

by the total area of the doublet in both spectra is identical in the two states. The ratio of the integrated intensity of this Trp doublet to the intensity of the Tyr signal is the same in both states. For this reason, the dramatic change in the relative strength of the two components of the doublet must be interpreted in terms of changes in the environment of the Trp residues rather than modification of the resonance condition. The insert in Figure 1 shows an enlargement of the spectra in the region of the Trp doublet and the resolution of the two peaks using a fitting program to define the relative contribution of the bands at 1341 and 1361 cm^{-1} . From these areas, one can calculate that approximately 50% of the low-frequency intensity is transferred to the high-frequency band upon going into the M state. Given the fact that this signal originates from eight Trp residues and assuming that the Raman signal of these eight residues is equally enhanced, the change observed implies that approximately four Trp residues are perturbed by the bR \rightarrow M reaction. The relative intensities of this doublet in proteins have been shown to be altered upon Trp exposure to the aqueous environment.⁹ The retinal pocket includes four Trp residues (W86, W138, W182, W189).^{10,11} These are the Trp residues likely to be perturbed by the bR \rightarrow M reaction, and we propose that their environment is becoming more hydrophobic in the M state. The bR568 \rightarrow M reaction corresponds to the deprotonation of the Schiff base that transfers its proton to the nearby aspartate D85. The increase of the retinal pocket hydrophobicity indicated by our results could be due to the disappearance of charges in the retinal pocket.

Other features are found in the 1550–1630 cm^{-1} region of the UVRR difference spectrum (Figure 1). Because the intensities of the 1550 and 1620 cm^{-1} bands of Trp vary with the environment, these bands are very likely to contribute to the difference spectra. However, because of the complexity of this region where three Trp and two Tyr bands contribute, these changes are difficult to assign and interpret at the present time.

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Palladium(II) Catalysts for Living Alternating Copolymerization of Olefins and Carbon Monoxide

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Several Pd(II) catalyst systems have been reported^{1,2} which effect perfectly alternating copolymerization of olefins with carbon monoxide to yield polyketones $[\text{C}(\text{O})\text{CH}(\text{R})\text{CH}_2]_n$. There has been increasing interest in these polymers, particularly the

(1) For reports of $(\text{CH}_2\text{CH}_2\text{CO})_n$, see: (a) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1982**, *104*, 3520–22. (b) Sen, A.; Lai, T.-W. *Organometallics* **1984**, *3*, 866–70. (c) Sen, A. *Adv. Polym. Sci.* **1986**, *73/74*, 125. (d) Drent, E.; van Broekhoven, J. A. M.; Doyle, M. J. *J. Organomet. Chem.* **1991**, *417*, 235–51. (e) Klabunde, U.; Ittel, S. D. *J. Mol. Catal.* **1987**, *41*, 123–34. (f) For leading references to earlier work and the extensive patent literature, see 1c,d.

(2) For reports of $(\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{CO})_n$ and related polymers, see: (a) Drent, E. Eur. Pat. Appl. 0229408, 1986. (b) Drent, E. U.S. Patent 4,788,279, 1988, and references therein. (c) Corradini, P.; De Rosa, C.; Panunzi, A.; Petrucci, G.; Pino, P. *Chimia* **1990**, *44*, 52–54.

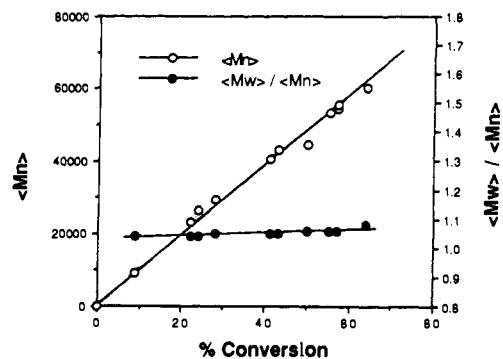
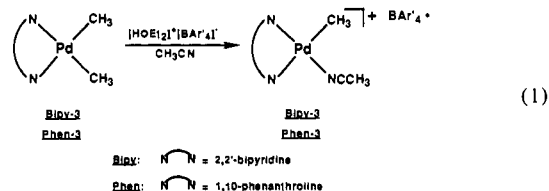


Figure 1. Molar masses and molar mass distribution as a function of conversion for 4-*tert*-butylstyrene and carbon monoxide. (M_n) values were determined by GPC relative to polystyrene standards, and % conversion was determined by ^1H NMR spectroscopy. Conditions: 0.2 mmol of Phen-3 and 20 g of 4-*tert*-butylstyrene in 80 mL of chlorobenzene under 40 psi of CO, 25 $^\circ\text{C}$.

$\text{C}_2\text{H}_4/\text{CO}$ copolymer ($T_m = 257$ $^\circ\text{C}$),^{1d} due to their unusual properties, the low cost of monomers, the presence of the carbonyl functionality, and the potential for further functionalization.^{1c,d,3a} The catalyst systems used have typically employed Pd(II) salts in methanol or chloroform in combination with acids, mono- or bidentate phosphines, or bidentate nitrogen ligands and frequently oxidants such as benzoquinone. Little has been reported concerning molecular weights or molecular weight distributions,^{3b} however, the nonliving nature of these systems can be inferred from the facile chain termination steps that have been identified, including alcoholysis of acyl intermediates.^{1b-d,4} We report here the synthesis of well-defined Pd(II) catalysts that operate in aprotic solvents to yield living alternating copolymers of olefins and CO. In situ spectroscopic studies have established mechanistic details including the identity of the catalyst resting state. We illustrate our investigations with 4-*tert*-butylstyrene/CO, which yields the soluble polymer $[\text{CHArCH}_2\text{C}(\text{O})]_n$, **1**, where Ar = 4- $((\text{CH}_3)_3\text{C})\text{C}_6\text{H}_4$.

Treatment of (2,2'-bipyridine)Pd(CH₃)₂, Bipy-2, or (1,10-phenanthroline)Pd(CH₃)₂, Phen-2, with 1 equiv of Et₃OH⁺Ar'₄⁻ [Ar' = 3,5-(CF₃)₂C₆H₃] in acetonitrile followed by solvent removal gives the monomethyl salts **3** as colorless solids⁵ (eq. 1). Exposure



of solutions of either Bipy-3 or Phen-3 (0.1 mmol) and *tert*-butylstyrene (62 mmol) in chlorobenzene (40 mL, 25 $^\circ\text{C}$) to 1 atm of CO results in uptake of CO and formation of **1**. The initial rate of CO uptake (ca. 0.2 turnover/min under these conditions) is proportional to *tert*-butylstyrene concentration and suggests chain growth is first order in olefin.

The copolymer can be precipitated from methanol as a white solid ($T_g = 158$ $^\circ\text{C}$), which has been characterized by ^1H and ^{13}C NMR spectroscopy.⁶ Both the ^1H and ^{13}C spectra of **1** suggest

(3) (a) Sen, A.; Jiang, Z.; Chen, J.-T. *Macromolecules* **1989**, *22*, 2012. (b) In one case, Sen has indirectly measured molecular weight and molecular weight distribution of the ethylene/CO copolymer by conversion to a soluble derivative.^{3a}

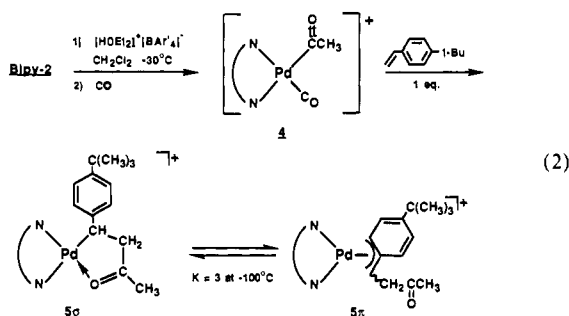
(4) (a) Barsacchi, M.; Consiglio, G.; Medici, L.; Petrucci, G.; Suter, U. *W. Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 989–91. (b) For related work, see: Pisano, C.; Mezzetti, A.; Consiglio, G. *Organometallics* **1992**, *11*, 20–22.

(5) See supplementary material for preparation and complete characterization.

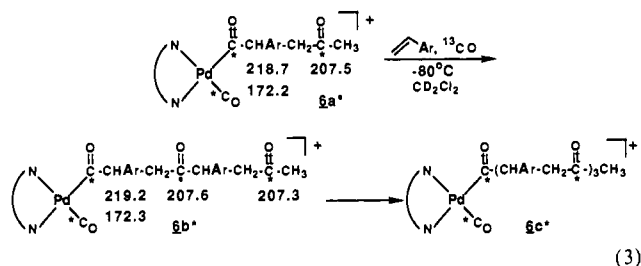
(6) **1**: ^1H NMR (CD_2Cl_2) δ 1.23 (s, 9 H), 2.63 (br dd, 1 H), 2.98 (br dd, 1 H), 4.08 (br q, 1 H), 6.57 (d, 2 H), 6.98 (d, 2 H); ^{13}C NMR (CD_2Cl_2) δ 31.5 ($(\text{CH}_3)_3\text{C}$), 34.6 ($(\text{CH}_3)_3\text{C}$), 43.4 (CH_2), 53.0 (CH), 125.9 (C_{ortho}), 128.3 (C_{meta}), 134.7 (C_{ipso}), 150.2 (C_{ipso}), 206.9 (CO); ν_{CO} (CH_2Cl_2) 1708 cm^{-1} . Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}$ (found): C, 82.93 (82.36); H, 8.57 (8.53).

a substantial degree of stereoregularity at C₂.⁷ For example, in the decoupled ¹³C spectrum, CH₂ shows a single major resonance at 43.4 ppm, with minor bands (ca. 5%) appearing at 44.7 and 44.2 ppm. Epimerization of **1** using (NaOH/CH₃OH, THF) and reprecipitation yields an atactic polymer which exhibits multiple bands for CH₂: 46.1, 44.9, 44.7, and 43.4 ppm. Similarly, the ¹H NMR spectrum exhibits major doublets for H_{ortho} and H_{meta} at δ 6.16 and 7.10 and minor doublets at δ 6.85, 6.97, 7.16, and 7.25. The atactic polymer shows a complex envelope of bands in the δ 6.5-7.5 range.

A ¹³C NMR study has revealed details concerning the chain growth process and the catalyst resting state. For the mechanistic study, an acetonitrile-free catalyst **5** was prepared as shown in eq 2. The chelate species **5σ** is in very rapid equilibrium with



the π -benzyl complex **5π**; static ¹H and ¹³C spectra can be obtained below -80 °C indicating a **5σ**:**5π** ratio of ca. 3:1.^{5,8} Intermediate **4** has been spectrally identified.^{9a,b} Preparation of **5*** using 99% ¹³CO followed by exposure to ¹³CO (1 atm) in CD₂Cl₂ at -80 °C yields the labeled carbonyl acyl complex **6a*** which shows three characteristic carbonyl bands at 172.2, 218.7, and 207.5 ppm for the PdCO, the α -acyl carbonyl, and CH₂C(O)CH₃, respectively. Treatment of a CD₂Cl₂ solution of **6a*** with ca. 6 equiv of *tert*-butylstyrene under 1 atm of ¹³CO results in chain growth which can be monitored by ¹³C NMR spectroscopy at temperatures between -80 and -60 °C.^{9a} The first species detected upon insertion is **6b*** followed by **6c***. In a related ¹³C NMR experiment, unlabeled **5** was reacted with ¹³CO and ca. 10 equiv of 4-*tert*-butylstyrene. The first two insertion products, analogous to **6b*** and **6c*** but with unlabeled end groups, confirmed the assignments for ¹³C(O)CH₃ bands in **6a,b*** and allowed identification of the internal carbonyl resonances of **6c***. Further insertions led to an envelope of bands in the 207-208 ppm range continually increasing in intensity relative to the PdCO and PdCO(R) bands. These experiments clearly indicate that the carbonyl acyl complex form of the catalyst, **6**, is the resting state and that olefin insertion is the slow step in chain growth. The structure of **5** establishes the regiochemistry of the insertion reaction which is confirmed by structural assignment of **6a**.



(7) Stereoregularity has also been noted by Corradini^{2c} for insoluble fractions of (CH(C₆H₅)CH₂CO)_n from the mixture of polymers obtained using the Drent procedure.^{2a}

(8) For Pd(II) chelate structures related to **5a**, see: (a) Brumbaugh, J. S.; Whittle, R. R.; Parvez, M.; Sen, A. *Organometallics* **1990**, *9*, 1735-57. (b) Ozawa, F.; Hayashi, T.; Koide, H.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1991**, 1469-70.

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These systems¹⁰ represent a rare example of a living alternating copolymerization.¹¹ The living nature of the polymerization has been verified by demonstrating a linear relationship between $\langle M_n \rangle$ and the degree of monomer conversion together with $\langle M_w \rangle / \langle M_n \rangle$ values for **1** which approach 1.0. Figure 1 illustrates data for a typical polymerization carried out at 4 atm of CO with Phen-**3** as catalyst. The compatibility of these catalysts with a variety of functional groups and the presence of readily modified carbonyl groups suggest that a variety of functionalized polymers with well-defined structures and narrow molecular weight distributions will be accessible.

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Supplementary Material Available: Details of synthesis and listings of spectral data for **1**, Bipy-**3**, Phen-**3**, **4**, **4***, **5σ**, **5π**, **5***, **6a**, **7**, and **7*** and listing of ¹³C NMR data for chain growth experiments **5** → **6a** → **6b** → **6c** (14 pages). Ordering information is given on any current masthead page.

(10) Other chlorobenzene-soluble co- and terpolymers prepared using these catalysts include norbornene/CO, styrene/ethylene/CO, styrene/propylene/CO, and *p*- and *m*-methylstyrene/CO.

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[Ru(η^5 -C₅Me₅)(η^5 -C₅F₅)]: The First Transition-Metal Complex Containing a Perfluorocyclopentadienyl Ligand

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Since the discovery of ferrocene,¹ the η^5 -cyclopentadienyl ligand and its substituted analogues have become the most ubiquitous in organometallic chemistry, and many derivatives are now readily accessible.² While most cyclopentadienyl complexes are prepared by reaction of the appropriate cyclopentadiene or cyclopentadienyl anion with a suitable transition-metal complex, the first perhalocyclopentadienyl complexes were prepared by repetitive metalation/halogenation exchange reactions.³ A subsequent approach to complexes containing η^5 -C₅X₅ (X = Cl, Br, I) ligands has involved reactions of diazotetrahalocyclopentadienes with the appropriate metal halide,⁴ and permercuration/perhalogenation of ferrocene has also been used to prepare perhaloferrocenes.⁵

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