TABLE II

APPARENT ASSOCIATION CONSTANT OF POTASSIUM IODIDE AND PEO-6000 IN METHANOL AT 35°

Polymer concn, %	Ratio of potassium iodide to PEO	Apparent association constant (K)
1	0.22	2.28
1	0.44	1.29
1	0.88	0.74
1	1.76	0.43
1	2.64	0.31
2	0.11	4.20
2	0.22	1.76
2	0.44	0.88
2	0.88	0.47
2	1.32	0.37
5	0.09	3.78
5	0.18	1.39
5	0.35	0.54
5	0.53	0.34
10	0.04	Very large
10	0.09	1.84
10	0.17	0.84
10	0.27	0.50

$$K = \frac{[\text{complex}]}{[\text{PEO}]_f[\text{K}^+]} \qquad (2)$$

this excess is 10% PEO (2.27 M) and 0.05 or 0.10 M potassium iodide. From these values, X_f and X_b may be calculated for all systems, and the K value may be obtained from eq 2, where $[\text{K}^+]$ is the concentration of the free potassium ion; the [complex] and $[\text{PEO}]_f$ are, respectively, the concentrations of the complexed and free PEO. These calculated formation constants are summarized in Table II. It is clearly shown that the apparent formation constant decreases as the ratio of the potassium iodide to PEO increases, while the total polymer concentration was kept constant. The K value also decreases as the polymer concentration increases at the same salt to polymer ratio. These phenomena are commonly found in polyelectrolyte solutions.[1,6,10]

The Δ values of PEO-6000 were also measured in aqueous solutions. They are all zero after the bulk magnetic susceptibility corrections using cyclohexane as standard. On this basis, it may be concluded that PEO does not form a complex with potassium iodide in water. Previous viscometric measurements in aqueous systems led to the same conclusion.[6]

Acknowledgment. The author would like to acknowledge Dr. Lewis Siegel of VA Hospital, Ann Arbor, Mich., for his kind help to carry out the electrophoresis experiments in his laboratory. The author also expresses his appreciation to Dr. Robert Ullman for valuable discussions and to Miss S. J. Lignowski for experimental help.

(10) K. J. Liu and H. P. Gregor, *J. Phys. Chem.*, **69**, 1252 (1965).

Polyoxamides. I. Preparation and Characterization of Cyclic Oxamides

O. Vogl[1] and A. C. Knight

Plastics Department, Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Delaware 19898.

Received March 7, 1968

ABSTRACT: Cyclic oxamides of various diamines have been prepared and characterized. From hexamethylenediamine and oxalyl chloride the first three cyclic oligomers were obtained in pure form. These are designated *c*-62, *c*-6262, and *c*-626262. *c*-22, *c*-43, *c*-82, and 4-methoxy-*c*-62 were prepared from ethylenediamine, tetramethylenediamine, octamethylenediamine, and 3-methoxyhexamethylenediamine with oxalyl chloride.

Cyclic oxamides, notably the cyclic oxamides of hexamethylenediamine, have been prepared for polymerization studies. Poly(hexamethylene oxamide) is of interest because of its high melting point, stiffness, and low moisture sensitivity relative to common nylon resins. It is, however, thermally unstable at its melting point with gas evolution and loss of molecular weight. For this reason the possibility seemed attractive of making 62 polymer directly by polymerization of the cyclic monomer, 1,4-diazacyclodecanedione-2,3, hereafter referred to as *c*-62. This monomer had not previously been prepared nor had the ring-opening polymerization of cyclic oxamides been investigated.[2] This paper describes the preparation and characterization of cyclic oxamides and the following paper their polymerization.

Lactams with more than one amide group in the ring have been known for a long time. An excellent review was recently written by Dale.[3a] The best method for the preparation of cyclic diamides was described by Stetter;[3b] it is an extension and improvement of Ziegler[4] and Ruggli's[5] dilution technique for the preparation of

---

(1) Central Research Department, Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Del. 19898.

(2) P. W. Morgan, "Condensation Polymers," Interscience Publishers, Inc., New York, N. Y., 1965.

(3) (a) J. Dale, *Angew. Chem.*, **78**, 1078 (1966); (b) H. Stetter and J. Marx, *Ann.* **607**, 59 (1957).

(4) K. Ziegler in Houben-Weyl–Müller's "Methoden der organischen Chemie, Vol. 4, Part 2, G. Thieme, Stuttgart, 1955, p 738.

(5) P. Ruggli, *Ann.*, **392**, 92 (1912).

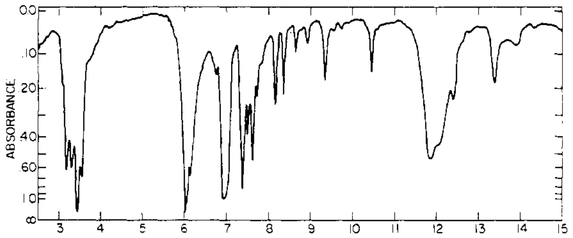


Figure 1. Infrared spectrum of *c*-62 (Nujol mull).

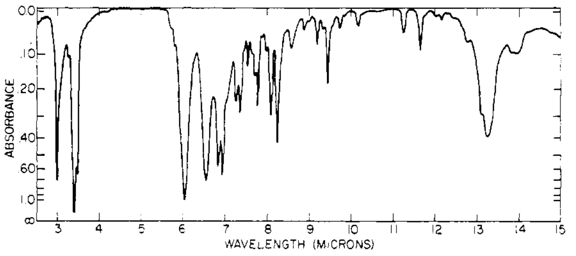


Figure 2. Infrared spectrum of *c*-6262 (Nujol mull).

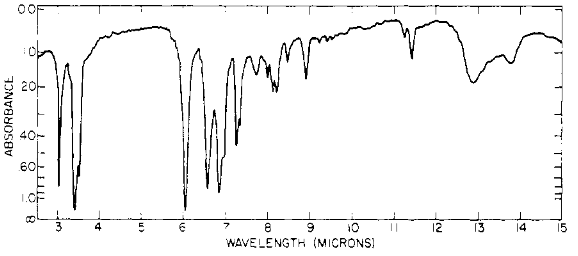


Figure 3. Infrared spectrum of *c*-626262 (Nujol mull).

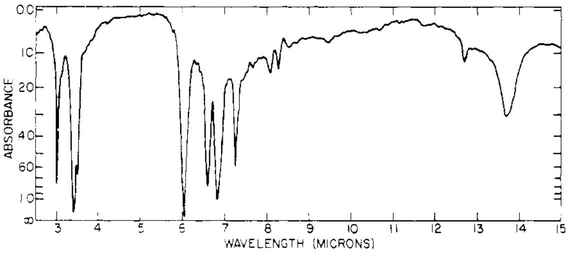


Figure 4. Infrared spectrum of 62 polymer (Nujol mull).

medium-sized rings. Diacid chlorides and diamines were allowed to react in benzene, and cyclic diamides in up to 75% yield were obtained. The yields dropped substantially when the ring size was smaller than 12 members. Noticeably absent from this study were the cyclic oxamides and malonamides. The two lower dicarboxylic acids malonic acid and oxalic acid have different chemical behavior than the higher aliphatic dicarboxylic acids. They are stronger acids, and their derivatives are much more reactive. It was expected that the cyclic oxamides, because of the ring strain caused by the adjacent amide groups, would be highly reactive and could be easily polymerized.

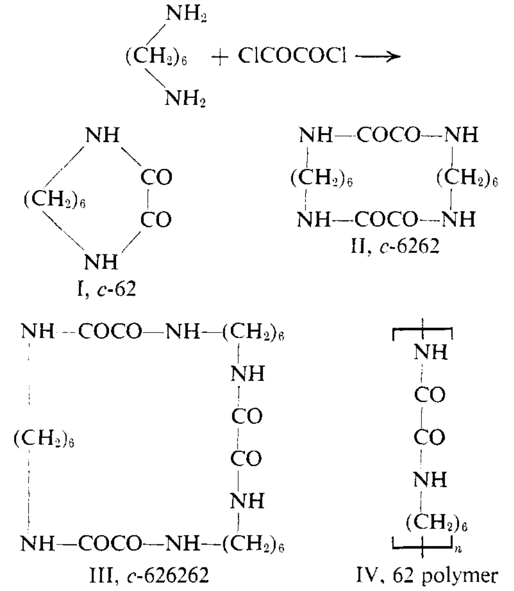
Results and Discussions

Cyclization to form cyclic diamides can be accomplished in several ways: (1) direct reaction of a reactive dicarboxylic acid derivative with a diamine; (2) preparation of an intermediate aminoamide acid derivative followed by cyclization; (3) equilibration of linear polymer with the cyclic diamide and (4) rearrangement of cyclic dioximes.

The first three methods have now been investigated for the preparation of 1,4-diazacyclodecanedione-2,3 (*c*-62). The last method was expected to give mixtures or the "wrong isomer" [6] and was not tried.

Stetter's procedure had not been applied to the preparation of cyclic oxamides. Difficulties could be foreseen because of ring strain, which would favor polymer formation. We have found, in fact, that Stetter's reaction conditions led mainly to polymer, with only traces of *c*-62 (Scheme I). To avoid this, greater dilutions seemed desirable to counterbalance the high reactivity of oxalyl chloride and decrease in reaction rate. Success was attained by carrying out the cyclization at 100 times the original scale and running the reaction slower. This resulted in an effective 100-fold dilution which led to a 14% yield of products extractable with dioxane. The extract was found to contain not only the cyclic monomer *c*-62, but also the cyclic dimer and trimer which are designated *c*-6262 and *c*-626262, respectively. The ratio of monomer–dimer–trimer in the original extract was 4:3:1.

Scheme I



The melting point of *c*-62 is 232°. The cyclic dimer, *c*-6262 (1,4,11,14-tetraazacycloeicosatetrone-2,3,12,13), melts at 303°, and the cyclic trimer at 345°. These three cyclic oligomers have distinct differences from each other and from 62 polymer in the infrared fingerprint region (see Figures 1–4).

c-62 is most characteristically distinguished from the three other compounds (Figure 1). The 2.9- or 3.0-μ peak is absent, and two absorption peaks appear at 3.2 and 3.3 μ. This seems to suggest that *c*-62 is present in the *cis*-amide form. In concurrence with this suggestion is the absence of the 6.55-μ peak which is present in the other three cyclic amides including the open chain polymer. The carbonyl peak of *c*-62 at 6.1 μ is also split. Most useful for the differentiation of *c*-62 from *c*-6262, *c*-626262, and polymer is the absorption at 12 μ.

---

(6) M. Rothe, *Collect. Czech. Chem. Commun.*, **24**, 148 (1959).

TABLE I

PREPARATION OF CYCLIC DIAMIDES[a]

Lactam	Prepared from: Diacid chloride	Prepared from: Diamine	% of theoretical yield	Mp, °C
c-62	Oxalyl chloride	HMD[b]	15	232[e]
c-82	Oxalyl chloride	Octamethylenediamine-1,8	31	260[e]
c-42	Oxalyl chloride	Tetramethylenediamine	10	405[e]
c-22	Oxalyl chloride	Ethylenediamine	8	
3-Methoxy-*c*-62	Oxalyl chloride	3-Methoxy-HMD	34	250,[e] 264[d]
c-6262	Oxalyl chloride	DAD[c]	21	303,[e] 308, 310[d]
c-6266	Adipoyl chloride	DAD	46	238,[e] 245[d]

[a] Rate of addition: 0.8–1.7 ml/min of 0.1 *M* dichloride and of 0.2 *M* diamine into 1500 ml of benzene; reaction time, 5–8 hr. [b] HMD = $H_2N(CH_2)_6NH_2$. [c] DAD = $H_2N(CH_2)_6NHCOCONH(CH_2)_6NH_2$ added in dioxane solution at 50°. [d] DTA melting point heating rate. 15°/min. [e] Melting point taken in capillary, aluminum block, heating rate 2°/min.

TABLE II

ELEMENTAL ANALYSIS OF DIAMIDES

Lactam	Formula	Calcd, %: C	Calcd, %: H	Calcd, %: N	Found, %: C	Found, %: H	Found, %: N
c-62	$C_8H_{14}O_2N_2$	56.45	8.29	16.46	56.4	8.1	16.5
					56.6	8.2	16.4
c-6262	$C_{16}H_{28}O_4N_4$	56.45	8.29	16.46	56.5	8.4	16.7
					56.4	8.2	16.9
c-626262	$C_{24}H_{42}O_6N_6$	56.45	8.29	16.46	56.8	8.0	16.6
					56.6	8.1	
c-22	$C_4H_6O_2N_2$	42.10	5.30	24.55	42.6	5.6	24.7
c-42	$C_6H_{10}O_2N_2$	50.69	7.09	19.71	51.0	7.6	20.2
3-Methoxy-*c*-62	$C_9H_{16}O_3N_2$	54.39	8.05	13.98	54.7	8.3	14.1
							13.9
c-82	$C_{10}H_{18}O_2N_2$	60.58	9.15	14.13	60.8	9.2	14.0

It is actually a triple peak with the main maximum at 11.85 μ and shoulders at 12.05 and 12.4 μ. The intensity of this peak was used for our quantitative work. *c*-6262 has its characteristic peak at 13.25 μ with a shoulder at 13.1 μ (Figure 2). *c*-626262 has a broad peak at 12.85 (Figure 3) and the 62 polymer at 13.7 μ (Figure 4).

Additional chemical proof that *c*-6262 was the compound melting at 303° was desirable. N,N′-Bis(6-aminohexyl)oxamide (DAD, V) was then prepared by reacting ethyl oxalate with excess hexamethylenediamine. DAD was cyclized with oxalyl chloride and gave (in addition to 62 polymer) a good yield of *c*-6262, identical in all respects with the compound (mp 303°) obtained as one product from the hexamethylenediamine and oxalyl chloride reaction. This preparation of *c*-6262 from DAD was, of course, free of *c*-62 and *c*-626262 (Scheme II).

SCHEME II

$H_2N(CH_2)_6NHCOCONH(CH_2)_6NH_2$
V, DAD

$ROOCCONH(CH_2)_6NHCOCOOR$
VI, ADA, R = CH_3, C_2H_5

$ROOCCONH(CH_2)_6NH_2 \cdot HCl$
VII, alkyl AD·HCl, R = CH_3, C_2H_5

DAD was also cyclized with adipoyl chloride and gave in good yields a mixed cyclic tetramide, *c*-6266, which contains the oxalyl and adipoyl part separated by two hexamethylenediamine units.

N,N′-Dioxalylhexamethylenediamine esters (ADA, VI) were also prepared. Attempted cyclization with hexamethylenediamine gave only 62 polymer but no *c*-6262.

TABLE III

CRYOSCOPIC MOLECULAR WEIGHT DETERMINATION OF CYCLIC DIAMIDES (SOLVENT, *m*-CRESOL)

	Molecular weight: Calcd	Molecular weight: Found	Formula
c-62	170.21	158[b]	$C_8H_{14}O_2N_2$
		166	
c-6262	340.42	320[a]	$C_{16}H_{28}O_4N_4$
c-626262	510.63	465[a]	$C_{24}H_{42}O_6N_6$
c-22	114.10	111	$C_4H_6O_2N_2$
		123	
c-42	142.16	140	$C_6H_{10}O_2N_2$
3-Methoxy-*c*-62	200.23	221	$C_9H_{16}O_3N_2$
		223	
c-82	198.26	193	$C_{10}H_{18}O_2N_2$

[a] Rast determination in borneol. [b] Polymerizes rapidly.

Several other cyclic oxamides were prepared in the course of this investigation. Their preparation and properties are summarized in Tables I–III.

Attempts were also made to prepare *c*-62 in a two-step synthesis.[7] First, the monoalkyloxalatoamide·HCl (VII) was prepared from hexamethylenediamine·HCl and ethyl (or methyl) oxalate. Several attempts failed to cause ring closure to *c*-62. When a solution of the salt was dropped into a large volume of alcohol containing KOH, 62 polymer, but not a trace of *c*-62, was obtained.

---

(7) E. Wünsch, *Collect. Czech. Chem. Commun.*, **24**, 60 (1959).

It is known that equilibration of a polyamide melt in the presence of an anionic catalyst produces some cyclic oligomer. An attempt was made to make *c*-62 from extracted 62 polymer.[3a] The polymer was heated to 350° in a sublimation apparatus at 0.1 mm in the presence of 1% of $NaOCH_3$. The sublimate collected on the cold finger was investigated after 1 hr heating. It contained *c*-6262 and hexamethylenediamine carbonate but not a trace of *c*-62.

Experimental Section

Hexamethylenediamine, hexamethylenediamine dihydrochloride, and dimethyl oxalate were used from freshly opened bottles (Eastman, reagent grade) without further purification. All other reagents were fractionated before use. Benzene (reagent grade unless otherwise stated) was topped in the reaction vessel before use.

Analytical Procedures. Purity of the cyclic oxamides was judged by the constancy of their infrared spectra after two consecutive recrystallizations. Melting point and its sharpness could not be used as a criterion of purity. If *c*-62 was melted rapidly (3–5°/min) with insertion of the melting point tube 10° below the melting point, a fairly sharp melting point of 231–232° was obtained. Melting in 234° vapor bath occurred in 1.5 min and gave a stable melt. Heating of the sample at the commonly recommended 1°/min, while inserting the sample at 150°, caused a melting range beginning at 220°. The melting was accompanied by polymerization, and the melt did not clarify even at 240° but continued to solidify.

Thin layer chromatography and paper chromatography could not be adapted to determine cyclic oxamide purity. The detection of lactams requires cleavage with chlorine followed by dipping in tolidine solution to give a purplish blue spot.[8] Unfortunately, oxamides cannot be cleaved under these conditions.

Molecular weights were determined by the Rast method for molecular weights higher than 300. The cryoscopic method in *m*-cresol (0.4% solution) gave good results in the 150–300 molecular weight range; at higher molecular weights, the values are low. Attempts to confirm the molecular weight determination by mass spectroscopy failed because of extensive fragmentation.

Infrared Spectra. Nonstrained lactams show a normal spectrum in the infrared region, with individual differences in the 10–13-μ fingerprint region. This region was mainly used for the differentiation of various cyclic oxamides (see Figures 1–4).

Preparation of *c*-62. Into a stirrer-equipped, corrosion-resistant vessel containing 200 l. of dry benzene (topped and distilled nitration grade), blanketed with nitrogen, were added separate streams of 635 g of oxalyl chloride (5 mol) in 36 l. of dry benzene and 1160 g of hexamethyldiamine (10 mol) in 36 l. of dry benzene at a uniform rate of 40 ml/min for each stream over a period of 15 hr. Rotameters were used to assure exact and constant delivery of the reactants. After the reaction was complete, the gelatinous precipitate was isolated by filtration. The filter residue, which consisted of cyclic oxamides, 62 polymer, hexamethylenediamine dihydrochloride, and excess solvent, was dried to a weight of about 3 kg, broken into $^1/_8$ to $^1/_4$ in. pieces, and extracted for 24 hr with dioxane. (Drying the filter cake to constant weight (1.8 kg) is undesirable. It sinters to a hard cake, which can be broken up only with difficulty. Usually a fine powder results which is not very suitable for a Soxhlet extraction.) Most of the cyclic oxamides were extracted in 24 hr. After 50 hr the extracts were evaporated to dryness, yield 124 g (14.5% of theory). Infrared analysis of the mixture showed *c*-62, *c*-6262, and *c*-626262 in a ratio of 4:3:1.

Fractional Crystallization. The mixture of cyclic oxamides (5 g) was dissolved in 100 ml of glacial acetic acid. The hot, slightly yellow solution was filtered from a small amount of flocculent precipitate. It was set aside and allowed to cool slowly to room temperature in about 2 hr. Filtration gave pure *c*-6262 (1.65 g, 33%). The filtrate was diluted with 100 ml of distilled water, and the precipitate of *c*-626262 was filtered (0.75 g, 15%). Vacuum evaporation left 2.15 g of *c*-62 (44%). It was recrystallized twice from alcohol to give a pure sample. When even a pure sample of *c*-62 is dissolved in alcohol at its boiling point, a small amount of insoluble residue is always found. This is 62 polymer, and the cloudy solution must be filtered in order to obtain an uncontaminated sample of *c*-62. The polymer is formed during the dissolution of *c*-62. Infrared investigation showed that a sample of *c*-62 which did not contain any 62 polymer contained about 5% of 62 polymer after recrystallization (without filtration) from alcohol.

Laboratory Runs. Oxalyl chloride (6.3 g, 0.05 mol) was dissolved in 500 ml of dry benzene. HMD, hexamethylenediamine (11.6 g, 0.1 mol), was also dissolved in 500 ml of benzene. Both solutions were dropped simultaneously from dropping funnels (which were equipped with regulators tipped with Teflon tetrafluoroethylene resin) with vigorous stirring during 9 hr into 1500 ml of benzene. This reaction was run in a four-necked, 5-l. round-bottom flask equipped with a nitrogen inlet and exit, a mechanical stirrer, and the two dropping funnels on opposite necks on the flask. After the reaction was complete, the slurry was filtered, dried, and extracted in a Soxhlet with tetrahydrofuran, yield of cyclic diamides 1.1 g (12%). The benzene solution was evaporated to dryness, and 0.1 g of residue was left. Only a small amount of it was *c*-62, according to its ir spectrum.

Other Cyclizations. Similar experiments were carried out in the laboratory equipment with various other diamines to prepare various cyclic oxamides. The results are shown in Tables I and II.

N,N′-Bis(6-aminohexyl)oxamide (DAD, V). In a 750-ml erlenmeyer flask was dissolved 120 g of hexamethylenediamine in 190 ml of benzene. A solution of 36 g of diethyl oxalate in 150 ml of benzene was added with mechanical stirring during 5 min. An exothermic reaction occurred, and a white solid precipitated. After 1 hr, the slurry was filtered and 56 g of polymer was removed. The filtrate was transferred to a 1-l. erlenmeyer flask, heated to boiling, and 360 ml of petroleum ether (bp 40–60°) was added. White crystals of V (17 g, 23%) precipitated when the solution was chilled in ice. Additional 7 g was obtained when the original filter cake was extracted with 100 ml of boiling water. Recrystallization from water (fivefold, filtration to remove a small amount of polymer) gave pure V, mp 117–118°.

Anal. Calcd for $C_{14}H_{30}O_2N_4$: C, 58.6; H, 10.5. Found: C, 58.6; 58.5; H, 10.4, 10.4.

N,N′-Dioxalylhexamethylenediamine (ADA, VI). In a 1-l. beaker, 200 ml of diethyl oxalate was dissolved in 200 ml of toluene. A solution of 50 g of hexamethylenediamine in 125 ml of toluene was added with stirring. During the addition, the temperature rose and a solid precipitated. After the addition was complete, the mixture was heated gently on a hot plate, and the precipitate went into solution. The solution was cooled in ice and allowed to crystallize. White crystals (114 g, 92%) were obtained, mp 92–93°.

Anal. Calcd for $C_{14}H_{24}O_6N_2$: C, 53.1; H, 7.7; N, 8.9. Found: C, 53.2; 53.4; H, 7.7, 7.8; N, 9.2, 9.2.

Ethyl N-(6-Aminohexyl)oxamate Hydrochloride (Ethyl AD ·

---

[8] F. Reindel and W. Hoppe, *Chem. Ber.*, **87**, 1103 (1954); H. N. Rydon and P. W. G. Smith, *Nature*, **169**, 922 (1952).

HCl, VII). In a 2-l. erlenmeyer flask, 6.6 g of hexamethylenediamine dihydrochloride and 4.1 g of hexamethylenediamine were dissolved in 500 ml of absolute alcohol. The solution must be kept hot to avoid precipitation of the dihydrochloride. A solution of 10.2 g of diethyl oxalate in 100 ml of absolute alcohol was added with stirring during a period of 5 min. The solution was concentrated on a hot plate to 100 ml and brought to dryness under reduced pressure.

The dry material was powdered and extracted with 400 ml of acetone. The suspension was filtered [the solid (30–35%) contains 62 polymer (IV), DAD·2HCl, and hexamethylenediamine dihydrochloride] and the filtrate allowed to crystallize in an ice bath. Filtration gave relatively pure ethyl AD·HCl. Additional material may be obtained by adding 150 ml of anhydrous ether, total yield 25–30%.

Anal. Calcd for $C_{10}H_{21}O_3N_2Cl$: C, 47.7; H, 8.4; Cl, 14.0. Found: C, 47.7, 47.9; H, 8.2, 8.4; Cl, 13.9, 14.1.

When a similar reaction of a 1:1 mixture of hexamethylenediamine and hexamethylenediamine dihydrochloride was carried out with dimethyl oxalate in methanol, the corresponding methyl ester was obtained in 32% yield, mp 152–153°.

Anal. Calcd for $C_9H_{19}O_3N_2Cl$: Cl, 15.0. Found: Cl, 14.7.

Polyoxamides. II. Polymerization of Cyclic Diamides[1a]

O. Vogl[1b] and A. C. Knight

Plastics Department, Experimental Station, E. I. du Pont de Nemours and Co.,
Wilmington, Delaware 19898. Received March 7, 1968

ABSTRACT: Poly(hexamethylene oxamide) and related polyoxamides were prepared by ring-opening polymerization of appropriate cyclic oxamides. They polymerized rapidly in the melt with ionic catalysts to form solid polymers and copolymers. Slow thermal decomposition, with evolution of CO and CO_2, was observed in polymerization mixtures. Poly(hexamethylene oxamide) was also found to undergo thermal decomposition well below its melting temperature. *c*-62 also polymerized in the crystalline state.

A mild polymerization method is essential for the preparation of polyoxamides. They are unstable in the melt and even below their melting points. For example, poly(hexamethylene oxamide) (hereafter called 62 polymer) starts to degrade significantly at 280°. High molecular weight polyoxamides cannot be prepared directly from oxalic acid and diamine by dehydrating the acid salt because oxamides decompose at temperatures lower than that necessary for the dehydration of polymeric oxalate salts. The most frequently used technique for the preparation of polyoxamides is the reaction of oxalate esters with diamines.[2–18] Interfacial and emulsion polymerization using oxalyl chloride and diamines have also been explored. Recently, an intriguing method was devised by Solokov and his coworkers.[19,20] This is a gas–liquid phase type of interfacial polymerization in which gaseous oxalyl chloride with the carrier gas nitrogen is bubbled into an aqueous solution of the diamine.

Ring-opening polymerization of cyclic oxamides had not previously been used to prepare polyoxamides. This is probably due at least partially to the fact that the cyclic oxamides were not available. A ring-opening polymerization of 1,4-diazacyclodecanedione-2,3, subsequently designated *c*-62, seemed an attractive method to produce 62 polymer. The cyclic monomer was expected to melt enough lower than the polymer to avoid the region of thermal instability and thus allow polymerization directly to high polymer.

In the preceding paper[1a] we have described the preparation of 1,4-diazacyclodecanedione-2,3 and other cyclic oxamides.

The literature on lactam ring-opening polymerization is extensive, particularly the work on caprolactam polymerization. Lactam polymerization as commonly carried out is an anionic polymerization and can be cocatalyzed with acylating agents. The cocatalytic polymerization can be carried out at 150°, whereas the normal anionic polymerization requires 220°. Lactams can also be polymerized with cationic initiators but much less effectively. Ring size and strain in

---

(1) (a) Polyoxamides. I: O. Vogl and A. C. Knight, *Macromolecules*, **1**, 311 (1968). (b) Central Research Department, Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Del. 19898.

(2) I. G. Farben, A.-G., Belgian Patent 444,942 (1942).

(3) I. G. Farben, A.-G., Belgian Patent 450,369 (1943).

(4) P. Schlack, German Patent 924,536 (1955).

(5) S. J. Allan, J. G. N. Drewitt, C. Dreyfus, and F. Bryans, Canadian Patent 496,211 (1953).

(6) S. J. Allan, J. G. N. Drewitt, and C. Dreyfus, Canadian Patent 496,210 (1953).

(7) G. S. Stamatoff, British Patent 737,939 (1955); U. S. Patent 2,704,282 (1955); Canadian Patent 566,778 (1958).

(8) D. Coleman, British Patent 781,289 (1957); Canadian Patent 568,528 (1959); German Patent 1,157,393, I9,492 (1963).

(9) C. R. Lindegren, U. S. Patent 2,977,339 (1961).

(10) J. R. Caldwell and C. C. Dannelly, U. S. Patent 2,945,009 (1960).

(11) J. H. Fisher and V. F. G. Cooke, French Patent 1,204,350 (1959).

(12) J. Lincoln, British Patent 870,057 (1961).

(13) S. D. Bruck, U. S. Patent 2,977,340 (1961).

(14) S. D. Bruck, *Ind. Eng. Chem. Prod. Res. Develop.*, **2**, 119 (1963).

(15) F. Becke and K. Wick, German Patent 1,154,625, B49,681 (1963).

(16) F. K. Duxbury, French Patent 1,250,897 (1960); British Patent 888,150 (1962); U. S. Patent 3,139,417 (1964).

(17) Monsanto Canada, British Patent 851,659 (1960).

(18) H. K. Hall and J. H. Berge, *J. Polym. Sci., Part B*, **1** (6), 277 (1963).

(19) L. B. Solokov, L. V. Turetskii, and T. V. Kudim, *Vysokomol. Soedin.*, **2**, 1744 (1960).

(20) L. B. Solokov, *J. Polym. Sci.*, **58**, 1253 (1962).