

Atropisomeric P[^]N Ligands for the Palladium-Catalyzed Copolymerization of Styrene with Carbon Monoxide

Preliminary Communication

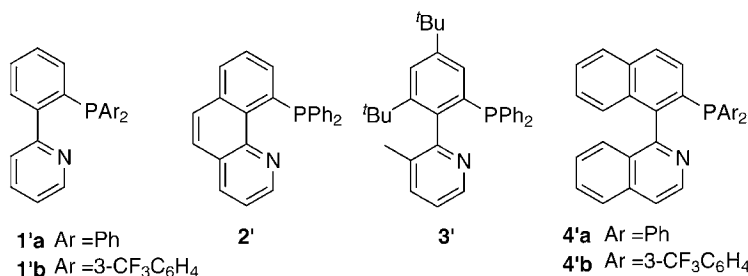
by Achim Gsponer and Giambattista Consiglio*

Eidgenössische Technische Hochschule, Institut für Chemie- und Bioingenieurwissenschaften,
ETH Hönggerberg, CH-8093 Zürich
(e-mail: consiglio@tech.chem.ethz.ch)

Achiral and chiral cationic palladium catalysts, modified with atropisomeric P[^]N ligands with different steric and electronic properties, can efficiently produce poly(styrene-*alt*-CO) with essentially complete regioregularity and variable tacticity, depending on the ligand geometry; the electronic effect on catalytic activity depends on the geometry of the ligand.

The alternating copolymerization of styrene with carbon monoxide to poly[1-oxo-2-phenylpropane-1,3-diyl] has attracted much attention in recent years [1–10]. The catalyst precursors used to produce stereoregular copolymers were [Pd(N[^]N)(S)(CH₃)](X) [11] or [Pd(N[^]N)(S)₂](X₂) [12] complexes (S = solvent molecule; X = weakly coordinating anion). N[^]N Ligands such as bipyridine or phenanthroline result in syndiotactically specific copolymerization [13], whereas a bis-oxazoline type of ligand [14][15] or atropisomeric diketo imines [8] result in isotactically specific copolymerization. Cationic palladium complexes of the type [(P[^]N)Pd(S)₂](X)₂ (P[^]N = 4-substituted 4,5-dihydro-2-phosphinooxazole ligand) also produce highly isotactic copolymers. In contrast to the above-mentioned N[^]N modified compounds, these complexes can be used under high carbon monoxide pressure to achieve higher polymer yields [16]. However, the substituent at C(4) of the dihydrooxazole moiety is necessary for the isotactic microstructure of the copolymer, but also causes rate reduction [17]. In an attempt to combine the good catalytic activity of the bipyridine systems [10] with the stabilizing effect of the diphosphine, without losing the isotactic steric control, we tried to exploit atropisomeric ligands and to compare them with their achiral counterparts. We, therefore, synthesized [Pd(P[^]N)(H₂O)₂](OTf)₂ complexes **1–4** [17][18], where P[^]N are the corresponding ligands **1'–4'**, and used them as catalyst precursors for the copolymerization of styrene with carbon monoxide.

The *Table* lists the results of the copolymerization experiments. They were carried out at high carbon monoxide pressure (320 bar), after identifying the positive order of the carbon monoxide concentration of catalyst precursor **1a**, as found for the other P[^]N ligands [16][19]. The achiral catalyst precursor **1a** has the highest catalytic activity of the ligands with diphenylphosphino substituents. It is noteworthy that system **2**, with the planar ligand, is not catalytically active. Analogously, for the N[^]N ligand systems under comparable reaction conditions, the phenanthroline catalyst is less active than



the bipyridine catalyst [20]. The catalyst precursor **1a** also produces copolymers with the highest molecular masses. Indeed, for these copolymers, no unsaturated end groups, formed as a consequence of chain termination through β -H elimination, were identified in the ¹H-NMR spectrum [16]. Such terminations are also rare in copolymers produced with phenanthroline or bipyridine [12][21] but were found in high concentrations when other hybrid P[^]N ligand systems were used [16][19].

Table. Copolymerization of Styrene with Carbon Monoxide Using **1–4**^a)

Ligand	Reaction time [h]	Copolymer [g]	Productivity [g/g Pd · h]	$M_n \cdot 10^{-3}$
1a ^b)	40	21	46.5	24
1b	17	7.7	84.8	13
2	143	–	–	–
3	26.3	4	18	5.5
4a	5.6	25	20	19
4b	46	2.1	8.5	6.2

^a) Reaction conditions: 50 ml of styrene in 10 ml of MeOH; 0.05 mmol of catalyst precursor unless otherwise stated; 320 bar CO (initial pressure at room temperature); 2 mmol of 1,4-benzoquinone; 50°. ^b) 0.10 mmol of catalyst precursor. M_n = average molecular weight.

The Figure shows the ¹³C-NMR spectrum of the produced copolymers in the region of the C(1)–Ph signals. It is remarkable that the three effective catalyst precursors used, **1a**, **3**, and **4a**, give copolymers that show essentially the three possible microstructures, namely prevalingly syndiotactic, isotactic, and completely atactic, respectively [22]. The P[^]N ligand **1'** is the first to produce as catalyst precursor **1**, a prevalingly syndiotactic copolymer. The difference in behavior of catalysts **3** and **4** is also remarkable. Despite its chirality, **4** gives a completely atactic copolymer with similar concentrations of the four possible triads (*ll*, *ul*, *lu*, and *uu*) [22]. In contrast, **3** gives a copolymer with good isotacticity; none of the signals belongs to the *uu* triad. The different behavior of ligands **3'** and **4'a** in other enantioface-discriminating catalytic reactions, such as the hydroboration, was discovered recently and was attributed to differences in the dihedral angle in the coordinated atropisomeric ligands [23].

Another remarkable aspect of the catalysis is related to the contrasting electronic effect on the catalytic activity, as shown by catalyst precursors **1b** and **4b** with respect to **1a** and **4a**. However, the decrease in basicity of the phosphorus ligating moiety has no influence on the stereochemistry of the copolymerization reaction.

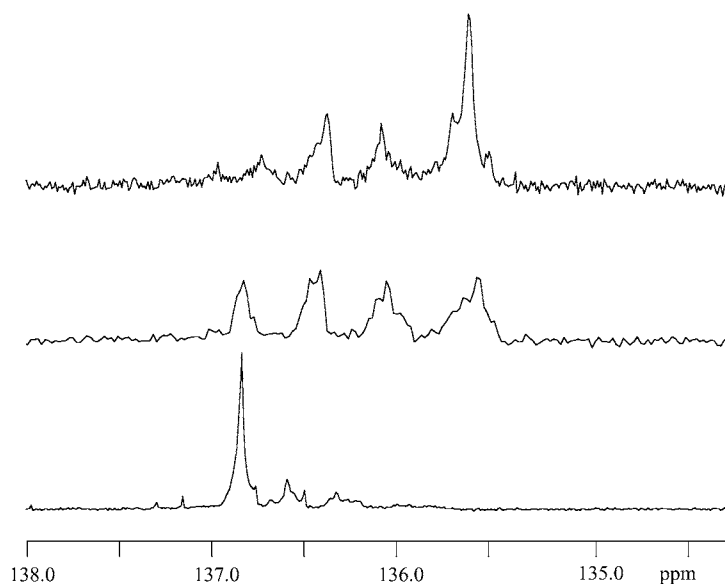


Figure. ^{13}C -NMR Spectra (125 MHz, $(\text{CF}_3)_2\text{CDOD}$) of the $\text{C}(1)\text{-Ph}$ region of poly(styrene-alt-CO) prepared with catalysts **1a**, **4a**, and **3** (from the top to the bottom)

REFERENCES

- [1] B. Milani, A. Scarel, G. Mestroni, S. Gladiali, R. Taras, C. Carfagna, L. Mosca, *Organometallics* **2002**, *21*, 1323.
- [2] F. Yao, C. Xu, L. Geng, Y. Bai, J. Zhang, J. Sun, *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 642.
- [3] A. Bastero, A. Ruiz, C. Claver, S. Castellón, *Eur. J. Inorg. Chem.* **2001**, 3009.
- [4] C. R. Baar, M. C. Jennings, R. J. Puddephatt, *Organometallics* **2001**, *20*, 3459.
- [5] J.-C. Yuan, S.-J. Lu, *Organometallics* **2001**, *20*, 2697.
- [6] C. Carfagna, G. Gatti, D. Martini, C. Pettinari, *Organometallics* **2001**, *20*, 2175.
- [7] K. Nozaki, H. Komaki, Y. Kawashima, T. Hiyama, T. Matsubara, *J. Am. Chem. Soc.* **2001**, *123*, 534.
- [8] M. T. Reetz, G. Aderlein, K. Angermund, *J. Am. Chem. Soc.* **2000**, *122*, 996.
- [9] C. Bianchini, A. Meli, *Coord. Chem. Rev.* **2002**, *225*, 35.
- [10] E. Drent, P. H. M. Budzelaar, *Chem. Rev.* **1996**, *96*, 663.
- [11] M. Brookhart, F. C. Rix, J. M. DeSimone, J. C. Barborak, *J. Am. Chem. Soc.* **1992**, *114*, 5894.
- [12] M. Barsacchi, G. Consiglio, L. Medici, G. Petrucci, U. W. Suter, *Angew. Chem., Int. Ed.* **1991**, *30*, 989.
- [13] P. Corradini, C. De Rosa, A. Panunzi, G. Petrucci, P. Pino, *Chimia* **1990**, *44*, 52.
- [14] M. Brookhart, M. I. Wagner, G. G. A. Balavoine, H. A. Haddou, *J. Am. Chem. Soc.* **1994**, *116*, 3641.
- [15] S. Bartolini, C. Carfagna, A. Musco, *Macromol. Rapid Commun.* **1995**, *16*, 9.
- [16] M. Sperrle, A. Aeby, G. Consiglio, A. Pfaltz, *Helv. Chim. Acta* **1996**, *79*, 1387.
- [17] A. Aeby, G. Consiglio, *Inorg. Chim. Acta* **1999**, *296*, 45.
- [18] M. Sperrle, V. Gramlich, G. Consiglio, *Organometallics* **1996**, *15*, 5196.
- [19] A. Gsponer, T. M. Schmid, G. Consiglio, *Helv. Chim. Acta* **2001**, *84*, 2986.
- [20] A. Macchioni, G. Bellachioma, G. Cardaci, M. Travaglia, C. Zuccaccia, B. Dilani, G. Corso, E. Zangrando, G. Mestroni, C. Carfagna, M. Formica, *Organometallics* **1999**, *18*, 3061.
- [21] V. Busico, P. Corradini, L. Mandriani, M. Trifuoggi, *Makromol. Rapid Commun.* **1993**, *14*, 261.
- [22] M. Barsacchi, A. Batistini, G. Consiglio, U. W. Suter, *Macromolecules* **1992**, *25*, 3604.
- [23] F. Y. Kwong, Q. Yang, T. C. W. Mak, A. S. C. Chan, K. S. Chan, *J. Org. Chem.* **2002**, *67*, 2769.

Received January 23, 2003