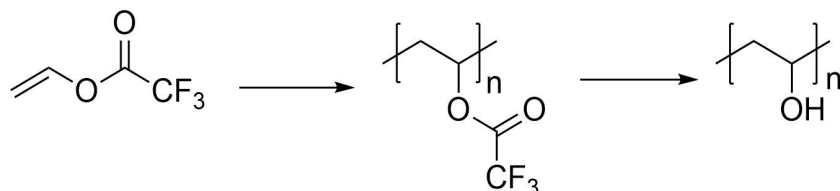


Stereoregular Poly-(vinyl trifluoroacetate) and Poly(vinyl alcohol)

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A. Polymerization of Vinyl Trifluoroacetate

1. Procedure

In each of four 200 x 25 mm heavy-walled Pyrex[®] test tubes that have been narrowed at a point 1-1.5 in from the top are placed 0.54 g (0.6% by weight of monomer) of a 50% paste of 2,4-dichlorobenzoyl peroxide in dibutyl phthalate (Note 1), and 45 g of vinyl trifluoroacetate (Note 2). *Caution! Acyl peroxides are strong oxidants and must be handled with care.* A small wad of glass wool is placed in the top of each tube and they are attached to a vacuum line, constructed as shown in Fig. 1, through which high purity nitrogen is flowing at a moderately rapid rate. The tubes are then immersed in a Dry Ice - trichloroethylene or Dry Ice - carbon tetrachloride/chloroform bath under positive nitrogen pressure. *Caution! Trichloroethylene, carbon tetrachloride and chloroform are toxic and should be handled with gloves in an efficient fume hood.*

After cooling for about 15 min, the tubes are evacuated to a pressure of about 0.5 torr by reversing the three-way stopcock shown in Fig. 1. The system is then flushed with nitrogen by *cautiously* reversing the stopcock again until a slight positive pressure is attained. This procedure is repeated twice to ensure an inert atmosphere in the tubes. After the pressure is again reduced to 0.5 torr, the tubes are sealed at the constriction using a hand torch. When the glass seals have cooled, the tubes are permitted to warm to room temperature and are shaken vigorously to dissolve as much of the initiator as possible. The tubes are then inserted in metal shields (Note 3) and placed in a constant temperature bath at 40°. An occasional *cautious* (Note 4) agitation of the tubes during the first half hour will complete the dissolution of the initiator. After 1 day, the tubes are filled with purple to brown solid polymer. They are chilled in powdered Dry Ice to release the polymer from the walls, and the poly(vinyl trifluoroacetate) is removed by breaking the tubes. *Caution! Wear heavy gloves to protect the hands and break the tubes behind a safety shield in case internal pressure has developed.* Conversions to polymer of the order of 90-100% are achieved with an η_{red} in cyclohexanone of 3-4 dl/g.

2. Notes

1. Available from the Lucidol Division of Wallace and Tiernan, Inc., under the name Lupercio CDB.
2. The vinyl trifluoroacetate can be purchased, or prepared by the reaction of acetylene with trifluoroacetic acid in the presence of mercuric oxide.³ *Caution! Vinyl trifluoroacetate should be handled in an efficient fume hood and should not come in contact with the skin.*
3. These can be conveniently made from standard 8 in. iron pipe nipples fitted with caps and perforated to permit the water to flow around the tube.

4. The agitation of the tubes (which are not removed from the metal shields) should be carried out behind a safety shield, heavy gloves being used to protect the hands. A gentle inversion of the tubes several times usually provides adequate stirring.

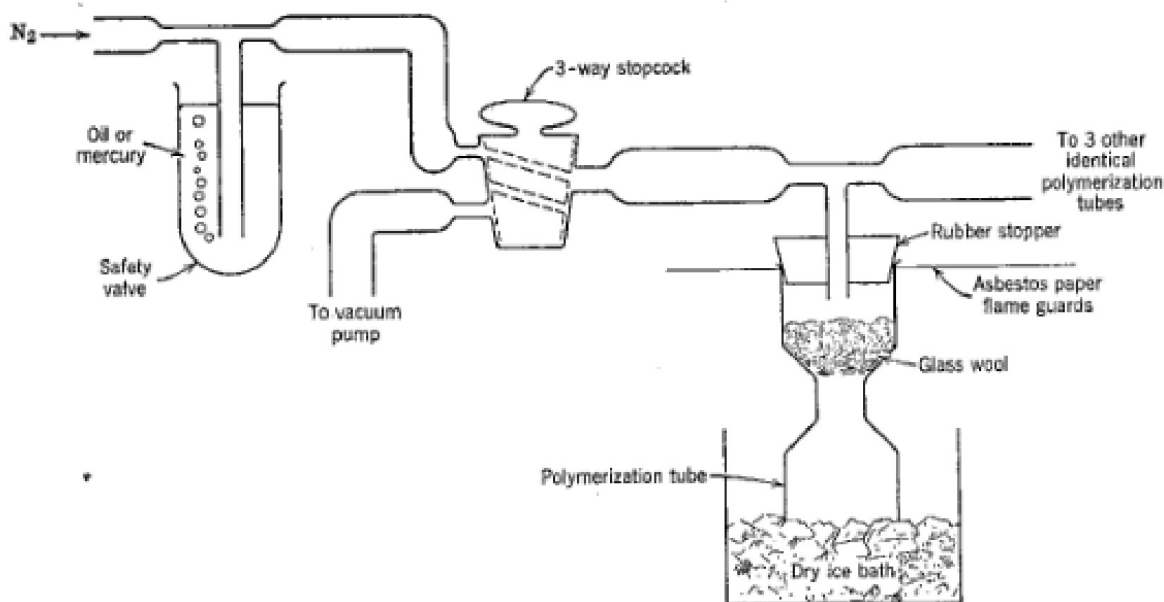


Fig. 1.

3. Methods of Preparation

Vinyl trifluoroacetate has been polymerized in bulk with benzoyl peroxide as the initiator⁴ and with ultraviolet radiation.⁵ In addition, this monomer has been polymerized in acetone solution.⁴

B. Conversion of Poly(vinyl trifluoroacetate) to Poly(vinyl alcohol)

1. Procedure

Poly(vinyl trifluoroacetate) (ca 180 g) is dissolved in 1800 ml of redistilled tetrahydrofuran (Note 1) with good agitation, at the reflux temperature of the solvent. *Caution!* The dissolving and alcoholysis steps must be carried out in an efficient hood to avoid building up a hazardous concentration of tetrahydrofuran vapor. The alcoholysis reaction is carried out in a 5 l, four-necked, round-bottomed flask equipped with a stirrer, a reflux condenser, a 150 ml addition funnel containing 120 ml of a 5% solution of sodium methoxide in methanol, and a 1 l addition funnel, which is either jacketed and heated by circulating hot water or wrapped with electrical heating tape (Note 2). In the flask are placed 660 ml of redistilled tetrahydrofuran, 20 ml of dry methanol, and 10 ml of a 10% solution of sodium methoxide in methanol. The mixture is heated to reflux and about one-half of the hot polymer solution is added through the large addition funnel over a period of 1.5 h. This is repeated with the remainder of the polymer solution, using small additional quantities of fresh tetrahydrofuran to rinse residual poly(vinyl trifluoroacetate) from the dissolving flask and funnel into the alcoholysis vessel. Small amounts of the 5% sodium methoxide solution (Note 3) are added as required to keep the reaction faintly basic, as determined with pH paper. After all the polymer solution has been introduced, the white to light yellow slurry is kept at reflux for an additional 2 h. At the end of this period, the mixture is neutralized with glacial acetic acid and permitted to cool. The finely divided poly(vinyl alcohol) is separated by filtration, washed with

several portions of methanol, and dried in a vacuum oven at 50°/20 torr. The yield of poly(vinyl alcohol) is about 50 g, 90% of theoretical, based on 180 g of poly(vinyl trifluoroacetate).

2. Notes

1. Commercial tetrahydrofuran must be purified by distillation because the inhibitor present will cause the poly(vinyl alcohol) to be discolored.
2. The polymer solution must be kept at about 50° to prevent gelation.
3. A lighter colored poly(vinyl alcohol) will result if an equivalent amount of a 1% sodium methoxide solution is used, but a constant addition of this catalyst solution throughout the reaction period is required.

Ed. Note: Since this procedure was published, controversy has arisen over the tacticity of poly(vinyl trifluoroacetate) and the derived alcohol. The original submitter feels that some of the more recent work confirms the earlier thesis that these polymers are more syndiotactic than those made *via* vinyl acetate.

3. Methods of Preparation

A thin film of poly(vinyl trifluoroacetate) has been converted to a film of poly(vinyl alcohol) (PVA) by ammonolysis in dry, gaseous ammonia.^{4,6} It has also been reported that sodium carbonate can be used as the catalyst for the alcoholysis.⁵

The preparation of highly syndiotactic PVA *via* cationically polymerized vinyl trimethylsilyl ether has been reported.⁷ PVA has also been prepared from syndiotactic poly(vinyl formate) prepared by low temperature, free radical polymerization,⁸ and from free radical polymerization of vinyl esters of C₄ to C₆ ω-hydrofluorocarboxylic acids.⁹ Isotactic PVA has been obtained from cationically polymerized vinyl benzyl ether.¹⁰

4. References

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