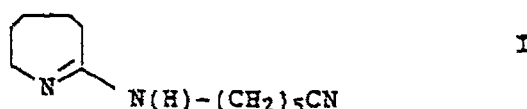


Preparation of polycaprolactam

- 5 The present invention relates to an improved process for preparing polycaprolactam by reacting 6-aminocapronitrile with water.

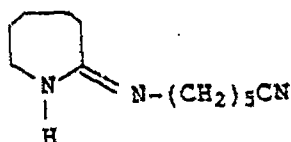
On heating or storage at room temperature, 6-aminocapronitrile forms a brown tetrahydroazepine derivative (THA derivative I) of the formula

10



THA derivative I shall also encompass its tautomeric form

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- EP-A-497,333 describes the direct polymerization of polycaprolactam starting from 6-aminocapronitrile. The problem to be solved in the process mentioned was the removal of tetrahydroazepine ("THA") before the polymerization step, since tetrahydroazepine leads to discoloration of the polymer obtained on polymerizing caprolactam in the presence of tetrahydroazepine.

- 25 EP-A-497,333 proposes solving the problem by means of a treatment with a basic compound such as an alkali metal hydroxide or an alkali metal alkoxide. Following the treatment, 6-aminocapronitrile can be conveniently separated from the reaction mixture by distillation, which is not possible without such a treatment.

- 30 EP-A 502,439 solves the problem of removing THA in the presence of 6-aminocapronitrile by treatment with sodium borohydride. Here too 6-aminocapronitrile can be readily separated from the reaction mixture by distillation after the treatment.

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Altogether and on the basis of experience with THA it might therefore be expected that THA derivative I would lead to discolored polycaprolactam in the direct
 5 conversion of 6-aminocapronitrile into polycaprolactam, unless separated off before the cyclization and before the polymerization step.

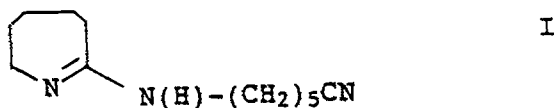
It might further be expected that THA derivative I would reduce the lifetime of the catalyst used in the polymerization, since it was known from US 5,162,567 that
 10 heating THA produces high boilers, ie. compounds or mixtures with a higher boiling point than 6-aminocapronitrile (accordingly making it easy to remove the 6-aminocapronitrile). High boilers, however, tend to form polymeric or oligomeric decomposition products which can form deposits on catalyst surfaces and so reduce not only the lifetime but also the activity of the catalysts.

15

It is an object of the present invention to provide a process for preparing polycaprolactam avoiding the above mentioned disadvantages.

We have found that this object is achieved by a process for preparing
 20 polycaprolactam by reacting 6-aminocapronitrile with water, which comprises using a starting mixture of 6-aminocapronitrile and the tetrahydroazepine derivative of the formula.

25



and conducting the reaction in liquid phase.

The present invention also provides the use of THA derivative I for preparing
 30 polycaprolactam.

The amount of water used is generally at least 0.01 mol, preferably from 0.1 to 20 mol, in particular from 1 to 5 mol, per mole of THA derivative I.

Advantageously THA derivative I is used in the form of a from 1 to 50% strength by weight, in particular from 5 to 50% strength by weight, particularly preferably
5 from 5 to 30% strength by weight, solution in water (in which case the solvent is then also the reactant) or in water-solvent mixtures. Examples of suitable solvents are alkanols such as methanol, ethanol, n- and i-propanol, n-, i- and t-butanol and polyols such as diethylene glycol and tetraethylene glycol, hydrocarbons such as petroleum ether, benzene, toluene, xylene, lactams such as pyrrolidone or
10 caprolactam or alkyl-substituted lactams such as N-methylpyrrolidone, N-methylcaprolactam or N-ethylcaprolactam and also carboxylic esters, preferably of carboxylic acids having from 1 to 8 carbon atoms. Ammonia too can be present in the reaction. It is of course also possible to use mixtures of organic solvents. Mixtures of water and alkanols in a water:alkanol weight ratio of 1-75:25-99,
15 preferably 1-50:50-99, have been determined to be particularly advantageous in some cases.

The THA derivative I content in the 6-aminocapronitrile of the starting mixture can be within the range from 0.01 to 95% by weight, in particular from 0.1 to 50% by
20 weight, particularly preferably from 0.5 to 20% by weight.

The starting mixture customarily has, depending on the level of THA derivative I, a UV number (sum of all absorbances of a 10% by weight solution in ethanol at wavelengths from 280 to 400 nm, based on a pathlength of 5 cm) within the range
25 from 5 to 40,000.

The starting mixture is obtainable by heating 6-aminocapronitrile with or without solvent. From experience to date, the temperature can be within the range from 20 to 280°C, in particular within the range from 50 to 250°C, particularly preferably
30 within the range from 100 to 230°C. The reaction times are customarily within the range from 10 minutes to 20 hours. As expected, shorter reaction times are possible at higher temperatures. The reaction can be carried out at pressures within the range from 100 kPa to 25 MPa, preferably from 500 kPa to 20 MPa. It can further

be advantageous to carry out the reaction in the presence of acidic homogeneous or heterogeneous catalysts such as mineral acids, carboxylic acids, sulfonic acids,
5 titanium dioxide, aluminum oxide, acid ion exchangers or Lewis acids.

If desired, pure THA derivative I can be obtained for example by distillation of unconverted 6-aminocapronitrile, solvents and any by-products.

10 The abovementioned starting mixture as aqueous solution and THA derivative I alone can be directly converted into polycaprolactam by heating by known methods, for example described in EP-A-150,295.

The advantage of the process of the present invention is that it provides a convenient
15 way of processing THA-derivative-I-containing reaction mixtures with 6-aminocapronitrile into polycaprolactam. The products and product mixtures thus obtained are free of troublesome THA derivative I. Thus there is no need for further process steps in the use of additional agents, compared with the removal of THA from corresponding reaction mixtures.

20

Example

400 g of 6-aminocapronitrile (ACN) were heated to 200°C for 8 h. Distillation yielded as second fraction at 0.1 mbar and 140°C 40 g of THA derivative I (yield
25 10%) as a pure compound. The characterization was carried out by means of NMR spectroscopy:

¹H-NMR (250 MHz, DMSO-d₆, TMS, ppm):

4.2 (s, broad, 1 H), 3.2 (m, 2 H), 2.9 (t, 2H), 2.45 (t, 2H),
30 2.25 (m, 2H), 1.7 - 1.1 (m, 12 H).

¹³C-NMR (62.9 MHz, DMSO-d₆, TMS, ppm):

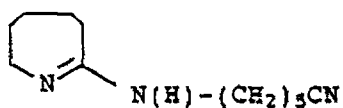
163.3 s, 120.6 s, 47.0 t, 41.6 t, 32.9 t, 30.6 t,
29.7 t, 28.4 t, 26.0 t, 25.6 t, 24.8 t, 16.2 t.



We claim:

- 5 1. The use of tetrahydroazepine derivatives (I) for preparing polycaprolactam.
2. A process for preparing polycaprolactam by heating an aqueous solution of 6-aminocapronitrile, which comprises including THA derivative (I)

10



in the aqueous solution.