The (Co)Polymerization of the Cyclic Diamide 1,6-Diazacyclododecane-7,12-Dione

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ABSTRACT

It is demonstrated for the first time that the cyclic diamide 1,6-diazacyclododecane-7,12-dione (c-4) can be polymerized. Polyamide 46 was prepared by thermal or hydrolytic ring-opening polymerization of c-4. c-4 polymerized in the melt to form polyamide 46, containing approximately one-third of the original c-4. Due to possible degradation of c-4 near its melting point, the polyamide 46 formed possibly contained a crosslinked fraction which was insoluble. Therefore, the thermal behavior deviated from that of Stanyl (a commercial polyamide 46 from DSM, The Netherlands). Furthermore, polyamide 46 was prepared by anionic polymerization of c-4 in N-methyl-2-pyrrolidone solution at 202°C. c-4 polymerized with NaH and 1,6-hexamethylene diisocyanate as catalysts. Almost all c-4 was converted to polyamide 46. Due to possible crosslinking, the polyamides had difficulties in dissolving. Furthermore, the thermal behavior of this low molecular-weight polyamide 46 deviated from that of Stanyl, but solid-state postcondensation had a positive effect on the melting point. Then copolyamides of ϵ-caprolactam (CL) and c-4 were prepared by anionic ring-opening copolymerizations. The cyclic monomers polymerized in the melt with lactam magnesium bromide and isophthaloyl-bis-caprolactam as catalysts. It was demonstrated that approximately all c-4 was copolymerized with CL at 180°C. At 200°C only ~30% was incorporated. The copolymerization of a maximum of 8.5 mol% c-4 in polyamide 6 showed no effect on the thermal behavior and crystallinity as compared to polyamide 6.

INTRODUCTION

In general, the synthesis of polyamides is conducted by the polymerization of amino acids or their amide-forming derivatives, or by reacting diamines with dicarboxylic acids or amide-forming derivatives of dibasic carboxylic acids [1]. Polyamide 46 (Stanyl), for instance, is obtained by reacting 1,4-diaminobutane (DAB) with adipic acid (ADA) [2]:

$$H_2N-(CH_2)_4-NH_2 + HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH \rightarrow -[\overset{H}{\overset{|}{N}}-(CH_2)_4-\overset{H}{\overset{|}{N}}\underset{\underset{O}{\|}}{C}-(CH_2)_4-\underset{\underset{O}{\|}}{C}]_n- \qquad (1)$$
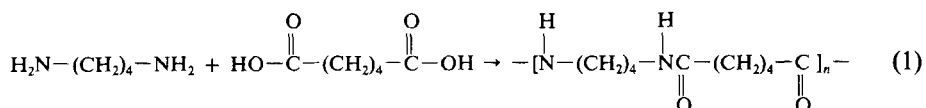
In addition, polyamides are obtained by ring-opening polymerization of the corresponding lactams (in principle, an amide-forming derivative of an amino acid). The literature on lactam polymerization is extensive, particularly the work on ε-caprolactam (CL) [3]. Lactam ring-opening polymerization can be performed by thermal, hydrolytic, or anionic reaction routes. The anionic polymerization can be cocatalyzed with acylating agents and can then be carried out at 150°C [for instance, in reaction injection molding (RIM) technology of polyamides [4]] whereas normal anionic polymerization requires 220°C.

The ring-opening polymerization of cyclic diamides for the preparation of polyamides has been used only sparingly. Greenewalt [5] described the hydrolytic polymerization of 1,8-diazacyclotetradecane-9,14-dione and the corresponding tetraamide to form polyamide 66 by heating the cyclic oligomer for 2 hours (wrongly interpreted as 200 hours by Vogl and Knight [6]) at 250°C under 1 mm pressure:

$$\begin{array}{l} \overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}} \\ | \qquad\qquad\quad | \\ N-(CH_2)_6-N \\ | \qquad\qquad\quad | \\ H \qquad\qquad\quad H \end{array}$$

$$\rightarrow -[\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}\underset{\underset{O}{\|}}{C}-(CH_2)_4-\underset{\underset{O}{\|}}{C}]_n- \qquad (2)$$

$$\begin{array}{l} \overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}} \\ | \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ N-(CH_2)_6-\underset{\underset{H}{|}}{N}\underset{\underset{O}{\|}}{C}-(CH_2)_4-\underset{\underset{O}{\|}}{C} \\ | \qquad\qquad\quad | \\ H \qquad\qquad\quad H \end{array}$$

Iwakura et al. [7] polymerized 1,5-diazacyclooctane-2,4-dione hydrolytically in the solid state to produce linear poly(trimethylene malonamide):

$$\begin{array}{l} \overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}} \\ | \qquad\qquad\quad | \qquad \rightarrow -[\overset{H}{\overset{|}{N}}-(CH_2)_3-\overset{H}{\overset{|}{N}}\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}]_n- \qquad (3) \\ N-(CH_2)_3-N \\ | \qquad\qquad\quad | \\ H \qquad\qquad\quad H \end{array}$$

This cyclic diamide and 7,7-dimethyl-1,5-diazacyclooctane-2,4-dione were also polymerized in the melt. The main driving force for polymerization was considered to be the internal strain of the 8-membered cyclic diamide.

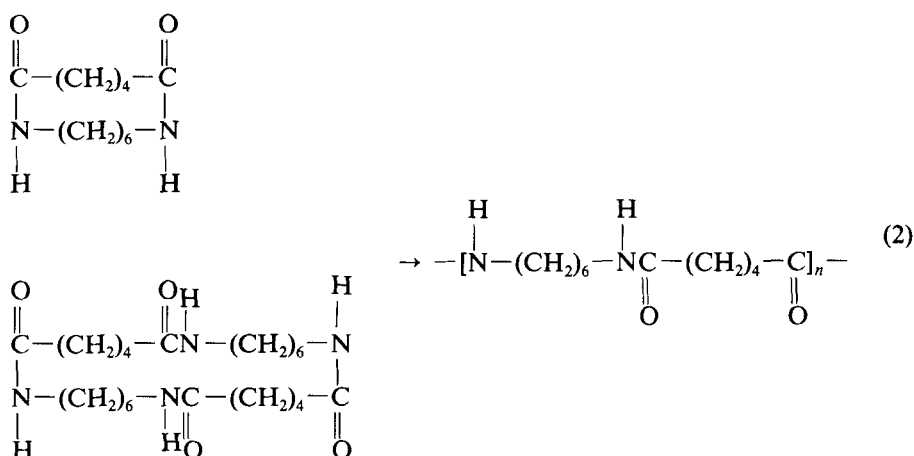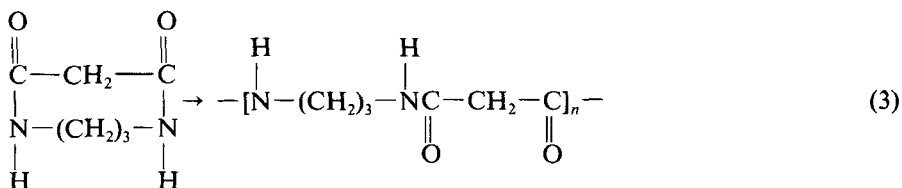In this work, polymerizations of the cyclic diamide 1,6-diazacyclododecane-7,12-dione, hereafter referred to as c-4, to polyamide 46 (Eq. 4), and copolymerizations of c-4 with CL to copolyamides (Eq. 5), are presented for the first time.

$$
\begin{array}{c}
\underset{\substack{\text{O} \\ \parallel \\ \text{C}-(\text{CH}_2)_4-\text{C} \\ \mid \qquad\qquad \mid \\ \text{N}-(\text{CH}_2)_4-\text{N} \\ \mid \qquad\qquad \mid \\ \text{H} \qquad\qquad \text{H}}}{} \rightarrow \underset{}{-[\overset{\text{H}}{\underset{}{\text{N}}}-(\text{CH}_2)_4-\overset{\text{H}}{\underset{}{\text{N}}}\underset{\substack{\parallel \\ \text{O}}}{\text{C}}-(\text{CH}_2)_4-\underset{\substack{\parallel \\ \text{O}}}{\text{C}}]_n-}
\end{array} \qquad (4)
$$

$$
\begin{array}{c}
\underset{\substack{\text{O} \\ \parallel \\ \text{C}-(\text{CH}_2)_4-\text{C} \\ \mid \qquad\qquad \mid \\ \text{N}-(\text{CH}_2)_4-\text{N} \\ \mid \qquad\qquad \mid \\ \text{H} \qquad\qquad \text{H}}}{} + \left[\underset{\text{(CH}_2)_5}{\overset{\substack{\text{H} \; \text{O} \\ \mid \; \parallel \\ \text{N}\text{C}}}{}}\right] \rightarrow -[\overset{\text{H}}{\text{N}}-(\text{CH}_2)_4-\overset{\text{H}}{\text{N}}\underset{\substack{\parallel \\ \text{O}}}{\text{C}}-(\text{CH}_2)_4-\underset{\substack{\parallel \\ \text{O}}}{\text{C}}]_n-[\overset{\text{H}}{\text{N}}-(\text{CH}_2)_5-\underset{\substack{\parallel \\ \text{O}}}{\text{C}}]_m-
\end{array} \qquad (5)
$$
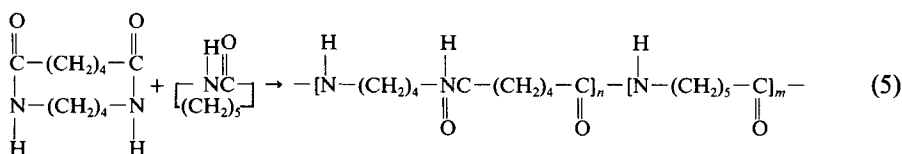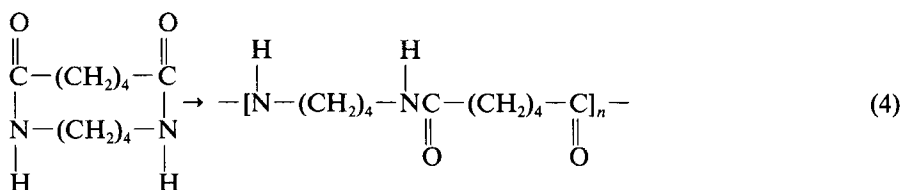
As already suggested by Iwakura et al. [7], the internal ring strain in c-4 can be considered the main driving force for polymerizations.

EXPERIMENTAL

Materials

The cyclic diamide 1,6-diazacyclododecane-7,12-dione (c-4) was obtained by thermal depolymerizations of Stanyl (DSM, The Netherlands), following for the greater part the method of Langhammer et al. [8]. The cyclic diamide was recrystallized from ethanol to constant purity ($\geq 99.9\%$) as evidenced by high-pressure liquid chromatography (HPLC). N-Methyl-2-pyrrolidone (NMP, Janssen, Belgium) was distilled from CaH_2 and kept on Molecular Sieves 4 Å prior to use. Caprolactam magnesium bromide (LMB, Grant Chemical, USA), ϵ-caprolactam (CL, DSM, The Netherlands), 1,6-hexamethylene diisocyanate (HMD, 98%, Aldrich, Belgium), isophthaloyl-bis-caprolactam (IBC, DSM in-house laboratory scale production, The Netherlands), and sodium hydride (NaH, 95%, Aldrich, Belgium) were used as received.

Polymerizations

(a) Thermal Polymerization

One part of c-4 was placed in a suitable vessel and the air replaced by nitrogen. The product was then heated to above its melting temperature (305°C). The vessel was cooled to room temperature at the end of polymerization and the solid formed was removed.

TABLE 1.   Anionic Polymerization in 10% NMP Solution at 202°C

Batch	c-4, g	NaH, g	HMD, μL	$\tau_{reaction}$	Conversion, %
AP1	10	0.10	50	3.5'	a
				6.5'	a
				23.50'	a
				28.5'	43
AP2	10	0.10	100	92.30'	8
AP3	10	0.10	100	11.30'	a
				27.30'	a
				35.30'	a
				43.30	a
				51.30'	a
				59.30'	a
				67.30'	35
AP4	10	0.03	200	19.30'	a
				43.30'	a
				67.30'	a
				91.30'	a
				115.30'	a
				139.30'	66
AP5	5	0.012	80	28	23

[a]Sample = 200 mg.

(b)   Hydrolytic Polymerization

One part of c-4 and one part of water were placed in a suitable vessel equipped with a reflux condenser and nitrogen inlet. The reaction mixture was then heated from 25 to 300°C at a rate of 180°C/h, followed by 15 hours isothermally at 300°C, and finally cooled to 25°C at a rate of 100°C/h. At the end, the solid formed was removed from the vessel.

(c)   Anionic Polymerization

Amounts of c-4, NaH, and NMP (see Table 1) were supplied to a suitable vessel equipped with mechanical agitation, reflux condenser, and nitrogen inlet. The contents were heated to NMP reflux conditions (202°C). After complete dissolution, HMD was added with a syringe. During polymerization, samples were taken for analysis. At the end of the reaction time, the reaction mixture was added to a tenfold excess of methanol to precipitate the polymer formed. The polymer was collected and washed with methanol. Subsequently, the polymer was dried at 45°C *in vacuo* for at least 24 hours. One batch (AP3) was also postcondensed in the solid state according to the following procedures: From room temperature to 250°C in 1 hour, then isothermal at 250°C for 7 hours (SSPC1); or from room temperature to 220°C in 1 hour, isothermal at 220°C for 1 hour, then from 220 to 250°C in 1 hour, and next, isothermal at 250°C for 5 hours (SSPC2).

TABLE 2.   Anionic Copolymerization Conditions

Batch	T_{mix}, °C	$T_{reaction}$, °C	CL, g	c-4, g	τ_{cryst}, min	$\tau_{reaction}$, min
COP1[a]	100	180	9.125	0.5	2	10
COP2	140	180	9.17	1.56	0	10
COP3	150	180	9.17	0.5	5	15
COP4	180	180	9.17	1.56	0	15
COP5	190	190	9.17	1.56	0	30
COP6	140	200	9.17	1.56	2.5[b]	5
COP7	200	200	9.17	1.56	6[b]	30

[a]IBC 0.125 g.
[b]Spherulite formation.

(d)   Anionic Copolymerization

The total amount of monomers (see Table 2) was divided and supplied separately to one tube containing 0.75 g LMB and another tube containing 0.08 g IBC. The contents in both tubes were then melted at T_{mix}. After complete dissolution, the contents from the tubes were supplied at the same time at $t = 0$ to the polymerization vessel at $T_{reaction}$. The reaction mixture was mixed thoroughly. At the start of the polymerization, the polymer formed began to crystallize (τ_{cryst}). The crystallized polymer was removed from the vessel at the end of the copolymerization ($\tau_{reaction}$).

Characterization and Analysis

All polymers were dried at 45°C *in vacuo* overnight prior to analysis.

Extractions

(a)   Water-Soluble Extracts (WSE).   Pieces of polyamide, with a diameter of ≤ 1 mm, were extracted intermittently with water at ambient temperature eight times for 20 minutes with 6 minute intervals in a Fritten extractor. The extracts were then analyzed for carbon content by a carbon analyzer (DC-80: UV oxidation followed by CO_2 detection) or were analyzed by HPLC.

(b)   Methanol-Soluble Extracts (MSE).   Pieces of polyamide, with a diameter of ≤ 1 mm, were extracted with methanol at ambient temperature for at least 24 hours in a Soxhlet extractor. The extracts were then analyzed by HPLC.

Measurements

Melting points were determined on a Gallenkamp Melting Point Apparatus in closed capillaries, or by a polarization microscope, equipped with a hot stage, and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AC200 (200 MHz) in acetic acid-d_2 (CDOOD). Viscosity numbers (η_{vn}) were measured in 0.5% formic acid (90%) solutions at 25°C. Differential scanning calorimetry (DSC) mea-

surements were recorded on a Perkin-Elmer PC Series DSC 7 with a heating/cooling rate of 20°C/min (T_m^1 from the first heating curve, T_c from the cooling curve, and T_m^2 from the second heating curve). The HPLC measurements were carried out with a HP 1090 DR 5 high-pressure liquid chromatography instrument using one column Nucleosil 120-5C_{18} (250 × 4 length/i.d., in millimeters). The HPLC analysis was performed with a 7.5% acetonitrile solution in a 10-mM H_3PO_4 mobile phase and applying a flow rate of 2.0 mL/min at 40°C (pressure drop 260 atm).

RESULTS AND DISCUSSION

Cyclic Diamide

In the past, starting in 1939 [9], several methods have been applied to the preparation of c-4. The high-dilution procedures [10] and Beckmann and Schmidt rearrangements [11, 12] suffer from serious drawbacks; e.g., special design apparatus required, use of large quantities of benzene, exclusion of water and CO_2, starting materials not readily available, multistep syntheses required which form isomeric cyclic oligomers which are difficult to separate. Although not yet applied to the synthesis of c-4, the procedure described by Langhammer et al. [8] looked promising for the preparation of c-4. Different polyamides were thermally converted into cyclic oligomers at 280 to 330°C. The reaction is catalyzed by small amounts of salts of different carboxylic acids and is supposed to take place by an anionic depolymerization mechanism. The degradation product of polyamide 66 reportedly contained more than 50 wt% of the 14-membered cyclic diamide and about 25 wt% of the corresponding cyclic tetraamide. Dale and Coulon [13] prepared c-4 by simple pyrolytic depolymerization of polyamide 46 in the presence of metallic sodium as catalyst. This method is analogous to Carothers' cyclic ester synthesis by depolymerization of polyesters [14, 15], but is more limited in scope and gives poorer yields. The above-mentioned thermal catalytic depolymerization reactions seemed very suitable for the depolymerization of Stanyl to c-4 [16]. Simple recrystallization from ethanol yielded c-4 with a purity ≥99.9%, as evidenced by HPLC.

(a) Thermal Polymerization and   (b) Hydrolytic Polymerization

Thermal and hydrolytic polymerizations were carried out for the greater part by following the method described by Greenewalt [5]. c-4 was not stable in the melt and seemed to partly decompose. For instance, c-4 became black during determination of the melting point ($T_m = 295°C$ according to Stetter and Marx [10], and Dale and Coulon [13], $T_m \approx 295°C$ according to the author's own observations), possibly due to degradation. Nevertheless, low molecular-weight polyamide was obtained at the end of polymerization. The polyamides contained significant amounts of unreacted c-4 as determined in methanol extractions (MSE); see Table 3.

The polyamides formed were identified by ^{13}C-NMR as polyamide 46. The chemical shift assignments were in agreement with published ones [17]. All polymerizations were accompanied by sublimation of c-4, starting at ~180°C at atmospheric pressure. In one experiment the decomposite on the inner side of the top of the reactor was analyzed by ^{13}C-NMR (see Table 5, HP1sub), and it was shown that the material was composed of only c-4.

TABLE 3. MSE, Viscosity Numbers, and DSC Analysis for Polymers Prepared by Thermal/Hydrolytic Polymerization

Batch	MSE, %	η_{vn}, mL/g	DSC, °C; J/g				
			T_m^1	ΔH	T_c	T_m^2	ΔH
TP1	26						
TP2	25						
HP1[a]	30	18	238	24	180	227	16
Stanyl		±200	294	155	259	287	81

[a]Extracted with methanol (MSE).

The MSEs were analyzed by HPLC. It was demonstrated that besides some original c-4, some corresponding tetraamide and the linear oligomers of DAB-ADA (diaminobutane-adipic acid), DAB-ADA-DAB, ADA-DAB-ADA, and DAB-ADA-DAB-ADA were present, indicating that c-4 was ring-opened. For HP1* (the asterisk indicates extraction with methanol), it was noticed that not all material was soluble in formic or sulfuric acid. Therefore, only the viscosity number of the soluble part of HP1* was determined and found to be 18 mL/g, corresponding to $\overline{M}_n \approx 2000$. The existence of a fraction not soluble in formic or sulfuric acid suggested the occurrence of crosslinking during polymerization. Due to this particular fraction, the thermal behavior of HP1* deviated from that of Stanyl. The polyamide 46 formed by hydrolytic polymerization of c-4 had a lower melting point and was less crystalline.

(c) Anionic Polymerization

Polyamide 46 was obtained by anionic ring-opening polymerization of c-4 in NMP solution at 202°C. First, a suitable solvent for the anionic polymerization of c-4 had to be found. From the literature it was known that c-4 is soluble in benzene and THF [9, 18], in a mixture of THF/cyclohexane/water (186/14/10) [11], and sparingly soluble in ethanol and ethanol/ether mixtures. It was found by the author's own observations that c-4 is soluble in ethanol, dichloromethane, DMF, DMSO, methanol, NMP, and water, and not soluble in ether, cyclohexane, THF, toluene, or xylene. Furthermore, the solubility of c-4 in CL is limited to a maximum of 27 wt% at 200°C. NMP was chosen as solvent for the anionic polymerizations due to the high solubility of c-4 in NMP (≥ 10 wt%). Furthermore, it was anticipated that c-4 and CL would copolymerize in one system given their similarity and the solubility of c-4 in CL (see Section d below).

c-4 polymerized slowly in a 10% solution of NMP at reflux conditions with NaH and HMD as catalysts to yield low molecular-weight polyamide; see Table 4. The polyamide did not precipitate during the polymerizations, but it precipitated after addition to methanol, thus indicating the synthesis of low molecular-weight products, which is in accord with the measured viscosity numbers. Below 202°C no polyamide was formed that precipitated in methanol, evidenced by HPLC analysis, which showed that the original amount of c-4 was recovered from the methanol solution. This phenomenon was also observed by Krajník et al. [19] when CL was

TABLE 4.   MSE, Viscosity Numbers, and DSC Analysis for Polymers Prepared by Anionic Polymerization[a]

Batch	τ_{reaction}, h	MSE, %	η_{vn}, mL/g	DSC, °C; J/g				
				T_m^1	ΔH	T_c	T_m^2	ΔH
AP1	3.5′			278	100	246	271	73
	6.5′			277	101	247	274	78
	23.50′			272	94	242	267	73
	28.5′		18	271	141	242	267	73
	28.5′[b]	7.5	18	271	120	243	269	77
AP2	92.30′[b]	18	16.5	260	96	222	252	54
AP3	11.30′			270	97	240	266	70
	27.30′		n.s.	269	104	240	265	71
	67.30′[b]	11	16.6	273	108	244	269	82
	SSPC1		n.s.	277	96	243	269	75
	SSPC2		n.s.	292	113	243	273	75
AP4	19.30′		30.1	279	103	247	273	82
	43.30′		21.3	276	107	242	270	89
	67.30′		19.7	273	104	237	265	78
	91.30′		20.4	273	96	236	264	76
	115.30′		19.7	280	116	243	272	93
	139.30′		21.1	276	117	242	269	87
AP5	28		16.6	273	93	242	268	70
Stanyl			●200	294	155	259	287	81

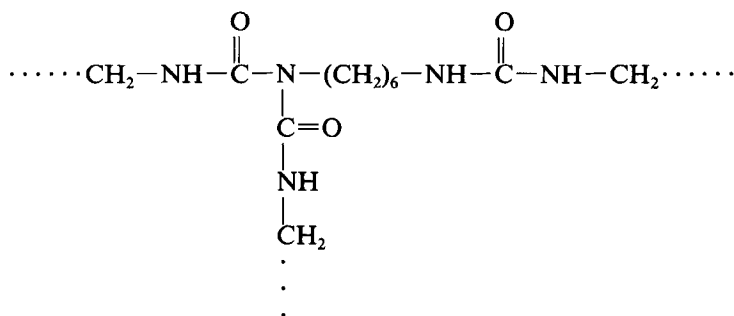[a]n.s. = not soluble.
[b]Extracted with methanol (MSE).

copolymerized with 1,8-diazacyclotetradecane-2,9-dione. A very slow decrease in monomers occurred at 230 and 260°C, while the rate of decrease was much higher at 280°C. Although no kinetic treatment of the results was possible, it was obvious that a significant change in reactivity of the cyclic dilactam took place in the 260–280°C temperature range. ^{13}C-NMR analysis confirmed that the structure of the polyamide formed was similar to that of Stanyl; see Table 5.

The MSEs were analyzed by HPLC. It was demonstrated that besides some original c-4, the linear oligomers of ADA-DAB-ADA, DAB-ADA-DAB-ADA, and ADA-DAB-ADA-DAB-ADA were present, indicating that c-4 was ring-opened. By determination of the viscosity numbers, it was found that not all polyamide 46 was soluble in formic or sulfuric acid (see AP3 SSPC1 and SSPC2). Increasing the temperature to 60°C did not solubilize the gel that was formed. This indicated the existence of a crosslinked fraction or very high molecular-weight products. The use of HMD as catalyst possibly enhanced the formation of crosslinks through biuret-type links:

TABLE 5. ^{13}C-NMR Data for Polyamides, Shifts in ppm

Batch		C=O	CO—$\underline{C}H_2$—	CO—CH₂—$\underline{C}H_2$—	NH—$\underline{C}H_2$—	NH—CH₂—$\underline{C}H_2$—
TP1		177.0	35.2	25.0	39.7	25.8
TP2		177.1	35.3	25.1	39.8	25.9
HP1		176.9	35.3	25.2	39.6	25.8
HP1[a]		177.0	35.5	25.2	39.7	26.0
HP1sub		178.1	34.9	25.0	39.4	25.2
AP1	3.5′	177.0	35.2	25.1	39.7	25.8
	6.5′	177.0	35.2	25.0	39.7	25.8
	23.50′	177.0	35.2	25.0	39.7	25.8
	28.5′	177.0	35.2	25.0	39.7	25.8
	28.5′[a]	177.0	35.4	25.1	39.7	25.9
	SSPC2	177.0	35.2	25.1	39.7	25.8
c-4		178.2	35.1	25.1	39.6	25.3
Stanyl		177.0	35.3	25.1	39.8	25.8

[a]Extracted with methanol (MSE).

$$\cdots\cdots CH_2-NH-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle \overset{|}{C}=O}{|}}{N}-(CH_2)_6-NH-\overset{\overset{\displaystyle O}{\|}}{C}-NH-CH_2\cdots\cdots$$

Due to the possible existence of biuret crosslinks, the polyamide 46 formed by anionic solution polymerization of c-4 had lower melting temperatures and was less crystalline. Solid-state postcondensation of polyamide 46 had an effect — although minor — on the melting point (see Table 4).

(d)   Anionic Copolymerization

The anionic copolymerization of c-4 with CL to yield copolyamides was carried out analogously to the anionic copolymerization of CL with Hycar [poly(butadiene-co-acrylonitrile) from B.F.Goodrich Co.] [20]. To obtain a homogeneous reaction system, it was necessary to dissolve all c-4 in CL prior to polymerization. It was observed that the solubility of c-4 in CL was ~9 wt% at 150°C, going to a maximum of 27 wt% at 200°C. The time required for complete dissolution varied from 5 to 10 minutes. After complete dissolution, the different components were mixed together and the copolymerization was started. The cyclic monomers polymerized rapidly in the melt with LMB and IBC as catalysts to form solid copolymers. After a small induction period (τ_{cryst}), the reaction mixture became cloudy

TABLE 6.   WSE and HPLC Analysis for Copolymers[a]

Batch	WSE, %C	CL unreacted, %	c-4 unreacted, %	c-4 incorporated, mol %
COP1	1.9	2.6 (2.9)	0.5 (10)	2.8
COP2	1.9	1.7 (2.1)	0.05 (0.4)	6.3
COP3	2.4	2.8 (3.1)	1.0 (20)	2.4
COP4	2.8	2.9 (3.7)	0.03 (0.2)	8.5
COP5	7.0	3.5 (4.4)	7.2 (53)	4.2
COP6	17.9	17.2 (21.7)	9.4 (70)	3.2
COP7	16.3	22.4 (28.2)	9.0 (67)	3.8

[a]Figures in parentheses relate to the original amount of starting monomers.

and viscous. At the end of copolymerization, the mixture was solid due to crystallization of the copolyamide formed. In some cases the reaction mixture became cloudy immediately after mixing of the different components ($\tau_{cryst} = 0$). This early cloudiness was due to crystallization of c-4 in the probably saturated CL-solution at a specific temperature ($T_{mix} < T_{reaction}$). The cloudiness disappeared shortly after the reaction mixture was at $T_{reaction}$, but then the solution became cloudy again and also viscous, indicating that copolymerization had started.

The copolyamides formed were extracted with water to determine the amount of unreacted monomers (WSE); see Table 6. The amount of CL found in the WSEs was in accord with the values measured by, for instance, Andrews et al. [21] who found ~3 wt% cyclic oligomers in polyamide 6, or Reimschuessel [3] who found 2.73% cyclic oligomers as MSE of polyamide 6. The amount of residual c-4 in the copolyamides was low for copolymers prepared at 180°C, while it was substantial for the copolyamides prepared at 200°C. At 200°C, the amount of unreacted CL was also significant. With these results it was possible to calculate the amount of c-4 incorporated in the copolyamides. It was demonstrated that almost all c-4 was incorporated at 180°C, yielding a copolyamide of polyamides 6 and 46 with a maximum of 8.5 mol% incorporated polyamide 46, while only ~30% was incorporated at 200°C.

TABLE 7. ^{1}H-NMR Data for Extracted Copolyamides, Integration Ratios

Batch	NHC$\underline{H}_2$	CO$-$C$\underline{H}_2$	CH$_2$C$\underline{H}_2$CH$_2$	(CH$_2$)$_2$C$\underline{H}_2$(CH$_2$)$_2$	c-4 incorporated
COP1	2.0	2.0	4.3	2.0	2.2 ± 1.6
COP2	2.2	2.2	4.2	2.0	4.0 ± 1.5
COP3	2.0	2.0	4.1	2.0	0.9 ± 0.2
COP4	2.0	2.0	3.9	2.0	0
COP5	2.2	2.2	4.2	2.0	4.2 ± 1.5
COP6	2.1	2.0	4.1	2.0	2.5 ± 1.2
COP7	2.1	2.1	4.1	2.0	1.7 ± 0.3

TABLE 8.   DSC Analysis for Extracted Copolyamides

Batch	T_m^1, °C	ΔH, J/g	T_c, °C	T_m^2, °C	ΔH, J/g	T_g, °C
COP1	213		167	208		54
COP2	220	56	165	217	51	51
COP3	214		172	211		51
COP4	220	50	166	215	54	50
COP5	214	75	157	210	39	51
COP6	216	72	157	212	38	49
COP7	215	76	161	211	37	50
Nylon 6	215 ± 2	66 ± 12	164 ± 2	212 ± 3	45 ± 4	51 ± 2

From ^{1}H-NMR spectra it was clear that the as-polymerized copolyamides contained small amounts of unreacted cyclic monomers. After extraction, these unreacted monomers were removed totally, as evidenced by NMR spectroscopy. The assignment of the different chemical shifts was easy [22], and from the integral intensities the amount of c-4 incorporated could be calculated. Because it was impossible to determine the amount of c-4 in the copolyamides quantitatively (only qualitatively) by ^{13}C-NMR, ^{1}H-NMR spectra were used (besides data from the WSE) to calculate the amount of c-4 incorporated; see Table 7. The results were in close agreement, except for COP4. There is no adequate explanation at the present time for this discrepancy. The error in the amount of c-4 incorporated, calculated from NMR data, was rather large due to the subtraction of two large peak areas, whereas this was not the case for the calculation from WSE data.

The thermal behavior was studied by using a polarization microscope equipped with a hot stage and by means of DSC (see Table 8). All copolyamides showed an average T_g of 50°C, a T_m of 213°C, and T_c of 163°C, which were identical to values determined for polyamide 6. Literature values [3] for polyamide 6 are T_m = 215–228°C and $T_g \approx$ 50°C. It seemed that the copolymerization of a maximum of 8.5 mol% polyamide 46 in polyamide 6 showed no effect on the thermal behavior and crystallinity as compared to polyamide 6.

CONCLUSIONS

It was demonstrated for the first time that 1,6-diazacyclododecane-7,12-dione (c-4) was polymerized thermally, hydrolytically, and anionically to polyamide 46 by ring-opening polymerizations. Due to possible crosslinking, some polyamide 46 had difficulties in dissolving in formic or sulfuric acid, and showed a thermal behavior that deviated from that of Stanyl (lower melting points). Furthermore, copolyamides of polyamide 6 and polyamide 46 were successfully prepared by anionic ring-opening polymerization of c-4 with ε-caprolactam. The copolyamides with a maximum of 8.5 mol% incorporated polyamide 46 showed no effect on the thermal behavior and crystallinity as compared to polyamide 6.

From the results mentioned herein, it seems that the coexistence of a solvent for c-4 is required during polymerization. c-4 melts at a high temperature ($\sim$295°C) and therefore a bulk melt process like RIM still seems incompatible with the homo-

polymerization of this cyclic diamide. Further experiments have to be performed to obtain further insight into the possibilities of polymerizing c-4 to polyamide 46 or copolyamides.

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