[CONTRIBUTION NO. 210 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Polytetrafluoroethylene

BY W. E. HANFORD[1] AND R. M. JOYCE

Polytetrafluoroethylene, first described by Plunkett,[2] possesses unusual physical properties in addition to the chemical inertness characteristic of highly fluorinated saturated organic compounds. In this paper we report an improved method for the preparation of polytetrafluoroethylene and present a discussion of its physical properties and structure.

Tetrafluoroethylene was first characterized by Ruff and Bretschneider,[3] who prepared it from tetrafluoromethane. It has also been prepared by the dechlorination of *sym*-dichlorotetrafluoroethane.[4,5] The synthesis of tetrafluoroethylene by the pyrolysis of difluorochloromethane has recently been reported.[6,7]

Polymerization

The polymerization of tetrafluoroethylene was first observed in monomer maintained under superatmospheric pressure at room temperature.[2] A detailed investigation of its polymerization was then undertaken in order to develop a rapid, controllable procedure. This polymerization has been successfully carried out under superatmospheric pressure in the presence of water and such polymerization initiators as ammonium, sodium, or potassium persulfates, hydrogen peroxide, oxygen, or organic peroxy compounds.[8,9]

Polymerization of Tetrafluorethylene.—A solution containing 2.0 g. of 30% aqueous hydrogen peroxide in 300 cc. of distilled water was charged into a 400-cc. silver-lined pressure bomb. The bomb was then closed, evacuated, and charged through a valve in the head with 70 g. of tetrafluoroethylene (b. p. −76.3°). The bomb was agitated in a shaker tube while heating at 60° for seventeen hours, the initial pressure being 700 pounds per square inch, and falling as the polymerization proceeded. The bomb was then cooled and opened. The polymer was separated from the aqueous phase by filtration, washed with water, and dried in an oven at 150°. The yield was 63 g. of white granules which were not wetted by water.

In order to minimize hazards, it is essential to maintain complete control of the polymerization at all times. Good temperature control, adequate cooling facilities, and efficient agitation are essential to safety in conducting the polymerization on any but a very small scale. Failure to exercise such control may result in an increasingly rapid reaction, leading to a violently explosive decomposition of the monomer. Since the rate of polymerization increases with pressure, these precautions are of prime importance at elevated reaction pressures. Particular care should be taken to provide adequate control of the reaction at pressures above about 1000 pounds per square inch.

Properties of Polytetrafluoroethylene[10]

Polytetrafluoroethylene is a highly crystalline linear polymer. Evidence for its crystalline character is provided by X-ray diffraction patterns. A high degree of crystallinity is also indicated by the appearance of thin films, which can be prepared in a specially insulated Carver press at 400°. These are milky and translucent if cooled slowly from the pressing temperature, but almost completely clear if cooled rapidly by quenching. Films so prepared have a characteristic slippery feel. Linearity is indicated by the fact that thin sections of the polymer can be cold drawn as much as 400%, thereby becoming highly oriented. Moreover, the polymer undergoes a sharp, reversible transition at 327°, changing from a stiff, translucent or opaque substance to a transparent, rubbery material; the transition from a stiff to a rubbery state is a recognized characteristic of crystalline linear polymers.[11] Despite evidence that this is a first order transition, the polymer retains its shape and does not undergo viscous flow. The application of compressive stress above this temperature brings about some elastic deformation coupled with a very slow plastic deformation; an increase in the stress, or an attempt to force the polymer through large angular deformations, serves only to fracture the polymer mass. Under tensile stress above 327°, the polymer elongates slightly, then tears or breaks. As the temperature is raised above 327°, the rubbery state persists unaltered until thermal degradation of the polymer chains sets in. This thermal degradation, which occurs slowly at about 450°, and more rapidly at higher temperatures,[12] is accompanied by the formation of volatile products.[13]

The chemical inertness of polytetrafluoroethylene is so great that thermal degradation in air at temperatures ranging from 450–700° takes place without any carbonization. Polytetrafluoroethylene is not attacked by such reagents as hydrochloric, hydrofluoric and chlorosulfonic acids,

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[1] Present Address: M. W. Kellogg Co., New York, N. Y.

[2] Plunkett, U. S. Patent 2,230,654.

[3] Ruff and Bretschneider, *Z. anorg. allgem. Chem.*, **210**, 173 (1933).

[4] Locke, Brode and Henne, THIS JOURNAL, **56**, 1726 (1934).

[5] Henne and Midgley, *ibid.*, **58**, 882 (1936).

[6] Downing, Benning and McHarness, U. S. Patent 2,384,821.

[7] Torkington and Thompson, *Trans. Faraday Soc.*, **41**, 236 (1945).

[8] Brubaker, U. S. Patent 2,393,967.

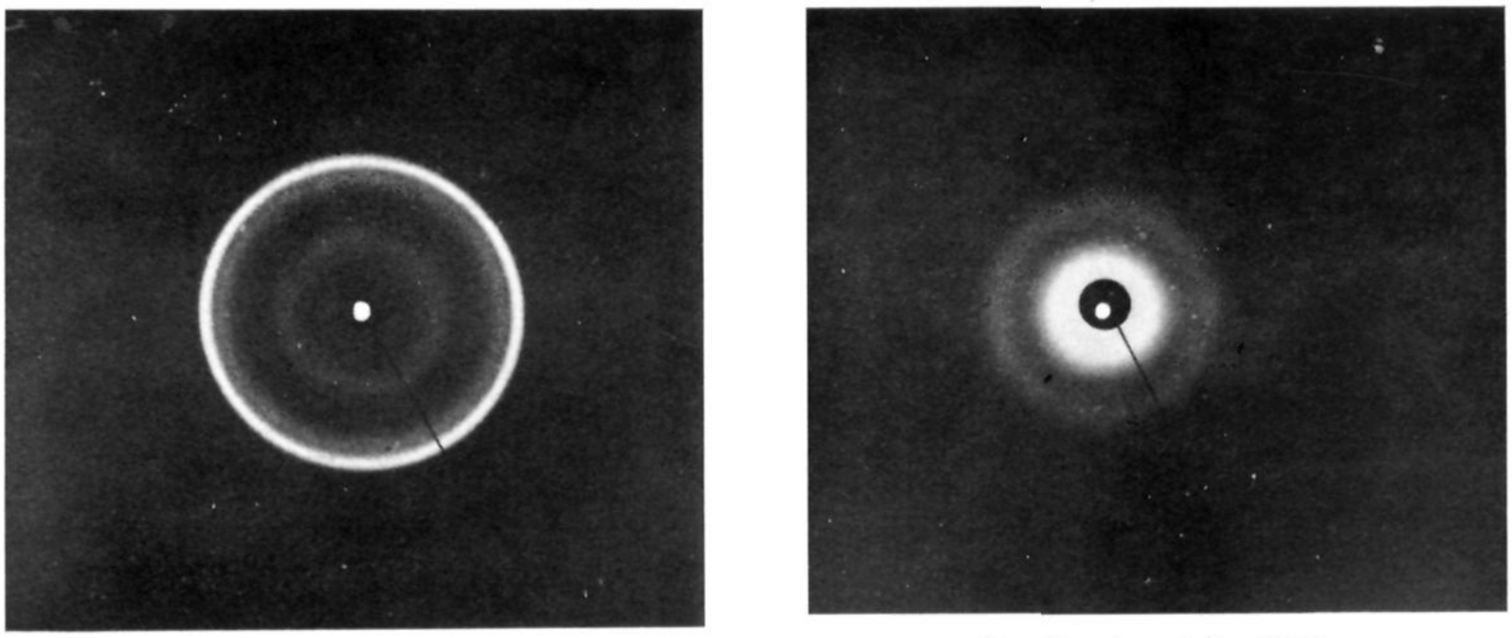
[9] Joyce, U. S. Patent 2,394,243.

[10] A more detailed description of the properties of polytetrafluoroethylene is being published by Renfrew and Lewis in *Ind. Eng. Chem.*

[11] K. H. Meyer, "High Polymeric Substances," Interscience Publishers, New York, N. Y., 1942, p. 159.

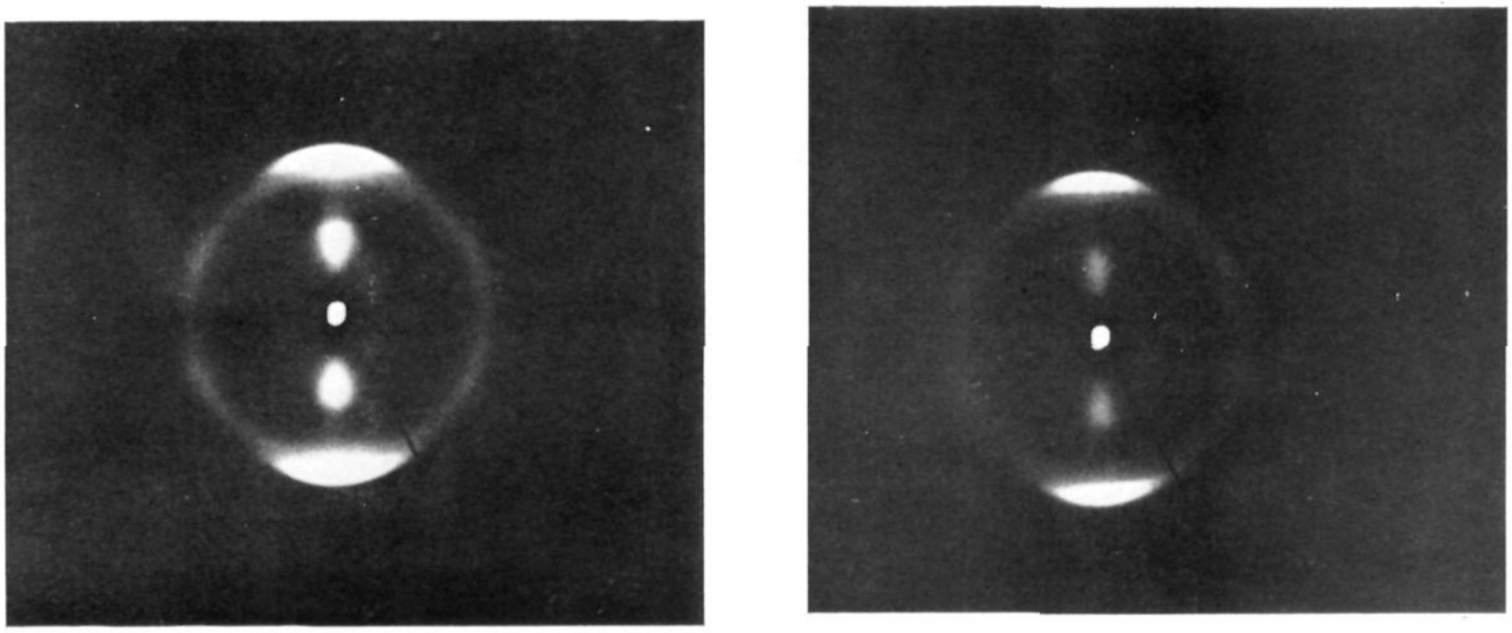
[12] Downing, Benning and Park, U. S. Patent 2,394,581.

[13] Since the volatile products of this thermal degradation have not been completely characterized, and may be toxic, manipulations of the polymer at such temperatures should always be carried out in a hood, and inhalation of the vapors should be avoided. Because of the possibility that toxic products may be evolved slowly at lower temperatures, it is recommended that adequate ventilation be provided for manipulations of sizeable quantities of polymer at temperatures over 200°.



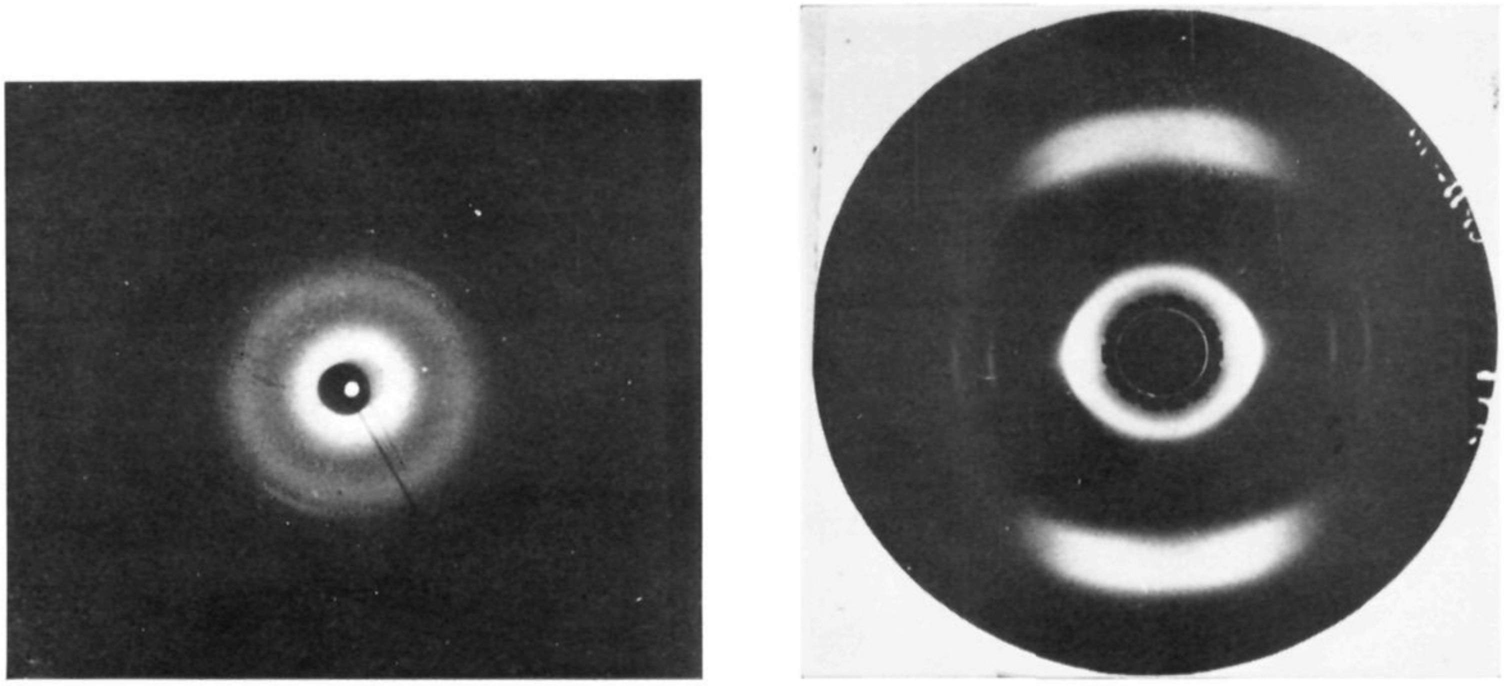
A. Unoriented film 25°.

B. Unoriented film 330°.



C. Oriented film 25°.

D. Oriented film 280°.



E. Oriented film 330°.

F. Oriented film 25°.

Fig. 1.

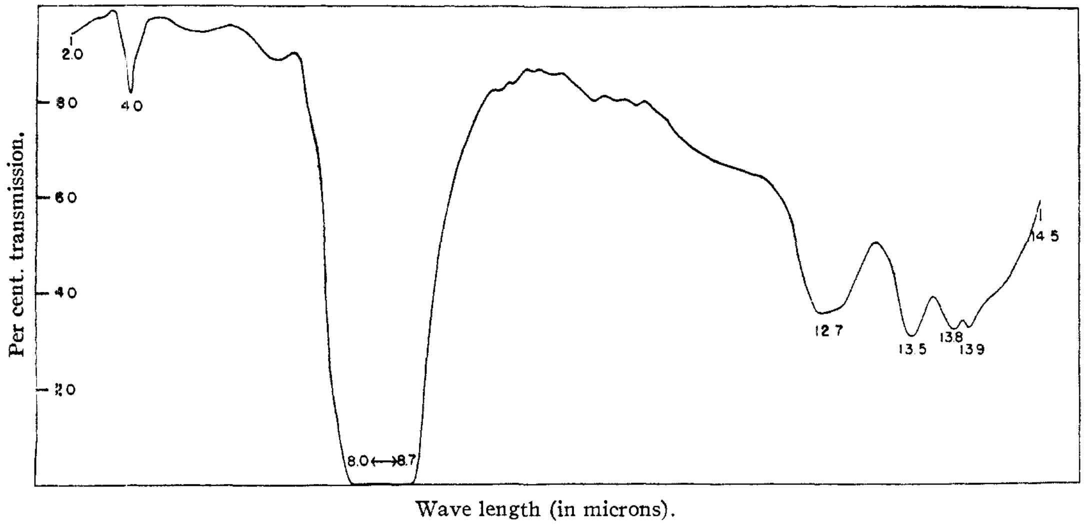


Fig. 2.

aqua regia, chlorine or boiling nitric acid. Even at 300°, sulfuric acid, fused caustic, or oxygen have no effect. Molten sodium attacks it slowly around 200°, more rapidly as the temperature is raised, with the formation of sodium fluoride and carbon.

Polytetrafluoroethylene is neither dissolved in nor swelled by organic solvents, such as hydrocarbons, chlorinated hydrocarbons, esters and phenols, even at temperatures above the transition point at 327°. This insolubility has precluded an estimate of the molecular weight of the polymer. The polymer has not been found compatible with any of a wide variety of plasticizers or with other polymeric substances.

The dielectric loss factor of polytetrafluoroethylene, 0.0002, is one of the lowest known for solid substances, and has no dispersion over the frequency range 60–10^6 cycles or the temperature range 25–310°. Neither the power factor, *ca.* 0.0001, nor the dielectric constant, 2.0, shows any variation within experimental error over these ranges. It is noteworthy that this dielectric constant is considerably greater than 1.891, the square of 1.375, the refractive index of the polymer. From the refractive index and the density, 2.2, the refractivity of the CF_2CF_2 unit in the polymer is calculated to be 10.4. Subtracting from this 4.84, the atomic refractivity for two carbons, we find 5.57 as the refractivity for four fluorine atoms, or 1.39 as the atomic refractivity of fluorine in this polymer.

X-Ray Diffraction

X-Ray diffraction patterns for polytetrafluoroethylene are shown in Fig. 1. Diagrams A and B were obtained from samples of unoriented films at 25 and 330°, respectively, and diagrams C, D and E were obtained from previously oriented films at 25, 280 and 330°, respectively, all at 5-cm. specimen to camera distance. In both series, the absence of crystallinity at 330° is clearly evident. Diagram F, obtained from a previously oriented film at 25° with a 3-cm. specimen to camera distance, shows two sets of layer lines which correspond to identity periods along the axis of orientation of 2.49 and 2.60 Å. The principal ring in diagram A corresponds to a spacing of 4.86 Å., and the diffuse inner ring to 5.36 Å. Three faint rings corresponding to spacings of 2.83, 2.40 and 2.17 Å. can also be discerned.

The infrared absorption spectrum of a 0.002″ polytetrafluoroethylene film is shown in Fig. 2. The polymer has no absorption bands of consequence from the visible region up to the strong unresolved region of opacity at 8–8.7 μ, attributable to the C–F bond. Weaker bands are found at 4.0, 12.8, 13.5, 13.8 and 13.9 μ. Polytetrafluoroethylene has no absorption bands in the ultraviolet, although the transmission falls steadily from 64% at 5000 Å. to 4% at 2200 Å. This probably arises from Rayleigh scattering of the incident light by the crystallites which cause the slight haze in the polymer film.

Transition Point

The transition at 327° has the characteristics of a melting point. This is indicated by the loss of crystallinity shown in the X-ray diagrams, and by the fact that the polymer cannot be oriented above this temperature. Previously oriented samples relax to their unoriented dimensions when heated to this temperature, indicating a first order transition with the acquisition of an additional degree of freedom. The sharpness of this transition is illustrated by curve 1 in Fig. 3, in which the current developed by a photoelectric cell activated by a beam of light traversing a film of polytetrafluoroethylene in a molten salt bath is plotted against temperature. Curve 2 was obtained as the sample cooled; it is seen that the transition is reversible, but that considerable su-

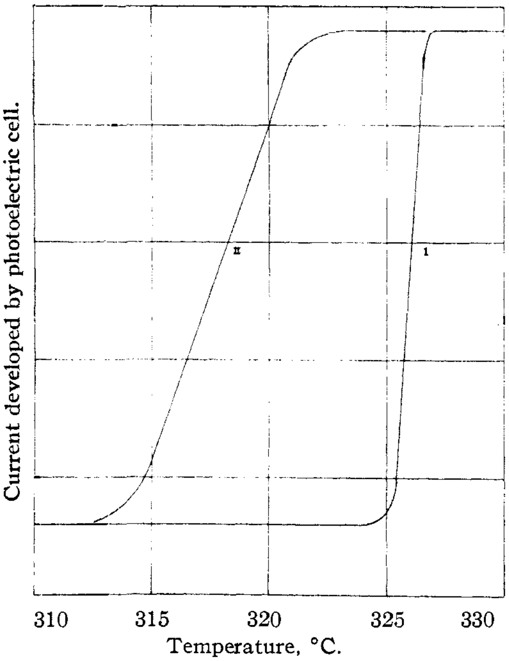


Fig. 3.

percooling is encountered. Additional evidence for a first order transition is provided by the fact that cold-pressed compacts can be sintered to tough moldings which are essentially non-porous above this temperature.[14] The significant difference between polytetrafluoroethylene and other thermoplastics above their melting points is that the latter exhibit viscous flow and relatively rapid plastic deformation, whereas polytetrafluoroethylene does not undergo viscous flow at a measurable rate, and is capable of only very slow plastic deformation. In consequence, polytetrafluoroethylene is thought to have a melt viscosity of a different order of magnitude from those of the common thermoplastics. No technique for the measurement of this melt viscosity has been devised.

Structure and Viscosity of Polytetrafluoroethylene

Evidence that polytetrafluoroethylene is a linear non-cross-linked polymer is provided by its high degree of crystallinity, its ability to be oriented, and its sharp transition point. Chain branching is considered improbable because any mechanism postulated therefor would involve the rupture of the very strong carbon–fluorine bond. Except for the end groups, the nature of which is unknown, the structure of polytetrafluoroethylene is therefore believed to be accurately represented by $-(CF_2CF_2)-_n$.

The high melt viscosity of the polymer is considered essentially a consequence of this structure rather than of great chain length. Although the chain length is not known this hypothesis is predicated on the observation that polymer properties known to depend on chain length, such as tensile strength and elongation, can be materially decreased by controlled thermal degradation with but little effect on the melt viscosity. We believe that the factor basically responsible for the high melt viscosity is the restricted rotation of the carbon atoms in the fluorocarbon chain.

The postulate of restricted rotation in a fluorocarbon chain is based on the following considerations. First, the mutual electrostatic repellence of fluorine atoms should act to oppose free rotation of the CF_2 groups. Second, the size of the substituent fluorine atoms should bring about considerable steric interaction between adjacent CF_2 groups, much more, for example, than between CH_2 groups in a hydrocarbon chain. Since the restriction to rotation resulting from these effects is cumulative along the fluorocarbon chain, the absolute magnitude of the restriction for a pair of CF_2 groups need not be grossly greater than that for a pair of CH_2 groups to bring about a considerable difference in polymer properties. Tuckett[15] has considered such effects in polymers of the type $(CH_2CXY)_n$; the effects are much more pronounced in the present case because they are not "diluted" by the alternate CH_2 groups. Because of this restricted rotation, the statistical segments of the polymer chain, which have been postulated as the basic units in the viscous flow of polymer molecules[16] are believed extremely long, hence the activation energy for viscous flow is very high.

Kauzmann and Eyring[16] and Kistler[17] have considered the viscous flow of long-chain molecules as an activated process in which the unit of flow is a chain segment of 25–30 carbon atoms, rather than the entire molecule. In considering the viscosities of certain hydrocarbons and polyesters Kauzmann and Eyring mention the possible contribution to the activation energy for flow of restricted rotation about the carbon–carbon bonds in the linear chains, and indicate that such contributions can probably be neglected for these types of compounds. They also point out that articulation about chain bonds is essential to a flow mechanism involving the successive motion of chain segments. This requirement of articulation for flow is important. In the case of a long-chain molecule in which rotation between all adjacent chain carbons is much more highly restricted than in hydrocarbons, the activation energy for such rotation may make a major contribution to the activation energy for flow. Because of the restricted rotation thought to exist between all carbons of the polytetrafluoroethylene chain, it is believed that the statistical flow segment for this polymer is extremely long and that the activation energy required to initiate viscous flow is so high that such flow is not observed below the temperature of thermal degradation.

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[14] Brubaker and Hanford, U. S. Patent 2,400,099.

[15] Tuckett, *Trans. Faraday Soc.*, **38**, 310 (1942).

[16] Kauzmann and Eyring, THIS JOURNAL, **62**, 3113 (1940).

[17] Kistler, *J. Applied Phys.*, **11**, 769 (1940).

Cohesion

All of the substituent fluorine atoms in the polytetrafluoroethylene chain have strong, identical electrostatic fields which are mutually repellent. Because of this effect, interchain bonding forces (except for van der Waals forces) are absent in the polymer, and the molecular cohesion is very low. As a result the polymer is easily fractured above the transition point at 327°. The polymer is mechanically anisotropic; applied stresses are localized along certain lines within the mass and fracture of the mass occurs along these lines as the stress is increased. These fracture lines can be observed by heating a block of polymer to about 350°, subjecting it to compression in a chamber having an orifice, then cooling and sectioning. Once the polymer mass is fractured, the high viscosity and absence of interchain bonding preclude its fusing together except very slowly and under considerable direct pressure.

Insolubility

Polytetrafluoroethylene resembles polyethylene in being insoluble in organic solvents at room temperature, but it has not been found to exhibit the increased solubility at elevated temperatures that is shown by polyethylene around 70°.[18] The separation of polymer chains from each other when a non-polar, crystalline polymer is dissolved must involve the same relative motion of the chains as that occurring in the viscous flow of the molten polymer, hence the surmounting of the same energy barrier in both situations. While this factor should not affect the equilibrium solubility of the polymer, it would make the rate of solution of polytetrafluoroethylene in any solvent extremely low. However, it is probable that polytetrafluoroethylene is not just slowly soluble, but is quite insoluble, because of the very low order of associative forces between a fluorocarbon and other organic molecules.

Acknowledgment.—We wish to acknowledge the assistance of Mr. H. S. Young in the high pressure work on the polymerization of tetrafluoroethylene, of Miss Janice Sutter for X-ray diffraction data, and of Dr. J. R. Downing for the infrared spectrum of polytetrafluoroethylene.

Summary

An improved method for the polymerization of tetrafluoroethylene is described.

The properties of polytetrafluoroethylene include abnormally high melt viscosity, insolubility in all organic solvents, extreme chemical inertness, and very low dielectric loss factor.

Evidence that the polymer is a linear, highly crystalline fluorocarbon, and an explanation of its properties in terms of such a structure, are presented.

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[18] Ref. 11, p. 98.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Reaction between Ferric Oxide and Barium Carbonate in the Solid Phase. Identification of Phases by X-Ray Diffraction[1]

BY MICHAEL ERCHAK, JR.,[2] I. FANKUCHEN AND ROLAND WARD

An investigation of the kinetics of the reaction between barium carbonate and ferric oxide in presence of oxygen was made by Struthers and Ward.[3] By chemical analysis, they inferred that one of the products was probably $BaFeO_3$. Rosenstein[4] further investigated this system and established, by X-ray analysis, the presence of barium oxide in many of the products and the existence of a compound which seemed to have a perowskite-like structure. The latter was taken as further evidence for the compound $BaFeO_3$. In these preparations, however, the valence number of iron rarely exceeded 3.3 and never reached 4. A more thorough investigation of this system seemed to be called for especially with regard to the determination of the solid phases produced in the reaction at various temperatures with a wide range of mixtures. Chemical analysis has decided limitations for this purpose. X-Ray analysis, on the other hand, permits not only of the recognition of phases and their intersolubilities but also an approximate determination of the relative extent to which the phases are formed. Structural changes in a phase may also be observed. H. Forestier[5] found that a compound corresponding to $BaOFe_2O_3$ crystallized in a hexagonal close-packed lattice. Hilpert[6] also found evidence of formation of crystalline products. Hüttig[7] prepared many ferrites of the alkaline earth metals. Calcium ferrite was identified as having a spinel structure. Adelsköld[8] found evi-

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[1] Abstracted from a thesis submitted by Michael Erchak, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy to the Graduate School of the Polytechnic Institute of Brooklyn, 1945.

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[3] R. Ward and J. D. Struthers, THIS JOURNAL, **59**, 1849 (1937).

[4] R. D. Rosenstein, Thesis for Bachelor of Science degree at Polytechnic Institute of Brooklyn, 1943.

[5] H. Forestier, *Compt. rend.*, **192**, 842 (1937).

[6] S. Hilpert and A. Wille, *Z. physik. Chem.*, **18 B**, 291 (1932).

[7] G. F. Hüttig, *et al.*, *Z. Elektrochem.*, **40**, 306 (1934); THIS JOURNAL, **57**, 2470 (1935).

[8] V. Adelsköld, *Arkiv. Kemi Mineral. Geol.*, **12A**, No. 29 (1938).