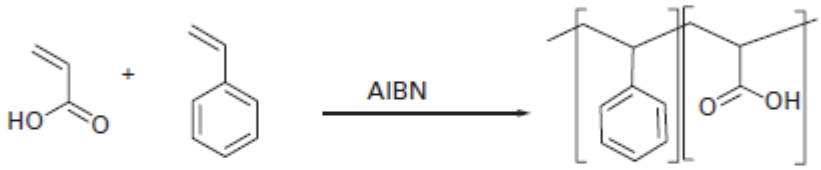
Preparation of a poly(styrene–acrylic acid) copolymer by free-radical polymerization (Scheme 7)

Caution! Carry out all procedures in a well-ventilated fume-hood, wear appropriate disposable gloves, a lab-coat, and safety glasses. All vacuum-line work should be performed while standing behind a protective Perspex screen.



Scheme 7 A copolymer formed from styrene and acrylic acid.

Equipment

- Dual manifold (nitrogen/vacuum)
- Vacuum source
- Source of dry nitrogen
- Thermostatted water-bath
- Apparatus for filtration under reduced pressure: Buchner flask, sintered-glass funnel, and water aspirator
- Lab-jack
- Polymerization tube
- Dewar containing liquid nitrogen
- Beaker (500 mL)
- Erlenmeyer flasks (250 mL)
- Vacuum oven

Materials

• Acrylic acid, 1.7 mL, 25 mmol	**flammable, causes burns**
• Styrene, 25.55 mL, 223 mmol	**flammable, irritating to eyes and respiratory system**
• AIBN, 0.41 g, 2.5 mmol	**toxic, harmful, explosive, highly flammable**
• Methanol, ca. 150 mL	**highly flammable, toxic by inhalation and if swallowed**
• Acetone, ca. 20 mL	**highly flammable**
• Petroleum ether 60/80, ca. 300 mL	**highly flammable**
• Liquid nitrogen for cooling	**Extremely cold liquid, vapour can cause rapid suffocation**

Method

Preparation: Styrene and acrylic acid should be purified to remove inhibitors prior to use. Both may be distilled under reduced pressure, but styrene can be washed with a dilute aqueous solution of potassium carbonate.

1. Place styrene (25.55 mL, 223 mmol), acrylic acid (1.7 mL, 25 mmol), and AIBN (0.41 g, 2.5 mmol) in a polymerization tube. A protective netting sleeve is then placed over the tube to minimize danger from glass should the tube shatter. Attach the tube to the manifold and close the Young's tap at the top of the tube.
2. Place the polymerization tube into the liquid nitrogen Dewar and evacuate the manifold by closing the nitrogen supply and opening the vacuum tap.
3. Once frozen, open the tap to the polymerization tube and allow the air to be pumped out of the tube, with the liquid nitrogen Dewar still in place. After a few minutes the air will be removed from the system (generally this can be detected by the sound of the pump). Close the tap on the polymerization tube, the upper tap, and the access to the pump.
4. Remove the nitrogen Dewar from under the polymerization tube and allow the system to warm to room temperature. Any sudden contact with the polymerization tube at this stage may cause the tube to shatter.

5. Allow nitrogen into the system by opening the N_2 inlet tap; then carefully open the upper tap and then the lower tap in sequence, being particularly careful to ensure that a sudden influx of gas does not cause the tube to become detached from the manifold.
6. Repeat steps 2–5 two more times to ensure complete removal of oxygen from the system.
7. When nitrogen has been passed into the system for a third time, place the polymerization tube into the liquid nitrogen Dewar and evacuate the manifold by closing the nitrogen supply and opening the vacuum tap.
8. Close the Young's tap on the polymerization tube and warm to room temperature. Place the tube in a thermostatted water-bath at 55°C for 1 hr.[a]
9. Remove the tube from the water-bath and allow to cool to room temperature.
10. Pour the viscous solution drop-wise into 150 mL methanol contained in a beaker (500 mL) cooled in ice. Dissolve the polymer in a small quantity of a suitable solvent (no more than 10 mL per gram polymer), in this case acetone, and precipitate from a suitable non-solvent for the polymer (in this case, petroleum ether 60/80).
11. Dissolve the polymer once again in a suitable solvent and re-precipitate. Collect the white polymer by filtration at the water pump using a clean dry sintered-glass funnel and dry the sample in the vacuum oven at 60°C for 24 h.

[a]It is important that the polymerization not be allowed to proceed to high yield since the different reactivities of the two monomers will result (in most cases at least) in a changing composition as a function of time as one of the monomers is depleted more rapidly than the other.