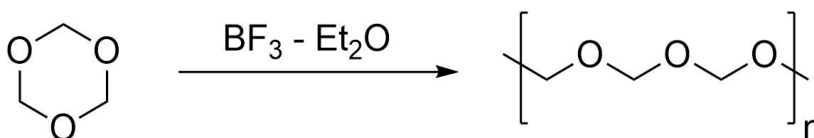


# Cationic Polymerization of 1,3,5-Trioxane

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## 1. Procedure

To a flame-dried, 500 ml, round-bottomed flask equipped with a serum stopper are charged, under anhydrous conditions in an efficient hood, pure anhydrous trioxane (90 g, 1.0 mol, Note 1) and 210 g of ethylene dichloride, which has been refluxed and distilled over phosphorous pentoxide. *Caution! Many chlorinated hydrocarbons are toxic and should be used with adequate precaution.* Boron trifluoride-etherate (70 mg, 0.5 mmol) in 7 ml of ethylene dichloride is injected with a syringe while the mixture is shaken vigorously (Note 2). The flask is then immersed in a bath at 45°C.

After an induction period of about 2 min, during which small amounts of formaldehyde are formed, precipitation of insoluble polyoxymethylene begins. The reaction mixture solidifies within 10 min (Note 3). After a total of 60 min at 45°C, sufficient acetone is added to form a slurry. The slurry is filtered and the polymer is thoroughly washed several times with acetone on a glass filter and sucked dry. To remove catalyst residues, which may degrade the polymer, it is boiled for 30 min with 1 l of ether containing 2 wt-% of tributylamine; yd 40-50 g.

## 2. Characterization

Polyoxymethylene is a white powder of melting temperature 176-178°C (in a sealed glass tube); it is soluble in phenol at 115°C, in N,N-dimethylformamide (DMF) or benzyl alcohol at 140°C.<sup>3</sup> Because of the unstable hemiacetal hydroxyl end-groups and unremoved catalyst residues, the polymer decomposes to formaldehyde almost entirely within 2 h at 190° even under pure nitrogen. It is recommended that molecular weights be determined by viscosity measurement after stabilizing the polymer by acetylation, otherwise degradation will interfere.

## 3. Stabilization by End-Group Acetylation<sup>4</sup>

Polytrioxane (1 g) is mixed with 100 ml of DMF, 40 ml of pure acetic anhydride, (*Hood!*) and 8 ml of N,N-dimethylcyclohexylamine or a similar high-boiling tertiary amine (Note 4) in a 250 ml flask equipped with a reflux condenser and a calcium chloride tube. The polymer is dissolved at about 145°C by short and cautious heating over a free flame. The flask is then immersed in a bath at 140°C for 30 min. The polymer precipitates on cooling, is filtered, washed with acetone, refluxed for 30 min with 100 ml of fresh acetone and dried. About 950 mg of acetylated polymer is recovered that undergoes less than 10% decomposition during heating at 190°C for 16 h under pure nitrogen (Note 4).

The stabilized polymer in a 1% solution in DMF at 140° has  $\eta_{inh} = 0.50$  dl/g, corresponding to a molecular weight  $M_w \sim 50,000^5$  (Note 5).

#### 4. Notes

1. Trioxane (mp 64°C) can be purified and dried by very careful distillation (bp 115°C) through an efficient column (bp of azeotrope containing 30 wt-% water, 91.3°C). Crystallization of trioxane during distillation and storage causes partial polymerization and should therefore be avoided. Trioxane is also conveniently purified with chemical reagents; e.g., refluxing for 20 h over 5 wt-% sodium or calcium hydride or with 10-20 wt-% naphthalene-1,5-diisocyanate and 0.3% of dibutyl tin dilaurate or triethylenediamine as catalyst, followed by fractional distillation. In all cases, care is taken to avoid adherence of water or methanol-containing condensates to the upper portion of the reflux condenser.
2.  $\text{SnCl}_4$  may be used instead of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ .
3. The rate of polymerization depends greatly on purity and dryness; if polymerization is slow, more initiator is added.
4. The checkers used tributylamine and obtained 875 mg of acetylated polymer,  $\eta_{inh} 0.42$  dl/g. The initial decomposition rate at 190° under pure nitrogen was 0.6%/min.
5. The molecular weights obtained are extremely dependent on the dryness of the trioxane solution; careful exclusion of water during the polymerization procedure is required.

#### 5. Methods of Preparation

Polyoxymethylene of high weight can also be made by anionic or by cationic polymerization of anhydrous formaldehyde.<sup>6,7,8</sup> Purification, handling, and polymerization of trioxane, however, are much easier than for anhydrous formaldehyde. Polycondensation of aqueous formaldehyde solutions yields polymers of low molecular weight (paraformaldehyde).<sup>6</sup>

#### 6. References

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