Amorphous Polystyrene

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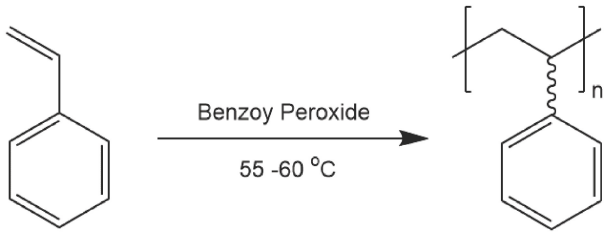

A. Bulk Polymerization with Peroxide Catalysis

1. Procedure

A glass polymerization tube (Note 1) is charged with 25.00 ml (22.68 g) of freshly distilled styrene (Note 2) and 0.50 g of benzoyl peroxide. *Caution! Benzoyl peroxide is a strong oxidant and can ignite or explode if not properly treated.*

The tube is connected to a three-way stopcock and the other two inlets of the stopcock are connected to a vacuum pump and a balloon containing nitrogen, respectively. The contents of the polymerization tube are then degassed and sealed under vacuum (Note 3).

The monomer is polymerized by heating the sealed tube at 55-60°C for 66 h (2.75 days).

At the end of the reaction period the plug of polymer is obtained by breaking the glass tube with a hammer (Note 4) and separating the broken glass from the plug.

The polymer is dissolved in 300 ml of benzene at room temperature with stirring, and the solution (Note 5) is then added dropwise to 3 l of methanol (Note 6) with vigorous stirring to precipitate the polymer. The polystyrene is collected by filtering through a sintered glass funnel (coarse porosity). The polymer is further purified by redissolving it in benzene and reprecipitating it by addition to methanol.

After drying overnight in a vacuum oven at 60°C, the polymer weighs 22.5 g, and has η_{inh} = 0.37-0.38 dl/g at 29.4° in a 0.5% benzene solution.

2. Notes

1. The polymerization tube has a bulb 12 cm in length and 2.5 cm in diameter. A constricted neck 15 cm long is connected to the bulb.
2. It is necessary to distill the styrene under reduced pressure to free the monomer of inhibitor and other impurities. The first 5% of styrene distilled is discarded and the middle fraction is saved. An alternate procedure is to wash the styrene with a 5% aqueous sodium hydroxide solution and to then dry the monomer over anhydrous calcium sulfate.
3. The contents of the tube are frozen by immersing the tube in a Dry Ice-acetone bath. After freezing, the tube is evacuated, nitrogen is introduced, the monomer is thawed, refrozen, and re-evacuated. This procedure is repeated several times. Before the tube is sealed, the monomer is refrozen and the tube is re-evacuated.
4. The tube should be wrapped in a towel to prevent flying glass from being a hazard.
5. The solution may be freed of dust particles by filtering it through a sintered glass funnel. The non-solvent is used in a volume ten times that of the solvent to ensure complete precipitation of the polymer.

B. Solution Polymerization with Cationic Catalysis

1. Procedure

The Catalyst. Into a 2 oz screw-cap bottle (Note 1), which has been thoroughly dried in an oven, is pipetted 20 ml of reagent grade carbon tetrachloride from a newly opened bottle (Note 2). The bottle and its contents are then accurately weighed.

Stannic chloride catalyst (0.6 ml, 1.32 g, Note 3) is withdrawn with a 5 ml hypodermic syringe and immediately injected into the 2 oz bottle without unscrewing the cap. The bottle is then accurately reweighed to determine the exact amount of catalyst transferred. Sufficient carbon tetrachloride is added to the bottle with a syringe to bring the solution to a concentration of 2.14 wt % in catalyst. The catalyst solution is immersed in an ice bath until needed (Note 4).

The Monomer. Freshly distilled styrene (6.5 ml, Note 2, Part A) is pipetted into a thoroughly dried 4 oz screw-cap bottle (Note 1). With a pipet, 20 ml of carbon tetrachloride and 25.5 ml of nitrobenzene (Note 5) are added to the monomer. The bottle cap is closed tightly, and the bottle is shaken briefly. The bottle is then placed in the same ice bath with the catalyst solution.

After about 10 min to allow for the contents of both bottles to cool to 0°, 4 ml (6.5 g) of the catalyst solution is withdrawn with a hypodermic syringe. The contents of the syringe are injected into the 4 oz bottle of monomer solution (Note 6). After standing for a period of 5 h in an ice bath, the solution is added to 500 ml of methanol (Note 6, Part A) with vigorous stirring to precipitate the polymer. The polystyrene is collected by filtering through a sintered glass funnel. The polymer is further purified by redissolving in 50 ml of methyl ethyl ketone and reprecipitating into 500 ml of methanol. This process is repeated twice.

Drying overnight in a vacuum desiccator (Notes 7 and 8) gives the product; weight 5 g, η = 0.19-0.20 dl/g at 29.2° as 0.5% benzene solution.

2. Notes

1. The cap of the bottle should be perforated and fitted with two rubber gaskets. The lower gasket, exposed to the contents of the bottle, must be chemically inert to the solvents, and the upper gasket is a puncture-sealing rubber material such as butyl rubber.
2. The carbon tetrachloride should be stored over anhydrous calcium chloride if it is not used immediately after opening the bottle.
3. The main supply of stannic chloride catalyst should be stored in a screw-top bottle, fitted at the cap as described in Note 1 with two rubber gaskets. If the main supply of catalyst becomes contaminated, it may be purified by refluxing over phosphorous pentoxide for 1-2 h and then distilling under reduced pressure.
4. A more elaborate procedure than that described above for preparing the catalyst is reported in the literature.[3]
5. If the nitrobenzene is not obtained from a newly opened reagent grade bottle, it must be purified according to standard procedures.[4]
6. The polymerization mixture consists of a 10.0 mol-% solution of styrene in solvent (an equimolar mixture of carbon tetrachloride and nitrobenzene) containing 0.1 mol-% of stannic chloride catalyst. The molar ratio of monomer to catalyst is 100:1.
7. Paraffin chips and phosphorous pentoxide are placed in the desiccator to absorb any solvent adhering to the polymer. The pressure in the desiccator is 0.5 torr.
8. Care must be taken when admitting air to the desiccator because the polymer is powdery. It is helpful to cover the polymer container with a piece of porous filter paper held in place with a rubber band.

3. Methods of Preparation

Polystyrene has also been prepared by suspension,[5] emulsion,[6] solution,[7] and thermal polymerization.[8]

4. References

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