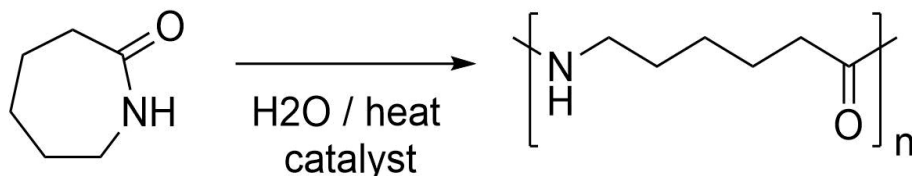# *Poly-ε-Caprolactam*

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1. Procedure

ε-Caprolactam (50 g, Note 1) and 2.0 g of a 50 wt % aqueous solution of catalyst (Note 2) are placed in a 38 x 300 mm Pyrex® test tube fitted with 8 mm Pyrex® inlet and exit tubes. The tube is swept with nitrogen for 5 min before adjusting the rate to 350 cc/min (Note 3). The tube is immersed to a depth of 9 in in a vapor bath at 280-285°C (Note 4). After 4 h (Note 5) the test tube is removed from the bath and allowed to cool to room temperature under nitrogen. The test tube is then broken away from the polymer by wrapping in a towel and gently breaking the glass with a hammer. The polymer plug can be cut to the desired particle size (Note 6). After extraction, the polymer has a crystalline melting point of 227° and a density at 23°C of 1.13 g/ml (Note 7).

2. Notes

1. Caprolactam is commercially available in pure form as a white crystalline substance with a melting point of 68-69 °C when dry. The easiest ways to ascertain adequate lactam purity is to carry out the polymerization and note whether a high molecular weight polymer of good color is obtained.
2. Amine salts are effective initiators leading to a polymer with a Flory molecular weight distribution after extraction. Because this polymerization is carried out at an elevated temperature in an atmosphere constantly swept with fresh nitrogen, it is important to use high-boiling components. It is also important to use difunctional components to avoid introduction of non-reactive ends that limit the molecular weight. The product is normally a copolymer comprising ca 98 wt-% polycaprolactam and 2 wt-% initiator residues, unless the catalyst chosen is ε-aminocaproic acid, which can be obtained by hydrolysis of the lactam.[3] The 50 wt-% solution is convenient for preparation of the initiator. The amine and acid (stoichiometric equivalents or a 1% excess of amine if somewhat volatile) are dissolved or dispersed in water, and one solution is then slowly added to the other with stirring. The resulting solution can then be treated with Darco G-60 carbon black to remove impurities, and the filtrate can be used directly in the polymerization. Suitable amines are hexamethylene diamine, piperazine, 3,3′-(methylimino)bispropylamine, 3,3′-iminobispropylamine, and *m*-xylylene diamine. Representative acids are adipic and sebacic acids. Also suitable are amino acids which have little tendency to participate in ring-closure reactions such as ε-aminocaproic acid or 11-aminoundecanoic acid. Salts from these amines and acids should give equivalent products.
3. Within reasonable limits the nitrogen flow rate is not critical.
4. A suitable vapor bath is made from an 80 mm Pyrex® glass tube 13 in long, rounded at one end, and fitted with a side arm of 15 mm tubing located 4 in below the open end and bent at a 90° angle so it extends 4 in above the open end. This tube can be heated with a Glass-Col

400 ml beaker heating mantle. The tube should be wrapped with insulating material. A sheet of asbestos or other suitable material can be cut to sit on top of the bath with a hole just big enough to accommodate the test tube. Diphenylene oxide is placed in the bath so its liquid level is just below the top of the heating mantle and brought to reflux.

5. Sublimed monomer will accumulate in the exit tube but should not cause plugging; any accumulation is readily removed by wiping with a damp swab or pipe cleaner. A number average MW of about 11,000 is reached in 2 h and 16,000 in 4 h as determined for extracted polymer by end-group analysis using the method of Waltz and Taylor,[4] or as estimated from solution viscosity.[5] A convenient empirical relationship observed for extracted resin is

$$\overline{M}_n = 15,600 \times \eta_{inh}^{1.49}$$

where η_{inh} is the inherent viscosity at 25° of 0.5 g of resin in 100 ml of *n*-cresol (98%, freshly distilled). Longer reaction times result in only slightly higher molecular weight and cause significant variation in MW from the top to the bottom of the plug.

6. If a uniform particle size is not required, the plug can be fragmented for convenient handling by freezing in Dry Ice and compressing the cold plug in a hydraulic press or simply wrapping it in a towel and striking it with a hammer. Polycaprolactam in equilibrium at 280° contains over 10 wt-% of water-extractable monomer and cyclic oligomers.[6] Under the reaction conditions described here, some of the relatively volatile monomer is removed, but the higher cyclic oligomers are not. Essentially complete extraction of the polymer can be accomplished by boiling for 16 h in ten times its weight of water if the particles have dimensions not over one-sixteenth of an inch. Drying to a sufficiently low moisture content for melt pressing is achieved without discoloration or change in MW by heating overnight at 100° under nitrogen or reduced pressure.

7. The crystalline melting point can be determined microscopically on a Kofler hot state[7] or estimated by the simpler ASTM method,[8] but the criterion of melting in this method is less certain and the values less reliable. The density is readily measured in a gradient tube[9] made from solutions of carbon tetrachloride (C) and toluene (T): lower layer = 46.3/53.7 C/T (v/v); upper layer = 25.9/74.1 C/T (v/v).

3. Methods of Preparation

The procedure described here is extremely simple in that it avoids special equipment and sealed systems, and yields a polymer of normal Flory MW distribution. Hydrolytic polymerization under pressure and catalytic polymerization in evacuated sealed tubes using alkali or alkaline earth metal salts of ε-caprolactam as catalyst have been described.[10] The latter method yields a polymer whose molecular weight decreases on continued heating.[11] High viscosity polycaprolactam has been obtained with very short reaction times by using an alkali metal hydride as catalyst, but the subsequent decrease in viscosity with time, denoting a peculiar initial distribution of molecular weights, was again observed.[12] The imide-promoted anionic polymerization of caprolactam takes place at relatively low temperatures but yields products of uncertain molecular weight distribution.[13] The non-hydrolytic polymerization of caprolactam via acid catalysis has been carried out in sealed tubes, but the molecular weights achieved were below 5000.[14] A two-step process involving alkali catalysis in a nitrogen atmosphere followed by catalyzed redistribution in a sealed tube has been reported.[15] Elimination of the amine and acid end-groups to reduce the rate of depolymerization to monomer at melt temperatures can be accomplished by reaction with an isocyanate in N,N-dimethyl formamide.[16] Additional information on the synthesis, characterization and utility of a variety of nylons is now available.[17]

4. References

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