosphate (0.44 g, 1.2 mmol) dissolved in dichloromethane (2 mL). After adding the catalyst to the stirred solution, polymer started precipitating from solution as a white powder to give a viscous "cake" within about 5 s. The reaction exothermed to a maximum of 64 °C. After 60 min, methanol (100 mL) was added to destroy the catalyst. The polymer cake was added to stirring acetone to afford the product as a white powder which was filtered off and washed with acetone and then methanol. The polymer was then dried overnight in a heated (60 °C) vacuum oven. Yield: 228.6 g (99.4%). ^{1}H NMR (1,2-dichlorobenzene-d_4, 50 °C): δ 2.38 (br m, 2H), 2.1−0.9 (br m, 8H). GPC: $M_\mathrm{w} = 1\,640\,000$; $M_\mathrm{n} = 436\,000$.

Norbornene Polymerization Procedure Using Ni(dpm)$_2$, AlEt$_3$, and B(C$_6$F$_5$)$_3$. In a typical polymerization procedure, norbornene (5.0 g, 53 mmol) was added to a vial equipped with a magnetic stirbar in the drybox. The norbornene was diluted with 1,2-dichloroethane to give a 0.9 M solution of monomer. To this solution was added Ni(dpm)$_2$ (0.0055 g, 0.013 mmol), followed by triethylaluminum (0.077 mL of a 1.7 M solution in cyclohexane) and $\mathrm{B(C_6F_5)_3}$ (2.64 mL of a 3.15 wt % solution in Isopar E). The polymerization was halted after the appropriate time by pouring the contents of the vial into an excess of methanol. The polymer was isolated by filtration and dried under vacuum. Yield: 4.85 g (97%). ^{1}H NMR (1,2-dichlorobenzene-d_4, 50 °C): δ 2.38 (br m, 2H), 2.1−0.9 (br m, 8H). Attempts to determine the molecular weight of this polymer in 1,3,5-trichlorobenzene were unsuccessful due to incomplete dissolution in this solvent.

Norbornene Polymerization Procedure in the Presence of Ethylene Using $(\eta^6$-toluene)Ni(C$_6$F$_5$)$_2$. To a 100 mL glass vial equipped with a magnetic stirbar, 5.1 g of norbornene (54 mmol) was added in the drybox. The norbornene was dissolved in 50 mL of toluene. The solution was charged with 5 psi ethylene pressure, and a toluene solution (10 mL) of $(\eta^6\text{-toluene})\mathrm{Ni(C_6F_5)_2}$ was injected. The reaction was stirred for 1 h at room temperature. The higher molecular weight polymer was precipitated by addition of the reaction solution to methanol (300 mL). The solid was collected by centrifugation. The resulting methanol fraction was separated and allowed to evaporate. From the methanol fraction 0.4 g of solid was collected. Methanol-insoluble fraction: ^{1}H NMR (*o*-dichlorobenzene-d_4): δ 6.0−5.7 (two br s, 1H), 5.0 (br s, 2H), 3.3 (br s, 1H), 2.8−0.9 (aliphatic protons). ^{19}F NMR (*o*-dichloroben-

Table 1. Polymerization of Norbornene Using Multicomponent Catalyst Systems

expt[a]	nickel complex	cocatalyst	activator	conv (%)	activity[c]	M_w	M_w/M_n
1	$[(\eta^3\text{-crotyl})Ni(1,4\text{-COD})]PF_6$, 0.47 mM			99	191 000	1 640 000	3.76
2	$Ni(dpm)_2$, 0.22 mM	$AlEt_3$, 2.2 mM	$B(C_6F_5)_3$, 2.0 mM	97	373 000[d]	1 050 000[e,f]	5.95
3	$Ni(dpm)_2$, 0.22 mM		$B(C_6F_5)_3$, 2.0 mM	95	366 000[d]	619 000[f]	2.40
4	$Ni(dpm)_2$, 0.22 mM		$B(C_6F_5)_3$, 0.22 mM	48	186 000		
5	$Ni(dpm)_2$, 0.22 mM		$B(C_6F_5)_3$, 0.22 mM	54	206 000		
6	$Ni(dpm)_2$, 0.22 mM		$B(C_6F_5)_3$, 0.22 mM	46	178 000		
7	$Ni(dpm)_2$, 0.22 mM		$BF_3 \cdot Et_2O$, 2.0 mM	0[g]			
8	$Ni(dpm)_2$, 0.22 mM		$B(OEt)_3$, 2.0 mM	0			
9	$Ni(dpm)_2$, 0.22 mM		$B(OC_6F_5)_3$, 2.0 mM	0			
10	$Pd(dpm)_2$, 0.22 mM		$B(C_6F_5)_3$, 2.0 mM	95	366 000	h	
11	$Pd(dpm)_2$, 0.22 mM		$B(C_6F_5)_3$, 0.22 mM	11	44 000		
12	$Ni(dpm)_2$, 0.22 mM		$B(C_6F_5)_3 \cdot 3H_2O$, 0.22 mM	91	352 000	418 000	2.43
13	$Ni(dpm)_2$, 0.22 mM		$B(C_6F_5)_3 \cdot 3H_2O$, 0.22 mM	87	331 000	314 000	1.73
14[b]	$[Ni(Ph)(PPh_2CH{=}C(O)Ph)]_2$, 0.16 mM		$B(C_6F_5)_3$, 1.6 mM	16	79 000	2 230 000	4.11
15[b]	$[Ni(Ph)(PPh_2CH{=}C(O)Ph)]_2$, 0.16 mM		$B(C_6F_5)_3 \cdot 3H_2O$, 0.33 mM	86	412 000[d]	1 250 000[f]	7.78

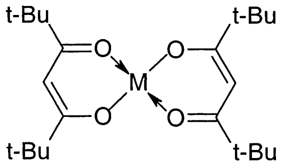
[a] All runs were carried out in 1,2-dichloroethane for 1 h at room temperature at 0.9 M norbornene concentration. [b] Run carried out in toluene. [c] In g of polymer produced/(mol of Ni h). [d] Likely to be much higher since a solid formed within 1 min of mixing. [e] Not completely dissolved. [f] Partially excluded from column. [g] No high polymer obtained upon addition to methanol. [h] Insoluble.

zene-d_4): −133.1 and −133.8 (singlets, 1 F), −139.3 (s, 1 F), −158.1 (s, 1 F), −162.7 (s, 2 F). GPC: $M_w = 7900$, $M_n = 3800$.

Results and Discussion

Norbornene Polymerization. Polymerization of norbornene using $[(\eta^3\text{-crotyl})Ni(1,4\text{-COD})]PF_6$ in 1,2-dichloroethane resulted in essentially quantitative conversion to polymer (experiment 1 in Table 1). The determined polymerization activity of $[(\eta^3\text{-crotyl})Ni(1,4\text{-COD})]PF_6$ was 191 000 g of polymer/(mol of Ni h). However, the actual activity of the catalyst system is likely to be much higher since during the polymerization a viscous mixture formed within 5 s after addition of the catalyst. Nevetheless, the polymerization was allowed to continue for a full hour to ensure complete conversion before the reaction was terminated. The molecular weight of the isolated polymer was very high ($M_w = 1\,640\,000$).

Tris(pentafluorophenyl)boron[26] is a very strong Lewis acid and as such is effective in a number of chemical transformations.[27] Tris(pentafluorophenyl)boron probably has found great utility as an activator in olefin polymerization. Marks and co-workers have shown that $B(C_6F_5)_3$ can abstract the methyl ligand from $(Me_5C_5)_2ZrMe_2$ to form a cationic zirconocene complex.[28] Following this logic, we investigated mixtures of an organic soluble nickel salt such as Ni(2,2,6,6-tetramethyl-3,5-heptanedionate)$_2$ (or $Ni(dpm)_2$), $AlEt_3$, and $B(C_6F_5)_3$ as catalyst components for the polymerization of norbornene. It was reasoned that $AlEt_3$ would alkylate nickel and $B(C_6F_5)_3$ would then abstract an anionic ligand and form a cationic nickel species, similar to $[(\eta^3\text{-crotyl})Ni(1,4\text{-COD})]PF_6$, which should be active in norbornene polymerization.[29]



$M(dpm)_2$

M = Ni (**1**) or Pd (**2**)

In polymerization experiment 2 (Table 1), the catalyst employed was a mixture of $Ni(dpm)_2$, $AlEt_3$, and $B(C_6F_5)_3$ in a 4000:1:10:9 norbornene:Ni:Al:B molar ratio. Near quantitative conversion (97%) and high activity were achieved just as in the case of $[(\eta^3\text{-crotyl})Ni(1,4\text{-COD})]PF_6$. In fact, the activity observed is in all likelihood higher than the determined 373 000 g of polymer/(mol of Ni h) since the polymerization reaction became solid within 1 min of addition of the catalyst components, indicating high conversion in a very short amount of time. Nevertheless, the polymerization was allowed to continue for a full hour before the polymer was isolated. The observed molecular weight of the polymer obtained is extremely high. However, the sample was not completely soluble in 1,3,5-trichlorobenzene at 135 °C and was partially excluded from the GPC column; therefore, the exact value of the molecular weight is unclear. This observation is in contrast to the poly(norbornene) isolated using $[(\eta^3\text{-crotyl})Ni(1,4\text{-COD})]PF_6$, which is completely soluble in 1,3,5-trichlorobenzene.

Janiak and co-workers found that mixtures of $B(C_5F_5)_3$ and $AlEt_3$ in combination with Ni(acetylacetonate)$_2$ or Ni(ethylhexanoate)$_2$ gave high norbornene polymerization activities.[18b]

NMR Characterization of Poly(norbornene). The ^1H and ^{13}C NMR spectra for poly(norbornene) (PNB1) made using $[(\eta^3\text{-crotyl})Ni(1,4\text{-COD})]PF_6$ are presented in Figures 1a and 2a, respectively. The ^1H and ^{13}C NMR spectra for poly(norbornene) (PNB2) made using a mixture of **1**, $AlEt_3$, and $B(C_6F_5)_3$ are given in Figures 1b and 3a, respectively. Both polymers are vinyl addition in nature since no olefinic resonances are observed in the isolated polymer (i.e., no ROMP polymer was formed). Their ^{13}C NMR spectra show that both polymers are *exo* enchained; the spectra do not exhibit resonances in the 20−24 ppm region. The presence of such resonances has been taken as evidence of *endo* enchainment on the basis of model studies.[30] Despite these similarities, the NMR spectra of the two polymers are distinctly different in appearance.

Assignment of methylene and methine resonances ^{13}C NMR resonances of both polymers is readily made using DEPT editing of the ^{13}C NMR spectra (see Figures 2 and 3). For the PNB1, the peaks between about 55 and 38 ppm are assigned to methine carbons, and those peaks between about 38 and 28 are assigned to methylene protons. The ^{13}C NMR spectrum of PNB2 can be similarly divided into methine (55−38 ppm) and

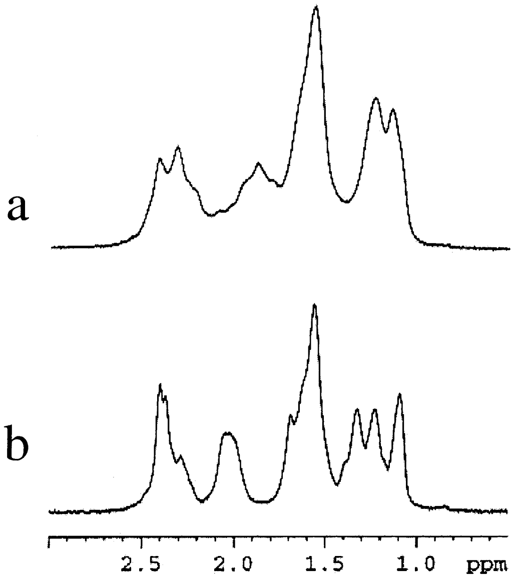


Figure 1. ^{1}H NMR spectra of addition poly(norbornene) PNB1 (a) and PNB2 (b) at 90 °C in *o*-dichlorobenzene-d_4.

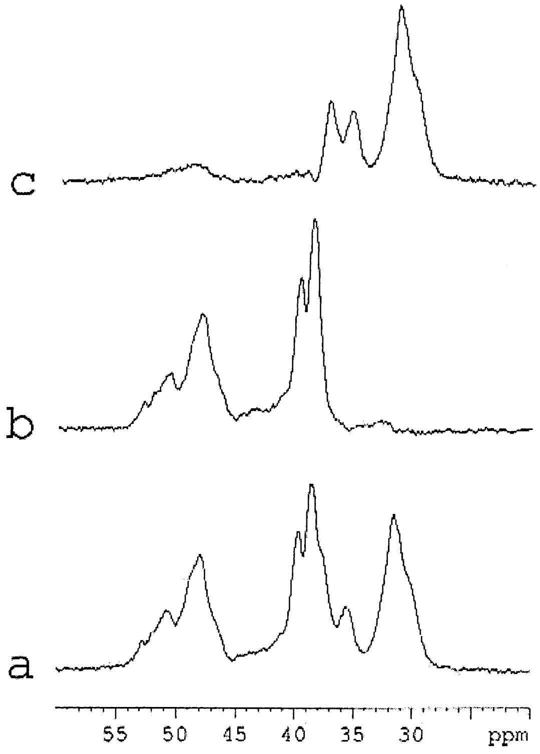
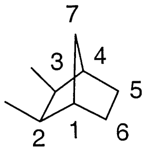


Figure 2. DEPT edited ^{13}C NMR spectra for PNB1: (a) full spectrum, (b) methine carbons, (c) methylene carbons.

methylene (38−28 ppm) regions. With the help of assignments reported by Arndt for hydrotrimers of norbornene[31] and integration of the DEPT spectra, assignments of carbons 1−7, based on the following numbering scheme, can be made for each polymer (see Table 2).



It is noteworthy that the chemical shift assignments are essentially the same for each polymer but that, within each chemical shift region, the number of resonances observed is different for each polymer. For example, C7 (chemical shift region 38−34 ppm) exhibits two peaks in spectrum of PNB1 and only one peak in PNB2.

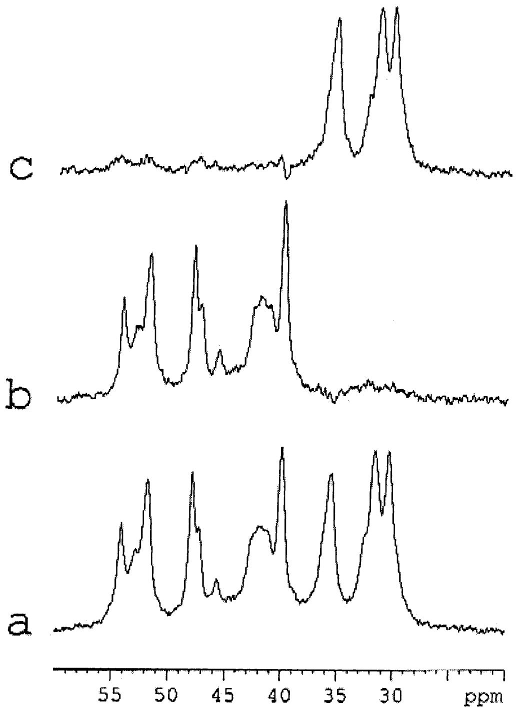


Figure 3. DEPT edited ^{13}C NMR spectra for PNB2: (a) full spectrum, (b) methine carbons, (c) methylene carbons.

Table 2. ^{13}C NMR Assignments for Poly(norbornene) Made Using [(η^3-crotyl)Ni(1,4-COD)]PF$_6$ and Ni(dpm)$_2$, AlEt$_3$, and B(C$_6$F$_5$)$_3$

carbon number	PNB1[a] (ppm)	PNB2[b] (ppm)
C2, C3	54−45	55−45
C1, C4	45−38	45−38
C7	38−35	38−34
C5, C6	34−29	34−28

[a] Catalyst = [(η^3-crotyl)Ni(1,4-COD)]PF$_6$. [b] Catalyst = Ni(dpm)$_2$, AlEt$_3$, and B(C$_6$F$_5$)$_3$.

We attribute the distinctions in these spectra to differences in polymer architectures. Unfortunately, the broad, unresolved nature of the spectra made it difficult to assign exact stereochemistry to the enchainment of norbornene in the polymers with absolute certainty. The best resolved peaks in both spectra are assigned to C7. In PNB1, two peaks of equal intensity are observed for C7. Again, on the basis of assignments for hydrotrimers of norbornene by Arndt, one would expect two peaks of equal intensity for C7 if the polynorbornene enchainment was equally divided between *mm* and *mr* placements or between *rr* and *mm*.[32] Two major peaks were observed below 40 ppm for C1 and C4 in PNB1. According to Arndt, only the *mm* and *mr* triads of the hydrotrimers of norbornene exhibit C1 and C4 resonances below 40 ppm. Thus, the microstructure of PNB1 is best described as a mixture of *mm* and *mr* triads of more or less equal population. To further confirm the microstructure assignment, the solid-state CPMAS−^{13}C NMR spectrum of PNB1 was acquired (see Supporting Information). The spectrum is essentially identical to that published by Arndt for nickel as well as some zirconocene-catalyzed poly(norbornene) for which microstructures of low disyndiotacticity were claimed.[33]

For PNB2, the peak assigned to C7 appears as a single peak. This observation is consistent with a microstructure containing a composite of two norbornene triads with overlapping peaks due to C7. This is possible for the *rr* and *mr* triads given the close proximity of their C7 resonances assigned by Arndt. The dearth of substantial population of *mm* triads in PNB2 is confirmed by the absence of peaks near 39 ppm. According to Arndt, the C1 and C4 peaks of the central norbornene of the *mm* triad of hydronorbornene trimers resonate at 39.03. Thus, the microstructure of PNB2 is best described as containing low diisotacticity. For comparison purposes, the solid-state CPMAS−^{13}C NMR spectrum of PNB2 is included in the Supporting Information and shows substantial differences from PNB1.

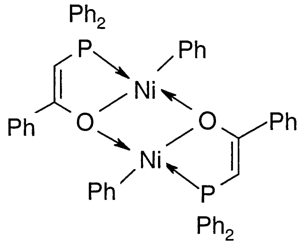
Norbornene Polymerization Using Nickel and Palladium Complexes and $B(C_6F_5)_3$. A possible explanation for the two different microstructures observed for PNB1 and PNB2 is found in the differences in the catalysts employed. Evidence supporting the creation of a unique type of active species in the latter case was obtained upon discovering that it was entirely *unnecessary* to add $AlEt_3$ to **1** and $B(C_6F_5)_3$ to obtain excellent yields of polymer. In run 3, 95% conversion and a very high activity were obtained when a 4000:1:9 norbornene:Ni:$B(C_6F_5)_3$ molar ratio was employed. NMR spectral characteristics of this polymer sample were identical to that obtained in run 2. The conversion to polymer was reduced when a lower concentration of $B(C_6F_5)_3$ was used, for example, when a monomer:Ni:B molar ratio of 4000:1:1 was used, the conversion decreased to 48% (experiment 4, Table 1). Repeats of run 4 (see experiments 5 and 6) show that the conversion is reproducible; conversions of 54% and 46% were obtained, respectively. Clearly, alkylation of **1** by $AlEt_3$ was not necessary to create an active species, contrary to what was originally proposed above. Other nickel complexes will also initiate norbornene polymerization in the presence of only $B(C_6F_5)_3$.[18b]

Evidently, an electron-withdrawing aryl subsituent is necessary for creation of the active species since neither $BF_3{\cdot}Et_2O$, $B(OEt)_3$, nor $B(OC_6F_5)_3$ in combination with Ni(dpm)$_2$ yielded polymer upon addition of the reaction mixture to methanol.[34] See experiments 7−9. Janiak and co-workers found that $B(C_6H_5)_3$ also does not activate Ni(acetylacetonate)$_2$ or Ni(ethylhexanoate)$_2$ toward norbornene polymerization.[18b]

Polymerization experiments carried out using Pd(dpm)$_2$ also showed that norbornene was polymerized quite effectively in the absence of $AlEt_3$ at a 4000:1:9 monomer:Pd:$B(C_6F_5)_3$ ratio. The yield drops from 95% to 11% when only 1 equiv of $B(C_6F_5)_3$ per Pd is used as shown in runs 10 vs 11. A marked decrease in solubility was noted for the Pd-based polymers, though the polymer was soluble enough at 50 °C in *o*-dichlorobenzene to obtain a ^{1}H NMR spectrum (see Supporting Information). No olefinic resonances were observed, confirming the formation of addition poly(norbornene). However, given the solubility difficulties encountered, no further work was done on palladium-based poly(norbornene).

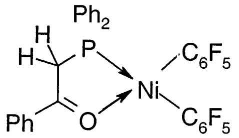
We investigated the effect of water on the polymerization system using $B(C_6F_5)_3$. Delivery of precise quantities of water was enabled by Siedle and co-workers, who reported that $B(C_6F_5)_3$ forms a trihydrate.[35] Surprisingly, it was discovered that addition of $B(C_6F_5)_3{\cdot}3H_2O$ actually doubles the conversion to polymer when compared to $B(C_6F_5)_3$. In experiment 12, in which a 4000:1:1 ratio of monomer:Ni:$B(C_6F_5)_3{\cdot}3H_2O$ was employed, a conversion of 91% was obtained. A repeat of this experiment gave 87% conversion (see experiment 13). This should be compared to experiments 4−6 in which an average of 49% was obtained when $B(C_6F_5)_3$ is substituted for $B(C_6F_5)_3{\cdot}3H_2O$. The molecular weights of polymer produced with $B(C_6F_5)_3{\cdot}3H_2O$ are significantly lower than those of previous samples. Apparently, the same type of active species is created since the NMR signature of polymers from runs 11 and 12 are identical to the samples produced in experiments which used $B(C_6F_5)_3$, i.e., PNB2.

Nickel complexes that are activated by $B(C_6F_5)_3$ toward addition polymerization of norbornene are not limited to Ni(dpm)$_2$. The dimer complex [Ni(Ph)(PPh$_2$CH=C(O)Ph)]$_2$ (**3**) forms an active species upon addition of 10 equiv of $B(C_6F_5)_3$ although the conversion is low (16%). See experiment 14. However, the activity of the complex is boosted by almost an order of magnitude by addition of 2 equiv of $B(C_6F_5)_3{\cdot}3H_2O$ per Ni complex. In this experiment, the conversion is 86% and the activity climbs to 412 000. See experiment 15. The NMR characteristics of this polymer were consistent with formation of PNB2.



3

This was an important result since, on the basis of previous work, $B(C_6F_5)_3{\cdot}3H_2O$ was known to react with [Ni(Ph)(PPh$_2$CH=C(O)Ph)]$_2$ to form Ni(C_6F_5)$_2$(PPh$_2$CH$_2$C(O)Ph) (**4**) via an unprecedented transfer of two pentafluorophenyl groups from B to Ni.[21]



4

Norbornene Polymerization Using Single-Component Complexes. Complex **4** was tested for norbornene polymerization activity. Addition of **4** (2000:1 norbornene:Ni molar ratio) in toluene to norbornene at room temperature gave 39% conversion in 1 h (0.9 M norbornene in toluene). The polymer NMR spectra showed production of PNB2. *Thus, nickel complexes containing C_6F_5 ligands are active for norbornene polymerization.*

This result prompted a search for a more active system. It was postulated that polymerization is probably initiated by insertion into the Ni−C bond of the pentafluorophenyl ligand and that coordination of the norbornene to the metal center would be required before initiation ensued. If ligand loss is a prerequisite, approach of the norbornene substrate to Ni would be hampered by coordination of the neutral, chelating P∼O ligand in **4**. Presumably, a more active catalyst should

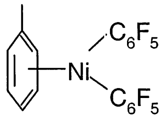
Table 3. Comparison of Copolymerization of Norbornene and 5-Triethoxysilylnorbornene (80:20 Molar Ratio) Using Multicomponent and Single-Component Catalysts

experiment[a]	nickel complex	cocatalyst	activator	conv (%)	M_w	M_w/M_n
16	Ni(ethylhexanoate)$_2$, 0.45 mM	AlEt$_3$, 4.5 mM	B(C_6F_5)$_3$, 4.1 mM	52	837 000	4.33
17	Ni(ethylhexanoate)$_2$, 0.45 mM	AlEt$_3$, 4.5 mM	B(C_6F_5)$_3$, 4.1 mM	58	784 000	3.96
18	Ni(ethylhexanoate)$_2$, 0.45 mM	AlEt$_3$, 4.5 mM	B(C_6F_5)$_3$, 4.1 mM	50	741 000	4.14
19	(η^6-toluene)Ni(C_6F_5)$_2$, 0.45 mM			79	423 000	2.42
20	(η^6-toluene)Ni(C_6F_5)$_2$, 0.45 mM			73	461 000	2.63
21	(η^6-toluene)Ni(C_6F_5)$_2$, 0.45 mM			78	428 000	2.92
22[b]	Ni($C_6H_3(CF_3)_3$)$_2$(1,2-dme), 0.30 mM			37	1 023 000	7.23

[a] Molar ratio of norbornene to 5-triethoxysilylnorbornene is 80:20. Total monomer concentration was 0.9 M in cyclohexane. Polymerizations were carried out for 5 h at room temperature. GPC determinations were made in C_6H_5Cl at room temperature. [b] Total monomer concentration was 1.2 M in toluene. Polymerization was carried out for 1.5 h at room temperature.

contain pentafluorophenyl ligands and a labile ligand or ligands that can be readily displaced by norbornene. The fact that experiment 15 gave 86% conversion upon addition of 2 equiv of B(C_6F_5)$_3$ to **3** is consistent with this notion. It is entirely possible that excess of the Lewis acidic B(C_6F_5)$_3$ may compete with Ni for the $P\sim O$ ligand, thus producing a more accessible Ni species.

Our search for a more active system led us to nickel bis(pentafluorophenyl) complexes originally reported by Klabunde and co-workers in the 1980s.[36] One of the more interesting complexes reported was (η^6-toluene)Ni(C_6F_5)$_2$ (**5**). Toluene can be readily replaced by a number of neutral, electron donors including xylene, mesitylene, THF, PEt$_3$, and norbornadiene. In fact, Klabunde noted that formation of (norbornadiene)Ni(C_6F_5)$_2$ was accompanied by an intractable polymer. Klabunde speculated that vinyl addition polymerization occurred with possible cross-linking. Unfortunately, the insolubility of the polymer prevented further analysis.



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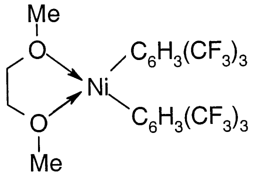
Thus, we synthesized and tested toluene complex **5** and found that it is effective for the polymerization of norbornene-type monomers. A comparison of a three-component system with **5** was made for the copolymerization of norbornene and 5-triethoxysilylnorbornene in an 80:20 molar ratio (see Table 3). (Copolymerizations were carried out in order to make the final product more soluble.) In this case, the three-component system employed was Ni(ethylhexanoate)$_2$, AlEt$_3$, and B(C_6F_5)$_3$ in a 2000:1:10:9 monomer:Ni:Al:B ratio while with the single-component catalyst the molar ratio of monomer to Ni was 2000:1. The polymerizations were carried out in cyclohexane for 5 h at room temperature in triplicate in order to determine reproducibility.

The data in Table 3 demonstrate that the single-component complex is significantly more active than the three-component system; a 23% increase in conversion is observed on average. Consistent with this conclusion, the molecular weights of the polymers made using the single-component complex were substantially lower and their polydispersities were much narrower.

The NMR spectra of the norbornene homopolymer produced by **4**, **5**, and mixtures of **1** and B(C_6F_5)$_3$ with or without AlEt$_3$ are identical (i.e., PNB2), again suggesting that the active species in all the systems are related, i.e., nickel species containing C_6F_5 ligands. To obtain direct evidence of C_6F_5 transfer from tris(pentafluorophenyl)boron to nickel in the Ni(dpm)$_2$ system, we monitored the reaction mixture of B(C_6F_5)$_3$·3H_2O and Ni(dpm)$_2$ (1:1 molar ratio) in benzene-d_6 by ^{19}F NMR spectrometry. While the reaction mixture changed from purple to green, indicating formation of the water adduct of Ni(dpm)$_2$, no peaks were observed in the −115 to −120 ppm region which would be expected for the *ortho* aryl fluorines on C_6F_5 attached to nickel.[21] The reaction of Ni(dpm)$_2$ was repeated with B(C_6F_5)$_3$ in the presence of Me$_2$Si(OEt)$_2$ (in order to mimic the silyl groups in 5-triethoxysilylnorbornene); a reddish-brown color resulted. The ^{19}F NMR spectrum of this mixture exhibited a small resonance at −117 ppm indicative of a Ni−C_6F_5 species (assigned to the *o*-fluorine in the Ni-(C_6F_5)) along with unreacted B(C_6F_5)$_3$. Evidently, Me$_2$Si(OEt)$_2$ stabilizes the Ni(C_6F_5) moiety. For Pd(dpm)$_2$, reaction with B(C_6F_5)$_3$·3H_2O (1:1 molar ratio) in benzene-d_6 produced ^{19}F NMR signals consistent with formation of a Pd(C_6F_5)-containing species: −120.5 (2 F), −161.0 (1 F), and −162.0 (2 F).[37] Thus, we established that in the multicomponent systems transfer of C_6F_5 groups from boron can occur.

Polymerization of norbornene-type monomers is not restricted to nickel complexes containing C_6F_5 ligands. We have found that substituted electron-withdrawing aryl ligands such as tris(2,4,6-trifluoromethylphenyl)[38] is quite effective in copolymerizing norbornene and 5-triethoxysilylnorbornene, for example. At a 4000:1 monomer-to-nickel ratio, Ni(2,4,6-tris(trifluoromethyl)-phenyl)$_2$(1,2-dimethoxyethane) (**6**) gave 37% conversion to polymer from an 80:20 norbornene:5-triethoxysilylnorbornene monomer mixture. See run 22 in Table 3 for details.



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Thus, we discovered the unusual activation of nickel toward the polymerization of norbornene-type monomers by C_6F_5 transfer from B(C_6F_5)$_3$ to nickel,[39] a reaction manifold that typically is a decomposition route for transition metal catalysts.[40] This discovery led to the development of a class of neutral, single-component nickel complexes containing an electron-withdrawing group such as C_6F_5 that are effective for the polymerization of norbornene-type monomers.

Norbornene Polymerization in the Presence of Ethylene. Our interest next turned to the polymerization initiation step. The most direct proof of the initiation mechanism would come from elucidation of the end-

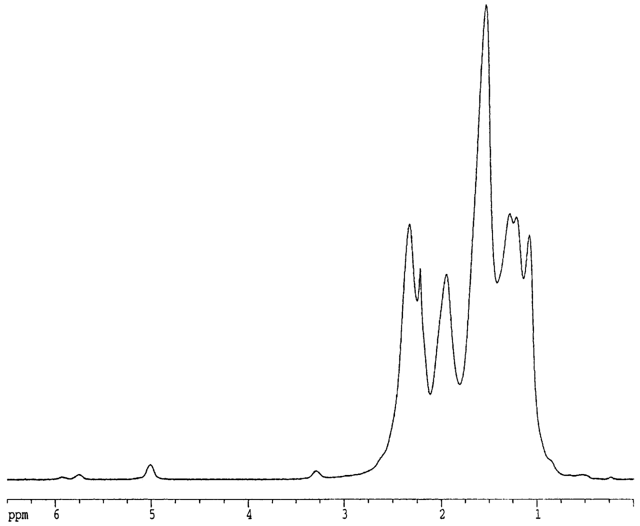


Figure 4. ^{1}H NMR spectrum in *o*-dichlorobenzene-d_4 at 25 °C of the methanol-insoluble fraction from polymerization of norbornene using (η^6-toluene)Ni(C_6F_5)$_2$ in the presence of ethylene.

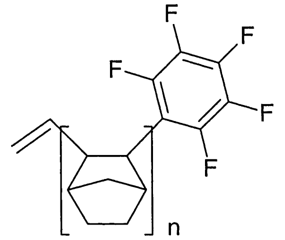
group structure of the polymer, PNB2, produced using (η^6-toluene)Ni(C_6F_5)$_2$. Unfortunately, the molecular weights of the polymers in Table 3 produced therefrom were much too high for NMR determination of end groups. In an effort to lower the molecular weight of the polymer chain, homopolymerization of norbornene was carried out in the presence of ethylene. Norbornene polymerizations catalyzed by cationic nickel catalysts such as [(η^3-crotyl)Ni(1,4-COD)]PF_6 are quite susceptible to acyclic olefins as chain transfer agents. Addition of decene-1, for example, to these reactions produces substantially reduced molecular weight olefin-terminated poly(norbornenes).[6]

Thus, norbornene was polymerized under 5 psig of ethylene on a 5 g scale using (η^6-toluene)Ni(C_6F_5)$_2$ at a 500:1 norbornene to nickel molar ratio. Precipitation into methanol produced a low yield (8%) of a methanol-insoluble fraction. From the filtrate, a smaller amount of a methanol soluble fraction was isolated.

NMR analysis of the methanol-insoluble fraction was quite informative. While the aliphatic region of the ^{1}H NMR spectrum was essentially identical to the high molecular weight polymer made in the absence of ethylene, there were three new resonances observed: broad singlets at 3.3 and 5.0 ppm and a pair of broad singlets at 5.95 and 5.75 ppm (see Figure 4). The relative intensities of these signals were about 1:2:1, respectively. The two downfield resonances are consistent with vinyl groups at the end of the polymer chain. The origin of the resonance at 3.3 ppm was not clear at this stage of our investigation and required further analysis (see below).

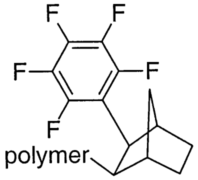
The ^{19}F NMR spectrum of the methanol-insoluble fraction was especially illuminating. Four distinct groups of resonances were observed: singlets at −162.7 (2 F), −158.1 (1 F), and −139.3 ppm (1 F) and two signals at −133.1 and −133.8 ppm (1 F). These resonances were consistent with the presence of a C_6F_5 group appended to the polymer, presumably at the end of the polynorbornene chain. The exact assignments are discussed in more detail below.

The methanol-soluble fraction was of sufficiently low molecular weight that peaks could be observed in the field ionization mass spectrometry experiment (see Supporting Information). Analysis of the predominant series of peaks was consistent with the following structure:



where the end groups are $-CH{=}CH_2$ and $-C_6F_5$ and *n* = 2, 3, 4, 5, 6, and 7 (*m*/*z* = 382, 476, 570, 664, 758, and 852, respectively).

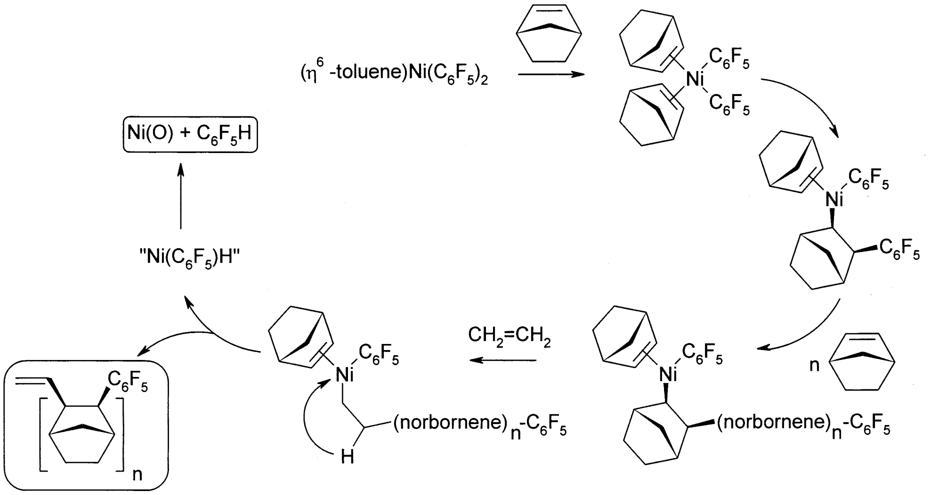
The ^{19}F NMR spectrum of the methanol-insoluble fraction is consistent with a vinyl addition poly(norbornene) with an *exo*-enchained pentafluorophenyl end group (see structure below). The *para*-fluorine is assigned to the peak at −158.1 ppm (1F). The two *ortho*-fluorines should be inequivalent; one fluorine is *syn* to the norbornene bridging methylene, and the other is *anti*. If the pentafluorophenyl end group experiences hindered rotation around the phenyl *ipso* carbon−norbornene carbon single bond, separate resonances would be expected for the *ortho*-fluorines. Indeed, two groups of signals are observed at −133.1 and −133.8 ppm (1F) and at −140.8 ppm (1F) and are assigned to the two *ortho*-fluorines. The chemical shift of the *ortho*-fluorine *syn* to the polynorbornene chain could potentially be influenced by the stereochemical placement of the penultimate norbornene monomer. This monomer is enchained such that a *meso* configuration results; the *ortho*-fluorine *syn* to the polymer backbone would resonate at a different chemical shift than if the enchainment resulted in a *racemic* configuration. As such, one of the *ortho*-fluorines appears as two resonances (−133.1 and −133.8 ppm) of almost equal intensity. The two *meta*-fluorines, which theoretically should also be inequivalent, are evidently accidentally degenerate and resonate at −162.7 ppm (2F) and apparently are not affected by the stereochemistry of the last two norbornene units.[41]



The electrophilic C_6F_5 substituent appended to the end of the poly(norbornene) chain also affects the ^{1}H NMR chemical shifts of selected protons on the adjacent norbornene unit. In the methanol-insoluble fraction, a downfield resonance at 3.3 ppm was observed. This shift is assigned to the proton on the methine carbon bearing the C_6F_5. The inductive effect of C_6F_5 explains the downfield shift of this proton.

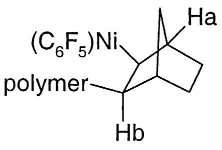
It is interesting to note that, once the end groups of the low molecular weight polymers were established, we could calculate the molecular weight of the methanol-insoluble fraction. The calculated molecular weight, 3600, was in good agreement with the number-average molecular weight determined by GPC, 3800, thus substantiating the assignment of the polymer end-group structure.

Scheme 1



Mechanism. The isolation, separation, and unambiguous characterization of the end groups for poly(norbornene) synthesized using (η^6-toluene)Ni(C_6F_5)$_2$ in the presence of ethylene enabled us to construct a mechanism of chain initiation and termination (see Scheme 1). The fact that each isolated norbornene oligomer in the mass spectrum contains a C_6F_5 and a vinyl end group and the observation of such end groups in the higher molecular weight fractions supports the hypothesis that initiation of the norbornene polymer chain occurs via insertion of the *exo* face of the norbornene monomer into the Ni−C bond of the C_6F_5 ligand. Presumably, coordination of norbornene to Ni occurs prior to insertion and thus explains the higher activity observed for (η^6-toluene)Ni(C_6F_5)$_2$ with a labile toluene ligand compared to a complex like Ni(C_6F_5)$_2$($PPh_2CH_2C(O)Ph$) which contains a chelating ligand.

After the first norbornene insertion, propagation ensues and molecular weights grow to large values, suggesting that little or no chain termination occurs. For cationic nickel catalysts such as [(η^3-crotyl)Ni(1,4-COD)]PF_6 similar behavior was observed since β-hydrogens were unavailable for elimination. It appears that this also applies here. H_a is in a bridgehead position, and its elimination would violate Bredt's rule by forming a bridgehead double bond. H_b is *anti* to Ni and is improperly oriented for elimination. In fact, even if H_b should occur in the *syn* orientation, it is extremely unlikely that β-hydride elimination would occur since it would result in forming a norbornene end group on the polymer which is energetically unfavorable.



After insertion of ethylene occurs, presumably after coordination to Ni, a (C_6F_5)Ni−CH_2−CH_2− capped norbornene polymer intermediate is formed. Free rotation about the −CH_2−CH_2− bond of this intermediate offers two β-hydrogens that can be readily eliminated to form a neutral NiH(C_6F_5) species and a vinyl-terminated poly(norbornene) chain. A similar hydride intermediate has been proposed by Klabunde for the dimerization of ethylene and propylene.[42]

The fate of the neutral NiH(C_6F_5) species became of primary interest. If this species were capable of coordinating and inserting norbornene into the Ni−H bond, many turnovers could be attained (i.e., many polymer chains per nickel center). However, it appears that under the conditions employed NiH(C_6F_5) was not sufficiently stable to undergo further norbornene polymer initiations. We see no evidence for the formation of hydride-initiated poly(norbornene) chains, i.e., H−(norbornene)$_n$−vinyl, by mass spectrometry. The absence of such polymer chains, the formation of black solutions (presumably nickel metal) during norbornene polymerization in the presence of ethylene, and the presence of C_6F_5H in the mass spectrum of the reaction mixture supports the notion that the NiH(C_6F_5) moiety decomposes via reductive elimination of pentafluorobenzene and nickel metal.

These data suggest strongly that (η^6-toluene)Ni(C_6F_5)$_2$ should be thought of as an initiator of norbornene polymerization rather than a catalyst. Chain transfer to ethylene apparently does not occur, only chain termination. In fact, calculations show that the expected number-average molecular weight of the polymers obtained in runs 19−21 in Table 3 should be about 190 000, assuming that every metal center initiates a polymer chain.[43] This value is close to the observed 166 000 average M_n determined from data in Table 3 for these runs.

If the second C_6F_5 remains coordinated to nickel and does not initiate further polymerization of norbornene, then what indeed is its role? Perhaps the second pentafluorophenyl ligand influences the enchainment of the norbornene monomer units which is manifested in the microstructure of the polymer. Certainly on the basis of NMR spectra, the microstructure of poly(norbornene) made using (η^6-toluene)Ni(C_6F_5)$_2$ (PNB2), for example, is substantially different than PNB1 produced by [(η^3-crotyl)Ni(1,4-COD)]PF_6 (see Figures 1−3). In the case of [(η^3-crotyl)Ni(1,4-COD)]PF_6 all of the ligands are presumably replaced by norbornene.

Polymer Properties. Polymers made using (η^6-toluene)Ni(C_6F_5)$_2$ exhibited interesting mechanical properties. In particular, a copolymer containing an 80:20 molar ratio of norbornene and 5-triethoxysilylnorbornene had a tensile modulus of 1.4 GPa, an elongation to break of 15%, and a T_g of 355 °C.[44] This material exhibited excellent transparency with greater than 90%

average transmission between 400 and 700 nm and a low dielectric constant (2.67), suggesting that this material could find utility in optical and electronic applications.

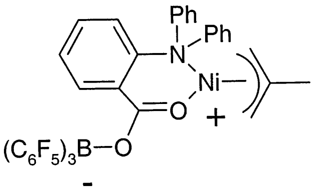
An 80:20 norbornene:5-triethoxysilylnorbornene copolymer made with [(η^3-crotyl)Ni(1,4-COD)]PF_6, while possessing similarly good optical and dielectric properties, however, gave completely brittle polymers, despite being equivalent in molecular weight.

The mechanical property differences observed for these two polymers may well be due to differences in their microstructure. Ludovice et al. have studied the effect of intrinsic viscosity vs molecular weight for PNB1 and PNB2.[45] The scaling exponent of the logarithm of intrinsic viscosity vs the logarithm of molecular weight is 0.53 for PNB1 (from [(η^3-crotyl)Ni(1,4-COD)]PF_6) and 0.97 for PNB2 (from (η^6-toluene)Ni(C_6F_5)$_2$). Thus, PNB1 represents a random coil morphology, while PNB2 is more semirigid in nature. Simulation of these results by Ludovice suggests that PNB1 is more atactic, while PNB2 is more stereoregular. These architectural differences may be responsible for the mechanical properties dissimilarities.

Concluding Remarks. We have shown that $B(C_6F_5)_3$ activates both Ni and Pd toward the vinyl polymerization of norbornene. In sharp contrast to early transition metal metallocenes, the activation of Ni has been shown unambiguously to occur by a rare transfer of C_6F_5 from B to Ni. The development of single-component initiators containing electron-withdrawing aryl ligands, such as (η^6-toluene)Ni(C_6F_5)$_2$, resulted from this discovery. Initiation of polymerization was proven to occur via insertion of norbornene into the Ni$-C_6F_5$ bond. The polymer microstructure as revealed by ^{1}H and ^{13}C NMR spectrometry is entirely different from that produced using the cationic nickel catalyst, [(η^3-crotyl)Ni(1,4-COD)]PF_6. This microstructure difference impacts the resulting polymer mechanical properties.

The functional tolerance of the complexes described herein has allowed the development of poly(norbornenes) containing pendant esters, anhydrides, sulfonamides, acids, alcohols, and amines that are useful as photoresist matrix polymers and NLO-active polymers, for example.[14,46] More details regarding these types of materials will be forthcoming.[47]

In closing, a recent publication presented data regarding the vinyl addition poly(norbornene) catalyzed by a zwitterionic $B(C_6F_5)_3$ adduct of a N$\sim$O chelated methallyl nickel complex.[48] Given the similarities of the structure of this complex to that of [(η^3-crotyl)Ni(1,4-COD)]$^+$, one would have predicted a polymer microstructure similar to PNB1. However, the ^{13}C CPMAS NMR spectrum of the poly(norbornene) presented therein is clearly more like PNB2, suggesting that the zwitterionic complex is acting more like (η^6-toluene)Ni(C_6F_5)$_2$. Clearly, further investigation of complexes such as these is warranted.



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Supporting Information Available: FI-MS of norbornene oligomer fraction, ^{1}H NMR, and solid-state ^{13}C NMR spectra of poly(norbornene). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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