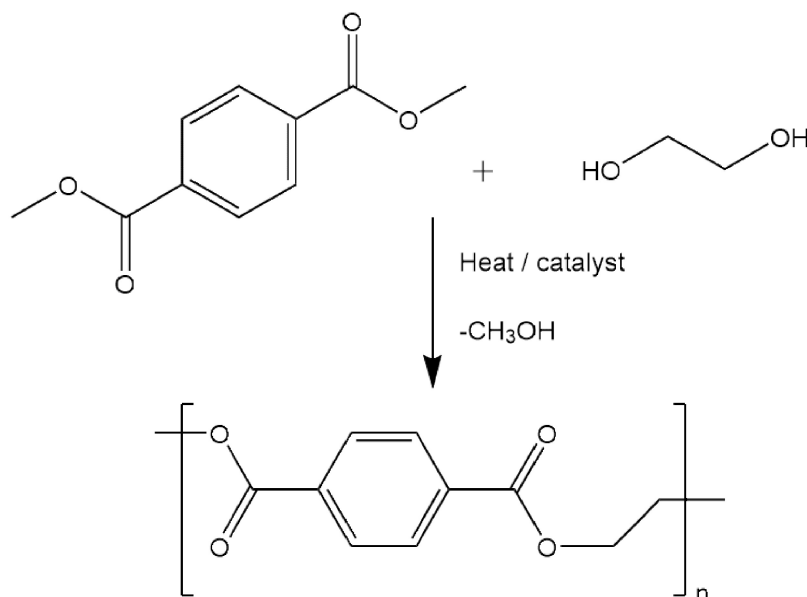


# Poly(ethylene terephthalate)

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## 1. Procedure

The condensation may be conveniently carried out in a glass "polymer tube" about 25 mm x 250 mm, sealed to a 10 mm x 70 mm neck carrying a side arm for distillation. Into the tube is charged dimethyl terephthalate (DMT 13.6 g, 0.07 mol, Note 1), ethylene glycol, (10 g, 8.8 ml, 0.16 mol, Note 2), calcium acetate dihydrate, (0.022 g, 0.15% based on DMT, Note 3), and antimony trioxide, (0.005 g, 0.035% based on DMT, Note 4). The charge is melted by submerging the tube about halfway (Note 5) in the vapors (Note 6) of boiling ethylene glycol (197°), and a fine capillary (Note 7), connected to nitrogen under pressure, is introduced through the neck of the tube. A vacuum-tight seal is made with a piece of heavy-walled rubber tubing well-lubricated with silicone grease. The capillary must be adjusted to reach the very bottom of the polymer tube. Methyl alcohol distills rapidly for a few minutes. After 1 h, the tube is adjusted to be heated as completely as possible by the glycol vapors, and heating at 197° is continued for 2 h more (Note 8). The polymer tube is then transferred to a 222° (methyl salicylate) vapor bath for 15 min, during which time excess glycol distills and polymerization begins (Note 9).

The side arm of the polymer tube is now connected by means of a short piece of heavy-walled tubing to a receiver having a side arm for vacuum. The tube is now heated at 283° (dimethyl phthalate). Polymerization proceeds and glycol distills slowly. After 5-10 min vacuum is applied very cautiously (Note 10) and the pressure is brought to 0.2 torr or less in about 15 min. Polymerization should be complete within 3 h (Note 11). The tube is then filled with nitrogen, removed from the vapor bath (Note 12), and allowed to cool. The glass is cracked away from the mass of polymer by wrapping it in a towel and tapping with a hammer. Residual glass, which adheres very tenaciously, must be removed with a coarse file. The polymer may then be sawed or chopped into small pieces with a knife, hammer, and wooden block. The pieces, mixed with Dry Ice to prevent heating and fusion, may be further ground in a Wiley mill.

When the polymerization is properly carried out, the yield is quantitative except for mechanical losses (Note 13). An inherent viscosity ( $\eta_{inh}$ ) of about 0.7 dl/g is obtained at 30° as a 0.5% solution in *s*-tetrachloroethane-phenol (40-60). This corresponds to an intrinsic viscosity of 0.62 dl/g and a number average molecular weight of about 16,000. Polymers having  $\eta_{inh}$  above about 0.5 dl/g may be melt-spun or pressed into flexible films. The crystalline melting point (hot-stage, polarizing microscope) of polymer prepared as described is about 258°.

## 2. Notes

1. All ingredients must be of the highest purity. DMT may be purified by crystallization from methanol or dioxane.
2. Satisfactory glycol may be prepared by dissolving 1% of metallic sodium in the commercial product under nitrogen, heating under reflux for 1 h, and distilling through a short Vigreux column.
3. At the temperature used for the first ester exchange reaction, basic catalysts are most effective. Calcium acetate is most satisfactory for laboratory work. Reagent grade chemicals should be used as catalysts to ensure best color in the final polymer.
4. Although the polymerization is also an ester exchange reaction, it cannot be driven to completion with calcium acetate. The simultaneous addition of the basic and acidic catalysts does not result in mutual interference, however.<sup>3</sup> Zinc acetate alone may be used for both ester exchange and polymerization catalysts, but darker colored polymer usually results.
5. There is a strong tendency for DMT to co-distill with methyl alcohol. This can lead to clogging of the side arm, and to altered composition when copolymers are made.
6. Pyrex<sup>®</sup> test tubes (50 x 400 mm) make convenient vapor baths. In use, the upper wall acts as an air condenser to prevent loss of vapors. Electrical heating is safest and easiest to control. The reaction should be carried out so any of the refluxing vapors that leave the tube enter an exhaust system leading to a hood.
7. Commercial heavy-walled capillary tubing, small enough to fit inside the neck of the polymer tube, is drawn to a fine tip after softening in a gas-oxygen flame. The shoulder of the heavy capillary tubing is kept above the side arm of the polymer tube so flow of methanol and glycol vapors is not impeded. The extremely fine tip of the capillary makes additional control of nitrogen flow unnecessary.
8. It is essential to remove the last traces of methyl alcohol with the nitrogen sweep before processing if high viscosity is to be obtained. With ethylene glycol terephthalate, this step can be allowed to proceed overnight. With more unstable monomers, the heating cycle can be shortened by using a larger excess of glycol which often entrains the last traces of methyl alcohol in the next step.
9. If the charge solidifies at any of the intermediate stages, it will remelt without difficulty when transferred to the next higher temperature.
10. If vacuum is applied too rapidly, material will splatter to the top of the tube and solidify, and bis(hydroxyethyl)terephthalate will distill.
11. The melt may be too thick to bubble at 283° when an  $\eta_{inh}$  of 0.8 dl/g is approached. Separation of calcium terephthalate will cause the melt to become hazy, and decomposition products of antimony oxide may cause a grayish-green color. On cooling, the polymer should crystallize and become opaque. The glass polymer tube may shatter violently because of differential shrinkage. Flying glass may be confined by wrapping the tube in a towel during cooling.
12. The glass capillary may be withdrawn from the melt before it cools; "manual spinning" of a filament may thus be observed. The phenomenon of "necking down" may be demonstrated by hand-drawing the filament in contact with a warm hot plate.

13. This type of polyesterification is applicable to any system in which monomers and polymers are thermally stable at temperatures above the polymer melting point, and the glycol is sufficiently volatile to permit the excess to be completely removed under vacuum.

### 3. Methods of Preparation

Polyethylene terephthalate has been prepared by direct esterification of ethylene glycol with terephthalic acid,<sup>4</sup> by the condensation of bis(hydroxyethyl)terephthalate prepared from terephthalic acid and ethylene oxide,<sup>5</sup> from terephthalic acid and ethylene carbonate,<sup>6</sup> from monomethyl terephthalic acid ester and ethylene carbonate,<sup>7</sup> from terephthalic acid and ethylene glycol,<sup>8</sup> by self-condensation of methyl hydroxyethyl terephthalate<sup>9</sup> or mono(hydroxyethyl)terephthalic acid,<sup>10</sup> from terephthalic acid and bis(hydroxyethyl)terephthalate,<sup>11</sup> from disodium terephthalate and ethylene chlorohydrin,<sup>12</sup> and from terephthaloyl chloride and ethylene glycol.<sup>13</sup>

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