

New olefin polymerization and copolymerization catalysts. Effect of coordinating functionalities*

Ayusman Sen

Department of Chemistry, The Pennsylvania State University, University Park,
Pennsylvania 16802, USA

Abstract: The coordination of the functionalities that may be present either in the monomer or in the growing polymer chain to the metal center is a key impediment in the development of new transition metal-based catalysts for the insertion polymerization of polar monomers. Several examples are discussed to illustrate this problem. Additionally, it is shown that the reduction of the electrophilicity of the metal center is one way to decrease this interaction.

INTRODUCTION

Polyolefins with a high density of functional groups along the backbone are of great interest because of their many desirable properties [1]. These are most easily synthesized by the polymerization of polar monomers. Among the polymerization procedures, transition metal-catalyzed routes are particularly attractive because of the potential ability to (a) control polymer tacticity and chirality, and (b) incorporate both polar and nonpolar monomers into the polymer chains. Unfortunately, most transition metal-based olefin polymerization systems are not very tolerant of functionalities present in polar monomers, especially if the functionality is close to the C=C bond [2]. In particular, early transition metals are highly oxophilic resulting in inhibition of polymerization by oxygen-containing functionalities in the monomer. Even with late transition metals, inhibition of polymerization due to coordination of functionalities in the monomer or in the polymer chain can and does occur. Below, we cite examples of this phenomenon and describe our attempts at circumventing this problem by controlling the electrophilicity of the metal center.

RESULTS AND DISCUSSION

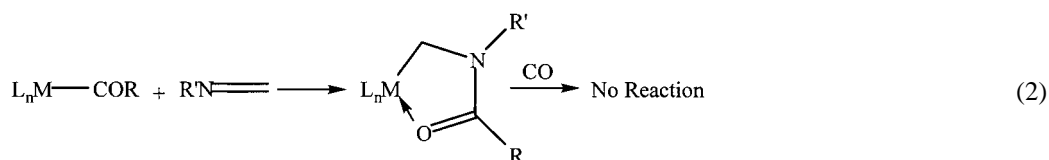
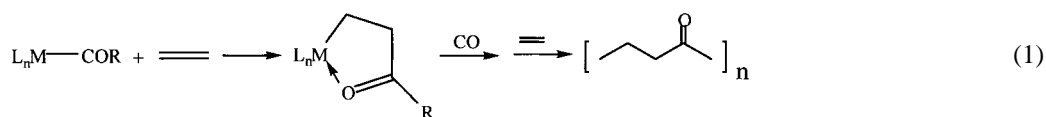
The palladium(II)-catalyzed alternating copolymerization of olefins with carbon monoxide is, by now, well documented [3]. The usual catalyst employed is a cationic palladium(II) species incorporating a bisphosphine or a bisamine ligand. The chain-growth occurs by alternate insertions of carbon monoxide and olefin into an initial Pd–C bond (eq. 1). We and others have examined the olefin insertion step [3a,4,5]. As shown in eq. 1, following insertion the newly formed ketone coordinates to the metal through the oxygen. However, the Pd–O interaction is weak, and the coordinated oxygen is easily displaced by an incoming monomer, allowing the copolymerization to proceed.

A very different situation pertains to the alternating copolymerization of imines with carbon monoxide. This reaction is of interest because, if successful, it would constitute a new general procedure for the synthesis of polypeptides. The sequence of steps leading to chain growth are similar to those observed for the alternating olefin–carbon monoxide copolymerization, with the insertion of the imine into the metal–acyl bond replacing the corresponding olefin insertion step. Indeed, imine inser-

*Lecture presented at the XIXth International Conference on Organometallic Chemistry (XIX ICOMC), Shanghai, China, 23–28 July 2000. Other presentations are published in this issue, pp. 205–376.

†E-mail: asen@chem.psu.edu

tion into the metal–acyl bond in cationic bisphosphine or a bisamine-Pd(II) complexes does occur readily [6]. As with the insertion of olefin into metal–acyl bonds, the corresponding imine insertion results in a metal-bound amide in which the oxygen of the amide carbonyl group is coordinated to the metal (eq. 2). Unlike the situation in olefin–carbon monoxide copolymerization, however, the Pd–O interaction is fairly strong and cannot be disrupted by an incoming monomer (carbon monoxide) and further chain growth ceases. The difference lies in the greater negative charge and, therefore, stronger coordinating ability of the carbonyl oxygen of an amide fragment. Interestingly, the insertion of carbon monoxide apparently occurs readily in analogous species where the amide carbonyl is not coordinated to the metal [7]. It is also interesting to note that while imine insertion into Pd(II)-acyl bonds was observed, the corresponding insertion into Pd(II)-alkyl bonds did not occur [6]. Almost certainly, the formation of the very strong amide linkage constituted the added driving force in the former reaction.



A similar inhibition, but not cessation, of polymerization was observed by Brookhart in his work on the copolymerization of ethylene with methyl acrylate that is catalyzed by cationic bisimine-Pd(II) complexes [8]. Here again, the coordination of the oxygen atom of the ester group of acrylate significantly slows down polymerization and leads to lower-molecular-weight materials.

A common theme in all three systems described above is that the palladium species employed is cationic and, therefore, relatively electrophilic. One of the reasons why cationic metal species are employed for polymerizations is that they usually have weakly bound solvent molecule(s) in place of more strongly coordinating anion(s). This allows greater accessibility of the metal center to the incoming monomer. However, the higher electrophilicity of the cationic metal center also causes a stronger binding of any functionality that may be present either in the monomer or in the growing polymer chain.

It is clear from the above description of the problem that a metal catalyst for the homo- and copolymerization of polar monomers should have one or more weakly bound ligands that are easily displaced by the incoming monomer and, at the same time, be neutral to reduce the electrophilicity of the metal center. Accordingly, in collaboration with Prof. Pablo Espinet's group in Spain, we have been investigating the use of weakly ligated neutral palladium(II) complexes in the polymerization of polar monomers [9]. One such complex, Pd(L)(MeCN)(C₆F₅)(Br) (L = monodentate phosphine or amine), appears to be the first known metal species to catalyze the homopolymerization of acrylate esters through an insertion mechanism [2c]. The 2,1-insertion of methyl acrylate into the Pd–C₆F₅ bond in the parent compound, Pd(MeCN)₂(C₆F₅)(Br), occurs but is followed by rapid β-hydrogen abstraction to yield CH(CO₂Me)=CHC₆F₅, along with the precipitation of metallic palladium. However, when 1 equiv of a monodentate phosphine or amine was added to Pd(MeCN)₂(C₆F₅)(Br) along with excess methyl acrylate, there was no precipitation of metallic palladium, and the formation of poly(methyl acrylate) occurred. Evidently, the presence of the ligand suppresses β-hydrogen abstraction in favor of further monomer insertions.

The reaction of methyl methacrylate with Pd(MeCN)₂(C₆F₅)(Br) also leads to a β-hydrogen abstraction product, CH₂=C(CO₂Me)CH₂C₆F₅. Note that the β-hydrogen abstraction occurs from the methyl group following 2,1-insertion of the olefin. A competition experiment involving the simultane-

ous addition of both methyl acrylate and methyl methacrylate to $\text{Pd}(\text{MeCN})_2(\text{C}_6\text{F}_5)(\text{Br})$ revealed that the reaction with methyl acrylate proceeded *ca.* 1.25 times faster than the corresponding reaction with methyl methacrylate. Since the coordination of the bulkier methyl methacrylate must be disfavored compared to methyl acrylate, this result suggests that β -H abstraction from the CH_3 group in the inserted methyl methacrylate is much faster than that from the $\text{CH}_2\text{C}_6\text{F}_5$ group in either inserted acrylate or methacrylate. Indeed, in the reaction with methyl methacrylate, the possible competing β -H abstraction product $\text{MeC}(\text{CO}_2\text{Me})=\text{CHC}_6\text{F}_5$ was not observed, which suggests that the rates of β -H abstraction from the two possible sites differ by at least one order of magnitude, in favor of CH_3 (see Fig. 1). Consistent with the above was our failure to polymerize methyl methacrylate under conditions employed for the polymerization of methyl acrylate. Even in the presence of 1 equiv of a monodentate phosphine or amine, only the β -hydrogen abstraction product was observed.

We wish to end this section with a final illustration of the effect of functionalities on the polymerization of olefins by cationic metal complexes. The species, $[\text{Pd}(\text{PR}_3)(\text{Me})]^+$, generated *in situ* by halide abstraction from $[\text{Pd}(\text{PR}_3)(\text{Me})(\text{Cl})]_2$, is an extremely active catalyst for the insertion polymerization of norbornene with a rate exceeding 1000 tons norbornene/mol Pd \cdot hour at 25 °C [10]! However, the polymerization rate was found to decrease dramatically for norbornene derivatives with pendant oxygen functionalities on the side opposite to the C=C bond. Because of the way they are synthesized, functionalized norbornene derivatives sold commercially consist of *exo* and *endo* isomers with the latter predominating. The drop in polymerization rate for functionalized norbornene derivatives may be ascribed to the formation of a chelate by coordination of the metal to the functionality and the C=C bond along the *endo* face (see Fig. 2). 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 [3a,5]. Consistent with this hypothesis has been our observation of the preferential uptake of the *exo* isomer in the polymerization of functional norbornene derivatives by $[\text{Pd}(\text{PR}_3)(\text{Me})]^+$. Indeed, under certain conditions a polymer can be obtained from the *exo* isomer but not the *endo* isomer [10a].

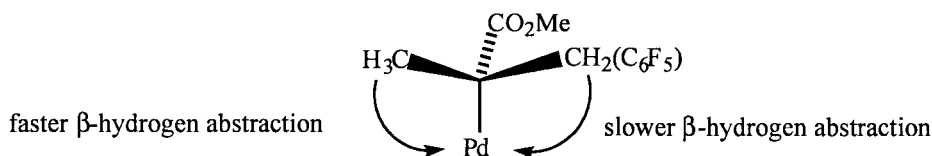


Fig. 1

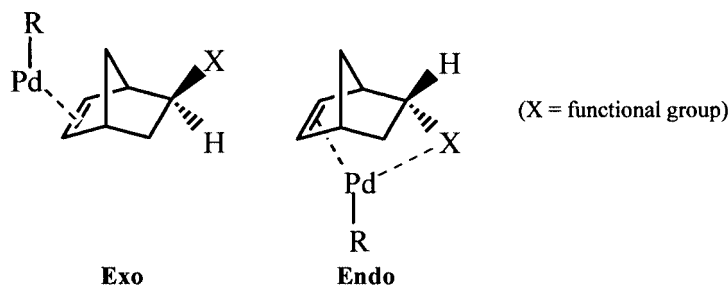


Fig. 2

CONCLUSION

The coordination of the functionalities that may be present either in the monomer or in the growing polymer chain to the metal center is a key impediment in the development of new transition metal-based catalysts for the insertion polymerization of polar monomers. Additionally, it is shown that the reduction of the electrophilicity of the metal center is one way to decrease this interaction.

REFERENCES

1. Reviews: (a) A. O. Patil, D. N. Schulz, B. M. Novak (Eds.). *Functional Polymers: Modern Synthetic Methods and Novel Structures*, American Chemical Society, Washington, DC (1998); (b) A. Akelah and A. Moet. *Functionalized Polymers and Their Applications*, Chapman & Hall, New York (1990); (c) D. E. Bergbreiter and C. R. Martin (Eds.). *Functional Polymers*, Plenum, New York (1989); (c) D. C. Sherrington and P. Hodge. *Syntheses and Separations using Functional Polymers*, Wiley, New York (1988).
2. (a) H. H. Brintzinger, D. Fischer, R. Mulhaupt, B. Rieger, R. M. Waymouth. *Angew. Chem., Int. Ed. Engl.* **34**, 1143 (1995); (b) G. W. Coates and R. M. Waymouth. In *Comprehensive Organometallic Chemistry II*, E. W. Abel, F. G. A. Stone, G. Wilkinson (Eds.), Vol. 12, p. 1193, Elsevier, New York (1995); (c) L. S. Boffa and B. M. Novak. *Chem. Rev.* **100**, 1479 (2000).
3. (a) A. Sen. *Acc. Chem. Res.* **26**, 303 (1993); (b) E. Drent and P. H. M. Budzelaar. *Chem. Rev.* **96**, 663 (1996) and references to patents therein.
4. (a) C. S. Shultz, J. Ledford, J. M. DeSimone, M. Brookhart. *J. Am. Chem. Soc.* **122**, 6351 (2000); (b) F. C. Rix, M. Brookhart, P. S. White. *J. Am. Chem. Soc.* **118**, 4746 (1996); (c) P. Margl and T. Ziegler. *J. Am. Chem. Soc.* **118**, 7337 (1996).
5. (a) B. A. Markies, D. Kruis, M. H. P. Rietveld, K. A. N. Verkerk, J. Boersma, H. Kooijman, M. T. Lakin, A. L. Speck, G. van Koten. *J. Am. Chem. Soc.* **117**, 5263 (1995); (b) R. van Asselt, E. E. C. G. Gielens, R. E. Rülke, K. Vrieze, C. J. Elsevier. *J. Am. Chem. Soc.* **116**, 977 (1994).
6. (a) S. Kacker, J. S. Kim, A. Sen. *Angew. Chem., Int. Ed. Engl.* **37**, 1251 (1998); (b) R. D. Dghaym, K. J. Yaccato, B. A. Arndtsen. *Organometallics* **17**, 4 (1998).
7. M. Beller, M. Eckert, F. Vollmüller, S. Bogdanovic, H. Geissler. *Angew. Chem., Int. Ed. Eng.* **36**, 1494 (1997).
8. S. Mecking, L. K. Johnson, L. Wang, M. Brookhart. *J. Am. Chem. Soc.* **120**, 888 (1998).
9. A. Sen and P. Espinet. Unpublished.
10. A. D. Hennis, J. D. Polley, A. Sen. *Polym. Prepr. - Am. Chem. Soc., Div. Polym. Chem.* **40**(2), 782 (1999); (b) A. D. Hennis and A. Sen. *Polym. Prepr. - Am. Chem. Soc., Div. Polym. Chem.* **41**(2), 1933 (2000).