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PAPER

Oligomerization and polymerization of 5-ethylidene-2-norbornene by cationic palladium and nickel catalysts

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Nickel- and palladium-based catalyst systems were developed to convert 5-ethylidene-2-norbornene (ENB) to oligomers and polymers with highly controllable molecular weights. Depending on the choice of central metal ion, supporting ligand, and α -olefin chain transfer agent (CTA), ENB-derived materials ranging from dimers (ca. 270 Da) to high molecular weight polymers (>100,000 Da) were prepared. Typical reactions utilized $[(\eta^6\text{-mesitylene})M(\eta^3\text{-2-R-allyl})]^+$ ($M = \text{Pd}$, $R = \text{H}$; $M = \text{Ni}$, $R = \text{Me}$) in dichloromethane solution at ambient temperature, with tertiary phosphine co-ligands and α -olefins controlling the enchainment. Access to oligomers of cycloolefins with $M_n < 2,000$ Da is noteworthy, particularly considering that ENB is much less reactive than norbornene itself.

Introduction

Oligomers derived from alkenes find applications in a range of materials including surfactants, lubricants, resins, and adhesives.^{1–4} Those oligomers derived from rigid bicyclic monomers (e.g. norbornene) are particularly valuable in specialized applications due to their unusually high glass transition temperature (T_g) values.^{5–9} It can be challenging to control the molecular weight of norbornene-derived materials, however, particularly in the low molecular weight regime of oligomers.

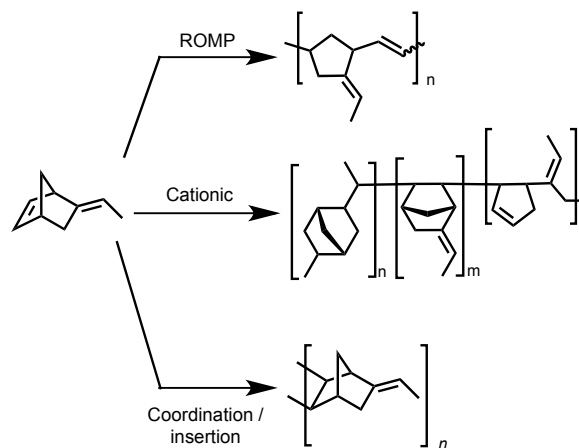
With the aim of improving access to norbornene-derived oligomers, we set out to develop readily tunable catalysts capable of controllably producing materials spanning a wide range of molecular weights. Within this goal, we particularly targeted oligomers derived from 5-ethylidene-2-norbornene (ENB) since, remarkably, they have received little attention.^{7,8,10–15}

ENB is readily available as it is derived from Diels-Alder reaction of butadiene with cyclopentadiene and is used as a crosslinking agent in ethylene/propylene/diene monomer (EPDM) rubber production.^{16,17} The rigid bicyclic repeat units of oligomeric ENB should give rise to physical properties that are similar to, and perhaps complementary to, the well-studied parent norbornene (NB) and dicyclopentadiene (DCPD) oligomers.^{5,18} The distinguishing ethylidene fragment contained in every repeat unit of ENB-derived materials could provide

complementary properties or perhaps facilitate late stage installation of additional functional groups.^{19,20}

The physical properties of low molecular weight oligomers are strongly affected by chain length,²¹ but selective oligomerization of ENB is challenging. To access ENB-derived oligomers of low molecular weight, we sought to promote rapid chain termination in an active ENB polymerization catalyst.

The polymerization of norbornenes typically occurs via ring opening metathesis, carbocation/alkene coupling, or coordination-insertion pathways, Scheme 1.^{8,10,7} Ring-opening metathesis polymerization (ROMP) produces unsaturated linkages and a cyclopentane core, leading to distinct physical properties relative to materials containing rigid bicyclic cores. Cationic polymerization has been reported to create linkages indiscriminately, including crosslinking through the ethylidene unit, often generating insoluble and nonuniform materials.⁷ The various reported methods^{6,22} for production of norbornene-based oligomers (particularly those based on DCPD, which find applications as resins)^{22,23} generally utilize harsh thermal and Lewis acidic reaction conditions and suffer from poor molecular weight control and low yields.



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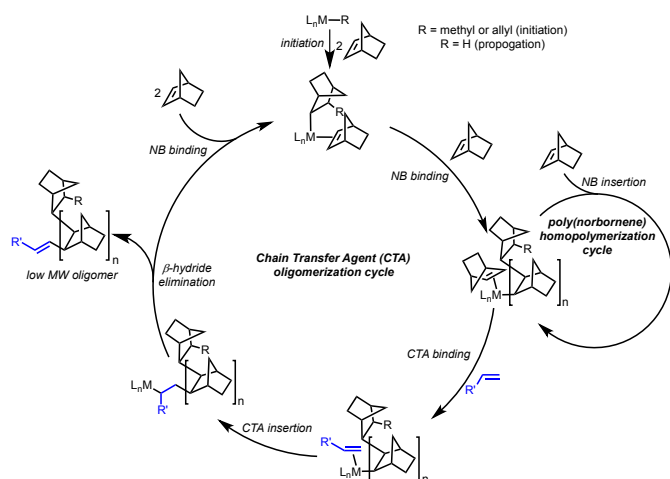
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Scheme 1. Three different mechanisms produce three distinct ENB polymer structures. Only coordination/insertion polymerization maintains both the bicyclic structure and vinylic functionality.

Oligomer production via a coordination/insertion mechanism is promising because the reaction conditions are mild and the bicyclic structure and vinylic functionality of ENB are maintained.¹² Goodall and coworkers,^{24–26} Brookhart and coworkers,^{27–29} and others^{8,30–34} have shown that cationic Ni and Pd complexes are excellent coordination/insertion catalysts for the polymerization of NB. Comparatively little work has been reported on metal-catalyzed polymerizations of ENB.^{7,8,10–15}

The controlled coordination/insertion oligomerization of norbornene derivatives is still challenging, however. Catalysts operating by this mechanism typically produce extremely high molecular weight poly(norbornene),^{8,12,30–32,35,36} the result of exceptionally slow β -hydride elimination relative to chain propagation in the metal bicyclic alkyl intermediates. Goodall has pioneered a strategy in which α -olefins can function as chain transfer agents (CTAs) in the coordination/insertion polymerization of norbornenes.^{25,37,38} α -Olefin insertion into an intermediate metal-bicyclic alkyl complex yields a linear alkyl complex that undergoes β -elimination to terminate the chain with an olefinic end group (Scheme 2). The effectiveness of the α -olefin chain transfer reagent in reducing molecular weights will depend on the relative rates of insertion of the α -olefin versus the norbornene monomer. Furthermore, the catalyst must undergo rapid β -hydride elimination of the flexible alkyl that results from α -olefin insertion, or else block copolymers will be produced.³⁹ While α -olefins can curtail growing NB polymer chains during polymerization by Pd^{II}- or Ni^{II}-allyl-based catalysts,²⁴ access to oligomers with molecular weights less than 5,000 Da was impractical and not reported due to the need for very high α -olefin:norbornene ratios in that system.⁴⁰



Scheme 2. Chain transfer of α -olefins clips growing poly(norbornene) chain via chain transfer.

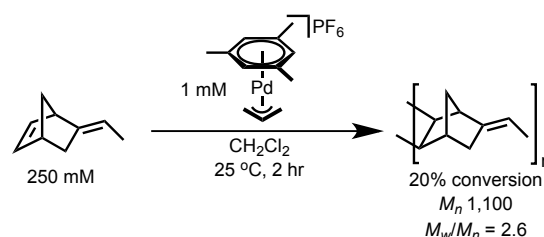
We hypothesized that Ni^{II} or Pd^{II} catalysts with bulky ligands would have less accessible active sites that would favor insertion of the less encumbered α -olefin over insertion of norbornenes, leading to lower molecular weight oligomers

without the requirement of exceptionally high α -olefin concentrations.^{37,38} We therefore paired known η^6 -mesitylene-capped cationic Ni and Pd η^3 -allyl catalysts²⁸ with bulky tertiary phosphine supporting ligands and used α -olefins as chain transfer agents to target controlled generation of low molecular weight oligomers derived from ENB. The catalyst system reported here generates ENB-derived oligomers with molecular weights ranging from 270 Da (dimers) to polymers >100,000 Da in a controlled fashion. The Ni and Pd systems offer complementary reactivity patterns, enabling access to low molecular weight materials with high glass transition temperatures.

Results and Discussion

Homopolymerization of ENB by Cationic Palladium Catalysts

The Pd precatalyst $[(\eta^6\text{-mesitylene})\text{Pd}(\eta^3\text{-allyl})][\text{PF}_6]$ (denoted $[(\text{mes})\text{Pd}(\text{allyl})][\text{PF}_6]$ hereafter) was selected for initial studies because it does not require an activator and can be used in conjunction with various tertiary phosphine ligands. After synthesizing $[(\text{mes})\text{Pd}(\text{allyl})][\text{PF}_6]$ according to literature methods,²⁸ the homopolymerization of ENB was investigated to establish the potential of this system for the planned studies utilizing α -olefin chain transfer agents.



Scheme 3. Homopolymerization of ENB (250 mM) catalyzed by $[(\text{mes})\text{Pd}(\text{allyl})][\text{PF}_6]$ (1 mM) in CH_2Cl_2 at $25\text{ }^\circ\text{C} \pm 1\text{ }^\circ\text{C}$ for two hours, and quenched with methanol. Identity of chain ends unknown.

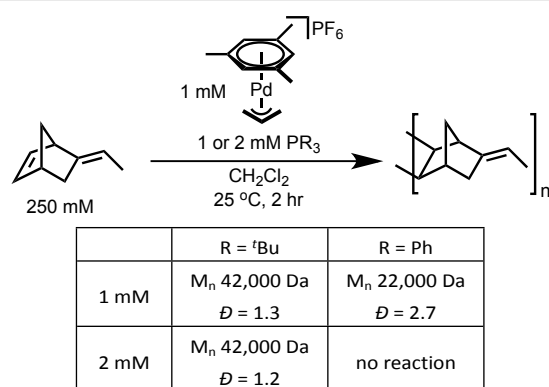
Polymerizations were carried out using 250 mM ENB and 1 mM catalyst in CH_2Cl_2 under 1 atm N_2 at room temperature. The conversion of ENB was determined via ^1H NMR spectroscopy of a 100 μL aliquot using mesitylene as internal standard and methanol to quench the reaction. Additional characterization, such as gel permeation chromatography (GPC) in THF, was performed after the polymer was precipitated from the reaction medium with methanol, washed vigorously with additional methanol, and dried *in vacuo*.

The homopolymerization of ENB with $[(\text{mes})\text{Pd}(\text{allyl})][\text{PF}_6]$ under standard conditions proceeded to only 20% conversion (Scheme 3). GPC analysis provided the mass-average molecular weight, $M_w \sim 3,000$ Da, and a number-average molecular weight, M_n of $\sim 1,100$ Da. The ratio M_w/M_n provides a dispersity, $\mathcal{D} = 2.6$, that is suggestive of poor catalyst control. While increased monomer conversion was observed (51%) in a separate homopolymerization allowed to react for 24 h under the same conditions, the polymer had a similar M_n (1400 Da) and an even higher dispersity ($\mathcal{D} = 3.4$).

The low activity of the Pd catalyst might be attributed to chelation of the ENB monomer, which has been suggested for

related catalysts.¹⁰ To test this hypothesis, homopolymerization of NB itself was carried out with [(mes)Pd(allyl)][PF₆] under standard conditions. A precipitate formed shortly after initiation, and NMR spectroscopy confirmed complete conversion of NB. High molecular weight poly(norbornene) generally exhibits low solubility,^{12,26} so detailed characterization was not pursued. The high activity towards NB underscores the challenges of controlled ENB enchainment. The poor activity and broad dispersity led us to consider ligated variants of [(mes)Pd(allyl)][PF₆] as catalysts.

Including 1 equiv P^tBu₃ together with [(mes)Pd(allyl)][PF₆] under the standard conditions resulted in complete conversion within 2 h to polymeric material with $M_n = 42,000$ and $\mathcal{D} = 1.3$ (Scheme 4). Similar yields were obtained with 1 equiv PPh₃.



Scheme 4. Homopolymerization of ENB catalyzed by [(mes)Pd(allyl)][PF₆] and PR₃ (1 or 2 mM) in CH₂Cl₂ at 25 °C ± 1 °C for 2 h. Identity of chain ends unknown.

Including 2 equiv PR₃ led to contrasting results. The conversion and M_n values were nearly identical regardless of whether 1 or 2 equiv P^tBu₃ was added. In contrast, the use of 2 equiv PPh₃ completely inhibited the reaction (Scheme 4). These findings suggest that the smaller size of PPh₃ relative to P^tBu₃ results in 2:1 PPh₃:Pd complexation that poisons the catalyst. In contrast, P^tBu₃ is sufficiently bulky to enforce 1:1 binding and maintain activity in the presence of excess ligand. On the basis of the greatly improved polymerization activity of ENB relative to the phosphine-free catalyst system, and the insensitivity to free ligand, subsequent studies focused on P^tBu₃ as a supporting ligand.

A pre-formed 1:1 P^tBu₃:Pd complex, (P^tBu₃)PdMeCl, was selected as an alternative precatalyst, based on Nozaki's previous report of *in situ* chloride abstraction by NaBAR₄^F to yield an active cationic catalyst for NB homopolymerization.³³ Homopolymerization of ENB with the (P^tBu₃)PdMeCl/NaBAR₄^F catalyst system showed analogous reactivity to the [(mes)Pd(allyl)][PF₆]/P^tBu₃ catalyst system, likely indicating access to the same active species.

The ¹H NMR spectra of the ENB-derived polymers feature a broad resonance at δ 5.2 corresponding to an intact ethylidene unit that integrates ca. 1:12 relative to the broad aliphatic resonances (δ 1.0–3.1), consistent with an ENB homopolymer without significant cross-linking.⁷ The good solubility of the

polymer in aromatic solvents is further evidence against cross-linking.

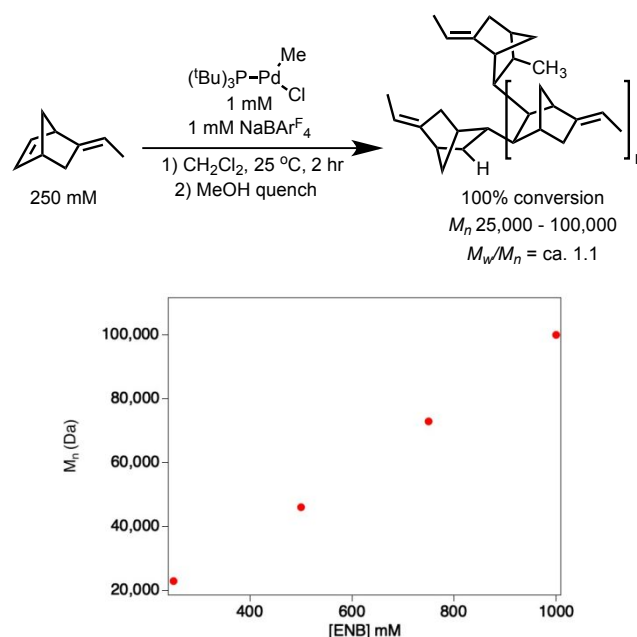


Figure 1. M_n as a function of ENB concentration in the homopolymerization of ENB by (P^tBu₃)PdMeCl/NaBAR₄^F. Conditions: 250–1000 mM ENB, 1 mM (P^tBu₃)PdMeCl/NaBAR₄^F, 2 h at 25 °C ± 1 °C under N₂.

Several experiments are consistent with a highly controlled homopolymerization when Pd is ligated by P^tBu₃. First, homopolymerization at four different initial concentrations of ENB resulted in complete conversion within 5 min to give polymers with narrow dispersity ($\mathcal{D} \sim 1.1$) and M_n values that increased with increasing initial concentration of ENB (Figure 1). Second, as shown in Figure 2, M_n increases linearly as a function of percent conversion. Third, in reactions charged with additional monomer (2.2 mmol ENB) at the conclusion of a typical polymerization reaction (1.1 mmol ENB), the polymer exhibited an increase in M_n from 22,000 (\mathcal{D} 1.2) to 56,000 (\mathcal{D} 1.3). The combined data point to a highly controlled homopolymerization of ENB when cationic Pd catalysts are used in conjunction with P^tBu₃. The chain-ends are thus assigned as the initiating methyl group from the Pd catalyst and a proton introduced upon quenching with methanol.

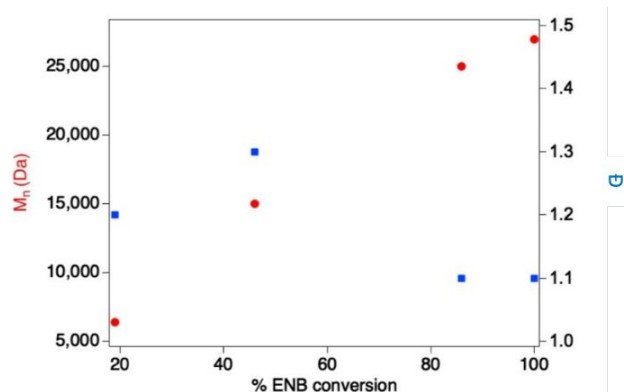


Figure 2. M_n (red circles) and \mathcal{D} (blue squares) as a function of % conversion. Conditions: 250 mM ENB, 1 mM (P^tBu₃)PdMeCl/NaBAR₄^F, 2 h at 25 °C ± 1 °C under N₂.

Controlling Molecular Weight in Palladium-Catalyzed ENB Enchainment

With a well-defined ENB polymerization system in hand, we explored the use of α -olefins as CTAs to reduce chain length. Whereas the bulky, geometrically constrained bicyclic metal alkyl complex formed upon ENB insertion does not undergo β -hydride elimination rapidly (as evidenced by the controlled homopolymerization to high molecular weight), the flexible linear metal alkyl complex formed upon α -olefin insertion was expected to undergo extremely rapid β -hydride elimination from the cationic Pd center. Such a β -hydride elimination would result in a poly(ENB) chain bearing a single terminal alkene unit and a metal hydride species capable of re-entering the catalytic cycle (see Scheme 2, above). This strategy has proved fruitful to generate variable molecular weight NB polymers.^{26,37,38}

A liquid α -olefin, 1-hexene was selected as an initial CTA because the concentration can be easily varied. Polymerizations of ENB in the presence of varying amounts of 1-hexene each proceeded to full conversion within 2 h at room temperature with the $(P^tBu_3)PdMeCl/NaBARF_4$ catalyst system (Figure 3). A broad singlet in 1H NMR spectra (δ 0.9) corresponds to a methyl group on the hexene chain-end. The ratio of the terminal methyl resonance to the broad aliphatic resonances increases with decreasing oligomer weight, as expected. The $^{13}C\{^1H\}$ NMR spectra feature new internal olefin resonances attributed to the hexenyl terminus (δ 130).

As shown in Figure 3, a decrease in M_n was observed as the concentration of 1-hexene increased from 30 mM to 250 mM. The \mathcal{D} increased with increasing 1-hexene concentration, consistent with increased chain transfer at high α -olefin concentrations. At the highest tested 1-hexene concentration of 250 mM (1:1 CTA:monomer ratio), the M_n was approximately half of that observed in the absence of the CTA.

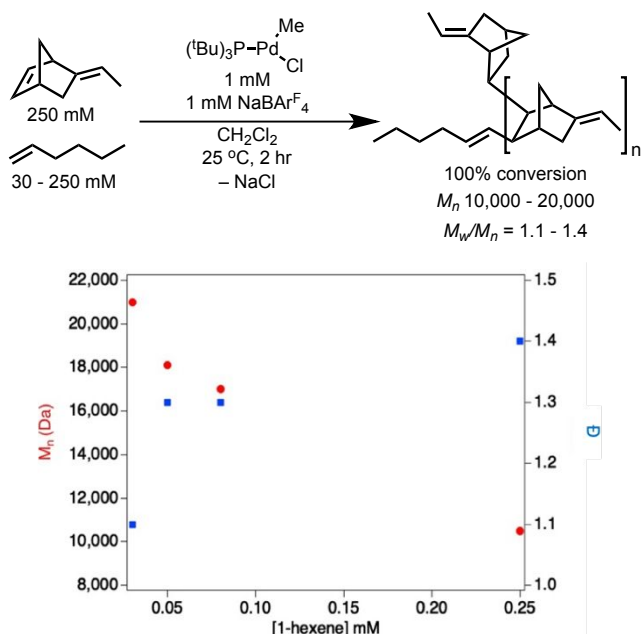
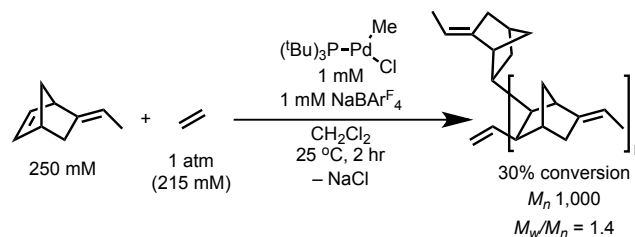


Figure 3. Change in M_n (red circles) and \mathcal{D} (blue squares) as a function of 1-hexene concentration, [1-hexene], added to Pd-catalyzed ENB polymerization.

Conditions: 250 mM ENB, 1 mM $(P^tBu_3)PdMeCl/NaBARF_4$, and 30, 50, 80, or 250 mM 1-hexene, 2 h at $25 \text{ }^\circ\text{C} \pm 1 \text{ }^\circ\text{C}$ under nitrogen.



Scheme 5. Ethylene as a chain transfer reagent leads to low ENB conversion. Conditions: 250 mM ENB, 1 mM $(P^tBu_3)PdMeCl/NaBARF_4$, and 1 atm C_2H_4 , two hours at $25 \text{ }^\circ\text{C} \pm 1 \text{ }^\circ\text{C}$.

We hypothesized that ethylene would insert more rapidly into the Pd alkyl intermediate than 1-hexene and thus more efficiently curtail chain growth. A CH_2Cl_2 solution of $(P^tBu_3)PdMeCl/NaBARF_4$ was added to an ethylene-saturated CH_2Cl_2 solution ($\sim 215 \text{ mM } C_2H_4$ based on an independent measurement, see Supporting Information Section II) containing 250 mM ENB, and the reaction was stirred for 2 h (Scheme 5). The yellow solution turned dark, presumably due to the formation of Pd black. This observation stands in contrast to ENB homopolymerizations and ENB/1-hexene oligomerizations, which retain a yellow color throughout the polymerization reaction without any visible formation of Pd black. Also consistent with catalyst decomposition under ethylene was the low ($\sim 30\%$) conversion. The resulting ethylene-terminated oligomer did, however, feature a significantly lower molecular weight ($M_n \sim 1,000 \text{ Da}$, $\mathcal{D} \sim 1.4$) than the homopolymer prepared without the CTA ($M_n \sim 25,000$, $\mathcal{D} \sim 1.1$) and the hexene-terminated oligomer prepared with 250 mM 1-hexene ($M_n \sim 10,000$, $\mathcal{D} \sim 1.4$). The ethylene-derived vinylic chain-ends were apparent by 1H NMR spectroscopy and by MS-APCI (mass spectrometry-atmospheric pressure chemical ionization). Oligomeric ENB fragments containing a C_2H_4 fragment plus a proton could be observed from dimers (m/z 269.22) to 16-mers (m/z 1951.54).

The role of ethylene in promoting catalyst decomposition was probed in the absence of ENB. When a Teflon-sealed NMR tube containing $(P^tBu_3)PdMeCl$ and $NaBARF_4$ in CD_2Cl_2 was charged with 1 atm ethylene, an immediate color change from bright yellow to dark brown was accompanied by the release of free P^tBu_3 . Despite a promising reduction in M_n under ethylene, the low conversion and catalyst decomposition led us to consider alternative catalysts for accessing light oligomers.

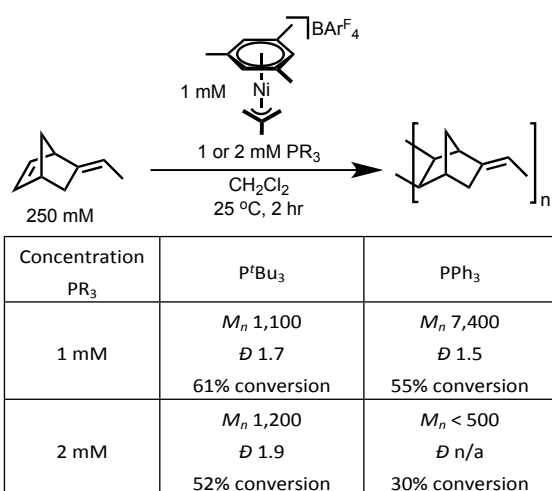
Homopolymerization of ENB by $[(mes)Ni(Me-allyl)][BARF_4]$

The nickel precatalyst $[(\eta^6\text{-mesitylene})Ni(\eta^3\text{-2-methylallyl})][BARF_4]$ (denoted $[(mes)Ni(Me-allyl)][BARF_4]$ hereafter) was pursued next on the basis of previous reports of 1,3-diene polymerization and norbornene hydrovinylation.^{27,28,41-43} Like the closely related Pd precatalysts described above, $[(mes)Ni(Me-allyl)][BARF_4]$ can be used in conjunction with various supporting ligands.

The homopolymerization of ENB by $[(mes)Ni(Me-allyl)][BARF_4]$ was pursued initially. Following the standard conditions introduced above resulted in only 10% conversion of

ENB after 2 h. When allowed to react for 24 h, the conversion increased to 60%. Each reaction produced a material with M_n ca. 2,000 Da. The materials produced in a series of experiments varying the initial concentrations of ENB exhibited a modest increase in conversion with increasing ENB concentration, but consistently low M_n values (2,200–3,900 Da, \bar{D} between 1.4 and 2.5, Table S7 in the SI). It is apparent that the reaction suffers from poor catalyst control. The low activity and frequent chain termination are tentatively attributed to chelation of ENB.¹⁰ Consistent with this hypothesis, homopolymerization of NB itself resulted in complete conversion after 2 h and formation of a polymeric material that was insoluble in hydrocarbon, ethereal, and chlorinated solvents.^{12,26}

Hoping to increase the activity of the Ni catalyst towards ENB, tertiary phosphine supporting ligands were introduced. Under the standard conditions and in the presence of 1 equiv P^tBu_3 , ENB underwent 61% conversion to low molecular weight oligomers ($M_n = 1,100$) in 2 h, Scheme 6. Improved activity was also observed in the presence of 1 equiv PPh_3 (Scheme 6). The Ni catalyst tolerates 2 equiv P^tBu_3 , but shows diminished activity in the presence of 2 equiv PPh_3 , just as was observed for the Pd catalyst.



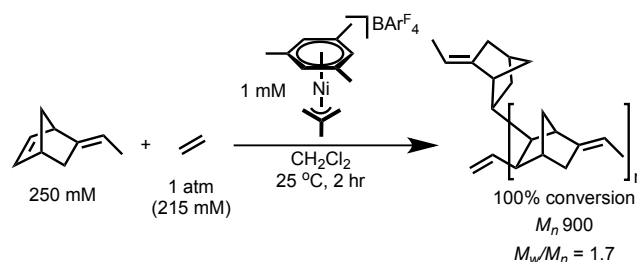
Scheme 6. Influence of PR_3 identity and concentration of ENB homopolymer M_n (Da). Conditions: 250 mM ENB, 1 mM [(mes)Ni(Me-allyl)](BARF₄) and PR_3 (1 or 2 mM) mixture in CH_2Cl_2 at 25 °C ± 1 °C for 2 h. Identity of chain ends unknown.

Controlling Molecular Weight in Nickel-Catalyzed ENB Enchainment

The reactivity of [(mes)Ni(Me-allyl)](BARF₄) in the presence of ethylene as a possible CTA was explored next. Under standard conditions with [(mes)Ni(Me-allyl)](BARF₄) (and no additional ligand), and under 1 atm ethylene, full conversion of ENB was observed within 2 h (Scheme 7). This result was somewhat unexpected, given the relatively low conversion of homopolymerization of ENB observed in the absence of ethylene. The material produced in high yield from ENB/ethylene mixtures had $M_n \sim 900$ Da. The ¹H NMR spectrum featured broad resonances (δ 5.0 and δ 5.2) corresponding to intact ethylidene units, as well as a broad resonance (δ 5.8) corresponding to the vinyl chain end. Ethylene-capped ENB oligomers from dimers (269.23) up to decamers (m/z 1258.01)

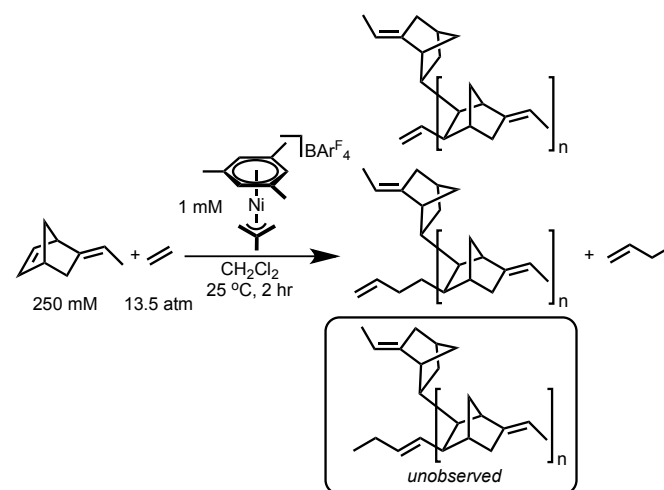
were identified by MS-APCI. Whereas the Pd system underwent decomposition under ethylene, in contrast, the Ni system exhibits improved activity and access to the desired light oligomers of ENB.

An analogous reaction with parent NB also gave full conversion. The ethylene-terminated oligomers, however, were approximately twice the molecular weight ($M_n = 2000$ Da) as the ENB oligomers produced under the same conditions. This is consistent with NB undergoing faster insertion than ENB.



Scheme 7. ENB oligomerization under 1 atm C_2H_4 . Conditions: 250 mM ENB, 1 mM [(mes)Ni(Me-allyl)](BARF₄), 1 atm C_2H_4 , stirred for 2 h at 25 °C ± 1 °C.

With a promising initial reaction in hand, we sought to vary conditions to tune the average molecular weight of the oligomer. The average degree of oligomerization should be sensitive to the ENB/ C_2H_4 ratio, with lower ratios favoring more chain termination and thus smaller oligomers. Lowering the initial concentration of ENB from 250 mM to 125 mM under 1 atm C_2H_4 led to a reduction in M_n from 900 Da to 740 Da after Ni-catalyzed oligomerization (Table S11 in the SI).



Scheme 8. Increased C_2H_4 pressure decreases ENB oligomer chain length. Conditions: 250 mM ENB, 1 mM [(mes)Ni(Me-allyl)](BARF₄), 200 psi C_2H_4 , stirred for 2 h at 25 °C ± 1 °C.

Alternatively, the concentration of ethylene can be increased relative to ENB to decrease M_n . When oligomerization was performed under 13.5 atm ethylene, the reaction proceeded to ca. 80% conversion after 2 h (Scheme 8). The M_n value of this oligomeric material was too low for GPC analysis, showing that the elevated ethylene pressure successfully curtailed the chain length. Both 1-butene and 2-butene were also apparent in ¹H NMR spectra, presumably formed via an ethylene dimerization process that was insignificant at 1 atm

ethylene. According to MS-APCI, the major ENB-containing species were ethylene-capped or butene-capped dimers of ENB and ethylene- or butene-capped trimers of ENB (Figure S37). We propose that the butene-coupled oligomers are the product of a second insertion of ethylene into the growing ENB chain prior to β -hydride elimination, due to the lack of evidence for internal olefin chain-ends in the $^{13}\text{C}\{^1\text{H}\}$ NMR and ^1H NMR spectra that would indicate butene insertion (Scheme 8 and Figures S35 and S36).

To better understand the role of the CTA in Ni-catalyzed ENB oligomerization, chain transfer was studied using variable concentrations of 1-hexene. Under N_2 , solutions of ENB containing 30–250 mM 1-hexene and 1 mM [(mes)Ni(Me-allyl)][BARF₄] produced oligomers of variable molecular weight. Figure 4 shows the relationship between oligomer M_n and the initial concentration of 1-hexene, which illustrates that increasing the concentration of 1-hexene produces materials with lower M_n (lowest M_n observed \sim 1000 Da). These reactions only proceed to ca. 50% conversion, in contrast to the nearly quantitative conversion seen with ethylene. Allowing reactions to stir at room temperature for 24 h increased conversion to \sim 80%, with a similar molecular weight distribution (See Experimental Section).

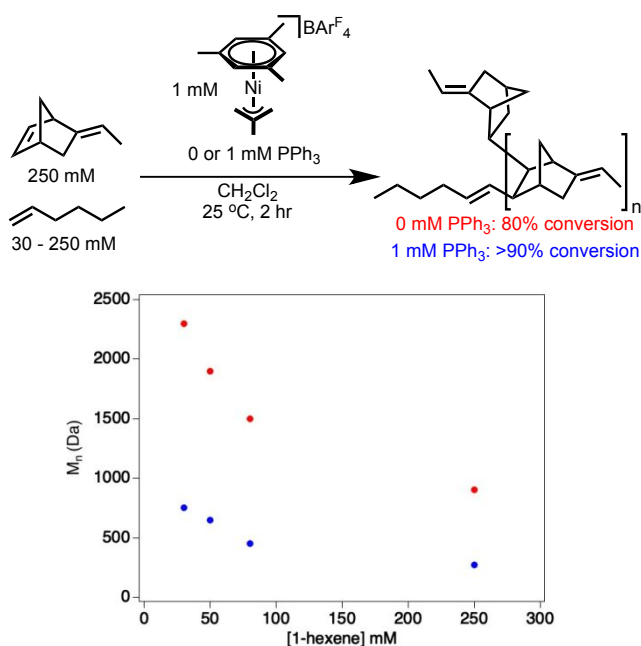
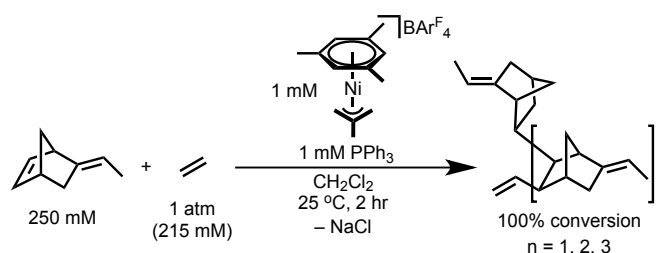


Figure 4. M_n decreases with increasing [1-hexene] (red circles), and shorter oligomers are obtained in the presence of a PPh₃ co-ligand (blue circles). Conditions: 250 mM ENB, 1 mM [(mes)Ni(Me-allyl)][BARF₄] and 0 or 1 mM PPh₃. 30, 50, 80, or 250 mM 1-hexene in CH₂Cl₂, 2 h at 25 °C \pm 1 °C.

Including PPh₃ as a supporting ligand for [(mes)Ni(Me-allyl)][BARF₄] leads to high yields of very light ENB-derived oligomers. An ethylene-saturated CH₂Cl₂ solution containing 250 mM ENB under 1 atm ethylene was treated with [(mes)Ni(Me-allyl)][BARF₄] and 1 equiv PPh₃ (Scheme 9). Oligomeric material with molecular weights too low to measure by GPC were obtained in high yield. MS-APCI revealed predominantly ethylene-capped dimers and trimers of ENB.



Scheme 9. Ni-catalyzed ENB oligomerization with PPh₃ supporting ligand.

Chain termination with 1-hexene was investigated next for the Ni/PPh₃ catalyst system. Under standard conditions including 1-hexene and 1 equiv PPh₃ relative to Ni catalyst, reactions proceed to ca. 60–70% conversion after 2 h. (Nearly quantitative conversion was observed in reactions allowed to run for 24 h.) MS-APCI spectra of these materials revealed masses corresponding to hexene-terminated ENB oligomers. Figure 4 shows how binding PPh₃ to the Ni center reduces M_n by a factor of ca. 3 relative to phosphine-free conditions. This is presumably the result of an increase in the 1-hexene binding affinity (and thus overall insertion rate) relative to ENB at the bulkier Ni center containing a PPh₃ ligand.

Comparing the Nickel and Palladium Catalyst Systems

Based on either nickel or palladium precursors, variations in supporting ligand and CTA concentration provide access to ENB-derived materials that span an impressive range of molecular weights. Chains ranging in length from two units (ca. 270 Da) to over 800 units (ca. 100,000 Da) were accessed in this study.

It is instructive to compare the overall reactivity patterns of the nickel- and palladium-based catalyst systems. Both arene-capped Ni and Pd allyl catalysts exhibit low activity for ENB homopolymerization alone (c.f. Scheme 3 and Table S7), but give improved ENB conversion in the presence of a tertiary phosphine supporting ligand (c.f. Schemes 4 and 6). The products of the PR₃-supported homopolymerization are distinct, however. The Pd system produces high molecular weight polymers with narrow polydispersity in highly controlled fashion. Depending on the ratio of catalyst to monomer, poly(ENB) M_n values ranged from 22,000 to 136,000 Da. In contrast, the Ni system does not produce ENB homopolymers in a controlled manner (broad dispersity and short chains, M_n 4,900–7,400 Da).

In the presence of ethylene, the Pd catalysts rapidly decompose to Pd black, even in the presence of PR₃. Conversely, the Ni catalysts exhibit *increased* activity in the presence of ethylene (c.f. Schemes 5 and 7), giving quantitative conversion of ENB to low molecular weight oligomers. The positive influence of phosphine supporting ligands in the nickel system was surprising, given that many Ni(allyl)(halide) dimers are unstable in the presence of phosphine ligands.⁴⁴ In this context, it is important to note that the order of reagent addition is important with respect to Ni catalyst stability: addition of PR₃ to CH₂Cl₂ solutions of [(mes)Ni(Me-allyl)]⁺ leads to decomposition, but addition of PR₃ to a CH₂Cl₂ solution of ENB followed by

addition of $[(\text{mes})\text{Ni}(\text{Me-allyl})]^+$ leads to clean and controlled reactivity.

Physical properties of ENB-derived materials

Part of the motivation for preparing ENB-derived oligomers and polymers with controllable molecular weight is the promise of unusual and valuable materials properties provided by the rigid bicyclic cores of hydrocarbon chains. We anticipated that the variations in chain length and chain end composition provided by the present catalyst systems would provide access to materials with a range of properties. As the chain length and molecular weight of a polymer increase, the theoretical maximum glass transition temperature (T_g) is approached according to the Flory-Fox equation.²¹ With ENB-derived materials ranging from M_n ca. 270 to 100,000 Da in hand, several representative materials were analyzed to probe variation in T_g values.

Ten ENB-derived materials were selected for detailed characterization. To ensure no catalyst was present during analysis, the materials were precipitated from the reaction mixture with methanol, dissolved in toluene at room temperature, filtered through a short silica plug, and dried *in vacuo*.

Four ethylene-terminated ENB oligomers prepared with the Ni catalyst system with varying M_n (400, 800, 1,000 and 1,700 Da) were examined. The shortest ethylene-terminated oligomer, M_n 400 Da, was a viscous, sticky material, whereas the longest ethylene-terminated material (M_n 1,700 Da) was a white powder that became a clear colorless brittle film upon heating to 200 °C and cooling back to 25 °C. Four analogous hexene-terminated materials prepared with the Ni catalyst system were also examined (M_n 600, 1,000, 1,900, and 2,500 Da). The shortest hexene-terminated oligomer was a tacky paste, whereas the longest hexene-terminated oligomer was a white powder that transforms into a transparent, brittle material upon melting and cooling. Finally, one higher M_n hexene-terminated ENB polymer (M_n 20,000 Da) and one ENB homopolymer (M_n 25,000 Da) prepared with the $(\text{P}^t\text{Bu}_3)\text{PdMeCl}$ catalyst were examined. Both of these materials appear as off-white powders that can be solution-cast out of dichloromethane as transparent films.

Differential Scanning Calorimetry (DSC) was performed on the ten ENB-derived materials to determine the T_g of each material. Figure 5 shows the relationship between T_g and M_n . In the low molecular weight range, increasing the polymer chain length results in an increase in the glass transition temperature. The T_g values span a wide range, with the lowest molecular weight material (mostly ENB tetramer, M_n 400 Da) having a T_g below room temperature (-18 °C) and the highest molecular weight polymer ($M_n \sim 25,000$ Da) exhibiting a T_g of approximately 178 °C. The T_g value of the high molecular weight polymer is similar to T_g values reported for closely related high molecular weight polymers of norbornene derivatives.^{7,12} The thermal measurements correlate with the physical properties of the materials, with the low T_g materials appearing as viscous pastes at room temperature and the high T_g materials melting into hard, transparent films.

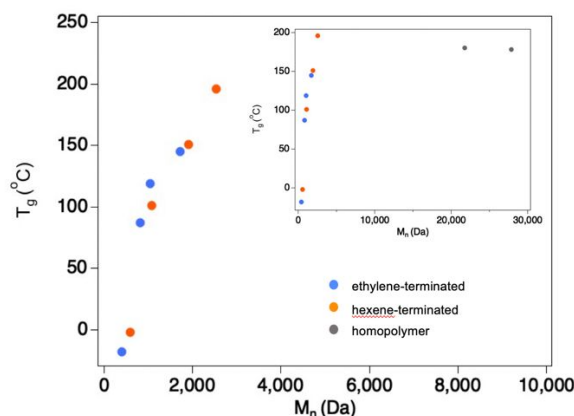


Figure 5. T_g of ethylene-terminated ENB oligomers (blue circles), hexene-terminated ENB oligomers (orange circles), and ENB homopolymer (grey circles) as a function of M_n .

To examine the influence of the ethylidene units on the physical properties, hydrogenation of one of the oligomeric samples and one of the polymeric samples was carried out. The ENB-derived materials (M_n of 500 or 25,000 Da) were each dissolved in CH_2Cl_2 , sparged with H_2 at 0 °C, and treated with five 1 mM portions of $[\text{Ir}(1,4\text{-cyclooctadiene})(\text{PCy}_3)(\text{pyridine})][\text{PF}_6]$ over 1 h.⁴⁷ Both materials were ca. 99% hydrogenated on the basis of ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. The T_g of the hydrogenated materials did not differ from their unsaturated parent materials. The fully saturated ENB-derived materials would be expected to show enhanced stability towards oxidative degradation.^{45,46}

Conclusions

A series of Ni and Pd catalyst systems were developed that convert ENB to materials ranging in molecular weights from dimers (ca. 270 Da) to high molecular weight polymers (>100,000 Da). These reactions proceed in high yields at room temperature in the presence of tertiary phosphine co-ligands, with molecular weights controlled by α -olefin chain transfer agents. Notably, oligomers ranging in molecular weight 270 – 2,000 Da can be controllably and selectively prepared using the catalyst $[(\text{mes})\text{Ni}(\text{Me-allyl})][\text{BAR}^F_4]$ in the presence of ethylene, where the molecular weight of the oligomer is controlled by the relative ratio of ethylene to monomer in solution, and the presence and identity of added phosphine co-ligands. The present catalyst system is noteworthy for offering a convenient method for preparing oligomers of cycloolefins with $M_n < 2,000$ Da.

The monomer ENB is much less reactive than NB itself, presumably due to unproductive metal coordination by the ethylidene unit. By introducing phosphine ligands, the catalyst systems described here achieve high conversion of ENB to oligomers and polymers with controlled molecular weights. Given that Pd and Ni polymerization catalysts are often deactivated by polar or Lewis basic functional groups,^{12,48} ENB-derived materials hold promise for future exploration of post-

functionalization at the unsaturated ethylidene units contained throughout the chains.

Conflicts of interest

There are no conflicts to declare

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