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POLYMERIZATION OF LACTAMS—XVI*.

CYCLIC OLIGOMERS IN COPOLYMERS OF 6-CAPROLACTAM WITH 8-OCTANELACTAM AND THEIR DETERMINATION BY MASS SPECTROSCOPY

J. MAŘÍK, J. MITERA and J. KRÁLÍČEK
Institute of Chemical Technology, Prague 6, Czechoslavakia

and

J. STEHLÍČEK
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague 6, Czechoslovakia

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Abstract—The methanolic extract of a copolymer of 6-caprolactam with 8-octanelactam was analyzed; cyclic oligomers were identified by mass spectroscopy. The cyclic homodimers and codimer were separated by thin-layer chromatography. The quantitative analysis of methanolic extract involved direct evaporation into the ion source of mass spectrometer.

INTRODUCTION

Cyclic and linear oligomers of ω-aminoacids may be isolated from the extractable portion of polyamides prepared by lactam polymerization. These compounds have chemical properties similar to those of the polymer itself but physical properties which differe sufficiently for individual oligomers to be separated. The content of oligomers in an equilibrium polymer is fixed; their content in an extract depends on the extraction agent used. Linear oligomers are often preferred to polymers in model reactions.

The cyclic dimers, particularly the dimer of 6-caprolactam, have much higher melting points than the corresponding polymer and cause difficulties in manufacturing of polyamides. However, the formation of cyclic dimer can be affected by a simple optimization criterion [1]. Recently, the cyclic dimers have been considered in determination of more accurate kinetic parameters of polymerization [2] and those of higher lactams seem to be important in the polymerization mechanism [3]. For this reason, considerable attention has been given to separation, isolation, analysis and synthesis of the oligomers of ω-aminoacids. Heikens [4] used fractional sublimation for separation of individual cyclic oligomers of nylon-6; paper chromatography [5–12] has also been used. Higher oligomers were resolved by stepwise crystallization [13]. The cyclic and linear oligomers were obtained from nylon-6 by selective extraction and further separated by ion exchange [14, 15]. The oligomers were also determined by i.r. spectroscopy [16, 17].

Modern chromatographic methods are less time-consuming and thin-layer [18, 19], gel permeation [1, 19–21] and gas chromatographies [1, 22, 23] were employed for separation of nylon-6 oligomers. There are many difficulties with these methods particularly in quantitative work, e.g. selection of solvent or conversion to derivatives suitable for gas chromatography.

The oligomers of higher lactams have been little studied. The analysis of nylon-12 extracts has been mentioned [20, 23–25] and also that for nylon-11 [24, 26]. Only cyclic dimers [27, 28] were described in polyamides of lactams with nine- to eleven-membered rings. Cyclic codimers were synthesized from *N*-(α-aminoacyl) lactams by Rothe [29].

Individual components of a mixture may be metered into the ion source of mass spectrometer using the same principle as in fractional sublimation. The method of recording spectra of selected ions of a mass spectrum as a temperature—or time—function allows following the sublimation kinetics selectively for particular components of the mixture. This new technique was employed for analysis of mixtures of polycyclic aromatic compounds [30].

We tried to separate cyclic dimers and trimers from the methanolic extract of a copolymer of 6-caprolactam and 8-octanelactam. The oligomers were identified by MS and the above mentioned technique was used for quantitative determination of cyclic dimers.

EXPERIMENTAL

The copolymer was prepared by polymerization of 0.5 mole parts of caprolactam with 0.48 mole parts of 8-octanelactam with catalysis by 0.2 mole parts of 8-aminooctanoic acid at 250° for 36 hr. Slices of copolymer 0.5–1 mm thick were extracted with methanol (analytical grade) at room temperature for 24 hr with five changes of solvent. The extract (5.61%) was evaporated to dryness and used for MS analysis as a methanolic stock solution (44.9 mg/10 cm^3). This solution together with the solution of standard were metered by a syringe (5 μl) into micro test tubes provided with a heating coil and employed for direct evaporation into the ion source of spectrometer. For TLC, the extract was freed of the major part of monomers by sublimation at 85° and 10 Pa.

Cyclic dimers of 6-caprolactam and 8-octanelactam were obtained according to Ref. [4, 31]. 2,2'-Dinaphthol (Loba-Chemie, Viena) had m.p. 215°, mol.wt. 286.33.

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Table 1. TLC of cyclic oligomers on Kieselgel G; developed ascendingly with the mixture tetrahydrofuran–heptane–water (88.6:6.6:4.8 vol. parts)

Cyclic oligomer		M^+, m/e	R_F
1,10-diazacyclooctadecan-2,11-dione (dimer of octanelactam)	$C_{16}H_{30}N_2O_2$	282	0.70–0.75
1,8-diazacyclohexadecan-2,9-dione (codimer)	$C_{14}H_{26}N_2O_2$	254	0.64–0.68
1,8-diazacyclotetradecan-2,9-dione (dimer of caprolactam)	$C_{12}H_{22}N_2O_2$	226	0.51–0.57
1,8,15-triazacycloheneicosan-2,9,16-trione	$C_{18}H_{33}N_3O_3$	329	0.41
1,8,15-triazacyclotricosan-2,9,16-trione	$C_{20}H_{37}N_3O_3$	367	0.32
			0.24
1,8,17-triazacyclopentacosan-2,9,18-trione	$C_{22}H_{41}N_3O_3$	395	0.13–0.14
1,10,19-triazacycloheptacosan-2,11,20-trione	$C_{24}H_{45}N_3O_3$	423	

Separations and isolations of cyclic oligomers by TLC were carried out on glass plates 50 × 200 mm coated with Kieselgel G (Merck) layers 0.5-mm thick, activated by storage over solid potassium hydroxide. The mixture of cyclic and linear oligomers was applied to the layers as a 5% solution in 2,2,2-trifluoroethanol in strips 23 × 2-3 mm containing 6–7 mg of mixture per plate. The chromatograms were developed by a mixture tetrahydrofuran–heptane–water 88.6:6.6:4.8 (volume ratio) and detected by spraying with 2% ethanolic solution of iodine. The individual detected bands were scraped down after desorption of iodine (20 hr, 25°) and extracted in microcolumns with methanol. The clear extracts were evaporated, dried at 25° and 7 Pa and used for MS.

The preparative separation of cyclic codimer (1,8-diazacyclohexadeca-2,9-dione) was carried out on three plates with Kieselgel G layers 400 × 200 × 0.8 mm, by applying 80 mg of the mixture on each plate and using conditions as above. The scraped material of a band was extracted by methanol and the evaporated extract was sublimed at 7–10 Pa. The pure codimer (purity 95%, content of the cyclic dimer of 8-octanelactam 5%) was obtained after two further refinings on plates with Kieselgel G layers 50 × 200 × 0.2 mm and the final sublimation; the codimer

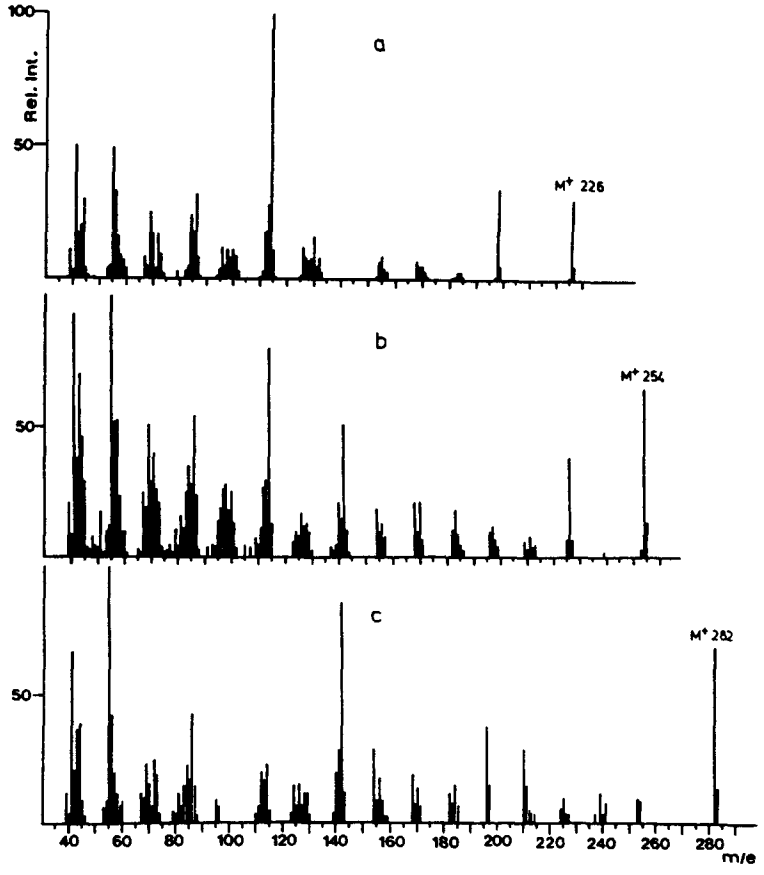

Fig. 1. Mass spectra of (a) cyclic dimer of 6-caprolactam (1,8-diazacyclotetradecan-2,9-dione), (b) cyclic codimer of 6-caprolactam and 8-octanelactam (1,8-diazacyclohexadecan-2,9-dione) and (c) cyclic dimer of 8-octanelactam (1,10-diazacyclooctadecan-2,11-dione).

has m.p. 225–8°, sublimes above 154° (7 Pa) and is well soluble in methanol and dichloromethane.

Mass spectra were recorded during the direct evaporation of sample into the ion source of GS-MS LKB 9000 apparatus. The evaporation temperature was controlled manually from 20 to 200° by the voltage applied to the heating coil of a micro test tube. The temperature of the ion source was 250°, pressure 10^{-4} Pa, energy of ionizing electrons 70 eV, current 20 mA, width of the collector slot 0.3 mm, and voltage at the electron multiplier 3.7 kV. Spectra were recorded by oscillograph at the speed of one decade of mass units in 10 sec within 1 min intervals. Integral areas were calculated by the method of gradual integration using the table calculator Hewlett-Packard Model 9830 A.

RESULTS AND DISCUSSION

It was proved that, as with homopolymers [3, 15], methanol effectively extracts from the 6-caprolactam-8-octanelactam copolymers, not only monomers but also cyclic dimers. Study of mass spectra of extracts showed the presence of two cyclic homodimers, the mixed dimer (codimer), two cyclic homotrimers and mixed trimers (cotrimers).

Cyclic oligomers were separated by thin-layer chromatography. The mass spectra of materials obtained from the upper three bands of the chromatogram permitted unambiguous identification of three cyclic dimers in the order shown in Table 1. Although the individual trimeric fractions behaved as chromatographically homogeneous, they were always contaminated with larger amounts of other cyclic trimers and all four expected molecular ions were consequently found in each fraction. The mixed cyclic oligomers (co-oligomers) of lactams have been here identified in copolymers for the first time.

The method of direct sample evaporation into the ion source of a mass spectrometer had the following advantages: (a) Direct analysis of extract (b) evaporation of monomers, dimers and trimers proceeds stepwise in fractions (c) all compounds present in the fraction and differing in molecular mass are recorded.

Mass spectra of homodimers isolated by TLC were identical with those of homodimers obtained from the corresponding homopolyamides (Fig. 1a and c). Interpretation of these spectra together with the spectrum of codimer (Fig. 1b) enabled the quantitative determination of cyclic dimers and the estimate of trimers directly in the extract from copolymer.

It is necessary to eliminate possible interferences with ions chosen for the quantitative evaluation, i.e. of the molecular ions in our case, by the fragment ions of compounds of higher molecular mass. All dimers have intense molecular ions (m/e 226, 254 and 282), which were chosen for quantitative analysis of mixture. Other very intense ions of dimer spectra are m/e 114 and 142 corresponding to the protonated molecules of 6-caprolactam and 8-octanelactam. We consider the fragment ions $(M - 28)^+$ of codimer and $(M - 28)^+$ and $(M - 42)^+$ of 8-octanelactam dimer for interference with molecular ions of lower dimers. The ratio of intensities (i) of molecular ions and $(M - 28)^+$ ions decreases with increasing molecular mass of dimer. The intensities of fragment ions were expressed by means of intensity of the corresponding molecular ion and used in calculation of corrected intensities (I) of molecular ions of the dimers in the spectrum as follows:

$$I_{282} = i_{282}$$

$$I_{254} = i_{254} - 0.137\, i_{282}$$

$$I_{226} = i_{226} - 0.585\, I_{254} - 0.063\, i_{282}.$$

The quantitative representation of dimers in mixtures was found by the method of gradual integration of areas P under curves of corrected intensities I plotted against time t:

$$P = \sum_{j=0}^{n} P_j = \sum_{j=0}^{n} (t_{j+1} - t)(I_j + I_{j+1})/2$$

where P_j is the area of the section below the curve of corrected intensity in the time interval t_j to t_{j+1}. The intensities of individual molecular ions changing

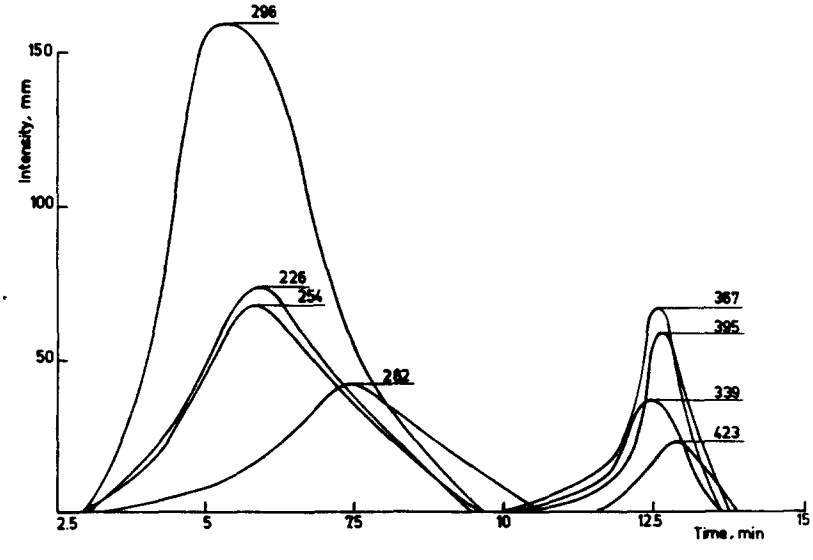

Fig. 2. Time course of molecular ion intensities of cyclic oligomers and the standard (2,2'-dinaphthol) during the direct evaporation into ion source; monomers already volatilized.

Table 2. Calibration with a known mixture of cyclic dimers and the standard: $c_{226}:c_{254}:c_{282}:c_{286} = 1:0.95:1.05:0.1$

Analysis no.	Integral areas P				Molar response factors $f = (c/c_{286})(P_{286}/P)$		
M^+ (e/m)*	226	254	282	286†	226	254	282
1	6397	4306	6899	5052	7.90	11.15	7.69
2	3649	2385	4960	2973	8.15	11.84	6.29
3	5658	3728	7138	4659	8.23	11.87	6.85
		Average factors			8.09	11.62	6.94
		Standard deviation			±0.17	±0.41	±0.70

* For oligomers corresponding to individual M^+ see Table 1.
† 2,2'-Dinaphthol as standard.

Table 3. Analysis of the oligomeric fraction (2.245×10^{-5} g) of copolymer prepared from 0.5 mol 6-caprolactam, 0.48 mol 8-octanelactam and 0.02 mol 8-aminooctanoic acid at 250° (36.5 hr); standard 2,2'-dinaphthol (7.46×10^{-8} g)

Analysis no.	Integral areas P				Absolute amount*			
Dimers† M^+ =	226	254	282	286§	226	254	282	
1	1358	2629	2027	7375	17.3	48.1	20.3	
2	853	1566	991	3843	20.9	54.9	19.0	
3	638	1197	806	3037	19.7	53.2	19.7	
4	632	1055	757	2844	20.9	50.0	19.7	
		Average			19.7	51.6	19.7	
		Standard dev.			±1.7	±3.1	±0.5	
Trimers†, ‡ M^+ =	329	367	395	423	329	367	395	423
1	717	1231	1049	422	(10.1	17.2	14.7	5.9)
2	374	638	520	199	(10.1	17.1	14.0	5.3)
3	321	524	475	177	(10.9	17.8	15.6	6.0)
4	317	513	451	170	(11.5	19.2	16.3	6.2)
		Average			(10.6	17.8	15.2	5.9)
		Standard dev.			±0.7	±1.0	±1.0	±0.4

* Micromoles of oligomers in 1 g of extractables.
† For oligomers corresponding to individual M^+ see Table 1.
‡ P from uncorrected I_j values; absolute amounts were roughly estimated by means of an average response factor for dimers $f = 8.9$.
§ Standard.

with the time of evaporation into the ion source are plotted in Fig. 2.

The relative concentrations of dimers thus calculated need further correction for the "spectral response" of individual molecular ions, i.e. the intensities of molecular ions have to be related to the response of the chosen ion of a suitable standard (e.g. dinaphthol) which is added in known amount. This calibration of spectral response of individual oligomers can be expressed as the molar response factor (f)

$$f = (c/c_s)(P_s/P),$$

where c/c_s is the molar ratio of the determined oligomer and standard in the calibration mixture and P and P_s are the corresponding integral areas. Table 2 shows the determination of factors f for single dimers by means of 2,2'-dinaphthol as the standard and Table 3 illustrates the determination of cyclic dimers in the copolymer extract where these factors were applied.

Cyclic trimers and cotrimers may be determined by this method only with certain limitations. Since we failed to separate individual pure trimers even in the small amounts required for mass spectra, it was necessary to use the measured uncorrected intensities of molecular ions for estimation of the trimer representation.

It was mentioned for dimers that the relative intensity of $(M - 28)^+$ ions decreases with increasing molecular mass. By extrapolating this dependence to the spectra of lactam trimers, we can assume that the interference of fragment and molecular ions does not cause errors greater than 10 relative percent. The error could be further reduced by decreasing the energy of ionizing electrons down to near the ionization potential of molecules. However, the disadvantage of this procedure consists in the reduced sensitivity of recording, and this is critical because trimers are present in the extract in smaller amounts than dimers. Another rough simplification is the use of the mean value of response factors for dimers (i.e. 8.9) to estimate the absolute amounts. It is necessary to

consider that the factors for dimers differ from one another by up to 67%. Nevertheless, the estimates of trimers in Table 3 are illustrative and show the way for improvement of the method.

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