Living 1,2-Olefin-Insertion Polymerizations Initiated by Palladium(II) Alkyl Complexes: Block Copolymers and a Route to Polyacetylene–Hydrocarbon Diblocks

Adam L. Safir and Bruce M. Novak*

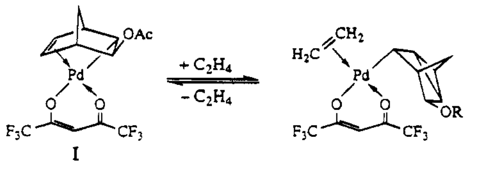
Polymer Science and Engineering Department and the Materials Research Science and Engineering Center, University of Massachusetts, Amherst, Massachusetts 01003

Received May 11, 1995
Revised Manuscript Received May 19, 1995

A key objective of synthetic polymer chemists is the development of new living polymerization systems.[1] Emphasis is placed on this goal because it is only through living systems that one can readily prepare polymers with defined end groups, predetermined molecular weights, and molecular weight distributions and prepare polymers and block copolymers of higher architecture. Gaining the requisite control over the polymerization of olefinic substrates by organometallic complexes has proved most challenging in this regard.[2] To this end, we report a highly air- and moisture-stable, living 1,2-insertion polymerization of olefins initiated by palladium(II) alkyl complexes and the use of these complexes to prepare novel hydrocarbon–polyacetylene block copolymers.

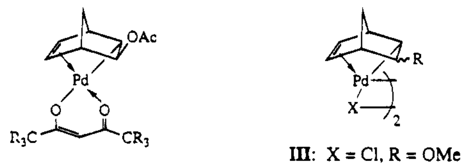
Although considerable effort has gone into studying the insertion of olefins into Pd–C bonds,[3] as well as the dimerization of olefins catalyzed by Pd(II) compounds containing Pd–C bonds,[4] the majority of the work in the area of Pd(II)-initiated olefin polymerizations has utilized the cationic palladium(II) species $[Pd(CH_3CN)_4][BF_4]_2$ which has been shown to initiate via a cationic mechanism.[5] Because of the needs to control the polymer end groups and develop fast initiating systems, we have been studying the polymerization of bicyclic olefins catalyzed by palladium(II) alkyl complexes. Unfortunately, the majority of literature palladium alkyl complexes are stabilized by either chelation or strong donor ligands[6] which often inhibit polymerizations. In order to eliminate these stabilizing ligands, we have focused on alkyl groups containing an internal olefin to stabilize the palladium center through chelation.[7] We have looked at a number of these Pd(II) complexes, focusing on variations of the σ,π-bicyclic structure (Figure 1), and have found them to be efficient initiators for living polymerizations. In addition, they produce very stable palladium end groups, so much so that the polymers can be isolated and stored with the Pd(II) center still attached and reused at a later time as an active initiator.

In the presence of olefins such as ethylene, the hexafluoroacetylacetonato σ,π-bicyclic complex, **I**, was shown to undergo tricyclic rearrangement of the σ,π-alkyl ligand in a reversible manner (eq 1).[8] This suggested that the coordination site filled by the olefin of the σ,π-bicyclic ligand would be available for monomer association after initiation.



I

(1)

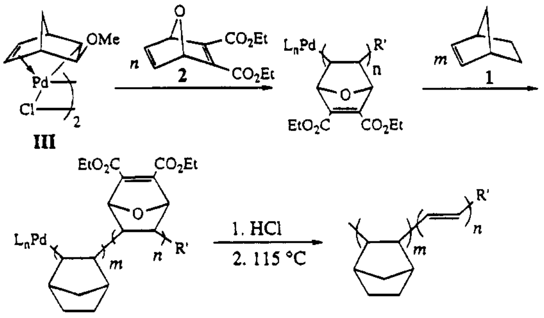


I: R = F
II: R = H

III: X = Cl, R = OMe
IV: X = Br, R = OMe
V: X = I, R = Ph

Figure 1. Palladium σ,π-alkyl complexes used to initiate 1,2-olefin-insertion polymerizations.

Scheme 1



Based on these observations, the monomeric σ,π-bicyclic complexes **I**[7e] and **II**[9] as well as the dimeric σ,π-bicyclic complexes **III**,[7b] **IV**,[7b] and **V**[10] were synthesized and screened as initiators for the 1,2-olefin-insertion polymerizations of a number of bicyclic olefins. We found that bicyclo[2.2.1]hept-2-ene (**1**) and diethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**2**) (see Scheme 1) could be quantitatively polymerized by these σ,π initiators in less than 15 min using wet solvents (THF or tetramethylurea (TMU)) in the presence of air. The importance of the preformed σ-Pd–C bond in determining the activity of these complexes can be demonstrated by comparing the activity of **I** in control experiments with analogous complexes lacking the σ bond. For example, polymerizations using (bicyclo[2.2.1]hepta-2,5-diene)$PdCl_2$ failed to polymerize **1** and gave only 33% yields of poly-**2** after 2 days. Other monomers such as bicyclo[2.2.1]hepta-2,5-diene (**3**) and diethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**4**) can also be polymerized using these σ,π complexes, albeit with significantly attenuated rates.

Not surprisingly, the activities of these complexes depend on both the solvent and the auxiliary anionic ligand. Not all of these polymerizations are necessarily living (*vide infra*) and/or well-behaved, and the outcome of a polymerization is strongly dependent on these aforementioned factors. More specifically, deactivation of the chain ends (as evidenced by diminutive yields) and mutation of the organometallic chain ends into two types of independently propagating species (as evidenced by bimodal molecular weight distributions) are both observed under less than ideal conditions. Polar, coordinating solvents are preferred, but ethereal solvents such as THF deactivate the more active catalysts.[11] This can be seen by comparing entries 5–7 in Table 1. We have found TMU to be unusual in that it acts to increase the rate of polymerization and suppress catalyst decomposition and mutation side reactions (Table 1, entries 7 vs 10). In TMU where decomposition is suppressed, the anionic ligand activity trend, I > Br > Cl, is revealed.

Figure 1b shows a typical gel permeation chromatography (GPC) trace of a bimodal polymer isolated from the polymerization of **2**. This bimodal character is observed in THF with all these complexes and even in TMU for initiators **III**–**V**. This bimodal profile evolves

0024-9297/95/2228-5396$09.00/0

Table 1. Polymerization of Monomer 2 Initiated Using Palladium σ,π Complexes at a Fixed Monomer/Initiator Ratio[a]

entry	initiator	solvent	time	yield (%)	living	M_m[b] (×10^3)	PDI[c]
1	**I**	THF	2 h	99	yes	6.9, 43.4	
2	**II**	THF	20 min	99	yes	8.1, 36.4	
3	**I**	TMU	40 h	99	yes	15.6	1.2
4	**II**	TMU	4 h	98	yes	15.8	1.5
5	**III**	THF	4 h	95	yes	6.9, 32.7	
6	**IV**	THF	24 h	53	no	9.8, 28.2	
7	**V**	THF	24 h	13	no		
8	**III**	TMU	20 min	99	yes	10.8, 37.1	
9	**IV**	TMU	4 min	97	yes	13.2, 40.0	
10	**V**	TMU	2 min	99	yes	13.4, 43.7	

[a] [**6**] = 1.9 M; [Catalyst] = 0.027 M; M/I = 70. [b] M_m is defined as the molecular weights of the peak maximum. [c] PDIs are not calculated for samples showing bimodal distributions.

over the lifetime of the polymerization, and the distribution of polymer between the two peaks is dependent upon the initial concentrations of monomer and initiator. This suggests that the active chain end mutates into two types of propagating species in solution. The exact nature of this process is not readily apparent and is still under investigation. The presence of distinct propagating species in solution does not detract from the livingness (*vide infra*) of these polymerizations in that the purported mutation constitutes neither a chain termination nor a chain transfer side reaction.[12] Nevertheless, we found that complexes **I** and **II** would initiate these polymerizations in TMU to yield monomodal polymer with PDIs as low as 1.2.

The most interesting aspect of these polymerizations is the stability of the palladium centers. Not only are these initiators air and moisture stable and thus suitable for bench top polymerizations (initiators **I**–**V** are all atmospherically stable for more than 12 h, and no variations are observed when the polymerizations are conducted under an inert atmosphere) but they also remain active as the chain ends, even after isolation and storage in the solid state. These "polymeric reagents" can be used for the preparation of block copolymers by dissolving them in a solution containing the second monomer (Scheme 1).

Living polymerizations are polymerizations lacking kinetically significant chain-transfer and chain-termination steps. Of the several accepted ways to demonstrate the absence of these two side reactions, the preparation of well-resolved block copolymers is one of the best,[1a] and we use this approach here. Moreover, the unusual stability of these organometallic chain ends allows us to run either block or chain-extension polymerizations by isolating the living chains between monomer additions. The GPC traces of an "AA" chain-extension experiment of poly-**2** (showing both fast and quantitative initiation and also that all polymer chains retain an active palladium center) conducted in the presence of air and moisture are shown in Figure 2. First, 5 equiv of **2** was added to the palladium(II) initiator, and after isolation 90% yield of oligomer with M_n = 1100 (relative to polystyrene) was isolated as a yellow powder (Figure 2a). This oligomer was then used to initiate the polymerization of a second aliquot of monomer. When an additional 65 equiv of **2** per palladium (original initiator) was added to a solution of the oligomeric initiator, a 90% yield of polymer was obtained with M_n = 16 000 (relative to polystyrene) (Figure 2b). These two GPC traces are fully resolved, proving that the palladium(II) center remains living as the polymer chain end and is fully stable under atmospheric conditions. With the exception of initiators **IV** and **V** in THF (which undergo decomposition), all of these complexes propagate polymerization in a living manner.

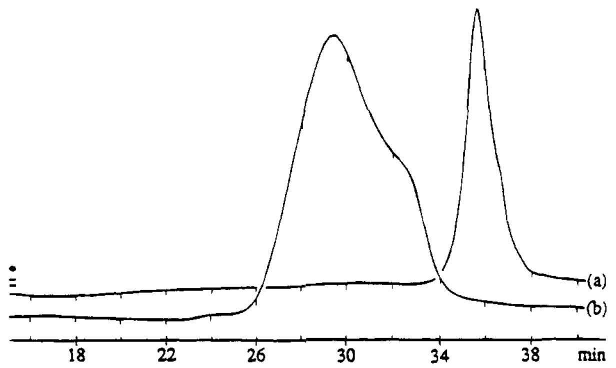


Figure 2. GPC traces of poly-**2**. (a) Initial block of oligomeric poly-**2** (M/I = 5). (b) Poly-**2** after addition of 65 equiv of **2** to a solution of the oligomeric poly-**2** shown in a.

We have previously shown that poly-**2** and poly-**4** are actually "protected" polyacetylenes that will undergo deprotection through retro-Diels–Alder reactions at 100 and 165 °C, respectively.[13] Similarly, we have now found that the diblock copolymers, poly-(**2**-*b*-**4**) and poly-(**2**-*b*-**1**), prepared using these living systems,[14] can be heated at 115 °C to produce novel polyacetylene–hydrocarbon diblock copolymers (Scheme 1). Heating a sample of poly-(**2**-*b*-**4**) where the poly-**2** block was large (M/I = 65) and the poly-**4** block was small (M/I = 5) at 115 °C in 1,2,4-trichlorobenzene produced a visible absorbance that red-shifted over time, culminating in an ultimate wavelength of 524 nm. Heating the same sample of poly(**2**-*b*-**4**) at 115 °C under vacuum as a thin film on NaCl plates produced a sample with an IR spectrum that showed both the major stretches from the poly-**4** block and a signal at 1010 cm^{-1} from the *trans*-polyacetylene block. By shortening the size of the poly-**2** block, we were able to produce copolymers with visible absorbances in the yellow (400 nm) and orange (470 nm) regions. Thus, this living system allows us to synthesize diblock copolymers containing hydrocarbon segments and polyacetylene segments of controlled size. Control over the morphology and, hence, bulk properties of these diblocks is currently being investigated.

Acknowledgment. We gratefully acknowledge support of this work from the Office of Naval Research, the NSF, the Alfred E. Sloan Foundation, DuPont, 3M, BFGoodrich, Procter & Gamble, Exxon, and the Lawrence Berkeley Laboratories. A.L.S. acknowledges the Department of Education for a predoctoral fellowship.

Supporting Information Available: Experimental procedures for the synthesis of complexes **II** and **V** (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) For a general overview of living polymerizations and criteria, see: (a) Quirk, R. P.; Lee, B. *Polym. Int.* **1992**, *27*, 359. (b) Webster, O. W. *Science* **1991**, *251*, 887.
(2) For selected examples of organometallic-initiated living olefin systems, see: (a) Doi, Y.; Suzuki, S.; Soga, K. *Macromolecules* **1986**, *19*, 2896. (b) Hadjiandreou, P.; Julemont, M.; Teyssie, Ph. *Macromolecules* **1984**, *17*, 2455.
(3) (a) Markies, B.; Wijkens, P.; Kooijman, H.; Spek, A.; Boersma, J.; Koten, G. *J. Chem. Soc., Chem. Commun.* **1992**,

1420. (b) Brombaugh, J.; Whittle, R.; Parvez, M.; Sen, A. *Organometallics* **1990**, 1735. (c) Hughes, R.; Powell, J. *J. Organomet. Chem.* **1973**, *60*, 387.

(4) (a) Jiang, Z.; Sen, S. *Organometallics* **1993**, *12*, 1406. (b) Jiang, Z.; Sen, A. *J. Am. Chem. Soc.* **1990**, *112*, 9655.

(5) (a) Sen, A.; Jiang, Z. *Macromolecules* **1993**, *36*, 911. (b) Risse, W.; Breunig, S. *Makromol. Chem.* **1992**, *193*, 2915. (c) Risse, W.; Mehler, C. *Macromolecules* **1992**, *25*, 4226. (d) Sen, A.; Lai, T.-W.; Thoman, R. *J. Organomet. Chem.* **1988**, *358*, 567. (e) Brookhart, M.; Rix, F.; DeSimone, J. *J. Am. Chem. Soc.* **1992**, *114*, 5894. (f) Markies, B.; Verkerk, K.; Rietveld, M.; Boersma, J.; Kooijman, H.; Spek, A.; Koten, G. *J. Chem. Soc., Chem. Commun.* **1993**, 1317.

(6) (a) Ladipo, F.; Anderson, G. *Organometallics* **1994**, *13*, 303. (b) Kim, Y-J.; Osakada, K.; Yamamoto, A. *J. Organomet. Chem.* **1993**, 247. (c) Cavell, K.; Jin, H.; Skelton, B.; White, A. *J. Chem. Soc., Dalton Trans.* **1993**, 1973. (d) Reger, D.; Garza, D.; Lebioda, L. *Organometallics* **1991**, *10*, 902.

(7) (a) Omae, I. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 889. (b) Green, M.; Hancock, R. *J. Chem. Soc A* **1967**, 2054. (c) Anderson, C.; Burreson, B. *J. Organomet. Chem.* **1967**, *7*, 181. (d) Segnitz, A.; Kelly, E.; Taylor, S.; Maitlis, P. *J. Organomet. Chem.* **1977**, *124*, 113. (e) Hughes, R.; Powell, J. *J. Organomet. Chem.* **1973**, *60*, 427.

(8) (a) Carturan, G.; Zanella, R.; Graziani, M.; Belluco, U. *J. Organomet. Chem.* **1974**, *82*, 421. (b) Ban, E.; Hughes, R.; Powell, J. *J. Organomet. Chem.* **1974**, *69*, 455.

(9) Complex **II** was synthesized by treating di-μ-acetobis(*exo*-6-acetoxy-2-norbornene-*endo*-5σ,2π)dipalladium(II)[7c] with sodium acetylacetonate. For complete synthesis and characterization see supporting information.

(10) Complex **V** was synthesized from di-μ-chlorobis(*endo*-6-phenyl-2-norbornene-*endo*-5σ,2π)dipalladium(II)[7d] via halide exchange with tetrabutylammonium iodide. For complete synthesis and characterization, see the supporting information.

(11) Portnoy, M.; Ben-David, Y.; Rousso, I.; Milstein, D. *Organometallics* **1994**, *13*, 3465.

(12) (a) Müller, A. H. E. In *Comprehensive Polymer Science*; Pergamon: New York, 1989; Vol. 3, Chapter 26. (b) Böhm, L. L. *Z. Phys. Chem. (Frankfurt)* **1970**, *72*, 199; **1974**, *88*, 297.

(13) Safir, A.; Novak, B. *Macromolecules* **1993**, *26*, 4072.

(14) These diblock copolymers (poly(**2**-*b*-**4**) and poly(**2**-*b*-**1**)) were synthesized in the same manner as the "AA" chain-extension polymerizations described in the text.

MA9506400