TABLE I

UNSATURATED ESTERS OF TRINITROETHANOL

Compound	B.P.	M.P.	Yield, %	Formula	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
Trinitroethyl acrylate	80/2 mm.	...	41	$C_5H_5N_3O_8$	25.53	2.21	17.87	25.25	2.18	17.90
Trinitroethyl methacrylate	95/5 mm.	26	54	$C_6H_7N_3O_8$	28.92	2.83	16.87	28.60	2.76	16.78
Trinitroethyl crotonate	97/5 mm.	...	60	$C_6H_7N_3O_8$	28.92	2.83	16.85	29.90	2.88	16.32
Ditrinitroethyl fumarate	...	150	18	$C_8H_6N_6O_{16}$	21.71	1.35	19.00	22.05	...	18.45
Ditrinitroethyl itaconate	...	97	9	$C_9H_8N_6O_{16}$	23.68	1.75	18.42	...	...	18.00

Polytrinitroethyl N-isopropenylcarbamate. Three grams (0.019 mole) of trinitroethanol, 0.85 g. (0.01 mole) of isopropenyl isocyanate[4] and 0.005 g. of trinitrobenzene were allowed to stand 1 week at 24°, and the mixture was then diluted with ether. A small amount of material which did not dissolve was discarded. Washing the solution with water until the water layer was colorless, drying with anhydrous calcium sulfate, and distilling *in vacuo*, left a dark semisolid which did not distill at 100° and 2 mm. It was purified by washing with hot petroleum ether (b.p. 60–70°).

Anal. Calcd. for $C_6H_8N_4O_8$: C, 27.28; H, 3.05, N, 21.21. Found: C, 27.35; H, 3.38; N, 21.18.

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[4] D. D. Coffmann, U. S. Patent, **2,334,476** (Nov. 16, 1943).

Polymerization of Perfluorobutyne-2[1]

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High molecular weight polymers of perfluorobutyne-2 have not been previously reported although recent publications[2–4] have described the thermal and catalytic preparation of trimers and tetramers of this bis(perfluoroalkyl)acetylene.

It has now been found that perfluorobutyne-2 forms a new, thermally stable, high molecular weight polymer under the influence of γ-radiation. Exposure of perfluorobutyne-2 to a Co^{60} source for sixty-seven hours at a rate of 3.6×10^5 r./hr. produced, in quantitative yield, a white, inert, solid polymer that is not attacked or wetted by boiling concentrated sulfuric acid, concentrated nitric acid or 50% sodium hydroxide solution. The polymer is insoluble in ether, carbon tetrachloride, methyl alcohol, benzene, and all other common laboratory solvents.

Preliminary data indicate that the thermal behavior of this polymer, polyperfluorobutyne, is quite different from that of polytetrafluoroethylene. The decomposition curve obtained from a thermogravimetric analysis in nitrogen showed an initiation point at 425°, approximately the same temperature as was found for polytetrafluoroethylene; at the 50% decomposition point, however, the curve for polyperfluorobutyne was about 75° above that of polytetrafluoroethylene.

Pyrolysis of polyperfluorobutyne and polytetrafluoroethylene in an evacuated system showed a more marked difference in behavior. Production of gaseous products from polytetrafluoroethylene began at 430°; the temperature was raised to 550°, and after six hours, one-half of the polytetrafluoroethylene had formed gaseous products; three hours at 630° completed the decomposition of this polymer sample. In contrast, with the same heating schedule, polyperfluorobutyne did not form gaseous products until a temperature of 550° had been reached, and after four hours at 630° only about 40% of the weight of the sample was converted to gaseous products. This pyrolysis does not necessarily indicate greater thermal stability in polyperfluorobutyne but does show a type of decomposition different from that of polytetrafluoroethylene.

The infrared spectrum of polyperfluorobutyne resembled that of polytetrafluoroethylene in the position of its major absorption peaks; there was a shift, however, to somewhat higher frequencies than those found for polytetrafluoroethylene.

Elemental analysis confirmed the assumption that this new product is a polymer of perfluorobutyne and that neither carbon nor fluorine was lost by fragmentation in the irradiation process. An empirical formula of C_4F_6 was obtained from the analysis.

Assumptions of the structure of this new polymer are at the present only speculative. As perfluorobutadiene is known to polymerize rather easily,[5] the possibility that perfluorobutyne-2

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[1] This work was supported in part by the Office of Naval Research, Chemistry Branch, under Contract N-onr 580(03); NR 356-333 with the University of Florida. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] H. C. Brown, H. L. Gewanter, D. M. White, and W. G. Woods, *J. Org. Chem.*, **25**, 634 (1960).

[3] J. F. Harris, Jr., R. J. Harder, and G. N. Sausen, *J. Org. Chem.*, **25**, 633 (1960).

[4] J. F. Harris, Jr., U. S. Patent **2,923,746**, February 2, 1960.

[5] C. Slesser and S. R. Schram, *The Preparation, Properties, and Technology of Fluorine and Organic Fluorine Compounds*, McGraw-Hill Book Company, New York, New York, 1951, pp. 624–626.

might isomerize to perfluorobutadiene and subsequently polymerize was considered. A 1,4-linear polymerization of perfluorobutadiene would leave one carbon-carbon double bond in each monomer unit and this should be detectable in the infrared spectrum. The spectra of the new polymer showed no absorption in this region. The known homopolymers of perfluorobutadiene decompose at approximately 300° and thus do not resemble the polymer obtained in the present work.

There was no apparent phase change when polyperfluorobutyne was heated in a melting point tube to 500°. This fact and the lack of unsaturation seem to indicate a highly branched and highly cross-linked structure.

Small yields of polyperfluorobutyne (*ca.* 7%) have been obtained also in the thermal preparation of hexa(trifluoromethyl)benzene from perfluorobutyne-2.[2]

EXPERIMENTAL

Polyperfluorobutyne. Hexafluorobutyne-2 (2.25 g., 0.0139 mole) was condensed in a previously evacuated heavy-wall Pyrex tube 40 cm. × 1.3 cm. (*ca.* 50 ml. capacity). The reaction tube was then sealed and placed in the Co^{60} irradiation tank for 67 hr. to receive γ-radiation at a rate of 3.6×10^5 r./hr. (total dosage 2.4×10^7 r.).

The polymerization tube was then opened and 0.24 g. of unchanged perfluorobutyne-2 recovered. Remaining in the tube was 2.0 g. of a white, solid polymer. This polymer was refluxed with concd. sulfuric acid, with concd. nitric acid and with 50% sodium hydroxide solution with no apparent degradation. It was insoluble in ethyl ether, carbon tetrachloride, methyl alcohol, benzene, and a variety of other common laboratory solvents.

The infrared spectra of solid polyperfluorobutyne shows strong absorption peaks at 8.05, 8.36, and 8.50 μ; a weak absorption peak was found at 8.80 μ. These peaks are in the same region as the major peaks for polytetrafluoroethylene but at slightly higher frequencies.

Anal. Calcd. for C_4F_6: C, 29.63; F, 70.37. Found: C, 29.14; F, 70.27.

Comparative pyrolysis of polyperfluorobutyne and polytetrafluoroethylene. Polyperfluorobutyne, 2.0 g. and polytetrafluoroethylene, 2.0 g. were placed in individual heavy-wall Pyrex tubes and each tube was connected by Tygon pressure tubing to its own liquid-air cooled trap for condensation of gaseous pyrolysis products. The pyrolysis tubes were then bound together, placed in a vertical tube furnace, and the system evacuated.

The temperature of the furnace was raised to 100° and held at this temperature for 1 hr. while the system was pumped to remove residual moisture or air from the polymer samples. The furnace temperature was then raised to 524°, to 550°, and to 630° in steps as shown in Table I. Moles of gaseous products were determined in following the course of the reaction.

TABLE I

PYROLYSIS OF POLYPERFLUOROBUTYNE AND POLYTETRAFLUOROETHYLENE

		Moles, gaseous product, $\times 10^3$	
Temp.	Time, Hr.	Polytetrafluoroethylene	Polyperfluorobutyne
524–550	3.5	10.1	0.0
550	5.5	14.9	0.0
550	11.5	17.4	0.0
550–630	13.3	—	3.1[a]
630	14.5	20.0	—
630	16.3	(Completely pyrolyzed)	6.9[b]

[a] Av. mol. wt., 116. [b] Av. mol. wt., 123.

Pyrolysis of polytetrafluoroethylene resulted in an almost quantitative decomposition to tetrafluoroethylene. The infrared spectra of the polyperfluorobutyne gaseous decomposition products indicated that it was largely hexafluoroethane, though other compounds, at least one of which showed C=C unsaturation, were also present.

In addition to the volatile products, the pyrolysis of polyperfluorobutyne produced 0.95 g. of a tan powder, collected from the upper part of the pyrolysis tube and the connecting tubing that evidently contained unsaturation as it decolorized an acetone solution of potassium permanganate. Further investigation of this pyrolysis product will be reported in a subsequent publication.

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