Fluoroelastomers: synthesis, properties and applications

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Abstract

The review seeks to cover recent developments in the area of fluorinated elastomers. It reports that, except for isolated cases, most fluoroelastomers are synthesized by radical co-, ternary or tetrapolymerizations. Hence, after reminding the most known syntheses of fluoroalkenes involved in the preparation of these fluoropolymers and recent achievements of block, graft and alternating copolymers, several academic laws and concepts (e.g. kinetics) of the copolymerization are presented. The section dealing with the synthesis of fluoroelastomers is divided into two parts: the first one covers the preparation of fluorinated copolymers containing tetrafluoroethylene, while the second one extensively describes the preparation of fluoroelastomers based on vinylidene fluoride. This section also points out recent syntheses on novel reactive functional trifluorovinyl or vinyl ether monomers for easy curing of original fluoropolymers. Then, heteroatom-containing fluoroelastomers are briefly summarized. Various methods of curing are reported in the following section while the next one describes ingredients used in formulations of fluoroelastomeric systems. This review also covers compounding and processing of this class of fluoropolymers. Finally, a summary of various properties and applications of fluoroelastomers is presented showing how such products resistant to severe conditions are useful in modern industries. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Fluoroelastomers; Fluoroalkenes; Copolymers; Cure site monomers; Kinetics of copolymerization; Crosslinking; Processing; Synthesis–properties relationship; Applications

Contents

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1. Introduction

In contrast to the organic or inorganic fluorine chemistries (dating from 1670), that of fluorinated polymers is rather recent: the first discoveries were achieved in the late 1930s with the synthesis of low-molecular weight polychlorotrifluoroethylene (PCTFE) [1] followed by that of high-molecular weight polytetrafluoroethylene (PTFE) by Plunkett [2] in 1938. Then, several homopolymers were obtained and further generations of (co)polymers made of various (per)fluorinated base units were prepared. Nowa-days, functional polymers bringing new properties have found novel applications and are expanding. A brief history of the evolution of fluoropolymers, based on these last 65 years, enables one to understand their extraordinary development and is presented in Table 1.

Fluorinated polymers are particularly interesting and attractive compounds because of their versatility (they range as a wide scope of thermoplastics, elastomers, plastomers, thermoplastic elastomers and can be semi crystalline or totally amorphous) and their unique combination of relevant properties [3] (mainly linked to the low polarizability and the strong electronegativity of the fluorine atom, to its small Van Der Waals

Nomenclature

CSM	Cure site monomer
CTFE	Chlorotrifluoroethylene
E	Ethylene
HFP	Hexafluoropropylene
HFPO	Hexafluoropropylene oxide
IR_FI	α,ω-Diiodoperfluoroalkane
ITP	Iodine transfer polymerization
M	Monomer
NMR	Nuclear magnetic resonance
P	Propene
PAVE	Perfluoroalkyl vinyl ether
PAAVE	Perfluoroalkoxy alkyl vinyl ether
PFPE	Perfluoropolyether
PMVE	Perfluoromethyl vinyl ether
PPVE	Perfluoropropyl vinyl ether
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
R	Alkyl group
R_F	Perfluorinated group
R_FI	Perfluoroalkyl iodide
Sty	Styrene
TAC	Triallyl cyanurate
TAIC	Triallyl isocyanurate
TFE	Tetrafluoroethylene
TFS	α,β,β-Trifluorostyrene
T_{dec}	Decomposition temperature
T_g	Glass transition temperature
VDF (or VF_2)	Vinylidene fluoride (or 1,1-difluoroethylene)
Δ	Heating

radius (1.32 Å) and to the strong C–F bond (485 kJ mol^{-1}). Hence, fluoroplastics with high fluorine contents exhibit high thermal, chemical, ageing and weather resistance, excellent inertness to solvents, hydrocarbons, acids and alkalies, low dielectric constants, low flammability, low refractive index, low surface energy (interesting oil and water repellency) and moisture absorption. Furthermore, the presence of the strong C–F bond [3] has a crucial impact on the high resistance to oxidation and to hydrolytic stability.

Hence, these specialty polymers have been used in many applications: building industries (paints and coatings resistant to UV and graffiti), petrochemical and automotive industries, aerospace and aeronautics (use of elastomers as seals, gaskets, O-rings used in extreme temperatures for tanks of liquid hydrogen for space shuttles), chemical engineering (high-performance membranes), optics (core and cladding of optical fibers), treatment of textile, stone (expecially for old monuments), microelectronics. In spite of their high price (mainly linked to unusual processes of polymerization, to the cost of purifying

Table 1
Historical development of fluorinated polymers

1st Generation: Fluorinated homopolymers	
1934–1938	PCTFE (C_2F_3Cl), PTFE (C_2F_4)
1950	PVDF ($C_2H_2F_2$), PVF (C_2FH_3), PTrFE (C_2F_3H)

2nd Generation: Fluorinated copolymers	
1950–1960	VDF/CTFE ($C_2H_2F_2$–C_2F_3Cl)
	VDF/HFP ($C_2H_2F_2$–C_3F_6)
	FEP (C_2F_4–C_3F_6)
	PFA (C_2F_4–CF_2=CF–OC_3F_7)
1980	ETFE (C_2H_4–C_2F_4)
	E/CTFE (C_2H_4–C_2F_3Cl)
	Elastomers (see Table 2)
	Copolymers of fluorinated acrylates
1989	Amorphous transparent copolymers: Cytop® and Teflon® AF (then Hyflon® AD, 1996)

3rd Generation: Fluorinated functional polymers	
1980	Ion exchange membranes; room temperature crosslinkable paints
1995	Crosslinkable resins and elastomers

the gaseous monomers and to the small scale of production), these polymers have found major developments in modern technologies.

Various books [4–9], chapters of books [10] or reviews [11–14] have provided useful and exhaustive data on homopolymers and are not detailed in this review.

However, fluoroplastics have various disadvantages: the homopolymers are often crystalline, exhibit a poor solubility in common organic solvents and are not cured or crosslinked easily. This is why the generation of fluorinated copolymers [15–26] (involving a mixture of comonomers that induces disorder of the macromolecule and thus reduces or gets rid off the high crystallinity of the homopolymer) has extensively grown without possessing the drawbacks of homopolymers mentioned above. After presenting various fluoroolefins involved in copolymerization and reminding several theoretical laws and concepts on the copolymerization, the objective of this review deals with the synthesis, characterization, properties, curing and applications of numerous fluoroelastomers (including perfluoroelastomers and those containing heteroatoms).

2. Fluoroelastomers

2.1. Combination of fluoroalkenes

Table 2 lists various comonomers which constitute today's commercial elastomers. This table exhibits lines associated to columns for which most intersections lead to fluoroelastomers [16–23]. The fluorinated comonomers can be chosen for specific properties of the co-, ter- or tetrapolymers. To obtain

Table 2

Main commercially available fluoroelastomers (CTFE — chlorotrifluoroethylene ($F_2C=CFCl$); HFP — hexafluoropropene ($F_2C=CFCF_3$); HPFP — 1-hydropentafluoropropene ($HCF=CFCF_3$); P — propene ($H_2C=CHCH_3$); PMVE — perfluoromethyl vinyl ether ($F_2C=CFOCF_3$); TFE — tetrafluoroethylene ($F_2C=CF_2$); VDF — vinylidene fluoride (or 1,1-difluoroethylene) ($F_2C=CH_2$); X — CSM (G is a halogen atom or a functional group) ($F_2C=CF–R–G$))

	HFP	PMVE	CTFE	P	HPFP
VDF	Daiel[®] 801 (Daikin) Fluorel[®] (3M/Dyneon) Tecnoflon[®] (Ausimont) SKF[®]-26 (Russia) Viton[®] A (DuPont)	–	Kel F[®] (Dyneon) SKF[®]-32 (Russia) Voltalef[®] (Elf Atochem)	–	Tecnoflon[®] SL (Ausimont)
TFE	–	Kalrez[®] (DuPont)	–	Aflas[®] (Asahi Glass)	–
VDF + TFE	Daiel[®] 901 (Daikin) Fluorel[®] (Dyneon) Tecnoflon[®] (Ausimont) Viton[®] B (DuPont) + E: Tecnoflon[®] (Ausimont) + X: Viton[®] GH (DuPont)	Viton[®] GLT (DuPont)	–	–	Tecnoflon[®] T (Ausimont)

elastomeric properties (i.e. amorphous material with a low glass transition temperature), basic monomers such as vinylidene fluoride or 1,1-difluoroethylene (VDF or VF$_2$) and tetrafluoroethylene (TFE) (lines) can be copolymerized with other fluorinated co-monomers of topological similarity with sometimes a bulky group attached to a vinyl functionality [17,22–24]. One efficient example concerns the introduction of hexafluoropropene (HFP) into highly crystalline PVDF to reduce the crystallinity and for sufficient incorporated HFP a totally amorphous rubbery polymer is obtained. If improved low-temperature flexibility is required, perfluoroalkyl vinyl ethers (PAVEs) (and especially those containing more than one oxygen atoms) are preferred over HFP. It is well-known that poly(hexafluoropropylene), PHFP can be produced under "exotic" conditions [4] (high pressure and temperature or special electron beam irradiations). Except for VDF/hexafluoroisobutylene, CTFE/ethylene (E), CTVE/vinyl ethers, TFE/E and TFE/propene which possess an alternating structure (see Section 3.2.3.), all other copolymers are random. In several cases, another reactive monomer is added in small amount to provide functional groups suitable for curing or crosslinking. This cure site monomer (CSM), which is more difficult to prepare, is usually added in few mole percents (less than 5%).

Table 2 also supplies fluoroelastomers trademarks produced by main important companies involved in fluorine chemistry.

This review illustrates numerous examples of fluoropolymers and mainly those of TFE- and VDF-based copolymers (Sections 4 and 5).

2.2. Synthesis of fluoroalkenes

This section focuses on the preparation of most known fluoroalkenes, while the more exotic ones are detailed later: especially PAVEs or PAAVEs described in Section 4.5 or fluorinated nitroso or phosphazene monomers (reported in Section 6.3).

Fluoroalkenes [4,10,11,22] are obviously the raw materials for obtaining fluorinated cotelomers [27] or fluoroelastomers.

2.2.1. Vinyl fluoride

Vinyl fluoride can be prepared either in a two-step process by the addition of two moles of HF onto acetylene leading to 1,1-difluoroethane (CFC 152) which undergoes a dehydrofluorination [28], or in a one-step reaction catalyzed by mercury catalyst [29–31]:

$$HC \equiv CH + HF \xrightarrow{Hg} H_2C = CHF$$

$$CH_3CHF_2 \quad -HF$$
$$CFC\ 152$$
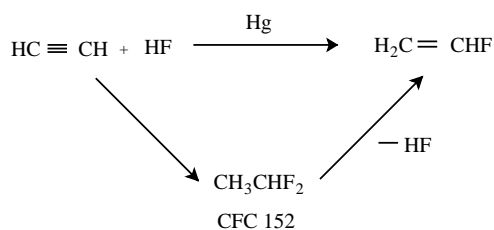
This olefin can also be obtained from the dehydrochlorination of 1-chloro-1-fluoroethane [32] or 1-chloro-2-fluoroethane in vapor phase [33]. Other procedures have also been proposed [34].

2.2.2. Vinylidene fluoride (VDF or VF$_2$)

Various syntheses are possible to prepare VDF.

First, the chlorination of CFC 152 to 1-chloro-1,1-difluoroethane (CFC 142) [35] followed by a dehydrochlorination at about 700–900°C in the gas phase [36–39] is the most typical process:

$$\text{CFC 152} + Cl_2 \longrightarrow CH_3CF_2Cl + HCl$$
$$\Delta \downarrow$$
$$H_2C=CF_2$$
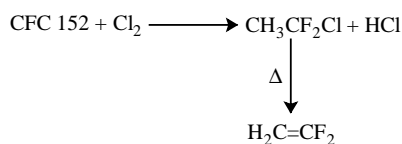
The elimination can also be performed either at higher temperatures [36], in the presence of copper catalyst [40] or at lower temperatures in the presence of steam.

Second, the hydrofluorination of 1,1,1-trichloroethane yields CFC 142 [41] which is subsequently dehydrochlorinated as above:

$$CH_3CCl_3 + HF \rightarrow CH_3CF_2Cl \underset{\Delta}{\rightarrow} \underset{VDF}{H_2C=CF_2}$$
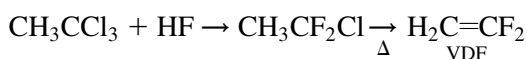
Third, the catalytic pyrolysis (at 400°C in the presence of CrF$_3$·3H$_2$O) of 1,1,1-trifluoroethane requires specific conditions but produces VDF in high yield and purity [42–44].

Fourth, the dechlorinations of 1,2-dichloro-1,1-difluoroethane [45–47] and of other intermediates [48] were also achieved:

$$ClCF_2CH_2Cl \overset{Zn}{\rightarrow} F_2C=CH_2$$
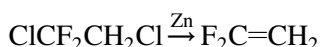
In this review, Section 5 is devoted to copolymers from VDF.

2.2.3. Chlorotrifluoroethylene (CTFE)

CTFE can be synthesized from the hydrofluorination of perchloroethane leading to 1,1,2-trichloro-1,2,2-trifluoroethane (CFC 113) subsequently dechlorinated in the presence of zinc/methanol [49–51] or in the gas phase involving aluminum fluoride-nickel phosphate [52] or metal oxide catalysts in the presence of hydrogen [53]:

$$\underset{CFC\ 113}{Cl_3C–CCl_3 + HF \rightarrow Cl_2CF–CF_2Cl}$$

$$\text{CFC 113} \underset{CH_3OH}{\overset{Zn}{\rightarrow}} F_2C=CFCl + ZnCl_2$$
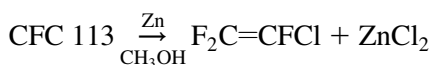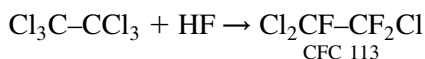
2.2.4. Tetraflouroethylene (TFE) and hexafluoropropylene (HFP)

TFE can be produced from a non-catalytic gas-phase pyrolysis of chlorodifluoromethane (CFC 22) at high temperatures (600–900°C) and atmospheric or subatmospheric pressures [37,54]. Steam or other inert gas may be used as diluents. The reaction is assumed to occur via the formation and dimerization of difluorocarbene and high yields (95%) are achieved:

$$2CHClF_2 \underset{\Delta}{\rightarrow} F_2C=CF_2 + 2HCl$$
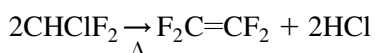
According to the reaction conditions (thermal profiles of the pyrolyzer and temperatures) TFE can add to difluorocarbene or decomposes itself.

Hence, major by-products, including HFP, highly toxic perfluoroisobutylene (the lethal concentration (LC 50) of which is only few parts per billion [55]), octafluorocyclobutane and also chlorofluoroalkanes are removed by a complex distillation [56,57].

HFP, obtained as a co-product in the production of TFE [58], is also prepared by heating TFE to 700–900°C under reduced pressure [59–62]:

$$3F_2C=CF_2 \rightarrow 2F_3C–CF=CF_2$$
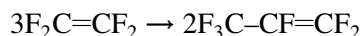
The relative amounts of TFE and HFP from the pyrolysis processes can be controlled by the reaction conditions. HFP has also been prepared by pyrolysis of 2-chloro-1,1,1,3,3,3-hexafluoropropane [63]. Other syntheses of TFE and HFP have been reported already [54,64], but they are not practiced commercially. The copolymers of TFE are described in Section 4.

While 2-hydropentafluoropropene is prepared by Ausimont [65] from HFP, trifluoroethylene is prepared from 1,1,1,2-tetrafluoroethane (CFC 134a), produced by various companies [66].

Regarding hazards and price, TFE, which may deflagrate with considerable violence under pressure, heat and in the presence of oxygen (the reaction is exothermic to the extent of 276 kJ mol^{-1}) [65], as trifluoroethylene [66], is according to certain companies at least 10 times more expensive than VDF.

2.2.5. 3,3,3-Trifluoropropene

As mentioned above, the preparation of such a monomer has been reported already in the patent literature [67]. This fluoroolefin has been involved in the copolymerization of various other fluorinated alkenes such as TFE [68–72] which will not be detailed in this review. However, it is an extremely useful precursor of methyl(3,3,3-trifluoropropyl)dichlorosilane (by hydrosilylation reactions) for the preparation of commercially available fluorosilicones as described in Section 6.5.

2.2.6. Fluorinated styrenic monomers

Fluorinated aromatic monomers are scarce and examples are given hereafter considering styrenic monomers where the fluorine atoms are linked to the ethylenic carbon atom, only.

Regarding α,β,β-trifluorostyrene (TFS), various ways of synthesis have been proposed. A one-step method consists in the addition of TFE to LiC_5H_6 leading to TFS [73]. Other routes start from trifluor-oacetic acid fluoride either via a Friedel and Craft reaction [74] or via an organomagnesian [75], leading to $CF_3C(O)C_6H_5$ as a useful intermediate of TFS.

The organometallic approach was also suggested by Burton et al. [76,77] who isolated TFS in 74% yield, as follows (X = Cl or Br):

$$F_2C=CFX + Zn \xrightarrow{DMF} F_2C=CFZnX \xrightarrow{Pd(PPh_3)_4} F_2C=CFC_6H_5$$
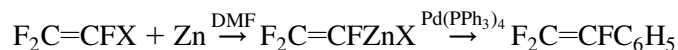
Although homopolymerization of such trifluorovinyl aromatic monomers is difficult, except in emulsion [78,79] or plasma [80] processes, the copolymerization with $F_2C=CFY$ (with Y = Cl, F, CF_3) was successfully achieved leading to novel sources of energetic materials [81].

Poly-TFS possesses much better resistances to oxidation and to chemicals than those of halogenated homologues. On the other hand, a wide range of functional groups can be attached to the aromatic ring. A sulfonated polymer was successfully used as a membrane for fuel cells by General Electric Co. [75,79].

Other fluoroaromatic monomers are synthesized from the reaction of triphenylphosphorane with chlorodifluoromethane, leading to $F_2C=CRPh$ (R = H or CH_3) [82].

2.3. Polymerization of fluoroalkenes

Direct radical co- or terpolymerization of fluoroalkenes has been further proved to be a versatile way that offers many opportunities for obtaining a wide range of fluoropolymers.

Homopolymerization or copolymerization of fluoroolefins have been described previously [8–12,17–24,67], mainly from aqueous dispersion techniques (emulsion or suspension) or by solution as processes. Random copolymers can be obtained by feeding into the autoclave one or a mixture of comonomers. In the case of copolymerization, reaching a more constant composition of the copolymer can be achieved by adjusting the composition of the monomers in the autoclave according to their reactivity ratios (see Sections 4 and 5 and Tables 5 and 7 for copolymers involving TFE or VDF, respectively).

As known earlier the (co)polymerization of fluoroolefins is carried out in a radical way. Basically, this reaction is composed of four main steps: initiation, propagation, transfer and termination, already described in main text books or reviews.

Initiators can be commonly used, such as potassium or ammonium persulfates (emulsion process) or peroxides (suspension and solution processes). Interestingly, the use of fluorinated telechelic peresters [83–85], synthesized by the oxidation of fluorinated acid chlorides [83–85] or by the direct addition of acid fluorides [86] to hydrogen peroxide, were successfully used by Rice and Sandberg in the copolymerization of VDF and HFP leading to original fluoroelastomers [83,87], as follows:

$$F_3CCH_2O_2C(CF_2)_3\overset{O}{\overset{\|}{C}}Cl \xrightarrow[\text{NaOH, H}_2\text{O}]{\text{H}_2\text{O}_2} F_3CCH_2O_2C(CF_2)_3-\overset{O}{\overset{\|}{C}}O-O\overset{O}{\overset{\|}{C}}-(CF_2)_3CO_2CH_2CF_3$$

$$\xrightarrow[-5°C]{\text{VDF / HFP}} F_3CCH_2O_2C(CF_2)_3\left[(VDF)_{0.65}(HFP)_{0.35}\right]_n(CF_2)_3-CO_2CH_2CF_3$$
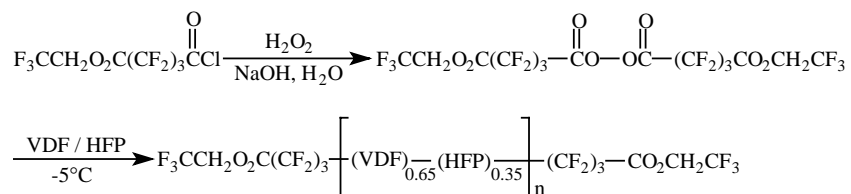
The average molecular weight determined by vapor pressure osmometry (VPO) was ca. 4000.

More recently, hydrogen peroxide was used to prepare novel α,ω-dihydroxylated poly(VDF-*co*-HFP) in a two-step procedure [88] (G designates CH_2OH or CO_2H):

$$H_2O_2 + n\ VDF + p\ HFP \longrightarrow HO\left[(VDF)_x(HFP)_y\right]_z G$$

$$\underline{A}$$

$$\underline{A} \xrightarrow{\text{AlLiH}_4} HO\left[(VDF)_x(HFP)_y\right]_z CH_2OH$$
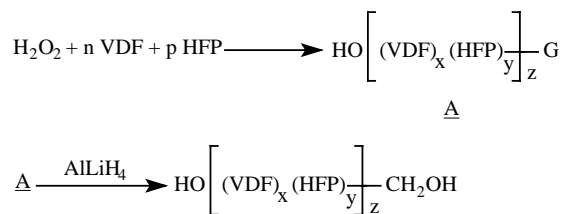
While propagation of monomers occurs in a classical way (although the propagation-rates of all monomers have not yet been assessed even if various reactivity ratios have been determined already, Tables 5 and 7), termination step proceeds by recombination, only.

Obviously, the use of chain transfer agent enables one to obtain lower molecular weights and, according to the nature of this reactant, functional compounds can be obtained or a better control of the copolymerization can be achieved [27,89]. According to the amount and of the transfer-efficiency of such a reagent, conditions of telomerization [90–93] can be realized. Such a reaction represents a very interesting model of polymerization since it leads to low-molecular weight polymers with well-defined end-groups. A quasi-exhaustive list of chain transfer agents used in the telomerization of main fluoroalkenes was previously reported [27].

3. Copolymerization

3.1. Introduction

As mentioned in Section 1, fluorinated homopolymers are often crystalline and insoluble in common organic solvents. However, as indicated in this review, the introduction of a comonomer enables the resulting polymer to loose its crystallinity. Indeed, copolymerization is the most general and powerful method to perform effective systematic changes in polymer properties, and is widely used in the production of commercial polymers and in basic investigations of structure–properties relationships. As a result, copolymerization modifies the symmetry of the polymeric chain and modulates both intramolecular and intermolecular forces, so that properties such as melting point, glass transition temperature, crystallinity, stability, elasticity, permeability and chemical reactivity may be varied within wide limits. Literature dealing with copolymerization is abundant in books [94] or reviews [95–99].

3.2. Various kinds of fluorinated copolymer

As shown in this review, most fluorinated copolymers are random. But, it has been found that block, grafted or alternated fluorocopolymers have been synthesized already and few examples are supplied below.

3.2.1. Fluorinated block copolymers

Several examples are given hereafter regarding block copolymers, although others are reported in Sections 6.2 and 6.5.

Tatemoto et al. [100] prepared poly(VDF-*co*-HFP)-*b*-PVDF block copolymers by controlled (or pseudo-living) iodine transfer polymerization [101–103] using an α,ω-diiodoperfluoroalkane (IR$_F$I) which generated a first elastomeric block **1**. This was then able to initiate the polymerization of VDF (Fig. 1), as follows:

$$I\,R_F\,I \;+\; a\,VDF + b\,HFP \longrightarrow I\left[(VDF)_x(HFP)_y\right]_z R_F \left[(VDF)_x(HFP)_y\right]_z I$$

$$\underline{\mathbf{1}}$$

$$\underline{\mathbf{1}} \;+\; c\,VDF \longrightarrow I(VDF)_n\left[(VDF)_x(HFP)_y\right]_{2z} R'_F (VDF)_m I$$
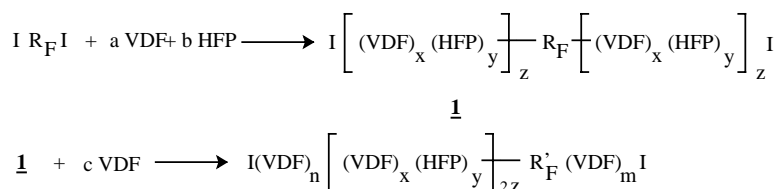
These special fluoropolymers, called thermoplastic elastomers, launched by the Daikin Company in

1984, under the Daiel® trademark, are composed of soft segments (containing the VDF/HFP blocks) and hard ones composed of PVDF or E/TFE blocks [103].

In a similar process, various models of multiblock copolymers containing VDF, trifluoroethylene and HFP were proposed from controlled step-wise (co)telomerization of fluoroolefins [104].

On the other hand and involving the cleavage of the C–Br bond regarded as stronger than the C–I one, two processes have been used to prepare di- or triblock copolymers. The first one, as mentioned above, lies on the controlled radical polymerization by bromine transfer [105] (called atom transfer radical polymerization, ATRP) of styrene from α,ω-dibrominated intermediates **2** regarded as "macroinitiators" [106]. These dihalogenated compounds were prepared by telomerization of VDF with 1,2-dibromotetrafluoroethane [107], as follows:

$$BrCF_2CF_2Br \;+\; n\,VDF \xrightarrow{\text{peroxide}} Br\,R_F\,(VDF)_n\,Br$$

$$\mathbf{2}$$

$$\mathbf{2} \;+\; p\,H_2C=CH \xrightarrow{\text{ATRP}} Br(Sty)_x\,R_F\,(VDF)_n\,(Sty)_y\,Br$$
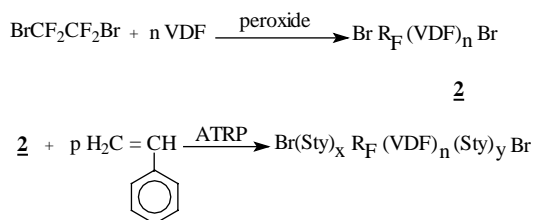
The second process involving a C–Br cleavage was used by Moggi et al. [108] who telomerized VDF with ω-bromoperfluorinated polyethers in a non-controlled process:

$$CF_3(OC_2F_4)_m(OCF_2)_p Br \;+\; n VDF \xrightarrow{\text{rad.}} \text{poly(fluoroether)-}b\text{-PVDF}$$

These above diblock copolymers exhibit a heterogeneous morphology with two amorphous zones assigned to both blocks. That attributed to perfluorinated polyether had a T_g of $-143°C$ in all the cases, while the second one depended upon the chain length of VDF blocks, hence varying from -82 to $-52°C$ for a number of VDF units ranging from 13 to 71.

A similar investigation leading to PFPE-*b*-poly(VDF-*co*-HFP), from the radical cotelomerization of VDF and HFP with PFPE-I (where PFPE stands for perfluoropolyether), is reported in Section 6.2.

Another example of synthesis [109] of diblock copolymers (**4**) also deals with the chlorine transfer radical polymerization (via a CCl$_3$ end-group) of various monomers (M) (styrene, MMA, methyl acrylate and butyl acrylate) initiated by VDF telomers (**3**) with $\overline{DP}_n$ ranging between 5 and 16:

$$Cl_3C–H \;+\; n VDF \xrightarrow{\text{rad.}} Cl_3C–(VDF)_n–H$$
$$\mathbf{3}$$

$$\mathbf{3} \;+\; pM \xrightarrow{\text{CuCl,bipyrid.}} \text{PVDF-}b\text{-poly(M)}$$
$$\mathbf{4}$$
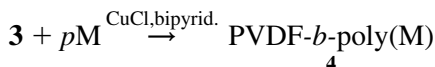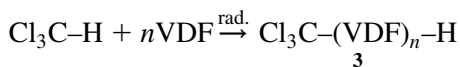
Interestingly, whatever the VDF telomer/M couple, the average molecular weight in number ($\bar{M}_n$) of **4** increased with the monomer conversion and experimental values where close to the theoretical ones. In addition, narrow molecular weight distributions and low polydispersities ($\bar{M}_w/\bar{M}_n < 1.2$) were obtained as evidence of a controlled radical polymerization.

Another attempt of synthesis of fluorinated diblock copolymers was recently achieved in our laboratory by a controlled radical step-wise copolymerization involving Tempo as a counter radical [110]. Its structure was the following:

$$H_3C-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-(Sty)\overline{_n}(CH_2CH)\overline{_p}-O-N$$

with pendant group $CH_2OC_2H_4C_8F_{17}$
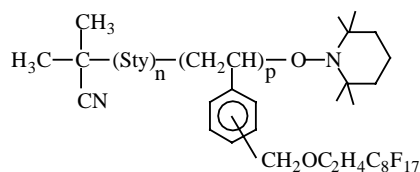
The following example was suggested by Oestreich and Antonietti [111] who allowed poly(styrene)-*b*-(polybutadiene) "block copolymers" (SB) containing 90% of 1,2-butadienic units in the polybutadiene block (prepared by anionic polymerization) to be fluorinated via two two-step procedures from the pendant double bonds of the butadienic block (leading to rather "grafted" segments). The first method consists in achieving a hydroboration in the presence of 9-bicyclononyl borane (9-BBN) followed by an oxidation that generated hydroxy side groups. Esterification of these functions with perfluorinated carboxylic acid chlorides introduced fluorinated side groups in the butadienic blocks. The second route deals with the epoxidation of 1,2-double bonds in the presence of metachloroperbenzoïc acid (MCPBA) followed by the opening of the oxirane by the same above fluoroacid chlorides. Both ways are summarized in the following scheme, where one 1,2-pendant double bond of the butadiene block is presented only (R_F represents C_7F_{15}):

$$-(Sty)\overline{_p}(CH_2-CH)\overline{_n}$$
with pendant $CH=CH_2$

1. 9-BBN
2. $H_2O_2/\overline{O}H$ MCPBA

$$-(Sty)\overline{_p}(CH_2-CH)\overline{_n}$$
with pendant C_2H_4OH

$$-(Sty)\overline{_p}(CH_2-CH)\overline{_n}$$
with epoxide O

$R_F COCl$
pyridine

$R_F COCl$
$Bu_4 N^+ Cl^-$

$$-(Sty)\overline{_p}(CH_2-CH)\overline{_n}$$
with pendant $C_2H_4OCOR_F$

$$-(Sty)\overline{_p}(CH_2-CH)\overline{_n}$$
with pendant $CHCl$ — CH_2OCOR_F
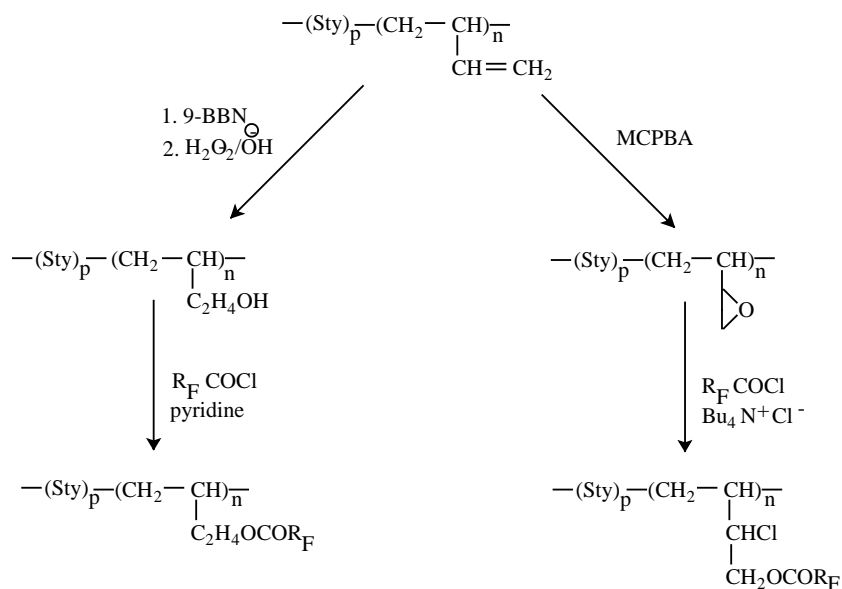
The last example chosen was proposed by De Simone and co-workers [112,113] who prepared

amphiphilic block copolymers by controlled radical polymerization either from benzyl *N,N*-diethyl dithiocarbamate [112] (by heating in supercritical CO_2 or under photoinitiation) or from brominated agents [113] as follows:

$$5 + H_2C=CH–CO_2CH_2C_7F_{15} \longrightarrow poly(M_1)\text{-}b\text{-}P(FOA)$$
$$\text{FOA}$$
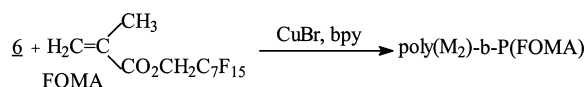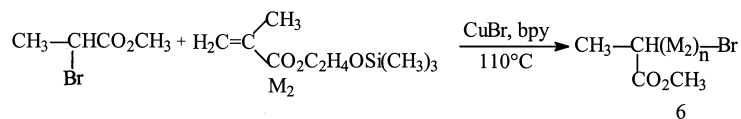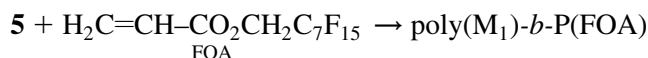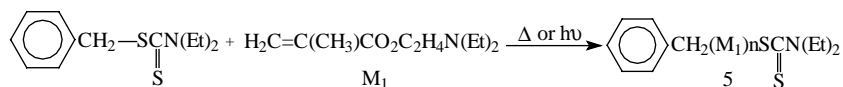
By atom transfer radical polymerization, various poly(M_1)-*b*-PFOMA were obtained, M representing MMA, 2-hydroxyethyl methacrylate, styrene, *tert*-butyl acrylate, ethyl hexyl acrylate with average molecular weights ranging from 40,000 to 56,000.

3.2.2. Fluorinated graft copolymers

Although various possibilities of fluorinated graft copolymers have been achieved [114,115], one of the rare examples of elastomeric graft copolymers was discovered by the Central Glass Company which produces Cefral Soft®. Its synthesis first involves the terpolymerization of VDF and HFP with an olefinic peroxicarbonate. This last monomer was first reactive with its double bond at low temperatures (50°C) leading to a fluorinated elastomer (**7**) bearing peroxicarbonate side groups, followed by a further step that enabled the peroxicarbonate to initiate the polymerization of VDF yielding PVDF grafts, as follows [116]:

$$7 + q\text{VDF} \overset{95°C}{\rightarrow} poly(\text{VDF-}co\text{-CTFE})\text{-}g\text{-PVDF}$$
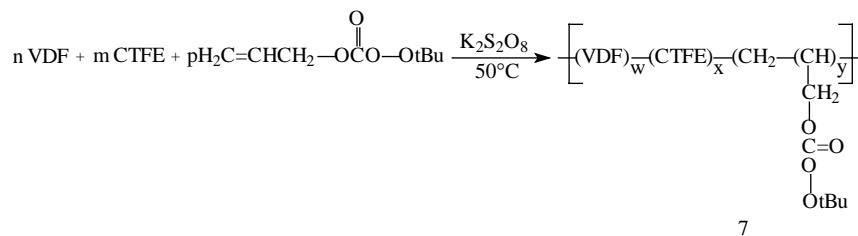
3.2.3. Fluorinated alternating copolymers

As for alternating fluorinated copolymers, many examples have been provided in various reviews

[95,96,99,117–119] showing mainly that alternating copolymerization occurs between donor and acceptor monomers that have high positive or negative value of *e* parameter of the Alfrey and Price [120] *Q–e* scheme (see Section 3.3.5). As fluorinated alkenes are electron-withdrawing olefins, they are intent on reacting easily with donating monomers such as vinyl ethers. The best example lies on the CTFE/vinyl ether couple which has already led to industrial Lumiflon® (Asahi Glass), Fluorobase® (Central Glass), Zeffle® (Daikin), Fluonate® (Dainippon Ink) or DX 2000® (Elf Atochem) products as efficient anti-aging coatings.

In the same way, TFE/propylene [121] copolymers are alternating, produced by the Asahi Company (and called Aflas®), and is going to be extensively described in Section 4.2.

Other industrial copolymers also result from such "acceptor–donor" copolymerization. These are Halar® (E/CTFE) or Tefzel® (E/TFE) produced by Ausimont or Dupont, respectively. These two fluorinated copolymers are thermoplastic in contrast to elastomeric Aflas®.

Although VDF does not react with vinyl ethers as CTFE, 1,1-dichlorodifluoroethylene, perfluoroacrylonitrile, TFE or methyl perfluoroacrylate (MPFA) do, it is able to produce, with hexafluoroisobutylene, alternating thermoplastic copolymers commercialized by Allied under the CMX® trademark [122–124]. However, various examples of couples of fluoroolefins/non-fluorinated monomers leading to alternating copolymers are listed in Table 3 and their physical properties have been investigated: some of them are crystalline while others exhibit elastomeric behaviors.

3.3. Kinetics of copolymerization

The copolymerization of two monomers M_1 and M_2 results in the formation of copolymers having compositions and monomer unit sequence distributions which depend on the relative concentrations of a variety of species and on their relative reactivities towards each other. Depending on the species considered to be important, a number of copolymerization models have been proposed [95,96]. Most of them are reminded hereafter.

3.3.1. Terminal model

In the simplest case (restricting all subsequent discussion to free-radical initiated processes), only the relative rates of addition of M_1 and M_2 monomers to growing polymeric radicals need to be considered. This situation, called "ideal copolymerization" requires two propagation rates and can be characterized by a single reactivity ratio *r*.

$$\sim\!\sim\!\sim M_1^{\bullet} + M_1 \xrightarrow{\;k_1\;} \sim\!\sim\!\sim M_1 M_1^{\bullet}$$

$$\sim\!\sim\!\sim M_2^{\bullet} + M_2 \xrightarrow{\;k_2\;} \sim\!\sim\!\sim M_2 M_2^{\bullet}$$
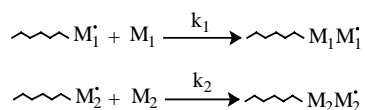
where $r = k_1/k_2$

Ideal copolymerization produces copolymers with Bernouillian monomer unit sequence distribution [95,96].

The terminal model for copolymerization is the most used [145,146]. It involves the four propagation

Table 3
Examples of fluorinated alternating copolymers

Monomer[a]	Comonomer[b]	Properties[c]	References
CTFE	E	Cryst.	[125]
CTFE	P	–	[126]
CTFE	IB	Cryst.	[127]
CTFE	NVP	Cryst.	[128]
CTFE	VAc	–	[129]
CTFE	VE	$T_g \leq 20°C$	[117,130,131]
$F_2C=CCl_2$	VE	–	[132]
$F_2C=CFCN$	α-olefin[d]	–	[133]
$F_2C=CFCN$	VE[d]	–	[134]
HFIB	VAc	$T_g = 50°C$	[135]
HFIB	VDF	Cryst.	[122–124]
MPFA	E	–	[136]
MPFA	P[d]	Rubber	[137]
MPFA	VAc	–	[138]
MPFA	VE[d]	–	[134]
TFE	E	Cryst.	[139]
TFE	P[d]	$T_g = 0–5°C$	[121,140]
TFE	IB	Cryst.	[141]
TFE	VAc	–	[142]
TFE	VE[d]	$T_g < -10°C$	[143]
α-F acrylonitrile	1,3-chd	–	[144]

[a] CTFE: chlorotrifluoroethylene; HFIB: hexafluoroisobutylene; MPFA: methyl perfluoroacrylate; TFE: tetrafluoroethylene.
[b] IB: isobutylene; NVP: N-vinyl pyrrolidone; VAc: vinyl acetate; VE: vinyl ether; VDF: vinylidene fluoride; 1,3-chd: 1,3-cyclohexadiene.
[c] Cryst.: crystalline; T_g: glass transition temperature.
[d] Initiation under γ-irradiation.

steps, macroradicals and M_1 and M_2 monomers. The four equations can be written as follows:

$$\sim\sim\sim M_1^\bullet + M_1 \xrightarrow{k_{11}} \sim\sim\sim M_1 M_1^\bullet$$

$$\sim\sim\sim M_1^\bullet + M_2 \xrightarrow{k_{12}} \sim\sim\sim M_1 M_2^\bullet$$

$$\sim\sim\sim M_2^\bullet + M_1 \xrightarrow{k_{21}} \sim\sim\sim M_2 M_1^\bullet$$

$$\sim\sim\sim M_2^\bullet + M_2 \xrightarrow{k_{22}} \sim\sim\sim M_2 M_2^\bullet$$
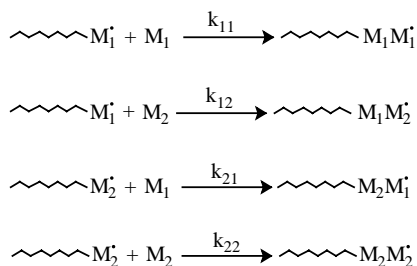
where k_{ij} represents the rate constant of addition of macroradical $M_i^\bullet$ onto M_j.

Copolymerization obeying to the terminal model produces copolymers with monomeric unit sequence distributions that can be described from the first order statistics of Markov [96,97].

At least, 90% of known copolymerization systems can be represented adequately by the ideal or terminal copolymerization models, but copolymerizations involving polar monomers or monomers with large steric requirements often need more complicated ones [97,98].

From writing differential equations which correspond to the rate of disappearance of monomers M_1 and M_2, and from assuming steady-state concentrations of the radical centers $\dot{M_1}$ and $\dot{M_2}$ a more simple equation can be obtained, relating the ratio of monomers in the copolymer ($d[M_1]/d[M_2]$) to the concentrations of monomers in the feed ($[M_1]$ and $[M_2]$):

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]}$$

the parameters r_1 (or r_{12}) and r_2 (or r_{21}) are regarded as reactivity ratios defined as follows:

$$r_1 = k_{11}/k_{12} \qquad \text{and} \qquad r_2 = k_{22}/k_{21}$$

In 1965, Tidwell and Mortimer [147] proposed to classify methods of experimental determination of reactivity ratios r_1 and r_2 in copolymerization from the Mayo and Lewis' differential equation [145], as follows:

$$F_1 = f_1 \frac{f_1(r_1 - 1) + 1}{f_1^2(r_1 + r_2 - 2) + 2f_1(1 - r_2) + r_2} \tag{1}$$

where F_1 and f_1 represent the molar fractions of monomer 1 in the copolymer and in feed, respectively.

Tidwell and Mortimer distinguished five groups of methods summarized below:

(a) Approximative methods. The methods proposed by Kuo and Chen [148], Bauduin and Meghabar [149], Kennedy and Lo [150] lead to approximative values of r_i and are not able to supply any interval of confidence on these values. However, they may give useful data to choose the most adapted experiments to assess the reactivity ratios from other ways.

(b) Curve fitting methods. These methods consist in finding the r_1 and r_2 which lead to the polymer–monomer composition curve that fits with the experimental data. Alfrey et al. [151] and later Braun et al. [152] also suggested similar methods, the latter authors considering that experimental results for which $f_1 < 0.5$ are more representative of r_2 while the others are more directed towards r_1. Although such methods assess r_1 and r_2 values in more accurate ways than that above, no interval of confidence can be supplied.

(c) Curve crossing method. Historically, that method is the oldest one and was proposed by Mayo and Lewis [145].

Then, Joshi and Joshi [153] suggested more accurate solutions for which an interval of confidence on the r_i values can be assessed.

(d) Methods by linearization. Linearization methods are based on mathematical changes of Eq. (1) where r_1 and r_2 reactivity ratios appear in the coefficients of linear equations, the variables being functions of f_1 and F_1 experimental values.

The most known and the oldest method was proposed by Fineman and Ross [154] and was improved by Tosi [155], then by Yezreliev et al. [156] and also by Kelen and Tudos [157].

Non-linear regression method by the least square method. This method has been initially proposed by Behnken [158], as a modification or extension of the method by adjustment of curve. This method, also detailed in Tidwell and Mortimer's review [147], indicates how the surface in which all the couples composed of r_1 and r_2 values are located with a chosen probability (regarded as the domain of confidence) can be drawn in the (r_1, r_2) plane.

3.3.2. Penultimate model

Merz et al. [159] proposed the penultimate model, reviewed by Tirrell [96]. Indeed, the propagation step should take into account four distinct active enters, which are defined by the identities of their terminal and penultimate units, given by eight equations, as follows:

$$\sim\!\sim\!\sim M_1M_1^\bullet + M_1 \xrightarrow{k_{111}} \sim\!\sim M_1M_1M_1^\bullet$$

$$\sim\!\sim\!\sim M_1M_1^\bullet + M_2 \xrightarrow{k_{112}} \sim\!\sim M_1M_1M_2^\bullet$$

$$\sim\!\sim\!\sim M_1M_2^\bullet + M_1 \xrightarrow{k_{121}} \sim\!\sim M_1M_2M_1^\bullet$$

$$\sim\!\sim\!\sim M_1M_2^\bullet + M_2 \xrightarrow{k_{122}} \sim\!\sim M_1M_2M_2^\bullet$$

$$\sim\!\sim\!\sim M_2M_1^\bullet + M_1 \xrightarrow{k_{211}} \sim\!\sim M_2M_1M_1^\bullet$$

$$\sim\!\sim\!\sim M_2M_1^\bullet + M_2 \xrightarrow{k_{212}} \sim\!\sim M_2M_1M_2^\bullet$$

$$\sim\!\sim\!\sim M_2M_2^\bullet + M_1 \xrightarrow{k_{221}} \sim\!\sim M_2M_2M_1^\bullet$$

$$\sim\!\sim\!\sim M_2M_2^\bullet + M_2 \xrightarrow{k_{222}} \sim\!\sim M_2M_2M_2^\bullet$$
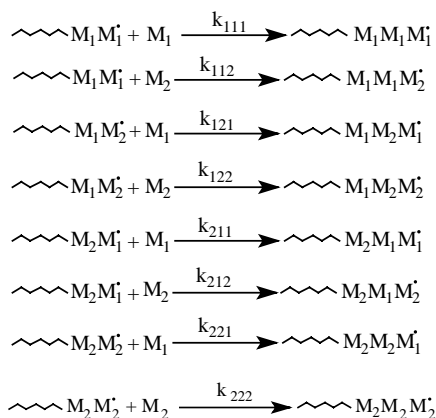
Hence, the copolymer composition determined by the relative rates of the monomer consumption is becoming more complex [96].

The prediction of monomer sequence length by the penultimate model is conceptually identical to that described for the terminal model. The probability (P_{BAA}) that a $\sim\!\sim\!\sim M_BM_A^\bullet$ chain end adds M_A is:

$$P_{BAA} = \frac{[M_A]}{[M_A] + [M_B]/r_{BA}}$$

Thus, the knowledge of the copolymerization reactivity ratio allows calculation of copolymer compositions and sequences as functions of the ratio of monomer concentration in the feed.

3.3.3. Complex participation model in the acceptor donor copolymerization

Radical copolymerization of electron rich alkenes (called "donor monomers") with electron poor olefins (case of fluoroalkenes, called "acceptor monomers") offer alternating copolymers over the entire range of the feed composition [160], called AD copolymerization.

In such systems, one often observes a marked sensitivity of the overall copolymerization rate to temperature, solvent and monomer concentrations [161]. However, Butler et al. [162] have also noted anomalies in the stereochemistry and regiochemistry [163] of certain systems.

A mechanistic scheme that accounts for this behavior involves the participation of 1:1 alkenic electron [DA] complexes in the propagation step. It is proposed that the 1:1 complex competes with free monomers for the growing chain end. Modification of the terminal model in this way requires consideration of eight propagation steps well summarized by Tirrell [96].

It is well known that there are two major theories concerning AD copolymerization. Scheme 1 represents the copolymerization occurring either via the propagation of a complex (1) [164] or via the propagation by free monomers (2) [165].

$$A + D \rightleftarrows [DA] \text{ complex}$$

$$(2) \downarrow \quad -[A-D]_n- \quad \downarrow (1)$$
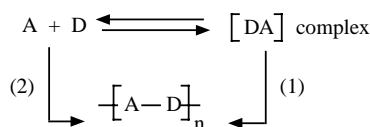
Scheme 1.

Both these mechanisms are controversial even with classical monomers usually involved in copolymerization (e.g. maleimides, vinyl ethers).

Matsuda et al. [166] performed a very interesting study on the terpolymerization of methyl trifluoroacrylate with TFE and E, considering that E only is able to copolymerize with both fluoromonomers and they investigated both kinetics taking into account these two mechanisms: that from free monomers and that involving the charge transfer complex (CTC) assuming that both complexes also copolymerize. The authors observed that the experimental values were closer to the model proposed from the complex than from the free monomer mechanism.

The CTC can be evidenced by several spectroscopic techniques such as UV [167] or ^{19}F nuclear magnetic resonance (NMR) [131]. Usually, the constant of this CTC is ranging between 0.05 and $1.00\, l\, mol^{-1}$ at 20°C.

3.3.4. Other copolymerization models

Two additional models — the complex dissociation [168,169] model and the depropagation model [170] (which may occur at a temperature close to the ceiling temperature) — have not been considered as extensively as the models above, but each of them is physically plausible and each has been analyzed in sufficient detail so that compositions and sequences may be calculated [96].

The excellent review of Tirrell [96] also details the evaluation of the copolymerization models (composition and sequence, measurements of absolute rate constants) and the reader is directed to it for a better description.

3.3.5. Q *and* e *parameters and other concepts*

Alfrey and Price [120] suggested two parameters assigned to each monomer involved in copolymerization: these are the Q and e factors. Q is devoted to the resonance effect or stabilization and to the life time of the radical formed (having a crucial influence on the reactivity of the monomer) while e denotes the permanent electric charge carried by the entity (radical or molecule).

The Alfrey and Price equation leads to the determination of Q and e from the reactivity ratios [171] by both the following equations:

$$r_{12} = \frac{Q_1}{Q_2} \exp[-e_1(e_1 - e_2)]$$

$$r_{21} = \frac{Q_2}{Q_1} \exp[-e_2(e_2 - e_1)]$$

This Alfrey and Price Q–e scheme is useful for the interpretation of radical and monomer reactivities and for the prediction of the monomer reactivity ratios in radical copolymerization. This remains the most used model.

Table 4
e and Q values of fluorinated monomers

Monomer	e	Q	References
$H_2C=CHCF_3$	0.42	0.130	[174]
$H_2C=C(CF_3)OAc$	1.51	0.069	[175]
$H_2C=CFC_6H_5$	−0.70	0.900	[176]
	−2.04	2.49	[177]
$H_2C=CFCONH_2$	1.45	0.540	[178]
$H_2C=C(CF_3)CO_2CH_3$	2.90	0.800	[179]
	2.50	0.740	[180]
$H_2C=C(CF_3)C_6H_5$	0.40	0.780	[172,173]
	0.90	0.430	[181]
$HFC=CH_2$	0.60	0.250	[182]
	0.72	0.008	[171,174]
	1.28	0.012	[171]
	−0.05	0.016	[183]
	−0.80	0.010	[184]
$H_2C=CFCF_2OR_F$	0.75	0.030	[185]
$F_2C=CH_2$	0.50	0.015	[173]
	0.40	0.008	[183]
	1.20	0.036	[186]
$F_2C=CCl_2$	2.10	0.041	[171]
$CF_3CF=CFH$ (cis)	2.10	0.002	[184]
$F_2C=CFH$	1.15	0.009	[183]
$F_2C=CHCF_3$	0.31	0.002	[187]
$F_2C=CFCH_2OH$	1.52	0.011	[188]
$F_2C=CFC_3H_6OH$	1.04	0.008	[188]
$F_2C=CFC_3H_6OAc$	1.14	0.060	[189]
$F_2C=CFC_3H_6SAc$	1.68	0.045	[190]
$F_2C=CFCl$	1.84	0.031	[183]
	1.56	0.026	[172–174]
	1.48	0.020	[171]
$F_2C=C(CF_3)COF$	2.35	0.011	[186]
$F_2C=CFCO_2CH_3$	2.37	0.035	[137]
	1.20	0.048	[172–174]
	1.5–2.1	0.01–0.20	[191]
	2.2–2.6	0.04–0.06	[138]
$F_2C=CFOCF_3$	3.01	0.250	[192]
$F_2C=CFOC_3F_7$	2.48	0.031	[192]
$F_2C=CFO(HFP)OC_3F_7$	1.37	0.004	[193]
$F_2C=CFO-R_F-CO_2R$	1.08	0.006	[194]
$F_2C=CFO-R_F-SO_2F$	2.26	0.047	[192]
$F_2C=CFCF_3$	4.09	0.047	[174]
	1.50	0.005	[195]
$F_2C=CF_2$	1.22	0.049	[191]
	1.63	0.032	[172,196]
	1.84	0.031	[183]
$H_2C=CFCH=CH_2$	−0.42	2.100	[171]
	0.63	1.880	[174]
$F_2C=CF-CF=CF_2$	0.58	0.820	[174]

Table 4 (*continued*)

Monomer	e	Q	References
$F_2C=CF-CF=CF_2$ (cont.)	4.09	0.047	[183]
	0.47	0.930	[197]
$F_2C=CF-C_6H_5$	0.95	0.380	[171]

Compilations of Q and e values have been published by various authors, the most recent ones being Refs. [172,173], both by Greenley. However, few values of fluoromonomers have been reported in these compilations and we find it interesting to supply a more exhaustive list (Table 4).

The general tendency shows that the more fluorine atoms onto the double bond, the higher the e value. In most cases, Q values are very small except for those of styrenic and acrylic monomers. It is, however, difficult to rationalize these values since various processes, methods of initiation, temperatures, solvents and different ways to determine the corresponding reactivity ratios have been used. The low Q values are good evidences of the poor ability of a fluorine atom for resonance stabilization of the radical on the adjacent carbon atom.

In addition to the Q and e values of fluoroolefins, the literature also quotes such parameters for fluorinated (meth)acrylates [136,171,198–205] (e.g. the fluorinated group is located in the β or γ position about the ester function), styrenics [171,177,206], maleimides [207,208] or fumarates [209] which are not detailed in this review.

As several authors underlined, the Q–e scheme is probably too simplified to discuss the reactivity of a monomer in free radical reactions based only on separate resonance and polarity factors [210–213].

This is why other concepts have been proposed, e.g. by Jenkins.

The "Patterns of reactivity" scheme, originally proposed in 1959, seems to provide a more accurate prediction of monomer reactivity ratios than the Q–e scheme does.

4. Fluoroelastomers from TFE

4.1. Introduction

Polytetrafluoroethylene (PTFE) is one of the most attractive fluoropolymers, thanks to its outstanding properties of thermal stability, inertness and low surface tension. Most copolymers containing TFE are melt processable [56,214] evidenced by, for example, those containing up to 6 mol% of HFP, PMVE or perfluoropropylether, (FEP®, MFA® or PFA®, respectively). They have high melting points of 265, 285 or 305°C, respectively.

However, FEP® polymers [56] do not have the same thermostability as that of PTFE and this enabled TFE/PAVE copolymers to find useful development [17–24,215]. Indeed, these latter ones possess heat stability and high-temperature properties close to that of PTFE, and can be used at the same continuous service.

Although TFE copolymerizes easily with E to produce an alternating highly crystalline copolymer (Tefzel® from DuPont), it also copolymerizes with propylene leading to an alternating elastomeric material (Aflas® from Asahi).

Besides these melt processable TFE-based copolymers, fluorocarbon elastomers containing TFE have also been produced. For example those having both VDF and HFP have been of considerable commercial interest since the 1950s [216,217]. They are described in the following sections (see Section 5.3). Due to the shielding of the polymer backbone by the fluorine atoms, these elastomers exhibit far superior chemical resistance and thermal stability over their hydrocarbon analogues. In spite of their extreme inertness towards many chemicals, these polymers are readily attacked by bases and can easily be dehydrofluorinated. Besides, both diamine or diphenol-base cure systems generate a lot of unsaturations in the polymer backbone, which are proned to nucleophilic attack by many additives (e.g. amines, succinimides) that are used in engine oils.

To avoid the presence of base-sensitive sites in VDF/HFP elastomers, two different ways are possible: to prepare fluorocarbon elastomers without any HFP or to synthesize fluorocarbon elastomers without any VDF [218,219].

The first group encompasses copolymers of TFE/P, VDF/TFE/P or VDF/TFE/PMVE [15–24,89,220,221]. The second group comprises elastomers based on TFE with PAVEs: TFE/PAVE, TFE/PAVE/olefin [15–24,221,222].

In all these fluorocarbon elastomers, the main monomer is TFE.

4.2. Fluoroelastomers from TFE and propylene

In the early 1960s it was found that TFE readily copolymerizes with propylene (P) to give fluoroelastomers, commercialized by the Asahi Glass Company as Aflas® elastomers [17–22]. This rubber contains 54–57 mol% of fluorine, less than VDF/HFP (see Section 5.3) and other TFE-based fluoroelastomers.

These copolymers have been prepared by emulsion polymerization with perfluorocarbon surfactants and a modified persulfate redox system as the initiator [223–224]. The redox system consists of ammonium persulfate, ferrous sulfate, ethylene diaminotetraacetic acid and sodium hydroxymethane sulfinate, and the copolymerization was performed at a temperature range of 0–50°C. The molecular weight of copolymers obtained is rather high (higher than 1.5×10^5) and the vulcanizates have good physical properties [225]. At higher temperatures, other redox systems can be used but chain transfer reactions start to dominate and, consequently, lower molecular weight polymers are produced [226,227].

A polymerization recipe containing water-soluble peroxydisulphates, thiosulphates or sulphites, ferrous salts, pyrophosphate and ammonium perfluorooctanoate is also employed in the temperature range of 0–50°C [228,229].

A new initiating system, containing *tert*-butyl peroxybenzoate and redox catalyst has also been used successfully to copolymerize TFE with P in bulk [230] and emulsion [231–233] processes. It was found that it exceeds considerable catalytic activity at low temperatures, increasing the alternating character of copolymers obtained with improved thermal and chemical resistances [234].

The copolymerization of P and TFE initiated by γ-radiations (from ^{60}Co) or electron beams led to elastomers with an alternating structure [234–238]. In the wide range of monomer compositions, (30–90 mol% of TFE) the alternating copolymers were obtained and the TFE content in the monomer feed affected the copolymerization rate and molecular weight of the copolymers. The reactivity ratios were found to be $r_P = 0.10$ and $r_{TFE} = 0.01$ [236].

The copolymers can be crosslinked by high-energy radiations at room temperature [239], a reaction accompanied by a HF-release.

Radiation-induced emulsion copolymerization of TFE with P has been studied extensively by Matsuda et al. [240–244]. The rate of polymerization is proportional to the dose rate (0.3– 5.3) $\times 10^5$ R/h of ^{60}Co source but the molecular weight of the copolymer does not depend on the dose rate [245].

In the presence of oxygen, the radiation polymerization was accompanied by HF evolution [242,246] from TFE oxidation followed by the hydrolysis of COF_2. By increasing the surfactant concentration, the rate of radiation polymerization increases and the molecular weight of the copolymer increases with the temperature.

TFE/P polymers are usually cured by a peroxide coagent (radical trap). The system and radiation are discussed more precisely in Section 7. To improve the curability, a third comonomer (CSM) has also been included into the chain. TFE/P fluoroelastomers with small amount of CSM have also been reported by various authors. Kojima et al. [247] have shown that a CSM such as glycidyl vinyl ether may be introduced in the polymer without disturbing the predominant alternating structure of the copolymer. These TFE/P/glycidyl vinyl ether terpolymers can be cured at room temperature with tris(dimethylaminomethyl) phenol in the presence of phenol accelerators or at 170°C by diamines. The same researchers [248] reported TFE/P/VDF terpolymers as a means of improving the low-temperature properties.

Different CSMs such as carboxylic [248], hydroxy [249], ester type monomers [249] or containing a chlorine [248] terminal atom can be incorporated in the elastomeric macromolecules without upsetting the alternating structure of TFE/P units.

A series of investigations by incorporation of a third comonomer with symmetric or pendant lateral groups to TFE/P binary copolymers to decrease the glass transition temperature and the low-temperature resilience has also been achieved [250–253]. The best results with improved thermal stability and T_gs lower than -20°C were obtained by TFE/P/perfluoropropyl vinyl ether (PPVE) terpolymers [253].

Aflas® TFE/P elastomers are endowed with interesting properties. They are resistant to H_2S, oil and gas, amine corrosion inhibitors, acid used in acidifying operations, steam/hot water/brine and CO_2 and methane gases [21]. TFE/P elastomers are replacing other elastomers in oil field applications because of their resistance to the wide range of chemicals, heat and pressures that can be encountered in these applications.

Polymers based on TFE, P and VDF show improved low-temperature properties, but give up some chemical resistance and resistance towards polar solvents [254,255]. An interesting comparison of elastomeric properties between such terpolymers and VDF/TFE/HFP was achieved by Grooteart et al. [256]. They showed that these latter ones were much more base-sensitive than the former ones. Prereacted bisphenol curatives have been used in TFE/P/VDF terpolymers [257].

4.3. TFE-based fluoroelastomers containing ethylene (E)

As mentioned in Section 4.1, TFE/E copolymers are crystalline and alternating, developed by DuPont under the Tefzel® trademark.

Fluoroelastomers based on TFE, PMVE and E were also introduced by the DuPont Company in 1986. The peroxide curing was possible by incorporation of bromine-containing CSMs [219]. The elastomers have better low-temperature properties than TFE/PMVE and TFE/P and are suitable for long-time service in hostile environments.

Copolymerization of PAVE such as CF_2=$CFO(CF_2)_3OC_3F_7$ and E was carried out in emulsion and yielded elastomers having an alternating structure (E/PAVE molar ratio of 53/47) with improved

low-temperature properties ($T_g = -42°C$) [258]. When PAVE was partially replaced by perfluoropropylvinyl ether or VDF, terpolymers of higher T_g ($T_g = -27°C$) were formed and another type of fluoroelastomers, comprising olefins with perfluorinated monomers were developed (such as Aflas[®] 200 with 59% fluorine (developed by Asahi Glass)).

To reduce the regularity of HFP/VDF/HFP triads, which are base-sensitive sites, Arcella et al. [89,220] introduced hydrogenated olefins (mainly E) as suitable protecting monomers. In this case, the monomer sequence, e.g. HFP/VDF/HFP/E (regarded as the most probable) is a less base-sensitive material.

The polymerization reaction was carried out with a monomer mixture of VDF, HFP, TFE and E. To overcome the low reaction kinetics and to obtain a low-molecular weight product, a special "microemulsion" polymerization technique was involved. A first product developed by this method in an industrial scale is the Technoflon[®] BRX 915N of Ausimont. A bromoperfluoroalkyl vinyl ether CSM was used to afford peroxide curability [259,260].

However, these fluoroelastomers still contain a non-negligible amount of hydrogen that renders them more vulnerable to chemical and oxidative attacks than PTFE does. Nevertheless, DuPont's efforts have led to "elastomeric Teflon[®]" thanks to Kalrez[®] perfluoroelastomer composed of TFE and PMVE (see Section 4.5). Such a polymer is resistant to hostile environments.

Hence, fluoroelastomers endowed with high resistance to polar solvents and to bases were synthesized at Ausimont by Albano et al. [261] They copolymerized in emulsion TFE (33–75 mol%) with PVE, mainly PMVE (15–45 mol%), 10–22 mol% of VDF, and optionally 0.05–2 mol% of a CSM (containing iodine and/or bromine atoms present in the chain and/or in the terminal position). The reaction proceeds in the presence of a microemulsion of perfluoropolyoxyalkylenes and others. The terpolymer obtained is vulcanized by peroxide with an excellent resistance to methyl *tert*-butylether and bases with a low compression set properties.

4.4. Thermoplastic fluoroelastomers

Fluorinated thermoplastic elastomers (TPE) have been reported scarcely in most books dealing with TPE [262,263].

Since the 1990s Daikin has introduced new fluorinated thermoplastic elastomers under the trade name of Daiel[®] by applying their "iodine transfer polymerization" technology [100–103]. These copolymers have triblock structure, B–A–B, where A is a fluorinated rubber and B is a fluorinated resin. Block copolymers were obtained by a free-radical polymerization process of fluorinated monomers in the presence of iodo-substituted fluorocarbons (see Section 3.2.1). In this case, the free radical polymerization reaction behaves as a pseudo living or controlled polymerization, thus leading to continuous stepwise chain growth. $I(CF_2)_nI$ ($n = 4$ or 6) is usually used as the diiodo reactant. In the first stage iodine-terminated TFE/VDF/HFP terpolymers were synthesized by emulsion polymerization. In the second step the polymerization of the hard segment component takes place in the presence of the iodine-terminated terpolymer emulsion. One type contains E/TFE/HFP (Daiel[®] T530), while the other one is composed of PVDF blocks (Daiel[®] T-630) [264].

Recently, triblock fluorinated thermoplastic elastomers were synthesized using pseudo-living technology, called "branching and pseudo-living approach" [265,266], starting from diiodinated compounds. However, in this process, a small amount of a fluorinated diene was added leading to original fluoroelastomers, the morphology of which was deeply modified with improved mechanical and sealing properties [89].

4.5. Perfluoroelastomers from TFE and PAVE monomers

The second group of fluoroelastomers without any VDF is based on TFE/PAVE or, to a less extent, on TFE/PAVE/olefin compositions.

Perfluoroelastomers (mainly TFE/PAVE copolymers) offer the highest protection against high service temperatures and oxidative environments by combining the resilience and sealing force of an elastomer and the chemical inertness and thermal stability of PTFE [19]. These perfluoroelastomers are similar to Teflon® PFA fluoropolymers as they have a fully fluorinated backbone but with 20–40 mol% vinyl ether incorporated vs. 1–5 mol% of Teflon® PFA. The latter, because of the lack of interpolymeric bonds and "crosslinking" sites, is a typical thermoplastic. Conversely, perfluoroelastomers employ a crosslinking network or a curing system, which provides the molecule with the combination of elastomeric behavior and chemical resistance [221]. The commercially available perfluoroelastomers are based on a copolymer of TFE and PAVE. The most commonly used ether is perfluoromethyl vinyl ether (PMVE), due to its favorable polymerization properties, commercialized by DuPont under the trademark of Kalrez®. The copolymerization of TFE with PMVE is readily initiated by free radicals in either fluorocarbon solvents or aqueous emulsion systems [267]. The reactivity of both monomers towards radicals are sufficiently similar so that no difficulty is experienced in obtaining homogeneous copolymers at high conversions of monomers in systems producing polymers containing up to 50 mol% of the vinyl ether monomer. Higher molecular weight PAVE may also produce elastomeric copolymers with TFE, however, at considerably slower polymerization rates. A small amount (less than 5 mol%) of a third functional reactive monomer (CSM) is added in the polymerization to create a crosslinking site on the polymer. The following polymeric chain is fulfilled by using either redox or thermally generated free radicals.

$$-(CF_2-CF_2)_n-(CF_2-\underset{\underset{\underset{CF_3}{|}}{\overset{|}{O}}}{CF})_m-(CF_2-\underset{\underset{X}{|}}{CF})_z-$$

TFE PMVE CSM
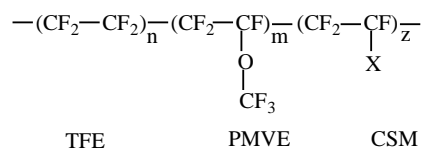
This third monomer is usually added to make these polymer crosslinkable. It is required that this monomer has the right functionality to enable the crosslinking reaction to take place. It is also important that it copolymerizes with TFE and PAVE in a random fashion and causes no chain transfer reaction [24]. The synthesis of the three classes of CSM that meet the above requirements is reported in Section 4 while the crosslinking is discussed in Section 7.

The most thermally stable perfluoroelastomer available employs a nitrile-containing CSM. Perfluoroelastomers containing bromine or iodine cure sites can be cured with peroxides in the presence of co-agents and perfluorophenoxy or hydrogen cure sites may be cured using stable bisphenols (Section 7). Many patents have been deposited dealing with the use of different types of CSM improving the properties of perfluoroelastomers [268–274].

Aqueous emulsion polymerization systems, employing ammonium perfluorooctanoate as the dispersing agent and persulfate or the persulfate–bisulfite redox couple as the initiator, have been employed typically to give high conversions of monomers in a few hours at temperatures ranging from 40 to 100°C and the pressure within 5–7 Mpa and to lead to a product latex containing 25–30% of solid polymer [226,227,231–233]. The

polymer is isolated by coagulation either by freezing or adding an electrolyte to the emulsion (e.g. magnesium chloride or brine) followed by washings with water and with alcohol [232,233].

Aqueous suspension or dispersion methods result in increased occurrence of carboxylic acid end-groups that are deleterious to the products during melt-processing steps and to the function of the polymer. The reason is that PAVE undergoes a free-radical catalyzed rearrangement [67] shown below (in the case of PPVE):

$$\dot{R}_F + CF_2{=}CFOC_3F_7 \rightarrow R_FCF_2\dot{C}FOC_3F_7 \qquad (a)$$

$$R_FCF_2\dot{C}FOC_3F_7 \rightarrow R_FCF_2CFO + \dot{C}_3F_7 \qquad (b)$$
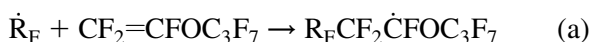
This reaction, if not controlled, would lead to unacceptably low-molecular weight copolymers. Fortunately, the reaction is quite temperature dependent, so that the control of the polymerization temperature in the range of 70–95°C keeps the unimolecular transfer to a tolerable level [67]. The second important modification is the use of chain transfer agents. The solution process used for the synthesis of TFE/PPVE copolymers employs CFC 113 as the solvent and perfluoropropionyl peroxide (3P) as the initiator at temperatures of 40–65°C [270,275,276]. To control the molecular weight methanol has been added as a suitable transfer agent.

Another possibility is to use supercritical CO_2 as medium of the polymerization [277] of fluoroolefin. This process seems to avoid any formation of perfluorinated acid flouride and hence leads to high molecular weights.

The first perfluoroelastomer grades were notably for setting new standards of thermal stability with excellent resistance to almost all chemicals [19,22–24,222]. The second generation of perfluoroelastomers which has been developed in these last 15 years is Perlast® (from DuPont) [222]. It is a copolymer of TFE with irregularly placed pendant perfluorocarbon ether groups which are the key to promote both low T_g (−19°C) and low-temperature flexibility. The iodine-based cure system used with Perlast® is unique and, while not affording the levels of extreme high-temperature resistance associated with the triazine-cured Kalrez® 4079, the Perlast® system has the great advantage of not containing either metal oxide or other metal-based catalysts.

Perfluoroelastomers can handle the widest variety of chemical reagents of any elastomer available today. In addition to the broad range of applications in the chemical processing industry they are used in aircraft/aerospace, semiconductor chip manufacturing, chemical transportation, petrochemical industries, nuclear power plants and analytical and process instrumentation (see Section 11).

4.5.1. Synthesis of comonomers

Among perfluorovinyl ethers two families can be distinguished. Those which are non-functional and usually exhibit a perfluorinated group [278] (such as PMVE, $F_2C{=}CFOCF_3$ or $F_2C{=}CFOC_nF_{2n+1}$, $n = 2, 3$) and those which bear an ω-functionalized end-group such as sulfonyl fluoride, carboxy, phosphonic acid, hydroxy, cyano, pentafluorophenoxy or trifluorovinyl groups.

The synthesis of non-functional ones has been reviewed in the literature [4,5,8,9,13,279] (starting from hexafluoropropylene oxide (HFPO)); that of several functional ones are described hereafter.
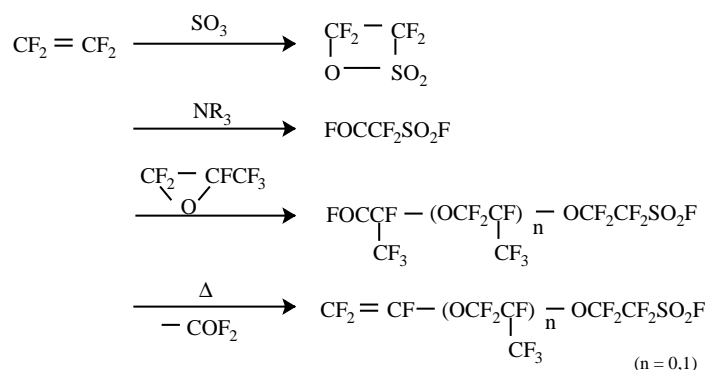
The co- or ter- or tetrapolymers produced from them may fall into two classes: those acheived from

trifluorovinyloxy monomers bearing sulfonyl fluoride, carboxy, phosphonic acid functions leading to membrane applications mainly; and those obtained from the other monomers mentioned above yielding (per)fluoroelastomers. Although the first kind of copolymers are a bit far from the present topic, we have found it interesting to recall them and hence to report briefly on the synthesis of the functional monomers.

Functionalized perfluorovinyl ethers have already reached an industrial production scale and three main companies start their syntheses from TFE [279–284].

4.5.1.1. Sulfonic acid perfluoroalkoxyvinyl monomers. In the DuPont and Dow Chemical technologies, a fluorinated sultone is a key reactant while the last step deals with a pyrolysis, as follows:

(a) DuPont technology. This sultone allows to introduce further a sulfonyl fluoride end-group and an acid fluoride. The latter reacts to HFPO and, after pyrolysis leads to the sulfonyl fluoride perfluorovinyl ether, as follows:

$$CF_2 = CF_2 \xrightarrow{\ SO_3\ } \begin{matrix} CF_2 - CF_2 \\ | \quad\quad | \\ O \;-\!\!-\; SO_2 \end{matrix}$$

$$\xrightarrow{\ NR_3\ } FOCCF_2SO_2F$$

$$\xrightarrow{\ \overset{CF_2 - CFCF_3}{\underset{O}{\diagdown\ \diagup}}\ } \underset{\quad CF_3 \quad\quad\quad CF_3}{FOCCF - (OCF_2CF)_n - OCF_2CF_2SO_2F}$$

$$\xrightarrow[-\ COF_2]{\ \Delta\ } \underset{\quad\quad\quad\quad\quad\quad CF_3}{CF_2 = CF - (OCF_2CF)_n - OCF_2CF_2SO_2F} \quad \text{(n = 0,1)}$$

(b) Dow chemical technology. This company uses chloropentafluoropropylene oxide (CPFPO) instead of HFPO to promote the formation of $F_2C=CFO$ end-group more easily.

$$CF_2 = CF_2 \xrightarrow{\ SO_3\ } \begin{matrix} CF_2 - CF_2 \\ | \quad\quad | \\ O \;-\!\!-\; SO_2 \end{matrix} \xrightarrow{\ F^-\ } FCOCF_2SO_2F \xrightarrow{\ CPFPO\ }$$

$$\underset{}{\overset{CF_2Cl}{\underset{|}{FCO-CFOCF_2CF_2SO_2F}}} \xrightarrow[-COFCl]{\ \Delta\ } CF_2 = CFOCF_2CF_2SO_2F$$
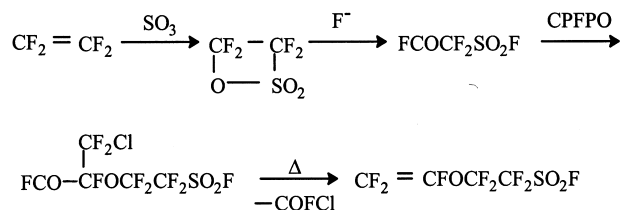
The radical copolymerization of this fluorinated sulfonyl fluoride monomer with TFE was successfully achieved [285].

(c) Asahi glass technology. The Asahi Glass company has two ways: first, the electrochemical fluorination of a hydrogenated cyclic sulfone led to $FOC(CF_2)_2SO_2F$ (in high yields) which reacted with HFPO and underwent a pyrolysis to yield $F_2C=CFO(CF_2)_3SO_2F$.

The second procedure generates a fluorinated thioether which is then oxidized as follows:

$$CF_2 = CF_2 \xrightarrow[\text{(CH}_3\text{O)}_2\text{CO}]{\text{RSNa}} HOOCCF_2CF_2SR \xrightarrow[\text{2. SOCl}_2]{\text{1. Cl}_2/\text{H}_2\text{O}} ClCOCF_2CF_2SO_2Cl$$

$$\xrightarrow{\text{NaF}} FCOCF_2CF_2SO_2F \xrightarrow{\text{HFPO}} \overset{\overset{\text{CF}_3}{|}}{FCOCFOCF_2CF_2CF_2SO_2F}$$

$$\xrightarrow[-\text{COF}_2]{\Delta} CF_2 = CFOCF_2CF_2CF_2SO_2F$$
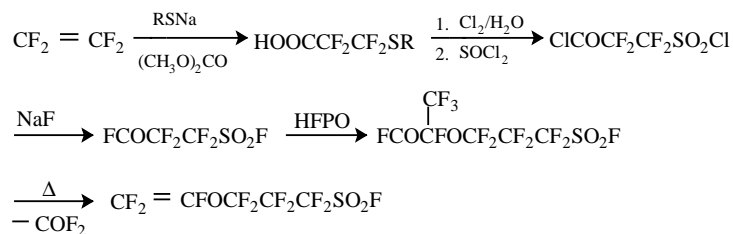
Other synthetic methods have been achieved on a research scale.

First, Krespan and England [286] synthesized perfluoroallyl fluorosulfate from HFP and sulfur trioxide catalyzed by BF_3 and then isolated $F_2C=CFCF_2OC_2F_4SO_2F$ according to the following process:

$$FSO_2CF_2COF + KF \rightarrow FSO_2CF_2CF_2OK \rightarrow FSO_2C_2F_4OCF_2CF=CF_2$$

In addition, Kostov et al. [287] prepared $FOCCF_2SO_2F$ (from the isomerization of the tetrafluoroethane-β-sultone) that was reacted with $F_2C=CFCF_2OSO_2F$ (prepared from the addition of HFP onto SO_3, catalyzed by $B(OCH_3)_3$ as the catalytic complex) leading to $F_2C=CFCF_2OC_2F_4SO_2F$. Nguyen and Wakselman [288] used another way of synthesis and introduced various HFPO units.

More recently DesMarteau [289] achieved the synthesis of original $F_2C=CFOCF_2CF(CF_3)OC_2F_4-G$ where G represents $SO_2NHSO_2CF_3$, $N(Na)SO_2CF_3$ or $N(Na)SO_2C_4F_8SO_2N(Na)SO_2CF_3$.

In addition fluorinated monomers such as $R_F-CF=CF-SO_2F$ were also depicted [290].

4.5.1.2. Carboxylic perfluoroalkoxyvinyl monomers. In contrast to the preparation of sulfonated perfluorovinyl ethers, the synthesis of carboxylated perfluorovinyl ether is difficult.

The three companies above also share the market of these monomers.

For DuPont and Dow Chemical the difference is only in the difluorination step, as described below:

(a) DuPont technology. The reaction first led to methyl-3-methoxy 2,2,3,3–tetrafluoropropionate (yield = 74%) but the yield of the third step is low (8–15%). However, improvements were achieved by the use of different aprotic solvents producing the perfluoroacid fluoride in 30–40% [291].

$$CF_2 = CF_2 \xrightarrow[\text{(CH}_3\text{O)}_2\text{CO}]{\text{CH}_3\text{ONa}} CH_3OCF_2CF_2COOCH_3 \xrightarrow{\text{SO}_3} FCOCF_2COOCH_3$$

$$\xrightarrow{\text{2HFPO}} \overset{\overset{\text{CF}_3}{|}\quad\overset{\text{CF}_3}{|}}{FCOCFOCF_2CFOCF_2CF_2COOCH_3}$$

$$\xrightarrow[-\text{COF}_2]{\Delta} \overset{\overset{\text{CF}_3}{|}}{CF_2 = CFOCF_2CFOCF_2CF_2COOCH_3}$$
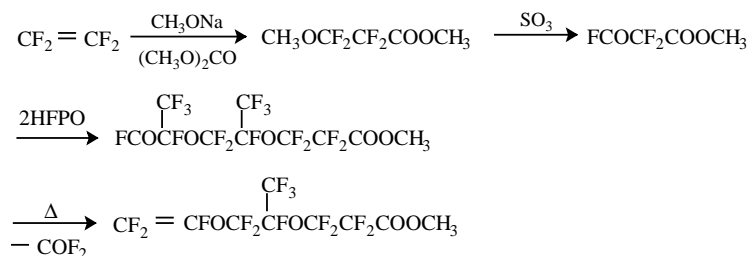
(b) Dow chemical technology. The first two steps are similar to these above, but this company used CPFPO instead of HFPO:

$$CF_2 = CF_2 \xrightarrow[\text{(CH}_3\text{O)}_2\text{CO}]{\text{CH}_3\text{ONa}} CH_3OCF_2CF_2COOCH_3 \xrightarrow{SO_3} FCOCF_2COOCH_3$$

$$\xrightarrow{CPFPO} \underset{}{FCOCFOCF_2CF_2COOCH_3}$$
$$\overset{CF_2Cl}{|}$$

$$\xrightarrow[-\text{COFCl}]{\Delta} CF_2 = CFOCF_2CF_2COOCH_3$$
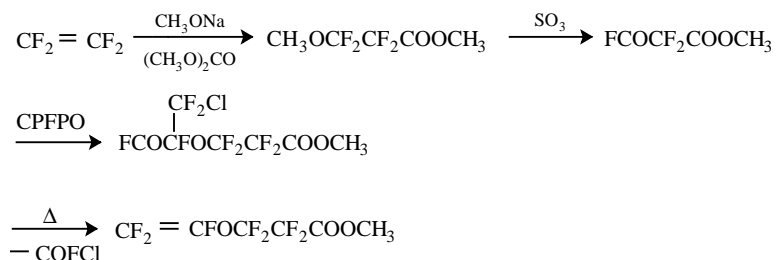
(c) Asahi glass technology. Interestingly, for Asahi Glass, the telomerization of TFE with iodine followed by a sulfonation brings an originality of synthesis, as follows:

$$CF_2 = CF_2 \xrightarrow{I_2} I(CF_2CF_2)_2I$$

$$\xrightarrow{CH_3OH} FOCCF_2CF_2CO_2CH_3$$

$$\xrightarrow{\underset{O}{CF_2 - CFCF_3}} \underset{CF_3}{FOCCF} - (OCF_2CF)_n - O(CF_2)_3CO_2CH_3$$
$$\overset{|}{CF_3} \quad \overset{|}{CF_3}$$

$$\xrightarrow{\Delta} CF_2 = CF - (OCF_2CF)_n - O(CF_2)_3CO_2CH_3$$
$$\overset{|}{CF_3} \quad (n = 0,1)$$
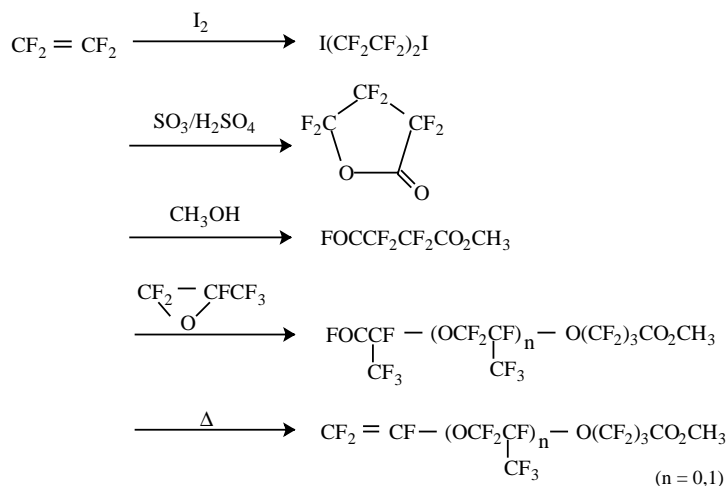
Such a novel process enables this company to produce Flemion® membrane in an industrial scale [279]. The cyclic lactone is obtained in high yields (70–80%) and the controlled addition of methanol to the lactone generated 3-methoxycarbonyl perfluoropropionyl fluoride selectively, to which HFPO was added.

An alternative way from the lactone to the vinyl ether was proposed to improve the yield [279,292]. The addition of 1 mol of HFPO to the lactone occurred almost quantitatively and pyrolysis of the

asymmetric diacid fluoride led to the perfluorovinyl ether in ca. 70% yield:

$$\text{lactone} \xrightarrow{\text{HFPO}} \text{FOCC(CF}_3\text{)O(CF}_2\text{)}_3\text{COF} \xrightarrow[\text{2) CH}_3\text{OH}]{\text{1) }\Delta} \text{F}_2\text{C=CFOC}_3\text{F}_6\text{CO}_2\text{CH}_3$$

A research scale route involving an original final step of deiodofluorination was described by Ukihashi et al. [293], as follows:

$$\text{FOCC}_2\text{F}_4\text{CO}_2\text{CH}_3 \xrightarrow[\text{KF/I}_2]{\text{TFE}} \text{IC}_2\text{F}_4\text{OC}_3\text{F}_6\text{CO}_2\text{CH}_3 \xrightarrow{-\text{ IF}} \text{F}_2\text{C=CFOC}_3\text{F}_6\text{CO}_2\text{CH}_3$$
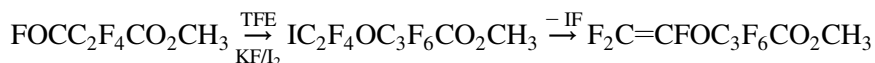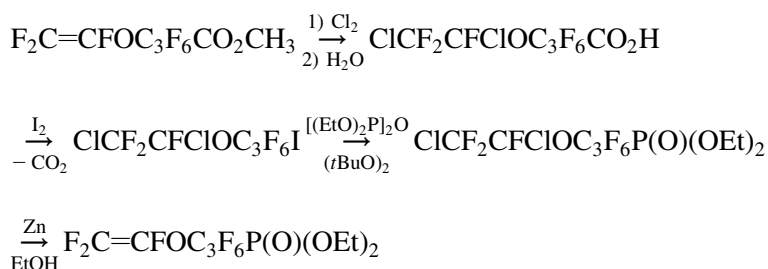
4.5.1.3. Phosphonic acid perfluoroalkoxyvinyl monomers. Besides most important carboxylic and sulfonic groups novel perfluorovinyl ethers bearing a ω-phosphonic acid group were synthesized.

The first one was achieved from the chemical change of carboxylic acid into phosphonic acid function involving an iodinated intermediate as follows [293,294]:

$$\text{F}_2\text{C=CFOC}_3\text{F}_6\text{CO}_2\text{CH}_3 \xrightarrow[\text{2) H}_2\text{O}]{\text{1) Cl}_2} \text{ClCF}_2\text{CFClOC}_3\text{F}_6\text{CO}_2\text{H}$$

$$\xrightarrow[-\text{CO}_2]{\text{I}_2} \text{ClCF}_2\text{CFClOC}_3\text{F}_6\text{I} \xrightarrow[(t\text{BuO})_2]{[(EtO)_2\text{P}]_2\text{O}} \text{ClCF}_2\text{CFClOC}_3\text{F}_6\text{P(O)(OEt)}_2$$

$$\xrightarrow[\text{EtOH}]{\text{Zn}} \text{F}_2\text{C=CFOC}_3\text{F}_6\text{P(O)(OEt)}_2$$

Then, the synthesis of dimethyl perfluoro(3-vinyloxypropyl) phosphonate was achieved and co- or terpolymerized with TFE and perfluoro (propyl vinyl ether) [294].

Another alternative was proposed by Petersen et al. [295]; the iodides being converted into the corresponding phosphonites using a photoreaction in the presence of tetraethyl pyrophosphite, followed by an oxidation with hydrogen peroxide to prepare the desired diethyl phosphonate esters.
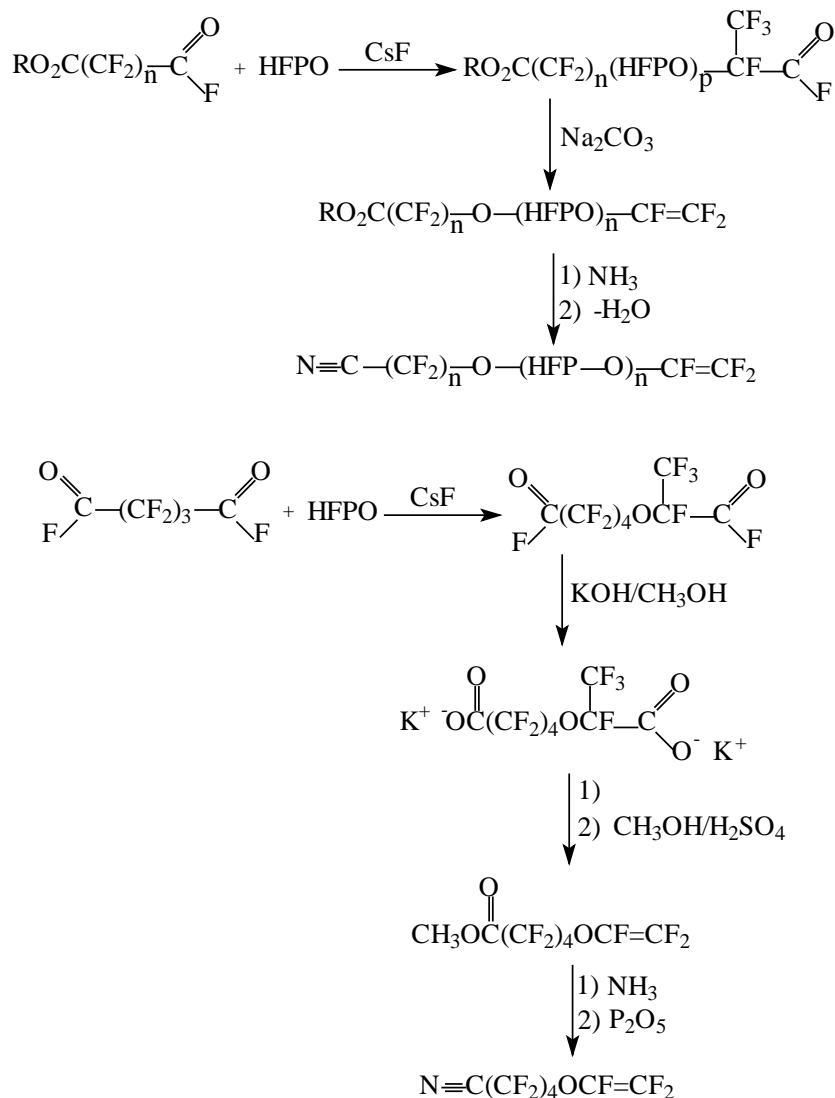
Other exotic functional perfluorovinyl ethers were reported in the very interesting review published by Ikihashi and Yamabe [281].

As a matter of fact, most applications [279–283] have been obtained from copolymers containing TFE and perfluorinated vinyl oxy-ω-sulfonyl fluoride or ω-carboxy (or derivatives): membranes for chlorine–alkali electrolysis, perfluorinated ion exchange materials, hydrogen–oxygen solid polymer electrolyte fuel cells or applications in space, ground (for vehicles) and undersea power sources.

4.5.1.4. Other functional PAVEs. They may contain other functional groups such as nitrile or hydroxyl ones. Various ways of synthesis are reported below.

4.5.1.4.1. Nitrile-type. Many efforts have been made by Nottke [296] or Breazeale [297] who could

synthesize ω-nitrile perfluoro(vinyloxy) monomers. Two reaction schemes are presented below:

$$RO_2C(CF_2)_n\text{--}\overset{\displaystyle O}{C}{-}F \quad + \quad HFPO \quad \xrightarrow{\text{CsF}} \quad RO_2C(CF_2)_n(HFPO)_p\text{--}\overset{\displaystyle CF_3}{CF}{-}\overset{\displaystyle O}{C}{-}F$$

$$\downarrow Na_2CO_3$$

$$RO_2C(CF_2)_n\text{--}O\text{--}(HFPO)_n\text{--}CF{=}CF_2$$

$$\downarrow \begin{array}{l} 1)\ NH_3 \\ 2)\ \text{-}H_2O \end{array}$$

$$N{\equiv}C\text{--}(CF_2)_n\text{--}O\text{--}(HFP\text{--}O)_n\text{--}CF{=}CF_2$$

$$\overset{\displaystyle O}{C}{-}(CF_2)_3{-}\overset{\displaystyle O}{C}{-}F \quad + \quad HFPO \quad \xrightarrow{\text{CsF}} \quad \overset{\displaystyle O}{C}(CF_2)_4OCF\text{--}\overset{\displaystyle O}{C}{-}F$$

$$\downarrow KOH/CH_3OH$$

$$K^+\ {}^-O\overset{\displaystyle O}{C}(CF_2)_4O\overset{\displaystyle CF_3}{CF}{-}\overset{\displaystyle O}{C}{-}O^-\ K^+$$

$$\downarrow \begin{array}{l} 1) \\ 2)\ CH_3OH/H_2SO_4 \end{array}$$

$$CH_3O\overset{\displaystyle O}{C}(CF_2)_4OCF{=}CF_2$$

$$\downarrow \begin{array}{l} 1)\ NH_3 \\ 2)\ P_2O_5 \end{array}$$

$$N{\equiv}C(CF_2)_4OCF{=}CF_2$$

Both these cyanoperfluoro(vinyloxy) monomers were successfully co- or terpolymerized with TFE and PMVE [296–301] or with VDF and PMVE [302] leading to crosslinked fluoroelastomers via triazine rings (see Section 7.6) endowing them with outstanding thermal and oxidative stabilities [303].

To circumvent this additional curing, Watakabe et al. [304] first synthesized an original $F_2C{=}CFOC_3F_6CN$ (according to Sullivan's method [305] which was the first reported way to prepare ω-cyano-perfluoro(vinyloxy) monomers) that was further cyclized in two steps to produce a fluorinated telechelic bis(trifluorovinyloxy)triazine.

4.5.1.4.2. Hydroxylated-type. Researchers at DuPont [284] succeeded in the preparation of ω-hydroxy

Table 5
Reactivity ratios of TFE and monomers (E, propylene and mainly fluoroalkenes) in copolymerization

M	r_{TFE}	r_M	References
$H_2C=CH_2$	0.10	0.15	[315]
$H_3CCH=CH_2$	0.06	1.00	[236]
$F_3C-CH=CH_2$	0.12	5.0	[71,316]
$C_3F_7CH=CH_2$	0.21	2.3	[316,317]
$FCH=CH_2$	0.06	0.30	[183]
tr-$HFC=CHCF_3$	22	0.18	[316]
$F_2C=CH_2$	3.73	0.23	[318]
	0.28	0.32	[183]
$(F_3C)_2C=CH_2$	0.58	0.09	[316]
$F_2C=CHF$	1.14	0.46	[183]
$F_3CCF=CH_2$	0.37	5.4	[316]
$F_2C=CFCl$	0.75	1.04	[319]
	0.80	1.10	[183]
	1.0	1.0	[171]
$F_2C=CFBr$	0.82	0.24	[319]
$F_2C=CFCH_2OH$	2.47	0.41	[188]
$F_2C=CFC_3H_6OH$	1.57	0.45	[188]
$F_2C=CFCO_2CH_3$	5.0	0.10	[320]
	3.0	0.15	[191]
$F_2C=CFCF_3$	15	0	[321]
	65	0	[183]
	3.5	0	[322]
$F_2C=CFCF_2OR_FSO_2F$	10	0.3	[287]
$F_2C=CFOCF_3$	1.73	0.09	[193]
$F_2C=CFOC_3F_7$	8.72	0.06	[193]
$F_2C=CFOCF_2CF(CF_3)OC_3F_7$	15.60	0.02	[193]
$F_2C=CFO-R_F-CO_2R$	7.0	0.14	[194,323]
$F_2C=CFO-R_F-SO_2F$	8.0	0.08	[280,323]

perfluorovinyl ethers such as $F_2C=CFOCF_2CF(CF_3)(O)(CF_2)_2CH_2OH$ or $F_2C=CFOC_3F_6CH_2OH$ by the reduction, in the presence of sodium borohydride, of the corresponding methyl perfluoro (*i*-oxa-*i* + 1-alkenoate) in high yields (86%), as follows:

$$F_2C=CFO-R_F-CO_2CH_3 \xrightarrow{NaBH_4} F_2C=CFO-R_F-CH_2OH$$
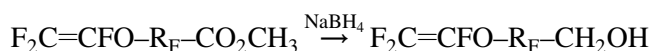
These ω-hydroxyperfluorovinyl ethers can also be functionalized into various original derivatives. The –OH end-group can be chemically changed into –OR, where R represents $C\equiv CH$, $COC(CH_3)=CH_2$, $CH_2-C_6H_4-CH=CH_2$ [284].

4.5.1.5. Trifluorovinyl-type. The Asahi Company develops the very interesting perfluoro-3-oxa-1,6-heptadiene as an valuable intermediate which ring cyclizes to produce Cytop® as an amorphous perfluoroplastic, combining high optical clarity and solubility with outstanding chemical, thermal and electrical properties [279].

Almost similar fluorinated non-conjugated diene $F_2C=CFOCH_2CF_2CF=CF_2$ was prepared by Smart et al. [306] in four steps (the last step deals with the dechlorination of $ClCF_2CFClCF_2CH_2OCF=CF_2$ in the presence of zinc) and was easily homopolymerized and copolymerized with various fluoromonomers, the produced copolymers being useful in coatings and encapsulants.

On the other hand, the Ausimont Company also develops a soluble, transparent, fluorocyclic copolymer containing TFE and fluorinated dioxolane under the Hyflon® AD trademark [307].

4.5.1.6. Aryl trifluorovinyl ethers. Phenyl trifluorovinyl ether (PTVE) has been synthesized in a two-step procedure: 3-phenoxy-2,2,3,3-tetrafluoropropionic acid methyl ester was converted into its potassium salt and pyrolyzed to yield PTVE [308].

Aryl trifluorovinyl ethers have been prepared usually by direct reaction of sodium areneoxides with TFE [309] or by addition of arene oxides to 1,2-dibromotetrafluoroethane yielding 2-bromotetrafluoroethyl ethers, followed by elimination of "BrF" in the presence of zinc [310]. In certain conditions, 1,3-bis(fluorovinyloxy) benzene was obtained.

Pattison [311] disclosed the synthesis of the following CSM:
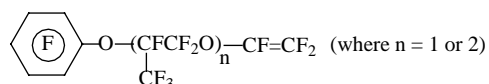
and could terpolymerize it with TFE and PMVE. Interestingly, the pentafluorophenoxy side groups were efficiently crosslinked [311] to promote fluoroelastomers with better mechanical properties [312].

Additional syntheses and molecules including aromatic α,ω-bis(trifluorovinyl ethers) were summarized in the chapter of Babb [313].

Other exotic functional perfluorovinyl ethers were reported in the very interesting reviews published by Yamabe et al. [281], Kirsh et al. [282] or Hung et al. [284].

4.5.1.7. Hydrofluoroalkyl vinyl ethers. Few hydrofluoroalkyl vinyl ethers $F_2C=CHOR_F$ have been reported. To our knowledge, the Ausimont Company only has protected this invention [314] from the dehydrochlorination of $ClCF_2CH_2OR_F$.

For example, this company mentions the synthesis of various amorphous copolymers TFE/$F_2C=CHOCF_2CFHOC_2F_4OCF_3$ (mol% in the copolymer 79/21); TFE/$F_2C=CHOCF_2CFHOCF_3$ (mol% 80/20) and TFE/$F_2C=CHOCF_2CFHOC_2F_4O(CF_2O)_4CF_3$ (mol% 85/15) displaying T_gs of -24.7, -6.4 and $-80.0°C$, respectively.

4.5.2. Copolymerization of TFE

Usually, most copolymers containing TFE are crystalline (melt processable copolymers are TFE/PAVE as PFA® materials, TFE/HFP as FEP® or MFA®) while certain terpolymers are amorphous, having elastomeric properties: besides TFE/P or TFE/PMVE, they contain VDF and HFP and are developed in Section 5.

Regarding the kinetics of copolymerization, Table 5 displays the reactivity ratios of TFE and comonomers. One of the most interesting works was investigated by Naberezhnykh et al. [183] who suggested the decreasing reactivity series of various alkenes about a polymeric TFE chain as follows:

$$H_2C=CH_2 > H_2C=CHF > H_2C=CF_2 > F_2C=CFCl > F_2C=CF_2 > F_2C=CFH \gg F_2C=CFCF_3$$
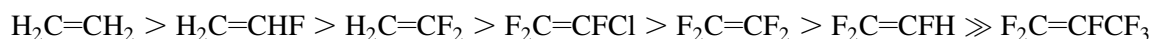
Hence, it can be deduced that the more the double bond is substituted by fluorine atoms, the more reactive the TFE in copolymerization.

5. Fluoroelastomers from VDF (or VF$_2$)

5.1. Introduction

Poly(vinylidene fluoride), PVDF or PVF$_2$, is a thermoplastic that exhibits very interesting piezo-, pyro- and ferroelectrical properties [325–328], is inert to various solvents, oils, acids and shows low permeabilities to gases and liquids. Its T_g is about −40°C while its melting temperature varies from 158 to 197°C [329]. PVDF crystallizes in its called alpha form and can only give the beta form by stretching at moderate temperature or when a certain amount of trifluoroethylene is added to it.

Homopolymers derived from VDF (or VF$_2$) are long chain macromolecules endowed with a high crystallinity rate rendering them unsuitable as elastomers. In contrast, copolymers of VDF with various comonomers can fall into three categories: (i) when the amount of comonomers in the copolymer is as small as that of VDF the resulting materials are thermoplastic with a lower crystallinity than that mentioned above [25,26]; (ii) for a slightly higher content of comonomer thermoplastic elastomers are obtained; (iii) for higher proportion of comonomers the produced copolymers are elastomeric, amorphous with low intermolecular forces [17–24].

Moreover, although PVDF has found interesting applications, three major disadvantages are noted: the high melting temperatures generate energetic costs for processing this polymer; the poor solubility in common organic solvents (PVDF is soluble in DMF or dimethyl acetamide) and the difficult curing of this material.

Hence, fluorocopolymers derived from VDF have drawn more interest. The first copolymers of VDF were patented as early as 1946 [330], followed by various generations of more and more VDF-based copolymers. Tables 2 and 6 list various fluorinated elastomers and thermoplastics and show the great versatility of compounds. In addition, the historical development of fluorinated copolymers from non-fluorinated monomers [25,26,118] or from fluoroolefins [17,19,21–23,119] have been reported already.

A large variety of fluoroolefins or functional comonomers can be successfully co-, ter- or tetrapoly-merized and some examples are reported below.

Copolymers of VDF and CTFE or HFP represent the most important production, nowadays, among the thermoplastic copolymers of VDF (those from vinyl fluoride [331] or TFE are also thermoplastic, the latter ones being studied more due to their interesting ferroelectric behavior [332–337]), while such a positive fate was reached for VDF/HFP elastomers produced by most fluoropolymer industries.

As a matter of fact, four types of VDF-based fluoroelastomers are manufactured:

1. the earliest types of fluorocarbon elastomers are those prepared from VDF and HFP (type-A);
2. later, the B types were developed; they contain VDF, HFP and TFE base units;
3. fluoroelastomers designated as type-C were prepared to improve the solvent resistance; they contain a higher fluorine content and CSM such as bromotrifluoroethylene in addition to VDF, TFE and HFP;
4. the most recent ones are called type-D fluoroelastomers endowed with low-temperature resistance and containing PAVE instead of HFP.

Table 6
Commercial copolymers of VDF: Thermoplastics (HFA — hexafluoroacetone)

Monomers	Composition (mol%)	Trade name	Producer	Melting point (°C)
VDF/CTFE	90/10 or 95/5	FORAFLON®	Atofina	165–167
	90/10 or 95/5	KF POLYMER®	Kureha	–
		SOLEF®	Solvay	150–165
VDF/TFE	80/20	KYNAR® SL, 7200	Atofina N.A.	120
VDF/HFA	88/12	–	Central Glass	121
VDF/HFP	95/5 or 85/15	KYNARFLEX®	Atofina N.A.	135–160
		SOLEF®	Solvay	130–160
VDF/TFE/HFP	72/18/10	KYNAR® ADS	Atofina N.A.	90
VDF/TFE/HFP	30/55/15	HOSTAFLON® TFB	Dyneon	160–185
(VDF/CTFE)-*g*-VDF	(37.5/12.5)/50	CEFRAL SOFT®	Central Glass	170

Regarding the behavior in solution of fluoroelastomers, little data is given in the literature [338,339] in contrast to the Mark–Houwink relationships to determine molecular weights of PVDF [101,340,341]. To our knowledge, the most pertinent studies were achieved by Zinbo and Theodore [338] and by Maccone et al. [339] who determined key molecular weight parameters by size exclusion chromatography, such as the average molecular weights and molecular weight distributions. The latter team recently investigated on the branching of PVDF from the transfer to the polymer and then the cross-linking in the presence of a fluorodiolefin [339].

5.2. VDF/CTFE copolymers

The first copolymers of VDF/CTFE were produced for military interest from 1955 [342–346]. At this time, these materials were the first commercially available fluoroelastomers (called Kel® F) with vulcanizate properties higher to any of those existing.

Nowadays, according to the properties and applications required, various VDF/CTFE copolymers are proposed: the amount of CTFE being crucial. Obviously, the elastomeric behavior is reached at 30–50 mol% of CTFE while thermoplastic copolymers are obtained when containing less than 15 mol% of CTFE [347] and are called flexible PVDF (Table 6).

In addition, a terpolymer of VDF, CTFE and a peroxide-functional allyl monomer has been synthesized and subsequently grafted to PVDF to form a tough, flexible thermoplastic material, commercialized by the Central Glass Company under the Cefral® trademark [116] (see Section 3.2.2).

VDF-based fluoroelastomers have outstanding resistance to flame, chemicals, solvents, heat and oxidation. These materials can be cured by bis-nucleophiles such as bisphenols or diamines or by peroxides, as reported in Section 7.

5.3. VDF/HFP copolymers

The first VDF/HFP copolymer was produced by DuPont de Nemours under Viton® trademark in 1957 with a better thermal stability and inertness to chemicals and a lower swelling to oils and petroleum than those mentioned above [348].

In 1958, the 3M Company commercialized Fluorel® and, later, Ausimont and Daikin produced their Technoflon® and Dai-El® products, respectively.

VDF/HFP copolymers have also led to various kinds of product according to the content of HFP. As above, at less than 15 mol% of HFP, the resulting copolymers show thermoplastic properties [349] (Table 6), while those containing 30–40 mol% behave as elastomers [216,350–352]. Ajroldi et al. [353] have demonstrated that a composition of 20–21 mol% HFP represents the best compromise between the requirements of a low T_g and a fully amorphous elastomer.

Today, at least 25 grades are supplied depending on the nature of the comonomer, its content and its distribution, molecular weights, state (powder or pellets) or presence of additives. Tables 2 and 6 list the producers and tradenames of these copolymers.

On both academic and applied points of view, Apostolo et al. [354] recently performed interesting investigations on the kinetics of emulsion copolymerization of VDF and HFP, monitoring all the parameters of the experimental conditions and using an appropriate model.

Further original terpolymers based on VDF, HFP and TFE have also been produced [339,355,356].

For example, elastomeric terpolymers of VDF, TFE and HFP [217] provide gum stocks for high-performance fluoroelastomers while for various amounts of these three fluoroolefins, thermoplastic elastomers can be produced, as reported by Hull et al. [356].

Indeed, according to the respective amounts of monomers, the elastomeric behavior [the region of the triangle (the summits of which are VDF, HFP and TFE) encompasses a composition of 20–70% of VDF, 20–60% of HFP and 0–40% of TFE] [19] may fall into a thermoplastic elastomeric one (composition of 15–20 or 70–80% of VDF; 13–25 or 80–85% of HFP and 15–30 or 80–85% of TFE) as explained by Logothetis [19] or Hull et al. [356].

For a structural point of view it is required that the microstructure of the elastomers contains about one HFP unit for every two to four of the other monomer units to prevent any crystallization of the terpolymer and to insure an amorphous macromolecule. This can be shown by ^{19}F NMR as described in various articles dealing with co- or terpolymerization [355,357,358] or with telomerization [27,104,359–363]. Although no adjacent HFP units were found in the microstructure (its reactivity ratio worth 0, Table 7), more recent telomerization of HFP gives evidence of the presence of two consecutive HFP units when the reaction was carried out at higher temperatures [361–363] in the presence of α,ω-diiodoperfluorobutane.

Regarding the thermal properties an interesting comparison of the T_gs of fluoroelastomers containing VDF was realized by Van Cleeff [368] but showing that their T_gs could not be lower than $-29°C$.

5.4. VDF/pentafluoropropene

Copolymers of VDF and 1-hydropentafluoropropene ($CF_3CF{=}CFH$) have been produced by 3M [369] or Montedison [370] to compete with those obtained from VDF and HFP, leading to original fluoroelastomers, but their lower thermostability could not allow these materials to find effective development. Nevertheless, little basic research has been achieved [187], especially on the kinetics of copolymerization that assessed the reactivity ratios of both comonomers (Table 7) showing that VDF is more reactive than its pentafluorinated partner.

Ter- or tetrapolymers containing 23–65% of VDF, 25–75% of $F_2C{=}CFOR_F$, 0.3–0.5% of 2-hydro-pentafluoropropene and optionally, 0–30% of TFE were prepared by Bowers and Schmiegel [371].

These copolymers exhibit excellent low-temperature properties and processability when cured with polyhydroxy compounds or amines.

5.5. VDF/TFE/propylene

As shown above, an HFP unit surrounded by two VDF units or by VDF and TFE units was shown to be a useful structure curable by dinucleophiles [19,24,89], since the $-CF_2CF(CF_3)CH_2CF_2-$ may be dehydrofluorinated, leading to a reactive inner double bond.

This is why researchers at Asahi [372] substituted HFP by propene which enables the resulting terpolymers to be resistant to dehydrofluorination. Such a phenomenon is explained because CH_3 is a less electron-withdrawing group than CF_3 and hence contributes to a lower acidity of the adjacent methylene and methine functionality. As a result, this terpolymer has been crosslinked with difficulty in the presence of conventional nucleophilic cure systems [256,257,372].

5.6. VDF/trifluoroethylene and VDF/hexafluoroacetone copolymers

In contrast to the fluoropolymers mentioned above these copolymers are thermoplastics.

VDF can copolymerize in all proportions with trifluoroethylene (TrFE) [365] leading to random crystalline copolymers. Nowadays, only VDF/TrFE copolymers containing a TrFE amount ranging from 17 to 50 mol% have a slight commercial development limited to few tons per year. Although expensive because of the price and hazards of TrFE, these copolymers have found applications in various fields thanks to their piezo-, ferro- and pyroelectrical properties [373].

Copolymers of VDF with hexafluoroacetone [374–376] are crystalline and attractive for their electrical properties.

5.7. VDF/PAVE

5.7.1. Copolymerization of VDF with non-functional PAVE

As indicated in Section 4, functional PAVE or perfluoroalkoxy alkyl vinyl ethers (PAAVE) easily copolymerize with TFE leading to novel materials useful for membrane applications. In contrast to these copolymers which are not elastomeric, those obtained from the copolymerizations of PAVE (or PAAVE) with VDF exhibit interesting elastomeric properties, although little development has been achieved.

Indeed, the ether group brought by the PAVE (or PAAVE) comonomer allows the macromolecule to exhibit a low glass transition temperature and in certain cases, elastomers resistant to low temperature endowed with good thermal stability have been obtained.

First, Albin and Gallagher [377] from Du Pont, pioneered this research in the 1960s from an emulsion process, yielding copolymers containing PMVE with a temperature of flexibility ranging from -28 to $-24°C$. This reaction evidences the poor reactivity of PMVE ($r_{PMVE} = 0$; $r_{VDF} = 3.4$; Table 7). However, adding traces of TFE led to commercially available Viton® GLT (from DuPont) having outstanding properties [23,378]. This terpolymer exhibits the following repeating unit structure:

$$-(CH_2CF_2)_x[CF_2CF(OCF_3)]_y(C_2F_4)_z- \qquad \text{with } x = 4; \ y = 1 \text{ and } z = \text{trace}$$
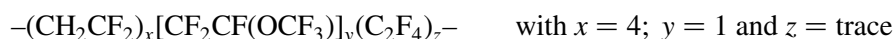
In 1966, NASA [379] published a report describing similar interest, dealing with the copolymerizations

Table 7
Monomer reactivity ratios for copolymerization of VDF (A) with other fluoromonomers (B) (and E)

Monomer B	r_A	r_B	$r_A r_B$	$1/r_A$	References
$H_2C=CH_2$	0.05	8.5	0.42	20.00	[315]
$FCH=CH_2$	0.17	4.2–5.5	0.71–0.94	5.88	[184]
	0.20–0.43	3.8–4.9	0.76–2.11	2.33–5	[364]
$H_2C=CFCF_2OR_F$	0.38	2.41	0.92	2.63	[185]
$F_2C=CFH$	0.70	0.50	0.35	1.43	[365]
$F_2C=CHCF_3$	9.0	0.06	0.54	0.11	[187]
$F_2C=CHC_6F_{13}$	12.0	0.90	10.80	0.08	[366]
$CFCl=CF_2$	0.73	0.75	0.55	1.37	[318]
	0.17	0.52	0.09	5.88	[367]
$CFBr=CF_2$	0.43	1.46	0.63	2.33	[318]
$CF_2=CF_2$	0.23	3.73	0.86	4.35	[318,321]
	0.32	0.28	0.09	3.13	[183]
$CF_3-CF=CF_2$	6.70	0	0	0.15	[196]
	2.45	0	0	0.40	[321]
	2.90	0.12	0.35	0.34	[195]
$F_2C=CFOCF_3$	3.40	0	0	0.29	[192]
$F_2C=CFOC_3F_7$	1.15	0	0	0.86	[192]
$F_2C=CFO(HFP)OC_2F_4SO_2F$	0.57	0.07	0.04	1.75	[192]
$CF_2=CF(CH_2)_3OAc$	0.17	3.26	0.59	5.56	[189]
$F_2C=CF(CH_2)_3SAc$	0.60	0.41	0.25	4.07	[190]
$F_2C=C(CF_3)COF$	7.60	0.02	0.15	0.13	[186]

of VDF with $F_2C=CFOC_nF_{2n+1}$ ($n = 1, 2, 3$) initiated by AIBN at high pressure ($P > 1000$ atm). This synthesis led to fluoroelastomers with T_gs ranging from −25 to −20°C.

More recently, PMVE or perfluoro-*n*-propyl vinyl ether was shown to readily copolymerize with VDF in solution, initiated by peroxides, and yielded elastomers with interesting elastomeric behavior since T_gs were as low as −44°C [192,380].

PAAVE was also copolymerized with VDF and produced original copolymers having low T_gs. For example, Yamabe et al. [381] from Asahi performed the following emulsion copolymerization:

$$VDF + F_2C=CFOCF_2CF(CF_3)OC_3F_7 \rightarrow poly(VDF\text{-}co\text{-}PAAVE)$$

which led to fluoroelastomers, the T_gs of which ranged from −36 to −29°C. They showed excellent low-temperature resistance, alcohol resistance and high thermostability ($T_{dec} = 390–415$°C). In certain cases, these authors carried out ternary polymerization of these above comonomers with either perfluoro-*n*-propyl vinyl ether or 2-bromo-perfluoroethyl vinyl ether.

Researchers at the Daikin Company [271] used a comonomer with three ether bridges such as $F_2C=CF[OCF_2CF(CF_3)]_2OC_3F_7$ to be copolymerized in a solution process (in 1,2,2-trifluorotrichloroethane), initiated by a chlorofluoroperester. The T_gs of certain copolymers could reach −44°C.

5.7.2. Copolymerization of VDF with functional PAVE or PAAVE

Functional perfluoroalkoxyalkyl vinyl ethers and mainly those containing a sulfonyl fluoride or their derivatives were also successfully copolymerized with VDF in various processes.

First, Ezzel and Carl [382] encompassed copolymers of VDF and perfluorovinyl ethoxy sulfonyl fluoride.

Then, Connolly and Gresham [383] disclosed the copolymerization of VDF with perfluorosulfonyl fluoride ethoxy propyl vinyl ether (PSEPVE) and the terpolymerization involving HFP, in an emulsion process, but using a small amount of functional comonomer so that only 0.2–5.0 mol% was present in the copolymer.

Recently Feiring et al. [384,385] have also investigated on the copolymerization of VDF with various functional comonomers as $F_2C=CFOCF_2CF(CF_3)OC_2F_4R$ where R represents $NHSO_2CF_3$ (described by Desmarteau [289] or Xue [386]), $SO_2CLi(SO_2CF_3)_2$, $SO_2NLiSO_2CF_3$ and SO_2F (PSEPVE) [385]. In the case of the last system, the copolymers have a T_g of $-20°C$ and no weight-loss was noted up to $375°C$.

Hence, these copolymers with pendant groups containing fluorosulfonyl methide or fluorosulfonyl imide derivatives are original fluorinated ionomers that can be used in applications such as batteries, fuel cells, electrolysis cells, ion exchange membranes, sensors, electrochromic windows, in electrochemical capacitors and for modified electrodes.

More recently, we have disclosed that VDF copolymerizes with PSEPVE [387] in all proportion and have been able to assess their reactivity ratios (Table 7). More interestingly, the addition of HFP in this system enabled the functional PSEPVE monomer to improve its reactivity and to produce original elastomers with a higher thermostability [388].

5.8. VDF/functional perfluorovinyl monomers

In contrast to the above-mentioned perfluorovinyl ethers that propagate with difficulty in radical polymerization (only hydroxy-terminated perfluorovinyl ethers homopolymerize under ionic conditions [284]), several attempts of copolymerizations of VDF with $F_2C=CF–R–G$ (where G and R represent a functional group and a hydrogenated spacer, respectively) have shown that these latter homopolymerize easily. Such original monomers enable the resulting copolymers to be efficiently crosslinked with routes different from those usually involved (by means of diamines, bisphenols, peroxydes or by radiations, as reported in Section 7).

Pioneering work was carried out by researchers at Daikin [389] from various functional monomers such as: $F_2C=CF(CF_2)_n(CH_2)_mOH$ where $n = 0, 1, 2$ and $m = 1–3$.

The synthesis of the monomers was described in the same patent, while the optimization of $F_2C=CF(CH_2)_3OR$ (with R = H or Ac) was recently achieved [390]. Other functional trifluorovinyl monomers have also been prepared: either bearing an ω-insaturation [391–393], or a carboxylic [394–396], an amide [392], a sultone [391], an epoxide [397], a hydroxyl [188,394,398], a thioacetoxy [190] and a phosphonate group [399]. More exotic routes to trifluorovinyl end-group have been reviewed recently [400]. In addition, trifluorovinyl monomers bearing nitrogenated heterocycle have been reported already [401]. Copolymerizations of VDF with $F_2C=CF(CH_2)_3OR$ [189,389] or with $F_2C=CF(CH_2)_3SCOR$ [190,402] were achieved leading to elastomeric materials (according to the nature and the amount of the functional monomer, T_gs were ranging from -23 to $-8°C$ [389]). Their kinetics of copolymerization were also investigated, showing that the reactivity ratio of VDF was lower than that of the functional comonomer [189,190] (Table 7). Indeed, it was worth supplying a reactivity series of

fluorinated monomers about VDF. The traditional method for the determination of relative reactivity of a macroradical to several monomers was used. Indeed, it is common to compare the values $1/r_A = k_{AB}/k_{AA}$ as the ratio of rate constants of crossed propagation to that of propagation (k_{AA}). Thus, the higher the $1/r$ value, the more able the radical is to react with the second monomer. Table 7 allows one to suggest the following series of relative reactivities of monomers to $\sim\sim\sim$VDF$^\bullet$ radicals.

$F_2C=CHC_6F_{13} < F_2C=CHCF_3 < HFP < PMVE < PPVE < VDF < TrFE < CTFE$ (recent value) $\approx$ BrTFE $< H_2C=CFCF_2OR_F < TFE < F_2C=CFC_3H_6SCOCH_3 < F_2C=CFC_3H_6OAc < H_2C=CHF \approx$ CTFE (old value) $<$ E, although numerous kinetics still deserve to be investigated, as that involving VDF and $F_2C=CFCO_2CH_3$, showing in a first attempt that VDF incorporates the copolymer better [320].

6. Fluoroelastomers containing heteroatoms

Besides the common fluorinated elastomers described above, containing carbon, fluorine, hydrogen, and in several cases, small quantities of oxygen, other elastomers having heteroatoms have also been developed. Five main families are summarized below, including "fluoroinorganic" elastomers such as fluorophosphazenes and fluorosilicones.

6.1. Poly(thiocarbonyle fluoride)s

The C=S bond is able to be polymerized by means of an anionic initiation [403,404] at low temperatures to lead to fluorinated polymers containing low T_gs. Various examples of structures are the following [403,405–407]: $-(CF_2S)_n-$; $-[C(CF_3)_2S]_n-$ and $-[CF(R_F)S]_n-$ where R_F designates a perfluoroalkyl group.

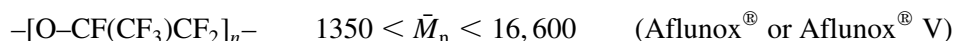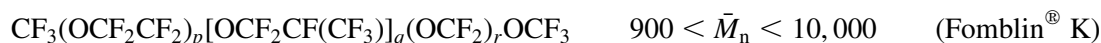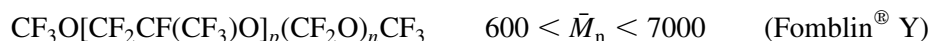### 6.2. Fluorinated polyethers and perfluoropolyethers (PFPEs)

PFPE, which also constitute a special class of fluoropolymers, have found various applications such as lubricants [408], elastomers [409], pump fluids and heat transfer fluids under demanding conditions.

Four main families of fluorinated polyethers are produced in an industrial scale. These are Fomblin$^\circledR$, Krytox$^\circledR$, Denmum$^\circledR$ and Aflunox$^\circledR$ produced by Ausimont, Du Pont, Daikin and NOK Corp. (or Nippon Mektron Ltd), respectively [409]. These polymers are prepared by anionic ring opening polymerization of HFPO (PFPE-K) [409–412], by polymerization of TFE or HFP in the presence of oxygen under UV(PFPE-Y and PFPE-Z) [408,409] or by Lewis acid-catalyzed ring opening polymerization of 2,2,3,3-tetrafluorooxetane followed by a direct fluorination under UV light (PFPE-D) [413]. Lagow et al. [414,415] also achieved their syntheses by direct fluorination of hydrogenated polyethers; this process requiring much care to avoid side-reactions such as cleavages of chains. Nowadays, the production of the PFPE from this last way is developed by Exfluor Research Corp. [416,417].
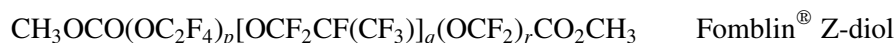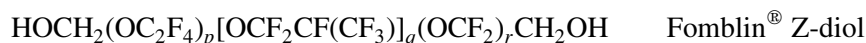
Their interesting characteristics are their low T_gs (lower than $-50°C$) and their totally amorphous state thanks to their aliphatic structure and ether links [409,415]. In addition, these products, endowed with high thermostability, excellent chemical inertness and low surface tension, find relevant applications as lubricants and heat carrier-fluids in hostile conditions.

PFPE can be homopolymers or copolymers and can exhibit linear or branched structures, as follows:

$$CF_3(OCF_2CF_2)_p(OCF_2)_qOCF_3 \qquad 4000 < \bar{M}_n < 13,000 \qquad (\text{Fomblin}^{\circledR} \text{ Z})$$

$$CF_3CF_2CF_2O(CF_2CF_2CF_2O)_nCF_2CF_3 \qquad 1600 < \bar{M}_n < 7000 \qquad (\text{Demnum}^{\circledR})$$

$$CF_3CF_2[OCF_2CF(CF_3)]_nF \qquad 1300 < \bar{M}_n < 10,300 \qquad (\text{Krytox}^{\circledR})$$

$$CF_3O[CF_2CF(CF_3)O]_p(CF_2O)_nCF_3 \qquad 600 < \bar{M}_n < 7000 \qquad (\text{Fomblin}^{\circledR} \text{ Y})$$

$$CF_3(OCF_2CF_2)_p[OCF_2CF(CF_3)]_q(OCF_2)_rOCF_3 \qquad 900 < \bar{M}_n < 10,000 \qquad (\text{Fomblin}^{\circledR} \text{ K})$$

$$-[O-CF(CF_3)CF_2]_n- \qquad 1350 < \bar{M}_n < 16,600 \qquad (\text{Aflunox}^{\circledR} \text{ or Aflunox}^{\circledR} \text{ V})$$

In a smaller scale, the Hoescht Company develops HFPO polymers leading to fluorinated polyether acryl fluoride which, after hydrolysis and decarboxylation, becomes Hostinert$^{\circledR}$ PFPE [418].

Functionalized PFPEs are well reported by Scheirs [409] while most investigations have been performed by Ausimont [419]. They are:

$$HO_2C(OC_2F_4)_p[OCF_2CF(CF_3)]_q(OCF_2)_rCO_2H \qquad \text{Fomblin}^{\circledR} \text{ Z-diac}$$

$$HOCH_2(OC_2F_4)_p[OCF_2CF(CF_3)]_q(OCF_2)_rCH_2OH \qquad \text{Fomblin}^{\circledR} \text{ Z-diol}$$

$$CH_3OCO(OC_2F_4)_p[OCF_2CF(CF_3)]_q(OCF_2)_rCO_2CH_3 \qquad \text{Fomblin}^{\circledR} \text{ Z-diol}$$

In addition DuPont develops a PFPE with an iodo end-group, leading to original PFPE-*b*-poly(VDF-*co*-HFP) diblock copolymers under telomerization conditions [420]:

$$\text{PFPE–I} + n\text{VDF} + p\text{HFP} \overset{\text{rad.}}{\rightarrow} \text{PFPE-}b\text{-poly(VDF-}co\text{-HFP)}$$
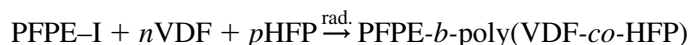
According to the nature of the initiator and to the stoichiometry of the reaction, molecular weights ranging between 1900 and 30,000 were obtained [420] (starting from a PFPE-I having a $\bar{M}_n = 1300$).

More recently, an interesting study regarding the synthesis of poly(ϵ-caprolactone)-*b*-PFPE-*b*-poly(ϵ-caprolactone) was achieved from the ring opening polymerization of ϵ-caprolactone by using hydroxyl-telechelic PFPEs in the presence of various catalyst/initiators [421].

Interesting reviews [408,409,422–424] or articles [425–429] supply pertinent information on the syntheses, the properties and applications of these PFPEs.

More exotic fluorinated polyethers are those prepared by DuPont from the ionic addition of hydroxy end-group to trifluorovinyl ethers [284]. The monomers have the following formula:

$$F_2C{=}CFOCF_2CF(CF_3)OC_2F_4CH_2OH \qquad \text{or} \qquad F_2C{=}CFOC_3F_6CH_2OH$$

The polymerization proceeds quickly at ambient temperature leading to oligomers ($\bar{M}_w = 4000$–6000). Useful data is reported in the interesting chapter of Hung et al. [284].

These hydrogenofluorinated polyethers were photochemically fluorinated leading to original PFPEs [430].

More exotic process, performed in supercritical CO_2 was reported, enabling the produced PFPEs to be involved in coating applications [431].

6.3. Fluoro nitroso elastomers

Nitroso fluoroelastomers are heterochain polymers applied mainly to situations where a non-flammable elastomer is needed or to ambient temperature conditions where resistance to hydrocarbon or strong oxidizing reagents is required. The ultimate characteristic of the nitroso polymer is failing to burn in pure oxygen and has resulted in its extensive use for the NASA in the Apollo spacecraft.

The most important of this series is the copolymer resulting from the spontaneous alternated copolymerization of trifluoronitrosomethane with TFE [432–434] leading to the intermediate oxazetidine:

$$CF_3-N-\!\!-\!O$$
$$|\qquad|$$
$$CF_2-CF_2$$
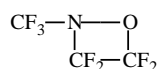
to yield the following branched nitroso elastomer:

$$\left[\begin{array}{c} CF_3 \\ | \\ N-O-CF_2-CF_2 \end{array}\right]_n$$
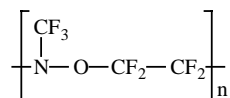
This polymer has a T_g of $-51°C$ and has demonstrated excellent resistance to corrosive chemical environments such as hydrogen-bearing solvents, acids, oxidizing agents, fire and ozone [435,436]. Other analogs utilizing variously substituted nitroso monomers and different olefins were also prepared [437–442]. In some cases, the obtained fluoropolymers reached an average molecular weight of 100,000 [440], as elastomeric gums.

Other polyfluorinated nitrosoalkanes were developed by 3M [443].

The only effective crosslinking agents were found to be diamines but some degradation took place during the cure and the final products had relatively low tensile strength. A terpolymer in which pendant carboxyl groups were incorporated afforded a system susceptible to vulcanization by a large selection of agents. However, the presence of carboxyl groups resulted in somewhat decreased oxidative stability as compared to the original copolymer system [444].

The nitroso fluoroelastomers are not commercialized yet and the future of these materials would seem to be limited to that of specialty elastomers although numerous investigations have been performed since more than 60 polymers have been synthesized already [442,445].

6.4. Polyfluoroalkoxyphosphazene polymers

The polyfluoroalkoxyphosphazenes represent a recent commercial addition to the fluorinated elastomer family. Early work culminated in studies of polymerization conditions conducive to the production of linear high-molecular weight ($\bar{M}_n > 10^6$) dichlorophosphazene polymers $-[N=P(Cl_2)]_n-$ known as inorganic rubber [446]. They can be prepared by heating the hexachlorocyclotriphosphazene cyclic trimer under vacuum at 250°C and terminating the reaction at moderate ($<70\%$) conversions before crosslinking occurs. Surprisingly, polyphosphazenes $-[N=P(X_2)]_n-$ have low glass transition temperatures and many can crystallize (e.g. when X = F, $T_g = -96°C$ and $T_m = -60$ to $-40°C$; when X = Cl, $T_g = -63°C$ and $T_m = -30°C$). Commercial interest as specialty rubbers stems from the preparation of

poly(fluoroalkoxyphosphazene) elastomers, reported in 1968 [447]. The linear phosphazene polymers are substituted with fluorocarbon alcohols as shown in the following reaction:

$$-[N=P(Cl_2)]- + R_1CH_2ONa \rightarrow -[N=P(OCH_2R_1)_2]_n-,$$
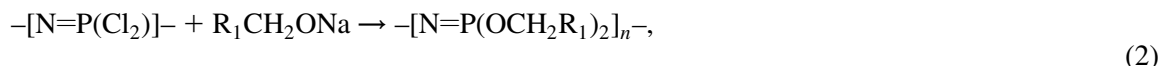
$$\text{where } R_1 = CF_3, C_3F_7; R_1 = CF_3, T_g = -68°C \tag{2}$$

Commercial introduction was achieved by Firestone from 1975 and one of the most well-known fluorophosphazenes has OCH_2CF_3 and $OCH_2(CF_2)_4H$ groups born by the phosphorous atom ($T_g = -68°C$). These elastomers are vulcanizable (by peroxide via incorporation of a CSM) and offer a unique set at low-temperature properties, similar to those of the fluorosilicones, with improved oil and solvent resistance properties from -65 to $+175°C$. The polymers can be processed on conventional equipment, vulcanization being achievable via the use of organic peroxides, sulfur with accelerators or high-energy radiations [448–450]. Excellent resistance is shown by fluorinated polyphosphazenes (PNF® elastomers) to ozone, N_2O_4, hydrolysis by water, flame and radiation, but strong mineral acids lead to a loss of their properties. The solvent and hydrocarbon resistances, low-temperature flexibility and wide service-temperature range of PNF® elastomers should lead to their utilization in O-rings, fuel hoses, seals, gaskets, diaphragms and vibration damping.

6.5. Fluorosilicones

As in the previous family, fluorosilicones are regarded as "fluoroinorganic" elastomers in which polymeric chains are composed of "inorganic" repeating units exhibiting organic fluorinated pendant groups. The most important properties are the retention of tensile properties at high-temperature and the exceptional low-temperature flexibility [451,452]. In addition, the introduction of fluorine atoms improves the solvent resistance, although depolymerization occurs from 230°C. As fluorophosphazenes, these polymers contain a fluorine amount ranging from 30 to 40%, hence enabling them to get a good chemical inertness.

Discovered in 1950, regarded as the most common fluorosilicones, and leading the market of such a class of fluoropolymers, Silastic® polymers, commercialized by the Dow Corning Company and prepared from cyclosiloxane D_3 [453] has the following repeating base unit:
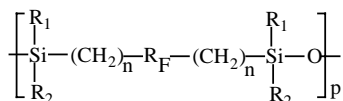
$$\begin{array}{c} CH_3 \\ | \\ -(Si-O)- \\ | \\ CH_2CH_2CF_3 \end{array}$$
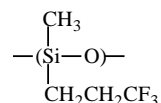
The T_g of this poly(methyl trifluoropropyl siloxane) ranges from -75 to $-65°C$ and unlike poly(dimethyl siloxane)s, it does not exhibit a low-temperature crystallization at $-40°C$, due to the inability of the polymeric chain to pack into a crystalline lattice [451]. It can be crosslinkable from various classical processes of the chemistry of silicones such as in the presence of peroxides or from the $SiH/Si-CH=CH_2$ systems [452].

However, the relatively low strength limits the use of fluorosilicones to static applications such as seals for fuel line [454].

To improve the thermostability of such fluoropolymers, researchers at the Dow Corning Company

synthesized "hybrid" fluorinated silicones with the following structure [455,456]:

$$\left[\begin{array}{c} R_1 \\ | \\ Si-(CH_2)_{\overline{n}}-R_F-(CH_2)_{\overline{n}}-Si-O \\ | \\ R_2 \end{array} \begin{array}{c} R_1 \\ | \\ \\ | \\ R_2 \end{array}\right]_p$$

where R_1, R_2 : CH_3, $C_2H_4CF_3$ and R_F : $(CF_2)_x$ x = 1 or $C_2F_4OC_2F_4$

n = 2

Recently, our laboratory has supplied novel hybrid fluorosilicones based on fluorinated telomers containing VDF, TFE and HFP base units [104]. The fluoropolymers are rather stable in a wide range of temperatures ($T_g \sim -40°C$ and $T_{dec} = 400°C$) [457–461]. Their structure is similar to that above with $n = 2$ or 3; R_1, R_2: CH_3, $C_2H_4CF_3$ or $C_2H_4C_4F_9$ and R_F: $(VDF)_a$ $(TFE)_b$ $(HFP)_c$ with $a = 0, 1$; $b = 2, 3$; $c = 0, 1$.

7. Crosslinking of fluoroelastomers

7.1. Introduction

Fluoroelastomers, like all other thermosetting elastomers, require curing in order to get useful and enhanced properties. A considerable amount of effort has been devoted over the 40 years of existence of fluoroelastomers towards the development of practical crosslinking systems. Fluoroelastomers can be cured by nucleophiles such as diamines or bisphenols, with peroxides and by radiation.

Irrespective of the curing system the best vulcanizate properties are obtained by a two-step process. The first step comprises both heat (150–180°C) and pressure (10–30 MPa), by molding a specimen in a press (e.g. compression molding). The second step (post-cure) is carried out in air at 200–250°C at atmospheric pressure for 12–24 h. Post-curing is utilized to develop optimum physical properties. The cure chemistry for a variety of fluoroelastomers is rather different but there are two basic mechanisms: ionic and radical curing. These mechanisms are generally considered while the specific features of the curing of various groups of fluororubbers have been detailed by various authors [15,19,22,221,348,462–466].

The largest group of fluoroelastomers, VDF-based fluorocarbons, can be crosslinked by ionic curing; however, radical curing can also be possible if the polymer has been prepared in the presence of a CSM bringing a functional group susceptible of a radical attack, such as bromine or iodine [20,22–24].

The cure chemistry of VDF-based fluoroelastomers is connected with the strong polarity of the C–F bond and specific polarization of molecules, which determined their selective ability to split off hydrogen fluoride under the influence of internal factors (e.g. temperature, bases, etc.).

7.2. Ionic curing

VDF/HFP and VDF/HFP/TFE fluorocarbon elastomers can be crosslinked by bisnucleophiles, such as bisphenols and diamines. Schmiegel, in 1979, identified the triad monomer sequences as "base-sensitive sites" by ^{19}F NMR spectroscopy [358,467]. He observed that solution reaction of VDF/HFP copolymers in the presence of base results in the decrease of the integral intensity of the signals at −75.2 and −108.6 ppm in the ^{19}F NMR spectra, corresponding to HFP/VDF/HFP sequence, or in the case of copolymer with TFE to the following triad sequences: HFP/VDF/TFE and TFE/VDF/TFE.
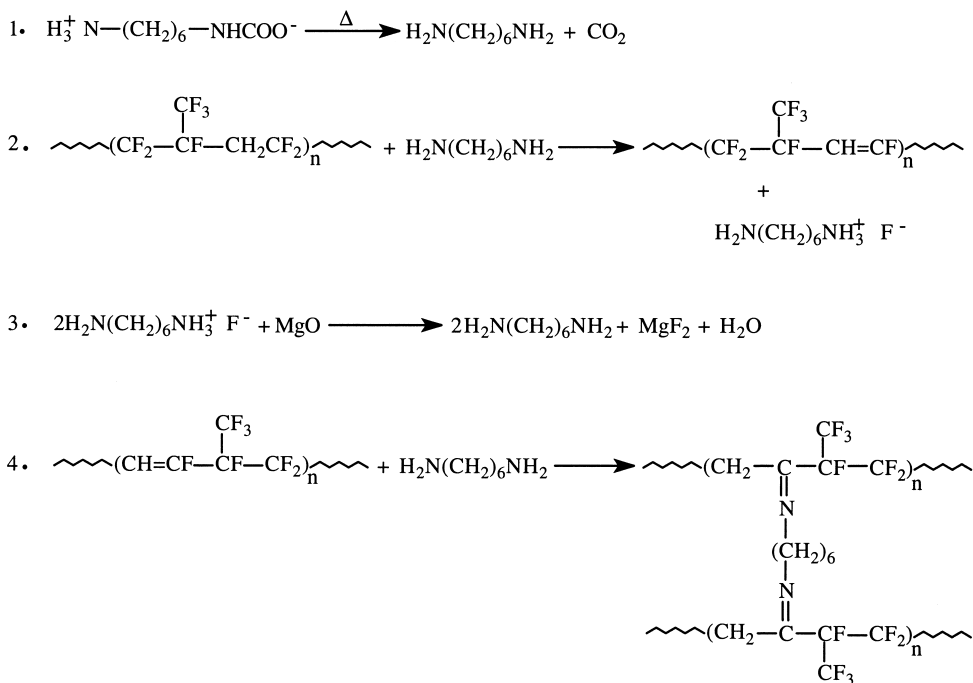
1. $H_3^+N{-}(CH_2)_6{-}NHCOO^- \xrightarrow{\Delta} H_2N(CH_2)_6NH_2 + CO_2$

2. $\sim\!\!\sim\!\!\sim(CF_2{-}\underset{\underset{CF_3}{|}}{CF}{-}CH_2CF_2)_n\!\!\sim\!\!\sim + H_2N(CH_2)_6NH_2 \longrightarrow \sim\!\!\sim\!\!\sim(CF_2{-}\underset{\underset{CF_3}{|}}{CF}{-}CH{=}CF)_n\!\!\sim\!\!\sim$

$+$

$H_2N(CH_2)_6NH_3^+\ F^-$

3. $2H_2N(CH_2)_6NH_3^+\ F^- + MgO \longrightarrow 2H_2N(CH_2)_6NH_2 + MgF_2 + H_2O$

4. $\sim\!\!\sim\!\!\sim(CH{=}CF{-}\underset{\underset{CF_3}{|}}{CF}{-}CF_2)_n\!\!\sim\!\!\sim + H_2N(CH_2)_6NH_2 \longrightarrow \sim\!\!\sim\!\!\sim(CH_2{-}\underset{\underset{N}{\|}}{C}{-}\underset{\underset{CF_3}{|}}{CF}{-}CF_2)_n\!\!\sim\!\!\sim$

$(CH_2)_6$

$\sim\!\!\sim\!\!\sim(CH_2{-}\underset{\underset{CF_3}{|}}{\overset{\overset{N}{\|}}{C}}{-}CF{-}CF_2)_n\!\!\sim\!\!\sim$

Fig. 1. Curing of VDF-containing fluoroelastomers with diamines.

According to the currently accepted mechanism the crosslinking reaction consists of two steps:

1. dehydrofluorination of the polymer by the base, to generate double bonds in the backbone chain:

$$>CH{-}CF< \xrightarrow[-HF]{base} >C{=}C<$$
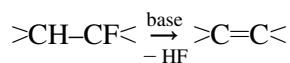
2. nucleophilic addition of the Nu–R–Nu bis-nucleophile to the double bond, yielding crosslinks:

$\sim\!\!\sim Nu{-}R{-}Nu\sim\!\!\sim$
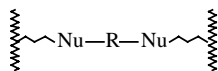
The accelerator, which has the typical structure of phase transfer catalysts (PTC), is thought to act as the cation of the base, making it able to diffuse through the rubber.

The formation of double bonds in the presence of a base from these base-sensitive sites is the starting step in the ionic crosslinking of these fluoroelastomers. The following reaction mechanism has been proposed recently by Arcella et al. [22] on the basis of a broad study involving solution investigations using ^{19}F and ^{1}H NMR, FT-IR techniques, coupled with solid-state curing experiments [468]. The mechanism is depicted above where the Nu–R–Nu bis-nucleophile represents a bisphenol or a diamine crosslinker.

In the first step, the formation of –C(CF$_3$)=CH– double bond by elimination of fluorine from the

tertiary carbon is suggested. Double bond is shifted, catalyzed by fluorine ion and the formation of –CH=CF– double bond occurs. Then, the nucleophilic addition of a crosslinker to the –CH=CF– double bond proceeds with:

1. the allylic shift of fluorine providing the new $-C(CF_3)=CH-$ double bond;
2. addition onto the double bond followed by elimination of fluorine from the same double bond.

7.2.1. From amino systems

Amines or amine-based compounds are used as curatives for fluoroelastomer compounds [469–472] and they are always used in conjunction with magnesium oxide. Aliphatic amines and polyamines were the earliest curing agents of FKM[®] elastomers but they are too much reactive, i.e. they tend to scorch during cure. This drawback has led to the development of carbamate salts of amines and other Schiff bases [473] which are less reactive. Because of the processing difficulties and the relatively poor retention of physical properties at high temperatures (200°C), the importance of the diamine cure has decreased.

The mechanism of crosslinking involving 1,6–hexanediamine is shown in Fig. 1.
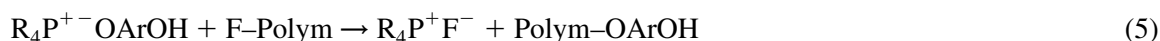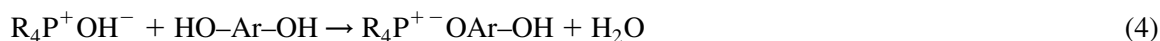
7.2.2. From bisphenol system

Bisphenol cures were developed in the late 1960s and started replacing the diamine cure in the early 1970s.

Schmiegel [358] found that the bisphenol does not react with the polymer without any accelerator, which is an onium (phosphonium, ammonium, etc.) salt in combination with a metal compound as an activator. The bisphenol reacts with the metal oxide to give the phenolate ion which, in turn, reacts with the phosphonium or tetraalkylammonium ion to give the intermediate I or II, respectively. These intermediates are strong bases which have some compatibility with the polymers and abstract hydrogen fluoride from the polymer backbone:

$$R_4P^{+\,-}OArOH \qquad R_4N^{+\,-}OAr–OH$$
$$\quad\;\; I \qquad\qquad\qquad\;\; II$$

The double bonds rearrange and a second molecule of HF can be abstracted from the polymer to give a diene too. Such reactions are only possible when the CH_2 group on the backbone is flanked by CF_2 or $CF(CF_3)$ groups rendering the hydrogen atoms acidic enough to be abstracted by the base. The resulting anion will then eliminate a fluorine ion and form a double bond and eventually a diene. Formation of the unsaturation in the polymer backbone is the rate determining step of the curing reaction [19].

The use of a phase transfer catalyst (onium salt) determines the phenolate-anion generation in the curing reaction to its use up in the rubber compound. For example, the mechanism is as follows:

$$R_4P^+X^- + Ca(OH)_2 \rightarrow R_4P^{+\,-}OH + CaXOH \tag{3}$$

$$R_4P^+OH^- + HO–Ar–OH \rightarrow R_4P^{+\,-}OAr–OH + H_2O \tag{4}$$

$$R_4P^{+\,-}OArOH + F–Polym \rightarrow R_4P^+F^- + Polym–OArOH \tag{5}$$

The $R_4P^+F^-$ obtained diffuses on the $Ca(OH)_2$ surface, where it enters in reactions (3) and (4), and the

cycle is repeated till full exhaust of the bisphenol as a crosslinking agent. The rate and the product of the reaction depends on the rate of desorption of the ion-pair $R_4P^{+-}OArOH$ from the surface of $Ca(OH)_2$ particles and its diffusion into the rubber phase [474,475].

It is suggested [358,467] that the crosslinking reaction proceeds on the macromolecular chain fragments where the HFP/VDF/HFP triads were formed. Under the action of the anion, the reactions of dehydrofluorination, double bond rearrangement and again dehydrofluorination, take place consecutively. The substitution for fluorine atoms at unsaturated carbon atoms with phenolate-ion results in crosslinking. The quaternary salt catalyst regenerates repeatedly, hence its amount in the compound is several times lower than that of the stoichiometric one. The reaction of crosslinking continues to the use up of the bisphenol.

Because of processing and property advantage, the most commonly used compound is "bisphenol-AF" (2,2$'$-bis(hydroxyphenyl) hexafluoropropane) [475]. Others, like hydroquinone, substituted hydroquinones and 4,4$'$-disubstituted bisphenols are used commercially to a lesser extent [476]. The bisphenol reacts with polymer in the presence of an accelerator (PTC), such as phosphonium or ammonium salt, a compound having the formula:

$$\left[\begin{array}{c} R_2 \\ | \\ R_1\!-\!P\!-\!R_3 \\ | \\ R_4 \end{array} \right]^{+}_{n} \quad X^{(-)}_n$$
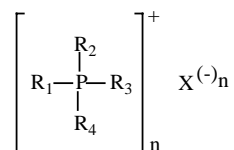
where P is mainly selected from phosphorous, arsenic, and antimony; R_i are substituents such as alkyl, aryl, aralkyl, and alkenyl; and X is selected from the following groups: halide, sulfate, sulfite and carbonate [462]. The accelerator is preferably benzyl triphenyl phosphonium chloride or bromide.

The metal compound, as an activator of ionic curing, is composed of a divalent metal oxide, such as MgO, ZnO, CaO or PbO, or a divalent metal hydroxide or a mixture of oxide and/or hydroxide with a metal salt of weak acid [462]. The metal compound serves a dual purpose. It absorbs certain gaseous and acidic materials which are involved during the curing and can chemically attack and weaken the fluoroelastomers. It also provides a long-term aging stability. In the process of curing with diamines, the acid acceptors have been found to play a multirole, since these compounds can affect dehydrohalogenation, assist in hydrolysis of the Schiff base and regenerate the free amine from its hydrofluoride [464].

Fluoroelastomers containing PAVE are not usually cured with bisphenols [23]. They would loose trifluoromethoxide (especially in the most used PMVE) during the dehydrofluorination step [477]. Trifluoromethanol is further degraded to HF and CO_2, which results in the formation of large amount of volatiles and sharply deteriorate sharply the physical properties of these vulcanizates. Patent literature describes some degree of success when using bisphenol cures with tetrapolymers, containing the four major monomers: TFE, VDF, HFP and PMVE [478,479].

The main drawback of bisphenol cures is the presence of some unsaturation in the vulcanized parts.

Dehydrofluorination which occurs in the ionic crosslinking reaction produces double bonds beyond that which are strictly required for the crosslinking itself. While Smith and Perkins [480] found that four moles of F^- per mole of crosslink during the curing by diamines, Schmiegel [358,467] predicted six moles of F^- were necessary per mole of crosslink by bisphenol-AF in the presence of quaternary
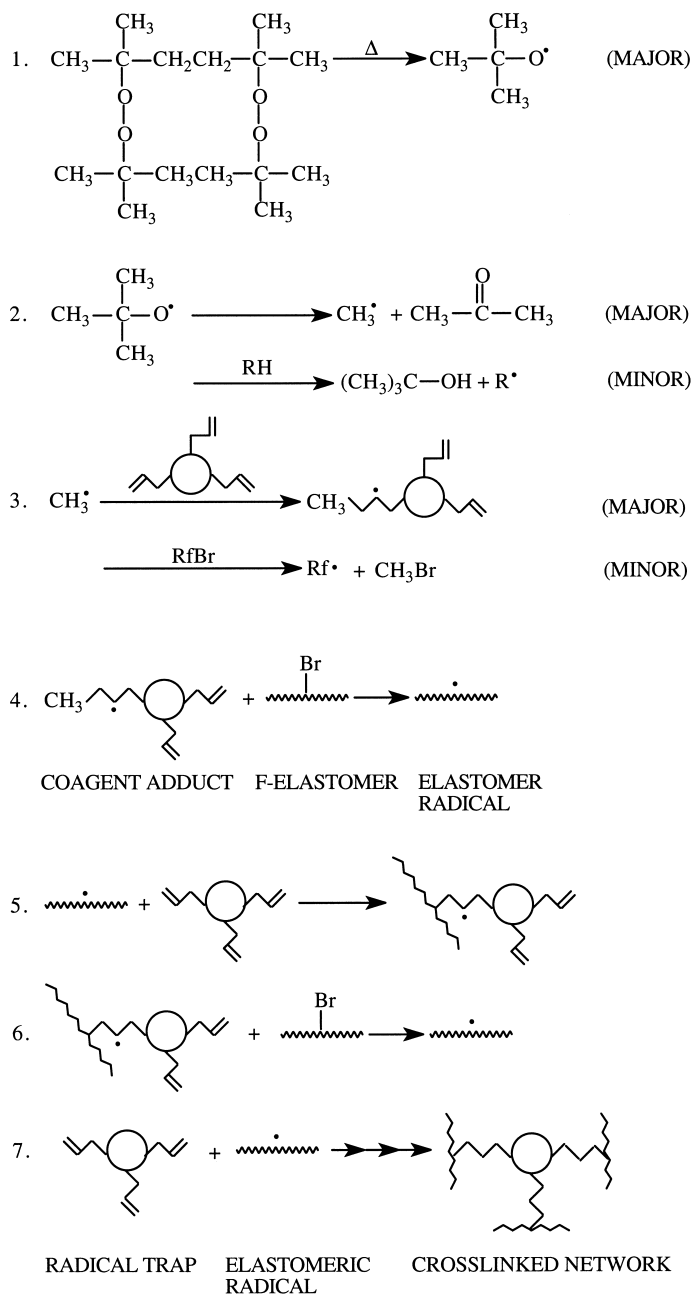
Fig. 2. Main reactions of proposed crosslinking mechanism of brominated fluoroelastomers from peroxides/trially(iso)cyanurate system.

phosphonium salt. Other authors found even higher amount in bisphenol crosslinking depending on the relative amount of a phosphonium salt [474]. Excess of unsaturations formed in ionically crosslinked elastomeric parts represent weak points susceptible to further nucleophilic attack by basic substances present in the contact fluid.

There are different ways to overcome that "Achilles' heel". One of the possibilities which has been achieved already lies in forming different fluorocarbon elastomer structures, such as fluorocarbons without VDF [218,219] or fluorocarbon elastomers without HFP [e.g. TFE/P (Aflas®), TFE/PAVE copolymers (perfluoroelastomers), etc.].

An interesting approach was developed by Arcella et al. [220] of so-called protective monomers. The basic idea was to introduce a monomer able to alter the base-sensitive monomer triads, and produced new monomer sequences with a lower weakness to nucleophiles [89]. Alternatively, bisamidoxime compounds were interestingly acting as vulcanizing agents when the copolymer contains nitrite side groups [481].

But the main route to avoid the presence of unsaturations after the crosslinking reaction is radical curing, mainly by peroxides.

7.3. Radical curing

7.3.1. Peroxide curing

Peroxide crosslinking is basically a free radical process. It involves the thermal decomposition of peroxide to provide free radicals which abstract hydrogen from the methylene groups along the polymer chain, and the resultant polymeric radicals interact, directly or through the intermediary of radical traps to form crosslinks.

Two different pathways to increase the efficiency of peroxide cure vulcanization of fluoroelastomers have been developed. The first one concerns the increase of the content of hydrogen-containing groups in the copolymer, such as in TFE/P copolymers (Aflas®). The hydrogen of tertiary carbon atom in propylene units is a little screened (only from one side from fluorocarbon groups the energy of the C–H bond is lowered by the induction effect of CH_3 groups). So, these types of H atom are easily accepted by free radicals with a high yield of polymeric radicals and formation of crosslinks.

These polymers are cured by a peroxide coagent (i.e. radical trap) system. Among the various peroxides and coreagents, α,α'-bis(*t*-butyl-peroxy)diisopropyl benzene and triallyl isocyanurate (TAIC) and triallyl cyanurate (TAC) (Fig. 2) are most suitable, respectively [20–24,365,464].

Peroxides, in the presence of acid acceptors, appear to afford good vulcanizates, both with Viton® and Kel®-F fluoroelastomers. This is mainly true for aromatic peroxides since the results with the aliphatic compounds do not seem to be very encouraging. Investigations were essentially centered on benzoyl peroxide formulations, although a limited effort was developed using 2,4-dichlorobenzoyl peroxide [464].

Attempts were made to determine the extent of peroxide crosslinking in the absence of an acid acceptor, but the properties were not satisfactory. In analogy with the amine series, the optimum properties are reached [464] only after post-curing.

To make these elastomers better curable by peroxides, a CSM susceptible to free-radical attack has been introduced [220,482–485]. Bromine-containing monomers such as bromotrifluoroethylene [218,268,319,484–490], 1-bromo-2,2-difluoroethylene [489], perfluoro(2-bromoethyl vinyl ether) [220,259,260,491–496] and others [268,273,482,483,486,496–499] provide such cure sites (Fig. 2).

Adding tributyl stananne or triethyl silane improves the curing [496]. It is desirable that the bromomonomers copolymerize to high conversion with minimum chain transfer and inhibition. For good curing performance, an aliphatic peroxide, a suitable radical trap, and an inorganic acid acceptor are required. Among the various peroxides tried, 2,5-dimethyl-2,5-di-*t*-butylperoxyhexane (peroxide I) and 2,5-dimethyl-2,5-di-*t*-butylperoxyhex-3-yne (peroxide II) were found to be the most suitable. Peroxides that contain aromatic substituents such as dicumyl peroxide, give variable results, and may be linked to their sensitivity to acid catalyzed decompositions. The preferred coreagent or radical trap is TAIC. The other common radical traps are similarly effective in formation of crosslinks, but the resulting networks are less stable, as determined by compression set resistance measurements at 230°C [269].

The crosslinkers are usually di- or trifunctional electron-rich olefins [269], such as TAIC (Diak® 17), TAC and trimethallyl isocyanurate (Diak® 8) [269]. The radical trap (coagent) concentration is important to maintain both a good cure rate and a final cure state.

The introduction of iodine-containing fluoroelastomers facilitates the molding process considerably and makes possible injection molding of fluoroelastomers. I/Br-fluoroelastomers combine the properties from iodine as chain end [100–104,497,500] and from Br in the polymer chain [107,108,464]. The reaction mechanism of peroxide curing with coagent is well known and described in the literature [15,17–24,269].

The radical produced from the initiator may abstract an X-atom from the polymer (minor reaction) or add to the radical trap (e.g. TAIC) to give a more stable radical (Fig. 2). These more stable radical intermediates, in turn, abstract X atoms from the polymer, generating polymeric radicals. The driving force for such a chain reaction during propagation is the transfer of an X atom from the electron-poor fluoropolymer to the electron-rich hydrocarbon radical on the radical trap. The radical trap, therefore, becomes the crosslinker and to give optimum properties should be efficient (multifunctional and electron-rich) and thermally and oxidatively stable.
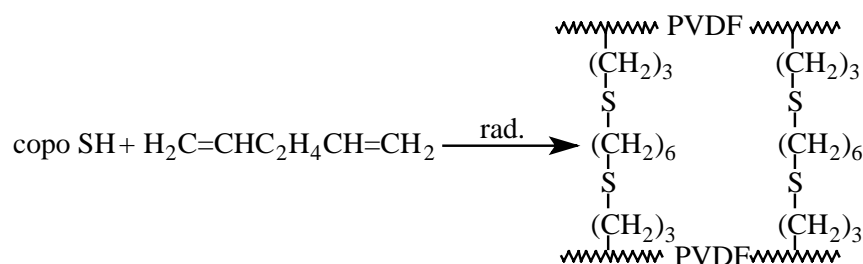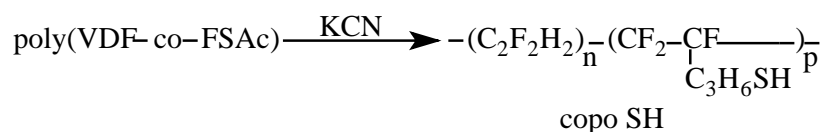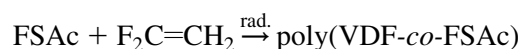
Metal oxides are useful in absorbing any traces of HF generated during the curing process [269]. As a result, such polymers show a marked improvement in steam and acid resistance, together with good physical properties of vulcanizates.

Arcella et al. [220,259] suggested an interesting idea to prepare mixed hydroxilic/peroxidic network to reduce double bond formation of ionic crosslinking. In this way, it is possible to reduce the amount of onium salt and compensate the reduced crosslinking density by curing of brominated chain-ends using a peroxide system. A new peroxide cure system was introduced by Saito et al. [501] for VDF-based fluoroelastomers. It is a combination of radical curing system, promoted by a special organic onium compound and acid acceptor. A radical generated from organic peroxide adds to TAIC to give a TAIC-radical. Simultaneously, dehydrofluorination of the elastomer backbone occurs in the presence of onium compound and acid acceptor, followed by the addition of the TAIC radical across the generated fluoro-olefin cure site. These steps occur during the curing period.

7.3.2. Other system of radical curing

For example, although thiol-ene systems have easily led to vulcanize hydrogenated elastomers, this process has been used scarcely to cure fluoroelastomers because of the difficulty in the availability of mercapto side groups. However, we have recently used an original trifluorovinyl ω-thioacetate monomer (FSAc) able to copolymerize with VDF [190], and the resulting copolymer was hydrolyzed to generate elastomers bearing mercapto lateral groups (copo SH). Curing was performed in the presence of

non-conjugated dienes as follows [190,402]:

$$F_2C{=}CFCH_2CH{=}CH_2 + HSCOCH_3 \xrightarrow{UV} \underset{FSAc}{F_2C{=}CFC_3H_6SCOCH_3}$$

$$FSAc + F_2C{=}CH_2 \xrightarrow{rad.} poly(VDF\text{-}co\text{-}FSAc)$$

$$poly(VDF\text{-}co\text{-}FSAc) \xrightarrow{KCN} \underset{copo\ SH}{-(C_2F_2H_2)_n\text{-}(CF_2\text{-}\underset{C_3H_6SH}{CF}{-})_p\text{-}}$$

$$copo\ SH + H_2C{=}CHC_2H_4CH{=}CH_2 \xrightarrow{rad.}$$

Other systems of crosslinking more adapted to TFE-containing elastomers are detailed in Section 7.6.

7.4. Radiation crosslinking of fluoroelastomers

Fluorinated polymers containing hydrogen (including VDF-base copolymers) and copolymers of TFE and HFP can be crosslinked with different degrees of effectiveness by high-energy radiation. In the last 15 years several outstanding reviews of radiation crosslinking of fluoropolymers have been published by Lyons [502–504] and many articles detail different aspects of this process, more recently reported by Logothetis [505] and Forsythe [506,507]. Indeed, Dixon et al. [348] were the first team to disclose that VDF/HFP elastomers could be cured successfully with high-energy radiation. Then, Florin and Wall [508] performed further studies of VDF-based copolymers and Yoshida et al. [509] studied the stress relaxation of irradiated fluorocarbon elastomers.

The mechanism of radiation crosslinking of fluoroelastomers is similar to that proposed for other elastomers: it is a typical radical mechanism closed to peroxide curing. In irradiated products, the free radicals were registered. But even at such high-energy irradiation the free fluorine was not found. Hydrogen fluoride is produced during the irradiation of VDF copolymers but having a great bond strength, it does not participate in exchange reactions along the polymer chains. Hence, in hydrogen containing fluoropolymers, it may be assumed that only exchange reactions of hydrogen atoms or main chain radicals can be expected [510]. Depending on the copolymer compositions, different doses are required for radiation curing: for VDF/CTFE copolymers, low doses up to 3 Mrad are enough, while for VDF/HFP elastomers, 10 Mrad and more [510] were necessary.

Post-curing is also needed to improve the technical properties of vulcanizates. The presence of radical traps (TAIC and others) increases the efficiency of radiation curing. Mainly carbon–carbon crosslinks
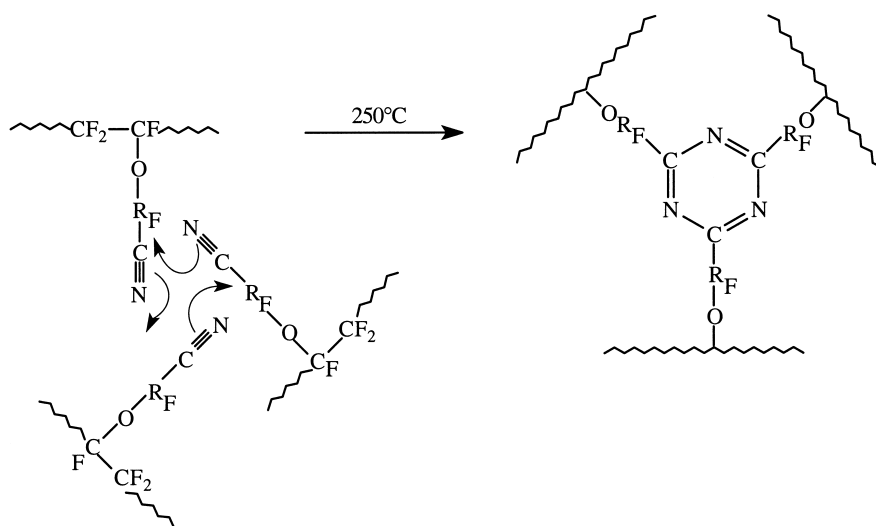
Fig. 3. Thermal curing of nitrile-containing fluoroelastomers.

are formed, and it may be expected to have a good resistance to heat aging, and a relative inertness to chemical and oxidative attack. This process was applied successfully for TFE/P copolymers [248].

Radiation vulcanization can be accelerated in the presence of the sensitizers, such as vinyl ethynyl-phenylol resins or other unsaturated compounds [511]. In this way, the total dose for optimum cross-linking can be lowered and the properties of gum can be considerably improved.

Doses of 10–15 Mrad are sufficient to give excellent properties and the cured parts remain clear and colorless [504]. There seems to be little selectivity, i.e. crosslinked parts with good properties have been made from polymers containing functionalities and from those without any functionality. The advantage of radiation cured materials is that they do not contain any filler or chemical, i.e. any impurity that can be extracted from the vulcanizates which is so important in the semiconductor industry [24].

7.5. Post-curing of fluoroelastomers

Post-curing of fluoroelastomers is more applied for chemical curing than for radiation crosslinking and leads to improvement of the mechanical properties of the final vulcanizate. Indeed, an increase (ca. 50%) is noted in the Young's modulus and the tensile strength at break, while a 50% decrease is seen in elongation at break and a substantial improvement in compression set resistance [477]. One of the essential functions of the oven cure is the removal of water, a by-product of the cure, the presence of which prevents full development of the diamine cure and causes reversion of the bisphenol cure [471,480]. Smith and Perkins [480] showed that post-cure would enhance another type of crosslinking. They suggested the formation of aromatic rings with loss of HF by a Diels–Alder addition. However, in other works [269,512–519] it was concluded that during post-cure a thermally induced bond-breaking and bond-making process occurs and this results in a more stable network. However, the present mechanism of post-curing reaction is not completely understood.

7.6. Curing chemistry of TFE-based perfluoroelastomers

Perfluoroelastomers (FFKM[®], Du Pont products [4,19]: Kalrez[®], Perlast[®] are based on copolymers of TFE (60–80 mol%) with PAVE (20–40 mol%) and a third CSM in less than 2 mol%. The most readily copolymerizable homolog is PMVE. The CSM comprises the following three classes of compounds [24]:

1. perfluoro(alkylvinyl ethers), $CF_2=CF-O-R_F-G$; where G designates $-COOR$, $-OC_6H_5$, $-O(CF_2)_nCN$, $-CN$, $-Br$;
2. substituted fluoroolefins such as $R_1CH=CR_2R_3$; R_1, R_2, R_3: H, Br, F, R_F, R_FBr;
3. fluoroiodo compounds, R_FI and IR_FI; R_F: perfluoroalkyl group.

For the curing process of FFKM[®] of great importance are perfluoroolefins containing Br and I atoms [520–522] or PAVE, containing nitrile groups. Vulcanization of perfluoroelastomers with nitrile groups is brought about by the catalytic interaction of tetraphenyltin or silver oxide on the pendant CN group, thereby creating a triazine crosslinked structure [19–24].

Typically, the $-CN$ end-groups of the grafts enable the fluoroelastomer to be cured leading to stable triazine rings as shown in Fig. 3. These cyano perfluorinated elastomers display outstanding thermal and oxidative [303] stabilities and continuing efforts have been directed to further modification of these polymers to broaden the areas in which they can be used (Section 10).

Perfluoroelastomers containing bromine or iodine cure site can be crosslinked with aromatic or aliphatic peroxides in the presence of radical traps, such as TAIC well detailed by Logothetis [19,20,24,273]. These types of vulcanizate have more universal chemical resistance while thermal stability is less important.

The iodine-based cure system used with Perlast[®] is unique and does not afford the level of extreme high-temperature resistance associated with the triazine-cured Kalrez[®] 4079. Thanks to this curing, Kalrez[®] 4079 is the only elastomer capable of extended service at 316°C. Perlast[®] system has the great advantage of containing neither metal oxide nor other metal-based catalysts [222,518].

Aromatic or aliphatic diamines and bisphenols (dipotassium salts) can be used to cure perfluoroelastomers containing perfluorophenoxy or hydrogen cure sites. This system, in order to act well, requires the presence of an accelerator such as polyethers or the cyclic polyether compounds.

Perfluoroelastomers may also be cured by high-energy radiation.

Clear cured parts can be made by curing perfluoroelastomers with a high-energy electron beam followed by a post-cure. The chemical resistance and compression set properties of these materials are excellent, but the tensile properties are lower because they do not contain any reinforcing fillers [24].

8. Formulations and ingredients of fluoroelastomer compounds

8.1. Introduction

Compounding of fluoroelastomers is relatively more simple when compared to other rubbers. Ingredients are obviously the result of the particular cure chemistry, final properties to be achieved and processing technology to be used. A summary of fluoroelastomer technology is available in the literature [523–527].

End-use requirements usually dictate the type of fluoroelastomers to be used: vulcanization system,

fillers and other process aids. The ingredients do not exert negative influence on chemical and thermal resistance of fluoroelastomers and the curing system has to give a network bonds with similar energy to the main polymer chain. There are no special stabilizers against heat or aging of fluoroelastomers but inorganic oxides and alkali-earth hydroxides can improve their thermal stability. The fillers used are not of any special type: they cannot considerably regulate the mechanical properties and the level of filling is not high. Different processing aids such as low-molecular weight polyethylenes or hydrocarbon waxes and pigments can also be used. Plasticizers are generally avoided since they influence negatively during post-cure processing aids. Usually, the standard chemicals are cure systems (curative and accelerators), acid scavengers (metal oxides), activators (hydroxides), filler(s), processing aids and pigments (if necessary for coloration).

A typical recipe of fluoroelastomers can be given as follows (in parts per hundred, phr): fluoroelastomer 100; curing system ca. 1–6; metal oxides ca. 3–15; fillers ca. 0–40; processing aids ca. 0–5; others (if needed) ca. 1–5.

The simplicity of the fluoroelastomer formulations requires an adequate choice of the ingredients of every group to satisfy the requirements of technological properties of rubber mixtures and operating properties of end vulcanizates.

This is why some aspects of the choice of different ingredients and their influence to the properties of rubber mixtures and end-articles are discussed.

8.2. Vulcanization systems

Since the mechanism and chemistry of curing are detailed in Section 7, only the technological aspects of the curing are reported below.

Three types of cure system used are from diamines, dihydroxy and peroxides. Radiation crosslinking has also been discussed in a preceding section. The most popular cured system (about 80% of all applications) is the nucleophilic one. It is based on the crosslinker (mainly bisphenol-AF [474,475]) and accelerator (a phase transfer catalyst).

8.2.1. Block polyfunctional amines

Diamine curing system is the first one applied for the fluoroelastomer vulcanization, and the most well known are DIAK[®] (trademark of DuPont Dow Elastomers) no. 1 (hexamethylene diamine carbamate), DIAK[®] no. 3 (dicinnamylidene diamine carbamate) and DIAK[®] no. 4 (4,4′-bis(aminocyclohexyl)-methane carbamate). The diamine cure system is characterized by good cures and good bondability, heat aging and compression set [21]. But they are scorchy (especially nos. 1 and 4), not stable during the storage, are all sensitive to heat history prior to final processing and prone to mold fouling [523]. Cured elastomers have relatively low stability to steam and hot water.

8.2.2. Bisphenolic systems

Bisphenolic systems were introduced around 1970 and they dominate the market today. Using these systems, fluoroelastomers can be cured rapidly with good scorchy stability, good compression set values and improved heat aging properties. They consist of two compounds: curative (usually bisphenol) and accelerators (quaternary phosphonium or ammonium salts). The most used is bisphenol-AF [2,2-bis(4-hydroxyphenyl)hexafluoropropylidene] in a combination with triphenylbenzyl phosphonium chloride (BTPPC) [474]. As curatives, others reactants can also be used such as hydroquinone, resorcin with

cation active surfactants (triethylbenzyl ammonium chloride, TEBAC) and others. Curatives and accelerators are available as dispersions in low-molecular weight fluorohydrocarbon elastomers (ASTMD-1418 designation FKM$^{®}$, but suppliers' precompounds dominate.

The recent precompounds have a low viscosity and contain cure systems, which are highly active above 200°C. They are designed for injection molding at high temperature where the thermally depressed viscosity allows excellent flow [523]. Bisphenolic vulcanization ensures good technological properties of rubber mixtures and production of articles with complicate configurations. At the same time they have a high scorchy stability, long-term storage, high rate of curing and excellent compression set/stress relaxation resistance.

The levels of the acid acceptor (MgO) and activator [Ca(OH)$_2$] in the case of bisphenol cure strongly affect not only the cure network as reflected by the final properties, but also the cure properties so that the cure system must be finely tuned to achieve the optimum balance of processing parameters [22].

8.2.3. Peroxide vulcanization

The peroxide cure system is the most recent of those available and is often combined with co-reagent (radical trap). In other variants, it requires fluoroelastomers where the CSM can be activated. Although peroxide-curable materials have provided new compound performance, they have not surpassed the bisphenol cure in many areas. The peroxide cure system consists of organic peroxides and co-reagent and has had industrial applications from 1976 when fluoroelastomers-containing monomers with a corresponding cure-active site group were developed. The safe processing peroxides most commonly used are mainly (50%) active 2,5-dimethyl-2,5-di(*t*-butyl peroxy) hexane or less active 2,5-dimethyl-2,5-di(*t*-butyl-peroxy) hexyne-3, typically Varox$^{®}$ DBPH or Luperco$^{®}$ 130 XL, respectively [523] (Fig. 2). The last one is considered to be more suitable for continuous vulcanization in air or in the presence of liquid curing medium. The other organic peroxides such as di-(*t*-butyl peroxide), dicumyl peroxide and 1,4-di(*t*-butyl peroxiisopropyl) benzene are also used. Co-reagents such as TAIC (DIAK$^{®}$ no. 7) or trimethallyl isocyanurate (DIAK$^{®}$ no. 8) enhance crosslink density and hence vulcanizate properties [523]. Peroxide vulcanizates are characterized with improved resistance to aggressive aqueous media, to certain lubricant additives and to nucleophilic reagents [527,528], but they give less scorch safety than the bisphenolic system does. They are required for elastomers, containing CSM such as Viton$^{®}$ GLT and GFLT, and TFE-P elastomers (Aflas$^{®}$). In the last case, a combination of 1,4-di-(*t*-butylperoxyisopropyl)benzene and TAIC are recommended [529]. Peroxide curing is preferred in co-vulcanization of fluoroelastomers with other synthetic rubbers (e.g. E/P, silicone and fluorosilicone rubbers).

Terpolymers, containing in the chain monomer units with nitrile functional end-groups (CF$_2$=CFO(CF$_2$)$_4$CN and F$_2$C=CFOCF$_2$CF(CF$_3$)OC$_2$F$_4$CN) are cured with tetraphenyltin, Sn(C$_6$H$_5$)$_4$ (3–6 phr) which is a catalyst of trimerization of CN groups, forming thermostable triazine rings [15,19] (Fig. 3).

Terpolymers, containing perfluoro-(2-phenyloxypropylvinyl ether), CF$_2$=CFOCF$_2$CF(CF$_3$)OC$_6$H$_5$ can be cured with polyfunctional amines (e.g. hexamethylene diamine) in 1–1.5 phr, introduced with MgO (10–15 phr) [15,19].

8.3. Metal oxides

Auxiliary active chemicals such as acid scavengers (MgO, PbO, CaO or different inorganic bases) act

at the same time as cure activators to give a high degree of crosslinking [469]. When amine cure system is used, 15 phr of a low-activity magnesia (iodine no. 20) is typical. For bisphenol cure systems, 3–6 phr of a high-activity grade (iodine no. 120 +) are preferred. Calcium oxide may be added to aid post-cure of thick components [523]. Where the resistance to aqueous media is needed, the best additive is lead oxide (fumed litharge), but the health hazards are sufficient reason to try to eliminate such products from the inventory. Viton® GBL 205 LF of DuPont (terpolymer of VDF, HFP and TFE containing 68 mol% of fluorine) was shown to have excellent resistance to acid without any need to use lead in the formulation [463].

Metal oxides also improve the efficiency of radiation curing of fluoroelastomers, but decrease to some extent the resistance to heat aging in strength state [530].

8.4. Fillers

Filler types and contents are directly dependent on the desired final properties while combinations of fillers are sometimes the key to the optimization of processing behavior. Generally, the fillers used in fluororubber compounds are rather different from those of conventional elastomers. The reinforced effect of active fillers in fluoroelastomers is very small and hence non-active or low active carbon black or mineral fillers in a typical level up to 50 phr are used [469]. Increasing of the filler content deteriorates the low-temperature properties and heat ageing of fluorovulcanizates [15].

MT-black (N-990) is usually the preferred one because of its large particle size and hence increases the modulus of the crosslinked fluoroelastomers.

The incorporation of fillers results in a higher compound viscosity, lower elongation at break, higher hardness, modulus and tensile strength [23]. The introduction of low active technical carbon as graphite decreases the shrinkage of rubber mixture during vulcanization and improved antifriction and wear resistance of end-products.

Adequate mineral fillers used in fluoroelastomer formulations are barium sulfate, Nyad® 400 (fibrous calcium silicate), Austin black, SRF black (N-774), titanium dioxide, red iron oxide, diatomaceous, silica and Teflon® powders. Incorporation of fiber fillers such as glass fibers (diameter of 0.5–3.8 μm, length of 3–50 mm, coated with organosilanes) and organic fibers such as phenylon, arimides MP, turlon in the amount of 5–50 phr improves the heat aging and low-temperature properties of fluorovulcanizates [530,531].

8.5. Processing aids

Fluoroelastomers differ from other synthetic rubbers by their high viscosity and stiffness which make their processing difficult. Hence, process aids are commonly used to assist flow and to improve release from molds and calenders, to provide a smooth finishing for extrudates. They are mainly composed of two types of ingredient: plasticizers and waxes.

The first one reduces viscosity to improve flow and provides lower hardness parts. The use of plasticizers in the fluoroelastomer formulations is not always expedient, as they deteriorate the mechanical properties, heat and chemical resistances of vulcanizates [532]. Moreover, the plasticizers are partially evaporated during the post-cure process and this results in poor resistance to compression set and creep, formation of cracks and pores, especially in thick items [469].

On the other hand, proven process aids include low-molecular polyethylenes, hard waxes such as

Carnauba (a natural wax from bean) or VPA No. 2 and sulfones such as VPA No. 3. Hard waxes in quantities of up to 1 phr especially assist in demolding, often with 0.5–1.0 phr of an organic sulfone [523].

A three-component system, specifically for peroxide-cured recipes contains 0.25 phr of stearic acid, 0.2–0.5 phr of fatty acid amide and 1–1.5 phr of hard wax [524,525]. In the literature of fluoroelastomer processing, study is shown that useful processing aids can be low-molecular weight fluoropolymers or fluorocarbon fluids, which have a good compatibility with the basic fluoroelastomer [526]. Viton$^{®}$ LM low-molecular weight copolymer of VDF and HFP (about 15 phr [469]), low-molecular weight copolymer of TFE and PMVE with a molecular weight lower than 3×10^4 (1–50 phr [533]) or thermoplastic elastomers (40–95% soft and 60–5% hard segments [534] can be used to improve the technological properties of fluororubbers, their molding, processability, tensile properties, etc.). Fluorine-containing poly(meth)acrylates [526,535] $CH_2=C(CH_3)C(O)OCH_2CF_2CHF_2$ and Dynamar PPA-790 [536] can also be used as a processing aids. Polymerizable oligoester acrylates (OEA) with a good compatibility to fluoroelastomers were suggested as suitable processing aids. In most cases [537,538], the viscosity of fluoroelastomers is reduced, the shrinkage of the vulcanizates is decreased to 2.5% at 20 phr OEA. In the stage of vulcanization, a graft polymerization of OEA takes place and network particles are formed. They are bonded with elastomeric macromolecules, acting as vulcanization knots to improve the thermal and mechanical properties of vulcanizates obtained. The OEA can be used effectively in the radiation curing of the level of 5–10 phr [539]. To overcome the poor low-temperature properties of fluoroelastomers, a blending with other elastomers (polar ones such as acrylic, epichlorohydrine, fluorosilicone and non-polar ones, mainly E/P and silicone rubbers) has been performed [540–542].

Development of peroxide cure systems considerably expands the co-vulcanization of fluoroelastomers with other elastomers, especially fluorosilicones and epichlorohydrines. Such products possess a high heat resistance (up to 200°C) [543], and are resistant to aggressive liquid media (oils, fuels, solvents) together with good low-temperature properties [527,543].

9. Processing of fluoroelastomers

9.1. Introduction

High polarity and molecular weights of the fluoroelastomers are their characteristic features over the other synthetic elastomers and result in a higher viscosity. Besides, the viscosity of rubber mixtures increases after mixing with a carbon black or with other fillers. The rheological properties of the elastomer are of paramount importance because they determine the flow characteristics during mixing, preforming and molding. The pecularities of fluoroelastomers in many cases require a special processing regime, to optimize the crosslinking density (lower elongation at break, low creep and stress relaxation) with a good tear strength at the demolding temperature (i.e. less crosslinking or lower-molecular weight [24,523]).

The manufacture of fluoroelastomeric items uses typical rubber technology equipment (i.e. that required for mixing, shaping and curing).

9.2. Mixing

The basic principles in the preparation of fluoroelastomer compounds are freedom from any source of

contamination, minimum exposure to water and energy input. Contamination of conventional elastomers in the course of mixing can deteriorate the serviceability of products made from the mixture. Contamination with unintended compounding ingredients or oils can influence the processing and vulcanization. Absorption of water from different sources (mainly condensation) accelerates the curing and gives less scorchy safety. Mixing procedures need to maximize energy input before the matrix becomes too soft [523].

9.2.1. Open mills

Open milling is quite popular for the processing of fluoroelastomers since it needs a lower capital investment, an easier cleaning of the machine and visual control by skilled operators. But, on the other hand, the open mills have limited productivity, environmental contamination and poor control [22].

Depending on the filler systems, polymer blends and the size of the mills, actual milling time should require ca. 25–40 min at maximum 80–90°C and a roll friction ratio of ca. 1.1–1.25 to 1.0. The procedure is rather simple. After formation of the rolling bank (temperature 50°C for 0.5–3 min) the metal oxides are added, followed by the filler(s), the plasticizers and finally the vulcanization system.

In some cases, to have a better distribution of the cure agent(s) in the mixture, they are introduced with a small amount of filler(s). Crossblends and cigars are rolled several times (e.g. six times). The mixture prepared is drawn to form a sheet with required thickness and is then cooled. The temperature of the sheet must be below 80–90°C. A formal rework of up to 5 min on cold mills after being allowed to stand 16–24 h is very important to disperse all ingredients completely [523].

9.2.2. Internal mixers

Fluoroelastomers have a high heat build up because of viscous shear and low elongation at break (called "green strength") [544]. When internal mixers are used, intensive cooling and low starting temperature are necessary to avoid prescorched compounds. A one-pass technique compounding of fluoroelastomers can be completed in a 3–5 min cycle. It comprises a charge of fluoroelastomer, introduction of precompounds of metal oxide and carbon black (0.5 min), mixing (1.5 min), addition of the cure system in the last minute and unloading (for 2–2.5 min at 110–125°C) [469]. Because of scorch, the amine curing system may be added on the open mills (at a temperature below 70°C) or in a separate internal mixer pass [469]. For the other vulcanization systems, one-pass mixing is used. A high shear mixing is required to obtain good dispersion, upon which processing and properties depend on a great extent. Reworking to complete dispersion by mills or internal mixers is recommended. When a cooling bath is used, it is necessary to remove the stock as soon as possible and to dry with force-air.

The granular beads of fluoroelastomers (e.g. Viton® A, A-35, A-HV, B, B-50, E-45, E-60, E-430, GH, etc) give the possibility of continuous mixing [545].

Fluoroelastomer compounds should only be sampled for rheometer (moving die rheometer, MDR) and other tests after the reworking step. Fluoroelastomers, their compounds and vulcanizates are tested according to ASTM or DIN procedures commonly used in the rubber industry.

9.3. Molding

Standard transforming technologies are all applicable for fluoroelastomers, such as compression, transfer and injection molding, extrusion and calendering.

Mass production for large consumption such as O-rings, seals and gaskets is steadily and rapidly moving towards injection molding [22]. Extruded tubes, hoses and profiles represent a small percentage (less than 10%) of the total fluoroelastomer consumption.

Molding is the most used process for fluoroelastomer compounds. Different factors, such as volume, tool and equipment amortization ratio of saleable products to scrap, have to be considered to choose the molding process. Molds should be made from a high-quality Cr/Ni tool steel supplied with a good temperature control. Mold design should take into account that fluoroelastomers may shrink at a different ratio, from 2.5 up to 3.0%.

9.3.1. Compression molding

About 60% of fluoroelastomers are transformed by compression molding. This process allows flexible, economic production of relatively small volumes of components. The investments in presses and molds are relatively modest.

The preparation of preforms requires extreme care. They must correspond to the shape and mass of the components [546]. To minimize scrap, a preform is generally cut or extruded. On the inside parts of the mold, silicon fluid or polyethylene glycol emulsions are usually dispersed. In classic procedures, molds are set at 170–200°C and the vulcanization time lasts from 30 s to 2 min.

Thanks to the rheological properties of fluoroelastomers, the compounds with apparent high Mooney viscosities (ML/100°C) can be transfer molded. This technique gives a better dimensional control of the finished part than those prepared by compression molding [523].

9.3.2. Injection molding

Recent development of fluoroelastomers (e.g. polymerization, facilitate cure systems, special fluorinated processing aids) contributes to their injection mold, applied for high-volume precision parts such as O-rings and shaft seals [18–24,496]. Fluororubbers compounds with a low viscosity (Viton[®] A-35 or B-50) can be processed easily than those of high viscosity. To improve the injection molding, a low-molecular weight polyethylene and waxes in the level of 0.5–2 phr is preferable [469]. Generally, injection molding is carried out at relatively low temperatures from 70 to 80°C.

Recently, the raw types of bisphenol-cured precompound have been available and the vulcanization time is only 30 s or less at the mold temperature of 200°C with an outstanding easy release. In the other cases, external mold release agents are necessary (e.g. with amine cure system, dispersions based on polyethylene (up to 180°C) or modified silicones are effective) [523].

The best results obtained from injection molding are achieved by vacuum, applied during the injection step in order to avoid air trapping, splitting and porosity. The mold must be designed to avoid as much as possible losses in flash, sprue and runners [24].

9.4. Calendering

Calendering is mostly used to produce sheets with or without fabric inserts. Compounds for calendering should be of medium or low viscosity and high elongation grades are preferred for such applications [523]. The fluororubber compounds are calendered at relatively cool rolls; e.g. the temperature of the top roll is 50–70°C, that of the central one is 45–65°C while the lowest one is not heated. If there is no danger of scorch, the temperatures of the top and central rolls can be higher. To avoid any presence of air in the fluororubber compounds and any presence of pores in the sheets, it is necessary to have a high

friction between the top and central rolls, the addition of 3–5 phr of low-molecular weight polyethylene, and the use of higher molecular weight fluoroelastomers (e.g. Viton[®] A-HV or Viton[®] B) to improve the "green strength".

9.5. Extrusion

Fluoroelastomers can also be shaped by extrusion [547]. The fully mixed stock is continuously forced through a shaping die below the curing temperature. The typical temperature pattern for fluoroelastomers is a gradual increase from the feeding zone to the die: from cold feed (40–65°C), then heating (75–85°C) to die (for a maximum temperature of about 100°C). A roller feed is required. To minimize the frictional adhesion of hot compounds to the die and to prevent surface fractures the elastomer composition (processing aids and polymer green strength) and the extruder/die characteristics have to be carefully regulated [524,547]. As no practical continuous vulcanization method is used, the cure of extruded tubes, hoses and profiles is achieved by steam or air autoclaving.

9.6. Vulcanization

Generally, the vulcanization of fluoroelastomers is composed of two stages. The first one consists of either shaping under pressure in the presses and heating, or vulcanization in autoclave or continuous curing of sheets and radiation curing. The second step, called post-curing, is provided in a thermostated oven, usually in air, to develop optimum properties of vulcanizates.

Vulcanization in presses is performed from 170 to 200°C with a vulcanization time ranging from 5 to 60 min and a pressure from 10 to 30 MPa, depending on the type of curing system, configuration and size of the parts. Thin parts require up to 4 min at 200°C, but thick ones need 30–60 min at 150–170°C.

Autoclave vulcanization in steam or pressurized hot air is applied for the length parts (tubes, sleeves) for which the post-cure stage is usually not necessary. The vulcanization temperature ranges from 120 to 155°C with the time from 20 min to 4 hr. Vulcanization that occurs in hot air is mainly applied for compounds involving peroxide cure systems.

The vulcanization of TFE-P (Aflas[®]) elastomers can be performed at higher temperatures (165°C for 30 min to 195°C for 3 min). The optimum is reached at 170°C for 15 min while post-curing at 200°C for 3 h [529].

The vulcanization of perfluorocarbon Kalrez[®]-type elastomers depends on the CSM and on the cure system. For example, in the case of fluorinated terpolymers containing a CSM that bears nitrile groups and requiring a vulcanization agent such as tetraphenyltin, the conditions of press vulcanization are 160–210°C, 0.5–18 h and pressure of 7 MPa, followed by a post-curing at 200–290°C for 24–36 h.

The iodine-based cure system used for Perlast[®] is unique and, whilst not affording the levels of extreme high-temperature resistance associated with the triazine-cured Kalrez[®] 4079, the Perlast[®] system has the major advantage to contain neither metal oxide nor other metal-based catalysts. The bisphenol-AF system allows the vulcanizates to withstand temperatures of above 270°C and the more recent triazine-based system affords vulcanizates which can bear prolonged use around 316°C depending on other conditions [222].

In the second post-cure stage, an increasing of degree of crosslinking is observed. It is suggested that crossbonds are formed by the Diels–Alder reactions between adjacent dehydrofluorinated units, separation of side-volatile products such as HCl or HF, H_2O. Post-curing considerably improves mechanical

Table 8
Chemical resistance of different types of fluoroelastomer [221,222,526]: A — excellent; B — good; C — unsuitable for use

Fluid type	Fluoroelastomer			
	FFKM®	FKM®	TFE/P	Fluorosilicone
Solvents				
Acetone	A	C	B	C
Benzene	A	A	B	C
Ethyl acetate	A	C	–	C
Formaldehyde	A	C	–	C
Hexane	A	A	B	A
Methanol	A	B	A	B
Methylene chloride	A	B	–	B
Methyl isobutyl ketone	A	B	C	C
Methyl *tert*-butyl ether	A	B	C	C
Pyridine	A	C	C	C
Water	A	A	A	A
Acid–base				
Acetic acid	A	B	A	C
Sulfuric acid	A	A	A	B
Aniline	A	B	A	C
Sodium hydroxide	A	B	A	B
Oil and others				
Oxidizers	A	B	B	C
Oils and greases	A	A	A	A
Halogenated refrigerents	B	C	C	C

properties of end-products: the longer the post-curing time, the greater the tensile strength and the lower the compression set.

Temperatures are typically 200°C (for amine cures and bonded parts), from 230 to 260°C (bisphenol and peroxide cures) for 16–24 h [523]. Thick parts may also require inclusion of 1–3 phr of CaO to prevent fissuring. Ovens must be positively vented to atmosphere (10 air changes per hour) and not overloaded (the fluoroelastomers cannot exceed 10% of the volume of the oven).

A serious problem for fluoroelastomers deals with their high shrinkage and the anisotropy of the shrinkage from the mold being higher than that of hydrocarbon rubbers. Actually, the anisotropy is increasing during the post-curing. The reason lies in the different thermal coefficients of expansion of mold and rubber mixture. Fillers, notably graphite, decrease the shrinkage, but other fillers do not decrease it as in the case of conventional elastomers. During post-curing as a result of extra crosslinking, loss of process aids, curatives, moisture and other volatile products is observed and the shrinkage grows. In the press forming, the shrinkage is about 2% and, additionally, in the post-cure oven, it is 1%. For the fluoroelastomers, a shrinkage anisotropy is typical. The shrinkage in thickness is higher than that in length. With the increase of temperatures of the press and of the post-curing process, and by the introduction of fillers (e.g. graphite), the shrinkage anisotropy decreases [548]. The shrinkage should be considered when part tolerances are specified.

Table 9
Temperature of service, massic amounts of fluorine and hydrogen in elastomers

Type[a]	Temperature of service, (°C)[b]	F (%)	H (%)
Fluorocarbon elastomers			
VDF/HFP	−18–210	66	1.9
VDF/HFP/TFE	−12–230	66.5–69.5	1.1–1.9
VDF/PMVE/TFE	−27–230	64–66.5	1.1–1.7
TFE/propene	0–200	54–57	4.3
TFE/PMVE	0–280	73	0
TFE/PMVE/E	−15–230	66	1.1
Fluorosilicone	−65–175	37	4.5
Fluorophosphazenes	−65–175	55	1.4

[a] VDF, vinylidene fluoride; HFP, hexafluoropropylene; TFE, tetrafluoroethylene; PMVE, pefluoromethyl vinyl ether.
[b] Range of temperature in continuous service.

9.7. Safety and environmental considerations

Fortunately, fluoroelastomers are non-toxic and non-irritating under normal conditions. They can be compounded and cured with standard precautions, such as temperature control, adequate ventilation and so on. Safety information of polymer and ingredient suppliers should always be studied prior to process fluoroelastomers for the first time or before introducing a new grade.

10. Properties of fluoroelastomers

10.1. Introduction

Fluoroelastomers account for 4% only of the consumption of specialty rubbers but they give excellent performance under severe conditions requiring great resistance to high temperature and chemical environments and have a great place in the progress of modern industries. Generally, their properties are determined versus the fluorine content, the structure of the copolymer chain, the fluoroelastomer compounds and their network.

The most commonly used fluoroelastomers are usually referred to as A and B types. A types are dipolymers of VDF and HFP and have a nominal fluorine content of 66% by weight. B types are terpolymers containing VDF, HFP and TFE in a ratio which gives a nominal fluorine content of 68 wt%. The decreased hydrogen content of the B-type polymers results in improved chemical resistance. B-type polymers also have superior high-temperature stability. Adjusting the ratio of VDF, HFP and TFE to give 70% by weight of fluorine results in polymers which are generally referred to as F types. F-type polymers possess a fluid resistance which is superior to those of both A and B types 401 [549].

There are many other specialty grades of fluoroelastomers available, which use additional or different monomers to impact specific qualities. Fluorel® fluoroelastomers from 3M/Dyneon and Viton®

fluoroelastomers from DuPont have the ASTM designation FKM® while perfluoroelastomers are designated FFKM®.

The following sections exhibit several examples of properties such as the chemical inertness, the thermal stability and the mechanical properties of various (per)fluoroelastomers.

10.2. Fluid and chemical resistance

Chemical attack results in the swelling of the elastomer (regarded usually as a reversible event). Swelling up to ca. 10% can beneficially increase the sealing force produced by an elastomeric gasket, but too much swell can cause the seal to become damaged leading to a premature failure. Chemical attack can degrade the material and this should be avoided at all costs.

As a class, fluoroelastomers are notably resistant to swelling in aliphatic, aromatic and chlorinated hydrocarbons, fuels, oils and many other organic liquids. They display good to excellent resistance to chemical attack, flame propagation, oxidation, ozone and weathering. Resistance generally increases with increasing the fluorine content and FKM® elastomers are unaffected by almost all solvents and reagents such as alcohols, ketones, esters, amines and other polar solvents which considerably swell, or in the case of amines react with other types of elastomers (Table 8).

Peroxide-curable types of Viton® were originally invented to offer higher performance properties than could be obtained by standard grades of fluoroelastomers. The range of properties that these types can achieve is very exciting. In addition, peroxide-curable types have always offered higher tensile strengths and shorter cure cycles [463]. Compared with others of their group, peroxide-cured type elastomers have considerably greater resistances to swelling in organic media and to degradation in hot aqueous media.

One particularly outstanding fluoropolymer used in elastomeric applications is that prepared from TFE and PAVE, and particularly PMVE (Table 9). To facilitate the crosslinking of these copolymers (FFKM®) essential to achieve better elastomeric properties, a small percentage of termonomer is generally incorporated, such as a cyano- or nitrile-containing fluoroolefins [273,303]. These cyano-perfluoroelastomers exhibit outstanding thermal and oxidative stabilities. Fluoroelastomers having iodine cure sites do not have a high concentration of ionic end-groups, such as carboxylic or sulfonic acid moieties, which are introduced from the initiating system. Conventional chain transfer agents can be used to lower the concentration of the ionic end-groups and also to lower the polymer viscosity [303].

The main properties of uncured TFE/PMVE elastomers and fluid resistance of vulcanizates at 25°C have been discussed by Barney et al. [267]. Indeed, the copolymer is totally soluble in a variety of highly fluorinated liquids, including perfluorokerosene, perfluorodiisopropyl ketone, perfluorotributyl-amine, etc. It is essentially completely resistant (less than 2% swelling) to most other liquids, including strong aqueous bases, concentrated nitric or sulfuric acids, hydrazine, alcohols, ketones, esters, acids, amines, amides, ethers, aliphatic or aromatic hydrocarbons and partially chlorinated derivatives. The polymer wets Teflon® and Teflon® FEP readily.

The cured polymer is slightly attacked at temperatures around 250°C by di- and polyamines acting as reducing agents.

However, there are some distinct differences in the swelling under extreme conditions for FKM items obtained with different cure systems. The bisphenol-cured pieces swell most in glacial acetic acid and water and least in ethylene diamine. The peroxide-cured stocks swell least in high-temperature water under pressure. Thus, one can choose the system that gives the optimum properties for a practical application. All FKM® swell to some degree in chlorofluorocarbons or fluorocarbon solvents [24].
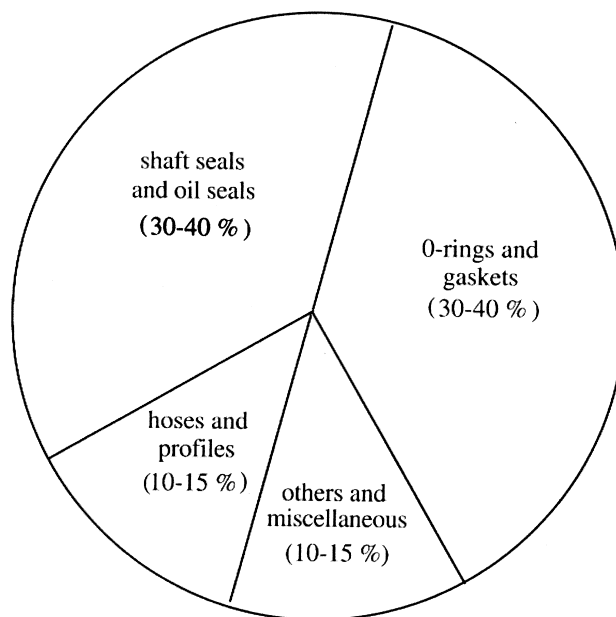
Fig. 4. Diagram of fluoroelastomer item-distribution.

Up to 210°C, fluoroelastomers remain serviceable indefinitely offering excellent resistance in most solvents and chemicals (Table 8). New fluoroelastomers offer easily processable and low compression set high-fluorine terpolymers, contradicting the previous statement that the higher the fluorine content, the better the chemical resistance at the expense of processability and compression set. Heat and oil resistances are obviously to be considered together with other properties such as tensile or compression set [23].

Perlast[®] is affected by strong oxidizing and reducing agents. Boiling tertiary amines and molten alkali metals (Li, K, Na, etc.) should be avoided as it is for all fluorinated polymers.

Extremely strong oxidizing agents such as fluorine gas and related compounds can produce volatile mixtures after reacting with fluoropolymers. Chemicals which would cause a large volume change should be avoided (they include HCFC, CFC, fluorinated oils, CTFE oils). Such a change is not necessarily fatal to the product: the effect is one of swell rather than degradation. Strong oxidizing agents such as fuming nitric acid will attack carbon black: a non-black filler should be used in such environments [222].

Both Perlast[®] and other FFKM[®] perfluoroelastomers performed quite satisfactorily over this extended test and the values of three physical measurements taken remain within narrow bands. In contrast, the FKM[®] swells rapidly before the 336 h interval [222].

The major advantages of TFE/P elastomers (Aflas[®]) compared to FKM[®] fluoroelastomers are a better chemical resistance to automotive oils and lubricants combined with a more consistent response to different types and brands of these fluids [529]. It maintains the good high-temperature resistance for which FKM fluoroelastomers are noted. Engine oils, transmission fluids and gear lubricants are complex formulations of base stocks and additive packages. A new type of engine oil designated by the SG term was introduced in 1988 and nowadays there are various oil formulations that meet these specifications.

Table 10
Mechanical properties of different types of fluoroelastomer [15,221]

Property	Fluoroelastomers			
	FFKM[®]	FKM[®]	TFE/P	Fluorosilicone
100% Modulus (MPa)	6.2–13.1	2.1–15.2	2.5–3.5	1.0–6.1
Tensile strength (MPa)	14.5–16.8	9.0–18.6	18.0–20.0	6.2–8.6
Elongation (%)	120–240	100–500	250–350	100–500
Compression set (%) 70 h, 200°C	35–50	≥ 10	45–50	60
Hardness (Shore A)	70–95	90–95	65–75	50–75
Brittle temp. (°C)	-40 to -30	-59 to -18	-40	-66

Accordingly, elastomeric parts have to be exposed to many different oil and lubricant chemical envir-
onments. Interestingly, TFE/P elastomers are resistant to a wide variety of engine oils and lubricants.

In contrast to the FKM[®] elastomers, TFE/P ones are not dehydrofluorinated in engine oils and they
maintain stable properties after exposure to a wide variety of engine oils.

Mechanical properties after exposure to engine oils are much better (Table 10). Various oils have little
impact on TFE/P with elongation changes varying from -10.5 to -5.0%. In contrast, FKM[®] elongation
changes vary from -41.3 to -75.2% [529]. There is no evidence of surface attack on the TFE/P test
specimens but FKM[®] shows evidence of surface crazing or cracking. The same trend was observed
during chemical resistance. The changes in tensile strength and volume swell are that the volume swell
of Aflas[®] reach an equilibrium very quickly and is stable over the duration of the test.

TFE/P exhibits very good transmission fluid resistance and also consistent resistance to the various
automatic transmission fluids [529]. Peroxide-curable fluoroelastomer FKM[®] 5927 exhibits the superior
fluid-resistance as Viton[®] GF and low-temperature performance with improved processability [550].
FKM[®] 5958 shows excellent low-temperature flexibility and compression set resistance maintaining the
outstanding fluid-resistance of the solvent-resistance-type fluoroelastomers.

Broad and extensive research has been realized since the time of development of standard fluoroe-
lastomers and their crosslinking to solve processing problems and to obtain easy processing products for
high performances requiring a higher chemical stability against aggressive oils, together with optimum
mechanical properties and aging at high temperatures. For the "critical" injection molding technology, a
new type of Technoflon[®] P 189 N has been commercialized [259].

A new family of improved base-resistant VDF fluorocarbon elastomers has been developed by
Ausimont as a commercial product called Technoflon[®] BRX 915 N. Heat aging at 275°C is in compar-
ison with a standard peroxide-curable VDF fluorocarbon elastomer (e.g. Technoflon[®] P 819 N). The new
grade has a higher resistance to high-temperature aging in a basic engine coolant [89].

A fluoroelastomer endowed with high resistance to polar solvents and to bases, excellent compression
set at high temperatures, low glass transition temperature and good processability was synthesized from
suitable ratio of TFE, PAVE and VDF, the last one being 10–20 mol% in the terpolymer. PAVEs are
preferably chosen among the first three homologs (C_1–C_3). Such fluoroelastomers are particularly
suitable for the manufacture of sealing elements for plants intended to methyl *tert*-butyl ether production
[261].

Table 11
Fluoroelastomers: trademarks and properties

Trademark	Comonomers in copolymer	% F	T_g (°C)	Advantages/drawbacks
Viton®				Good chemical resistance at high T
Fluorel®	VDF/HFP	64	−18	Resistance to oxidation, solvents, flames
Tecnoflon®				May swell
Dai-el®	VDF/HFP/TFE	70	−7, −13, −21	High thermostability, better resistance to swelling
FKM®	VDF/HFP/TFE with CSM	67	−16	Better mechanical properties
	VDF/HFP/TFE/E(5%)	Variable		E protects from alkaly attack
	VDF/PAVE	Variable	−40	Resistance to oxidative attack
Tecnoflon®	VDF/HCF=CFCF₃	Variable		Heat resistance, as above and to solvents
	VDF/TFE/HCF=CFCF₃	62–70		
Kel F®	VDF/CTFE	Variable	−15	Vulcanization: better heat and chemical resistance
Atlas®	TFE/P	54–57		Chemical, heat and pressure resistance

10.3. Thermal resistance

Fluoroelastomers have outstanding resistance to heat compared with other elastomers. VDF-based fluoroelastomers and fluorosilicones are capable of long-term service in dry heat at 200°C, while FKM® elastomers are stable for many months at 260°C (and Kalrez® for continuous use at 316°C). The fluorophosphazenes have a lower long-term service temperature (<175°C). Of course, all are capable of useful short-term service at higher temperatures (Table 9) [15,22,23].

The use at low temperatures obviously depends on the application. Service in static applications is often satisfactory at temperatures appreciably lower than those used in dynamic applications. The fluorosilicones and fluorophosphazenes (PNF®) have lower T_gs and higher flexibility than those of FKM® rubber (their T_gs are in the range of −10 to −30°C) while VDF/TFE/PMVE have a wide temperature operating interval [15,23,24].

Actually, Van Cleeff [23] has interestingly reviewed the situation of the T_gs of Viton® elastomers versus the hydrogen content. From those containing TFE, VDF and PMVE base units, the author showed that the higher the H mol%, the lower the T_g (the lowest T_g was observed for Viton® GLT containing 1.7 H mol%, $T_g = −29$°C). From the terpolymers involving TFE, VDF and HFP, a similar tendency as above was noted. For example, the T_g of Viton® A is −17°C (H mol% = 1.9) while that of Viton® B-70 is −20°C (H mol% = 1.8). Obviously, for the same H content, the T_gs of the first series are always lower than those of the second one.

Cured perfluoroelastomers show exceptional thermal stability and are differentiated by the robustness of their crosslinks. The perfluoroelastomers with pendent nitrile groups as cure sites retain their properties in the best way after they are exposed to high temperatures. The triazine crosslinks are stable enough

to show little or no change from the original post-cure properties after 18 days at 288°C in air. Even after short exposure to 316°C useful properties are maintained [221].

Perfluoroelastomers cured with bisphenols are less stable to heat and after 20 days at 280°C in air the 100% modulus is reduced by about 25% and the tensile strength by about 15%, while the elongation is increased by about 120%. The peroxide-curable polymers are less thermally stable, starting to loose properties significantly after few days at about 220°C in air. The radiation-cured parts still have lower thermal resistance, limiting their use to around 200°C.

The differences in thermal resistance are attributed to curing chemistry and to the stability of the crosslink structures, since all of the polymers are perfluoroelastomers and have almost the same backbone structure (Table 11). Thus, the triazine structure is the most thermally stable. The bisphenol crosslinks are also thermally stable, but a little inferior to those of the triazines [15,221].

The crosslink structure generated during a peroxide-cure is related to the structure of the coagent being used. Since the coagents have a hydrocarbon skeleton, their thermal stability in air is limited. The irradiation-cured parts appear to have a carbon–carbon crosslink structure and are expected to have good thermal resistance. However, during irradiation, some chain scissions occur, and result in the formation of carboxylic acids, which lowers the thermal stability of the crosslinked parts [23,24].

The advantageous low-temperature properties of Perlast® have important implications for sealing performance because the wide majority of applications for perfluoroelastomers exist below 200°C [222] (Fig. 4).

10.4. Mechanical properties

The tensile properties of the fluoroelastomers are generally satisfactory; TFE/PMVE and TFE/P having the highest ones while fluorosilicones and fluorophosphazenes show the lowest tensile strength at room temperature. The polymers with inorganic backbones do retain a higher proportion of their tensile properties at higher temperatures. Resistance to compression set is an important property of fluoroelastomers because the largest end-use concerns seals (particularly O-rings) [15–24]. The introduction of bisphenol-curing system considerably improves the compression set resistance. VDF- and TFE-based elastomers give materials with compression sets as low as 10–15% after 70 h at 200°C in air. TFE/P elastomers have poor resistance to compression set and FFKM® copolymers show slow recovery from compression at temperatures below about 150°C [15].

The physical properties of the chemically cured parts compare well with each other and typical values are shown in Table 10. Some formulations are better than others, and pronounced differences are obvious when the testing conditions change. Items cured by high-energy irradiation have similar properties as the heat-cured articles, except for hardness and tensile properties. The absence of reinforcing fillers in these objects is the cause of lower stress at 100% elongation (3 MPa), tensile strength (10 MPa) and hardness Shore A (65) and higher values in elongation at break (250%) [24,476].

A new type of fluoroelastomer, Technoflon® P 819N [89,261], exhibits a mixed hydroxylic/peroxide network. The reducing of the amount of onium salt (decreasing the amount of unsaturations) is compensated by peroxide curing of brominated chain ends by synthesizing the copolymer in the presence of a brominated chain transfer agent. The processing problem of peroxide-cured fluoroelastomers has been overcome by introduction of fluorinated substances. The other possibility is bromine or iodine-polymer development using "di-iodo techniques" of Tatemoto [100–103]. Polymers having iodine-terminated chain ends cure very efficiently with peroxides giving good processing properties in terms of fast cure

rate and easy moldability. However, when resistance to heat is considered, the network obtained with diiodo-terminated chain ends appears to be considerably less stable. Technoflon® P 819 N is an excellent elastomer for injection molding together with higher resistance to aggressive oils [261].

Perfluoroelastomers (such as those containing TFE/PMVE base units) having iodine cure sites exhibit outstanding thermal and oxidative stability [463].

Viton® GF 3000 is the improved processing and lower viscosity version of Viton® GF [463]. It is similar to the latter (containing VDF/HFP/TFE units) but, except for bromine CSM, it incorporates additional enhanced proprietary brought by the CS moiety. Viton® GF 300 exhibits lower compounded viscosity and faster cure rate. At the same time, the low-temperature properties are similar to those of Viton® GF. Elongation increasing at 200 and 250°C are worse than that of Viton® GF but they have the same fluid resistance (automotive fluids, water, steam and acids). Viton® GF 205 NP is the no post-cure Viton® type with very good physical properties. Viton® GF 205 NP has a faster cure rate than either Viton® A 401 C or Viton® GBL 200 with similar scorch safety as that of Viton® GBL 200. Compression set values of no post-cure compared to standard bisphenol-cure type (Viton® A 401 C) are better. Original physical properties, such as tensile strength and elongation without post-cure are good but heat aging results are not as good as those of standard Viton®. The fluid resistance data show that the Viton® GF 205 NP acts as much as a 70% fluorined material [463]. Viton® GBL 205 LF is a VDF/HFP/TFE terpolymer and contains a proprietary acid acceptor system so that metal oxides are neither required nor recommended in the formulations.

Viton® GBL 205 LF has excellent resistance to acids without the need to use lead. Regarding all other physico-chemical and rheological properties, it behaves similarly as a peroxide-curable Viton® B-type. Interestingly, this product is significant for the development of rubber processors and it provides an environmentally friendly method to obtain excellent resistance to steam and acids [463].

11. Applications of fluoroelastomers

Fluoroelastomers were originally developed for use as fuel tank hatch and joint sealants, fuel vapour seals and O-rings for hydraulic systems in aircraft and aerospace applications. Fluoroelastomers are now widely used in the industry as O-rings, V-rings, gaskets and other types of static and dynamic seal, as diaphragms, valve seals, hoses, coated cloth, shaft seals [496], expansion joints, etc. They are also used in cars as O-rings for fuel and shaft seals and other components of fuel and transmission systems [15,19–24,409].

Commercial applications of fluoroelastomers reflect their rather special combination of properties: excellent resistance to heat, fluids, oxidizing media combined with good physical properties.

Today, VDF/HFP and VDF/HFP/TFE polymers are produced and marketed internationally by different companies such as Du Pont Dow Elastomers (Viton®), Ausimont (Technoflon®), Dyneon (Fluorel®) and Daikin (Daiel®) (Table 2). Lower capability is attributed to products from other countries: Russia (SKF® 26, SKF® 32, SKF® 260), China and Japan (Nippon Mektron and Asahi) [22] (Table 11).

The main types of fluoroelastomer part used are shown in Fig. 4.

The main consumer (60%) of the fluoroelastomer parts is the automotive industry [463,467,538,547,551]. In most sealing applications, an elastomeric seal is the most susceptible component to the seal assembly. Several factors are considered when the elastomers have to be chosen for seal: operating temperature, thermal cycling, pressure range, seal environmental, fluid type, etc. Oxygenates

used in gasoline (e.g. methyl *tert*-butyl ether, MTBE) required higher-performance elastomeric materials to prevent equipment leakage, equipment failure and costly downtime [261].

In MTBE environments, FFKM® behaves considerably better than conventional fluoroelastomers do, leading to a longer seal life and improved protection against seal failure.

The chemical and petrochemical industries also represent a promising market (10%) for fluoroelastomer items. These industries expose elastomers to a wide variety of chemical reagents and operating conditions [15,17,19–24].

In many applications, chemical plants must retrofit existing values or replace them with new valves that conform to the more stringent standards. The chemical resistance provided by a FFKM® combined with the lighter sealing load results in longer service life and reduced fugitive emissions (over 33% of all air-toxic volatiles) in different valves of chemical industry using now PTFE sealings.

Energy-consuming industries for control systems require fluoroelastomers for joints and lining resistant to corrosive materials.

Fluoroelastomers and especially FFKM® play an important role in sealing applications in both commercial and military aircraft industries (10%).

Aerospace propellant systems often utilize very aggressive fuels and oxidizers which are incompatible with all currently available elastomers, including fluoroelastomers. FFKM® are often used in these systems due to their oxidative stability and compatibility with both oxidizers and hydrazine-type fuels.

Fire-resistant lubricants containing phosphate esters and lubrication oils-containing amines are both interesting applications where the use of FFKM® greatly extends seal life.

FFKM® are the most suitable materials available for use in semiconductor processing equipment [552,553]. In these applications, the elastomer comes in direct contact with dry process chemicals and reactive plasmas. The elastomer is typically exposed to aggressive wet chemical environments such as sulfuric acid/hydrogen peroxide or ammonium hydroxide/hydrogen peroxide/ultra pure deionized water mixtures. In such applications, limiting the contaminants to only parts per billion is crucial. The use of FFKM® that combines chemical resistance and minimum release of contaminants becomes the most cost effective sealing material for the semiconductor chip fabrication process [222,554].

Although discovered more than 20 years ago, perfluoroelastomers represent a production of only a few thousand kilograms a year. However, they are growing at a fast pace in terms of applications and introduction of new composition to meet industrial needs. Perfluoroelastomers represent less than 1% of the total fluoroelastomer field, dominated by VDF-base copolymers.

Most of the current research efforts are directed to improve the properties of fluoroelastomers and their processability. It is expected that new fluoropolymeric materials and new curing chemistry will be developed in the future due to continued escalation at severe service conditions and improvements in broad temperature damping characteristics and low-temperature resilience [21]. Blends of fluoroelastomers with other polymers and recyclability features will also contribute to their continuing success in many engineering and aggressive service environments.

12. Conclusions

Among fluoropolymers, elastomers, which represent a more recent generation, have shown relevant properties. In spite of the fact that they are highly priced, they are useful since they exhibit poor swelling in oils, hydrocarbons, solvents, but are resistant to heat, aging, concentrated acids and alkalies and have

useful mechanical and compression set properties. Hence, they open up prospects of new applications in numerous fields: oil, automotive, chemical, aerospace and aeronautic industries.

Thus, most companies involved in fluorine chemistry devote funds and research to challenging products to which fluoroelastomers belong to. A wide range of fluoroelastomers are commercially available or synthesized in a small scale; basically, they can fall into three main categories: (i) fluor-ocarbons containing mainly carbon, fluorine and to a less extent hydrogen and oxygen atoms (most of them are produced from the radical copolymerization of VDF or TFE or from the terpolymerization involving both of them). However, maintaining their outstanding properties at low temperature remains a great challenge that (ii) fluorosilicones have overcome. (iii) concerns the fluorinated polyphosphazenes endowed with excellent fire resistance.

The synthesis of fluorocarbon elastomers by direct radical co- or terpolymerization of fluoroolefins has been further proved to be a versatile way that offers many opportunities for obtaining a wide range of fluoropolymers.

The production and demand of fluorinated elastomers are having an increasing market for novel applications: seals and O-rings inert to oils and hostile environments.

However, to enhance their properties, curing reactions are required. Usually, they occur in the presence of various reactants, or a mixture of reagents (e.g. bisphenols, polyamines, peroxides/TAIC) at rather high temperatures.

Hence, a new generation of more easily crosslinkable fluoroelastomers has been achieved from novel reactive monomers which exhibit halogen atoms (bromine or iodine, mainly) or functional groups (e.g. hydroxy, carboxy, mercaptan). Although such monomers are the most expensive counterpart in the preparation of the fluoroelastomers, generally just 1–5% of them is required in the copolymer to allow it to be crosslinked. Thus, their reactivity in co- or terpolymerization has to be taken into account to utilize them fully while it is sometimes neglected or not regarded as a crucial parameter.

Thus, further work in synthesizing more reactive co-monomers with adequate function and kinetic factors should be expected to enable one to go to the next generation of fluoroelastomers.

The availability of this new class of fluoropolymers should open many interesting opportunities for exploiting the unique properties of these elastomers in many uses.

This offers additional chances to a technology that already forms the basis of the commercial production of classes of chemicals which are among the most advanced and successful products in fluorine chemistry. Such new targets are real challenges and should attract the interest of many academic and industrial researchers in this fascinating area.

Acknowledgements

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