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Ring-Opening Polymerization of Heterocycles with Palladium Insertion Catalysts: Observation of a Multifunctional Polymerization Initiator

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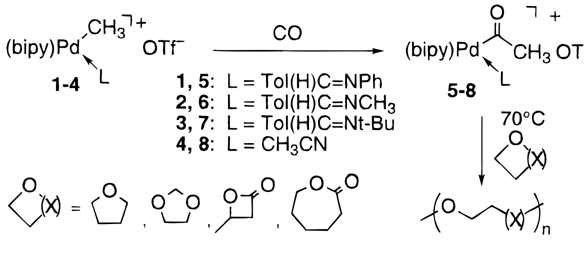
Summary: The palladium insertion polymerization catalysts (bipy)Pd(CH_3)L^+OTf^- have been found to mediate a second class of polymerization reaction: the ring-opening polymerization of heterocycles. Unlike traditional cationic ring-opening processes, this polymerization is found to proceed via an unusual series of metal-based reactions, including novel steps which allow the coupling of insertion monomers (CO and norbornene) with ring-opened polymers.

The cationic ring-opening polymerization of heterocycles has become of significant importance in polymer synthesis, due in part to the diverse variety of functionalized materials that can be prepared by this method, including natural and/or biodegradable polymers.[1] In contrast to the well-known transition-metal-catalyzed synthesis of polyolefins, where the catalyst can affect various polymerization properties (e.g., sequential monomer selectivity, polymer molecular weight and tacticity),[2] the synthesis of ring-opened heterocycles is often mediated by compounds whose role is to initiate the polymerization process. This provides less opportunity to “tune” polyheterocycle properties through catalyst choice and has stimulated research to develop initiators which function beyond the simple activation of polymerization, such as living polymerization initiators,[1] chiral initiators,[3] enzyme initiators,[4] and ring-opening insertion systems.[5,6] We report here that the organo-palladium complexes (bipy)Pd(R)L^+OTf^-, which are known insertion polymerization catalysts,[2] can mediate a second type of polymerization reaction: the ring-opening polymerization of heterocycles. In contrast to typical initiators, mechanistic studies suggest this polymerization proceeds via an unusual series of metal-based reactions. The manipulation of these steps provides significant control over polymer molecular weight and end groups, and allows the novel combination of cationic ring-opening polymerization with sequential olefin/CO insertion to generate new polymers.

Cationic palladium−methyl complexes with various dative ligands, (bipy)Pd(CH_3)L^+OTf^- (bipy = 2,2′-bipyridyl; OTf = OSO_2CF_3; **1**−**4**), can be prepared by reaction of (bipy)Pd(CH_3)Cl with AgOTf in the presence of L (eq 1).[7] The addition of 1 atm of CO to CH_2Cl_2 solutions of **1**−**4** leads to the formation of acyl complexes (bipy)Pd($COCH_3$)L^+OTf^- (**5**−**8**). When this reaction of **1**−**4** (ca. 20 mg, 0.05 mmol) with 1 atm of CO is performed at 70 °C in THF, the reaction solution slowly darkens and becomes viscous. Filtration and removal of solvent yields 0.33−0.98 g of a glassy solid (Table 1).[8] The ^1H and ^{13}C NMR of this material shows it to be the ring-opened polymer of tetrahydrofuran. As shown in eq 1, complexes **1**−**4** under 1 atm of CO are effective for the cationic ring opening of a number of heterocycles, such as dioxolane and lactones.



(1)

Metal complexes that can mediate two distinct types of polymerizations, i.e., insertion and heterocyclic ring-opening polymerization, have been observed in rare instances.[6,9] These systems typically involve highly electropositive metal centers, which mediate ring-opening polymerization as Lewis acid initiators, by binding strongly to the heteroatom to begin the cationic ring-opening process. In contrast, palladium complexes such as **1**−**4** are considered to interact only weakly with heteroatom substituents (e.g. ethers and esters), a feature that has made them of much interest in the insertion polymerization of functionalized olefins.[2] It is

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[1] For reviews, see: (a) *Cationic Polymerization*; Matyjaszewski, K., Ed.; Marcel Dekker: New York, 1996. (b) *Ring-Opening Polymerization*; Brunelle, D. J., Ed.; Hanser: Munich, 1993. (c) Yagci, Y.; Mishra, M. K. In *Macromolecular Design: Concept and Practice*; Mishra, M. K., Ed.; Polymer Frontiers: New York, 1994; p 391.

[2] (a) Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663. (c) Abu-Surrah, A. S.; Rieger, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2475.

[3] For examples, see: (a) Nakano, T.; Okamoto, Y.; Hatada, K. *J. Am. Chem. Soc.* **1992**, *114*, 1318. (b) Novak, B. M.; Goodwin, A. A.; Patten, T. E.; Deming, T. J. *Polym. Prepr.* **1996**, *37*, 446.

[4] Bisht, K. S.; Deng, F.; Gross, R. A.; Kaplan, D. L.; Swift, G. *J. Am. Chem. Soc.* **1998**, *120*, 1363.

[5] Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1985**, *107*, 1358.

[6] Yasuda, H.; Tamamoto, H.; Yamashita, M.; Yokota, K.; Nakamura, A.; Miyake, S.; Kai, Y.; Kanehisa, N. *Macromolecules* **1993**, *26*, 7134.

[7] (a) Dghaym, R. D.; Yaccato, K. J.; Arndtsen, B. A. *Organometallics* **1998**, *17*, 4. (b) van Asselt, R.; Gielens, E. E. C. G.; Rulke, R. E.; Vrieze, K.; Elsevier, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 977.

[8] Isolated polymers were washed with organic solvents and/or precipitated from methanol until the only ^1H and ^{13}C NMR peaks noted were those of the polymer.

[9] For examples of cationic and insertion polymerization catalysts, see: Hayakawa, M.; Mitani, M.; Yamada, T.; Mukaiyama, T. *Macromol. Rapid Commun.* **1996**, *17*, 865. Quyoum, R.; Wang, Q.; Tudoret, M. J.; Baird, M. C. *J. Am. Chem. Soc.* **1994**, *116*, 6435.

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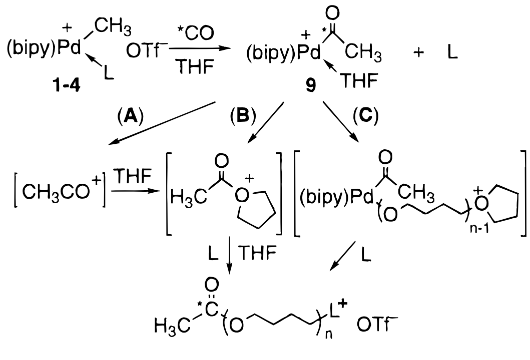
Table 1. Polymerization with Complexes 1-4 and 12[a]

substrate	initiator	[L], mmol	yield, g	M_n[b]	M_w[b]
THF	**1**		0.44	2.4	4.9
THF	**2**		0.06	1.3	1.9
THF	**3**		0.55	3.3	7.2
THF	**4**		0.92	3.5	7.8
THF	**4**	0.25[c]	0.13	1.1	2.1
THF	**4**	0.50[c]	0.07	8.2	1.5
THF[d]	**4**		1.42	13.8	19.6
dioxolane	**4**		8.02	1.4	3.3
butyrolactone	**4**		4.33	0.5	0.75
ϵ-capralactone	**4**		1.06	2.8	4.1
THF	**4**	0.05[e]	3.01	19.1	26.7
THF	**12**		3.12	15.5	22.1

[a] Conditions: 10 g of substrate, 0.05 mmol of catalyst, and 1 atm of CO heated to 70 °C for 24 h. [b] $\times 10^4$. [c] Added PhN=C(H)Tol. [d] 100 g of substrate. [e] Added norbornene.

Scheme 1



also interesting to note that when **1**−**4** are heated to 70 °C in THF for several days in the absence of CO ligand, only traces (<20 mg) of polymer are obtained, providing an unusual carbon monoxide "on" switch for the polymerization. These data all suggest an unusual role of the palladium complexes in initiating ring opening and prompted our closer examination of the polymerization process.

Monitoring the reaction of THF with (bipy)Pd(CH_3)-$NCCH_3^+OTf^-$ (**4**; 7 mg, 0.02 mmol in 1 mL of d_8-THF and 1 atm of ^{13}CO) by ^{1}H and ^{13}C NMR reveals the immediate quantitative formation of free acetonitrile and a new palladium−acyl fragment, (bipy)Pd($^{13}COCH_3$)$^+$ (**9**), at room temperature.[10] The ^{13}C NMR of this complex shows a single labeled ^{13}CO resonance (δ 218.3, Pd$^{13}COCH_3$), implying that the THF solvent, rather than a second ^{13}CO, occupies the fourth coordination site (Scheme 1). Heating of **9** to 70 °C reveals no further reaction intermediates and instead leads to the slow disappearance of **9** and gelling of the solvent due to formation of poly-THF. This rapid insertion of CO into the palladium−methyl bond prior to ring opening suggests the palladium−acyl complex **9** is the active initiator for polymerization. Further evidence for the involvement of the **9** in the polymerization is found in the structure of the poly-THF (vide infra).

Closer examination of the isolated poly-THF reveals these palladium complexes allow more control over the ring opening than simply providing the correct initiation conditions. Variation of the dative ligand (L) on **1**−**4** leads to significantly different poly-THF molecular weights, ranging from $M_w = 8.8 \times 10^4$ for **4** to $M_w = 1.9 \times 10^4$ with **2** (Table 1). In addition, the ^{1}H NMR of the poly-THF generated with **1** shows the incorporation of the PhN=C(H)Tol ligand into the polymer as an immonium group (^{1}H NMR: δ 2.38 (s, 3H), 4.45 (t, 2H), 7.3−7.8 (m, 9H), 9.34 (s, 1H)).[11] When >0.06 M PhN=C(H)Tol is added to the polymerization, the incorporation of this immonium moiety into the polymer is quantitative.[12] Similarly, a $-CH_2(CH_3)N{=}C(H)Tol^+$ unit is formed in the poly-THF generated with **2**.[13] No evidence for ^{t}BuN=C(H)Tol or $NCCH_3$ incorporation is noted with **3** and **4**, respectively, and instead small amounts of bipy (<20%) are found in the larger M_w polymers. COSY and TOCSY NMR experiments demonstrate these immonium units are end groups on the alkyl terminus of the poly-THF. The incorporation of imine into the poly-THF as an immonium group and the lower polymer M_w observed with the more basic imines on initiators **1** and **2** suggest that this ligand (L) is involved in termination of THF cationic polymerization by nucleophilic attack on the growing polymer. To test this hypothesis, increasing amounts of free Tol(H)C=NPh were added to THF polymerization with **2**. This results in similarly decreasing polymer M_w (Table 1), consistent with the role of free imine in polymer termination.

The poly-THF generated with **1**−**4** also has a ^{1}H NMR resonance at δ 2.01 (s) which integrates to one methyl group per polymer chain.[12] This resonance becomes a doublet ($^2J_{C-H} = 6.9$ Hz) when ^{13}CO is employed in the polymerization. Both IR (ν_{CO} 1739.9 cm^{-1}) and ^{13}C NMR (δ 171.2) analysis show that a carbonyl is also incorporated on the polymer. These spectral features correlate with a [CH_3CO] moiety on the poly-THF in the form of an ester end group.[14] The presence of this unit as the other polymer end group was determined by ^{13}C NMR decoupling experiments, which shows three-bond coupling between the ^{13}C-labeled carbonyl carbon and the $-OCH_2-$ hydrogens on the poly-THF ($^3J_{C-H} = 2.7$ Hz). Considering the incorporation of ^{13}CO into this end group, the ester undoubtedly arises from coupling of the poly-THF with the palladium−acyl ligand.

While the mechanistic details of this reaction have not been fully elucidated, the incorporation of two palladium ligands from **1**−**4** (Pd−imine and Pd−methyl), and external CO, into the poly-THF suggests ring-opening polymerization occurs via a series of steps. Plausible mechanisms to account for our observations are outlined in Scheme 1. Palladium−acyl complexes have been previously postulated by Tanaka to react with THF via free RCO$^+$ to form 4-chlorobutyl alkyl acetate, suggesting MeCO$^+$ (path **A**) as a possible intermediate.[15] Nevertheless, the formation of intermediate **9** implies THF coordination to Pd is also important to the polymerization. Indeed, it was found that the chloride-substituted (bipy)Pd(COMe)Cl, which does not coordinate THF to Pd, is also inactive for THF polymerization

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[10] ^{1}H NMR of **9**: δ 2.82 (d, 3H), 7.70 (t, 2H), 8.19 (t, 2H), 8.48 (d, 2H), 8.57 (d, 2H).

[11] For comparison, ^{1}H NMR of Tol(H)C=N(Ph)$CH_3^+OTf^-$: δ 2.38 (s, 3H), 4.16 (s, 3H), 7.2−7.8 (m, 9H), 9.30 (s, 1H).

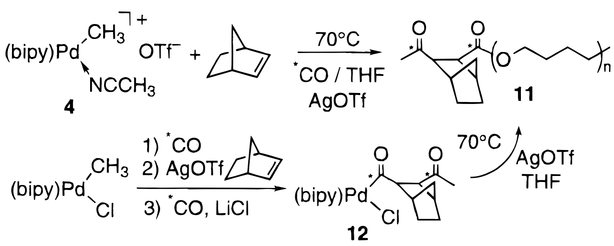
[12] End-group quantitation was determined by comparison of M_n calculated from ^{1}H NMR to M_n from GPC data. For complete polymer characterization, see the Supporting Information.

[13] ^{1}H NMR of Tol(H)C=N(CH_3)CH_2^+ end group: δ 2.49 (s, 3H), 3.76 (s, 3H), 4.20 (t, 2H), 7.2−7.8 (m, 4H), 9.15 (s, 1H).

[14] Ethyl acetate: ν_{CO} 1742 cm^{-1}; δ 170.3 (*C*O).

[15] Tanaka, M.; Koyanagi, M.; Kobayashi, T. *Tetrahedron Lett.* **1981**, *22*, 3875 and references therein.

Scheme 2



under our conditions. The initiation of ring opening from **9** could occur through direct acylation of THF (path **B**), or the polymerization of THF on palladium (path **C**), followed by reductive elimination.[17] The termination of either of these ring-opening reactions by nucleophilic attack of L would generate the observed immonium end groups. Further studies are currently in progress to distinguish between these mechanistic possibilities.

A particularly exciting aspect of this polymerization is the coupling of the acyl fragment in **9** with the THF polymer. Since this acyl moiety is also the ligand into which olefin/CO insertion polymerization has been found to occur,[2] the coupling step suggests these palladium complexes could provide a unique system to combine monomers polymerized by two distinct mechanisms, insertion (olefin and carbon monoxide) and cationic ring opening (THF), into novel copolymers.[1,6] Experiments toward this end were performed in a controlled manner by reaction of **4** (0.05 mmol) with 1 equiv of norbornene (0.05 mmol), AgOTf, and 1 atm of ^{13}CO in THF at 70 °C (Scheme 2). This yields 3.01 g of a white solid, which ^{1}H NMR analysis shows to be poly-THF (**11**) with the quantitative incorporation of a single norbornyl (δ 1.17−3.22 (m)) and methyl ketone (δ 2.13 (d, 3H)) fragment. An identical polymer (**11**) can be generated by first carrying out the sequential insertion of ^{13}CO, norbornene, and ^{13}CO into (bipy)Pd(CH$_3$)Cl to form **12**,[18] followed by addition of AgOTf in THF and heating to 70 °C. ^{13}C NMR of the isolated polymer **11** reveals the presence of ^{13}C label in both a ketone (δ 207.7) and ester (δ 174.9) end group, while COSY and ^{13}C decoupling experiments show connectivity between the ester carbonyl carbon and both the norbornyl to poly-THF fragments, demonstrating this polymer is indeed the novel product of *coupling of olefin and CO insertion monomers with ring-opening polymerization*.

In conclusion, the palladium insertion polymerization catalysts (bipy)Pd(R)L$^+$OTf$^-$ have been found to initiate THF ring-opening polymerization with significant ligand control over polymer molecular weights and end groups. In addition to mediating two distinct classes of polymerization on a single metal site, these palladium complexes provide a single-pot method to couple insertion monomers onto ring-opened heterocycles. To our knowledge, the latter is not precedented in metal-mediated polymerizations[6,19] and provides potential access to new classes of block copolymers incorporating insertion and ring-opened monomers. Experiments directed toward the generation of these materials with complexes **1**−**4** are currently underway.

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Supporting Information Available: Text and figures giving preparation details and characterization data on **1**−**3**, **5**−**7**, **9**, and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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[17] The role of CO insertion in path **C** could be to effect the Lewis acidity of palladium. Such ancillary ligand effects have been previously observed for THF ring opening: Borkowsky, S. L.; Jordan, R. F.; Hinch, G. D. *Organometallics* **1991**, *10*, 1268.

[18] Markies, B. A.; Kruis, D.; Rietveld, M. H. P.; Verkerk, K. A. N.; Boersma, J.; Kooijman, H.; Lakin, M. T.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1995**, *117*, 5263.

[19] Organic initiators for simultaneous free radical and ring-opening polymerization have been recently prepared: (a) Weimer, M. W.; Scherman, O. A.; Sogah, D. Y. *Macromolecules* **1998**, *31*, 8425. (b) Mecerreyes, D.; Moineau, G.; Dobois, P.; Jerome, E.; Hedrick, J. L.; Hawker, C. J.; Malmstrom, K. E.; Trollsas, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1274.