Addition Polymerization of Functionalized Norbornenes: The Effect of Size, Stereochemistry, and Coordinating Ability of the Substituent

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The effect of the substituent on the palladium(II)-catalyzed addition polymerization of functionalized norbornene derivatives was examined. *Endo*-substituted norbornenes are polymerized more slowly than their corresponding *exo* isomers. The size of the substituent plays a role. However, the coordinating ability of the functionality plays an even bigger role in attenuating polymerization than its size. The formation of chelates upon the coordination of the *endo*-functionalized norbornene is responsible, in part, for the observed decrease in polymerization rate. A further, and even greater, reason for the diminution of activity of *both* the *endo*- and the *exo*-functionalized isomers is simply the coordination of the functionality to the metal center.

Introduction

Metal-catalyzed addition polymerization of functionalized olefins is an area of great current interest in synthetic polymer chemistry because the addition of functionalities to a polymer that is otherwise nonpolar can greatly enhance the range of attainable properties.[1] One particular area of interest has been the addition polymerization of functionalized norbornene derivatives.[2] The resultant polymers exhibit superior etch resistance and thermal stability and are attractive candidates for deep UV photolithography.[3] A key problem in the development of metal-catalyzed routes to functionalized olefin polymers is the possibility of the coordination of the functionality present both in the monomer and in the resulting polymer. This has the effect of attenuating polymerization activity because it hinders the incoming monomer from coordinating to the metal center.

An additional issue relating to the polymerization of functionalized norbornenes is the presence of *exo* and *endo* isomers. Because they are synthesized by Diels−Alder reaction, functionalized norbornene derivatives sold commercially consist of *exo* and *endo* isomers with the latter predominating (approximate molar ratio: 1:3−1:4).[4] Earlier work in others labs[5] as well as our own[6] have shown that the *endo*-functionalized norbornenes are polymerized more slowly. Thus, the drop in polymerization rate for commercial functionalized norbornene mixtures has previously been ascribed to the formation of a chelate by coordination of the metal to the functionality and the C=C bond along the *endo* face (Figure 1).[5,6] This has two detrimental effects on polymerization. First, chelation strengthens metal−olefin interaction, thereby raising the barrier for the insertion step. Second, it forces insertion through the *endo* face, in sharp contrast to the known propensity for norbornene to insert into metal−carbon bonds through the less hindered *exo* face.[7] Indeed, we had earlier isolated and characterized a platinum complex formed by the insertion of *endo*-5-ethyl ester-2-norbornene into a Pt−H bond.[6] Herein, we report the results of an investigation of the factors influencing the palladium(II)-catalyzed polymerization of functionalized norbornene derivatives. The study allows us to separately assess the different ways that a substituent can influence polymerization activity.

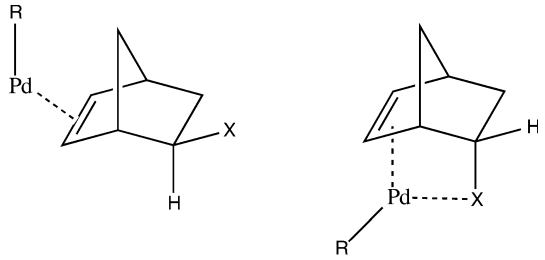

Figure 1. Modes of bonding for functionalized norbornene derivatives (X = coordinating functionality).

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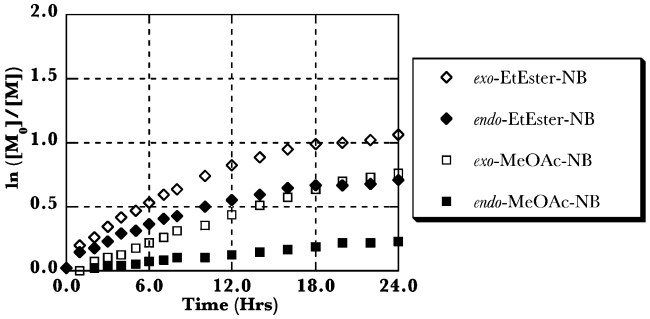


Figure 2. First-order kinetic plot of monomer conversion vs time for the homopolymerization of EtEster-NB and MeOAc-NB.

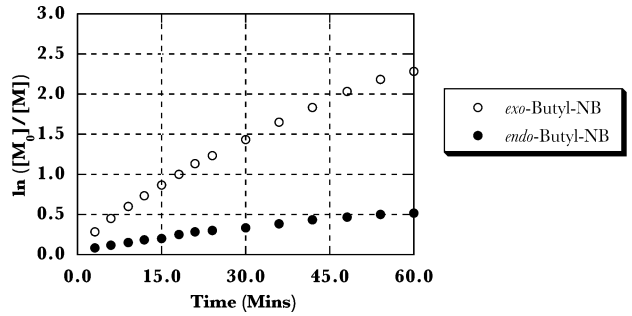
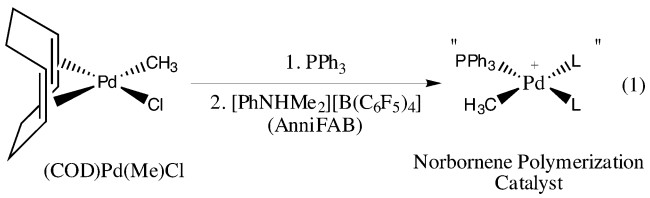


Figure 3. First-order kinetic plot of monomer conversion vs time for the homopolymerization of Butyl-NB.

Results and Discussion

The catalyst system chosen for our study was formed in situ, as shown by eq 1. We had previously shown that such systems are extremely active for the polymerization of norbornene, but the activity is sharply attenuated for norbornene derivatives with pendant oxygen functionalities on the side opposite the C=C bond.[6] On the basis of the ^{13}C NMR shifts, one can surmise that the electronic effect of the substituent on the C=C bond is minimal (not surprising given the distance between the two). Thus, the vinyl carbons of the norbornene resonate at 135.5 ppm, while those of 5-ethyl ester-2-norbornene (EtEster-NB) appear at 137.7 and 132.5 ppm (*endo*) and 138.1 and 135.9 ppm (*exo*).



(1)

As anticipated, we observe the preferential uptake of the *exo* isomer in the homo- and copolymerization of 5-ethyl ester-2-norbornene (EtEster-NB, NB-$COOCH_2$-CH_3) and 5-methyl acetate-2-norbornene (MeOAc-NB, NB-$CH_2OC(O)CH_3$) (e.g., Figure 2). Unexpectedly, however, 5-*n*-butyl-2-norbornene (Butyl-NB), which *does not* have a coordinating functionality, exhibits an even larger preference for *exo* uptake (Figure 3). Furthermore, the rate of polymerization was found to decrease in the order Butyl-NB > Hexyl-NB > Decyl-NB (Figure 4). Clearly, the coordination of the *endo* functionality cannot be the *sole* explanation for the observed preferential uptake of the *exo*-substituted functional norbornenes.

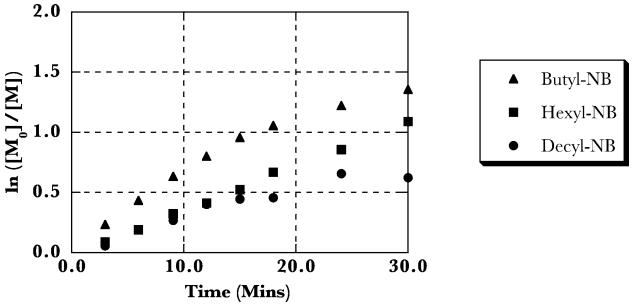


Figure 4. First-order kinetic plot for the homopolymerization of the *n*-alkyl-functionalized norbornenes.

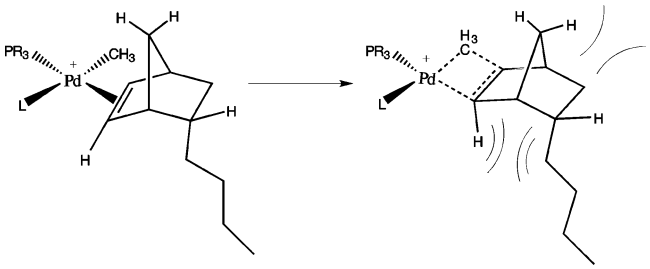


Figure 5. Steric compression in the insertion of *endo*-Butyl-NB.

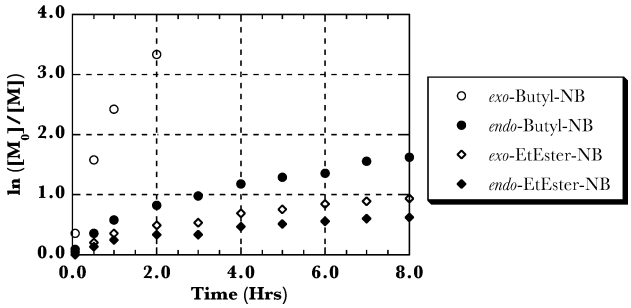


Figure 6. First-order kinetic plot for the copolymerization of Butyl-NB and EtEster-NB.

As shown in Figure 5, even for coordination and insertion through the *exo* face, in the *endo* isomer there is an unfavorable interaction between the substituent and the vinylic hydrogen that is being rehybridized from sp^2 to sp^3 upon coordination and insertion into the palladium−alkyl bond. This raises the energy barrier for the insertion of the *endo* isomer, resulting in a decreased polymerization rate.

While the experiments with Butyl-NB clearly demonstrate the importance of the steric size and placement of the substituent, this is not the whole explanation for substituents with coordinating functionalities. For example, the rate of Butyl-NB homopolymerization is several orders of magnitude faster than both EtEster-NB and MeOAc-NB and is retarded in the copolymerization with either EtEster-NB (Figure 6) or MeOAc-NB (Figure 7). Thus, in addition to steric effects, the coordinating ability of the substituent must also play a role in attenuating catalytic activity. The latter effect can take one of two forms: (a) the monomer can chelate through the *endo* face and (b) the functional group can simply coordinate *without* chelation; the latter possibility is supported by the observation that coordinating solvents, such as acetonitrile or ethyl acetate, sharply attenuate polymerization activity of the catalyst.[6]

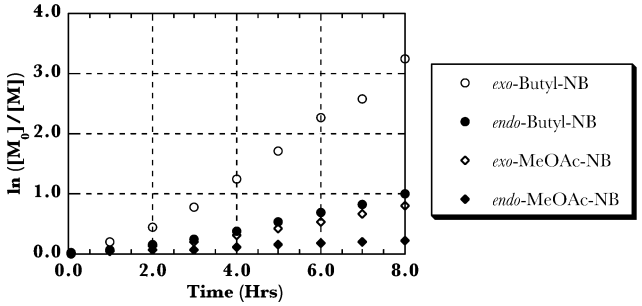


Figure 7. First-order kinetic plot for the copolymerization of Butyl-NB and MeOAc-NB.

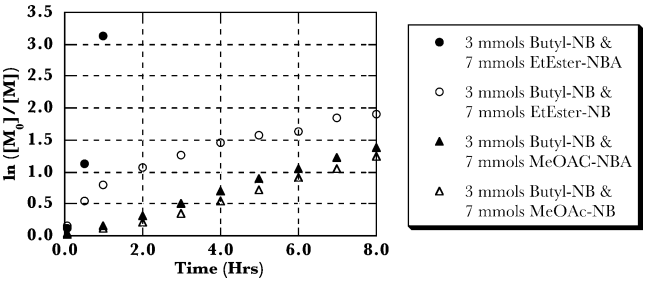


Figure 8. First-order kinetic plots for the conversion of 3.0 mmol of Butyl-NB in the presence of either 7.0 mmol of EtEster-NB or MeOAc-NB as well as their corresponding norbornane analogues, EtEster-NBA or MeOAc-NBA.

To differentiate between the above two possibilities, we examined the rate of uptake of Butyl-NB in the presence of either the norbornene derivative with a coordinating functionality or the corresponding saturated norbor*nane* analogue. If inhibition were primarily due to chelate formation, then the unsaturated norbornene derivative would be the stronger inhibitor. On the other hand, both the norbornene and norbornane derivatives will be equally effective inhibitors if the simple coordination of the functionality (without chelate formation) was responsible for the inhibition.

As shown in Figure 8, EtEster-NB was significantly more (5.9×) effective at attenuating the uptake of *n*-butylnorbornene than its saturated analogue. On the other hand, MeOAc-NB was only a marginally better (1.1×) inhibitor than its saturated analogue (Figure 8). Clearly, chelation plays a significant role in the case of EtEster-NB but not for MeOAc-NB. We propose that the reason for this interesting difference between the two substrates lies in the ring sizes for the possible chelates. As shown in Figure 9, an optimal six-membered ring is formed with EtEster-NB, while a less stable eight-membered ring is expected of MeOAc-NB.[8]

Finally, even though MeOAc-NB does not form an effective chelate upon coordination like EtEster-NB, the former is better at attenuating polymerization activity (see Figures 6 and 7). We believe this is because the ester group of MeOAc-NB is less sterically hindered, allowing it to coordinate more easily to the metal center (Figure 10). A comparison of the carbonyl stretching frequencies of MeOAc-NB (1741 cm^{-1}) and EtEster-NB (1734 cm^{-1}) demonstrates that the higher basicity of the EtEster-NB is not nearly as important as the steric accessibility of the ester functionality.

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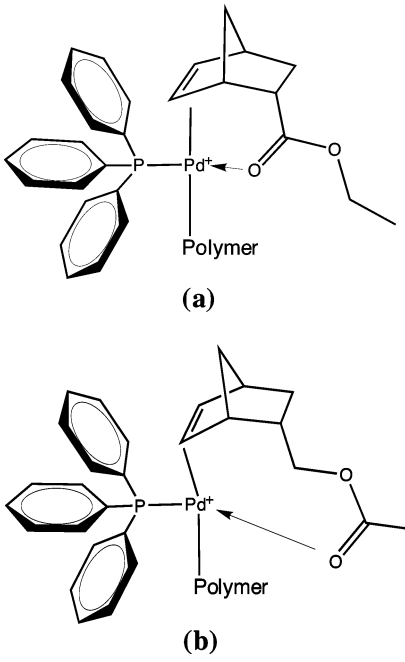

Figure 9. Chelate formation by (a) *endo*-EtEster-NB and (b) *endo*-MeOAc-NB.

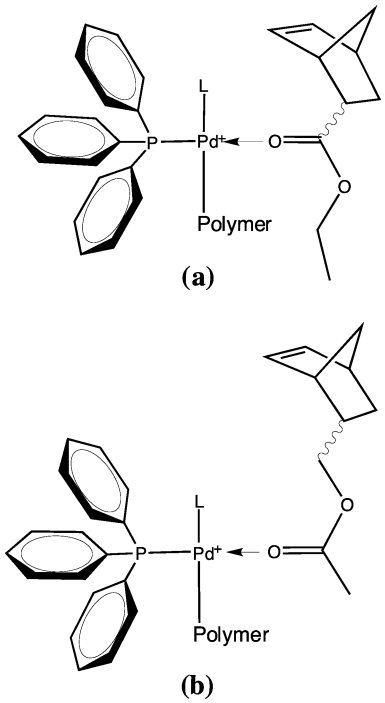

Figure 10. Steric hindrance involved in the coordination of the ester functionality of (a) *exo*/*endo*-EtEster-NB and (b) *exo*/*endo*-MeOAc-NB.

Conclusion

In conclusion, for the first time we are able to separately assess the effect of regiochemistry, size, donor, and chelating ability of the substituent in the polymerization and copolymerization of substituted norbornenes. *Endo*-substituted norbornenes are polymerized more slowly than the corresponding *exo* isomers. The size of the substituent also plays an important role. However, the coordinating ability of the functionality plays an even bigger role in attenuating polymerization than its size. The formation of chelates upon the

coordination of the *endo*-functionalized norbornene is responsible, in part, for the observed decrease in polymerization rate. A further, and even greater, reason for the diminution of activity of *both* the *endo*- and the *exo*-functionalized isomers is simply the coordination of the functionality to the metal center.

Experimental Section

General Methods. All work involving air- and/or water-sensitive compounds was carried out using standard Schlenk and/or drybox techniques under a dinitrogen atmosphere. (1,5-Cyclooctadiene)Pd(CH_3)Cl [(COD)Pd(Me)Cl] was synthesized according to published procedures.[9] Chlorobenzene (ACS grade) from EM Sciences was dried using a Grubbs-type solvent purification system.[10] 1,1,2,2-Tetrachloroethane (99%) from Aldrich was dried over CaH_2, distilled, and degassed (freeze−pump−thaw) three times prior to use. Tricyclohexylphosphine (97+%) and triphenylphosphine (99%) were used as received from Strem Chemicals. Acetone (ACS grade) was used as received from EM Sciences. *N*,*N*-Dimethylanilinium tetra(pentafluorophenyl)borate (AnniFAB) were used as received from Promerus PLC. 5-Butyl-2-norbornene (Butyl-NB), 5-ethylester-2-norbornene (EtEster-NB), 5-methyl acetate-2-norbornene (MeOAc-NB), 5-hexyl-2-norbornene (Hexyl-NB), and 5-decyl-2-norbornene (Decyl-NB) were received as generous gifts from Promerus PLC and were degassed (freeze−pump−thaw) three times prior to use.

The saturated norbornanes, 2-ethyl ester norbornane (EtEster-NBA) and 2-methyl acetate norbornane (MeOAc-NBA), were prepared by hydrogenation of their corresponding norbornenes under an atmosphere of 300 psi H_2 at 50 °C for 3 days using a 5% Pd/carbon catalyst. After the reaction was complete the norbornanes were centrifuged and filtered through a 0.2 μm syringe filter to remove the Pd/carbon catalyst. The norbornanes were then degassed (freeze−pump−thaw) three times prior to use.

The *exo* and *endo* norbornene isomers were separated and quantified using gas chromatography (GC) with 1,1,2,2-tetrachloroethane (TCE) as an internal standard. GC data were obtained on a Hewlett-Packard 5890 Series II instrument fitted with an Alltech EC-5 column and a FID detector.

Polymer molecular weights were obtained using a Waters SEC system using a three-column bank (Styragel 7.8 × 300 mm columns, 100−5000 D, 500−30 000 D, 2000−4 000 000 D), a Waters 600 controller, a Waters 486 UV detector, and a Waters 410 differential refractometer. Size exclusion chromatography was performed in chloroform at ambient temperature and calibrated to poly(styrene) standards.

Homopolymerization of Butyl-NB, EtEster-NB, and MeOAc-NB. Under an inert atmosphere, 0.019 mmol of (COD)Pd(Me)Cl, 1 equiv of PPh_3, 1.0 mmol of TCE, 10.0 mmol of functionalized norbornene (∼8:2 *endo*:*exo*), and 9 mL of chlorobenzene were added to a 30 mL scintillation vial. An initial sample (∼5 drops) of solution was diluted in ∼1 mL of acetone for GC analysis. The scintillation vial was then placed in a temperature-controlled silicone oil bath at 70 °C and allowed to equilibrate for ∼15 min. After equilibrating, 0.019 mmol of AnniFAB in 1 mL of chlorobenzene was added to the solution. Samples of the reaction mixture (∼0.1 mL) were removed from the reaction, and the polymerization reaction was halted in ∼1 mL of acetone for GC analysis. At the end of the reaction (1 h for the Butyl-NB, 24 h for the MeOAc-NB and EtEster-NB monomers), a sample of the reaction mixture was removed and prepared for SEC analysis as above. The polymerization was then halted and the polymer precipitated from solution by rapid addition of the reaction mixture into an excess volume of methanol (∼400 mL). The polymer was subsequently separated from solution by filtration or centrifugation and then dried under vacuum. Butyl-NB: M_w = 13 000, PDI = 2.4. EtEster-NB: M_w = 4300, PDI = 1.3. MeOAc-NB: M_w = 4300, PDI = 1.2).

Homopolymerization of Butyl-NB, Hexyl-NB, and Decyl-NB. For the comparison of alkyl-NB polymerization rates, PCy_3 was used instead of PPh_3 for the palladium catalyst and quenched after 1 h. Butyl-NB: M_w = 260 000, PDI = 1.7. Hexyl-NB: M_w = 200 000, PDI = 2.8.

Copolymerization of Functionalized Norbornenes. Under an inert atmosphere, 0.019 mmol of (COD)Pd(Me)Cl, 1 equiv of PPh_3, 1.0 mmol of TCE, 3.0 mmol of Butyl-NB, 7.0 mmol of EtEster-NB or MeOAc-NB, and 9 mL of chlorobenzene were added to a 30 mL scintillation vial. An initial sample (∼5 drops) of solution was diluted in ∼1 mL of acetone for GC analysis. The scintillation vial was then placed in a temperature-controlled silicon oil bath at 70 °C and allowed to equilibrate for ∼15 min. After equilibrating, 0.019 mmol of AnniFAB in 1 mL of chlorobenzene was added to the solution. Samples of the reaction mixture (∼0.1 mL) were removed from the reaction, and the polymerization reaction was halted in ∼1 mL of acetone for GC analysis. At the end of the reaction (24 h), a sample of the reaction mixture was removed and prepared for SEC analysis as above. The polymerization was then halted and the polymer precipitated from solution by rapid addition of the reaction mixture into an excess volume of methanol (∼400 mL). The polymer was subsequently separated from solution by filtration or centrifugation and then dried under vacuum. Butyl-NB/EtEster-NB: M_w = 5200, PDI = 1.9. Butyl-NB/MeOAc-NB: M_w = 3400, PDI = 1.5.

Polymerization of Butyl-NB in the Presence of Functionalized Norbornanes. Polymerizations of Butyl-NB in the presence of norbornanes were set up similar to their corresponding copolymerization reactions with either EtEster-NB or MeOAc-NB. Butyl-NB/EtEster-NBA: M_w = 2000, PDI = 2.1.

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