TABLE VII The Effect of Catalyst/Initiator Stoichiometry on Intercept Values for Equation 7

Catalyst (initiator)	-Intercept, [C] [I]	$mol/l. \times 10^{3}$ [C] <sup>1/2</sup> [I]
Bromomagnesium caprolactan	n	
(N-acetylcaprolactam)	-6.7	+0.2
Sodium caprolactam (N-carbanilinocaprolactam)	-0.3	+0.5
Sodium caprolactam (N-acetylcaprolactam)	-2.5	+0.1

Reevaluation of the data using eq 7 resulted in positive intercepts and  $K_d$  values. As further verification, two sodium caprolactam catalyzed polymerizations were run at 100° with N-acetylcaprolactam as the initiator (Figure 9). The resulting changes in intercept values are summarized in Table VII.

These facts suggest that two imide functions occupy coordination sites around one catalyst molecule and lead to the conclusion that there may be simultaneous growth of two polymer molecules from a catalyst site if an initiator/catalyst ratio of 2 is employed. If ratios of less than 2 are employed or the polymer chain with its imide end group is removed from the catalyst, degradative and branching<sup>12</sup> processes should be

(12) E. H. Mottus, R. M. Hedrick, and J. M. Butler, *Polym. Preprints*, **9**, 390 (1968). Papers presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

enhanced due to the ability of the polymer amide groups to compete more favorably with monomer for coordination sites than they could with imide functions.

Activation Energies. From the reaction path scheme it is expected that polymerization activation energies should be essentially identical for a given catalyst after the initial addition to an initiator species. This was not found to be true for sodium caprolactam with N-carbanilinocaprolactams and N-acetylcaprolactam. This anomaly may be explained in part by a coordination mechanism. The urea end group formed from the carbanilinoimide would more readily coordinate with the catalyst than the amide end group resulting from the N-acyllactam. At temperatures higher than  $120^{\circ}$ it has been shown<sup>13</sup> that disubstituted ureas react with the catalyst to form an imide and an amine, the latter acting as a polymerization modifier.

## Conclusions

Although this kinetic equation does not specifically account for all of the many possible side reactions and equilibria, <sup>1, 4</sup> it does satisfactorily describe the initiated, anionic polymerization of  $\epsilon$ -caprolactam with regard to the rate-determining steps.

Acknowledgment. We wish to thank Dr. R. M. Hedrick for his encouragement.

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# Polyimides. Synthesis and Polymerization of 4-Carboxy-2-piperidone

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ABSTRACT: A new polyimide, poly[(2,5-dioxo-1,3-pyrrolidinediyl)dimethylene], has been obtained by thermal polymerization of 4-carboxy-2-piperidone, which was synthesized from dialkyl itaconate *via* cyanomethyl succinate. A possible mechanism of polymerization is discussed that involves isomerization of the 4-carboxy-2-piperidone and step-growth polymerization of the isomerization product.

**R** ecent reports from this laboratory have been concerned with synthesis and polymerization of  $\beta$ -carboxymethylcaprolactam.<sup>1-4</sup> The corresponding polymer was identified as a poly[(2,6-dioxo-1,4piperidonediyl)trimethylene],<sup>2</sup> the formation of which has been explained by a mechanism that involved an initial isomerization of the caprolactam derivative to a reactive species and subsequent polymerization of the

latter by condensation.<sup>8</sup> Since to our knowledge this type of mechanism was unique in the area of condensation polymerization, it was of interest to determine the scope of this new polymerization process. A research program concerned with the study of lactams containing carboxylic functions has therefore been initiated. In this paper we shall report on the synthesis and polymerization of 4-carboxy-2-piperidone.

## Discussion

Monomer. The synthesis of 4-carboxy-2-piperidone (IV) consisted of the addition of hydrogen cyanide to dialkyl itaconate I and reductive cyclization of the resulting dialkyl cyanomethylsuccinate II to afford

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<sup>(3)</sup> H. K. Reimschuessel, Advances in Chemistry Series, American Chemical Society, Washington, D. C., in press.
(4) H. K. Reimschuessel, J. P. Sibilia, and J. V. Pascale,

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the corresponding 4-alkoxycarbonyl-2-piperidone III which upon saponification yielded the monomer IV (Scheme I). The structure of IV was verified by ele-



mental and spectral analyses and by comparison of IIIa with an authentic sample obtained by a modification of a method previously reported by Takahashi and Kariyone.<sup>3</sup> This multistep preparation, commencing with 4-ethylpyridine, resulted in extremely low yields. The reactions according to Scheme I, in contrast, resulted in high yields; the reductive cyclization of II afforded III in excess of 85%. Apparently, the formation of the piperidone III was more highly favored than that of the possible isomer, 3-alkoxycarbonylmethyl-2-pyrrolidone (V).

Polymer. IV polymerized readily by heating to temperatures above its melting point ( $\sim 175^{\circ}$ ). The polymerization proceeded rapidly both in the presence and absence of an inert solvent, and did not require any catalyst. Since it is known that six-membered lactams polymerize satisfactorily only when a combination of a strong base and an acylating agent was used as a catalyst,6 and that most substituted six-membered lactams did not polymerize at all,7.8 this polymerization can not be explained by one of the mechanisms that govern the conversion of the known lactams to polyamides. Considering the structure of IV, it was therefore reasonable to assume that the mechanism for this polymerization was analogous to that considered for the polymerization of  $\beta$ -carboxymethylcaprolactam.<sup>3</sup> The principal features of this mechanism consisted of an initial isomerization of the lactam and polymerization by condensation of the isomerized product. Thus, the isomerization may be an internal molecular rearrangement that involves a single monomer molecule according to Scheme II, in which this reaction may or may not



be acid catalyzed. Alternatively, it may involve proton

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transfer between two intramolecular protonated monomer molecules as shown in Scheme III.



The chain growth (polymerization) may then proceed by the known condensation reaction between the anhydride and amine functions and may involve either or both the amide-acid or iminolactone as intermediates, In analogy with the polymer derived from  $\beta$ -carboxymethylcaprolactam, this polymer must therefore be a poly[(2,5-dioxo-1,3-pyrrolidinediyl)dimethylene] having a repeat unit of the structure (Scheme IV).



Both infrared and nmr spectra of the obtained polymer were consistent with this structure. There were no absorptions indicating the presence of either or both NH and COOH groups. The polymer was found to be soluble in solvents such as formic acid, m-cresol, trifluoroethanol, and sulfuric acid; it was insoluble in the common organic solvents. The polymer did not show any tendency to crystallize. This was expected because of the presence of a center of asymmetry in the polymer repeat unit. Differential thermal analysis measurements indicated a glass transition temperature of 135° for the dry polymer. Thermal gravimetric analysis measurements showed that the polymer experienced a weight loss of only 1 % at 300° when heated at a rate of 10°/min in either air or nitrogen.

Employing conventional procedures, the polymer was converted into filaments and films which were transparent and exhibited very high tensile strength at relatively low elongation.

In conclusion, this study showed that the principal features identified for the polymerization of  $\beta$ -carboxymethylcaprolactam are also characteristic for the polymerization of 4-carboxy-2-piperidone and that, in all probability, we are dealing here with a more generally applicable concept for the synthesis of a new class of condensation polymers.

### Experimental Section<sup>9</sup>

**Dimethyl Cyanomethylsuccinate (IIa).** To a stirred and cooled solution of 79.0 g (0.5 mol) of distilled dimethyl itaconate in 400 ml of methanol was added dropwise 65.1 g (1 mol) of potassium cyanide in 400 ml of water. After 0.5 hr, 65 ml (0.75 mol) of cold concentrated hydrochloric acid was added. The reaction mixture was stirred at room temperature for 72 hr and then extracted with three portions of ether. The ethereal extracts were combined, dried (MgSO<sub>4</sub>), and condensed. The resulting oil was distilled to afford 71.4 g (77%) of IIa: bp 113–117° (0.8 mm); ir (neat) 2260 (C=N) and 1745 (C=O); nmr (CCl<sub>4</sub>)  $\delta$  2.45–3.40 (m, 5, CH<sub>2</sub>CH(CO)CH<sub>2</sub>), 3.68 (s, 3, OCH<sub>3</sub>), 3.74 ppm (s, 3, OCH<sub>3</sub>).

Anal. Calcd for  $C_{8}H_{11}NO_{4}$ : C, 51.88; H, 5.99; N, 7.57. Found: C, 51.58; H, 5.76; N, 7.76.

**4-Methoxycarbonyl-2-piperidone** (IIIa). Dimethyl cyanomethylsuccinate (46.3 g, 0.25 mol) hydrogenated at 400 psi and 100° for 5 hr using a Raney nickel catalyst (4 g). The solution was filtered to remove catalyst and condensed *in vacuo*. The resulting solid was recrystallized from petroleum ether (bp 30–60°)-methylene chloride to give 33.8 g (85%) of IIIa: mp 126.5–127°; ir (KBr) 1740 (ester C=O), 1665 (lactam C=O), 1640 (C=N);<sup>10</sup> nmr (CDCl<sub>3</sub>)  $\delta$  2.0–3.2 (m, 5, CH<sub>2</sub>CH(CO)CH<sub>2</sub>), 3.36 (m, 2, CH<sub>2</sub>N), 3.73 (s, 3, OCH<sub>3</sub>), 7.86 ppm (s, 1, NH).

Anal. Calcd for  $C_7H_{11}NO_3$ : C, 53.49; H, 7.06; N, 8.91. Found: C, 53.33; H, 7.14; N, 8.92.

**Independent synthesis of IIIa** was accomplished by using a modification of the method of Takahashi and Kariyone.<sup>5</sup> A mixture melting point of samples from the two different routes was undepressed and the infrared spectra of the two samples were superimposable.

**4-Carboxy-2-piperidone (IV).** To a stirred solution of 12.3 g (0.22 mol) of potassium hydroxide in 150 ml of methanol was added 31.4 g (0.2 mol) of 4-methoxycarbonyl-2-piperidone in 150 ml of methanol. The solution was refluxed 6 hr and allowed to stir at room temperature for 16 hr. The solvent was removed *in vacuo*. The resulting solid was dissolved in 50 ml of water, cooled below 0°, and acidified with concentrated hydrochloric acid. Three recrystallizations of the precipitate from ethanol-water yielded 25.5 g (89%) of IV: mp 174.5-5.5°; ir (KBr) 1695 (acid C=O) and 1635 (lactam C=O); nmr (D<sub>2</sub>O)  $\delta$  1.7-3.4 (m, 5, CH<sub>2</sub>CH(CO)CH<sub>2</sub>) and 3.5 ppm (m, 2, CH<sub>2</sub>N).

Anal. Calcd for  $C_6H_3NO_3$ : C, 50.34; H, 6.34; N, 9.79. Found: C, 50.36; H, 6.36; N, 9.60.

**Diethyl Cyanomethylsuccinate (IIb).**<sup>11</sup> As described above for the preparation of IIa, diethyl itaconate (37.2 g, 0.2 mol) was converted to 32.2 g (75%) of IIb: bp 106–109° (0.3 mm); ir (neat) 2265 (C=N) and 1740 (C=O); nmr (CCl<sub>4</sub>)

 $\delta$  1.26 (t, 6, OCH<sub>2</sub>CH<sub>3</sub>), 2.50–3.25 (m, 5, CH<sub>2</sub>CH(CO)CH<sub>2</sub>), 4.11 (q, 2, OCH<sub>2</sub>), 4.16 ppm (q, 2, OCH<sub>2</sub>).

Anal. Calcd for  $C_{10}H_{15}NO_4$ : C, 56.32; H, 7.09; N, 6.57. Found: C, 56.35; H, 7.02; N, 6.53.

**4-Ethoxycarbonyl-2-piperidone (IIIb).** As above for IIIa, 21.4 g (0.1 mol) of IIb afforded 15.4 g (90%) of IIIb: mp  $108-109^{\circ}$ ; ir (KBr) 1740 (ester C=0), 1660 (lactam C=O), 1635 (C=N); nmr (CDCl<sub>3</sub>)  $\delta$  1.27 (t, 3, OCH<sub>2</sub>CH<sub>3</sub>), 1.60-3.10 (m, 5, CH<sub>2</sub>CH(CO)CH<sub>2</sub>), 3.33 (m, 2, CH<sub>2</sub>N) 4.17 (q, 2, OCH<sub>2</sub>) 7.98 ppm (s, 1, NH).

Anal. Calcd for  $C_{3}H_{13}NO_{3}$ : C, 56.12; H, 7.65; N, 8.18. Found: C, 56.16; H, 7.61; N, 8.07.

**Polymerization of IV. 1.** 4-Carboxy-2-piperidone (5 g) and 4 drops (0.2 cc) of water were placed in a  $20 \times 200$  mm Pyrex tube fitted with an 8-mm inlet tube. The tube was swept with nitrogen for 5 min and immersed to a depth of 6 in. in an oil bath maintained at a constant temperature of 220°. After 24 hr the polymerization tube was removed from the bath and allowed to cool at room temperature under a continuous nitrogen sweep. The tube was then broken away from the polymer plug which was ground. After extraction in boiling ethanol with subsequent drying at 100° and 30 mm, the polymer sample exhibited a reduced viscosity value of 0.8, when measured using 0.13 g in 25 cc of *m*-cresol solution at 25°.

The spectral data of the polymer samples were consistent with the polyimide structure: ir (film) 1700–1740 cm<sup>-1</sup> (imide C=O); nmr (15% polymer in formic acid)  $\delta$  1.17–2.13 (m, NCH<sub>2</sub>CH<sub>2</sub>CH), 2.44 (m, COCH<sub>2</sub>) 3.26 ppm (m, NCH<sub>2</sub>).

2. Two 5-g samples of 4-carboxy-2-piperidone were heated at 200 and  $220^{\circ}$ , respectively, for 20 hr, as described above in example 1, and then heated at constant temperature an additional 20 hr under pressure (2 mm). The polymer samples, when subjected to the work-up as described above, gave reduced viscosity values of 1.0 and 1.4, respectively, when measured using 0.13 g in 25 cc of *m*-cresol at 25°. The infrared spectra of these samples were identical with those of polymer from **1**.

**3.** 4-Carboxy-2-piperidone (100 g) was suspended in 2000 cc of dichlorobenzene for 48 hr. Nitrogen was bubbled through the suspension during the active polymerization period. The water formed during the condensation process was removed by refluxing solvent through a Soxhlet apparatus containing anhydrous magnesium sulfate. After cooling the reaction to room temperature, the solvent was decanted and the polymeric material dissolved in formic acid. The resulting solution was filtered and the filtrate added dropwise to ether. The precipitated polymer was washed with ethanol and extracted with boiling ethanol. After drying at 100° and 30 mm, the reduced viscosity of the polymer sample was 0.5, when measured using 0.13 g in 25 cc of *m*-cresol at 25°.

4. 4-Carboxy-2-piperidone (50 g) was polymerized in refluxing trichlorobenzene, as described for the polymerization of example 3. The resulting polymer had a reduced viscosity of 1.5 when measured using 0.13 g in 25 cc of *m*-cresol at 25°. Differential thermal analysis measurements indicated the polymer to have a glass transition temperature of 127°, when heated at a rate of 20°/min. When heated to 250°, quenched and reheated at 20°/min, the glass transition temperature of the polymer sample was 135°. Thermal gravimetric analysis measurements showed that the polymer experienced a 1% weight loss in either air or N<sub>2</sub> at 300°, when heated at a rate of 10°/min.

<sup>(9)</sup> Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were determined with a Perkin-Elmer Model 21 spectrometer either neat or in potassium bromide. Nmr spectra were obtained with a Varian Associates Model A-56/60 spectrometer with tetramethylsilane as the internal standard.

<sup>(10)</sup> This band could be attributed to the tautomeric lactam of III. Similar absorptions have been observed in the ir spectra of other valerolactams and caprolactams.

<sup>(11)</sup> E. Hope [*Proc. Chem. Soc.*, 28, 192 (1912)] has reported the quantitative addition of hydrogen cyanide to diethyl ita-conate.