

Calcium Oxide as an Initiator for Acrylonitrile Polymerization

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1. Procedure

A 100 ml three-neck flask is equipped with a precision-ground stirrer (glass paddle) and a nitrogen inlet. The third opening is stoppered and used for introducing the reactants. To provide a constant positive nitrogen pressure, the inlet line is attached to the flask via a T-tube, the third end of which is attached to a vent trap containing an inert dry liquid hydrocarbon such as cyclohexane. The flask is flamed and purged with nitrogen, and 1 g of calcined, free-flowing, powdered calcium oxide is introduced (Note 1). The flask is then cooled. N,N-Dimethylformamide (DMF, Note 2, 30 ml) and acrylonitrile (Note 3, 10 ml) are introduced by pipet. The reaction is stirred under nitrogen overnight (16 h). As polymerization proceeds, the suspended particles of calcium oxide become coated with white to slightly yellow polymer. The suspension stays quite fluid and is milky in appearance.

To isolate the polymer, the contents of the flask are added to 100 ml of 1N HCl to give a copious, white, coherent precipitate. This mixture is then agitated in a blender for 5 min to free the polymer of calcium oxide. The polymer is collected by filtration and is retreated with an additional 100 ml of 1N HCl, agitated for 5 min in the blender, and collected. The filter cake is washed with water until the filtrate is neutral, and then with acetone. After drying in an oven at 80° for 1 h under reduced pressure (<100 mm), a yield of 2.5-6 g (31-75%) of polyacrylonitrile is obtained (Note 4).

2. Characterization

The inherent viscosity of the polyacrylonitrile varies from 1 to 2 or higher in DMF solution at 30° at a concentration of 0.5%. Concentrated solutions of polyacrylonitrile to be used for forming films may be prepared from a solution of 1-2 g of polymer in 8-9 ml of DMF. Ice-cold DMF is added to the finely divided polymer in a screw cap vial, which is then stoppered and warmed on the steam bath for several hours to effect solution. Film is cast from the viscous solution by use of a 10- or 20-mil doctor knife. After evaporation of the solvent, the brittle films (1-4 mils thick) may be cut into strips on a warm (90-100°) glass plate without fracturing, and oriented by drawing 6-10 times at 160° on a heated rod or bar. The film still contains residual DMF, most of which may be removed by soaking overnight in methanol. The authenticity of the sample may be checked by the infrared spectrum.³ The material cannot be melted but undergoes an exothermic condensation on heating.⁴

3. Notes

1. A reagent grade or technical grade calcium oxide (e.g., Mallinckrodt N.F. lumps) is suitable, but the latter is preferred. The material is ground to a fine powder with a mortar and pestle.

Directly before use, the oxide sample is heated strongly with a Fisher burner in a platinum crucible until a *free-flowing* dry powder is obtained. This takes 10-60 min. The contents of the hot crucible are added directly to the reaction flask.

2. The commercial material (200 ml) is refluxed at reduced pressure over 1-5% by weight of phosphoric anhydride for 30 min and then distilled, bp 63°/39 torr. A simple Vigreux column is adequate. The center fraction is stored under dry nitrogen and is used soon after distillation because the product can absorb water.
3. The commercial product (100 ml) is freed of inhibitor and traces of water by refluxing over (for about 30 min) and distilling from, 1-5% by weight of phosphoric anhydride through a short Vigreux column. The pure, constant-boiling center fraction is stored under dry nitrogen and is used promptly to avoid spontaneous polymerization.
4. Variations in yield and viscosity depend on the grade of calcium oxide used (see Note 1), the fineness of the particles, and the extent to which the oxide has been dried before using.

4. Methods of Preparation

Acrylonitrile polymerizes by free radical or anionic initiation in suspension or in solution. Detailed procedures for polymerization are given by Sorenson and Campbell.⁴ A number of types of initiators, including calcium oxide, are described in Table 1 of the article by Bohn, Schaeffgen, and Statton.⁵

5. References

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