Well-Controlled Block Polymerization/Copolymerization of Alkenes and/or Carbon Monoxide by Cationic Palladium Methyl Complexes

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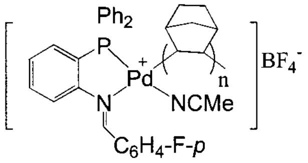
Summary: Cationic palladium imine−phosphine complexes [Pd(P−N)(CH$_3$)(CH$_3$CN)]$^+$ catalyze the living block polymerization and copolymerization of olefins and/or carbon monoxide. The palladium-capped polymers, intermediates of the polymerization, were isolated.

Strategies for well-defined transition metal catalyzed block polymerization and oligomerization of alkenes, leading to useful functionalized polymeric materials, have been receiving much attention.[1−7] However, block polymers built by the subsequent insertion process of olefin and/or CO allowed to grow into the living block polymer of various substrates, which requires the suppression of β-elimination, have been less explored.[8,9] We recently reported that the new palladium imine−phosphine complexes [Pd(P−N)(CH$_3$)(CH$_3$CN)](BF$_4$) (**1**, P∼N = *o*-C$_6$H$_4$(PPh$_2$)(N=CHC$_6$H$_4$F-*p*)) can catalyze copolymerization of CO−ethylene (E−CO) and CO−norbornylene under mild reaction conditions as well as provide well-characterized oligomeric intermediates of stepwise insertion.[10] The nonsymmetric P−N bidentates are keen to confer the reactivity difference at the trans sites, thereby allowing us to fine-tune the metal complex catalyzed reactions. For instance, the imino moiety can stabilize the alkyl group better than does the phosphine. Therefore, the insertion intermediates may have longer lifetimes than in the diphosphino systems. Herein we report our results of the palladium alkyl complex catalyzed triblock polymerization/copolymerization of olefins and carbon monoxide.

Polymerization of norbornylene is first mediated by the palladium imine−phosphine complex **1**. In a typical run, a mixture of norbornylene (2 g) and **1** (180 mg) in dichloromethane (40 mL) was stirred at room temperature for 10 h to provide **2a** ($n \approx 5$) (297 mg). Complex **2a** is a stable white powder and is obtained by decanting a solution of hexane and dichloromethane. The FAB mass spectrum of **2a** shows that the oligomer chains range from $n = 1$ to $n = 9$, indicating the formation of an oligomeric chain. In addition to the signals of the ligand part, the ^{1}H NMR spectrum of **2a** in CDCl$_3$ has broad signals in the range δ 2.4−0.35 corresponding to the oligomeric norbornylene. The integration ratio of norbornylene to the imine proton (ligand) allows us to calculate the average repeating unit of norbornylene as 4−5, which is consistent with the maximum intensities at *m*/*z* 880.6 ($n = 4$) and 974.6 ($n = 5$). Acid washing of this material gave oligomeric norbornylenes, and GPC analysis of the oligomers gives $M_n = 453$ ($M_w/M_n = 1.45$), which also verifies the chain length proposed. Under similar conditions but a longer period of time (20 h), the palladium complex **2b** ($n \approx 10$) with a longer norbornylene chain was isolated. Upon Pd−C cleavage, the GPC determination shows $M_n = 985$ ($M_w/M_n = 1.16$) for oligomeric norbornylene.



2a (n ∼ 5)
2b (n ∼ 10)
2c (n ∼ 20)

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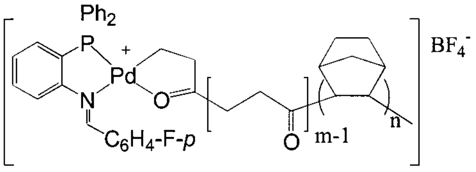
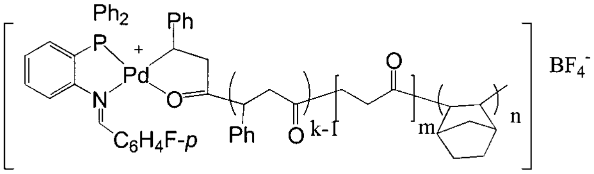
Since the active metal center remains on the oligomeric species, ethylene (50 psi) and carbon monoxide (50 psi) in dichloromethane at room temperature for 8 h provide a block copolymer of polynorbornylene and E−CO, **3a** ($n \approx 5$, $m \approx 10$).[11] Characterization of this block polymer was established by spectroscopic methods. An infrared absorption at 1711 cm^{-1} for the C═O stretching mode supports the formation of polyketones. ^{13}C NMR shifts at 234.1 (C═O) and 36.4 ($-CH_2$-CO−) also confirm the insertion of ethylene and carbon monoxide. The molecular weight determined by ^{1}H NMR from the ratio of integrated peak area of the norbornyl group or imine proton versus $-CH_2CH_2CO-$ is about 1400 g/mol, suggesting that each polymer chain has been incorporated with an average of 9−10 units of $-CH_2CH_2CO$-. The attachment of a palladium center on the oligomeric chain is confirmed by ^{31}P NMR and mass spectroscopy. A single shift at δ 37.4 (relative to 85% H_3PO_4) in the ^{31}P NMR spectrum suggests that the coordination environment should resemble that of $[(P{\sim}N)PdCH_2CH_2COCH_3]^+$ (δ 36.1).[10] The FAB mass spectrum shows that the peaks of the ions are consistent with the mass units. Peaks appearing in the FAB mass spectrum of this sample are consistent with the formula $[(P{\sim}N)Pd(CH_2CH_2CO)_n(C_7H_{10})_mCH_3]^+$. For example, the masses and isotopic abundance around the peak at m/z 1554.8 ($m = n = 7$) are identical with those calculated for the formula $C_{96}H_{120}O_7NPFPd$ (the FAB mass spectrum of **3a** is included in the Supporting Information). Upon acidic workup, the polymeric materials become insoluble in most organic solvents, which makes further identification difficult.



3a n ~ 5, m ~ 10
3b n ~ 10, m ~16

Complex **3a** can undergo further insertion with other olefins and CO. For example, **3a** was treated with styrene/CO (50 psi) in dichloromethane at room temperature. The product, **4a** ($n \approx 5$, $m \approx 10$, $k \approx 3$), precipitated as a white solid from the reaction mixture.



4a n ~ 5, m ~ 10, k ~3
4b n ~10, m ~ 16, k ~3

However, the measurement of nuclear magnetic resonance signals in CD_2Cl_2 is still feasible. The incorporation of styrene/CO was confirmed by both spectroscopic and FAB mass analyses. However, the integration ratio of the imino proton versus aromatic ones in ^{1}H NMR shows only 2−3 units of styrene/CO incorporated. The fewer units of styrene incorporated is presumably due to the poor solubility of the material in solution. Upon acid washing of the sample, a white powder was obtained that dissolved in THF, and GPC determination of the molecular weight (M_n) was 1880, indicating the increase of molecular weight from **3a**.

In fact, the longer polymeric chain can be achieved with a longer reaction period. Complexes **2b**, **3b** ($n \approx 10$, $m \approx 16$), and **4b** ($n \approx 10$, $m \approx 16$, $k \approx 3$) were obtained and characterized similarly, but the solubilities of these species are much poorer than for those with shorter chains, particularly with **3b** and **4b**. The acid-washed samples of **3b** and **4b** become insoluble in most organic solvents, which causes a problem in the determination of their molecular weights. Nevertheless, the M_w/M_n values of the acid-washed samples of **2b** and **4a** are 1.16 and 1.17, respectively, which also clearly suggests the living polymerization nature of the catalyst.

In conclusion, the cationic palladium complexes chelated through an *o*-phenylene linkage of phosphine−imine exhibit moderate activities in the living polymerization of various olefins and/or carbon monoxide, which allows us to isolate the intermediates of polymerization. A detailed study concerning the catalysts toward various olefins and the property of the polymers are currently under investigation.

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Supporting Information Available: Text and figures giving experimental details, including the preparation of palladium complexes and ^{1}H NMR and FAB mass spectra of **2a** and **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) **3a**: IR (KBr) 2952, 2872 (ν_{C-H}), 1711($\nu_{C=O}$), 1635 (coordinating C═O) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 9.18 (br, 1 H), 8.36−8.29 (br, 2 H), 7.85−7.20 (br, 16 H), 3.06−2.86 (m, 2.2 H), 2.62 (br, 30.1 H), 2.45−2.25 (br, 5.8 H), 2.19 (br, 6.5 H), 1.83−0.69 (br, 45.7 H); ^{31}P NMR δ 37.4 (br).