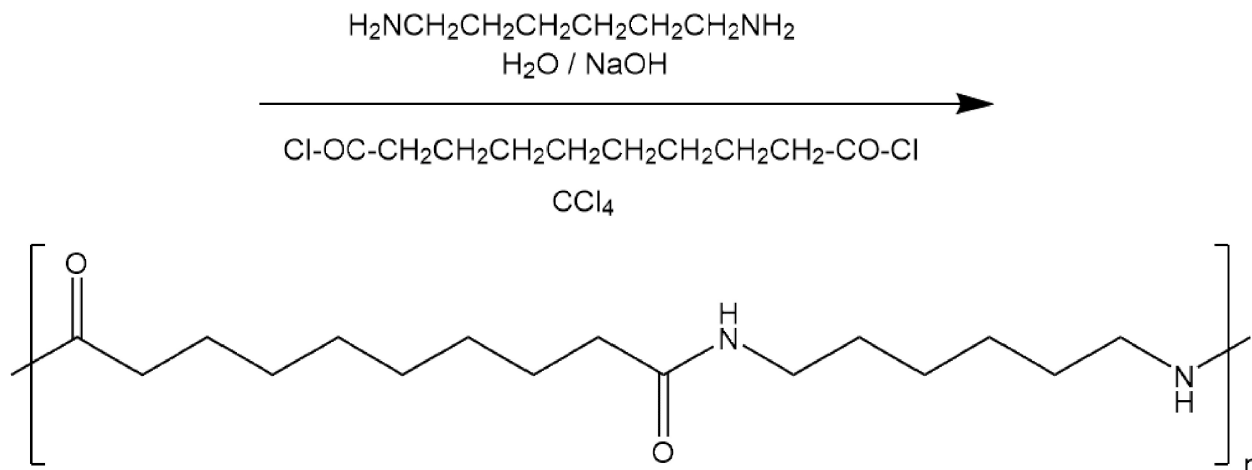


Poly(hexamethylenesebacamide) by Interfacial Polycondensation

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1. Procedure

In a 1 qt explosion-proof blender (Note 1) is placed a solution of hexamethylenediamine (2.32 g, 0.02 mol) and sodium hydroxide (1.60 g, 0.04 mol, Note 2) in 330 ml of water. The blender is turned to high speed with a rheostat, and there is added (Note 3) over a period of about 15 s a solution of sebacoyl chloride (4.78 g, 0.02 mol, Note 4) in 250 ml of tetrachloroethylene (Note 5).

After the mixture has been stirred for 2 min (Note 6), the polymer is collected on a fritted glass filter (Note 7) and washed with water until free of alkali and salt (Note 8). The granular polymer is dried in air at a temperature below 100° or in a vacuum oven; yd 4.8 g (85%).

2. Characterization

Solubility. The polymer is insensitive to most common low-boiling organic solvents but is soluble in formic acid, concentrated sulfuric acid, trifluoroacetic acid, phenol, *m*-cresol, and hot benzyl alcohol. Viscous solutions are formed at 5% to 50% solids.

Dilute Solution Viscosity. The inherent viscosity (η_{inh}) is 1.0-1.8 dl/g (Note 9) determined in *m*-cresol at 30° and 0.5 g of polymer per 100 ml of solution. The intrinsic viscosity and weight average molecular weight can be approximated from the equations:

$$\eta_{inh} = [\eta] + 0.42[\eta]^2c \quad \text{and} \quad \overline{M}_n = 10,750[\eta]^{1.05}$$

which were derived for polymer formed by melt polymerization.

Melt Temperature. The polymer melt temperature (T_m) on a hot metal surface is 220° (Note 10). The crystalline T_m by loss of birefringence of an oriented film under a polarizing microscope is 215°.

Number Average Molecular Weight. \bar{M}_n determined for a polymer with $\eta_{inh} = 1.87$ dl/g by the osmotic method was $19,300 \pm 250$. The total end groups were 115 (88 mol of carboxyl and 27 mol of amine) per 10^6 g, which gives an \bar{M}_n of 17,400.

3. Notes

1. Vigorous stirring and high shearing action are needed to disperse the reactants rapidly and break down the tough film of polymer as it forms. Inefficient stirring will reduce the molecular weight and the yield of polymer. Detergents may be added to assist stirring, but they may interfere with the polymerization and the final polymer will not be stable to melting. Flammable solvents should not be used in an electrically-driven blender unless the motor is isolated from the fumes, or the housing is modified as suggested in ref. 12, p. 409.
2. Other strong inorganic bases may be used, although some adjustment in the ratio of the phase volumes may be necessary to obtain the highest polymers. Sodium carbonate is acceptable if 1 mol is used for each mol of hydrogen chloride. Excesses of inorganic base up to 10% can be used without detriment to the properties of the product.
3. A smooth addition without loss of product may be made by adding the solution through a powder funnel inserted in a hole made in the plastic cover of the blender. It is also helpful to place a foil of aluminum on top of the jar but under the cover.
4. Liquid acid chlorides are most easily measured out in graduated pipets or in calibrated syringes. The volume of sebacyl chloride to be used is 4.28 ml at 25°. Diamine and base may be prepared as a concentrated aqueous solution (0.2 g/ml) and dispensed from automatic burets equipped with stopcocks of Teflon® (Note 11) fluorocarbon resin. Intermediates of adequate purity may be obtained from reagent supply houses.^{3,4}
5. For best results the solvent should be distilled to free it of traces of water and other minor impurities. Various other water-immiscible solvents such as carbon tetrachloride, dichloromethane, xylene, and benzene may be used, but adjustments in the reactant ratios must be made to obtain the highest molecular weight polymers.^{4,5}
6. Stirring may be continued for a longer time, but for an unhindered aliphatic polyamide there is little change after 5 min. The narrowest molecular weight distribution is obtained by stopping the polymerization at about 2 min. Cessation of polymerization may be assured by adding 100 ml of 3% aqueous hydrochloric acid to the blender at 2 min and continuing the stirring for 1 min more.
7. Paper filters contaminate the product with cellulose fiber that degrades and discolors if the polyamide is later melted.
8. The washing may be hastened by the use of such organic solvents as acetone or alcohol, or mixtures of these with water. They help to remove the water-immiscible solvent. Stirring in the blender will also speed the washing. A final rinse with ethyl ether yields a fluffier form of dried product. Deionized water should be used in the washing if end groups are to be determined or the polymer is to be melted.
9. A lower viscosity indicates lower molecular weight. This may result from impure reactants or solvents, incorrect material balance, failure to stir rapidly, or degradation by careless after-treatment.
10. Absorbed moisture acts as plasticizer and lowers T_m .
11. Teflon® is a trademark of the DuPont Company.
12. The transfer of solvents, the polymerization and the recovery of polymer should be carried out in a well-ventilated hood. The waste solvents should be collected and disposed of suitably.

4. Methods of Preparation

High molecular weight, aliphatic polyamides were first made by melt polycondensation.⁶ This commercial process is a useful laboratory procedure, but longer times and special equipment are required.

The preparation of aliphatic polyamides by an unstirred interfacial polycondensation has been described as a lecture demonstration experiment.^{3,5} The unstirred system has also been used to study polymerization variables and mechanism.⁴ Variations in procedure that may be used or that may be necessary to favor other polyamides have been reported.^{7,8,9,10,11,12,13}

5. References

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