Poly[methylene bis(4-phenylene) sebacamide

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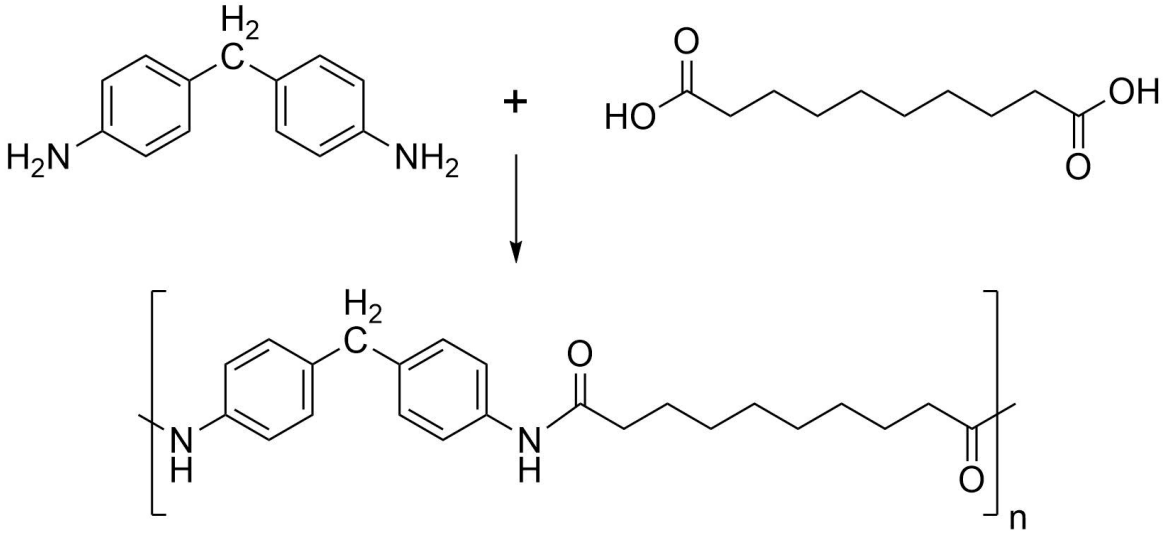

1. Procedure

A heavy-walled Pyrex test tube (Note 1) approximately 300 mm x 35-40 mm ID is fitted with Neoprene rubber stopper. Holes are bored through the stopper to accept a glass capillary (350 mm x 6 mm, 1/4-3/4 mm bore), a glass thermocouple well (350 mm x 6 mm OD), and a gas exit tube (6 mm OD). The capillary and thermocouple well are inserted through the stopper so they extend to within 1/4 in. of the bottom of the test tube. The gas exit tube is bent at a 135° angle, and one end of the tube is inserted just to the bottom of the stopper. A mixture of 9.91 g (0.0500 mol) of 4,4′-diaminodiphenylmethane (*Caution! The National Institute for Occupational Safety and Health has included this chemical in a list of 1500 substances shown to cause cancer in animals. A possible link between this compound and toxic hepatitis has also been cited.*) and 10.62 g (0.0525 mol) of sebacic acid is added to the test tube (Notes 2 and 3). The reactor is then assembled (Note 4) and connected to the manifold system as shown in Fig. 1 (Note 5). Valve A and stopcock C are closed, and valve B is opened slowly to evacuate the system. A check is made for leaks, particularly where the tubes are inserted through the stopper. When the apparatus is free from leaks, the system is alternately evacuated and purged with nitrogen in the following manner. Valve B is closed, and valve A is slowly opened (Note 6) to admit nitrogen. When atmospheric pressure is reached in the system, valve A is again closed and valve B is opened until a pressure of 5 torr or less, is attained. After the fourth evacuation, the system is returned to atmospheric pressure and stopcock C is opened. The nitrogen flow is adjusted (valve A) to give a gentle sweep through the reactor. A heating bath (preferably a heated, fluidized bed of sand) is mounted around the lower half of the test tube (Note 7).

The contents of the reactor are heated rapidly (40-50 min., Note 8) to 285°. The temperature of the polymer melt is held at 285° for 30 min. at atmospheric pressure. Stopcock C is then closed

and valve B is opened slowly, while allowing valve A to admit a very slow flow of nitrogen to sweep through the molten polymer. The pressure is reduced to 5-15 torr over a period of 25 min. (Note 9). The melt temperature (285°) and pressure (5-15 torr) are held constant for 15-30 min. to finish the polymerization while continuing to sweep nitrogen through the melt. Valve B is then closed, and by regulating valve A the system is slowly brought to atmospheric pressure. Stopcock C is opened, and the heating bath is removed. The polymer is allowed to cool to room temperature by removing the stopper and introducing a blanket of nitrogen directly into the mouth of the test tube (Note 10). The polymer is removed after cooling by wrapping the test tube with a heavy towel and breaking the glass tube.

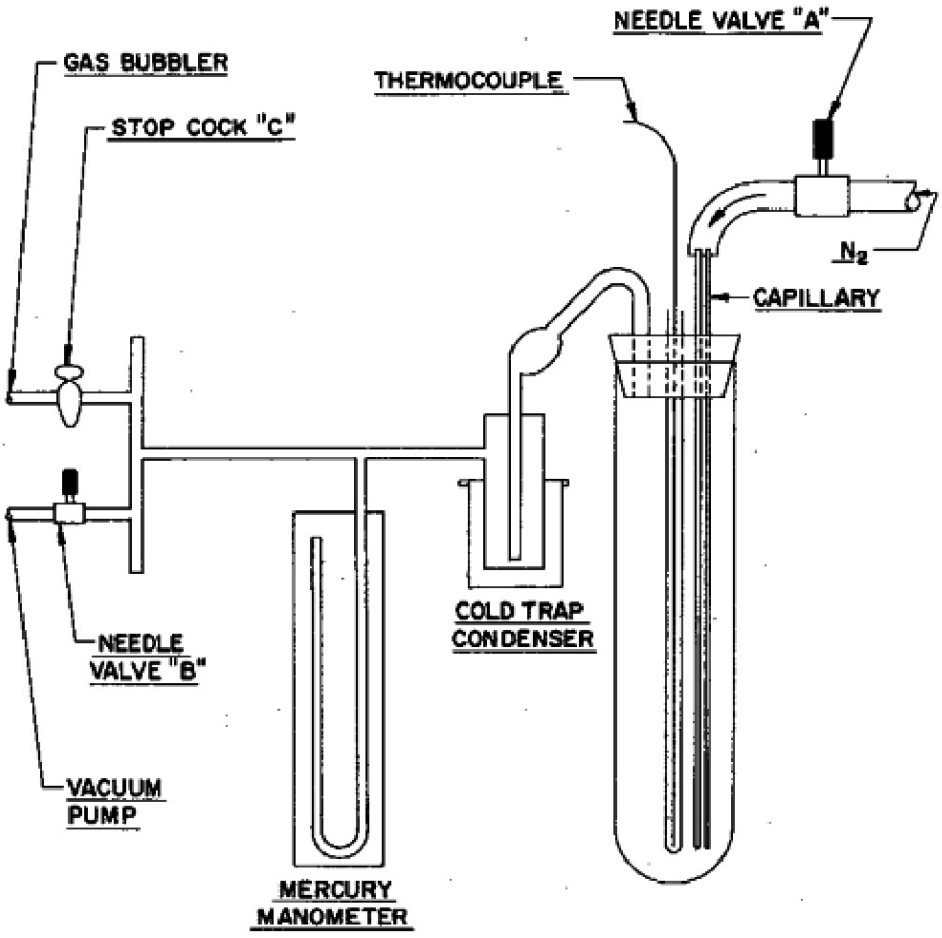

Figure 1. Polymerization apparatus for synthesis of poly[methylene bis(4-phenylene)sebacamide].

2. Characterization

The opaque, cream-colored polymer (Note 11) has an inherent viscosity of 0.70-0.90, determined at 30° on a 0.5% solution in *N,N*-dimethylacetamide containing 5% dissolved lithium chloride (Note 12).

Differential elemental analysis (Note 13) shows the polymer to have a crystalline melting point of 270°. In addition, polymer which has been rapidly quenched from the melt shows a crystallization exotherm at 140°.

Fibers and films may be obtained by melting the polymer in an inert atmosphere and spinning or extruding through a suitable apparatus.

3. Notes

1. This test tube should be fabricated, by a competent glass blower, from tubing with a minimum wall thickness of 2 mm.
2. 4,4′-Diaminodiphenylmethane was obtained from Allied Chemical Company. It was recrystallized twice from toluene (100 g/500 ml), decolorized with charcoal, and dried for 48 h. in a vacuum oven at 50° to remove the last traces of solvent. The capillary melting point was 93-94°.
3. Sebacic acid (reagent grade) was obtained from Matheson, Coleman, and Bell and used without further purification. A 5 mol % excess of sebacic acid served to inhibit gel formation during polymerization.
4. Care must be exercised in assembling the reactor to prevent plugging the capillary with the reactants. The tube for introducing nitrogen can also be just above the surface of the polymer. If this is done and the thermocouple well is raised from the melt at the end of the polymerization, it is not necessary to remove the stopper during cooling. The chance of oxygen contacting the polymer and causing color is reduced.
5. A Dry Ice-methanol bath was used to cool the cold trap. Care must be taken not to plug the condenser during the reaction. A safety shield mounted in the front of the reactor and bath is recommended.
6. Care should be taken during purging and evacuation to prevent reactants from being swept from the test tube.
7. It is generally desirable to secure a second thermocouple to the lower outside wall of the test tube (with a high-temperature glass tape) to prevent possible degradation from overheating.
8. The heating rate is rather critical. If the mixture is heated too slowly, the prepolymer will solidify ("phase out"). If the reaction mixture is heated too rapidly, excessive foaming will result. A crust of prepolymer frequently forms on the surface of the polymer melt because of cooling by the refluxing water of condensation. This crust will generally melt when the reaction temperature reaches 285°.
9. Care should be exercised during the pressure reduction to prevent excessive foaming of the melt.
10. On cooling, the polymer frequently pulls glass from the walls of the tube. Hence the test tube should be wrapped with a towel to prevent loss of product or injury from flying glass.
11. Color varies from white to cream to light yellow, depending on the quality of the 4,4′-diaminodiphenylmethane used and the content of oxygen in the polymerization system.
12. This value was determined with a Cannon-Fenske Series 100 viscometer.
13. A DuPont Model 900 Differential Thermal Analyzer was used. The heating rate was 20°/min., in nitrogen.

4. Methods of Preparation

In addition to this procedure for poly[methylene bis(4-phenylene)sebacamide],[3,4] the polymer may be prepared from dimethyl (or diethyl) sebacate and 4,4′-diaminodiphenylmethane, using a similar melt polycondensation scheme.[5,6]

The polymer may also be prepared by the Schotten-Baumann reaction, using sebacoyl chloride and 4,4′-diaminodiphenylmethane in a water-tetrahydrofuran system.[7]

5. References

1. *Monsanto Textiles Company, Pensacola, FL 35202.*
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