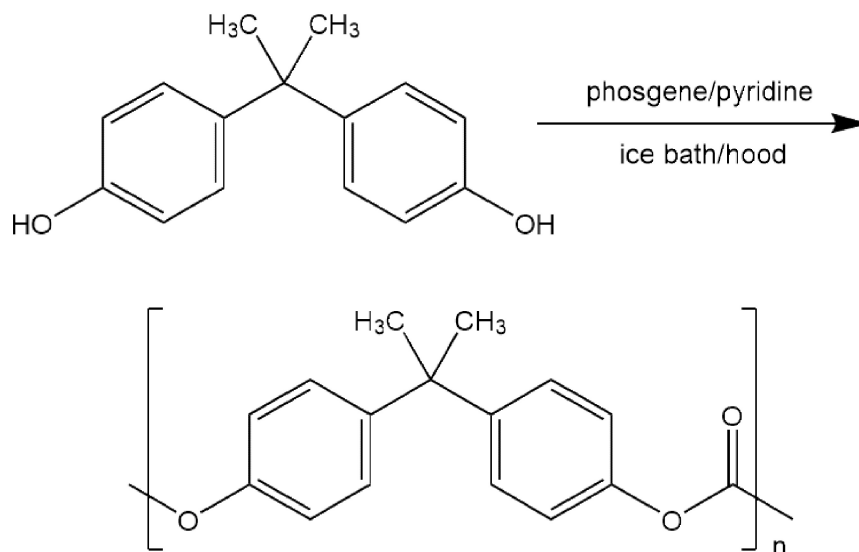


Bisphenol-A Polycarbonate (*p,p'*-Isopropylidene Bisphenol Polycarbonate)

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1. Procedure

Caution! The reaction should be conducted in a hood.

A 500 ml four-necked flask (or resin pot) equipped with a stirrer, a thermometer, a wide-bore gas inlet tube (Note 1), and a gas outlet (Note 2) is charged with bisphenol-A (22.8 g, 0.10 mol, Note 3) and 228 ml of pyridine (Note 4). Phosgene, at a rate of ca. 0.25 g/min (Note 5), is passed into the rapidly stirred reaction mixture, which is maintained at 25-30° with a water bath (Note 6). *Caution! Phosgene is a toxic, irritating gas and should be used only in an efficient fume hood.* Pyridine hydrochloride begins to separate after about 25 min. This indicates that the reaction is about 60% complete. Approximately 15 min later a marked increase in viscosity will be noted over a period of 2-3 min; the polymerization is then essentially complete (Note 7).

The polymer may be precipitated directly in the reaction flask. A dropping funnel containing 250 ml of methanol is substituted for the gas inlet tube, and methanol is added to the stirred reaction mixture over a period of 2-3 min. (Note 8). The polymer suspension is stirred for 5 min after precipitation and recovered by filtration on a Büchner funnel. General purpose filter paper may be used. The polymer may be conveniently freed of residual pyridine and pyridine hydrochloride by two or three successive cycles of agitation in an explosion-proof blender with 250 ml portions of methanol (Note 9). The filtered product is dried overnight in a vacuum oven at 125°; yd 22 g.

2. Characterization

The intrinsic viscosity of bisphenol-A polycarbonate determined in dioxane at 30° is 0.46 dl/g. The melting range is 225-250° (determined on a melting point block, Note 10). It is soluble in

methylene chloride, chloroform, tetrachloroethane, chlorobenzene, dioxane, and pyridine. Colorless transparent films may be conveniently cast on glass from methylene chloride solution. The polymer may be pressed into films between aluminum foil at 240-260°.

3. Notes

1. A 7 mm inside-diameter tube was used with the end positioned just above the stirring blade. A gas diffuser or smaller tube is undesirable because pyridine hydrochloride and/or the pyridine-phosgene complex tends to clog the inlet.
2. A length of rubber tubing may be connected to the gas outlet to carry escaping phosgene to a scrubber consisting of an empty trap connected to a second trap containing well-stirred ammonium hydroxide. The entrance to this trap should be above the liquid level to prevent formation of urea from clogging the opening.
3. The melting point of bisphenol-A may vary from 148-157°. The monomer used in the reaction described melted at 156.2°. Recrystallization (chlorobenzene) may be used for purification.
4. Reagent grade pyridine was used. A technical grade may also be used. Dimethyl aniline may be substituted for pyridine, and part of the tertiary amine may be replaced with chlorinated aliphatic hydrocarbons or chlorobenzene.
5. The rate of phosgene addition is not critical and, in fact, need not be measured. A dry trap between the phosgene cylinder and the reaction vessel is recommended to prevent the reaction mixture from being drawn into the cylinder if the phosgene flow is stopped.
6. Temperature is not critical, but high temperatures promote color.
7. The exact end point is difficult to characterize. Somewhat more than the theoretical 10 g of phosgene is usually required. A marked increase in viscosity is a good indication. Overshooting of the end point may be visually determined if the yellow color of the transient phosgene-acid chloride complex does not dissipate rapidly. The reaction may essentially be back-titrated by adding a small quantity of the original reaction mixture or, alternatively, the product may be precipitated at, or past, the end point.
8. Some degradation of the polymer may occur if the precipitation with alcohol is too slow. A stringy, sticky ball of polymer may form if precipitation is too rapid. Other alcohols, acetone, and hydrocarbons may be used as precipitating solvents. Alternatively, the polymer may be precipitated in an explosion-proof blender by pouring the reaction mixture into stirred methanol.
9. An alternative purification procedure may be followed involving one or more cycles of dissolution in methylene chloride, precipitation, and washing with methanol. The adequacy of washing in either procedure may be determined by checking the wash liquor for chloride ion with alcoholic silver nitrate.
10. The melting point is approximately 15° lower when measured in a capillary tube. The melting point is affected by extent of crystallinity and by molecular weight. Use of acetone to precipitate the polymer may promote crystallization and raise the melting point. Slow drying rates also promote crystallinity. Polymer with an intrinsic viscosity of 1.0-3.0 dl/g will not flow until the temperature is above 250°.

4. Methods of Preparation

Bisphenol-A polycarbonate may also be prepared from bisphenol-A and diphenylcarbonate by a thermally induced ester interchange.

5. References

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