Preparation of 3-Phenacylpyridine.—To a solution of potassium amide, prepared from potassium (0.4 mole, 15.6 g.) dissolved in 350–400 ml. of anhydrous liquid ammonia, was added 3-picoline (0.4 mole, 37.2 g.) over a 15-minute period. The resulting blood-red mixture was stirred for two hours and then methyl benzoate (0.2 mole, 27.2 g.), diluted with an equal volume of anhydrous ether, was added over a 20-minute period. After the ester was added, the reaction mixture, which was violet in color, was stirred for an additional hour and then the reaction was quenched by the addition of solid ammonium chloride (22.0 g., 0.41 mole). The liquid ammonia was replaced by the addition of 200–300 ml. of ether and warming the reaction mixture on a water-bath until the ether started to reflux. Then the mixture was cooled, poured onto crushed ice, made strongly acid with concentrated hydrochloric acid, and extracted with several portions of ether. The combined ether extracts were dried over Drierite. The aqueous phase was made basic by the addition of solid sodium carbonate, extracted with chloroform, and the extracts dried over sodium carbonate. The solvent was removed from the combined ether extracts to give 3.3 g. of benzoic acid, m.p. 121–122° alone and when mixed with an authentic sample, and 1.4 g. of benzamide, m.p. 129–130° alone and when mixed with an authentic sample. The chloroform extracts were distilled at atmospheric pressure to remove the solvent and recovered 3-picoline (22.0 g., b.p. 135–143°). The residue was then distilled in vacuum to give 18.0 g. of a white solid mixture of 3-phenacylpyridine and benzamide, b.p. 141–175° at 2 mm. The mixture was washed with cold ether in which the benzamide (3.0 g., m.p. 130° alone and when mixed with an authentic sample) is insoluble and the 3-phenacylpyridine is soluble. The ether washings were distilled to give 15.0 g. (38.2%) of 3-phenacylpyridine, b.p. 170–175° at 3 mm., m.p. 48.6–49.5° (from 30–60° petroleum ether); picrate, m.p. 168.6–169.6° (from 95% ethanol); oxime, m.p. 154.2–155.2° (from ethanol–benzene).

Alkylation of 3-Picolylpotassium with Benzyl Chloride.—Benzyl chloride (0.2 mole, 25.3 g.), dissolved in an equal volume of anhydrous ether, was added to 3-picolylpotassium (0.4 mole), prepared as described above, and the reaction mixture was then stirred for one hour, quenched with solid ammonium chloride, and processed to give 2.8 g. (7.7%) of 3-(2-phenylethyl)-pyridine, b.p. 126–130° at 3 mm. (*Anal.* Calcd. for $C_{13}H_{13}N$: C, 85.20; H, 7.15. Found: C, 85.23; H, 7.42. Picrate m.p. 144.2–145.2° (from 95% ethanol). *Anal.* Calcd. for $C_{19}H_{16}N_4O_7$: C, 55.53; H, 3.88; N, 13.59. Found: C, 55.11; H, 4.04; N, 13.81) and 5.0 g. of what is probably slightly impure dibenzyl-3-pyridylmethane, b.p. 198–201° at 3 mm. *Anal.* Calcd. for $C_{20}H_{19}N$: C, 87.86; H, 7.00. Found: C, 87.09; H, 8.18.

Wolff–Kishner Reduction of 3-Phenacylpyridine.—A solution of 3-phenacylpyridine (0.057 mole, 11.2 g.), hydrazine hydrate (4.7 ml. of an 85% solution), sodium hydroxide (4.7 g.) and diethylene glycol (75.0 ml.) was refluxed for six hours, cooled to room temperature, and extracted with several portions of benzene. The solvent was removed and the residue distilled in vacuum to give 4.8 g. (46.2%) of 3-(2-phenylethyl)-pyridine, b.p. 126–130° at 2.75 mm. This material gave a picrate, m.p. 144.2–145.2° alone and when mixed with a sample prepared from the compound obtained by the benzylation of 3-picolylpotassium.

Preparation and Wolff–Kishner Reduction of Benzyl 3-Pyridyl Ketone.—3-Cyanopyridine (0.18 mole, 18.3 g.), dissolved in 200 ml. of anhydrous ether, was added over a one-hour period to 0.18 mole of benzylmagnesium chloride. A yellow solid precipitated and the solution refluxed during the addition of the 3-cyanopyridine. The reaction mixture was stirred for 24 hours at room temperature and then 50 g. of ammonium chloride in 200 ml. of water and 50 ml. of concentrated hydrochloric acid were added. Stirring was continued for an additional 24 hours and the phases separated. The aqueous phase was refluxed for an additional two hours, cooled to room temperature, and extracted with ether. The combined ether extracts were dried over sodium sulfate and the solvent removed. Distillation of the residue gave 5.0 g. (12.7%) of benzyl 3-pyridyl ketone, b.p. 155–158° at 3 mm.; oxime, m.p. 124.5–125.5°[6]; picrate, m.p. 126–126.8°. *Anal.* Calcd. for $C_{19}H_{14}N_4O_8$: C, 53.52; H, 3.24. Found: C, 53.62; H, 3.43. When this ketone was treated with hydrazine hydrate, sodium hydroxide, and diethylene glycol and processed as described in the previous experiment, there was obtained 1.7 g. of an oil which gave a picrate, m.p. 144.2–145.2° alone and when mixed with a sample of the picrate obtained from the reduction product of 3-phenacylpyridine and from the benzylation of 3-picolylpotassium.

Pittsburgh 13, Pennsylvania

[Contribution from the Research Institute of Temple University]

The Copolymerization of Highly Fluorinated Olefins with Ethylene Oxide[1]

By Murray Hauptschein[2a] and Joseph M. Lesser[2b]

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The copolymerizations of perfluoropropene and trifluorochloroethylene with ethylene oxide have been effected and studied in the presence of ultraviolet light or di-*t*-butyl peroxide (DTBP) as the initiators. Vinylidene fluoride did not copolymerize with ethylene oxide using DTBP as the initiator but the conversion to vinylidene fluoride homopolymer has been shown to be increased greatly by the presence of ethylene oxide. Perfluoropropene and vinylidene fluoride in the presence of DTBP react with ethyl ether to form telomers.

The purpose of this research was to investigate the possibility of synthesizing highly fluorinated polyether type polymers by the interpolymerization of fluorinated olefins with ethylene oxide. The only references to olefin–alkylene oxide copolymers are in the recent patent literature.[3a,b] Ethylene and vinylidene chloride formed copolymers with aliphatic epoxides utilizing azine catalysts at 200–300° in the former case, and using persulfate or peroxide aqueous emulsion systems in the latter case. In general, the copolymers contained a relatively small percentage of alkylene oxide units, which in the case of ethylene were shown to be joined together rather than to be interspersed among ethylene units.

Perfluoropropene, chlorotrifluoroethylene and vinylidene fluoride were the olefins investigated in

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[1] The work herein reported was carried out on Project NR 055-354 between the Office of Naval Research and the Research Institute of Temple University. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] (a) Pennsylvania Salt Mfg. Co., Whitemarsh Research Laboratories, Chestnut Hill P. O. Box 4388, Philadelphia 18, Pa.; (b) part of a thesis to be submitted to Temple University in partial fulfillment of the requirements for the Masters degree.

[3] (a) D. D. Coffman, U. S. Patent 2,516,960 (August 1, 1950); (b) G. W. Stanton and C. E. Lowry, U. S. Patent 2,556,048 (June 5, 1951).

the present study. It was found that only the first two completely halogenated monomers readily copolymerized with ethylene oxide.

Perfluoropropene has been converted to a trimer, tetramer and a pentamer by photochemical polymerization in a silica vessel,[4] and to a trimer or tetramer by exposure to irradiation of a nuclear reactor.[5] Aside from these references there is no record of perfluoropropene being homopolymerized, in spite of considerable study,[6] although copolymerization with "electron-rich" olefins has been shown to occur quite readily.[6]

We have now found that perfluoropropene will polymerize with ethylene oxide in the presence of di-*t*-butyl peroxide (DTBP) or ultraviolet light as the initiators. These interpolymers contain up to 50 mole % of perfluoropropene. The light-catalyzed reactions yielded much purer copolymers since there were no possible contaminants from the peroxide promoter. At initial ethylene oxide–perfluoropropene ratios of 1:1 to 1:2, fair yields of essentially 1:1 clear, viscous copolymers were obtained in the photochemical polymerizations. At an initial ratio of 4:1 the resulting copolymer contained about 30 mole % of perfluoropropene. In all experiments moderately good conversions (about 40–50% and higher) were obtained within five days exposure to ultraviolet light even though heavy-wall Pyrex (rather than silica) vessels were used. The composition of the true copolymers was established by elementary analysis with added support from infrared spectral examination. The 1:1 copolymer was insoluble in water but soluble in organic solvents such as ethyl ether, dichloromethane and benzene.

That the monomeric units of this 1:1 copolymer are interspersed uniformly and most probably are made up of alternating head-to-tail linkages, *i.e.*, $(-C_3F_6-OCH_2CH_2-)_n$, is supported by the following facts. This copolymer does not react noticeably with concentrated sulfuric acid nor is it cleaved by heating at 150° for 24 hours in a sealed tube containing excess 47% hydriodic acid. This is in contrast to the known susceptibility of polyethylene glycols, *i.e.*, $(-CH_2CH_2-OCH_2CH_2-)_n$, to these reagents. The fact that the infrared spectra of five different samples of copolymer (of varying degrees of polymerization) were identical is additional evidence that the repeating units are in a definite sequence, rather than being distributed at random.

In a similar manner, copolymers of trifluorochloroethylene and ethylene oxide have been prepared. Both the photochemical and DTBP induced copolymerizations gave excellent yields of product. For an initial ethylene oxide–trifluorochloroethylene molar ratio of 1.9:1 (DTBP run), the waxy polymer contained 56 mole % of chlorotrifluoroethylene. In the photochemical experiments initial ratios of 3.7:1 and 1:1.2 afforded jelly and glass-like copolymers containing 46.8 and 62.9 mole % of chlorotrifluoroethylene, respectively. These copolymers were insoluble in water, but soluble in organic solvents such as ethyl ether, dichloromethane and benzene. (Trifluorochloroethylene homopolymer is insoluble in benzene.) In contrast to the perfluoropropylene copolymer, the chlorotrifluoroethylene copolymer was attacked to a noticeable extent by concentrated sulfuric acid and 47% hydriodic acid at 150°.

Vinylidene fluoride is known to polymerize in rather poor conversions (about 20%) in the presence of acetyl peroxide[7] and benzoyl peroxide.[8] We have found that when DTBP was used as the promoter, polyvinylidene fluoride was formed in 54% conversion. Of much greater interest, however, was the fact that although vinylidene fluoride and ethylene oxide showed almost no tendency to copolymerize in the presence of DTBP at temperatures up to 140°, the conversion to vinylidene fluoride homopolymer was increased substantially to 70–100% for mole ratios of ethylene oxide to vinylidene fluoride over the wide range of 0.04 to 5.1. The yield is independent of the proportion of ethylene oxide present.

It is known that the presence of a suitable liquid in the system, in addition to the monomers added for interpolymerization, may afford a better environment for copolymerization. An experiment was therefore carried out similar to the above but in the presence of a large excess of ethyl ether. It was found, however, that a "telomerization" reaction with ethyl ether predominated. The free radical catalyzed reactions of tetrafluoroethylene and polyfluoroethylenes of general formula $CF_2{=\!=}CX_2$ (where X may be F, Cl or Br) with aliphatic ethers have been reported.[9] The extension of this reaction to $CF_2{=\!=}CH_2$ is now disclosed. Telomers of average ratio $CF_2{=\!=}CH_2{:}(C_2H_5)_2O$ of 3:1 and 4:1 have been characterized.

Of particular interest was the fact that the relatively non-polymerizable perfluoropropene interacted with ethyl ether in the presence of DTBP at 148° to give a 2:1 telomer. A possible structure is $C_2H_5OCH(CH_3)-[CF_2-CF(CF_3)]_2H$ which may be formed by abstraction of an α-hydrogen atom of the ether, and addition of the resulting $C_2H_5OCH(CH_3)$ radical to the CF_2 group of perfluoropropene, etc.[10] The findings of La Zerte and Koshar[11] on the free radical catalyzed addition of terminally unsaturated perfluoroölefins with alcohols ($R_fCF{=\!=}CF_2 + RCH_2OH \rightarrow R_fCFHCF_2CRHOH$ where R_f = perfluoroalkyl) support these conclusions.

Finally, since ethylene oxide did not readily copolymerize with vinylidene fluoride using DTBP as an initiator, two free radical catalysts containing hydroxyl groups, which are known to cause polymerization of ethylene oxide, were tried. The use of *t*-butyl hydroperoxide and succinic acid peroxide, however, resulted in the homopolymerization of both monomers rather than in a true copolymerization.

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(4) R. N. Haszeldine, *J. Chem. Soc.*, 3559 (1953).

(5) B. Manowitz, *Nucleonics*, **11**, 18 (1953).

(6) R. M. Adams and F. A. Bovey, *J. Polymer Sci.*, **9**, 481 (1952).

(7) E. T. McBee, H. M. Hill and G. B. Bachman, *Ind. Eng. Chem.*, **41**, 70 (1949).

(8) W. E. Hanford and D. E. Sargent in "Organic Chemistry," Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1953, p. 1115.

(9) W. E. Hanford, U. S. Patent 2,433,844 (January 6, 1948).

(10) See W. H. Urry, F. W. Stacey, E. S. Huser and O. O. Juveland, THIS JOURNAL, **76**, 450 (1954), for a detailed discussion of a related mechanism. Also see ref. 4 where radical attack is shown to be exclusively on the CF_2 group of hexafluoropropene.

(11) J. D. La Zerte and R. J. Koshar, THIS JOURNAL, **77**, 910 (1955).

Experimental[12]

Monomers.—Perfluoropropene was prepared in 93% yield by a previously reported procedure.[13,14] The pure olefin was transferred *in vacuo* into a stainless steel cylinder for storage. Vinylidene fluoride and chlorotrifluoroethylene were purchased from General Chemical Division. Ethylene oxide (99.5% pure) was obtained from the Matheson Company.

General Procedure.—The peroxide-catalyzed polymerizations were conducted in stainless steel bombs of approximately 250-ml. capacity under autogenous pressures. The gaseous olefins were introduced *in vacuo* into the bomb containing the required amounts of ethylene oxide and catalyst. The photochemical polymerizations were carried out in heavy-wall Pyrex vessels of 30–40 ml. capacity, placed 5 cm. from a Hanovia ultraviolet lamp used without the Woods filter. The reaction tubes were filled and sealed in an atmosphere of dry nitrogen.

In all experiments, prior to analysis, the polymers were washed exhaustively with water to remove any polyethylene glycols, *i.e.*, homopolymer of ethylene oxide, which may have been present. In most cases it was found that ethylene oxide homopolymer was not formed and, therefore, washing was actually unnecessary. Polymer compositions were established by elementary analysis, preference being given to the more accurately determinable carbon content.

The Polymerization of Vinylidene Fluoride in the Presence of Varying Mole Ratios of Ethylene Oxide.—Table I summarizes the results obtained for ten representative runs. The catalyst was DTBP (Lucidol Division) and the temperature was maintained at 135 ± 5°. The quantities of vinylidene fluoride used varied from 0.2–0.7 mole. In all runs the polymer had a softening point of approximately 150°, which did not change after washing with vigorously boiling water for several hours. Since the weight of polymer did not decrease after the washing period, the original crude material did not contain ethylene oxide homopolymer. The infrared spectra of the polymer obtained from both the 5.1:1 and 4.8:1 ethylene oxide–vinylidene fluoride mole ratio runs were identical to the spectrum of the polymer obtained in the first run of Table I, *i.e.*, for homopolymerization conditions. Thus, only homopolymerization of vinylidene fluoride occurred in all the runs.

TABLE I

THE POLYMERIZATION OF VINYLIDENE FLUORIDE IN THE PRESENCE OF VARYING MOLE RATIOS OF ETHYLENE OXIDE. TEMP. 135 ± 5°, CATALYST DTBP

Mole ratio C_2H_4O: $CF_2{=}CH_2$	Catalyst, % by wt.[a]	Reacn. time, hr.	Conversion, %[a]	Carbon, %	Hydrogen, %
0	9.1	140	53	38.5[b]	3.5[b]
0	7.9	60	54	...	..
0.04	9.1	24	84	...	..
.14	7.9	19	80	38.2	3.3
.46	1.3	60	71	...	..
.50	7.9	18	90	...	..
1.4	6.8	18	83	...	..
1.7	10	96	100	39.6	3.6
4.8	14	60	87	39.6	3.5
5.1	6.7	19	80	38.2	3.2

[a] Based on vinylidene fluoride only. [b] Calcd. for $-(CF_2\text{-}CH_2)_n-$, C, 37.51; H, 3.15. The higher carbon–hydrogen values found are undoubtedly due to the incorporation of end groups from the catalyst.

t-Butyl hydroperoxide and succinic acid peroxide (both obtained from the Lucidol Division) were also employed as initiators.

Vinylidene fluoride (38 g., 0.59 mole) and ethylene oxide (47 g., 1.07 moles) were polymerized in the presence of 4.4 g. of *t*-butyl hydroperoxide at 120° for 4 days. The crude polymer (39 g.) was washed with boiling water for several hours, and 20.5 g. (54%) of slightly impure polyvinylidene fluoride, softening point *ca.* 140° (C, 39.96, 39.90; H, 3.61, 3.50) were isolated.

Vinylidene fluoride (38 g.) and ethylene oxide (47 g.) were polymerized in the presence of 4 g. of succinic acid peroxide at 140° for 19 hours. The crude polymer (32 g.) was washed with boiling water, and 27.5 g. (72%) of slightly impure polyvinylidene fluoride (C, 39.77; H, 3.58) were isolated.

In both of the above experiments the water extract contained polyethylene glycols resulting from the homopolymerization of ethylene oxide.

An experiment was carried out in the presence of 100 ml. of ethyl ether; molar quantities of vinylidene fluoride and ethylene oxide as well as 4% DTBP were used. An ethereal solution of the crude product was extracted exhaustively with water, dried over anhydrous sodium sulfate, and rectified. Thirty-four grams of product boiling above 50° at <1 mm. were obtained, most of which boiled at 45–70° at <0.5 mm., $n^{18}\text{D}$ 1.376; C, 44.22, 44.29; H, 5.38, 5.53. This product is probably a telomer with ratio vinylidene fluoride to ethyl ether of 3–4:1. See below for a description of this telomerization reaction in the absence of ethylene oxide.

The Reaction of Vinylidene Fluoride with Ethyl Ether.—Vinylidene fluoride (38 g.), ethyl ether (50 g.), and DTBP (2 g.) were heated in a pressure vessel at 130° for 60 hours. In addition to the isolation of 6 g. of vinylidene fluoride homopolymer, two fractions (6 g. each) of wide boiling range were characterized: Fraction 1, b.p. 40–70° at 1 mm., $n^{21}\text{D}$ 1.3676, d^{22}_4 1.220, d^0_4 1.246. *Anal.* Calcd. for $3CF_2{=}CH_2{\cdot}(C_2H_5)_2O$: C, 45.11; H, 6.06. Found: C, 44.89; H, 5.64. Fraction 2, b.p. 70–140° at 1 mm., $n^{21}\text{D}$ 1.3746, d^{20}_4 1.316, d^0_4 1.339. *Anal.* Calcd. for $4CF_2{=}CH_2{\cdot}(C_2H_5)_2O$: C, 43.64; H, 5.49. Found: C, 43.35; H, 5.31.

Thus the average composition of these telomers is 3:1 and 4:1, respectively. In addition, there were obtained a large amount of lower boiling material (mostly 30–40° at 18 mm.), and 3 g. of a residue, which probably contained telomers of lower and higher molecular weights, respectively.

The Reaction of Perfluoropropene with Ethyl Ether.—Perfluoropropene (41 g.), ethyl ether (50 ml.) and DTBP (2 g.) were heated in a pressure vessel at 148° for 60 hours. Approximately 30 g. of the product was found to boil over 100°. This material was rectified in a Podbielniak column. Approximately 5 g. of material, b.p. 125–135° (middle cut, b.p. 132°, $n^{19}\text{D}$ 1.3342) were obtained, but the principal fraction (16 g.) was found to be a 2:1 telomer, b.p. 165–175° (middle cut b.p. 173°, $n^{19}\text{D}$ 1.3262, d^{22}_4 1.483, d^0_4 1.516).

Anal. Calcd. for $2C_3F_6{\cdot}(C_2H_5)_2O$: C, 32.10; H, 2.69; F, 60.93. Found: C, 32.51; H, 2.76; F, 59.9.

The infrared spectra of this telomer demonstrated the absence of double bonds and hydroxyl groups. The principal bands (in microns) are: 3.37, 6.84, 7.12, 7.51, 7.8, 8.1, 8.5–8.6, 9.05, 9.62, 9.8, 10.6, 11.55 (shoulder), 11.7, 12.01, 13.36, 13.8 (small), 13.99, 14.7–14.8.

The Photochemical Homopolymerization of Chlorotrifluoroethylene.—Chlorotrifluoroethylene, sealed in a small Pyrex tube so that there was much liquid phase, was exposed to ultraviolet light for 66 hours. A white solid polymer, m.p. 190–205°, was obtained in approximately 50% conversion. *Anal.* Calcd. for $(C_2F_3Cl)_n$: C, 20.62. Found: C, 20.98.

The Photochemical Copolymerization of Chlorotrifluoroethylene with Ethylene Oxide.—Chlorotrifluoroethylene (9.5 g., 0.082 mole) and ethylene oxide (13.4 g., 0.3 mole) were sealed in a Pyrex tube and exposed to ultraviolet light for 63 hours. A colorless viscous liquid (16.5 g.) was collected. No unreacted chlorotrifluoroethylene was detected. The liquid was dissolved in dichloromethane and extracted exhaustively with water. The lower layer was separated, dried with anhydrous sodium sulfate, and the methylene chloride evaporated off. The jelly-like solid was heated at 100° *in vacuo* in an Abderhalden pistol. *Anal.* Found: C, 30.83, 30.80; H, 2.83, 3.07. This corresponds to 46.8 mole % of chlorotrifluoroethylene in the copolymer.

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(12) Microanalyses by Clark Microanalytical Laboratory and Schwarzkopf Microanalytical Laboratory. The infrared analyses were taken with a Baird Associates Infrared Recording Spectrophotometer of Samuel P. Sadtler & Sons, Inc.

(13) J. D. La Zerte, L. J. Hals, T. S. Reid and G. H. Smith, *ibid.*, **75**, 4525 (1953).

(14) We are indebted to Mr. E. A. Nodiff of this Laboratory for carrying out this procedure and for other technical assistance.

Another experiment was carried out simultaneously under identical conditions, except that 14.2 g. (0.12 mole) of chlorotrifluoroethylene and 4.4 g. (0.1 mole) of ethylene oxide were used. Only traces of unreacted olefin were detected. The glass-like polymer (almost 100% yield) was treated as above. *Anal.* Found: C, 26.76, 26.85; H, 1.76, 1.81. This corresponds to 62.9 mole % of chlorotrifluorethylene in the copolymer.

The DTBP Catalyzed Copolymerization of Chlorotrifluoroethylene and Ethylene Oxide.—Chlorotrifluoroethylene (59.0 g., 0.51 mole), ethylene oxide (43 g., 0.98 mole) and DTBP (3.8 g.), were heated at 125° for 60 hours. A jelly-like polymer (72 g.), was formed. After washing and drying as above the resulting translucent wax was analyzed. Found: C, 28.48, 28.31; H, 2.08, 2.13. This corresponds to 56.0 mole % of chlorotrifluoroethylene in the copolymer.

The DTBP Catalyzed Copolymerization of Perfluoropropene and Ethylene Oxide.—Perfluoropropene (62 g.), ethylene oxide (47 g.) and DTBP (6 g.), were heated at 145° for 72 hours. Approximately 54 g. of an oily polymer, > b.p. 45° at < 0.5 mm. were collected. Approximately 35% of this material boiled at 45–100° at 0.5 mm., n^{24}D 1.3534. *Anal.* Found: C, 33.19. 32.98; H, 2.85. 2.79. This corresponds to 41.0 mole % of perfluoropropene in the copolymer. Approximately 50% of the crude polymer boiled at 100–145° at 0.5 mm., n^{24}D 1.3779, d^{22}_4 1.466, d^0_4 1.494. *Anal.* Found: C, 35.90, 35.74; H, 3.40, 3.14; F, 45.63, 45.57. This corresponds to 31.8 mole % of perfluoropropene in the copolymer.

The Photochemical Copolymerization of Perfluoropropene with Ethylene Oxide.—Perfluoropropene (27.0 g., 0.18 mole) and ethylene oxide (9.0 g., 0.204 mole), sealed in a Pyrex tube, were irradiated with ultraviolet light for 133 hours. (The sealed tubes were placed in wire gauze holders to lessen the chances of breakage of the mercury vapor tube in case of an explosion. Actually a number of tubes exploded in similar runs.) Approximately 16 g. of a clear, viscous polymer, b.p. > 60° at <0.5 mm., was collected. After washing with water and drying the product was rectified. Approximately 30% of this material boiled at 100–110° at <0.5 mm., n^{20}D 1.3699. *Anal.* Found: C, 33.63; H, 2.74. This corresponds to 39.0 mole % of perfluoropropene in the copolymer. Approximately 15% of the crude polymer boiled at 110–115° at <0.5 mm., n^{20}D 1.3631. *Anal.* Found: C, 32.56; H, 2.49. This corresponds to 43.1 mole % of perfluoropropene in the copolymer. Approximately 30% of the total crude boiled at 115–180° at 0.5 mm., n^{20}D 1.3620. *Anal.* Found: C, 31.96, 31.76; H, 2.27, 2.11; F, 56.87, 56.89. This corresponds to 46.1 mole % of perfluoropropene in the copolymer. The dark residue (*ca.* 25% of total), b.p. above 180° at 0.5 mm. was not investigated further.

The infrared spectra of these three fractions as well as two other (photochemically initiated) similar high boiling fractions, n^{20}D 1.3584 and 1.3594, respectively, were identical with the exception of certain intensity changes, particularly for the band at 3.4 μ, which varied as would be expected from the carbon–hydrogen analyses. It was significant to note that no band was present in the C=C stretching vibration region. Since Haszeldine[10] observed a strong band at 5.77 μ for the trimer to pentamer obtained from the photochemical homopolymerization of perfluoropropene, no homopolymerization of perfluoropropene could have occurred in the present case. The spectra also confirmed the absence of any ethylene oxide homopolymer. The principal absorption bands (in microns) are: 3.4, 6.83, 7.12, 7.79, 8.4–8.6, 9.06, 11.92, 12.82, 14.3 (shoulder), 14.7.

Perfluoropropene alone did not polymerize at all when exposed to ultraviolet light in a sealed Pyrex vessel (rather than a silica one[10]) for 120 hours. There was no reaction also, when equal volumes of perfluoropropene and ethylene oxide, sealed in a Pyrex tube, were heated for several hours at 100°, in the absence of ultraviolet light. Finally, no more than a trace of polymer was obtained when perfluoropropene in the presence of a trace of ethylene oxide was either heated in the presence of DTBP or exposed to ultraviolet light. This behavior should be compared with the effect of trace amounts of ethylene oxide on the homopolymerization of vinylidene fluoride.

Another experiment was carried out using 0.20 mole of perfluoropropene and 0.11 mole of ethylene oxide, which were irradiated with ultraviolet light for eight days. The bulk of the product was found to be a 1:1 copolymer. The two principal cuts boiled at 60–100° at <0.5 mm., n^{23}D 1.3410, % C, 31.2 (for a 1:1 copolymer, % C 30.94), and at 100–150° at <0.5 mm., n^{28}D 1.3568, % C, 31.2 (*i.e.*, 1:1 copolymer), % F, 60.1 (for a 1:1 copolymer, % F 58.74).

Ethylene oxide and perfluoropropene in the molar ratio of 4:1 were exposed to ultraviolet light for 64 hours. Only traces of unpolymerized olefin were recovered. The principal high boiling products after washing and drying were (a) b.p. 100–115° at <0.5 mm., n^{22}D 1.3840, % C, 36.95 (*i.e.*, 28.5 mole % of perfluoropropene) and (b) b.p. 115–150° at <0.5 mm., n^{21}D 1.3785, % C, 35.75 (*i.e.*, 32.0 mole % of perfluoropropene).

Kinematic Viscosities of Two Perfluoropropene–Ethylene Oxide Copolymers.—Viscosities were determined with calibrated Ostwald–Cannon–Fenske-type viscosimeters.

The DTBP catalyzed copolymer, n^{24}D 1.3534 (see above) gave experimental values of 2.22 centistokes (cts.) at 212.0°F., 61.15 cts. at 62.0°F., and 279.3 cts. at 32.0°F. These values lie on a nearly straight line when plotted on an ASTM (D341-43) viscosity chart. The slope of this line, showing the temperature dependence of viscosity, *i.e.*, the so-called ASTM slope, was 1.1.

A photochemically produced copolymer, n^{21}D 1.3631, b.p. 90–180° at <0.5 mm., gave values of 4.52 cts. at 290°F., 16.49 cts. at 212.0°F., and 186.9 cts. at 141.5°F. The ASTM slope was 1.0.

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PHILADELPHIA. PENNSYLVANIA