

# EFFECT OF THE CATION ON THE FORMATION OF KETO STRUCTURES DURING ACTIVATED ANIONIC POLYMERIZATION OF LACTAMS\*

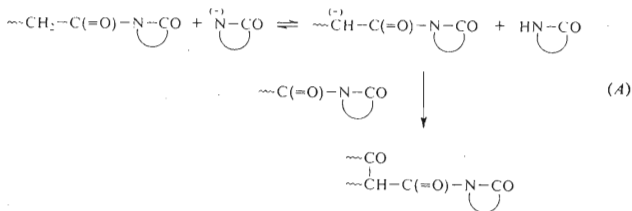
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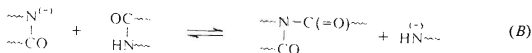
During the polymerization of caprolactam (activated with N-benzoylcaprolactam at 225°C) the content of the keto structures increases with decreasing ionization potential of the metal whose lactamate was used as initiator in the series  $Ba^{++} < BrMg^+ \ll Li^+ < Na^+ \cong K^+ \cong Cs^+$ . The order of the polymerization catalytic activity ( $Ba^{++} < Li^+ < BrMg^+ \gtrsim Na^+ < K^+ < Cs^+$ ) is only slightly different. The concentration of the diaminoketone structures formed in the polymers of 8-octanelactam and 12-dodecanelactam under comparable reaction conditions is three to four times lower than in polycaprolactam.

Condensation of diacylamine or acyllactam groups during the anionic polymerization of lactams gives rise to keto structures which are one of the causes of branching of macromolecules<sup>1</sup>. The extent of condensation is proportional to the initial concentrations of the catalytic components, temperature, and the time of heating<sup>2</sup>. Moreover, the formation of the keto groups also depends on the type of the activator used<sup>3</sup>. In the first stage of the activated polymerization, it is mainly the growth centres on macromolecules produced by the activator that participate in the condensation:

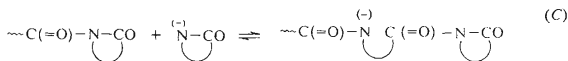


\* Part LIV in the series Alkaline Polymerization of 6-Caprolactam; Part LIII: This Journal 39, 539 (1974).

Later on, the condensation proceeds predominantly on the growth centres arising by the slow disproportionation reaction between the amide group of the monomer or of the polymer and the corresponding anion<sup>4</sup>:



Condensation (A), disproportionation (B) and polymerization (C) require the presence of a strong base which is consumed by side reactions<sup>5</sup> during the polymerization.



In order to suppress the condensation, the lowest possible concentration of the strong base is called for, however the strong base has to be present until the polymerization equilibrium is attained. It follows from the equilibria (A)–(C) that the rates of condensation, disproportionation and polymerization are proportional to the concentration of the lactam anions, so that the ratio of these reactions cannot simply be affected by a change in the initial concentration of the initiator. Under the usual polymerization conditions in the melt (0.3–0.5% of catalytic components, 220–250°C), the polymerization lasts only for a fraction of the time during which the sample is exposed to elevated temperatures. Thus, in such case the extent of the condensation reactions leading to the formation of the keto structures is not determined by the ratio of the rates of condensation and polymerization. The concentration of the keto structural units could be reduced *e.g.* by extending the polymerization time within the given reaction time, *i.e.* by relatively reducing the slower reaction (A) and the reaction (B), which is slower by an order of magnitude, with respect to (C). At a given concentration of the catalytic components, this may be achieved by reducing the dissociation of the lactamate, in the lactam medium at temperatures up to 200°C, for instance using the lactamate of an alkali metal of increased ionization potential<sup>6</sup>. To verify this hypothesis, we investigated in this paper the effect of the lactamate cation on the formation of the keto structural units in the polymer chain in the polymerization of caprolactam initiated with its cesium, potassium, sodium, lithium, or barium salt and activated with N-benzoylcaprolactam; caprolactam magnesium bromide was also used as initiator.

Two series of experiments were carried out at a concentration of the initiator 0.6 mol. % (related to the monomer). In the first series, the ratio of the activator concentration ( $c_A$ ) and initiator concentration ( $c_i$ ) was 0.25; at this ratio, 90% of

the initial basicity is still present on completion of the polymerization<sup>5</sup>. For alkali metal salts of caprolactam, disproportionation (*B*) plays an important role under these conditions during heating of the sample, so that the concentration of the keto groups increases with the duration of the process<sup>2</sup>. In the second series, the above ratio of the components was 3, when after a short polymerization time almost the whole catalytic activity of the system vanishes, and the characteristics of the polymer remains practically unchanged while the thermal process goes on. To ensure the same temperature course during the polymerization, a two-stage polymerization procedure was used; in the first stage the initial mixture of the components was heated in a bath of 175°C ( $T_s$ ) and after a short overheating due to the released heat of polymerization (by 4–11°C above the temperature of the bath, *i.e.* to a temperature

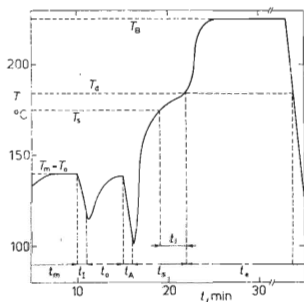


FIG. 1

Temperature Course of the Two-Stage Polymerization of Caprolactam Initiated with Caprolactam Magnesium Bromide

$c_1 = 52.3$  mmol/kg,  $c_A = 13.1$  mmol/kg; symbols are defined in the Experimental.

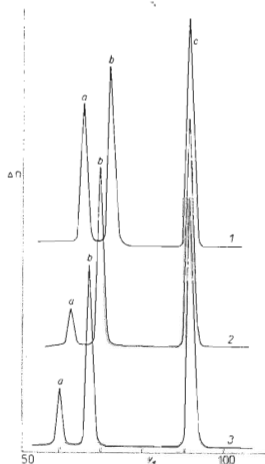


FIG. 2

GPC Analyses of Benzamide Fractions of the Poly(lactam Hydrolyzates

$V_e$  Elution volume (count),  $n$  differential refraction; 1 polycaprolactam, 2 poly(8-octanelactam), 3 poly(12-dodecanelactam); *a* dibenzamidoketones, *b* monobenzamidoketones and adducts of benzamide acids with tetrahydrofuran, *c* anthracene.

$T_d$  during a time  $t_i$  ranging from 1 to 5 minutes for alkali metal salts) the second stage was carried out in a bath of 225°C ( $T_B$ ). Such procedure allows the chosen final temperature of the polymerizate,  $T_B$ , to be attained in the fastest possible way without temporarily exceeding it. At the same time, it is possible to evaluate to some extent the polymerization rate in the first stage from the rate of overheating above  $T_s$  assuming that the conversions are neither too high nor too different at attaining  $T_s$ . A typical course of temperature at the moment of attaining the temperature  $T_s$  is given in Fig. 1.

It can be clearly seen from the values  $(T_d - T_s)/t_i$  (Table I) that in accordance with the published data<sup>7-9</sup> the catalytic activity of the salts increases in the series Ba < Li < Na < K < Cs, that is, with decreasing ionization potentials. If the rate value obtained for sodium caprolactam commonly used as initiator is taken as the standard value, then the catalytic activity under given conditions (in the monomer melt at 175°C) may be described for the above series by the ratio 0.16 : 0.50 : 1.00 : 1.69 : 2.92; different ratios, and consequently also participations of the anions may be determined for a different medium and temperature.

At a  $c_A/c_I$  ratio equal to 0.25, the concentration of the diaminoketone units in the polymerizate ( $c_D$ ) is practically the same for all alkali metal lactamates (Table II). The ionization difference which was reflected in the rate of the chain growth reaction

TABLE I

Polymerization of Caprolactam in the Presence of Its Various Salts (initiators)

$c_I$ ,  $c_A$  Are initiator and activator concentrations, respectively; the other symbols are defined in the Experimental.

| Cation            | $c_I$<br>mmol/kg | $c_A$<br>mmol/kg | $t_s$<br>min | $t_d$<br>°C | $T_B$<br>°C | $t_e$<br>min | $(T_d - T_s)/t_i$<br>K · s <sup>-1</sup> |
|-------------------|------------------|------------------|--------------|-------------|-------------|--------------|--|
| Cs <sup>+</sup>   | 52.2             | 13.0             | 2.4          | 182.5       | 224.7       | 119.8        | 0.31                                     |
| K <sup>+</sup>    | 52.4             | 13.1             | 3.0          | 183.7       | 224.7       | 118.4        | 0.18                                     |
| Na <sup>+</sup>   | 52.5             | 13.1             | 3.7          | 180.8       | 224.7       | 122.2        | 0.11                                     |
| Li <sup>+</sup>   | 52.6             | 13.2             | 4.9          | 182.7       | 225.2       | 119.2        | 0.05                                     |
| Ba <sup>++</sup>  | 26.2             | 13.1             | 10.0         | 176.0       | 225.1       | 120.0        | 0.02                                     |
| BrMg <sup>+</sup> | 52.3             | 13.1             | 5.7          | 184.3       | 225.7       | 119.8        | 0.08                                     |
| Cs <sup>+</sup>   | 48.8             | 151.9            | 2.1          | 181.8       | 225.0       | 60.6         | —  |
| K <sup>+</sup>    | 50.9             | 152.6            | 3.0          | 180.9       | 226.0       | 61.3         | —  |
| Na <sup>+</sup>   | 50.9             | 152.7            | 1.6          | 185.2       | 226.5       | 61.0         | —  |
| Li <sup>+</sup>   | 51.0             | 152.8            | 3.0          | 178.8       | 225.6       | 61.2         | —  |
| Ba <sup>++</sup>  | 25.4             | 152.2            | 6.0          | 182.2       | 225.8       | 61.0         | —  |
| BrMg <sup>+</sup> | 50.7             | 152.0            | 1.2          | 185.9       | 226.5       | 61.4         | —  |

does not affect the side reactions (condensation or disproportionation) to any important degree. A considerable drop in the rate of polymerization, condensation, and disproportionation in the case of the barium salt is also reflected in the half value of  $c_D$ . Although in this case the monomer-polymer equilibrium is still achieved, the ratio of the polymerization period to the overall reaction time increases considerably compared to polymerizations carried out with the alkali metal lactamates.

The decay of the catalytic activity for  $c_A/c_I = 3$  is obvious from the fact that the monomer-polymer equilibrium was not attained (Table II). Although in this case the disproportionation may be neglected, the comparatively balanced  $c_D$  values indicate the parallel character of the chain growth and condensation reaction in the presence of any alkali metal salt of caprolactam; a perceptible drop in the concentration of the monoaminoketone units in the polymerizate ( $c_M$ ), which are formed at the very beginning of the polymerization when the initial activator is still present,

TABLE II

Characterization of Polymers Prepared in the Presence of Various Caprolactam Salts

$c_D, c_M$  Respective concentrations of diamino and monoaminoketone units in the polymerizate (mmol/kg),  $p$  the fraction of the water insoluble polymerizate (%),  $\bar{P}_n$  the number-average degree of polymerization, [B] and [C] concentrations of basic and acidic groups, respectively (mmol/kg)  $M_0$  mol. weight of the monomer,  $E$  concentration of the end groups (mmol/kg).

| Cation            | $c_D^a$ | $c_M$ | $p$   | $\bar{P}_n^b$ | [B]  | [C]  | $2/M_0E^c$ |
|-------------------|---------|-------|-------|---------------|------|------|------------|
| $c_A/c_I = 0.25$  |         |       |       |               |      |      |            |
| Cs <sup>+</sup>   | 62.8    | —     | 91.22 | 230.7         | 40.7 | 23.0 | 231.3      |
| K <sup>+</sup>    | 62.2    | —     | 91.24 | 236.6         | 36.4 | 25.4 | 237.0      |
| Na <sup>+</sup>   | 61.9    | —     | 91.32 | 221.0         | 42.4 | 25.4 | 219.3      |
| Li <sup>+</sup>   | 65.9    | —     | 91.31 | 209.2         | 45.6 | 21.5 | 221.2      |
| Ba <sup>++</sup>  | 30.2    | —     | 90.90 | 277.0         | 22.9 | 12.6 | 265.3      |
| BrMg <sup>+</sup> | 44.4    | —     | 91.72 | 172.3         | 66.0 | 14.7 | 189.2      |
| $c_A/c_I = 3$     |         |       |       |               |      |      |            |
| Cs <sup>+</sup>   | 43.1    | 11.8  | 88.99 | 105.7         | 14.6 | 18.0 | 95.8       |
| K <sup>+</sup>    | 44.2    | 11.0  | 90.18 | 110.3         | 14.4 | 19.0 | 96.1       |
| Na <sup>+</sup>   | 42.8    | 10.6  | 89.61 | 102.5         | 13.4 | 27.0 | 92.0       |
| Li <sup>+</sup>   | 39.5    | 10.2  | 89.56 | 101.5         | 15.4 | 15.0 | 97.0       |
| Ba <sup>++</sup>  | 17.3    | 5.5   | 68.22 | 56.5          | 4.2  | 37.4 | 73.6       |
| BrMg <sup>+</sup> | 19.4    | 4.1   | 90.74 | 94.6          | 27.4 | 61.1 | 74.4       |

<sup>a</sup> Determined with a deviation from the average of  $\pm 0.5\%$  rel. <sup>b</sup>  $\bar{P}_n = 116.8[\eta]^{1.115}$  (osmometry)<sup>13</sup>. <sup>c</sup>  $E = 100\sigma \cdot \varrho_A \cdot c_A/p + [B] + [C]$ , where  $\sigma = 0.89$  and  $\varrho_A = 1.0$  (ref.<sup>17</sup>).

proceeds parallel with the decrease of the ionization potentials. For barium, half values of  $c_D$  and  $c_M$  were found again. If both the concentrations of the acidic and basic groups and the average degrees of polymerization of the equilibrium polymerizates are taken into account, one may deduce that the dissociation of the ion pair of barium caprolactam to yield nonassociated ions is on the average half of the less dissociating alkali salts.

In the polymerization initiated with caprolactam magnesium bromide the individual parameters depart from the regular sequence in the series of the other salts under investigation, so that the initiation with complex compounds should be evaluated quite independently; neither can a different mechanism be ruled out (*cf.*<sup>10</sup>). The character of the polymerization products is completely different. Unlike the yellowish products prepared in the presence of alkali salts, they are white and on cooling of the melt do not exhibit the usual contraction.

Lactam cycles of different sizes differ by their conformation: In caprolactam (1-aza-2-cycloheptanone), the amide group has a planar *cis* conformation, in 12-dodecanolactam (1-aza-2-cyclotridecanone) its conformation is *trans*, while in 8-octanolactam (1-aza-2-cyclononanone) the conformer with the nonplanar *trans*-amide group is represented to an important extent besides the conformer with the *cis*-amide group<sup>11</sup>. Moreover, the process of ionic reactions of various lactams may be affected by a change of their dielectric constant, *i.e.* by the dielectric constant of the medium. Both the acyllactam ends of the growing chains and the original acyllactam used as activator participate in the formation of the keto structural units by condensation. The monomeric lactam or its anion are reaction components of the disproportionation reactions leading to diacylamines capable of condensation; they may also participate in the other cyclically repeating side reactions having as a consequence regeneration of the growth centres. The role played by the monomer and its anion in partial

TABLE III

Characterization of Poly lactams.

Reaction conditions see the Experimental.  $[\eta]$  intrinsic viscosity (dl/g); the other symbols *cf.* Table II.

| Monomer           | $c_D$ | $\rho$ | $[\eta]$ | [B]            | [C]            | $\bar{P}_n$ | $2/M_0E$ |
|-------------------|-------|--------|----------|----------------|----------------|-------------|----------|
| Caprolactam       | 55.9  | 91.56  | 2.02     | 30.8           | 31.1           | 256         | 224      |
| 8-Octanolactam    | 16.5  | 98.66  | 2.36     | 48.8           | 13.6           | —           | —        |
| 12-Dodecanolactam | 19.8  | 98.67  | 5.07     | — <sup>a</sup> | — <sup>a</sup> | —           | —        |

<sup>a</sup> Polymer insoluble both in the phenol-propanol mixture and in benzylalcohol.

reactions of the overall process of the equilibrium polymerization quite naturally depends on the monomer-polymer equilibrium at a given temperature. On attaining the equilibrium at 225°C the caprolactam polymerizate contains approximately 8.5% of the extractables, of which about 70% consists of monomer. For 12-dodecanelactam the equilibrium is shifted to the polymer, and the extractables, predominantly the monomer, amount to some 1.5%, while for 8-octanelactam no monomer is present on completion of the polymerization<sup>12</sup>. It follows from Table III that although the concentration of the diaminoketone units in polycaprolactam is much higher than in the polymers of nine- and thirteen-membered lactam, it is in no case proportional to the equilibrium content of the monomer. It seems rather that the lower  $c_D$  values for both higher lactams are due to the decreased mutual accessibility of reacting groups during the condensation reactions leading to the keto structures.

## EXPERIMENTAL

### Initiators

Sodium, potassium, and cesium caprolactam were prepared each time in the amount necessary for the given polymerization. The caprolactam was dissolved in a measured volume of a 0.05 to 0.15M methanol solution of methoxide, and the solvent was evaporated (15 min) at 0.5 Torr and room temperature. During the following 15 minutes the temperature was raised to 120°C at 0.1–0.2 Torr. These conditions were maintained for another 15 minutes. All operations were carried out in argon; the distillation proceeded with stirring. The initial molar lactam to methoxide ratio was 20 : 1; the residual lactam was determined by weighing the product (average excess 80% by wt., at 0.04–0.12 g of lactamate). In parallel initiator samples, the residual methanol was determined on dissolution in cyclohexanol (1 ml) and acetic acid (40  $\mu$ l) by means of GLC (column 1 m, 3 mm with Carbowax 2M (10%) on Chromosorb W); the methanol concentration did not exceed 0.5 mol %.

Caprolactam magnesium bromide was obtained similarly from an ether solution of ethylmagnesium bromide (*cf.*<sup>10</sup>); after dissolution of the reference sample in methanol (2 ml) and acidifying with acetic acid (0.05 ml) the lactam content was checked by GLC (the same column as for the determination of methanol) with benzophenone as the internal standard. Lithium caprolactam was prepared from solid lithium tert-butoxide in a similar manner: the mixture of butoxide and lactam was kept at 80°C and 0.1 Torr for the first 15 minutes. Barium caprolactam was obtained similarly from barium hydride (94%); the removal of the excess lactam by distillation followed after two hours of dissolution at 120°C under normal pressure.

### Polymerization

Caprolactam used and the caprolactam polymerization technique (Procedure B) *cf.*<sup>13</sup>. The monomer was melted at 140°C ( $T_m$ ) for 10 minutes ( $t_m$ ), the initiator was dissolved during 1 minute ( $t_i$ ) and the solution was thermostated in a bath at 140°C ( $T_0$ ) for 4 minutes ( $t_0$ ); after dissolving of N-benzoylcaprolactam (activator) during 1 minute ( $t_A$ ) a part of the reactor containing the melt was immersed into a bath ( $T_s = 175^\circ\text{C}$ ) for a period  $t_s$  and on exceeding the temperature of the melt by 5–10°C above  $T_s$  (attaining the temperature  $T_d$  during a period  $t_i$ ) it was transferred into a bath having 225°C ( $T_B$ ) (Fig. 1). The polymerization process was interrupted by

immersing a part of the reactor containing the polymerize into cold water; as an effective time of the process ( $t_e$ ), we regarded the interval between attaining  $T_d$  at the beginning of the polymerization and the cooling of the polymerize. The polymerizations of the 7-, 9- and 13-membered lactam were carried out in the presence of 0.40 mol. % of sodium salts and 0.20 mol. % of N-benzoyl derivatives<sup>14,15</sup> of the respective lactams. 8-Octanelactam (BASF, Ludwigshafen), m.p. 73.0 to 74.5°C (twice from acetone); 12-dodecanelactam (Chemische Werke Hüls A.G.), m.p. 151.0 to 151.5°C (three times from 1,2-dimethoxyethane); their sodium salts were prepared by a procedure described for sodium caprolactam<sup>7</sup>. The preparation conditions of the polymerization mixture and the polymerization itself are defined by the following temperatures and time intervals (*cf.* the preceding paragraph and Fig. 1): for all lactams,  $t_m = 10$  min,  $t_1 = 2$  min,  $t_0 = 3$  min,  $t_A = 30$  s,  $T_s = 160^\circ\text{C}$ ,  $T_B = 225.3^\circ\text{C}$ ; for caprolactam,  $T_m = T_0 = 125^\circ\text{C}$ ,  $t_s = 310$  s,  $t_e = 151.5$  min (where  $t_e$  is the interval between the beginning of dissolution of the activator and the attaining of  $T_0$  at the final cooling of the polymerize); for 8-octanelactam,  $T_m = T_0 = 90^\circ\text{C}$ ,  $t_s = 2$  min,  $t_e = 153$  min; for 12-dodecanelactam,  $T_m = T_0 = 160^\circ\text{C}$ ,  $t_s = 1.5$  min,  $t_e = 151.5$  min.

### Model Compounds

8-Benzamidooctanophenone, 1,15-dibenzamido-8-pentadecanone, and 8-benzamidooctanoic acid were isolated from the polymerize of 8-octanelactam, 1,23-dibenzamido-12-tricosanone and 12-benzamidodecanoic acid were obtained from the polymerize of 12-dodecanelactam. The polymerizations of lactams were carried out in the presence of the corresponding sodium salts and N-benzoyl derivatives (25 mol. % related to the monomer) at 225°C (reaction times 2 h and 1 h in the first and second case, respectively). The polymerizes were hydrolyzed (4 and 7 g in 16 and 27 ml, respectively, of dilute hydrochloric acid 1 : 1) and benzoylated (7 and 8.4 ml of benzoyl chloride) for three hours as described elsewhere<sup>16</sup>. On dilution with water, the reaction mixtures were extracted with chloroform (for 12-dodecanelactam after addition of NaCl). The solvent was removed from chloroform solutions at reduced pressure; the evaporation residues were treated chromatographically — in the first case by preparative layer chromatography (Kieselgel GF<sub>254</sub> layer 400 . 200 . 1 mm, chloroform-ether system 9 : 1), in the second case by GPC (repeated injections of 0.5 ml of a concentrated solution in tetrahydrofuran by using an analytical method, *cf.* below). Alkaline aqueous layers were acidified by conc. hydrochloric acid (10 and 28 ml, respectively), raw acids were removed by filtration and purified by crystallization.

*8-Benzamidooctanophenone*: 70 mg, m.p. 72.5–85°C (cyclohexane); mass spectrum:  $M^+$  323.1899, for  $C_{21}H_{25}NO_2$  calculated 323.1885. *1,15-Dibenzamido-8-pentadecanone*: 106 mg, m.p. 127–128°C (benzene); mass spectrum:  $M^+$  464.3033, for  $C_{29}H_{40}N_2O_3$  calculated 464.3039. *8-Benzamidooctanoic acid*: 1.13 g, m.p. 87–88.5°C (water). For  $C_{15}H_{21}NO_3$  (263.3) calculated: 68.42% C, 8.04% H, 5.32% N, found: 68.47% C, 8.18% H, 5.37% N.

*1,23-Dibenzamido-12-tricosanone*: 90 mg, m.p. 112.5–114°C (tetrahydrofuran); mass spectrum:  $M^+$  576.4282, for  $C_{37}H_{56}N_2O_3$  calculated 576.4291. *12-Benzamidodecanoic acid*: 1.19 g, m.p. 99–100°C (acetone). For  $C_{19}H_{29}NO_3$  (319.4) calculated: 71.44% C, 9.15% H, 4.39% N; found: 71.46% C, 9.23% H, 4.20% N.

### Characterization of Samples

The concentration of keto groups in the polymerizes was determined by a procedure described earlier<sup>16</sup>. The water extractables of polymerizes, concentrations of the basic and acidic groups in the polymers and viscometric measurements were carried out as usual<sup>13</sup>; the polymerizes of 12-dodecanelactam were first extracted with boiling benzene and only then with water.



*Determination of the diamino-ketone units in poly lactams by GPC.* After hydrolysis of 0.5 g of the polymerizate and benzylation<sup>16</sup>, the reaction mixture was neutralized (pH 5–7) by hydrochloric acid, the mixture was evaporated *in vacuo* to dryness, the evaporation residue was dissolved in a minimum volume of water with sodium carbonate added (8–25 mmol), the solution was evaporated to dryness, the residue was dried *in vacuo* and extracted ten times 30 minutes each time with 50 ml of freshly purified tetrahydrofuran (by boiling with sodium) under reflux. The extraction fractions were filtered under pressure through an S4 fritted glass disc and evaporated to dryness. The solution of a mixture of the evaporation residue with 10 mg of anthracene (internal standard) in 1.5 ml of tetrahydrofuran was injected (0.3 ml) into the chromatograph columns (5 columns 8 × 1000 mm connected in series, packed with an S-Gel 832 produced in the Institute of Macromolecular Chemistry); tetrahydrofuran was used as eluent. The ratios of the peak areas of the compound under investigation and of the standard obtained from a differential refractometer record were used for evaluation (Fig. 2). It was found that the molar coefficients of the differential refraction are the same for 1,12-dibenzamido-6-undecanone (preparation *cf.*<sup>16</sup>), 1,15-dibenzamido-8-pentadecanone, and 1,23-dibenzamido-12-tricosanone. The method was calibrated by employing a mixture of caprolactam and 1,12-dibenzamido-6-undecanone.

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