Polymers with Main-Chain Chirality. Synthesis of Highly Isotactic, Optically Active Poly(4-*tert*-butylstyrene-*alt*-CO) Using Pd(II) Catalysts Based on C_2-Symmetric Bisoxazoline Ligands

M. Brookhart* and Mark I. Wagner

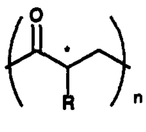
Department of Chemistry
University of North Carolina at Chapel Hill
Chapel Hill, North Carolina 27599-3290

Gilbert G. A. Balavoine and Hassan Ait Haddou

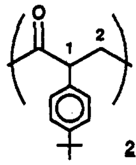
Laboratoire de Chimie de Coordination du CNRS
205 route de Narbonne, 31077 Toulouse Cedex, France

Received December 27, 1993

Polymerization of vinyl monomers using chiral catalysts can result in polymers with highly stereoregular isotactic microstructure; a prime example is the production of isotactic polypropylene from various chiral metallocenes.[1] These isotactic polymers effectively possess mirror planes of symmetry and therefore do not exhibit optical activity even when enantiomerically pure catalysts are employed.[2] The alternating copolymerization of vinyl monomers with carbon monoxide yields polyketones of general structure **1** which possess true stereogenic centers along the polymer backbone.[3] Such systems thus present an oppotunity to employ simple vinyl monomers in combination with chiral, enantiomerically pure metal catalysts to prepare optically active polymers with main-chain chirality.[4-7] We report here that palladium catalysts based on enantiomerically pure C_2-symmetric bis-oxazoline ligands copolymerize *p*-*tert*-butylstyrene (TBS) and carbon monoxide to yield alternating copolymer **2** with a highly isotactic microstructure and high optical activity.



1



2

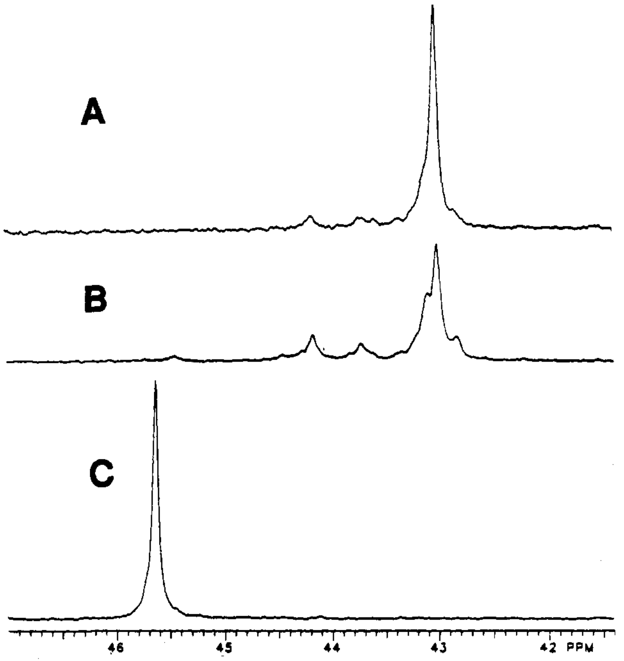
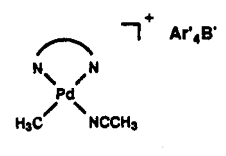
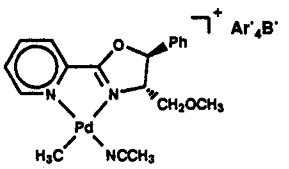


Figure 1. ^{13}C NMR spectra in the region of the C(2) resonance of poly(4-*tert*-butylstyrene-*alt*-carbon monoxide) (**2**) produced from (a) $[(2,2'\text{-bipyrimidine})Pd(CH_3)(NCCH_3)]^+[BAr'_4]^-$ (**3c**), (b) $[((4S,5S)\text{-4-(methoxymethyl)-5-phenyl-2-(2-pyridinyl)-1,3-oxazoline})Pd(CH_3)(NCCH_3)]^+[BAr'_4]^-$ (**4**), and (c) $[(2,2\text{-bis}[2\text{-}[4\text{-}(S)\text{-methyl-1,3-oxazolinyl}]]\text{propane})Pd(CH_3)(NCCH_3)]^+ [BAr'_4]^-$ (**6b**).

We previously reported[8] that copolymerization of TBS and CO with **3a** or **3b** yields copolymer **2** with substantial stereoregularity (ca. 85%), to which we tentatively assigned a syndiotactic microstructure based on earlier work of Corradini on poly(styrene-*alt*-CO).[9] Catalyst **3c** prepared from 2,2'-bipyrimidine gives a polymer with the same syndiotactic microstructure and somewhat higher stereoregularity (ca. 90%); the ^{13}C spectrum in the region of the C(2) resonance is shown in Figure 1a. Since catalysts **3a–c** are achiral, stereoregularity must be achieved by a chain-end control mechanism.



3a-c



4

= **3a** 1,10-phenanthroline
3b 2,2'-bipyridine
3c 2.2'-bipyrimidine

Ar' = $3,5\text{-}(CF_3)_2C_6H_3\text{-}$

Initial attempts to prepare an optically active TBS/CO alternating copolymer were made using catalyst **4** prepared from the bidentate ligand shown.[11] Complex **4** (0.05 mmol) in 20 mL of CH_2Cl_2 and 5 mL of TBS was exposed to 1 atm of CO at 25 °C for 22 h. Precipitation from methanol gave 4.1 g of copolymer, with $\bar{M}_n$ = 14 000 and $\bar{M}_w$ = 25 000.[12] Examination of the ^{1}H

---

(1) (a) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355. (b) Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. (c) Rieger, B.; Mu, X.; Mallin, D. T.; Rausch, D. T.; Chien, J. C. W. *Macromolecules* **1990**, *23*, 3559. (d) Erker, G.; Nolte, R.; Aul, R.; Wilker, S.; Kruger, C.; Noe, R. *J. Am. Chem. Soc.* **1991**, *113*, 7594. (e) Chien, J. C. W.; Llinas, G. H.; Rausch, M. D.; Lin, G. Y.; Winter, H. H. *J. Am. Chem. Soc.* **1991**, *113*, 8569. (f) Soga, K.; Shiono, T.; Takemura, S.; Kaminsky, W. *Makromol. Chem. Rapid Commun.* **1987**, *8*, 305. (g) Ewen, J. A.; Haspeslagh, L.; Atwood, J. L.; Zhang, H. *J. Am. Chem. Soc.* **1987**, *109*, 6544. (h) Coughlin, E. B.; Bercaw, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 7606.

(2) Wulff has shown that certain complex microstructures of polymers generated from simple vinyl monomers will possess main-chain chirality. These complex microstructures cannot be achieved with simple single-site catalysts. Wulff, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 27.

(3) For general references to these polymers, see: (a) Sen, A. *Acc. Chem. Res.* **1993**, *26*, 303. (b) Sen, A. *Adv. Polym. Sci.* **1986**, *73/74*, 125. (c) Drent, E.; Van Broekhoven, J. A. M.; Doyle, M. J. *J. Organomet. Chem.* **1991**, *417*, 235. (d) Barsacchi, M.; Batistini, A.; Consiglio, G.; Suter, U. W. *Macromolecules* **1992**, *25*, 3604.

(4) Consiglio has reported preparation of an isotactic propylene/CO copolymer using a chiral bidentate phosphine ligand, but no data concerning optical properties are given. Barsacchi, M.; Batistini, A.; Consiglio, G.; Suter, V. W. *Macromolecules* **1992**, *25*, 3604.

(5) Synthesis of poly(trityl methacrylate) using chiral, optically active initiators has led to a chiral, optically active polymer due to conformationally stable helical chains. Nakano, T.; Okamato, Y.; Hatada, K. *J. Am. Chem. Soc.* **1992**, *114*, 1318 and references therein.

(6) Waymouth has reported that chiral zirconium catalysts can be used for the enantioselective cyclopolymerization of 1,5-hexadiene to optically active poly(methylene-1,3-cyclopentane) possessing main-chain chirality: (a) Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 91. (b) Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 6270.

(7) (a) De, B. B.; Sivaram, S.; Dhal, P. K. *Polymer* **1992**, *33*, 1756. (b) Reference 2. (c) Ciardelli, F. In *Encyclopedia of Polymer Science*; Kroschwitz, J. I., Ed.; John Wiley and Sons: New York, 1987; Vol. 10, p 463.

(8) Brookhart, M.; Rix, F. C.; DeSimone, J. M.; Barborak, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 5894.

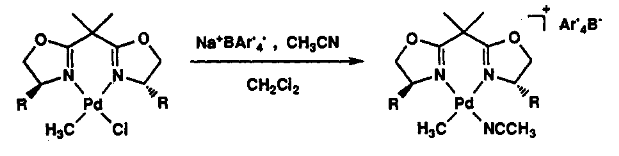
(9) Corradini, P.; DeRosa, C.; Panuzzi, A.; Petrucci, G.; Pino, P. *Chimia* **1990**, *44*, 52.

(10) The bipyrimidine complex **3c** (0.04 mmol) (see supplementary material for preparative details) was stirred for 20 h in 10 mL of TBS and 20 mL of CH_2Cl_2 under 1 atm CO. Copolymer **2** (10 g) was precipitated from methanol.

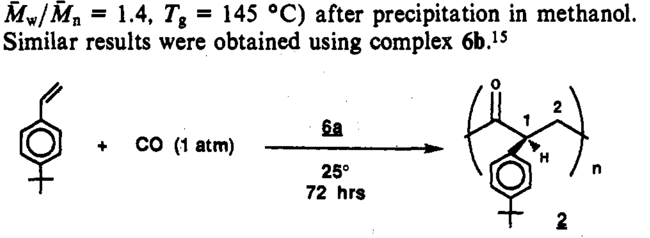
0002-7863/94/1516-3641$04.50/0 © 1994 American Chemical Society

and ^{13}C NMR spectra revealed that this polymer is less stereoregular than those prepared from **3a–c** but that the microstructure is still largely syndiotactic. This is illustrated by the ^{13}C spectrum shown in Figure 1b. Interestingly, this polymer did exhibit optical activity, with $[\alpha]^{25}_{589}$ −29° (c = 0.5, CH_2Cl_2) and a molar optical rotation of $[\Phi]^{25}_{589}$ −54°.[13] Since optical activity was observed in the case of **4**, we were encouraged to examine potentially more stereodiscriminating ligands possessing C_2 symmetry.

Complexes **5a,b** were prepared from the corresponding enantiomerically pure bisoxazoline ligands.[14] Treatment of either **5a** or **5b** with $Na^+BAr'_4{}^-$ (Ar′ = 3,5-$(CF_3)_2C_6H_3$) in CH_2Cl_2/CH_3CN resulted in conversion to the cationic acetonitrile catalysts **6a** and **6b**, respectively.[14d] In a typical copolymerization, exposure of **6a** (0.1 mmol) in 10 mL of stirring TBS to CO (1 atm) at 25 °C for 72 h gave 1.9 g of copolymer ($\bar{M}_n$ = 26 000, $\bar{M}_w$ = 38 000, $\bar{M}_w/\bar{M}_n$ = 1.4, T_g = 145 °C) after precipitation in methanol. Similar results were obtained using complex **6b**.[15]



5a R = -CH(CH₃)₂, **5b** R = -CH₃ **6a,b**

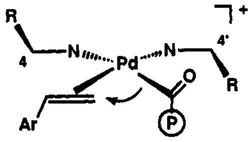


2

Isotactic, $[\Phi]^{25}_{589}$ −536°

Examination of the ^{1}H and ^{13}C NMR spectra[16] of this polymer revealed a very high degree of stereoregularity but with a different microstructure than that observed for copolymers prepared from **3a–c**. The ^{13}C NMR spectrum in the C(2) region is shown in Figure 1c; stereoregularity is greater than 98%. The polymer exhibits a high molar rotation of $[\Phi]^{25}_{589}$ −536° (c = 0.50, CH_2Cl_2), which confirms the isotactic microstructure.

Based on previous mechanistic studies[3,8] a transition state for acyl insertion similar to **7** below can be proposed. The C_α–C_β double bond must lie in or nearly in the square plane to accommodate migratory insertion. Models suggest that a methyl or isopropyl substituent at C(4) would sterically enforce the aryl ring to orient as shown. An *R* configuration is predicted for the isotactic copolymer produced from **6a,b**.[17]



7

In summary, the alternating copolymerization of styrene with CO by Pd(II)-based complexes containing bidentate nitrogen ligands represents a unique situation. Use of planar, achiral ligands such as phenanthroline or bipyrimidine results in chain-end control of polymer microstructure and production of a syndiotactic copolymer. This chain-end control mechanism can be overridden by use of enantiomerically pure C_2-symmetric ligands, as in **6a,b**, which provides strict enantiomorphic site control and produces highly isotactic, optically active copolymers.

Acknowledgment. We thank the National Science Foundation for financial support (CHE-8705534), F. C. Rix and O. Hoareau for assistance in synthesis, the laboratory of J. M. DeSimone (M. Hunt, M. Clark, R. Phillips) for polymer characterization by GPC, and Professors E. Eliel and J. M. DeSimone for useful comments.

Supplementary Material Available: Synthesis and spectral data for **2**, **3c**, **4**, **5a,b**, and **6a,b** (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(11) The pyridine–oxazoline ligand was treated with (TMEN)$Pd(CH_3)_2$ in benzene to produce ((4*S*,5*S*-4-(methoxymethyl)-5-phenyl-2-(2-pyridinyl)-1,3-oxazoline)$Pd(CH_3)_2$. This neutral complex was then treated with CH_3Br and $Na^+BAr'_4{}^-$ in CH_2Cl_2 and CH_3CN to form the cationic acetonitrile complex, [(4*S*,5*S*-4-(methoxymethyl)-5-phenyl-2-(2-pyridinyl)-1,3-oxazoline)-$Pd(CH_3)(NCCH_3)]^+[BAr'_4]^-$. Details are contained in supplementary material. For ligand synthesis, see: Balavoine, G.; Clinet, J. C.; Lellouche, I. *Tetrahedron Lett.* **1989**, *30*, 5141.

(12) A Waters 150-CV gel permeation chromatograph with Ultrastyragel columns of 100-, 500-, 10^3-, 10^4-, and 10^5-Å porosities in tetrahydrofuran was used with poly(styrene) standards (Showa Denko) for the determination of molar mass and molar mass distribution.

(13) The molar optical rotation of the polymer is $[\Phi]T_\lambda = [\alpha]T_\lambda(M/100)$, where M is the molecular weight of the repeating polymer unit.

(14) (a) Pfaltz, A. *Acc. Chem. Res.* **1993**, *26*, 339. (b) Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 726. (c) Corey, E. J.; Imai, N.; Zhang, H.-Y. *J. Am. Chem. Soc.* **1991**, *113*, 728. (d) Experimental details of preparation and characterization of **5a,b** and **6a,b** are in the supplementary material.

(15) Catalyst **6b** (0.1 mmol) was placed in a Schlenk tube under 1 atm of CO. TBS (10 mL) was added, and the solution was stirred for 72 h. Precipitation in methanol gave 1.1 g of polymer.

(16) Isotactic poly(4-*tert*-butylstyrene/CO): ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C) δ 7.17 (d, J = 8.3 Hz, 2H, H_β or H_γ), 6.84 (d, J = 8.3 Hz, 2H, H_γ or H_β), 3.87 (dd, J = 9.5 Hz, J = 3.4 Hz, CH), 3.04 (br dd, J = 18.2 Hz, J = 7.8 Hz, 1H, CH_2), 2.60 (br dd, 1H, CH_2), 1.21 (s, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C) δ 207.0 (-C(O)-), 149.8 (C_δ), 134.5 (C_α), 127.7 (C_γ), 125.6 (C_β), 51.7 (CH), 45.6 (CH_2), 34.3 ($\mathit{C}(CH_3)_3$), 31.3 ($C(\mathit{CH}_3)$).

(17) A 2, 1 mode of insertion for **6a,b** is assumed based on mechanistic investigations of **3a,b**.[8] Other transition-state models can be proposed which predict an *S* configuration. These issues are under investigation.