Polyacrylonitrile from a Slurry Polymerization

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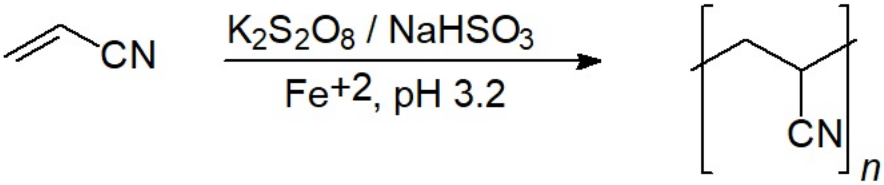

1. Procedure

Deaerated distilled water (0.4 l) and distilled acrylonitrile (50 ml, 40 g) are placed in a 1 l 3-neck flask equipped with a stirrer, a stopper, and a reflux condenser (Notes 1, 2 and 3). The flask is placed in a thermostat in the hood at 50 ± 1°, and a constant pressure of nitrogen equal to 1 in of water is applied to the top of the condenser. A solution of 20-25 ml of water, 4.0 ml of 0.1*N* sulfuric acid and 0.001 g of ferrous ammonium sulfate hexahydrate is added quickly through the stopper (Note 4). When the contents of the flask are at 50°, 25 ml of water containing 0.10 g of potassium persulfate and then 50 ml of water containing 0.50 g of sodium metabisulfite are added quickly to the rapidly stirring mixture. Within 1 min the appearance of opalescence indicates that the reaction has started. Stirring is continued at 50-200 rpm for 1 h, during which time a thick slurry develops. A 1% solution of sodium carbonate to reach pH 7-10 is added to stop the reaction (Note 5). The slurry is vacuum filtered and washed with 200 ml of water followed by 200 ml of acetone or ethanol. The polymer is crumbled into a drying tray and dried below 100°; yd 65-75%; intrinsic viscosity (in DMF) 1.5-1.7 dl/g (Note 6).

Copolymers may also be made by this procedure if there is not too great a deviation of the comonomer from acrylonitrile in solubility characteristics or copolymerization reactivity ratios (Note 7).

2. Notes

1. The water is deaerated by bubbling nitrogen through it for 2-3 min at a rate of at least 50 ml/min. Failure to deaerate may cause low conversions and erratic molecular weights.
2. Larger runs should be attempted only with great caution, because the heat of polymerization may exceed the cooling capacity of the thermostated bath, causing violent boiling of the acrylonitrile.
3. Distilled acrylonitrile is prepared by adding 1 ml of 85% phosphoric acid per liter of monomer and distilling rapidly through a simple Claisen head to remove inhibitors. It is not necessary to distill most commercial grades of acrylonitrile to remove inhibitors, although the resulting product have a slightly lower molecular weight which may be compensated for by using less persulfate.
4. Sulfuric acid must be added to obtain good rate and molecular weight control. The best range is pH 2.4-4.0 with best reproducibility at pH 2.8 ± 0.05. If the sulfuric acid is added after the bisulfite, molecular weight control will be erratic because of rapid bisulfite addition to acrylonitrile at pH 6 and above. The iron salt is a catalyst for persulfate decomposition and must be present above 0.2 ppm Fe^{2+} based on the total volume.

5. Adjustment to pH > 7 stops polymerization by allowing bisulfite addition to acrylonitrile and lowering the iron content. Alternatively, sequestering agents or phenolic inhibitors may be used.
6. Raising the molecular weight may be simply achieved by lowering the amount of persulfate or both persulfate and bisulfite used; a lower rate of polymerization will be observed. The maximum range of intrinsic viscosity is 0.05-20 dl/g.
7. A mixture of comonomers may be used including vinyl acetate, acrylamide, methyl vinyl ketone, and methyl acrylate. Others may be used by slight pH adjustment (e.g., vinylidene chloride at 30° or 2-vinyl pyridine with enough acid to reach pH 3.2).

3. References

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