Novel Palladium(II)-Catalyzed Direct Synthesis of Polymers with Oxamide and Urea Linkages

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Polyoxamides and polyureas are interesting classes of polymers because the high concentration of hydrogen bonds present results in high melting points and superior mechanical properties. A variety of methods are currently employed for the synthesis of polyoxamides, including interfacial polycondensation and solution techniques, and involve the reaction of either oxalyl chloride, oxalic acid, or oxalic esters with diamines.[1] However, the thermal polycondensation reaction which is the most commonly employed procedure for polyamide synthesis does not work well in this case due to the relatively facile thermal decarbonylation of the oxalate monomer. Polyureas are made either through the reaction of diisocyanates with diamines or by interfacial polycondensation between phosgene and diamines.[2] All of the above 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 (eqs 1 and 2).

$$H_2N\text{-}R\text{-}NH_2 + CO \rightarrow (\text{-}HN\text{-}R\text{-}NHCO\text{-})_n + 2H^+ + 2e^- \quad (1)$$

$$H_2N\text{-}R\text{-}NH_2 + 2CO \rightarrow (\text{-}HN\text{-}R\text{-}NHCOCO\text{-})_n + 2H^+ + 2e^- \quad (2)$$

Herein, we report novel palladium(II)-catalyzed carbonylation of α,ω-diamines leading to the synthesis of (a) polyureas and (b) polymers with *both* oxamide and urea linkages, the relative proportions of which can be varied rationally. The reactions were carried out under an oxidative condition using iodine as promoter.[3] Remarkably, the ratio of oxamide to urea linkages in the resultant polymers was a sensitive function of the added iodine, with the ratio decreasing from 1.5 to 0 with increasing iodine concentration. Unreacted amines constituted the end groups, and, thus, further reactions of the polymers through reactions of the termini should be possible.

Experimental Section. General Procedures. The IR spectroscopy was done on an IBM FTIR-32 spectrometer using KBr pellets. ^{1}H- and ^{13}C{^{1}H}-NMR spectra were obtained on a 300-MHz Bruker spectrometer using CF_3COOD as solvent. The viscometry was performed using an Ubbelohde viscometer with CF_3COOH as the solvent. $\eta_{inh} = \ln \eta_r/c$ (c = 0.5 g/dL at 25 (1) °C).

Synthesis of Polymers with *both* Oxamide and Urea Linkages (Procedure 1). In a glovebox, under nitrogen, the reactants were placed in a glass liner made to fit a 125-mL Parr high-pressure vessel in the following order: $Pd(OAc)_2$ (0.1 mmol, 22 mg), K_2CO_3 (0.2 mmol, 28 mg), Ph_3P (0.2 mmol, 52 mg), 50 mL of THF, followed by 1,6-hexanediamine (3 mmol, 349 mg). The liner was then brought out of the glovebox, and I_2 (0.1 mmol, 25 mg) was added. The liner was then placed in the high-pressure vessel, stirred for 5 min, and O_2 purged through, and then the vessel was charged with 150 psi of O_2. Finally, the vessel was charged to a total of 1000 psi with carbon monoxide. This was kept stirring for 2 h at 100 °C in an oil bath. After 2 h the vessel was removed from the oil bath and allowed to cool to room temperature slowly, usually 15 min. The pressure dropped 400 psi during the reaction. The gray precipitate was filtered off from the maroon liquid and was washed with 75 mL of H_2O, 75 mL of benzene, and 75 mL of THF, leaving a gray solid. This solid was stirred in 50 mL of HNO_3 for 5 min, and then NaCl was added slowly to a total of about 10 mg. The solution turned a bright yellow-orange, and the gray precipitate totally dissolved. This was added to 200 mL of H_2O, and the white yellow precipitate formed was filtered and washed with distilled H_2O followed by THF and dried under high vacuum overnight. Anal. Calcd for polymer with 58% oxamide and 42% urea linkages: C, 58.0; H, 9.2; N, 18.3; I, 0.0; Pd, 0.0. Found: C, 56.5; H, 8.9; N, 16.2; I, 0.04; Pd, <0.1. The results of such experiments are summarized in Table I.

IR (cm^{-1}): 3324 (m), 2926 (s), 2857 (m), 1629 (s), 1573 (m), 1476 (m), and 1252 (m). ^{1}H NMR (ppm): protons on α-carbon next to an oxamide linkage, 3.38; next to a urea linkage, 3.30; next to a terminal amine, 3.26; protons on β-carbon next to an oxamide or urea linkage, 1.62; next to a terminal amine, 1.71; all other protons on methylene groups, 1.34 (br). ^{13}C{^{1}H} NMR (ppm): oxamide, carbonyl, 162.36; α-C, 42.78; β-C, 28.20; γ-C, 30.40; urea, carbonyl, 161.05; α-C, 44.04; β-C, 27.99; γ-C, 30.51; terminal amine, α-C, 42.89; β-C, 28.26; γ-C, 30.30.

Synthesis of Polyureas (Procedure 2). In a glovebox, under nitrogen, the reactants were placed in a glass liner made to fit a 125-mL Parr high-pressure vessel in the following order: K_2CO_3 (0.2 mmol, 28 mg), Ph_3P (0.2 mmol, 52 mg), and 1,8-hexanediamine (3 mmol, 433 mg), followed by 50 mL of THF. The liner was then brought out of the glovebox, and I_2 (3.0 mmol, 761 mg) and $Pd(OAc)_2$ (0.1 mmol, 22 mg) were added. The color was maroon. The liner was placed in the high-pressure vessel and allowed to stir for 5 min. The vessel was then purged with CO three times and finally charged with 1000 psi of CO. The vessel was placed in a hot oil bath at 100 °C overnight, after which it was removed from the bath and allowed to cool slowly for 15 min until it reached room temperature when the pressure was released. The reaction mixture was filtered and washed as with the oxamide–urea polymer. This left a dark brown solid which was not further reprecipitated due to its insolubility in HNO_3. The Pd content of the polymer was found to be <0.3% by analysis. The results of such experiments are summarized in Table II.

IR (cm^{-1}): 3334 (m), 2922 (s), 2847 (s), 1622 (s), 1560 (s), 1462 (s), and 1247 (m). ^{1}H NMR (ppm): protons on α-carbon next to a urea linkage, 3.31; on β-carbon next to a urea linkage, 1.62; on γ- and δ-carbons next to a urea linkage, 1.34; on α-carbon next to a terminal amine, 3.21; on β-carbon next to a terminal amine, 1.76; all other protons on methylene groups, 1.34 (br). ^{13}C{^{1}H} NMR (ppm): urea, carbonyl, 160.77; α-C, 43.84; β-C, 27.98 γ-C, 30.22; δ-C, 30.46; terminal amine, α-C, 43.39; β-C, 27.98; γ-C, 30.33.

Results and Discussion. The oxamide–urea polymer synthesis gave very high turnovers in a short period of time. For example, the reaction of 1,8-hexanediamine gave a rate of 59.7 g of polymer/g of Pd per h and was complete in 2 h. The results are included in Table I. Yields as high as 86% (based on the initial amount of diamine; diamine: catalyst = 30) were attained, with as much as 58% of the linkages being oxamide. A 79% yield was obtained even with a diamine to catalyst ratio of 100.

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Table I
Data on the Synthesis of Polymers with Both Oxamide and Urea Linkages Using an I_2:Pd(II) Ratio of 1

diamine	% yield[a]	% oxam	M_n[b]	DP[b]	η_{inh}[c]	^{13}C-Ox[d]	^{13}C-Ur[d]
1,4	48.0	43.7	1060	8.5	0.11	162.49	
1,6	79.9	58.0	3480	21.2	0.32	162.36	161.05
1,8	75.1	30.0			0.55	162.58	161.18
1,10	85.6	35.8			0.58	162.55	161.11
1,12	79.9	42.2			0.42	162.47	161.05

[a] Yields based on the initial amount of diamine (diamine:catalyst = 30). [b] Number-average molecular weight and degree of polymerization found by integrating the absorbance of protons on an α-carbon. [c] $\eta_{inh} = \ln \eta_r/c$ (c = 0.5g/dL at 25 (1) °C). Samples prepared by dissolving in CF_3CO_2D, filtering, reprecipitating, and then using the proper weight for viscometry. [d] ^{13}C-NMR carbonyl absorbances in ppm.

Table II
Data on the Synthesis of Polymers with Urea Linkages Only Using an I_2:Pd(II) Ratio of 30

diamine	% yield[a]	M_n[b]	DP[b]
1,4	6.9	860	6.4
1,6	89.7	1886	13.5
1,8	61.9	1730	10.3
1,10	96.0	1210	5.2
1,12	88.7	1250	4.6

[a] Yields based on the initial amount of diamine (diamine:catalyst = 30). [b] Number-average molecular weight and degree of polymerization calculated from ^{1}H-NMR spectra.

The pure polyurea synthesis required overnight stirring to give greater than high oligomers. A self-imposed cutoff was utilized in the values for percent yield. All oligomers which were soluble in THF were separated and not counted in the reported figures. The results are summarized in Table II.

Table III and Figure 1 show a remarkable direct correlation between the ratio of iodine to metal and the percent of dicarbonylated (i.e., oxamide) linkages along the polymer chain. Similar results were also observed when *n*-butylamine was used as the model, with the ratio of di-*n*-butyloxamide to di-*n*-butylurea changing from 2.1 to 0.05 as the I_2/Pd(II) ratio was increased from 1 to 30.

Table III[a]
Relationship between the Percentage of Oxamide Linkages in the Polymer and the I_2:Pd(II) Ratio in the Reaction Mixture

I_2 (mol)/Pd (mol)	% oxamide[b]	M_n[b]	DP[b]	% yield[c]
1[d]	58	3480	21.2	79.9
2[d]	43	2520	15.6	74.2
4[e]	30	3040	19.4	79.1
30[e]	0	1886	13.5	89.7

[a] Reactions performed on 1,6-hexanediamine. [b] Calculated from ^{1}H-NMR spectra. [c] Yields based on the initial amount of diamine (diamine:catalyst = 30). [d] Procedure 1 in the Experimental Section. [e] Procedure 2 in the Experimental Section.

Several solvents were employed in order to improve the polymer molecular weight and percent yield. Since the end group in the polymers was the active amine functionality, the molecular weight was only limited by the precipitation of the polymers. The yield decreased in the order THF > CH_3CN > benzene, while M_n was independent of the solvent. The reaction also occurred in the presence of water; however, the yields decreased significantly.

For polymers with molecular weights of less than 3500, ^{1}H NMR proved to be the most reliable method for obtaining the ratio of oxamide to urea linkages. In

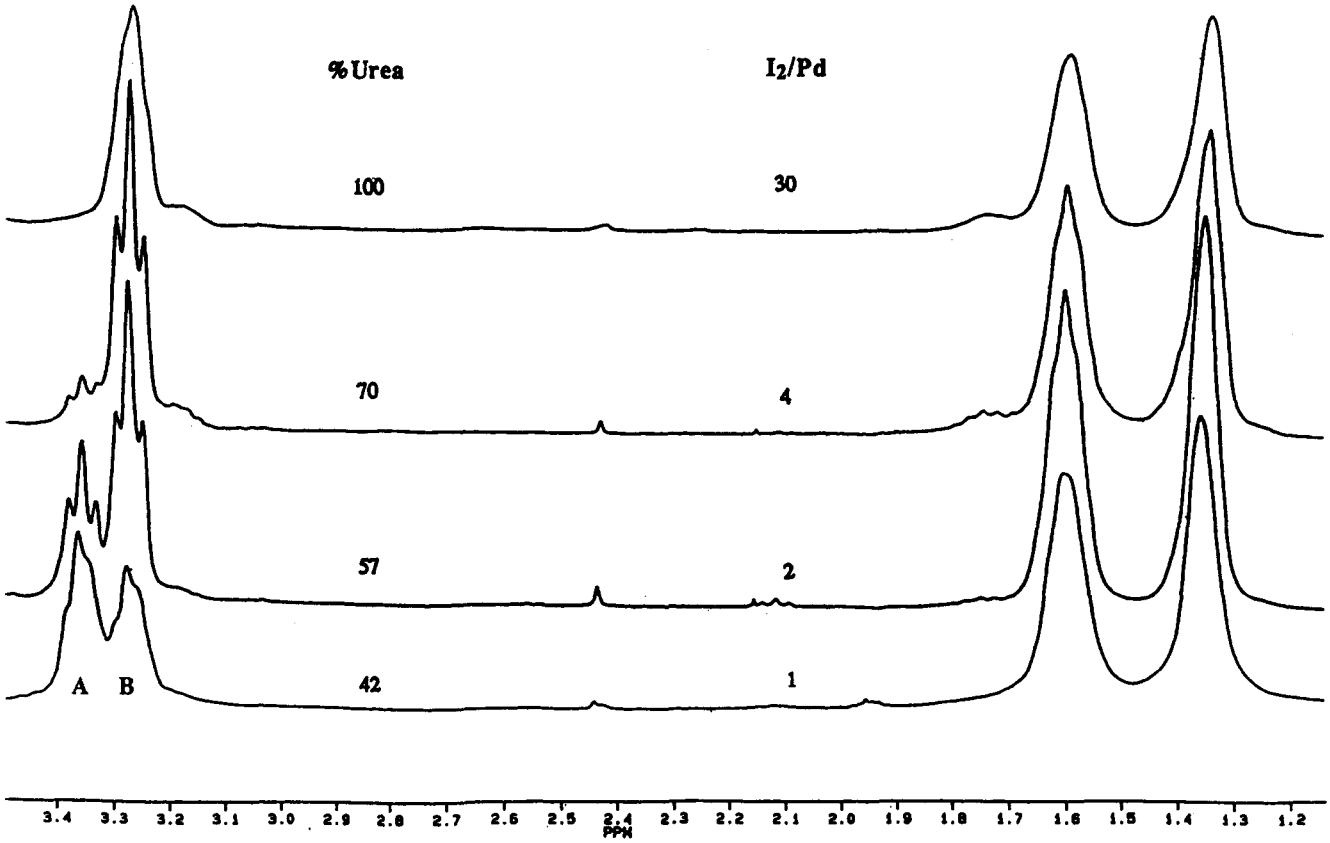

Figure 1. ^{1}H-NMR spectra demonstrating the increase in the ratio of urea to oxamide linkages in the polymer with an increasing iodine to palladium ratio in the reaction mixture. The protons on the α-carbons are labeled "A" for oxamide and "B" for urea linkages.

particular, distinct resonances were observed for the protons on the α-carbon (next to nitrogen) corresponding to oxamide, urea, or the amine end group. With higher molecular weights, the corresponding resonances for the urea and the amine end groups overlapped. End-group analysis by ^{1}H-NMR spectroscopy also provided a means for obtaining number-average molecular weights and degrees of polymerization for the polymers. ^{13}C-NMR spectroscopy does give the advantage of having a greater difference in the chemical shifts of the α-carbon; however, the noise of the base line made the integration unreliable.

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References and Notes

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(3) For related Pd(II)-catalyzed carbonylation of monoamines using iodine as promoter, see: Pri-Bar, I.; Alper, H. *Can. J. Chem.* **1990**, *68*, 1544 and references therein.