William T. Miller

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Professor Miller was born in Winston-Salem, North Carolina, educated in the schools of the area, and graduated from Duke University with a Bachelor's degree in 1932. He did graduate work with Lucius A. Bigelow at Duke, one of the first to use elemental fluorine in organic synthesis, receiving his Ph.D. degree in 1935. He was then a Lilly Fellow at Stanford University, and in 1936, he came to Cornell as an Instructor in the Department of Chemistry. He then initiated a vigorous research program in fluorine chemistry to show that the uniquely high chemical reactivity of this element could be used to form an unusual variety of compounds with uniquely high chemical stability.

World War II broke out soon after Miller came to Cornell, and at the age of 30, he was recruited for the supersecret Manhattan Project, supposedly to synthesize "special materials that would lubricate bullets". Actually, a major objective of this project was to separate the fissionable U–235 from the stable isotope U–238 using "gaseous diffusion". In this process, the different isotopes make their way through the torturous paths of a porous barrier at slightly different rates so that the U–235 can be enriched sufficiently to undergo a nuclear explosion. However, the only convenient gaseous form of the unusually heavy element uranium is UF6, which is nearly as reactive and corrosive as elemental fluorine itself. Worse yet, any fluorination with UF6 produces UF4, a solid that clogged the diffusion membrane. Although stainless steel could be used for many parts of the diffusion plant, UF6 resistant materials with other physical properties, such as oils, greases, and gaskets, were also critically needed.

The resistance of the new polymer Teflon that contains only carbon and fluorine initially appeared to be very promising, but at that time, it turned out to be very hard to fabricate, was impure, and could only be produced as an intractable solid. Teflon gaskets leaked because the polymer exhibited "cold flow" under pressure. With Manhattan Project encouragement, other fluorine chemists tried to convert hydrocarbon oils, greases, etc. to fluorocarbons by replacing the hydrogen atoms with fluorine atoms; however complete replacement was nearly impossible, and a single remaining hydrogen atom was a fatal link in the chain of chemical stability.

Miller devised a brilliant alternative approach to this problem. He emulated the synthesis of Teflon, in which molecules are built up by polymerizing tetrafluoroethylene, C_2F_4. To achieve modified physical properties, he used C_2F_3Cl rather than C_2F_4. By 1943, the Miller approach appeared to be the only promising route, and his research group was moved to the Manhattan Project at Columbia University, "inside" the secret project where they could interact directly with the diffusion plant designers on their specific material requirements. In an intensive day-and-night research effort, they synthesized a wide variety of UF_6-resistant products: liquids for vacuum pump oils (the diffusion process was carried out entirely under vacuum), heat exchange fluids, greases and waxes for lubricants, and solids for gaskets, valve seats, and windows (UF_6 attacks glass). Critical to this was their basic research that determined how such physical properties depend on composition and molecular weight.

Polymer chemistry in the 1940s was an infant field; nylon and polystyrene had just been invented. The Miller group pioneered in solving polymer chemistry problems involving these unique new materials, such as separation, purification, and characterization. For these critical research contributions, Miller received the personal commendation of Major General Leslie Groves, the Manhattan Project military commander: "these materials were essential to our success".

Miller's research constituted an important part of Cornell's early and continuing leadership in polymer science. Peter Debye, who received the Nobel Prize before coming to Cornell, developed during WWII, the method of light scattering to determine the molecular weight of polymers, a method that had a very important impact on the synthetic rubber program. Paul Flory, who joined the Cornell chemistry faculty in the late 1940s, received the Nobel Prize for his basic polymer research. These were the first of many world class polymer research programs at Cornell.

On his return to Cornell as a full Professor in 1946, Miller embarked on a broad scale basic research program that established his laboratory as a world center in organofluorine chemistry. He pioneered and illustrated the broad applicability of elemental fluorine syntheses; the extension of these basic concepts developed by his research group showed that an unlimited number of highly fluorinated carbon compounds could exist, and that such compounds exhibited a diverse and exciting chemistry. They demonstrated that fluoroolefins were also unusual in the great ease with which they suffer nucleophilic attack on the unsaturated carbon, with even halide anions showing useful reactivity. Contrary to the mechanistic expectations of the time, fluoride ion was shown by far the most reactive, with addition and rearrangement reactions analogous to those of a proton as an electrophile for unsaturated hydrocarbons. His research made possible elegant syntheses of a variety of interesting fluorohalo compounds. In later research, he discovered and exploited fluoroorganometallic compounds involving metals such as copper, mercury, and silver that showed unusual chemical reactivity.

For the Cornell Department of Chemistry, Miller played a key role in our only building project since 1923, overseeing the construction of the S.T. Olin Laboratory in the mid 1960s and the subsequent renovation of

Baker Lab. Miller visited recently constructed chemistry buildings around the country and recommended the architectural firm that had also designed the chemistry building at Brookhaven National Laboratory. Convincing the Cornell administration of this choice was a first, as the architect was not a Cornell alumnus. A unique part of Professor Miller's plan for the building was a new style of small teaching laboratory, optimized for the interaction of a small group of students with a single teaching assistant. Miller also took a very active role in construction oversight and in obtaining construction materials of far greater quality and at far lower cost, such as acid-resistant stainless steel ductwork for the chemical exhaust hoods, at nearly the cost of much inferior galvanized material through his industrial contacts. Twice, Miller was a Chemistry delegate to the Faculty Council of Representatives.

The uniquely reactive element fluorine was discovered by the French chemist Henri Moissan in 1886, for which he received the Nobel Prize. In 1986, Professor Miller received the Moissan Centenary Medal, as Moissan's worthy successor in fluorine chemistry. Miller also received the American Chemical Society Award for Creative Work in Fluorine Chemistry in 1976, the year of his retirement, and a special Festschrift issue of the *Journal of Fluorine Chemistry* was dedicated to him on his 70th birthday in 1981. He was a member of the American Chemical Society and the Royal Society of Chemistry of Britain.

The home that the Millers built next to Sunset Park in Cayuga Heights with its spectacular view of the Cayuga Lake valley was a tribute to their unusually good taste and to their passionate attention to detail. Here, Miller's love of the most challenging problems was also shown by his outstanding success with prized varieties of grapes, walnut trees, persimmons, and espaliered pears.

He is survived by his wife of 47 years, Betty Robb Miller; his brother, Robert L. Miller, of Panama City, Florida; his nephew, Robert Miller, of Belfast, Northern Ireland; and his niece, Katherine Johnston, of Opelika, Alabama.

Jerrold Meinwald, Charles F. Wilcox, Fred W. McLafferty