

# Palladium(II)-Catalyzed Terpolymerization of Alkane- $\alpha,\omega$ -Dinitrite Esters, Alkenes, and Carbon Monoxide to Polysuccinates

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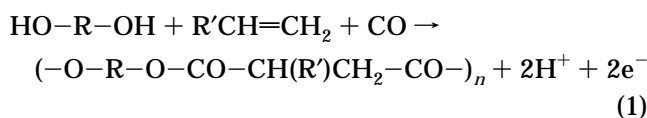
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Aliphatic polysuccinates in the molecular weight ( $M_w$ ) range of 1,000–11,000 were produced from alkane- $\alpha,\omega$ -dinitrites, alkene, and carbon monoxide using bis(benzonitrile)palladium(II) chloride as a homogeneous catalyst. The alkane dinitrites may be synthesized from the corresponding aliphatic diols by reaction with either aqueous nitrous acid or nitrogen oxides. Nitric oxide, given off as a byproduct during polymerization, can be recycled to produce additional monomer.

## Introduction

Polysuccinates are specific type of polyester<sup>1</sup> containing a two-carbon chain between the carbonyl groups of the ester functionality. Present interest in polysuccinates, such as poly(tetramethylene succinate) (trade-name, Bionelle), derive from their biodegradability, ionic conductivity, and high mechanical strength when crystalline.<sup>2</sup>

Current synthetic routes to polysuccinates entail polycondensations involving the reaction of either succinyl chloride, succinic acid, or succinic esters with diols.<sup>3</sup> Thus, the procedures employ relatively expensive organic compounds as the source for the carbonyl functionality. In principle, it should be possible to replace these simply with carbon monoxide under oxidative conditions (eq 1). Such a pathway would be

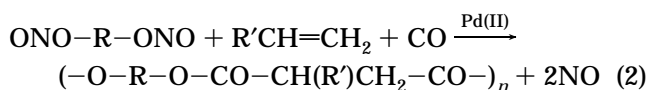


particularly attractive for the synthesis of substituted polysuccinates due to the high price differential between the succinate precursor and the corresponding  $\alpha$ -alkene.

The preparation of succinate esters from alcohols and alkenes by oxidative carbonylation using a palladium-based catalytic system has been reported.<sup>4</sup> However, these systems are not catalytic with respect to palladium and/or require the use of a cocatalyst (mercury or iron salts). Even where the process is catalytic, low yields result from catalyst deactivation due to interaction with water, which is formed as a byproduct. An alternative route to succinic esters would be the reaction

between alkane- $\alpha,\omega$ -dinitrites, alkene, and carbon monoxide.<sup>5</sup> In this procedure, nitric oxide would be the only byproduct and can be reused to synthesize the alkyl nitrite from the corresponding alcohol.

We have previously reported the synthesis of aliphatic polyoxalates through palladium-catalyzed carbonylation of alkane- $\alpha,\omega$ -dinitrites.<sup>6</sup> As described herein, we have now discovered that the addition of alkenes under controlled conditions to the above system resulted in the formation of polysuccinates in accordance with eq 2.



## Experimental Section

**Materials.** Bis(benzonitrile)palladium dichloride,<sup>7</sup> hexane-1,6-dinitrite,<sup>6</sup> and cyclohexane-1,4-dinitrite<sup>6</sup> were synthesized using literature procedures. All reagents and solvents were dried and degassed using standard inert atmosphere techniques and stored under nitrogen. Carbon monoxide (CP grade, MG industries) and ethylene (CP grade, Air Products) were used without further purification. All other materials were used without further purification.

**General Procedures.** Polymerization reactions were performed in a 125 mL Parr high-pressure stainless steel vessel fitted with a glass liner that was equipped with a magnetic stir bar. The loading and assembly of the reactor was carried out in a glovebox under an inert atmosphere. During reactions, the vessel was heated in an oil bath that was maintained at the stated temperature (usually 80 °C). The IR spectroscopy

(4) (a) Fenton, D. M.; Steinwand, P. J. *J. Org. Chem.* **1972**, *37*, 2034. (b) Heck, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 2712. (c) James, D. E.; Hines, L. F.; Stille, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 1806. (d) Biale, G.; Fenton, D. M.; Olivier, K. L.; Schaeffer, W. D. U.S. Patent 3,381,030, 1968. (e) Medema, D.; van Helden, R.; Kohll, C. F. *Inorg. Chim. Acta* **1969**, *3*, 255.

(5) For previous work on reactions involving monofunctional nitrites, see: (a) Brechot, P.; Chauvin, Y.; Commereuc, D.; Saussine, L. *Organometallics* **1990**, *9*, 26. (b) Umemura, S.; Matsui, K.; Ikeda, Y.; Masunaga, K.; Kadota, T. U.S. Patent 4,234,740, 1980. (c) Umemura, S.; Matsui, K.; Ikeda, Y.; Masunaga, K.; Kadota, T. U.S. Patent 4-138,580, 1979. (d) Umemura, S.; Matsui, K.; Ikeda, Y.; Masunaga, K.; Kadota, T.; Fujii, K.; Nishihara, K.; Matsuda, M. U.K. Patent Appl. 2,024,821, 1979.

(6) (a) Pawlow, J. H.; Sadow, A. D.; Sen, A. *Organometallics* **1997**, *16*, 1339. (b) Pawlow, J. H.; Sadow, A. D.; Sen, A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1996**, *37* (2), 198.

(7) Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic: London, 1985; p 17.

<sup>Ⓢ</sup> Abstract published in *Advance ACS Abstracts*, November 15, 1997.

(1) Reviews: (a) Odian, G. *Principles of Polymerization*; Wiley: New York, 1991; p 123. (b) Seymour, R. B.; Carraher, C. E., Jr. *Polymer Chemistry: An Introduction*; Marcel Dekker: New York, 1988; p 245.

(2) (a) Pranamuda, H.; Tokiwa, Y.; Tanaka, H. *Appl. Environ. Microbiol.* **1995**, *61*, 1828. (b) Ihn, K. J.; Yoo, E. S.; Im, S. S. *Macromolecules* **1995**, *28*, 2460. (c) Ichikawa, Y.; Suzuki, J.; Washiyama, J.; Moteki, Y.; Noguchi, K.; Okuyama, K. *Polymer* **1994**, *35*, 3338. (d) Ueda, A. S.; Chatani, Y.; Tadokoro, H. *Polym. J.* **1971**, *2*, 387. (e) Huang, F.; Wang, X.; Li, S. *J. Macromol. Sci.—Chem.* **1991**, *A28*, 175.

(3) Review: Jedlinski, Z. J. In *Handbook of Polymer Synthesis*; Kricheldorf, H. R., Ed.; Marcel Dekker: New York, 1992; Part A, p 647.

was done on a Perkin Elmer Series 1600 FTIR spectrometer using KBr pellets or NaCl plates.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were obtained on a 300 MHz Bruker AM-300 spectrometer using  $\text{CDCl}_3$  as the solvent. Molecular weights were determined using a Waters Associates liquid/gel permeation chromatographic system fitted with a column bank containing Styragel HR2 and HR3 GPC columns and a differential refractometer detector. HPLC grade  $\text{CHCl}_3$  (Aldrich) was used as the mobile phase. The samples were calibrated using narrow molecular weight distribution polystyrene standards from Polymer Laboratories (Church Stretton, U.K.), American Polymer Standards (Mentor, OH), and Polymer Standards Service (Silver Spring, MD).

**Synthesis of Poly(hexamethylene succinate).** In a glovebox, a 125 mL Parr high-pressure vessel fitted with a glass liner was charged with the following reactants:  $\text{Pd}(\text{PhCN})_2\text{Cl}_2$  (51 mg, 0.13 mmol), hexane-1,6-dinitrile (1.0 g, 5.7 mmol), 100 psi of CO, 200 psi of  $\text{C}_2\text{H}_4$ , and 5 mL of  $\text{CH}_3\text{NO}_2$ . The reactor was heated in an oil bath at 80 °C for 48 h. The vessel was then cooled to ambient temperature, the excess gases vented, and the vessel opened, revealing a heterogeneous mixture of black Pd precipitate and a light yellow solution. The solution was filtered through Celite, and the precipitate was washed twice with  $\text{CH}_3\text{OH}$  and acetone. The filtrate was concentrated using a rotary evaporator, leaving a light brown oil. The oil was dissolved in a minimal amount of  $\text{CHCl}_3$  and precipitated in 100 mL of  $\text{CH}_3\text{OH}$  at 0 °C. The white solid was stirred overnight, collected by filtration, washed 3 times with cold  $\text{CH}_3\text{OH}$  and 3 times with cold ether, and dried *in vacuo*. Yield: 0.43 g (50%). Anal. Calcd for succinate polymer ( $\text{C}_{10}\text{H}_{16}\text{O}_4$ )<sub>n</sub>: C, 60.00; H, 8.05; Pd, 0.0. Found: C, 58.28; H, 7.57; Pd, 0.16.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 4.07 (4H, t,  $J = 6.6$  Hz), 2.60 (4H, s), 1.73 (4H, br), 1.36 (4H, br).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , ppm): 172.3, 64.8, 30.1, 28.3, 25.1. IR (KBr,  $\text{cm}^{-1}$ ): 2937, 2866, 1726, 1420, 1332, 1162, 991, 668.

**Synthesis of Poly(hexamethylene methyl succinate).** In a glovebox, a 125 mL Parr high-pressure vessel fitted with a glass liner was charged with the following reactants:  $\text{Pd}(\text{PhCN})_2\text{Cl}_2$  (41 mg, 0.11 mmol), hexane-1,6-dinitrile (1.1 g, 6.0 mmol), 23.0 g of propene (150 psi), 5 mL of  $\text{CH}_3\text{NO}_2$ , and 100 psi of CO. The vessel was placed in an oil bath at 80 °C and heated for 48 h. The reactor was then removed from the oil bath and allowed to cool to ambient temperature. Excess gases were vented, and the reaction vessel was opened, revealing a black precipitate and a pale yellow solution. The mixture was filtered through Celite and washed 3 times with  $\text{CH}_3\text{NO}_2$  and then 3 times with acetone. The solution was concentrated using a rotary evaporator, leaving a viscous light brown oil. The oil was dried *in vacuo*. Attempts to precipitate out a solid were not successful. Yield: 1.40 g (92%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 4.00 (4H, t,  $J = 6.5$  Hz), 3.60 (t, terminal  $\text{CH}_2$ ), 2.75 (1H, m), 2.60 (1H, dd,  $J = 5.5, 6.4$  Hz), 2.35 (1H, dd,  $J = 5.5, 13.0$  Hz), 1.50 (4H, br), 1.30 (4H, br), 1.15 (3H, d,  $J = 6.5$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , ppm): 175.3, 171.8, 64.5, 37.5, 35.7, 28.3, 25.5, 16.9. IR (NaCl,  $\text{cm}^{-1}$ ): 2938, 2865, 1733, 1557, 1463, 1258, 1167, 989.

**Synthesis of Poly(hexamethylene ethyl succinate).** In a glovebox, a 125 mL Parr high-pressure vessel fitted with a glass liner was charged with the following reactants:  $\text{Pd}(\text{PhCN})_2\text{Cl}_2$  (40 mg, 0.10 mmol), hexane-1,6-dinitrile (1.0 g, 5.7 mmol), 1-butene (4.1 g, 73 mmol), 5 mL of  $\text{CH}_3\text{NO}_2$ , and 500 psi of CO. The vessel was placed in an oil bath at 80 °C and heated for 36 h. The reactor was then removed from the oil bath and allowed to cool to ambient temperature. Excess gases were vented, and the reaction vessel was opened, revealing a yellowish solution with a black precipitate. The solution was filtered through Celite and washed 3 times with  $\text{CH}_3\text{NO}_2$ . The solution was concentrated using a rotary evaporator, leaving a viscous yellow oil, which was dried *in vacuo*. Attempts to precipitate out a solid were not successful. Yield: 0.88 g (68%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 4.10 (4H, t,  $J = 6.6$  Hz), 3.62 (t, terminal  $\text{CH}_2$ ), 2.72 (2H, m), 2.39 (1H, m), 1.35 (4H, br), 1.13

(2H, m), 1.12 (4H, br), 0.89 (3H, t,  $J = 6.5$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , ppm): 174.8, 172.1, 64.5, 42.6, 35.5, 28.4, 25.6, 24.5, 11.2. IR (NaCl,  $\text{cm}^{-1}$ ): 2938, 2864, 1733, 1558, 1461, 1258, 1166, 986.

**Synthesis of Poly(hexamethylene phenyl succinate).** In a glovebox, a 125 mL Parr high-pressure vessel fitted with a glass liner was charged with the following reactants:  $\text{Pd}(\text{PhCN})_2\text{Cl}_2$  (40 mg, 0.10 mmol), hexane-1,6-dinitrile (1.0 g, 5.7 mmol), styrene (2.0 g, 19.6 mmol), 5 mL of  $\text{CH}_3\text{NO}_2$ , and 500 psi of CO. The vessel was placed in an oil bath at 80 °C and heated for 48 h. The reactor was then removed from the oil bath and allowed to cool to ambient temperature. Excess gases were vented, and the reaction vessel was opened, revealing a yellow solution with a black precipitate. The solution was filtered through Celite and washed 3 times with  $\text{CH}_3\text{NO}_2$ . The solution was concentrated using a rotary evaporator, leaving a viscous yellow oil, which was dried *in vacuo*. Attempts to precipitate out a solid polymer were not successful. Yield: 0.95 g (62%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 7.41 (5H, m), 4.06 (4H, t,  $J = 6.5$  Hz), 3.64 (1H, m), 3.60 (t, terminal  $\text{CH}_2$ ), 3.23 (1H, dd,  $J = 5.5, 16.8$  Hz), 2.65 (1H, dd,  $J = 5.5, 14.8$  Hz), 1.31 (4H, br), 1.13 (4H, br).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , ppm): 172.9, 171.6, 137.8, 128.4, 127.7, 125.8, 64.6, 47.0, 37.6, 32.1, 25.4, 23.2. IR (NaCl,  $\text{cm}^{-1}$ ): 3455, 3062, 2938, 2864, 1731, 1635, 1556, 1454, 1259, 1166, 1071, 991, 986, 853, 767, 700.

**Synthesis of Triblock Poly(succinate-oxalate-succinate).** In a glovebox, a 125 mL Parr high-pressure vessel fitted with a glass liner was charged with the following reactants:  $\text{Pd}(\text{PhCN})_2\text{Cl}_2$  (40 mg, 0.10 mmol), hexane-1,6-dinitrile (1.25 g, 7.1 mmol), 5 mL of  $\text{CH}_3\text{NO}_2$ , and 1000 psi of CO. The vessel was placed in an oil bath at 80 °C and heated for 6 h. After this period, the CO pressure was reduced to 100 psi and 200 psi of ethene was charged. The reaction was removed from the oil bath and allowed to cool to ambient temperature. Excess gases were vented, and the reaction vessel was opened, revealing a pale yellow solution and a black precipitate. The mixture was filtered through Celite and washed 3 times with  $\text{CH}_3\text{NO}_2$ . The solution was concentrated using a rotary evaporator, leaving a light tan solid, which was dried *in vacuo*. Yield: 0.76 g (57%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 4.26 (t,  $J = 6.6$  Hz), 4.07 (t,  $J = 6.5$  Hz), 3.60 (t, terminal  $\text{CH}_2$ ), 2.60 (s), 1.74 (br), 1.57 (br), 1.35 (br).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , ppm): 172.3, 157.9, 66.9, 64.6, 29.0, 28.4, 27.8, 25.5, 25.3. IR (KBr,  $\text{cm}^{-1}$ ): 3443, 2937, 2863, 1743, 1726, 1420, 1166, 992.  $M_n = 1,860$ ,  $M_w = 4,690$ , PDI = 2.5.

**Synthesis of 3,3'-Biisoxazoline.** In a glovebox, a 125 mL Parr high-pressure vessel fitted with a glass liner was charged with the following reactants: hexane-1,6-dinitrile (1.0 g, 5.7 mmol) and 5 mL of  $\text{CHCl}_3$  solvent. The reactor was charged with 500 psi of ethylene and heated in an oil bath at 100 °C for 24 h. After the reactor was cooled to ambient temperature, the excess gas was vented and the vessel opened, revealing a brown-yellow solution. The solution was concentrated on a rotary evaporator, and the product was separated from 1,6-hexanediol byproduct using flash chromatography on a silica column using 50/50 hexane/ethyl acetate as the mobile phase. The product was a white crystalline solid. Mp 170 °C. Yield 0.79 g (99%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 4.52 (4H, t,  $J = 10.4$  Hz), 3.31 (4H, t,  $J = 10.4$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , ppm): 150.9, 70.2, 32.8. IR (KBr,  $\text{cm}^{-1}$ ): 3002, 2890, 1550, 1467, 1424, 925, 872, 825.

## Results and Discussion

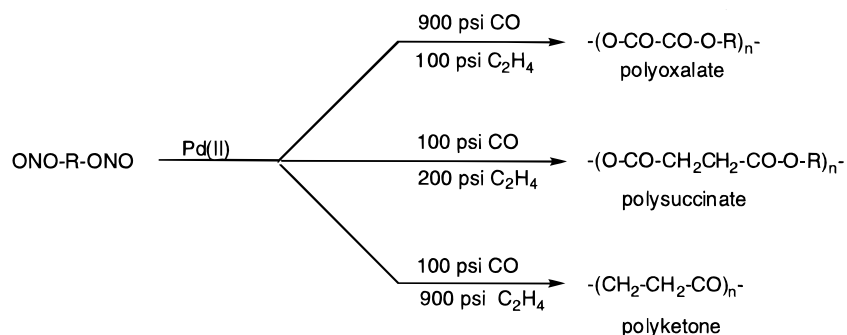
Our results on the palladium(II)-catalyzed synthesis of polysuccinates are summarized in Table 1. The  $^1\text{H}$  NMR spectra of the polymers, as synthesized, exhibited both nitrite and alcohol end groups, the latter due to the decomposition of the nitrite functionality. Upon work-up, all the nitrite end groups were converted to

**Table 1. Palladium(II)-Catalyzed Synthesis of Polysuccinates<sup>a</sup>**

Monomer	Alkene <sup>b</sup>	Solvent	Conversion <sup>c</sup> %	TON <sup>d</sup>	M <sub>n</sub> <sup>e</sup>	M <sub>w</sub> <sup>e</sup>	PDI <sup>e</sup>
	=	CH <sub>3</sub> NO <sub>2</sub>	50	23	5,910	10,680	2.0
	=	CH <sub>3</sub> NO <sub>2</sub>	12	7	4,350	5,800	1.3
	=	CH <sub>3</sub> NO <sub>2</sub>	50	25	2,030	4,450	2.2
	=	CH <sub>3</sub> CN	71	36	1,860	4,690	2.5
	=	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	30	12	1,050	2,730	2.6
		CH <sub>3</sub> NO <sub>2</sub>	92	50	1,180	2,530	1.8
		CH <sub>3</sub> NO <sub>2</sub>	68	34	990	3,290	1.9
		CH <sub>3</sub> NO <sub>2</sub>	62	35	700	1,330	1.9
		CH <sub>3</sub> NO <sub>2</sub>	16	8	760	1,320	1.7

<sup>a</sup> General conditions: alkane dinitrite, 1.0–1.25 g; Pd(PhCN)<sub>2</sub>Cl<sub>2</sub>, 40–50 mg; solvent, 5 mL; CO, 100 psi; 80 °C oil bath; 36–48 h. <sup>b</sup> Ethene, 200 psi; other alkenes, 2–23 g. <sup>c</sup> Based on alkane- $\alpha,\omega$ -dinitrite employed; for reactions involving ethene, it was based on isolated solid polymer. <sup>d</sup> Turnovers with respect to Pd. <sup>e</sup> Relative to narrow molecular weight polystyrene standards.

### Scheme 1. Polymer Product Obtained as a Function of the Alkene:Carbon Monoxide Ratio



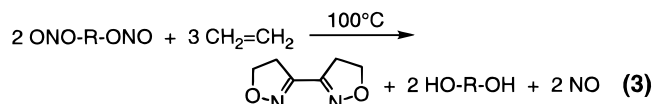
the corresponding alcohol. However, this opens up the possibility of further modifications and extensions of the polymers through additional reactions of the termini.

As discussed below, the system was sensitive to a number of reaction variables, with the formation of polysuccinate occurring only under a specific set of conditions.

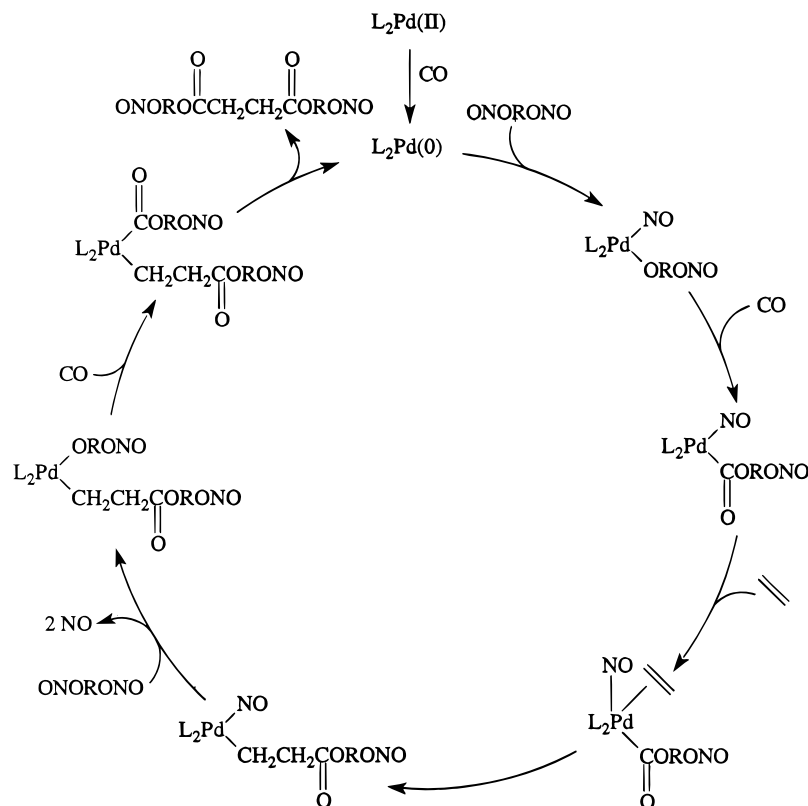
**Catalyst.** The most effective catalyst for the synthesis of polysuccinates, regardless of the alkene used, was Pd(PhCN)<sub>2</sub>Cl<sub>2</sub>. No other palladium(II) complex examined was able to produce comparable yields of product. Thus, cationic Pd(II) complexes, such as [Pd(CH<sub>3</sub>CN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub>, [Pd(PPh<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, and [Pd(dppp)(CH<sub>3</sub>CN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> (dppp = 1,3-bis(diphenylphosphino)propane), were not effective catalysts. Additionally, several palladium(II) complexes that were effective catalysts for the oxidative carbonylation of alkane- $\alpha,\omega$ -dinitrites to polyoxalates,<sup>6</sup> such as Pd(acac)<sub>2</sub> and Pd(PPh<sub>3</sub>)<sub>2</sub>(OAc)<sub>2</sub>, were not optimal for polysuccinate synthesis. Several research groups have suggested that the presence of chloride ions was essential for optimal yields for this class of reactions.<sup>4</sup> However, palladium(II) chloride was not effective, nor was the complex Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, most likely due to the former's limited solubility and the latter compound's lack of easily dissociable ligands. It

is possible that the effectiveness of Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> was due to the ideal combination of high solubility and labile ligands.

**Reaction Temperature.** The choice of reaction temperature was critical to the formation of polysuccinates. At lower temperatures (< 60 °C), catalyst reactivity was poor and only low yields of dimers and trimers were formed; a significant quantity of the alkane dinitrite also remained unreacted after 48 h. The optimal (oil bath) temperature was determined to be 80 °C, at which the highest molecular weight and highest yields were obtained. At temperatures above 80 °C, the polymer yield dropped precipitously for ethene. At elevated temperatures, the byproduct, 3,3'-biisoxazoline, was formed via a thermal reaction between the alkane dinitrite and ethene (eq 3).<sup>5a</sup> Quantitative yield of the



3,3'-biisoxazoline byproduct occurred even in the absence of palladium and carbon monoxide. This reaction, however, did not occur with higher  $\alpha$ -alkenes.

**Scheme 2. Proposed Mechanism for Palladium(II)-Catalyzed Synthesis of Polysuccinates**

**Alkene:Carbon Monoxide Ratio.** As shown in Scheme 1, varying the alkene:carbon monoxide ratio had a dramatic effect on the type of polymer formed. When equal amounts of ethene and carbon monoxide were used (100 psi of CO, 100 psi of ethene), very low molecular weight oligomers consisting of a mixture of carbonate and succinate linkages formed. When the ethene pressure was doubled to 200 psi under identical reaction conditions, polysuccinates were formed exclusively. Thus, a 2:1 alkene:carbon monoxide ratio was optimal for polysuccinate synthesis. A large ratio of ethene:carbon monoxide (900 psi of ethene, 100 psi of CO) resulted in the formation of the alternating ethene-carbon monoxide copolymer in moderate yield (420 mg). A variety of palladium(II) complexes are known to catalyze the formation of this copolymer.<sup>8</sup> Finally, under excess carbon monoxide (900 psi of CO, 100 psi of ethene), polyoxalate was formed exclusively. This is consistent with our previous report on palladium(II)-catalyzed polyoxalate synthesis.<sup>6</sup> Presumably, polysuccinate formation did not take place due to the preferential coordination of carbon monoxide to the metal when it was in excess.

From the above observations, it is clear that an unprecedented degree of control over which specific polyester linkage is made can be achieved through careful selection of the alkene:carbon monoxide ratio. This is illustrated by the synthesis of a triblock polymer containing both polyoxalate and polysuccinate segments. The polyoxalate segment was formed first by carbonylation of hexane-1,6-dinitrite under a high pressure of carbon monoxide.<sup>6</sup> The resultant polymer contained reactive RONO groups at the two ends, which

were utilized to initiate further polymerization. After 6 h under high pressure of carbon monoxide (1000 psi), the pressure was reduced to 100 psi and 200 psi of ethene was added. This resulted in the formation of polysuccinate blocks on either end of the polyoxalate segment. The integration of the  $^1H$  NMR ( $CDCl_3$ ) spectrum revealed the presence of succinate and oxalate linkages in the ratio of 60:40. The formation of a triblock polymer was confirmed by gel permeation chromatography which showed a unimodal polymer distribution, indicative of a single polymeric species ( $M_n = 1,860$ ,  $M_w = 4,690$ , PDI = 2.5).

**Alkene- $\alpha,\omega$ -dinitrite and Alkene Employed.** Variation in alkene structure had a significant impact on both the molecular weight and the properties of the polymer formed. Ethene was the most reactive alkene, yielding the highest molecular weight product ( $M_w = 10,700$ ). This polymer was a powdery, white solid material. Powder X-ray diffraction and DSC analysis indicated that the polymer was amorphous and low-melting (mp = 66.5 °C), respectively. The use of  $\alpha$ -alkenes, such as propene, 1-butene, styrene, and allylbenzene, resulted in the formation of polymers that were low molecular weight viscous liquids ( $M_w = 1,000$ –3,500). The decreased reactivity of these alkenes is most likely due to their decreased tendency to coordinate to the metal and/or due to their reduced insertion rates compared to ethene (see Scheme 2). The liquid state of the polymers derived from  $\alpha$ -alkenes is attributable to both low molecular weight and interference in chain packing by the substituent.

Since the polysuccinate synthesis is a condensation polymerization, high monomer purity is also essential for the formation of long polymer chains. The hexane-1,6-dinitrite used was approximately 98.5% pure, as

(8) Reviews: (a) Sen, A. *Acc. Chem. Res.* **1993**, *26*, 303. (b) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663.

determined by  $^1\text{H}$  NMR spectral integration. On the basis of monomer purity, the highest degrees of number average polymerization ( $X_n$ ) expected is 65 (based on  $X_n = 1/(1 - p)$ ). However, this equation assumes equal amounts of bifunctional monomers with identical reactivities. Using ethene as the alkene, we observed a maximum degree of polymerization of approximately 40. On the other hand, the use of  $\alpha$ -alkenes led to a lower degree of polymerization due their reduced reactivity.

**Mechanism.** The mechanism of palladium(II)-catalyzed reactions of alkenes with alkyl nitrites and carbon monoxide has been investigated by Chauvin and co-workers.<sup>5a</sup> On the basis of this work and that of

Waller,<sup>9</sup> a possible mechanism for polysuccinate synthesis is shown in Scheme 2. It has been established that a Pd(0) species is the active carbonylation catalyst, and we believe that the Pd(II) precursor is reduced *in situ* by carbon monoxide.

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(9) Waller, F. J. *J. Mol. Catal.* **1985**, *31*, 123.