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Palladium(II)-Catalyzed Carbonylation of Alkane Dinitrite Esters to Polyoxalates

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Summary: Aliphatic polyoxalates in the molecular weight (M_w) range of 5000−15 000 were produced from alkane α,ω-dinitrites and carbon monoxide, using a homogeneous palladium(II)-based catalytic system. The alkane dinitrites were 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.

Polyoxalates are an interesting class of polymers with two adjacent carbonyl groups in the repeating unit. They currently are under study as bioabsorbable materials.[1] Several methods are currently employed for the synthesis of polyoxalates, and these involve the reaction of either oxalyl chloride, oxalic acid, or oxalic esters with diols.[2] 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).

$$\text{HO-R-OH} + 2\,\text{CO} \longrightarrow (\text{-O-R-O-CO-CO-})_n + 2\,\text{H}^+ + 2\,e^- \tag{1}$$

The preparation of carbonate and oxalate esters from alcohols by oxidative carbonylation using transition metal catalysts has been widely reported.[3] However, catalyst deactivation occurs over time due to interaction with the water which is formed as a byproduct. An alternative route is the carbonylation of alkane nitrites using heterogeneous palladium(0) catalysts.[4] In the latter procedure, nitric oxide is the only byproduct and can be reused to synthesize the alkane nitrite from the corresponding alcohol.

We report here a new procedure for the synthesis of aliphatic polyoxalates based on palladium-catalyzed carbonylation of alkane α,ω-dinitrites derived from α,ω-diols (eq 2). These reactions, both homogeneous and heterogeneous, were performed in a variety of solvents and were catalyzed by several palladium species. Decomposition of the nitrite functionality occurs with some regularity at elevated temperatures due to protonolysis and thermal homolytic cleavage of the O−NO bond, resulting in the formation of alcohol end-groups and release of nitric oxide.[5] However, this opens up the possibility of further modifications and extensions of the polymers through additional reactions of the termini.

$$\text{ONO-R-ONO} + 2\text{CO} \xrightarrow{\text{Pd(II)}} (\text{-O-R-O-CO-CO-})_n + 2\,\text{NO} \tag{2}$$

Experimental Section

Materials. The reagents 10% palladium on carbon, palladium acetylacetonate, and bis(triphenylphosphine)palladium acetate (Aldrich) were dried under vacuum. Bis(benzonitrile)palladium dichloride was synthesized using a literature preparation.[6] Toluene (Aldrich) was dried with sodium/benzophenone. Nitromethane (Aldrich) and chloroform (Fisher) were dried using CaH_2 and P_2O_5, respectively, and vacuum distilled. All reagents and solvents were stored under nitrogen. Carbon monoxide CP grade (MG Industries) was 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 vessel fitted with a glass liner and assembled in a glovebox under an inert atmosphere. The IR spectroscopy was done on a Perkin-Elmer Series 1600 FTIR spectrometer using KBr pellets or NaCl plates. ^{1}H and ^{13}C{^{1}H} NMR spectra were obtained on a 300 MHz Bruker AM-300 spectrometer using $CDCl_3$ as the solvent. Differential scanning calorimetry was performed using a Perkin-Elmer DSC 7 calorimeter. Powder X-ray diffraction of the polymer samples was performed using a Philips X'Pert X-ray diffractometer. Molecular weight determination was performed using a Waters Associates liquid/gel permeation chromatographic system fitted with an Ultrastyragel 10^3 Å GPC column and a differential refractometer detector. HPLC grade chloroform (Aldrich) was used as the mobile phase. The samples were calibrated using narrow molecular weight distribution polystyrene standards from Polymer Laboratories

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[1] Johnson, R. A.; Shalaby, S. W. In *Polymers of Biological and Biomedical Significance;* Shalaby, S. W., Ikada, Y., Langer, R., Williams, J., Eds.; American Chemical Society: Washington, DC, 1994; p 202.

[2] Review: Jedlinski, Z. J. In *Handbook of Polymer Synthesis*; Kricheldorf, H. R., Ed.; Marcel Dekker: New York, 1992; Part A, p 666.

[3] (a) Review: Shaikh, A.-A. G.; Sivaram, S. *Chem. Rev.* **1996**, *96*, 951. (b) Fenton, D. M.; Steinwand, P. J. *J. Org. Chem.* **1974**, *39*, 701. (c) Ugo, R. In *Catalysis in C1 Chemistry*; Keim, W., Ed.; D. Reidel: Dordrecht, The Netherlands, 1983; p 156. (d) Romano, U. S. *Chim. Ind. (Milan)* **1993**, 75. (e) Rivetti, F.; Romano, U. Eur. Pat. Appl. EP. 534,545, 1992. (f) Delledonne, D.; Rivetti, F.; Romano, U. *J. Organomet. Chem.* **1995**, *488*, C15. (g) Rivetti, F.; Romano, U. *Chim. Ind. (Milan)* **1980**, *62*, 7. (h) Cavinato, G.; Toniolo, L. *J. Organomet. Chem.* **1993**, *444*, C65. (i) Romano, U.; Tesei, R.; Mauri, M. M.; Rebora, P. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 396. (j) Watanabe, E.; Murayama, K.; Ida, K.; Wada, K.; Kasori, Y. Eur. Pat. Appl. EP 532,861, 1993. (k) Morris, G. E.; Oakley, D.; Pippard, D. A.; Smith, D. J. H. *J. Chem. Soc., Chem. Commun.* **1987**, 410. (l) Gaffney, A. M.; Leonard, J. J.; Sofranko, J. A.; Sun, H.-N. *J. Catal.* **1984**, *90*, 261. (m) Burk, P. L.; Van Engen, D.; Campo, K. S. *Organometallics.* **1984**, *3*, 493. (n) Chen, G.-S., Cheng, H.-D.; Yan, H.-M.; Xue, B. *J. Nat. Gas. Chem.* **1993**, *4*, 321. (o) Graziani, M.; Uguagliati, P.; Carturan, G. *J. Organomet. Chem.* **1971**, *27*, 275.

[4] (a) Review: Jiang, X.-Z. *Plat. Met. Rev.* **1990**, *34*, 178. (b) Nishimura, K.; Uchiumi, S.; Fujii, K.; Nishihira, K. *Am. Chem. Soc., Prep. Div. Pet. Chem.* **1979**, *24*, 355. (c) Nishimura, K.; Fujii, K.; Nishihira, K.; Matsuda, M.; Uchiumi, S. U.S. Pat. 4,229,591, 1980. (d) Nishimura, K.; Fujii, K.; Yamashita, M.; Itatani, H. U.S. Pat. 4,229,589, 1980. (e) Waller, F. J. *J. Mol. Catal.* **1985**, *31*, 123. (f) Shiomi, Y.; Matsuzaki, T.; Masunaga, K. U.S. Pat. 4,874,888, 1989. (g) Tahara, S.; Fujii, K.; Nishihira, K.; Matsuda, M.; Mizutare, K. U.S. Pat. 4,461,909, 1984. (h) Tahara, S.; Fujii, K.; Nishihira, K.; Matsuda, M.; Mizutare, K. U.S. Pat. 4,467,109, 1984.

[5] (a) Nussbaum, A. L.; Robinson, C. H. *Tetrahedron* **1962**, *17*, 35. (b) Allen, A. D. *J. Chem. Soc.* **1954**, 1968.

[6] Heck, R. F. *Palladium Reagents in Organic Syntheses;* Academic: London, 1985; p 17.

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(Church Stretton, U.K.). Elemental analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN).

Synthesis of Hexane 1,6-Dinitrite. Alkane α,ω-dinitrites derived from water-soluble diols were synthesized using a procedure modified from that in the literature.[7] A 150 mL aqueous solution of 1,6-hexanediol (10.0 g, 85 mmol) and sodium nitrite (12.8 g, 186 mmol) was prepared. A 6 N HCl solution (31 mL) was added dropwise to the mixture over 30 min at 0 °C. A green liquid formed at the bottom of the flask. The product alkane dinitrite was extracted using three 10 mL portions of CH_2Cl_2. The CH_2Cl_2 solution changed to yellow after being washed with 5% $NaHCO_3$. The alkane dinitrite solution then was dried over anhydrous Na_2SO_4. The solvent was removed, and the monomer was purified by vacuum distillation (bp 30 °C at 1 mmHg), yielding a clear yellow liquid which was stored under nitrogen. Yield: 14.0 g (96%). ^{1}H NMR ($CDCl_3$) (ppm): 4.65 (t), 1.67 (br), 1.39 (br). ^{13}C NMR ($CDCl_3$)(ppm): 68.0, 28.8, 25.4. IR (NaCl) (cm^{-1}): 2945 (s), 2864 (s), 1641 (s), 1601 (s), 1461 (m), 1304 (m), 971 (m), 789 (s).

Synthesis of Butane 1,2-Dinitrite. The synthesis of alkane dinitrites containing functionalities on adjacent carbons must be performed with additional caution due to increased tendency of decomposition. A 50 mL aqueous solution of 1,2-butanediol (4.8 g, 54 mmol) and sodium nitrite (8.2 g, 118 mmol) was prepared. A 6 N HCl solution (20 mL) was added dropwise to the mixture over 15 min at 0 °C. A green liquid formed at the bottom of the flask. The product alkane dinitrite was extracted using three 25 mL portions of CH_2Cl_2. The CH_2Cl_2 solution changed to yellow after being washed with 5% $NaHCO_3$. The alkane dinitrite solution then was dried over anhydrous Na_2SO_4. The solvent was removed, and the monomer was purified by vacuum distillation (bp 24 °C at 1 mmHg), yielding a clear yellow liquid which was stored under nitrogen. Yield: 3.9 g (50%). ^{1}H NMR ($CDCl_3$) (ppm): 5.56 (m), 4.92 (d), 1.79 (m), 0.96 (t). ^{13}C NMR ($CDCl_3$) (ppm): 78.8, 69.1, 24.3, 9.5. IR (NaCl) (cm^{-1}): 2976 (s), 2885 (m), 1662 (s), 1464 (m), 1349 (m), 1127 (w), 1053 (m), 989 (m), 920 (s), 770 (s).

Synthesis of Cyclohexane 1,4-Dinitrite. An alternative synthetic route to the alkane dinitrite was required when the diol precursor had limited solubility in water. A solution of 1,4-cyclohexanediol (20.0 g, 172 mmol) in 100 mL of CH_2Cl_2 was prepared and cooled to 0 °C in an ice bath. Brown nitrogen oxide gas (NO_2), generated by mixing NO and O_2 at room temperature, was bubbled into the diol solution for 20 min, when the solution turned dark green. The organic solution was washed with three 20 mL portions of ice water and 5% $NaHCO_3$ to remove impurities. After drying of the solution over Na_2SO_4, the solvent was evaporated, leaving a clear yellow liquid. The product was purified by several extractions into benzene since it was not possible to perform vacuum distillation due to decomposition. Yield: 27.0 g (79%). ^{1}H NMR ($CDCl_3$) (ppm): 5.41 (br), 2.05 (m), 1.80 (m). ^{13}C{^{1}H} NMR ($CDCl_3$) (ppm): 75.4, 28.1, 27.8. IR (NaCl) (cm^{-1}): 2950 (s), 2870 (m), 1640 (s), 1448 (m), 1375 (s), 1266 (w), 1070 (m), 781 (s).

Synthesis of Poly(1,6-hexamethylene oxalate). In a glovebox, a 125 mL Parr high-pressure vessel fitted with a glass liner was charged with the following reactants: Pd(acac)$_2$ (25 mg, 0.08 mmol), hexane 1,6-dinitrite (1.5 g, 8.5 mmol), and 5 mL of $CHCl_3$ solvent. The reactor then was charged with 1000 psi of CO and heated in an oil bath at 100 °C for 24 h. After cooling of the sample to ambient temperature, the CO was vented and the vessel opened, revealing a clear solution, black Pd precipitate, and brown-yellow mixture of nitrogen oxides. The black precipitate was filtered out and washed with $CHCl_3$. The solvent was evaporated using a rotary evaporator, leaving a light tan solid. Purification of the polymer was achieved by dissolving the solid in a minimal quantity (1 mL) of $CHCl_3$ and precipitating it with 150 mL of CH_3OH. After it had been stirred overnight, the solid turned white, at which point it was collected by filtration and dried *in vacuo*. Yield: 1.0 g (70%). Anal. Calcd for pure oxalate polymer $(C_8H_{12}O_4)_n$: C, 55.80; H, 7.03; Pd, 0.0. Found: C, 55.05, H, 7.24; Pd, 0.18. ^{1}H NMR ($CDCl_3$) (ppm): 4.26 (t), 1.74 (br), 1.42 (br), 3.62 (t, OH end groups). ^{13}C{^{1}H} NMR ($CDCl_3$) (ppm): 157.8, 66.8, 28.0, 25.2. IR (KBr) (cm^{-1}): 3473 (w), 2939 (m), 2869 (m), 1751 (s), 1475 (w), 1225 (s), 1182 (s). Mp: 66.5 °C.

Synthesis of Poly(1,4-cyclohexanediyl oxalate). In a glovebox, Pd(acac)$_2$ (50 mg, 0.16 mmol), cyclohexane 1,4-dinitrite (1.7 g, 9.9 mmol), and 5 mL of $CHCl_3$ were placed into a Parr bomb and pressurized with 1000 psi of CO. The reactor was heated at 100 °C for 24 h. After cooling and venting of gases, the bomb was opened, revealing a dark brown solution and black precipitate. The Pd metal was filtered off, and the solution was concentrated to 1 mL using a rotary evaporator and added dropwise to 300 mL of CH_3OH, precipitating the oxalate polymer. After it had been stirred overnight, the off-white solid was collected by filtration, washed with CH_3OH and ether, and dried *in vacuo*. Yield: 0.7 g (43%). Anal. Calcd for pure oxalate polymer $(C_8H_{10}O_4)_n$: C, 56.47; H, 5.88; Pd, 0.0. Found: C, 54.95, H, 6.15; Pd 0.0. ^{1}H NMR ($CDCl_3$) (ppm): 5.05 (br), 2.15 (m), 1.80 (br), 3.80 (br, OH end groups). ^{13}C{^{1}H} NMR ($CHCl_3$) (ppm): 157.3, 73.6, 26.9, 26.8. IR (KBr) (cm^{-1}): 3473 (w), 2954 (w), 2872 (w), 1736 (s), 1449 (m), 1304 (m), 1178 (s). Mp: 139.6 °C. Note that the calculated elemental analysis is for a polymer with *only* oxalate linkages and does not account for the presence of some carbonate linkages and end-groups.

Synthesis of 2-Oxo-4-ethyl-1,3-dioxolane. In a glovebox, a 125 mL Parr high-pressure vessel fitted with a glass liner was charged with the following reactants: Pd(acac)$_2$ (25 mg, 0.08 mmol), butane 1,2-dinitrite (1.0 g, 6.9 mmol), and 5 mL of $CHCl_3$ solvent. The reactor then was charged with 1000 psi of CO and heated in an oil bath at 100 °C for 24 h. After cooling of the sample to ambient temperature, the CO was vented and the vessel opened, revealing a brown solution, black Pd precipitate, and brown-yellow mixture of nitrogen oxides. The black precipitate was filtered out and washed with $CHCl_3$. The solvent was evaporated using a rotary evaporator, leaving a pale yellow oily liquid. Yield: 0.8 g (100%). ^{1}H NMR ($CDCl_3$) (ppm): 4.60 (m), 4.39 (t), 3.95 (t), 1.70 (m), 0.96 (t). ^{13}C{^{1}H} NMR ($CDCl_3$) (ppm): 155.0, 77.9, 68.9, 26.9, 8.4. IR (NaCl) (cm^{-1}): 2975 (s), 2884 (s), 1747 (s), 1553 (m), 1463 (s), 1377 (s), 1306 (s), 1182 (s), 973 (s), 860 (m), 775 (s).

Results and Discussion

The synthesis of aliphatic polyoxalates was performed by carbonylation of alkane dinitrites using a number of palladium-based catalysts in several solvents. The results are shown in Table 1. Moderate to good yields of polymer were obtained by this procedure. Several variables such as catalyst composition, solvent, carbon monoxide pressure, and monomer were examined, and our observations are detailed below.

Catalyst composition proved to be of critical importance to the success of the polymerization. Initial experiments showed that 10% Pd on carbon was an active catalyst but *only* in the absence of solvent. However, the molecular weight of the polymer was limited to around 6000, presumably due the inclusion of the catalyst in the polymer matrix, thereby preventing further reaction. Attempted polymerization in either polar or nonpolar solvents using Pd on carbon failed, only oligomers being formed in low yield. The major part of the monomer decomposed into the original diol starting material, the rest remained unreacted.

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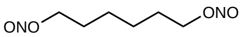
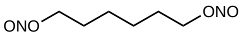
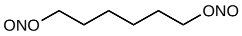
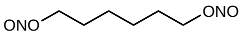
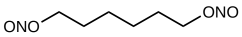
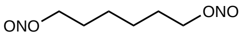
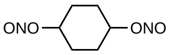
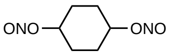
[7] (a) Kuhn, L. P.; Wright, R.; DeAngelis, L. *J. Am. Chem. Soc.* **1956**, *78*, 2719. (b) Kuhn, L. P.; DeAngelis, L. *J. Am. Chem. Soc.* **1954**, *76*, 328.

Table 1. Catalyst and Solvent Effects on Polyoxalate Synthesis[a]

monomer	catalyst[b]	solvent	% yield	turnovers[c]	M_n[d]	M_w[d]	PDI[d]
	10% Pd/C	neat	50	70	3160	6020	1.9
	$Pd(acac)_2$	toluene	82	46	5300	8520	1.6
	$Pd(acac)_2$	$CHCl_3$	71	36	9310	15380	1.7
	$Pd(acac)_2$	CH_3NO_2	30	12	4750	6170	1.3
	$Pd(PPh_3)_2(OAc)_2$	$CHCl_3$	64	54	7560	13210	1.8
	$Pd(PhCN)_2Cl_2$	$CHCl_3$	68	64	3460	6480	1.9
	$Pd(acac)_2$	$CHCl_3$	43	26	3780	5230	1.4
	$Pd(acac)_2$	CH_3NO_2	16	8	4210	5420	1.3

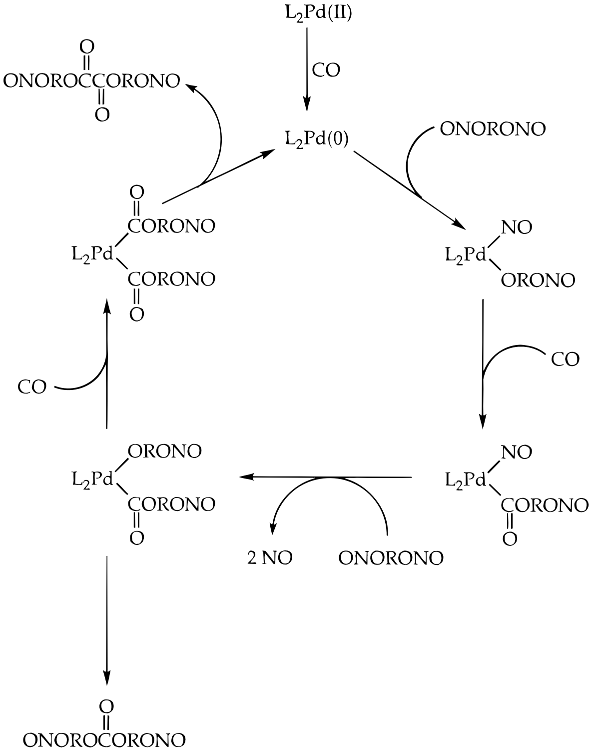
[a] General Conditions: 1.0−1.5 g of alkane dinitrite, 5 mL of solvent, 1000 psi of CO, 100 °C, 24 h. [b] 25 mg of catalyst for hexane-1,6-dinitrite, 50 mg of catalyst for cyclohexane 1,4-dinitrite. [c] Turnovers with respect to Pd. [d] Relative to polystyrene standards.

Failure of polymerization in a solvent using palladium on carbon possibly was due to the inability of the monomer to come into contact with the heterogeneous catalyst with enough frequency to enable polymerization to occur.

Simple palladium(II) salts also proved to be ineffective in producing high polymer. The use of either $PdCl_2$ or $Pd(OAc)_2$ as the catalyst produced oily oligomers in the molecular weight range of 1000. The brown oil, consisting of oligomer, catalyst, dinitrite, and diol, proved to be very difficult to purify. Complexes derived from $PdCl_2$ and phosphine or amine ligands, such as $(PPh_3)_2PdCl_2$, $[Ph_2PCH_2CH_2CH_2PPh_2]PdCl_2$, and [2,2′-bipyridine]$PdCl_2$, showed no catalytic activity. One possible reason for the inactivity of these complexes is the absence of easily dissociable ligand(s) on the metal. Catalysts successfully employed for the synthesis of polyoxalates include $Pd(PhCN)_2Cl_2$, $Pd(acac)_2$ (acac = acetylacetonate) and $(PPh_3)_2Pd(OAc)_2$. The catalytic activity of the latter is surprising since palladium phosphine complexes were reported to be ineffective as catalysts for the reaction between a nitrite ester and carbon monoxide.[4b] The corresponding cationic compound, $[(PPh_3)_2Pd(MeCN)_2](BF_4)_2$, yielded only low molecular weight oligomers under identical reaction conditions.

The reaction system was sensitive to the pressure of carbon monoxide employed. High selectivity toward monocarbonylation (i.e., formation of carbonate linkages) was never observed; instead, a mix of both carbonate and oxalate linkages was produced at lower CO pressures. When CO was bubbled through a solution of the catalyst and monomer, no polymer was produced. Instead, an orange palladium carbonyl complex was formed from the catalyst. The alkane dinitrite did not react in any appreciable extent under these conditions. At 100 psi of CO pressure, monocarbonylation predominated. However, the reaction proceeded in low yield with oily oligomers with molecular weights < 2000. At 500 psi of CO pressure, white, powdery polymer with 92% oxalate linkages (by ^1H NMR analysis) was produced. When the pressure was increased to 1000 psi, carbonate formation was almost completely suppressed; > 97% oxalate linkages were seen in the polymer product as determined by ^1H NMR analysis.

Scheme 1. Proposed Mechanism for Palladium-Catalyzed Carbonylation of Alkane Dinitrites



Solvent effects in the polymerization were significant. The effective catalysts, $Pd(acac)_2$, $Pd(PhCN)_2Cl_2$, and $Pd(PPh_3)_2(OAc)_2$, were soluble in a variety of organic solvents. The liquid dinitrite monomer also was miscible with both polar and nonpolar solvents. As a result, polymerization occurred in various solvents such as toluene, benzene, chloroform, tetrahydrofuran, and nitromethane. However, in some solvents, such as toluene, the molecular weight of the polymer did not exceed 8500, presumably due to precipitation of the polymer. On the other hand, in chloroform, molecular weights ranged up to 15 000 as a result of the high solubility of catalyst, monomer, and polymer. In highly polar nitromethane, a low number of turnovers as well as low molecular weight polymer resulted.

Since the polymerization reaction is essentially step-growth, monomer purity is critical in order to achieve

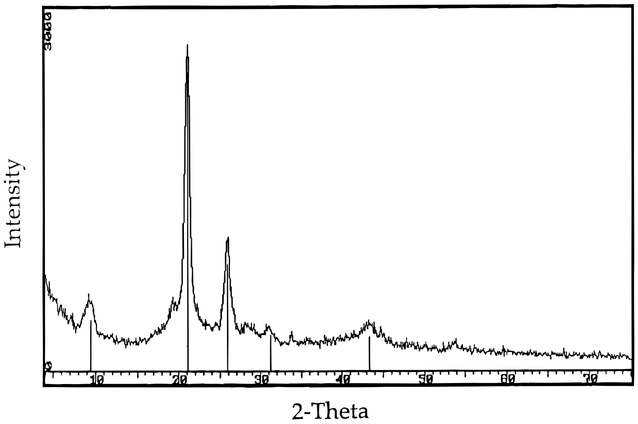
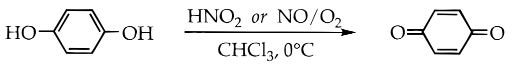


Figure 1. X-ray powder diffraction pattern obtained for poly(hexamethylene oxalate).

a high molecular weight. The purities of hexane 1,6-dinitrite and cyclohexane 1,4-dinitrite used were approximately 98.5% and 96.0%, respectively. The higher boiling nitrites proved to be difficult to purify by distillation since they tend to decompose at higher temperatures. Instead, they were purified by multiple extractions. On the basis of monomer purity, the highest degrees of number average polymerization (X_n) observed (55 and 25, for hexamethylene and 1,4-cyclohexanediyl derivatives, respectively) were close to that calculated from theory (65 and 25, respectively, based on $X_n = 1/(1 - p)$). Presumably, the use of higher purity dinitrites would lead to higher molecular weight polymers in the appropriate solvent.

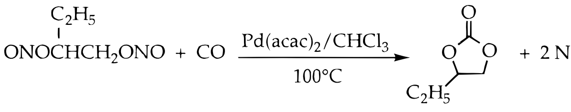
The mechanism of the palladium-catalyzed carbonylation of monofunctional alkane nitrites to oxalate esters has been investigated by several groups, and on the basis of Waller's proposal,[4e] a possible mechanism for the conversion of alkane dinitrites to polyoxalates is shown in Scheme 1. It has been established that a Pd(0) species is the active carbonylation catalyst,[4] and we believe that the Pd(II) precursor is reduced *in situ* by carbon monoxide. The dependence of the ratio of carbonate to oxalate linkages in the backbone on carbon monoxide pressure (vide supra) derives from the competition between reductive elimination versus carbonylation of the Pd(COORONO)(ORONO) species.

Variation in the structure of the alkane dinitrite resulted in dramatic differences in product selectivity, as well as the physical characteristics of the polymer. Use of cyclohexane 1,4-dinitrite as the monomer produced a polyoxalate with a melting point significantly higher than that for a polymer with a linear backbone. The former had a melting point of 139.6 °C as determined by DSC, a significant increase compared to that for a polymer derived from hexane 1,6-dinitrite (66.5 °C). Presumably, this was due to the increased rigidity of the polymer backbone. Powder X-ray diffraction of the polymers showed that the poly(hexamethylene oxalate) was considerably more crystalline than the polymer based on cyclohexane 1,4-dinitrite (Figure 1). Polymers derived from aromatic dinitrites would be expected to be much more crystalline. Unfortunately, the synthesis of aromatic dinitrites using nitrogen oxides or aqueous nitrous acid proved unsuccessful. It has been demonstrated previously that 1,4-hydroquinone is converted to benzoquinone quantitatively by similar oxidative systems (eq 3).[8]



(3)

Carbonylation of butane 1,2-dinitrite did not produce a polymer. Instead, a five-membered cyclic carbonate was produced in quantitative yield under the reaction conditions (eq 4). This result was expected since carbonylation of vicinal diols produces cyclic carbonate esters.[9] The selectivity for this reaction was nearly 100%; no oxalate linkages or cyclic oxalates were produced. It is probable that formation of the ring occurs by reductive elimination from a cyclic intermediate (cf. Scheme 1). This is most likely due to favorable kinetics as well as thermodynamic stability of the ring.



(4)

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[8] (a) Bosch, E.; Rathore, R.; Kochi, J. K. *J. Org. Chem.* **1994**, *59*, 2529. (b) Beake, B. D.; Moodie, R. B.; Sandall, J. P. B. *J. Chem. Soc., Perkin Trans 2* **1994**, 958.

[9] (a) Tam, W. *J. Org. Chem.* **1986**, *51*, 2977. (b) Mizuno, T.; Nakamura, F.; Egashira, Y.; Nishiguchi, I.; Hirashima, T.; Ogawa, A.; Kambe, N.; Sonoda, N. *Synthesis* **1989**, *8*, 636.