

## Polymerization of Laurinolactam. I. Impurities in Industrial Laurinolactam and Their Influence on Anionic Polymerization

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### Synopsis

Fractions containing predominantly cyclododecanone (0.02%), C<sub>24</sub> hydrocarbons (0.02%), and probably isomers of the mono- and diunsaturated 13-membered lactam (0.05%) were isolated from industrial laurinolactam. Both the cyclic ketone and unsaturated lactams slow down the anionic polymerization of laurinolactam, but they exert only insignificant or no effects on the molecular weight of the resulting polymer if the polymerization has been activated with N,2-disubstituted 3-oxoamide. On the other hand, the molecular weight is greatly affected by the type of catalytic system. Of the purification techniques tested, the most effective and advantageous one was crystallization from 1,2-dimethoxyethane.

### INTRODUCTION

It is known that polymerization of industrial laurinolactam gives rise to a crosslinked polymer, which has been attributed to the presence of impurities.<sup>1,2</sup> A number of purification techniques (mainly described in the patent literature<sup>3-14</sup>) have been developed to remove these impurities both for laurinolactam and other lactams. Since these methods have not been critically evaluated and the impurities present in laurinolactam have not been identified, we have been dealing in the present work with the isolation and identification of principal impurities in order to establish their influence on the course of the anionic polymerization and the molecular weight of the polymer thus obtained.

### EXPERIMENTAL

**Chemicals.** Laurinolactam (Hüls, Germany; acidity 0.27  $\mu$ mole/kg); 1,2-dimethoxyethane distilled with CaH<sub>2</sub>. The other solvents were analytical purity grade. Silicagel (Merck), activity 7-8 Brock. Sodium caprolactam was prepared from sodium methoxide.<sup>15</sup> Cyclopentadecanone, mp 62-63°C. N,2-Diethyl-3-oxohexanamide was prepared according to ref. 16.

**Gas Chromatography.** The gas-chromatographic analysis of solutions of laurinolactam was performed at 180°C on a 1-m column or at 200°C on

a 2-m column (10% of silicone rubber XE-60 on Chromosorb W, 80–100 mesh) on a Perkin-Elmer Model F 11 apparatus. The injection temperature was 250°C. Benzophenone was added to the individual samples as an internal standard for quantitative measurements.

**Fractional Crystallization from a Concentrated Solution.** A crystallization tube (50 mm diam., 600 mm long) provided with a thermostating jacket and sealed with a Teflon stopper was filled with a solution of 480 g laurinolactam and 500 ml dry methylcellosolve or 1,2-dimethoxyethane. The crystallizer with the solution was first thermostated to 80°C and then cooled at a rate of 2°C/hr to 50°C. The mother liquor was then discharged while the crystallizer was heated to 80°C at a rate of 5°C/hr. A corresponding amount of the new solvent was added to the crystals remaining in the crystallizer, and the crystallization was carried out in the same way. The impurities content in the mother liquors from each crystallization was determined by gas chromatography.

**Crystallization for Polymerization.** Laurinolactam for polymerization purposes was crystallized three times from 1,2-dimethoxyethane (200 ml/100 g lactam) in a simple laboratory apparatus under dry argon freed from the last traces of oxygen. The yield of each crystallization was 90% by weight. The quality of the product was tested by determination of impurities in the individual mother liquors. The last mother liquors contained impurities lying close to the limit of perception.

**Purification by Zone Melting.** A glass ampoule (10 mm diam., 160 mm long) was filled with laurinolactam and passed five times through the melting zone at a rate 2 cm/hr (Zone-Refining Unit, Baird-Tatlock).

**Hydrogenation.** A solution of 3 g laurinolactam in 100 ml ethanol was hydrogenated at a pressure of 5 atm H<sub>2</sub> in the presence of 6.25 g Raney nickel for 8 hr.

**Ozonization.** Approximately 1 g ozone was introduced into a solution of 5 g laurinolactam in 100 ml methanol while stirring at room temperature for 1 hr (Ozone-Generator, Fischer, Germany).

**Purification by Polymerization.** Laurinolactam (50 g) was melted in a 100-ml flask under an inert gas (at 160–165°C). A 50% dispersion of sodium hydride in mineral oil (0.125 g) was then dissolved in the melt. The polymerization mixture was heated to 200°C for 1 hr, while in another experiment it was heated for 2 hr. In still another experiment, with 1.75 mol-% sodium laurinolactam, the thermostating lasted 20 min. Then the mixture was poured into 300 ml xylene and cooled to room temperature. The crystals obtained were filtered off and dissolved in methanol. Carboraffin was added and the solution was filtered. The solvent was evaporated from the filtrate in vacuo and the residue was recrystallized from benzene. The impurities content was at the limit of perception according to gas-chromatographic data.

**Accumulation of Impurities.** Industrial laurinolactam (1 kg) was crystallized from 2 liters 1,2-dimethoxyethane. The crystals were filtered off, the mother liquor was diluted to 2 liters with fresh solvent, and 1 kg

TABLE I

Fraction	I	II	III	IV	V
Amount, g	0.131	0.123	0.110	0.310	0.263
Main component	hydrocarbons	cyclodecanone	laurinolactam	unsaturated lactams (M = 193 and 195)	— (acidity 0.13 mole/—kg)

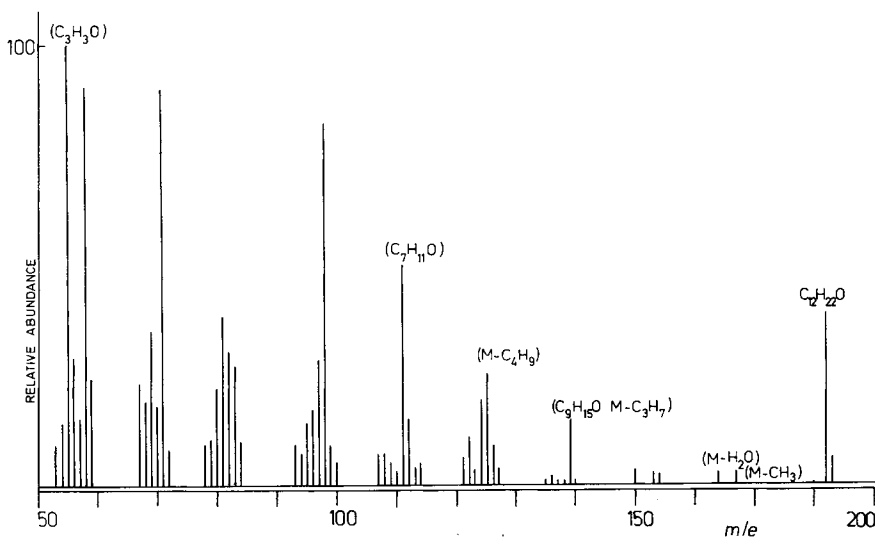


Fig. 1. Mass spectrum of the crystalline chromatographic fraction II.

industrial laurinolactam was dissolved in the solution thus obtained. After cooling the warm solution to 20°C, the lactam crystals were separated. This procedure was repeated three times more, yielding mother liquor from 5 kg industrial laurinolactam. The resulting mother liquor was concentrated in vacuo and more crystalline laurinolactam was filtered off. Gradual concentration and separation of laurinolactam crystals, followed by evaporation of the solvent from the last mother liquor, gave 11.7 g concentrated impurities which still contained about 50% laurinolactam. According to the conductometric titrations, these concentrated impurities (A) contained 5.2 mmole acid groups per kg.

**Separation of Impurities.** Concentrated impurities A (1 g) were chromatographed on a silica gel column (25 × 600 mm) and successively developed with *n*-heptane, with the mixtures heptane: dimethoxyethane 4:1 and 1:1, with dimethoxyethane, and with methanol. The IR and mass spectra of the individual fractions (I–V) were recorded (Infracord, Perkin-Elmer and Mass Spectrograph AEI MS-902), as shown in Table I.

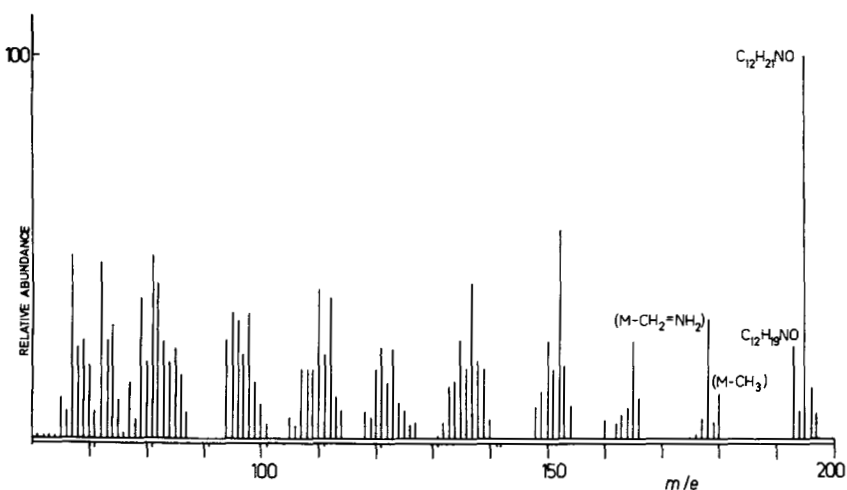


Fig. 2. Mass spectrum of the purified chromatographic fraction IV.

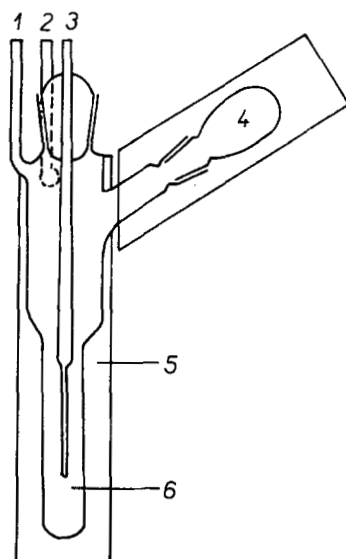


Fig. 3. Polymerization vessel with heating: (1) inlet; (2) outlet of inert gas; (3) tube for the thermocouple; (4) flask for the initiator or activator; (5) heated mantle; (6) polymerization tube.

Fraction II was chromatographed once more, yielding a compound of the formula  $C_{12}H_{22}O$  (Fig. 1), mp  $55-56^{\circ}C$ ; this compound exhibited strong absorption at  $1710\text{ cm}^{-1}$  and gave a 2,4-dinitrophenylhydrazone, mp  $149-150^{\circ}C$  (cyclohexane). Similarly, fraction IV was also chromatographed once again, and its IR, NMR, and mass spectra (Fig. 2) were recorded.

**Polymerization.** After several preliminary experiments, the polymerization was carried out in a polymerization cell shown in Figure 3. The

temperature of both the laurinolactam melt and an essential part of the polymerization cell was maintained 3–9°C above the melting point of laurinolactam (Table II). A solution of sodium laurinolactam was then produced by rinsing the cell containing sodium caprolactam with the laurinolactam melt (155–160°C). Preparation of this solution took 1.5–2.0 min on the average. In the solution of the sodium salt thus produced, an activator was dissolved at 153–161°C during 50–70 sec. Impurities, if added, were dissolved together with the activator.

TABLE II  
Effect of Impurities<sup>a</sup>

Impurities						
Designation	Concn., mg/g	$T_0$ , °C	$t_{\max}$ , min	$\Delta T_{\max}$ , °C	$p$ , %	$[\eta]$ , dl/g
A	1.00	158.0	4.0	6.6	98.3	2.80
A	5.00	157.5	5.2	6.6	97.9	2.87
A	12.5	159.0	9–13	0.5	12.4	0.80
II <sup>b</sup>	6.3	158.5	7.1	3.4	73.0	2.43
II <sup>b</sup>	9.7	161.0	8–10	0.6	18.5	0.86
IV <sup>b</sup>	10.0	157.0	7.2	2.3	56.7	1.99
V <sup>b</sup>	5.0	158.5	—	—	—	—
<sup>c</sup>	—	157.5	4.2	7.1	98.8	2.74
<sup>d</sup>	—	158.5	3.6	7.0	99.0	2.80
	—	158.5	3.5	6.6	98.9	2.74
Cyclopenta- decanone	10.3	157.5	6.1	7.6	93.5	3.12
<sup>e</sup>	—	159.5	5.2	1.8	98.8	5.30

<sup>a</sup> Polymerization at 200°C in the presence of an equimolar amount of sodium caprolactam and N,2-diethyl-3-oxohexanamide (0.3 mole-%). Time: 30 min at 200°C and 4 hr at 150°C. Laurinolactam was crystallized three times from 1,2-dimethoxyethane (200 ml/100 g).

<sup>b</sup> Chromatographic fractions.

<sup>c</sup> Unpurified lactam.

<sup>d</sup> Lactam crystallized once.

<sup>e</sup> Activated with 0.3 mole-% of N-benzoyllaurinolactam.<sup>20</sup>

The polymerization mixture was immersed into a salt bath (200° ± 0.1°C) and thermostated 30 min while measuring the temperature difference between the reaction mixture and the bath. Heating and cooling of laurinolactam and polymerizate were recorded in the same way. After 30 min, the product was cooled to 150°C, kept at this temperature 4 hr, and then left to cool spontaneously to room temperature.

The polymerizate in the form of filings (0.15 × 2 mm) was extracted with boiling methanol (3 × 15 min, 60 ml/g polymerizate) and dried at 50°C at 1 torr for 12 hr.

The intrinsic viscosity in tricresol at 25°C was determined by a standard procedure described for caprolactam.<sup>17</sup>

## DISCUSSION

**Purification of Lactam. Accumulation and Identification of Impurities**

Gas chromatography allowed direct determination of impurities in laurinolactam if their amount exceeded 0.01%. For identification, the impurities were accumulated and separated into pure components by crystallization and column chromatography. Preliminary crystallization tests have shown that the optimum purifying effect is found with 1,2-dimethoxyethane or 2-methoxyethanol, whereas acetone, pyridine, dichloroethane, ethyl acetate, acetonitrile, and dimethylformamide were less efficient. Dimethoxyethane was then used for the preparation of pure laurinolactam for polymerization and also for the accumulation and fractionation of impurities. During these operations, there arises the danger of formation of further impurities due to the oxidation with air oxygen or peroxide from the solvent. This is why crystallization, accumulation of impurities, as well as column chromatography were carried out under argon. Peroxides and moisture that may have been present were removed from the solvent by adding calcium hydride during distillation.

The other purification methods investigated are altogether less advantageous. Some of them, such as, e.g., oxidation or reduction methods, contaminate the product rather than purify it. The polymerization technique which gives otherwise good results is complicated and uneconomical.

During the fractionation of accumulated impurities by column chromatography, the individual fractions were isolated quantitatively if possible, so that the nonvolatile compounds that may be present would not escape determination.

A colorless, oily liquid was obtained as the first fraction; its infrared spectrum did not exhibit any absorption in the frequency region of the NH or CO group. According to the mass spectrum, C<sub>24</sub> hydrocarbons are present in crude laurinolactam in an amount of about 0.02%. It seems that these compounds are side products of the cyclotrimerization of butadiene followed by hydrogenation. Owing to the high boiling point, one part of these hydrocarbons are codistilled with laurinolactam. After repeated chromatographic separation, a further fraction (about 0.02% related to the crude lactam) yielded a crystalline compound C<sub>12</sub>H<sub>22</sub>O which exhibited an intensive carbonyl frequency ( $\nu_{C=O} = 1710 \text{ cm}^{-1}$ ) and gave a 2,4-dinitrophenylhydrazone. As can be seen from the mass spectrum (Fig. 1), the fragmentation of M<sup>+</sup> ( $m/e = 182.1672$ , C<sub>12</sub>H<sub>22</sub>O) fully corresponds to an alicyclic ketone.<sup>18</sup> Since the NMR measurements indicated that the molecule contains no protons bonded to a branched carbon atom, the compound in question was identified as cyclododecanone. This ketone is one of the intermediates in the preparation of laurinolactam and can get into the product during the final laurinolactam distillation.

Another oily fraction contains a mixture of several compounds which could not be separated even by repeated chromatographic fractionation. This fraction is strongly enriched by compounds of  $m/e = 195$  and  $m/e = 193$

and exhibits an intensive absorption at  $1680\text{ cm}^{-1}$ ,  $1550\text{ cm}^{-1}$ , and  $3400\text{ cm}^{-1}$ , similarly to the starting laurinolactam. In the rechromatographed fraction,  $M^+$  ( $m/e = 195.1618$ ) was determined which corresponds to the composition  $C_{12}H_{21}NO$  along with a smaller participation of compound  $M^+$ ,  $m/e = 193.1463$  and the composition  $C_{12}H_{19}NO$  (Fig. 2). According to the NMR spectra, the protons are present also on double-bonded carbon atoms. It seems therefore that the compound in question could be laurinolactam with one or two unsaturated bonds. Since, however, the analyzed compounds were present in a mixture, the constitution of the compounds of the isolated fraction cannot be described with certainty.

The last acid fraction was not investigated in more detail with respect to the possible content of some other compounds which may arise during the process of isolation.

### Effect of Impurities on the Anionic Polymerization

The anionic polymerization is very sensitive toward impurities; and, therefore, the effect of small quantities of impurities on its course and molecular weight will be easy to establish. After preliminary tests, simple non-isothermal calorimetry was chosen for following the course of polymerization. *N*,2-Diethyl-3-oxohexanamide was used as activator<sup>19</sup> and was sufficiently active at  $200^\circ\text{C}$  to achieve equilibrium within 30 min, while its activity at the temperature of preparation of the polymerization mixture ( $155\text{--}160^\circ\text{C}$ ) was sufficiently low.

When evaluating the polymerization course from the course of temperature, it should be noted that the thermal conductivity of the polymerizate is lower than that of laurinolactam (Fig. 4). If the major part of polymeriza-

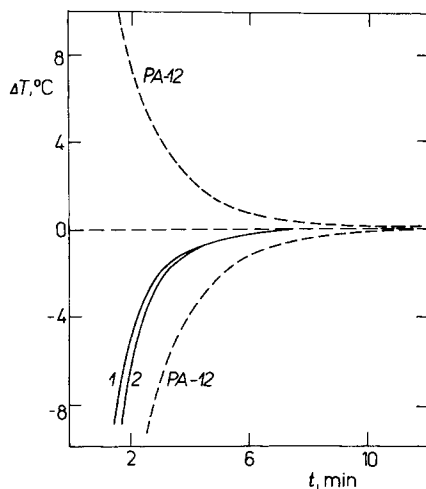


Fig. 4. Heating and cooling curves of laurinolactam and nylon 12. Bath temperature  $200^\circ\text{C}$ . Laurinolactam:  $T_0 = 162^\circ$  (1) and  $156^\circ\text{C}$  (2). Nylon 12:  $T_0 = 160^\circ$  and  $228^\circ\text{C}$ .

tion takes place during thermostating of the polymerization mixture to the bath temperature, the polymerizate attains this temperature later than during heating of the monomer. In such case, the temperature maximum is lower or absent, since the greatest part of the heat of polymerization is released during thermostating.

The accumulated impurities contain acid compounds which are present in the chromatographic fractions. There is therefore a possibility that the inhibiting action of the impurities (or chromatographic fractions) is also partly due to these acid components. Under polymerization conditions, the impurities can undergo a number of reactions (e.g., condensation) which give rise to acid products which can lead to the decay of one or both components of the catalytic system.

The comparatively high inhibitive activity of cyclopentadecanone (Table II) indicates the decay of lactam anions. The chromatographic fraction containing cyclododecanone inhibits the polymerization much more than cyclopentadecanone (Table II). This difference can be explained by the fact that the latter fraction contains acid compounds or that the condensation of cyclododecanone is faster.

The highest content of acid compounds was detected in chromatographic fraction V (0.13 mole/kg); even a small quantity of this fraction completely prevented polymerization. Similarly, as in the preceding case, the cause of the inhibitive effect cannot be seen in acidity only ( $5.0 \text{ mg} \times 0.13 \text{ mole/kg} = 0.65 \text{ mmole/kg}$ , while the sodium salt content in the polymerization mixture is 15 mmole/kg). It is possible that in this fraction, too, some other compounds are present, the condensation reactions of which yield acid products consuming lactam anions.

Despite the fact that the inhibitive effect of some impurities is large, there is, with respect to their low amount, no substantial difference between the course of polymerization of the industrial and crystallized lactam. It could seem, therefore, that there is no need for further purification of industrial laurinolactam. However, the polymerization mixture obtained from industrial lactam is of brown color, while that obtained from crystallized lactam is almost colorless. Similar differences have been observed with the resulting polymers; it can therefore be expected that the degradation behavior of the polymers will also depend on the purity of the monomers.

### Effect of Impurities on Molecular Weight

The presence of impurities affects the intrinsic viscosity of polymers much less than they affect the rate of polymerization (Table II). The addition of a small amount of impurities to pure laurinolactam causes a change in the intrinsic viscosity by only 1–2%, while the position and height of the temperature maximum are much more affected (Figs. 5 and 6). The molecular weight remained unaffected even if a fraction of unsaturated lactams was added, in which case branching or crosslinking could be expected.



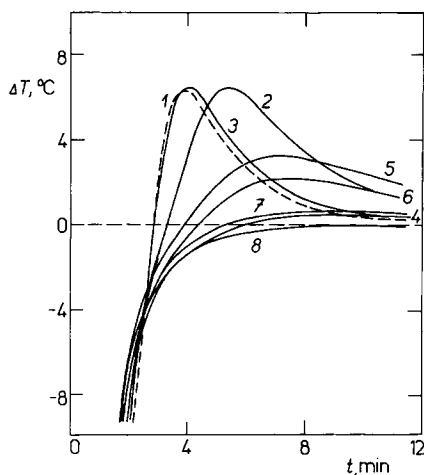


Fig. 5. Effect of impurities on polymerization at 200°C in the presence of 0.3% mole sodium caprolactam and 0.3% mole of N,2-diethyl-3-oxohexanamide. Polymerization without any addition (1); with impurities A, 5 mg/g (2); with 1.0 mg/g (3); with 12.5 mg/g (4); with 6.3 mg/g of fraction II (5); with 10.0 mg/g of fraction III (6); with 9.7 mg/g of fraction II (7); with 5.0 mg/g of fraction III (8).

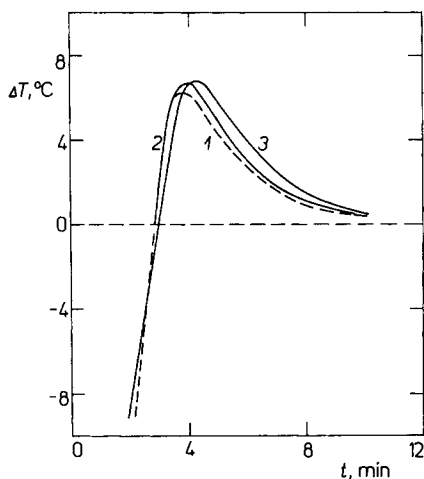


Fig. 6. Polymerization at 200°C in the presence of 0.3% mole sodium caprolactam and 0.3% mole N,2-diethyl-3-oxohexanamide with laurinolactam of different purity: (1) crystallized three times; (2) crystallized once; (3) industrial.

If N, 2-disubstituted 3-oxoamide was used as the activator, all polymers prepared at 200°C were quite soluble. On the other hand, if the polymerization was activated with N-benzoyllaurinolactam, the intrinsic viscosity of the resulting polymer was twice as high (Table II). Hence, the type of catalytic system affects the molecular weight much more than the impurities.

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