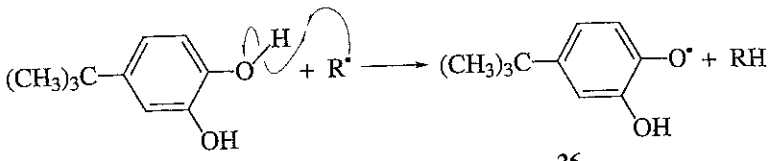


(22.13)

25
tert-Butycatechol

26

In the discovery experiment that follows, you will explore an important aspect of polymer chemistry by preparing polystyrene (**24**) under different reaction conditions and test whether it, like many polymers, may be produced in a variety of physical forms such as an amorphous solid, a film, and a clear glass.

EXPERIMENTAL PROCEDURES

Preparation of Polystyrene

Discovery Experiment

Purpose To demonstrate the synthesis of polystyrene by free-radical polymerization under different conditions.

SAFETY ALERT

1. **Wear safety glasses or goggles and suitable protective gloves while performing the experiment.**
2. **The free-radical initiator *tert*-butyl peroxybenzoate is a safe material to use in this experiment because it decomposes at a moderate rate when heated. Nonetheless, do not heat this catalyst excessively when performing the polymerization.**

MINISCALE PROCEDURE

Preparation Refer to the online resources to answer Pre-Lab Exercises, access videos, and read the MSDSs for the chemicals used or produced in this procedure. Review Sections 2.9, 2.17, 2.19, 2.21, and 2.22.

Apparatus A separatory funnel, small soft-glass test tube, 25-mL round-bottom flask, microburner, apparatus for magnetic stirring, heating under reflux, and *flameless* heating.

A ■ *Removal of the Inhibitor from Commercial Styrene*

Place about 10 mL of commercial styrene in a small separatory funnel and add 4 mL of 3 *M* sodium hydroxide and 15 mL of water. Shake the mixture thoroughly, allow the layers to separate, and withdraw the aqueous layer. Wash the organic layer sequentially with two 8-mL portions of water, carefully separating the aqueous layers after each wash. Dry the styrene by pouring it into a small Erlenmeyer

flask containing a little *anhydrous* calcium chloride and then swirling the flask. Allow the mixture to stand for 5–10 min, decant the liquid from the drying agent, and use the dried styrene in the following experiments.

Analysis Obtain IR and NMR spectra of styrene and compare them with those of an authentic sample (Figs. 22.1 and 22.2).

WRAPPING IT UP

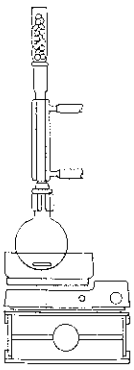
Allow the volatiles to evaporate from the *calcium chloride* by placing it on a tray in the hood; then discard it in the container for nontoxic solids. Neutralize the **aqueous layers** before flushing them down the drain.

B ■ *Polymerization of Pure Styrene*

Place about 2–3 mL of dry styrene in a small soft-glass test tube, and add 2 or 3 drops of *tert*-butyl peroxybenzoate. Clamp the test tube in a *vertical* position over a wire gauze, insert a thermometer so that its bulb is in the liquid, and heat the styrene and catalyst with a *small* burner flame. When the temperature reaches 140 °C, temporarily remove the flame. If boiling stops, resume heating to maintain gentle boiling. The exothermicity of the polymerization increases the rate of formation of free radicals by thermal decomposition of the initiator, and this in turn increases the rate of polymerization. Thus be watchful for a rapid increase in the rate of boiling and remove the flame if the refluxing liquid nears the top of the test tube.

After the onset of polymerization, the temperature should rise to 180–190 °C, much above the boiling point of styrene. The viscosity of the liquid will increase rapidly during this time. As soon as the temperature begins to decrease, remove the thermometer and pour the polystyrene onto a watchglass. Do not touch the thermometer *before* the temperature decreases, because moving it in the boiling liquid might cause a sudden "bump," which could throw hot liquid out of the tube. Note the formation of fibers as the thermometer is pulled out of the polymer. The rate of solidification of the polystyrene depends on the amount of catalyst used, the temperature, and the length of time the mixture is heated.

C ■ *Solution Polymerization of Styrene*



Place about 2 mL of dry styrene and 5 mL of xylene in a 25-mL round-bottom flask and add 7 drops of *tert*-butyl peroxybenzoate from a Pasteur pipet. Assemble the apparatus for heating under reflux and heat the mixture under reflux for 20 min. Cool the solution to room temperature and then pour about *half* of it into 25 mL of methanol. Collect the white precipitate of polystyrene that forms by decantation or by vacuum filtration if decantation is not practical. Resuspend the polystyrene in fresh methanol and stir it vigorously. Collect the polystyrene by filtration and allow it to dry in the hood.

Pour the remaining *half* of the polystyrene solution onto a watchglass or the bottom of a large inverted beaker and allow the solvent to evaporate. A clear film of polystyrene should form.