

Fluoropolymers functionalized by phosphorous and silicon groups: syntheses, characterization and applications

Mohammad Wehbi

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THÈSE POUR OBTENIR LE GRADE DE DOCTEUR DE L'UNIVERSITÉ DE MONTPELLIER

En Institut Charles Gerhardt – UMR 5253

École doctorale Sciences Chimiques Balard

Unité de recherche Chimie Moléculaire et Organisation du Solide (CMOS) et Ingénierie et Architectures Macromoléculaires (IAM)

En partenariat international avec Université Libanaise, Liban

Fluoropolymères fonctionnalisés par des groupes phosphore et silicium. Synthèses, caractérisation et applications.

Présentée par Mohammad WEHBI Le 30 November 2018

Sous la direction de Ahmad Mehdi/Ali Hachem et Bruno Ameduri/Ali Alaaeddine

Devant le jury composé de

- M. Didier Gigmes, DR, Aix-Marseille Université
 M. Kamal H. Bouhadir, Pr, Université Americaine de Beyrouth
 M. Rodolphe Sonnier, MA, Ecole des Mines d'Alès
 M. Salem Kharrat, MCF, Université Saint Joseph de Beyrouth
 M. Ahmad Mehdi, Pr, Université de Montpellier
 M. Ali Hachem, Pr, Université libanaise
 M. Bruno Ameduri, DR, ENSCM
- M. Ali Alaaeddine, Pr, Université libanaise

Rapporteur Rapporteur Examinateur Examinateur Directeur de thèse Directeur de thèse Co-encadrant de thèse Co-encadrant de thèse



Look up at the stars and not down at your feet. Try to make sense of what you see and wonder about what makes the universe exist. Be curious.

Stephen hawking

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Abbreviations

AA: Acetic acid

AIBN: 2,2'-Azobis(isobutyronitrile)

APTES: Aminopropyltriethoxysilane

ATRP: Atom transfer radical polymerization

BHT: 2,6-di-*tert*-butyl-4-methylphenol

BrTMSPr: 3-Bromo-1-(trimethylsilyl)-1-propyne

BTP: 2-Bromo-3,3,3-trifluoro-1-propene

CEVE: 2-Chloroethyl vinyl ether

C-Ph: Tetraethyl (2,5-dihydroxy-1,4-phenylene) diphosphate

C-Ph-BC: (2,5-bis(diethoxyphosphoryl)-1,4-phenylene bis(propylcarbamate))

CQ: Camphorquinone

CTFE: Chlorotrifluoroethylene

DDA.HCl: Dodecylamine hydrochloride

DEBAAP: N,N-diethyl-1,3-bis(acrylamido)propane

DHP: Dimethyl (hydroxymethyl)phosphonate

DMC: Dimethyl carbonate

DMF: Dimethylformamide

DMSO: Dimethyl sulfoxide

DTBPH: 2,5-dimethyl-2,5-di(tert-butylperoxy) hexane

ECTFE: Ethylene chlorotrifluoroethylene

EDAB: Ethyl 4-(dimethylamino)benzoate

ETFE: Ethylene tetrafluoroethylene

EVE: Ethyl vinyl ether

FEP: Fluorinated ethylene propylene

FEP: Fluorinated ethylene propylene

FEVE: Fluoroethylenevinylether

HAP: Hydroxyapatite

HEA: 2-Hydroxyethyl acrylate

HEMA: 2-Hydroxyethyl methacrylate

HFC: 1,1,1-Trichloroethane

HFP: Hexafluoropropylene

IPP: Diisopropyl peroxydicarbonate

LDA: Lithium diisopropylamide

LOI: Limiting oxygen index

MADIX: Macromolecular design for interchange of xanthates

MAF: 2-(Trifluoromethyl)acrylic acid

MAF-COCI: Dimethyl 2-(trifluoromethyl)acryloyl Chloride

MAF-cyCB: (2-Oxo-1,3-dioxolan-4-yl)methyl 2-(trifluoro methyl) acrylate

MAF-DMP: Dimethyl (dimethoxyphosphoryl)methyl 2-(trifluoromethyl) acrylate

MAF-TBE: tert-butyl 2-trifluoromethacrylate

NMP: Nitroxide mediated polymerization

OCRP: Organostilbine-mediated radical polymerization

PCTFE: Polychlorotrifluorethylene

PEMFC: Polymer exchange membranes for fuel cells

PFA: Perfluoroalkoxy alkylvinylethers

PFS: Polypentafluorostyrene

PMMA: Poly(methyl methacrylate)

PPVE: Perfluoro(propyl vinyl)

PPVE: Perfluoropropylvinylether

PSU: Polysulfone

PTFE: Polytetrafluoroethylene

PVBC: Polyvinylbenzyl chhoride

PVDF: Polyvinylidenefluoride

PVF: Polyvinylfluoride

RAFT: Reversible addition fragmentation transfer

(R)ITP: (Reversible) Iodine transfer polymerization

RFGD: Radio frequency glow discharge plasma treatment

RH: Relative humidity

SBS: Shear bond strength

TAPE: Tert-amyl peroxy-2-ethylhexanoate

TBPPi: Tert-butyl peroxypivalate

TFE: Tetrafluoroethylene

TFMAN: α-Trifluoromethacrylonitrile

TFS: Trifluorostyrene

THV: Terpolymer of tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride.

TSP: Tris(trimethylsilyl) phosphite

VBC: Vinylbenzyl chhoride

VDF: Vinylidene difluoride

VDMP: Vinyldimethylphosphonate

VTEOS: Vinyltriethoxysilane

Introduction

Fluorinated compounds have an important impact on our daily lives and found applications in fluorinated water, fluoride toothpaste, drugs (such as Sevofluorane®, Ciprofloxacin®, and Prozac®), as well as fluoride additives (separators, binders and electrolytes) in lithium ion batteries.¹⁻⁴ Fluoropolymers are one of the most important materials from the family of fluorinated compounds. They are attractive macromolecules due to their specific properties (attributed from the low polarizability and strong electronegativity of the fluorine atom, due to its small van der Waals radius (1.32 Å), and to the strong C-F bond (485 kJ \cdot mol⁻¹). Thus, these polymers exhibit high thermal, chemical, aging, and weather resistance, excellent inertness to solvents, to hydrocarbons, to acids, and to alkalies, low surface energy (oil and water repellency), low dielectric constants, low flammability, low refractive index, and moisture absorption. These properties led for the use of fluoropolymers in building industries, petrochemical and automotive industries, aerospace and aeronautics, chemical engineering, optics, textile treatment, stone, and microelectronics and cables and wires industries.⁵⁻⁸ As technology is often only limited by the materials available, fluoropolymers have made a major contribution to the world we live in today, often performing roles no other material is capable of. However, high crystallinity, poor solubility, difficulty in crosslinking and the lack of functionality, impart these polymers major weakness that tend to limit some of their applications.⁸ To overcome these limitations, the copolymerization of commercially available fluoromonomers with other comonomer bearing a functional group has gained a lot of interest.⁷⁻¹¹ These comonomers introduce a (bulky) functional group that induces disorder in the macromolecule, thus reducing the high crystallinity of the homopolymer.⁷⁻¹¹ In addition, these comonomers brings a functional group such as acetoxy,¹² thioacetoxy,¹³ hydroxyl, esters, ethers,¹⁴ halogens,¹⁵ cyclic carbonates,¹⁶ or carboxylic acid^{18,19} to name a few. These functions

can also improve some of the properties of the resulting copolymers such as thermal stability,¹⁷ proton conductivity^{18,19} or hydrophobicity¹⁷ compared to pristine homopolymers.

Based on this concept, the demand for the development of new functional fluoropolymers to explore new potential applications is relatively high. Due to the relevant properties of the phosphorous atom, phosphonate functional polymers have found applications in dispersants, corrosion inhibiting agents,²⁰ as flame retardants,²¹ as adhesion promoters for paints,²² polymer electrolyte membranes for fuel cells,²³⁻²⁵ and biomedical fields.²⁶ Although several examples of phosphorous functional fluoropolymers have been reported, most of these studies showed these copolymers employed in fuel cell membranes. Thus, it would be interesting to see what other properties these copolymers possess that could open the door for new applications.

In addition, the crosslinking of such copolymers would ensure more durability, thermal and chemical stability. The crosslinking of fluoropolymers is usually a complicated process requiring multistep reactions or modifications to the polymer's backbones. Triethoxysilane groups can offer a more elegant and simple method for polymers crosslinking through the solgel process.²⁷ Few studies are found regarding triethoxysilyl-functionalized fluoropolymers, mainly for enhanced adhesion,²⁸ water and oil repellence,²⁹⁻³¹ solvent resistance³² and for amines functionalizations.³³⁻³⁶ Thus the objective of this thesis work is the synthesis of phosphorous or silane functional fluoropolymers. The co/terpolymers are prepared through radical polymerization of functional monomers with vinylidene fluoride (VDF). The obtained co/terpolymers showed promise in anticorrosion coatings, enhanced adhesion to substrate and lanthanide extractions.

To provide a common footing for the chapters that follow, chapter 1 is a general state of the art which introduces the origin and the significance of fluorinated polymers, an over view on phosphorous functional fluoropolymers, and finally, the Sol-Gel transformation and triethoxysilane functional fluoropolymers.

Chapter 2 is a fundamental study on the kinetics of copolymerization of VDF and and *tert*butyl 2-trifluoromethacrylate (MAF-TBE) to better understand how these monomers behave.

Chapter 3 introduces a new phosphonate functional monomer (MAF-DMP) followed by its copolymerization with VDF to obtain poly(VDF-*co*-MAF-DMP) copolymer. This copolymer's anticorrosion property was studied by its coating over steel plates.

Chapter 4 demonstrate the synthesis of cyclic carbonate functional PVDF. The cyclic carbonate ring was then modified into a triethoxysilane group to obtain Poly(VDF-*co*-MAF-Si(OEt)₃). This polymer showed a very strong adhesion over various substrates.

Chapter 5 deals with the terpolymerization of VDF with both phosphorous and silane functional monomers (poly(VDF-ter-VDMP-ter-VTEOS) terpolymers). This terpolymer was then crosslinked under acidic conditions and it shows promising results with europium extraction from water.

Finally, the Conclusion recaps all the results obtained during this thesis and the perspectives consists on the future works regarding other potential applications for these co/terpolymers.

Chapter I: STATE OF THE ART

1.1. Fluoropolymers

1.1.1 History of fluoropolymers

While mineral fluorides traces back to the 16th century, fluorochemicals were not properly developed until the early-to-mid twentieth century.³⁷ Moisson's isolation of elemental fluorine in 1886, and few years later, Swarts use of SbF₃ in a Cl/F exchange reaction to prepare fluorinated aromatics and the first chlorofluorocarbon gas (CF₂Cl₂), drew attention to the importance of fluorinated compounds.³⁷ In 1928, General Motors Corporation in the US wanted to find a replacement for their dangerous and toxic refrigerants (ammonia and sulfur dioxide), and their research team led by Midgley Jr selected CF₂CCl₂ as a first candidate.³⁸ The gaseous fluorocarbon proved to be an ideal refrigerant, and in 1931 General Motors in partnership with E. I du Pont de Nemours & Co., formed a new corporation, Kinetic chemicals Inc., to produce commercial quantities of the newly trademarked product Freon-12[®].³⁸ Throughout the 1930s other developed several Freons were including dichlorotetrafluoroethane (CClF₂CClF₂) commercially known as Freon-114[®] a precursor of tetrafluoroethylene (TFE). During this period researchers from IG-Farbenindustrie in Hoechst/Frankfurt Germany, while studying the polymerization of fluoroethylenes, discovered that chlorotrifluoroethylene (CTFE) could be polymerized to form polychlorotrifluorethylene (PCTFE), an inert, chemical and heat resistant polymer plastic and thus the first patent for a fluoropolymer was filed in 1934 by Schloffer and Scherer.³⁹ In 1938, Plunkett, a DuPont chemist working on new types of Freons, accidentally discovered PTFE while attempting to chlorinate gaseous TFE.⁴⁰ He obtained a white waxy polymeric substance that was chemically inert, extremely heat resistant, non-adherant, and virtually insoluble in any solvent.⁴⁰ However, PTFE struggled to find a market in the US due to its excessive cost.

Year	Event	Ref
1886	Isolation of elemental fluorine and preparation of fluorinated aromatics and the first chlorofluorocarbon gas (CF ₂ Cl ₂)	37
1925	Usage of CF ₂ CCl ₂ as a refrigerant gas	38
1930s	Development of Freon-114 (CClF ₂ CClF ₂) a precursor of tetrafluoroethylene (TFE).	38
1934	Discovery of PCTFE	39
1938	Discovery of PTFE	40
1946	Scale up of PTFE production after its usage in the Manhattan project	41
1953	Introduction of Polychlorotrifluoroethylene (PCTFE)	14
1960	Introductio of Fluorinted ethylene propylene (FEP)	42
1961	Introduction of PVF and PVDF	7,42
1965	Introduction of the first commercial graded PVDF Kynar 500	43
Late 1960's	Discovery of Nafion [®]	44
1970's	Introduction of perfluoroalkoxy alkylethers (PFA) copolymers	7,42
1980's	Developed fluoroethylenevinylether (FEVE) resins	45
1993	Release of VDF/TFE/HFP terpolymer	7,42

Table 1.1. Timeline of important events throughout the history of fluorinated polymers.

During World War II, over 25000 people worked on the Manhattan Project that focused on the development of the first Atomic bomb. A key component of the process was the use of UF₆ to separate U²³⁵ fromU²³⁸.^{41,46} The problem was that UF₆, prepared from uranium oxide (UO₂), HF, and fluorine gas, was difficult to handle and purify and extremely corrosive to metal. As such new corrosion resistant materials were needed if the 'Project' was to succeed. PTFE proved to be an excellent candidate due its unique chemical resistance properties under extreme conditions which led to a government contract being issued for scale-up production.⁴¹ Following the war, DuPont made PTFE available commercially under the tradename Teflon. In 1953 the Kellog Co. introduced polychlorotrifluoroethylene (PCTFE) under the trade name

Kel-F 81. PCTFE, a homopolymer of chlorotrifluoroethylene (CTFE), contained chlorine in the fluoropolymer backbone which introduced film forming properties, making it a more processable alternative to PTFE.¹⁴ PCTFE was harder and less permeable than PTFE, possessed outstanding moisture barrier properties, and could be produced in bulk solution and suspension forms.¹⁴

In 1960 FEP (fluorinated ethylene propylene) a copolymer made from TFE and hexafluoropropylene (HFP) was introduced as the first copolymer of TFE. FEP contains ,5% of HFP which introduce a trifluoromethyl side group along the polymer chain and thus is melt processable in contrast to PTFE.⁴² The following year the Dupont company released polyvinylfluoride (PVF) which contained only one fluorine in the ethylene monomer unit, and polyvinylidenefluoride (PVDF) which contained two.^{7,42} PVF and PVDF have lower amounts of fluorine compared with other fluoropolymers but maintain many of the chemical and thermal resistance properties of PTFE. They also possess enhanced mechanical strength more akin to hydrocarbon-based polymers. The first commercially available PVDF, Kynar 500[®], was introduced in 1965 by Pennsalt Co.⁴³ In the late 1960s Grot at DuPont discovered Nafion[®], a copolymer of TFE with perfluorovinyl ether containing sulfonate groups.⁴⁴ Nafion[®] was the first synthetic ionic polymer (ionomer) and was found to be highly conductive to protons. This made it suitable for membrane applications and it soon found use in industrial electrolysis and fuel cells.⁴⁷ Modified fluoroionomers such as Flemion[®] and Aquivion[®] were later developed by asahi glass and solvay specialty polymers companies to overcome some of the solvent and operating temperature limitations of Nafion.^{44,48}

In the 1970s, Dupont introduced perfluoroalkoxy alkylvinylethers (PFA) copolymers made from TFE and perfluoropropylvinylether (PPVE). This melt processable copolymer was transparent in thin sections and possessed a broad range of properties encompassing both FEP and PTFE.^{7,42} This polymer was used in the chemical and semiconductor industries as pipes, fittings, linings, and as specialized films. Around the same time, Dupont also introduced ethylene chlorotrifluoroethylene (ECTFE) and ethylene tetrafluoroethylene (ETFE), copolymers of ethylene (E) and CTFE and TFE, respectively. These polymers were the first fluoropolymers to contain non-fluorinated subunits and possessed a mix of hydrocarbon and fluorocarbon polymer properties. Also, in certain cases these polymers were alternated.

In the early 1980s, Asahi Glass developed a new generation of fluoroethylenevinylether (FEVE) resins⁴⁵ as alternating copolymers composed of acceptor fluorinated ethylene monomers (CTFE) and a mix of donor vinyl ethers monomers that can be varied depending on applications. FEVE resins were the first fluoropolymers to be soluble in organic solvents and can be cured at room temperature. Asahi Glass marketed such resins under lumiflon[®] tradename. To compete with such poly(CTFE-*alt*-VE) copolymers, almost Similar FEVE resins were later introduced by Daikin under the tradename Zeffle[®]. During this period new fluoropolymers were developed to meet the technology demands of growing industries.

In 1993, Hoechst partnered with Dynean company (a subsidiary of the 3M Group) to release THV, a semicrystalline three component terpolymer of tetrafluoroethylene (TFE), hexafluoropropylene (HFP) and vinylidene fluoride (VDF). THV is highly flexible, soluble in polar organic solvents, and has excellent adhesive properties making it very useful for thin film coatings and multilayer constructions.^{7,42}

Since the 1990s, trademarked ranges of fluoropolymers have been developed to meet the needs of emerging technologies in construction, electronics, and energy sectors. The number of companies specializing in the production of one or two fluoropolymers, particularly PTFE, are increasing.

1.1.2 Poly(vinylidene fluoride) (PVDF)

Poly(vinylidene fluoride) (PVDF) is the second most produced fluoropolymer after polytetrafluoroethylene (PTFE).^{6,7,11,49,50} VDF is regarded as an attractive monomer, is one of the most commonly used fluoroalkenes.^{8,51,52} The reactivity of VDF is close to that of tetrafluoroethylene and chlorotrifuoroethylene, however it is much less dangerous: not explosive and has a lower toxicity (the lethal concentration required to kill 50% of the population of mice, LC50 > 200,000 ppm) than the other two. Thus, VDF-based (co)polymers are extensively used in piezoelectric devices,^{53,54} binders and separators for Li-ion batteries,^{11,55} membranes for water treatment,^{8,56,57} in petrochemical industry and photovoltaic devices.¹¹ Figure 1.1 illustrates the structure of PVDF.



Figure 1.1. Structure of PVDF.

However, PVDF suffers from (i) high crystallinity (leading to increased processing cost), (ii) poor solubility (except in *N*,*N*-dimethylformamide, dimethyl sulfoxide, N-methylpyrrolidone and dimethylacetamide), (iii) difficulty in crosslinking (presence of toxic telechelic diamines or bisphenolates¹⁹) (iii) difficulty in tuning properties for targeted applications (due to the lack of functionality).^{8,11} These drawbacks can be overcome by (i) incorporating vinyl monomers containing functional groups⁸ such as hydroxyl, acetoxy,¹² thioacetoxy,¹³ ethers, esters, halogens, carboxylic acid⁵⁸ or aryl groups as comonomers in the radical copolymerization of VDF or (ii) cross-linking via cure site comonomers containing trialkoxysilane,⁵⁹ cyanato or

isocyanato groups or using bisamines or bisphenates.¹⁹ By this approach, some of the properties of the resulting copolymers^{8,50,60} can be improved such as adhesion, thermal stability,¹⁷ proton conductivity^{18,61} or hydrophobicity,¹⁷ to name a few.

1.1.2.1 Synthesis of Vinylidene Fluoride (VDF or VF2)

VDF (figure 1.2.) is a colorless, flammable, and nearly odorless gas that boils at -82 °C and freezes at -144 °C. It is a nontoxic, environmentally friendly fluorinated gas in contrast to chlorotrifluoroethylene (CTFE) and bromotrifluoroethylene (BrTFE), nonexplosive contrarily to tetrafluoroethylene (TFE) or trifluoroethylene (TrFE), and can easily homopolymerize and copolymerize under radical initiation.⁶²



Figure 1.2. Structure of Vinylidene Fluoride (VDF)

Various synthetic methods of VDF are possible (Scheme 1.1). i) through the chlorination of chlorofluorocarbon (CFC 152) to 1-chloro-1,1-difluoroethane (CFC 142),⁶³ followed by a dehydrochlorination at about 700-900 °C. (Scheme 1.1-A). ii) the hydrofluorination of 1,1,1-trichloroethane (HFC) yields CFC 142⁶⁴ (Scheme 1.1-B), which is subsequently dehydrochlorinated as above. Third, the dehydrobromination of 1-bromo-1,1-difluoroethane and dechlorination of 1,2-dichloro-1,1-difluoroethane (Scheme 1.1-C) in the presence of a Zn catalyst.⁶⁵



Scheme 1.1 Synthetic routes of Vinylidene Fluoride (VDF)

1.1.2.2 Radical Homopolymerization of VDF

The easiest and most common method for the synthesis of PVDF is through the radical polymerization of VDF, however, its polymerization is not completely regiospecific. The asymmetric structure of VDF leads to orientation isomers during the polymerization (scheme 1.2). The configuration of the monomer in the chain can either be $-CH_2CF_2-CH_2CF_2$ - (head-to-tail) normal addition (92-95 %) or $-CH_2CF_2-CF_2CH_2$ - (head-to-head) and $-CF_2CH_2-CH_2CF_2$ - (tail-to-tail) reverse addition (5-8 %) VDF-VDF dyads.⁸ Cais and Kometani^{66,67} synthesized PVDF homopolymers with reverse additions concentrations ranging from 0.2 to 23.5 mol % and studied the effect of the defect concentration on the crystal structures. ^{66,67} Below a defect percentage of ca. 11 mol %, the α phase was obtained for melt processed films while above 11 mol %, the copolymers exhibited the β phase, as predicted by Farmer *et al.*⁶⁸

Scheme 1.2. The head-to-tail normal and head-to-head or tail-to-tail reverse VDF-VDF dyads. These head-to-head or tail-to-tail defects are influenced by the conditions of polymerization process and temperature. The different configurations can be assessed by ¹⁹F NMR spectroscopy (Figure 1.3.).^{69,70}



Figure 1.3. ¹⁹F nuclear magnetic resonance spectrum of pristine PVDF.⁷⁰

The homopolymerization of VDF usually proceeds by a radical initiated polymerization process in aqueous emulsion or suspension (involving pressures of 10-300 atm) at temperatures of 10-130 °C, requiring a fluorinated surfactant, Chain transfer agents, buffers, or both. This reaction can be achieved in water⁷¹ or in organic solvents⁷² depending on the solubility of the

initiator. In addition, solution polymerization has also been investigated. It is initiated by organic peroxides in which the oxygen-oxygen bond undergoes a homolytic scission, in the presence of chlorofluorinated solvents.⁷⁰ The quality and the characteristics of the product are influenced by the polymerization procedures, temperatures, pressure, recipe ingredients, monomer feeding strategy, and postpolymerization processing.^{9,62}

1.1.2.3 Properties of PVDF

PVDF is a thermoplastic that exhibits interesting properties that can be altered by the molecular weights, molecular weight distributions, chain configurations, crystalline and defects of chaining.^{8,73} PVDF is inert to various solvents, oils, and acids and shows low permeability to gases and liquids. The glass transition (T_g) and melting (T_m) temperatures of the amorphous and crystalline PVDF regions are in the range of -40 to -30 and 155-192 °C respectively.⁶² PVDF is typically 50-70% crystalline with five distinct crystal polymorphs named α , β , γ , δ , and ε , though α , β , and γ are the most frequent ones (Figure 1.4).⁸ The α -phase is the most common polymorph of PVDF and is normally obtained by crystallization from the melt at moderate or high undercooling.⁸ The α -phase is frequently established when mechanical performance is required. Among others, it shows greater stability. It is a nonpolar phase and it has a conformational chair structure of the type trans-gauche (TGTG').

From the α -phase, by means of thermal, mechanical or electrical treatments, other phases can be obtained.^{54,74} The α -form is the PVDF conformation used in the production of Flexwear[®] (Unifirst Corporation) and Flexbarrier[®] (Midsun Group, Inc.).



Figure 1.2 Schematic structures of the α , β , and γ forms of PVDF.

The β -phase is used extensively in piezoelectric and pyroelectric applications.⁵⁴ It is routinely obtained by mechanical deformation of melt-crystallized films.⁸ Materials having piezoelectric property are part of a class that can convert mechanical energy into electrical energy or electrical energy into mechanical energy. The piezoelectric effect is constituted by a linear coupling between an electric field applied to an induced voltage, or a mechanical energy producing an electrical polarity. The β -phase is a polar phase with conformational structure of the planar zig-zag, type (TTT) with unit cell also in the orthorhombic form.

The microstructure of PVDF in the β -phase strongly depends on the way in which the phase is obtained.⁷⁵ By stretching from the α -phase at precise stretch ratios, at defined temperatures, the microstructure changes from a spherulitic to a microfibrillar structure, from α -phase to β -phase. No further information was found in the literature regarding these conditions, beside that as described by Serrado Nunes *et al.*⁷⁶

1.1.2.4 Radical Copolymerization of VDF

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-property relationships. As a result, copolymerization

usually modifies properties such as molecular weights, melting point, glass transition temperature, crystallinity, stability, elasticity, permeability, and chemical reactivity may be varied within wide limits. It is well-known that copolymerization of fluoroalkenes is carried out by a radical method. Such as its homopolymerization, the copolymerization of VDF with different comonomers is usually performed by radical polymerization. The literature shows that VDF have been copolymerized with different fluorinated and non-fluorinated monomers.⁸ Table 1.2 shows examples of some fluorinated comonomers than can successfully copolymerize with VDF.

Comonomers	structure	reference
Chlorotrifluoroethylene		8
	F F	
Trifluoroethylene		8,77
Hexafluoropropylene		8
1H-Pentafluoropropene	F F F F	8,78
4,5,5- Trifluoro-4-ene pentyl acetate	F F C ₃ H ₆ OCOCH ₃	12

Table 1.2. Some Comonomers of VDF.



1.1.3 2-(Trifluoromethyl)acrylic acid (MAF), a suitable comonomer to VDF.

Among the various comonomers for VDF, 2-(trifluoromethyl)acrylic acid (MAF) and/or alkyl 2-trifluoromethacrylates (MAF-esters) are particularly attractive.⁶⁰ MAF or MAF-esters containing copolymers exhibit outstanding outdoor stability/aging resistance and adhesion property.⁶⁰ Interestingly, MAF and MAF-esters does not homopolymerize under radical conditions,⁸¹ however it is possible to do so via cationic polymerization.⁸²⁻⁸⁴ Since MAF copolymerize well with VDF, our group has carried out the copolymerization of MAF derivatives with VDF *via* both conventional radical polymerization^{80,85,86} and reversible deactivation radical polymerization (RDRP)^{87,88} techniques. The reactivity ratios of VDF (*r*_{VDF} = 0.33 ± 0.09) and MAF (*r*_{MAF} = 0) at 55 °C were also reported (Figure 1.5),⁸⁵ which confirmed

that MAF does not homopropagate under radical conditions,⁸⁹ but in certain cases these monomers can produced copolymers containing an interesting alternating structure.^{60,85,87}



Figure 1.3 Monomer/copolymer composition of VDF/MAF determined by 19F NMR spectroscopy.⁵⁵ The resulting copolymers have potential applications in nanocomposites,⁹⁰ fuel cell membranes,¹⁸ and binders for Li-ion batteries.⁵⁵ Thus, MAF or MAF-esters have emerged as classic comonomers to prepare functional VDF-based copolymer with tunable properties.⁶⁰

1.1.3.1 Synthesis of MAF

Various methods have been reported for the synthesis of MAF. The first one describes the conversion of trifluoroacetone into the cyanhydrin and a thermal elimination of acetic acid (AA) from cyanhydrin-acetate to α -trifluoromethacrylonitrile (TFMAN).^{82,91} Hydrolysis of TFMAN generates 2-(trifluoromethyl)acrylic acid (MAF). Another method for preparation of MAF involves the hydrocarboxylation of BTP, easily accessible from commercially available TFP,⁹² under Heck reaction conditions.⁹³ This reaction required PdCl₂(PPh₃)₂ as the catalyst and was performed at 80 °C under 40 atm-carbon monoxide in the presence of triethylamine (TEA) and water (Scheme 1.3).



Scheme 1.3. Synthesis of 2-(trifluoromethyl)acrylic acid (MAF) from 3,3,3- trifluoropropene (TFP).

1.1.3.2 Modification of MAF into functional MAF-esters.

Another interesting property of MAF is that it can be easily modified to prepare fluorinated monomers bearing different functional groups depending on the desired application.¹⁷ Thus various studies are reported dealing with the modifications of MAF into Functional MAF-esters (Table 1.3). Typically, the carboxylic acid function in MAF is first converted into acyl chloride using thionyl chloride or Phthaloyl chloride. The following step is the esterification reaction of the obtained acyl chloride with a functional alcohol in the presence of a weak base (to trap HCl gas generated during the reaction) to obtain a functional MAF-esters (Scheme 1.4).



Scheme 1.4. Synthesis of MAF-Esters from MAF.

MAF-ester	structure	reference
2-trifluoromethacrylates bearing benzoyl group	$ \begin{array}{c} CF_{3} \\ 0 \\ 0 \\ -CF_{2} \\ 0 \\ F_{3}C \end{array} $	94
2-trifluoromethacrylates bearing a fluorinated group.	$ \xrightarrow{CF_3} = 0 \\ \xrightarrow{O} = 0 \\ \xrightarrow{O} = C_n F_{2n+1} $	95
2-trifluoromethacrylates bearing an epoxy group.		96
2-trifluoromethacrylates bearing an Oligo(oxyethylene) group.		97
2-trifluoromethacrylates bearing a Phenyl group.		98
2-trifluoromethacrylates bearing a Methyl group.	\sim	96

Table 1.3. Different prepared MAF-esters.


1.1.3.3 Radical copolymerization of MAF with VDF.

The radical copolymerization of VDF and MAF was first reported by Watanabe *et al.*¹⁰⁰ was initiated by ⁶⁰Co rays. Recent copolymerizations of these monomers is usually initiated by peroxides in compatible organic solvents.⁸⁵

Another interesting approach for the copolymerization of VDF and MAF is the controlled radical polymerization since it produces controlled polymer structures, well-designed polymers that have narrow polydispersities and can also lead to diblock or graft copolymers. Several techniques of controlled radical polymerization have been developed such as nitroxide mediated polymerization (NMP),^{101,102} atom transfer radical polymerization (ATRP),¹⁰³ reversible addition fragmentation transfer (RAFT),¹⁰⁴ macromolecular design for interchange of xanthates (MADIX),¹⁰⁵ organocobalt- or organostilbine-mediated radical polymerization (OCRP)^{106,107} and (reversible) iodine transfer polymerization ((R)ITP).^{87,108,109}

1.2. Phosphorous containing fluoropolymers.

In recent years, a lot of interest was given to phosphorous-containing monomers and polymers^{26,110-112} due to the relevant properties of the phosphorous atom and have found applications in dispersants, corrosion inhibiting agents, for preventing deposit formation,²⁰ as flame retardants,²¹ as adhesion promoters for paints,²² superlubricity coatings,¹¹³ as water repellent and intrinsically photostable coating materials for stone,¹¹⁴ polymer electrolyte membrane fuel cells,²³⁻²⁵ and in biomedical fields.²⁶ Due to its high electronegativity, the presence of fluorine atoms either on polymers back bones or on a spacer connected to this backbone can increase the electron density of adjacent functional groups, thus enhancing its properties,¹¹⁵⁻¹¹⁷ This led to a rising interest in combining the properties of both fluorine and phosphorous elements to evaluate if synergetic effects could be achieved. Literature reports

five main approaches to the synthesis of fluorinated polymers functional with phosphorous groups: (i) blends of fluoropolymers and a phosphorous source (ii) by radical homopolymerization of monomers containing both fluorine and phosphorous atoms, (iii) telomerization of fluorinated polymers with phosphorated end groups. (iv) by direct radical copolymerization of fluoromonomers and phosphorous-based monomers, (v) by chemical modification of fluorinated copolymers with phosphorated reactants. Finally, since fluorine and phosphorous atoms bring complementary relevant properties (low refractive index and dielectric constants, chemical inertness, high electrochemical, soils, and heat resistances, electroactivity from fluorine and high acidity, complexation, anticorrosion, flame retardant, biomedical properties from phosphorous), synergetic characteristics have been targeted allowing such fluoro-phosphorous (co)polymers to be used as novel materials involved in various applications as polymer exchange membranes for fuel cells, self-etching adhesives for dental materials, adhesion promoters, flame retardant products, polymer blends, and anticorrosive coatings.

1.2.1. Poly(vinylidene fluoride) with Phosphonated Copolymer Blends

Blends of PVDF and phosphorous containing methacrylate copolymers were prepared by Brondino et al.¹¹⁸ Initially, dimethyl(2-methacryloyloxyethyl)phosphonate (I) was obtained by the methacrylation of a phosphonated alcohol, followed by the chemical conversion of the dimethyl phosphonate phosphonic acid groups (2 group to to vield methacryloyloxyethyl)phosphonic diacid (II) and methyl(2-methacryloyloxyethyl)phosphonic hemiacid (III) (Figure 1.6.). The hemiacid was obtained using three different reagents: (i) bromotrimethylsilane (III-a), (ii) chlorotrimethylsilane (III-b) and (iii) sodium iodide in acetone (III-c). These monomers were then copolymerized with methyl methacrylate under radical conditions using AIBN as an initiator. The amount of phosphorous in the copolymers was also determined by ¹H NMR spectroscopy and titration with KOH/ethyl alcohol solution (Table 1.4).

Figure 1.6. Chemical structures of dimethyl(2-methacryloyloxyethyl)phosphonate (**I**), (2 methacryloyloxyethyl)phosphonic diacid (**II**) and methyl(2-methacryloyloxyethyl)phosphonic hemiacid (**III**).¹¹⁸

Table 1.4. Final Composition of the Copolymers prepared from the copolymerization of (**I**), (**II**) and (**III**) with methyl methacrylate.¹¹⁸

Final Molar Composition of Phosphonated and

Non-Phosphonated Units in Copolymers (x/y)

No.	Monomers (initiator molar ratio)	¹ H-NMR	Elemental Analysis (%P _{found})	Titration by Conductemetry	I _α (mg KOH/g)
1	I-MMA (20/80)	24/76	17/83 (4.3)	nd ^a	nd
2	II-MMA (20/80)	5/95	8/92 (2.4)	9/91	92
3	III-a-MMA (20/80)	11/89	nd	nd	56
4	III-b-MMA (20/80)	pr^{b}	8/92 (2.2)	9/91	46
5	III-c-MMA (20/80)	24/76	17/83 (4.4)	17/83	80

^and: not determined.

^bpr: poor resolution NMR signals.

Finally, the obtained copolymers were dissolved with PVDF in DMF and applied onto galvanized steel plates using a bar-coater followed by solvent evaporation in an oven at 280 $^{\circ}$ C, leading to a film with 20-25 µm thickness. Different blends were prepared using various copolymers and their adhesive and anticorrosive properties where evaluated and summarized in Table 1.5. The cross-cut testing allow the evaluation of the strength of the coating by perfoming some two perpendicular sets of parallel cuts to obtain a matrix, which by applying and removing a scotch tape onto, gives an idea of the adhesive strength of a coating. This test

results displayed an improvement in the adhesive properties of the blends containing phosphonated groups compared to those of virgin PVDF and the PVDF–PMMA blends (column 4). This improvement can be explained mainly by the polarity and the hydrophilicity of the phosphonated functional groups. Indeed, the T values resulting from the conical mandrel bend tests (column 5) revealed the good film properties of the PVDF–organophosphorus copolymer coatings. In addition, these results indicate that the phosphonic acid function gave better adhesive properties than the dialkyl phosphonate ones.

sample	Percentage of additives blend (% by weight)	Percent of Phosphorus (% by weight)	I _a of Blends (mg KOH/g)	Cross-cut Testing (Quotation/5 ^a)	Conical Mandrel Bend Testing T Value	Water Immersion Testing (Quotation/5)	Boiling Water Testing (Quotation/5)
Virgin PVDF				5	> 3	5	5
PVDF paint without any primer				5	> 3	5	S.
PVDF paint + primer				0	0	0	0
PVDF + 5% PMMA	5	0	0	56			
PVDF + 10% PMMA	10	0	0	56			
PVDF + 30% PMMA	30	0	0	5^{b}			
PVDF + 5% No. 1	5	0.22	0	56			
PVDF + 10% No. 1	10	0.43	0	5^{b}			
PVDF + 30% No. 1	30	1.29	0	0-1	0.8	0	0
PVDF + 10% No. 2	10	0.24	9.2	0	1.1	0	0
PVDF + 5% No. 3	5	0.13	2.8	0	0	nd ^c	1
PVDF + 10% No. 3	10	0.25	5.6	0	0	0	0
PVDF + 30% No. 3	30	0.75	16.8	0	0.4	0	0
PVDF + 5% No. 4	5	0.11	2.3	0	0	pu	3
PVDF + 10% No. 4	10	0.22	4.6	0	1.0	pu	0
PVDF + 30% No. 4	30	0.66	13.8	0	2.8	pu	1
PVDF + 5% No. 5	5	0.22	4.1	1	0.4	pu	5
PVDF + 10% No. 5	10	0.44	8.2	0	2.8	pu	1
PVDF + 30% No. 5	30	1.32	24.6	0	1.8	nd	4

Table 1.5. PVDF-PMMA and PVDF-Organophorus Copolymer Blends with Adhesion Tests results Compared with a PVDF Paint Reference Coated With or Without Adhesion Primer. Reproduced with permission from John Wiley & Sons, Inc.¹⁰⁸

 a Notation; 0, best adhesive properties; 5, worst adhesive properties. b Further tests not performed. c nd for not determined.

The blends with the higher adhesion properties underwent salt spray tests to evaluate their anticorrosive properties. The results (Table 1.6) show that the percentage of corroded surfaces, increased when the acid value and the percentage of phosphorus in blends increased. This is may be due to the semipermeable membrane behaviour of the polymer film, however films that maintained some level of adhesion, result in prevention of corrosion.

Table 1.6. Salt Spray Tests on PVDF Blend Coatings.¹¹⁸

	Salt Spray Test	
Sample	Percentage of corroded	
	Surface (70)	
PVDF paint + primer	Delamination	
PVDF + 10% No. 2	99	
PVDF + 5% No. 3	84	
PVDF + 10% No. 3	31	
PVDF + 10% No. 4	96	
PVDF + 10% No. 5	99	

1.2.2. Chemical modification of Fluorinated copolymers by Phosphorous

containing reactants.

Another approach for the introduction of phosphorous atoms into fluoropolymers dealt with the chemical modification of these copolymers to introduce phosphonic acid function via click chemistry or through the ionization of polymers surface to increase the functionalization on the polymers surface.

1.2.2.1. Intorduction of Phosphonic Acid Groups onto Fluorinated Polymers

Bearing Iodine Atoms.

A simple approach for the incorporation of phosphates to polymers is through the post polymerization modification of a polymer by a phosphorous containing reactant.¹¹⁹⁻¹²¹ Tayouo *et al.*²⁴ reported the Arbuzov chemical modification of an iodine containing fluorinated polymers into ionomers functionalized with phosphonic acid groups. Initially, two types of iodine bearing fluorinated copolymers were prepared: (i) by radical copolymerization of chlorotrifluoroethylene (CTFE) with 2-chloroethyl vinyl ether (CEVE) (Scheme 1.5); (ii) the radical terpolymerization of CTFE with CEVE and ethyl vinyl ether (EVE). ^{24,122} This was followed by the modification of chlorine atoms into iodine atoms by nucleophilic substitution using NaI (Finkelstein reaction). The average molecular weights of both copolymers: initially, the substitution of iodine atom into phosphonate group through the Arbuzov reaction^{123,124} at 130 °C in the presence of triethylphosphite followed by the hydrolysis of dialkylphosphate into phosphonic acid in the presence of BrSi(Me)₃.¹²⁵ The nucleophilic substitution of halogenated alkyl compounds into phosphonate groups was achieved by the presence of iodine atom as a better leaving group than the chlorine one.



Scheme 1.5. Synthetic Pathway to Chemically Graft Phosphonic Acid Groups onto Fluorinated Copolymers Obtained by Radical Copolymerization of CTFE with CEVE.²⁴

TGA thermogram (Figure 1.7) of the fluorinated copolymers bearing a phosphonic acid side groups showed three degradation steps: (i) 5% at 100 °C due to desorption of water adsorbed by hygroscopic phosphonic acid groups. (ii) the main degradation (70%) between 250 and 400 °C due to the cleavage of the C-P bond followed by the degradation of the fluorinated backbone, and (iii) above 400 °C arises from self-condensation reactions which form water molecules as well as phosphonic anhydride bonds.¹²⁶ In addition, isotherms at 130 °C (operational temperature of fuel cells) for several days only showed 5% loss (desorption of water) evidencing the high polymer stability at this temperature. Interestingly, only one glass transition temperature (Tg) was observed for each copolymer. This result shows that no phosphonic acid proper phase is observed due to the alternated structure of the fluorinated copolymers. The Tg values ranged from about 50 to 75 °C, depending on the phosphonic acid to those of the iodinated fluorinated copolymers as well as to the copolymers in the ester form (about 15 °C). This evidences the hydrogen bonding between the phosphonic acid groups.



Figure 1.7. TGA thermograms of $[(F:Cl)_{0.07}$ -co- $(F:POH)_{0.93}]$ and $[(F:Cl)_{0.07}$ - co- $(F:P)_{0.93}]$ (ester form) recorded under air at 10 °C/min.²⁴

Finally the author reports the preparation of membranes processed from the obtained co- and terpolymers. The hydration number vs the phosphonic acid content, i.e. IEC, revealed two behaviors: at relative humidity (RH) 100%, when IEC became high, the morphology of the membrane changed to increase the water uptake. At low RH, however, water sorption was very low even at high IEC, and self-condensation took place. This typical hydration behavior for phosphonic acid polymeric membranes caused a decrease of the protonic conductivity. Indeed, this decrease in RH from 95 to 25%, led to a decrease in the conductivity values by about 1 order of magnitude. However, an increase of the temperature (from 90 to 120 °C) doubles the proton conductivity in the same range of RH (Figure 1.8). This result indicates that water molecules and phosphonic acid hydrogen bonding are involved in the proton conduction mechanism. Finally, the proton conductivity increased by 3 orders of magnitude by increasing IEC (from 2.5 to 7 meq/g) to reach 20 mS.cm⁻¹ at 25 °C and 95% RH. It can be concluded that the high IEC is the key factor to significantly change the water sorption and, consequently, to enhance proton conductivity.²⁴



Figure **1.8** Proton conductivity of phosphonic acid grafted fluorinated membrane as a function of relative humidity at 90 $^{\circ}$ C (•) and 120 $^{\circ}$ C (•).

1.2.2.2 PEMFC from Radiografting of Fluoropolymers followed by grafting of phosphonated synthons

Another strategy lies on the irradiation-grafting technique, starting from the irradiation of poly(TFE-*co*-HFP) or poly(E-*co*-TFE) copolymers, fluorinated ethylene propylene (FEP) or ethylene tetrafluoroethylene (ETFE), respectively, at irradiation dosage of 50 kGy.¹²⁷ Then, the activated polymer films bearing radicals was immersed into vinylbenzyl chloride (or chloromethyl styrene, VBC) to lead to an *in situ* grafting of poly(vinylbenzylchhoride) onto ETFE and FEP films. The produced PVBC grafts then underwent an Arbuzov reaction (in the presence of triethyl phosphite at rather high temperature 140 °C) to introduce dialkyl phosphonate that were subsquently hydrolyzed into phosphonic acid functions. The phosphonation reached 90 %. The phoshonated FEP grafted films had a better stability than the ETFE ones and their conductivities were comparable to those of Nafion® film while their water uptakes were much lower.

1.2.2.3 Grafting of phosphonated poly(pentafluorostyrene) on to polysulfone.

The grafting of a phosphonated fluoropolymer onto polysulfone was repoted by Dimitrov *et al.*¹²⁸ The fluoropolymer (PFS-A) was prepared by the ATRP homopolymerization of 2,3,4,5,6-pentafluorostyrene in bulk at 110 °C (Scheme 1.6). The reaction was initiated by 3-bromo-1- (trimethylsilyl)-1-propyne (BrTMSPr) and CuBr/2,2'-bipyridyl was used as a catalytic system. After the end of the reaction, the alkyne end group was deprotected in acidic conditions. The overall yield of the reaction reached 82% and fairly good molecular weights of 10500 was obtained. The following step was the grafting of the fluorinated polymer to a polysulfone polymer bearing a pedant 3-(azidomethyl)benzoyl groups (PSU-N, M_n=43100), by a click reaction between the azide group (in PSU-N) and the alkyne group in (PFS-A). Finally, the postpolymerization modification of the fluorinated styrene rings in the grafted PFS was achieved by its reaction with excess amount of tris(trimethylsilyl) phosphite (TSP) at 150 °C. Two grafted polymers were prepared having differing in the size of the PFS used with PSU-*g*-PhPFS-1 having 31 repetitive units and PSU-*g*-PhPFS-2 having 54 repetitive units.



Scheme 1.6. Synthetic procedure for the preparation of polysulfone grafted with phosphonated poly(pentafluorostyrene)copolymers (PSU-*g*-PhPFS).¹²⁸ The TGA thermograms (Figure 1.9) indicate that the degradation of PSU-*g*-PhPFS polymers starts from 400 °C due to the cleavage of the C-P bonds followed by PFS decomposition, which

is slightly better than that of Nafion[®] NRE212 (378 °C), but lower than pristine PSU (501 °C).



Figure 1.9. TGA curves for: a) the phosphonated graft copolymer PSU-g-PhPFS-1; b) the phosphonated graft copolymer PSU-g- PhPFS-2; c) the native PSU; d) Nafion[®] NRE212.¹²⁸

The electrochemical properties for membranes prepared from these polymers showed a higher swelling rate but slightly lower conductivity than Nafion®NRE212 AT 100 °C. (Figure 1.10.).



Figure 1.10. Proton conductivity of graft copolymer membranes and Nafion® NRE212 versus reciprocal temperature, measured under fully immersed conditions.

1.2.3. Telechelic bis(phosphonic-acid) P(VDF-co-CTFE) Copolymers.

Since The operation of modern society depends highly on electrical energy, the demand for more efficient devices and materials for electric charge storage is of great interest.¹²⁹ Among current technologies, capacitors possess the advantage of high-power density due to the fast-electrical energy storage and discharge capability. Recently the employment of polymers as dielectric materials in such devices shows an advantage compared to ceramics due to their low cost, great processability and lightweight.¹³⁰ Due to the effect of the electronegative fluorine atoms, poly(vinylidene fluoride) (PVDF)-based ferroelectric polymers exhibit large spontaneous polarization and high dielectric constants, which make it an attractive alternate to ceramics dielectric materials for capacitors. Li *et al.* ¹³¹ reported the preparation of Telechelic bis(alkyl phosphonate) poly(VDF-*co*-CTFE) copolymers by the radical polymerization of VDF

and CTFE using a phosphonate functional benzoyl peroxide initiator (Scheme 1.7). This latter was first prepared from the oxidation of 4-carboxyphenylphosphonate with DCC. The authors obtained α, ω -bis(alkyl phosphonate) poly(VDF-*co*-CTFE) copolymer with a molecular weight of 28,000 g/mol in 38% yield. Actually, the authors did not report on the possible primary termination and the bisfunctionality is questionable since a non-negligible amount of transfer can be expected. The phosphonate groups were then hydrolyzed into phosphonic acid using iodotrimethylsilane/methanol (Scheme 1.7).



Scheme 1.7. Synthesis of the functional initiator and telechelic bis(alkyl phosphonic acid) poly(VDF*co*-CTFE) copolymers.¹³¹

The phosphonic acid terminals of these polymers was complexed onto ZrO₂ in DMF followed by thermal treatment for the preparation of membranes. ³¹P NMR spectrum (Figure 1.11) shows that the signal shifts from 45 ppm in the phosphonic acid terminated P(VDF-CTFE) to 28 ppm in the nanocomposites, due to the bidentate binding mode of terminal phosphonic acids to ZrO₂.



Figure 1.11. ³¹P solid-state NMR spectra of (a) phosphonic-acid-terminated P(VDF-CTFE); (b) P(VDF-CTFE)- ZrO2 nanocomposites.¹³¹

Studying the Dielectric Properties of the membrane the authors noted that no notable change in the dielectric permittivity for the membranes with low amount of ZrO_2 . This is attributed to the comparable dielectric permittivity of both PVDF and ZrO_2 . As the amount of ZrO_2 increased above 17 %, an improvement in the dielectric permittivity was observed. Interestingly, it was found that the incorporation of ZrO2 nanoparticles into the polymers leads to significant increase in the energy density of the materials (figure 1.12.) at high electric field, where it reached its maximum of 11.2 J/cm³ in the membrane containing 9.1% of ZrO₂.



Figure 1.12. Stored energy density of the polymer and the nanocomposites as a function of the applied field.¹³¹

1.2.4. Homopolymerization of phosphorous containing fluoromonomers for flame retardant applications.

Recent studies focused on the development of halogen free flame retardants due to the risen environmental threat by the release of toxic gas from the process of combustion of materials^{132,133}. Intensive research has been focused on phosphonated materials as flame retardants. Even though the presence of phosphorus usually leads to a decrease in thermal stability but it promotes charring through dehydration of cellulose¹³⁴. Phosphorylated (co)polymers have been involved in flame retardant materials¹³⁵⁻¹³⁷ but only two papers concerning fluorophosphorous ones have been reported. Timperley *et al.* claims the preparation of a series of phosphorous containing fluoromonomers from the esterification reaction of bis(fluoroalkyl) phosphites with 2-hydroxyethyl acrylate (HEA) or 2-hydroxyethyl methacrylate (HEMA).¹³⁸ Initially, several bis(fluoroalkyl) phosphites were prepared from the esterification of phosphorous trichloride.¹³⁹ Then, the prepared bis(fluoroalkyl) phosphites

were reacted with either HEA or HEMA to obtain the fluorinated monomers (Scheme 1.8) in yields ranging from 29% to 64%.¹³⁸



Scheme 1.8. Synthesis of different fluorinated acrylic esters.

These monomers were then homopolymerized, using 2,2'-azobis(isobutyronitrile) (AIBN) as an initiator, to obtain an elastic rubbery polymer in yields up to 95%. The flame retardance property of the obtained monomers and polymers were evaluated. Cotton samples were treated with either 5% of monomers or 1 % of polymer to access their limiting oxygen index (LOI). The increase in the LOI value implies that the material is more resistive to burn. In general, materials can be characterized according to their LOI value as: (i) less than 25% LOI indicate that the material burns in air, while 25% to 30% value means it can burn under hot air, whereas for greater than 30% LOI, the material is flame retardant. Compared to untreated fabric (17% LOI), the sample treated with 1% polymer showed 5% increase in its LOI value (22%) while the one treated with 5% of the monomer displayed 8% increase in its LOI value (25%), indicating an enhanced flame retardancy of the materials.

1.2.5 Copolymerization of phosphate and/or fluorine containing monomers.

1.2.5.1 Perfluorovinyloxy substituted phosphonate esters (VE)

Yamabe *et al.*^{140,141} reported the synthesis of dimethyl (3-trifluoroethenoxyhexafluoropropyl) phosphonate (Scheme 1.9) from 3-(methoxycarbonyl)-1,1,2,2,3,3-hexafluoropropyl trifluorovinyl ether (M₀), in seven steps, as one of the first phosphonate containing fluoromonomer. The overall yield of the reaction was 17% and the structure of the monomer was confirmed by ¹⁹F NMR spectroscopy (Figure 1.13.) highlighted by the doublet of doublets centered at -135 ppm corresponding to $CF_2=C\underline{F}O$ - while those at -122 and -114 ppm are assigned to both non-equivalent fluorine atoms in $CF_2=CFO$ -. The signals at -124, -121, and -84 ppm are attributed to $CF_2=CFO-CF_2-CF_2-CF_2-P(O)(OCH_3)_2$, $CF_2=CFO-CF_2-CF_2-CF_2-P(O)(OCH_3)_2$, $CF_2=CFO-CF_2-CF_2-CF_2-P(O)(OCH_3)_2$, respectively.



Scheme 5.9. Synthesis of dimethyl (3-trifluoroethenoxyhexafluoropropyl) phosphonate from 3-(methoxycarbonyl)-1,1,2,2,3,3-hexafluoropropyl trifluorovinyl ether.^{140,141}



Figure 1.13. ¹⁹F NMR spectrum of dimethyl (3-trifluoroethenoxyhexafluoropropyl) phosphonate.¹⁴¹

Although Yamabe et al.^{140,141} successful synthesis, the overall yield of the reaction was low due to the formation of significant amounts of mono- and bis-dealkylated products during the oxidation of the phosphonate. In addition, hydrolysis of phosphonate occurred while trying to deprotecting the trifluorovinyl ether moiety. To overcome this problem the mixture of phosphonate, monophosphonic acid, and phosphonic acid were reacted with phosphorus pentachloride to produce a mixture of phosphoryl chlorides. However, the isolation of the desired phosphoryl chlorides was limited and led to low overall yield. Pedersen *et al.*¹⁴² demonstrated that the deprotection of the trifluorovinyl ether moiety prior to its oxidation prevents the dealkylation of the phosphonate (Scheme 1.10). Initially, the deprotection of the double bond occurs, followed by oxidation of the phosphonate, thus avoiding the dealkylation of the phosphonate group, which allows the synthesis of perfluorinated diethyl phosphonate in good yields (69% based on the starting iodide), avoiding the isolation of the troublesome phosphoryl chlorides.



Scheme 1.10. Modified method for the preparation of perfluorinated diethyl phosphonate.¹⁴² Yamabe *et al.* then successfully radical copolymerized (M₀) with tetrafluoroethylene (TFE) (Figure 1.14) ¹⁴³ in 1,1,2-trichloro-1,2,2-trifluoroethane (R-113) using AIBN as an initiator, with 25% yield. Capillary viscosimetry of different polymer samples showed that the increase in the phosphate content in the copolymer (typically increasing M₁ compared to TFE) induced an increase in the volumetric flow rate (Q) which means that the molecular weights of the polymers increased for higher M₂ content. Thermogravimetric analysis (TGA) was studied and the authors observed two decomposition temperatures at: (i) at T_{d1}= 180 °C assigned to the decomposition of phosphonate residue to phosphonic acid and (ii) at T_{d2}= 308 °C due to the cleavage in the CF₂-P linkage.



Figure. 1.14: Copolymer of tetrafluoroethylene and dimethyl (3-trifluoroethenoxyhexafluoropropyl) phosphonate (M₀). Since the preparation of films from the copolymer by melt processing lacked adequate flexibility and thus perfluoro(propyl vinyl) (PPVE) was introduced of as new monomer to the polymer system.¹⁴¹ The conditions for the terpolymerization reaction was identical to that of the copolymerization and the resulting terpolymer (Figure 1.15) showed the same melt flow index and thermal decomposition behavior as those of the copolymers. The stress-strain curve shows that the terpolymer displays an enhanced elongation (110%) compared to that of the copolymer (30%) at the same tensile strength (2.1 kg/cm^2) indicating that the flexibility of the terpolymer increased by the introduction of PPVE termonomer.



Fig. 1.15 Terpolymer of tetrafluoroethylene, dimethyl (3-trifluoroethenoxyhexafluoropropyl) phosphonate (M₀) and perfluoro(propyl vinyl).¹⁴¹ The potential application of the terpolymer as an ion exchange membrane was achieved by measuring the conductivity of these membrans after the hydrolysis of the phosphonate groups into phosphonic acid. The results obtained by Yamabe *et al.* Table 1.7 summarizes the proton conductivity of three types of prefluorinated cation exchange membranes in 1N-hydrochloric acid. The conductivity of the perfluorophosphonic acid membrane (3.5 x $10^{-2} \Omega^{-1} \text{ cm}^{-1}$) in acidic media was close to that of perfluorosulfonic acid (9.0 x $10^{-2} \Omega^{-1} \text{ cm}^{-1}$).¹⁴¹

Cation exchange membrane	Functional group (relative activity)	Ion exchange capacity (meq/g.dry polymer)	Ionic conductivity $(\Omega^{-1}.cm^{-1})$
Phosphonic acid type	-CF ₂ -P(O)(OH) ₂ (10)	1.44 1.95	3.5 x 10 ⁻³ 2.7 x 10 ⁻²
		2.05	7.0 x 10 ⁻²
Carboxylic acid type	-CF ₂ -COOH (1)	1.44	3.4 x 10 ⁻⁵
Sulphonic acid type	-CF ₂ -SO ₃ H (430)	0.91	9.0 x 10 ⁻²

Table 1.7. Proton conductivities of perfluorinated cation exchange membranes in 1N-hydrochloric acid.¹⁴¹

Inspired by Yamabe *et al.*, Kotov *et al.*²³ prepared three different perfluorinated diethyl phosphonate monomers, diethyl (3-trifluoroethenoxyhexafluoropropyl) phosphonate (M_1), diethyl (2-trifluoroethenoxytetrafluoroethyl) phosphonate (M_2) and diethyl (trifluoroethenoxy-4-trifluoromethyl-3-oxa-perfluoropentyl) phosphonate (M_3) (Figure 1.16).



Figure 1.16. Structures of (3-trifluoroethenoxyhexafluoropropyl) phosphonate (M1), diethyl (2-trifluoroethenoxytetrafluoroethyl) phosphonate (M2) and diethyl (trifluoroethenoxy-4-trifluoromethyl-3-oxa-perfluoropentyl) phosphonate (M3).

The prepared monomers M_1 , M_2 and M_3 (Figure 1.16) was then copolymerized and terpolymerized with TFE and TFE/PPVE, respectively. The polymerizations were carried out in emulsion, using C₇F₁₅CO₂Na as an emulsifier, Na₂HPO₄.7H₂O as a buffer and Na₂S₂O₈-NaHSO₃ as a redox initiating system. The yield of the polymerization reached up to 59%. The decomposition of the polymers usually occurs between 240 and 310 °C (Figure 1.17.) due to the loss of ethylene groups in the diethyl phosphate function. The phosphonate group was then

hydrolyzed to phosphonic acid and after hot pressing, the terpolymer was processed into films of 0.1-0.13 mm thickness.



Figure 1.17. TGA thermogram of a fluoropolymeric bearing diethylphosphonate side groups.

Compared to the values in table. 1.7, the conductivity and water absorption of the films processed by Kotov *et al.*²³ were superior (Table 1.8). The poly(TFE-*co*-M₁ or M₂) copolymers had fairly higher absorption of water, and a proton conductivity similar to that of commercially available Nafion[®]. When PPVE was introduced in a polymer involving functional monomer M_1 or M_2 , a decrease was noted in both the water adsorption and proton conductivity. The films based on TFE and functional monomer M_3 displayed high water uptake values. In contrast, low proton conductivity compared to those of polymers containing M_1 or M_2 or Nafion[®] was observed. This arises from to the poor cluster formation of the film during its preparation using hot pressing.²³

Monomers employed	IEC of acid film (meq g ⁻¹)	Water uptaake (%) ^a	Proton conductivity (S.cm ⁻¹) ^b
1, TFE	2.8	22	0.076
1, TFE, PPVE	2.5	17	0.051
2, TFE	2.7	21	0.069
2, TFE, PPVE	2.8	11	0.035
3, TFE	3.0	54	0.006
Nafion	-	30	0.07-0.08

Table 1.8. Electrochemical evaluation of fluoropolymer phosphonic acid films, where TFE and PPVE stands for tetrafluoroethylene and perfluoropropyl vinyl ether respectively.²³

^aMeasured after boiling in deionized water for 4 h. ^bMeasured at 80 °C under saturated water vapor

A newer generation of fluorophosphonated vinyl ethers with a CF₃ group present on the phosphorous atom was presented by Creager *et al.*¹⁴⁴ The preparation of this monomer was achieved from the modification of phosphonic acid, P-(trifluoromethyl)-diethyl ester (scheme 1.11.). First the ester was treated with PCl₅ to prepare phosphonic dichloride, P-(trifluoromethyl)- which was later modified through a Grignard reaction to give the bis-fluoroalkyl-phosphinic acid monomer in 64% overall yield.

$$F_{3}C \xrightarrow{P}{-}OEt + PCI_{5} \xrightarrow{PhCN} F_{3}C \xrightarrow{P}{-}CI \xrightarrow{1)}{E_{1}C_{1}} \xrightarrow{1)}{E_{1}C_{2}OH_{5}} \xrightarrow{F}_{6}C \xrightarrow{F}_{7}C \xrightarrow{F}_{7}C$$



He then performed the emulsion polymerization of the fluoroalkylphosphonic monomer with tetrafluoroethylene (TFE) in water using a fluorinated surfactant and a persulfate initiator (Scheme 1.12.).¹⁴⁵ However, the author recorded no data regarding the thermal or the chemical stability of such copolymers.



Scheme 1.12. Preparation of Fluoroalkylphosphonic acid ionomers from the emulsion copolymerization of a phosphonated fluoromonomer with tetrafluoroethylene in water.

The proton conductivity of membranes processed from these copolymers showed a slightly better results Compared to Nafion[®], at 100% RH (relative humidity) (Figure 1.18.). DFT-based BOMD simulations for the CF₃PO(OH) group showed faster proton diffusion compared to oxygen, which is a characteristic of Grotthuss proton transport mechanism.^{144,145}



Figure 1.18. Ionic conductivity data for ionomer P-18 (blue), and Nafion® (red).¹⁴⁵

1.2.5.2 Synthesis of perfluoroalkyl vinyl phosphonic acid monomer.

Daikin industries¹⁴⁶ claimed the preparation of functional fluorinated copolymers. Initially, a phosphorous containing fluoromonomer was prepared from the modification of chlorotrifluoroethylene (CTFE) as shown in Scheme 1.13. The first step deals with the addition of iodine monochloride onto CTFE to prepare chloroiodo fluoroalkanes which then reacts onto tetrafluoroethylene (TFE) to lead to 1,2-dichloro-1,1,2,3,3,4,4-heptafluoro-4-iodobutane. Finally, the halogenated fluoroalkane is converted into fluoroalkyl vinylphosphonic acid after phosphorylation and dechlorination using zinc.

IC1 +
$$F_2C=CFC1$$
 \longrightarrow CICF₂CFCII $\xrightarrow{C_2F_4}$ CICF₂CFCI-CF₂CF₂I
AIBN, 60 °C
1) P/I₂, 145 °C
2) H₂O₂/H₂O
3)Zn
 $F_2C=CF-C_2F_4-P(O)(OH)_2$

Scheme 1.13. Synthesis of fluorinated vinylphosphonic acid monomer.

Since VDF is a gas, its copolymerization with fluorinated vinyl phosphonic acid monomer was performed in an autoclave.¹⁴⁶ The polymerization reaction was initiated by diisopropyl peroxydicarbonate (IPP) in a fluorinated solvent. After the introduction of all the monomers into the autoclave, it was heated up to 50 °C ($t_{1/2}$ = 10 hours for the initiator at this temperature). The yield of the reaction was quite low (17%) and the content of phosphorous in the copolymer was 8% (accessed by ¹⁹F NMR spectroscopy). Surprisingly, the authors carried out only one experiment, leading to a molecular weight of the copolymer was 19,000 g mol⁻¹.¹⁴⁶

1.2.5.3 Synthesis of dimethylphosphate-1,2,2 trifluorostyrene monomer

The preparation of dimethylphosphate-1,2,2 trifluorostyrene in 50% yields is reported by stone *et al.* in a two steps reaction (Scheme 1.14.).¹⁴⁷ First, 4-iodobenzene phosphonic acid dimethyl ester was prepared from the reaction of phosphorous trichloride with paradiiodobenzene using

aluminum chloride as a catalyst (yield 75%). This product was then reacted with trifluoroethylenylzinc reagent while using tetrakis(triphenylphosphine)palladium(0) as a catalyst using method described by Heinze *et al.*¹⁴⁸ to obtain dimethylphosphate-1,2,2 trifluorostyrene.



Scheme 1.14. Synthesis of dimethylphosphate-1,2,2 trifluorostyrene. ¹⁴⁷

The radical homopolymerization of dimethylphosphate-1,2,2-trifluorostyrene was achieved in a sealed glass tube using AIBN as an initiator.¹⁴⁷ ¹H NMR spectrum confirmed the formation of a polymer (obtained in 34% yield) with signals at 3.50-3.76 ppm attributed to CH₃ groups of the phosphonate group and signals between 5.3 and 8.1 ppm assigned to the aromatic ring.¹⁴⁷ The phosphonate groups on the polymer were then hydrolysed into phosphonic acid in 95% conversion. However, the hydrolyzed homopolymer tends to dissolve in aqueous medium and thus lacks the suitable physical properties to be used as an electrolyte. The monomer was then copolymerized with trifluorostyrene (TFS) (Scheme 1.15.) to enhance its properties. The emulsion copolymerization reaction was initiated by potassium persulfate and dodecylamine hydrochloride emulsifier (DDA.HCl) with rather low yield 21% and M_w= 105,902 g.mol⁻¹ (relative to polystyrene standards).^{147,149}



Scheme 1.15. Radical copolymerization of dimethylphosphate-1,2,2-trifluorostyrene with trifluorostyrene followed by the hydrolysis of the phosphonate groups into phosphonic acid (where DDA stands for dodecylamine hydrochloride).¹⁴⁷

Since the molecular weight of the resulting copolymer was significantly higher than that of the homopolymer, the hydrolysis of its phosphonate groups into phosphonic acid did not induce water solubility. The fuel cell performance of the hydrolyzed homopolymer and copolymer were studied. Although the homopolymer showed superior conductivity compared to the copolymer, (due to the better water uptake), it had inferior results compared to commercially available sulfonic acid based ionomers (Figure 1.19).¹⁴⁷



Figure 1.19. Polarization data comparing the homo and copolymer of dimethylphosphate-1,2,2 trifluorostyrene with commercially available fuel cell membranes.

1.2.5.4 Synthesis of diisopropyl (1,1-difluoro-5-methacryloyloxypentyl)-

phosphonate (PCF₂MA).

Though phosphonated monomers and polymers have been used for dental applications¹⁵⁰, a few articles report those also containing fluorine atoms. Lequeux's team designed a quite interesting series of monomers bearing a $-CF_2P(O)(OR)_2$ end-group. First, they reported¹⁵¹ the synthesis of a difluorophosphonylated monomer in two steps followed by the esterification of

equimolar amounts of diisopropyl(1,1-difluoro-5-hydroxypentyl)phosphonate and methacryloyl chloride in dichloromethane at 0 $^{\circ}$ C (Scheme 1.16).



Scheme 1.16. Synthesis of diisopropyl (1,1-difluoro-5-methacryloyloxypentyl)- phosphonate.¹⁵¹

To assess the role of the linker in the adhesive strengths of the fluorophosphated acrylate monomers, the author compared the photopolymerization of a series of three phosphonated 5-(methacryloyloxy)pentylphosphonic 5methacrylate monomers: acid (1), (methacryloyloxy) pentylidenebisphosphonic acid (2),and 1,1-difluoro-5-(methacryloyloxy)pentylphosphonic acid (3) (Figure 1.20., prepared as shown in scheme 1.16). ¹⁵¹ They were able to efficiently to adhere to hydroxyapatite (HAp) crystals by formation of ionic interactions between the corresponding salt and HAp calcium ions according to a certain organization during the polymerization. Furthermore, dentin shear bond strength measurements (Table 1.9.) showed that primers based on the telechelic bisphosphonic acid and the difluoromethylphosphonic acid 3 are significantly more efficient than the one based on the corresponding phosphonic acid 1. Thus, the nature of the acidic group has a great influence on dentin adhesion. Moreover, the use of adhesives based on monomers 2 and 3 were found to lead to significantly higher SBS than when employing a commercially available formulation (AdheSE) bonding resin. Therefore, these

two monomers appear to be great candidates to enter adhesive formulations. Due to their chelating properties, bisphosphonic and difluorophosphonic acids should also improve dentin adhesion durability.



Figure 1.20. phopshorated monomers involved in photopolymerization for dental applications.

Primer	Mean SBS (MPa)	S.D. (MPa)
AdheSE primer	14.5	3.6
Primer 1	15.4	5.5
Primer 2	19.7	5.2
Primer 3	20.6	2.1

Table. 1.9. Dentin shear strength measurements (SBS) using primers 1-3 and AdheSE primer.

The same research group also studied the effect of the linker on the potential dental applications of these fluorophosphonated acrylates.¹⁵² Thus various monomers with different linker lengths were prepared by various methods (Scheme 1.17): (i) 1,3- dipolar cycloaddition Reaction of 8 to obtain 9 and 11 intermediates followed by conversion to 10 and 12, respectively in to methacrylates; (ii) alkylation of the carbanion 5 with bromoalkanes to obtain 13 followed by its reaction with Amberlyst H-5 to obtain 14; iii) the alkylation of the carbanion 5 with dibromoalkanes to yield 15a-f followed by the modification of the bromine atom into acrylamide function for 16e-f monomers; and finally (iv) the reaction of 5 with caprolactone in THF followed by the conversion of the alcohol group into a methacrylate group.



Scheme 1.17. different synthetic routs for the preparation of difluorophosphonylated monomers with different spacers.

The photopolymerization of new monomers with N,N-diethyl-1,3-bis(acrylamido)propane (DEBAAP) using camphorquinone (CQ) as a photoinitiator, ethyl 4-(dimethylamino)benzoate (EDAB) as a coinitiator and 2,6-di-*tert*-butyl-4-methylphenol (BHT) as a stabilizer. The shear bond strength (SBS) of these primers was then determined for various polymers prepared from fluorinated and nonfluorinated monomers (Figure 1.21.). The SBS of the fluorinated polymers was greater than the nonfluorinated polymers, which means a more efficient and stronger binding. The author also states the effect of the spacer and claims that the increase in the spacer size correlates with the better SBS (monomer 10, fig 1.21). In addition, the presence of a hetrocycle even in large spacers usually tends to decrease the SBS values (23 fig 1.21.), which can be addressed by the presence of a bismethacrylate function (22 fig 1.21.). Finally, the best SBS value was obtained in the presence of a ketophosphonic acid function.



Figure 1.21. Mean SBS (MPa) and standard deviation (MPa) for fluorophosphonate acids primers.

1.2.5.5 Phosphonate containing methacrylate fluoromonomer

Due to the presence of electron-withdrawing difluoromethylene adjacent to phosphonic acid makes more acidic that functional group, Toyota¹⁵³ claimed the preparation of a phosphonate methacrylate fluoromonomer. The objective of this study was to (co)polymerize such monomer for proton exchange membranes.

The monomer was prepared in a three-step procedure (Scheme 1.18.): i) the reaction of $HCF_2PO(OEt)_2$ with CO_2 in the presence of Lithium diisopropylamine (LDA) and BuLi, followed by ii) the reduction of the obtained carboxylic acid group using NaBH₄ into a primary ω -hydroxyl 2,2-difluorodialkyl phosphonate, and finally iii) its condensation with an acyl chloride group to obtain a phosphonate functional methacrylate fluoromonomer.



Scheme 1.18. Synthesis of phosphonate-functionalized methacrylate fluoromonomer.¹⁵³

The prepared monomer was homopolymerized using AIBN in 62% over all yield. The molecular weights of the polymer ranged between 9800 and 21500 g.mol⁻¹. Then, the phosphonate groups were further hydrolyzed using bromotrimethylsilane into phosphonic acid groups (Scheme 1.19.). The polymers were drop casted on a substrate and immersed in water to remove any organic solvent and obtain electrolyte films.



Scheme 1.19. Radical polymerization of phosphonate-containing methacrylate fluoromonomers followed by the hydrolysis of the phosphonate groups into phosphonic acids.¹⁵³

The proton conductivity of the homopolymer was studied to determine its potential application as a PEMFC (Figure 1.22.). The polymer electrolytes were placed between two platinum plates and their conductivity was calculated according to equation (1):

$$Conductivity (S/cm) = \frac{\text{Distance between platinym plates (cm)}}{(Sw (cm) x St (cm)x Resistance (\Omega))}$$
(1)

Where Sw is the sample film width and St is the sample film thickness. The conductivity of the fluoropolymer was compared to that of a polymer containing an aromatic phosphonic acid groups (Figure 1.22.). The fluoropolymer showed an improved conductivity under low humidity conditions (up to 60%), making it suitable for applications of low humidity mediums.



Figure 1.22. Proton conductivity phosphonic acid functional fluoropolymer compared to phosphonic acid functional aromatic polymer.¹⁵³

1.2.5.6 Aromatic Phosphorus containing monomer

Two methods for the preparation of phosphonated poly(aryl ether) were reported by Abouzari-Lotf et al.¹⁵⁴ Initially, these authors synthesized two phosphonated monomers: tetraethyl (2,5dihydroxy-1,4-phenylene) diphosphate (C-Ph) and its derivative (2.5 bis(diethoxyphosphoryl)-1,4-phenylene bis(propylcarbamate)) (C-Ph-BC) (Scheme 1.20.). Phosphonated monomer (C-Ph) was first prepared from diphosphorylation of hydroquinone by diethylphosphate using Atherton-Todd method,¹⁵⁵ followed by phosphate phosphonate rearrangement in the presence of strong base.¹⁵⁶ Since masked compounds give better results in nucleophilic substitution polymerization reactions,¹⁵⁷ (C-Ph) was reacted with npropylisocyanate to give the corresponding bispropylcarbamate-masked compound (C-Ph-BC) (Scheme 1.20.).



Scheme 1.20. Preparation of phosphonate ester functionalized bisphenol (C-Ph) and bispropylcarbamate derivative (C-Ph-BC).¹⁵⁴

The prepared monomers (C-Ph) and (C-Ph-BC) were copolycondensed with decafluorobiphenyl by nucleophilic aromatic substitution reaction in DMAc at temperature below 140 °C (Scheme 1.21.).¹⁵⁴ Two types of polymers were prepared (using the same
synthetic method) by either using a bisphenol or a biscarbamate in the reactants. The polymer prepared from carbamate was advantageously more interesting than the bisphenols one since they are: (i) a shorter reaction time under mild conditions, (ii) no water generation during the polymerization, and (iii) formation of higher molecular weight polymers (37,900 g.mol⁻¹) compared to (28,400 g.mol⁻¹) for polymers prepared using bisphenols. The hydrolysis of the phosphonate groups into phosphonic acid took place in acidic medium and the authors evidenced the enhanced thermal properties of the acid functional polymer (T_{d10%} = 430 °C) compared to the phosphonic ester functional one (T_{d10%} = 290 °C due to the loss of four ethyl groups).



Scheme 1.21. Polycondensation of aromatic fluorinated polymers bearing two phosphonate groups.

Proton conductivities of membranes prepared from poly(Ar-co-(C-Ph) and (C-Ph-BC)) under both fully hydrated and dry conditions were investigated.¹⁵⁴ The authors wanted to see the effect of increasing the phosphonic acid groups in the repetitive unit of the polymer from one (Liu *et al* work) to two. Accordingly, they observe an increase in the conductivity value for the acid functional membranes, reaching 92 mS/cm when fully hydrated at ambient temperature. High proton conductivity demonstrates that the high and localized concentration of phosphonic acids was effective for water-assisted proton transport. In addition, it was found that the level of conductivity of the membrane under fully hydrated conditions increased with temperature and reached 150 mS/cm around 100 °C and stays almost constant up to 140 °C. Proton conductivity of the membrane under dry (no external humidification) conditions increased exponentially with temperature from nearly 2 x 10^{-3} mS.cm⁻¹ at 25 °C to 2.2 mS.cm⁻¹ at 120 °C. The combination of all these properties makes this phosphonated polymer electrolyte potentially useful in fuel cell technology.

1.3. The Sol-Gel Technology

The sol-gel process is a versatile wet chemical process to prepare ceramic and glass materials. This synthesis technique involves the transition of a system from a colloidal liquid, named sol, into a solid gel phase.¹⁵⁸⁻¹⁶⁰ The sol-gel technology allows to prepare ceramic or glass materials in a wide variety of forms: ultra-fine or spherical shaped powders, thin film coatings, ceramic fibres, microporous inorganic membranes, monolithics, or extremely porous aerogels. An overview of the sol-gel process is illustrated in Figure 1.23.



Figure 1.23. Overview of the sol-gel process.¹⁶¹

This technique offers many advantages among them the low process temperature, the ability to control the composition on molecular scale, the porosity to obtain high surface area materials, and the homogeneity of the final product up to atomic scale. Moreover, it is possible to synthesize complex composition materials, to form higher purity products through the use of high purity reagents.¹⁵⁸⁻¹⁶⁰ Three approaches are used to make sol-gel monoliths: method 1, gelation of a solution of colloidal powders; method 2, hydrolysis and polycondensation of alkoxide or nitrate precursors followed by drying of gels; method 3, hydrolysis and polycondensation of alkoxide precursors followed by aging and drying under ambient atmospheres.¹⁶²

The sol-gel process allows obtaining high quality films up to micron thickness, which is difficult to obtain using the physical deposition techniques. Moreover, it is possible to synthesize complex composition materials and to provide coatings over complex geometries.¹⁵⁸⁻¹⁶⁰ The starting materials used in the preparation of the sol are usually inorganic metal salts or metal organic compounds that by hydrolysis and poly-condensation reactions form the sol. Further processing of the sol enables one to make ceramic materials in different

forms. Thin films can be produced by spin-coating or dip-coating. When the sol is cast into a mold, a wet gel will form. By drying and heat-treatment, the gel is converted into dense ceramic or glass materials. If the liquid in a wet gel is removed under a supercritical condition, a highly porous and extremely low-density aerogel material is obtained. As the viscosity of a sol is adjusted into a suitable viscosity range, ceramic fibers can be drawn from the sol. Ultra-fine and uniform ceramic powders are formed by precipitation, spray pyrolysis, or emulsion techniques.¹⁵⁸⁻¹⁶⁰

1.3.1 The Sol-Gel definition

Sols are dispersions of colloidal particles (solid particles with diameters of 1-100 nm) in a liquid.¹⁶² A gel is an interconnected, rigid network of polymeric chains with pores of submicrometer dimensions. The term "gel" can be classified into 4 catigories: i) well-ordered lamellar structures, ii) covalent polymeric networks, iii) polymer networks formed through physical aggregation and iv) particular disordered structures.¹⁶³ Commonly, the most preferred starting reagents are alkoxides with general formula " $M_x(OR)_y$ " where M is the element with valence y and R is the alkoxide group. These alkoxides must exhibit useful properties to control the chemical synthesis of oxides:

1. Easy to purify, a lot of alkoxides can be distilled to obtain highly pure products;

2. Wide variety, it is possible to choose R among a large number of alkylic groups in order to obtain the required reactivity;

3. Possible control, of the alkoxides hydrolysis and the polycondensation of hydrolysed species;

4. Mixed alkoxides, as a further control means of the stoichiometry and homogeneity of the final products.¹⁶⁴

1.3.2 Hydrolysis and polycondensation.

The transition from sol to gel involves two key steps, the hydrolysis and polycondensation. The hydrolysis takes place by small amounts of water. Because water and alkoxides are immiscible, a mutual solvent such as alcohol, is normally used as a homogenizing agent. In the hydrolysis reaction, the alkoxide groups (OR) are replaced stepwise by hydroxyl groups (OH) (Scheme 1.22.).¹⁶⁴

Scheme. 1.22. hydrolysis reaction, the alkoxide groups (OR) are replaced stepwise by hydroxyl groups (OH).

The hydrolysis rate depends on many factors such as charge density on the metal, the number of metal ions bridged by a hydroxo- or oxo-ligand, and the size of the alkyl groups.^{165,166} Simultaneously to the hydrolysis, the polycondensation reactions occur (Scheme 1.23.).

$$-\overset{i}{\underset{i}{\text{si-oh}}} -\overset{i}{\underset{i}{\text{si-oh}}} -\overset{i}{\underset{i}{\text{si-o-si-}}} + \text{Hoh}$$
$$-\overset{i}{\underset{i}{\text{si-or}}} -\overset{i}{\underset{i}{\text{si-o-si-}}} -\overset{i}{\underset{i}{\text{si-o-si-}}} + \text{Hor}$$

Scheme. 1.23. Polycondensation reactions of silanes.

The polycondensation reactions or gelation involve hydroxyl groups and result in M-O-M' linkages which, in turn, yield a three-dimensional network. The gel state is then best described as a viscoelastic material composed of interpenetrating solid and liquid phases.¹⁶⁷ The physical characteristics of the gel network depend greatly upon the size of particles and extent of cross-linking prior to gelation. At gelation, the viscosity increases sharply, and a solid object is obtained.

For alkoxysilane-based gels, size, structures and cross-linking of polymers are dependent on the ratio of the SiOR-to-SiOH hydrolysis rate and the rate of condensation. During acidcatalyzed sol-gel conditions, a fast protonation of the alkoxy group is formulated as a first step. The alkoxy group is substituted by water according to an SN2 reaction accompanied by inversion of the silicon tetrahedron. Acid-catalyzed condensation is directed preferentially towards the ends of oligomers resulting in a preferred formation of linear polymers. At basic conditions, polycondensation is much faster than at acidic conditions and the reactivity increases with a decreasing number of alkoxy groups. A nucleophilic hydroxyl anion interacts with the silicon of the alkoxysilane. The hydrolysis reaction proceeds via a pentavalent negatively charged intermediate. Condensation of the silanols preferentially continues along the inner centers of oligomers and not at the ends, which results in highly branched dense polymers. The branched nanostructures lead to the formation of small, spheric particles (Figure 1.24.).^{168,169}



Figure 1.24. Gel structure: crosslinked linear chains (left); branched clusters (right).

The gelation step is followed by aging, which involves maintaining the gel for a period of time, hours to days, completely immersed in liquid. During aging, polycondensation continues along with localized solution and reprecipitation of the gel network, which increases the density of crosslinking and decreases the porosity. The strength of the gel thereby increases with aging. An aged gel must develop sufficient strength to resist cracking during drying.¹⁶⁴

The wet gel, obtained after the aging step, is not the final product. In fact, a drying stage is necessary and depending on the thermal treatment performed, wide variety of products can be obtained like glass or ceramic. In the drying process, the aged gel is heated at about 100° C to allow the desorption of water and residual alcohol physically linked to the polymeric network. Many difficulties arise during the drying stage, mainly caused by the removal of large amounts of solvent trapped in the polymeric network. The transformation of the wet gel into dried gel leads to a volume decrease, and it is often associated with the formation of cracks. This can be avoided by controlling the drying by i) decreasing the liquid surface energy by addition of surfactants or elimination of very small pores, ii) by hypercritical evaporation, which avoids the solid-liquid interface, iii) obtaining monodisperse pore sizes by controlling the tracts of hydrolysis and condensationor iv) drying by slow heating rate v) and for coatings, the thickness usually must not exceed 10 μ m. ¹⁶⁴ Usually, the dried gel is annealed in the temperature range 300–500 °C to remove the residual organic groups. During these heat-treatments, condensation reactions among residual alkoxides groups, both on surface and inside the gel, can take place.

1.3.3 Triethoxysilane functional fluoropolymers

1.3.3.1 Introduction of triethoxysilane onto PCTFE surface.

The interest of using chemically resistant (unreactive) polymers for applications in surface protection is very interesting. Fluoropolymers also brings hydrophobicity as an added value for their applications for substrate coatings. Based on these concepts Lee *et al.* reported the design and synthesis of a poly(chlorotrifluoroethylene) PCTFE film that possess a strong adhesive property to glass via silane coupling agent.²⁸ First, PCTFE-OH film samples were prepared by the oxidation of the polymer using chromium(V1) oxide. The OH modified films was then reacted with a mixture of dibutyltin dilaurate (catalyst) and (3-isocyanatopropyl)triethoxysila in THF to obtain PCTFE polymer functional with triethoxysilane via a urethane linkage. The

pedant triethoxysilane groups was then hydrolyzed by placing the films in 0.05 M HCl for 24 h. The obtained film was sandwiched between two layers of glass and Mylar films and placed in hydraulic press at 80 °C, and 500 psi of pressure was applied for the first 4 hours followed by 100 psi for the next 8 hours. The author claims that urethane is the sole product of this reaction and that the triethoxysilane moiety does not condense with surface hydroxyl groups on the polymer films under these conditions. This was proved by IR spectroscopy by the loss of hydroxyl groups in PCTFE-OH (band at 3335 cm⁻¹) and presence of the urethane N-H stretching modes (3450 cm-' (free N-H) and 3341 cm-' (hydrogenbonded N-H). The adhesive strength of such polymers was also noted, and the results showed superior adhesion to glass in which the obtained film couldn't be removed without damaging it, in comparison, films of PCTFE and PCTFE-OH showed no adhesion and pealed directly off the glass thus showing that the presence of triethoxysilane is the main cause of such strong adhesion of these films.

1.3.3.2 fluorescein functional expanded poly(tetrafluoroethylene) (ePTFE) via a silane linkage.

Vargo *et al.* previously reported the functionalization of the surface of expanded poly(tetrafluoroethylene) (ePTFE) films with OH groups via the radio frequency glow discharge plasma treatment (RFGD).³³ The author went on to exploit the presence of such groups that act as an anchoring point by their reaction with functional silanes. In fact, they showed that it is possible to efficiently introduce a fluorescein FITC group onto aminopropyltriethoxysilane by its reaction with fluorescein-isocyanate to prepare FITC-APTES.³⁴ The OH functional ePTFE films was then dip coated with a solution of 1% of FITC-APTES in hexane, however the author mentions that no refluxing, stirring, or hydrolytic catalysis is required to hydrolyze the triethoxysilane group. Finally, the study mentions that the washing of the coated films with NaOH (0.1 M) till the loss of its fluorescence, allows the determination of the amount of OH groups present on the starting films, However the author might be a little bit optimistic by assuming that no more free OH groups are present on the

surface of the films and that the concentration of FITC groups correlates to that of initial OH. In addition, no Yields, percent, or any specific data was given throughout the study. The author proposes that such films can find applications in antifouling applications.

Another approach for the modification of PTFE to carry abundant surface hydroxyl groups was investigated by Kallury *et al.*³⁵ in which they used aluminum deposition and subsequent washing with NaOH to introduce the required OH groups into the surface of Teflon. The authors aim was the introduction of amino moieties for the immobilization of amino acids or enzymes through their carboxylic acid side group onto the surface of Teflon which acts as a substrate (Scheme 1.24.).



Scheme 1.24. Generation of amino functional Teflon surface.

In order to avoid any undesired side products, first, the amino group of 11- aminoundecanoic acid has to be protected by trifluoroacetyl protective group. This as followed by the modification of the carboxylic acid side group into an acyl chloride, that reacts to the amine group of APTES in the presence of triethyl amine as a catalyst. Tinally the trifluoroacetyl protective group was removed by treatment with aqueous methanolic potassium carbonate to obtain the desired Teflon product. This system was used for the immobilization of Urease is a

nickel-dependent metalloenzyme, through the amine function present on the substrate surface.³⁵

1.3.3.3 FEP Surface Refunctionalization

The same team of Vargo *et al.* followed the same approach as with PTFE (see section 3.3.2) for the functionalization for silane functionalization of Poly(tetrafluoroethylene-co-hexafluoropropylene) FEP.^{36,170} The same approach was employed in which plasma treatment (RFGD) was used to introduce OH onto FEP surface followed by the incorporation of APTES onto its surface (Figure 1.25.). These films was then attached to a polystyrene dish and sterilized with 0.1 N hydrochloric acid or 70% ethanol for 1 h. Mouse neuroblastoma was then cultured on the dish, and results showed that these cells adsorbs very well to the surface of the film and in some cases neurite outgrowth only at surface chemically modified regions.^{36,170}



Figure 1.25. X two-step method for refunctionalizing fluoropolymers with aminopropyl triethoxysilane.

1. Conclusion

Fluoropolymers are unique class of polymers that due to their desirable properties found applications in various applications. However, these polymers suffer from high crystallinity, poor solubility in organic solvents, and lack of functionality. To overcome these drawbacks, the focus on the copolymerization of these polymers with functional monomers have grabbed the attention of researchers. Because of its excellent properties, PVDF a member of the fluoropolymer's family, a rising interest is given to the functionalization of this monomer. Despite the plethora of functions that have been introduced into PVDF, few examples have been present for its functionalization with phosphonate or triethoxysilane groups. Since a phosphorous function usually brings various unique properties (flame retardancy, anticorrosion, dental applications, chelation and electron conductivity in fuel cell membranes), it is of interest to prepare phosphonate functional PVDF to assess the synergistic effects of the F and P atoms. In addition, a triethoxysilane can facilitate the crosslinking of such polymers and a unique mixtures of properties could be achieved by combining all of these groups in one polymer.

A promising approach for the preparation of such functional co/terpolymers is by the copolymerization of VDF with MAF-esters containing either phosphorous or silicon. Other commercially available functional monomers could also prove viable for the preparation of phosphorous and silicon functional PVDF. The obtained co/terpolymers would be studied for various applications such as anticorrosion of steel, enhanced adhesion to substrates and lanthanides extraction. But first it is quite interesting to deeply study the kinetics of polymerization of VDF with the MAF esters to better understand how they behave through a polymerization reaction, which will be the focus of the next chapter.



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"Kinetics of Radical Copolymerization of Vinylidene fluoride with *tert*-butyl 2trifluoromethyl Acrylate A Suitable Pair for the Synthesis of Alternating Fluorinated Copolymers " Mohammad Wehbi *et al.*, *Polym. Chem.*, 2018, **9**, 3754-3761.

2.1. Abstract

The kinetics of radical copolymerization of vinylidene fluoride (VDF) with *tert*-butyl 2trifluoromethacrylate (MAF-TBE) initiated by *tert*-butyl peroxypivalate in solution is presented. The evolutions of the microstructure and molecular weights of such resulting poly(VDF-*co*-MAF-TBE) copolymer were monitored by ¹⁹F nuclear magnetic resonance spectroscopy and by gel permeation chromatography over the whole conversion range. In the early stage of the polymerization, an equimolar composition of VDF and MAF-TBE in the copolymer was observed till the total conversion of the latter. Subsequently, polymerization of VDF was achieved leading to a mixture of poly(VDF-*alt*-MAF-TBE) copolymers and PVDF homopolymer chains. Closer investigation of the copolymerization was performed by synthesizing a series of seven copolymerization reactions from initial [VDF]_o/[MAF-TBE]_o molar ratios ranging between 25/75 and 90/10. The kinetics of copolymerization led to the assessment of the reactivity ratios of both comonomers according to the Mayo-Lewis method and yielded r_{VDF}=0.0399 and r_{MAF-TBE}=0.0356, at 57 °C, evidencing of an alternating copolymerization. Q and e values of MAF-TBE were deduced to be 1.312 and 3.0, respectively.

2.2. INTRODUCTION

During the last decades, fluorine-containing monomers and polymers have been the epicenter of extensive research due to their outstanding properties for high value added applications. The unique properties of fluoropolymers emerge from the strongly polarized C-F bond that induces a strong and short bond (~490 kJ mol⁻¹) due to its highly ionic character. This characteristic render these materials attractive for a wide range of special applications such as petrochemicals, textile, aeronautics, aerospace, optics, textile, chemical engineering, microelectronics, automotive, and building industries.^{49,171-173}

Fluorinated monomers consist of conventional olefins or alkenes, or commercially available (meth)acrylic, styrenic, or cyclic monomers that contain one or several fluorine atoms. Conventional polymerization methods have been mainly used for the polymerization of these elegant monomers. However, in the last few years, substantial progress has been reported of their (co)polymerization via controlled radical polymerization methods such as iodine transfer polymerization,¹⁰⁸ RAFT,^{88,174,175} and organometallic polymerizations.¹⁷⁶

Among commercially available functional monomers, *tert*-butyl 2-trifluoromethacrylate (MAF-TBE) is a valuable fluorinated monomer which has been widely used for photoresist applications.^{60,177-180} A main characteristic of 2-trifluoromethylacrylates and hence MAF-TBE is that they fail to homopolymerize under radical conditions,^{89,181} while anionic polymerization is successful.^{83,84} Therefore, MAF-TBE has been vastly copolymerized with a plethora of fluorinated or non-fluorinated monomers, such as methacrylonitrile,¹⁷⁷ vinyl ethers,¹⁸² 3,4-dihydrofuranes,^{182,183} α -olefins,¹⁸⁴ fluorinated monomers,^{185,186} and norbornenes¹⁸³ resulting in random or alternating copolymers. On the other hand, VDF is a well-known fluorinated monomer, the homo- and copolymers of which are synthesized *via* traditional radical polymerization approaches.^{8,108,176,187-190} PVDF has shown interesting properties such as chemical resistance to acids and organic solvents, thermal stability, low dielectric constants

and dissipation factors, excellent weather or age resistance.^{8,11,173} However, as many fluorinated homopolymers, PVDF exhibits several disadvantages such as a high crystallinity, a lack of functionality and difficulty to cross-link. Previous studies indicated that MAF-TBE is a suitable candidate for a successful copolymerization with VDF which after hydrolysis of the *tert*-butyl groups can be further functionalized giving to the copolymer the desired properties.^{60,80,86,88}

Though such interesting applications have been highlighted for both monomers, limited references have been reported in the academic literature regarding their copolymerization. First, the radical copolymerization of VDF with MAF-TBE was investigated in the presence of a branched perfluoro-3-ethyl-2,4-dimethyl-3-pentyl persistent radical that releases an efficient source of •CF₃ radicals able to initiate the copolymerization. The molecular weights of the resulting poly(VDF-co-MAF-TBE) copolymers were calculated via ¹⁹F NMR spectroscopy and ranged from 22,000 to 105,000 g mol^{-1,191} In a related study,⁸⁰ radical copolymerization of VDF with MAF-TBE was investigated under various experimental conditions: initiators, temperatures, and solvents. Polymerization using peroxides produced poly(VDF-co-MAF-TBE) copolymers with different molar compositions in satisfactory yields having a high VDF content. Subsequent hydrolysis of ester groups enhanced the hydrophilicity of these copolymers as it was evidenced by water contact angle studies.⁸⁰ A more detailed study of the RAFT copolymerization of VDF with MAF-TBE was reported,⁸⁸ initiated by bis (4-tertbutyl cyclohexyl) peroxydicarbonate and controlled by 2-mercaptopropionic acid methyl ester O-ethyl dithiocarbonate (i.e. xanthate) as chain transfer agent. Results have shown relatively high yields and molar masses that ranged between 1,500 to 5,000 g mol⁻¹ while dispersity were lower than 2. The livingness of macroradicals was tested by further sequential controlled radical (co)polymerizations of vinyl acetate (VAc) or VDF that led to poly(VDF-co-MAF-TBE)-b-PVAc and poly(VDF-co-MAF-TBE)-b-PVDF block copolymers, respectively. The

block copolymers were obtained with well-defined molecular weights and still narrow dispersities as evidenced by gel permeation chromatography. However, all the aforementioned reports do not investigate in depth the copolymerization of both fluorinated monomers.

Towards this direction, this chapter deals with the kinetics of radical copolymerization of VDF with MAF-TBE. The evolutions of molecular weights and molar compositions of the resulting poly(VDF-*co*-MAF-TBE) copolymers were studied by *in situ* gel permeation chromatography and ¹⁹F nuclear magnetic resonance spectroscopy, respectively. The Mayo-Lewis model was used to calculate the reactivity ratios of both fluorinated comonomers. Moreover, Alfrey and Price equation enabled to determine the Q and e values of both comonomers. Interestingly, it was found that the copolymerization of this fluorinated monomer pair showed a tendency of cross-propagation leading to alternating copolymers.

2.3. Results and discussion

2.3.1. Kinetics of conventional copolymerization of VDF with MAF-TBE

The conventional radical copolymerization of VDF with MAF-TBE was performed in dimethyl carbonate (DMC) using *tert*-butyl peroxypivalate (TBPPi) as initiator at 57 °C (Scheme 2.1.), from an initial [VDF]_o/[MAF-TBE]₀ molar ratio of 90/10. At that temperature, the half-life of the initiator corresponds to ca. 10 h.

$$H_{2}C=CF_{2} + H_{2}C=CF_{2} + H_{2}C=CF_{2} + H_{2}C=CF_{2} + H_{2}C=CF_{2} + H_{2}C=CF_{2} + CH_{2}-CF_{2} + CH_{2}-CF_{2$$

Scheme 2.1. Conventional radical copolymerization of VDF with MAF-TBE initiated by *tert*-butyl peroxypivalate (TBPPi) in dimethyl carbonate (DMC).

In order to get a deeper insight on the copolymerization of VDF with MAF-TBE, a kinetic study was performed covering the whole conversions of comonomers. Thus, aliquots were collected from the autoclave throughout the course of the reaction and characterized by GPC in order to monitor the evolution of the number average molecular weights (M_n) and dispersities (M_w/M_n) as a function of polymerization time. Specifically, in order to investigate further the critical early stage of the polymerization, aliquots were taken every 15 min for the first hour of polymerization and subsequently every hour till the end of the reaction (after 7 h). At this point, it should be stressed that the collection of aliquots did not induce any significant effect on the progress of the polymerization as it can been clearly seen from the graph of the recorded pressure of the autoclave as a function of polymerization time where a smooth exponential decay is noted. (See Appendix 1 Figure S2.3). The GPC profiles of the aliquots taken during the copolymerization displayed unimodal distributions (Figure 2.1a). The GPC eluograms exhibited negative refractive index signals because the refractive index increment of PVDF in DMF is negative and confirms previous studies.¹⁹²⁻¹⁹⁴ Figure 2.1b illustrates the evolution of M_n s and M_w/M_n s versus the polymerization time (Table 1). It can been clearly observed that even in a very early stage of polymerization (15 min), high-molecular weight (20,500 g/mol) poly(VDF-co-MAF-TBE) copolymers were formed with relatively low dispersities, which is a well-known characteristic of free radical polymerization.¹⁹⁵ The M_n s increased up to 1 h where a maximum value was reached (24,100 g/mol) followed by a linear decrease from 24,100 to 11,200 g/mol accompanied with a simultaneous increase of dispersity (Figure 2.1b) as the polymerization progressed. A possible explanation of this behavior might be attributed to transfer reactions leading to the interruption of the growth of the polymer chain resulting in a decrease in the size of propagating chains.¹⁹⁵ During this process, new radicals were formed, able to reinitiate the polymerization with consequent limitation of the molecular weights and

thus a broadening of the dispersity. The above hypothesis is further supported by the noticeable growth of the dispersity (from 1.31 to 1.78) during the course of the polymerization.



Figure 2.1 a) GPC eluograms of poly(VDF-*co*-MAF-TBE) copolymers b) Number-average molecular weights and dispersities at different polymerization times, for the conventional radical copolymerization of VDF with MAF-TBE.

¹⁹F NMR spectroscopy enables to monitor the evolution of the molar composition of poly(VDF-*co*-MAF-TBE) copolymers during the polymerization. Figure 2.2 exhibits a stack of the ¹⁹F NMR spectra of the synthesized copolymers for different interval periods.



Figure 2.2 Stack of ¹⁹F NMR spectra of crude poly(VDF-*co*-MAF-TBE) copolymers at different polymerization times recorded in DMF-d₇ at room temperature.

At the early stage of polymerization, specific signals assigned to both VDF and MAF-TBE units in the copolymer are clearly observed. Specifically, a broad peak at -93.8 ppm assigned to $-CF_2$ group of VDF in VDF-MAF-TBE dyad³¹ while the broad signal at -68 ppm assigned to the fluorine atoms in $-CF_3$ of MAF-TBE. A smaller peak centered at -66 ppm might be attributed to the reversible addition of MAF-TBE.⁸⁸ The sharp peak at -65 ppm is characteristic of residual MAF-TBE monomer. After 2 h of polymerization, a new peak at -92.5 ppm assigned to the normal addition or head-to-tail (H-T) of VDF–VDF dyads ($-CH_2-CE_2-CH_2-CE_2-)_n$ accompanied by the appearance of two new high field peaks at -114 and -116 ppm attributed to the reverse head-to-head (H–H) VDF–VDF dyads ($-CH_2-CE_2-CH_2-)_{.88,188,189,196,197}$ Moreover, at the same time, the subtle appearance of a doublet of multiplets centered at -115.5 ppm is attributed to chain transfer reactions ($CF_2-CH_2-CE_2-H$) or back-biting.³³ The assessment of the molar composition of each monomer was determined by comparing the integrals of the signals characteristic for VDF and MAF-TBE units which are present at each stage of polymerization (eq. 2.3 in the experimental section). The results are summarized in Table 2.1.

Entry	Polymerization time (h)	VDF composition (mol %) ^a	M_n (g/mol) ^b	$M_w/M_n^{ m b}$	
1	0.25	48	20,500	1.31	
2	0.5	47	21,700	1.30	
3	0.75	49	24,100	1.29	
4	1	52	24,100	1.34	
5	2	61	23,500	1.48	
6	3	87	19,700	1.53	

Table 2.1 VDF compositions, number average molecular weights, and dispersities of the conventional radical copolymerization of VDF with MAF-TBE in DMC at 57 °C at different polymerization times.

7	4	91	17,200	1.58
8	5	89	16,800	1.51
9	6	89	15,200	1.62
10	7	90	11,200	1.78

^a Calculated by ¹⁹F NMR (from eq. (2.3) in experimental section), ^b determined by GPC calibrated with PMMA standards.

Figure 2.3 illustrates the mole fraction of VDF in the poly(VDF-*co*-MAF-TBE) copolymers *versus* polymerization time as it was evaluated by ¹⁹F NMR spectroscopy. These results showed that the composition of VDF and MAF-TBE in the copolymer during the first hour of polymerization has almost one-to-one ratio suggesting that the monomers copolymerize each other forming alternating copolymers. As the polymerization proceeds, the molar ratio of VDF gradually increases to finally obtain the theoretical molar ratio (90%). The latter hypothesis is also supported by ¹⁹F NMR spectra where signals assigned to VDF-MAF-TBE dyads are only present up to 1 h of polymerization. After this period, the concentration of MAF-TBE has significantly depleted as evidenced by the absence of signal at -65 ppm. At the same time, the presence of new peaks centered at -92.5, -113 and -116 ppm are attributed to the normal H-T addition and reversed H–H VDF–VDF dyads, respectively. This is due to the enrichment of the alternating copolymers with VDF monomer units and the formation of new PVDF chains. At this point is should be stressed that the *M_n* reached a maximum value during the copolymerization of MAF-TBE and VDF and subsequently decreased as the polymerization of VDF progressed.



Figure 2.3 Molar ratio of VDF in the poly(VDF-*co*-MAF-TBE) copolymers *versus* polymerization time.

2.3.2. Mechanism of polymerization

Scheme 2.2 illustrates a schematic presentation of the possible routes during the first stage of the radical copolymerization.



Scheme 2.2 Propagations of VDF or MAF-TBE monomers during the first steps of conventional radical copolymerization.

The mechanism of the radical copolymerization of VDF and MAF-TBE is shown in Scheme 2.2. As the temperature of the reaction approach 57 °C, TBPPi dissociate releasing radicals that could initiate the reaction. These radicals can initiate the polymerization reaction by their addition to either VDF or MAF-TBE, generating propagating radicals A and B, respectively. The radical A can react either onto VDF or onto MAF-TBE. However the results obtained from ¹⁹F NMR spectroscopy, it is observed the absence of the characteristic signal assigned to VDF H-T (92.5 ppm) addition up to 2h. Therefore MAF-TBE is much more reactive than VDF with respect to radical A. Radical B cannot react with MAF-TBE since this monomer can not homopolymerize,^{15,16} but react efficiently with VDF. Both routes lead to the formation of propagating macroradical which are C and D. Iterative step-wise cross propagation occurs forming alternating poly(VDF-*alt*-MAF TBE) copolymers up to high molecular weights (M_n =24,100 g/mol).

2.3.3. Determination of the reactivity ratios of VDF and MAF-TBE

In order to further support our assumptions of the alternation of VDF and MAF-TBE, the monomer reactivity ratios were determined using eq 3 (in general experimental setup and characterizations section in the annexe). Therefore, a series of seven poly(VDF-*co*-MAF-TBE) copolymers was synthesized from initial [VDF]₀/[MAF-TBE]₀ molar ratios ranging from 25/75 to 90/10 in DMC. The copolymer conversion was limited to less than 10% to minimize the drift of copolymer makeup. Table 2.2 lists the reactivity ratios obtained for different fluorinated monomers bearind a CF₃ at the ethylene double bond. The traditional way to compare the reactivity of these monomers towards a macroradical terminated by VDF is to consider $1/r_{VDF}$ and thus a higher tendency for cross propagation. Values greater than 1 indicate a higher reactivity of M comonomers toward such a macroradical. Hence, the increasing reactivity

series of the comonomers is as follows: $CH_2=C(CF_3)F < CH_2=C(CF_3)CO_2H < CH_2=(CF_3)CH < H_2C=C(CF_3)_2 < CH_2=C(CF_3)CO_2t$ -Bu, showing that MAF-TBE appears as an excellent partner comonomer of VDF. This alternation seems still difficult to explain from conventional theories of the electronic delocalization of fluoromonomers and from known rules of alternation.

Table 2.2 Monomer reactivity ratios and polymerization temperatures from the radical copolymerization of VDF with other monomers (M).

$\mathbf{P} \stackrel{\text{in}}{=} \mathbf{R}$	T (°C)	r _{VDF}	r _M	1/ r _{VDF}	ref
K III K					
 F	74	0.76	1.23	1.31	197
CO ₂ H	55	0.33	0	3.03	85
Н	75	0.28	2.35	3.57	198
CF ₃	-15 to 80	0.136	0.047	7.35	199
CO ₂ t-Bu	57	0.039	0.035	25.64	This work

The Q-e values of a monomer refer to its stabilization by resonance and polar effects, respectively. They were calculated for MAF-TBE using Alfrey and Price equations (eq. 2.1-2.2).²⁰⁰

$$r_{VDF} = \frac{Q_{VDF}}{Q_{MAF-TBE}} \exp[-e_{VDF}(e_{VDF} - e_{MAF-TBE}) \qquad (eq. 2.1)$$

$$r_{MAF-TBE} = \frac{Q_{MAF-TBE}}{Q_{VDF}} \exp[-e_{MAF-TBE}(e_{MAF-TBE} - e_{VDF}) \qquad (eq. 2.2)$$

According to the literature, Q-e values of VDF have been reported to be 0.015 and 0.5, respectively.²⁰¹ The latter values were incorporated to equations 3 and 4 for the calculation of the respective Q-e values of MAF-TBE which were found to be 1.3 and 3.0, respectively which are in accordance with previous reported values of MAF-TBE.^{181,202,203}

At this point, it should be stressed that the e values of both monomers do not exhibit opposite signs which is a point of prime importance in order to rationalize theoretically their tendency toward alteration during the polymerization. However, this peculiar behavior is also observed for the radical VDF and hexafluoroisobutylene (HFiB) that leads to commercially available alternating copolymers under the CMX[®] trademark, as well as copolymers of MAF and MAF-TBE with other fluorinated monomers that show such a tendency (Table 2.3). These results are rather unexpected and the actual mechanism for this behavior remains speculative. Deeper theoretical calculations deserve to be achieved to support such a hypothesis. The experimental results provided compelling evidences and confirmed that MAF-TBE and VDF indeed form perfect alternating copolymer structure in the whole tested range of comonomer feeds.

Table 2.3 Monomers reactivity ratios (M_i) and Q-e values of conventional radicalcopolymerization of VDF with MAF and MAF-TBE with other fluorinated monomers.

M_1	M ₂	\mathbf{r}_1	r ₂	\mathbf{Q}_1	e ₁	Q ₂	e_2	Ref
MAF	VDF	0.000	0.330	0.150	2.94	0.015	0.5	85
MAF	VDF	0.000	1.600	0.020	2.59	0.015	0.5	204
HFiB	VDF	0.047	0.136	0.330	2.74	0.015	0.5	199
FAV8	MAF-TBE	0.030	0.00	0.008	0.15	1.300	3.0	205
FATRIFE	MAF-TBE	0.000	1.720	0.240	1.27	1.300	3.0	206
VDF	MAF-TBE	0.039	0.035	0.015	0.50	1.312	3.0	This work

3,3,3,4,4,4-hexafluoroisobutylene (HFiB), 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-(vinyloxy)decane (FAV8), 2,2,2-trifluoroethyl-fluoroacrylate (FATRIFE)

2.4. Experimental

2.4.1. Materials

Tert-butyl 2-trifluoromethacrylate (MAF-TBE) and 1,1-difluoroethylene (VDF) were kindly provided as gifts from Tosoh FineChemicals Corproration (Shunan, Japan) and Arkema (Pierre

Bénite, France), respectively. *Tert*-butyl peroxypivalate (TBPPi, 75%) was purchased from AkzoNobel. ReagentPlus grade dimethyl carbonate (DMC, >99%, Merk), dimethylformamide (DMF, 99.9%, Merk) and *n*-pentane (95%, Sigma Aldrich) were used as received. Deuterated dimethylformamide 99.5% (DMF-*d*₇) used for NMR spectroscopy was purchased from Euroiso-top.

2.4.2. Radical Copolymerization of VDF with MAF-TBE

First check section 3 autoclave operations in General Experimental setup and Characterizations (annexe). Initially, a solution of TBPPi (0.362 g, 2.08 mmol, 1 mol % to monomers mixtures) and MAF-TBE (4.00 g, 20.1 mmol) were added in a round bottom Schlenk flask equipped with a stir bar followed by the addition of DMC (70 mL) and the mixture was degassed by bubbling nitrogen for 30 min. The solution was then introduced into the autoclave through a funnel tightly connected to the inlet valve of the autoclave. The reactor was then cooled in a liquid nitrogen bath, and VDF gas (12.00 g, 187.5 mmol) was transferred into it under weight control. Subsequently, the autoclave gradually heated to 57 °C while the reaction solution was mechanically stirred. During the polymerization, aliquots were taken rapidly through a special steel pipe adapted on the outlet valve at an interval of 15 min until the first hour of polymerization and then after 1 h and were immediately frozen in liquid nitrogen to quench the polymerization. Finally, the polymerization was terminated by immersing the autoclave in an iced bath and after depressurization was opened to air. The purified product was obtained after two repeated precipitations in chilled pentane and was recovered by centrifugation followed by drying under vacuum overnight and was characterized by ¹H and ¹⁹F NMR spectroscopy and GPC.

¹H NMR (400 MHz, DMF- d_7 , appendix 1 Figure S2.1), δ :1.50 (s, 9H, CH₂C(CF₃)(CO₂C(C<u>H</u>₃)₃) of MAF-TBE); 2.30 to 2.50 (m, $-CF_2CH_2-CH_2CF_2-$ reverse VDF-VDF T-T dyad addition); 2.70 to 3.20 (m, $-CH_2CF_2-CH_2CF_2-$, normal VDF-VDF H-

T dyad addition); 2.90 (s, 2H, $-C\underline{H}_2C(CF_3)(CO_2C(CH_3)_3)$ of MAF-TBE); 6.05 to 6.45 (tt, ${}^2J_{HF}$ = 55 Hz , ${}^3J_{HH}$ = 4.6 Hz), $-CH_2CF_2-\underline{H}$ end-group originated from the transfer of proton to solvent or polymer or from the back biting.²⁰⁷

¹⁹F NMR (376 MHz, DMF-*d*₇, appendix 1 Figure S2.2), δ : -66.5 (-C<u>F</u>₃ of MAF-TBE reverse addition to VDF); -68.4 (-C<u>F</u>₃ of MAF-TBE normal addition to VDF); -92.5 (-CH₂C<u>F</u>₂-CH₂C<u>F</u>₂- normal VDF gamma H-T dyad addition); -92.9 (-C<u>F</u>₂ of VDF in -CH₂C<u>F</u>₂-CH₂CF₂-CF₂-CH₂-); -93.8 (-C<u>F</u>₂ of VDF in VDF-MAF-TBE dyad); -95.5 (-CH₂C<u>F</u>₂-CH₂C<u>F</u>₂- normal VDF beta H-T dyad addition); -114.5 (-CH₂C<u>F</u>₂-CF₂CH₂-CH₂, reverse VDF-VDF H-H dyad addition); -115.4 (dtt, ²J_{HF} = 55 Hz, ³J_{HF} = 16 Hz and ⁴J_{FF} = 6 Hz, CF₂-CH₂C<u>F</u>₂-H, chain-end from transfer); -116.8 (-CH₂CF₂-C<u>F</u>₂CH₂-CH₂, reverse VDF-VDF H-H dyad addition).

The molar fractions of VDF base units in the copolymer were determined using equation (2.3) by taking the ratios of the integrals of all signals of $-CF_2$ in VDF monomer units with respect to those of the signals of $-CF_3$ on MAF-TBE units in the ¹⁹F NMR spectra:^{17,80,88,204}

mol% VDF in copolymers =
$$\frac{(\int_{-92.5}^{-96} CF_2 + \int_{-113}^{-118} CF_2)/2}{(\int_{-92.5}^{-96} CF_2 + \int_{-113}^{-118} CF_2)/2 + \int_{-66}^{-71} CF_3/3} \times 100 \qquad \text{eq. (2.3)}$$

2.4.3. Determination of the reactivity ratios of VDF and MAF-TBE

In order to determine the reactivity ratios of VDF and MAF-TBE, seven copolymerizations of VDF with MAF-TBE were performed at various [VDF]_o/[MAF-TBE]_o molar feed ratios (25/75, 40/60, 50/50, 60/40, 70/30, 80/20, 90/10) as described in section 4 Determination of the reactivity ratios in General Experimental setup and Characterizations section. In all cases the concentration of monomers to solvent was kept constant to 0.42 gr/mL in order to ensure similar polymerization conditions for all the polymerizations. TBPPi (1 mol % to monomers mixtures) was employed as an initiator and DMC as a solvent.

2.4.4. Characterizations

All performed characterizations are present in the general experimental set up and characterizations (Annexe).

2.5. Conclusion

The present study reports the kinetics of radical copolymerization of MAF-TBE with VDF in DMC using TBPPi as the initiator. GPC studies showed that high molecular weight copolymers were formed in the very early stage of the copolymerization with relatively narrow dispersities. As polymerization proceeded, a decrease of molecular weight was noted with a broadening of the dispersities signifying the presence of chain transfer reactions which in turn led to limitation of molecular weights. The molar compositions of the copolymers, assessed by ¹⁹F NMR spectroscopy, were equimolar in both monomers until MAF-TBE was converted. Subsequently, the reaction progressed by homopolymerization of VDF. The kinetics of radical copolymerization enabled to assess the monomer reactivity ratios equal to rvDF=0.0399 and r_{MAF-TBE}=0.0356 at 57 °C denoting a strong tendency for the formation of alternating copolymers. From the results of the literature, a compared reactivity of $H_2C=C(CF_3)R$ monomers toward macroradicals terminated by VDF was suggested, showing that MAF-TBE is an excellent partner for VDF. Finally, the Q-e values, calculated by Alfrey and Price equations, were in accordance with those mentioned in literature for MAF-TBE. The copolymerization of VDF and MAF-TBE is currently studied via controlled radical copolymerization methods (RDRP) and the results will be described in forthcoming publications.

Chapter III: Poly(vinylidene fluoride) Containing Phosphonic Acid Function for Application as Corrosion Resistance Coating for Steel



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3.1. ABSTRACT

The synthesis of vinylidene fluoride (VDF)-based copolymers bearing pendant phosphonic acid function for potential application as anti-corrosion coatings was achieved via radical copolymerization of VDF with a new phosphorous containing 2-trifluoromethacrylate monomer, (dimethoxyphosphoryl)methyl 2-(trifluoromethyl)acrylate (MAF-DMP). MAF-DMP was prepared from 2-trifluoromethacrylic acid (MAF) in 60% overall yield. Radical copolymerizations of VDF with MAF-DMP using tert-amyl peroxy-2-ethylhexanoate at varying comonomer feed ([VDF]₀/[MAF-DMP]₀) ratios led to several poly(VDF-co-MAF-DMP) copolymers of different VDF molar percentages (79-96%) with molecular weights $(M_n s)$ ranging between ca. 6000 and 10000 g mol⁻¹ and fair yields (47-54%). The compositions and microstructures of all the synthesized copolymers were determined by ¹H and ¹⁹F NMR spectroscopies. The reactivity ratios of this new monomer pair were also determined (r_{VDF} = 0.76 ± 0.34 and $r_{\text{MAF-DMP}} = 0$ at 74 °C). The resulting poly(VDF-co-MAF-DMP) copolymers exhibited high melting temperature (162-171 °C, with respect to the VDF content) and the degree of crystallinity reached up to 51%. The thermal stability of the copolymers increased with incremental VDF content in the copolymer, reaching up to 268 °C, under air. Finally, the pendant dimethyl phosphonate ester groups of poly(VDF-co-MAF-DMP) copolymer were hydrolyzed quantitatively under mild conditions using bromotrimethylsilane to prepare novel phosphonic acid-functionalized PVDF-PA. Compared to hydrophobic poly(VDF-co-MAF-DMP) copolymers (the water contact angle, WCA, was 98°), the hydrophilic character of the PVDF-PA was found to be surprisingly rather pronounced, exhibited lower WCA (15 °). Finally, steel plates coated with PVDF-PA displayed excellent corrosion resistance properties under simulated sea water environment.

3.2. INTRODUCTION

Due to their outstanding strength and ductility, metals are commonly employed in the engineering and construction of industrial materials and structures. steel is widely used as a construction material in industry due to its comprehensive performance, low cost, and good plasticity.²⁰⁸ However, in humid and harsh conditions, the corrosion of steel inevitably takes place, significantly impacting the durability of such materials. Corrosion is usually a phenomenon concerns the metal degradation due to its oxidation by its surrounding environment.²⁰⁹ To reduce the rate of this process, metals are often treated with coatings that protect against such harsh environments.^{210,211} Organic composites with dispersed inorganic fillers such as epoxy (EP) resins are widely used as anti-corrosion coatings due to their favorable mechanical properties, excellent corrosion resistance, and stable chemical properties.²¹²⁻²¹⁴ However, all powerful corrosion inhibitors are harmful to both environment and health because of their toxic and carcinogenic nature.²¹⁵ In recent years, attention has been given to polymers used as anti-corrosion coatings or additives to traditional organic coatings due to them being cheap, easily processed and possess sufficient mechanical strength.^{111,216-218} Several polymer families have been used as anticorrosion coatings such as polyanilines,²¹⁹ polyurethanes²²⁰, polyimides²²¹, and polystyrene (PS)/ graphene-based nanocomposites.²²²

The main property that characterizes a corrosion protective coating is its adhesion to the substrate.¹¹¹ However, Diffusion of water through the coating-metal interface could result in a decrease of adhesion leading to defects of organic coatings related to metal corrosion (e.g., blistering, delamination). Due to the chelating properties of the phosphonate group, phosphorous containing (co)polymers²²³ have been widely studied for anticorrosion applications of steel.^{224,225} In recent years, phosphorus-containing polymers^{110,226,227} have received great interest^{112,228,229} due to their interesting complexing properties²³⁰ and have found

applications as dispersants, corrosion inhibiting agents, for preventing deposit formation,²⁰ as flame retardants,²¹ as adhesion promoters for paints,²² superlubricity coatings,¹¹³ as water repellent and intrinsically photostable coating materials for stone,¹¹⁴ polymer electrolyte membrane fuel cell,²³⁻²⁵ and in biomedical fields.²⁶ Having high hydrophobicity along with impressive mechanical strength and stability, few studies on phosphorous functional fluoropolymers have been reported for anticorrosion applications. Brondino *et al.*²³¹ employed as-synthesized phosphorus-based poly(meth)acrylates as additives in PVDF as a good anticorrosive coating for galvanized steel plates. Timperley *et al.*¹³⁸ reported synthesis of bis(fluoroalkyl)acrylic and methacrylic phosphate monomers and their polymers for potential application as flame retardant.

Poly(vinylidene fluoride) (PVDF) is the second most produced fluoropolymer after polytetrafluoroethylene (PTFE).^{6,7,49} It is prepared from the radical polymerization of VDF^{8,51,52} whose reactivity is close to that of tetrafluoroethylene and chlorotrifuoroethylene, however it is much less dangerous being not explosive and has a lower toxicity (the lethal concentration required to kill 50% of the population, LC50 > 200,000 ppm) than the other two. Thus VDF-based (co)polymers are extensively used in piezoelectric devices,⁵³ binders and separators for Li-ion batteries,^{11,55} membranes for water treatment,^{8,56,57} in petrochemical industry and photovoltaic devices.¹¹ However, PVDF suffers from (i) high crystallinity (leading to increased processing cost), (ii) poor solubility (except in N,N-dimethylformamide, dimethyl sulfoxide and dimethylacetamide), (iii) defficulty in tuning properties for targeted applications (due to the lack of functionality).^{8,11} These above drawbacks can be overcome by (i) incorporating vinyl monomers containing functional groups⁸ (such as hydroxyl, acetoxy,¹² thioacetoxy, ethers, esters, halogens, -CO₂H⁵⁸ or aryl groups as comonomers in the radical copolymerization of VDF or (ii) cross-linking via cure site comonomers containing trialkoxysilane,⁵⁹ cyanato or isocyanato groups or using bisamines or bisphenates.¹⁹ By this approach, some of the properties of the resulting copolymers^{8,50,60} can be improved such as adhesion, thermal stability,¹⁷ conductivity¹⁸ or hydrophobicity,¹⁷ to name a few.

Among, the various comonomers for VDF, 2-(trifluoromethyl)acrylic acid (MAF) and/or alkyl 2-trifluoromethacrylates (MAF-esters) are particularly attractive.⁶⁰ MAF or MAF-esters containing copolymers exhibit outstanding outdoor stability/aging resistance and adhesion property.⁶⁰ Thus, our group has carried out the copolymerization of MAF derivatives with VDF *via* both conventional radical polymerization^{80,85,86} and reversible deactivation radical polymerization (RDRP)^{87,88} techniques. Thus, MAF or MAF-esters have emerged as classic comonomers to prepare functional VDF-based copolymer with tunable properties.

To our knowledge, there is no report of phosphorous functional MAF-ester neither phosphorous containing VDF-based copolymer exhibiting anti-corrosion properties. Therefore, the main objective of this chapter is the development of novel PVDF containing phosphonic acid functionality, as well as use of the resulting copolymers as corrosion resistance coating for steel in marine environment.

3.3. RESULTS AND DISCUSSION

First, the synthetic pathways for dimethoxyphosphoryl)methyl 2-(trifluoromethyl)acrylate (MAF-DMP) monomer are discussed, followed by its radical copolymerization with vinylidene fluoride (VDF). Finally, spectroscopic characterizations, molar masses, thermal and surface properties of the phosphorous containing PVDF are described.

3.3.1. Synthesis of MAF-DMP.

MAF-DMP monomer was first synthesized from 2-trifluoromethyl acrylic acid (MAF) using a strategy described in Scheme 3.1. First, dimethyl phosphite was reacted with paraformaldehyde to obtain dimethyl (hydroxymethyl)phosphonate quantitatively (step A).²³² Parallely, MAF was converted into MAF-COCl using thionyl chloride in 65% yield (step B).¹⁷ Then, the esterification reaction of the as-synthesized dimethyl (hydroxymethyl)phosphonate with MAF-COCl in the presence of pyridine (to trap HCl gas generated during the reaction) led to MAF-DMP (step C) in high purity and fair overall (60%) yield.



Scheme 3.1. Synthesis of MAF-DMP

MAF-DMP was characterized by ¹H, ¹⁹F and ³¹P NMR spectroscopy (Figures S3.2-S3.4, details are provided in the Experimental Section). ¹H NMR spectrum (Figure S3.4) of MAF-DMP exhibits characteristic signals for $-OCH_3$, $-OCH_2PO(OCH_3)_2$ and $H_2C=C(CF_3)(CO_2CH_2PO(OCH_3)_2)$ protons centered at 3.78, 4.53, 6.48 and 6.75 ppm, respectively. The ¹⁹F (Figure S3.5) and ³¹P (Figure S3.6) NMR spectrum displays singlets centered at -67 and 20.50 ppm assigned to the -CE₃ and -P(O)(OCH_3)_2, respectively.

3.3.2. Synthesis of Poly(VDF-co-MAF-DMP) Copolymers.

Initial attempts to homopolymerize MAF-DMP under free radical conditions failed. This was expected and in accordance with earlier literature stating that MAF or MAF-esters does not undergo homopolymerization under radical polymerization conditions.^{17,80,81} The radical copolymerization of VDF with MAF-DMP was initiated by *tert*-amyl peroxy-2-ethylhexanoate (TAPE) at 74 °C in dimethyl carbonate (DMC) (Scheme 3.2).



Scheme 3.2. Radical Copolymerization of VDF with MAF-DMP Initiated by TAPE

DMC was chosen as the polymerization solvent as Asandei's group recently established that it was the most suitable solvent for iodine transfer polymerization of VDF, since it swells VDF well and regarded as a green solvent.^{52,196,233} Furthermore, DMC is regarded as a "green" solvent²³⁴ that swells PVDF. Since VDF is gas, all the copolymerizations were carried out under pressure in autoclaves. The detailed experimental conditions, results and several characteristics of the obtained poly(VDF-*co*-MAF-DMP) copolymers (P1-P5) are summarized in Table 3.1. In all reactions (P1-P5, Table 3.1) an initial increase of pressure with increase in temperature was noted, followed by a decrease of pressure (indicating consumption of the gaseous monomers) along the progress of the copolymerization.

 Table 3.1. Experimental Conditions and Results (Molecular Weights, Dispersities, and

 Thermal Properties) of the Radical Copolymerization of VDF with MAF-DMP^a

entry	VDF mol%		P _{max} ^c (bar)	ΔP^d (bar)	yield (%)	$M_{n,SEC}^{e}$	D^e	<i>T_{d10%}^f</i> (°C)	T_m^g (°C)	χ ^g ([%])
	feed	copolymer ^b								
P1	75	79	18	8	53	9300	1.59	235	171	24
P2	80	83	20	9	50	8200	1.51	241	162	29
P3	85	86	28	19	48	8700	1.54	249	167	30
P4	90	92	29	21	47	5700	1.52	254	165	50
P5	95	96	31	23	51	5900	1.48	268	164	51

Acronyms: VDF: vinylidene fluoride; MAF-DMP: (dimethoxyphosphoryl)methyl-2-(trifluoromethyl)acrylate; TAPE: *tert*-amyl peroxy-2-ethylhexanoate; Solvent, DMC: dimethyl carbonate; Temperature: 74 °C; Time: 16 h. ^aConditions: Solvent used = 25 mL; Initiator = 1.5 mol% with respect to total monomer; ^bCopolymer compositions were assessed by ¹⁹F NMR spectroscopy using equation 2; ^cP_{max}: maximum pressure observed during the polymerization; ^d Δ P: pressure drop observed in the autoclave between maximum pressure and pressure at the end of the polymerization. ^eMolecular weights (*M_n*s) and dispersities (*Ds*) were determined by SEC in DMF using poly(methyl methacrylate) standards. ^fAssessed by thermogravimetric analysis (TGA), under air; 10 °C/min. ^gDetermined by differential scanning calorimetry (DSC); χ : crystallinity determined from equation 1.

In order to study the effect of comonomer feed ratio on the reaction, copolymerizations were carried out using various initial $[VDF]_0/[MAF-DMP]_0$ molar ratios (P1–P5, Table 3.1). In all cases, the poly(VDF-*co*-MAF-DMP) copolymers were obtained in fair to good yields (47-53%). In all cases, VDF content in the copolymer was slightly higher than that in the starting comonomer feed, suggesting higher reactivity of VDF compared to MAF-DMP. Molecular weights (M_n s) and dispersities (Ds) of poly(VDF-*co*-MAF-DMP) copolymers ranged between 5,700 and 9,300 g mol⁻¹, probably caused by the high concentration of initiator and 1.48 to 1.59, respectively, as assessed by size exclusion chromatography (SEC) (Table 3.1 and Figure S3.7).

3.3.3. Characterization of Poly(VDF-*co*-MAF-DMP) Copolymers by ¹H and ¹⁹F NMR Spectroscopies.

P1-P5 copolymers were characterized by ¹H, ¹⁹F, and ³¹P NMR spectroscopy. The ¹H NMR spectrum of the poly(VDF-*co*-MAF-DMP) copolymers (Figure 3.1) mainly exhibits four characteristic signals: (i) at around 2.15-2.40 ppm attributed to the reverse (tail-to-tail, T-T) addition of VDF repeat units ($-CF_2CH_2-CH_2CF_2-$),^{52,86,196,233,235,236} (ii) a small signal at 2.62 ppm assigned to the [$-CH_2CF_2-CH_2C(CF_3)(CO_2CH_2PO(OCH_3)_2)-$]; (iii) a broad signal ranging between 2.70 and 3.20 ppm for the overlapping of normal (head-to-tail, H-T) addition of VDF ($-CH_2CF_2-CH_2CF_2-$), (iv) at around 3.72 ppm attributed to the $-OCH_3$ in phoshonate function and (v) at 4.55 ppm corresponding to the $-OCH_2PO(OCH_3)_2$. A tiny triplet of triplets centered at 6.3 ppm was assigned to $-CH_2CF_2-H$, suggesting negligible transfer to monomer,

solvent or copolymer.237



Figure 3.1. Representative ¹H NMR spectrum of poly(VDF-*co*-MAF-DMP) copolymer prepared by free radical copolymerization of VDF and MAF-DMP using TAPE in DMC at 74 °C (P2, Table 3.1), recorded in DMSO- d_6 at 20 °C. (*) Solvent (DMSO) peak.


Figure 3.2. Representative ¹⁹F NMR spectrum of poly(VDF-*co*-MAF-DMP) copolymer prepared by free radical copolymerization of VDF and MAF-DMP using TAPE in DMC at 74 °C (P2, Table 3.1), recorded in DMSO- d_6 at 20 °C.

The microstructures of the synthesized copolymers were determined by ¹⁹F NMR spectroscopy (see Experimental Section for details). The ¹⁹F NMR spectrum of the poly(VDF-*co*-MAF-DMP) copolymers (Figure 3.2 depicts a representative spectrum) mainly exhibits a number of characteristic signals: (i) at –69 ppm assigned to the fluorine atoms in –CF₃ of MAF-DMP in the copolymer; (ii) at –91.5 ppm attributed to the normal or Head-to-Tail (H-T) VDF-VDF dyads (–CH₂C<u>F</u>₂–CH₂C<u>F</u>₂–) of the PVDF chains; (iii) at –95 ppm corresponding to the fluorine atoms of the –CF₂ groups of VDF in VDF-MAF-DMP alternating dyads,^{85,87,88} (iv) at –113.2 and –116.5 ppm assigned to the reverse or H-H VDF-VDF dyads (–CH₂C<u>F</u>₂–C<u>F</u>₂CH₂–), and (v) a doublet (${}^{2}J_{FH} = 55$ Hz) of triplets (${}^{3}J_{FH} = 16$ Hz) of triplet (${}^{4}J_{FF} = 6$ Hz) centered at -114.8 ppm corresponding to the -CH₂C<u>F</u>₂-H chain-ends.^{60,196,207,233,236,238} The ³¹P NMR spectrum (Figure S3.8) reveals the characteristic signal centered at ca. 20 ppm attributed to the phosphorous atom of the dimethyl phosphonate pendant groups of the MAF-DMP units in the copolymers.

3.3.4. Determination of Reactivity Ratios.

To gain more insight into the copolymerization, the reactivity ratios of VDF/MAF-DMP comonomer couple was determined (details are provided in the Experimental Section Figure S3.1). The copolymer-comonomer composition curve (Figure 3.3) reveals the variation of MAF-DMP content in the copolymer composition vs. the feed composition. These data points fitted with the Mayo-Lewis copolymerization equation (2) (general experimental setup and characterization section in the annexe) provide the following reactivity ratios: $r_{VDF} = 0.76 \pm 0.34$ and $r_{MAF-DMP} = 0$ at 74 °C.



Figure 3.3. Evolution of copolymer-comonomer composition curve at instantaneous composition (<10% conversion) for the radical copolymerization of VDF with MAF-DMP using TAPE as the initiator in DMC at 74 °C.

These values confirm the inability of MAF-DMP to undergo homopolymerization under radical condition, like MAF and other MAF-esters.^{60,81} The reactivity ratio values shows that the copolymers obtained from the copolymerization of MAF-DMP and VDF are random, unlike the alternating ones obtained in chapter 2 with MAF-TBE and VDF. This shows that the reactivity of MAF derivatives with VDF changes greatly upon changing the functional groups on the MAF-esters. This may be attributed to higher transfer, solvent solubility and bulkiness of the ester group. Other comparisons of the obtained reactivity ratios with those of the literature for the radical copolymerization of VDF with other monomers are provided in Table S3.1.

3.3.5. Thermal Properties of Poly(VDF-co-MAF-DMP) Copolymers.

The thermal stabilities of P1-P5 poly(VDF-*co*-MAF-DMP) copolymers were assessed by thermogravimetric analysis (TGA) under air (Figure S3.9). Interestingly, the thermal stability

of the poly(VDF-*co*- MAF-DMP) copolymers increases with increase of VDF content in the copolymer from P1 (79 mol% VDF) to P5 (96 mol% VDF), as evidenced by the $T_{d,10\%}$ (temperature for a 10% weight loss, Table 3.1). VDF-based copolymers bearing *tert*-butyl 2-trifluoromethacrylate (MAF-TBE) revealed a significant weight loss (14%) when the sample was heated just above 150 °C due to the decomposition of the *tert*-butyl ester group into a carboxylic acid group and concomitant release of isobutylene.^{80,239} Whereas, VDF-based copolymer containing a 2-trifluoromethacrylate monomer containing a C₆F₁₃ side chain, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-2-(trifluoromethyl)acrylate (MAF-C₆F₁₃) exhibited superior thermostability and hydrophobicity.¹⁷ Hence, such poly(VDF-*co*-MAF-DMP) copolymers exhibit intermediate thermal stability between those of poly(VDF-*co*-MAF-TBE)^{80,88} and poly(VDF-*co*-MAF-C₆F₁₃).¹⁷

Surprisingly, all the copolymers exhibited melting temperatures (T_m s), as revealed by differential scanning calorimetry (DSC) analysis (Figures S3.8-S3.12) and their crystallinity were determined using equation (1).²⁴⁰ The results revealed that the degree of crystallinity (χ) was increased from 24 to 51% with an increase of VDF mol% in the copolymer from P1 (79 mol%) to P5 (96 mol%).

3.3.6. Synthesis of Phosphonic Acid Functionalized PVDF (PVDF-PA).

Hydrolysis of the dimethyl phosphonate ester groups of poly(VDF-*co*-MAF-DMP) copolymer (P2, Table 3.1) was carried out using bromotrimethylsilane at room temperature (Scheme S3.1, the detailed procedure is given in the Experimental Section), using a modification of the procedure reported earlier by McKenna *et al.*²⁴¹



Figure 3.4. ATR-IR spectra of poly(VDF-*co*-MAF-DMP) copolymer (P2, Table 3.1) before (bottom spectrum) and after hydrolysis (top spectrum) of the phosphonate ester groups.

The presence of dimethyl phosphonate ester group in poly(VDF-*co*-MAF-DMP) copolymer was confirmed in the IR spectrum (Figure 3.4) by the frequencies for ester P=O stretching at 1320 cm⁻¹ and P-O-C stretching bands at 1010 cm⁻¹.^{23,141,242} The successful complete hydrolysis of such a phosphonate ester was confirmed by the vanishing the P-O-C stretching bands and the appearance of O-H stretching frequency. ¹H NMR spectra (Figure S3.15) revealed disappearance of the frequency at 3.72 ppm characteristic of –OCH₃ group of the phosphonate ester of poly(VDF-*co*-MAF-DMP) copolymer, indicating successful hydrolysis of the dimethyl phosphonate ester groups. The extent of hydrolysis was further confirmed by ³¹P NMR analysis. The ³¹P NMR spectrum (Figure S3.8) revealed that the signal of phosphonate function underwent a high field shift from 20.50 ppm to 15.4 ppm after hydrolysis.¹¹⁸ Thus, IR and NMR characterizations confirmed the quantitative hydrolysis of the dimethyl phosphonate ester of the poly(VDF-*co*-MAF-DMP) offering original PVDF-PA.

3.3.7. Thermal Properties of PVDF-PA.

The thermal stabilities of the poly(VDF-*co*-MAF-DMP) copolymers before (P2, Table 3.1) and after hydrolysis of the dimethyl phosphonate groups were studied by thermogravimetric analysis (TGA), under air (Figure 3.5). The TGA thermogram of the poly(VDF-*co*-MAF-DMP) copolymer revealed an initial weight loss above 220 °C , which is likely due to the decomposition of the dimethyl phosphonate ester group to phosphonic acid (Scheme S3.2), as reported in earlier studies.^{23,243,244} This is followed by a rapid continuous weight loss resulting from the cleavage of the CH₂-P linkage between 270 and 330 °C.¹⁴¹

As for PVDF-PA copolymer, a significant loss of 10% between 90 and 200 °C is due to the evaporation of adsorbed water and then a stability is observed up to ca. 265 °C, assigned to the condensation of two phosphonic acid function from two chain resulting in a phosphonic anhydride that yields a crosslinking.²⁴ This is followed by a rapid decomposition above 300 °C. This further confirms the successful hydrolysis of the dimethyl phosphonate ester groups of poly(VDF-*co*-MAF-DMP) copolymer.



Figure 3.5. (A) TGA thermograms of poly(VDF-*co*-MAF-DMP) copolymer (P2, Table 3.1) before (solid line) and after (dashed line) hydrolysis of the phosphonate ester groups, heated at 10 °C min⁻¹ under air.

The DSC analysis of PVDF-PA, poly(VDF-*co*-MAF-PA) copolymer (Figure S3.16) did not reveal the first endotherm, as exhibited by that of the poly(VDF-*co*-MAF-DMP) copolymer at 155 °C (Figure S3.11, P2, Table 3.1). Thus, it was concluded that the initial endotherm in DSC analysis were due to the loss of methyl from the phosphonate esters to form the corresponding phosphonic acids.²³

3.3.8. Surface Properties of the Poly(VDF-co-MAF-DMP) Copolymer

before and PVDF-PA.

The surface properties of the films made from the poly(VDF-*co*-MAF-DMP) copolymer (P2, Table 3.1) and PVDF-PA were examined by means of water contact angle (WCA) measurements. The results were compared to that of pure PVDF (Figure 3.6). Thin films of the polymers were prepared by spin-coating onto a glass slide. Results revealed that, expectedly, the pure PVDF film is hydrophobic, as suggested by the earlier calculations²⁴⁵ (exhibiting a

high WCA value of 130 °). Incorporation of the MAF-DMP moieties onto the backbone of PVDF resulted in a decrease of the hydrophobicity, as evidenced by a WCA value of 98 °.



Figure 3.6. Evolution of water contact angles (WCA) vs. time in case of pure PVDF (a, final WCA = 130°), poly(VDF-*co*-MAF-DMP) copolymer (P2, Table 3.1) before (b, final WCA = 98°) and PVDF-PA (c, final WCA = 15°). The images on the right show the final state of the water drop after 40 s in each case.

Finally, hydrolysis of the dimethyl phosphonate groups of the poly(VDF-*co*-MAF-DMP) copolymer offered the superhydrophilic²⁴⁶ PVDF-PA, displaying a decrease of WCA value with time, to as low as 15 ° after 40 s. This decrease of WCA is indicative of the surfactant property of the phosphonic acid functionalized PVDF which reduces the surface tension of the water droplet. By controlling (i) the MAF-DMP amount in the copolymer and (ii) the extent of hydrolysis of the dimethyl phosphonate ester groups, it could be possible to prepare phosphorous containing "semi-hydrophilic, hydrophilic or super-hydrophilic" PVDF coatings exhibiting tunable wettability.

3.3.9. Adhesion and Anti-corrosion Studies of PVDF-PA Coated Steel.

It was worth attempting to verify if PVDF-PA could increase adhesion^{118,231,247} of PVDF onto metallic substrates. This can be useful in applications in corrosion resistance coatings, proton exchange membranes for polymer electrolyte membrane fuel cells ¹⁴¹, especially to enhance adhesion of electrode materials onto the membrane to favour the electrode membrane assembly, binders for Li-ion batteries and membranes for water treatment.⁵⁰ Thus, the adhesion and anti-corrosion properties of this copolymer were studied.



Scheme 3.3. Procedure for Preparing Coated Steel Plates for Anti-Corrosion Study

For the adhesion and anti-corrosion study, a photocrosslinkable special formulation was prepared in methyl ethyl ketone comprising of PVDF-PA, tri(propylene glycol) diacrylate (TGDPA), 1,4-butanediol diacrylate (BDDA), and 2-hydroxy-2-methylpropiophenone (Darocur 1173) and benzophenone as photoinitiators. Thin films were casted on galvanized steel plates and then UV crosslinked (Scheme 3.3, details are provided in the Experimental Section and S3.2-S3.3). Notably, the coating surface consisted of mostly phosphonic acid

function which is adhering to the steel plate is more hydrophilic (WCA = 41°) compared to the coating surface facing the air (WCA = 93°), consisted of more hydrophobic domains (Scheme 3.3).



Figure 3.7. Status of the steel plate vs. time under marine (simulated sea water) environment during corrosion experiment. (A-C) Steel plates coated with phosphonic acid functionalized PVDF at the start of the experiment (A), after 1 h (B) and after 18 h (C). (D): Uncoated steel plate after 1 h.

Adhesion properties were characterized using the D3359 ASTM standard test method (tape test, Figure S3.17). The terpolymer displayed very good adhesion properties, classified 4 on the ASTM scale (that ranges from 0 to 5, for which 5 indicating the best adhesion properties of the film). This good adhesion property can be ascribed to the chelation of the metal surface atoms by the phosphonic acid groups.

The thickness of the coating was estimated by Scanning Electron Microscopy measurement.

As shown in Figure 3.8, the coating is highly homogenous with a thickness of $85 \,\mu m$.



Figure 3.8. SEM images showing the homogeneity of the coating (left) and the estimation of his thickness (right).

The anti-corrosive behavior of the PVDF-PA was evaluated in accordance with the Salt Spray Test under accelerated conditions in simulated sea water environment (Figure S3.3). Results of corrosion tests on the galvanized steel plates (Figure 3.7) show that the phosphonic acid groups maintain some level of adhesion, thereby preventing the spread of corrosion, whereas bare surfaces were full of corrosion within 1 h only. The coated surface was bright, transparent, and without porosity, even after 18 h.

In order to evaluate the state of the coated and uncoated surfaces, the coating was mechanically removed, and an image of the boundary was achieved by SEM (Figure 3.9). The oxidation level was calculated by the estimation of iron and oxygen contents by means of the Energy X-Ray dispersive spectroscopy (EDXS). It was found that, the Fe/O atomic ratios were 58 and 2 for treated and untreated surfaces, respectively. This results show clearly the efficiency of the coating toward the oxidation of steel.



Figure 3.9. SEM image of the boundary between the uncoated (left) and coated surface (right).

3.4. EXPERIMENTAL SECTION

3.4.1. Materials.

All reagents were used as received unless stated otherwise. 2-trifluoromethyl acrylic acid (MAF) was kindly offered by Tosoh F-Tech Company (Shunan, Japan). 1,1-Difluoroethylene (vinylidene fluoride, VDF) was kindly supplied by Arkema (Pierre Benite, France). *Tert*-amyl peroxy-2-ethylhexanoate (TAPE, 95%) was purchased from AkzoNobel (Chalons sur Marne, France). Dimethyl phosphite (DMP, purity 98%), paraformaldehyde (purity 95%), tri(propylene glycol) diacrylate (TGPDA), 1,4-butanediol diacrylate (BDDA, purity 90%), 2-hydroxy-2-methylpropiophenone (Darocur 1173, purity 97%) and benzophenone (purity ≥99%) were purchased from Aldrich (Aldrich Chimie, 38299 Saint Quentin-Fallavier, France). ReagentPlus grade dimethyl carbonate (DMC, purity >99%), methyl ethyl ketone (MEK), dichloromethane, pyridine, thionyl chloride, hydrochloric acid and laboratory reagent grade methanol were purchased from Sigma-Aldrich. Deuterated chloroform (CDCl₃) and deuterated

dimethyl sulfoxide (DMSO-*d*₆) used for NMR spectroscopy were purchased from Euroiso-top (Grenoble, France) (purity >99.8%).

3.4.2. Characterizations.

The general procedures and conditions for all the characterizations is described in General experimental setup and characterizations section (Annexe).

3.4.3. Synthesis of (Dimethoxyphosphoryl) methyl 2 (Trifluoromethyl) acrylate.

3.4.3.1. Synthesis of Dimethyl (hydroxymethyl)phosphonate (DHP).

Dimethyl (hydroxymethyl)phosphonate (DHP) was synthesized using a method reported earlier by Jeanmaire *et al.*²³² Typically, dimethyl phosphite (20.8 mL, 227 mmol), paraformaldehyde (6.820 g, 227 mmol) and potassium carbonate (1.560 g, 11.3 mmol) were added to methanol (50 mL) in a round bottom flask equipped with a magnetic stirring bar. It was stirred at room temperature for 1 h. The reaction mixture was then filtrated, and the solvent was removed under vacuum in a rotary evaporator. The product, as a colorless liquid, was further dried under vacuum at 50 °C for 16 h.

3.4.3.2. Synthesis of Dimethyl 2-(trifluoromethyl)acryloyl Chloride (MAF-COCl).

The procedure is described in section 2 Modification of MAF into MAF-ester (General experimental setup and characterizations section)

3.4.3.3. Synthesis of Dimethyl (dimethoxyphosphoryl)methyl 2-(trifluoromethyl) acrylate (MAF-DMP).

The procedure of this reaction is described in section 2 Modification of MAF into MAF-ester (General experimental setup and characterizations section) using Dimethyl (hydroxymethyl) phosphonate (20.0 g, 143 mmol), pyridine (12.6 mL, 157 mmol), and MAF-COCl (143 mmol) as reactants and dichloromethane (40 mL) as solvent to obtain MAF-DMP (yield = 60%).

MAF-DMP, as a brownish viscous liquid, was characterized by ¹H, ¹⁹F and ³¹P NMR spectroscopy.

¹H NMR (400 MHz, CDCl₃, δ ppm, Figure S3.4): 3.78 (m, 6H, $-OCH_3$); 4.53 (d, 2H, $-O-CH_2-PO(OCH_3)_2$; 6.48 and 6.75 (2 s, 2H, $H_2C=C(CF_3)(CO_2CH_2PO(OCH_3)_2)$.

¹⁹F NMR (376 MHz, CDCl₃, δ ppm, Figure S3.5): peak centered at -67 (-C<u>F</u>₃).

³¹P NMR (162 MHz, CDCl₃, δ ppm, Figure S3.6): peak centered at 20.50 (-<u>P</u>(O)(OCH₃)₂).

3.4.4. Radical Copolymerization of VDF with MAF-DMP.

A typical copolymerization of VDF with MAF-DMP (P2, Table 3.1) was performed in a 50 mL Hastelloy autoclave Parr system (HC 276) as follows (Scheme 3.1): A solution of TAPE (0.400 g, 1.8 mmol) and MAF-DMP (5.4 g, 23.4 mmol) in DMC (25 mL) was degassed by N₂ bubbling for 30 min. This homogeneous solution was then transferred into the autoclave under vacuum using a funnel tightly connected to the autoclave introductory valve. The reactor was cooled in a liquid nitrogen bath, and VDF gas (6.0 g, 93.7 mmol) was introduced into the autoclave under weight control. After this, the reactor was stirred mechanically and gradually heated up to 74 °C, and the evolutions of pressure and temperature were recorded. The maximum pressure, P_{max} reached 20 bar. The reaction was stopped after 24 h by placing the autoclave in an ice bath. The unreacted gaseous monomer was purged off. Then, the autoclave was opened, the solvent and unreacted liquid monomer (if there was any) was completely removed under vacuum. The crude product was then dissolved in acetone and precipitated from chilled pentane, centrifuged, and then dried under vacuum (20×10^{-3} bar, 50 °C) for 16 h. The yield of the polymerization was determined by gravimetry (mass of copolymer obtained/mass of monomers introduced in the reactor) (yield = 50%). The poly(VDF-co-MAF-DMP) copolymer, as a off white powder, was characterized by ¹H, ³¹P and ¹⁹F NMR spectroscopy.

¹H NMR (400 MHz, DMSO-*d*₆, δ ppm of P2, Table 3.1, Figure 3.1): 2.15 to 2.40 (m, $-CF_2C\underline{H}_2-C\underline{H}_2CF_2-$ reverse VDF–VDF T-T dyad addition); 2.62 ($-CH_2CF_2-C\underline{H}_2C(CF_3)(CO_2CH_2PO(OCH_3)_2)-$]; 2.70 to 3.20 (m, $-C\underline{H}_2CF_2-C\underline{H}_2CF_2-$, normal VDF–VDF H-T dyad addition), 2.80 ($-C\underline{H}_2C(CF_3)(CO_2CH_2 PO(OCH_3)_2)$ of MAF-DMP); 3.72 (m, 6H, $-OC\underline{H}_3$); 4.55 (d, 2H, $-O-C\underline{H}_2-PO(OCH_3)_2$; 6.05 to 6.45 (tt, ${}^2J_{HF}=$ 55 Hz , ${}^3J_{HH}=$ 4.6 Hz, $-CH_2CF_2-\underline{H}$ end-group originated due either to the transfer of proton to solvent or polymer or from the back biting.²⁰⁷

¹⁹F NMR (376 MHz, DMSO-*d*₆, δ ppm of P2, Table 3.1, Figure 3.2): from -66 to -71 (-C<u>F</u>₃ of MAF-DMP in the copolymer), from -91.5 to -93.5 (-CH₂C<u>F</u>₂-CH₂C<u>F</u>₂-normal VDF-VDF H-T dyad addition); from -93 to -95 (-C<u>F</u>₂ of VDF in the alternating VDF-MAF-DMP dyad); -113.2 (-CH₂C<u>F</u>₂-CF₂CH₂-CH₂, reverse VDF-VDF H-H dyad addition); -114.8 (dtt, ²*J*_{HF} = 55 Hz, ³*J*_{HF} = 16 Hz and ⁴*J*_{FF} = 6 Hz, CF₂-CH₂C<u>F</u>₂-H, chain-end from transfer); -116.5 (-CH₂CF₂-C<u>F</u>₂CH₂-CH₂, reverse VDF-VDF H-H dyad addition).

³¹P NMR (162 MHz, DMSO-d6, δ ppm of P2, Table 3.1, Figure S3.8): signal centered at 20.5 ppm (-CO2CH2PO(OCH3)2 of MAF-DMP).

The molar fractions of VDF base units in the copolymer was determined using equation (3.1) by taking the ratios of the integrals of all signals of $-CF_2$ in VDF monomer units with respect to the integrals of the integrals of $-CF_3$ on MAF-DMP units in the ¹⁹F NMR spectra:⁸⁸

mol% VDF in copolymers =
$$\frac{(\int_{-91}^{-96} CF_2 + \int_{-113}^{-118} CF_2)/2}{(\int_{-91}^{-96} CF_2 + \int_{-113}^{-118} CF_2)/2 + \int_{-66}^{-71} CF_3/3} \times 100 \quad (3.1)$$

3.4.5. Determination of the Reactivity Ratios of VDF and MAF-DMP.

First, refer to the section determination of the reactivity ratios in general experimental setup and characterizations in the annexe. For the determination of reactivity ratios of VDF/MAF-DMP monomer pair, seven copolymerizations of VDF with MAF-DMP at seven [MAF- DMP]₀/[VDF]₀ molar feed ratios (15/85, 30/70, 40/60, 50/50, 70/30, 80/20, 90/10) were performed in thick borosilicate Carius tubes (see Figure S3.1 for the image of Carius tube) as described in section 4 in General Experimental setup and Characterizations section. In all tubes, TAPE (1.5 mol % with respect to the monomers) was used as an initiator, and DMC as a solvent.

3.4.6. Synthesis of Phosphonic Acid Functionalized PVDF (PVDF-PA).

Hydrolysis of the dimethyl phosphonate ester groups of poly(VDF-*co*-MAF-DMP) copolymer was carried out using bromotrimethylsilane in dimethyl sulfoxide (DMSO) at room temperature, using a modification of the procedure reported earlier by McKenna *et al.*²⁴¹ A typical example is as follows: In a round bottom, a fine powder of poly(VDF-*co*-MAF-DMP) copolymer (2.0 g) (P2, Table 3.1) was added into DMSO (20 mL). It was kept stirring magnetically under N₂ purging at room temperature until complete dissolution of the polymer. The polymer solution was then treated with 3 equivalents of bromotrimethylsilane, added dropwise under stirring over a period of 1 h. Then, the in situ formed trimethylsilyl ester was treated with 10 equivalents of chilled H₂O. The solution was centrifuged, and then dried under vacuum (20×10^{-3} bar, 50 °C) for 16 h to obtain the corresponding PVDF-PA copolymer, as an off white powder powder. The hydrolyzed product was characterized by ¹H (Figure S3.15) and ³¹P (Figure S3.8) NMR spectroscopy.

3.4.7. Adhesive and Anticorrosive Properties.

The formulation of the coating were achieved as follows: TGDPA (2.0 g, 6.6 mmol), BDDA (3.0 g, 15 mmol), Darocur 1173 (0.15 g, 0.9 mmol), benzophenone (0.14 g, 1.17 mmol) and poly(VDF-co-MAF-DMP) (0.28 g, 0.33 mmol w.r.t. phosphonate) were dissolved in 5.0 mL MEK in a flask and stirred magnetically at room temperature for 30 mins to make a homogeneous solution. This solution was deposited onto galvanized steel plates using a BarCoater (120 mm Braive Instruments). The thickness of the films obtained was about 20–25

mm Coated steel plates were left at room temperature for 24 h. The coated film was UV-cured for 12 min using Fusion UV systems (Figure S3.2). The adhesive properties were assessed by the Cross-cut Testing. The anticorrosive behaviour of PVDF-PA was evaluated in accordance with the Salt Spray Test (DIN 50021) that provided a controlled accelerated corrosive environment to evaluate the relative corrosion resistance of the coating and the steel plate. The steel plates were placed inside a chamber (Figure S3.3) at 45 °C and an aqueous sodium chloride solution (with a concentration by mass of 50 g L-1) is continuously sprayed by means of compressed air for a specified period to evaluate the resistance to corrosion.

3.5. CONCLUSION

Hydrophilic phosphonic acid-functionalized PVDF (PVDF-PA) was synthesized by a simple "mild condition" hydrolysis of the poly(VDF-co-MAF-DMP) copolymers. First, a new monomer, dimethyl (dimethoxyphosphoryl)methyl 2-(trifluoromethyl)acrylate (MAF-DMP), was synthesized from 2-trifluoromethyl acrylic acid (MAF) in satisfactory yield. Then, free radical copolymerizations of VDF and MAF-DMP led to a wide range of poly(VDF-co-MAF-DMP) copolymers of various molar masses, dispersities and comonomer contents. This study also reports for the first time the determination of reactivity ratios of (VDF;MAF-DMP) couple: $rVDF = 0.76 \pm 0.34$ and rMAF-DMP = 0 at 74 °C. These features show that: (i) VDF is more reactive than MAF-DMP and (ii) MAF-DMP does not homopolymerize under radical polymerization conditions. In addition, the MAF-DMP content in the copolymers affects the degree of crystallinity (χ) of such phosphate containing PVDF. χ value increased from 24% to 51% with an increase in VDF molar percentages from 79 to 96%. By controlling the MAF-DMP amount and the extent of hydrolysis of the dimethyl phosphonate ester group, semihydrophilic, hydrophilic or superhydrophilic PVDF with tunable wettability could be achieved. Furthermore, phosphonic acid functionalized PVDF coating exhibited excellent corrosion resistance in marine environment. This work opens the route to new phosphorous containing fluorinated materials for emerging applications in corrosion resistance coating.



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4.1. ABSTRACT

Vinylidene fluoride (VDF)-based copolymers bearing pendant trialkoxysilane groups for potential applications for coatings were synthesized via a free radical copolymerization of VDF with functional 2-trifluoromethacrylate cyclic carbonate monomer, (MAF-cyCB), followed by introduction of silane pendant groups. MAF-cyCB was prepared from 2-trifluoromethacrylic acid with 55% overall yield. Radical copolymerization of VDF with MAF-cyCB initiated by tert-amyl peroxy-2-ethylhexanoate at varying [VDF]₀/[MAF-cyCB]₀ ratios led to several poly(VDF-co-MAF-cyCB) copolymers having different molar percentages of VDF (77-96%). The average molecular weights $(M_n s)$ reached up to ca. 19,000 g mol⁻¹ in fair to good yields (45-74%). Determination of the compositions and microstructures of all synthesized copolymers were achieved by ¹H and ¹⁹F NMR spectroscopies. The resulting poly(VDF-co-MAF-cyCB) copolymers exhibited moderately high melting temperature (131-161 °C, with respect to the VDF content) while the degree of crystallinity that reached up to 34%, decreased with increasing MAF-cyCB. Finally, the pendant cyclic carbonate ester groups of the synthesized poly(VDF-co-MAF-cyCB) copolymers were quantitatively converted into novel triethoxysilane-functionalized PVDF that could be further hydrolyzed under acidic conditions to trihydroxy silane -functionalized PVDF. Finally, steel plates were coated with the silvlated PVDF and displayed improved adhesion properties compared to those of pristine PVDF.

4.2. INTRODUCTION

Adhesion is the interatomic and intermolecular interaction at the interface of two surfaces.²⁴⁸ recently, interest have been given toward polymers and epoxy resins with adhesive properties due to their bulk and surface properties, low cost and good mechanical properties.^{249,250} Adhesion between the polymer surface and a substrate is dependent on the chemical groups at or near the interface.²⁵¹ As a matter of fact, the design of highly adhesive polymers is highly desirable for the automotive,²⁵² aerospace, building,²⁵¹ engineering²⁵³ and biomedical industries.²⁵⁴ Poly(vinylidene fluoride) (PVDF) is one of the most important fluoropolymers due to its unique properties.^{7,49} Currently, VDF-based (co)polymers are extensively used in membranes for water purification,^{8,57} Li-ion batteries (as binders and separators),^{11,55} piezoelectric devices,^{53,54} and photovoltaic devices.¹¹

However, extensive use of PVDF as adhesion promoting agents, printer inks, and paints²⁵⁵ is often restricted by some disadvantages: (i) high crystallinity leading to costly processing, (ii) low solubility, and (iii) laborious tuning properties for targeted applications (especially due to the lack of functionality).^{8,10,11} However, these drawbacks can be overcome by (i) the incorporation of functional vinyl monomers⁸ such as acetoxy,^{12,13} thioacetoxy,¹³ hydroxyl, esters, ethers, halogens, carboxylic acid^{18,58} or (ii) cross-linking via cure site comonomers containing trialkoxysilane,⁵⁹ and by using bisamines or bisphenates.¹⁹ These approaches can lead to improvement of some of the properties of the resulting copolymers such as adhesion, thermal stability,¹⁷ proton conductivity¹⁸ or hydrophobicity.¹⁷ As a matter of fact, Whang *et al.*²⁵⁶ studied the adhesive strength of PVDF/aminopropyltriethoxy silane blends onto silicon wafers deposited via spin coating, dip coating or drop casing. He obtained films with moderately weak adhesion due to the lack of chemical bonding between PVDF and the silane groups. Better results was obtained by, Boutevin *et al.*²⁵⁷ studied the adhesive strength of ozone treated PVDF homopolymer followed by its copolymerization with other monomers such as

styrene, acrylic acid, glycidyl methacrylate or methyl methacrylate. The author mentioned that the obtained blends shows excellent adhesive behavior onto glass substrate. In a more recent study, Ribeiro *et al*²⁵⁸ reported the adhesive strength of PVDF/hydroxyapatite composite coating on titanium substrates. The coating showed strong attachment to the substrate since no detachment was observed under three-point bending test.

In recent years, increased attention has been given to polymers that contain five membered cyclic carbonate ring²⁵⁹⁻²⁶⁴ and found applications in enzyme immobilization,^{265,266} as electrolytes,²⁶⁷ photopolymerization²⁶⁸ and polymeric blends.²⁶⁹ One of the methods to introduce cyclic carbonates into polymer backbone is through the (co)polymerization of monomers containing the cyclic carbonate groups.²⁷⁰ The main interest of cyclic carbonate groups in polymers is their reaction with amines to prepare hydroxyurethanes without the use of harmful isocyanates.²⁷¹⁻²⁷³ In addition, the presence of a hydroxyl groups gives hydroxyl urethane further advantages compared to regular urethanes such as lower porosity,²⁷⁴ excellent adhesion,²⁷⁵ abrasion resistance and good anticorrosive properties.²⁷⁶ Depending on the functional group present on amine-bearing materials, various functions can be introduced into the polymers. Campagne et al. reported synthesis, processing, crosslinking, and characterization of original proton conducting membranes composed of crosslinked fluorinated copolymer bearing dangling cyclocarbonate and triazole functions.²⁷⁷ Among them silane functionality is of great significance. In fact, Tachibana²⁷⁸ reported that the preparation of hydroxyalkyl terminated silanes can be achieved by the reaction of 3-aminopropyl alkoxysilanes with ethylene carbonate. Recently, Aguiar et al.²⁷⁹ reported the development of hybrid urethanes coatings for inorganic surfaces produced by isocyanate free and sol-gel routes via ring opening of cyclic carbonate. Buller *et al.*²⁸⁰ synthesized oligo(ethylene glycol) copolymers bearing benzophenone units to achieve biocompatible polymer coatings on organic surfaces. Polymers containing silanes can benefit from its further ability to hydrolyze and

condensate and thus crosslinking into a stable, three-dimensional siloxane network.^{281,282} In addition, alcoxysilanes are excellent adhesion promoters,²⁸³ since they form a stable covalent bonds with hydroxyl groups present on metal or glass substrates.²⁸⁴ Therefore, the main objective of this chapter is the development of silane-functional PVDF exhibiting improved adhesion onto steel plates.

4.3. RESULTS AND DISCUSSION

4.3.1. Synthesis of MAF-cyCB.

Synthesis of MAF-cyCB was achieved by the esterification reaction of 2-trifluoromethyl acrylic acid (MAF) with glycerol carbonate (Scheme 4.1). First, MAF was modified into 2-(trifluoromethyl)acryloyl chloride (MAF-COCl) using thionyl chloride and the overall yield of this step was 65% (step A).⁸ Then, the esterification reaction of MAF-COCl with glycerol carbonate in the presence of pyridine (to trap HCl gas generated during the reaction) led to MAF-cyCB, in 85% yield (step B).



Scheme 4.1. Synthesis of 2-oxo-1,3-dioxolan-4-yl)methyl 2-(trifluoromethyl)acrylate (MAF-cyCB) from 2-(trifluoromethyl)acrylic acid (MAF).



Figure 4.1. ¹H NMR spectrum of MAF-cyCB recorded in CDCl₃ at 20 °C.

The purified MAF-cyCB was characterized by ¹H and ¹⁹F NMR spectroscopies. ¹H NMR spectrum (Figure 4.1) of MAF-cyCB exhibits characteristic signals centred at 3.74, 4.54, 4.29, 4.96, 6.47, and 6.72 ppm assigned to $-O-CH_2-CH(O)-CH_2-O-$, $-O-CH_2-CH(O)-CH_2-O-$, $-O-CH_2-CH(O)-CH_2-O-$, $-O-CH_2-CH(O)-CH_2-O-$ and $H_2C=C(CF_3)(CO_2CH_2-$, respectively. The ¹⁹F NMR spectrum (Figure S4.1) shows a singlet at -65.8 ppm, attributed to $-CE_3$ group in MAF. ^{17,60,80,87,88}

4.3.2. Synthesis of Poly(VDF-co-MAF-cyCB) Copolymers.

The radical copolymerization of VDF with MAF-cyCB was initiated radically by *tert*-amyl peroxy-2-ethylhexanoate (TAPE) at 74 °C in dimethyl carbonate (DMC) in various comonomers feed ratios (Scheme 4.2). Similar to MAF and other MAF-esters, ^{17,60,80,87,88} the homopolymerization MAF-cyCB under radical conditions failed.

entry	VDF mol%		P_{max}^{c} (bar)	<i>∆P</i> ^d (bar)	yield (%)	$M_{n,SEC}^{e}$	D^e	$T_{d10\%}^{f}$ (°C)	T_m^g (°C)	χ ^g (%)
	feed	copolymer ^b	_							
P1	75	77	37	13	45	6500	1.47	261	131	2
P2	80	83	33	11	47	8000	1.52	272	133	8
P3	85	87	30	13	45	9000	1.56	277	135	18
P4	90	91	33	18	57	13000	1.61	287	150	30
P5	95	96	34	24	74	19000	1.67	308	161	34

Table 4.1. Experimental Conditions and Results (Molecular Weights, Dispersities, and Thermal Properties) of the Radical Copolymerization of VDF with MAF-cyCB^a at 74 °C in DMC for 16 h.

Acronyms: VDF: vinylidene fluoride; MAF-cyCB: (2-oxo-1,3-dioxolan-4-yl)methyl 2-(trifluoromethyl)acrylate; TAPE: *tert*-amyl peroxy-2-ethylhexanoate; Solvent, DMC: dimethyl carbonate; Temperature: 74 °C; Time: 16 h. ^aConditions: Solvent used = 70 mL; Initiator = 1.5 mol% with respect to total monomer; ^bCopolymer compositions were assessed by ¹⁹F NMR spectroscopy using equation 2; ^cP_{max}: maximum pressure observed during the polymerization; ^d Δ P: pressure drop observed in the autoclave between maximum pressure and pressure at the end of the polymerization. ^eMolecular weights (*M_n*s) and dispersities (*Ds*) were determined by SEC in DMF using poly(methyl methacrylate) standards. ^fAssessed by thermogravimetric analysis (TGA), under air; 10 °C/min. ^gDetermined by differential scanning calorimetry (DSC); χ : crystallinity rate determined from equation 1.



Scheme 4.2. Radical Copolymerization of VDF with MAF-cyCB Initiated by *tert*-amyl peroxy-2-ethylhexanoate (TAPE).

All copolymerizations were carried out under high pressure autoclaves since VDF is a gas. Table 4.1 summarizes the experimental conditions, results, and characteristics of all prepared poly(VDF-*co*-MAF-cyCB) copolymers (**P1-P5**). In the course of all the polymerizations (**P1-** **P5**), an initial increase in pressure along the increase in temperature was noted, followed by a decrease in pressure when the temperature reached ca. 68-70 °C. This is due to the dissociation of the initiator (hence releasing radicals) at this temperature that allowed the copolymerization to start, and then the consumption of the monomers. All polymerizations were achieved in DMC as the solvent because it is regarded as a green solvent^{11,52,196} that swells PVDF well. The effect of comonomer feed ratio was studied by preparing five poly(VDF-*co*-MAF-cyCB) copolymers from various [VDF]₀/[MAF-cyCB]₀ molar ratios (**P1–P5**, Table 4.1). The yield of the copolymerization reaction ranged from 45 to 74% and increased with the increase of VDF

content due to its higher reactivity compared to that of MAF-cyCB. As MAF and MAF-TBE which are known not to homopolymerize ($r_{MAF}^{85} = r_{MAF-TBE}^{285} = 0$), MAF-cyCB behaves similarly. In all cases, VDF content in the copolymer was slightly higher than that in the comonomer feed, confirming such a higher reactivity. Molecular weights (M_n s) and dispersities (Ds), determined by size exclusion chromatography (SEC) (Table 4.1), ranged between 6500 and 19000 g mol⁻¹ and between 1.47 and 1.67, respectively.

4.3.3. Characterization of Poly(VDF-co-MAF-cyCB) Copolymers by ¹H and ¹⁹F NMR Spectroscopies.

The purified poly(VDF-*co*-MAF-cyCB) copolymers (**P1-P5**) were characterized by ¹H and ¹⁹F NMR spectroscopies (Figures 4.2-4.3 and Figures S4.2-S4.9). The ¹H NMR spectrum of the poly(VDF-*co*-MAF-cyCB) copolymers (Figure 4.2) mainly exhibits seven characteristic signals: (i) in 2.15-2.40 ppm range attributed to the reverse (tail-to-tail, T-T) addition of VDF repeat units ($-CF_2CH_2-CH_2CF_2-$),^{10,12,13,52,53,58,59,236} (ii) a small signal at 2.62 ppm assigned to the [$-CH_2CF_2-CH_2C(CF_3)(CO_2CH_2CH(O)CH_2O)-$]; (iii) a broad one ranging between 2.70 and 3.20 ppm corresponding to normal (head-to-tail, H-T) addition of VDF ($-CH_2CF_2-CH_2CF_2-$)^{10,12,13,52,53,58,59,236}, (iv) at 3.73 ppm attributed to one of the two protons in $-CO_2CH_2CH(O)CH_2O$ in the cyclic carbonate function,²⁵⁹⁻²⁶⁴ and (v) between 4.2 and 4.55

ppm characteristic of the $-CO_2CH_2CH(O)CH_2O$. ²⁵⁹⁻²⁶⁴ (vi) at around 4.6 ppm attributed to the second protons of $-CO_2CH_2CH(O)CH_2O^{259-264}$ and (vii) at 5.07 ppm assigned to $-CO_2CH_2CH(O)CH_2O$ in the cyclic carbonate function. A tiny triplet of triplets, centered at 6.3 ppm, corresponding to $-CH_2CF_2-H$, suggesting negligible back-biting²⁰⁷ or transfer to monomer, solvent or copolymer.



Figure 4.2. Representative ¹H NMR spectrum of poly(VDF-*co*-MAF-cyCB) copolymer prepared by free radical copolymerization of VDF and MAF-cyCB initiated by TAPE in DMC at 74 °C (**P5**, Table 4.1), recorded in DMSO- d_6 at 20 °C. (*) Solvent (DMSO) peak.

The microstructures of the resulting copolymers were determined by ¹⁹F NMR spectroscopy (see Experimental Section for details). The ¹⁹F NMR spectrum of the poly(VDF-*co*-MAF-cyCB) copolymers (Figure 4.3) mainly exhibits the following characteristic signals: (i) a broad signal centered at –66 ppm assigned to –CF₃ in MAF-cyCB units in the copolymer; (ii) at –91.5 ppm attributed to the normal or Head-to-Tail (H-T) VDF-VDF dyads (–CH₂C<u>F</u>₂–CH₂C<u>F</u>₂–) of

the PVDF chains; (iii) at -95 ppm corresponding to the fluorine atoms of the -CF₂ groups of VDF in VDF-MAF-cyCB alternating dyads,^{55,85,87,88} (iv) at -113.2 and -116.5 ppm assigned to the reverse or H-H VDF-VDF dyads (-CH₂C<u>F₂-CF₂CH₂-), and (v) a doublet (${}^{2}J_{FH} = 55$ Hz) of triplets (${}^{3}J_{FH} = 16$ Hz) of triplets (${}^{4}J_{FF} = 6$ Hz) centered at -114.8 ppm as fingerprint of the -CH₂C<u>F₂-H</u> chain-ends.^{60,80,196,207,233,236,238} The molar fractions of VDF base units in the copolymer were determined from equation (2), provided in the experimental section.</u>



Figure 4.3. Representative ¹⁹F NMR spectrum of poly(VDF-*co*-MAF-cyCB) copolymer prepared by free radical copolymerization of VDF and MAF-cyCB initiated TAPE in DMC at 74 °C (**P5**, Table 4.1), recorded in DMSO-*d*₆ at 20 °C.

4.3.4. Thermal Properties of Poly(VDF-co-MAF-cyCB) Copolymers.

The thermal stabilities of **P1-P5** poly(VDF-*co*-MAF-cyCB) copolymers were studied by thermogravimetric analysis (TGA) under air (Figure 4.4) and differential scanning calorimetry

(DSC). Similar to the reported case of poly(VDF-*co*-MAF-DMP), the thermal stability (demonstrated by $T_{d,10\%}$ temperature for a 10% weight loss, Table 4.1) of the poly(VDF-*co*-MAF-cyCB) copolymers increased with the increase of VDF content in the copolymer from **P1** (77 mol% VDF) to **P5** (96 mol% VDF). Upon heating just above 150 °C, the copolymers with higher content of MAF-cyCB, **P3-P5**, exhibited a significant weight loss. This is probably due to the decomposition of the cyCB pendant groups via ring opening,²⁶² similar to the formation²⁶² of carboxylic acid group after decomposition of the *tert*-butyl ester group via concomitant release of isobutylene.^{80,239}



Figure 4.4. TGA thermograms of poly(VDF-*co*-MAF-cyCB) copolymers prepared by free radical copolymerization of VDF and MAF-CyCB initiated by *tert*-amyl peroxy-2-ethylhexanoate in dimethyl carbonate at 74 °C (**P1-P5**, Table 4.1) heated at 10 °C min⁻¹ under air.

The melting temperatures (T_m s) of the copolymers were assessed by differential scanning calorimetry (DSC) (Figures S4.10-S4.14) and their crystallinity were determined using equation (1).^{240,286} As expected for PVDF or copolymers containing a high VDF amount, the glass transition temperature, T_g , was not observed. However, the results revealed that the T_m

ranged from 131 to 162 °C and the degree of crystallinity (χ) varied from 2 to 34% with an increase of VDF mol% in the copolymer from 77 (**P1**) to 96 (**P5**), respectively (Figure 4.5). This non-surprising results arise from the increasing amount of bulky MAF-cyCB pendant groups that hinders the organization of PVDF moieties and thus reducing the crystalline zone brought by PVDF.



Figure 4.5. Plots of T_m and degree of crystallinity (%) vs VDF mol% in the poly(VDF-*co*-MAF-cyCB) copolymer (**P1-P5**, Table 4.1) prepared by free radical copolymerization of VDF and MAF-CyCB initiated by *tert*-amyl peroxy-2-ethylhexanoate in dimethyl carbonate at 74 °C.

4.3.5. Ring opening of Cyclic Carbonate in Poly(VDF-co-cyCB) Copolymers.

The aminolysis of cyclic carbonates is becoming more important in the preparation of isocyanate-free hydroxyurethanes.^{263,272,287,288} Endo *et al.* demonstrated ring opening polymerization of cyclic carbonate in a recent review.²⁶² Cornille *et al.*²⁸⁹ reported that C₅ cyclic carbonates is more reactive than C₆ cyclic carbonates, justifying our choice of using C₅ cyclic carbonates. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was chosen as a catalyst to lower the activation energy of the ring opening reaction while avoiding the hydrolysis of the triethoxysilane groups and the dehydrofluorination of PVDF moieties.^{290,291} Using a reported

procedure by Cornille *et al.*,²⁷⁵ the ring opening of cyCB groups in poly(VDF-*co*-MAF-cyCB) copolymer (**P2**, Table 4.1) was carried out involving (3-aminopropyl)triethoxysilane in the presence of DBU at room temperature in DMF for 3 days (see Scheme 4.3 for schematic representation of the entire process and Scheme S4.1 for the chemical structures for cyCB ring opening).



Scheme 4.3. Preparation of Poly(VDF-*co*-MAF-Si(OEt)₃) from the reaction of Poly(VDF-*co*-MAF-cyCB) with (3-Aminopropyl)triethoxysilane (APTES) and the subsequent Hydrolysis and Condensation to form Poly(VDF-*co*-MAF-SiO_{1.5}) networks.

The reaction was monitored by ¹H NMR and IR spectroscopies. The first technique (Figure S4.15) shows the disappearance of the signals ranging between 3.8 ppm and 5.0 ppm characteristic of the cyclic carbonate protons. This was concomitant to the appearance of the peaks at 1.1 ppm and 3.5 ppm assigned to ethyl group in $-Si-(O-Et)_3$ and the other signals centered at 3.1 ($-O-C(O)-NH-CH_2-$), 3.4 ($-CH_2-CH(OH)-CH_2-O-C(O)-NH-CH_2-$), 3.7 ($-CH_2-CH(OH)-CH_2-O-C(O)-NH-CH_2-$) and 5.5 ppm ($-CH_2-CH(OH)-CH_2-O-C(O)-NH-CH_2-$) characteristic for hydroxyurethanes, indicating the successful quantitaive opening of the

carbonate ring and the formation of primary and secondary hydroxyurethanes.

4.3.6. Hydrolysis-Condensation of triethoxysilane functions for the Crosslinking of in poly(VDF-co-MAF-SiOEt)3 into poly(VDF-co-MAF-SiO1.5) Networks.

The triethoxysilane groups in the resulting poly(VDF-*co*-MAF-Si(OEt)₃) copolymers into poly(VDF-*c*o-MAF-Si(OH)₃ were hydrolyzed by the addition of aqueous HCl solution to maintain the solution pH at 1.5 at room temperature in DMF (Schemes 4.3 and S4.2). In such an acidic medium, PVDF is known to be stable.^{8,11,52} The polymer solution was then casted onto steel plates and the solvent was evaporated by heating progressively up to 80 °C, allowing the condensation and network formation to take place, thus enabling the formation of poly(VDF-*co*-MAF-SiO_{1.5}) network which adheres on the steel plates through an –Si-O-Metal bond.

The formation of the urethane function in a poly(VDF-*co*-MAF-Si(OEt)₃) copolymer was confirmed by the IR spectroscopy. The IR spectrum (Figure S4.16) dsiplays the frequencies at 1755, 1670, and 1670 cm⁻¹ assigned to the C=O stretching²⁸⁹, the stretching for the H bonding disorder, and the H bond order in urethanes, respectively.^{292,293} In addition, the presence of absorption bands at 1078 cm⁻¹ (Si-O-) and 840 cm⁻¹ ²⁹⁴ (Si-O-Si group) evidences the incorporation of silane.

4.3.7. Thermal Properties of Poly(VDF-co-MAF-SiO1.5) Network.

The thermal stabilities of the poly(VDF-*co*-MAF-cyCB) copolymers before (**P3**, Table 4.1) and after modification into poly(VDF-co-MAF-SiO_{1.5}) network were studied by TGA, under air (Figure 4.6). The TGA thermogram of the poly(VDF-*co*-MAF-cyCB) copolymer exhibits an initial weight loss above 190 °C, which is probably due to the decomposition of the cyclic carbonate²⁹⁵ ring. This is followed by a continuous weight loss between 200 and 550 °C resulting from the degradation of the polymer backbone.

As for poly(VDF-*co*-MAF-SiO_{1.5}) network, a similar weight loss trend as that of poly(VDF*co*-MAF-cyCB) copolymer is observed until ca. 200 °C. However, a better thermal stability of poly(VDF-*co*-MAF-SiO_{1.5}) network was observed above 200 °C due to the presence of siloxane groups in the polymers.²⁹⁶ This is followed by decomposition above 450 °C.



Figure 4.6. TGA thermograms of poly(VDF-*co*-MAF-cyCB) copolymer (**P3**, Table 4.1) before (red solid thermogram) and after (black dashed thermogram) modification to poly(VDF-*co*-MAF-SiO_{1.5}), heated at 10 °C min⁻¹ under air.

The DSC thermogram of poly(VDF-*co*-MAF-SiO_{1.5}) network (Figure S4.17) shows a melting temperature ($T_m = 158$ °C), higher than that of the poly(VDF-*co*-MAF-cyCB) copolymer (133 °C) (Figure S4.12, **P3**, Table 4.1). This increase is due to the crosslinking of the copolymer by the silane functions.²⁹⁷ This result along with that from TGA confirms the successful introduction of silane groups and the further crosslinking in the poly(VDF-*co*-MAF-cyCB) copolymer.

4.3.8. Adhesion Properties of Poly(VDF-co-MAF-SiO1.5) Network.

The adhesive property of such a modified PVDF onto metal plates was evaluated according to the ASTM standard protocol by a cross cut adhesion test. Initially, three individual polymer solutions were prepared by dissolving PVDF, poly(VDF-*co*-MAF-cyCB) copolymer and poly(VDF-*co*-MAF-Si(OH)₃) in DMF. The solutions were then separately casted onto metal plates and placed under vacuum while gradually heating up to 80 °C for three hours to remove the solvent and to allow crosslinking of poly(VDF-*co*-MAF-Si(OH)₃) into PVDF containing silicate networks.



Figure 4.7. (a) PVDF, (b) poly(VDF-*co*-MAF-cyCB) copolymer and (c) poly(VDF-*co*-MAF-SiO_{1.5}) coated on steel plates. Cross cut adhesion test on (d) poly(VDF-*co*-MAF-cyCB) copolymer and (e) poly(VDF-*co*-MAF-SiO_{1.5}) network.

Pristine PVDF polymer coating (Figure 4.7a) peeled off immediately with no external pressure applied and scored a 0 out of 5 on the ASTM D3359-02 classifications indicating that no adhesion occurred on the steel plate. This expected behavior is due to the lack of function in such PVDF homopolymers. In contrast, poly(VDF-*co*-MAF-cyCB) copolymer (Figure 4.7b) and poly(VDF-*co*-MAF-SiO_{1.5}) network (Figure 4.7c) formed uniform and solid coatings. However, poly(VDF-*co*-MAF-SiO_{1.5}), due to its crosslinking, led to a more homogenous coating than that obtained from poly(VDF-*co*-MAF-cyCB) copolymer. A lattice pattern of cuts

with similar spacing was processed on the coating surface of poly(VDF-*co*-MAF-cyCB) copolymer (Figure 4.7d) and poly(VDF-*co*-MAF-SiO_{1.5}) network (Figure 4.7e) by using a cross hatch cutter followed by applying a commercial scotch tape over the lattice. The substrate was then examined and displayed no loss in the squares from the lattice part, on both poly(VDF-*co*-MAF-cyCB) copolymer and poly(VDF-*co*-MAF-SiO_{1.5}) network, thus scoring 5 on the ASTM D3359-02 classifications. Hence, the presence of silane functions confirmed the satisfactory adhesion onto steel by the presence of strong Si-O-Metal bonds.

In case of isocyanate-free poly(hydroxyurethane), reported by Cornille *et al.*,²⁸⁹ of good adhesion originated from the dangling surface hydroxyl groups.^{298,299} In our case, the source of improved adhesion of the poly(VDF-*co*-MAF-cyCB) copolymer is the bonding between carbonyl group (having higher electron cloud density due to electron donating mesomeric effect of two nearly ester "oxygen" atom of the carbonyl group⁷⁷) of MAF-cyCB with the metal. After ring opening, hydrolysis, and crosslinking, the resulting poly(VDF-*co*-MAF-SiO_{1.5}) copolymer forms strong Si-O-Metal bond with the metal surface, resulting in an improved adhesion. Although the adhesion properties of poly(VDF-*co*-MAF-cyCB) and poly(VDF-co-MAF-SiO_{1.5}) copolymers were estimated to be similar via the Scotch test, the latter can form up to three Si-O-M bonds with the metal substrate^{283,300,301} per silane group while cyclic carbonate³⁰² can form only one. In addition poly(VDF-co-MAF-SiO_{1.5}) has an improved thermal stability compared to poly(VDF-*co*-MAF-cyCB) (Figure 4.6). This indeed justifies the exhaustive ring opening/hydrolysis/crosslinking strategy.

4.3.9. maximum capacity of MAF- cyCB in the poly(VDF-*co*-MAF-cyCB) copolymer.

In all copolymerization reactions discussed so far, the copolymers prepared contains a maximum of 25% of MAF esters (MAF-DMP or MAF-cyCB). It is to our interest to prepare copolymers with higher amount of MAF-ester to enhance the possible application of this

copolymer. Attempts to copolymerize VDF with high amount of MAF-cyCB (above 25% in the polymerization feed) have been attempted (scheme 4.4). The reaction was attempted using either dimethyl carbonate (DMC) or 1,1,3,3,3- pentafluorobutane (PFB) as solvents and *Tert*-amyl peroxy-2-ethylhexanoate (TAPE), *tert*-butyl peroxypivalate (TBPPi) and 2,5-dimethyl-2,5-di(*tert*-butylperoxy) hexane (DTBPH) as initiators.



R[•] = TAPE, TBPPi, DTBPH

x = 0.3-0.5

Scheme 4.4. Radical Copolymerization of VDF with high amount of MAF-cyCB.

The obtained product at the end of the reaction was a brown viscous liquid. ¹⁹F NMR spectroscopy (Figure S4.18) showed the appearance of a peak at -65 ppm attributed to the CF₃ of the unreacted MAF-cyCB Monomer, a signat at -68 ppm attributed to the CF₃ of MAF-cyCB in a MAF-cyCB-VDF dayad and a signal at -95 ppm corresponding to the CF₂ of VDF in VDF-MAF-cyCB dayad. The disappearance of normal and reverse addition VDF peaks at -91 ppm and -113 ppm respectively, shows that no polymer is obtained, but rather only small oligomers are present. This inhibition may be attributed to the high transfer occurring in the reaction when the amount of MAF-cyCB increase. Also it is interesting to check the molecular weights of the polymers P1 to P5in table 4.1 where we can see that the molecular weight of the polymers decrease from 19000 to 6500 as the amount of MAF-cyCB increase from 5 to 25%. This drawback in VDF and MAF-cyCB copolymerization was also noticed with other MAF esters, which means different monomers pair should be used in the terpoymerization with VDF

to obtain a terpolymer with sufficient enough functionality. The monomers used to overcome this limitation is discussed in chapter 5.

4.4. EXPERIMENTAL SECTION

4.4.1. Materials.

All reagents were used as received unless stated otherwise. 2-Trifluoromethyl acrylic acid (MAF) and 1,1-difluoroethylene (vinylidene fluoride, VDF) were kindly offered by Tosoh F-Tech Company (Shunan, Japan) and Arkema (Pierre Benite, France), respectively. *Tert*-amyl peroxy-2-ethylhexanoate (TAPE, purity 95%) was bought from AkzoNobel (Chalons sur Marne, France). (3-Aminopropyl)triethoxysilane (APTES, purity 99%) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, purity 98%) were purchased from Aldrich (Aldrich Chimie, 38299 Saint Quentin-Fallavier, France). Glycerol 1,2-carbonate (purity >90%) was acquired from TCI Europe N.V. (Paris, France). ReagentPlus grade dimethyl carbonate (DMC, purity >99%), dichloromethane (DCM), pyridine, thionyl chloride, hydrochloric acid and laboratory reagent grade methanol were purchased from Sigma-Aldrich. Deuterated chloroform (CDCl₃) and dimethyl sulfoxide (DMSO-*d*₆), used for NMR spectroscopy, were purchased from Euroiso-top (Grenoble, France) (purity >99.8%).

4.4.2. Characterization.

All characterization conditions and details are present in the General Experimental setup and Characterizations.

4.4.3. Synthesis of (2-oxo-1,3-dioxolan-4-yl)methyl 2-(trifluoro methyl) acrylate (MAF-cyCB).

4.4.3.1 Synthesis of 2-(trifluoromethyl)acryloyl chloride (MAF-COCl). The procedure is described in section 2 Modification of MAF into MAF-ester (General

experimental setup and characterizations section)
4.4.3.2. Synthesis of (2-oxo-1,3-dioxolan-4-yl)methyl 2-(trifluoro methyl)acrylate (MAF-cyCB).

The procedure of this reaction is described in section 2 Modification of MAF into MAF-ester (General experimental setup and characterizations section) using Glycerol 1,2-carbonate (25.27 g, 214 mmol), MAF-COCl (214 mmol) and pyridine (19.0 mL, 235 mmol) as reactants and dichloromethane (40.0 mL) as solvent to obtain MAF-cyCB (yield = 85%) as a brownish viscous liquid, characterized by ¹H and ¹⁹F NMR spectroscopies.

¹H NMR (400 MHz, CDCl₃, δ ppm, Figure 4.1): 3.74 and 4.54 (2m, 2H, -O-CH₂-CH(O)-C<u>H</u>₂-O-); 4.29 (m, 2H, -O-C<u>H</u>₂-CH(O)-CH₂-O-); 4.96 (m, 1H, -O-CH₂-C<u>H</u>(O)-CH₂-O-); 6.47 and 6.72 (2 s, 2H, <u>H</u>₂C=C(CF₃)(CO₂CH₂-).

¹⁹F NMR (376 MHz, CDCl₃, δ ppm, Figure S4.1): peak centred at -65.82 (-C<u>F</u>₃).

4.4.4. Radical Copolymerization of VDF with MAF-cyCB.

First check the section 3 autoclave operations in the General experimental setup and characterization section. A typical copolymerization of VDF with MAF-cyCB (**P2**, Table 4.1) was performed in a 100 mL Hastelloy autoclave Parr system (HC 276) equipped with a manometer, a mechanical Hastelloy anchor, a rupture disk (3000 PSI), inlet and outlet valves and a Parr electronic controller (for stirring speed and heating control). A solution of TAPE (0.72 g, 3.12 mmol) and MAF-cyCB (5.00 g, 20.83 mmol) prepared in DMC (70 mL) was degassed by N₂ bubbling for 30 min. This solution was transferred into the autoclave under vacuum through a funnel tightly connected to the introduction valve of the autoclave. The reactor was then cooled in a liquid nitrogen bath, and VDF gas (12.00 g, 187.5 mmol) was transferred into it under weight control. After this, the vessel was stirred mechanically and gradually heated up to 74 °C, and the evolutions of pressure ($P_{max} = 33$ bar) and temperature were recorded. The reaction was stopped after 16 h by placing the autoclave in an ice bath. The

unreacted gaseous monomer was purged off. Then, the autoclave was opened, the solvent and unreacted liquid monomer (if there was any) was completely removed under vacuum. The crude product was then dissolved in acetone and precipitated from chilled pentane, centrifuged, and then dried under vacuum (20×10^{-3} bar, 50 °C) for 16 h. The yield of the polymerization was determined by gravimetry (mass of the copolymer obtained/mass of monomers introduced in the reactor) (yield = 47%). The poly(VDF-*co*-MAF-cyCB) copolymer, as an off white powder, was characterized by ¹H and ¹⁹F NMR spectroscopies.

¹H NMR (400 MHz, DMSO-*d*₆, δ ppm of **P2**, Table 4.1, Figure 4.2): 2.15 to 2.40 (m, -CF₂C<u>H</u>₂-C<u>H</u>₂CF₂- reverse VDF-VDF T-T dyad addition); 2.70 to 3.20 (m, -C<u>H</u>₂CF₂-C<u>H</u>₂CF₂-, normal VDF-VDF H-T dyad addition), 2.80 (-C<u>H</u>₂C(CF₃)(CO₂CH₂) of MAF-cyCB); 3.73 and 4.60 (2m, 2H, -O-CH₂-CH(O)-C<u>H</u>₂-O-); 4.30 (m, 2H, -O-O-C<u>H</u>₂-CH(O)-CH₂-O-); 5.07 (m, 1H, -O-CH₂-C<u>H</u>(O)-CH₂-O-); 6.05 to 6.45 (tt, ²J_{HF} = 55 Hz , ³J_{HH}= 4.6 Hz), -CH₂CF₂-<u>H</u> end-group originated from the transfer of proton to solvent or polymer or from the back biting.²⁰⁷

¹⁹F NMR (376 MHz, DMSO-*d*₆, δ ppm of **P2**, Table 4.1, Figure 4.3): -66 (-C<u>F</u>₃ of MAF-cyCB in the copolymer), -91.5 to -95.5 (-CH₂C<u>F</u>₂-CH₂C<u>F</u>₂-normal VDF-VDF H-T dyad addition); -93 to -95 (-C<u>F</u>₂ of VDF in the alternating VDF-MAF-cyCB dyad); -113.2 (-CH₂C<u>F</u>₂-CF₂CH₂-CH₂, reverse VDF-VDF H-H dyad addition); -114.8 (dtt, ²*J*_{HF} = 55 Hz, ³*J*_{HF} = 16 Hz and ⁴*J*_{FF} = 6 Hz, CF₂-CH₂C<u>F</u>₂-H, chain-end from transfer); -116.5 (-CH₂CF₂-C<u>F</u>₂CH₂-CH₂, reverse VDF-VDF H-H dyad addition).

4.4.5. Synthesis of Poly(VDF-co-MAF-Si(OEt)₃) via cyCB Ring Opening.

Ring opening of cyCB groups in poly(VDF-*co*-MAF-cyCB) copolymer was carried out by using APTES with DBU as a catalyst in DMF at room temperature using the method reported earlier by Tachibana.²⁷⁸ Typically, in a round bottomed flask, fine powder of poly(VDF-*co*-MAF-cyCB) copolymer (**P2**) (2.0 g; $M_n = 8000$ g mol⁻¹) was dissolved in DMF (15 mL). It was

stirred under nitrogen at room temperature until the complete dissolution of the copolymer and then 1.5% of DBU (0.6 μ L was added. The polymer solution was then treated with one equivalent of APTES (6 μ L, 0.006 mmol) with respect to cyCB content in the copolymer, and the reaction mixture was kept under magnetic stirring and under nitrogen atmosphere for three days to obtain poly(VDF-*co*-MAF-Si(OEt)₃) copolymer. The color of the solution became dark brown indicating the quantitative ring opening.

4.4.6. Hydrolysis of Poly(VDF-*co*-MAF-Si(OEt)₃) to Poly(VDF-*co*-MAF-Si(OH)₃).

The hydrolysis of the Si(OEt)₃ groups in poly(VDF-*co*-MAF-Si(OEt)₃) copolymer was carried out by treating the polymer solution (in DMF) with an acidic water solution (pH=1.5; 0.5 mL), while stirring magnetically for 1 h (Scheme S4.1). This hydrolyzes the triethoxysilane groups into trihydroxysilyl groups³⁰³ to prepare poly(VDF-*co*-MAF-Si(OH)₃). The solution was then deposited onto steel plates and the solvent was removed in a vacuum oven at 80 °C for 3 h, to obtain brown film with a very strong adhesion.

4.4.7. Adhesion Properties.

The adhesion property was characterized using the D3359 ASTM standard test method (tape test) using a TQC CC2000 cross cut adhesion test kit. Initially, the coatings were wiped with a dry piece of tissue, then two series of parallel cuts cross angled to each other was performed to obtain a pattern of 25 similar squares. Following that a piece of transparent adhesive tape was applied over the squares area and then quickly removed. The results of this test was compared to the D3359 ASTM standard test classifications that ranges from 0 to 5, for which 5 indicates the best adhesion properties of the film.

4.5. CONCLUSION

A new way of crosslinking PVDF as novel coating onto steel was suggested. Triethoxysilanefunctionalized PVDF was synthesized by a simple post-polymerization modification of the assynthesized poly(VDF-co-MAF-cyCB) copolymers. First, a new monomer, MAF-cyCB was developed in satisfactory yield followed by its conventional radical copolymerizations with VDF to prepare a series of poly(VDF-co-MAF-cyCB) copolymers of various comonomer compositions and molecular weights. These results revealed that: (i) VDF has a higher reactivity than MAF-cyCB and (ii) MAF-cyCB was unable to homopolymerize under radical conditions. Additionally, the degree of crystallinity (χ) of such copolymers was affected by the MAF-cyCB content. χ value increased from 2% to 34% when an increase in VDF molar percentages ranged from 77 to 96%. Thus, just by tuning the MAF-cyCB amount in the monomer feed and post-polymerization modification extent, silane functionalized PVDF of various compostions can be synthesized. Furthermore, such a resulting functionalized PVDF coating exhibited excellent adhesion to steel. This work opens the route to new silanecontaining fluorinated materials for emerging applications in functional coatings. However, further studies showed that the copolymerization of VDF with MAF-esters is limited to 25% MAF-ester in the copolymer which implies a different monomer should be used for the preparation of phosphorous and silane functional PVDF.

Chapter V: Solid-Liquid

Europium ions extraction Via Phosphonic acid and silane functional Polyvinylidene fluoride.

5.1. Abstract

Vinylidene fluoride (VDF)-based terpolymers bearing pendant triethoxysilane (-Si(OEt)₃) and dimethyl phosphonate groups for potential applications in Eu ions extraction from water were synthesized *via* a conventional radical copolymerization of VDF with vinyltriethoxylsilane (VTEOS) and vinyldimethylphosphonate (VDMP). Though the radical copolymerization of VTEOS and VDMP failed, the successful terpolymerization was initiated by 2,5-dimethyl-2,5di(tert-butylperoxy) hexane at varying monomers ratios to obtain poly(VDF-ter-VDMP-ter-VTEOS) terpolymers having different molar percentages of VDF (70-90%), VTEOS(5-20%) and VDMP (10%) with 49-81% yields. Determination of the compositions and microstructures of all synthesized copolymers were achieved by ¹H, ¹⁹F, ²⁹Si and ³¹P NMR spectroscopies. The resulting poly(VDF-ter-VDMP-ter-VTEOS) terpolymers were further crosslinked via inorganic polymerization (sol-gel) thanks to the hydrolysis and condensation of the triethoxysilane groups to obtain a 3D network characterized by solid state ²⁹Si and ³¹P NMR spectroscopies, TGA and DSC. The terpolymer exhibited moderately high thermal stability (300 °C) before and after crosslinking, while the degree of crystallinity slight increased from 9.7 % to 12.1%. Finally, the dimethyl phosphonate groups were successfully hydrolyzed into phosphonic acid functions. Finally, europium ion uptake of the terpolymer (P_{20}) was investigated and the polymer showed excellent removal capacity of Eu(III) ions from water upto total removal at low ionic concentrations.

5.2. INTRODUCTION

Metal ions are one of the most dangerous pollutants in aqueous environments due to their high toxicity, their persistence and susceptible carcinogenic effect.³⁰⁴ This opened the door for various studies³⁰⁵ focusing on the development of methods for the removal of these metals from heterogenous media such as liquid–liquid extraction and solid–phase extraction,³⁰⁶⁻³⁰⁹ chemical precipitation,³¹⁰ membrane filtration,³¹¹ flotation,³¹² electrochemical³¹³ and biofiltration methods.³¹⁴

A great interest is given to solid–phase extraction (SPE) where ion exchange or chelating materials are employed for metal ion separation since it simplifies the separation, cost effective, and reduces the solvent use.³¹⁵ The concept of polymers bearing chelating functions for their employment as SPE has been reported.³¹⁶ Multiple approaches have been investigated for the preparation of such functional polymers such as impregnation³¹⁷, grafting of the desired functional group,^{318,319} copolymerization of functional monomers with a crosslinker.³²⁰⁻³²³

Recently, a great interest has been given to phosphorous-containing monomers and polymers^{26,110-112} finding applications in corrosion inhibiting agents, ^{22,324} flame retardants,²¹ adhesion promoters for paints, superlubricity coatings,¹¹³ as water repellent,¹¹⁴ polymer electrolyte membrane fuel cells,^{23-25,141} and in biomedical fields.²⁶ in addition, phosphonates and phosphonic acids are known for their excellent chelating properties.³²⁵ Thus, examples of phosphorous functional polymers employed as SPEs are quite abundant. Kabanov *et al.*³²⁶ reported the preparation of crosslinkable polymers from the copolymerization of diethyl vinyl phosphonate and acrylic acid with *N*,*N* -methylene diacrylamide for the extraction of Cu²⁺. Goto *et al.*³²⁷ showed the preparation of polymers based on the polymerization of 1,12-dodecanediol-O,O'-diphenyl-phosphonic acid (DDDPA) with divinylbenzene to successfully extract zinc ions from aqueous media. Inspired by the work of Goto, Zhu *et al.*³²⁸ demonstrated

the emulsion polymerization of DDDPA and 4-vinylpyridine to prepare polymers with high selectivity to lead ions.

As a matter of fact, Fluorinated polymers are high performing speciality polymers that found applications in petrochemicals, textile, aeronautics, aerospace, optics, textile, chemical engineering, microelectronics, automotive, and building industries.^{49,171-173} Recent studies focused on the development of these polymers to fully take advantage of their unique properties. One of the most important member to these polymers family is poly(vinylidene fluoride) which is second most produced fluoropolymer (PVDF) the after polytetrafluoroethylene (PTFE).^{6,7,49} This is because PVDF almost shares the same properties as PTFE, but its starting monomer, vinylidene fluoride (VDF) is is much less dangerous than TFE (not explosive and has a lower toxicity) while being comparable in terms of reactivity.⁸ This led PVDF to find a wide range of applications including treatment of waste water. Zhao et al.^{329,330} demonstrated the preparation of melamine-diethylenetriaminepentaacetic acid/PVDF (MA–DTPA/PVDF) chelating membrane bearing polyaminecarboxylate groups for the removal of Ni(II) from waste water. In addition, studies by Wang et al.³³¹ showed the chelation of Pd/Fe by polyacrylic acid/ PVDF membranes. Both authors mentioned that the hydrophobicity of the copolymers (arisen from the fluorine atoms) led to easier separation and material retrieval from the solution. Multiple studies also illustrated the functionalization of PVDF based membranes by multiple functional groups for waste water treatment,³³²⁻³³⁵ however no records are present for phosphorous functional PVDF being employed for this application.

Finally, in order to achieve high durability and materials reusability, it is essential for polymers employed as SPEs to be crosslinked. In addition, this crosslinking ensures the heterogeneity of such materials in complex aqueous media. PVDF crosslinking has been carried out through i) amines and diamines, ii) bisphenols, iii) via epoxides and iv) radiation.¹⁹ However, a more simple approach is highly desirable for the crosslinking of PVDF. As a matter of fact, triethoxysilane groups can offer a more elegant and simple method for polymers crosslinking through the sol-gel process.²⁷ A few studies are reported regarding triethoxysilylfunctionalized fluoropolymers, mainly for enhanced adhesion,²⁸ water and oil repellence,²⁹⁻³¹ solvent resistance³², fuel cell membranes³³⁶ and for amines functionalizations.³³⁻³⁶ Earlier, Asandei et al.³³⁷ reported the limited polymerization of VDF with vinyltriethoxylsilane initiated by tert-butyl peroxide. Inspired by this authors work, this chapter highlights the synthesis of phosphonate and triethoxysilyl-functionalized PVDF terpolymers, poly(VDF-ter-VDMP-ter-VTEOS), to demonstrate the synergistic effects of phosphorous, silicon and fluorine atoms. The terpolymers is prepared through the radical polymerization of VDF, dimethylvinylphosphonate, and vinyltriethoxysilane using 2,5-dimethyl-2,5-di(tertbutylperoxy) hexane as an initiator. A detailed NMR spectroscopy (¹H, ¹⁹F, ³¹P and ²⁹Si) and thermal study has been performed to the terpolymers before and after their crosslinking. The obtained materials were used to extract europium ions from aqueous media.

5.3. Results and Discussion

5.3.1. Synthesis of poly(VDF-ter-VDMP-ter-VTEOS) terpolymers.

The synthesis of poly(VDF-*ter*-VDMP-*ter*-VTEOS) terpolymers was achieved through the conventional radical terpolymerization of vinylidene fluoride (VDF), vinyldimethylphosphonate (VDMP) and vinyltriethoxylsilane (VTEOS) at 115 °C using 2,5-dimethyl-2,5-di(*tert*-butylperoxy) hexane (DTBPH) as an initiator and dimethyl carbonate (DMC) as a solvent (Scheme 5.1).

Scheme 5.1. Radical terpolymerization of VDF, VDMP, and VTEOS Initiated by 2,5-dimethyl-2,5-di(*tert*-butylperoxy) hexane (DTBPH).

Since VDF is a gas, the polymerization took place in high pressure autoclaves. Different reaction conditions were tested such as different reaction solvent (Dimethyl carbonate or 1,1,1,3,3-pentafluorobutane), temperature (57 to 135 °C depending on the often used initiator), initiator (*tert*-butyl peroxypivalate (TBPPi at 57 °C), *Tert*-amyl peroxy-2-ethylhexanoate (TAPE at 73 °C), and 2,5-dimethyl-2,5-di(*tert*-butylperoxy) hexane (DTBPH between 115-135 °C)), and varying monomer ratios in the reaction feeds. Table 5.1 summarizes the different reactions attempted for the polymerization. To keep the reaction system simple, initially, copolymerizations of the different monomers present were attempted. The copolymerization of VTEOS and VDMP (**P**1-3) failed no matter what kind of initiator, solvent or reaction temperature used. The same conclusion can be obtained regarding the copolymerization of VDF and either VDMP or VTEOS when TAPE or TBPPi was used as an initiator (**P**4-6, **P**11-12, **P**16-17).

Feed (%)								
Entry	VDF	VTEOS	VDMP	Initiator	Solvent	T(°C)	Yield (%)	Δp (bar)
P 1	0	50	50	TBPPi ^a	DMC	57	0	-
P ₂	0	50	50	TAPE ^b	DMC	75	0	-
P 3	0	50	50	DTBPH ^c	DMC	115	0	-
P 4	90	10	0	TBPPi ^a	DMC	57	0	-
P 5	90	10	0	TAPE ^b	DMC	75	0	-
P 6	90	10	0	TBPPi ^a	PFB	57	0	-
P 7	90	10	0	DTBPH ^c	PFB	135	62	25
P 8	80	20	0	DTBPH ^c	PFB	135	56	22
P 9	50	50	0	DTBPH ^c	PFB	135	49	23
P ₁₀	90	10	0	DTBPH ^c	DMC	115	75	26
P 11	90	0	10	TBPPi ^a	DMC	57	0	-
P ₁₂	90	0	10	TAPE ^b	DMC	75	0	-
P ₁₃	90	0	10	DTBPH ^c	DMC	115	80	24
P 14	70	0	30	DTBPH ^c	DMC	115	81	28
P ₁₅	50	0	50	DTBPH ^c	DMC	115	79	27
P 16	80	10	10	TBPPi ^a	DMC	115	0	-
P 17	80	10	10	TAPE ^b	DMC	115	0	-
P ₁₈	85	5	10	DTBPH ^c	DMC	115	78	27
P 19	80	10	10	DTBPH ^c	DMC	115	77	28
P ₂₀	70	20	10	DTBPH ^c	DMC	115	80	25

Table 5.1. Reaction conditions and yields for the radical terpolymeriation of VDF, VTEOS and VDMP.

Acronyms: VDF: vinylidene fluoride; VTEOS: vinyltriethoxylsilane; VDMP: vinyldimethylphosphonate; a) TBPPi: *tert*-butyl peroxypivalate; b) TAPE: *tert*-amyl peroxy-2-ethylhexanoate; c) DTBPH: 2,5-dimethyl-2,5-di(*tert*-butylperoxy) hexane; Solvent, DMC: dimethyl carbonate; PFB: 1,1,1,3,3-Pentafluorobutane,

The first successful reaction between VDF and VTEOS was achieved when DTBPH was used as an initiator (**P**7-10). Interestingly, similar to TBPPi and TAPE, DTBPH is also a peroxide, but the terpolymerization was only initiated by the later. Looking at the structure of DTBPH, it is worth noting that it is a difunctional initiator compared to monofunctional TBPPi and TAPE, meaning that it is capable of releasing more radicals into the reaction medium³³⁸ (Scheme 5.2) increasing its density and thus ensuring that the reaction could initiate more efficiently. In addition, the higher dissociation temperature of its peroxide bond (t_{1/2}= 10 h at 115 °C compared to 57 °C and 75 °C for TBPPi and TAPE, respectively) leads to a higher overall pressure in the reactors which can ensure the success of the polymerization of gaseous monomer.

$$\xrightarrow{\text{CH}_{3}}_{\text{H}_{3}\text{C}-\overset{\text{CH}_{3}}{\underset{\text{C}}{\text{H}_{3}}}, \overset{\text{CH}_{3}}{\underset{\text{C}}{\text{H}_{3}}}, \overset{\text{CH}_{3}}{\underset{\text{C}}{\text{H}_{3}}}, \overset{\text{CH}_{3}}{\underset{\text{C}}{\text{H}_{3}}}, \overset{\text{A}}{\xrightarrow{\text{C}}{\text{H}_{3}}} \xrightarrow{\text{C}}_{\text{2}} \overset{\text{CH}_{3}}{\underset{\text{C}}{\text{H}_{3}}}, \overset{\text{CH}_{3}}{\underset{\text{C}}{\text{H}_{3}}}, \overset{\text{C}}{\underset{\text{C}}{\text{H}_{3}}}, \overset{\text{C}}{\underset{C}}$$

Scheme 5.2. Dissociation mechanism of 2,5-dimethyl-2,5-di(tert-butylperoxy) hexane (DTBPH).³³⁸

The same results were also obtained when attempting the polymerization of VDF with VDMP (**P**₁₃₋₁₅), which confirms that DTBPH is a suitable initiator for this polymerization system. It is worth noting that changing the polymerization solvent did not affect the polymerization, thus we opted to use dimethyl carbonate (DMC) since is considered as a green solvent^{11,52,196} and swells PVDF well. However, the variation of the reaction temperature between 115-135 °C showed that the former tends to give better yields foe the overall reaction (75 % at 115 °C (**P**₁₀) compared to 62 at 135 °C (**P**₇)) which may be attributed to the initiators half-life ($t_{1/2}$ = 10 h at 115 °C while 1h at 135 °C) and its ability to release radicals for an extended amount of time at lower temperatures. Based on the obtained results, poly(VDF-*ter*-VDMP-*ter*-VTEOS) terpolymer synthesis was successful. Interestingly, the presence of VDF in the reaction medium

allows the terpolymerization of VTEOS and VDMP, a pair that failed to copolymerize under any conditions.

5.3.2. Characterization of poly(VDF-*ter*-VDMP-*ter*-VTEOS) terpolymers by ¹H and ¹⁹F NMR Spectroscopies.

The purified poly(VDF-ter-VDMP-ter-VTEOS) terpolymer were characterized by ¹H, ¹⁹F, ³¹P, and ²⁹Si NMR spectroscopies. The ¹H NMR spectrum of the poly(VDF-ter-VDMP-ter-VTEOS) terpolymer (Figure 5.1) mainly exhibits eight characteristic signals: i) at 0.4 to 0.7 ppm attributed to the proton present on the carbon adjacent to the Si atom, ii) 1.1 to 1.3 ppm for the CH₃ groups of the triethoxysilyl units, iii) 1.7 ppm corresponding to the CH group adjacent to the PO group, iv) 2.15 to 2.40 ppm range attributed to the reverse (tail-to-tail, T-T) addition of VDF repeat units (-CF2CH2-CH2CF2-),10,12,13,52,53,58,59,236 v) 2.70 to 3.10 ppm corresponding (head-to-tail, H-T) addition of VDF to normal (-CH₂CF₂-CH₂CF₂-)^{10,12,13,52,53,58,59,236} vi) 2.80 ppm protons of ethylene CH₂ in VDF and VTEOS or VDMP dyad, vii) 3.65 ppm attributed to the CH₂ of triethoxysilane group and finally viii) 3.7 ppm signals of the CH₃ protons in the dimethyl phosphonate side group. However, this peak is overlapping with DMC peak which can not be removed due to the polymers highly viscous nature. The small triplet (${}^{2}J_{HF}$ = 45 Hz) of triplets (${}^{3}J_{HH}$ = 7 Hz), centered at 6.3 ppm, correspondS to -CH₂CF₂-H, and suggests back-biting²⁰⁷ or transfer to monomer, solvent or copolymer.



Figure 5.1. Representative ¹H NMR spectrum of poly(VDF-*ter*-VDMP-*ter*-VTEOS) terpolymer (P_{20} , Table 5.1), recorded in DMF- d_7 at 20 °C.

¹⁹F NMR spectrum shows the characteristic peaks of PVDF (**P**₂₀, Figure 5.2), centered between -91.5 to -93.5 ppm assigned to for the normal VDF–VDF H-T dyad addition, while that at -94.5 ppm attributed for VDF in the alternating VDF–VDMP/VTEOS dyad, a small peak at 107.5 ppm corresponding to CH₃CF₂C<u>F₂CH₂–,³³⁹ and signals between -114 and -116.5 ppm for reverse VDF–VDF H-H dyad addition.</u>

On the other hand, the ³¹P NMR spectrum (P_{20} Table 5.1, Figure 5.3) displays only a single peak at 37.5 ppm attributed to the pendant phosphonate group on the polymer's backbone.



Figure 5.2. Representative ¹⁹F NMR spectrum of poly(VDF-*ter*-VDMP-*ter*-VTEOS) terpolymer (P_{20} , Table 5.1), recorded in DMF- d_7 at 20 °C.



Figure 5.3. Representative ³¹P NMR spectrum of poly(VDF-*ter*-VDMP-*ter*-VTEOS) terpolymer (P_{20} , Table 5.1), recorded in DMF- d_7 at 20 °C.

The ²⁹Si NMR spectrum (**P**₂₀ Table 5.1, Figure 5.4) displays two peaks, centered at -44 ppm attributed to the triethoxysilane group ($-\underline{Si}(OCH_2CH_3)_3$) next to normal addition VDF dyad, while the second peak at -46 ppm is for a triethoxysilane group ($-\underline{Si}(OCH_2CH_3)_3$) adjacent to a reverse addition VDF dayad. The ²⁹Si NMR spectrum exhibits no peak at between -50 and -70 ppm which means no crosslinking of the pedant silyl groups have took place yet.



Figure 5.4. Representative ²⁹Si NMR spectrum of poly(VDF-*ter*-VDMP-*ter*-VTEOS) terpolymer (P_{20} , Table 5.1), recorded in DMF- d_7 at 20 °C.

5.3.3. Crosslinking of poly(VDF-ter-VDMP-ter-VTEOS) terpolymer.

The crosslinking of poly(VDF-ter-VDMP-ter-VTEOS) terpolymer was achieved via the hydrolysis and condensation of the pendant triethoxysilyl groups. The sol-gel transformation enables the preparation of a 3D network by the formation of the strong Si–O–Si bonds. For the crosslinking to occur, H^+ , OH^- or a nucleophile such as F^- or Lewis base is required to act as a

catalyst for this transformation to occur.³⁴⁰ First, tetrabutylammonium fluoride (TBAF)/water system was used as a catalyst for the crosslinking of poly(VDF-ter-VDMP-ter-VTEOS) terpolymer in DMF, because it is an excellent source of the nucleophilic $F^{.341}$ However, upon the addition of TBAF, the polymeric solution turned black and no successful gelation occurred. This is due to the F^{-} extracting protons from the highly acidic PVDF backbone (CF₂CH₂CF₂), leading to dehydrofluorination instead of hydrolysis of the triethoxysilyl groups.³⁴² To overcome this issue, highly concentrated HCl (12 M) was used as a catalyst mainly because PVDF is well known to be stable against acids.^{8,11} The choice of such a strong acid is due to the effect of pH on the kinetics of hydrolysis and condensation of silanes (Figure 5.5).



Figure 5.5. pH effect on the rate of hydrolysis and condensation of silanes.¹⁵⁸

Usually at acidic pH, hydrolysis occurs rapidly, while the condensation step is slow. However, by using strong acidic conditions (pH<2), the condensation step becomes fast, and thus crosslinking of the polymer.³⁴³ This was noted by the rapid gel formation upon the addition of two drops of HCl into a solution of the terpolymer (10.02 g) in DMF (7 ml) (Figure 5.6). The gel was kept to age for 1 week to make sure complete crosslinking occurred. All the tested terpolymers with 5, 10, and 20 % of triethoxysilane was capable of forming strong gels, but it was noted that the strength of the gel was dependent on the percentage of triethoxysilane group present, where higher the amount, the stronger the gel formed. The solvent was then removed

by thermal treatment under vacuum (80 °C, 20×10^{-3} bar) for 24 h to obtain a solid yellow resin (Figure 5.6).



Figure 5.6. Sol-Gel transformation of poly(VDF-ter-VDMP-ter-VTEOS) terpolymer (**P**₂₀) in DMF using HCl as a catalyst followed by solvent removal via thermal treatment (80 °C at 20×10^{-3} bar).

The obtained resins were characterized by ²⁹Si and ³¹P solid state NMR spectroscopy. The Si NMR (Figure 5.7) spectrum shows the presence of two broad peaks: the first one at -50 to -60 ppm attributed to the $T^2 Si(OH)(OSi)_2$ groups while the peak at -60 to -70 ppm is attributed to T^3 substructures -<u>Si</u>(OSi)₃. One would expect to only obtain T^3 substructures. However, as the amount of crosslinking increases during the condensation step, the polymer chains lose its flexibility and thus is unable to fold to allow the total condensation of the triethoxysilyl groups (Figure 5.8).



Figure 5.7. OP-MAS solid state ²⁹Si NMR of poly(VDF-*ter*-VDMP-*ter*-VTEOS) terpolymer (**P**₂₀, Table 1) after crosslinking.



Figure 5.8. Sketch of hydrolysis and the inorganic polymerization of the pendant triethoxysilane groups.

The ³¹P NMR spectrum (Figure 5.9) displays the presence of three P signals: i) that at -24 ppm attributed to totally hydrolyzed phosphonic acid groups (-PO(OH)₂), ii) the one at -35 ppm corresponding to partially hydrolyzed phosphonate groups ((-PO(OMe)(OH)), and iii) that at -44 ppm for the dimethyl phosphonate group (-PO(OMe)₂).²³ The hydrolysis of the phosphonate groups into phosphonic acid and partially hydrolyzed phosphonate is due to the use of strong acidic conditions during the crosslinking step. However, this is not a problematic since the desired product is phosphonic acid functional terpolymer, poly(VDF-ter-VPA-ter-VTEOS) terpolymer.



Figure 5.9. OP-MAS Solid state ³¹P NMR of poly(VDF-*ter*-VDMP-*ter*-VTEOS) terpolymer (**P**₂₀, Table 5.1) after crosslinking.

5.3.4. Thermal properties of poly(VDF-*ter***-VDMP-***ter***-VTEOS) terpolymer.** The thermal stabilities of poly(VDF-*ter*-VDMP-*ter*-VTEOS) terpolymer before and after its cross-linking were assessed by thermogravimetric analysis (TGA) under air (Figure 5.10). Before cross-linking, an initial loss was observed at 130 °C due to the loss of the trapped solvent (DMC) in the polymer chains. A second degradation is also observed at 300 °C mainly attributed to the degradation of the fluorinated polymer backbone,³⁴⁴⁻³⁴⁶ which continues till the total degradation of the terpolymer at about 580 °C. After crosslinking, a single degradation is noticed at 180 °C, which is much steeper than that in the case of the uncrosslinked terpolymer up to 400 °C. This is surprising because it was expected that the crosslinking should enhance the thermal properties of the terpolymer, which is only noted above 400 °C where no more

degradation is noted and 20 % of residue remain. This residue is the thermally stable Si-O-Si groups from the crosslinking of the triethoxysilyl groups.



Figure 5.10. TGA thermograms of poly(VDF-*ter*-VDMP-*ter*-VTEOS) terpolymer (P_{20} , Table 5.1) heated at 10 °C min⁻¹ under air.

The melting temperatures (T_m) of the terpolymer before and after coss-linking were assessed by differential scanning calorimetry (DSC) (Figures 5.11) and their crystallinity were determined using equation (1) (General experimental setup and characterization section).^{286,347}

Degree of crystallinity
$$(\chi) = \frac{\Delta H_m}{\Delta H_c} \times 100$$
 (1)

As expected for PVDF or copolymers containing a high VDF amount, the glass transition temperature, Tg, was not observed. However, no real difference in the T_m before crosslinking (133 °C) and after crosslinking (136 °C) of the terpolymer was observed. Regarding the degree of crystallinity (χ), a slight increase was noted from 9.7 % to 12.1% after crosslinking, maybe due to the formation of a stiff non-flexible network which can slightly increase the crystallinity of the terpolymer or due to several oligo(VDF) hydrophobic zones that gather with each others.



Figure 5.11. DSC thermogram of poly(VDF-*ter*-VDMP-*ter*-VTEOS) terpolymer (**P**₂₀, Table 1) before and after crosslinking.

5.3.5. Hydrolysis of phosphonate groups into phosphonic acid in poly(VDFter-VDMP-ter-VTEOS) terpolymer.

The full hydrolysis of the phosphonate groups into phosphonic acid function in the crosslinked terpolymers was attempted using bromotrimethylsilane at room temperature (Figure 5.12) (the detailed procedure is given in the Experimental Section), using a modification of the procedure reported earlier by McKenna *et al.*²⁴¹ The solid state ³¹P NMR spectrum (Figure 5.13) shows that it is not possible to totally hydrolyze all the phosphonate groups as evidenced by the presence of two peaks at –44 ppm attributed to the remaining dimethyl phosphonate group and the broad peak at –25 ppm corresponding to the totally hydrolyzed phosphonic acid groups. Attempts for this hydrolysis using highly concentrated HCl (12 mol.L⁻¹) while heating at 60 °C also gave the same results. The signal of phosphonic acid appears broadened with a shoulder on one side due to the hydrogen bonding of the POH group. The deconvolution of the peaks in the NMR spectrum allows the determination of the exact amount of each phosphorous species present and results that 31% of the phosphonate species failed to fully hydrolyse. This maybe the inaccessibility of phosphonate groups imbedded inside the terpolymer network.



Figure 5.12. Sketch of silanols modification in crosslinked poly(VDF-*ter*-VPA-*ter*-VTEOS) terpolymer by Me₃SiBr.



Figure 5.13. Solid state ³¹P NMR of crosslinked poly(VDF-ter-VPA-ter-VTEOS) terpolymer (**P**₂₀, Table 5.1).

Interestingly, the ²⁹Si NMR spectrum (Figure 5.14) showed that after the treatment with bromotrimethylsilane, the T² peaks disappear and a new one at 12 ppm appears while the T³ peaks remain intact between -60 and -70 ppm. This new peak corresponds to the bromotrimethylsilyl group that reacted onto T₂ silane groups. In the same time, this explains the disappearance of T² substructures since they convert into T³ substructures after their reaction with bromotrimethylsilane. This means that the structure of the polymer networks backbone was not affected by the partial hydrolysis reaction of the phosphonate groups, and thus this material could be employed for Eu(III) ion extraction from water.



Figure 5.14. Solid state ²⁹Si NMR spectrum of poly(VDF-ter-VPA-ter-VTEOS) terpolymer (**P**₂₀, Table 5.1).

5.3.6. Study of Eu(III) uptake from aqueous medium.

Considering the affinity between phosphonate ligands and trivalent lanthanides, it is attractive to use coordinating polymers bearing organophosphorus ligands as a binding site for lanthanides separations.³⁴⁸⁻³⁵⁰ The various studies on the matter focoused on organic-inorganic hybrid Zirconium(IV)–Benzene based polymers,³⁴⁸ fluorinated acrylate and styrene-based copolymers³⁴⁹ showed promise in the removal of different lanthanide including Eu(III) ions. Thus, the extraction of Eu³⁺ onto the polymer network as a function of the lanthanide concentration was investigated at room temperature. The interest in our polymer system compared to the aforementioned examples is the hetrogenious process of extraction (since our material does not dissolve). Various solutions with different metal concentration (2, 4, 6, 8, 10 mmol.L⁻¹) was prepared in a mixture of water and acetic buffer at pH 5.8 to allow Xylenol Orange changes color in the complexometric titration.³⁵¹ All ion exchange experiments were performed by the batch method, with the solid/liquid ratio of 0.25 g of polymer (**P**₂₀, Table 5.1) /25 mL of metal ion solution. Polymer P₂₀ was chosen for the study because it had strong

rigidity and showed less swelling affinity in watter. Since the crosslinked polymer contains only 10 % of phosphorous atoms, and assuming that each Eu^{3+} atom requires three ligands groups to form a complex,³⁵² the maximum concentration (C_{theo}) of the extracted ion could be determined (3.5 mmol.L⁻¹) using equations (5.1, 5.2, 5.3 and 5.4) as well as the theoretical uptake (α_{theo} %) of each concentration can be calculated (Table 5.2).

$$m = n_1 M_1 + n_2 M_2 + n_3 M_3 \quad (5.1)$$
$$n_1/7 = n_2/2 = n_3 \quad (5.2)$$
$$n_{Eu} = n_3/3 \quad (5.3)$$
$$C_{theo} = n_{Eu} / V_{sol} \quad (5.4)$$

Where m is the mass of the terpolymer (0.25 g), n_1 , n_2 , n_3 and n_{Eu} are the number of moles of VDF, VTEOS, VDMP and theoretical number of moles of Eu extracted respectively, M_1 , M_2 , and M_3 are the molecular weights of VDF (64.04 g.mol⁻¹), VTEOS (190.3 g.mol⁻¹) and VDMP (136.09 g.mol⁻¹) respectively. V_{sol} is the volume of the solutions prepared equal to 25 mL.

Table 5.2. Theoretical and experimental ion uptake by $poly(VDF_{0.7}$ -*ter*-VPA_{0.1}-*ter*-VTEOS_{0.2}) terpolymer (**P**₂₀, Table 5.1) in various concentrations of Eu³⁺.

Solution concentration	α_{theo} %	α %	
$(mmol.L^{-1})$			
2	100	99.5	
4	87.5	76.2	
6	58.3	52.2	
8	43.7	43.7	
10	35.0	43	

The amount of Eu³⁺ ions remaining in the liquid phase when reaching equilibrium after 24 h has been measured in the filtrates by complexometric titration with EDTA using xylenol orange as an indicator. Upon reaching the equivalence point, the color of the solution changes from purple to yellow. The uptake degree of the terpolymer at different Eu³⁺ concentrations is summarized in Figure 5.15.



Figure 5.15. The removal efficiency of Eu^{3+} ions by poly(VDF-ter-VPA-ter-VTEOS) terpolymer (**P**₂₀, Table 5.1) (**■**) and theoretical removal (**●**) versus their initial concentration.

Pristine PVDF showed no Eu ion extraction, which verifies that any metal removal is due to the phosphorous atoms present on the polymer. At low metal concentration (2 mmol.L⁻¹), the terpolymer exhibits excellent ion uptake, confirmed by the absence of any free Eu in the

solution, which was expected according to the theoretical calculations. As the lanthanide ion concentration in the solution increases, a decrease in the uptake capacity is witnessed, however this decrease is in accordance with the theoretical results, which shows that the terpolymer is capable of performing efficiently up to 8 mmol.L⁻¹. To our surprise, at concentration of 10 mmol.L⁻¹, the obtained Eu extraction was better than the theoretical one. At this concentration, the immobilization of the lanthanide ions is due to the complexation with the pendant phosphorous atoms and adsorption in the polymer network.³⁵³ Considering that in the present theoretical calculations only the effect of complexation is considered, at high concentration, the effect of adsorption becomes more prominent which explains why the polymer surpassed the expected extraction values. These data show that this terpolymer can be employed efficiently for lanthanide extractions from heterogenous medium.

5.4. EXPERIMENTAL SECTION

5.4.1. Materials.

All reagents were used as received unless stated otherwise. 1,1-difluoroethylene (vinylidene fluoride, VDF) were kindly offered by Arkema (Pierre Benite, France. *Tert*-amyl peroxy-2-ethylhexanoate (TAPE, purity 95%), *tert*-butyl peroxypivalate (TBPPi, purity 75%) and 2,5-dimethyl-2,5-di(*tert*-butylperoxy) hexane (DTBPH, purity 90%) were bought from AkzoNobel (Chalons sur Marne, France). Vinyltriethoxylsilane (VTEOS, purity 97%) and Europium(III) chloride hexahydrate (Purity 99.9%) were purchased from Aldrich (Aldrich Chimie, 38299 Saint Quentin-Fallavier, France). Vinyldimethylphosphonate (VDMP, purity 90%) was acquired from ABCR (Karlsruhe, Germany). Reagent Plus grade dimethyl carbonate (DMC, purity >99%), 3,3'-bis[N,N-bis(carboxymethyl)aminomethyl]-o-cresolsulfonephthalein tetrasodium salt (Xylenol orange), (Ethylenedinitrilo)tetraacetic acid tetrasodium Salt (EDTA), hydrochloric acid and pentane were purchased from Sigma-Aldrich. Deuterated acetone and

dimethylformamide (DMF-*d*₇), used for NMR spectroscopy, were purchased from Euroiso-top (Grenoble, France) (purity >99.8%).

5.4.2. Characterization.

All characterization conditions and details are present in the General Experimental setup and Characterizations.

5.4.3. Radical Copolymerization of VDF with VTEOS and VDMP.

First please check the section 3 autoclave operations in the general experimental setup and characterization section. A typical copolymerization of VDF with VDMP and VTEOS (P₂₀, Table 5.1) was performed in a 100 mL Hastelloy autoclave Parr system (HC 276) equipped with a manometer, a mechanical Hastelloy anchor, a rupture disk (3000 PSI), inlet and outlet valves and a Parr electronic controller (for stirring speed and heating control). A solution of DTBPH (0.77 g, 2.7 mmol), VDMP (3.60 g, 26.7 mmol) and VTEOS (10.20 g, 53.5 mmol) in DMC (70 mL) was degassed by N₂ bubbling for 30 min. This solution was transferred into the autoclave under vacuum through a funnel tightly connected to the introduction valve of the autoclave. The reactor was then cooled in a liquid nitrogen bath, and VDF gas (12 g, 187.5 mmol) was transferred into it under weight control. After this, the autoclave was stirred mechanically and gradually heated up to 115 °C, and the evolutions of pressure (Pmax = 36 bar (P_{20} , Table 5.1)) and temperature were recorded. The reaction was stopped after 16 h (Pmin=11 bar) by placing the autoclave in an ice bath. The unreacted gaseous monomer was purged off before opening the autoclave and its content was transferred into a schlenk tube where the solvent and unreacted liquid monomer (if there was any) was completely removed under vacuum while avoiding the exposition of the polymer to the humid atmosphere. The crude product was then dissolved in dry acetone and chilled pentane was added through a cannula under vacuum to precipitate the polymer, and then dried under vacuum $(20 \times 10^{-3} \text{ bar},$

50 °C) for 24 h. (yield = 80%). The poly(VDF-*ter*-VDMP-*ter*-VTEOS) terpolymer, as a white wax, was characterized by ¹H and ¹⁹F NMR spectroscopies.

¹H NMR (400 MHz, DMF- d_7 , δ ppm of **P20**, Table 5.1, Figure 5.1): 0.4 to 0.7 (s, 1H -CF₂CH₂-CH₂C<u>H</u>-Si(OCH₂CH₃)₃), 1.1 to 1.3 (m, 9H -CF₂CH₂-CH₂CH-Si(OCH₂C<u>H₃)₃), 1.7 (m, 1H -CF₂CH₂-CH₂C<u>H</u>-PO(OCH₃)₂), 2.15 to 2.40 (m, -CF₂C<u>H₂-CH₂CF₂- reverse</u> VDF-VDF T-T dyad addition); 2.70 to 3.10 (m, -C<u>H₂CF₂-CH₂CF₂-, normal VDF-VDF H-</u> T dyad addition), 2.80 (-C<u>H₂CH-(Si(OCH₂CH₃)₃) and (-CH₂CH-(PO(OCH₃)₂)); 3.65 (s, 6H, -CF₂CH₂-CH₂CH-Si(OC<u>H₂CH); 3.7 (s, 6H, -CF₂CH₂-CH₂CH-PO(OC<u>H₃)₂); 6.05 to 6.45</u> (tt, ²J_{HF} = 55.0 Hz , ³J_{HH}= 4.6 Hz), -CH₂CF₂-<u>H</u> end-group originated from the transfer of proton to solvent or polymer or from the back biting.²⁰⁷</u></u></u>

¹⁹F NMR (376 MHz, DMF- d_7 , δ ppm of **P20**, Table 5.1, Figure 5.2): -91.5 to -93.5 (-CH₂C<u>F</u>₂-CH₂C<u>F</u>₂-normal VDF-VDF H-T dyad addition); -94.5 (-C<u>F</u>₂ of VDF in the VDF-VDMP/VTEOS dyad); -114 (-CH₂C<u>F</u>₂-CF₂CH₂-CH₂, reverse VDF-VDF H-H dyad addition); -115 (dtt, ²*J*_{HF} = 55.0 Hz, ³*J*_{HF} = 16.0 Hz and ⁴*J*_{FF} = 6 Hz, CF₂-CH₂C<u>F</u>₂-H, chain-end from transfer); -116.5 (-CH₂CF₂-C<u>F</u>₂CH₂-CH₂, reverse VDF-VDF H-H dyad addition).

³¹P NMR (162 MHz, DMF- d_7 , δ ppm of P20, Figure 5.3): peak centered at 37.5 ppm (–<u>P</u>(O)(OCH₃)₂).

²⁹Si NMR (80 MHz, DMF-*d*₇, δ ppm of **P**₂₀, Figure 5.4): -44 (s, -<u>Si</u>(OCH₂CH₃)₃), -46 (s, -<u>Si</u>(OCH₂CH₃)₂)(OH)).

5.4.4. Crosslinking of poly(VDF-ter-VDMP-ter-VTEOS) terpolymer.

The crosslinking of poly(VDF-*ter*-VDMP-*ter*-VTEOS) terpolymer was achieved via the hydrolysis and polycondensation of the pendant triethoxysilyl groups present on the polymers backbone. Typically, the terpolymer (5 g) was dissolved in DMF using a vortex mixer followed by the addition of 1 drop of hydrochloric acid (12 M) as water source and catalyst. The mixture

was immediately mixed for a couple of seconds and then kept stationary to avoid any disturbance for the network formation. The obtained milky gel after 2 hours was kept to age for 1 week at room temperature, followed by three washings with acetone prior to solvent removal under reduced pressure (20×10^{-3} bar, 80 °C) for 24 h. The final product obtained was a yellowish resin, which was characterized by solid state ²⁹Si and ³¹P NMR spectroscopies.

OP-MAS Solid state ²⁹Si NMR (80 MHz, δ ppm of **P**₂₀ after crosslinking, Figure 5.7): -50 to -60 (T₂ -<u>Si(OH)(OSi)₂</u>, -60 to -70 (T₃ -<u>Si(OSi)₃</u>).

OP-MAS Solid state ³¹P NMR (162 MHz, δ ppm of **P**₂₀ after crosslinking, Figure 5.9): -24 (-PO(OH)₂), -35 (-PO(OMe)(OH)), -44 (-PO(OMe)₂).

5.4.5. Hydrolysis of phosphonate groups into phosphonic acid functions in poly(VDF-*ter*-VDMP-*ter*-VTEOS) terpolymer.

Hydrolysis of the dimethyl phosphonate groups of poly(VDF-*ter*-VDMP-*ter*-VTEOS) terpolymer was carried out using bromotrimethylsilane. In a round bottom, poly(VDF-*ter*-VDMP-*ter*-VTEOS) terpolymer (2.0 g) was mixed till its totally swells in DMF (20 mL) under N₂ purging at room temperature. The polymer solution was then treated with 3 equivalents of bromotrimethylsilane, added dropwise under stirring over a period of 1 h and the reaction was allowed to proceed for 16 h at room temperature. Then, the reaction was quenched with 10 equivalents of MeOH. The polymer then filtered, and then dried under vacuum (20×10^{-3} bar, 50 °C) for 16 h to obtain poly(VDF-*ter*-VPA-*ter*-VTEOS) terpolymer (2.0 g), as a brown resin. The hydrolyzed product was characterized by solid state ³¹P (Figure 5.14) and ²⁹Si (Figure 5.15) NMR spectroscopy.

5.4.6. Complexometric Titration

The ion exchange capabilities of poly(VDF-*ter*-VPA-*ter*-VTEOS) terpolymer were determined through complexometric titration. The ion exchange process was performed by equilibration of poly(VDF-*ter*-VPA-*ter*-VTEOS) terpolymer with aqueous solutions of Eu(III) at various initial concentrations (2, 4, 6, 8 and 10×10^{-3} mol.L⁻¹). The lanthanide solutions were prepared by dissolving the appropriate amount of europium (III) chloride hexahydrate in a mixture of 10 ml water and 15 ml acetic buffer (pH 5.8). 0.25 g of the terpolymers was then added into each lanthanide solution and stirred for 24 h to allow the ion exchange to occur. The filtrates were then titrated with EDTA (0.01 M) in the presence of few drops of xylenol orange as an indicator. The addition of EDTA ceased when the color of the solution turned from violet to yellow. The uptake (α %) was determined by equation (5.5):

$$\alpha \% = \frac{Ci - Ce}{Ci} x \ 100 \tag{5.5}$$

Where Ci is the initial concentration of Eu(III) in the solution before the ion exchange and Ce is concentration of Eu(III) remaining in the solution after the ion exchange.

5.5. CONCLUSION

Novel functional PVDF based terpolymers for metal extraction application were synthesized, characterized and used for Eu³⁺ etxraction. These terpolymers were synthesized by a simple radical terpolymerization of VDF with commercially available VTEOS and VDMP. Appropriate choice of the initiator enabled to reach upto 85% yield. Poly(VDF-*ter*-VPA-*ter*-VTEOS) terpolymer was synthesized with different monomer compositions ranging from 70 to 80% PVDF, 5 to 20% VTEOS and 10% VDMP. The obtained waxy terpolymer, was crosslinked under acidic conditions to obtain a solid network that can not dissolve under any conditions. Additionally, the crosslinked terpolymer exibit a slight weaker thermal stability

while its degree of crystallinity (χ) was slightly higher than the uncrosslinked one. The phosphonate groups were partially hydrolyzed into phosphonic acid functions using bromotrimethyl silane, to obtain phosphonic acid functional poly(VDF-*ter*-VPA-*ter*-VTEOS) terpolymers. Furthermore, such functional terpolymer exhibited excellent europium extraction from water. This work opens new route to the application of materials for emerging applications in water decontamination.

Conclusion and perspectives

This PhD thesis work investigates the synthesis of new phosphorous or silane functional fluoropolymers for anticorrosion, enhanced adhesion and lanthanide ions extraction. In this work, the preparation of such functional PVDF was achieved by the co/terpolymerization of VDF with commercial phosphorous or silane functional monomers of by the modification of 2-(Trifluoromethyl)acrylic acid (MAF) to incorporate such functions. To have a better insight regarding such copolymerization a fundamental study dealing with the kinetics of radical copolymerization of VDF with MAF-TBE (a MAF derivative) in DMC using TBPPi as the initiator. Interestingly NMR spectroscopy studies showed that alternate copolymer is obtained, and a mechanism is proposed to illustrate the copolymerization route. This was further supported by the determination of the reactivity ratios for both monomers and the Alfrey and Price equations allowed the calculations for the Q and e values for both monomers.

Since the phosphorous function could bring potential applications in flame retardance, complexation, anticorrosion and adhesion, the preparation of phosphorous functional PVDF is presented in chapter 3 via the synthesis of new phosphonate functional MAF derivative (MAF-DMP). A detailed procedure for the preparation of MAF-DMP and its conventional polymerization with VDF is explicated. In addition, the reactivity ratio of the monomers was determined to compare the impact of different functions on the polymerization, while thermal properties of the copolymers showed relatively high thermal stability (which is expected for PVDF based polymers) that increases with the increase of VDF content in the monomers feed. The copolymers were then processed into films coated onto steel plates and a salt spray test was performed to access the anticorrosion properties of the polymers.

Chapter 4 demonstrate a new strategy for the introduction of a triethoxysilane function onto the polymer chains of PVDF. For this work, we opted for the post-polymerization modification
of cyclic carbonate functional PVDF with aminopropyltriethoxysilane (APTES) to introduce a pedant triethoxysilane function linked through a urethane group to the polymer's backbone. First the synthesis and the characterization of the cyclic carbonate functional MAF is achieved, followed by the copolymerized with VDF. The pedant cyclic carbonate rings present on the polymers surface was the modified with APTES to introduce the triethoxysilane group. Finally, hydrolysis of the triethoxysilane group was performed using acidic water (pH 1.5) to obtain a polymer colloidal solution which was casted into steel plates to assess its adhesive strength through the AsTM adhesion test.

Chapter 5 deals with the terpolymerization of VDF with both phosphorous and silane functional monomers to see the synergistic effect of such combination. However due to achieve a terpolymer with sufficient functional groups, vinyltriethoxylsilane (VTEOS) and vinyldimethylphosphonate (VDMP) monomer pair was chosen along VDF for such terpolymerization, since its polymerizations with MAF esters caps with 25% of the functional monomer in the polymerization feed. The terpolymerization proceeded in DMC and initiated by DTBPH. The obtained poly(VDF-ter-VDMP-ter-VTEOS) terpolymers was then crosslinked under acidic conditions to obtain a stable polymer network that cant dissolve in any solvent. The phosphonate groups were then hydrolyzed into phosphonic acid and the europium extraction abilities of such material was investigated and showed excellent results which means that such system can be employed for decontamination of water.

Since the demand for polymers tailored for specific applications is always high, MAF derivatives could be a compelling solution for the functionalization of PVDF. Although not reported in this current thesis, other functions such as PEG, furane, and sulfonic acid could be introduced for potential applications in Li ion batteries, self-healing PVDF and fuel cell

membranes respectively. The possibilities to introduce variety of functional groups is limitless and MAF could be the key for simple and efficient way for PVDF functionalization.

Due to the phosphorous atoms properties, multiple applications can be investigated for poly(VDF-*co*-MAF-DMP) and poly(VDF-*co*-VDMP) copolymers. For instance, the coating of metal nanoparticles could be investigated to change their surface properties such as hydrophobicity or oxidative stability. In addition, these polymers can also be used as additives to fabric and textile to improve their flame retardancy and hydrophobicity and oleophobicity. Since the position of the Phosphorous group on both polymers is different with one directly linked to the polymers back bone (case of poly(VDF-*co*-VDMP) copolymer) while the other connected through a linker (in poly(VDF-*co*-MAF-DMP) copolymer), it is interesting to see what effect this difference could bring to the effectiveness of these polymers in the applications they could be used to.

The cyclic carbonate functions on Poly(VDF-*co*-MAF-cyCB) copolymer, this polymer could be exploited to investigate a new method to crosslink the PVDF by the reaction of the pedant groups with a diamine crosslinker. Different functional and nonfunctional diamines could be studied to see the difference of effect of crosslinker size, effect of the newly introduced functions on the rate, swelling ratios and stability of such crosslinking. In addition, due to the electrical stability of PVDF, such copolymer could be investigated for Li ion transport via cyclic carbonate groups in Li ion batteries.

In regards for the lanthanide extraction studies for the poly(VDF-ter-VDMP-ter-VTEOS) terpolymer, although positive results was achieved a more detailed study should be performed to further support the already achieved results. For instance, since PVDF is stable in acids, studies on different pH could be performed to check for the optimal ion extraction pH ranges

and to investigate the metal release mechanism. Finally, the same system could be checked in the extraction for different types of metals (lanthanides or transition metals).

ANNEXE

General Experimental setup and Characterizations.

1. Characterizations

Nuclear Magnetic Resonance (NMR) Spectroscopy.

The compositions and microstructures of the copolymers were determined by ¹H and ¹⁹F NMR spectroscopies, recorded on a Bruker AC 400 Spectrometer (400 MHz for ¹H and 376 MHz for ¹⁹F) using DMSO- d_6 as a solvent. Coupling constants and chemical shifts are given in Hertz (Hz) and parts per million (ppm), respectively. The experimental conditions for recording ¹H [or ¹⁹F] NMR spectra were as follows: flip angle 90 ° [or 30 °, acquisition time 4.5 s [or 0.7 s], pulse delay 2 s [or 5 s], number of scans 32 [or 64], and a pulse width of 5 µs for ¹⁹F NMR.

Fourier Transform Infrared (FTIR) Spectroscopy.

FTIR analyses of the polymer were performed using a PerkinElmer Spectrum 1000 in ATR mode, with an accuracy of ± 2 cm⁻¹.

Size Exclusion Chromatography (SEC) Measurements.

Molecular weights (M_n s) and dispersities (Ds) of the poly(VDF-*co*-MAF-DMP) copolymers were assessed from size exclusion chromatography (SEC) with triple-detection GPC from Agilent Technologies using a PL0390-0605390 LC light scattering detector with two diffusion angles (15° and 90°), a PL0390-06034 capillary viscometer, and a 390-LC PL0390-0601 refractive index detector and two PL1113-6300 ResiPore 300 × 7.5 mm columns. DMF (containing 0.1 wt % of LiCl) was used as the eluent at a flow rate of 0.8 mL min⁻¹ and toluene as the flow rate marker. The entire SEC-HPLC system was thermostated at 35 °C. Poly(methyl methacrylate) standards were used for calibrating the SEC instrument and the results were processed using the corresponding Agilent software.

Thermogravimetric Analysis (TGA).

The thermogravimetric analysis of the purified and dried polymer samples were performed under air using a TGA 51 apparatus from TA Instruments at a heating rate of 10 $^{\circ}$ C min⁻¹ from room temperature to 580 $^{\circ}$ C.

Differential Scanning Calorimetry (DSC).

DSC analyses of the poly(VDF-*co*-MAF-DMP) copolymers were carried out using a Netzsch DSC 200 F3 instrument under N₂ atmosphere. The DSC instrument was calibrated with noble metals and checked before analysis with an indium sample ($T_m = 156$ °C). The heating or cooling range was from -40 °C to 200 °C at a scanning rate of 10 °C min⁻¹. Melting transitions were determined at the maximum of the enthalpy peaks and its area determined the melting enthalpy (ΔH_m).

The degrees of crystallinity of the copolymers were determined using equation 1:

Degree of crystallinity
$$(\chi) = \frac{\Delta H_m}{\Delta H_c} \times 100$$
 (1)

where ΔH_c (104.5 J g⁻¹) corresponds to the enthalpy of melting of a 100% crystalline PVDF^{286,347} and ΔH_m is the heat of fusion (determined by DSC in J g⁻¹), respectively.

Water Contact Angle (WCA).

WCA measurements were carried on the polymer thin film prepared by spin-coating (rpm = 3000, time = 30 s) from acetone solution (20 wt%) of the polymers on glass slides. The coated glass slides were then dried at room temperature for 12 h. WCA measurements were carried out at ambient temperature on Contact Angle System OCA-Data Physics using the water sessile drop method. The probe liquid was water (θ_{H2O}) and the dispensed drop volume was 5.0 µL. The average CA value was determined from five different drops per sample deposited on the same sample.

2. Modification of MAF into MAF-ester

(*i*) Synthesis of Dimethyl 2-(trifluoromethyl)acryloyl Chloride (MAF-COCl). In a typical procedure, MAF (1 equiv) and SOCl₂ (1.2 equiv) were taken in a 50 mL round bottomed flask equipped with a vertical condenser. An oil bubbler was attached on the top of the condenser to monitor the evolution of the gases during the progress of the reaction (HCl and SO₂). The reaction was stopped when evolution of gases ceased (almost after 4 hours). The product (MAF-COCl), as a yellowish liquid, was used as it is without further purification in the following step.

(*ii*) Synthesis of Functional MAF-Ester. The primary alcohol (1 equiv) and pyridine (1.1 equiv) were added to dichloromethane (40 mL) in a two-necked round bottom flask equipped with a dropping funnel. The mixture was stirred magnetically while purging with nitrogen for 20 mins. It was then cooled to -10 °C in an ice-salt bath and kept under nitrogen atmosphere. MAF-COCl (1 equiv) was transferred to the dropping funnel and added slowly to the reaction mixture (for 30 mins) while maintaining the flask at -10 °C. The reaction mixture was stirred magnetically at -10 °C for another 2 h and then at room temperature for additional 16 h. At the end of the reaction, 8 mL methanol was added to quench it. The reaction mixture was then washed three times with 40 mL dilute HCl, once with saturated NaHCO₃ solution and then finally with water (until neutral to pH). The organic layer was collected and dried over MgSO₄, filtered and the solvent was removed under vacuum.

3. Autoclave Operations.

The radical copolymerizations of VDF with MAF-esters were performed in a 50 mL Hastelloy autoclave Parr system (HC 276) which is equipped with a manometer, a mechanical Hastelloy anchor, a rupture disk (3000 PSI), inlet and outlet valves and a Parr electronic controller (for regulating the stirring speed and heating). Before the start of the reaction, the autoclave was checked for any leaks by pressurizing it with 30 bars of nitrogen. It was then put under vacuum

 $(40 \times 10^{-6} \text{ bar})$ for 30 min to remove the residual trace of oxygen. The dimethyl carbonate solution of the initiator and monomers was transferred into the autoclave under vacuum via a funnel tightly connected to the introduction valve of the autoclave. After this, the reactor was cooled in a liquid nitrogen bath, and VDF was transferred by double weighing (i.e., the difference of mass before and after filling the autoclave with VDF). The reactor was then allowed to warm up to ambient temperature and heated to the target reaction temperature under mechanical stirring.

4. Determination of the reactivity ratios

The determination of reactivity ratios was achieved by doing series of reactions in thick borosilicate Carius tubes (length 130 mm, internal diameter 10 mm, thickness 2.5 mm, total volume 8 mL). In a typical copolymerization, the different reactants including the initiator, solvent, and monomers were added in the tubes. The tubes were then degassed by three thaw-freeze cycles, the contents of the tubes were frozen in a liquid N₂ bath and VDF was transferred via a manifold from an intermediate cylinder from which the drop of pressure was calibrated beforehand with the amount of VDF (in g). Subsequently, the tubes were sealed under vacuum while keeping the content frozen in a liquid N₂ bath. The tubes were then inserted in thick metallic tubes placed in a heating and shaking apparatus regulated at the desired reaction temperature. After the reaction, the tubes were frozen and opened, and the instantaneous copolymer compositions were determined by measuring the conversions of the monomers by ¹⁹F NMR spectroscopy using equation (2).

$$mol\% VDF in copolymers = \frac{\left(\int_{-91}^{-96} CF_2 + \int_{-113}^{-118} CF_2\right)/2}{\left(\int_{-91}^{-96} CF_2 + \int_{-113}^{-118} CF_2\right)/2 + \int_{-66}^{-71} CF_3/3} \times 100$$
(2)

These low conversion (< 5 %) composition data points were then employed to plot the copolymer-monomer composition curve This curve was then fitted to the Mayo-Lewis³⁵⁴ copolymerization equation (3) using the least squares method, depicted by the red dotted line³⁵⁵

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \tag{3}$$

where F_1 , f_1 , f_2 , r_1 and r_2 stand for the molar percentage of monomer 1 in the copolymer, molar percentage of monomer 1 and monomer 2 in the comonomer feed, reactivity ratio of monomer 1 and monomer 2, respectively.

APPENDIX 1



Figure S2.1 ¹H NMR spectrum, recorded in DMF-d₇, of final poly(VDF-*co*-MAF-TBE) copolymer.



Figure S2.2¹⁹F NMR spectrum, recorded in DMF-d₇, of final poly(VDF-*co*-MAF-TBE) copolymer.



Figure S2.3 Evolution of autoclave pressure *versus* polymerization time of the radical copolymerization of VDF with MAF-TBE in DMC at 57 °C.

APPENDIX 2

Monomer (M)	acronym	temp. (°C)	r _{VDF}	r _M	References
H ₂ C=CHCO ₂ H	AA	50	0.11	305	356
H ₂ C=CHOCOCH ₃	VAc	45 (scCO ₂)	-0.40	1.67	357
H ₂ C=CHCF ₃	TFP	75	0.35	2.40	198
H ₂ C=C(CF ₃)CO ₂ H	MAF	55	0.33	0	85
H ₂ C=CHF	VF	45	0.17	4.2-5.5	358
H ₂ C=CFCF ₂ OR _F		120	0.38	2.41	359
FHC=C(F)CO ₂ H	DiFAA	74	0.34	0.86	360
$F_2C=CHC_6F_{13}$	-	74	12.0	0.9	361
F ₂ C=CHBr	BDFE	74	1.2	0.4	362
F ₂ C=CFH	TrFE	22	0.70	0.50	77
F ₂ C=CFCl	CTFE	80	0.73	0.75	363
F ₂ C=CFBr	BTFE	80	0.43	1.46	363
$F_2C=CF_2$	TFE	80	0.23	3.73	363
			0.32	0.28	364
F ₂ C=CF-CF ₃	HFP	70	5.0	0.0	365
		85	2.45	0	366
		120	2.90	0.12	367
		55 (scCO ₂)	5.13	0	368
		35 (scCO ₂)	3.6-4.6	0	369
		40 (scCO ₂)	3.2	0	370
F ₂ C=CF-OCF ₃	PMVE	120	3.40	0	371
		75	2.5	0	237
F ₂ C=CF-OC ₃ F ₇	PPVE	120	1.15	0	371
F ₂ C=CF-CO ₂ CH ₃	-	50	0.30	0	372
F ₂ C=CF-CH ₂ OH	-	50	0.83	0.11	373
F ₂ C=CF-(CH ₂) ₃ OAc	-	120	0.17	3.26	12
H ₂ C=C(CF ₃)COF	-	-	7.60	0.02	374
H ₂ C=C(CF ₃)OCOC ₆ H ₅	-	50	0.77	0.11	375
H ₂ C=C(CF ₃)CO ₂ CH ₂ PO(OCH ₃) ₂	MAF-DMP	74	0.76	0	Ch.3

Table S3.1. Reactivity Ratios of VDF with other Monomers in Radical Copolymerizations

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Supplementary Figures



Carius tube

Manifold

Water bath/Mechanical Shaker

Figure S3.1. Pictures of the Carius tube, manifold used to prepare the sealed Carius tubes and water bath/mechanical shaker to carry out radical copolymerization of VDF with MAF-DMP for the determination of the reactivity ratios.



Figure S3.2. Picture of the Fusion UV system for crosslinking coating formulations on steel plates for the corrosion study.



Figure S3.3. Pictures of Ascott Corrosion Test Chamber for Salt Spray Test (left) and the steel plate inside the chamber before the corrosion study (right).



Figure S3.4. ¹H NMR spectrum of MAF-DMP, recorded in CDCl₃ at 20 °C. (* Solvent (chloroform) peak)



Figure S3.5. ¹⁹F NMR spectrum of MAF-DMP, recorded in CDCl₃ at 20 °C.



Figure S3.6. ³¹P NMR spectrum of MAF-DMP, recorded in CDCl₃ at 20 °C.



Figure S3.7. SEC traces of poly(VDF-*co*-MAF-DMP) copolymers prepared by free radical copolymerization of VDF and MAF-DMP (see P1-P5, Table 3.1 for polymerization conditions and number average molecular weight characterization data). Because poly(VDF-*co*-MAF-DMP) copolymers have lower refractive indices (RIs) compared to the eluent and the detector is RI, the SEC signals are negative.



Figure S3.8. ³¹P NMR spectra of poly(VDF-*co*-MAF-DMP) copolymer (P2, Table 1) before (bottom) and after (top) hydrolysis of the phosphonate ester groups.



Figure S3.9. TGA thermograms of poly(VDF-*co*-MAF-DMP) copolymers prepared by free radical copolymerization of VDF and MAF-DMP using *tert*-amyl peroxy-2-ethylhexanoate in dimethyl carbonate at 74 °C (P1-P5, Table 1) heated at 10 °C min⁻¹ under air.



Figure S3.10. DSC thermogram of poly(VDF-*co*-MAF-DMP) copolymer containing 79 mol% VDF (P1, Table 1).



Figure S3.11. DSC thermogram of poly(VDF-co-MAF-DMP) copolymer containing 83 mol%

VDF (P2, Table 1).



Figure S3.12. DSC thermogram of poly(VDF-*co*-MAF-DMP) copolymer containing 86 mol% VDF (P3, Table 1).



Figure S3.13. DSC thermogram of poly(VDF-co-MAF-DMP) copolymer containing 92 mol%





Figure S3.14. DSC thermogram of poly(VDF-*co*-MAF-DMP) copolymer containing 96 mol% VDF (P5, Table 1).



Figure S3.15. ¹H NMR spectra of poly(VDF-*co*-MAF-DMP) copolymer (P2, Table 1) before (lower spectrum) and after (upper spectrum) hydrolysis of the phosphonate ester groups.



Figure S3.16. DSC thermogram of PVDF-PA, obtained by hydrolysis of the dimethyl phosphonate ester groups of poly(VDF-*co*-MAF-DMP) copolymer (P2, Table 1).



Before the test Plate with Scotch

After the test

Figure S3.17. Photographs of PVDF-PA films on steel plate before (A), with scotch tape (B) and

after (C) the adhesion test.

APPENDIX 3



Scheme S4.1. Ring opening of the cyclic carbonate groups by APTES in the presence of DBU to prepare poly(VDF-*co*-MAF-Si(OEt)₃) in DMF at room temperature.



Scheme S4.2. Hydrolysis of triethoxysilane groups into hydroxysilane in poly(VDF-*co*-MAF-Si(OEt)₃) to prepare poly(VDF-*co*-MAF-Si(OH)₃).



Figure S4.1. ¹⁹F NMR spectrum of MAF-cyCB, recorded in CDCl₃ at 20 °C.



Figure S4.2. ¹H NMR spectrum of poly(VDF-*co*-MAF-cyCB) copolymer prepared by free radical copolymerization of VDF and MAF-cyCB using TAPE in DMC at 74 °C (**P1**, Table 1), recorded in DMSO- d_6 (*) at 20 °C.



Figure S4.3. ¹⁹F NMR spectrum of poly(VDF-*co*-MAF-cyCB) copolymer prepared by free radical copolymerization of VDF and MAF-cyCB using TAPE in DMC at 74 °C (**P1**, Table 1), recorded in DMSO- d_6 at 20 °C.



Figure S4.4. ¹H NMR spectrum of poly(VDF-*co*-MAF-cyCB) copolymer prepared by free radical copolymerization of VDF and MAF-cyCB using TAPE in DMC at 74 °C (**P2**, Table 1), recorded in DMSO- d_6 (*) at 20 °C.



Figure S4.5. ¹⁹F NMR spectrum of poly(VDF-*co*-MAF-cyCB) copolymer prepared by free radical copolymerization of VDF and MAF-cyCB using TAPE in DMC at 74 °C (**P2**, Table 1), recorded in DMSO- d_6 at 20 °C.



Figure S4.6. ¹H NMR spectrum of poly(VDF-*co*-MAF-cyCB) copolymer prepared by free radical copolymerization of VDF and MAF-cyCB using TAPE in DMC at 74 °C (**P3**, Table 1), recorded in DMSO- d_6 (*)at 20 °C.



Figure S4.7. ¹⁹F NMR spectrum of poly(VDF-*co*-MAF-cyCB) copolymer prepared by free radical copolymerization of VDF and MAF-cyCB using TAPE in DMC at 74 °C (**P3**, Table 1), recorded in DMSO- d_6 at 20 °C.



Figure S4.8. ¹H NMR spectrum of poly(VDF-*co*-MAF-cyCB) copolymer prepared by free radical copolymerization of VDF and MAF-cyCB using TAPE in DMC at 74 °C (**P4**, Table 1), recorded in DMSO-*d*₆ at 20 °C.



Figure S4.9. ¹⁹F NMR spectrum of poly(VDF-*co*-MAF-cyCB) copolymer prepared by free radical copolymerization of VDF and MAF-cyCB using TAPE in DMC at 74 °C (**P4**, Table 1), recorded in DMSO- d_6 at 20 °C.



Figure S4.10. DSC thermogram of poly(VDF-*co*-MAF-cyCB) copolymer containing 77 mol% VDF (**P1**, Table 1).



Figure S4.11. DSC thermogram of poly(VDF-co-MAF-cyCB) copolymer containing 83 mol% VDF

(**P2**, Table 1).



Figure S4.12. DSC thermogram of poly(VDF-*co*-MAF-cyCB) copolymer containing 87 mol% VDF (**P3**, Table 1).



Figure S4.13. DSC thermogram of poly(VDF-co-MAF-cyCB) copolymer containing 91 mol% VDF

(**P4**, Table 1).



Figure S4.14. DSC thermogram of poly(VDF-*co*-MAF-cyCB) copolymer containing 96 mol% VDF (**P5**, Table 1).



Figure S4.15. ¹H NMR spectra of poly(VDF-*co*-MAF-Si(OEt)₃) copolymer, recorded in DMSO at 20°C.



Figure S4.16. ATR-IR spectra of poly(VDF-*co*-MAF-cyCB) copolymer (**P3**, Table 1) (top spectrum) and that of poly(VDF-*co*-MAF-SiO_{1.5}) network (bottom spectrum).



Figure S4.17. DSC thermogram of poly(VDF-*co*-MAF-Si(OEt)₃ copolymer.



Figure 4.18. ¹⁹F NMR spectrum of poly(VDF_{0.7}-*co*-MAF-cyCB_{0.3}) copolymer prepared by free radical copolymerization of VDF and MAF-cyCB initiated TAPE in DMC at 74 °C (**3**, Table 2), recorded in DMSO- d_6 at 20 °C.

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Abstract

Fluorinated polymers are intresting macromolecules which due to their unique properties are often used in special applications in building industries, aerospace, chemical engineering, optics, textile treatment and microelectronics. This thesis focusses on the development of phosphorous and silane functional fluorinated polymers through the conventional radical co/terpolymerization of functional monomers with vinylidene difluoride (VDF). These functional monomers were prepared from the modification of 2-(Trifluoromethyl)acrylic acid (MAF) to prepare MAF-esters with the desired functional group. First a fundamental study regarding the kinetics of polymerization of VDF with MAF-TBE revealed that these monomer pair tends to cross propagate resulting in an alternating copolymer. Phosphonate functional MAF (MAF-DMP) was then prepared and its copolymerization with VDF led to phophonate functional PVDF, that after the consequent hydrolysis of the phosphonate group into phosphonic acid showed anticorrosion properties to steel. Following the same concept, a cyclic carbonate functional MAF monomer (MAF-cyCB) was also copolymerized with VDF. The cyclic carbonate groups in the obtained PVDF copolymer was then opened by aminopropyltriethoxysilane to introduce a silane group, that by its hydrolysis allowed the copolymer to adhere strongly onto substrates. Finally, a terpolymer based on PVDF functional with both a phosphonate and a triethoxysilane group is prepared. The silane group was then hydrolyzed and crosslinked to obtain a 3D network of polymers. Finally, the hydrolysis of the phosphonate group into phosphonic acid led to material that can be employed in Eu(III) ion extraction from water.

Keywords: Fluoropolymer, PVDF, Phosphonate, Silane, Polymerizations, Sol-Gel, Anticorrosion, Adhesion, Lanthanide extraction.

Résumé

Les polymères fluorés sont des macromolécules intéressantes qui, en raison de leurs propriétés uniques, sont souvent utilisées dans des applications spéciales dans les industries du bâtiment, de l'aérospatiale, du génie chimique, du traitement des textiles, optiques et de la microélectronique. Cette thèse se concentre sur le développement de polymères fluorés fonctionnels à base de phosphore et de silane par la co/terpolymérisation radicalaire conventionnelle de monomères fonctionnels avec le fluorure de vinylidène (VDF). Ces monomères fonctionnels ont été préparés à partir de la modification de l'acide 2-(trifluorométhyl) acrylique (MAF) pour préparer des MAF-ester avec le groupement fonctionnel souhaité. Tout d'abord, une étude fondamentale concernant la cinétique de polymérisation du VDF avec MAF-TBE a montré que ces paires de monomères ont une tendance à se propager de manière croisée, ce qui donne des copolymères alternés. On a ensuite préparé du MAF avec une fonction phosphonate (MAF-DMP) et sa copolymérisation avec du VDF a permis d'obtenir du PVDF à fonctionnalité phosphonate qui, après l'hydrolyse consécutive du groupe phosphonate en acide phosphonique, avait des propriétés anticorrosion sur l'acier. De facon similaire, un monomère de MAF porteur une fonction carbonate cyclique (MAF-cyCB) a également été copolymérisé avec du VDF. Les groupes carbonate cycliques dans le copolymère de PVDF obtenu ont ensuite été ouverts par l'aminopropyltriéthoxysilane pour introduire un groupe silane, qui, par son hydrolyse, a permis au copolymère d'adhérer fortement sur les substrats. Enfin, un terpolymère à base de PVDF fonctionnel porteur à la fois un groupe phosphonate et un groupe triéthoxysilane a été préparé. Le groupe silane a ensuite été hydrolyse et réticulé pour obtenir un réseau 3D de polymères. Enfin, l'hydrolyse du groupe phosphonate en acide phosphonique a conduit à une matière pouvant être utilisée dans l'extraction des ions Eu (III) de l'eau.

Mots clés: Fluoropolymère, PVDF, Phosphonate, Silane, Polymérisations, Sol-Gel, Anticorrosion, Adhérence, Extraction de Lanthanides.