BISLACTAMS, THEIR SYNTHESIS, POLYMERIZATION AND COPOLYMERIZATION WITH 6-CAPROLACTAM. II.*

BISLACTAMS DERIVED FROM 2,2'-ALKYLENE-BIS(CYCLOHEXANONES), THEIR HYDROLYTIC POLYMERIZATION AND COPOLYMERIZATION WITH 6-CAPROLACTAM

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In contrast with methylene-bis(1-aza-2-cycloheptanone), which according to an earlier communication was synthetized in the form of three constitutional isomers 7,7' (*I*), 3,3' (*II*) and 3,7' (*III*), synthesis of further bislactams led only to 7,7'-isomers, namely, 7,7'-bis(1-aza-2-cycloheptanone) (*IV*), 7,7'-ethylidene-bis(1-aza-2-cycloheptanone) (*V*) and 7,7'-tetramethylene-bis(1-aza-2-cycloheptanone) (*VI*). The polymerization of bislactams *I*—*VI* in the presence of 2 mol% 6-aminocaproic acid at 260°C led in all cases to almost 100% values of the polymer content; the rate of polymerization of bislactams decreased in the order $III > I > VI > V$. During the copolymerization of the above bislactams with 6-caprolactam under similar conditions the so-called crosslinking efficiency of bislactams was determined qualitatively; it decreased in the series $IV = VI > I = II = III > V$.

The properties of common polyamides are determined in the first place by the linear character of chains and by the presence of regularly arranged amide groups forming intramolecular hydrogen bonds. A change in the polyamide properties may be achieved by physical or chemical interferences with the structure of the macromolecules or with their mutual arrangement in bulk; however, such interferences are usually accompanied by deterioration of some mechanical properties. Similarly to the other polymers, essential changes in the structure and properties of polyamides may be caused by formation of a three-dimensional structure. A reduced mobility of the individual segments in the three-dimensional network leads to a decrease in the crystallization ability and rate; on the other hand, the formation of crosslinks is one of the bases of the increase in thermal stability and permanence of shape, and also — along with limited crystallinity — the cause of the increase in impact resistance. Owing to the other properties following from the three-dimensional character of polymers their preparation and application may be regarded as feasible only in the case of an additional crosslinking of the substance having a final shape, or if a product having a final shape is produced by polymerization. The solution of the problem of crosslinking of polyamides has become urgent after anionic polymerization in moulds in the presence of activators and under conditions close to the adiabatic conditions had been carried out on the industrial scale.

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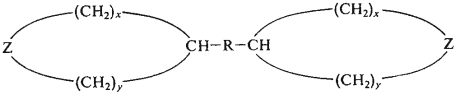
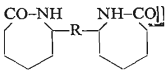
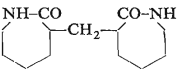
One of the possibilities of preparation of multidimensional polyamides based on 6-caprolactam which may be used both in the hydrolytic and in the anionic process is the copolymerization of 6-caprolactam with bislactams having the general formula[1-5] where Z denotes the CO—NH group and R is a simple covalent bond or a linear or branched hydrocarbon residue; x and y vary from 0 to 4. The possibility of crosslinking with bislactams has been treated only in patents[1-5,7-14], with the exception of a paper by Hopff and coworkers[6].



This work has been devoted to the preparation of bis-lactams and their polymerization and copolymerization with 6-caprolactam. In our introductory paper[15] we reported on the synthesis of methylene-bis(1-aza-2-cycloheptanone) and of its three constitutional isomers, *i.e.* of the isomer 7,7'-(*I*), 3,3'-(*II*) and 3,7'-methylene-bis(1-aza-2-cycloheptanone) (*III*). This paper is dealing with the synthesis of 7,7'-bis(1-aza-2-cycloheptanone) (*IV*), 7,7'-ethylidene-bis(1-aza-2-cycloheptanone) (*V*) and 7,7'-tetramethylene-bis(1-aza-2-cycloheptanone) (*VI*), and also with the hydrolytic polymerization of these bislactams and their copolymerization with 6-caprolactam.



I, R = —CH_2—
V, R = >CH—CH_3
VI, R = —$(CH_2)_4$—



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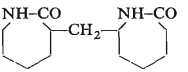

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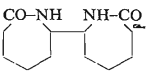


IV

Bislactam *IV* can be readily prepared from 6-caprolactam by radical dimerization with peroxides or UV-radiation[16-18]. We found for the reaction of 6-caprolactam with cumyl peroxide that the yield and purity of bislactam *IV* depend on the purity of the 6-caprolactam used and on the inertness of the medium; the yields increase considerably in nitrogen atmosphere (48·9% compared to 32% or 19·7% given in the literature[16,17]). A further increase in yields was obtained if 6-caprolactam crystallized several times was used at the same time (58·8%).

In the other cases, the synthesis of 2,2'-alkylene-bis(cyclohexanones) had to be carried out first. From these diketones, bislactams were prepared either directly by Schmidt's reaction or indirectly by Beckmann's rearrangement of the corresponding dioximes. 2,2'-Bis(cyclohexanone) was prepared by oxidative dimerization of cyclohexanone in the presence of lead dioxide according to the patent[19] in low yields (14·5% at the utmost); the yields were found to be greatly dependent on the quality of lead dioxide. 2,2'-Ethylidene-bis(cyclohexanone) was prepared by the condensation of cyclohexanone with acetaldehyde in an alkaline medium similarly to 2,2'-methylene-bis(cyclohexanone)[20]. The preparation of the latter diketone is much more difficult compared to the methylene derivative, owing to the easy intramolecular cyclization[21-22] leading to tricyclo-[7,3,1,$0^{2,7}$]-2-hydroxy-8-methyl-tridecane-13-one, which according to our observations becomes the only product if gaseous acetaldehyde is used. 2,2'-Ethylidene-bis(cyclohexanone) was obtained by a reaction of liquid acetaldehyde at 10°C. 2,2'-Tetramethylene-bis(cyclohexanone) was prepared by the alkaline condensation of ethyl 2-oxocyclohexane carboxylate with 1,4-dibromobutane followed by decarboxylation. An attempt to carry out direct alkylation of cyclohexanone with 1,4-dibromobutane in the presence of sodium amide[23] was unsuccessful[24]. Since all diketones described above contain in their molecules two asymmetric carbon atoms, they may exist in two diastereoisomeric forms, *viz.*, in the *meso*-form and as racemates. However, only 2,2'-bis(cyclohexanone) could be isolated in the form of two isomers; the crystalline isomer is probably a racemate and the isomer which is liquid at room temperature is a *meso*-form[25].

TABLE I

Yields of Bislactams (%) Obtained by Schmidt's Reaction and Beckmann's Rearrangement in Various Media

Operation	Medium	*Ia* + *Ib*[a]	*Ia* + *II* + *III*[b]	*IV*	*V*	*VI*
Schmidt	HCl	57·0	—	10·3	14·8	—
	H_3PO_4[c]	80·0	—	16·0	21·1	66·5
Beckmann	H_2SO_4	—	25·0	—	24·6	—
	H_3PO_4[c]	—	79·5	—	—	65·0

[a] Mixture of diastereoisomers. [b] Mixture of position isomers. [c] Polyphosphoric acid.

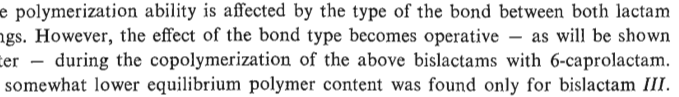
Dioximes were prepared by the common procedure, that is, by the reaction of diketones with hydroxylamino hydrochloride in the presence of bicarbonate in methanol.

The only compound that could not be prepared was 2,2′-bis(cyclohexanone)dioxime, probably owing to the easy cyclization of this compound with formation of a substituted pyrrol ring. (A model reaction of 2,2′-bis(cyclohexanone) with ammonium acetate yielded quantitatively 1,2,3,4,5,6,7,8-octahydrocarbazol).

The results of attempts to prepare bislactam are given in Table I. The least successful attempt was Beckmann's rearrangement in sulphuric acid where the maximum yield was 25%, if the extraction method of dosage of dioximes was used. The best results were obtained for the rearrangement in polyphosphoric acid; also Schmidt's reaction in polyphosphoric acid gave the highest yields. The low yields obtained in the case of 7,7′-bis(1-aza-2-cycloheptanone) are due to the simultaneous formation of 7-(2-oxocyclohexyl)-1-aza-2-cycloheptanone which, if the crystalline isomer 2,2′-bis(cyclohexanone) (m.p. 69–70°C) is used, may become the main product of Schmidt's reaction[25].

In contrast with methylene-bis(1-aza-2-cycloheptanone) which as has been mentioned above exists in the form of three position isomers *I*, *II*, and *III* (the isomer *I* was isolated in two diastereoisomeric forms *Ia* and *Ib*[15]), the other bislactams were isolated only in the form of a single isomer having the 7,7′ structure. The structure of bislactam *IV* obtained by Schmidt's reaction was proved by the identity of the product with bislactam obtained by the radical dimerization of 6-caprolactam, the structure of which has been proved earlier by Reinisch and coworkers[16]. Structures *V* and *VI* are favoured by the fact that the infrared spectra of these bislactams in the region of bands of free NH groups coincide with those of bislactam *Ia* or *Ib* (ref.[15]).

A surprisingly high equilibrium polymer content (96–99·9%) was found for the homopolymerization of bislactams in the presence of 2 mol% of 6-aminocaproic acid at 260°C (Fig. 1). These values are in fact only apparent ones, since they also include the portion of unreacted free lactam rings bonded in the polymer chain. Moreover, the fact cannot also be neglected that owing to the method used (extraction with water) the equilibrium polymer content in this case also involves all oligomers which however can be assumed to be very poorly soluble in water. The relatively small differences between the equilibrium polymer contents of the individual bislactams do not allow an unequivocal conclusion to be drawn to what extent the polymerization ability is affected by the type of the bond between both lactam rings. However, the effect of the bond type becomes operative – as will be shown later – during the copolymerization of the above bislactams with 6-caprolactam. A somewhat lower equilibrium polymer content was found only for bislactam *III*.



(*A*)

The finding satisfies the view of intramolecular cyclization[15] with formation of a stable pyrrolidone ring. This view is corroborated by an analysis of the infrared spectrum of the polymer which in contrast with the spectra of polymers of the other bislactams contains a band at 1700 cm^{-1} typical of the *cis*-amide bond of pyrrolidone.

As can be seen from Fig. 1*a*, the difference between the individual bislactams is markedly reflected in the polymerization rate which decreases in the order *III* > *Ia* = = *Ib* > *VI* > *V*; isomer *III* polymerizes faster than 6-caprolactam. This fact may be explained by the tendency of the monomer to undergo the above cyclization which may be the driving force of the polymerization of bislactam *III*. Since isomer *II* could be obtained in an insignificant amount[15], only a single homopolymerization was carried out, and after 24 h the polymer content was 94·7%, so that the effect of the position isomerism on the polymerization rate cannot be compared. Diastereoisomerism does not affect the polymerization rate, because isomers *Ia* and *Ib* polymerize at the same rate. The polymerization rate of bislactam *IV* at 260°C cannot be compared with the other bislactams, owing to the high melting point of this monomer (293°C). At temperatures above its melting point the other bislactams of this type have already a limited thermal stability; as can be seen in Fig. 1*b*, bislactam *IV* polymerizes considerably faster than bislactam *Ib*.

The polymers of all bislactams including bislactam *III* are brittle, yellowish, transparent and insoluble in common solvents of polyamides. Consequently, the

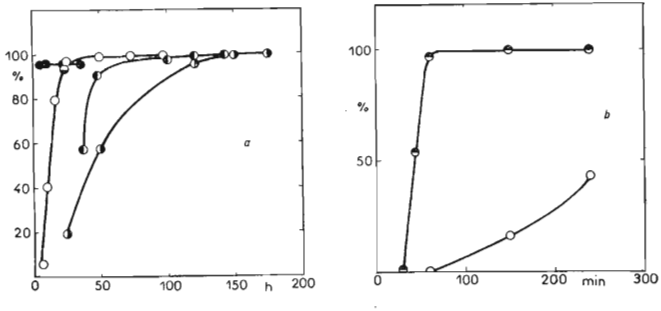


FIG. 1

Polymerization of Bislactams *I*—*VI*

Concentration of 6-aminocaproic acid 2 mol%. Polymerization at 260°C (*a*): ○ *Ia*, *Ib*, ◒ *II*, ● *III*, ◑ *V*, ◐ *VI*. Polymerization at 295°C (*b*): ○ *Ib*, ◓ *IV*.

product in the case of bislactam *III* is not a linear polymer, as could be inferred from reaction (*A*), but a multidimensional product. This indicates that the cyclization leading to a pyrrolidone ring is not quantitative, and copolymerization must also be taken into account. Analogous cases of copolymerization of nonpolymerizing lactams have been described in the literature[26,27].

The copolymerization of the above bislactams with 6-caprolactam was carried out at 260°C in the presence of 2 mol% of 6-aminocaproic acid. The concentration range was in most cases chosen so as to determine the "critical crosslinking efficiency", *i.e.* the minimum bislactam concentration at which a copolymer insoluble in common solvents of polyamides is formed. No differences in the polymerization rates or in the monomers–copolymer equilibria were established in the concentration range 0·2–1·0 mol% of bislactam; the copolymerization proceeds similarly to the homopolymerization of 6-caprolactam under comparable conditions. The bislactams investigated here can be presented in the following order reflecting their crosslinking efficiency: $IV = VI > Ia = Ib = II = III > V$.

TABLE II

Copolymerization of 6-Caprolactam with Bislactams (0·5 mol %) at 260°C
t Copolymerization time (h), *c* copolymer content (%).

t	*Ia*		*Ib*		*II*	
	c	η_{red}	*c*	η_{red}	*c*	η_{red}
6	76·6	1·65	80·9	2·14	—	—
12	85·1	1·95	87·0	2·64	88·3	2·00
24	88·2	2·44	89·3	3·20	89·2	2·37
48	88·9	3·14	89·3	4·03	89·3	2·25
72	89·1	3·71	89·3	4·05	89·4	2·59
96	89·1	3·00	89·3	2·90	89·7	2·77

The dependence of the copolymerization process on the concentration of bislactam was investigated in more detail for the individual isomers of methylene-bis(1-aza--2-cycloheptanone). The reduced viscosity of copolymer solutions in *m*-cresol increases with time (Table II) with increasing concentration of bislactam. At a concentration higher than the critical concentration of bislactam, polymers having a multidimensional structure and insoluble in common solvents of polyamides are formed in a certain region of conversions, before the equilibrium value has been attained. The rate at which bislactams are incorporated in the polyamide chain is difficult to determine from the participation of both lactams in the extract in the

region of real concentrations investigated here. Also the relative participation of bislactam in the copolymer is very low with respect to the concentrations used, and the accuracy of determination, *e.g.* by hydrolysis and chromatography, would therefore be considerably limited. A certain possibility for the evaluation of the character of copolymers in the initial stage of polymerization is offered by the values of the Huggins constant depending on intrinsic viscosity compared to similar values for the homopolymers of 6-caprolactam. This problem has been dealt with in another paper[28].

EXPERIMENTAL

The melting points were measured on Kofler's block, the boiling points were not corrected. The infrared spectra were recorded with a Zeiss-UR 10 apparatus.

Methylene-bis(1-*aza*-2-*cycloheptanone*). Isomers of methylene-bis(1-aza-2-cycloheptanone) were prepared by procedures described in an earlier paper[15] (*Ia*, m.p. 235–236°C, *Ib*, m.p. 195 to 197°C, *II*, m.p. 247°C and *III*, m.p. 174–182°C).

7,7′-*Bis*(1-*aza*-2-*cycloheptanone*) (IV). 2,2′-Bis(cyclohexanone) was obtained by oxidative dimerization of cyclohexanone with lead dioxide according to patent[19]. The partly crystalline distillate 165–175°C/14 Torr was divided into the liquid and the crystalline fraction. The liquid fraction was subjected to Schmidt's reaction by procedures described in ref.[15]. Bislactam *IV*, m.p. 293°C was obtained (2-propanol–water 3 : 1). Infrared spectrum (KBr): 1 195, 1 635–65, 3 290 cm^{-1}. For $C_{12}H_{20}N_2O_2$ (224·3) calculated: 64·25% C, 8·99% H, 12·49% N, found: 64·05% C, 9·06% H, 12·48% N. The use of the crystalline fraction of 2,2′-bis(cyclohexanone) for Schmidt's reaction during which 7-(2-oxocyclohexyl)-1-aza-2-cycloheptanone is predominantly formed, besides bislactam *IV* has been described in ref.[25]. In our case the mother liquors after the separation of raw bislactam *IV* contained about 3% of 7-(2-oxocyclohexyl)--1-aza-2-cycloheptanone.

Preparation of bislactam IV *by a modified procedure*[17]. A mixture of 113·1 g (1 mol) of 6-caprolactam and 11·6 g (0·043 mol) of cumyl peroxide was heated at the bath temperature 140°C for 20 h in nitrogen. On cooling, the crystalline reaction mixture was dissolved in acetone. Formation of crystals in solution set in immediately; the crystals were separated after being left to stand at 0°C for two days. 4·75 g (49·2% with respect to cumyl peroxide) of bislactam *IV* was obtained, m.p. 293°C (2-propanol–water). For $C_{12}H_{20}N_2O_2$ (224·3) found: 64·42% C, 9·18% H, 12·14% N. If 6-caprolactam crystallized four times was used instead of technical caprolactam, the yield was 58·5% of bislactam *IV*.

7,7′-*Ethylidene-bis*(1-*aza*-2-*cycloheptanone*) (V). 2,2′-Ethylidene-bis(cyclohexanone) was prepared after patent[29] as a viscous liquid, b.p. 169°C/4 Torr (dioxime, m.p. 167–168°C) and was used immediately for Schmidt's reaction or for the preparation of dioxime. Schmidt's reaction and Beckmann's rearrangement were carried out by procedures described in ref.[15] Bislactam *V*, m.p. 230–231°C (2-propanol) was obtained. Infrared spectrum of ($CHCl_3$): 1 200, 1 670, 3 400 cm^{-1}. For $C_{14}H_{24}N_2O_2$ (252·3) calculated: 66·63% C, 9·58% H, 11·10% N; found: 66·65% C, 9·50% H, 11·16% N.

7,7′-*Tetramethylene-bis*(1-*aza*-2-*cycloheptanone*) (VI). 2,2′-Tetramethylene-bis(cyclohexanone) was prepared by the condensation of ethyl 2-oxocyclohexane carboxylate with 1,4-dibromobutane with subsequent decarboxylation similarly to Kötz and Kayser[30] in a total yield 55%

or according to Ritchie and Taylor[31] in a total yield 69%. (2,2'-Ethoxycarbonyl-2,2'-tetramethylene-bis(cyclohexanone), b.p. 225°C/2 Torr, 2,2'-tetramethylene-bis(cyclohexanone), b.p. 191°C/1 Torr, dioxime, m.p. 159°C). Bislactam *VI* was prepared by Beckmann's rearrangement of dioxime or by Schmidt's reaction of diketone by procedures described in ref.[15] as a compound having m.p. 218—221°C (2-propanol). Infrared spectrum: ($CHCl_3$) 1200, 1670, 3400 cm^{-1}. For $C_{16}H_{28}N_2O_2$ (280·4) calculated: 68·53% C, 10·06% H, 9·99% N; found: 68·09% C, 10·28% H, 10·27% N.

Polymerization

The polymerizations and copolymerizations were carried out in evacuated sealed glass ampoules by the usual technique[32]. 2 mol% 6-aminocaproic acid was used as catalyst in all cases. The monomers were additionally dried for at least 12 h at 50°C/1 Torr prior to weighing. The polymer and copolymer contents were determined by a repeated extraction of dried polymer samples with boiling water according to the usual procedure[33]. (All bislactams used were found to be soluble in water). The viscosity measurements of soluble copolymers were carried out in *m*-cresol at concentrations 0·4 g/100 ml in an Ubbelohde viscometer with a capillary No II at 25 ± 0·005°C by the common technique[33].

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