Depolymerization of Poly-ϵ-caprolactam Catalyzed by Sodium Hydroxide

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Synopsis

Depolymerization of poly-ϵ-caprolactam chips was carried out at low pressures (3–15 mm Hg) and elevated temperature (225°–270°C) in the presence of sodium hydroxide as catalyst. The effects of variation of amount of sodium hydroxide, time, temperature, and pressure on ϵ-caprolactam yield were studied. With increase in alkali content the yield increases linearly, reaching a maximum at 1% (w/w) NaOH and then falls. The yield increases with time of depolymerization up to 4½ hr and then becomes practically constant. Between 240° and 250°C there is a sudden increase in depolymerization rate. Further increase in temperature has very little effect. Decrease in pressure from 15 to 3 mm Hg shows a nine-fold increase in yield. The optimum conditions for the depolymerization were a temperature of 250°C, a pressure of 3 mm Hg, and a time 4½ hr in the presence of 1% NaOH (w/w), which gave a 90.5% yield of ϵ-caprolactam. Physical properties, IR spectra, and behavior toward polymerization of the recovered monomer indicated the presence of some impurities.

INTRODUCTION

Poly(ϵ-caprolactam) has been found to undergo depolymerization under suitable conditions in the presence of catalysts to yield the monomer ϵ-caprolactam. In industry, orthophosphoric acid is normally used as catalyst, though a relatively large number of acids have been found to be effective as catalyst.[1–5] Although the depolymerization can also be carried out in presence of basic catalysts,[6–8] very little attention has been paid so far to this type of depolymerization. In the present study, depolymerization was carried out in presence of solid sodium hydroxide as catalyst, under low pressure and elevated temperature.

In the acid-catalyzed depolymerization, ϵ-caprolactam is obtained in the form of an aqueous solution, which must be made alkaline before the solution can be distilled for recovery of the monomer. In the present method, the caprolactam will be obtained directly as solid. Thus no postdepolymerization operation such as distillation will be necessary. Also, the bulk handling will be reduced considerably. These advantages might lead to savings in operating cost.

EXPERIMENTAL

Materials

Poly-ϵ-caprolactam chips as supplied by J. K. Synthetics Ltd., Kota, India, having a viscosity-average molecular weight of 16,000 were used for depolymerization.

Depolymerization Procedure

A known amount of polymer chips (with an equilibrium moisture content of 4%) and sodium hydroxide were heated in a silicone oil bath at desired temper-

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ature in a 100-ml round-bottom flask attached through an air condenser to another flask with suitable vacuum application accessories. The vapors were immediately removed from the reaction flask under vacuum and solidified in the air condenser and the flask. After a definite time interval, the solidified mass was collected. The remaining mass in the reaction flask was refluxed with water for 2 hr to extract any amount of ϵ-caprolactam left undistilled.

The ϵ-caprolactam yield was determined by the Kjeldahl method for nitrogen estimation, both in the sublimate as well as in the water extract. Gas-chromatographic analyses of the recovered as well as of a pure sample were carried out using the procedure of Friz et al.[9] The column length used, however, was 12 ft instead of 2.8 ft (80 cm). This was done to ensure better resolution of possible impurities present in the samples. The results indicated no difference between the samples, and hence it was concluded that ϵ-caprolactam was the only nitrogenous material in the recovered mass.

Analysis

The molecular weight of ϵ-caprolactam was determined by the freezing point depression method.

Both pure ϵ-caprolactam (as supplied by BDH) and recovered ϵ-caprolactam were polymerized in the usual way under the following conditions: water content 1% (w/w), temperature 270°C, time 24 hr, and pressure 3 mm Hg.

The molecular weights of the polymers were determined by the end-group method.[10]

RESULTS AND DISCUSSION

Dependence of ϵ-Caprolactam Yield on Sodium Hydroxide Concentration

Depolymerization of poly-ϵ-caprolactam was carried out for 4½ hr at 250°C under 3 mm Hg pressure. The amount of sodium hydroxide was varied 30-fold ranging from 0.5% to 15% (w/w). An experiment without addition of sodium hydroxide was also carried out under the same conditions. A plot of sodium hydroxide concentration versus % caprolactam yield is presented in Figure 1.

In the absence of sodium hydroxide, the yield was low, only 4.8%. With increase in alkali concentration, the yield linearly increased up to 1% (w/w) NaOH and then fell.

The depolymerization of poly-ϵ-caprolactam is an equilibrium reaction which may be represented as follows:

$$H\text{+}NH(CH_2)_5CO\text{+}_n OH \rightleftharpoons n\underbrace{(CH_2)_5\text{-}NH\text{-}CO} + H_2O$$

The equilibrium concentrations of the monomer and polymer are dependent upon the temperature and the amount of catalyst present.[11] The linear increase in yield with increase in NaOH up to 1% shows the increased effectiveness of the catalyst in this range and also indicates that in this range optimum catalyst concentration is not reached. The subsequent decrease in yield from 90.5% with 1% NaOH to 75% with 15% NaOH shows that the amount of catalyst present is more than that required for equilibrium.

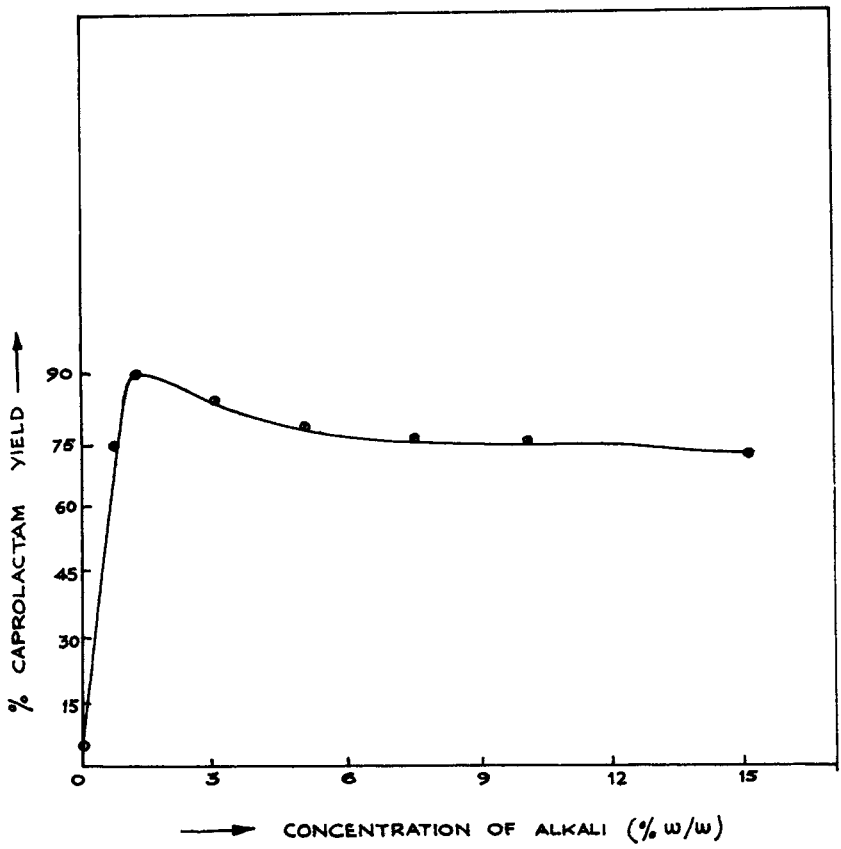

Fig. 1. Effect of sodium hydroxide concentration on ϵ-caprolactam yield: temp. 250°C, pressure 3 mm Hg, time 4½ hr.

The poly-ϵ-caprolactam used for depolymerization in the present study had an equilibrium moisture content of 4%. As hydrolysis of the amide bond is one of the mechanisms active during the degradation of polycaprolactam,[12,13] the amount of water present is highly effective as hydrolytic agent in the presence of NaOH at high temperature and low pressure.

The amount of volatile products remains essentially the same throughout (3–4%), indicating that excess NaOH does not lead to further degradation of ϵ-caprolactam.

Sumato and Inoue[8] have reported that ϵ-caprolactam can be obtained in nearly 100% yield using sodium hydroxide as catalyst at 95 mm Hg and 300°C and 130 mm Hg and 320°C. However, experiments done by the present authors at 300°C at several pressures between 50 and 100 mm Hg resulted in a very low yield of ϵ-caprolactam (less than 5%) and production of gaseous products. A charred, tacky residue was left in the reaction flask. This is expected because at 300°C, poly-ϵ-caprolactam depolymerizes by thermal decomposition only.[3,4] The chance of decomposition of ϵ-caprolactam itself also will increase with increase in temperature. A lower temperature and lower pressure, then, should give higher ϵ-caprolactam yield, which has been found in the present study.

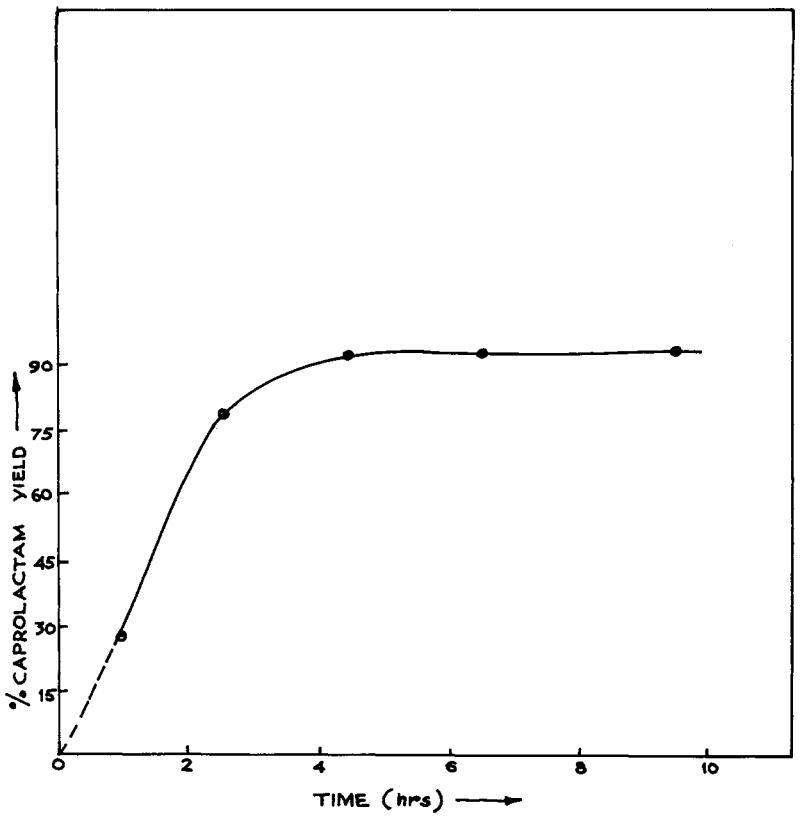

Fig. 2. Effect of depolymerization time on ϵ-caprolactam yield: NaOH 1% (w/w), temp. 250°C, pressure 3 mm Hg.

Dependence of ϵ-Caprolactam Yield on Time of Depolymerization

Poly-ϵ-caprolactam was depolymerized at 250°C with 1% (w/w) NaOH under 3 mm Hg pressure. The time was varied from 1 hr to 9½ hr. A plot showing percentage yield of ϵ-caprolactam versus time is presented in Figure 2.

The percentage yield increased at first linearly with time and reached 90.5% in 4½ hr. Increasing the time beyond that period up to 9½ hr only led to a marginal increase in the yield (92%). This shows that 4½ hr is sufficient for economic recovery of ϵ-caprolactam; beyond that, equilibrium is practically approached so that only marginal increase in yield takes place.

Dependence of ϵ-Caprolactam Yield on Depolymerization Temperature

Polyϵ-caprolactam was depolymerized for 4½ hr with 1% (w/w) NaOH under 3 mm Hg pressure. The temperature was varied from 225° to 270°C. Figure 3 presents a plot of percentage yield of ϵ-caprolactam versus temperature.

With increase in temperature from 225°C onward, there was a gradual increase in ϵ-caprolactam yield up to 240°C. Between 240° and 250°C, the increase in percentage yield is about three-fold (from 29.9% at 240°C to 90.5% at 250°C). Increasing the temperature above 250°C and up to 270°C does not lead to any

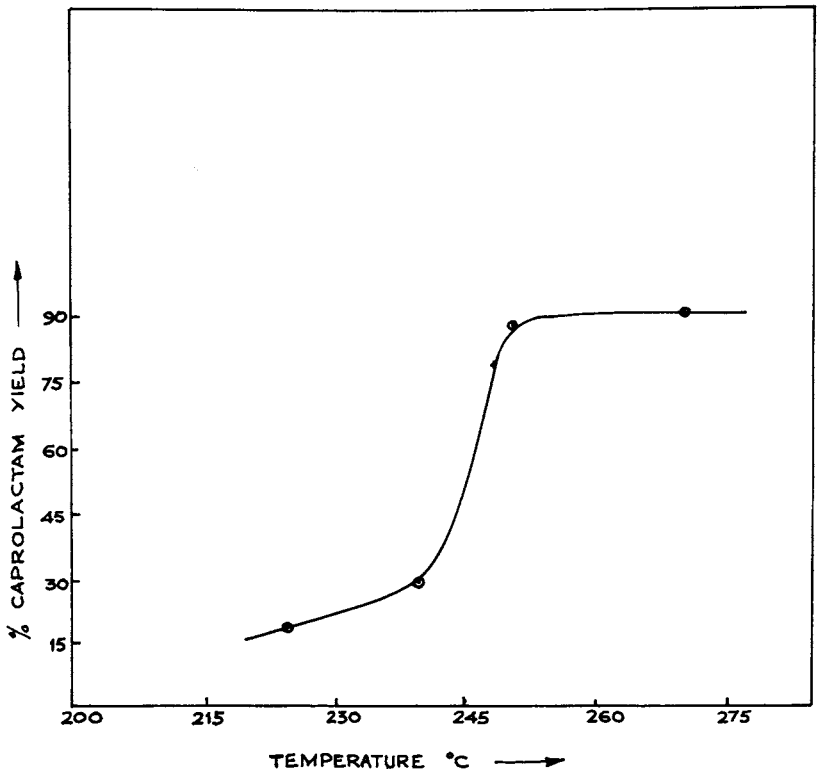

Fig. 3. Effect of temperature on ϵ-caprolactam yield: NaOH 1% (w/w), pressure 3 mm Hg, time 4½ hr.

appreciable increase in yield. The temperature range of 240°–250°C is thus critical, and 250°C may be considered as the optimum temperature.

Dependence of ϵ-Caprolactam Yield on Pressure

Depolymerization was carried out for 4½ hr with 1% (w/w) NaOH at 250°C. The pressure was varied fivefold, viz., from 3 to 15 mm Hg. Percentage yield versus pressure is plotted in Figure 4.

The decrease in pressure from 15 mm Hg to 3 mm Hg showed a ninefold increase in percentage yield of ϵ-caprolactam. An experiment conducted at atmospheric pressure under identical conditions showed that hardly any depolymerization was taking place. At 7.5 mm Hg, the yield is only about 16%. However, at 3 mm Hg, the yield is 90.5%, showing that below 7.5 mm Hg the yield increases enormously. This is due to quick removal of the ϵ-caprolactam produced from the reaction mass so that the poly(ϵ-caprolactam)–ϵ-caprolactam equilibrium is shifted more toward the ϵ-caprolactam side.

Characteristics of Recovered Caprolactam

Table I shows various properties of recovered ϵ-caprolactam as compared to pure ϵ-caprolactam. There was no difference in melting point and boiling point

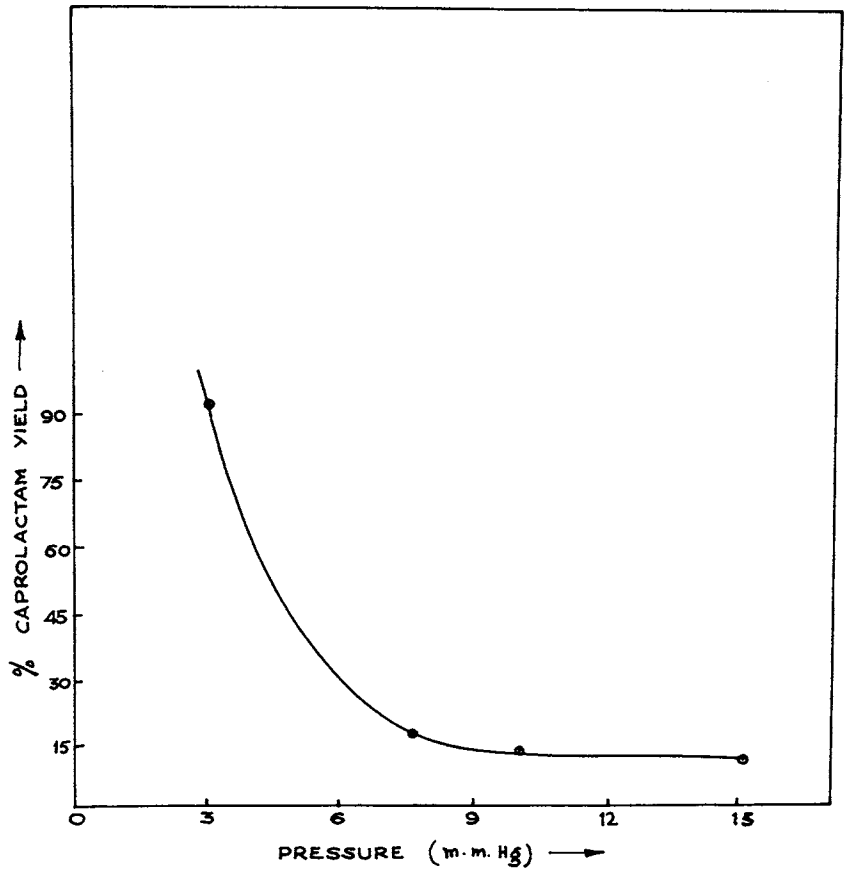

Fig. 4. Effect of pressure on ϵ-caprolactam yield: NaOH 1% (w/w), temp. 250°C, time 4½ hr.

between recovered ϵ-caprolactam and pure ϵ-caprolactam. However, there was a small difference in the cryoscopic molecular weight between the recovered ϵ-caprolactam and the pure one. The permanganate number was also higher for the recovered sample than for pure sample. The infrared spectra of pure ϵ-caprolactam, recovered ϵ-caprolactam, once vacuum-distilled recovered sample, and twice vacuum-distilled recovered monomer were strikingly similar, except for a strong band at 3250 cm^{-1} in case of the three latter samples, which may be assigned to polymeric association.

The behavior of the recovered ϵ-caprolactam toward polymerization was more

TABLE I
Physical Properties of Recovered and Pure ϵ-Caprolactam

Property	Recovered	Pure
Color	white	white
Molecular weight	112.8	113.2
Permanganate number	4.5	3.5
Melting point, °C	69	69
Boiling point/10 mm Hg, °C	135	135
Moisture, %	0.2	0.2

or less similar to that of a pure ϵ-caprolactam sample. However, the number-average molecular weight of the polymer as obtained by polymerization of recovered ϵ-caprolactam was 6600, whereas that obtained from pure ϵ-caprolactam was 8800.

The IR spectrum of both poly-ϵ-caprolactams were strikingly similar.

The lower molecular weight of the recovered sample indicates the presence of impurities in the sample. The higher permanganate number indicates presence of a greater amount of oxidizable impurities. Valk et al.[14] analyzed the products obtained by hydrolysis of depolymerized nylon 6 by thin-layer and gas chromatography analyses and found both basic (e.g., methylamine, ethylamine, etc.) as well as acidic (e.g., formic acid, adipic acid, acetic acid, etc.) and neutral (e.g., cyclopentanone, methyl succinate, etc.) impurities. However, gas-chromatographic analysis of the recovered sample in the present study did not indicate the presence of any of those impurities.

However, IR spectra indicate the presence of oligomers. Cyclic oligomers of caprolactam up to the nonamer are well known.[15–18] The cyclic oligomer concentration decreases very rapidly as the number of monomer units in the ring increases, thus, the oligomers which are found in poly(ϵ-caprolactam) are the dimer, trimer, and tetramer. The sublimation temperature at 2 mm Hg for monomer is 110°C, for dimer, 210–230°C, and for trimer, 260°C. A direct method for determination of monomer has been proposed by the sublimation technique.[19] In the present study, the method involved sublimation of ϵ-caprolactam at a pressure as low as 3 mm Hg. It seems that simple vacuum distillation of the product is not capable of yielding 100% pure ϵ-caprolactam, and that a trace amount of the oligomers accompanies it. As a result, the polymer obtained from such a sample was of lower molecular weight than that obtained from pure ϵ-caprolactam. These results also call for a more rigorous purification method of the recovered monomer than those which have been attempted so far.

CONCLUSIONS

The optimum conditions for the depolymerization of poly(ϵ-caprolactam) in the presence of sodium hydroxide as catalyst are a temperature of 250°C, pressure 3 mm Hg, time 4½ hr and sodium hydroxide 1% (w/w). Under these conditions, the yield of recovered ϵ-caprolactam is 90.5%.

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