ε-CYCLOHEXYLCAPROLACTAM*

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ε-Cyclohexylcaprolactam was prepared by Schmidt's reaction from 2-cyclohexylcyclohexanone. It was proved that this lactam does not polymerise at 255–280°C, either in the presence or in the absence of ε-aminocaproic acid, but undergoes cyclodimerization to form 7,14-dicyclohexyl--1,8-diaza-2,9-cyclotetradecanedione (*I*).

The rate of polymerization and the polymerization ability of substituted ε-caprolactams depend both on the position and the size of the substituent[1,2]. Recently, we have concerned ourselves with the study of the effect of voluminous substituents in the ε position, *i.e.* in the direct neighbourhood of nitrogen atom of the amide bond[3,4]. The results obtained, when studying the effect of 2-oxocyclohexyl and 2-hydroxycyclohexyl substituents, led us to study the polymerization of ε-cyclohexylcaprolactam for which a relatively high polymerization ability is quoted[5].

ε-Cyclohexylcaprolactam was prepared by Schmidt's reaction of 2-cyclohexylcyclohexanone in polyphosphoric acid, unlikely to Jansen[5] and Kelly and Mathews[6], who employed in their syntheses Beckmann's rearrangement of oxime. Its structure was checked both by infrared spectroscopy (the presence of the 3405 cm^{-1} band ($CHCl_3$) is characteristic for ε-substitution[7] of caprolactam derivatives) and by mass spectroscopy. The most intensive ion of the spectrum is the ion *m/e* 112. This fragment corresponds both to an ion which could have been formed by splitting off of the substituent on the carbon atom next to nitrogen atom and to an ion having the structure $^{(+)}NH_2{=}CH{-}\langle\bigcirc\rangle$, which could have been formed by α-splitting of the C—C bond with respect to nitrogen atom with simultaneous hydrogen transfer[8]. The GLC analysis of the crude product have shown that Schmidt's reaction gives selectively ε-derivative as the amount of side products was lower than 1%.

At the attempts of the polymerization of ε-cyclohexylcaprolactam in the presence of 2 mol % of ε-aminocaproic acid at the temperature range of 255–280°C the separation of a solid phase in the "polymerizing" liquid mass was observed. An analogous phenomenon was observed when heating anhydrous ε-cyclohexylcaprolactam at 255°C. This material, which is at 255–280°C only partially soluble in ε-cyclohexyl-

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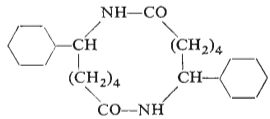
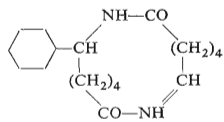
caprolactam, was obtained after monomer separation by extraction with benzene and identified as 7,14-dicyclohexyl-1,8-diaza-2,9-cyclotetradecanedion (*I*)



I

by elemental analysis and by mass and infrared spectra. Mass spectrum contained beside the M^+ *m/e* 390 ion also the most intensive ion *m/e* 307, which corresponds to fragment formed by splitting off of the substituent on the carbon atom next to nitrogen atom



II

and furthermore, it contained the ion type *m/e* 112 corresponding to the $^{(+)}NH_2{=}CH{-}$⟨⟩ fragment. The infrared spectrum of the dimer *I* is, with respect to the monomer spectrum, characterized by the same band shifts as it is observed in case of cyclic dimer of caprolactam when compared with caprolactam[9], including the new band at 1 545 cm^{-1}, which is typical for the presence of *trans*-amide bond.

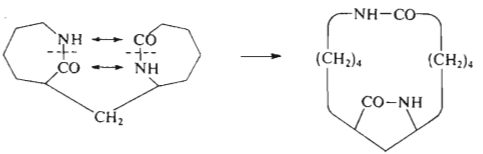
The content of the dimer *I* was at 255°C after 24 hours 17·8% and after 115 hours 60·8% irrespective of the way of monomer drying; *i.e.*, whether the monomer was dried by the usual way (see Experimental) or if an additional drying for 50 hours at 20°C/1 Torr was applied. The above mentioned values of the dimer content are slightly lower than the values obtained in the polymerization experiments of ε-cyclohexylcaprolactam performed under the same conditions in the presence of 2 mol % of ε-aminocaproic acid (Table I). This proves that the monomer used was free of water. In these cases the cyclic dimer *I* is also the main product as the ζ_{red} values of these "polymerizates" are practically independent of the temperature and the time of heating (0·22–0·27 dl/g) and identical with the viscosity of the dimer *I* (ζ_{red} = 0·23 dl/g); the results of mass spectroscopy are also the same.

Jansen[5] has also observed the formation of turbidity, but only after the repeated heating of cooled polymer samples even at 270°C, but he has not paid much attention to this phenomenon

as well as to the DTA measurements. The results of DTA measurements quoted by the author[5] give also the evidence about the presence of the dimer *I*. The DTA curves proceed through several maxima, which shift to higher temperatures with repeated heating. Also in our experiments the repeated heating of the samples prepared in the presence of ε-aminocaproic acid, which therefore contained, besides the dimer *I*, also the small amount of oligomers or of cooligomers of ε-aminocaproic acid, caused the shift of the melting point from its initial value of 235—245°C towards higher temperatures. Therefore the equilibrium content of "poly(ε-cyclohexylcaprolactam)" quoted by Jansen[5] (55% at 260°C) has to be taken as a pseudoequilibrium content of the dimer *I*.

This analysis shows that ε-cyclohexylcaprolactam at elevated temperature in the absence of catalysts cyclodimerises; the dimer *I* is also the main product of the polymerization of ε-cyclohexylcaprolactam in the presence of ε-aminocaproic acid or of water.

The formation of the dimer *I* in the absence of the catalyst can be explained by intermolecular transamidation reaction. The similar or the catalysed transamidation reaction was only described[7] in case of 3,7'-methylene-bis(1-aza-2-cycloheptanone), where even at the temperature as low as 90°C (at spectroscopic measurements) the formation of a stable five-member pyrrolidone ring was observed:



Internal transamidation could also explain the fact that analogous bislactam with such a highly unfavourable structure — 7,7'-bis(1-aza-2-cycloheptanone) — acts as a catalyst for the polymerisation of anhydrous caprolactam[10] at the concentrations of 5 mol % or higher. An analogous behaviour was also observed with ε-cyclohexylcaprolactam. The yield of the polymer at the polymerization of caprolactam in the presence of 5 mol % of this monomer and in the absence of other components was after 96 hours at 260°C approximately 50%.

In case of a bulky cyclic substituent, such as cyclohexyl, it seems, that caprolactam segment finds optimum conformational possibilities in the form of the cyclic dimer, rather than in its linear form; this is also evident from the study of calot models. Fourteen-member ring of the dimer, which is already beyond the transition region because of a small angle strain and the absence of interactions of hydrogen atoms inside the cycle, should therefore be more stable towards polymerization. Polymerization of more than thirteen-member lactam cycles has not yet been described in the literature, but a low polymerization ability of the caprolactam dimer has been quo-

ted[11,12]. In case of the dimer *I*, the presence of two bulky substituents could contribute to an enhanced stability of the cycle. Even if the content of the cyclic dimer *I* would depend on the reaction temperature, the limit values found (Table I) (with increasing tendency with decreasing temperature) could be taken only for a pseudo-equilibrium values, because of a heterogenity of the system during heating. The separation of the crystalline dimer *I*, which is even at high temperatures only partly soluble in the monomer, can shift the real equilibrium monomer–cyclic dimer, towards the dimer and can be in this way the driving force of the reaction leading to an unusually high yields of the fourteen-member ring compounds.

TABLE I

The Amount of the Residue Nonextractable by Benzene (c_I) in Products Obtained by Heating of ε-Cyclohexylcaprolactam in the Presence of ε-Aminocaproic Acid (2 mol %)

Time, h	c_I, % wt.	Time, h	c_I, % wt.	Time, h	c_I, % wt.
255°C		270°C		280°C	
90	67·3	96	62·6	90	59·6
140	74·3	120	65·7	110	60·2
170	71·6	210	69·5	135	60·1
240	75·1	260	71·8	160	61·9
340	72·8	350	71·8		

EXPERIMENTAL

Melting points (uncorrected) were determined on a Kofler block, infrared spectra were run on a Perkin-Elmer apparatus.

ε-Cyclohexylcaprolactam

2-(1-Cyclohexenyl)cyclohexanon, which was prepared according to Plešek[13] by autocondensation of cyclohexanone in the presence of *p*-toluensulphonic acid, was transformed to 2-cyclohexylcyclohexanone by pressure hydrogenation on a Pd/C catalyst. 2-Cyclohexylcyclohexanone was then transformed to the end product by Schmidt's reaction in polyphosphoric acid according to ref.[7]. ε-Cyclohexylcyprolactam was obtained in 95% yield; m.p. 148·5–148·9°C (ethanol; ref.[5] gives 146–147°C, ref.[6] gives 134–135°C). For $C_{12}H_{21}NO$ (195.3) calculated: 73·80% C, 10·84% H, 7·17% N; found: 74·10% C, 10·99% H, 6·84% N. Infrared spectra (KBr): 1200, 1655, 3060, 3200, 3280 cm^{-1}; ($CHCl_3$): 1200, 1655, 3405 cm^{-1}. Mass spectrum: M^+ ($C_{12}H_{21}NO$) *m/e* 195; the most intensive ion *m/e* 112.

Dimerization of ε-Cyclohexylcaprolactam

Dimerization of ε-cyclohexylcaprolactam, dried for 24 hours at 20°C/1 Torr, was performed at 255°C in evacuated sealed glass ampoules by the generally known method for hydrolytic polyme-

risation of caprolactam[14]. The mass was then crushed and the dimer *I* was obtained as a unsoluble residue after 24 hours' extraction with benzene at room temperature (the experimentally determined minimum time of extraction at 20°C was 10 hours; 1 g of ε-cyclohexylcaprolactam dissolves at this temperature in 32·2 ml of benzene, the dimer *I* is insoluble in benzene) in the 60·8% yield (after 115 hours of heating), m.p. 320–330°C. Analysis: $C_{24}H_{42}N_2O_2$ (390·7) calculated: 73·80% C, 10·84% H, 7·17% N; found: 73·75% C, 10·86% H, 7·20% N. Infrared spectrum (KBr): 1165, 1545, 1663 cm^{-1}. Mass spectrum: M^+ ($C_{24}H_{42}N_2O_2$) *m/e* 390; the most intensive ion *m/e* 307, ion type *m/e* 112.

The polymerization experiments with ε-cyclohexylcaprolactam in the presence of ε-aminocaproic acid were performed analogously to the dimerization. Viscosity measurements were performed according to the generally used procedure[15].

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