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

SYNTHESIS AND POLYMERIZATION OF ε-HEXYLCAPROLACTAM, ε-LAURYLCAPROLACTAM AND ε-ISOBUTYLCAPROLACTAM

J. KRÁLÍČEK, J. KONDELÍKOVÁ and V. KUBÁNEK

Department of Macromolecular Chemistry, Institute of Chemical Technology, Prague 6

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ε-Hexylcaprolactam, ε-laurylcaprolactam and ε-isobutylcaprolactam resp. have been synthetised *via* selectively proceeding Schmidt reaction of corresponding 2-alkylcyclohexanones. The structure of these lactams was determined using mass-spectrometry. The rate of polymerization catalysed by ε-aminocaproic acid is, in the case of ε-isobutylcaprolactam and ε-hexylcaprolactam resp., lower by more than an order of magnitude when compared with that measured for caprolactam. The equilibrium concentration of polymer was determined for ε-isobutylcaprolactam within the temperature range 240—270°C (72·8—63·7%), for ε-hexylcaprolactam within the range 226·8 to 260°C (84·0—79·5%) and for ε-laurylcaprolactam at 260°C (22·0%).

Both the polymerization rate and polymerization ability of substituted lactams depend, according to the literature published to date[1,2] upon the position of substituents and also upon the substituent size. Most of the authors, however, describe the polymerization of such lactams that contain relatively small substituents. The exception in a series of investigated ε-substituted caprolactams is practically only ε-cyclohexylcaprolactam[3] and 7-(2-hydroxycyclohexyl)perhydroazepin-2-one[4] resp. whose polymerization has been studied to some detail. In this paper we wish to report on the synthesis of some C-alkyl derivatives of caprolactam containing bulkier substituents such as ε-hexyl, ε-lauryl and ε-isobutylcaprolactam. We also studied the hydrolytic polymerization of these compounds.

EXPERIMENTAL

M. p. and b. p. are uncorrected. IR spectra were taken in chloroform using a Zeiss UR-10 spectrophotometer.

ε-Hexylcaprolactam (I). The solution of 48·9 g (1·28 mol) of sodium amide with 152·2 g (1·28 mol) of cyclohexanone in 200 ml of benzene was refluxed for 1 hour. Then 210·5 g (1·28 mol) of n-hexyl bromide was added dropwise and the mixture was boiled for 12 hours. After the neutralization by 10% acetic acid and dilution with water, the water layer was extracted with ether.

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Joined extracts were mixed with benzene layer and distilled. The *2-hexylcyclohexanone* yield was 144·6 g (62·1%), b.p. 138 to 142°C/15 Torr. Oxim, m.p. 95°C; for $C_{12}H_{23}NO$ (197·3) calculated: 73·09% C, 11·72% H, 7·11% N; found: 78·89% C, 11·80% H, 7·18% N.

To polyphosphoric acid, prepared by mixing 50 ml of 85% phosphoric acid and 50 g of phosphorous pentoxide, sodium azide (3·58 g; 0·055 mol) and 2-hexylcyclohexanone (10 g; 0·055 mol) were added simultaneously at room temperature, while stirring. The mixture was stirred for another hour and after 16 h standing it was first diluted with water and then neutralized with 25% solution of ammonium hydroxide keeping the temperature below 15°C. Crude lactam (1·7 g, 15·75%) was obtained from the chloroform extract after evaporation of the solvent by addition of light petroleum; m.p. 55°C. The *lactam* I (m.p. 68°C) resulted after seven times repeated crystallization from ether at lowered temperature. IR spectrum: 1660 and 3400 cm^{-1}. For $C_{12}H_{23}NO$ (197·3) calc.: 73·09% C, 11·72% H, 7·11% N; found: 72·83% C, 11·85% H, 7·12% N.

ε-*Laurylcaprolactam* (II). The procedure identical to that applied for synthesis of *I*. *2-Laurylcyclohexanone* was obtained in 36·2% yield, b.p. 152—158°C/1·5 Torr. Oxim, m.p. 110°C; for $C_{18}H_{35}NO$ (281·5) calculated: 76·80% C, 12·53% H, 4·98% N; found: 76·49% C, 12·40% H, 4·68% N. *Lactam* II was obtained in 25% yield, m.p. 63°C (light petroleum). IR spectrum: 1660 and 3400 cm^{-1}. For $C_{18}H_{35}NO$ (281·5) calculated: 76·80% C, 12·53% H, 4·98% N; found: 76·20% C, 12·27% H, 4·47% N.

ε-*Isobutylcaprolactam* (III). 2-Isobutylcyclohexanone was prepared from 2-ethoxycarbonylcyclohexanone and isobutyl bromide[5]. The Schmidt reaction of this compound (performed similarly as in the case of *I*) gave lactam *III* in 76·7% yield. The lactam *III* resulted as white crystalline compound, m.p. 69—70°C (ether). IR spectrum: 1660 and 3400 cm^{-1}. For $C_{10}H_{19}NO$ (169·3) calculated: 70·96% C, 11·31% H, 8·27% N; found: 70·46% C, 11·32% H, 8·21% N.

Polymerization

The polymerization was carried out in a usual manner[6] in glass ampoules sealed *in vacuo*, using ε-aminocaproic acid (2% mol) as a catalyst. The monomers were prior to polymerization dried at room temperature and at 1 Torr pressure for twelve hours. In order to determine the polymer content in a polymerizate the material was ground in an agate mortar at dry ice temperature, dried over phosphorus pentoxide to a constant weight and then extracted. The polymerizates obtained from *I* and *III* were extracted with water using the procedure described for the determination of polymers and copolymers of 7-(2-hydroxycyclohexyl) perhydroazepin-2-one with caprolactam[4]. The minimum amount of water necessary for extraction as well as minimum extraction time were found experimentally (overall extraction time is 7 hours for *III* and 60 hours for *I*). The polymerizate obtained from *II* was, because of its insolubility in water, repeatedly extracted with boiling light petroleum; (overall extraction time was 70 hours). The polymers were then dried to a constant weight over phosphorus pentoxide at 15 Torr.

RESULTS AND DISCUSSION

A simple condensation of alkylbromides with cyclohexanone in the presence of sodium amide[7] was employed for the preparation of 2-alkylcyclohexanones. A more detail study has, however, revealed that satisfactory yields are obtained only in such cases where linear alkyl bromide was used as an alkylation agent. When attempts were made to alkylate cyclohexanone using branched alkyl bromides (*e.g.*, isopropyl, isobutyl, cyclohexyl bromide) or alkylene bromides (ethylene dibromide or tetramethylene dibromide), only 2-(1-cyclohexenyl)cyclohexanone was formed as a rule. This compound is formed in the reaction mixture *via* basically catalysed autocondensa-

tion of cyclohexanone (this competing reaction proceeds also during the alkylation of cyclohexanone by linear alkyl bromides). This may be accounted for by a lower reaction rate of alkylation when branched alkyl halogenides or dihalogenides are used. The effect is due to sterical hindrances of these compounds. For these reasons 2-isobutylcyclohexanone was prepared by condensation of isobutyl bromide with 2-ethoxycarbonylcyclohexanone followed by decarboxylation[5]. The Schmidt reaction of 2-alkylcyclohexanones in polyphosphoric acid medium was employed for the preparation of lactams. The Beckmann rearrangement of corresponding oximes gave substantially lower results and also raw products of lower degree of purity.

The structure of ε-hexyl-(*I*), ε-lauryl-(*II*) and ε-isobutylcaprolactam (*III*) resp. was verified by using mass spectrometry; the mass spectrum of all the above mentioned compounds exhibited a pronounced base peak due to the 112 *m/e* ion. This fragment corresponds to the ion which was formed by splitting a substituent attached to carbon next to nitrogen atom[8]. The cracking pattern contained, besides fragments corresponding to hydrocarbon substituents fission and caprolactam ring fission, also ion *m/e* 114 (in the case of hexylderivative *I*) which was tentatively assigned to the $^{+}NH_2{=}CH{-}(CH_2)_5{-}CH_3$ ion. In the case of lauryl derivative *II* a peak *m/e* 198 was observed (structure $^{+}NH_2{=}CH{-}(CH_2)_{11}{-}CH_3$) whereas isobutylderivative *III* exhibited *m/e* 86 peak (structure $^{+}NH_2{=}CH{-}CH_2{-}CH(CH_3)_2$). These species were probably formed *via* α-splitting of C—C bond with regard to nitrogen (between the sixth and seventh atom of a heterocycle) and simultaneous hydrogen transfer as suggested by Gohlke and McLafferty[9]. The mass spectra in all cases confirm the structure of ε-alkyl derivatives of caprolactam. The suggested structure is further corroborated by the results of infrared spectroscopy; the absorption band at 3400 cm^{-1} indicates the substitution in position ε, whereas the 3420 cm^{-1}

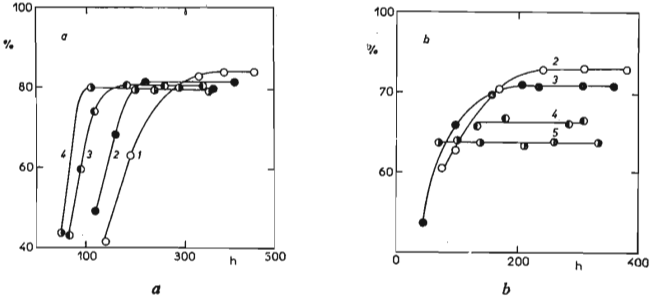

FIG. 1

The Dependence of Poly(ε-Hexylcaprolactam) (*a*) and Poly(ε-Isobutylcaprolactam) (*b*) Concentration upon the Polymerization Time

Polymerization temperature (°C): *1* 226·8, *2* 240, *3* 250, *4* 260, *5* 270.

band typical for α-substituted caprolactam is missing[10]. The selective formation of ε-derivatives during the Schmidt reaction of 2-alkylcyclohexanone containing bulky alkyl substituents is not surprising; similar conclusion was reached by Jansen[3] who studied the Beckmann rearrangement of some substituted cyclohexanoneoximes. The author assumes that 2-alkylcyclohexanoneoxime with a bulky substituent will rearrange to form ε-substituted caprolactam only, whereas homologues containing small alkyls will give a mixture of ε- and α-alkylcaprolactams. The polymerization rate of both ε-hexyl- and ε-isobutylcaprolactam is lower by approximately one order of magnitude than that of caprolactam. Thus the monomer–polymer equilibrium is, in both cases (*I* and *II*), reached at 250°C after almost 200 hours, at 260°C after 100 hours (Fig. 1). The decrease in the polymerization rate as a consequence of the substitution in vicinity of the amide bond is in agreement with the present opinion according to which the main cause of this effect are sterical reasons[11]. The equilibrium concentration of polymer in polymerizates obtained from *I* and *III* decreases proportionally to the increasing temperature (Fig. 2). Its value is in both cases unexpectedly high if we take into account the size of the hydrocarbon substituent. In the case of monomer *I* (80·6% at 250°C) it is close to equilibrium polymer concentration measured for ε-methylcaprolactam[11]. This is not in agreement with the present opinion according which the polymerization ability of first members in a series of ε-alkylcaprolactams decreases with the increasing size of alkyl group[1,12] (compare[2,11]). The increase in the polymerization ability with the increasing size of substituent next to the amide group, as it was observed on ε-cyclohexylcaprolactam[3] and 7-(2-hydroxycyclohexyl)perhydro-2-azepinone[4] cases, can thus be considered as being generally valid. Small substituents shift the equilibrium cycle-chain towards the cycle formation when compared with unstubstituted caprolactam. A branched substituent in an immediate vicinity of nitrogen even stabilizes the cyclic form. This effect however, is not so pronounced in the case of long or bulky substituents, the

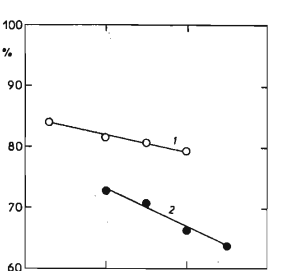

FIG. 2

The Dependence of Equilibrium Polymer Concentration upon the Polymerization Temperature

1 Poly(ε-hexylcaprolactam), *2* poly(ε-isobutylcaprolactam).

conformation possibilities being probably enhanced in a chain form. Both the size of substituent and the conformation possibility influence the polymerization ability of all substituted caprolactams; in the case of small substituents the negative effect of an increasing substituent size predominates whereas in the case of bulky substituent there is a pronounced difference between conformational possibilities of linear and cyclic form, the linear form being favoured. The position of carbon on which branching occurs is also important. The observed differences between zero polymerization ability of ε-isopropylcaprolactam[3] and that of *III* do not contradict this opinion. Polymerization is, in the latter case, made possible by greater distance between the branched substituents and by the overall increase in the substituent size.

ε-Laurylcaprolactam was used as a model of a C-alkylcaprolactam with an extremely long substituent. The equilibrium polymer concentration, is, in comparison with both previous alkylcaprolactams, substantially lower. The decrease in polymerization ability (equilibrium polymer content 22·0% at 260°C) can, in this case, be influenced by side reactions. The polymers were dark in colour and possessed a typical amine odour. The influence of a long aliphatic chain upon the equilibrium polymer content cannot, however, be neglected. The chain, thus can act as an inert diluent. It has been reported by Yumoto[13,14] and Čefelín and coworkers[11] that the equilibrium polymer content decreases with the increasing solvent concentration.

The equilibrium polymers obtained from all the ε-alkylcaprolactams were amorphous regardless the polymerization temperature; the softening temperature of these polymers is, low, *e.g.* in the case of poly-ε-isobutylcaprolactam its value was within 45—56°C.

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