

Fluoroelastomers: Today's Technology and Tomorrow's Polymers

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ABSTRACT: The history of fluoroelastomer development is briefly traced and the technology of many of today's fluoroelastomer products is discussed. An important theme in current research is the synthesis of fluoroelastomers with improved low temperature properties. The preparation of perfluorinated elastomers from perfluorovinyl ethers with glass transition temperatures as low as -76°C is discussed. Plasticization of these materials with perfluorinated polyether oils is also described.

KEY WORDS Fluoroelastomers / Low Temperature Properties / Fluorinated Polyethers / History / Crosslinking / Plasticizers /

Fluoroelastomers represent an active field of research—a fascinating area of polymer science with the promise of new discoveries and applications. This paper will outline some of today's fluoroelastomer technology and describe research activity on the preparation of low temperature fluoroelastomers which we believe point to some of tomorrow's products.

Applications requiring extreme resistance to heat and chemicals have driven the development of fluoroelastomers. Shapes such as "O" rings satisfy a great variety of sealing applications in hostile environments. Although frequently quite expensive relative to other elastomeric materials, the exceptional chemical resistance, heat stability and durability of these "O" rings often make them the most effective and least costly answer to sealing problems demanding resistance to corrosive high temperature environments. Another example of this is provided by the packer seals used in oil wells.

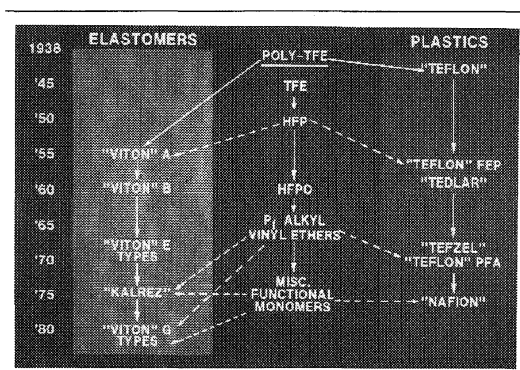
Kalrez[®] perfluoroelastomer seals reinforced with Kevlar[®] aramide fiber have proven very valuable in oil field exploration. Experience indicates that these assemblies withstand extended exposure to temperatures of 400°F and differential pressures of 15,000 psi in sour gas environments with very little change in properties. These seals retain their flexi-

bility and almost all of their tensile strength after three years downhole service.

Vinylidene fluoride (VF₂) based fluoroelastomers have recently found application in chimney coatings and flue duct expansion joints. The switch by many utilities to inexpensive high sulfur coal as a fuel source results in the production of many corrosive combustion products in power plants. At the 150—250°C temperatures commonly encountered in this application, metal joints fail quickly, but the fluoroelastomer joints will last 5 to 10 years in this corrosive atmosphere.

The fluoroelastomers are remarkable materials used when no other material will suffice. In the following, we will primarily discuss the fluoroelastomers developed at Du Pont because we are most familiar with these materials and, because, to date, they are illustrative of the most commonly used fluoroelastomers. Table I shows a chronological overview of major developments in monomer and polymer technology as it occurred in Du Pont. It also shows how intimately the major three branches of research—monomers, plastics and elastomers—are interconnected, however, we will concentrate on the elastomers branch.

The original Teflon[®] PTFE resin requires special fabrication methods because melt viscosities for

Table I. Chronological overview of major developments in monomer and polymer technology in Du Pont

poly(tetrafluoroethylene) (PTFE) are in excess of 10^{10} poise.¹ Fabrication techniques similar to powder metal sintering and ceramics are used rather than the much simpler extrusion and molding methods common to plastics.

Thus, the search commenced for an easier processing copolymer. This search was responsible for the synthesis of hexafluoropropylene (HFP) shown in the center column of Table I, and set the stage for the development of the copolymers. The TFE/HFP copolymers resulted in the discovery of melt processable Teflon® FEP resin but more to our interest, it made possible the discovery of the first fluoroelastomer, shown in the lefthand column of Table I, Viton® A fluoroelastomer. This product is a copolymer of HFP and VF_2 . Viton® B fluoroelastomer followed soon after and is a similar product that contains some TFE, in addition to VF_2 and HFP.

These early products were typically crosslinked with diamines or diamine carbamates and the crosslink in the elastomeric networks was often the chemically or thermally weak link. Therefore, efforts to develop improved crosslinking chemistry and cure sites were important research objectives. This resulted in a series of products during the late 60's, denoted as the Viton® E types, with more stable crosslinks derived from bisphenols.

The most recent developments are the peroxide curable Viton® G fluoroelastomers. These polymers contain further improvements in crosslink stability, as well as improved low temperature flexibility in the case of Viton® GLT fluoroelastomers.

Table II. Combination of fluorocarbon monomers for elastomer backbone

	$\text{CF}_2 = \overset{\text{CF}_3}{\text{CF}}$	$\text{CF}_2 = \overset{\text{OCF}_3}{\text{CF}}$	$\text{CF}_2 = \overset{\text{Cl}}{\text{CF}}$	$\text{CH}_2 = \overset{\text{CH}_3}{\text{CH}}$
$\text{CF}_2 = \overset{\text{H}}{\text{CH}_2}$	X	X (+ TFE)	X	
$\text{CF}_2 = \text{CF}_2$	X (+ VF_2)	X		X

However, these elastomers still contain significant amounts of hydrogen which make them more vulnerable to chemical and oxidative attack than is Teflon® resin. Because of a need for elastomers for exceedingly hostile environments, effort was also directed at developing an "elastomeric Teflon®," culminating in Kalrez® perfluoroelastomer. This advance was made possible by the preparation of perfluoroalkyl vinyl ethers and functionalized monomers to serve as cure sites.

This brief historical sketch brings us to the consideration of the synthesis and properties of today's fluoroelastomers.

CURRENT TECHNOLOGY

A primary objective in elastomer research is to create amorphous materials which have low glass transition temperatures. Homopolymers of VF_2 and TFE are highly crystalline and, therefore, not elastomeric, but the introduction of HFP into these polymer chains reduces that crystallinity. In the case of VF_2 , sufficient HFP can be incorporated into the polymers to yield a totally amorphous rubbery product. There are many other combinations of monomers that will also yield elastomeric materials and some of these are shown in Table II.

This table includes the monomers which constitute today's important fluorocarbon elastomers. The basic backbone monomers, vinylidene fluoride and tetrafluoroethylene, are shown in the first column. In order to confer the elastomeric property, these monomers are copolymerized with monomers shown in the first row, all of which have a certain structural similarity—a bulky group attached to the vinyl group.

The X's within Table II indicate commercially

available monomer combinations. The two on the far right represent KEL-F®, based on chlorotrifluoroethylene, a specialty product offered by 3M Company, and TFE/Propylene copolymers named Aflas®, currently available from Asahi Glass Company.

In the second column in the table, the first X represents the most common and widely used fluorocarbon elastomers. These are the copolymers of HFP and VF₂, and they are available from a number of manufacturers. The lower element in the second column represents a somewhat less common fluorocarbon elastomer, prepared from HFP, TFE, as well as some vinylidene fluoride.

The top element in the third column represents a polymer from perfluoromethyl vinyl ether (PMVE), VF₂, TFE, and a fourth cure site monomer. This is a relatively new fluorocarbon elastomer. Viton® GLT which is peroxide curable and has improved low temperature flexibility compared to the compositions shown in the second column. This may be just the first example of a new generation of fluoroelastomers employing perfluoroalkyl vinyl ether monomers to obtain good low temperature properties. This point is discussed in more detail below.

The lower element in the third column represents a very interesting class, namely, the Kalrez® perfluoroelastomers—elastomers which contain no hydrogen. These are polymers containing PMVE and TFE.

A graphical comparison of high and low temperature properties and chemical resistance for the fluoroelastomers with the more common heat and oil resistant elastomers^{2,3} is presented in Figure 1. The coordinates are fluid resistance and practical effective temperature range. In terms of their fluid resistance and effective upper service temperature, the fluoroelastomers readily outperform the other high performance elastomers shown here. This figure also points out one of the characteristic problems with fluoroelastomers mentioned above. As heat resistance increases the low temperature service capability decreases so that the total range of useful temperature remains about the same for each of the fluoroelastomers. Fluorosilicones and fluorinated polyphosphazines are commercially available elastomers with inorganic backbones instead of carbon backbones. Their novel structures provide excellent low temperature properties but somewhat poorer

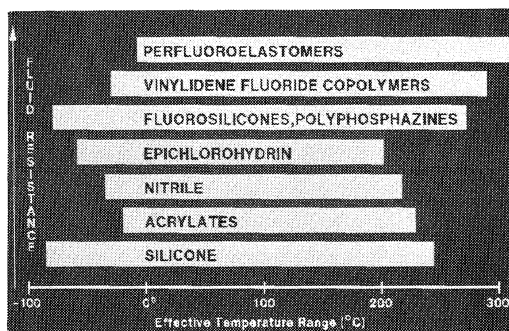


Figure 1. Comparison of high-performance elastomers in terms of effective temperature range.

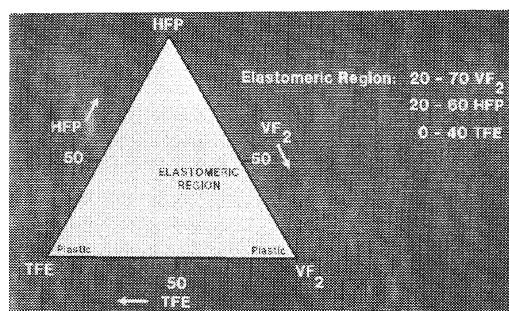
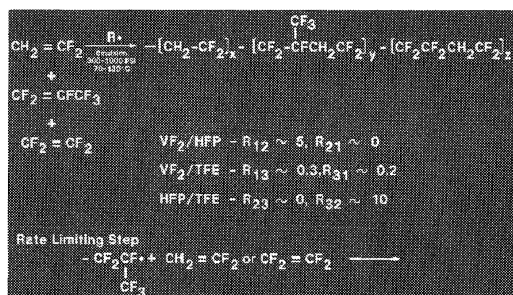


Figure 2. Composition map for the fluoroelastomers.

heat and chemical resistance relative to fluoroelastomers.

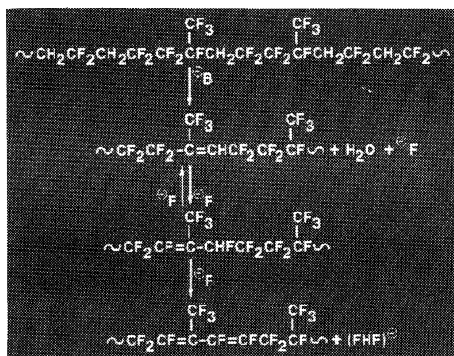
The useful compositional range to obtain an elastomeric backbone involving the three key monomers, TFE, HFP and VF₂, is shown in Figure 2. The region of interest is the one that is centered around a composition of 60% VF₂ and 40% HFP, and it may also contain as much as 40% TFE. On a molecular scale, one HFP unit occurs about every third monomer unit. This is sufficient to prevent crystallization of the polymer and assure an amorphous material.



(1)

These fluoroelastomers are prepared by free-radical polymerization in emulsion⁴ as depicted in eq 1. As the reactivity ratios indicate, when an HFP radical is on the end of the chain it does not react readily, and least of all does it react with itself. Thus, one does not find two or more HFP monomers adjacent to each other in the chain. In fact, a VF₂ residue flanked on both sides by HFP, or by HFP and TFE, respectively, turns out to be a very important structure. It is the cure site for this class of elastomers.

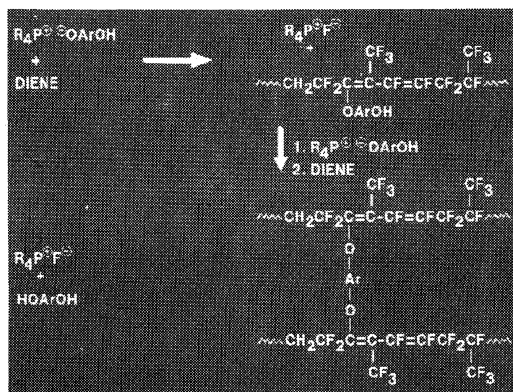
The crosslinking mechanism with diamines or bisphenols was elucidated in a number of recent papers by Schmiegel⁵ of Du Pont and is summarized in eq 2.



(2)

The primary cure site is a VF₂ residue between two HFP residues. NMR data, on a model system in solution support the base catalyzed dehydrofluorination of the VF₂ residue followed by rearrangement to yield the structure containing an allylic proton shown in the second line of eq 2. It was found that compounds such as ammonium or phosphonium salts accelerate this dehydrofluorination reaction which is the rate determining step. Fluoride ion then abstracts the allylic proton and elimination of another fluoride ion yields the conjugated diene as indicated in the last line of eq 2.

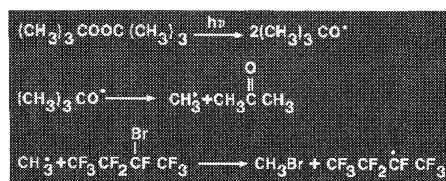
The diene structure generated is susceptible to nucleophilic attack and permits rapid substitution of a diamine or bisphenol, as shown in eq 3, to form a crosslink. Note that the polymer backbone in the crosslinked structure does contain some unsaturation. This is a potential weak spot in the polymer chain susceptible to oxidative attack. Also, the nature of these crosslinks, especially for the dia-



(3)

mine, is such that they are sensitive to attack by steam under certain conditions. The desire to eliminate unsaturation and to produce a more hydrolytically stable crosslink resulted in the development of the peroxide curing system.⁶

This necessitated the synthesis of polymer containing peroxide sensitive cure sites and led to development of the Viton® G types. Brominated monomers derived from fluorinated ethylenes or butenes were found to be the best for this purpose. In addition, a radical trap or coagent is required for optimum crosslinking. The coagent can be a variety of polyunsaturated materials but triallyl-isocyanurate is one of the best.

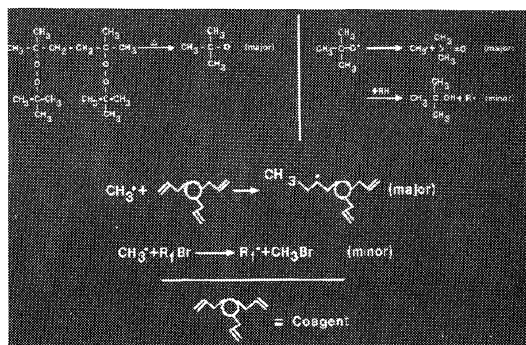


(4)

As shown in eq 4, model compound studies⁶ disclosed that methyl radicals generated by the decomposition of di-*t*-butyl peroxide react with 2-bromoperfluorobutane to yield methyl bromide and the fluorocarbon radical. The structure of the radical was confirmed by ESR spectroscopy.

Additional work with coagents and peroxide in rubber compounds indicates the curing chemistry is somewhat more complex than that suggested by the ESR studies. With reference to eq 5, a major volatile reaction product is acetone, but comparatively little methane or methyl bromide was observed. This

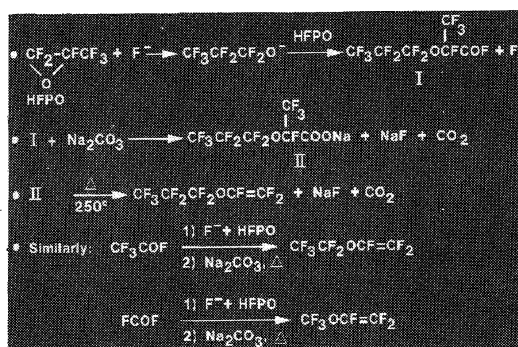
requires some species to absorb the methyl radicals produced. The authors propose the major reaction to be addition of methyl radical to the coagent to generate a new radical as shown schematically in eq 5.



(5)

Since crosslinking does occur and since the chemical stability of the resulting network does depend on the coagent, it seems very likely that the coagent radicals do attack the bromide cure site in the polymer starting chain reactions ultimately leading to crosslink formation. This is shown schematically in Figure 3.

The successful development of the peroxide curable elastomers has helped produce materials with improved heat and chemical resistance. However, to attain what is perhaps the ultimate in fluoroelastomer stability, it has been realized for a long time that a perfluorinated backbone would be required. This has led to the development of Kalrez[®] perfluoroelastomers. This advance in technology was made possible by the synthesis of perfluoroalkyl vinyl ether monomers. The preparation of these monomers is outlined in eq 6.



(6)

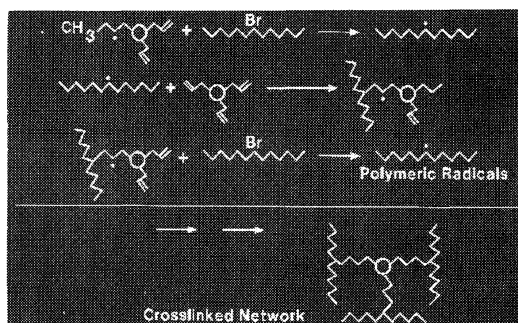
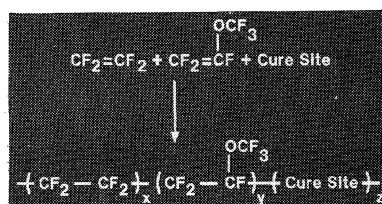


Figure 3. Crosslinking reaction mechanism of peroxides.

The first line shows the dimerization of hexafluoropropylene oxide (HFPO) to yield acid fluoride I. Reaction of the acid fluoride with sodium carbonate provides the sodium salt II, which when pyrolyzed, eliminates sodium fluoride and CO_2 to yield perfluoropropyl vinyl ether.⁷ This synthetic scheme can be generalized by using an acid fluoride, instead of HFPO, to first react with fluoride ion. The anion thus formed adds one molecule of HFPO to yield a new intermediate acid fluoride. Conversion of this to the sodium salt and pyrolysis forms a new perfluoroalkyl vinyl ether. The use of trifluoroacetyl fluoride and carbonyl fluoride to prepare perfluoroethyl- and perfluoromethyl vinyl ethers, respectively, is shown in the last two lines of eq 6.⁸

The discovery that these vinyl ethers were much more reactive in free radical polymerization with TFE than was HFP made it possible, for the first



(7)

time, to prepare a rubbery high molecular weight perfluorinated copolymer. For Kalrez[®] perfluoroelastomer, PMVE and TFE, as shown in eq 7, are used to obtain an elastomer with thermal stability⁹ to about 300°C, very similar to PTFE resin. The next challenge was to develop a cure site monomer as stable as the backbone. This took nearly ten years to accomplish. Some generalized

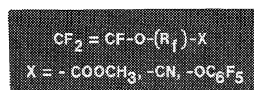


Figure 4. Curesite structure of perfluoroelastomers.

cure site structures which have been described in the literature¹⁰ are shown in Figure 4 in which X may be a carbomethoxy-, cyano-, or pentafluorophenoxy group and R_F is a fluoroalkyl or fluoroalkyl ether group. Crosslinking depends on the reactivity of the terminal functional group. In contrast to the VF₂ based elastomers, no unsaturation is generated in the polymer chain during crosslinking and this, coupled with its perfluorinated structure, is responsible for the excellent thermal and oxidative stability of the product.

This summarizes fluoroelastomer technology as it stands today, but this is not a static area. Work is presently progressing toward the development of fluoroelastomers with properties superior to today's products. Fluoroelastomers with improved low temperature properties are important goals in this work and will be important members in tomorrow's list of fluoropolymers. Indeed, attainment of low temperature flexibility, down to -50°C or below, has been a continuing challenge.

EXPERIMENTAL

Perfluorovinyl polyether monomers (PVPE)—These materials were prepared according to literature procedures¹⁸ and were purified by passing the crude PVPE monomers through a 1 × 10 cm column packed with neutral alumina. This gave product, C₃F₇O[CF(CF₃)CF₂O]_nCF=Cf₂, with a range of *n* values. Pure oligomers with a single value of *n*, were isolated by fractional vacuum distillation of the oligomer mixture in a 50 cm spinning band still. Thus, oligomers with *n*=2 or 3 were obtained with the respective boiling points 85–88°C/90 mm and 115–120°C/90 mm.

PVPE monomers were analyzed by ¹⁹F NMR using a Varian XL-100 spectrometer and by gas chromatography using a 1.8 m × 3.2 mm column packed with 20% FS-1265 on Gaschrom R 60/80, available from Supelco, Inc. By comparing the integrated NMR signal values for the tertiary fluorine atoms (-145 ppm relative to Freon®11) in PVPE with those for the vinylic fluorine atoms

(-115, -123, -136 relative to Freon®11) the value of *n* was determined. When a mixture of PVPE monomers having different values of *n* was used, an average value of *n* is calculated and used to calculate a number average molecular weight (*M_n*) for the monomer mixture. The concentration of each constituent present in such a mixture was determined by gas chromatography for moderate values of *M_n*. For example, chromatographic results for a PVPE mixture when the average *n* is 5.2 and *m_n* is 1130 are shown below.

Gas chromatographic analysis of PVPE

<i>n</i>	1	2	3	4	5	6	7	8
%	0.14	1.7	10.7	24.6	32.1	20.1	8.1	2.5

Analysis of a PVPE mixture when *n* was 10.9 and *M_n* was 2080 was unsuccessful because components with *n* larger than 10 did not pass through the chromatograph column. However, from the distribution of observable low molecular weight components and the *M_n* by NMR, we conclude this sample contained oligomers with *n* up to about 20.

Polymerizations—PVPE was weighed into a heavy walled 20 ml polymer tube. The tube was attached to a vacuum line and the PVPE was degassed by freezing under vacuum in liquid nitrogen. The desired amounts of TFE and PMVE were measured volumetrically into the vacuum line and then condensed into the polymer tube. Perfluoropropionyl peroxide (3P) in a stock solution of Freon® TF (1,1,2-trichloro-1,2,2-trifluoroethane), stored at 0°C, was added by means of a syringe to the polymer tube through a heavy walled rubber coupling connecting the polymer tube to the vacuum line. The tube was sealed and allowed to warm. When the tube warmed to about 0°C, it was placed on a shaker and the polymerization was allowed to proceed at room temperature for the desired length of time.

Alternatively, the PVPE, Freon® TF and 3P were added to a 75 ml stainless steel bomb. The bomb and its contents were cooled in an acetone/dry ice bath and alternately evacuated and filled with nitrogen three times to deoxygenate the bomb contents. The desired amounts of TFE and PMVE were then metered into the bomb which was then placed on a thermostated shaker at 60°C.

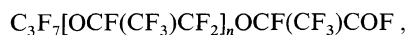
Experiment	1	2	3	4	5	6	7	8	9	10	11	12
Freon [®] TFD (ml)	10	10	10	10	10	10	5	5	5	5	3	3
PVPE (g)	9	9	15	20	9	9	18	15	9	8.1	7.6	15.6
<i>n</i>	5.2	5.2	5.2	5.2	5.2	5.2	10.9	10.9	5.2	2.0	3.0	3.0
PMVE (g)	4	6	4	—	4	1.3	4	2	4	3	2.8	2.3
TFE (g)	1.5	4	1.5	9.75	0.8	0.8	1.5	1.0	1.55	1.55	1.57	1.57
3P (g)	0.05	0.05	0.05	0.05	0.05	0.05	0.25	0.25	0.025	0.025	0.015	0.015
(I) (g) ^a	—	—	—	—	—	—	—	—	1.0	—	—	—
Conditions °C h ⁻¹	60/3	60/3	25/24	25/72	25/18	25/18	25/20	25/20	48/25	70/25	96/25	96/25
Polymer												
Wt (g)	1.7	2.8	2.0	1.3	0.72	2.0	0.83	0.94	1.6	0.46	2.7	4.3
Mole %												
PVPE	8	8	13	32	13	14	8	6.5	10	9	16	25
PMVE	13	26	15	—	27	12	20	18	15	12	23	8
TFE	79	66	72	68	60	74	72	76	72	78	61	67
(I)	—	—	—	—	—	—	—	—	3	—	—	—
<i>T_g</i> (°C)	-38	-43	-64	-76	-55	-67	-56	-63	-41	-9	-33	-61

^a (I): CF₂=CFOCF₂CF(CF₃)OCF₂CF₂CN.

In each case polymer was isolated by evaporating Freon[®] TF and some unconverted monomer under vacuum at 100°C. Polymers with high PVPE content were soluble in the residual monomer/Freon[®] TF mixture but not in pure Freon[®] TF. The final portions of monomer were removed from the polymer by extraction with 3 portions of Freon[®] TF. The polymer was then dried to constant weight in a vacuum oven at 110–120°C.

The quantities of material charged in each case and the results obtained are reported in the table above for several polymerizations. Polymers were analyzed by ¹⁹F NMR to determine composition. Solutions of the polymers in 2,2,4,4-tetrakis-(trifluoromethyl)-1,3-dithiatane containing Freon[®] 11 as an internal reference were used for this purpose. Glass transition temperatures were determined by differential scanning calorimetry using a Du Pont 990 instrument and the values reported are the average of one heat and one or two reheats of a given sample.

Plasticization experiments—sufficient perfluorinated polyether oil of formula



where *n* is 4 to 24 and *M_n* is 1130, was added to each of two vials containing 0.1 g of the polymer from experiment 1, to provide mixtures corresponding to 23% and 50% oil by weight. The mixtures were heated to 100°C and the oil was absorb-

ed by the polymer to form a uniform elastic solid at room temperature. To insure uniformity of the samples, each was pressed between sheets of Kapton[®] polyimide film in a heated press. The film thus formed was rolled into a cylinder, folded and repressed. This was repeated five times, and the sample was reweighed to verify that no significant weight loss had occurred. The *T_g* of each sample was then measured by DSC. The results plotted in Figure 7 show a regular decrease in *T_g* with increasing oil content.

THE DEVELOPMENT OF LOW TEMPERATURE FLUROELASTOMERS

Fluroelastomers have frequently been unsatisfactory for applications demanding really good low temperature properties. The search for suitable substitutes uncovered excellent low temperature properties with entirely different classes of polymers, namely, the fluorosilicones and fluorinated polyphosphazines. Representative structures for these polymers are presented in Figure 5.

The fluorosilicones, with alternating silicon and oxygen atoms in the backbone, have excellent low temperature properties and exhibit very low glass transition temperatures (*T_g* ~ -70°C) as do some of the polyphosphazines, first pioneered by Allcock,¹² and recently commercialized by the Firestone Company. Although these materials are excellent elastomers with exceptional low temperature capa-

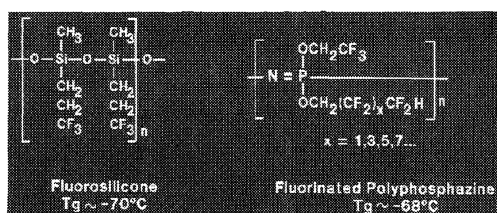


Figure 5. Representative structures for the fluorosilicone and fluorinated polyphosphazine.

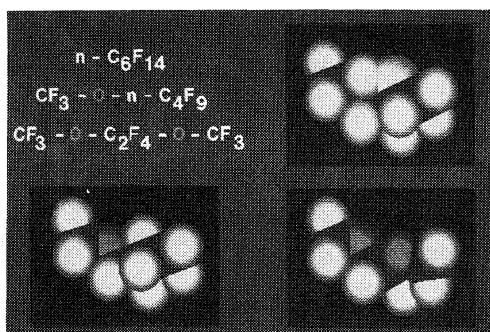


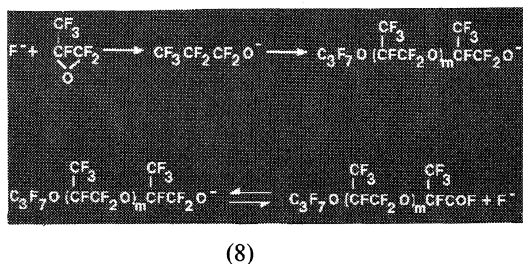
Figure 6. Computer drawn models of 3,4-gauche forms.

bilities, they compromise the thermal and chemical resistance offered by fluorocarbon elastomers.

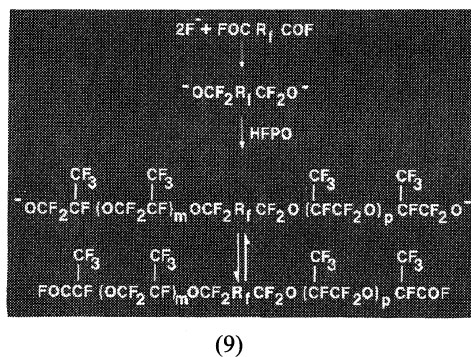
For this reason, many attempts have been made to modify fluorocarbon structures to obtain a good combination of low temperature properties as well as good heat and chemical resistance. The main thrust appears to have been based on HFPO chemistry since anionic polymerization of the epoxide places ether linkages in the polymer backbone.

The presence of the oxygen atom in the polymer backbone has a dramatic effect on T_g. This can be qualitatively illustrated by reference to the computer drawn models in Figure 6. The perfluorohexane model in the upper right of Figure 6, shows some rather severe interactions between fluorine atoms when the molecule is in the 3,4-gauche form. These high energy conformations will inhibit bond rotation and tend to raise the temperature where the polymer becomes glassy. Inserting oxygen atoms into the chain to replace CF₂ groups effectively reduces these interactions. Examination of the ether structures in the lower half of Figure 6 suggest much lower steric interactions, particularly when oxygen atoms occur about every third place in the chain. This tends to lower T_g and better low temperature

properties would be anticipated for the polyether structure.

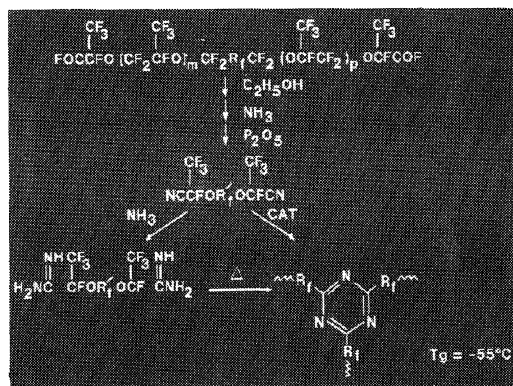


Equation 8 illustrates the anionic polymerization of HFPO as described by Hill.¹³ By analogy to certain hydrocarbon systems, we might anticipate any desired molecular weight can be obtained by selecting an appropriate monomer to initiator ratio. However, polymerization in the fluorocarbon system is complicated by the apparent equilibrium established between the growing alkoxide and the acid fluoride generated by eliminating a fluoride ion from the alkoxide. This equilibrium appears to have prevented preparation of truly high molecular weight elastomers.

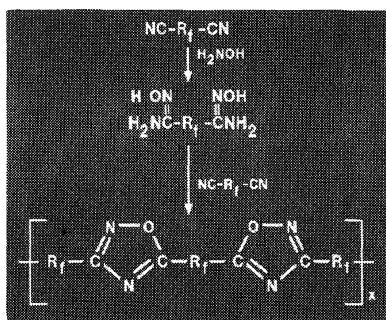


Recognition of the equilibrium suggested the use of difunctional initiators to provide intermediates to high polymers. As shown in eq 9, HFPO is added to both ends of the initiator and eventually a much larger diacid fluoride is made. The diacid fluoride can be used for chain extension to high molecular weight elastomers as shown in eq 10.

The diacid fluoride is converted sequentially to the diester, the diamide, and then to the dinitrile.¹³ The nitrile may be treated with more ammonia to yield the amidine which reacts to form the *s*-triazine or, alternatively, the dinitrile may be cyclized directly with the use of various metal catalysts. Such



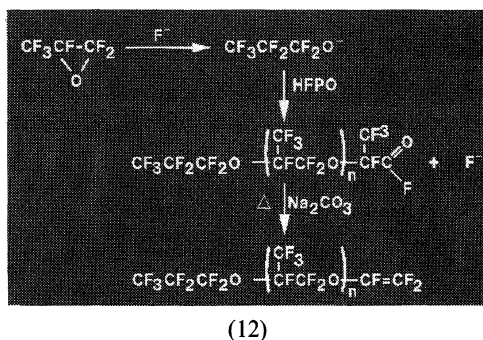
networks were found to have a T_g of -55°C although other properties were seen to be deficient.



Another example of chain extension chemistry recently developed at NASA¹⁴ is shown in the eq 11. In this case, the nitrile is converted to an amidoxime which reacts with another nitrile to form the oxadiazole. Other examples of chain extension chemistry are provided in the literature¹⁵; however, to our knowledge, none of these provide as yet, convenient routes to high polymers.

A newer approach to this problem is being investigated in Japan by workers at Asahi Glass¹⁶ and Daikin¹⁷ and in the U.S. by Du Pont. In this work, vinyl monomers with large fluorinated polyether groups are used to depress the glass transition temperature of the polymer. The preparation¹⁸ of such monomers with HFPO is illustrated in eq 12. Similar chemistry can be used to make analogous monomers from the epoxides of TFE, CTFE and other fluorinated olefins.

Since n in the formula for the monomer need not be very large in order to obtain elastomeric co-



polymers with low glass transition temperatures, the molecular weight limitations imposed by the alkoxide-acid fluoride equilibrium mentioned above in the anionic polymerization of HFPO are unimportant. High polymer molecular weight is achieved by free radical copolymerization of these vinyl polyether monomers with TFE, VF_2 or ethylene.^{16,17}

Examples of each type of copolymer are shown in the next Table III. In these cases, n , the number of ether units added onto the vinyl ether monomer is quite small, only 1 or 2, yet the glass transition temperatures are well below the -10 to -20°C values typically observed for VF_2/HFP elastomers. The effect of the polyether side chain length on copolymer low temperature properties is an interesting question which we have studied at Du Pont. Data are graphically presented in Figure 7.

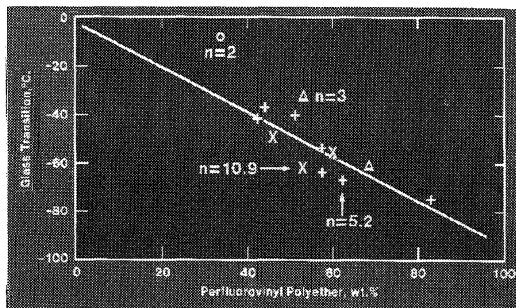
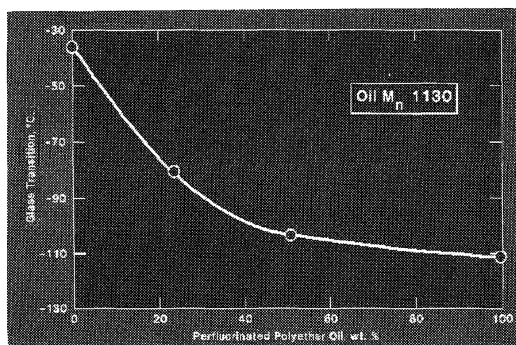
In this case, terpolymers of TFE, PMVE and the perfluorovinyl polyether (PVPE) were made. PMVE was added to insure a completely amorphous polymer. In this way, the thermal properties of polymers with wide variations in PVPE content could be studied without crystallization occurring at the lower concentrations of PVPE.

Figure 7 clearly shows the strong dependence of the glass transition temperature on the PVPE content of the polymer. Interestingly, we find that most of the data tend to fall near a single line after some minimum number of ether linkages are present in the side chain. Large deviations from the line are only observed when n is small, as shown by the circular and triangular points in figure 6 for $n=2$ or 3, respectively. The line was drawn to intercept the temperature axis near the value for the T_g of TFE/PMVE copolymers. Evidently, the effect of side chain length on the glass transition attenuates quickly with the effect for monomers with $n=3$ or 4

Table III. Fluorinated vinyl polyether copolymers

Comonomer	% Ether	n	T _g	Note
TFE	27	2	-32	1
VF2	51	2	-44	1
E	47	1	-41	2

1. Diakin
2. Asahi Glass

**Figure 7.** The relation between wt% of polyfluorovinyl polyether and glass transition temperatures.**Figure 8.** The relation between wt% of perfluorinated polyether oil and glass transition temperatures.

about the same as that for much large values of n .

As these data show, it is now possible to prepare perfluorinated elastomers with glass transition temperatures as low or lower than those of the fluoro-silicones or polyphosphazines.

These terpolymers have another interesting property. As shown in Figure 8, they can be effectively plasticized with perfluorinated ether oils derived from HFPO. Plasticization of fluoropolymers has not been satisfactory to date because plasticizers combining high heat and chemical resistance, low volatility and compatibility with fluoroelastomers

have not been found. The polyether side chains of these elastomers, however, make them compatible with oils derived from moderate molecular weight HFPO oligomers. These plasticizers do combine low volatility with heat and chemical resistance equivalent to the elastomer. In addition, the T_g for HFPO oligomers is extremely low. For example, the oil with $M_n = 1130$ has a $T_g = -111^\circ\text{C}$. As shown in Figure 8, an elastomer with $T_g = -38^\circ\text{C}$ can be plasticized to a T_g of -103°C by mixing equal parts of elastomer and oil. Compounding fluoroelastomers to obtain such drastic changes in T_g has not been possible before.

CONCLUSION

In conclusion, we have traced the discovery and development of fluoroelastomers from their beginnings in the mid-50's to the present day. The ever increasing performance goals for these products has spurred continuing development of new materials. This has resulted in materials with improved cross-linking chemistry and, more recently, in totally perfluorinated elastomeric products. Improved low temperature properties are seen as important goals in current fluoroelastomer research. We have discussed some recent work to develop such products and have discovered that it should be possible to combine excellent low temperature properties with the heat and chemical resistance commonly associated with perfluorinated polymers. Much has been accomplished but much remains to be done. Based on past and present activities, it seems clear that there is considerable potential for the continued evolution of new fluoroelastomers. As these materials are developed, it is certain the fluoroelastomers will play a continuing and, most likely, an increasingly important role in modern society.

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