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Effects of tris(pentafluorophenyl)borane on the activation of zerovalent-nickel complex in the addition polymerization of norbornene

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Abstract

The effects of $B(C_6F_5)_3$ on the activation of the Ni(0) and Ni(II) complexes were studied in the polymerization of norbornene. The Ni(0) complex, such as bis(1,5-cyclooctadiene)nickel ($Ni(COD)_2$ (**1**), biacetylbis(2,6-diisopropylphenylimmine)(1,3-butadiene)nickel (**2**), or tetrakis(triphenylphosphine)nickel (**5**), in combination with $B(C_6F_5)_3$, was determined to have high activity in the polymerization of norbornene. On the other hand, the Ni(II) complex with $B(C_6F_5)_3$ did not provide any activity at all under analogous conditions regardless of the structure of the Ni(II) complex. The use of other borane compounds, such as $B(C_6H_5)_3$, BEt_3, and BF_3 etherate, with $Ni(COD)_2$ (**1**) in place of $B(C_6F_5)_3$ clearly showed the main functions of $B(C_6F_5)_3$. The high Lewis acidity of $B(C_6F_5)_3$ enabled it to activate catalytic complexes, thus inducing polymerization. The study of the ^1H, ^{13}C, and ^{19}F NMR spectra of the polynorbornene produced with $Ni(COD)_2$ (**1**) and $B(C_6F_5)_3$, in the presence or absence of ethylene, showed that the initiation of addition polymerization occurred through the insertion of the *exo* face of the norbornene into the Ni–C bond of the C_6F_5 ligand. A new polymerization mechanism was proposed in norbornene polymerization, wherein the active complex formed from $Ni(COD)_2$ (**1**) and $B(C_6F_5)_3$ acts as a catalyst.

Keywords: Norbornene polymerization; Zerovalent-nickel complex; Tris(pentafluorophenyl)borane

1. Introduction

Bicyclo[2.2.1]hept-2-ene (norbornene) and its derivatives can be polymerized via ring-opening metathesis polymerization (ROMP) [1], cationic [2] or radical [3] polymerization, and vinyl addition polymerization [4,5]. The ROMP of norbornene provides a polymer containing unsaturation in the backbone. This makes it necessary to hydrogenate the polymer for the prospective application. The polynorbornenes obtained by ROMP have been commercialized with further modification through vulcanization or hydrogenation of double bonds in polymer chains [6]. Cationic or radical polymerization usually results in the formation of low molecular weight polymer with rearranged norbornene units in the backbone. On the other hand, vinyl addition polymerization provides a completely saturated polymer with no rearranged norbornene units. Consequently, the addition polymerization of norbornene (homo- and co-polymerizations) has been the subject of many studies. A number of catalysts based on the early transition metals Ti(IV)/AlR_3 [7], Zr(II)/methylaluminoxane (MAO) [8], and Cr(II)/MAO [9] as well as the late transition metals Co(II)/MAO [10], Ni(II)/MAO [4,11,12], and Pd(II)/MAO [4,13] have been investigated for the studies. As for the Ni(II) catalyst, organoaluminum compound, such as $AlEt_3$ or MAO, has been determined to be an essential ingredient for catalytic activity [4,14]. Exceptionally high activity was recently obtained using the salicylaldiminato Ni(II) complex with MAO or MMAO at $[Al]/[Ni]=2000$ [11,12]. Nonetheless, it is still important to have a low organoaluminum/metal ratio to reduce industrial operating costs and the amount of catalyst residues in the polymer. The latter leads to more advantages for the prospective optical applications of polynorbornenes [4,14].

Another method in activating the Ni(II) complex in the polymerization of norbornene is to use tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) in the presence [4,14] or absence [15] of the organoaluminum compound. Tris(pentafluorophenyl)-borane has been widely used in the metallocene-based olefin polymerizations due to its high efficiency [16]. Many studies have elucidated its role as a strong electrophile,

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capable of abstracting an alkyl ligand from a metal dialkyl to generate an active cationic form [16,17]. In addition, it was recently observed that even the single-component Ni(II) complex containing two pentafluorophenyl ligands, (η^6-toluene)Ni(C_6F_5)$_2$ [18], had high activity in the polymerization of norbornene-type monomers [15]. Little is known, however, regarding the ability of B(C_6F_5)$_3$ to function as an activator with the Ni(0) complex in norbornene polymerization.

The effects of B(C_6F_5)$_3$ on the activation of the Ni(0) and Ni(II) complexes (Figs. 1 and 2) were examined in the polymerization of norbornene. It was discovered that the Ni(0) complex **1**, **2**, or **5**, with B(C_6F_5)$_3$, had high activity and provided polynorbornene that had a high M_n even in the absence of AlR$_3$ and MAO. The Ni(II) complexes **6–10** with B(C_6F_5)$_3$, however, did not give any activity regardless of the structure of the Ni(II) complexes.

In this paper, the results of the activation of the Ni(0) complex with B(C_6F_5)$_3$ and the functions of B(C_6F_5)$_3$ in the polymerization of norbornene, together with the effects of the variation in the mol ratio of B(C_6F_5)$_3$ to the Ni(0) complex, were reported. The ^{19}F NMR studies showed that the Ni–C_6F_5 group, which was formed as a result of the transfer of C_6F_5 from B to Ni, initiated the polymerization.

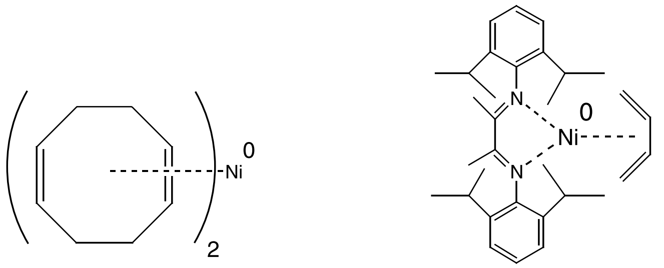
2. Experimental

2.1. General

Unless otherwise specified, all manipulations were performed under nitrogen using standard Schlenk or drybox techniques. Conversion was defined as the percentage by weight of the isolated polymer compared with the weight of the initially charged norbornene. The ^{1}H, ^{13}C, and ^{19}F NMR spectra were taken in CDCl$_3$ and recorded on a Varian unity Plus 400 NMR (400 MHz) spectrometer. Chemical shifts for the ^{1}H and ^{13}C NMR spectra were given in parts per million from the peak for internal trimethylsilane. The ^{19}F NMR spectra were referenced to external CFCl$_3$. Gel permeation chromatography data were obtained using a Waters Alliance GPC 2000, employing connected Waters columns packed with polystyrene, HT 5, HT 4, HT 3, and HT 2, with a refractive index detector. Trichlorobenzene was used as the eluent at a flow rate of 1.0 mL/min. Polystyrene standards in the 580–7,500,000 g/mol range were used for calibration.

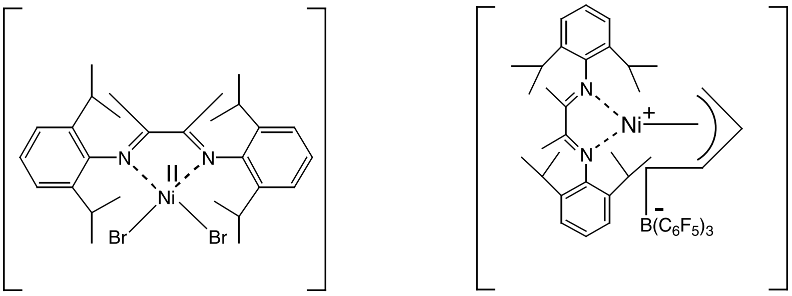
2.2. Materials

The following materials were purchased from Aldrich Chemicals: bis(1,5-cyclooctadiene)nickel (Ni(COD)$_2$) (**1**),



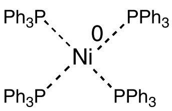
Bis(1,5-cyclooctadiene)nickel (**1**)

Biacetylbis(2,6-diisopropylphenylimmine)
(1,3-butadiene)nickel (**2**)



Biacetylbis(2,6-diisopropylphenylimmine)NiBr$_2$ (**3**)

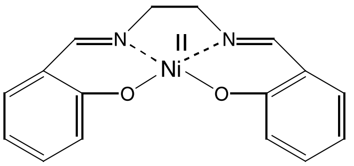
4



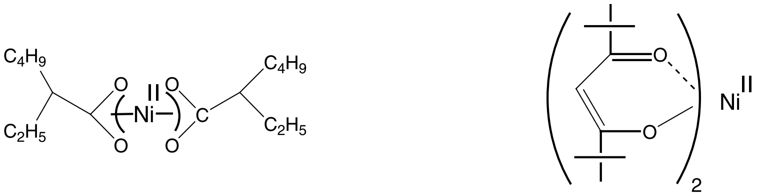
Tetrakis(triphenylphosphine)nickel (**5**)

Fig. 1. Structures of the Ni(0) complexes used for the polymerization of norbornene in combination with B(C_6F_5)$_3$.

Dibromobis(triphenylphosphine)nickel(II) (**6**) [1,2-Bis(diphenylphosphino)ethane]dichloronickel(II) (**7**)



N,N'-Bis(salicylidene)ethylenediamino nickel(II) (**8**)



Ni(2-ethyl hexanoate)$_2$ (**9**) Nickel(II) bis(2,2,6,6-tetramethyl-3,5-heptanedionate) (**10**)

Fig. 2. Structures of the Ni(II) complexes used for the polymerization of norbornene in combination with $B(C_6F_5)_3$ or $B(C_6F_5)_3$/MAO.

tetrakis(triphenylphosphine)nickel (**5**), dibromobis(triphenylphosphine)nickel(II) (**6**), [1,2-bis(diphenylphophino)ethane]-dichloronickel(II) (**7**), *N*,*N*'-bis(salicylidene)ethylenediamino nickel(II) (**8**), Ni(2-ethyl hexanoate)$_2$ (**9**), nickel(II) bis(2,2,6,6-tetramethyl-3,5-heptanedionate) (**10**), norbornene, tris(pentafluorophenyl)borane ($B(C_6F_5)_3$, 95%), triethylborane, triphenylborane, $BF_3 \cdot OBu_2$ and MAO. Biacetylbis(2,6-diisopropylphenylimmine)(1,3-butadiene)nickel (**2**) [19] was prepared starting from biacetylbis(2,6-diisopropylphenylimmine)$NiBr_2$ (**3**) [20] according to the literatures.

2.3. Polymerization

Polymerizations were performed in a 100 mL glass reactor sufficiently purged with nitrogen. The designated amount of Ni salt, polymerization solvent, norbornene, and borane compound was added sequentially to the reactor, and the polymerization was conducted at the mentioned temperature for 1 h (when using MAO together with Ni salt and borane compound, MAO was added after the addition of borane compound). The resulting polynorbornene was quenched with methanol containing a small amount of HCl.

2.4. Polymerization of norbornene with Ni(COD)$_2$/$B(C_6F_5)_3$ in the presence of ethylene

To a stirred solution of Ni(COD)$_2$ (1.06×10^{-4} mol, 29.2 mg) and norbornene (1.06×10^{-2} mol, 1.0 g) in 20 mL of toluene was added $B(C_6F_5)_3$ (1.06×10^{-4} mol, 57.1 mg) in 5 mL of toluene, and the reaction mixture was stirred for 1 h at 25 °C in the presence of ethylene (25 psi) under nitrogen. The termination of the polymerization with a small amount of methanol, followed by evaporation of solvent at reduced pressure, produced a vinyl-terminated polynorbornene, which was treated with a mixture of MeOH and pentane (4:1, V/V) to give a white solid in a yield of 18.2% (two more polymerizations were performed at the mol ratios of $[B(C_6F_5)_3]/[Ni]=5$ and 9 using the same conditions, where conversions were obtained in 56.8 and 71.9%, respectively): ^{1}H NMR ($CDCl_3$): δ 0.9–2.8 (aliphatic protons), 4.9 (br s, 2H), 5.7–5.9 (two br s, 1H). ^{19}F NMR ($CDCl_3$): -141.9, -142.1, and -143.5 (m, 1F), -142.7 (m, 1F), -158.5 (m, 1F), -163.5 (m, 2F).

3. Results and discussion

3.1. Activity of Ni(COD)$_2$/$B(C_6F_5)_3$

Table 1 shows the results of the polymerizations of norbornene performed with Ni(COD)$_2$/$B(C_6F_5)_3$ and Ni(II)/$B(C_6F_5)_3$/MAO. The Ni(0) complex **1** (Fig. 1), which has been used in tremendous organic transformations as an efficient catalyst [21], readily induced the polymerization with $B(C_6F_5)_3$. A high conversion of around 96% was obtained at the mol ratio of $B(C_6F_5)_3/Ni=5$ (entry 1 of Table 1). Both the ^{1}H and ^{13}C NMR spectra of the isolated polymer are shown in Fig. 3. The polymer was a vinyl addition in nature since no olefinic resonance was observed in the ^{1}H NMR spectrum (i.e. no ROMP polymer was formed). The ^{13}C NMR spectrum showed that the polymer was *exo* enchained. The spectrum did not exhibit resonances in the 20–24 ppm region. The presence

Table 1
Polymerizations of norbornene with $Ni(COD)_2/B(C_6F_5)_3$ and $Ni(II)/B(C_6F_5)_3/MAO$

Entry	Ni complex	Activator	Cocat.	Mol ratio	Conv. (%)	M_n ($\times 10^{-3}$)	M_w/M_n
1	**1**	$B(C_6F_5)_3$	–	1:5	96.0	322	3.21
2	**1**	$B(C_6F_5)_3$	–	1:3	89.6	438	2.48
3	**1**	$B(C_6F_5)_3$	–	1:1	90.0	421	2.58
4	**1**	$B(C_6H_5)_3$	–	1:5	0	–	–
5	**1**	BEt_3	–	1:5	0	–	–
6	**1**	$BF_3 \cdot OBu_2$	–	1:5	0	–	–
7	**6**	$B(C_6F_5)_3$	MAO	1:5:100	2.0	–	–
8	**7**	$B(C_6F_5)_3$	MAO	1:5:100	38.7	257	2.30
9	**8**	$B(C_6F_5)_3$	MAO	1:5:100	21.0	340	2.39
10	**9**	$B(C_6F_5)_3$	MAO	1:5:100	100	119	2.90
11	**10**	$B(C_6F_5)_3$	MAO	1:5:100	100	131	2.68

Polymerization conditions: polymerization solvent, toluene; solvent/norbornene (wt/wt), 4.3; polymerization temperature, 40 °C; norbornene, 2 g; concentration of Ni, 2.0×10^{-5} mol; polymerization time, 1 h.

of such resonances was used as an evidence of *endo* enchainment in model studies [22,23].

The effects of the variation in the mol ratio of $B(C_6F_5)_3$ to Ni on activity were not significant. A decrease in the concentration of $B(C_6F_5)_3$ did not change activity considerably (entries 1–3). Surprisingly, the polymerization performed even at $[B(C_6F_5)_3]/[Ni]=1$ provided high activity to give a conversion of around 90%. A significant decrease in conversion to around 50% was observed in the polymerization of norbornene when the mol ratio of $B(C_6F_5)_3$ to Ni(II) decreased to 1 [15]. It seemed that alkylation of **1** by MAO was totally unnecessary in the creation of active species, representing that the complex **1** with $B(C_6F_5)_3$ created a unique type of active species. The high Lewis acidity of $B(C_6F_5)_3$ plausibly made it play an important role in the formation of active complexes. Indeed, it was observed that the replacement of $B(C_6F_5)_3$ with the weaker Lewis acids, $B(C_6H_5)_3$ and BEt_3, or the stronger electron acceptor $BF_3 \cdot OBu_2$, did not result in any activity (entries 4–6). Evidently, an electron-withdrawing aryl substituent was necessary for the creation of active species. The polymerization performed with $B(C_6F_5)_3$ in the absence of $Ni(COD)_2$, however, did not give any activity at all.

Contrary to the Ni(0) complex **1**, the polymerizations of norbornene performed in toluene with the Ni(II) complexes **6–10** (Fig. 2) and $B(C_6F_5)_3$ at the mol ratio of $B(C_6F_5)_3/Ni=5$ did not result in any activity regardless of the structure of the Ni(II) complexes. These were done under the conditions specified in entry 1 of Table 1. The results were sharp contrast with those obtained from the polymerizations of norbornene performed in 1,2-dichloroethane [15] with nickel(II) bis(2,2,6,6-tetramethyl-3,5-heptanedionate) (**10**) and $B(C_6F_5)_3$, where conversions in the 46–97% range were obtained when the mol ratio of $B(C_6F_5)_3$ to Ni was 1–9.

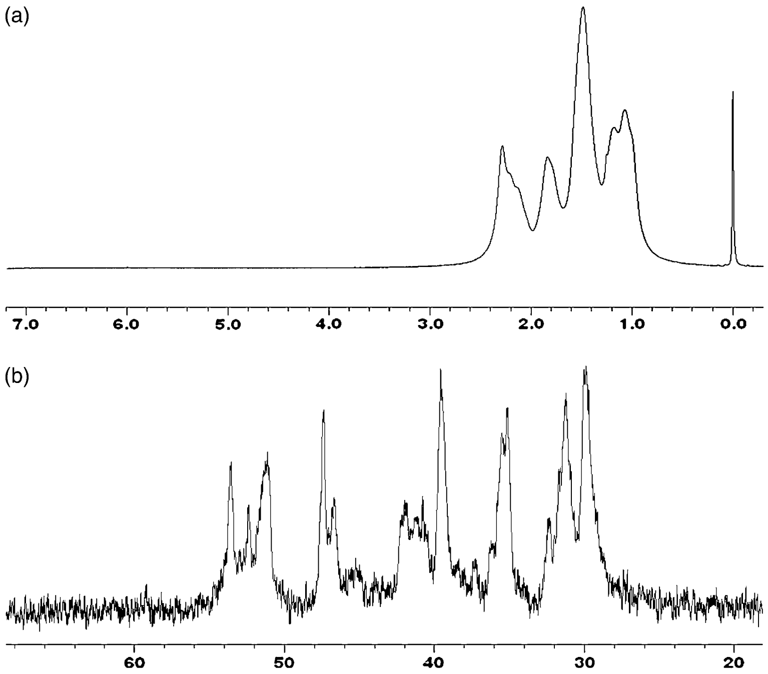


Fig. 3. (a) ^1H and (b) ^{13}C NMR spectra of the polynorbornene produced with $Ni(COD)_2/B(C_6F_5)_3$; polymerization temperature, 40 °C; polymerization solvent, toluene; solvent/norbornene (wt/wt), 4.3; norbornene, 2 g; concentration of Ni, 2.0×10^{-5} mol; polymerization time, 1 h; $[B(C_6F_5)_3]/[Ni]$, 5.

The polymerization, however, was readily induced upon the employment of MAO together with $B(C_6F_5)_3$ to give conversions in the 2–100% range (entries 7–11). Both the Ni(II) complexes **9** and **10** provided quantitative conversions, while the other three complexes **6–8** afforded conversions of below 50%. The ^{13}C NMR spectrum of the polynorbornene produced with **9**/$B(C_6F_5)_3$/MAO was essentially identical to that of the polynorbornene produced with $Ni(COD)_2/B(C_6F_5)_3$. This implied that the active complexes formed from $Ni(COD)_2/B(C_6F_5)_3$ and **9**/$B(C_6F_5)_3$/MAO were closely related. Quite lower activity was obtained when the polymerization was performed with **9**/MAO in the absence of $B(C_6F_5)_3$ ([MAO]/[9] = 100, conversion = ~73%). The ^{13}C NMR spectra of the two polynorbornenes produced with **9**/$B(C_6F_5)_3$/MAO and **9**/MAO were distinctively different in appearance. This represented that the active complexes formed from $Ni(COD)_2/B(C_6F_5)_3$ and **9**/$B(C_6F_5)_3$/MAO were quite different from those formed from **9**/MAO.

It was not clear why complexes **6–10**, in combination with $B(C_6F_5)_3$, reflected such a difference in activity compared to complex **1**, but the factors that might have caused the difference could be inferred. Presumably, the active complexes inducing the polymerization were formed through the reaction of the two ingredients, $Ni(COD)_2$ and $B(C_6F_5)_3$, with norbornene. The weakly bound cyclooctadienes in complex **1** could easily make the ligand exchange reaction with norbornene to take place. On the other hand, both the chelating and ionic donor ligands in complexes **6–10** would be displaced more awkwardly by norbornene due to their stronger coordination with Ni. If ligand loss is a prerequisite, approach of the norbornene substrate to Ni will be hindered considerably by the ligands in complexes **6–10**.

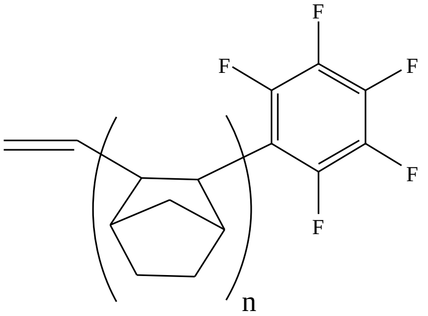
3.2. Study of the functions of $B(C_6F_5)_3$

Norbornene polymerizations catalyzed by cationic nickel catalysts such as [(η^3-crotyl)Ni(1,4-COD)]PF_6 have been known to undergo a facile chain transfer reaction with an α-olefin. The addition of 1-alkene to these reactions produced an olefin-terminated polynorbornene with a substantially reduced M_n [24].

In an effort to elucidate the working pathway of $B(C_6F_5)_3$, a polymerization of norbornene was conducted using $Ni(COD)_2$ and $B(C_6F_5)_3$ ($[B(C_6F_5)_3]/[Ni] = 1$), where the M_n of polynorbornene was intentionally decreased by introducing ethylene to make the analysis of polymer easier. The termination of polymerization using a small amount of methanol, followed by evaporation of solvent, produced a vinyl-terminated polynorbornene (the results of the polymerization will be discussed in a later). The ^1H and ^{19}F NMR spectra of the produced polymer were very informative (Fig. 4). The ^1H NMR spectrum of the produced polymer showed two new resonances although the aliphatic region was essentially identical to the high molecular weight polymer made in the absence of ethylene: broad singlet at 4.9 ppm and a pair of broad singlets at 5.7 and 5.9 ppm. The relative intensities of these signals were about 2:1. The two resonances apparently showed the presence of a vinyl group at the end of the polymer chain.

The ^{19}F NMR spectrum of the unpurified polynorbornene showed three distinct groups of resonances at −142.7, −158.5, and −163.5 ppm, besides many minor groups of resonances. The purification of the crude polynorbornene from the mixture solvent of MeOH and pentane (4:1, V/V) resulted in a white solid whose ^{19}F NMR spectrum showed four distinct groups of resonances: multiplets at −142.7 (1F), multiplets at −158.5 (1F), multiplets at −163.5 ppm (2F), and three signals at −141.9, −142.1, and −143.5 ppm (1F).

No absorption peak was observed in the ^{11}B NMR spectrum of the purified polynorbornene. This demonstrated that the resonances observed in the ^{19}F NMR spectrum came from a C_6F_5 group appended to the polymer, presumably at the end of the polynorbornene chain. The *para*- and *meta*-fluorines were assigned to the peaks at −158.5 ppm (1F) and −163.5 ppm (2F), respectively; the two *ortho*-fluorines were assigned to the peaks at −141.9, −142.1, −143.5 ppm (1F), and at −142.7 ppm (1F). The chemical shifts and the number of the absorption peaks assigned to the two *ortho* fluorines were somewhat different from those reported in the reference [15], which would be caused by the difference in the conformation of the pentafuorophenyl group with respect to the polymer chain in the two polymers. The analyses of the peaks observed in both the ^1H and ^{19}F NMR spectra were consistent with the following structure:



To sustain the inequivalence of the two *ortho*-fluorines on the phenyl ring observed in the ^{19}F NMR study, model studies were conducted on the compound shown below. Three conformers corresponding to the compound were discovered from the studies, using the CONFORMER SEARCH and ANALYSIS modules with the COMPASS force field in Cerius^2 [25]. Two of them (designated as conformers 1 and 2, respectively, for convenience) had localization energies that were quite similar to each other, and were relatively more stable than the third. The geometry of the two conformers was fully optimized using the density functional

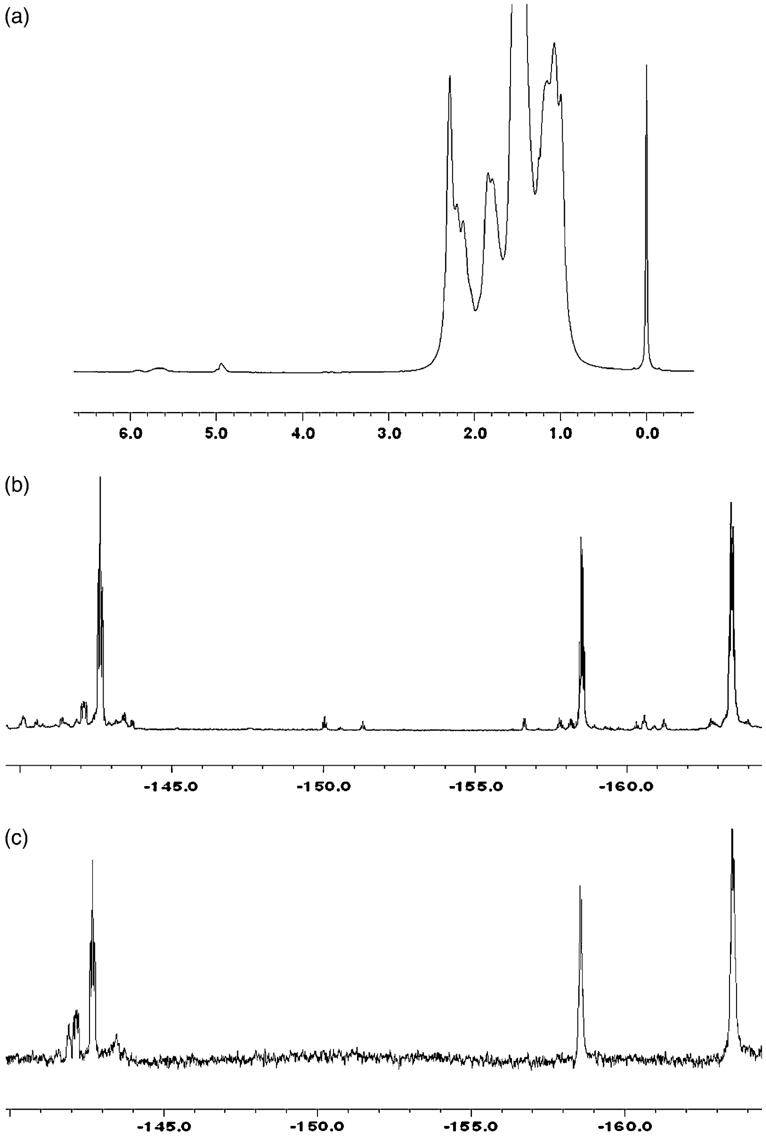
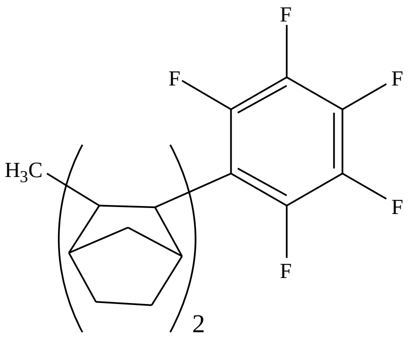


Fig. 4. (a) ^{1}H NMR spectrum of the purified polynorbornene and ^{19}F NMR spectra of (b) the unpurified and (c) purified polynorbornenes produced with $Ni(COD)_2/B(C_6F_5)_3$ in the presence of ethylene; polymerization solvent, toluene; solvent/norbornene(wt/wt), 17.3; polymerization temperature, 25 °C; norbornene, 1 g; concentration of $Ni(COD)_2$, 1.06×10^{-4} mol; polymerization time, 1 h; $[B(C_6F_5)_3]/[Ni]$, 1.

theory (DFT), B3LYP [26] with a basis set of 6-311G** [27,28].



The calculation of the ^{19}F NMR chemical shielding values of the two *ortho*-fluorines on each conformer was conducted using the individual gauges for atoms in molecules (IGAIM) [29] method implemented in Gaussian 98, with a basis set of 6-311+G** [27,28]. The chemical shifts of the two *ortho*-fluorines on each conformer were subsequently calculated, referring to the ^{19}F NMR chemical shielding value of $CFCl_3$ (154.7 ppm), which was calculated using the same methods as those used for the calculation of the model compound. The results are shown in Table 2. The two *ortho*-

Table 2
^{19}F NMR chemical shifts of the two *ortho*-fluorines on the model compound obtained from the theoretical calculation

Model compound	^{19}F NMR chemical shielding values of the two *ortho*-fluorines on the phenyl ring (ppm)[a]	Chemical shifts of the two *ortho*-fluorines on the phenyl ring (ppm)[b]
Conformer 1	−305.7, −305.8	−151.0, −151.1
Conformer 2	−300.9, −304.4	−146.2, −149.7

[a] Calculated with IGAIM-B3LYP/6-311+G**//B3LYP/6-311G** for the two conformers corresponding to the model compound.

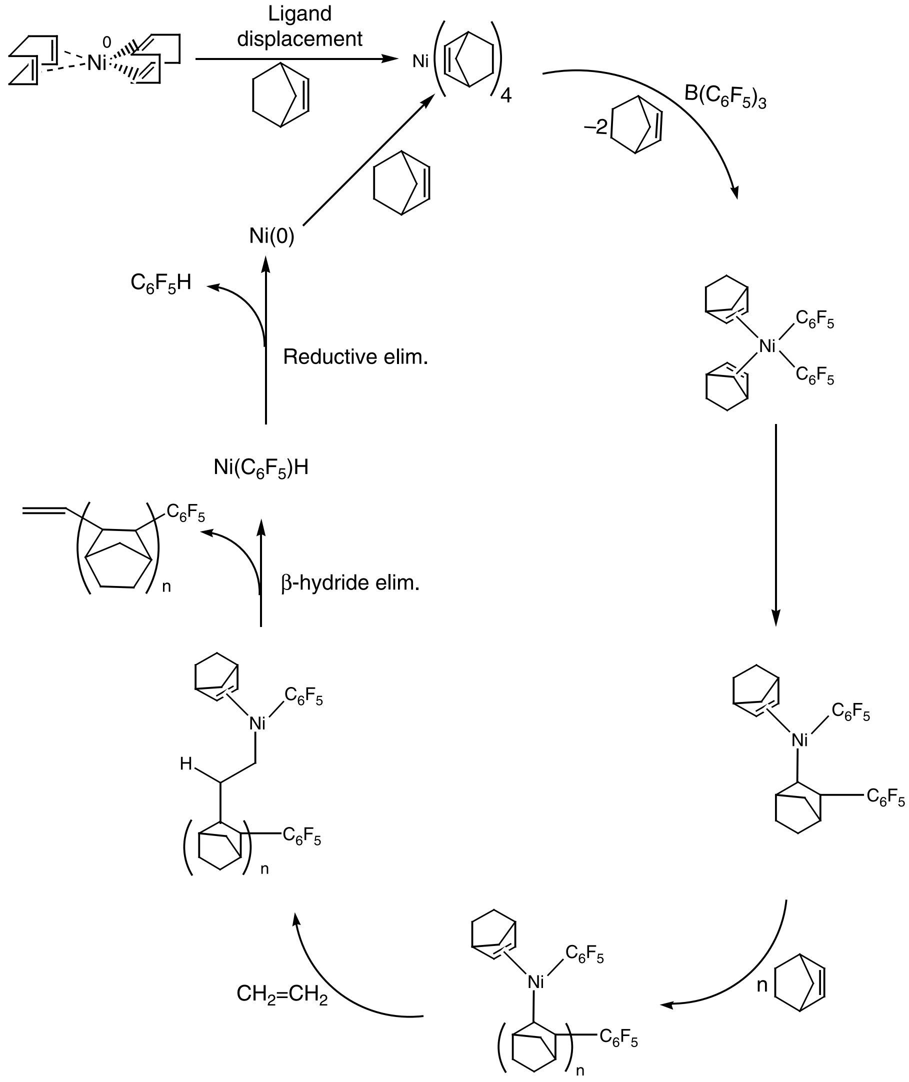
[b] The chemical shifts of the two *ortho*-fluorines on each conformer were determined, referring to the ^{19}F NMR chemical shielding value of $CFCl_3$.

fluorines on conformer 1 revealed two signals at −151.0 and −151.1 ppm. Those on conformer 2 showed two signals at −146.2 and −149.7 ppm. The actual ^{19}F NMR spectrum of the model compound was expected to show all the resonances for the two *ortho*-fluorines of the existing conformers. These results clearly showed why the two *ortho*-fluorines on the phenyl ring of polynorbornene exhibited several resonances (Fig. 4(c)). The differences in the chemical shifts between the theoretical and experimental studies were probably caused by the difference in the appearance of the model compound and the vinyl-terminated polynorbornene, and the effect of NMR solvent ($CDCl_3$) that was not considered in the theoretical calculation.

Contrary to the results of Goodall et al., however, the effect of the electrophilic C_6F_5 substituent appended to the end of the polynorbornene chain on the proton of the methine carbon bearing C_6F_5 was not observed in the ^1H NMR spectrum (Fig. 4(a)). A downfield resonance at 3.3 ppm was observed in the ^1H NMR spectrum of the polynorbornene produced with (η^6-toluene)$Ni(C_6F_5)_2$ in the presence of ethylene [15]. The peak was assigned to the proton on the methine carbon bearing the C_6F_5 group. It was not clear why the ^1H NMR spectrum did not show the signal of the proton on the methine carbon. Probably, the geometry of the pentafuorophenyl group in the polymer chain was such a state in which the transmission of its field effect to the proton of the methine carbon was not sufficient to create the downfield shift of the proton from the aliphatic region of polynorbornene. In general, the field effect of a substituent in the molecule is known to overwhelm its inductive effect in determining the acidity of the molecule [30]. The strength of the field effect mainly depends on the geometry of a substituent with respect to the part of the molecule considered.

3.3. Study of mechanism

The characterization of the end groups for polynorbornene synthesized using $Ni(COD)_2/B(C_6F_5)_3$ in the presence of ethylene enabled us to construct the mechanism of polymerization (Scheme 1). The coordination of monomer to Ni was



Scheme 1. Proposed mechanism of norbornene polymerization with a catalyst of $Ni(COD)_2/B(C_6F_5)_3$ in the presence of ethylene.

Table 3
Effects of variation in the level of $B(C_6F_5)_3$ on conversion and the M_n of polynorbornene in the presence of ethylene

Entry	$[B(C_6F_5)]_3/[Ni(COD)_2]$	Conv. (%)	Theoretical M_n	Observed M_n (MWD)	Theoretical M_n/ observed M_n
12	1	18.2	1720	2900 (1.66)	0.59
13	5	56.8	5360	2400 (1.61)	2.23
14	9	71.9	6780	2200 (1.72)	3.08

Polymerization conditions: polymerization solvent, toluene; solvent/norbornene (wt/wt), 17.3; polymerization temperature, 25 °C; norbornene, 1 g; concentration of $Ni(COD)_2$, 1.06×10^{-4} mol; polymerization time, 1 h.

expected to occur prior to the insertion [31,32]. This, therefore, explained the higher activity observed for $Ni(COD)_2$ with the labile COD ligands compared to the Ni(II) complexes **6–10**, which contained both the chelating and ionic donor ligands. The active $(norbornene)_2Ni(C_6F_5)_2$ species was presumably formed by a one-to-one reaction of the Ni(0) species with $B(C_6F_5)_3$ through C_6F_5 transfer from $B(C_6F_5)_3$ to Ni(0). The experimental results—polymerizations at $N(COD)_2/B(C_6F_5)_3$ ratios of 1:5 and 1:1 (Table 1, entries 1 and 3)—might indicate that the active Ni(II) species was formed by a one-to-one reaction of the Ni(0) species with $B(C_6F_5)_3$. The fact that the isolated polynorbornene contained a C_6F_5 group supported the proposition that the initiation of the norbornene polymer chain occurred through the insertion of the *exo* face of the norbornene monomer into the Ni–C bond of the C_6F_5 ligand. After the first norbornene insertion, propagation proceeded and polymer chains grew. A $(C_6F_5)Ni–CH_2–CH_2–$ capped norbornene polymer intermediate was formed upon the insertion of ethylene. A free rotation around the $–CH_2–CH_2–$ bond of this intermediate offered two β-hydrogens, which could readily be eliminated to form a neutral $NiH(C_6F_5)$ species and a vinyl-terminated polynorbornene chain. The neutral $NiH(C_6F_5)$ species was known to be not sufficiently stable to undergo further norbornene polymer initiations [15]. The species was observed to be readily decomposed to pentafluorobenzene and nickel metal via reductive elimination. This led Goodall et al. to suggest that $(\eta^6\text{-toluene})Ni(C_6F_5)_2$ should be thought of as an initiator of norbornene polymerization rather than a catalyst.

Indeed, the in situ ^{19}F NMR study on the reaction of $Ni(COD)_2$ with $B(C_6F_5)_3$ ($[Ni(COD)_2]/[B(C_6F_5)_3]=1$) in toluene-$d_8$, performed in the presence of a small amount of ethylene to obtain direct evidence of C_6F_5 transfer from $B(C_6F_5)_3$ to Ni, just showed the formation of C_6F_5H. No absorption peak was observed in the around −120 ppm region which would be expected for the *ortho* aryl fluorines on C_6F_5 attached to nickel [33]. The ^{19}F NMR spectrum of the reaction mixture showed three absorption peaks at −139.3 (br s, 2F), −154.4 (br s, 1F), and −162.7 (br s, 2F), except several resonances. The three absorption peaks were realized to come from C_6F_5H by comparison of their chemical shifts with those of authentic C_6F_5H. This again supported the fact that the $HNiC_6F_5$ species underwent reductive elimination to form C_6F_5H and Ni(0). The resulted Ni(0) would subsequently continue the polymerization cycle (Scheme 1), thus functioning as a catalyst.

To support the proposition on the polymerization mechanism the polymerization behavior was further studied with the variation in the level of $B(C_6F_5)_3$ in the presence of ethylene. The results are shown in Table 3. With the increase in the mol ratio of $B(C_6F_5)_3$ to Ni from 1 to 9, conversion was significantly increased from 18.2 to 71.9%, while the M_n of polynobornene was decreased from 2900 to 2200. The MWD (molecular weight distribution) of polynorbornene was maintained in the 1.61–1.72 range, showing that the active complex was single site [34].

A comparison of the theoretical M_n of polynorbornene, which was calculated from conversion and the ratio of initial monomer weight to the concentration of Ni, with observed M_n was conducted to determine whether the Ni(0) species was reactivated by the reaction with $B(C_6F_5)_3$ and whether the β-hydrogen elimination acted as a termination or a chain transfer reaction. The ratio of the theoretical M_n to the observed M_n of polynorbornene reveals the catalytic cycling times with the

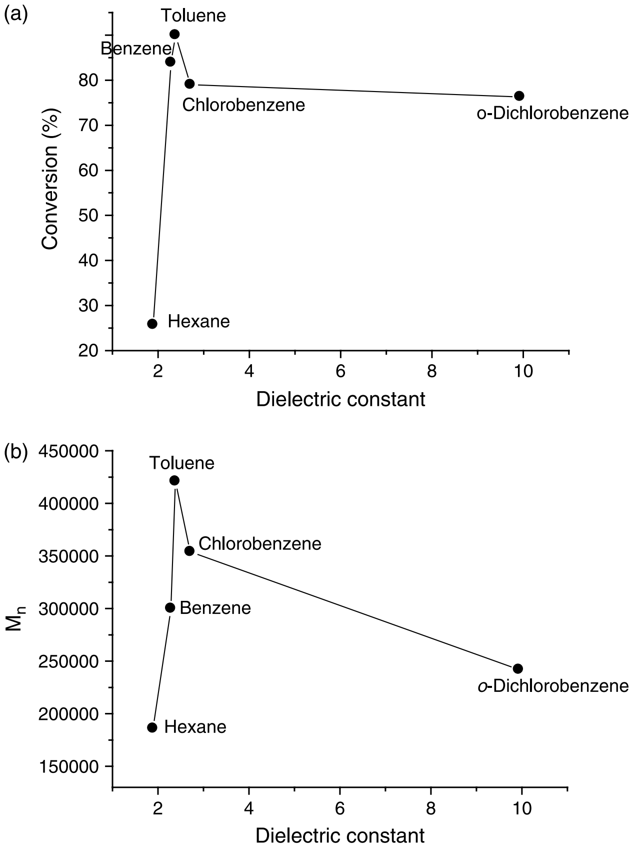


Fig. 5. Effects of solvent variation on (a) conversion and (b) the M_n of polynorbornene; solvent/norbornene (wt/wt), 4.3; polymerization temperature, 40 °C; norbornene, 2 g; concentration of $Ni(COD)_2$, 2.0×10^{-5} mol; polymerization time, 1 h; $[B(C_6F_5)_3]/[Ni]$, 1.

Table 4
Effects of other Ni(0) complexes on the polymerization of norbornene with $B(C_6F_5)_3$

Entry	Ni complex	Activator	Mol ratio	Conv. (%)	M_n	M_w/M_n
15	**2**	$B(C_6F_5)_3$	1:5	93.0	346,000	3.21
16	**2**	$B(C_6F_5)_3$	1:3	85.3	250,000	2.92
17	**2**	$B(C_6F_5)_3$	1:1	4.1	27,000	2.86
18	**5**	$B(C_6F_5)_3$	1:5	64.5	244,000	2.38
19	**5**	$B(C_6F_5)_3$	1:3	0	–	–
20	**5**	$B(C_6F_5)_3$	1:1	0	–	–

Polymerization conditions: polymerization solvent, toluene; solvent/norbornene (wt/wt), 4.3; polymerization temperature, 40 °C; norbornene, 2 g; concentration of Ni, 2.0×10^{-5} mol; polymerization time, 1 h.

variation in the level of $B(C_6F_5)_3$. The catalytic cycling times increased from 0.59 to 3.08 with increasing the mol ratio of $B(C_6F_5)_3$ to Ni (entries 12 and 14). This showed that the polymerization behavior in the presence of ethylene was very much dependent on the amount of $B(C_6F_5)_3$ due to the consumption of $B(C_6F_5)_3$ at every catalytic cycle, and the β-hydrogen elimination acted as a chain transfer reaction. Therefore, it was evident that the Ni(0), formed by β-hydrogen elimination of polymer end followed by reductive elimination of C_6F_5H, was reactivated by the reaction with $B(C_6F_5)_3$, as shown in Scheme 1.

3.4. Effect of solvent

The effects of polymerization solvent on the polymerization are shown in Fig. 5. Polymerization performed in aromatic solvents such as benzene, toluene, chlorobenzene, or *o*-dichlorobenzene gave a higher conversion and M_n than those of polymerization performed in aliphatic solvents such as hexane. Catalytic activity increased with an increase in the polarity of the solvent from hexane to toluene in the initial polymerizations. However, the employment of more polar solvents such as chlorobenzene and *o*-dichlorobenzene decreased the activity to give a conversion of around 75%, representing that there was no deep relation between solvent polarity and catalytic activity. This once more supported that the active complex was a neutral species, rather than an ionic one. The poor solubility of $Ni(COD)_2$ in hexane would cause such a lower conversion. The decrease in activity when using hexane was accompanied by a decrease in the M_n of polynorbornene.

Contrary to the results, an increase in catalytic activity and in M_n was observed with the increase in the polarity of the solvent using the catalyst of Ni(II)/MAO in norbornene polymerization, in which a zwitter ionic complex was proposed to act as the active species [4].

3.5. Polymerization with other Ni(0) complexes

To determine whether the activity of other Ni(0) complexes was comparable to that of complex **1** in norbornene polymerization, complexes **2** and **5** were employed. The results are shown in Table 4. Complex **2**, prepared according to the literature starting from complex **3**, has been realized to react with $B(C_6F_5)_3$ to form the zwitter ionic complex **4**, which was found to have high catalytic activity in the ethylene polymerization [19]. Complex **2** provided high activity to give a conversion of around 93% when the mol ratio of $B(C_6F_5)_3$ to Ni was 5 (entry 15). The use of a lower level of $B(C_6F_5)_3$, however, decreased the activity considerably. A conversion of around 4% was eventually obtained when the mol ratio of $B(C_6F_5)_3$ to Ni was 1 (entry 17). This result was totally different from that obtained from the polymerization with $Ni(COD)_2$ and $B(C_6F_5)_3$ at analogous conditions (entry 3 of Table 1). The zwitter ionic complex **4**, which was formed from the reaction of complex **2** and $B(C_6F_5)_3$, contains an η^3-Ni-allyl bond at the last polymerized unit, while the neutral active species formed from the reaction of complex **1** and $B(C_6F_5)_3$ has the η^1–Ni–C bond of the pentafluorophenyl ligand. The difference of the polymerized units presumably caused the difference in activity with the variation in the mol ratio of $B(C_6F_5)_3$/Ni. The use of a lower level of $B(C_6F_5)_3$ considerably decreased the M_n of polynorbornene as well (entries 15–17). The lower conversion and M_n clearly showed that the equivalent mol ratio of $B(C_6F_5)_3$ to complex **2** was not suitable for the generation of the matured active complexes in the polymerization. The polymer was also vinyl addition in nature since no olefinic resonance was observed in the isolated polymer.

Somewhat lower activity was obtained from the polymerization of norbornene with complex **5** and $B(C_6F_5)_3$ at the mol ratio of $B(C_6F_5)_3/Ni=5$ (entry 18). No olefinic resonance was observed in the ^1H NMR of the isolated polymer, confirming the formation of addition polynorbornene. The use of a lower level of $B(C_6F_5)_3$, however, did not result in any activity. The phosphine ligand in complex **5** would detrimentally act toward the active species. A similar decrease in activity was observed with the decrease in the mol ratio of BF_3 to Ni in the polymerization of norbornene performed with $Ni(PPh_3)_4/BF_3\cdot OEt_2$ [35], where BF_3 was proposed to act another function, a phosphine scavenger, besides a cocatalyst.

4. Conclusions

The Ni(0) complexes, in combination with $B(C_6F_5)_3$, were determined to have high activity and to provide high M_ns of polynorbornenes even in the absence of AlR_3 and MAO. The activity was obtained up to about 100 kg polynorbornene per mol Ni for an hour, which was comparable to that of the active Ni-based binary catalyst reported recently [4]. The required active-component (activator/cocatalyst) quantities were much less for Ni(0) than for Ni(II) in order to achieve similar monomer conversions, which was an important advantage for the prospective optical application of polynorbornene. Compared to the complex (η^6-toluene)Ni(C_6F_5)$_2$, which is known to be prepared by the co-deposition of nickel vapor with reagents [18] and to act as an initiator in norbornene polymerization, the meaning of the present system is that the readily accessible zerovalent Ni complex can be used, with B(C_6F_5)$_3$, as a precursor of catalyst in norbornene polymerization. Further studies on the polymerization of other polar norbornene monomers with this and related Ni-based catalysts are underway.

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