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]

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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

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TABLE I

ANIONIC POLYMERIZATION OF *c*-62[a]

Catalyst[b]	Time to polymerize, min
None	20
Methanol	20
$NaOCH_3$	0.3
KOH	1.3
LiH	0.4
$LiAlH_4$	Did not melt completely
CaH_2	2.0
K_2CO_3	1.3
Na	1.0
KCl	18.5
KI	18.0
HMD	6.5
HMD·2HCl	4.1
HMD carbonate	12
Triethylenediamine	18
Ph_3P	22
Iodine	15

[a] Catalyst concentrations, 1 mol %; time to melt, 20 sec; $T = 259°$. [b] HMD = hexamethylenediamine.

TABLE II

ANIONIC POLYMERIZATION OF *c*-62[a]

Catalyst[b]	Time to polymerize, min
LiAc	3.3
$NaAc \cdot 3H_2O$	3.7
KAc	3.2
$MgAc_2$	2.2
$CaAc_2$	4.5
$BaAc_2$	17.5
AgAc	0.3
$NiAc_2$	2
$CuAc_2$	3
$HgAc_2$	5
NaSt	2.7
$MgSt_2$	6.0
$AlSt_3$	2.3

[a] Catalyst concentration; 1 mol %; time to melt, 20 sec; $T = 259°$. [b] Ac = acetate, St = stearate; exact crystal water content was not always known.

lactam polymerization was discussed in the now classic work of Hall.[21]

Cyclic diamides have not been popular as intermediates for polyamide formation. It seems that ring opening of large cyclic diamides to the corresponding linear polymers is not very favored and long reaction times are required. Greenewalt described the polymerization of hexamethyleneadipamide by heating it for 200 hr at 250°.[22]

Results and Discussions

c-62 is stable in the melt for almost 30 min when nitric acid washed tubes are used. Then small gas bubbles form, and the melt slowly becomes viscous and solid polymer begins to deposit. This process begins in 5–10 min when new but not specially treated glass tubes are used. Addition of anionic initiators expectedly lowers the time of polymerization.

TABLE III

CATIONIC POLYMERIZATION OF *c*-62[a]

Catalyst	Time to polymerize, min
None	20
H_2SO_4	1.2
HBF_4	3
$NO_2^+BF_4^-$	6
$SnCl_4$	5
$SbCl_5$	1.7
$FeBr_3$	8.5
$BCl_3 \cdot P_2O_3$	5
P_2O_5	Some solid appeared immediately

[a] Catalyst concentration, 1 mol %; time to melt, 20 sec; $T = 259°$.

As can be seen in Table I, 1% of $NaOCH_3$ causes polymerization as soon as the monomeric *c*-62 is melted. In the case of $LiAlH_4$, polymerization occurs during the melting process. Other bases, KOH, CaH_2, K_2CO_3, and Na, are effective but somewhat slower. Primary aliphatic amines are less effective initiators, but they still catalyze the polymerization of *c*-62 in about 5 min. The ineffectiveness of *t*-amines like triethylenediamine, Table II, normally a very good anionic initiator, is surprising.

Table II summarizes the influence of the cation on the rate of polymerization. Acetate salts of alkali, alkaline earth metals, and various other cations were used as initiators. They all polymerize *c*-62 in 2–5 min, and no great significance should be placed on differences in this time range. Surprising, however, is the fast polymerization with silver acetate. We have no explanation at the present time for this phenomenon. Barium acetate is a poor initiator and may not be soluble enough in the medium.

Several typical cationic initiators were also used to polymerize *c*-62 in the melt (Table III). While none gave the fast polymerization seen with the best anionic initiators, H_2SO_4 and $SbCl_5$ initiated the polymerization in 1.5 min. P_2O_5, although not completely soluble in the melt, gave some polymer even during the melting process. It seems, however, that the cationic polymerizations were not as complete as the anionic polymerization.

In all these runs the temperature of polymerization was 259° (boiling diphenyl ether bath). For polymerization at higher temperatures, benzophenone (bp 306°) was used and for lower temperatures decyl alcohol (bp 234°). The rate of *c*-62 melting prior to polymerization seems most satisfactory at 259°.

Comparative experiments with $NaOCH_3$ as the catalyst at the three temperatures showed the expected increase in polymerization rate with increasing temperature. An increase in gas formation was also noted. At 234° incomplete melting was observed, indicating that polymerization had occurred before melting was complete.

All polymerizations were accompanied by gassing (bubble formation). In separate experiments the gas formation was investigated. It could be shown (Table

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TABLE IV

c-62 POLYMERIZATION. GAS EVOLUTION AT VARIOUS TEMPERATURES[a]

Sample wt, mg	Catalyst[b]	Gas evolved, ml —Bath temperature, °C— 234	259	306	Mol % of gas evolved/mol of monomer
80	$NaOCH_3$	0.71			1.6
104	$NaOCH_3$		1.10		2.8
126	$NaOCH_3$			2.2	3.6
114	KAc[c]	0.82			1.5
110	KAc		1.52		3.5

[a] Reaction time, 30 min. [b] Catalyst concentration, 1 mol %. [c] Ac = acetate.

TABLE V

c-62 POLYMERIZATION: 1% KAc CATALYST RATIO OF CO_2/CO EVOLUTION[a]

T, °C	CO_2/CO
306	76.24
	68.32
259	61.39

[a] Time, 15 min.

TABLE VI

POLYMERIZATION OF *c*-6262 (POLYMERIZATION TEMPERATURE, 306°)

Sample weight, mg	Catalyst type	Mol % of catalyst added	Time to polymerize, min
20	KAc[a]	0.5	13–17
40.2	NaSt[b]	4.7	30
20	DPE[c]	0.5	0
20	HMD·2HCl	1.0	0
20	$NaOCH_3$	1.0	8
20	Na_3PO_4	1.0	0
20	*d*	1.0	0[e]
20	KAc	1.0	6–17[f]

[a] Ac = acetate. [b] St = stearate. [c] DPE = *p,p'*-diaminodiphenyl ether. [d] Ethyl AD·HCl. [e] After solidification, no remelting in 306° bath. [f] Very viscous at 6 min; no solidification until 17 min.

TABLE VII

SOLID STATE POLYMERIZATION OF *c*-62 WITH AND WITHOUT 1% $NaOCH_3$ CATALYST

Time, hr	Conversion, % 153° Without	153° With	196° Without	196° With	222° Without	222° With
1	0	0	0	3	0	18.5
3	0	0	0	3	3	28
12	4.5	3	2.5	13	14.5	91
37	13.5	24	30.5	53	88	96

IV) that the gas formation is directly related to the polymerization temperature and not to the nature of the anionic catalyst. In 15 min 1.5 mol % of gas is evolved at 234° and as much as 3.5 mol % at 306°. Surprisingly, the gas is not CO, as would be expected from decarbonylation, but a mixture of CO_2 and CO (Table V). At 306° the ratio is approximately 3:1. Higher temperatures favor decarbonylation. Such side reactions account for lower molecular weights of 62 polymer. It was observed that the mass spectrum of *c*-62 has a large CO_2 peak but a small CO peak.

Gas evolution of 62 polymer (mp 320°) which was known to be unstable at the melting point was also investigated at 250°. It gave approximately the same amount of gas and the same CO_2/CO ratio as the polymerizing *c*-62 polymer.

Polymerization of *c*-6262 should also give 62 polymer. *c*-6262 melts at 303° and is much more melt stable than *c*-62. After 1 hr in the melt, no signs of polymerization were noticed. Consequently, the catalytic polymerization is also much slower. It takes 8 min for $NaOCH_3$, as initiator, to observe polymerization and 15 min for potassium acetate (Table VI), although the melt becomes viscous in about 6 min. Higher solubility of the polymer in the monomer is probably responsible for the later recognition of the polymerization. *c*-626262 was polymerized to 62 polymer with $NaOCH_3$ initiator in 30 min. The polymer was fairly dark, however.

During the preparation and purification of *c*-62, it was noticed that some 62 polymer was formed during recrystallization of *c*-62 from alcohol. It was also noticed that when freshly recrystallized *c*-62 was dried at 153° (0.1 mm) overnight, significant amounts of *c*-6262 and 62 polymer could be detected in the ir spectrum of *c*-62. Consequently, the polymer formation of highly purified samples of *c*-62 was investigated. Qualitative ir analysis had been worked out previously, and standardization was done with known mixtures of *c*-62 and 62 polymer.

Table VII shows that even at 150° (80° below the melting point of *c*-62) polymerization is noticeable. The rate even without the $NaOCH_3$ catalyst is about 0.4%/hr. The rate triples at 196° and is quite fast at 222°, particularly in the presence of catalyst. From these values an activation energy of 26 kcal can be calculated for the "uncatalyzed" polymerization. The activation energy for the catalyzed solid state polymerization of *c*-62 is only about 2–3 kcal lower.

Other cyclic oxamides have been polymerized at a bath temperature of 306° with 1 mol % of $NaOCH_3$ as the initiator; *c*-82 and 3-methoxy-*c*-62 begin to polymerize in 5 min. The polymerization was complete in 30 min.

c-62 readily copolymerizes with other cyclic oxamides and with other lactams. The following copolymers have been prepared. *c*-62 and *c*-82 give a copolymer with a melting range of 258–268°. *c*-62 copolymerizes with caprolactam, the copolymer melts at 260–270°, and the *c*-62 and 3-methoxy-*c*-62 copolymer melts at 268°. A copolymer from *c*-62 and *c*-42 was also prepared. These copolymers probably have the two diamines randomly distributed along the polyamide chain.

A regular copolymer of the ABAC type was obtained when *c*-6266 was homopolymerized with $NaOCH_3$ as the initiator. At a rate similar to the *c*-6262 polymerization, *c*-6266 forms the polymer at 259°. It is believed that *c*-6266 polymerizes exclusively through the oxamide link, and very little, if any, equilibration of the amide bonds occurs. Under the same condition and the same time, *c*-66 does not polymerize. The polymerization of mixed cyclic diamides appears to be an interesting way of getting to copolyamides of regular structure.

Experimental Section

Monomers. Monomers of high reactivity, for example, *c*-62, were recrystallized until two recrystallizations did not change the infrared spectrum of the compound. (Note: The melting point could not be used as a criterion of purity. *c*-62 starts to polymerize below the melting point and upon dissolution for recrystallization.)

Other cyclic monomers were recrystallized to constant melting point. The purity is believed to be better than 99%. Trace impurities of solvent and moisture were removed by drying the cyclic diamides over P_2O_5 at 0.1 mm and 100° overnight.

Cleaning of Glass Tubes. Glass tubes (4 mm o.d.) were placed into a bath of fuming nitric acid overnight. They were rinsed with distilled water, dried, flamed out, and placed in a 120° oven for several hours. Polymerization tubes of 5 in. length and sealed at one end were made from these glass tubes. *c*-62 is stable for 20 min in the melt at 259°. In nontreated tubes, polymerization starts in 5–10 min.

Polymerization Temperatures. Most polymerizations were carried out in a vapor bath of diphenyl ether (bp 259°). For higher polymerization temperatures, boiling benzophenone (bp 306°) and for lower polymerization temperatures, boiling 1-decanol (bp 234°) were used as the bath liquid. This polymerization temperature gave, however, incomplete melting of *c*-62 because polymerization occurred during the melting process.

Viscosity Measurements. Inherent viscosities of nylon 62 polymer were measured in 0.5% *m*-cresol solutions. The inherent viscosities (η) were between 0.3 and 0.5.

Gas Evolution. Gas evolution during the polymerization of molten *c*-62, *c*-6262, or from solid nylon 62 polymer was evaluated quantitatively as follows (see also ref 23 and 24). The polymerization of *c*-62 or *c*-6262 was carried out in a 2-ml glass tube closed with a serum stopper. Before polymerization the air in the tube was replaced with helium by repeated evacuation and refilling with helium. A 2-cc syringe (no. 17 needle) was inserted into the serum stopper, and the polymerization was carried out at elevated temperatures. The total gas evolution was measured in the syringe. The sample of the gas mixture of CO_2 and CO was analyzed by gas chromatography. Mass spectroscopy of *c*-62 gave as a major fragment CO_2 but not CO.

Solid-State Polymerization of *c*-62. Samples of 0.1 g of *c*-62 without and with 1 mol % of $NaOCH_3$ were placed into tubes and heated under nitrogen to 153° (bromobenzene bath), 196° (ethylene glycol bath), and 222° (methyl salicylate bath). Samples were taken out at different time intervals, and the ir spectrum in Nujol mull was determined. The ratios of the band at 11.8 μ (characteristic for the monomer) to the band at 13.8 μ (characteristic for the polymer) gave the amount of unchanged monomer. A standardization was carried out with known monomer polymer mixtures. No attempt was made to estimate the dimer content.

Polymerization. To a 0.5-ml glass tube were added 50 mg of the cyclic dioxamide and 1 mol % of the initiator in solution ($NaOCH_3$ in CH_3OH). The solvent was removed by evaporation. The polymer tube was repeatedly and alternately flushed with an inert gas and evacuated to remove oxygen. Nitrogen was commonly used as the inert gas, although hydrogen or helium have also been used. The tube was then sealed under one atmosphere of nitrogen and immersed in the condenser of a vapor bath containing refluxing diphenyl ether, bp 259°. The times necessary to form visible polymer using a variety of initiators are listed in Tables I–IV. After the polymerization was complete, the tube was cooled and the polymer removed from the tube. The polymer retains the shape of the cavity of the tube.

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Syntheses and Investigations of Polymers Containing the 1,2,4-Oxadiazole Nucleus

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ABSTRACT: Polymers containing the 1,2,4-oxadiazole nucleus were synthesized by the 1,3-dipolar cycloaddition of arylenedinitrile oxides to various dinitriles and by the homopolymerization of 3-cyanobenzonitrile oxide. Poly(arylene-1,2,4-oxadiazoles) were also synthesized by cyclodehydration of poly(arylene acyloylamidoximes), prepared by condensation polymerization of arylene diamidoximes and arylene diacid chlorides. Thermogravimetric analyses of polymers prepared by both methods showed thermal degradation below 400°. A number of model compounds were synthesized and their thermal properties were found to be similar to those of the polymers.

Early work by Tiemann and Krüger suggested that 3,5-diphenyl-1,2,4-oxadiazole was exceptionally stable to thermal, oxidative, and hydrolytic degradation.[1] Much later, Blomstrom reported the first synthesis of 1,2,4-oxadiazole polymers by the cyclodehydration of polymeric acyloylamidoximes, but made no mention of the thermal and oxidative stability of these products.[2] The copolymerization of terephthalonitrile di-N-oxide with terephthalonitrile[3] and the homopolymerization of 4-cyanobenzonitrile oxide[4]

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