Update on fluoroelastomers: from perfluoroelastomers to fluorosilicones and fluorophosphazenes

Bruno Ameduri, Bernard Boutevin

Update in Fluoroelastomers : from Perfluoroelastomers to Fluorosilicones and Fluorophosphazenes

Bruno Ameduri, Bernard Boutevin

Laboratoire de Chimie Macromoléculaire, UMR 5076
Ecole Nationale Supérieure de Chimie de Montpellier
8, Rue Ecole Normale
34296 Montpellier Cedex 5 – France
ameduri@enscm.fr

1-Introduction

Fluoropolymers [1-4] are particularly attractive because of their versatility (they range as a wide scope from thermoplastics to plastomers, elastomers, and thermoplastic elastomers) and of their unique combination of relevant properties : high thermostability (the higher the content of fluorine, the more thermostable the polymer), hydrophobicity, lypophobicity, oleophobicity, resistance to ageing and to oxidation, hydrolytic stability, chemical inertness, low permeability to gaz, low flamability, surface energy, moisture absorption and dielectric constants. Hence they have found many applications in building, automotive and petrochemical industries, microelectronics, aeronautics, aerospace, optics and for the treatment of textile, paper and stone. However, some of them are crystalline and are not cured or crosslinked easily. But, elastomers exhibit a non-organized structure linked to the monomers that decreased the crystallinity and can be more easily cured.

The objective of this review is to supply an update browse of the fluoroelastomers, ranging from (per)fluorocarbon elastomers to fluorophosphazenes, and fluorosilicones.

2-Fluorinated Elastomers

It is first required to recall various elastomers ranging from commercially available hydrogenated elastomers (polyisobutylene, polydienes, polyurethanes, to name a few) to (per)fluorinated ones (including F-phosphazenes, F-silicones, hybrid F-silicones, and thermoplastic elastomers, TPE, Table 1). As expected, the lower the price of the polymer, the higher its production. These « niche » fluorinated products exhibit exceptional properties and are regarded as high value added polymers used in high-tech applications.

INSERT Table 1

Two main kinds of F-elastomers are distinguished : those that required to be crosslinked and those are do not

2-1 Fluorocarbon elastomers.
Usually, fluorocarbon elastomers are synthesised from the radical copolymerisation of fluoroalkenes : vinylidene fluoride (VDF), hexafluoropropylene (HFP), tetrafluoroethylene (TFE), perfluoromethyl vinyl ether (PMVE), chlorotrifluoroethylene (CTFE), pentafluoropropylene (PFP) and propylene (P) [5,6]. Additional functional comonomers containing a crosslinking group (or cure site monomers) can be optionanlly introduced. In Table 1 the crossings between lines and columns represent elastomeric copolymers containing the corresponding comonomers, as comprehensively reviewed [5,6].

2-2 F-Phosphazenes.

Fluorinated polyphosphazenes are synthesized from the condensation of fluorinated alcohols with dichlorophosphazenes, as follows [6] :
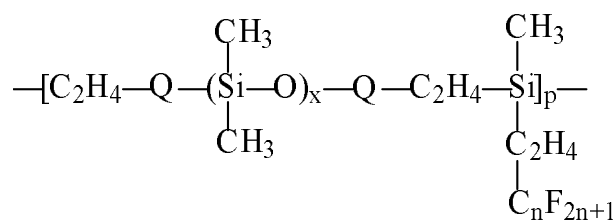
$$-[N=P]_n- + HO-R-R_F \longrightarrow -[N=P-]_n-$$

with Cl substituents on the left phosphazene and $O-R-R_F$ substituents on the product.
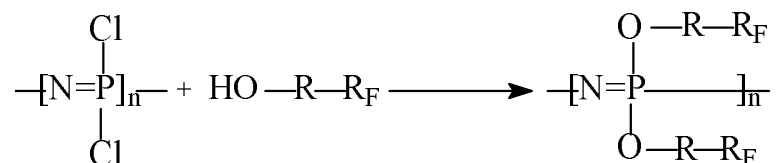
These PNF$^{®}$ phosphazenes, commercialized by Firestone [7], exhibit low Tgs (–70°C). Gleria *et al.* [8] recently reviewed the synthesis, properties and applications of fluorinated alkoxy and aryloxy substituted phosphazenes and also those of fluorinated phosphazene block copolymers [9] obtained either by sequential polycondensation or by hydrosilylation reaction [10].

2-3 F-Silicones.

Poly(methyltrifluoropropyl siloxane)s commercialised by the Dow Corning Corporation under Silastic$^{®}$ trademark (that represent ca. 96 % of fluorosilicones) have a Tg of –65°C but exhibit a medium thermal stability (T_{dec} is ca. 280°C leading to a depolymerisation). Their chemical structure is as follows :

$$-(Si-O)_p-$$

with CH_3 and $C_2H_4-CF_3$ substituents on Si.
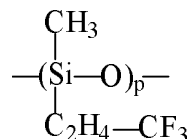
Various alternatives of hybrid fluorosilicones have been proposed by different teams. Those suggested by Kobayashi [11] allowed an improvement of the oleophobic, hydrophobic and surface properties :

$$-[C_2H_4-Q-(Si-O)_x-Q-C_2H_4-Si]_p-$$

with CH_3, CH_3 substituents on the first Si; and CH_3, C_2H_4, C_nF_{2n+1} substituents on the second Si.

with n = 4, 6 and Q variable spacer

Deeper investigations were achieved by Dow Corning and Shin-Etsu Companies [12] which suggested original structures, and interestingly, the poly(hexafluoropropylene oxide) segment, PHFPO, enables the resulting F-silicone to exhibit very low Tgs, while only one dimethyl siloxane unit per 100 HFPO units was found in the structure of Sifel polymers :

Dow Corning $\quad -[\overset{|}{\underset{|}{Si}}-C_2H_4-\overset{|}{\underset{\underset{R_F}{\wr}}{Si}}-C_2H_4]_x-(\overset{|}{\underset{|}{Si}}-O)_y$

$$R_F = -C_nF_{2n+1}$$

Shin Etsu $\quad -(\overset{|}{\underset{|}{Si}}\text{\textasciitilde}R_F\text{\textasciitilde}\overset{|}{\underset{|}{Si}}-O)_x-(\overset{|}{\underset{|}{Si}}-O)_y$
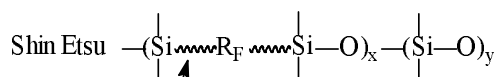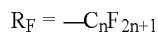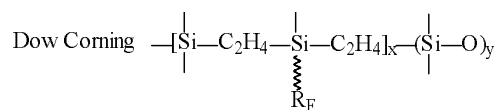
spacer

fluorinated chain

$$R_F = -[O-C_nF_{2n}]- \, , \quad n = 3 \text{ mainly}$$

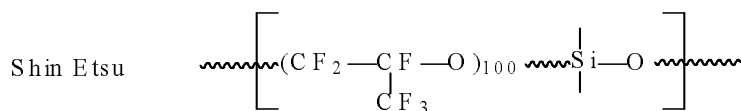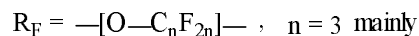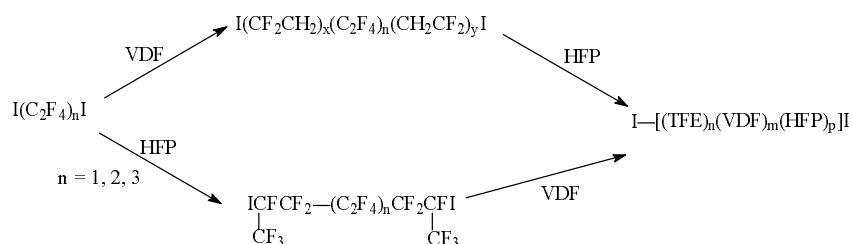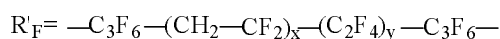Shin Etsu $\quad \text{\textasciitilde}\left[\text{\textasciitilde}(CF_2-\underset{\underset{CF_3}{|}}{CF}-O)_{100}\text{\textasciitilde}\overset{|}{\underset{|}{Si}}-O\text{\textasciitilde}\right]\text{\textasciitilde}$

To compete with these complex structures, we have proposed novel hybrid fluorosilicones bearing a fluorinated backbone obtained in three steps. The first one concerns the sequential thermal cotelomerisation [4] of VDF and HFP with fluorinated telechelic diiodides [13], as follows :

$$I(CF_2CH_2)_x(C_2F_4)_n(CH_2CF_2)_yI$$

VDF

HFP

$$I(C_2F_4)_nI$$

$$I-[(TFE)_n(VDF)_m(HFP)_p]I$$

HFP

$$n = 1, 2, 3$$

VDF

$$I\underset{\underset{CF_3}{|}}{CF}CF_2-(C_2F_4)_nCF_2\underset{\underset{CF_3}{|}}{CF}I$$

Then, these original fluorinated cotelomers were functionalized into fluorinated divinyl or diallyl nonconjugated dienes[14], and after hydrosilylation and (co)polycondensation, novel hybrid fluorosilicones were produced [15]:

$$-(\overset{\overset{CH_3}{|}}{\underset{\underset{\underset{\underset{R_F}{|}}{C_2H_4}}{|}}{Si}}-C_2H_4-R'_F-C_2H_4-\overset{\overset{CH_3}{|}}{\underset{\underset{\underset{\underset{R_F}{|}}{C_2H_4}}{|}}{Si}}-O)_x-(\overset{\overset{CH_3}{|}}{\underset{\underset{\underset{\underset{R_F}{|}}{C_2H_4}}{|}}{Si}}-O)_y-$$

$$R_F=C_nF_{2n+1} \, , \quad CF\overset{\diagup CF_3}{\diagdown CF_3}$$

$$R'_F= -C_3F_6-(CH_2-CF_2)_x-(C_2F_4)_y-C_3F_6-$$
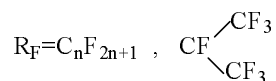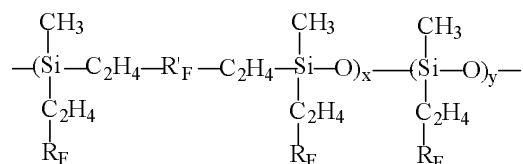
According to the nature of Rf', the spacer between the fluorinated chain and the silicon atom, a wide varieties of various hybrid fluorosilicones were prepared (Table 3). These oily fluorosilicones display Tgs of *ca.* −50 °C and a high thermal stability (Tdec > 390 °C, under air).
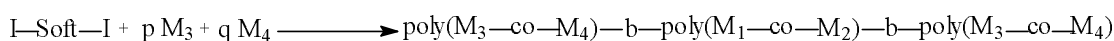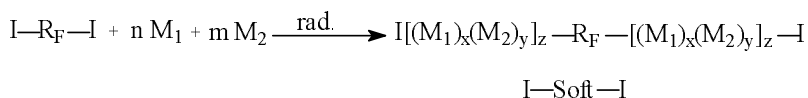
INSERT Table 3

2-4-Well-Architectured Fluorinated Thermoplastic Elastomers

This review also seeks to show how macromolecular architectures are required to fulfill demanding thermal, mechanical, and rheological characteristics. The searched macromolecules are block copolymers, graft copolymers or multiblock copolymers and variuos examples are presented hereafter. Non-exhaustive examples of thermoplastic elastomers are supplied below, produced from modern techniques of polymerization [4].

2-4-1 Triblock Copolymers by Iodine Transfer Polymerization

Triblock copolymers were prepared by sequential Iodine Transfer [16,17] of fluoroalkenes from I-Rf-I. Quasi-exhaustive exmples have recently been reviewed [bookBA BB]. The most relevant results were achieved from $I(C_2F_4)_nI$ (n = 4 or 6 mainly, which are thermally stable, and also because IC_2F_4I undergoes β-scission to generate iodine and tetrafluoroethylene (TFE) under radical conditions). These telomers are commercially available from the Daikin and Asahi Glass Companies but are also produced in a pilot plant at the Solvay Solexis Company.

These fluorinated triblock copolymers are synthesised in a two step-procedure : a novel α,ω-diiodofluoropolymer (usually an elastomeric I-Soft-I block) is produced from the first step and can further be successfully utilised as an original initiator in a second reaction as follows :

$$I\text{—}R_F\text{—}I \ + \ n\,M_1 + m\,M_2 \xrightarrow{\text{rad.}} I[(M_1)_x(M_2)_y]_z\text{—}R_F\text{—}[(M_1)_x(M_2)_y]_z\text{—}I$$

$$I\text{—}Soft\text{—}I$$

$$I\text{—}Soft\text{—}I \ + \ p\,M_3 + q\,M_4 \longrightarrow poly(M_3\text{—}co\text{—}M_4)\text{—}b\text{—}poly(M_1\text{—}co\text{—}M_2)\text{—}b\text{—}poly(M_3\text{—}co\text{—}M_4)$$

The process can be emulsion, suspension, microemulsion, or solution. Various companies have already shown much interest in this research.

Daikin's pioneering works from 1979 [16] were confirmed out at the DuPont Company [17] and at Ausimont (now Solvay-Solexis) [19].

INSERT TABLE 4

A *quasi*-exhaustive summary of these investigations is given in Table 4 where M_1, M_2, M_3 and M_4 (fluoro)alkenes can be equally well chosen among TFE, vinylidene fluoride (VDF), hexafluoropropylene (HFP), perfluoromethyl vinyl ether (PMVE), chlorotrifluoroethylene (CTFE), ethylene (E) and propylene (P). Typical combinations of comonomers by pair, trio or quartet enabled the authors to obtain both soft and hard segments. In the case of the preparation of blocks by the above copolymerisation of two olefins above, the authors were able to synthesise soft or hard segments by varying the amounts of comonomer [16-22]. It is recalled that a poly(VDF-co-HFP) copolymer containing less than 15 mol. % HFP is a thermoplastic (or hard block) while that having an HFP content higher than 15 mol. % exhibits elastomeric properties [5,6].

Usually, the central elastomeric segments have molar masses of 30,000 or more while those of the plastomeric (or hard) blocks are higher than 10,000, although Yagi *et al.* [21] already claimed molar masses of TPE up to 1,000,000. As a consequence, original thermoplastic elastomers, TPE, composed of soft and hard segments (as for the well-known PS-b-PBut-b-PS or SBS triblock), were produced in a living fashion by sequential ITP. They are endowed with a negative glass transition temperature, Tg, and high melting temperatures, Tm, sometimes higher than 250°C (Table 4).Both amorphous and crystalline zones can be seen in Dai-el[®] (from Daikin, now Dai-Act) or Tecnoflon[®] FTPE XPL supplied by Ausimont (now Solvay-Solexis).

The obtained A-B-A fluorocopolymers are phase segregated with an amorphous zone and crystalline domains (Figure 2), and they combine various advantages inducing a wide range of temperatures of service.

The hard segment can be composed of PVDF or PTFE, or a combination of VDF (in high quantity) with HFP or CTFE, or copolymers of TFE with E, PMVE, VDF or with HFP, or terpolymers TFE/E with P, isobutylene, HFP, pentafluoropropene, PMVE, 3,3,3-trifluoropropene or hexafluoroisobutylene.

Additional advantages of using ethylene as the comonomer are i) its low cost, ii) the livingness of the polymerisation [23] and iii) the fact that this monomer reduces the base sensitivity of VDF-containing copolymers [18,24] which is a further key-advantage.

Although not all the reactions have been carried out in the same experimental conditions, it is observed that polydispersities of the final TPE as low as 1.73 could be achieved from diiodides. Interestingly, when a fluorinated nonconjugated diene [19,24,25] was involved in terpolymerisation of fluoroalkenes, the PDI is even lower (1.4). This improved control of ITP, called « pseudo living and branching technology » [24,25], was extensively studied at Ausimont (now Solvay-Solexis S.A.) and enabled prodution of competitive thermoplastic elastomers. This is the case for example of Tecnoflon$^®$ FTPE XPL.

INSERT FIGURE 2

Table 4 also lists the Tgs and Tms of these fluorinated thermoplastic elastomers. Even when PMVE was added in the soft block, the Tg could not be significantly lowered. Further, the introduction of a small amount of nonconjugated diene slightly lowered the Tg and increased the Tm by a few degrees[19].

Most of these TPEs could be used from –30°C to 250°C [20] and can be used in continuous service at 200°C (in contrast to conventional elastomers that decompose at this temperature).

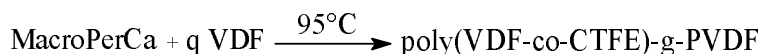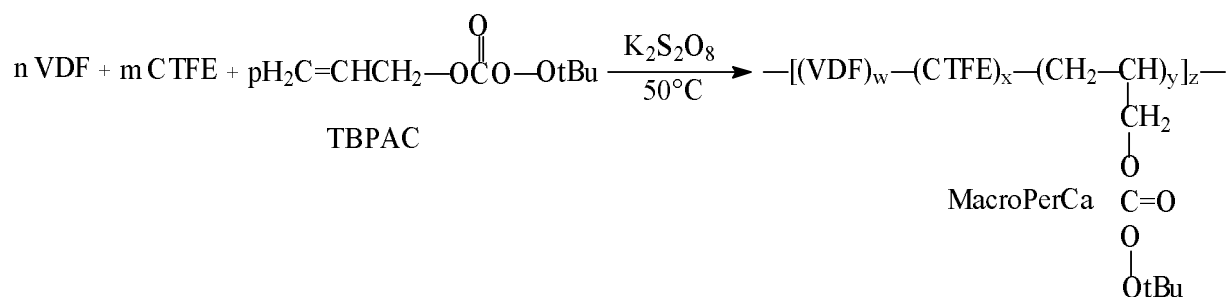Tatemoto [21] compared the thermal decomposition of three TPEs and supplied the following order :

poly(E-alt-TFE)-b-poly(VDF-co-HFP)-b-poly(E-alt-TFE) ; T_{dec} = 345°C < poly(E-alt-CTFE)-b-poly(VDF-co-HFP)-b-poly(E-alt-CTFE) ; T_{dec} = 379°C < PVDF-b-poly(VDF-co-HFP)-b-PVDF ; T_{dec} = 410°C.

Further, these TPEs have already led to numerous applications in high tech areas such as aerospace, aeronautics and engineering or in optics, arising from their outstanding properties are listed in Table 4.

These TPEs are useful as O-rings, hot melts, pressure-sensitive adhesives, tough transparent films, sealants having good chemical and ageing resistance, shaft seals for combustion engine in aggressive media and for oil wells applications, protective coatings for metals, or even for denture plates (since Dai-el$^®$ T530 is claimed to show neither erythrocyte hemolysis nor cytotoxicity, and does not generate any harmful substances).

2-4-2 Fluorinated Graft Copolymers

An original synthesis of fluorinated graft copolymers was suggested by the Central Glass Company, Ltd [26]. It consists of a two step-procedure in which the first one generates fluorinated macroinitiators. The Japanese authors claimed that this was realised by carrying out a suspension terpolymerisation of two fluoroalkenes and an allylic monomer (bearing a peroxycarbonate group at low temperature) to enable the reaction of the hydrogenated double bond of *tert*-butyl peroxyallyl carbonate (TBPAC) without decomposing the peroxycarbonate function, as follows :

$$n\ VDF + m\ CTFE + p\ H_2C{=}CHCH_2{-}O{-}\overset{\displaystyle O}{\overset{\|}{C}}O{-}OtBu \xrightarrow[50°C]{K_2S_2O_8} {-}[(VDF)_w{-}(CTFE)_x{-}(CH_2{-}CH)_y]_z{-}$$

TBPAC

MacroPerCa, with the pendant group $CH_2{-}O{-}C({=}O){-}O{-}OtBu$

$$MacroPerCa + q\ VDF \xrightarrow{95°C} poly(VDF{\text -}co{\text -}CTFE){\text -}g{\text -}PVDF$$

In the various examples, VDF, CTFE and HFP were chosen as the fluoroalkenes to give massic yield of the macroperoxycarbonate (MacroPerCa) was 60-80%.

Tgs of poly(VDF-co-CTFE-co-TBPAC) and poly(VDF-co-HFP-co-TBPAC) were –21 and –19°C, respectively. The presence of the peroxycarbonate groups was evidenced i) by DSC (an exothermic peak was noted at 160-180°C linked to the peroxycarbonate decomposition) and ii) by the content of the active oxygen of the terpolymer (0.042 and 0.063%, respectively).

However, neither the molecular weights nor the contents of the three monomers in the terpolymer was given. In addition, the obtaining of high molecular weight-polymers may be questionable since in the course of the terpolymerisation, allylic transfer (arising from the TBPAC) [27] should occur and hence should lead to oligomers.

The preparation of the fluorografted copolymer, composed of a fluoroelastomeric backbone and fluorinated thermoplastic grafts, was achieved from the polymerisation of VDF in solution initiated by the macroperoxycarbonate at 95°C. These thermoplastic elastomers obtained in high massic yields (81-91%) exhibit a melting point of 155-160°C.

Unfortunately, no information on the presence (or the absence) of PVDF produced from the direct addition of the *tert*-butoxy (or methyl) radical onto VDF was given as reported in previous study [27].

Conversely, these Japanese authors [28] synthesised poly(CTFE-co-TBAPC)-g-poly(VDF-co-HFP) grafted copolymers in high yield showing a low Tg (-19°C). In that case, the polymeric backbone consists of a thermoplastic PCTFE copolymer while the grafts are elastomeric.

Interestingly, all those fluorografted copolymers were kneaded and press-shaped at 200°C leading to semitransparent, elastic and flexible sheets that were compared to those prepared from commercially available fluoroelastomers. These original thermoplastic elastomers exhibit much better mechanical properties (break strength and elongation at break).

2-4-3 Multiblock Copolymers

Tonelli *et al.* synthesed original fluorinated polyurethane containing perfluoropolyethers (especially Fomblin) blocks [29]

Finally, by polyhydrosilylation of telechelic non-conjugated diene polyimides containing hexafluoroisopropylidene groups with fluorinated polyhybrid siloxane bearing Si-H end groups, a new generation of fluorinated (polyimide-b-polysiloxane) multiblock copolymers was achieved (Figure 3)[30]. The thermal (Table 5) and dynamicomechanical properties were investigated and show exceptional properties when compared to commercially available thermoplastic elastomers as Hytrel (poly(ether) –poly(ether) and SBS block copolymers (Figure 4). Such hydrib F-copolymers exhibit slightly higher Tg that these commercial copolymers but the rubbery plateau is rather wide (from –50 to 230 °C).

3-Conclusions and Perspectives

Although fluoroelastomers are costly and « niche » products, their outstanding properties make them usable in high tech fields. A wide variety of different fluoroelastomers such as fluorocarbon elastomers, F-phosphazenes or F-

silicones or hybrid silicones are nowadyas used in various applications. Their comparison in term of thermal properties leads to the following breakthrough : fluorocarbon elastomers exhibit high thermal stability (up to 360-390 °C) but their Tgs cannot be lower than –30 °C. In contrast, fluorophosphazenes and F-silicones are not quite thermostable (they degradate from ca. 230 and 280 °C, respectively) but their Tgs are satisfactory. To lower the Tgs, introduction of soft segments is necessary to avoid any crystallisation of these macromolecules. Hence, the introduction of fluorinated side groups is required to break the crystallinity. For example, Sifel F-silicone is a very interesting polymer regarding its thermal stability but its synthesis is quite difficult. However, a nice alternative lies on the preparation of hybrid silicones (Tg= -50 °C) and decomposition temperature of ca. 350-380 °C).

The conception of macromolecular architectures enables these products to reach better performance. Introducing soft segments *via* fluorinated *telechelic* intermediates has led to elastomeric *blocks* or from fluorinated *grafts*, original thermoplastics were obtained. The tremendous amount of work carried out in the preparation of phosphazenes or siloxane-fluorinated chain *block* copolymers was driven by the need to synthesise high-performance elastomers. Indeed, the term « high performance » implies the ability to withstand very low temperatures (Tg ≤ –60°C), to preserve elastomeric properties in the space and to resist at high temperatures [32]. For example, from Mach 2.05 (as for Concorde) to Mach 2.4, the requirement for these materials are to preserve a good thermal stability from 110 °C to 177 °C for 60,000 hrs. Meeting such a challenge is not trivial. In addition, the copolymers must possess good mechanical properties but also show excellent swelling-resistance whatever the nature of the solvent (polar or non polar). All these numerous and impressive investigations are not yet conclusive and several decades might still be needed to reach a satisfactory goal.

4-Acknowledgements :

5- References

[1] Scheirs, J. Modern Fluoropolymers, Wiley & Sons, New-York ,**1997**.

[2] Hougham, G; Cassidy, R; Johns, K; Davidson, T. Fluoropolymers, Kluvert, New-York, **1999**.

[3] Ebnesajjad, S. Melt Processible Fluoropolymers, **2000**, Vol. 2, Plastic Design Library, Warwich (USA).

[4] Ameduri, B. Boutevin, B. Well-Architectured Fluoropolymers : Synthesis, Properties and Applications (F-Telomers, Telechelics, and Alternated, Block and Graft Copolymers),   Elsevier, Amsterdam, **2004**.

[5] Logothetis A. L., *Prog. Polym. Sci.*, **1989**, *14*, 251.

[6] Ameduri, B; Boutevin, B; Kostov, G. *Prog. Polym. Sci.*, **2001**, *26*, 105.

[7] a) Kyker, G.C. ; Antkowiak, T.A. *Rubber Chem. Techno.* **1974**, *47*, 32 ; b) Tate, DP. *Rubber World*, **1975**, *172*, 41.

[8] Gleria, M; Bertani, R; De Jaeger, R; Lora, S. *J. Fluorine Chem.*, **2004**, *125*, 329.

[9] a) Matyjaszewski, K; Moore, M.K; White, M.L.*Macromolecules*, **1994**, *26*, 6741 ; b) Allcock, H.R; Crane, C.A; Morissey, C.T; Nelson, J.M; Reeves, S.D; Honeyman,

      C.H; Manners, I. *Macromolecules*, **1996**, *29*, 7740.

[10] Allcock, H.R; Prange, R. *Macromolecules*, **2001**, *34*, 6858.

[11]Kobayashi H. *Eur. Pat.*, 0,665,270 **1995** (Dow Corning Torray).

[12]Uritani, P. *Eur. Pat.*, 0,967,251 **1999** (Shin Etsu).

[13]Manseri, A; Ameduri, B; Boutevin, B; Caporiccio, G. *J. Fluorine Chem.*, **1995**, *74, 59 ; J. Fluorine Chem.,* **1996***, 78,*145 ; *J. Fluorine Chem.,* **1999***, 94*, 175.

[14]Manseri, A; Boulahia, D; Ameduri, B; Boutevin, B; Caporiccio, G. *J. Fluorine Chem.,* **1995**, *73*, 151 ; *J. Fluorine Chem.,* **1997**, *81*, 103.

[15] a) Guida-Pietrasanta, F; Boutevin, B; Caporiccio,G; Ratsimihety. *Macromol. Chem. Phys.*, **1998**, *199*, 61 ; b) Ameduri, B; Boutevin, B; Caporiccio, G; Guida-Pietrasanta, F; Ratsimihety A. « Use of Original Fluorinated Telomers in the Synthesis of Hybrid Fluorosilicones », in Hougham, G; Cassidy, R; Johns, K; Davidson, T. Fluoropolymers, Kluvert, New-York, **1999**, Chapt. 5, pp. 67-80. ; d) Guida-Pietrasanta, F; Boutevin, B; Ratsimihety A., « Side group modified polysiloxanes » in Chojnowski J. Silicon Containing Polymers : The Science and Technology of the Syntheisi and Applications, 2001, ? ? Ville ? ?

[16] a) M. Tatemoto, in: J.C. Salamone, Ed., *Polymeric Materials Encyclopedia*, CRC

Boca Raton, FL, **1996**, *Vol. 5*, 3847-3862; b) M. Tatemoto, T. Nakagawa, German Pat 2,729,671 (assigned to Daikin Kogyo Co., Ltd) 12011978 (Chem. Abstr. 88 (1978) 137374m); c) M. Oka, M. Tatemoto, *Contemp. Top. Polym. Sci.,* **1984**, *4,* 763-769.

[17] K.A. Davis, K. Matyjaszewski, *Adv. Polym. Sci.,* **2002**, *159.*

[18] Carlson, D.P. *USP,* 5,284,920 **1994** (DuPont).

[19] a) V. Arcella, G. Brinati, M. Albano, V. Tortelli, Eur. Pat. Appl. 0,661,312 A1 (assigned to Ausimont S.p.A.) 05-07-1995; b) V. Arcella, G. Brinati, M. Albano, V. Tortelli, Eur.Pat.Appl. 0,683,186 A1 (assigned to Ausimont S.p.A.) 09-05-1995; c) U. Gayer, T. Schuh, V. Arcella, M. Albano, Eur.Pat.Appl. EP1,231,239 A1 (assigned to Ausimont S.p.A.), 14-08-2002..

[20]   M. Tatemoto, *Int. Polym. Sci. Technol.,* **1985**, *12,* 85-91 translated into English from *Nippon Gomu Kyokaishi,* **1984**, *57,* 761-767.

[21] Yagi T.; Tsuda N. ; Noguchi T. ; Sakaguchi K. ; Tanaka Y. ;Tatemoto, M. *Eur. Pat.,* 0,422,644 **1990** (Daikin).

[22]   M. Tatemoto, Eur. Pat. 399,543 (assigned to Daikin Ind. Ltd) 28-11-**1990**.

[23]   Y. Yutani, M. Tatemoto, Process for preparing polymer, *Eur. Patent Appl. 0489370 A1* (assigned to Daikin), **1991**.

[24]   M. Apostolo ; S. Arrigoni, V. Arcella, Trends Polym. Sc., 7 (**2002**) 23.

[25]   a) V. Arcella, G. Brinati, M. Apostolo, *Chim.   Oggi,* **1997,** *79,* 345-351; b) G. Brinati, V. Arcella, *Rubber World,* **2001**, *224,* 27-32.

[26] S. Kawashima, T. Yosamura, Jpn. Kokai Tokkyo Koho JP 59 30, 847 (assigned to Central Glass Co., Ltd), 18-02-**1984** (*Chem. Abst.* 101 : 73689v).

[27]   J. Guiot, B. Ameduri, B. Boutevin, *Macromolecules,* **2002**, *35,* 8694-8707.

[28] Kawashina, C. *USP,* 4,472,557 **1984** (Central Glass).

[29] C. Tonelli, T. Trombetta, M. Scicchitano, G. Simeone, G. Ajroldi, J. Appl. Polym. Sc., 59 (1996) 311

[30] Andre, S; Guida-Pietrasanta, F; Rousseau, A; Boutevin, B; Caporiccio, G. *J. Polym. Sci., Part A, Polym. Chem.,* **2004**, *42,* 200.

[31] Andre, S; Guida-Pietrasanta, F; Rousseau, A; Boutevin, B; Caporiccio, G. *J. Polym. Sci., Part A, Polym. Chem.,* **2002**, *40,* 4485.(Tg versus n of units)

[32] Hergenrother, P.M. *Trends Polym. Sci.,* **1996**, *4,* 104.

TABLE CAPTIONS

Table 1 : Non-exhaustive list of elastomers ; produced amounts *versus* price (arbitary scale)

Table 2: Main commercially available fluoroelastomers

Table 3 : Thermal data for Hybrid F/Silicone homopolymers

Table 4 : Iodine transfer polymerisation of fluoroalkenes for the synthesis of fluorinated
Hard-b-Soft-b-Hard triblock copolymers (n.g. stands for not given).

Table 5 : Characteristics and thermal properties of multiblock Polyimide-b-poly(F-siloxane)
copolymers