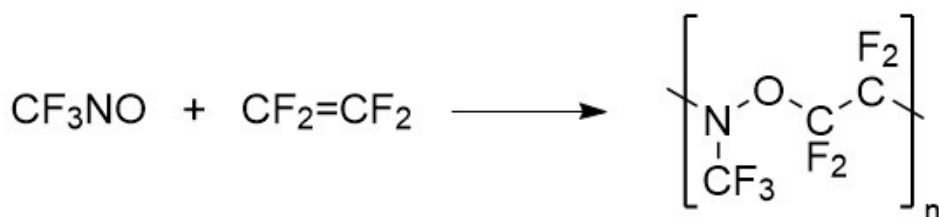


# Trifluoronitrosomethane-Tetrafluoroethylene Copolymer

Submitted by: C. D. Padgett and E. C. Stump<sup>1</sup>  
Checked by: G. H. Crawford and D. E. Rice<sup>2</sup>

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*Caution! Tetrafluoroethylene, particularly in the uninhibited state, has been reported to detonate unpredictably. All operations involving this compound should be carried out behind a suitable shield. For detailed information concerning the use of tetrafluoroethylene see Kirk-Othmer, Encyclopedia of Chemical Technology.<sup>3</sup> Although toxicity data on trifluoronitrosomethane has not been reported, it should be considered as extremely toxic and handled accordingly.*

## 1. Procedure

### A. Suspension Polymerization

A 2 l stirred autoclave with an internal cooling coil is charged with water (1000 g), lithium bromide (530 g), and magnesium carbonate (35 g, Note 1). It is then cooled to  $-183^\circ$ , evacuated, and charged with pure trifluoronitrosomethane (94 g, 0.095 mol, Note 2) and pure tetrafluoroethylene (95 g, 0.95 mol, Note 3). The autoclave is sealed and allowed to warm to  $-23^\circ$ , at which temperature it is maintained while the contents are stirred for 36 h. It is then vented in an efficient hood, allowed to warm to ambient temperature, and opened (Note 4). The product mixture is carefully acidified by the addition of 1:1 hydrochloric acid; there is no coagulation of polymer until the mixture becomes acidic. The polymer is removed from the reaction mixture and again washed with 1:1 hydrochloric acid to remove occluded magnesium carbonate. It is then dried in a vacuum desiccator to give 104 g (56% conversion) of an opaque white elastomeric gum. Attempts to effect solution in Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane) and FC-43 (perfluorotributylamine) were not successful, because some insoluble material remained even after stirring for several days (Notes 5 and 6).

### B. Bulk Polymerization

A 900 ml, soft-iron cylinder is evacuated, cooled to  $-183^\circ$ , and charged with pure trifluoronitrosomethane (53.5 g, 0.54 mol, Note 2) and pure tetrafluoroethylene (54.0 g, 0.54 mol, Note 3) and then sealed and placed in a  $-35^\circ$  bath for 24 h. The cylinder is then vented while it is allowed to warm to ambient temperature, opened, and found to contain 82 g (76% conversion) of a clear colorless gum (Note 4). Intrinsic viscosity in FC-43, was found to be 1.15 dl/g and, represents a molecular weight of  $1.5 \times 10^6$  (Notes 6 and 7).

## 2. Notes

1. The lithium bromide serves as an antifreeze and the magnesium carbonate as a suspending agent. No initiator is required, because the diradical trifluoronitrosomethane<sup>4</sup> itself serves as an initiator.
2. Unless the purity of the trifluoronitrosomethane is above 99%, low molecular weight polymers result. One of the major impurities that must be removed is trifluoronitromethane. Commercial trifluoronitrosomethane is purified by passing the gas through a train of traps containing, first, a 5% aqueous sodium hydroxide solution; then, calcium chloride; and finally, No. 4A Linde Molecular Sieves maintained at -78°. The purified trifluoronitrosomethane is collected in a trap cooled in liquid air.
3. Commercial tetrafluoroethylene contains a terpene inhibitor that must be removed before polymerization. Pure tetrafluoroethylene is obtained by passing the commercial product through concentrated sulfuric acid and condensing the gas in a trap cooled in liquid air. A laboratory preparation of tetrafluoroethylene is given in Kirk-Othmer, **Encyclopedia of Chemical Technology**.<sup>3</sup>
4. The unreacted monomers should be vented as the reaction mixture warms because they may react explosively at room temperature.
5. The insoluble material is polymeric, but it probably contains particles of magnesium carbonate that are extremely difficult to remove. A discussion of the problem connected with effecting solution of the copolymer is given by Ball, et al.<sup>5</sup>
6. NMR analysis showed that the product is a 1:1 copolymer consisting primarily of alternating units of trifluoronitrosomethane and tetrafluoroethylene. A study of structural irregularities frequently found in the copolymer by NMR analysis has been reported.<sup>6</sup>
7. A determination of molecular weight in relation to intrinsic viscosity in Freon 113 or FC-43 has been reported by the 3M Company.<sup>7</sup>

## 3. Methods of Preparation

As first reported by Barr and Haszeldine,<sup>8</sup> trifluoronitrosomethane and tetrafluoroethylene react exothermically at room temperature to give mostly perfluoro-2-methyl-1,2-oxazetidine with some low molecular weight copolymer of alternating trifluoronitrosomethane and tetrafluoroethylene units. At lower temperatures, the formation of higher molecular weight copolymer is favored.

The reaction was thoroughly investigated by the 3M Company<sup>4,7,9,10</sup> and later by Thiokol Chemical Corporation,<sup>11</sup> where, after carrying out polymerization in solution, bulk, and suspension systems, more than 200 lb of copolymer was made in successive suspension polymerizations. As much as 39 lb of copolymer was produced in a single run.

At Peninsular ChemResearch, Inc.,<sup>12</sup> it was found that for the production of small quantities (100 g) of the copolymer the bulk system was preferable because of simplicity plus easy isolation and purification of the product. The copolymers produced in these small-scale bulk systems were comparable to those produced in the suspension systems. The suspension system, however, is easier to scale up to larger amounts. Bulk polymerizations on a multipound scale have been successfully carried out at PCR, Inc. using a "thin film" polymerization technique.<sup>13</sup> In this process, the monomers are charged into metal cylinders that are then rotated about their longitudinal axis in a cold bath. As the polymer is formed, it is deposited as a film on the cylinder wall. In this way no large amounts of insulation are formed between unreacted monomer and coolant, and the heat of polymerization is efficiently dissipated.<sup>14</sup>

#### 4. References

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4. G. H. Crawford, D. E. Rice and B. F. Landrum, **J. Polym. Sci.**, A1, 565 (1963).
5. G. L. Ball, III, I. O. Salyer, J. V. Pustinger and H. S. Wilson, "Physical and Rheological Properties of Fluoronitroso Rubbers," Technical Report 67-63-CM, U.S. Army Natick Laboratories, Natick, MA.<sup>14</sup>
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10. D. E. Rice (3M Company), U.S. Patent 3,213,050 (October 19, 1965) [**Chem. Abstracts**, 59, 14126f (1963)]; G. H. Crawford, (3M Company), U.S. Patent 3,399,180 (August 27, 1968) [**Chem. Abstracts**, 60, 7009e (1964)].
11. J. Paustian et al, "Nitroso Rubber Research, Development and Production," final report under contract DA-19-129-AMC-69(X).<sup>14</sup>
12. E. C. Stump and C. D. Padgett, "Synthesis of New Fluorine-Containing Nitroso Compounds, Copolymers and Terpolymers," final report under contract DA-19-129-AMC-152(N) (AD 666801).<sup>12</sup><sup>14</sup>
13. C. D. Padgett and J. R. Patton, "Manufacturing Methods for Carboxy Nitroso Rubber," AFML-TR-72-185, final report under contract F-33615-71-C-1166, 1972.
14. Copies of these Government reports may be obtained by writing to Defense Documentation Center, Cameron Station, Alexandria, VA 22314.