Preparation and Polymerization of Thiocarbonyl Fluoride

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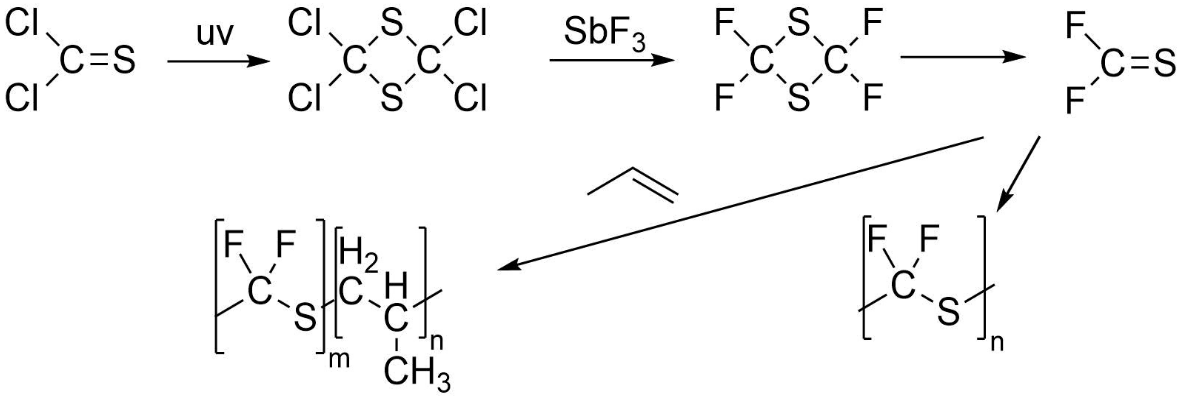

1. Procedure

A. 2,2,4,4-Tetrachloro-1,3-dithietane

2,2,4,4-Tetrachloro-01,3-dithietane is formed by ultraviolet dimerization of thiophosgene.[3] A Pyrex® glass test tube 4 in. ID and 18 in. long[4] is equipped with a water jacket and mounted vertically on a tripod. The top of the tube is closed with a rubber stopper fitted with a stirrer. The stirrer should be a sturdy glass rod to which a paddle of Teflon® fluorocarbon resin is attached at the lower end. A vent tube is also inserted through the stopper and protected with a Drierite drying tube. Six ultraviolet lamps (GE-H85-C3), each fitted with a parabolic reflector and connected to 550-volt transformers, are placed vertically around the reaction tube about 1/4 in. from its water jacket. Then 4000 g of thiophosgene (*Caution!*, Note 1) is placed in the tube and stirred slowly (Note 2) with the stirrer paddle about 3 in. below the top of the liquid. At the start, the lamps (*Caution!*, Note 3) are arranged so that their tops are level with the surface of the liquid thiophosgene. Water at 20° of slightly below is circulated through the jacket to keep the contents of the tube cool. The lamps are turned on and, as irradiation proceeds, crystals of 2,2,4,4-tetrachloro-1,3-dithietane form. The lamps are adjusted to maintain their tops even with the liquid level as it drops. The stirrer paddle is also lowered.

After approximately 215 h. dimerization is about 75% complete. At this point, the stirrer is stopped to allow the crystals to settle. Irradiation is continued for an additional 2 h. to form a crust over the solid. The temperature of the water circulating in the jacket is then reduced to 5°, the lamps are shut off, and the stirrer is removed. The liquid fraction is poured into a brown bottle for recovered thiophosgene. The tube is placed at an angle of 30° for about 30 min. to allow more liquid to drain. The solid 2,2,4,4-tetrachloro-1,3-dithietane is then removed from the tube and stored in a brown bottle until it is used in the next step. This solid fraction should weigh 2930 g (75% of the theoretical amount).

B. 2,2,4,4-Tetrafluoro-1,3-dithietane[5]

A three-necked, 12 l flask is equipped with a glass stirrer with a Teflon® paddle, a thermometer, a nitrogen, inlet, and a condenser connected to three cold traps in series. The first two traps are cooled with ice, and the third trap is cooled with solid carbon dioxide in acetone. The flask is charged with 7500 g of tetramethylene sulfone. Air is displaced by passage of dry nitrogen through the system. Nitrogen flow is maintained during the addition of all ingredients and until the apparatus is closed. After adding 4500 g of antimony trifluoride, the 2,2,4,4-tetrachloro-1,3-dithietane from the first reaction (3000 g) is added through the condenser, and up to 900 g of additional tetramethylene sulfone is used to wash all of it into the reaction flask. The reaction flask is heated to 67° with a Glas-Col mantle. The heat source is removed when bubble formation indicates that the reaction has started, and stirring is continued until bubbling decreases. Heating is then resumed at a rate such that the inside temperature reaches 180° over a 1 h. period. Crude tetrafluorodithietane fractions that collect in traps are combined, dried with magnesium sulfate (1 g/100 g of product), filtered, and distilled. Distillation is easily done with a column 24 in. long and 1.25 in. in diameter, packed with 1/8 in. glass helices, with an attached 3 l pot. The fraction that boils at 45-50° is collected for further purification.

Impurities are oxidized and removed by the addition of hydrogen peroxide. A 5 l, three-necked flask is equipped with a condenser, a thermometer, and a glass stirrer with a Teflon® paddle. Tetrafluorodithietane from the above distillation is added to the flask. As the diethietane is vigorously stirred, a solution of 20 cc of 30% hydrogen peroxide in 100 ml of 10% sodium hydroxide is added through the condenser over a period of about 3 min. The flask temperature rises with the addition of the caustic-peroxide mixture, but the temperature is maintained at 35-40° with an ice bath. Additional caustic-peroxide mixture is added frequently to maintain the temperature of the reaction mixture between 35° and 40° with continual ice-bath cooling. When the color is the heavy liquid layer is only a faint yellow, an additional 120 ml of the caustic-peroxide mixture is added and stirring is continued for 3 h. There are two layers in the reaction mixture; the heavy lower layer is separated and dried with magnesium sulfate, and the upper layer is discarded. The dried, lower layer is distilled, and the fraction boiling at 47.3-47.7° is collected as pure 2,2,4,4-tetrafluoro-1,3-dithietane. The yield is 1300 g (Note 4), which is 65% of the theoretical amount.

C. Thiocarbonyl Fluoride

Caution! Although toxicity studies have not been made, thiocarbonyl fluoride is undoubtedly dangerous because it quickly hydrolyzes to hydrogen fluoride and carbon oxysulfide.

An unpacked platinum tube 0.5 in. in diameter (Note 5) and 20 in. long is mounted at a 30° angle and fitted at the upper end with a T-tube that is connected to a dropping funnel and a nitrogen source. The lower end is fitted to a coiled tube trap of stainless steel that is cooled with an ice bath. The outlet from this trap is connected to a glass trap cooled with solid carjon dioxide in an acetone bath. The outlet from the second trap is protected with a drying tube. The platinum tube is heated to 500° over a 12 in. section, and nitrogen is passed through the tube at a rate of about 100 ml/min. to purge all moisture. Then 100 g of 2,2,4,4-tetrafluoro-1,3-dithiethane is added dropwise to the tube from the funnel over a 5 h. period. Thiocarbonyl fluoride, which condenses in the trap cooled with solid carbon dioxide and acetone, is purified by fractionation through a 2 ft. x 9 mm vacuum-jacketed column, which is packed with glass helices and equipped with a still head kept at a low temperature with solid carbon dioxide in acetone. Pure monomer boils at -54°, and the amount obtained is at least 90 g. This compound must be protected from moisture and should be kept very cold until used. Because impurities are slowly formed by this very reactive monomer, storage for more than a week is not advisable, even at low temperatures.

D. Anionic Polymerization [6]

A 300 m, round-bottomed flask having two necks, one with a 29/26 spherical ground glass joint and the other with a T_s 10/30 joint, is connected through a larger neck to a glass tee made from 27 mm tubing. The tee is constructed so that one end of the crossbar is bent 90° parallel to the stem and is terminated with a 29/26 ground glass male joint. The other end of the crossbar is connected by a three-way stopcock to a vacuum pump and a source of dry nitrogen. A glass-coated stirrer bar is added to the flask, and the entire assembly dried by flaming as nitrogen is passed through the system. Nitrogen flow is continued as the equipment cools, and then 100 ml of diethyl ether dried over sodium is added through the 10/30 neck with a large hypodermic syringe. (The syringe is previously dried by baking in a vacuum oven at 125° and cooled in a stream of dry nitrogen.) A serum stopper is immediately placed in the 10/30 neck, the nitrogen stream to the tee and flask is closed, and a 100 ml flask with 100 g of thiocarbonyl fluoride is attached to the 29/26 male ground glass joint of the tee. The contents of the polymerization flask and the monomer flask are frozen with liquid nitrogen, and the system is evacuated. Then the monomer-containing flask is allowed to warm, and the thiocarbonyl fluoride distills into the polymerization flask. After all the monomer has been transferred, the liquid nitrogen bath around the polymerization flask is replaced with a solid carbon dioxide-acetone bath. The contents of the flask melt as they warm; when they are completely melted, dry nitrogen is admitted until the pressure inside the system is at atmospheric level. The stirrer is then started, and 5 drops of dimethylformamide is added from a No. 22 hypodermic needle. Polymer formation, which begins almost immediately, is completed after 2 h. The white, spongy polymer is removed from the flask and boiled in about 200 ml of water which contains 5 ml of 50% nitric acid. After drying, the weight of the polythiocarbonyl fluoride is 95-98 g. The molecular weight of the polymer is very high as indicated by an inherent viscosity of 4-6 dl/g for a 0.5% solution in chloroform (Note 6).

E. Free-Radical Polymerization

Free radicals can be used to homopolymerize thiocarbonyl fluoride and to copolymerize thiocarbonyl fluoride with a variety of unsaturated compounds.[7] Copolymerization with propylene is illustrative of this process.

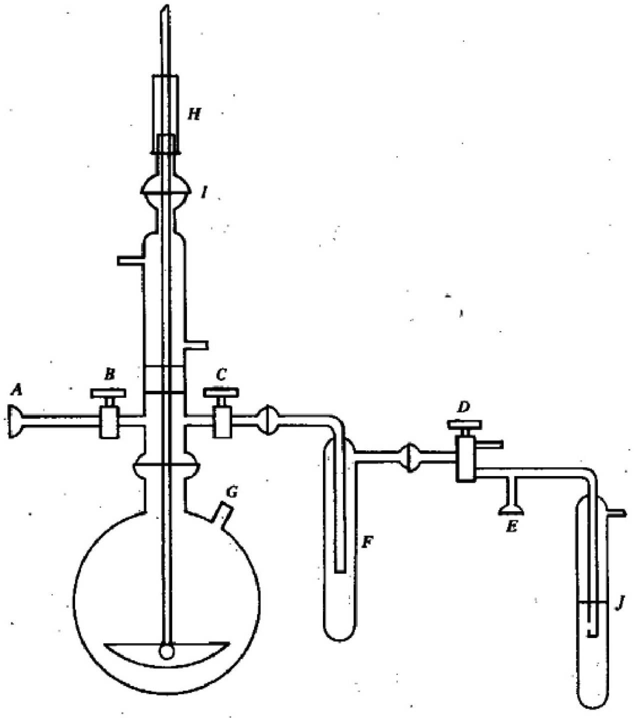

Figure 1. Apparatus for free-radical polymerization of thiocarbonyl fluoride.

The apparatus for this copolymerization is sketched in Fig. 1. The main elements are a 500 ml polymerization flask having a small neck at G for serum stopper and a True-Bore stirrer with a Teflon® paddle modified to hold a vacuum of about 0.3 mm. This modification involves sealing a 28/12 outer spherical joint to the top of the True-Bore condenser at I and slipping the corresponding inner spherical joint over the stirrer shaft and sealing it to the shaft with a rubber sleeve at H (Note 7). This joint is clamped together when the system is under vacuum and must be allowed to run free when the stirrer is operating. At A there is an 18/9 outer spherical joint; B and C are stopcocks, D is a two-way stopcock connected to a helium cylinder at E and to a vacuum pump, and J is a helium bubbler with mineral oil to about the level indicated. Before polymerization, all the glassware to the left of stopcock D is dried overnight in a vacuum oven at 125°. The apparatus is assembled hot under a stream of dry helium entering at E. The helium stream is maintained throughout preparation for polymerization and allowed to exit through the bubbler when not needed to fill the polymerization flask.

A cylinder of dichlorodifluoromethane (Freon®-12) is connected at A with a stainless steel line having an 18/9 stainless steel spherical joint. Stopcock D is turned to the vacuum pump, and the system is evacuated to about 0.4 torr. Next, the system is filled with helium by reversing stopcock D. This process is then repeated (Note 8). After being reevacuated, the polymerization flask is surrounded with a solid carbon dioxide-acetone bath, and the cylinder of Freon®-12 is opened carefully to allow the contents to distill into the flask until 300 ml has been collected (Note 9). The cylinder valve is closed, and helium is admitted through D as far as the cylinder valve. Then B is closed, and Freon®-12 freezes, the system is evacuated to the propylene cylinder and then filled with helium. Stopcock B is closed, and 70 ml of propylene is distilled from the cylinder into the graduated trap; then the propylene is cooled with a liquid nitrogen bath. Stopcock B is opened, the system is evacuated to about 0.4 torr, and stopcock C closed. The cooling bath is removed from the propylene trap; as the trap warms, propylene distills into the polymerization flask. The system is again filled with helium, stopcock B is closed, the propylene cylinder and graduated trap are removed, and a trap containing 35 ml of thiocarbonyl fluoride is connected at A. The thiocarbonyl fluoride is frozen with liquid nitrogen; then stopcock B is opened, and the system is evacuated, filled with helium, and evacuated again. Stopcock C is closed and the thiocarbonyl fluoride is allowed to warm, whereupon it distills into the polymerization flask. Stopcock B is closed, trap F is immersed in liquid nitrogen, stopcock C is opened, and the system is evacuated. The liquid nitrogen bath is removed from the polymerization flask, and a stream of acetone is directed at the outside of the flask to warm the contents and bring about melting as quickly as possible (Note 10). When melting is complete, the polymerization flask is reimmersed in liquid nitrogen, and the bath surrounding trap F is removed. Material collected in the trap redistills into the polymerization flask (Note 11). The system is again filled with helium, the liquid nitrogen bath surrounding the polymerization flask is replaced with a solid carbon dioxide-acetone bath, the clamp is removed from the stirrer joint at I, and the rubber sleeve at H is raised to free the stirrer shaft. As soon as the flask contents melt, the stirrer is started.

One and five-tenths milliliters of 0.5 *M* diethyl (ethylperoxy)borane (7.5×10^{-4} mol) in heptane[7] (*Caution!*, Note 12) is added with a syringe through the serum stopper at G, followed by similar addition of 0.7 ml of 1.86 M triethylborane (*Caution!*, Note 12, 13×10^{-4} mol) in heptane. Polymer formation begins almost immediately and is complete at the end of 2.5 h. Cold methanol is then added to the reaction mixture, and the whole mass is allowed to warm to room temperature. Freon®-12 and excess propylene are removed by distillation. The solid polymer is removed from the flask, dried, dissolved in 300 ml of chloroform, and reprecipitated by pouring the chloroform solution into methanol. After drying, the precipitated polymer weighs 50-51 g. It has a sulfur content of 32.02%, corresponding to a 2.34:1 mol ratio of thiocarbonyl fluoride to propylene.

2. Characterization

High molecular weight polythiocarbonyl fluoride[8] is soluble in chloroform and tetrahydrofuran. Inherent viscosities of 4-6 correspond to $\overline{M}_n$ of well over 500,000 and perhaps over 1,000,000. Inherent viscosities of 0.5% in chloroform solutions are preferred because the polymer is stable in chloroform but degrades quite rapidly in tetrahydrofuran. The degradation can be overcome if the tetrahydrofuran is saturated with dry hydrogen chloride. The polymer has a crystalline melting point of about 35°, at which temperature it changes from an opaque plastic to a very resilient elastomer. In the amorphous elastomeric form, it can be molded but only at a relatively high temperature.

Typical film-forming conditions are to heat the platens of a Carver press to 150° and press the polymer between aluminum sheets in the platens under a ram pressure of 10,000 lb. for several hours. As removed from the press, the films are elastomeric. At room temperature, they slowly crystallize to a non-elastomeric form. Reheating above 35° reconverts these films into the elastomeric form. An outstanding characteristic of this elastomer is high resilience (95% as measured by the Yerzley method, ASTM-D945). The T_g of the polymer measured by the torsion pendulum method is -118°.

The thiocarbonyl fluoride-propylene copolymer[8] is also soluble in chloroform. Inherent viscosities in 0.5% chloroform solutions typically fall between 2 and 3 dl/g. The compositions of these polymers range from about 2.2 molecules of thiocarbonyl fluoride per propylene molecule to much higher ratios. With a very large excess of propylene, copolymers having very nearly a 2:1 ratio can be prepared. The products are all soft polymers that stiffen only to a small extent at temperatures as low as -55°.

3. Notes

1. *Caution! Thiophosgene is very toxic. Because it can cause permanent injury by contact, ingestion, or inhalation, it should be used only in a forced-draft hood.* If it comes into contact with the skin, it should be immediately neutralized with ammonia, and the affected area washed with soap and water. If the eyes are affected, they should be washed with sodium bicarbonate solution.
2. If agitation is too vigorous, the dimer will remain suspended in the liquid and will block the entrance of ultraviolet light.
3. *Caution! Because ultraviolet light damages eyes, the apparatus should be shielded to prevent experimenter exposure. When working behind the shield, he should wear glasses that filter ultraviolet light.*
4. The product is colorless, has a refractive index of 1.3902^{26}-1.3919^{24}, and does not develop color when several drops are mixed with an alcohol solution of tripropylphosphine.
5. Stainless steel ball joints are friction-fitted to each end of the platinum tube, and the fit is sealed by silver soldering. A female joint on the upper end is connected to an appropriate glass joint on the T-tube, and the male joint on the lower end is connected to its opposite number on the stainless steel trap. The platinum tube was obtained under special agreement from Engelhard Industries, 700 Blair Road, Carteret, NJ 07008.
6. High inherent viscosities are obtained only if anhydrous conditions are maintained during polymerization.
7. The rubber sleeve is wired to both the stirrer shaft and the inner spherical joint for a tight fit.
8. This operation is repeated because it is important to remove all atmospheric oxygen. Any residual oxygen will react with the triethylborane that is to be used later and thereby will unbalance the stoichiometry of the redox initiating system.
9. It is convenient to mark the flask ahead of time at a level that corresponds to 300 ml.
10. This operation serves to degas the polymerization mixture and thus remove traces of atmospheric oxygen.
11. This material is presumed to be mostly thiocarbonyl fluoride. It is lower boiling than either Freon®-12 or propylene.
12. This solution can be made by cooling a 0.5 M solution of triethylborate (*Pyrophoric! Handle with extreme care.*) in heptane in a solid carbon dioxide-acetone bath and then carefully adding oxygen. Only 1 mol of oxygen reacts at this low temperature. After reaction, excess oxygen over the solution is replaced with helium or other inert gas. These solutions should be standardized by iodimetric titration.

4. Methods of Preparation

A number of methods have been developed for the preparation of thiocarbonyl fluoride.[9] In one method,[10] thiophosgene is chlorinated to trichloromethanesulfenyl chloride, followed by fluorination to obtain chlorodifluoromethanesulfenyl chloride, which is then dechlorinated. The reaction of bis(trifluoromethylthio)mercury and iodosilane gives trifluoromethylthiosilane, which decomposes to thiocarbonyl fluoride and fluorosilane.[11] Thiocarbonyl fluoride is formed when tetrafluoroethylene[5] or chlorofluoromethane[12] reacts with sulfur at high temperatures. Polymerization through the carbon-sulfur double bond, including thiocarbonyl fluoride, has been reviewed.[13]

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