Communication

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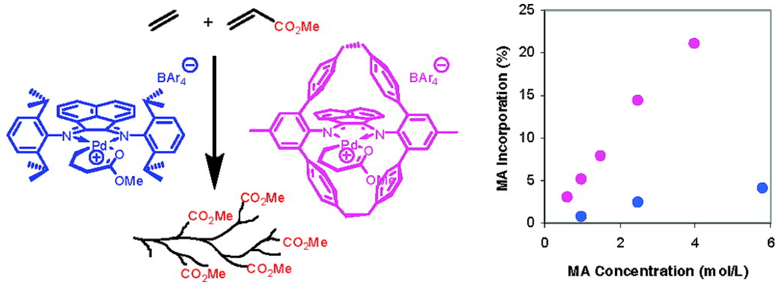

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Efficient Incorporation of Polar Comonomers in Copolymerizations with Ethylene Using a Cyclophane-Based Pd(II) α-Diimine Catalyst

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This communication reports our polymerization and mechanistic studies of a cyclophane-based Pd(II) α-diimine catalyst for efficient copolymerization of ethylene with polar olefins. Incorporation of polar monomers into polyolefins can significantly enhance important physical properties such as toughness and adhesion, thereby increasing the utility of olefin-based polymers. Currently, polar olefin copolymers are commercially manufactured through free radical polymerization but under very harsh conditions. As a result, there remains a tremendous driving force for developing milder transition-metal-catalyzed polymerizations that can produce polar olefin copolymers in a controllable manner. While early transition metal polymerization catalysts are in general not very effective for direct copolymerization with polar olefins because of their oxophilicity,[1] the polar functional group tolerance of recently developed late transition metal catalysts is highly promising.[2] Indeed, a few late metal catalysts have been reported for olefin copolymerization with polar monomers, prominent examples being the palladium(II) complexes[3−6] and the neutral nickel(II) systems.[7−10] Although these catalyst systems can incorporate polar olefins, efficiencies of functional olefin incorporation are usually low, which warrants further search of new catalysts.

Our laboratory has recently developed a cyclophane α-diimine ligand **2** for late transition metal polymerization catalysis.[11] The Ni(II) complex of **2** exhibited significantly increased thermal stability and reduced chain transfer,[12] even exhibiting living polymerization behavior at relatively high temperatures.[13] Encouraged by these positive results, we recently investigated the copolymerization of ethylene with polar olefins using cyclophane-based Pd(II) catalyst **2a**. The new system shows an unusually high efficiency in incorporating polar comonomers such as methyl acrylate (MA) and *tert*-butyl acrylate (TBA) as compared to the acyclic analogue **1a**. Furthermore, our low-temperature NMR studies revealed unique mechanistic origins for their increased efficiency for polar olefin incorporation.

In this study, a series of copolymerizations of ethylene with MA or TBA were carried out at 88 psi ethylene, 35 °C, for 18 h, but with different comonomer concentrations (Chart 1). The copolymers were analyzed by gel permeation chromatography (GPC) for molecular weight and NMR for composition and branching density (see the Supporting Information). The monomodal GPC traces and the characteristic chemical shifts in NMR spectra prove that these are statistical copolymers with the polar comonomers incorporated at the ends of branches. The incorporation level of polar monomer (mol % of polar comonomer incorporated) is plotted against the polar monomer feed concentration for both catalysts **1a** and **2a** (Figure 1). The comparison shows clearly that the cyclophane−Pd(II) catalyst **2a** is much more efficient in incorporating polar comonomers than the acyclic analogue **1a**. For example, **2a** afforded copolymer of over 20% MA at [MA] = 4.0 M, whereas catalyst **1a** achieved only 4% MA at 5.8 M. The contrast in incorporation efficiency is even bigger for copolymerization of ethylene with TBA, with **2a** again giving a polymer of high acrylate incorporation. The surprisingly high efficiency in incorporating acrylates for **2a** is most likely due to the unique microenvironment of the cyclophane ligand.

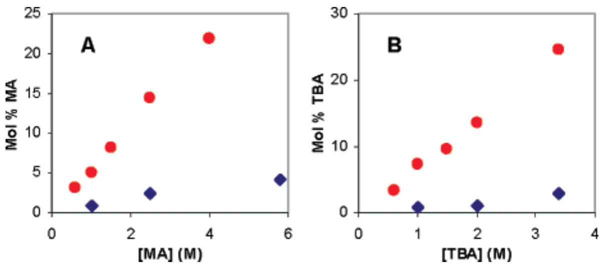
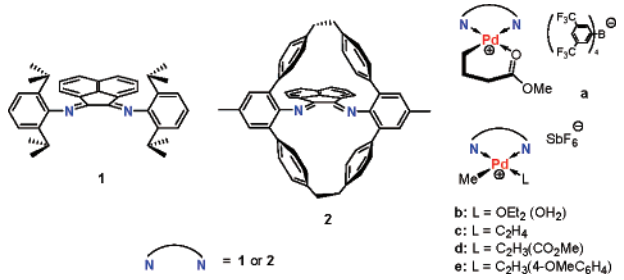


Figure 1. (A) Incorporation ratio of MA into copolymer versus MA concentration for catalysts **1a** and **2a**. (B) Incorporation ratio of TBA into copolymer versus TBA concentration for catalysts **1a** and **2a**. Red circle is for catalyst **2a**, and blue diamond is for catalyst **1a**.

Chart 1. Complexes Employed in the Copolymerization Study



To reveal the origin of the high efficiency for acrylate incorporation for the cyclophane−Pd(II) catalyst **2a**, a detailed comparative mechanistic study was undertaken. According to the established mechanistic model,[14] fast pre-equilibrium of monomers occurs before monomer insertion; therefore, incorporation will be related to the relative binding abilities of the olefins and their insertion rates. The labile adducts **1b** and **2b** served as suitable precursors to the corresponding ethylene or MA adducts (**1,2c** and **1,2d**, respectively) for our low-temperature NMR investigations.[15] The reactions to prepare the precursors proceeded far more sluggishly for the cyclophane-based systems than for their acyclic analogues, suggesting that ligand substitution is hindered by the cyclophane ligand. In particular, the formation of **2b** by silver(I) activation of the Pd(II) methyl iodide was complete after 2 days as opposed to only 2 h for the preparation of **1b**.

The rates of migratory insertion of ethylene and MA for both catalysts were measured by low-temperature ^{1}H NMR techniques. The first-order decay of the Pd−Me signal of the methyl olefin complexes was monitored at various temperatures, and the activation parameters, calculated from the Eyring plots, are shown in Table 1 (details in Supporting Information). The insertion barriers ($\Delta G^{\ddagger}$) agree with the polymerization data, with catalyst **2a** being 3 times

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Table 1. Kinetic Data for Olefin Insertion into the Pd−Me Bond

cat	olefin	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/mol·K)	$\Delta G^{\ddagger}$ (298 K, kcal/mol)
1c	C_2H_4	16.72 ± 0.35	−4.60 ± 1.44	18.14 ± 0.56
1d	MA	14.68 ± 0.60	−4.44 ± 2.81	16.05 ± 1.05
2c	C_2H_4	18.58 ± 0.49	−0.89 ± 1.92	18.58 ± 0.77
2d	MA	16.54 ± 0.35	+0.82 ± 1.62	16.29 ± 0.61

slower than **1a** for ethylene homopolymerization, for example (see Supporting Information, Table S1). The differences between the insertion barriers for ethylene and MA ($\Delta\Delta G^{\ddagger}$), however, are surprisingly similar for the two catalysts, suggesting that there must be other factors contributing to the unusually high efficiency in incorporating MA by catalyst **2a**.

Because the relative binding affinities of the olefins will also influence their incorporation ratio, we then carried out olefin exchange studies. Unlike the acyclic complexes,[14] olefin equilibria were not measurable for complexes of cyclic ligand **2** since displacement of one olefin by an added olefin did not occur up to the temperatures of olefin insertion (220−260 K, depending on monomer, see Supporting Information). As a result, we sought to obtain estimates of the rates of olefin exchange through one-dimensional inverse recovery NMR.[16] The method was successful in observing exchange between free and bound ethylene for the acyclic complex **1c** at temperatures as low as 200 K. No exchange, however, was discernible between free and bound ethylene for **2c** at temperatures up to 260 K. The lower limit for detectable exchange processes by this method is 10^{-2} s^{-1}, which is only 15-fold higher than the calculated insertion rate of ethylene into **2c** at 260 K, 6.9×10^{-4} s^{-1}. The exchange of MA was not observed, being too slow at the low temperatures in which complexes **1d** and **2d** are stable.

The evidence indicates a slow monomer equilibration for catalysts bearing ligand **2**, a conclusion also corroborated by the observations of reduced reactivity for ligand substitution in the preparation of **2b**. The rates of monomer exchange may approach or be less than the insertion rates, suggesting that fast pre-equilibrium of olefins does not occur for the cyclophane catalyst. As proposed previously by Brookhart and co-workers,[3,14] olefin exchange proceeds through association of a new olefin at the axial coordination sites followed by replacement of the olefin bound to the metal. The dramatic reduction of associative ligand substitution processes, critical steps in chain transfer, halide exchange, and olefin monomer exchange, is attributed to the effective steric blocking of the axial coordination sites of the metal by the bulky cyclophane ligand. Without the establishment of equilibrium prior to insertion, the catalyst's ability to discriminate between monomers of different steric and electronic properties would be suppressed. With this decrease in selectivity, the likelihood of one or the other comonomers binding should be less dependent on the relative energies of complexation, which would normally strongly favor ethylene, allowing a weakly binding comonomer higher incorporation.

In summary, we report on the unusually high efficient incorporation of polar olefins in copolymerizations with ethylene using a cyclic cyclophane-based Pd(II) catalyst. The unique structure of the cyclophane ligand, especially its ability to shield the axial binding sites, significantly reduces the rate of comonomer exchange. Presumably, this suppresses the catalyst's ability to discriminate between monomers for binding, thus enhances the incorporation for the polar olefins. Further mechanistic studies and structural modifications of the cyclic ligand are currently underway.

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Supporting Information Available: Experimental details for the synthesis and characterization of complexes, polymerization data, low-temperature NMR experiments, and complete ref 9. This material is available free of charge via the Internet at http://pubs.acs.org.

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