Suspension Polymerization of Vinyl Chloride

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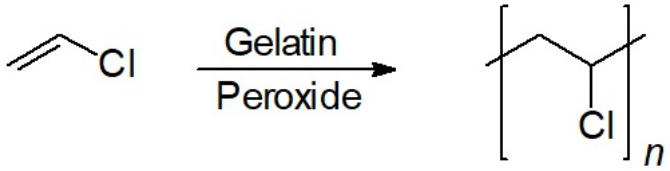

1. Procedure

Type A high bloom gelatin (0.3 g, Note 1) is slowly added to 300 ml of stirring distilled water in a 500 ml beaker. The mixture is heated to 70-80° to dissolve the gelatin. After cooling, 0.10 g of NH_4HCO_3 is added.

Into a 1 qt high pressure bottle (Note 2) are charged 0.25 g of lauryl peroxide and the prepared gelatin solution. *Caution! Peroxides are strong oxidants.* The bottle is stoppered and cooled in a deep freeze to freeze the gelatin-catalyst mixture (Note 3). To the frozen mixture is slowly added 100 g of vinyl chloride (*Caution!*) (Note 4). Vinyl chloride in excess of 100 g is allowed to evaporate, sweeping out the air in the bottle. The bottle is sealed with an aluminum foil lined cap, placed behind a safety shield and allowed to thaw (Note 5). After thawing, the bottle is agitated or tumbled end over end in a bottle polymerizer at 50° for 14-18 h (Note 6). The bottle is cooled and unpolymerized monomer carefully vented with a syringe needle inserted through the cap. The polymer is filtered on a Büchner funnel, washed with hot distilled water during filtration, and dried overnight at 40-50°; yd 85-95% of granular white polymer. The product has an intrinsic viscosity in the range 1.0-1.2 dl/g, measured in cyclohexanone at 25° (Note 7). The infrared spectrum and x-ray diffraction pattern of the polymer are similar to those reported.[3]

2. Notes

1. In place of the gelatin-ammonium bicarbonate combination, 0.5 g of Elvanol 50-42 may be used, with about equivalent results, except that a fine polymer powder is produced.
2. Duraglas bottles, available from the Owens-Illinois Glass Company, are able to withstand a pressure of 100-150 psi.
3. Bottle breakage during freezing of the contents can be minimized by tipping the bottle at a 45° angle during the freezing operation.
4. About a 10% excess of vinyl chloride is recommended to ensure good purging. The vinyl chloride may be distilled from shipping cylinders, condensed with a Dry Ice-acetone "cold finger" condenser, and collected in a flask cooled with Dry Ice. Rubber tubing should be avoided because it will lead to inhibition of the polymerization. Polyethylene or Teflon tubing is satisfactory.

Caution! Vinyl chloride boils at -14.6° and is highly flammable. All work should be conducted in a well-ventilated hood. Vinyl chloride is also a suspected carcinogen.[4]

5. *Caution! Placing a bottle with frozen contents in a warm bath can cause it to crack and explode. The bottle should be kept in a perforated metal cage or wrapped in wire mesh to contain glass fragments in the event that the bottle breaks.*
6. The purity of the vinyl chloride will affect the polymerization time which may be reduced by increasing the catalyst concentration, but with a concomitant reduction in molecular weight. Too slow or too rapid agitation may lead to agglomeration. The submitters' 1 qt bottle polymerizer rotates at 24 rpm. The checker's 1 pt bottle polymerizer rotates at 32 rpm.
7. The molecular weight of the polymer may be estimated from the expression $[\eta] = 2.4 \times 10^{-4} M_n^{0.77}$, where [η] is in deciliters per gram.[5]

3. References

1. *Diamond Shamrock Corp., Painesville, OH 44077; current address Rosen - Standard Oil Co., Cleveland, OH 44128.*
2. *Ethyl Corporation, Baton Rouge, LA 70821*
3. Natta, G.; Corradini, P. *J. Polym. Sci.* **1956**, *20*, 251; Krimm, S. *Fortschr. Hochpolymer.-Forsch.* **1960**, *2*, 51; Treiber, E.; Berndt, W.; Toplak, H. *Angew. Chem.* **1955**, *67*, 69.
4. *Regulation on Exposure to Vinyl Chloride*: Oct. 4, 1974; Federal Register, Vol. 39, p 35890 OSHA.
5. Danusso, F.; Moraglio, G.; Gazzera, S. *Chim. Ind. (Milan)* **1954**, *36*, 883.