TABLE III

CONSTANT COPOLYMERIZATION MIXTURE[a]

60.6 wt.% dichlorostyrene, 39.4 wt.% butadiene

Reaction time, hr.	Yield, %	$[\eta]$ at 30°	k'	$\overline{M}_n \times 10^3$	μ at 27°	Polymer Chlorine, %		Polymer Dichlorostyrene, %
15	7.2	0.64_2	0.36_4	90	0.42_1	24.99	24.75	60.7
25	11.6	$.66_6$	$.34_7$	100	$.40_4$	...	...	..
47	17.6	$.72_5$	$.36_4$	130	$.39_7$	...	...	..
57	31.4	$.89_0$	$.35_1$	160	$.39_5$	24.39	24.25	59.4

[a] In presence of 0.1 weight per cent. of benzoyl peroxide at 70°.

polymer composition is shown by the analytical results secured at the 7.2 and 31.4% extremes of conversion. The intrinsic viscosities were measured, and were found to remain relatively constant up to about 12% conversion and then showed a marked rise, a 40% increase being found at 31% conversion. A similar set of measurements with dichlorostyrene alone showed that the intrinsic viscosities were constant up to 21.0% conversion, the intrinsic viscosity being 0.77 ± 0.03. The number average osmotic molecular weights of the copolymers were determined and ranged from 90,000 to 160,000, increasing with degree of conversion. The viscosity, k', and osmotic pressure, μ, constants[6] indicate, among other properties, the shapes and flexibilities of the polymer in the solvent, toluene; they were found to be constant within experimental error.

Acknowledgment.—The authors wish to express their appreciation to the Dow, Monsanto and du Pont companies for the monomer samples; to Dr. Carl Tiedcke for micro-analyses of the butadiene copolymers, and to Miss Doris Linberg for her assistance in much of the laboratory work.

Summary

Experimental results on two olefin–diene copolymer systems show that the simple copolymer composition equation is obeyed. The values of α and β for the systems styrene–chloroprene, and dichlorostyrene–butadiene have been determined. An investigation was made of the change in viscosity and molecular weight with increasing degree of conversion of the constant copolymerizing mixture of the latter system.

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[6] Huggins, *Ind. Eng. Chem.*, **35**, 216 (1943); *J. Phys. Chem.*, **42**, 911 (1938); **43**, 439 (1939).

BROOKLYN, N. Y. RECEIVED MAY 27, 1946

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

The Preparation and Polymerization of Vinyl Fluoride

BY A. E. NEWKIRK

The polymerization of vinyl fluoride has been reported to be difficult or impossible.[1,2,3] There seemed to be no theoretical basis for this difficulty, and as the polymer should have useful properties an investigation was undertaken to prepare and polymerize vinyl fluoride.

Preparation of Vinyl Fluoride

Vinyl fluoride was prepared first by Swarts[4] by the reaction between 1,1-difluoro-2-bromoethane and zinc. This general reaction between an active metal and a halogenated ethane has been used by other investigators for the preparation of vinyl fluoride.[5,6,7,8] Swarts[9] has also used phenylmagnesium bromide in ether, and alcoholic potassium iodide, in place of the metal for removing halogen. The reaction of vinyl chloride or bromide with a metal fluoride is not described in the literature, and was tried with but slight success. Vinyl fluoride has been prepared by the addition of hydrogen fluoride to acetylene both without a catalyst[10,11,12], and with the aid of mercury (II) oxide on activated carbon.[13]

The catalytic reaction in the vapor phase over catalysts of mercury (II) chloride, or mixtures of this and barium chloride, supported on active carbon was used to prepare vinyl fluoride for the polymerization experiments. The latter catalyst was superior in all respects. It gave higher conversions, permitted higher space velocities, and had longer life. Typical results are shown in Table I. The mercury (II) chloride catalyst was active for from eight to twenty-four hours, after which its activity dropped to zero. Globules of mercury were observed in the spent catalyst.

The crude gas from the reactor, after removal of hydrogen fluoride, was mixed with ethane and fractionally distilled at atmospheric pressure in a low-temperature column. The addition of ethane permitted the removal of acetylene as an azeotrope.[14] The vinyl fluoride fractions had a purity

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[1] H. W. Starkweather, THIS JOURNAL, **56**, 1870 (1934).

[2] F. Schloffer and O. Scherer, German Patent 677,071 (1939).

[3] C. A. Thomas, U. S. Patent 2,362,960 (1944).

[4] F. Swarts, *Bull. acad. roy. Belg.*, 383 (1901).

[5] F. Swarts, *ibid.*, 728 (1909).

[6] A. L. Henne and T. Midgley, Jr., THIS JOURNAL, **58**, 882 (1936).

[7] A. L. Henne, *ibid.*, **60**, 2275 (1938).

[8] P. Torkington and H. W. Thompson, *Trans. Faraday Soc.*, **41**, 236 (1945).

[9] F. Swarts, *Bull. soc. chim.*, [4] **25**, 145 (1919).

[10] H. Plauson, U. S. Patent 1,425,130 (1922).

[11] A. V. Grosse and C. B. Linn, THIS JOURNAL, **64**, 2289 (1942).

[12] A. L. Henne, "Organic Reactions," Vol. 2, John Wiley and Sons, New York, N. Y., 1944, p. 66.

[13] J. Söll, German Patent 641,878 (1937), British Patent 469,421 (1937), U. S. Patent 2,118,901 (1938).

[14] W. A. McMillan, THIS JOURNAL, **58**, 1345 (1936).

Table I

Preparation of Vinyl Fluoride

Catalyst		$HgCl_2$	$HgCl_2$-$BaCl_2$	$HgCl_2$-$BaCl_2$
Temp., °C.		97–103	97–104	83–109[a]
Vapor input cc./min.	HF	460–540	460	860
	C_2H_2	440	440	880
Grams crude per hour		27.3	47.3	93.5
Wt. % vinyl fluoride		51.5	82.0	81.9
Wt. % 1,1-difluoroethane		16.0	4.1	..

[a] The reactor heater was disconnected at the start of this run, T = 83°. The temperature in the middle of the reactor rose gradually to 109° during 5.7 hr.

of 94 mole per cent. or better and were stored in steel cylinders. No trouble was experienced with samples of such purity stored for periods of over six months.

Experimental

Substitution Reaction.—Vinyl chloride was passed over a mixture of antimony (III) fluoride and antimony (V) chloride heated in an iron tube at temperatures from 26 to 470° without the formation of vinyl fluoride. Mercury (II) fluoride reacted with vinyl chloride at 200° to produce a very small amount of vinyl fluoride. Vinyl bromide and mercury (II) fluoride reacted when sealed in a small bomb to yield some vinyl fluoride, but the main reaction was the polymerization of the vinyl bromide.

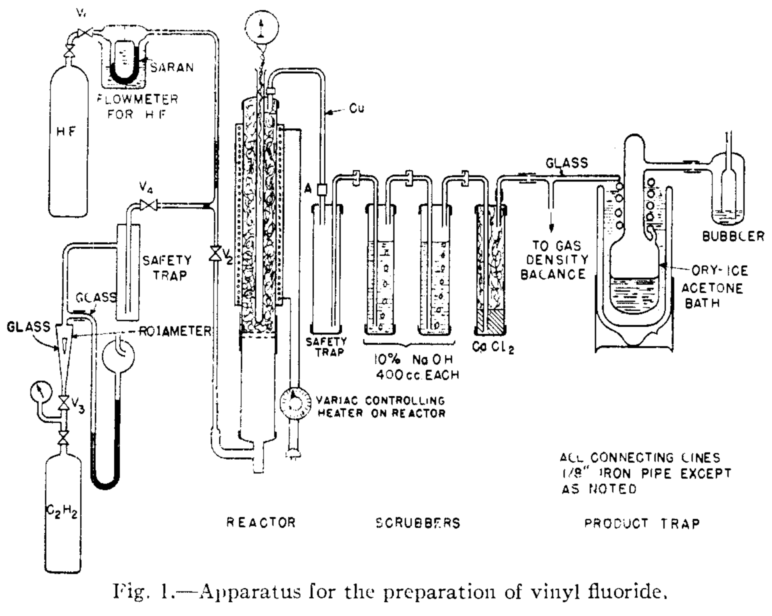

Fig. 1.—Apparatus for the preparation of vinyl fluoride.

Addition Reaction: Apparatus.—This is shown in Fig. 1. Commercial hydrogen fluoride from a cylinder was passed through needle valve, V_1, an orifice flowmeter, and was then mixed with acetylene which had been metered through a rotameter protected by a safety trap. The "Saran" manometer tube of the hydrogen fluoride flowmeter became dark after about each three days of use and was replaced. Liquid hydrogen fluoride was the manometer fluid. The valve, V_2, was used to control the pressure in the gas inlet system as indicated by the mercury manometer placed at the outlet to the rotameter. The gas mixture was passed into a reactor of two-inch diameter iron pipe three feet long which contained catalyst in the upper two-foot section. The reactor was fitted with a thermocouple well which permitted measurement of catalyst temperature at any point on the axis of the bed. The outlet gas from the reactor was scrubbed with 10% sodium hydroxide solution and dried over calcium chloride. It was then collected in a trap cooled to −85°, or by-passed to a gas density balance protected by a tube containing sodium fluoride and sodium hydroxide. When starting a run, the apparatus was disconnected at "A" and the reactor heated to 100° in a stream of hydrogen fluoride. Acetylene was then added, the scrubbers attached, and as soon as the gas density balance indicated an appreciable conversion (molecular weight = 40 or higher) the product trap was cooled. The effectiveness of the trap increased as the conversion of acetylene increased, and in one run in which high conversions were obtained, less than 2% of the total product was caught in a liquid nitrogen trap placed after the Dry Ice trap.

Catalysts: No. 1.—A solution of 145 g. of mercury (II) chloride in 800 cc. of boiling water was poured onto 535 g. of Columbia activated carbon pellets (grade 4SXW, 6 to 8 mesh). The water was evaporated from this mixture with slow stirring and the mass dried at 100° for two days. It was charged into the reactor and dried in a slow stream of hydrogen fluoride for eight hours starting at 100° and finishing at 130°. The system was then closed off until used.

No. 2.—A solution of 145 g. of mercury (II) chloride and 131 g. of barium chloride dihydrate in 350 cc. of boiling water was poured over 535 g. of carbon pellets, the water evaporated, the mass dried overnight at 135°, and then in a stream of hydrogen fluoride as described above.

Analysis.—Typical samples of vinyl fluoride purified by fractional distillation boiled in the range −73 to −70° and had the following compositions in mole per cent. acetylene, ethane and vinyl fluoride: (1) 2, 1, 97; (2) trace, 4, 96; (3) 0, 2, 98; and (4) 1, 5, 94. The composition of the vinyl fluoride samples and of some of the other fractions was determined as follows. The density of the gas was measured with an Edwards gas density balance, and the sum of acetylene and vinyl fluoride determined by absorption in bromine water. The composition was calculated assuming vinyl fluoride, ethane and acetylene to be the only substances present. This method had satisfactory accuracy. An analysis of an azeotrope fraction gave in mole per cent., C_2H_2 = 40.2, C_2H_6 = 59.0, ratio = 0.68, C_2H_3F = 0.8. The published data are 40.75, 59.25, 0.688.[14]

Polymerization of Vinyl Fluoride

Attempts to polymerize vinyl fluoride have been reported only very briefly in the literature. Starkweather[1] observed polymerization to "some extent" upon treating a toluene solution, saturated at −35°, at 67° and 6000 atmospheres for sixteen hours. Schloffer and Scherer[2] found vinyl fluoride very hard to polymerize, and Thomas[3] has reported that vinyl fluoride when heated in the presence of a peroxide catalyst undergoes substantially no polymerization. Resinous materials have been obtained in preparing vinyl fluoride from acetylene and hydrogen fluoride, but have not been identified further.[10,11,12]

In the present investigation vinyl fluoride was polymerized by exposure to light of wave length less than 2800 Å., and by the use of benzoyl peroxide, lauroyl peroxide and acetyl peroxide. Concentrated sulfuric acid caused charring of the monomer; dilute sulfuric acid had no effect. The conversion of monomer was increased from 2% to 40%, on the average, by the addition of a solvent for the monomer and catalyst. Acetone, ethanol and isopropanol were satisfactory.

Considerable difficulty in obtaining reproducible results was experienced with the acetone solvent, benzoyl peroxide catalyst polymerizations. This was due in part to the presence of both lower-boiling and higher boiling impurities in the vinyl fluoride which inhibited the polymerization as shown by a careful redistillation and polymerization of the three fractions obtained. Ten per cent. of ethane had no effect on the yield of polymer. Variability of results was also influenced by the amount of water in the acetone and it was found that the addition of 10% water was beneficial. Reproducible yields with different preparations of vinyl fluoride were obtained after adopting these two procedures.

The polymeric vinyl fluoride, after drying, was obtained in soft, friable white chunks which crushed very readily to a powder. The U.V. polymerized material remained white indefinitely, but samples polymerized with the aid of benzoyl peroxide turned brown on standing. Polymers prepared in dry acetone darkened more readily than those prepared in acetone containing 10% water. It was found that extraction of the polymer with ethanol for four hours eliminated the darkening on storage of the main portion of the polymer which was ethanol insoluble. The ethanol soluble portion was purified and dried in a vacuum desiccator. It became slowly dark brown in color, had a very pungent odor, and the glass container was etched. It seems likely that the extraction treatment fractionated the polymer and removed material of low molecular weight as well as other substances that catalyze the darkening, which is probably due to the splitting out of hydrogen fluoride acid. This behavior is comparable to that reported for vinyl chloride[15] which it is claimed can be made more stable toward heat and light by the extraction of the lower molecular weight polymer by the solvent action of aliphatic alcohols.

Several samples of polyvinyl fluoride prepared with benzoyl peroxide catalyst were heated in a Fisher-Johns melting point apparatus between microscope cover glasses. Softening started around 170°, and at 190° the samples were completely fluid. There was no evidence of decomposition. When worked on a steel-surfaced hotplate with a spatula, darkening set in around 100°, the polymer powders could be worked into a coherent mass at 140 to 150°, and were observed to string out at 180°. At the latter temperature they ranged in color from deep chocolate brown to black due to decomposition.

Calcium stearate and magnesium oxide were found to impart increased color stability to polyvinyl fluoride when used in an amount equal to 2% of the weight of the polymer.

When heated in a gas flame, polyvinyl fluoride melted and then burned with a yellow, very sooty flame. Combustion continued for several seconds after the removal of the flame, then ceased.

A brief study was made of the rate of decomposition of polyvinyl fluoride (prepared with benzoyl peroxide catalyst) in air and in nitrogen at 175°. The ethanol extracted polymer was much more stable than the crude polymer, and the polymer was more stable in nitrogen than air, Fig. 2.

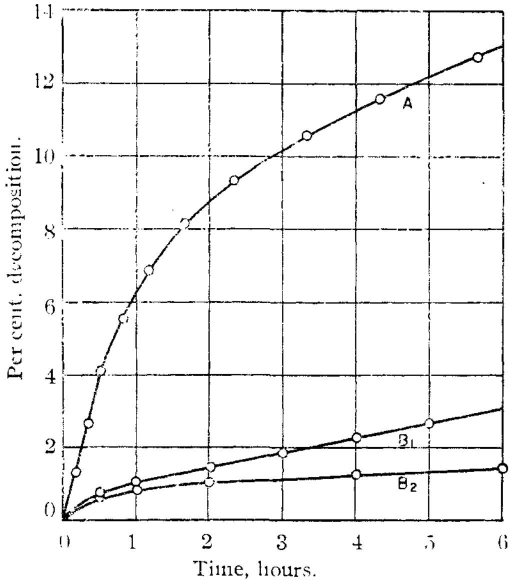

Fig. 2. Thermal decomposition of polyvinyl chloride at 175°: A, crude polymer in N_2; B, ethanol insoluble polymer, (1) in air, (2) in N_2.

A comparison with similar data for polyvinyl chloride[16] shows that except for an initial rapid decomposition of the fluoride, it decomposes at a slower rate than the chloride, Figs. 3 and 4.

The arrangement of monomer units in polymeric vinyl fluoride is probably of the head to tail type. The polymer did not liberate iodine from potassium iodide after refluxing for 100.5 hours in pure dioxane as might be expected from head to head tail to tail or random arrangements which would contain 1,2-difluoride structures in the molecule. The stability of the polymer might also be taken to indicate that the head to tail arrangement is most likely. Compounds containing a 1,2-difluoride structure are most unstable. Henne and Midgley,[17] for example, have reported that ethyl-

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(15) Deutsche Celluloid-Fabrik, German Patent 679,870 (1939).

(16) The curves showing the decomposition of polyvinyl chloride are taken from unpublished data of Dr. M. M. Sprung, who has kindly consented to their being used herein. The samples of polyvinyl chloride were obtained from the Carbide and Carbon Chemicals Corporation.

(17) A. L. Henne and T. Midgley, Jr., THIS JOURNAL, **58**, 882 (1936).

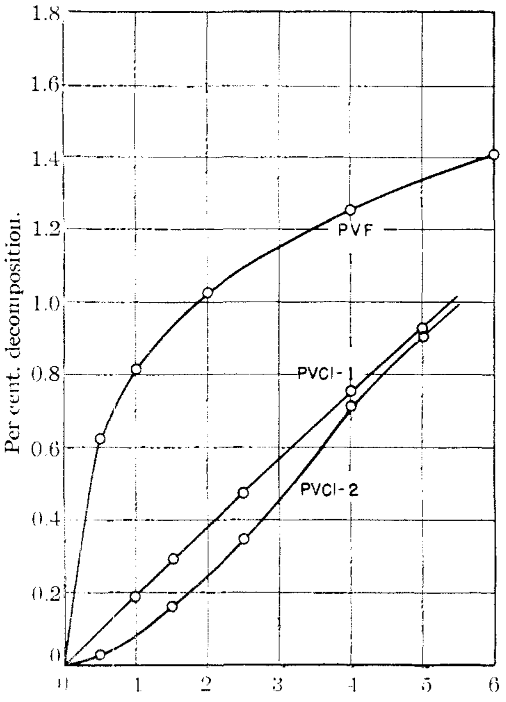

Fig. 3.—Thermal decomposition at 175° in nitrogen: PVF, polyvinyl fluoride, ethanol insoluble polymer; PVCl-1, polyvinyl chloride purified by extraction with hot isopropyl alcohol; PVCl-2 polyvinyl chloride, PVCl-1, plus 1.5% by weight of calcium butyl acetoacetate as inhibitor.

ene fluoride, 1,2-difluorocyclohexane, and 1,2-difluorodioxane decompose spontaneously to olefin and hydrogen fluoride at room temperature, and rapidly form the dihydroxy derivatives on being passed through water. While the head to tail arrangement might be expected to be more stable than the others in the present instance, the stability of the polymer is quite remarkable in view of the instability and ease of hydrolysis of monofluorides.

The density of polyvinyl fluoride determined pyknometrically on an ethanol extracted sample using ethanol as the fluid was 1.30 at 25°.

The solvent action of a number of compounds on polyvinyl fluoride has been qualitatively determined. It is not appreciably soluble at room temperature in any solvent tried, but will dissolve in hot dioxane, cyclohexanone, isophorone, phorone, fenchone, chlorobenzene, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane, and *m*-tricresyl phosphate. On cooling the solution, either precipitation of the polymer or gelation occurs. A 3% solution in hot 1,1,2-trichloroethane forms a soft gel at room temperature.

The molecular weight of the ethanol insoluble, methyl ethyl ketone soluble portion of the polymer was determined by the osmotic pressure method described by Mead and Fuoss[18] to be 23,000 ± 5,000.

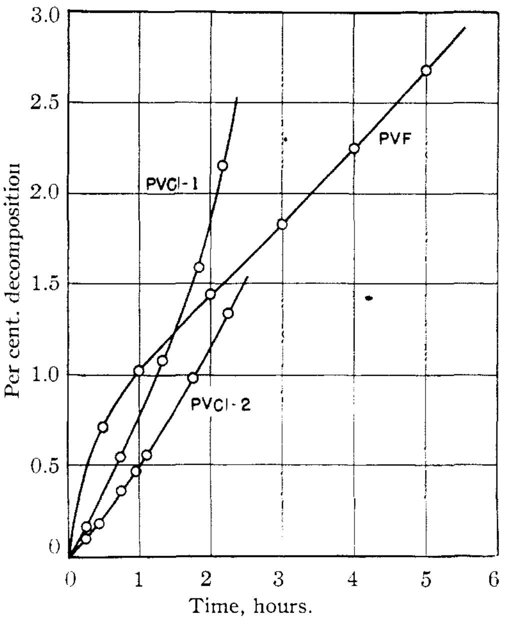

Fig. 4.—Thermal decomposition at 175° in air. Notation same as Fig. 3.

Polymeric vinyl fluoride appears to contain a crystalline arrangement for the most part. A film prepared by pressing a cover glass over a pool of molten polymer on a microscope slide, when examined after cooling, showed numerous small anisotropic areas. The X-ray powder diffraction pattern of the polymer powder had three sharp reflections. A fiber drawn from a pool of molten polymer gave a pattern with nine reflections. These showed that the fiber was only very slightly oriented.

Vinyl fluoride polymerized with vinyl acetate, vinyl chloride, and methyl methacrylate to form polymers containing fluorine. The copolymerization of vinyl chloride and vinyl fluoride has been disclosed by Thomas.[3]

Experimental

Polymerization by Ultraviolet Light.—Three types of ultraviolet lamps were used for these experiments. (1) the General Electric Type H-4 lamp which transmits no radiation at wave lengths less than 2800 Å., (2) the same lamp without the outer glass bulb, in which case considerable radiation below 2800 Å. is available, and (3) a four watt germicidal lamp with over 90% of the emitted radiation of wave length 2537 Å.

Vinyl fluoride liquid in quartz capillary tubes at 35° polymerized on exposure to 2 and 3, but not 1. The germicidal lamp caused polymerization of thirty-six per cent. of a 0.6203 g. sample of vinyl fluoride in two days at 27°.

Catalytic Polymerization.—Liquid vinyl fluoride sealed in a Pyrex capillary tube with from 1 to 3% of benzoyl peroxide was observed to have partially polymerized after sixteen hours at 55°. Three runs in a small steel bomb, 1, 2 and 3, Table II, gave only small yields of polymer. The addition of acetone as a solvent for catalyst and monomer improved the yield, runs 4 and 5, Table II. Sample 5 was analyzed: Calcd., C, 52.17; H, 6.56; F, 41.27. Found: C, 51.2; H, 6.8; F, 39.3. These results indicate that the product is polyvinyl fluoride. After modifying the procedure to give reproducible conversions

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[18] D. J. Mead and R. M. Fuoss, *J. Phys. Chem.*, **47**, 59 (1943).

and stability properties of the polymer results similar to those of run 6 were always obtained. Lauroyl peroxide and acetyl peroxide were also satisfactory catalysts, runs 7 and 8.

TABLE II

POLYMERIZATION OF VINYL FLUORIDE

Run	Time, hr.	Temp., °C.	Catalyst	Solvent	Conversion, %
1	37	51	1% benzoyl peroxide	None	0.5
2	112	62	1% benzoyl peroxide	None	4.0
3	89	85	1% benzoyl peroxide	None	1.7
4	23.5	64	1% benzoyl peroxide	Acetone	38.4
5	23.5	72	1% benzoyl peroxide	Acetone	47.8
6	23.5	71	1% benzoyl peroxide	10% H_2O in acetone	35
7	23.5	71	1% lauroyl peroxide	10% H_2O in acetone	44
8	117.5	43	0.8% acetyl peroxide	None	15

Thermal Decomposition.—The apparatus used for these experiments is shown in Fig. 5. Nitrogen and air were passed through the sample at 125 cc. per minute. The effluent gas was scrubbed with 0.1 or 0.02 *N* sodium hydroxide solution, and this was heated to a boil and back titrated with standard sulfuric acid to determine the loss in basicity due to absorption of hydrogen fluoride. The per cent. decomposition was calculated by comparing the hydrogen fluoride obtained with that which would be obtained if the polymer were completely decomposed to hydrogen fluoride and an unsaturated organic residue.

Molecular Weight.—A large sample of polymer prepared with benzoyl peroxide as catalyst was treated four hours with hot ethanol in a Soxhlet extractor; 3.02% dissolved in the alcohol. A sample of 45.61 g. of the ethanol insoluble portion was slurried with 3.8 liters of methyl ethyl ketone and heated at reflux for two hours. The slurry was allowed to settle and the cloudy liquid decanted into a vessel thermostated at 20°. The liquid was then centrifuged in 250-ml. portions, and the clear solution thus obtained evaporated to dryness in a vacuum desiccator. The polymer thus obtained was equivalent to 18.6% of the original sample.

The molecular weight of this polymer was obtained by re-dissolving 0.1402 g. in 199.937 g. of methyl ethyl ketone and measuring the osmotic pressure by the method of Mead and Fuoss.[18] The membrane was quite permeable to the polymer. Values of the extrapolated initial osmotic pressure in four runs were 0.89, 0.67, 0.67 and 0.79 cm. From these values the numerical average molecular weight may be calculated as 23,000 ± 5,000. Determinations of osmotic pressure were not made at different concentrations of polymer solution. The solution used was so dilute, and the solvent so poor, it was felt unlikely that any great change in molecular weight would be obtained in view of the large variation caused by the permeability of the membrane to the polymer.

Copolymers.—In these experiments, 0.11 mole of vinyl fluoride, 0.11 mole of the second monomer, and 1.2×10^{-4} mole of benzoyl peroxide was treated at 60°. After seventy-two hours, a 67% yield was obtained with vinyl acetate–vinyl fluoride, and a 61% yield with vinyl chloride–vinyl fluoride. The methyl methacrylate–vinyl fluoride mixture gave 82.3% of polymer in 113.5 hours at 60.5°.

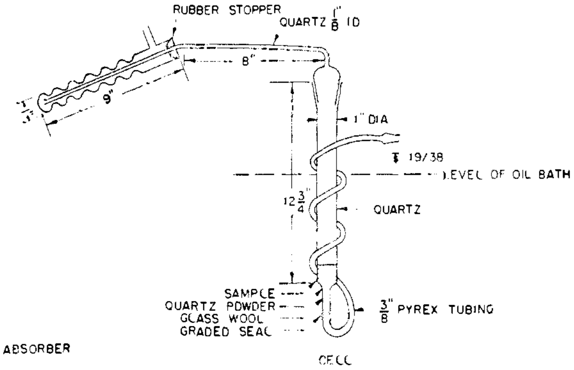

Fig. 5.—Thermal decomposition cell and absorber.

The vinyl fluoride–vinyl acetate polymer was a clear, colorless, soft solid which expanded to a porous sponge on being removed from the glass bomb liner. This effect was probably due to the unpolymerized vinyl fluoride. The polymer was completely soluble in acetone. After precipitation in water, resolution and evaporation of the acetone, the polymer was obtained as a clear, somewhat rubbery solid.

The vinyl fluoride–vinyl chloride polymer formed as a milky white, hard cylinder with a clear layer in the middle.

The vinyl fluoride–methyl methacrylate polymer was a porous, tough, colorless solid. It was very slightly soluble in acetone, toluene, and in a mixture of these solvents, but swelled in all three. Part of the polymer was pressed between steel plates at 165°, and then repressed at 145°. A clear, flexible sheet was obtained.

Acknowledgments.—The author wishes to thank Mr. L. B. Bronk for the determination of carbon and hydrogen, and Dr. D. Harker for X-ray diffraction data. The molecular weight determination was made with the assistance of Dr. D. W. Scott.

Summary

Vinyl fluoride has been prepared in good yields by passing an equimolar mixture of hydrogen fluoride and acetylene at 100° over carbon pellets impregnated with a mixture of mercury (II) chloride and barium chloride.

Vinyl fluoride has been polymerized by exposure to ultraviolet light at 27°, and by the use of peroxide catalysts.

The properties of polymeric vinyl fluoride have been investigated.

Vinyl fluoride has been found to polymerize with vinyl acetate, methyl methacrylate and vinyl chloride.

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