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Note

High-performance liquid chromatography of 12-dodecanelactam and its cyclic oligomers present in polyamide 12

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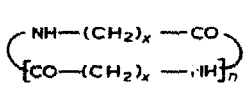
The equilibrium product of polymerization of lactams contains, in addition to the unreacted monomer, also linear oligomers and, in particular, cyclic oligomers:



I, $x = 11$, $n = 0$
II, $n = 1$
III, $n = 2$
IV, $n = 3$
V, $n = 4$

Most attention has been paid to the analysis of the cyclic oligomers formed in polymerization of ε-caprolactam ($x = 5$)[1]. There are few data on the cyclic oligomers of other lactams. Zahn and Gleitsmann[2] were the first to report the cyclic dimer (II) and trimer (III) of 12-dodecanelactam (I). Mori *et al.*[3] described the determination of cyclic oligomers of lactam I by gas chromatography after their previous reduction with $LiAlH_4$ in tetrahydrofuran (THF) solution. In industrial samples of polyamide 12, the contents of compounds I, II and III were 0.33, 0.94 and 0.25% (w/w), while the total amount of compounds extractable with ethanol was 1.70%. Feldmann and Feinauer[4] found, in polyamide 12 prepared at 260, 270 and 280°C, 0.83 ± 0.25% (w/w) of dimer II and 0.3 ± 0.18% (w/w) of trimer III in good agreement with values calculated from cyclization constants.

We have worked out a simple method for direct determination of cyclic oligomers of ε-caprolactam by means of high-performance liquid chromatography (HPLC)[1]. This method is applied here for the determination of oligomers of lactam I.

EXPERIMENTAL

Reagents and chemicals

The lactam I was crystallized three times from benzene and twice from acetone, dried at 50°C (2 kPa) for 50 h and then at 20°C (0.2 kPa) for 50 h. The equilibrium polyamide 12 was prepared by the polymerization for 600 h at 260°C of lactam I initiated with 2 mol. % of 6-aminocaproic acid in a sealed evacuated glass ampoule, according to ref. 5. The polymer was grated to shavings of thickness about 0.1 mm

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and extracted in a 125-fold (w/w) amount of methanol under reflux for 1 h. The completion of extraction was confirmed by repeated extraction. The extract was directly injected into a chromatographic column.

Equipment

The mixture of oligomers was separated in a Merck chromatographic column packed with LiChrosorb RP-18, using aqueous acetic acid (5 m*M*)–methanol (20:80, v/v) as eluent and a flow-rate of 0.7 ml/min. The injected volume was 10 μl. The Spectra-Physics SP 8000 liquid chromatograph was equipped with a SP 8400 UV–VIS variable-wavelength detector. The separation was monitored at 210 nm.

RESULTS AND DISCUSSION

As in the case of ε-caprolactam and its oligomers[1], a very good separation of the lactam I and its cyclic oligomers up to the hexamer was attained, as seen in Fig. 1. Individual peaks were identified by comparison with pure oligomers obtained by preparative gel chromatography on a column packed with the gel LH-20, using methanol as the eluent. The gel chromatographic separation of individual oligomers of lactam I may be assumed to proceed in order of their molecular weights.

The molar absorption coefficients of the individual cyclic oligomers at 210 nm are presented in Table I. The quantitative evaluation was carried out analogously to that of the oligomers of ε-caprolactam by Mori and Takeuchi[6]. The areas of individual peaks were multiplied by correlation factors obtained from the ratios of the molar absorption coefficients of individual oligomers to the molar absorption coefficient of the monomer. The resulting value, when divided by the total area, is proportional to the weight per cent of the given oligomer in the mixture. The weight per cents of the individual cyclic oligomers in the equilibrium polyamide 12 are given in Table I.

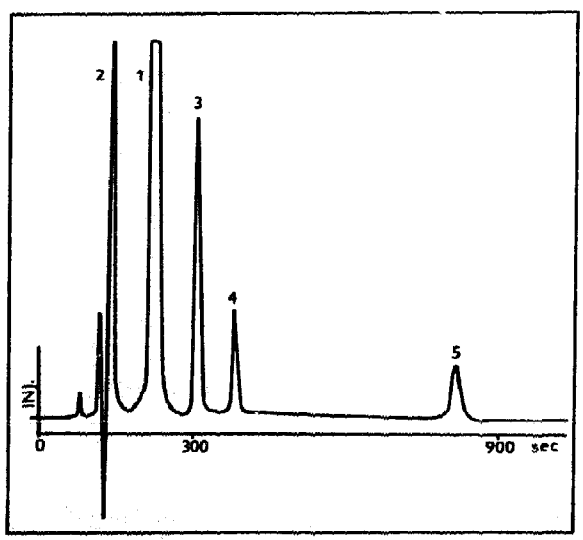

Fig. 1. HPLC separation of 12-dodecanelactam (I) and its cyclic oligomers. Peaks: 1 = I; 2 = dimer II; 3 = trimer III; 4 = tetramer IV; 5 = pentamer V.

TABLE I

CYCLIC OLIGOMERS OF 12-DODECANELACTAM

A = Molar absorption coefficient; k = correlation factor; p = content (%, w/w) in the equilibrium polyamide 12.

Oligomer	*A*	*k*	*p*
I	1497	1.0	0.41
II	1847	0.81	1.25
III	2812	0.53	0.31
IV	2946	0.50	0.12
V	2970	0.50	0.10

The described HPLC method was also used for the determination of cyclic oligomers of lactam I during its polymerization and also during its copolymerization with ε-caprolactam, where the presence of a codimer and of cotrimers was shown. The latter result will be published in a subsequent paper.

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