Polymerization of Ester-functionalized Norbornenes Using Neutral Nickel Catalysts

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ABSTRACT: Addition-type polynorbornenes have shown tremendous promise for a variety of applications; however, the direct polymerization of polar functionalized monomers is often challenging when using transition metal-based catalysts. This result is often ascribed to the oxophilic nature of many early transition metal species. Strategies to overcome this issue include the use of late transition metal catalysts, such as those containing Ni and Pd active sites, which generally exhibit greater monomer functional group tolerance. However, discrepancies in molecular weight and yield are still often encountered for the vinyl addition polymerization of polar vs. nonpolar functionalized norbornene monomers. While researchers have studied these effects for Pd-based complexes, analogous studies using neutral, single-site nickel-based catalysts are absent from the literature. Herein, we show that polar functionalized norbornenes and a variety of polar additives readily coordinate $L_nNi(C_6F_5)_2$ type vinyl-addition polymerization catalysts and affect their polymerization behavior. These results suggest that simple trends in polynorbornene molecular weight are observed as a function of coordinating ligand (L_n) strength for the polymerization of nonpolar substituted norbornenes when using O-donor ligands of moderate coordination ability, but do not fully explain why the polymerization of polar functionalized norbornenes routinely produce low molecular weight polymers in poor yields.

INTRODUCTION

Polyolefins are the most widely used and distributed polymers, reaching over 184 million tons produced globally in 2017.[1] This is due in part to their inexpensive monomer feedstocks and diversity of thermomechanical properties that may be accessed through tuning polymerization conditions and (co)monomer identity. Unfortunately, a commonly encountered issue when using early transition metal-based olefin polymerization catalysts is that they are often incapable of polymerizing, or copolymerizing, polar functionalized monomers. This is often ascribed to the highly oxophilic nature of early transition metals, therefore making them incompatible with polar functional groups such as alcohols, ethers, esters, and carboxylic acids.[2]

To circumvent these issues, researchers often use functional group protection-deprotection strategies or synthesize specialty monomers, for example, to enable the use of early transition metal catalysts.[2, 3] However, a promising strategy to access polar functionalized polyolefins via direct (co)polymerization is to shift from early transition metals to late transition metal-based catalysts. For example, cationic Pd diimine complexes originally reported by Brookhart and coworkers have been shown to copolymerize acrylates with ethylene.[4-6] Similarly, certain neutral nickel complexes have also been shown to facilitate the (co)polymerization of functional, olefinic monomers.[7-9] These, and numerous other research efforts, have enabled the development of myriad Pd and Ni catalysts capable of (co)polymerizing functionalized olefinic monomers.[10-14]

Detailed calculational studies of both cationic and neutral nickel and palladium complexes have been carried out to better understand the ability of these late transition metal-based catalysts to copolymerize simple olefins and polar comonomers.[15, 16] Therein, two coordination modes were considered for functional monomers, such as acrylates, to the active metal site: π-olefin and O-coordinated complexes. These studies suggest that complexes with strongly coordinating polar functionality (e.g., M-O-coordination) are inappropriate candidates for functional monomer copolymerization as this may hinder, or prevent, coordination of the functional monomer's olefinic double bond to the active metal site, which is a prerequisite for coordination-insertion polymerization.

Our interest in the area of functionalized polyolefins focuses primarily on polymers derived from cycloolefinic, norbornene-type monomers. In particular, polar functionalized norbornene-based polymers have shown promise as they, depending on the functional group, can exhibit improved adhesion to substrates or solubility in aqueous base, thus forming the basis for electronics packaging polymers and binder resins for photoresist formulations, respectively.[17-20] Complexes that are active for the polymerization of norbornene-based monomers traditionally include both cationic nickel and palladium complexes. However, in 2000, Rhodes and coworkers discovered the activation of nickel-based catalysts toward

the polymerization of norbornene by transfer of C_6F_5 from $B(C_6F_5)_3$ to Ni.[21] This discovery led to the development of a new class of single-site nickel catalysts bearing electron-withdrawing groups that propagate via a neutral Ni active site (e.g., **Ni1** and **Ni2** (Figure 1) that have C_6F_5 moieties), which are highly effective for the polymerization of substituted and unsubstituted norbornene monomers.[19, 22-25]

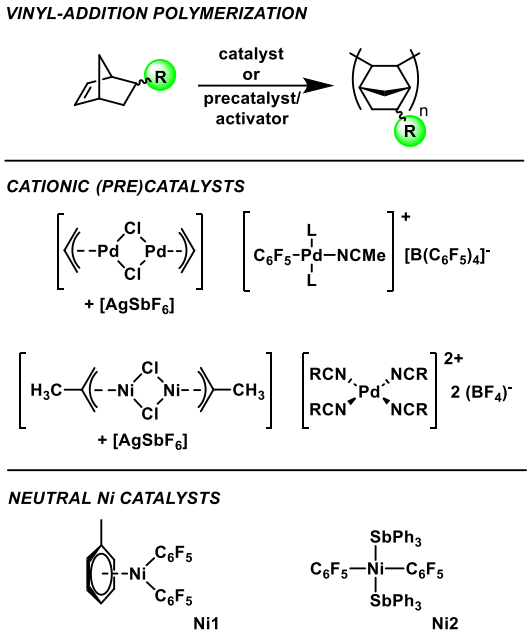


FIGURE 1. Vinyl-addition polymerization of polynorbornenes and examples of commonly used Ni- and Pd-based (pre)catalysts, which propagate via a cationic or neutral active metal site.

Despite the success of these neutral nickel catalysts, preliminary work in our labs has consistently shown a discrepancy in the vinyl-addition polymerization of polar functionalized norbornyl monomers using the neutral, single-site nickel catalyst (η^6-toluene)$Ni(C_6F_5)_2$ (**Ni1**), as compared to analogous polymerizations of nonpolar norbornene monomers. Similar effects have been reported for cationic palladium-based catalysts in which the presence of polar functional groups is found to have minimal electronic effect on the polymerizable norbornene C=C bond,[26] but rather the metal center is believed to coordinate the monomer's polar functional group (Figure 2), inhibiting further monomer coordination and insertion at the metal center.[26] Further complications arise in that norbornene-based monomers are commonly synthesized via Diels-Alder reaction that yields a mixture of *endo*- and *exo*-isomers.[27] Monomers having *endo*-substituted polar functional groups may form chelates via the simultaneous coordination of the metal to the polar functionality and bicyclic olefin. (Figure 2).[26, 28-31] Combined, these two modes of coordination, as well as other issues recently highlighted by Harth and coworkers,[2] are believed to lead to decreased polymerization activity when (co)polymerizing polar-substituted norbornene monomers.

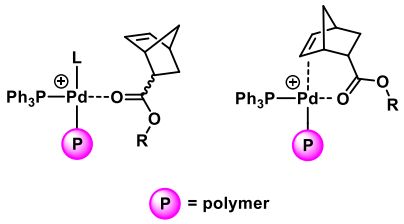


FIGURE 2. Proposed coordination modes when polymerizing prototypical *exo*- and *endo*-ester substituted norbornene monomers using Pd-based catalysts. Adapted from [26]. Copyright 2004 American Chemical Society.

While the coordination, and/or chelation, of polar-substituted norbornene monomers to cationic Pd catalyst centers has been investigated, similar studies have not been reported for Ni-based catalysts that propagate via a neutral Ni active site. Herein, we will describe these observed discrepancies between the vinyl addition polymerization of polar functionalized and nonpolar norbornene monomers and investigate the possibility of coordination, and/or chelation, of the polar functionality to the neutral nickel center as a possible explanation for this behavior. We then expand this study to a broader series of $(L)_nNi(C_6F_5)_2$ derivatives (where L = donor ligand) and evaluate their polymerization activity.

RESULTS AND DISCUSSION

Polymerization of Polar vs. Nonpolar Monomers. For the studies presented herein, 5-hexylbicyclo[2.2.1]hept-5-ene (**M1**) and *t*-butyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (**M2**) are used as prototypical nonpolar- and polar-substituted norbornene monomers, respectively. **M1** was chosen due to its propensity to yield highly soluble polymeric materials in common organic solvents, and **M2** was selected due to its commercial relevance for the production of photolithographic resists, wherein the *t*-butyl moiety may be readily removed via acid-catalyzed deprotection to yield carboxylic acid functionalized polynorbornenes. Each monomer was polymerized using **Ni1** at increasing monomer-to-catalyst ratios (Scheme 1). For each polymerization, we found that polymerization of nonpolar **M1** gives rise to high molecular weight polymer (M_n = 680-700 kg/mol) in high yield (Table 1, entries 1-3), while the polymerization of polar functionalized monomer **M2** produced only low molecular weight polymers (M_n = 9-17 kg/mol) in poor yield (Table 1, entries 4-6).

SCHEME 1. Polymerization of **M1** and **M2** using catalyst **Ni1**.

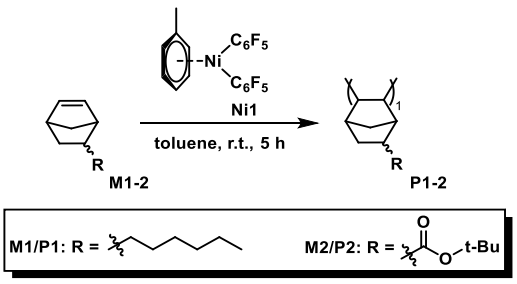


Table 1. Polymerization of norbornene monomers **M1** and **M2** to yield polymers **P1** and **P2**, respectively, using **Ni1**[a].

entry	monomer	M:cat	yield (%)	M_n[b] (kg/mol)	Đ [b]
1	**M1**	50:1	96 ± 6.4	700 ± 66	5.1 ± 2.1
2	**M1**	100:1	99 ± 0.6	680 ± 30	2.4 ± 0.9
3	**M1**	750:1	69 ± 2.6	690 ± 36	2.9 ± 0.4
4	**M2**	50:1	37 ± 6.4	8.7 ± 0.1	1.5 ± 0.1
5	**M2**	100:1	41 ± 0.7	15 ± 1.0	1.7 ± 0.1
6	**M2**	750:1	2.8 ± 2.1	17 ± 0.4	1.8 ± 0.1

[a] General polymerization conditions: total monomer = 0.14 mmol, 100 μL toluene; T_{rxn} = 20 °C, and t = 5 h. All polymerizations were run in triplicate. [b]Molecular weights and dispersity were measured using gel permeation chromatography at 40 °C in THF and reported relative to polystyrene standards.

As previously noted, the low molecular weights and yields observed for the polymerization of polar functionalized monomers using **Ni1** agree well with prior reports employing Pd(II)-based catalysts that propagate via a cationic metal site. Because of this, we hypothesized that a similar type of coordination, and/or chelation, may occur between the carbonyl moiety of ester functionalized monomer **M2** and the neutral active metal center of **Ni1**, as shown in Figure 3. If valid, these coordination modes may similarly inhibit productive monomer coordination, and/or insertion, and offer a plausible explanation for the lower molecular weight polymers and lower yields produced when polymerizing such polar functionalized monomers, as compared to analogous nonpolar monomer **M1**.

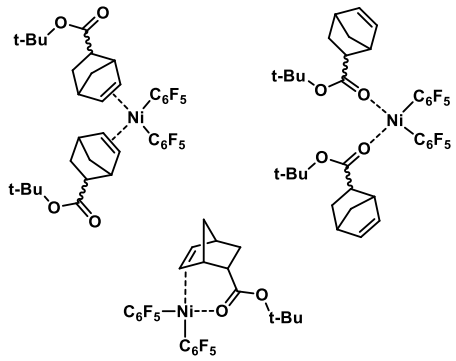
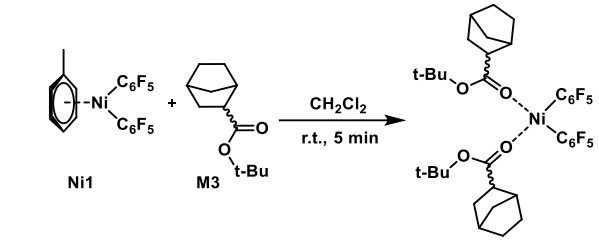


FIGURE 3. Potential coordination modes of ester functionalized monomer **M2** with **Ni1** following displacement of the labile, coordinated toluene.

Coordination Studies. Our initial investigations into the potential coordination of ester-substituted monomer **M2** to the active metal site of catalyst **Ni1** were conducted at low temperature to mitigate undesirable polymerization, which occurs readily at room temperature. Therein, excess **M2** was combined with in CH_2Cl_2 at -78 °C. The solvent and any volatile byproducts were then removed under vacuum to yield a yellow solid that was analyzed using IR spectroscopy and compared to the individual IR spectra of the native **Ni1** and **M2** (see Figure S17). If coordination of the carbonyl moiety of **M2** to the Ni-center occurs, we would expect to observe a shift of the carbonyl stretching frequency to lower wavenumbers as compared to that of free monomer **M2**, which occurs at 1724 cm^{-1}. Indeed, when **M2** was combined with **Ni1**, we observed two stretches at a lower frequency which could be ascribed to symmetric and asymmetric carbonyl stretches at 1636 cm^{-1} and 1614 cm^{-1}.[32] This shift, in addition to the asymmetric nature of the coordinated carbonyl peak, agrees with the coordination of two molecules of **M2** in a *cis* fashion to the $Ni(C_6F_5)_2$ fragment likely resulting in a square planar complex with pseudo-C_{2v} symmetry.[33, 34] Though these experiments were run at low temperatures in an attempt to avoid polymerization of the monomer, some polymerization was observed that complicated further analysis.

To avoid complications arising from monomer polymerization, monomer **M2** was hydrogenated using Crabtree's catalyst to yield *t*-butyl bicyclo[2.2.1]heptane-2-carboxylate (**M3**), which prevents the possibility of polymerization while still permitting ester coordination to the active Ni site. Therein, excess of **M3** was added to **Ni1** in CH_2Cl_2 at room temperature followed by removal of the solvent and any volatile byproducts under vacuum to yield a yellow solid (Scheme 2) that was analyzed by IR and ^{19}F NMR spectroscopy. Again, the single carbonyl stretch observed for **M3** at 1724 cm^{-1} was observed to shift and yield two new stretches at a lower frequencies (1638 cm^{-1} and 1615 cm^{-1}) that we ascribe to the symmetric and asymmetric carbonyl stretches (Figure 4), which also agrees with the coordination of two equivalents of **M3** in a *cis* fashion to the active $Ni(C_6F_5)_2$ site in a square planar complex with pseudo-C_{2v} symmetry.[33, 34]

SCHEME 2. Mixing of **M3** and **Ni1** to probe potential coordination modes via IR and NMR spectroscopy.



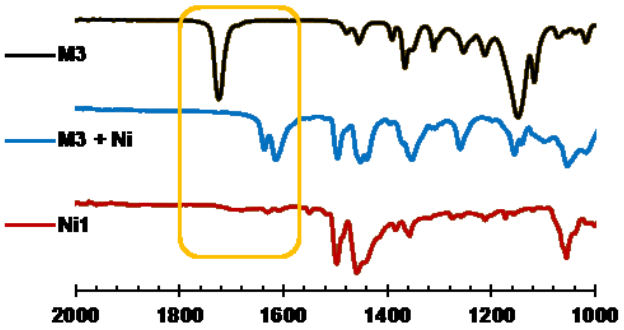


FIGURE 4. IR spectra of the hydrogenated monomer **M3** (top), **M3** + **Ni1** mixed in CH_2Cl_2 followed by removal of all volatiles in vacuo (middle), and **Ni1** (bottom).

The ^{19}F NMR spectrum of the product resulting from mixing **M3** + **Ni1** shows a shift in the ortho, para, and meta fluorine resonances

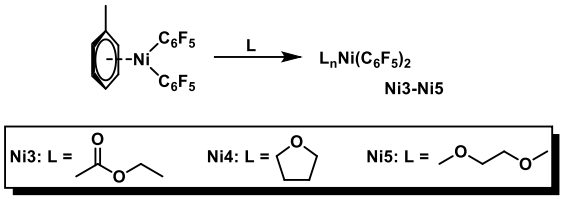
for the resultant new species, relative to the starting catalyst (Figure 5), with new resonances observed at ~ -119 ppm (*o*-fluorines), -162 ppm (*p*-fluorines), and -166 ppm (*m*-fluorines). These results similarly suggest coordination of the carbonyl of **M3** to the Lewis acidic Ni center. It should be noted that the ^{19}F NMR spectra of the products isolated after mixing **M2** + **Ni1** and **M3** + **Ni1** displayed broad signals and/or multiplets, which we attribute to the resultant product complexes bearing a mixture of coordinated *endo/exo* stereoisomers of **M2** or **M3**. Attempts to confirm the identity of these new complexes via X-ray crystallography were unsuccessful.

FIGURE 5. ^{19}F NMR spectra of **Ni1** (top) and the proposed coordinated species resulting from the mixing of excess **M3** with **Ni1** (bottom). Also present in the ^{19}F NMR spectrum are two additional sets of peaks from catalyst degradation. The first set of peaks (-137.91 ppm, -150.73 ppm, and -161.20 ppm) correspond to perfluoro-1,1'-biphenyl, which forms via reductive elimination at the Ni center. The second set of peaks (-139.05 ppm, -154.37 ppm, and -162.62 ppm) correspond to pentafluorobenzene that presumably results from protodemetallation that may have occurred during isolation and analysis of the product. Spectra were recorded in $CDCl_3$.

Because we were unable to fully confirm the identity of **Ni1**-**M2** or -**M3** coordinated complexes, we envisioned that simpler esters, such as ethyl acetate (EtOAc), that do not exist as isomeric mixtures might serve as an easily characterizable proxy for **M2** or **M3**. To test this hypothesis, excess EtOAc was combined with **Ni1** to yield an orange solid following removal of all volatiles under vacuum. Analysis of the resulting Ni complex by IR spectroscopy showed a shift in the single carbonyl peak from 1736 cm^{-1} to a lower frequency that can be ascribed to symmetric and asymmetric carbonyl stretches at 1662 cm^{-1} and 1647 cm^{-1}, which is similar to that observed when using monomers **M2** and **M3**. This data suggests coordination of two ethyl acetate molecules to the nickel center in a *cis* fashion. Similarly, ^{19}F NMR spectroscopy also showed shifts of the *ortho-*, *meta-*, and *para*-fluorine signals, as expected (Figures **S21** and **S4**, respectively).

Because these studies showed that even simple esters readily displace toluene and coordinate to **Ni1**, we became interested in how other donor ligands, L, might yield $L_nNi(C_6F_5)_2$ derivatives that might vary in their polymerization behavior for nonpolar and polar norbornene monomers. More specifically, we were interested in how ligands of varying coordinating strengths might impact the polymerization process. Based on this, catalysts **Ni3**, **Ni4**, and **Ni5**, were synthesized by dissolving **Ni1** in an excess of ethyl acetate, tetrahydrofuran, or 1,2-dimethoxyethane (DME), respectively (Scheme 3) following a modified literature procedure used to previously access **Ni4**.[35]

SCHEME 3. Synthesis of $L_nNi(C_6F_5)_2$ complexes **Ni3**-**Ni5**.



Catalysts **Ni3**, **Ni4**, and **Ni5**, which bear EtOAc, THF, and DME ligands, respectively, were characterized using ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy. X-ray crystallographic quality crystals of **Ni3** and **Ni5** were grown via layering of hexanes/EtOAc and hexanes/DME, respectively (Figure 6). **Ni4** was characterized by X-ray crystallography in a prior literature report.[35] Crystallography data of **Ni3** shows coordination of two ethyl acetate ligands in a *cis* - fashion through the oxygen of the carbonyl moiety to the active Ni center. (Figure S33) This coordination environment differs from the *trans*-environment observed for **Ni2**; however, it agrees nicely with our expectations from IR spectroscopy. Due to the potential for chelation of the DME ligand, **Ni5** was also expected to exist in a similar *cis*- coordination environment, which has been previously reported for the analogous catalyst bis(2,4,6-tris(trifluoromethyl)phenyl)Ni(1,2-dimethoxy-ethane).[36, 37] Indeed, X-ray crystallographic data of **Ni5** reveals chelation of the DME ligand resulting in cis-coordination of the C_6F_5 ligands (Figure S35).

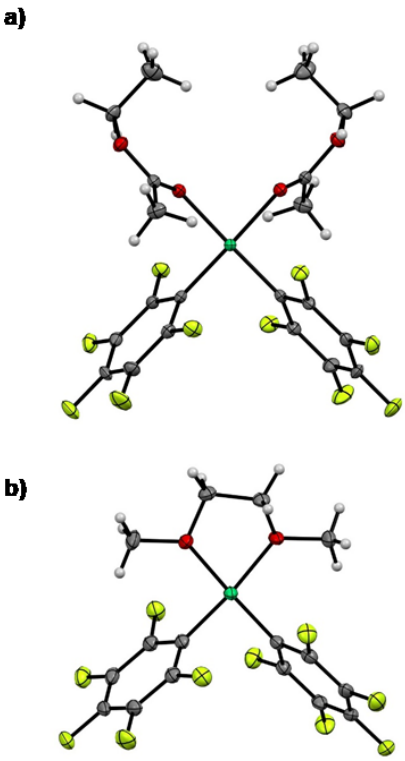


FIGURE 6. ORTEP representations of a) **Ni3** and b) **Ni5**. Thermal ellipsoids are drawn at 50% probability and all hydrogen atoms are included.

Polymerization and Equilibrium Studies. Monomers **M1** and **M2** were polymerized using catalysts **Ni2**, **Ni3**, **Ni4**, and **Ni5** following the procedure described above, and are compared to the results obtained using toluene ligated catalyst **Ni1** (see Table 2). Similar to the results obtained when using catalyst **Ni1**, polymerizations of nonpolar monomer **M1** using **Ni2, Ni3**, **Ni4**, and **Ni5** each produced high molecular weight polymers (M_n = 226 – 580 kg/mol) in high yield (88-97 %) (Table 2, entries 2-5). In contrast, analogous polymerizations of ester-containing monomer **M2** once again produced low molecular weight polymers (M_n = 14 – 16 kg/mol) in low yield (18 - 29%) (Table 2, entries 7-10). While these results confirm that neutral Ni catalysts **Ni3**, **Ni4**, and **Ni5** remain polymerization active, it suggests that pre-coordination of either polar ester or ether ligands to the active site does not strongly influence the polymer yield or molecular weights obtained when polymerizing polar monomer **M2**.

Table 2. Polymerization of norbornene monomers **M1** and **M2** to yield polymers **P1** and **P2**, respectively, using neutral nickel catalysts **Ni1**-**Ni5**.[a]

entry	Mon.	Cat.	yield (%)	M_n[b] (kg/mol)	$Đ$[b]
1	**M1**	**Ni1**	99 ± 0.6	680 ± 30	2.4 ± 0.9
2	**M1**	**Ni2**	95 ± 3.4	226 ± 53	1.7 ± 0.2
3	**M1**	**Ni3**	97 ± 1.5	460 ± 18	1.6 ± 0.1
4	**M1**	**Ni4**	88 ± 8.0	510 ± 36	1.9 ± 0.2
5	**M1**	**Ni5**	90 ± 1.5	580 ± 35	1.9 ± 0.4
6	**M2**	**Ni1**	41 ± 0.7	15 ± 1.0	1.7 ± 0.1
7	**M2**	**Ni2**	20 ± 3.5	14 ± 0.3	1.6 ± 0.1
8	**M2**	**Ni3**	21 ± 11	16 ± 0.8	1.5 ± 0.1
9	**M2**	**Ni4**	18 ± 6.5	14 ± 1.7	1.6 ± 0.2
10	**M2**	**Ni5**	29 ± 5.2	16 ± 0.5	1.6 ± 0.1

[a]General polymerization conditions: total monomer = 0.14 mmol, catalyst = 1.4 μmol, 100 μL toluene; T_{rxn} = 20 ^{0}C, and t = 5 h. All polymerizations were run in triplicate [b]Molecular weights and dispersity were measured using gel permeation chromatography at 40 ^{0}C in THF and reported relative to polystyrene standards.

Though polar-ligand coordinated catalysts **Ni3**, **Ni4**, and **Ni5** were unable to access high molecular weight **P2**, we noted that a trend of steadily increasing molecular weight polymers were obtained for catalysts **Ni3**, **Ni4**, and **Ni5** for the polymerization of monomer **M1**. To investigate this effect further, the K_{eq} between toluene coordinated **Ni1** and its polar ligand coordinated analogues ($L_nNi(C_6F_5)_2$) were each measured as a proxy to estimate the binding strength of each polar ligand to the Lewis acidic Ni center. For example, the K_{eq} between THF-coordinated **Ni4** and toluene-coordinated **Ni1** was measured by combining one equivalent of **Ni1** and two equivalents of THF and the equilibrium position was measured using ^{19}F NMR spectroscopy by integration of the aryl fluorine peaks assigned to each complex (Figure 7). At equilibrium, two sets of ^{19}F resonances were observed – the first set (-113.8 ppm, -160.2 ppm, and -164.0 ppm) corresponding to the toluene-ligated complex **Ni1** and the second set (-118.4 ppm, -161.2 ppm, and -165.1 ppm) corresponding to bis(THF) ligated **Ni4**. The measured K_{eq} values for **Ni1** in the presence of stoichiometric amounts of EtOAc, THF, and DME were 0.8, 2.7, and 19.0, respectively.

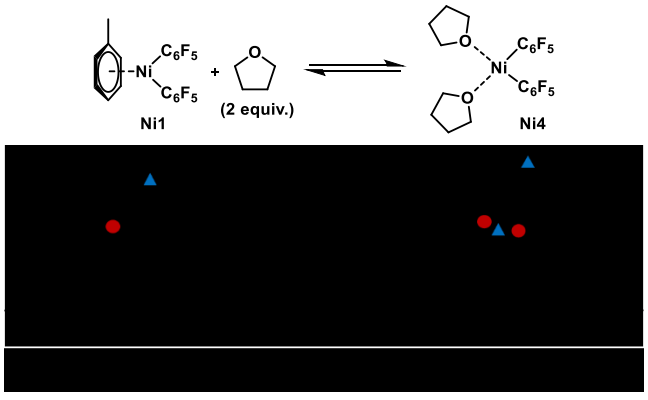


FIGURE 7. Representative example of determining K_{eq} via ^{19}F NMR spectroscopy for **Ni1** (red circles) in the presence of 2 equiv. of THF to form **Ni4** (blue triangles). Spectra were recorded in $CDCl_3$.

Plots of **P1** and **P2** molecular weight versus measured equilibrium constant (K_{eq}) of each $L_nNi(C_6F_5)_2$ are shown in Figures 8 and 9, respectively. Interestingly, we found that there is a clear linear trend between polymer molecular weight and measured K_{eq} values for **Ni3**, **Ni4**, and **Ni5** when polymerizing nonpolar monomer **M1** (Figure 8). While the exact mechanistic rationale for this observed behavior is yet unknown, we suspect that the presence of polar additives may

aid in the stabilization of the propagating Ni center, thereby preventing deleterious catalyst degradation and yielding higher molecular weight polymers. In contrast, no clear trend was observed for the polymerization of polar monomer **M2** (Figure 9), wherein the resultant molecular weights were not significantly different from one another based on the 1-sigma criterion.

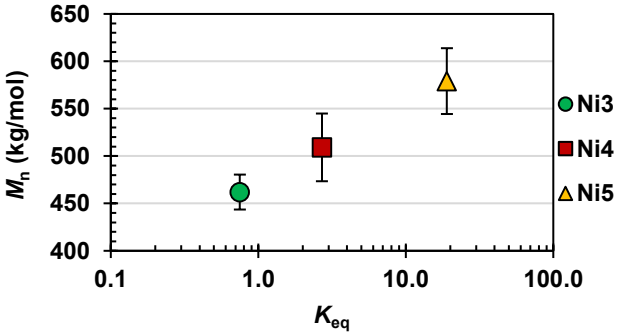


FIGURE 8. Plots of molecular weight (M_n) versus measured equilibrium constant (K_{eq}) of each $L_nNi(C_6F_5)_2$ for the polymerization of nonpolar monomer **M1**.

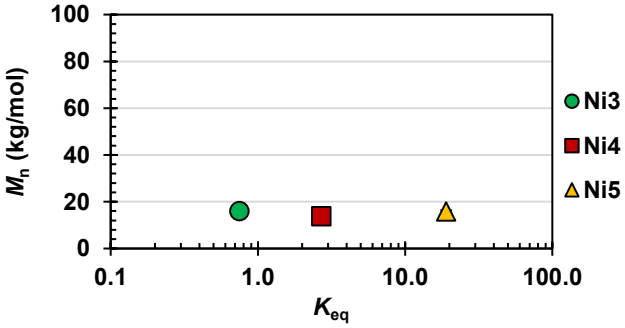


FIGURE 9. Plots of molecular weight (M_n) versus measured equilibrium constant (K_{eq}) of each $L_nNi(C_6F_5)_2$ for the polymerization of nonpolar monomer **M2**. NOTE: error bars for each data point are included in this plot but are hidden by the data markers.

These studies have focused primarily on oxygen-based ligands, due to the prevalence of polar norbornyl monomers bearing esters and ethers, for example. However, other neutral $L_nNi(C_6F_5)_2$ type complexes have recently seen increased interest for the vinyl addition of functionalized norbornenes, such as *trans*-$[Ni(C_6F_5)_2(SbPh_3)_2]$ (**Ni2**). This catalyst has been shown to tolerate a variety of functionalized norbornyl monomers, such as those bearing alkoxy silane-substituents,[24] and we were therefore interested in how the change in ligand type, from the hard, oxygen coordinating ligands of catalysts **Ni3**-**Ni5** to the soft stibine-based ligands of catalyst **Ni2** would impact the polymerization of monomers **M1** and **M2**.

To investigate this, we first ran equilibrium studies in which **Ni1** (1 equiv.) was mixed with $SbPh_3$ (2 equiv.) in CD_2Cl_2. The ^{19}F NMR spectrum of this mixture revealed rapid and complete ligand exchange of the toluene ligand of **Ni1** for the $SbPh_3$ ligands. The K_{eq} value was therefore unmeasurable, and its polymerization results could not be readily plotted alongside the results for catalysts **Ni3**-**Ni5**. Furthermore, ^{19}F NMR and IR spectroscopy both suggest that the coordinating $SbPh_3$ ligands are not readily displaced by **M3** or EtOAc, even when excess ester was used (See Figures S12, S13, S20 and S21).

In similarity to the results observed for catalysts **Ni1** and **Ni3**-**Ni5**, polymerization of nonpolar monomers using **Ni2** produced high molecular weight polymer **P1** (M_n = 230 ± 53 kg/mol) in high yield (90-99%), whereas polymerizations of polar monomer **M2** produced only low molecular weight **P2** (M_n = 14 kg/mol ± 0.3) in low yield (18-41 %). These polymerization results mimic those of catalysts **Ni3**-**Ni5**; however, **Ni2** does not seem to follow the same trend of increasing **P1** polymer molecular weight vs. ligand strength despite **Ni2** having an infinitely stronger coordinating ligand than any of the four other catalysts (**Ni1, Ni3**-**Ni5**). We anticipate that this discrepancy in observed behavior is likely due to the difference of hard vs. soft coordinating neutral ligands for catalysts **Ni3**-**Ni5** vs. **Ni2**, respectively, though further investigations will be required.

CONCLUSION

Norbornene-type monomers bearing polar and nonpolar functional groups were polymerized using a series of neutral, single-site nickel-based catalysts. The polymerization of the nonpolar monomer (**M1**) gave rise to high molecular weight polymer in high yield, whereas the polymerization of the polar, ester containing monomer (**M2**) gave rise to low molecular weight polymer in poor yield. The possibility of coordination/chelation of the polar functionality to the Lewis acidic metal center was investigated using IR and ^{19}F NMR spectroscopy. When excess **M2**, **M3**, or EtOAc were combined with **Ni1**, IR spectroscopy revealed a shift in the carbonyl stretch of the native ester to a lower frequency with symmetric and asymmetric carbonyl stretching. This, along with the shift in the ^{19}F NMR peaks of the coordinated species, suggests coordination of two molecules of **M2**, **M3**, or EtOAc in a *cis* fashion to the $Ni(C_6F_5)_2$ fragment.

Due to the facile displacement of the toluene ligand in **Ni1**, other $L_nNi(C_6F_5)_2$ catalysts were synthesized through simply dissolving **Ni1** in excess EtOAc, THF, or DME to yield **Ni3**, **Ni4**, and **Ni5**, respectively. To the best of the author's knowledge, **Ni3** and **Ni5** have not been previously described in the literature. These catalysts were thoroughly characterized using ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy, as well as X-ray crystallography. X-ray crystallography data of **Ni3** revealed coordination of two ethyl acetate ligands via the carbonyl oxygen to the nickel center in a *cis* fashion, which agrees with the results obtained from IR and ^{19}F NMR spectroscopy. X-ray crystallography data of **Ni5** revealed chelation of a single DME ligand to the nickel center in a *cis* fashion.

Monomers **M1** and **M2** were subsequently polymerized using **Ni2**, **Ni3**, **Ni4**, and **Ni5**, and these results were compared to the results obtained using **Ni1**. Polymerization of **M1**, again, gave rise to polymers with high molecular weights in high yield, whereas **M2** gave rise to polymers with low molecular weights in poor yield. Interestingly, polymerizations of nonpolar monomer **M1** presented a trend of increasing molecular weight as a function of ligand coordination strength, as was estimated by measured K_{eq} values for O-donor ligands of moderate coordination ability. In contrast, polymerizations of ester functionalized monomer **M2** produced polymers that were not significantly different from one another in molecular weight.

Finally, the results obtained for catalysts **Ni3**-**Ni5**, which bear ligands that coordinate the Ni center via oxygen atoms, were compared to polymerizations using the Sb-coordinated catalyst **Ni2**. Again, decreased molecular weight and yield were observed for the

polymerization of **M2**, as compared to **M1**. The coordination strength of this catalyst was also investigated; however, when compared to the coordinating strength of the ligands in **Ni1**, **Ni3**, **Ni4**, and **Ni5**, **Ni2** contains ligands that are infinitely stronger in their coordination strength. Surprisingly, however, this increase in ligand coordination strength did not follow the observed trend of increasing **P1** molecular weight noted for catalysts **Ni3**-**Ni5**, which we hypothesize may be due to the difference in ligand type (i.e. hard versus soft ligands). In sum, these results provide deeper insight into the discrepancies often observed when polymerizing polar vs. nonpolar norbornene-type monomers using neutral, single-site nickel catalysts, but future studies will be required to identify the exact mechanistic rationale leading to limited molecular weights and yields for the polymerization of polar monomers, such as **M2**. Furthermore, we have shown that $L_nNi(C_6F_5)_2$ complexes bearing O-donor ligands of moderate coordination ability may be attractive alternatives for the polymerization of norbornene-derived monomers, specifically those bearing nonpolar substituents.

EXPERIMENTAL SECTION

Materials and Methods. All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk technique or in an inert atmosphere using an MBraun glovebox filled with nitrogen gas. Monomers 5-hexylbicyclo[2.2.1]hept-5-ene (**M1**, endo: exo= 21:79) and *t*-butyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (**M2**, *exo:endo* = 23:77) were gifted from Promerus LLC and purified via vacuum distillation from CaH_2, degassed using iterative freeze-pump-thaw cycles (3×), and stored in the glovebox prior to use. The catalyst (η^6-toluene)$Ni(C_6F_5)_2$ (**Ni1**) was gifted from Promerus LLC, stored in a glovebox, and used as received. The catalyst *trans*-$[Ni(C_6F_5)_2(SbPh_3)_2]$ (**Ni2**) was synthesized following literature procedure.[23, 24] Dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), ethyl acetate (EtOAc), and toluene were purchased from Fischer Scientific, dried via passage through an Innovative Technologies PurSolv solvent purification system, and degassed via iterative freeze-pump-thaw cycles (3×) prior to use. Anhydrous dimethoxy ethane was purchased from Acros in Acroseal™ bottles and degassed via iterative freeze-pump-thaw cycles (3×) prior to use. Methanol for polymer precipitation was purchased from Fischer Scientific and used as received.

^{1}H NMR spectra of all monomers and polymers were obtained in $CDCl_3$ using a Varian 500 MHz spectrometer. ^{1}H NMR ^{13}C NMR, and ^{19}F NMR of all catalysts were obtained in $CDCl_3$ or CD_2Cl_2 using a Varian 500 MHz or 300 MHz spectrometer. All ^{1}H NMR spectra were referenced to the residual $CHCl_3$ peak at 7.26 ppm or the residual CD_2Cl_2 peak at 5.32 ppm. All ^{13}C NMR spectra were referenced to the residual $CDCl_3$ peaks at 77.16 ppm. IR spectra were obtained using an Agilent Technology Cary 630 FTIR with a diamond ATR sample cell. The IR spectrometer was used inside a nitrogen atmosphere glove box, and all samples were stored and analyzed under a nitrogen atmosphere. Polymer molecular weights were measured relative to polystyrene standards using Tosoh EcoSEC GPC system with a tetrahydrofuran eluent at 40 °C.

General Norbornene Polymerization Procedure using Ni1. In a typical polymerization procedure, **M2** (1.0014 g, 5.2 mmol) was added to a vial equipped with a magnetic stir bar in a glovebox. A solution of **Ni1** (2.5 mg, 0.05 mmol) in 3.7 mL of toluene was prepared in a separate vial, then added to the monomer. The final concentrations of **M2** and **Ni1** were 1.37 M and 0.0138 M, respectively. The reaction mixture was stirred at room temperature for 5 h before precipitating the reaction mixture into excess methanol. The precipitate was filtered and dried under vacuum at 65 ^{0}C overnight to yield 0.5589 g of the polymeric product (56 %).

Synthesis of *t*-Butyl bicyclo[2.2.1]hept-5-ane-2-carboxylate (M3). In a glovebox, **M2** (3.003 g, 15.5 mmol) was dissolved in CH_2Cl_2 (10.5 mL) in a vial equipped with a stir bar. [(1,5-cyclooctadiene) iridium(tricyclohexylphosphine)(pyridine)] PF_6 (Crabtree's Catalyst) (12.3 mg, 0.015 mmol) was weighed into a separate vial. The monomer solution was added to the vial containing Crabtree's catalysts. The vial containing the reaction mixture was placed in a stainless-steel Parr Reactor, sealed, and removed from glovebox. The reactor was then charged with hydrogen gas (300 psi) and stirred overnight. The hydrogenated product was distilled under vacuum between 35-40 °C at 300 mTorr to yield 1.6913 g of **M3** (56 %) as a colorless liquid. ^{1}H NMR ($CDCl_3$): *endo*-isomer δ= 2.66 (m, 1H), 2.50 (br s, 1H), 2.24 (br s, 1H), 1.45 (s, 9 H), 1.8-1.1 (m, 8H); *exo*-isomer δ= 2.45 (br s, 1H), 2.26 (br s, 1H), 2.19 (br d, 1H), 1.43 (s, 9H), 1.8-1.1 (m, 8H). IR: ν(CO) 1724 cm^{-1}. ^{13}C NMR ($CDCl_3$): δ=175.61, 174.53, 79.80 79.68, 47.61, 46.99, 41.03, 40.78, 40.36, 37.26, 36.48, 36.14, 34.21, 31.79, 29.57, 29.24, 28.82, 28.32, 28.23, 24.77. HRMS ESI +(m/z) $[M+H]^+$ Calculated for $C_{12}H_{20}O_2$:196.14633, Found:197.15378 CHNO elemental analysis for ($C_{12}H_{20}O_2$): C=73.09, H=9.82, O=17.19 (calculated, C= 73.43, H=10.27, O=16.30). Although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date.

Coordination of *t*-Butyl bicyclo[2.2.1]hept-5-ene-2-carboxylate to (η^6-toluene)$Ni(C_6F_5)_2$ (M2 + Ni1). In a glovebox, **Ni1** (0.1873 g, 0.39 mm) was dissolved in CH_2Cl_2 (3.6 mL) in a 50 mL Schlenk flask equipped with a magnetic stir bar to give a dark red-brown solution. The catalyst solution was cooled to -78 ^{0}C and **M2** (0.3031 mg, 1.6 mmol) was added. The solvent and any volatile byproducts were removed under vacuum to produce 0.2218 g of an orange powder (yield = 73% if calculated assuming two equivalents of **M2** are coordinated to **Ni1** with concomitant displacement of toluene). ^{19}F NMR (CD_2Cl_2): δ= -118.6 (m, 2F), -161.8 (bs, 1F), -165.5 (bs, 2F). IR:ν(CO) 1724 cm^{-1} (free monomer), 1636 cm^{-1}, 1614 cm^{-1} (coordinated monomer).

Coordination of *t*-Butyl bicyclo[2.2.1]hept-5-ane-2-carboxylate to (η^6-toluene)$Ni(C_6F_5)_2$ (M3 + Ni1). In a glovebox, **Ni1** (22.7 mg, 0.047 mmol) was dissolved in CH_2Cl_2 (1.0 mL) in a 5 mL Schlenk flask equipped with a magnetic stir bar to give a dark red-brown solution. **M3** (63.9 mg, 0.33 mmol) was added to the catalyst solution. The solvent and any volatile byproducts were removed under vacuum to produce 30.2 mg of orange powder (yield= 82 % if calculated assuming two equivalents of **M3** are coordinated to **Ni1** with concomitant displacement of toluene). ^{19}F NMR (CD_2Cl_2): δ= -118.6 (m, 2F), -162.0 (t, 1F), -165.9 (t, 2F). IR:ν(CO) 1638 cm^{-1}, 1615 cm^{-1}.

Coordination of EtOAc to $Ni(C_6F_5)$ (η^6-toluene)$Ni(C_6F_5)$ (EtOAc + Ni1). In a glovebox, **Ni1** (30.1 mg, 0.062 mmol) was dissolved in ethyl acetate (1.0 mL) in a 50 mL Schlenk flask equipped with a magnetic stir bar to give a dark red-brown solution.

The solvent and any volatile byproducts were removed under vacuum to produce 20.6 mg of an orange powder (yield= 58 % if calculated assuming two equivalents of EtOAc are coordinated to **Ni1** with concomitant displacement of toluene). ^{19}F NMR (CD_2Cl_2): δ -118.8 (d, 2 F), -160.4 (t, 1F), -164.5 (t, 2F). IR:ν(CO) 1662 cm^{-1}, 1647 cm^{-1}.

Synthesis of $(EtOAc)_2Ni(C_6F_5)_2$ (Ni3). In a glovebox, **Ni1** (0.1046 g, 0.21 mmol) was dissolved in 1.8 mL ethyl acetate in a 50 mL Schlenk flask equipped with a magnetic stir bar. The reaction was stirred for 5 minutes. The solvent and any volatile byproducts were removed under vacuum to produce 0.0586 g of orange powder (yield = 56 % if calculated assuming two equivalents of EtOAc are coordinated to **Ni1** with concomitant displacement of toluene. ^{1}H NMR ($CDCl_3$) δ= 4.12 (br s, 2H), 2.64 (br s, 3H), 1.21 (br s, 3H). ^{13}C NMR ($CDCl_3$) δ= 179.57, 150.09, 148.11, 138.24, 136.31, 135.74, 133.76, 101.51, 64.21, 22.84, 13.71. ^{19}F NMR (CD_2Cl_2): δ= -118.8 (d, 2 F), -160.4 (t, 1F), -164.5 (t, 2F). IR:ν(CO) 1662 cm^{-1}, 1647 cm^{-1}. CHN elemental analysis for ($C_{20}H_{16}F_{10}NiO_4$): C=42.44, H=3.08 (calculated, C= 42.22, H=2.83)

Synthesis of $(THF)_2Ni(C_6F_5)_2$ (Ni4). In a glovebox, **Ni1** (0.1065 g, 22.0 mmol) was dissolved in 6 mL of THF in a 50 mL Schlenk flask equipped with a magnetic stir bar. The reaction was stirred for 5 minutes. The solvent and any volatile byproducts were removed under vacuum to produce 0.1174 g of orange powder (yield = 99 % if calculated assuming two equivalents of THF are coordinated to **Ni1** with concomitant displacement of toluene. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra matched that of prior literature reports.[35]

Synthesis of $(DME)Ni(C_6F_5)_2$ (Ni5). In a glovebox, **Ni1** (17.1 mg, 0.035 mmol) was dissolved in 10 mL 1,2-dimethoxy ethane in a 50 mL Schlenk flask equipped with a magnetic stir bar. The reaction was stirred for 5 minutes. The solvent and any volatile byproducts were removed under vacuum to produce 15.8 mg of orange powder (yield = 92 % if calculated assuming one equivalent of DME is coordinated to **Ni1** with concomitant displacement of toluene). ^{1}H NMR (CDCl3): δ= 3.68 (br s, 4H), 3.02 (br s, 6H). ^{13}C NMR ($CDCl_3$): δ= 150.23, 148.34, 138.65, 136.70, 136.03. 133.96, 100.10, 71.65, 62.76. ^{19}F NMR (CD_2Cl_2): δ -118.8 (d, 2 F), -160.4 (t, 1F), -164.5 (t, 2F). CHN elemental analysis for ($C_{12}H_{10}F_{10}NiO_2$): C=39.79, H=2.09 (calculated, C= 40.12, H=2.44)

General Method for Determination of K_{eq} Values. In a typical procedure, **Ni1** (15.7 mg, 0.03 mmol) was dissolved in 700 μL of CD_2Cl_2. 10 μL of THF was mixed with 30 μL of CD_2Cl_2 (4 M). 10 μL of the THF solution was added to the catalyst solution. The solution was added to a J-Young NMR tube. NMR was obtained within 10 minutes of mixing. The peaks for the *ortho*-fluorines of the newly formed species were integrated to 1. The *ortho*-fluorines corresponding to **Ni1** were integrated and those values were used to calculate K_{eq} as the ratio of integrated products to reactants (K_{eq} = $I_{products}/I_{reactants}$).

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

NMR spectra, IR spectra, GPC traces, and X-ray crystallography (PDF)

Accession Codes

CCDC-2354741, 2354742, and 2348761 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: =44 1223 336033.

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Notes
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