phenone which was 9×10^{-4} M. The maxima are recorded in Table III.

Transesterification in Ethylene Chloride.—Approximately 0.20 M solutions of ethyl acetate and trifluoroacetic acid were prepared in pure dry ethylene chloride and their spectra were determined in an 0.05-mm. sodium chloride cell with a model 21 Perkin–Elmer infrared spectrophotometer. The ester absorbed at 5.76 μ and the acid at 5.56 μ. Equal volumes of the two solutions were mixed and the spectrum was recorded within two minutes. Carbonyl stretching bands characteristic of acetic acid monomer and dimer appeared near 5.9 μ. From the intensity of the ethyl acetate band before and after reaching equilibrium, and by comparison with known standards, the equilibrium constant $K = [CF_3CO_2Et][CH_3CO_2H]/[CH_3CO_2Et][CF_3CO_2H]$ was evaluated as 0.57. Similar experiments with acetonitrile solutions gave no evidence of transesterification after 12 hours under the same conditions.

Oxidation of Acetone with Trifluoroperoxyacetic Acid.—A solution of trifluoroperoxyacetic acid was prepared from 8.2 ml. (0.3 mole) of 90% hydrogen peroxide, 50.8 ml. (0.36 mole) of trifluoroacetic anhydride and 100 ml. of ethylene chloride. This solution was cooled in an ice-bath while 11.6 g. (0.2 mole) of acetone in 25 ml. of ethylene chloride was added dropwise. The resulting solution was kept at 5–10° for 20 hours and then was allowed to stand 2 hours at room temperature. The excess peracid was destroyed by addition of 30 g. of octene-1. The product, methyl trifluoroacetate, was obtained by careful fractionation of the reaction mixture using a center-rod column equipped with a capacitance controller for automatic take off; 17 g. (70%) of methyl trifluoroacetate, b.p. 42–43°, was obtained.

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Structural Effects on the Polymerization of Lactams

BY H. K. HALL, JR.

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The polymerizability of a number of lactams to polyamides was determined. When combined with literature data, these studies showed that: (1) Water and alkali metal catalysts were equally potent at temperatures above 200° (2) Rings with 8 or 9 members polymerized in all cases studied. About half of those with 7 atoms polymerized, while 6- or 5-membered rings failed to polymerize except in the case of pyrrolidone. (3) Alkyl or aryl substituents on the ring always decreased polymerizability. Hetero atoms in the ring either did likewise or had no effect. A mechanism was proposed for the alkali-catalyzed polymerization which has as its key step the attack of a lactam anion on an N-acyl-lactam chain end. It was suggested that the most important factor determining lactam polymerizability is the rate of cyclization of intermediates to reform the lactam. The intermediate may be aminoacid or acylaminoacid in the water-catalyzed polymerization, or an ω-aminoacyllactam in the alkali-catalyzed polymerization.

The polymerization of cyclic monomers[1] has received less attention than addition and condensation polymerizations. The available information on this subject was summarized by Small[2] and by Dainton and Ivin.[3] The polymerization of lactams, exemplified by the transformation of 6-caprolactam into poly-6-caproamide, forms the subject of this paper.

Two types of catalyst, namely, water and alkali metals or their hydrides, previously found to be effective[4] for the polymerization of lactams, were used in this study. A number of other potential catalysts, for example BF_3-etherate, litharge, etc., were tested but no catalytic activity was observed. However, effective cocatalysts for both the water- and alkali-catalyzed polymerizations were found (see below). In general, polymerization was carried out using molten monomers, since no useful solvents were discovered. The melting points of both lactam and resultant polyamide proved to be limiting factors for successful polymerization. If the melting points were excessively high, decomposition and inadequate contact of monomer and catalyst occurred.

The lactams studied are listed in Table I, the results of previous investigations being included in order to provide as complete a picture as possible of this field at the present time. Some generalizations can be made from the polymerization results summarized in Table I: (1) Water and sodium hydride were equally effective catalysts at temperatures above 200°. At room temperature water was ineffective but sodium hydride was still potent. (2) Ring-opening polymerization of lactams was a restricted technique, the majority of lactams failing to polymerize. (3) Of the five 8- and 9-membered ring compounds examined, all polymerized. Approximately one-half of the various 7-membered ring compounds which have been studied to date polymerized. Of the 6-membered rings, only 2,5-diketopiperazine is known to polymerize to any degree. 2-Pyrrolidinone was the only 5-membered lactam which polymerized. (4) Aryl or alkyl substituents on a ring decrease polymerizability, especially if they are on the nitrogen atom of the lactam. (5) Hetero atoms in a lactam ring either reduce polymerizability or have no effect. (6) Thiolactams (iminethiones) are markedly less prone to polymerize than the corresponding lactams. (7) Decomposition is particularly serious for lactams with hetero atoms β to the carbonyl group.

If a lactam fails to polymerize, the cause may be either an unfavorable equilibrium or a slow rate. We believe that water or alkali metals and their hydrides are sufficiently powerful to establish equilibrium between monomer and polymer, except where decomposition is extensive, at least above 200°. The following paragraphs attempt to show that the

(1) The expression "ring-opening polymerization" applies to polymerization mechanisms in which a ring adds to a growing chain.

(2) P. A. Small, *Trans. Faraday Soc.*, **51**, 1717 (1955).

(3) F. S. Dainton and R. J. Ivin, *Quart. Revs.*, **12**, 82 (1958).

(4) W. E. Hanford and R. M. Joyce, *J. Polymer Sci.*, **3**, 167 (1948).

TABLE I

RESULTS OF POLYMERIZATION EXPERIMENTS

Polymerized	Did not polymerize
	4-Rings
2-Azetidinone[b]	
	5-Rings
2-Pyrrolidinone[c]	1-Methyl-2-pyrrolidinone[a]
	5-Methyl-2-pyrrolidinone[a]
	5,5-Dimethyl-2-pyrrolidinone[a]
	5,5-Pentamethylene-2-pyrrolidinone[a]
	5-Carbethoxy-2-pyrrolidinone[a]
	2-Pyrrolidinethione (d.)[a]
	4-Thiazolidinone[a]
	2-Phenyl-4-thiazolidinone[a]
	2-Phenyl-4-thiazolidinone-1-dioxide[a]
	6-Rings
2,5-Piperazinedione[d]	1,4-Dimethyl-2,5-piperazinedione[a]
	1-Methyl-2,5-piperazinedione[d]
	3,6-Dimethyl-2,5-piperazinedione[d]
	1,4-Diphenyl-2,5-piperazinedione[d]
	2-Piperidone[a]
	3-Morpholone (d.)[a,e]
	3-Thiamorpholone (d.)[a]
	1-Isopropyl-5,5-dimethyl-2,3-piperazinedione[a]
	Benzo-2H-1,4-oxazin-3(4H)-one[a]
	Benzo-2H-1,4-thiazin-3(4H)-one[a]
	7-Rings
2-Oxohexamethylenimine[f]	1-Methyl-2-oxohexamethylenimine[a]
3-Methyl-2-oxohexamethylenimine[g,h]	1-Phenyl-2-oxohexamethylenimine[a]
4-Methyl-2-oxohexamethylenimine[a,g,h]	1-Methylol-2-oxohexamethylenimine[a]
5-Methyl-2-oxohexamethylenimine[a,g,h]	1-Ethylthiomethyl-2-oxohexamethyleninine[a]
6-Methyl-2-oxohexamethylenimine[h]	5-Isopropyl-2-oxohexamethylenimine[h]
7-Methyl-2-oxohexamethylenimine[h]	7-Isopropyl-2-oxohexamethylenimine[h]
5-Ethyl-2-oxohexamethylenimine[h]	5-*n*-Propyl-2-oxohexamethylenimine[h]
2-Hexamethyleneiminethione[i,j]	5-*t*-Butyl-2-oxohexamethylenimine[h]
Endomethylene-2-oxohexamethylenimine[k]	5-Phenyl-2-oxohexamethylenimine[a]
Endoethylene-2-oxohexamethylenimine[k]	5-Cyclohexylmethyl-2-oxohexamethylenimine[h]
	4-Methyl-7-isopropyl-2-oxohexamethylenimine[a]
	5-Methyl-2-hexamethyleneiminethione (d).[a]
	4,6-Dimethyl-2-hexamethyleneiminethione (d.)[a]
	2-Oxo-5-thiahexamethyleneimine (d.)[a]
	2-Oxo-5-thiahexamethyleneimine-5-dioxide (d.)[a]
	1-Benzenesulfonyl-1,4-diazepin-5-one[a]
	2,3-Benzo-1,4,5,6-tetrahydroazepin-7-one[h]
	Perhydro-3,4-benzazepin-7-one[a]
	2,3-Benzotetrahydro-1,4-thiazepin-5-one (d.)[a]
	2,3-Benzotetrahydro-1,4-thiazepin-5-one-1-monoxide (d.)[a]
	2,3-Benzotetrahydro-1,4-thiazepin-5-one-1-dioxide (d.)[a]
	8-Rings
2-Oxoheptamethylenimine[b]	
2-Heptamethyleneiminethione[a,i]	
1,5-Diazacyclooctane-2,6-dione[a]	
	9-Rings
2-Oxooctamethylenimine[f]	
2-Octamethyleneiminethione[a,i]	

[a] Present investigation. The lactams were treated with water at 200° or higher, and with sodium or sodium hydride at several temperatures between the melting point of the monomer and 250°. N-Acetylcaprolactam was added in many of the alkali-catalyzed experiments; (d.) signifies serious decomposition. [b] R. W. Holley and A. D. Holley, THIS JOURNAL, **71**, 2129 (1949). [c] W. O. Ney, Jr., W. R. Nummy and C. E. Barnes, U. S. Patent 2,638,463 (1953); W. O. Ney, Jr., and M. Crowther, U. S. Patent 2,739,959 (1956). [d] A. B. Meggy, *J. Chem. Soc.*, 1444 (1956). [e] R. Leimu and J. I. Jansson, *Suomen Kemistilehti*, **18B**, 40 (1945); *C. A.*, **41**, 769 (1947). [f] D. D. Coffman, N. L. Cox, E. L. Martin, W. E. Mochel and F. J. van Natta, *J. Polymer Sci.*, **3**, 85 (1948); W. E. Hanford and R. M. Joyce, *ibid.*, **3**, 167 (1948); H. R. Mighton, U. S. Patent 2,647,105 (1953). [g] Z. A. Rogovin, E. Khait, I. L. Knunyants and Y. Rymashevskaya, *J. Gen. Chem. U.S.S.R.*, **17**, 1316 (1947); *C. A.*, **42**, 4939 (1948). [h] A. Schäffler and W. Ziegenbein, *Ber.*, **88**, 1374 (1955); W. Ziegenbein, A. Schäffler and R. Kaufhold, *ibid.*, **88**, 1906 (1955). [i] N. L. Cox and W. E. Hanford, U. S. Patent 2,276,164 (1942). [j] Swiss Patents 270,546 and 276,924 (1951); 280,367 (1952). [k] But see C. E. Barnes, W. R Nummy and W. C. Ney, Jr., U. S. Patent 2,806,841 (1957). Repetition of this work gave only material which dissolved instantly in acetone to form non-viscous solutions and therefore was not polymeric.

most important factor influencing the equilibrium is the rate of cyclization to form the lactam. If this is high, the lactam will be favored at equilibrium and no polymer will be formed. If the cyclization rate is low, the polymer becomes the favored form at equilibrium.

The Water-catalyzed Polymerization.—The polymerization of a lactam by water occurs as[5]

$$\text{Lactam} + H_2O \underset{k_c}{\overset{k_H}{\rightleftharpoons}} \text{amino acid } (S_0)$$

$$\text{Lactam} + S_0 \underset{k'_c}{\overset{k_A}{\rightleftharpoons}} S_1$$

$$\text{Lactam} + S_1 \underset{k'_c}{\overset{k_A}{\rightleftharpoons}} S_2, \text{ etc.}$$

(These processes can occur without catalysis or with catalysis by carboxyl ends, and the lactam adds to amine ends.) It would be expected that variations in k_c would be paralleled by variations in k'_c, since both involve cyclization to the same product. Similarly, k_H and k_A would be expected to run parallel in a series of lactams, since the same ring is being attacked in each case.

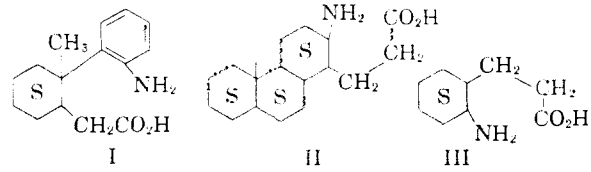
The rates of ring opening of lactams by water have not been studied, but Gordon[6] found that the rates of *alkaline* hydrolysis of lactams did not fall in the same order as their polymerizabilities (Table II). This points to variation in k_c and k'_c as the factor determining whether or not lactams will polymerize. As far as we know, no data on rates of cyclization of amino acids are available in the literature. However, striking differences have been reported for the behavior of amino acids on heating.

TABLE II

CONTRAST OF RATES OF HYDROLYSIS OF LACTAMS BY SODIUM HYDROXIDE AT 75° WITH THEIR POLYMERIZABILITIES

Lactam	Polymerizability	k_2, l. mole^{-1} sec.$^{-1}$ × 10^4
2-Pyrrolidinone	+	1.8
2-Piperidone	--	8.6
2-Oxahexamethylenimine	+	0.83

Some amino acids, such as 9-aminononanoic acid, give only polymer on prolonged heating. This behavior is typical of amino acids which cannot form 5-, 6- or 7-membered lactams on cyclization. In such cases, the cyclization rate is low; and if the lactam could be prepared, it doubtless could be polymerized. Other amino acids form the lactam slowly on prolonged heating. Here the cyclization rate is appreciable, but such lactams might be polymerizable, especially at lower temperatures. Examples of this type are 2-pyrrolidinone and 2,5-diketopiperazine. The rates of cyclization of such amino acids increase with increasing numbers of alkyl or aryl substituents on the ring, especially on the N atom. Finally, many amino acids cyclize to lactams spontaneously at room temperature. This is characteristic of amino acids with alicyclic or aromatic rings fused to the chain, such as I,[7] II[8] and III.[9] In such cases the cyclization rate has become so high that polymerization of the lactam would be difficult, if not impossible, to achieve.[10]



I II III

In every case, therefore, a substituent which increases the ease of cyclization of the amino acid decreases the ease of polymerization of the lactam. This conclusion lends support to our postulate that the magnitude of k_c is the factor determining whether or not a lactam will polymerize, and provides a working basis for the selection of new lactams as potential cyclic monomers.

Substituents enhance the cyclization rate primarily by a conformational effect.[11] The *gauche* conformations of the reactive groups are favored by introducing substituents, especially fused rings, on the intervening chain. In this way, the reactive groups are maintained in favorable positions for the cyclization reaction to occur.

Several effective catalysts for polyamidation reactions have been described in the recent literature.[12-14] These include phosphoric acid, sodium hypophosphite and boric acid. These catalysts in the presence of water polymerized caprolactam to poly-6-caproamide at 180°, at which temperature water alone effected little polymerization. Sodium phosphite and magnesium formate were also effective (Table III).

TABLE III

COCATALYSTS FOR POLYMERIZATION OF 2-OXOHEXAMETHYLENIMINE[a]

Cocatalyst	Polymer yield, %	M.p., °C.	η_{inh} (*m*-cresol)
Phosphoric acid	96	225	0.63
Boric acid	28.5	210	.33
Sodium hypophosphite	45.2	206	.33
Sodium phosphite	33.3	204	.28
Magnesium formate	21.5	202	.23
None	7.0	202	.21

[a] Conditions: 4.0 g. of lactam, 0.05 g. of water and 0.08 g. of cocatalyst heated at 180° for 21 hours.

The Alkali-catalyzed Polymerization.—Ney and Crowther[15] found that N-acyl lactams and other acylating agents enormously accelerated the alkali-catalyzed polymerization of pyrrolidinone to poly-4-butyramide. This interesting discovery provides the clue to the reaction mechanism shown. The essential feature of this mechanism is the attack of the lactam anion on the reactive imide end[16a]; this mechanism explains why N-alkyl

(5) (a) F. Wiloth, *Z. physik. Chem.*, **11**, 78 (1957); (b) P. H. Hermans, address at Brooklyn Polytechnic Institute Polymer Symposium, March, 1958.

(6) M. Gordon, Thesis, Manchester, 1950.

(7) R. A. Barnes and M. T. Beachem, THIS JOURNAL, **77**, 5388 (1955).

(8) B. M. Regan and F. N. Hayes, *ibid.*, **78**, 639 (1956).

(9) K. Bamberger and S. Williamson, *Ber.*, **27**, 1458 (1894).

(10) 5-Aminovaleric acid cyclizes to 2-piperidone about 40° below its interpolated melting point. This apparent enhancement in k_c, if upheld, explains the failure of 2-piperidone to polymerize.

(11) R. F. Brown and N. M. van Gulick, *J. Org. Chem.*, **21**, 1046 (1956).

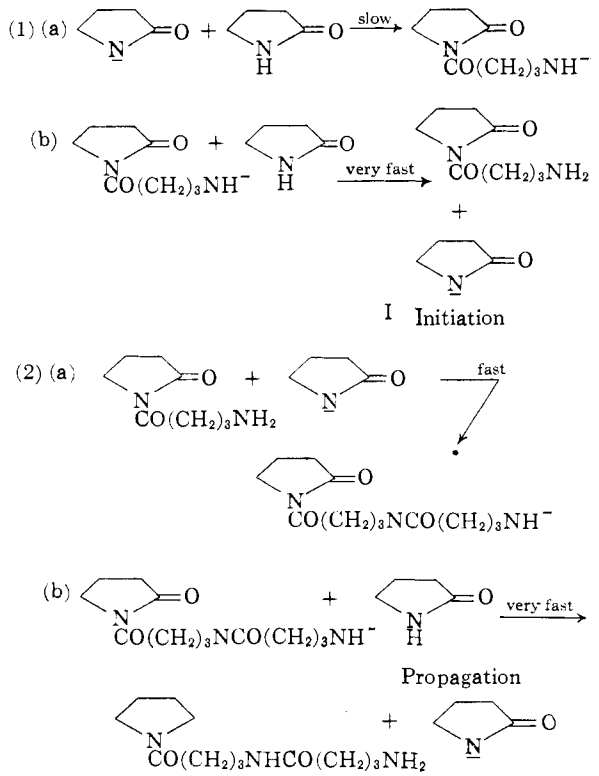
(12) S. W. Fox, *J. Chem. Educ.*, **34**, 476 (1957).

(13) M. Genas, German Patent 846,164 (1952).

(14) D. L. Cottle and D. W. Young, U. S. Patent 2,711,415 (1955).

(15) W. O. Ney, Jr., and M. Crowther, U. S. Patent 2,739,959 (1956).

(16) (a) Previous investigators have written step 2 as attack of the amine anion on the lactam. This overlooks the presence of the



lactams, which cannot form imides, are not polymerized by alkalies.[16a]

This mechanism was expected to apply to other lactams. In fact, it was found that a combination of sodium hydride and N-acetylcaprolactam caused caprolactam to polymerize at temperatures 100° below those required when N-acetylcaprolactam was absent. Curiously, in single experiments N-acyllactams failed to accelerate the polymerization of caprylolactam, but acetic anhydride and benzoyl chloride were effective.

The effect of substituents is to favor cyclization to lactam, thus reversing the polymerization.[17] Substituents will therefore depress polymerizability just as in the water-catalyzed polymerization.

Polymerizability of 5- *vs.* 6-Membered Cyclic Monomers.—Brown, Brewster and Schechter[18] suggested that cyclic carbonyl compounds with six ring atoms were markedly less stable than the corresponding compounds with five ring atoms. They cited the polymerizability of δ-valerolactone, as opposed to the non-polymerizability of γ-butyrolactone, in support of this thesis. The fact that pyrrolidone polymerizes with far more facility than 2-piperidone appears to contradict this generalization.

reactive imide grouping. (b) Since this paper was written, the same mechanism has been postulated by W. R. Nummy, C. E. Barnes and W. O. Ney, Abstracts of 133rd A.C.S. Meeting, San Francisco, Calif., April, 1958, p. 22R; by R. E. Noble, *Diss. Abs.*, **17**, 2823 (1957); Thesis, University of Colorado, 1957; and by J. Sebenda and J. Kralicek, *Coll. Czech. Chem. Comm.*, **23**, 766 (1958).

(17) That the alkali-catalyzed polymerization, at least in the case of 4-nylon, is reversible was shown by Dr. T. W. Campbell (unpublished results, these Laboratories). Heating 4-nylon with a little N-potassium pyrrolidinone under vacuum at 100° caused the complete conversion of the polymer to a distillate of monomeric pyrrolidinone; see also ref. 16b.

(18) H. C. Brown, J. H. Brewster and H. Schechter, THIS JOURNAL, **76**, 467 (1954).

This discrepancy can be rationalized as follows: In the lactones, the resonance is quite small and only one trigonal atom is present in the ring.[19] In the lactams the strong nitrogen–carbonyl interaction gives rise to two adjacent trigonal atoms.[20] The lactams should therefore be compared with the cycloalkenes. It is known that both cyclopentene and cycloheptene are less stable than cyclohexene by 4 kcal.,[21,21a] and this corresponds well to the polymerizabilities of the lactams.

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Experimental

Cyclic Monomers.—5-Methylpyrrolidinone.—γ-Valerolactone, 100 ml., was heated with 150 ml. of liquid ammonia for 4 hours in a bomb at 230°. The dark liquid was placed in a spinning-band flask and heated overnight at 160° to lactonize any hydroxyvaleric acid. Distillation gave 40 ml. of γ-valerolactone, b.p. 56° (0.5 mm.), and 25.7 g. of 5-methylpyrrolidinone, b.p. 81–82° (0.5 mm.), $n^{25}D$ 1.4742. This method gave yields equalling those obtained by hydrogenating levulinic acid in the presence of ammonia,[22] and avoided viscous products and high-boiling resins encountered in the latter preparation.

1-Benzenesulfonyl-1,4-diazepin-5-one.—With cooling, 6.0 g. of ethylenediamine was added to 8.6 g. of methyl acrylate. The mixture was held at room temperature overnight and was distilled; fraction 3 was analyzed.

Fraction	B.p., °C.	Pressure, mm.	Weight, g.
1	97	3.5	1.56
2	90	1.0	3.13
3	120	4.5	1.27

Anal. Calcd. for $C_6H_{14}O_2N_2$: C, 49.3; H, 9.7; N, 19.2. Found: C, 49.8; H, 9.3; N, 19.3.

After 3 weeks at room temperature, fractions 2 and 3 were treated with benzenesulfonyl chloride under Schotten–Baumann conditions to give 0.19 g. of crystals, m.p. 190–191°. Sublimation at 0.3 mm. and 160° raised the melting point to 196–197°. These experiments were reproducible only on this small scale.

Anal. Calcd. for $C_{11}H_{14}O_3N_2S$: C, 51.9; H, 5.5. Found: C, 51.6; H, 5.5.

2,3-Benzo-(1,6,7H)-5-thiazepinone Monoxide.—Oxidation, using 3.6 g. of 2,3-benzo-(1,6,7H)-5-thiazepinone, 13 ml. of acetic acid and 5.8 ml. of 30% H_2O_2, was performed according to Mayer and Horst.[23] On adding 13 ml. of water, a precipitate formed. Recrystallization from 30 ml. of water gave 2.74 g. of white crystals, m.p. 176–177°. Analyses and infrared spectrum showed this to be the sulfoxide, in contrast to Mayer and Horst's results.

Anal. Calcd. for $C_9H_9O_2NS$: C, 55.4; H, 4.7; O, 16.40. Found: C, 55.3; H, 4.6; O, 16.9.

2,3-Benzo-(1,6,7H)-5-thiazepinone Dioxide.—To a solution of 17.9 g. (0.10 mole) of 2,3-benzo-(1,6,7H)-5-thiazepinone in 400 ml. of acetic acid was added with stirring over 12 minutes a solution of 22.2 g. of $KMnO_4$ in 1 liter of water.

(19) Denys Cook (*ibid.*, **80**, 49 (1958)) has given evidence for this view from infrared studies. Further, the C–O–C angle in esters is 112°, almost the tetrahedral angle (P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 52 (1950)).

(20) R. J. Kurland and E. B. Wilson, Jr., *J. Chem. Phys.*, **27**, 585 (1957).

(21) J. G. Traynham and M. F. Sehnert, THIS JOURNAL, **78**, 4024 (1956).

(21a) P. von R. Schleyer, address at Delaware Valley Symposium, Philadelphia, Pa., February 5, 1958; THIS JOURNAL, **80**, 1700 (1958).

(22) A. R. Dunlop and R. Sherman, U. S. Patent 2,681,349 (1954).

(23) L. Mayer and C. Horst, *Ber.*, **56B**, 1415 (1923).

TABLE IV
SOURCES OF MONOMERS

Compound	Physical properties	Source or literature reference
2-Pyrrolidinone	B.p. 138° (20 mm.)	General Aniline and Film
1-Methyl-2-pyrrolidinone	B.p. 78° (10 mm.)	General Aniline and Film
5,5-Dimethyl-2-pyrrolidinone	B.p. 85° (0.40 mm.)	G. D. Buckley and T. J. Elliott, *J. Chem. Soc.*, 1508 (1947), give b.p. 140° (20 mm.)
5,5-Pentamethylene-2-pyrrolidinone	M.p. 133°	R. B. Moffett, THIS JOURNAL, **79**, 3186 (1957), gives m.p. 133°
5-Ethoxycarbonyl-2-pyrrolidinone	M.p. 54°	E. Fischer and R. Boehner, *Ber.*, **44**, 1332 (1911), give m.p. 54°
2-Pyrrolidinethione	M.p. 112–113°	J. Tafel and P. Lawaczek, *ibid.*, **40**, 2842 (1907), give m.p. 116°
4-Thiazolidinone	M.p. 96–97°	Supplied by Dr. W. R. Sorenson, these laboratories
2-Phenyl-4-thiazolidinone	M.p. 126–127°	A. R. Surrey and R. A. Cutler, THIS JOURNAL, **76**, 578 (1954), gave m.p. 126–128°
2-Phenyl-4-thiazolidone-1-dioxide	M.p. 160–161° (d.)	Method of Surry and Cutler, above.
3-Morpholone	M.p. 128–129°	R. Leimu and J. I. Jausson, *Suomen Kem.*, **18B**, 40 (1945); *C. A.*, **41**, 769 (1947), give m.p. 105°
3-Thiamorpholone	M.p. 88°	H. Bestian, *Ann.*, **566**, 242 (1950), gives m.p. 87–89°
Benzo-2H-1,4-oxazin-3(4H)-one	M.p. 168°	O. Aschan, *Ber.*, **20**, 1523 (1887), gives m.p. 169°
Benzo-2H-1,4-thiazin-3(4H)-one	M.p. 176°	A. W. Hofmann, *ibid.*, **13**, 1234 (1880), gives m.p. 176°
1-Isopropyl-5,5-dimethyl-2,3-diketopiperazine	M.p. 204–205°	J. L. Riebsomer, *J. Org. Chem.*, **15**, 68 (1950), gives m.p. 203°
1-Methyl-2-oxohexamethyleniminе	B.p. 120° (19 mm.)	R. E. Benson and T. L. Cairns, THIS JOURNAL, **70**, 2115 (1948)
1-Methylol-2-oxohexamethylenimine	M.p. 65–66°	Benson and Cairns, above
1-Ethylthiomethyl-2-oxohexamethylenimine	B.p. 138–141° (5–6 mm.)	Benson and Cairns, above
4-Methyl-7-isopropyl-2-oxahexamethylenimine	M.p. 119°	O. Wallach, *Ann.*, **278**, 304 (1893), gives m.p. 119–120°
2-Hexamethyleniminethione	M.p. 105–106°	L. Ruzicka, M. W. Goldberg, M. Hurbin and M. Furter, *Helv. Chim. Acta*, **18**, 659 (1935), give m.p. 107–109°
2-Oxo-5-thiahexamethylenimine	M.p. 113.0–115.0°	C. Barkenbus, V. C. Midkiff and R. M. Newman, *J. Org. Chem.*, **16**, 232 (1950); C. Barkenbus, J. F. Diehl and G. R. Vogel, *ibid.*, **20**, 871 (1955), give m.p. 115°
2,3-Benzo-(1,6,7H)-5-thiazepinone	M.p. 218°	W. H. Mills and J. B. Whitworth, *J. Chem. Soc.*, 2738 (1937), give m.p. 216°
2-Heptamethyleniminethione	M.p. 86°	L. Ruzicka, *et al.*, above, gives m.p. 82–83°
2-Octamethyleniminethione	M.p. 87–88°	L. Ruzicka, M. W. Goldberg, M. Hurbin and H. A. Boekenoogen, *Helv. Chim. Acta*, **16**, 1323 (1933), give m.p. 89°

Some warming occurred. The mixture was stirred for 1 hour at room temperature, was decolorized with SO_2, and evaporated under vacuum to one-half its volume. Filtration and rinsing with water gave 16.6 g. of white crystals, m.p. 255–257° (lit.[6a] m.p. 255°). The infrared spectrum showed the presence of a sulfone group.

Anal. Calcd. for $C_9H_9O_3NS$: C, 51.2; H, 4.3; O, 22.7. Found: C, 51.1; H, 4.5; O. 23.1.

1,5-Diazacycloöctane-2,6-dione.—Cyclohexane-1,4-dioxime ditosylate,[24] 10 g., was added to a solution of 3.90 g. of sodium acetate in 50 ml. of warm glacial acetic acid. The mixture was heated on a steam-bath for 25 minutes and was then pumped to dryness at 1 mm. to give 14 g. of a brown solid. This solid was sublimed at 240° and 0.5 mm. for 2.5 hours. The sticky yellow sublimate was rinsed with acetone to give 1.56 g. (49.4%) of granular white crystals, m.p. 298°.

Anal. Calcd. for $C_6H_{10}O_2N_2$: C, 50.7; H, 7.1; N, 19.7. Found: C, 50.6; H, 7.2; N, 19.3.

The dilactam, 0.33 g., was dissolved in 20 ml. of 6 *N* hydrochloric acid and heated for 48 hours on a steam-bath. Evaporation to dryness and washing with acetone gave 0.70 g. of β-alanine hydrochloride; its infrared spectrum was identical with that of an authentic sample.

2-Oxo-5-thiahexamethylenimine Dioxide.—2-Oxo-5-thiahexamethylenimine was oxidized[25] to the sulfone in 56% yield, m.p. 200.0–201.2° dec. from 90% ethyl alcohol.

Anal. Calcd. for $C_5H_9O_3NS$: C, 36.8; H, 5.6; N, 8.6. Found: C, 36.7; H, 5.3; N, 8.3.

(24) I. L. Knunyants and B. P. Fabrichnyi, *Dokl. Akad. Nauk S.S.S.R.*, **63**, 701 (1949).

(25) A. Pomerantz and R. Connor, THIS JOURNAL, **61**, 3388 (1939).

N-Phenylcaprolactam.—A mixture of 80 g. (0.7 mole) of dry caprolactam, 102 g. (0.5 mole) of iodobenzene, 76 g. (0.55 mole) of anhydrous potassium carbonate and 1 g. of freshly prepared moist copper powder[26] was heated with stirring at 180° for 8 hours. The warm mixture was filtered and distilled to give 52 g., b.p. 181–184° (9 mm.). The compound crystallized in the receiver. Two recrystallizations from a mixture of 100 ml. of ether and 50 ml. of petroleum ether gave 48.5 g. (51%) of white crystals, m.p. 75–76.5°.

Anal. Calcd. for $C_{12}H_{15}NO$: C, 76.2; H, 8.0; N, 7.4. Found: C, 76.2, 76.4; H, 8.1, 8.3; N, 7.0, 7.1.

These various lactams were prepared *via* Beckmann rearrangements: 2-piperidone, b.p. 108–110° (2–3 mm.), m.p. 41°; 5-phenyl-2-oxohexamethylenimine, m.p. 129–134° (*Anal.* Calcd. for $C_{12}H_{15}ON$: N, 7.4. Found: N, 6.9); perhydro-2,1-benzazepine-3-one (from β-decalone), m.p. 127° (*Anal.* Calcd. for $C_{10}H_{17}ON$: N, 8.4. Found: N, 8.3). These thiolactams were prepared by the method of Ruzicka and co-workers, cited in Table II: 5-methyl-2-hexamethyleniminethione, m.p. 76–77° (*Anal.* Calcd. for $C_7H_{13}NS$: S, 22.4. Found: S, 22.2); and 4,6-dimethyl-2-hexamethyleniminethione, m.p. 130° (*Anal.* Calcd. for $C_8H_{15}NS$: S, 20.4. Found: S, 19.9).

Polymerizations.—Polymerizations were carried out under nitrogen in long glass tubes which were heated by refluxing vapors of an appropriate liquid. The lactam, 2–4 g., was melted and a little sodium hydride was added. After it had dissolved, two drops of N-acetylpyrrolidinone were added. Alternatively, two drops of water were added and the tube was sealed. It was heated until the contents

(26) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 145.

became very viscous or solidified. The tube was then cooled and broken open and the polymer was washed thoroughly with warm water and acetone and dried. The polymerization results are summarized in Table I.

Poly-γ-butyramide from 2-Pyrrolidinone.—In an experiment without cocatalyst, sodium hydride, 0.10 g., was dissolved in 10.0 g. of anhydrous 2-pyrrolidinone with evolution of hydrogen. The resulting solution slowly became turbid. After being kept at room temperature overnight, it gave an 8% yield of poly-γ-butyramide, η_{inh} 0.20 in *m*-cresol.

The polymerization was accelerated strongly by the addition of cocatalysts (0.08–0.25 *M*) including N-acyl lactams, acyl halides, acid anhydrides, isocyanates, isothiocyanates, esters or dimethylcyanamide.[12] Other effective substances were nitriles, aromatic nitro compounds (purple color), fluorene, dialkyl amides, and polyhalo aliphatics. Compounds without effect included aromatics, halo aromatics, various salts, amides, lactams, ketones, ethers, sulfones, sulfoxides and amines. Inhibitors at these concentrations included acidic materials like alcohols or phenols. At high concentrations, the "indifferent" materials inhibited polymerization.

In a typical case of cocatalysis, acetic anhydride, 0.10 g., was added to a solution of 0.13 g. of NaH in 6.5 g. of pyrrolidinone. An exothermic reaction ensued, leading to the rapid formation of a hard white plug of polymer. This was broken into small pieces and extracted with water and acetone to give 5.7 g. of poly-γ-butyramide, η_{inh} 0.88 in *m*-cresol. Yields never exceeded 75–85% in such experiments, presumably because residual monomer became embedded in a matrix of polymer at these conversions.

Trapping Anionic Intermediate with Methyl *p*-Toluenesulfonate.—Sodium hydride, 0.75 g., was dissolved in 50 ml. of anhydrous pyrrolidone. With cooling, was added 5.0 g. of methyl *p*-toluenesulfonate, resulting in the precipitation of sodium *p*-toluenesulfonate. After 30 minutes, the mixture was distilled in a spinning band column. With a pot temperature of 150°, no distillation occurred, showing that no pyrrol*idine* or N-methylpyrrol*idine* had formed. Vacuum distillation gave 2.21 g. (71.3%) of N-methylpyrrol*idone*, $n^{27.5}D$ 1.4679 (authentic material $n^{27.5}D$ 1.4676). This result is consistent with the view that the anion present is always that of pyrrolidone.

Poly-ε-caproamide from 2-Oxohexamethylenimine.—2-Oxohexamethylenimine, 25.0 g., and sodium hydride, 0.60 g., were placed in a polymer tube which was evacuated and filled with nitrogen several times. The lactam then was melted and the sodium hydride dissolved with evolution of hydrogen. N-Acetylcaprolactam, 0.33 g., was added. The tube was shaken thoroughly and placed in a 139° vapor bath. The contents solidified quickly. After 30 minutes, the tube was cooled, and opened. The polymer was ground up, extracted with hot water, and dried to give 18.9 g. (74.7%) of polymer, η_{rel} 26.77 in formic acid. Other similar runs gave polymer in up to 80% yield, η_{inh} 1.0 in *m*-cresol. Blank experiments without the N-acetylcaprolactam gave no polymer below 150°.

At 202° a mixture of 4.0 g. of 2-oxohexamethylenimine, 2.0 ml. of 2-pyrrolidinone, 0.15 g. of NaH and 0.054 g. of N-acetylcaprolactam polymerized smoothly over a period of two hours, The polyamide was pure poly-ε-caproamide.

Anal. Calcd. for $C_6H_{11}ON$: N, 12.4. Found: N, 12.3.

Poly-β-alanine from 1,5-Diazacyclooctane-2,6-dione.—The dilactam, 0.85 g., was heated with two drops of water at 218° for 2.3 hours. The product was cooled, washed with water and dried, giving 0.30 g. polymer, η_{inh} 0.21 in sulfuric acid, m.p. 350° on a heated bar.[27]

Anal. Calcd. for C_3H_5ON: C, 50.7; H, 7.1; N, 19.7. Found: C, 49.1; H, 6.5; N, 17.6.

Poly-7-heptanethioamide from 2-Heptamethylenimine-thione.—The thiolactam was heated at 250° for 2 hours with sodium in the ratio of 30:1 to give a rubbery, tough polymer, m.p. 235°. Water at 180° for 120 hours gave a similar product, as did heating with sodium at 170° for 120 hours.

Poly-8-Octanethioamide from 2-Octamethylenimine-thione.—The thiolactam was heated at 180° for 48 hours with water or sodium in the ratios 10:1 and 20:1, respectively. The polythioamide was a brown rubbery solid which hardened somewhat on exposure to air.

(27) D. S. Breslow, G. E. Hulse and A. S. Matlock, THIS JOURNAL **79**, 376° (1957), give m. p. 340°.

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Polymerization of Cyclic Esters, Urethans, Ureas and Imides

BY H. K. HALL, JR., AND A. K. SCHNEIDER

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The polymerizations of a variety of cyclic esters, urethans, imides, anhydrides and ureas was studied. The 4-, 7- and 8-membered rings polymerized in almost every case, while the polymerizability of 5- and 6-membered rings depended on the class of compound.

The preceding article[1] described the polymerization of a variety of lactams to linear polymers. The present article describes the extension of this work to cyclic esters, urethans, ureas and imides.

The syntheses of the required monomers for the most part followed conventional methods. The experimental details and literature references are given in the Experimental section and in Table II.

Polymerizations were carried out with molten monomer since no useful solvents were found. Polymerization was undertaken at several temperatures between the melting point of the monomer and 250°, at which point decomposition usually became excessive. Sodium or sodium hydride catalyzed the polymerization of lactones, one urethan and one urea. The lactones also could be polymerized by a variety of other catalysts, including sulfonic acids, tetraisopropyl titanate, litharge, potassium carbonate and water. Tetramethyleneurea could be polymerized by heat alone. No conversion of a cyclic imide to a polymer could be effected.

The results of the polymerization studies are given in Table I, including for completeness the re-

Class of monomer	Polymerizability 5-Ring	6-Ring	Additional references
Lactam	+	−	Reference 1
Lactone	−	+	"Collected Papers of W. H. Carothers," Interscience Publishers, Inc., New York, N. Y., 1940
Urethan	Dec.	+	
Urea	+	−	
Imide	−	−	*Ibid.*
Anhydride	−	−	*Ibid.*

(1) H. K. Hall, Jr., THIS JOURNAL, **81**, 6412 (1959).