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Herbert S. Eleuterio^a

^a Petrochemicals Department Hickory Run, Wilmington, Delaware

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FLUOROPOLYMERS: AN EXPLORER'S VANTAGE POINT

HERBERT S. ELEUTERIO

Petrochemicals Department
Hickory Run, P.O. Box 80723
Wilmington, Delaware 19880-0723

Alfred Wallace, who proposed the theory of evolution about the same time as Charles Darwin, noted, "Man is the only animal capable of purposeful and directed evolution. He makes tools." Among the tools that man has made are synthetic polymeric materials. It is not surprising, therefore, that materials usage has tracked population growth, with an unmistakable growth spurt occurring at the time of the Industrial Revolution. Our discussion here will be limited to milestones in the purposeful and directed evolution of manmade perfluorinated materials. My vantage point or perspective is that of having been an explorer and discoverer of novel classes of perfluorinated monomers and polymers. To some observers, the innovation process in materials science and technology, especially fluoropolymers, resembles a Darwinian-like struggle in which human creativity has intervened in the process and influenced the outcome by making continuous improvements not only with known materials "species," but also by designing and producing unknown "species."

The first milestone in any discussion of fluoropolymers must begin with the serendipitous discovery of polytetrafluoroethylene (PTFE) in 1938. Unlike nylon, Teflon's commercial availability was impeded for about 10 years by difficulties in reacting the monomer safely as well as by limitations in fabricating the polymer. The severity of the hazards in handling (TFE) monomer was demonstrated by an explosion that killed two people, injured others, and demolished a (PTFE) semiworks in 1944. Safety has always been of uppermost concern in the development of fluoropolymers.

Teflon's intractability was another technical constraint that greatly influenced its development. A combination of high crystallinity, very

high molecular weight, and melt viscosity demanded that metallurgical and ceramic practices be employed in converting polymer to finished products. In order to reduce (PTFE) crystallinity, various perfluoro olefins were screened as copolymer candidates.

Since hexafluoropropylene (HFP) is obtained from the pyrolysis of (PTFE), it was fortuitous that (HFP) turned out to be the comonomer that reduced polymer crystallinity without significantly sacrificing (PTFE)'s other desirable properties. Thus a family of TFE/HFP copolymers evolved that could be processed by conventional thermoplastic processing techniques. A bit later, TFE/HFP resins will be revisited.

The early 1950s was a terribly exciting period to be doing chemistry, especially macromolecular chemistry. Professors Ziegler and Natta had captured the polymer world's attention with their transition metal catalyzed polymerization of olefins to high-molecular-weight polymers whose properties seemed to depend on the stereochemical control of substituents along the polymer backbone. While trying to learn more about the chemistry and physics of stereoregular and nonstereoregular polymers, I stumbled on to the fact that hexafluoropropylene, the fluorocarbon analog of propylene, had never been homopolymerized to high molecular weight.

Indeed, homopolymerization of (HFP) to high molecular weight had been generally regarded as not possible by many researchers who had tried and failed. Different catalysts and reaction conditions all gave low-molecular-weight liquids. By careful fractionation and coupling of telomer iodides, brittle waxes were among the highest-molecular-weight products obtained.

The use of very high pressures together with catalysts and reaction conditions that would not interfere with the growing polymer chain made possible the preparation of high-molecular-weight poly HFP. The synthesis of poly HFP and HFP-rich HFP/TFE copolymers filled a big gap in our fluoropolymer database. To illustrate just how wide a knowledge gap, *a priori* theoretical calculations had predicted that poly HFP if made would be a rubber. In fact, it is still the stiffest unfilled fluorocarbon polymer synthesized to date.

Although the unusual physical and mechanical properties of these amorphous materials have yet to be exploited commercially, an unexpected dividend of this exploratory research was the development of a quantitative infrared analytical method that could be used to control the quality of Viton and Teflon (FEP)-type resins. Prior to this time, the HFP content of these resins could not be measured with any degree of accuracy.

About the time that the exploratory phase of this work was being completed, the needs of the U.S. aerospace industry for thermally stable polymers that were functional over a wide temperature range (-60 to $+300^{\circ}\text{C}$) came to our attention. Our first attempts to make suitable candidates involved polymerizing TFE to low-molecular-weight fluids. However, these materials either were too volatile at high temperatures or became crystalline at low temperatures. Molecular models of these materials showed that fluorine atoms are relatively bulky and crowd the polymer backbone, stiffening the chain. Somehow flexibility had to be built into the polymer backbone without sacrificing its chemical or thermal stability. The clue that we were seeking was found in research work done at the University of Florida which reported the exceptional thermal stability of perfluorodiethyl ether upon attempted pyrolysis. Molecular models of perfluoropolyethers indicated that these materials might indeed be flexible enough. Since the charter of the Exploratory Research Section was to achieve breakthroughs in macromolecular science and technology, the route of choice, in my mind, was to epoxidize perfluoroolefins. Sporadic efforts had been made within Du Pont over the years to oxidize perfluoro-olefins to epoxides. Many of the early workers reported either no reaction or deflagrations, while later workers reported carbonyl compounds. In the meantime, extensive information had been built up which showed that fluoro-olefins, particularly hexafluoropropylene, were susceptible to nucleophilic attack. HFP's reactivity coupled with safety considerations tilted the odds toward hexafluoropropylene rather than tetrafluoroethylene as the target olefin to be epoxidized.

It was speculated that the hydroperoxy anion generated from alkaline hydrogen peroxide might be a strong enough nucleophile to add to the hexafluoropropylene double bond, and then, the perfluorocarbon anion generated would be a strong enough nucleophile to eliminate a hydroxide ion to form an epoxide. Our speculation turned out to be correct. Thus an entire new class of perfluorinated materials evolved! A fascinating facet of fluorocarbon chemistry is the dramatic difference in reactivity and properties of fluorocarbons opposite their hydrocarbon analogs. These differences in reactivity have been purposefully exploited by many investigators both scientifically and practically. A superb review article was published in 1985 in *Angewandte Chemie* by three Hoechst researchers which summarizes the remarkable chemical versatility of HFPO as a tool in the evolution of a host of perfluorinated progeny. A detailed account of HFPO science is beyond the scope of this paper. However, I have selected a few examples that illustrate HFPO's versatility as a basic building block.

Although other suppliers in Russia, Japan, China, Italy, Germany, and the United States have developed or licensed competitive processes and products for HFPO and its progeny, my examples will be drawn from Du Pont-developed technology. The products to be discussed briefly are derived from perfluoroalkyl polyethers, perfluorovinyl ethers, and perfluorosulfonyl fluorides. They are: Krytox fluids and lubricants, Kalrez elastomers, Teflon PFA resins, and Nafion membranes.

Krytox oils, greases, and fluids are end-capped perfluoroalkyl polyethers made from HFPO. They are used in industrial and aerospace applications where conventional lubricating products fail or where component failure or repair cannot be tolerated for either economic or safety reasons. To my delight, polyperfluoroether fluids are the coolant of choice in the Cray supercomputer.

Kalrez is a perfluoroelastomer that is a copolymer of tetrafluoroethylene, a perfluorovinyl ether, and a perfluorinated cure site monomer.

Kalrez components are essentially unaffected by all liquids. They prolong seal life in demanding chemical or corrosive environments and offer exceptional resistance to ozone, weather, and flame.

Teflon PFA resins are also copolymers of perfluoroalkyl vinyl ethers and tetrafluoroethylene. These readily moldable or extrudable thermoplastic resins were developed to extend the range of end-uses for Teflon resins. These polymers will be discussed in more detail in a bit.

Nafion resins are copolymers of fluorosulfonyl vinyl ethers and tetrafluoroethylene. Nafion membranes were first used as separators in fuel cells for power generation in U.S. satellites. In the mid-seventies, Nafion found increasing use in chloralkali plants. Functionally, the membranes permit migration of sodium ions from a cell's anode to its cathode compartments while blocking migration of hydroxyl ions. By properly tailoring polymer parameters Nafion membranes are able to function extremely well in a variety of hostile operations yet are environmentally sound and ecologically friendly, replacing asbestos diaphragms and mercury cells. Furthermore, Nafion membranes are energy efficient, have long life, and require low maintenance.

As mentioned earlier, more tractable perfluorinated copolymers of tetrafluoroethylene can be produced with HFP as the comonomer. By adjusting the HFP content and molecular weight, a variety of FEPs can be designed to satisfy desired end-use requirements, for example, low melt viscosity for injection molding, extrusion grade for tubing, wire coating, and cable jacketing; high melt viscosity with superior stress-crack resistance; and better mechanical properties for use as liners in

process equipment. However, the maximum continuous end-use temperature range for FEP resins does not quite match that of Teflon resins (205°C versus 250°C).

As previously mentioned, Teflon PFA fluoropolymers are copolymers of TFE and perfluoroalkyl vinyl ethers. These resins, which were introduced by Du Pont in 1972, have pendant perfluoroalkoxy (PFA) side groups which are very effective at reducing polymer crystallinity. Teflon PFA resins closely match the properties of PTFE resins yet have the processing advantages of thermoplastics. A portfolio of fluoropolymers have now evolved that satisfy nearly all the customers' needs. However, these perfluorinated materials are all partially crystalline with poor transmission of ultraviolet and visible light.

In 1989, Du Pont commercialized a new class of amorphous fluoropolymers. These materials are equal to or better than other amorphous polymers in optical clarity and mechanical properties. However, because they are fluoropolymers they have outstanding electrical properties and chemical resistance and can function over a wide range of temperatures.

Teflon AF resins are copolymers of bis-2,2-trifluoromethyl-4,5 difluoro-1,3-dioxole. The monomer is prepared from hexafluoroacetone and ethylene oxide, chlorinating the adduct, then fluorinating, and finally dechlorinating to the dioxole. In addition to the superior electrical chemical resistance and thermal properties associated with fluoropolymers, the Teflon AF family possesses glass transition temperatures as high as 300°C. The polymers have extremely high optical clarity and have limited solubility in commercially available perfluorinated ethers. Teflon AF polymers may be either solution cast into clear micron thin films or melt processed into a variety of forms.

A promising automobile application for Teflon AF is in fiber optic cables. Teflon AF is comparable to acrylics and polycarbonates in optical clarity as well as heat stable and chemically resistant. Major car companies are interested in fiber optic wiring harnesses that would allow increased use of microprocessors in cars without the shielding problems associated with metallic cables.

Thus far, I have commented only on completely perfluorinated polymers. A more representative overview of the evolution of fluoropolymers has been presented by ASAHI's Dr. Amabe. Dr. Amabe divides the chronological evolution of fluoropolymers into three periods: the era of homopolymers, the era of copolymers, and the era of functional polymers.

Time does not permit a detailed account of the historical development

of these materials, but a brief comment on how experimental work was typically carried out in industrial laboratories over this period of time is worth noting. The experimental design strategy from the 1930s to the 1950s was for the most part instrument limited. Experiments were executed in "Edisonian" or "trial and error" fashion. The experimental design protocol usually consisted of a repetitive series of approximations along with inferences drawn from a fragile and emerging scientific database. The revolutionary development of rapid, reliable information-rich instruments and experimental techniques such as programmed temperature GCs, NMRs, and time-of-flight mass specs shortened the time required to carry out definitive experiments and contributed significantly to the evolutionary advances made in fluoropolymer science and technology. For example, when HFP was first isolated, it was assigned a cyclic structure. It took months of tedious work to prove that HFP was a linear olefin.

Early on, I described materials research and development as an ongoing Darwinian-like struggle taking place in different parts of the world. Teflon PFA polymers are considered to be a major milestone, because in the opinion of one expert in the field of fluoropolymers, Carl Sperati: "With the discovery of PTFE resins, Du Pont scientists began focusing on perfluorinated copolymers which were truly melt fabricable like polyethylene and polyamides, but still had PTFE's extraordinary chemical stability as well as its mechanical and electrical properties." Although numerous copolymers were prepared, none had the desired combination of properties. The search for the elusive comonomer became feasible with the discovery of the synthesis of HFPO, some 20 years later. In sharp contrast to this lengthy search, shortly after Du Pont commercialized "PFA" resins, Hoechst entered the field with a terpolymer based on (TFE/HFP/PPVE). HOSTAFLOX TFA was marketed in 1978. Similarly, almost as soon as Nafion Du Pont membranes were commercialized, ASHAI Glass announced a competitive product, FLEMION. In 1989, Du Pont announced Teflon AF polymers based on dioxole chemistry. ASHAI quickly followed with CYTOP, novel fluoropolymers with cyclic structures. Previous attempts to produce cyclic structures gave greases or gelled mixtures containing six- and seven-membered rings. ASHAI's present approach is an innovation in the field of fluoropolymers. ASHAI has developed an extremely selective cyclopolymerization by using specially designed difunctional perfluoromonomers such as perfluorallyl vinyl ether. This monomer is readily derived from esters of perfluorovinyl ether.

Key features of these competing materials are their exceptional transparency with more than 95% UV and visible light transmission. CYTOP and Teflon AF films both enjoy a very low refractive index. The Darwinian struggle for market share is expected to take place in the optical lens, protective coatings, quartz glass, and insulation market arena.

Dr. Amabe goes on to ask what will come next in fluoropolymers. He suggests the era of molecular design. To illustrate his point, he describes the structural features and performance parameters of LUMIFLON polymers as examples of molecularly designed macromolecules. I would like to cite other examples of purposeful design that validate Amabe's thesis.

Gore-Tex is expanded polytetrafluoroethylene. As a breathable barrier material, it keeps liquid water out but lets water vapor through. Gore-Tex is the insulation material used in clothing designed for outdoor activities, such as skiing and mountain climbing. Advances in surface science measurement tools have enabled material scientists to find out why Gore-Tex works. What makes Gore-Tex function is its negative Poisson ratio, which means that when PTFE is stretched, it gets bulkier. A Poisson ratio is one of four numbers that define the elastic properties of a material; it relates stretching to thinning. Negative Poisson ratio materials permit stiffness without brittleness. Based on the data gathered thus far, research is underway to find even better candidates for use in artificial bones, shock absorbers, and polymeric sandwich panels. Sandwich panels currently used in construction and structural applications cannot be curved. Therefore, they must be laboriously installed in sections. One of the shortcomings of known fluorocarbon elastomers, seals, and gaskets is their low temperature embrittlement. This need represents another opportunity for negative Poisson ratio polymers.

Meeting the challenge of handling hazardous materials safely is the purpose of "challenge" 5200, a novel, flexible fluoropolymer composite. The polymeric matrix of this composite is based on Du Pont's TEFLON PTFE, FEP, and PFA fluorocarbon resins, and VITON fluoroelastomer. These materials along with woven fiberglass fabric are the basis for a totally encapsulating chemical protection suit (TECP) offering full body protection of the wearer. Incidentally, the suit's visor is made largely of TEFLON film.

Professor Fukui stated at the First Pacific Polymer Conference that a desirable future for science and technology is to address the "softside" of technology, "which relates the human sensation of touch to the molecular properties of macromolecular materials. . . . The research and de-

velopment methodology of soft technology will entail fusion and integration of science and technology, with art and various disciplines of the cultural sciences.”

Perfluorinated lubricants have been around for some time and are used in a variety of applications, for instance, in the space shuttle, in uranium-enrichment plants, and in semiconductor facilities. Montedison's Montefluos Division, a major producer of fluorine-based products, has used FOMBLIN perfluorinated polyether (PFPE) lubricant as a protective coating for preserving ancient marble and stone facades.

Now, Montefluos has modified the basic FOMBLIN formula for another preservative application. This time, the PFPE material is being used to protect and enhance human faces and bodies in such applications as sunscreens and cosmetics and to help protect workers' hands from a broad range of chemicals. This is the first time, Montefluos declares, that “fluorinated products have been used in cosmetics, apart from toothpaste.”

Market share in the world fluoropolymer market has always been determined on the basis of performance and price. Competition from more nonfluorinated polymer blends and alloys illustrates the ferocity of the ongoing Darwinian struggle in the insulated wire markets. The plenum area is the false ceiling in the airflow spaces in commercial buildings. After more than 10 years of enjoying unabated growth in the plenum and cable markets, fluoropolymer producers are beginning to feel the heat from polyvinyl chloride suppliers who are now marketing alloyed products at much lower prices. New developments in polymer alloys, blends, and composites, along with economics, decide the survival of the fittest! Just as selective breeding has produced plant and animal hybrids with inherent survival traits, polymer scientists and engineers are producing hybrid polymeric materials designed to survive in a globally competitive marketplace.

Environmental concerns can be either a problem or an opportunity. Krytox perfluoropolyethers demonstrate the advantages of recoverability and recycle. In an environmentally clean conscious world, recyclability of polymers is a must.

As materials science continues to evolve from the know-how and know-what age, which was dominated by skilled artisans, to the know-why age of the scientist-engineer, materials design and synthesis becomes more and more purposefully directed. Polymer science and technology enjoyed tremendous growth in the 1950s and 1960s as a result of hallmark discoveries in organometallic catalysis and mechanistic chemistry.

Researchers in Britain, the United States, and West Germany are carrying out experiments that show similar breakthrough potential in fluoropolymers. Perfluorinated macromolecules appear to have a bright future in optoelectronic applications. Compared to inorganic fibers, these fluoropolymers offer the potential of lower cost, more flexibility, and easier handling. The demand for faster signal-processing devices presents a wonderful market opportunity. Carbon fluorine bonds have less Rayleigh scattering and no overtone absorption compared to carbon hydrogen bonds. Research at the University of Durham and at MIT involving the ring-opening metathesis polymerization of fluorinated monomers excites the imagination! The synthesis of stereoregulated fluorinated polymers may be within reach in the not too distant future. Fifty years ago, control of polymer structure was the dream. Today, it is architectural polymer design!

In conclusion, progress in materials science and technology may set ultimate limits on the rate at which key sectors of the world economy can grow. Higher consumer expectations as well as increasing demands for materials performance have become more and more exacting. These demands can only be met by tailoring materials or combinations of materials for a specific function within the total operating system.

Wallace's theory of evolution differed from Darwin's in one critical respect. Wallace believed that man's mind was "specially created," in his view, the only exception to Darwin's theory of evolution. On the other hand, Nobel Laureate Herb Simon believes that "what chiefly distinguishes creative thinking in the basic physical sciences from more mundane forms are the willingness to accept vaguely defined problem statements and gradually structure them, a continuing preoccupation with problems over a considerable period of time, and an extensive background knowledge in relevant and potentially relevant areas."

I believe that the purposeful and directed evolution of perfluorinated materials validates Professor Simon's view of human creativity in the basic as well as the applied physical sciences.

Finally, in *The Ascent of Man*, Bronowski comments that "man ascends by discovering the fullness of his own gifts . . . what he creates, on the way, are monuments to the stages of his own understanding of nature and self." It is professionally gratifying to be among those who have explored those uncharted regions in science and technology that have resulted in a better understanding of fluoropolymers. I am grateful to the Du Pont Company, which has provided me with outstanding physical and people resources. Du Pont also gave me the chance to be

part of a rich research tradition in materials science. Materials science has evolved into an umbrella discipline that encompasses several disciplines whose core is made up of chemistry, physics, and engineering. Du Pont's Polychemicals Department commitment to materials synthesis, materials science, and materials engineering as an explicitly stated multidisciplinary objective dates back to 1950, when its Research Division was first formed. Fluorocarbon polymers were then and continue to be among the pacesetters in high-performance polymeric materials.