Poly(hexamethylene adipamide) by Melt Polymerization [Nylon 6,6]

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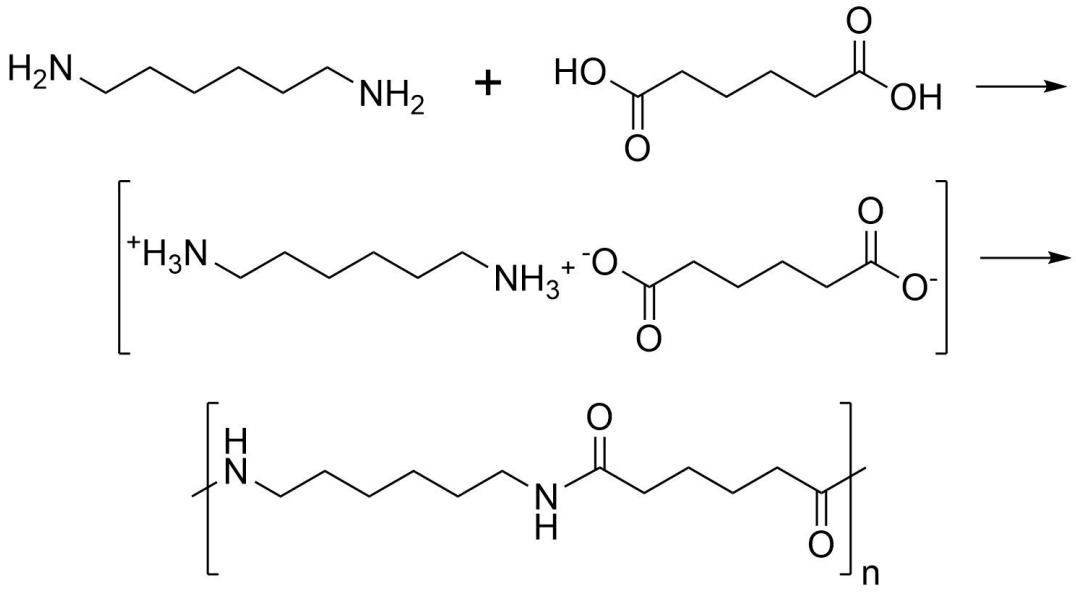

1. Procedure

A. Hexamethylenediamine-Adipic Acid Salt

In a 500 ml Erlenmeyer flask adipic acid (29.2 g, 0.2 mol; Note 1) is dissolved in 250 ml of warm ethanol, and the solution is cooled to room temperature. A solution of hexamethylenediamine (23.43 g, 0.202 mol; Notes 1 and 2) in 50 ml of ethanol is added to the adipic acid solution with gentle stirring (Note 3). Immediate precipitation of the salt takes place. The pH of the salt is adjusted to 7.6 (Note 4). The solvent is evaporated, and the salt is air-dried to constant weight. A quantitative yield of white, crystalline salt is obtained, mp 198-200°C. The pH of the dry salt (1% solution in water) is 7.6 (Note 4).

B. Poly(hexamethylenedipamide)

A glass polymer tube (Note 5) is charged with 32.0 g of hexamethylenediamine-adipic acid salt (Note 6). A constriction is made in the upper half of the neck of the tube with a glass-blowing torch. The tube is connected to a three-way stopcock; the other two inlets are connected to a vacuum pump and a source of low pressure nitrogen (about 1 atm), respectively. The polymer tube is placed on a 30° incline to the horizontal and purged of air by alternately evacuating and filling the tube with nitrogen (4-5 cycles). The tube is then sealed at the constriction with a torch while under vacuum (Note 7). The sealed polymer tube is clamped just below the neck in a vapor bath (Note 8). The polymer tube is heated in a vapor bath (naphthalene) at 218°C for 2 h (Note 9). *Caution! See Note 10.* When the heating cycle is completed, the polymer tube is allowed to cool to room temperature. The tube is opened about 1 in from the tip after scoring with a file. The rough edges are fire-polished.

A 60° bend is put in the neck of the polymer tube. The tube is clamped in an upright position in a vapor bath. The open end is connected to a trap by pressure tubing (Note 11). The trap is

connected with a three-way stopcock to a vacuum pump and a 1 atm source of nitrogen. The polymer tube is heated under nitrogen in the vapor bath (dimethyl phthalate) at 283°C for 2 h (Note 12). The polymer is then cooled to room temperature under nitrogen.

The polymer is obtained by wrapping the glass tube in a towel, and breaking it with a hammer (Note 13). The yield is quantitative except for mechanical losses.

The tough, white, opaque polymer has a crystalline melt temperature of 265°C. The inherent viscosity (η_{inh}), determined at 25°C in 0.5% solution in *m*-cresol is 1.0-1.4 dl/g and the number average molecular weight ($\bar{M}_n$, Note 14) is 18,700-20,000 (Note 15). End-group analysis gives the following: carboxyl ends, 40-51; amine ends, 56-61 (Note 16). The polymer is soluble in formic acid. Fibers and films may be obtained by melt methods or from formic acid solution.

2. Notes

1. All ingredients must be of the highest purity; adipic acid, mp 152°C, N.E. 72.1 ± 0.2; hexamethylenediamine, mp 41-42°C, bp 98-100°C (20 torr), N.E. 58.1 ± 0.2.
2. A small excess (1%) of diamine is added to ensure that the salt is rich in diamine. This is desirable because the diamine is the most volatile component.
3. Addition of the diamine solution is made quantitative by repeatedly rinsing the container holding the diamine with ethanol. About 100 ml of ethanol is used for this purpose.
4. The pH of the salt is determined on a 1% solution of the salt in water using a pH meter. This is accomplished by withdrawing from 1-2 g of wet salt from the slurry and dissolving it in 100 ml of distilled water and then determining the pH. A pH of 7.6 ± 0.2 is acceptable, although an imbalance on the basic side is more desirable. (See Note 2). Salt imbalance may be corrected by the addition of a small amount of the indicated component to the slurry and stirring well. The pH is then redetermined. A salt with a low pH gives a polymer containing a high carboxyl-end content; alternatively, a salt with a high pH produces a polymer with high amine-end content.
5. Heavy-walled polymer tubes, purchased from Labglass, Inc., Vineland, NJ have the following dimensions: 12 in long body with 38 mm O.D.; 12 in long neck with 13 mm O.D.
6. The salt is added to the polymer tube through a powder funnel connected to the neck of the tube by a short length of rubber tubing.
7. A thick, well-annealed heavy seal is necessary to withstand pressures that develop during heating.
8. The vapor bath consists of a 50 x 400 mm test tube about one-quarter filled with a suitable liquid. The upper walls of the test tube act as an air condenser to prevent loss of vapors. The vapor bath is heated with a mantle or other electrical heating device. For safety, considerations a steel tube vapor bath of these dimensions is recommended and heating should be conducted in a hood behind a shield.
9. The polymer tube is adjusted so that the bottom of the tube is not immersed in the boiling liquid, and so that the vapor rises to about 1 in above the solid in the polymer tube. The top of the vapor bath may be wrapped with aluminum foil to prevent vapors from escaping.
10. *Caution! This operation is extremely hazardous because there is a possibility that the sealed tube may shatter when heated because of the pressures that develop.* This may be caused by a poor seal, defects in the glass, or overheating. *The vapor bath containing the sealed tube must by shielded from all sides but left open at the top. It is recommended that this phase of the procedure by performed in a hood. The hand and arm used to manipulate the tube should be protected with leather, asbestos, or equivalent protective gloves.*
11. The trap consists of a 50 ml round-bottomed flask with an adaptor. A small vacuum trap suffices, however.
12. Higher molecular weight polymer can be obtained by applying vacuum for the last 15 min of the heating cycle.

13. The polymer pulls away from the glass on cooling.
14. The number average molecular weight is calculated from the equation

$$\overline{M_n} = \frac{2 \times 10^6}{\text{amine ends} + \text{carboxyl ends}}$$

15. Lower molecular weight polymer can be obtained by the addition of acetic acid to the salt during sealing. For example, 1 mol-% of acetic acid gives polymer having $\overline{M}_n$ 12,000.
16. Amine and carboxyl ends are reported as ends per 10^6 g of polymer as determined by pH and conductometric titrations, respectively.[3,4]

3. Methods of Preparation

Poly(hexamethylene adipamide) has also been prepared from hexamethylenediamine and adipoyl chloride by interfacial polymerization[5] and low-temperature solution polycondensation.[6]

4. References

1. *Carothers Research Laboratory, Textile Fibers Department, E.I. DuPont de Nemours and Co., Wilmington, DE 19898.*
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