Isomunchnone Polymerization. Poly(oxyvinylene)lactams from 1-(2-Chloroacetyl)lactams through a Mesoionic Intermediate

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We wish to report a new type of polymerization of the previously unexplored 1-(2-chloroacetyl)lactams. 1-(2-Chloroacetyl)-caprolactam (**1**) was prepared using a modification of the procedure of Sekiguchi and Courtin.[1,2] Surprisingly, the purified low-viscosity liquid solidified to a glassy solid after 2–3 days at room temperature. The monomer could also be polymerized in a matter of minutes upon heating, with noticeable evolution of gas (HCl). A previous description of the polymerization of simple *N*-acyl lactams employing carboxylic acid initiators and high temperatures gave ring-opened polyamides with *N*-acyl substituents.[3] These structures are completely different from polymers obtained from 2-chloroacetyl monomers.

Figure 1 shows a solid-state ^{13}C NMR spectrum of the polymer resulting from the polymerization of 1-(2-chloroacetyl)caprolactam.[4] Peaks observed in the monomer spectrum for the chloromethylene carbon (47.8 ppm) and one of the monomer carbonyls (177.1 and 168.7 ppm) are absent. Two new resonances appear in the polymer at 98.9 and 80.0 ppm corresponding to the oxyvinylene polymer backbone carbons. The β carbon at 80.0 ppm shows two signals due to *E* and *Z* isomerization similar to that reported for enamine derivatives.[5] The remaining upfield peaks are similar to those of a substituted lactam consistent with unopened rings attached to the α carbon. Further confirmation for the backbone structure comes from ^{1}H NMR. Gradual transformation was observed during polymerization of the exocyclic methylene protons of the chloroacetyl group (a two-hydrogen singlet at 4.51 ppm) to a one-hydrogen singlet at 4.15 ppm (in CDCl$_3$). The calculated value for this proton in the polymer is 4.18 ppm based on published additivity values.[6] Degradation studies of the polymer with refluxing 85% phosphoric acid indicate the formation of 6-aminohexanoic acid and hydroxyethanoic acid. The latter results from side-chain cleavage and isomerization of the formed polymer to poly(oxycarbonylmethylene), which is then degraded to hydroxyethanoic acid. The as-obtained oxyvinylene polymer demonstrated unexpected stability to refluxing methanolic KOH and refluxing benzylamine.

Figure 1. Solid-state ^{13}C NMR spectrum of poly(1-oxy-3-caprolactam vinylene) at 50.2 MHz with cross-polarization/magic angle spinning.

Figure 2. UV spectrum of neat 1-(2-chloroacetyl)caprolactam taken after fresh preparation and 24-, 72-, 96-, and 144-h reaction at ambient temperature.

Scheme I

In addition to the caprolactam-based 2-chloroacetyl derivative, 2-chloroacetyl compounds were prepared from the five-, six-, and eight-membered lactams as well. The 2-piperidone and 2-azacyclooctanone derivatives showed polymerization behavior similar to that of the caprolactam compound, while the 2-pyrrolidinone derivative failed to polymerize even at elevated temperature.

(1) Sekiguchi, H.; Coutin, B. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 1601–1614.

(2) Monomer preparation involved combining caprolactam and chloroacetyl chloride in a 2:1.126 mole ratio in benzene under nitrogen at 5 °C and allowing the solution to come slowly to room temperature and react for 24 h. Filtation of the insoluble caprolactam hydrochloride and evaporation of the benzene gave pure **1** in 85% yield (IR 2934, 2859, 1701, 1697, 1386, 1180, 1150, 980, 967, 779 cm^{-1}; ^{1}H NMR δ 4.51 (2 H, s), 3.78 (2 H, m), 2.69 (2 H, m), 1.70 (6 H, m); ^{13}C NMR δ 177.1, 168.7, 47.8, 43.6, 38.8, 28.8, 28.1, 23.4). Due to its inherent instability, this monomer was not submitted for elemental analysis; however, 1-(chloroacetyl)pyrrolidinone prepared under the same conditions gave the following results: Calcd for C$_6$H$_8$NO$_2$Cl: C, 44.60; H, 4.95; N, 8.67; Cl, 21.98. Found: C, 44.48; H, 4.69, N, 8.68; Cl, 21.05.

(3) Sebenda, J.; Hauer, J. *Polymer* **1979**, *20*, 1305–1306.

(4) Polymerization was carried out using a variety of procedures. Typically 9.94 g of **1** was charged to a 100-mL vacuum flask and heated at 100 °C for 1 h under 0.05 mmHg. The polymer was dissolved in methanol, precipitated into water, collected, and dried; yield, 7.36 g; inherent viscosity (0.5 g/dL in dimethyl sulfoxide), 0.051 dL/g. IR 3528 (br), 2934, 2865, 1703, 1457, 1423, 1368 cm^{-1}; ^{1}H NMR (in trifluoroacetic acid) δ 5.40 (1 H, s), 4.15 (2 H, m), 3.15 (2 H, m), 1.75 (6 H, m); ^{13}C NMR (in methanol, off-resonance decoupling) δ 169.1 (s), 98.9 (s), 80.0 (d), 40.3 (t), 35.3 (t), 29.4 [2 carbons](t), 21.5(t). Anal. Calcd for C$_8$H$_{11}$NO$_2$: C, 62.75; H, 7.19; N, 9.15. Found: C, 60.97, H, 7.16, N, 8.24, Cl, 0.04.

(5) Stradi, R.; Trimarco, P.; Vigevani, A. *J. Chem. Soc., Perkin Trans 1* **1978**, 1–4.

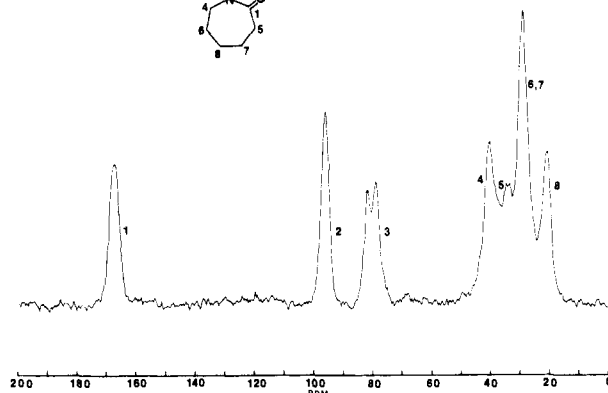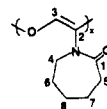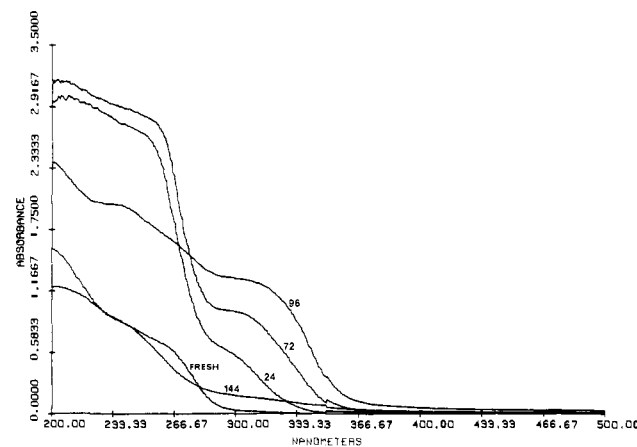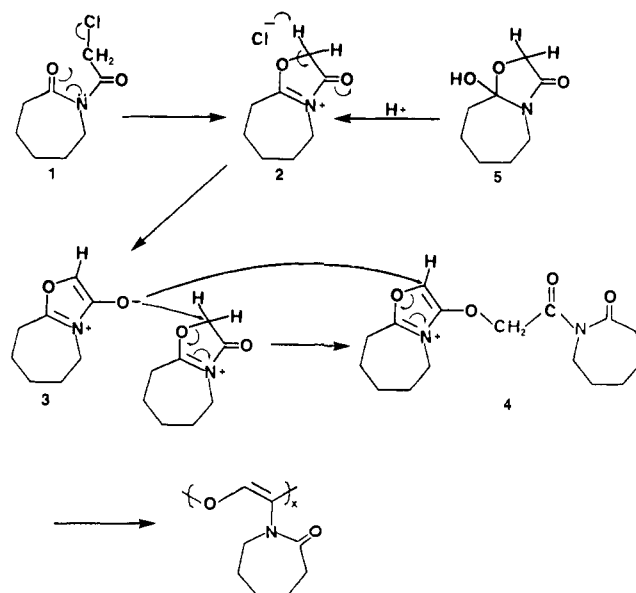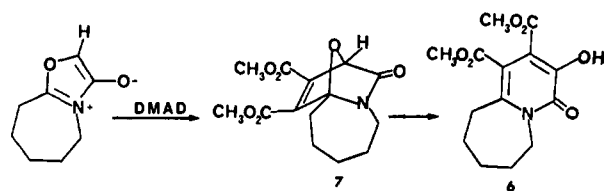(6) Pascual, C.; Meier, J.; Simon, W. *Helv. Chim. Acta* **1966**, 164.

Scheme II

Figure 2 shows the UV spectrum of neat 1-(2-chloroacetyl)-caprolactam taken shortly after preparation and during reaction at ambient temperature. The appearance of bands at 270 and 320 nm is similar to that reported by Griot and Frey, who studied the UV behavior of 7-hydroxy-8-oxa-1-azabicyclo[5.3.0]decanone (5) in sulfuric acid solution.[7] They interpreted the appearance of these bands as indication of the formation of the 5-hydro-1,3-oxazolium 4-oxide intermediate 2 as shown in Scheme I. This compound could also result from cyclization of the 2-chloroacetyl side chain of the 1-(2-chloroacetyl)lactam in an O-alkylation process as shown. We propose that further reaction of 2 with chloride anion and liberation of HCl results in the formation of the mesoionic 1,3-oxazolium 4-oxide or "isomunchnone" 3. Compounds of this type have been reported[8,9] to be unstable and highly reactive in 1,3-dipolar addition reactions with acetylenic and carbonyl compounds and alcohols.[10–12] This isomunchnone was trapped by reacting 1-(2-chloroacetyl)caprolactam with dimethylacetylenedicarboxylic (DMAD).[13] The crystalline product isolated from this reaction proved to be 7,8,9,10,11-pentahydro-3-hydroxy-4,5-bis(methoxycarbonyl)cyclohepta[a]pyridin-2-one (6). This compound results from rearrangement of the 1,3-dipolar cycloaddition product 7 as shown in Scheme II. The proposed polymerization process shown in Scheme I involves O attack of the isomunchnone 3 on the hydro-1,3-oxazolium 4-oxide 2 followed by successive propagation steps involving Michael-type addition of the isomunchnone 2 to the unsaturated moiety 4. To our knowledge, this represents the first reported polymerization involving a mesoionic 1,3-oxazolium intermediate.

The caprolactam-based polymer is white to yellow in color and has inherent viscosities of 0.07 to 0.03 dL/g (0.5 g/dL in dimethyl sulfoxide) depending upon the polymerization temperature. The 2-piperidone-based polymer is deep red in color, and the 2-aza-cyclooctanone-based polymer is yellow-gold.[14] Viscosities of these polymers are comparable to those of the caprolactam polymers. All polymers are soluble in a wide variety of organic solvents including methanol, benzene, and tetrahydrofuran. They are insoluble in water, appear to be noncrystalline, and do not possess

(7) Griot, R. G.; Frey, A. J. *Tetrahedron* **1963**, 1661–1673.

(8) Hamaguchi, H.; Ibata, T. *Tetrahedron Lett.* **1974**, 4475–4476.

(9) Potts, K. T.; Marshall, J. *J. Chem. Soc., Chem. Commun.* **1972**, 1000.

(10) Hamaguchi, H. *J. Chem. Soc., Chem. Commun.* **1978**, 247–248.

(11) Hamaguchi, H.; Ibata, T. *J. Chem. Soc., Chem. Commun.* **1980**, 230–231.

(12) Potts, K. T.; Marshall, J. L. *J. Org. Chem.* **1979**, 44, 626–628.

(13) Freshly prepared 1-(chloroacetyl)caprolactam, 6.00 g (0.0317 mol), was combined with 6.75 g (0.0475 mol) of DMAD and heated for 2 h at 80 °C under moderate vacuum. The ether-insoluble fraction was recrystallized from methanol to yield 1.56 g of 6 (16.7%): mp 200–201 °C; IR 3213, 1729, 1644, 1609, 1440, 1251, 1230 cm⁻¹; UV 315 nm (ε 9.2 × 10³), 277 (9.1 × 10³), 220 (1.5 × 10⁴); ¹H NMR δ 9.85 (1 H, s; exchanged D₂O), 4.37 (2 H, m), 3.74, 3.68 (6 H, s) 2.94 (2 H, m), 1.65 (6 H, m); ¹³C NMR (off-resonance decoupling) δ 166.3 (s), 165.4 (s), 157.9 (s), 143.6 (s), 142.0 (s), 117.7 (s), 107.2 (s), 52.4 (q), 43.8 (t), 28.8 (t), 28.2 (t), 27.0 (t), 26.2 (t). Long-range C–H coupling and COSY were used to assign the structure unambiguously. Anal. Calcd for C₁₄H₁₇NO₆: C, 56.95; H, 5.76; N, 4.75. Found: C, 56.82; H, 5.90; N, 4.82.

(14) The color experienced in some of the polymers is reflected in broad UV absorbances centered at 280 and 340 nm which are found in samples of caprolactam and azacyclooctanone polymers prepared at high temperature only. They are presumably due to side reactions of the polymer as it is formed. For the 2-piperidone-based polymer, the red color is seen in samples prepared at ambient and elevated temperature and cannot be removed by extraction. The 1-(2-chloroacetyl)piperidone monomer showed strong absorbances at 280 and 375 nm even after 2-months storage at ambient temperature. This may be indicative of a highly stabilized isomunchnone chain end or intermediate for this particular monomer.

sufficient molecular weight to form films or fibers. Further work is needed to confirm the proposed polymerization mechanism and improve product molecular weights.

Structure and Reactivity of [Ti{Ru(CO)₂(C₅H₅)}(NMe₂)₃]: A Direct Early–Late-Transition-Metal Bond Formed by Amine Elimination

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Condensation reactions in which a small molecule is eliminated have been recommended as a facile method for the preparation of heteronuclear metal–metal bonds.[1] We are exploring amine elimination (eq 1) as a potential method for forming bonds between early and late transition metals.

$$M-NR_2 + M'-H \rightarrow M-M' + R_2N-H \qquad (1)$$

early and late transition metals. Lappert and co-workers reported that Mo–Ti bonds were formed by reactions of [MoH(CO)₃(Cp)] with [Ti(NMe₂)(OCHMe₂)₃] or [Ti(NMe₂)(Cp)₂]₂.[2] However, in our hands [MoH(CO)₃(Cp)] invariably leads to "isocarbonyl" (Σ-CO)[3] linkages of the type Mo–CO–M$_{early}$, as illustrated by the structure of [Zr{(μ-CO)Mo(CO)₂(Cp)}₂(NEt₂)₂(NHEt₂)]₂,[4a] and many related compounds.[4b] We report here the first unambiguous example of a direct bond between an early and a late transition metal formed by amine elimination.

A solution of 2.35 mmol of [RuH(CO)₂(Cp)] (prepared from 0.50 g of [Ru₃(CO)₁₂] and excess cyclopentadiene)[5] in ca. 150 mL of n-heptane was gradually added to 0.50 g (2.23 mmol) of [Ti(NMe₂)₄].[6] The resulting yellow solution was stirred for 6 h at room temperature, filtered to remove a slight cloudiness, and then reduced to an oil and dried in vacuo for ca. 12 h. A minimum of toluene was added to dissolve the product, which crystallized upon concentration. Washing with a small amount of cold heptane and drying in vacuo gave 0.40 g (45%) of yellow [Ti{Ru(CO)₂(Cp)}(NMe₂)₃] (I).[7]

Spectroscopic characterization, particularly the absence of an infrared absorption at ca. 1600 cm⁻¹,[3] suggested formation of a direct Ru–Ti bond. This was confirmed by an X-ray diffraction study.[8] A plot of the structure of I is presented in Figure 1, and

(1) (a) Roberts, D. A.; Geoffroy, G. L. "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 6, Chapter 40, pp 763–877. (b) Gladfelter, W. L.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1980**, 18, 207. (c) Bruce, M. I. *J. Orgmet. Chem.* **1983**, 257, 417.

(2) (a) Cardin, D. J.; Keppie, S. A.; Lappert, M. F. *J. Chem. Soc. A* **1970**, 2594. (b) Lappert, M. F.; Sanger, A. R. *J. Chem. Soc. A* **1971**, 1314.

(3) Horwitz, C. P.; Shriver, D. F. *Adv. Orgmet. Chem.* **1984**, 23, 219.

(4) (a) Sartain, W. J.; Selegue, J. P. *Organometallics* **1984**, 3, 1922. (b) For [Zr{(μ-CO)Mo(CO)₂(Cp)}(Me)(Cp)₂] [Zr[(μ-CO)Mo(CO)₂(Cp)]-(Me)(Cp)₂] was prepared by methane elimination from [Zr(Me)₂(Cp)₂] and [MoH(CO)₃(Cp)]. Longato, B.; Martin, B. D.; Norton, J. R.; Anderson, O. P. *Inorg. Chem.* **1985**, 24, 1389.

(5) Humphries, A. P.; Knox, S. A. R. *J. Chem. Soc., Dalton Trans.* **1975**, 1710.

(6) Bradley, D. C.; Thomas, I. M. *J. Chem. Soc.* **1960**, 3857.

(7) Spectroscopic and physical data for I: mp 82–84 °C; IR (heptane) 1972 (s), 1911 (s) cm⁻¹; ¹H NMR (C₆D₆, 90 MHz) δ 4.81 (s, 5 H, Cp), 3.12 (s, 18 H, NMe₂); mass spectrum, m/e 403 (M⁺), 375 (–CO), 347 (–2CO), 360 (–CO, –CH₃), 332 (–2CO, –CH₃), 224 ([Ru(CO)₂(Cp)]).