Journal of Chromatography, 240 (1982) 539–542
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 14,717

Note

High-performance liquid chromatography of 6-caprolactam and its cyclic oligomers present in polyamide 6

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(Received January 11th, 1982)

Cyclic oligomers of 6-caprolactam, together with the monomer, are equilibrium products of its polymerization and form the greater part of oligomers in water extracts, *i.e.*, in the waste product from the production of fibres from polyamide 6. Our need to determine the individual cyclic oligomers in this waste product led us to seek a simple and rapid experimental method. Previously published methods are unsatisfactory because they are rather time consuming.

Ongemach and Moody[1] determined 6-caprolactam in water extracts of polyamide 6 by gas chromatography, and the content of cyclic oligomers together with 6-caprolactam by differential refractometry and IR spectrophotometry. Their method did not allow the determination of the individual cyclic oligomers, as was the case with the method of Anton[2], who determined the cyclic oligomers directly in water extracts. Reinisch *et al.*[3] used Craig's method of separation in the system *n*-heptane–methanol for direct determination of oligomers. Even when the long times and experimental requirements of this method are compensated by its absolute reliability, the method is not suitable for routine analyses. Heikens[4] determined the cyclic dimer, trimer and tetramer by a fractional sublimation of a methanolic extract, which was previously freed from monomer and linear oligomers. Rothe[5] separated cyclic oligomers by paper chromatography and determined the individual components by colorimetry. Both methods, fractional sublimation and paper chromatography, are complicated and time consuming.

Gas–liquid chromatography (GLC) was utilized in the determination of cyclic oligomers of 6-caprolactam for the first time by Mori *et al.*[6]. The monomer and oligomers were reduced to the corresponding amines which were then determined chromatographically. The method has again high experimental and time requirements. However, Mori and Takeuchi[7] published at the same time a method based on gel permeation chromatography (GPC). A good separation of 6-caprolactam and its cyclic oligomers up to the hexamer was attained on the gels Sephadex G-15, G-25 and Bio-Gel P-4 using 0.1 *N* HCl as the eluent. The method was experimentally simple and the analysis of one sample was relatively fast —it took 6 h. At the same time, Mulder and Buytenhuys[8] described the separation of cyclic oligomers of 6-capro-

0021-9673/82/0000–0000/$02.75

lactam on a column of Sephadex 20 with methanol as eluent, while Andrews *et al.*[9] used Sephadex G-25 and 50% acetic acid as eluent.

In spite of the good separation achieved, all methods based on gel permeation chromatography remain, due to their relatively high demand on time, just at the border of possible utilization for laboratory practice, and the more so for technological purposes.

In comparison with the above methods, high-performance liquid chromatography (HPLC) appears to be the method with lowest demand on time, and its application to the separation of cyclic oligomers of 6-caprolactam is described in this paper.

EXPERIMENTAL

Reagents and chemicals

6-Caprolactam (K.p. Spolana, Neratovice, Czechoslovakia) was recrystallized twice from acetone and three times from benzene, dried for 50 h at 50°C and 2 kPa and then for 50 h at 20°C and 0.2 kPa.

The cyclic dimer of 6-caprolactam (1,8-diaza-2,9-dioxocyclotetradecane) was obtained from concentrated extracts in the production of polyamide 6 (Chemlon n.p., Humenné, Czechoslovakia) by the procedure according to Fritzche and Körösi[10] followed by the recrystallization five times from methanol. It was dried similarly to 6-caprolactam; m.p. 339–342°C.

Polyamide 6 was prepared by polymerization of 6-caprolactam initiated with 2 mol. % of 6-aminocaproic acid and carried out at 260, 270 or 280°C for 24 h in a glass ampoule which was sealed under vacuum (0.2 kPa). Turnings of polyamide 6 of thickness *ca.* 0.1 mm were extracted in methanol (125:1, w/w) under reflux for 1 h. The extract was directly injected into a chromatographic column. The quantitative completeness of extraction was confirmed by repeated extractions.

Equipment

The mixture of oligomers was separated in a column from E. Merck packed with the carrier LiChrosorb having the anchored non-polar phase RP-18. Aqueous acetic acid (5 mmol/l)–methanol (70:30, v/v) was used as the eluent; flow-rate 0.64 ml/min. A 7-μl volume of the extracts was injected.

Separations were carried out with a Spectra-Physics SP 8000 liquid chromatograph and monitored with a SP 8400 UV–VIS detector at 210 nm.

RESULTS AND DISCUSSION

The HPLC method was used to solve this problem by Brodilová *et al.*[11], however they failed completely to separate the cyclic dimer and monomer. The ternary eluents tetrahydrofuran–heptane–water and 1-butanol–acetic acid–water and the less sensitive refractometric detection were used in that case. Consequently, separation was possible only with the concentrated mixture of cyclic oligomers of 6-caprolactam.

We have used the much more sensitive UV spectrophotometric detection which enables the direct quantitative analysis of extracts of 6-caprolactam polymers. Anoth-

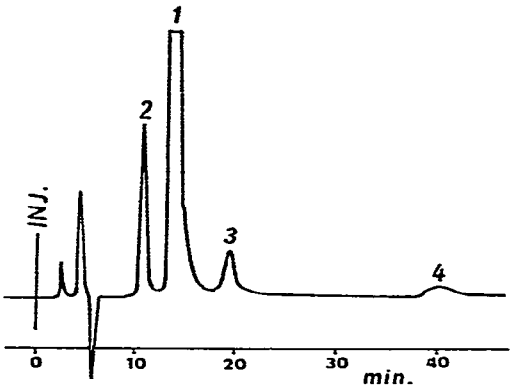

Fig. 1. HPLC separation of 6-caprolactam and its cyclic oligomers. Peaks: 1 = 6-caprolactam; 2 = cyclic dimer of caprolactam; 3 = cyclic trimer; 4 = cyclic tetramer.

er advantage of the procedure described is the application of methanol as the extraction agent and also as a component of the elution mixture. As shown in Fig. 1, a very good separation of 6-caprolactam and its cyclic oligomers was achieved (retention times of pentamer, hexamer and heptamer were 27, 37 and 45 min, respectively).

The peaks were identified by means of individual oligomers obtained by the GPC separation according to Mori and Takeuchi[7], where the cyclic oligomers were eluted in order of decreasing molecular weight. The method was tested with 6-caprolactam and the cyclic dimer as standards. The need for the complicated equipment is outweighed by the simplicity, rapidity and accuracy of the method.

It is known that the content of oligomers and monomer in polyamide 6 at equilibrium is constant and depends only on the polymerization temperature. Results

TABLE I

CONTENT OF 6-CAPROLACTAM (M_1) AND ITS CYCLIC OLIGOMERS (M_i) IN POLYAMIDE 6

A, B and C = equilibrium polyamide 6 prepared at 260, 270 and 280°C, respectively; D = industrial extract from production of fibres (Chemlon n.p.); a = content in the product of polymerization (%, w/w); b = content in extract (%, w/w).

Method	*Sample*	M_1	M_2	M_3	M_4	M_5	M_6	M_7 *and higher*
HPLC	A–a	7.1	1.3	0.6	0.3	0.1		
	A–b	75.5	13.8	6.4	3.2	1.1		
	B–a	7.4	1.3	0.6	0.4	0.1		
	B–b	77.1	12.5	6.3	3.1	1.0		
	C–a	8.3	1.3	0.6	0.3	0.1		
	C–b	78.3	12.3	5.7	2.8	0.9		
	D–b	67.1	6.5	11.0	8.2	4.5	1.3	0.6
GPC[7]	a	8.70	0.75	0.47	0.30	0.17	0.16	
GLC[6]	a	8.50	0.71	0.43	0.22	0.13	0.19	
Sublimation[12]	b	76.0	12.5		4.9	3.6	3.0	
Craig[13]	b*	–	23.3	27.9	23.3	25.6		

* After removal of the monomer.

of the quantitative HPLC analyses of equilibrium polymers of 6-caprolactam, prepared at 260, 270 and 280°C, are presented in Table I. However, exact comparison with the results of other methods is impossible, because the quoted authors mostly used unspecified industrial samples for analysis.

Table I shows that the equilibrium content of cyclic oligomers changes little with temperature, while that of the monomer changes substantially. The difference in the content of individual oligomers in the concentrated industrial water extracts from the production of polyamide 6 fibres and in the extract of equilibrium polyamide 6 prepared in the laboratory is obviously caused by the loss of the monomer and cyclic dimer which readily sublime during concentration of industrial water extracts.

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