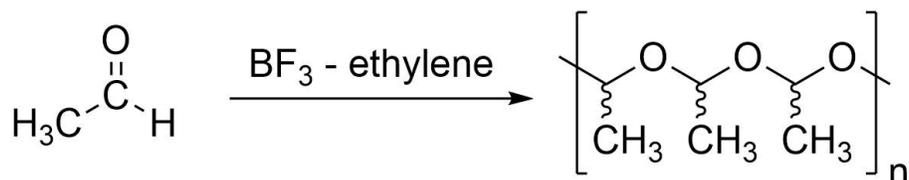


Amorphous Polyacetaldehyde

Submitted by: O. Vogl¹

Checked by: M. Goodman and G. C. C. Niu²

A. Boron Trifluoride as Catalyst



1. Procedure

Polymerization grade ethylene (250 ml), bp -104°C , is condensed with a liquid N_2 bath (Note 1) in a 1 l four-necked flask equipped with stirrer, thermometer (reading to -200°C), gas inlet tube, and short condenser (Note 2). The condenser terminates in a Claisen adapter connected with a glass T to a dry N_2 line and a double bubbler filled with mineral oil. Condensation of ethylene takes ca 10-20 min. The gas inlet tube is replaced by an adapter with a serum stopper cap.

Stirring is started, and acetaldehyde (39 g, 50 ml, 0.88 mol; Note 3) is injected slowly to avoid excessive boiling of the ethylene using a cooled syringe (polyethylene dry bag in refrigerator at 0°C). The internal temperature of the mixture is kept between -110° and -120°C by lowering and raising the liquid N_2 bath. Care is taken that no freezing of the mixture occurs. Gaseous BF_3 (3 ml, 0.13 mol) is injected with a syringe (Note 4).

In 10-20 min the stirrer stops because of polymer formation. The reaction is allowed to stand for an additional 30 min while the ethylene evaporates slowly. Excess ethylene is decanted with N_2 blanketing, and 100 ml of anhydrous pyridine added. Stirring at room temperature dissolves the polymer completely. The polymer may be isolated at this stage by pouring the solution into cold water.

For end-capping, 300 ml of acetic anhydride is added to the pyridine solution of polymer, and the mixture stirred under N_2 for 1-2 h. The brownish-green viscous solution is poured into 1 kg of ice and 1 l of water to precipitate polymer, which is then kneaded by hand in several changes of water and ice to destroy the acetic anhydride completely. Rubber gloves are worn during this operation. Washing is complete when the wash is colorless; yd 34-37 g (87-94%); $\eta_{\text{inh}} = 1-2$ dl/g (Notes 5 and 6).

2. Notes

1. Instead of using a liquid N_2 bath directly, which is difficult to control, it is advantageous to use other low-temperature baths. Methylcyclo-hexane (mp -126°C) can be used at -120°C with a liquid nitrogen cooling bath.
2. To obtain high molecular weights all operations must be carried out under rigorously dry conditions. The reaction flask should be flamed, the remaining parts of the apparatus and the syringes should be assembled while hot and then cooled in a stream of dry nitrogen.
3. Pure acetaldehyde is obtained by decomposition of paraldehyde³ or by careful fractional distillation of acetaldehyde.⁴ For the preparation of elastomeric polyacetaldehyde even of very high molecular weight, the latter procedure is adequate. Acetaldehyde, obtained from Eastman in a sealed vial, is stirred for 1 h at 0°C with $\text{Na}_2\text{CO}_3 \bullet \text{H}_2\text{O}$, followed by stirring with

MgSO₄ for 30 min. It is distilled in a low-temperature still from an antioxidant [0.1% of AgeRite White (Note 7)] in a nitrogen atmosphere, the first 20% of the distillate being discarded. The receiver is kept at 0°C, and the purified sample used immediately. The distillation apparatus is rinsed with soap solution or dilute NaOH solution after each distillation to eliminate acid buildup in the distillation column. Acidic cleaning solutions, particularly for the Dry Ice condenser, should be avoided. Acidity on the glass surface causes rapid polymer formation and plugging of the condenser.

4. BF₃ etherate may be used instead of gaseous BF₃. The etherate brings about polymerization much faster than does gaseous BF₃. Add the corresponding amount of catalyst (16 ml of BF₃ etherate) to the reaction mixture with a syringe.
5. The inherent viscosity of polyacetaldehyde is measured as a 0.5% solution in butanone. Polymers having η_{inh} up to 5 dl/g have been obtained by the method described in this preparation.
6. To obtain a stable polymer all impurities must be removed from the rubbery polymer. This is done by dissolving capped polymer in 10-20 times its volume of peroxide-free ether and washing as follows. Pyridine is removed by shaking the ethereal solution in a separatory funnel with water containing 1% acetic acid, followed by distilled water. Residual acetic acid and initiator are removed by shaking several times with 1% Na₂CO₃ solution, followed by repeated washings with distilled water. It is sometimes necessary to break the emulsions by adding NaCl. The polymer solution is dried over magnesium sulfate and filtered. Antioxidant (Note 7) and thermal stabilizer are added, and the solvent is evaporated under reduced pressure (vacuum pump) at room temperature.
7. This antioxidant is *sym*-di- β -naphthyl-*p*-phenylenediamine obtained from R.T. Vanderbilt Co., Inc., New York, New York.

3. Methods of Preparation

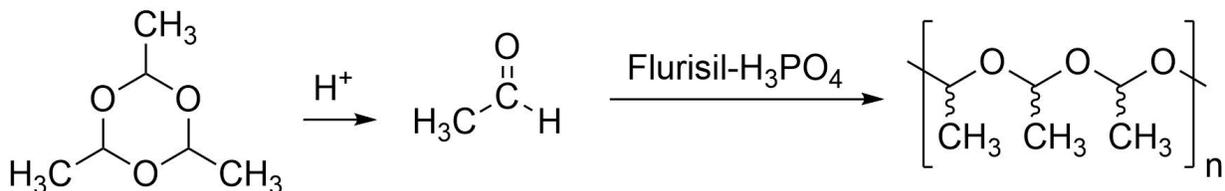
Elastomeric polyacetaldehyde has been prepared using other Lewis and protic acids as initiators.⁴ Aluminum alkyls, aluminum alkoxides, zinc alkyls, and phosphines also give polyacetaldehyde in good yield. The latter polymers, however, contain varying degrees of crystalline isotactic polyacetaldehyde. Acidic alumina and other metal oxides have been shown to give amorphous polyacetaldehyde.⁵

4. Merits of the Preparation

Although most methods of acetaldehyde polymerization give good yields of relatively low molecular weight amorphous polymer often containing some paraldehyde, the method described here gives high yields of very high molecular weight polymer free of paraldehyde. This method is also suitable for larger-scale preparation.

B. Fluorisil-Phosphoric Acid as Catalyst

Submitted by: J. Brandrup and M. Goodman⁶
Checked by: O. Vogl and L. Hammond¹



1. Procedure

A 50 ml, three-necked flask equipped with fractionating column (Note 1) 15-20 cm long, condenser, and a 25 ml, two-necked receiver are assembled hot (Note 2) under N_2 (Note 3). The system is closed by a bubble trap filled with mineral oil. Fluorisil (1 g) is placed in the receiver after disconnecting the bubble trap from the receiver (Note 4). A 5% solution of 100% H_3PO_4 (Note 5) in absolute ether (1 ml) is introduced the same way. Predried paraldehyde (25 ml, Note 6) is placed in the distilling flask under nitrogen, and dry cupric sulfate (1 g, Note 7) is added. The condenser is then cooled to approximately -60° to $-70^\circ C$ and the receiver placed in a Dewar flask filled with Dry Ice-acetone ($-78^\circ C$, Note 8). Distillation of paraldehyde commences. Decomposition of paraldehyde is regulated so that all acetaldehyde is cooled to at least $-50^\circ C$ before contacting the catalyst (Note 9). Distillation occurs over about a 1 h period.

After nearly all monomer is distilled, the receiver is disconnected and quickly stoppered. The receiver is kept at $-78^\circ C$ for 1-2 days; molecular weight increases with increasing reaction time. Very high molecular weight material forms from the glassy, clear solid (at -78°). The polymer is collected after 2-3 days. At the end of the reaction time, 20 ml of pyridine is added to the solution (Note 10) and the flask is warmed. The polymer is filtered from the Fluorisil and precipitated by decantation into water with agitation. It is advisable to redissolve the polymer in methanol and to add a methanolic solution of a stabilizer (Note 11). The stabilized polymer is precipitated into water, decanting and drying under reduced pressure at room temperature. Rubbery, amorphous polyacetaldehyde is obtained that has a reduced viscosity of 0.16 dl/g as a 0.1% solution in N,N-dimethylformamide, yd 8-13 g (40-70%). The polymer is unstable if it contacts acid. It should be stored in a cool place.

2. Notes

1. Any fractionating columns (Vigreux or packed) can be used.
2. All glassware must be washed with alkali to remove any trace of acid to avoid undesired polymerization. The glassware is dried at $120-150^\circ C$ overnight and is then immediately assembled under dry nitrogen starting with the three-necked flask to ensure dryness.
3. Oxygen-free, dry nitrogen is obtained by passing commercial prepurified nitrogen through conc sulfuric acid and NaOH.
4. Fluorisil (Floridin Company, Tallahassee, FL) is heated at $450-500^\circ C$ for 24 h, weighed hot, and immediately introduced into the flask.
5. Phosphoric acid (85%) is treated in ether with an appropriate amount of P_2O_5 to bring it to 100%; other protonic acids may be used.⁷
6. Paraldehyde from Baker and Adamson is stored over CaH. Before use it is decanted into a flask containing triisobutyl aluminum under N_2 (1-3% by volume based on paraldehyde). The paraldehyde is distilled immediately before use to remove any trace of water (bp 121° at 760 mm). *Caution! Aluminum alkyls are pyrophoric.*
7. Copper sulfate is dried shortly before use by heating over an open flame until the entire mass is white.
8. Methanol is circulated through a copper spiral kept at $-78^\circ C$ with Dry Ice-acetone.
9. If distillation occurs too rapidly, monomer is not cooled sufficiently and paraldehyde forms on contact with catalyst.
10. Amorphous polyacetaldehyde is very sensitive to acid degradation, which can occur during workup if the catalyst is not destroyed. Any basic substance (aniline, ammonia, amines) can be used in place of pyridine.
11. Ultramid 1C, BASF, Germany, is a methanol-soluble amide which forms a synergistic stabilizer with β -naphthylamine for aldehydes.⁸

3. References

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