THE INFLUENCE OF SUBSTITUENTS ON POLYMERIZATION OF SEVEN-MEMBERED LACTAMS. III.*

SYNTHESIS AND POLYMERIZATION OF 7-(2-HYDROXYCYCLOHEXYL)PERHYDRO-2-AZEPINONE

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Received July 8th, 1970

Schmidt reaction of 2-(1-cyclohexenyl)cyclohexanone in polyphosphoric acid gave, instead of the expected 7-(1-cyclohexenyl)perhydro-2-azepinone, a compound that was identified as 7-(2-hydroxycyclohexyl)perhydro-2-azepinone. The rate of hydrolytic polymerization of this lactam at 260°C catalysed by ε-aminocaproic acid is comparable with that found for ε-caprolactam. The equilibrium polymer concentration was determined to be 62·8%. The equilibrium concentration of copolymer during the copolymerization with ε-caprolactam decreases with the increasing concentration of substituted lactam. Simultaneous decrease of the molecular weight of the copolymers is accounted for by side reactions that may proceed during the copolymerization.

Information on the polymerization of substituted ε-caprolactams is, with the exception of methyl-derivatives[1–5], very scarce. The decrease of the polymerization ability of substituted ε-caprolactams is, in comparison with ε-caprolactam, usually related to the increasing size of the substituents[6,7]. ε-Cyclohexyl-ε-caprolactam[8] is regarded as an exceptional case. It gives relatively high conversion to polymer (55% at 260°C) which is in contrast with a sterically similar though not polymerizing ε-isopropyl-ε-caprolactam[8]. The differences between conformational possibilities of the monomer and that of the monomer segment in the polymer are, in the case of cyclic substituted derivative, probably greater than in the case of isopropyl derivative, similarly the geminal disubstituted ε,ε-caprolactams show discrepancies in the relationships between the polymerization ability and the character of substitution[9].

Comparing the known polymerization ability of ε-cyclohexyl-ε-caprolactam[8] with that of the corresponding cyclohexenylcaprolactam might show the influence of the expected small deformation of a cyclic substituent caused by the presence of the double bond. An attempt was made to prepare 7-(1-cyclohexenyl)perhydro-

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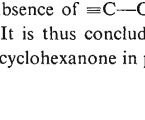
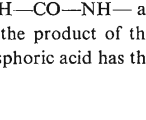
2-azepinone from easily accessible 2-(1-cyclohexenyl)cyclohexanone[10] by the Schmidt reaction in polyphosphoric acid but the expected compound was not isolated. Elementar analysis of the obtained crystalline product indicates that the compound contains one mole of water more than the expected 7-(1-cyclohexenyl)perhydro-2-azepinone. The hydrolytic reaction of possibly formed 7-(1-cyclohexenyl)perhydro-2-azepinone was ruled out because neither amino nor carboxylic groups were detected by the ninhydrin test, by conductometric titration or by the analysis of infrared spectra. A relatively broad 3315 cm^{-1} band in the infrared spectrum can be interpreted as the overlap of two bands corresponding to —OH and —NH groups forming intramolecular hydrogen bond. The shift of the amide containing carbonyl band from 1670 cm^{-1} to 1650 cm^{-1} can also be accounted for by the intramolecular hydrogen bond between the hydroxyl and amide bond. The maximum corresponding to the amide containing carbonyl group can be shifted back to 1670 cm^{-1} which is the absorption usually observed in other ε-caprolactam derivatives[11]. This effect occurs when the expected hydroxyl group is blocked by benzoylation. A similar phenomenon is seen in the case of the 3420 cm^{-1} band which corresponds to the NH group. The benzoylated compound shows also 1190 and 1735 cm^{-1} absorption bands that correspond to an ester group.

The presence of the hydroxyl group was further confirmed by the reaction with Agulhon reagent[12]. No double bond, however, was detected by chemical reaction. NMR spectroscopy revealed the presence of >CH—OH group (τ = 5·83 c/s) as well as $—CH_2—CO—NH—$ or $—CH_2—\underset{|}{CH}—NH—$ group (τ = 7·66 c/s and 6·72 c/s resp.) It also showed the absence of ≡C—OH, >CH—CO—NH— and $—CH_2—NH—$ groups respectively. It is thus concluded that the product of the Schmidt reaction of 2-(1-cyclohexenyl)cyclohexanone in polyphosphoric acid has the structure *I*.



I



II

These conclusions following from certain anomalies of the infrared spectrum of this compound are further confirmed by the infrared spectrum of another lactam *II* containing the hydroxyl group. This compound was also prepared by the Schmidt reaction of the corresponding ketone. The compound *II* shows a similar shift in the infrared spectrum from 1670 to 1650 cm^{-1} whereas in the region of 3200–3400 cm^{-1} there is only one band with the maximum at 3315 cm^{-1}.

The position of the substituent adjacent to the amide nitrogen is in agreement with the general experience with syntheses of substituted ε-caprolactam derivatives from cyclic ketones. It has recently been suggested[8] that both the Schmidt reaction of 2-alkylcyclohexanones and the Beckmann rearrangement of their oximes employed for the preparation of correspondingly substituted caprolactams lead to a mixture of α- and ε-alkylcaprolactams when the size of the substituents is small (proven in the case of methyl-[1,3] and isopropylcaprolactam[8] respectively). When, however, more bulky substituents are present then only ε-isomer is formed (proven in the case of tert-butyl-[8] and cyclohexylcaprolactam[8] respectively). Although the mechanism of 7-(2-hydroxycyclohexyl)perhydro-2-azepinone formation was not examined in detail, it seems plausible that in the first stage the addition reaction of polyphosphoric acid either to 2-(1-cyclohexenyl)cyclohexanone or to intermediately formed 7-(1-cyclohexenyl)perhydro-2-azepinone takes place being followed by the hydrolysis of the intermediate during the neutralization of the reaction mixture.

When substituents are present on the lactam cycle then the polymerization rate of ε-caprolactam derivatives decreases[1-4,7]. Čelefín and coworkers[4] observed substantial decrease in the polymerization rate of α- and ε-methyl-ε-caprolactam resp. in comparison with that of ε-caprolactam polymerized under similar conditions. They explain it by steric factors *i.e.* by the presence of a methyl group in the immediate

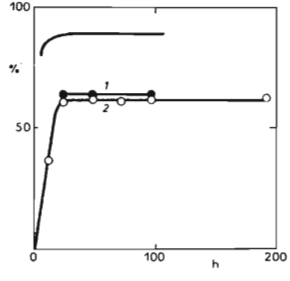


FIG. 1

Conversion of 7-(2-Hydroxycyclohexyl)perhydro-2-azepinone (*I*) into Polymer

ε-Aminocaproic acid concentration 2% mol, polymerization temperature 260°C: *1* copolymerization of lactam *I* with ε-caprolactam (equimolar ratio), ——— polymerization of ε-caprolactam, *2* polymerization of lactam *I*.

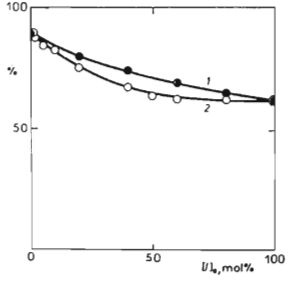


FIG. 2

Copolymerization of Lactam I with ε-Caprolactam. The Dependence of the Equilibrium Copolymer Contents upon the Monomer Mixture Composition

Concentration of ε-aminocaproic acid 2% mol, polymerization temperature 260°C, polymerization time 96 h. *1* theoretical values, *2* experimental values.

vicinity of the amide bond. The bulkier the substituent in this position the greater the decrease in the reaction rate. For example during the hydrolytic polymerization of isobutylcaprolactam at 260°C the monomer–polymer equilibrium is reached after as late as 150 hours[14]. Relatively high polymerization rate of the lactam *I* is, therefore rather surprising if we take into account the presence of a very bulky hydroxycyclohexylsubstituent in the close vicinity to the amide bond (compare Fig.1). The rate of polymerization of this monomer is very close to that of unsubstituted lactam. An explanation can be sought in the sterical arrangement of this molecule. The disadvantageous position of the hydroxyl substituent wedged in between two cycles is substantially improved by opening the lactam cycle during the polymerization.

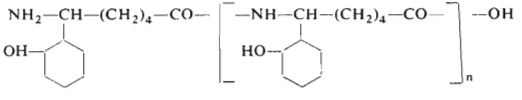
Equilibrium polymer concentration (Fig. 1) is at 260°C 62·8% which is very close to the value observed for ε-cyclohexyl-ε-caprolactam[8]. The polymer is transparent, amorphous, semirigid, soluble in chloroform and MeOH, insoluble in acetone, tetrachloromethane, benzene and toluene. Its low molecular weight indicated by low values of η_{red} is not surprising when the destructive reactions, that undoubtedly take place during polymerization, are taken into account (see lower).

The equilibrium copolymer concentration during copolymerization of the lactam *I* with caprolactam plotted against the initial composition of the mixture is presented in Fig. 2. The copolymer contents in the products are rather lower than those expected from the theoretically derived values of the equilibrium concentrations of the polymers with respect to the initial composition of the mixture. Also Čefelín and coworkers[5] when copolymerizing α-methyl-ε-caprolactam with ε-caprolactam have found lower values than the theoretical ones. It cannot be excluded, however, that the found differences may be, in our case, due to the increased solubility of mixed oligomers containing hydroxyl groups. These circumstances should be considered because in the calculation of the theoretical copolymer contents instead of the real monomer concentrations easily accesible values of low molecular fractions which were obtained by the extraction of both homopolymers by water were used[15].

With the increasing initial concentration of the lactam *I* the expected decrease in the molecular weight of copolymers is seen to occur (extracted by the products of copolymerization equilibrium). The dependence of η_{red} on the concentration of both monomers is too steep, particularly in the region of low concentrations of the lactam *I* (Fig. 3). The relationship between η_{red} and the contents of the comonomer reminds the general dependence of the molecular weight on the monofunctional substance concentration observed in the cases of polyaddition and polycondensation reactions. This fact cannot be ommited because both the polymerization and copolymerization of the lactam *I* are, under our reaction conditions, accompanied by side reactions that are quite pronounced when the polymerization time is long. The samples have then a yellow colour and have an amine odour. Although the character of these products was not closely examined it seems plausible that the mole-

cular weight decrease can be due to the water formed in the system either by the dehydration of the lactam *I* or by the dehydration of the polymer being formed. The plausibility of this assumption is further justified by the fact that the lactam *I* polymerises even without a catalyst, the polymerization being evidently initiated by water formed by dehydration. When the water free lactam *I* is kept for 70 hours at 260°C then the molecular weight of the formed equilibrium polymerizate, determined by the VPO method, is relatively low ($2{\cdot}28 \cdot 10^3$). This signifies that a considerable amount of water or other monofunctional products is formed *via* side reactions. The formation of water could also account for the high polymerization rate of the lactam *I*.

There are several alternative structures for the polymerizates formed in the presence of water or ε-aminocaproic acid. According to the first one the hydrolytic polymerization can take place, similarly as in the case of other lactams, leading to the formation of a polymer chain containing amide bonds



III

The presence of hydroxyl group in the side substituent does not, however, exclude the possibility of condensation reaction of the carboxylic end groups with the hydroxyl

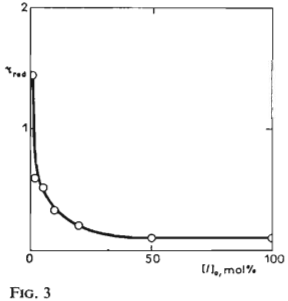


FIG. 3

The Dependence of Reduced Viscosity upon the Monomer Mixture Composition

For the copolymerization conditions see Fig. 2. *m*-Cresol used as a solvent for viscometry.

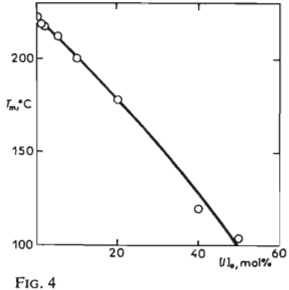
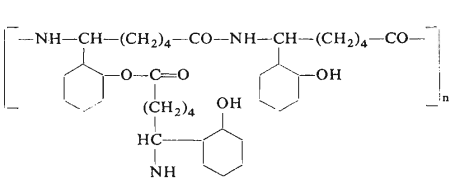


FIG. 4

The Dependence of the Melting Point upon the Monomer Mixture Composition

For the copolymerization conditions see Fig. 2.

groups of the substituent thus leading to the formation of a branched polymer *e.g.*



IV

The absence of the infrared absorption bands corresponding to the ester groups excludes the structure of the ester amide type and thus the structure *III* with local defects caused by the side reactions is assigned to the final product; the polymer may also contain cyclohexenyl groups formed by the dehydration of hydroxycyclohexyl substituent.

The changes in the concentration of both monomers and the overall decrease in the molecular weight with decreasing concentration of ε-caprolactam cause predictable changes in the crystallinity and melting points of the copolymers (Fig. 4). The copolymers with the amount of monomer units of the lactam *I* higher than 20% are amorphous and when this amount is more then 50% the copolymers are semi-rigid.

EXPERIMENTAL

Melting points (uncorrected) were measured on a Kofler block. Infrared spectra were taken in chloroform, NMR spectra measured in deuterated chloroform.

The Reaction of 2-(1-Cyclohexenyl)cyclohexanone with Azoimide

Polyphosphoric acid was prepared from 25 g of phosphorous pentoxide and 25 ml of phosphoric acid 85%. After the mixture had been cooled down to 15°C, 2-(1-cyclohexenyl)cyclohexanone[10] (5 g, 0·028 mol) was added slowly, dropwise into it while stirring. At the same time portions of sodium azide (1·8 g; 0·028 mol) were added. After 12 hours' standing at room temperature the reaction mixture was diluted with water and neutralized by 25% solution of ammonium hydroxide while keeping the maximum temperature at 20°C. The mixture was then extracted with chloroform and the crystalline residue after removing chloroform and washing with acetone yielded 3·25 g (59·5%) of raw 7-(2-hydroxycyclohexyl)perhydro-2-azepinone *I*, m.p. 184°C. After fourfold crystallization from acetone and twofold crystalization from water the melting point increased up to 190·5—191·5°C. For $C_{12}H_{21}NO_2$ (211·3) calculated: 68·22% C, 10·02% H, 6·63% N; found: 67·7% C, 10·25% H, 6·67% N.

The attempts to isolate the lactam *I* from the viscous dark product of the Beckmann rearrangement of 2-(1-cyclohexenyl)cyclohexanone oxim were unsuccessful.

The lactam *I* was benzoylated by treating it with benzoyl chloride in the presence of pyridine. The resulting product was used for spectral analysis.

The Polymerization of Lactam *I* and Its Copolymerization with ε-Caprolactam

The lactam *I* was for 24 hours at 80°C/1 Torr dried prior to polymerization, ε-caprolactam and ε-aminocaproic acid were dried at 50°C/15 Torr. Polymerization and copolymerization of the lactam *I* (always approximately 1 g) were carried out in a usual manner[16] in sealed glass evacuated ampoules (volume approximately 4 ml) always preserving the constant ratio between the liquid and gaseous phase; 2% mol of ε-aminocaproic acid were used as a polymerization catalyst. Copolymerizates containing more than 50% of the lactam *I* were half-rigid substances; thus they were before the extraction (0·6—0·8 g of sample in boiling water[17]) spread in form of a thin layer on the walls of pre-weighed beakers and then dried in a dessicator over phosphorous pentoxide to constant weight. Other copolymerizates were extracted using the usual methods[17]. Viscometric measurements were carried out in an Ubbelohde viscometer with No II capillary and using *m*-cresol as a solvent.

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Translated by J. Sedlář.