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Poly(vinylidene fluoride)-based Complex Macromolecular Architectures: From Synthesis to Properties and Applications

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ABSTRACT

This review highlights the synthesis, properties and applications, as well as the potential, of the rarely appeared in the literature poly(vinylidene fluoride) (PVDF)-based complex macromolecular architectures (CMAs). PVDF, the second in production fluoropolymer, is an attractive material due to its outstanding properties (high thermal stability and chemical inertness) along with its piezo-, pyro- and ferro-electrical performance. So far, although studies on the PVDF-based CMAs are limited, there is a growing interest in the synthesis/properties of non-linear structures (graft, miktoarm star, star and dendrimers), as well as their potential high-tech applications including drug/gene delivery, electronics and energy harvesting devices. The aim of this review is to present the primary strategies for the synthesis of PVDF-based polymer materials with CMAs and critically discuss the generation of avenues that may facilitate their commercialization. We anticipate shortly that PVDF-based CMA polymers will play a progressively important role in materials science and nanotechnology, both in academia and industry.

Keywords: poly(vinylidene fluoride), fluoropolymers, complex macromolecular architectures, properties, applications.

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Nomenclature

AAC	Acrylic acid
APCN	Amphiphilic polymer conetworks
ATRC	Atom transfer radical coupling
ATRP	Atom transfer radical polymerization
BDFO	8-bromo-1H,1H,2H-perfluorooct-1-ene
BCP	Block copolymer
BVPE	Bis(vinyl phenyl) ethane
BSA	Bovine serum albumen
CMA	Complex macromolecular architectures
CuAAC	Copper(I)-catalyzed azide-alkyne cycloaddition
CRP	Controlled radical polymerization
CTFE	Chlorotrifluoroethylene
DMA	Dimethyl acetamide
DMAEMA	2-(dimethylamino)ethyl methacrylate
DMAPS	N, N'-dimethyl-(methylmethacryloyl ethyl) ammonium propanesulfonate
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DVB	Divinylbenzene
EB	Electron beam
EGMA	Ethylene glycol methacrylate
GMA	Glycidyl methacrylate
GPE	Gel polymer electrolyte
HFP	Hexafluoropropylene
ITP	Iodine transfer polymerization
MF	Micro-filtration
MTFA	Methyl-1,1,2-trifluoroacrylate
MMA	Methyl methacrylate
MADIX	Macromolecular design through interchange of xanthate
MPS	3-Mercapto-1-propanesulfonic acid sodium salt
NIPAAM	N-isopropylacrylamide
NPs	Nanoparticles
NR	Nile Red
NMP	N-methyl pyrrolidinone

NMR	Nuclear magnetic resonance
PAAc	Polyacrylic Acid
PBIEA	Poly[2-(2-bromoisobutyryloxyethyl acrylate)]
PE	Polyethylene
PEGDME	Poly(ethylene glycol) dimethyl ether
PEGMA	Poly(ethylene glycol) methacrylate
PEG	Poly(ethylene glycol)
PGMA	Poly(glycidyl methacrylate)
PFPEs	Perfluoropolyethers
PMA	Propargyl methacrylate
PtBA	Poly(<i>tert</i> -butyl acrylate)
POMA	Poly(oxyethylene) methacrylate
PFSVE	Perfluoro(4-methyl-3,6-dioxaoct-7-ene) sulfonyl fluoride
PBIEA	Poly[2-(2-bromoisobutyryloxy)ethyl acrylate]
PLLA	Poly(lactic acid)
PMMA	Poly(methyl methacrylate)
PPMA	Poly(propargylmethacrylate)
PNIPAAM	Poly(N-isopropylacrylamide)
PS	Polystyrene
PSU	Polysulfones
PSSA	Poly(styrene sulfonic acid)
PTFE	Poly(tetrafluoroethylene)
PVBC	Poly(vinyl benzylchloride)
PVC	Polyvinyl chloride
PVDF	Poly(vinylidene fluoride)
RAFT	Reversible addition-fragmentation chain-transfer
St	Styrene
TFE	Tetrafluoroethylene
TFMAA	2-Trifluoromethacrylic acid
tBA	<i>tert</i> -butylacrylate
UF	Ultrafiltration
VDF	Vinylidene fluoride

1. Introduction

The synthesis of well-defined complex macromolecular architectures (CMAs) including graft, miktoarm star, star and dendritic architectures (**Figure 1**) is very important for material science since CMAs possess significantly different properties than the corresponding linear and thus provides a flexible platform in the fast-growing fields of nanotechnology, electronics, drug/gene delivery, biomedical materials or supersoft elastomers [1-5]. Besides, CMAs exhibit a variety of unique behavior, in solution and bulk, due to their ability to self-assemble into higher-order structures than the linear analogs [6].

Figure 1.

Fluorinated polymers are attractive specialty polymers in both industry and academia due to their : (i) outstanding high thermal stability, chemical inertness (to solvents, acids, and bases, except vinylidene fluoride (co)polymers), low dielectric constant, low surface energy (oil and water repellency), low flammability, low permittivity, low dissipation factor, and low water absorption as well as excellent weather resistance to oxidative and hydrolytic decomposition, (ii) behavior versatility: thermoplastics, elastomeric, plastomeric, or thermoplastic elastomers and crystallinity versatility: crystalline, semicrystalline or amorphous. These features are mainly related to the low polarizability, strong electronegativity, small van der Waals radius (1.31 Å) of the fluorine atom inducing strong C-F bond (energy dissociation is 485 kJ mol⁻¹) [7-12].

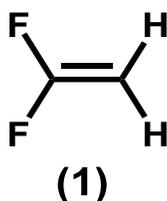
PVDF is an exceptional member of the fluoropolymer family with the second largest production volume of fluoroplastics after polytetrafluoroethylene (PTFE) [13]. In addition to its extraordinary properties and diverse range of applications, PVDF reveals piezoelectric (when is stretched), pyroelectric, and ferroelectric properties that can be implemented in electronics and energy harvesting devices [14-16], haptics and actuators [17]. However, PVDF deals with three major disadvantages: (i) high melting temperature corresponding to a high energy cost of processability; (ii) poor solubility in common organic solvents (PVDF is soluble only in dimethylformamide (DMF), dimethyl sulfoxide (DMSO), dimethylacetamide (DMA) and N-methyl pyrrolidinone (NMP), and (iii) difficult curing due to its high crystallinity [18]. To this direction, various fluorinated random/block copolymers and PVDF-based CMAs have been synthesized to enhance their properties and tune the adhesion, solubility, ion exchange, cross-linking ability, and so on [15]. While much attention was devoted to linear PVDF-based

materials, the number and type of CMA are limited [16, 19, 20]. Compared to linear analogs, complex systems are more intriguing owing to their compact structure, globular shape, and low viscosity.

PVDF-based CMAs are particularly exciting and present an attractive target in material synthesis. In order to facilitate the reader to understand the properties of the complex structures, we provide a brief introduction of linear PVDF-based homo/copolymers, which constitute the simplest structures of PVDF-materials. The developed synthetic routes towards PVDF-based CMAs, their properties, as well as current and potential applications over the last ten years are discussed.

2. PVDF-based Linear Polymers

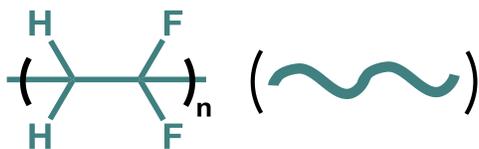
PVDF is formed by polymerization of vinylidene fluoride (VDF) monomer (**1**), a colorless, flammable, non-toxic, environment-friendly and odorless gas. VDF boils at -82 °C, freezes at -144 °C and its solubility in water is 6.4 cm³/100 g at 25 °C. VDF can be easily homopolymerized and copolymerized under radical initiation processes [21-25].



2.1. PVDF Homopolymers

PVDF (**2**) is commonly synthesized by a free radical polymerization process in aqueous emulsion or suspension at 15 - 350 atm and 20 - 140 °C) [14]. Solution polymerization in various organic solvents has been also investigated with organic peroxides initiators. Temperature, pressure, additives, as well as monomer feeding, are variables that influence product characteristics, as thoroughly discussed in an excellent review [21]. Due to the asymmetry of VDF monomer, and to compare to the hydrogen size of the fluorine atom VDF can be added to the growing macroradicals either by normal -CH₂CF₂-CH₂CF₂- (head-to-tail, H-T) or inverse -CH₂CF₂-CF₂CH₂- (head-to-head, H-H) and -CF₂CH₂-CH₂CF₂- (tail-to-tail, T-T) addition. The percentage of each addition, depending on the polymerization conditions [14, 26], can be evaluated by ¹H and ¹⁹F nuclear magnetic resonance (NMR) spectroscopy. According to the percentage of the chain “defects” (H-H and T-T), the crystallinity and consequently the

mechanical properties of PVDF such as strength, toughness, impact resistance and so on change. Successful controlled radical polymerizations (CRP) of VDF have also been reported including iodine transfer polymerization (ITP), reversible addition-fragmentation transfer (RAFT) polymerization and borane-mediated polymerization [19, 27, 28].



(2)

2.2. PVDF-based Random Copolymers

Copolymerization modulates both intramolecular and intermolecular forces so that properties such as melting point, glass transition temperature, crystallinity, stability, elasticity, permeability, and chemical reactivity may be varied over a wide temperature range [14]. The following fluoromonomers were radically copolymerized with VDF: hexafluoropropylene (HFP), tetrafluoroethylene (TFE), bromotrifluoroethylene (higher fluorine content cure-site monomer that improves solvent resistance), and perfluoroalkyl vinyl ether instead of HFP when low-temperature resistance is required [29, 30].

Among them, random copolymers such as poly(VDF-*co*-chlorotrifluoroethylene, CTFE), poly(VDF-*co*-trifluoroethylene), poly(VDF-*co*-HFP), poly(VDF-*co*-TFE), poly(VDF-*co*-pentafluoropropene), poly(VDF-*co*-3,3,3-trifluoropropene) and poly(VDF-*co*-1,1,1,2-tetrafluoropropene), poly(VDF-*co*-bromofluoroalkenes), poly(VDF-*co*-hexafluoroacetone), poly(VDF-*co*-perfluoroalkyl vinyl ether), poly(VDF-*co*-functional perfluorovinyl monomer), poly(VDF-*co*-fluoroacrylates) and poly(VDF-*co*-aromatic monomers) represent the most important synthetic attempts among thermoplastic copolymers of VDF and all these were prepared by conventional radical copolymerization [14]. Additionally, a few random copolymers were also synthesized by CRP including: poly(VDF-*co*-2-trifluoromethacrylic acid, TFMAA), poly(VDF-*co*-perfluoromethylvinylether) copolymers [31] and poly(VDF-*ter*-HFP-*ter*-F₂C=CFSF₅) terpolymers [14, 32, 33].

2.3. PVDF-based Block Co/Terpolymers

Block copolymers (BCPs), made of chemically different chains covalently linked each other, have received much attention since they provide new physical and thermodynamic

properties [34-38]. BCPs consisting of non-miscible blocks exhibit phase-separated microstructures, for example, a dispersed phase (spheres, gyroids or cylinders) of one block into a continuous matrix of the second one. Their special rheological and mechanical properties allow modification of solution viscosity, impact resistance, surface activity, and elasticity of polymers. Thus, a wide range of BCPs has been synthesized with tailorable properties depending on the nature and the length of the block sequences. BCPs have found significant applications in adhesives, sealants, surface modifiers for fillers and fibers, cross-linking agents for elastomers, additives for resin gelification and hardening, as well as compatibilizing agents or stable emulsifiers of homopolymer blends. Besides, the fluorinated BCPs, due to their exceptional properties, find applications in O-rings, shafts, diaphragms, sealants, gaskets, fuel cell membranes, surfactants, and other items (lenses, dental materials, etc.) [38].

The following four methods for the synthesis of PVDF-based BCPs are considered [14, 16]:

(i) *Conventional radical polymerization*: an example is the copolymerization of VDF with ω -iodoperfluorinated perfluoropolyethers (PFPEs) as macrotransfer agent in the presence of an adequate initiator (cleavage of C-I bond). The resultant PFPE-*b*-PVDF displays a phase-separated morphology leading to two glass transition temperatures: -143 °C (PFPE) and -82 to -40 °C (PVDF). Similarly, as above, the synthesis of PFPE-*b*-poly(VDF-*co*-HFP) diblock terpolymer was also reported [39].

(ii) *Controlled/living polymerization*: various diblock and multiblock *co*/terpolymers such as poly(VDF-*co*-HFP)-*b*-PVDF, PVDF-*b*-PHFP BCP or poly(VDF-*ter*-HFP-*ter*-TFE) triblock terpolymer, PVDF-*b*-PCTFE BCP [40], poly(TFE-*ter*-VDF-*ter*-HFP) triblock terpolymer, PVDF-*b*-polystyrene (PS) BCP [41], PVDF-*b*-poly(methyl methacrylate) (PMMA) and PMMA-*b*-PVDF-*b*-PMMA, poly(VDF-*co*-HFP)-*b*-PS, poly(VDF-*co*-HFP)-*b*-poly(styrene sulfonic acid) (PSSA), PSSA-*b*-PVDF-*b*-PSSA and PSSA-*b*-poly(VDF-*co*-HFP)-*b*-PSSA, PSSA-*b*-poly(VDF-*co*-HFP)-*b*-PSSA, PS-*b*-PVDF-*b*-PS, poly(VDF-*co*-HFP)-*b*-poly(VDF-*co*-HFP) and poly(VDF-*co*-HFP)-*b*-poly(vinyl acetate), poly(VDF-*ter*-HFP-*ter*-(perfluoro(4-methyl-3,6-dioxaoct-7-ene) sulfonyl fluoride (PFSVE)-*b*-poly(VDF-*co*-HFP) from poly(VDF-*ter*-HFP-*ter*-PFSVE), poly(VDF-*co*-TFP)-*b*-oligo(vinyl acetate) [42] and poly(VDF-*co*-TFP)-*b*-oligo(vinyl alcohol), PM-*b*-PVDF BCP and PM-*b*-PS-*b*-PVDF triblock terpolymer (PM : polymethylene) [43] were synthesized using controlled/living polymerization methods like ATRP, halogen transfer, RAFT

and ITP [14].

(iii) *Polycondensation*: a series of BCPs containing bisphenol A polysulfone and PVDF (PSF-*b*-PVDF) were synthesized by polycondensation of α,ω -dihydroxybisphenol A polysulfone homopolymer and α,ω -dibromo-PVDF. The synthesized BCPs, composed of rigid PSF and flexible PVDF segments, showed good thermal stability. Sulfonation of the PSF resulted in sulfonated PSFs-*b*-PVDF block copolymers while their potential use in proton conducting polymer fuel cell membranes was investigated [44].

(iv) “*Click*” *chemistry*. For example the copper (I)-catalyzed azide-alkyne cycloaddition (CuAAC) reactions, between alkyne- and azido-terminated homopolymers were applied for the synthesis of PVDF-*b*-PS [45], PVDF-*b*-PNIPAAM and PVDF-*b*-PtBA diblock copolymers [46]. Similarly, alkyne-terminated poly(lactic acid) (PLLA) and PVDF (N₃-PVDF-N₃) homopolymers “clicked” together to obtain double crystalline PLLA-*b*-PVDF-*b*-PLLA triblock copolymers [47]. The same strategy was applied for the synthesis of well-defined poly(3-hexyl thiophene)-*b*-PVDF-*b*-poly(3-hexyl thiophene) copolymers [16, 48].

2.4. PVDF-based Alternating Copolymers

Besides PVDF-based random copolymers and BCPs, alternating copolymers containing VDF units have been studied in academia and commercialized in industry. The radical copolymerization of VDF with other fluorinated comonomers having the appropriate reactivity ratios, produce alternating poly(VDF-*alt*-monomers) copolymers that can be used as thermoplastics, elastomers, and thermoplastic elastomers [14]. VDF was able to produce alternating copolymers with hexafluoroisobutylene, hexafluoroacetone, methyl 2-trifluoroacrylate or TFMAA [14]. Souzy *et al.* reported the alternating copolymerization of VDF with 2-trifluoromethacrylic acid (TFMAA), a non-homopolymerizable monomer [49]. Several years later, the same group fabricated polymer electrolyte membranes consisting of alternating copolymers of VDF, TFMAA, and HFP by adapting the following steps. In the first step, the conventional radical polymerization initiated by 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane was used to obtain poly(VDF-*alt*-TFMAA) alternating microblock structures separated by one HFP unit. The analysis of monomers sequence was proved by ¹⁹F-NMR spectroscopy. As a next step, the carboxylic acid groups of TFMAA were reduced into dangling hydroxyl ones. Finally, after etherification *via* a Mitsubishi reaction, these fluorinated polyols were converted to aryl

sulfonic acids grafted sites. Electrochemical and physicochemical properties of these poly[(VDF-*alt*-TFMAA)-*co*-HFP] materials were evaluated after mixing with commercially available poly(VDF-*co*-HFP) copolymers and casting into membranes [50]. It is worth mentioning that VDF, first monomer to be copolymerized with hexafluoroisobutylene in an alternating fashion, was commercialized by the Allied Co. (now Honeywell) under the CMX trademark [51].

3. PVDF-based Complex Macromolecular Architectures

Despite the fact that star structures are the simplest complex architectures, we decided to start from grafts since they are the most studied CMA.

3.1. Graft Polymers

A graft copolymer is a branched polymer in which one (miktoarm star) or more side chains are constitutionally or configurationally different from the main chain. Modification of commercial fluoropolymers such as PTFE, PVDF, etc. by grafting has attracted particular interest. Depending on the chemistry, number and molecular weights of branches, the properties of fluoropolymers, such as surface hydrophilicity, compatibility with other polymers, adhesion to metallic and inorganic substrates can be modified [52, 53]. The grafting of polymers onto PVDF backbone has been mostly accomplished by conventional radical polymerization *via* ozone treatment [52] or high energy technologies (ionizing radiation, γ rays, electron beam, and plasma) and later by controlled/living radical polymerization techniques with the most prominent that of ATRP.

3.1.1. Irradiation Grafting

Grafting on PVDF chains is mainly accomplished by first introducing free-radical moieties (initiating sites) along the PVDF chains (backbone), followed by polymerization of the side branch chain monomer, as shown in **Scheme 1**. Free radicals along the chain (backbone) can be generated either by radiation (e.g. corona, X-rays, γ -rays and electron beam) or by chemical treatment (peroxy/hydroperoxy method). In the case of radiation, formation of graft copolymers can be attempted either in steps (pre-irradiation and grafting) or simultaneously [53].

Scheme 1.

Radiation-induced graft copolymerization, in general, is a well-established technology dating back almost 60 years [54]. However, the first grafting onto PVDF chains can be found in 1986 in the seminal work of Niemöller *et al.*, where the authors studied the influence of different grafted chains of PVDF membranes on the separation of EtOH/H₂O by pervaporation process [55]. Initially, PVDF chains were exposed to ionizing radiation in order to randomly activate several sites along the backbone. These sites served as multimacroinitiators for the free radical polymerization of the side-chain monomer. Two decades later, Betz *et al.* inserted carboxylic acid groups in the side chains by grafting acrylic acid (AAc) onto PVDF backbone using either ion irradiation or electron beam. The synthesized amphiphilic graft copolymers were useful for the attachment of polypeptides with biological activity [56], or as drug carriers for substances such as dextran [57] and riboflavin [58].

3.1.2 Ionization Grafting

An alternative grafting strategy that can introduce peroxide initiating sites is the ozone treatment of PVDF backbone in solution. Ozonization of the PVDF backbone gives rise to the formation of alkyl peroxide and hydroperoxide groups along the PVDF chain (**Scheme 2**). However, the treatment is not so effective for fully fluorinated polymers such as PTFE and poly(tetrafluoroethylene-*co*-hexafluoropropylene), and poly(tetrafluoroethylene-*co*-perfluoroalkylvinyl ether) copolymers.

Scheme 2.

In one of the first attempts, Boutevin *et al.* activated PVDF after ozone treatment, followed by graft copolymerization of methyl methacrylate (MMA) to synthesize PVDF-*g*-PMMA copolymers (**Scheme 2**) [59]. The authors noted that the grafting rate in bulk is faster compared to that in solution. In the same work, PVDF parent block has been also grafted with other monomers such as styrene (St), AAc and glycidyl methacrylate (GMA). A couple of years earlier, the same group studied the reactivity of peroxides generated from PVDF compared to those generated from polyethylene (PE) and polyvinyl chloride (PVC), after ozonization, claiming that PVDF radicals are more reactive than PE and PVC based on the dissociation rate

constant (k_d) and activation energy (E_a) [60]. These two seminal works triggered the inspiration of two forthcoming contributions that describe the fabrication of micro-filtration (MF) membranes from PVDF backbone grafted with AAc [61] and N-isopropylacrylamide (NIPAAAM) by phase inversion technique [62]. The authors were able to manage the pore size and size distribution of the membranes by simply controlling the copolymer composition. The authors came to the conclusion, that the higher the duration and the temperature of ozone treatment, the higher the peroxide concentration. However, the danger of polymer degradation under extreme conditions exists [63].

Methoxy-poly(ethylene glycol) monomethacrylate was also grafted onto pretreated with ozone PVDF backbone to synthesize PVDF-*g*-PEGMA copolymer and used for the fabrication of ultrafiltration (UF) membranes [64]. The authors proved that even for grafting yield of 7%, the fabricated membrane is capable of preventing the adsorption of bovine serum albumin pointing out their utility as antifouling materials. Nah's group fabricated nanoporous polymer electrolytic membranes of PVDF-*g*-PtBA and studied the electrochemical stability and ionic conductivity [65]. The high values of conductivity, due to the solvation of Li by the oxygen atoms of PEG, PEGDME or PtBA chains, trigger the authors' interest to evaluate them as binders in electrodes of lithium-ion batteries [66]. By this common combination of ozone-treatment and phase-inversion technique, pH-sensitive membranes of PVDF-*g*-poly(4-vinylpyridine) and PVDF-*g*-PAAc were tested showing pH-sensitive permeability to aqueous solutions, but in an opposite manner [67]. For the former, the flow rate of aqueous solution (permeability) increased with the increase of pH value from 1 to 6. While for the latter one, the permeability through the membrane decreased and the decrease is more intensive between pH ranges of 2-4.

The development of ozone treatment as an activation method of PVDF backbone coincided with the advent of ATRP, a suitable technique for grafting monomers with functionalized groups. Zhai *et al.* [68] synthesized PVDF-*g*-poly[2-(2-bromoisobutyryloxy)ethyl acrylate] (PBIEA) which later has been used as ATRP macroinitiator for the polymerization of either sodium 4-styrenesulfonate (NaSS) or ethylene glycol methacrylate (EGMA) towards arborescent (-ar-) copolymer PVDF-*g*-PBIEA-*ar*-PNaSS and PVDF-*g*-PBIEA-*ar*-PEGMA, respectively. In the first case, membranes that cast from 1M aqueous NaCl solution had enriched with NaSS side chains and exhibited larger pore sizes compared to the membranes cast from water under the phase inversion process. In the second case, the authors claimed the improved

protein adsorption (c-globulin) due to the grafted PEGMA as quantified by XPS elemental analysis. By adopting the methodology of PVDF-*g*-PBIEA ATRP macroinitiator, the same group [69] attempted to graft DMAEMA monomer but with a low conversion (5%). Even though, the consecutive *n*-alkylation with hexyl bromide and nitromethane led to the quarternized PVDF-*g*-PBIEA-*ar*-QPDMAEMA membranes with polycation chains chemically tethered on the membrane surface that potentially prevent the bacterial growth and as a result can be used as an antibacterial assay. The same team [70] extended his studies by grafting polybetaines (zwitterionic polymers) onto the parent PVDF to produce temperature-dependent phase transition membranes. For the synthesis of these membranes, the authors applied thermally induced graft copolymerization of N,N'-dimethyl-(methacryloyl ethyl) ammonium propanesulfonate (DMAPS), a sulfobetaine monomer with electrolyte- and temperature-dependent behavior. The polymerization was carried out in a mixture of NMP and DMSO and the successful synthesis of the graft copolymer was confirmed by elemental analysis.

In addition to direct grafting, post-polymerization modification and subsequent “click” chemistry reactions were also applied for the synthesis of stimuli-responsive copolymer such as PVDF-*g*-[poly(glycidyl methacrylate) (PGMA)-*click*-poly(N-isopropylacrylamide) (PNIPAAM)] [71]. In this case, azide-functionalized GMA side chains were grafted *via* free radical-initiated graft copolymerization of GMA onto PVDF backbone, followed by reaction of the oxirane rings of GMA side chains with sodium azide (PVDF-*g*-P[GMA-(N₃)(OH)]). As a next step, previously prepared by ATRP alkyne-functionalized NIPAAM block reacted *via* “click” chemistry with the PGMA side chains to synthesize the thermoresponsive PVDF-*g*-P[GMA-*click*-PNIPAAM] copolymer (**Scheme 3**).

Scheme 3.

Using a slightly different methodology, the same group enriched the portfolio of “click” chemistry by using thiol-yne functionalized moieties, which previously introduced *via* graft copolymerization of propargyl methacrylate (PMA) using initiating sites along the PVDF backbone, created by ozonolysis. These PVDF-membranes were decorated either with thiol-functionalized 3-mercapto-1-propanesulfonic acid sodium salt (MPS) or azide-functionalized molecules such as azido- β -CD (where CD: cyclodextrin). The PVDF-*g*-P[PMA-*click*-MPS]

membranes exhibited electrolyte-dependent permeability for aqueous solutions, while the PVDF-*g*-P[*PMA-click-β*-CD] ones presented resistance to protein adsorption after surface inclusion of diadamantyl-poly(ethylene oxide) (AD-PEO) guest polymers [72].

Decoration of PVDF-based membranes with Au and Ag nanoparticles has been also achieved from a PVDF-containing graft copolymer as a precursor (**Scheme 4**). By using ozone-pretreatment, grafting copolymerization of pentafluorophenyl acrylate (PFA) led to the synthesis of PVDF-*g*-PFPA [73]. As a next step, amine/ester reaction of PFA pendant groups with dopamine hydrochloride converted to catechol functionalized PVDF-*g*-PDA membrane. The produced PVDF-*g*-PDA MF membranes used as a platform for the electroless plating and subsequent deposition of Au and Ag nanoparticles. An alternative NPs grafting *via* Michael addition and Schiff base reactions has been also followed by the same authors using three different types of functional polymers. The PVDF-*g*-PDA-Ag and -Au composite MF membranes were examined in specific antibacterial and thermo-responsive antifouling properties.

Scheme 4.

Recent advances in controlled/living polymerization have emerged tremendous opportunities over the synthesis of well-defined macromolecular architectures including linear, star-shape, comb and graft copolymers. Except for ATRP, RAFT method has been also used to prepare porous film having regular pore structure and size. The transfer of a dithioester moiety between the active and dormant species is described as a RAFT cycle resulting in well-defined architectures and controlled lengths of chains (predetermined molecular weight and low dispersity). Membranes that have been synthesized from RAFT-mediated process polymers were found to be much more uniform than that produced by “conventional” radical graft copolymerization process. For instance, Chen *et al.* were successfully synthesized amphiphilic PVDF-*g*-PEGMA copolymers by RAFT graft copolymerization of EGMA as a promising approach for the fabrication of antifouling MF membranes [74]. 1-Phenylethyl dithiobenzoate was used as the CTA while the polymerization was initiated by the previously ozone-activated PVDF backbone. To further ascertain the “living” character of polymerization, the authors consequently initiated block polymerization of St toward the synthesis of PVDF-*g*-(PEGMA-*b*-

PS). By adopting a slightly different strategy, the same group succeeded in the synthesis of PVDF-*g*-PAAc-*b*-PNIPAAM MF membranes [75]. In both cases, scanning electron microscopy of the cast by phase inversion MF membranes revealed higher uniformity over the pore size compared to the membranes of the conventional radical polymerization process.

3.1.3 Plasma and other radiation grafting methods

The immobilization of reactive groups along the parent PVDF backbone by argon-plasma process and the simultaneous graft polymerization has also been demonstrated (one-step plasma grafting technique). In principle, plasma polymerization is a process of high energy radiation that causes scission of chemical bonds (C-C and C-F) and generation of free radicals. Wang *et al.* reported the immobilization of PEG chains onto PVDF membranes by plasma initiated grafting technique [76]. The optimization of plasma conditions related to radio-frequency plasma power and the required time increased the surface PEG graft concentration. In 2007, Kaur *et al.* explored the capability of plasma-graft copolymerization of methacrylic acid (MAA) onto PVDF-based electro-spun nanofibrous membranes (ENM) to reduce the pore size. The synthesized PVDF-*g*-PMAA electro-spun membranes, when compared to commercially available PVDF ones exhibited “tighter” pored PVDF ENMs, while retaining their water flux performance [77]. Based on PVDF-*g*-PMAA, Gianelli’s group fabricated a hydrophilic UF membrane *via* the covalent attachment of super hydrophilic NPs to the PMAA grafts. In more details, silica NPs with external amine cationic ligands were anchored on the carboxylic groups of PMAA units *via* a dip-coating process [78]. The authors claimed that the transformation from hydrophobic to highly hydrophilic membrane was proved by the 100% increase of surface energy. Additionally, the hydration layer of hydrophilic silica NPs amplified the antifouling performance of these PVDF-based membranes as was proved after evaluation against BSA foulant.

A few additional methods have been proposed for initiating graft copolymerization along the PVDF backbone. For instance, several groups demonstrated the production of free radicals along the PVDF chain *via* electron beam and γ -rays treatment [79, 80]. Although a great deal of work has been carried out in the area of pre-irradiation treatment, none of these authors declared the synthesis of well-defined PVDF-based graft copolymers, since always the subsequent conventional radiation-induced grafting technique resulted in graft copolymers of little or no

control. In 2001, Holmberg *et al.* first combined a pre-irradiation treatment with ATRP to produce well-defined graft copolymers [81]. The benzylchloride groups of poly(vinyl benzylchloride) (PVBC) chains, previously grafted on PVDF stem, were utilized as ATRP initiators for the grafting of St followed by *tert*-butyl acrylate and thus giving rise to PVDF-*g*-(PVBC-*g*-PS) and PVDF-*g*-[PVBC-*g*-(PS-*b*-PtBA)] respectively. Kinetic studies showed that the degree of St grafting increased linearly with time to very high yield; the authors pointing out that such a high degree of grafting could not arise by conventional radiation-induced grafting method. Additionally, they supported their claim by exploiting the remaining chloride sides for the block polymerization of *tert*-butyl acrylate toward the fabrication of PVDF-*g*-[PVBC-*g*-(SSA-*b*-*tert*-butyl acrylate)] membranes after the sulfonation of PS grafts (**Scheme 5**). The same group also applied the electron beam (EB)/alkoxyamine concept to synthesize proton exchange membranes (PEMs) *via* Nitroxide-mediated controlled/living free radical graft polymerization (SFRP) [82]. The PVDF free radicals that formed from EB irradiation were immediately quenched with 2, 2, 6, 6-tetramethylpiperidinyl-1-oxy (TEMPO) which utilized as an initiator for the grafting of St or copolymerization of St and N-phenylmaleimide. In both cases, sulfonation was followed to synthesize PVDF-*g*-poly(St-*co*-phenylmaleimide) membrane while for the PVDF-*g*-PS, the alkoxyamines groups were converted to maleimide derivative before sulfonation. Thermogravimetric analysis (TGA) studies of the final PVDF-*g*-poly(SSA-*co*-phenylmaleimide) revealed that the addition of N-phenyl maleimide units increases the thermo-oxidative stability of the final PEMs.

Scheme 5.

In 2011, studies on the materials produced by graft copolymerization of 2-hydroxyethylmethacrylate onto EB preactivated PVDF backbone [79] revealed the improvement in dielectric properties by grafting PVDF. The poly(2-hydroxyethylmethacrylate)-*g*-PVDF copolymers were evaluated as capacitors for energy storage since at room temperature the measured dielectric constant is about 4.5 times higher as compared to pristine PVDF stem [79]. EB pre-irradiation method has also been used for the synthesis of cross-linked proton exchange membranes by grafting St onto fluoropolymers in the presence of different cross-linkers, followed by functionalization with sulfonic acid groups (SO₃H). The final properties of the

produced proton exchange membranes (PVDF-*g*-PSSA), such as crystallinity and mechanical strength, are influenced by the structure and concentration of the chosen cross-linkers [83]. For the same graft copolymer, in 2003, Qiu *et al.* [84] presented an alternative methodology of radicals activation based on solution grafting, free of any radiation treatment. Prior to grafting step, PVDF backbone was treated with an alcoholic solution of 0.5 M potassium hydroxide (KOH). The authors claimed that after a suitable time pretreatment, H and F atoms were stripped out from the PVDF chains while benzoyl peroxide in THF solution initiated the grafting of St. After sulfonation, the methanol permeability of PVDF-*g*-PSSA membrane, as tested by gas chromatography, was one magnitude lower than that of a typical perfluorosulfonated membranes, such as Nafion® [84]. Similar activation method by dipping PVDF powder into KOH solution was used by Chen *et al.* to proceed with the radical grafting of hydrophilic 4-methacrylamidobenzenesulfonic acid (MABS) monomer [85]. The synthesized amphiphilic PVDF-*g*-PMABS copolymer was mixed with PVDF homopolymer and even at low concentration (4wt. %) gave blends with significantly improved water flux in comparison with pure PVDF membrane.

The same PVDF-*g*-PSSA was used as a direct methanol fuel cell (DMFC) membrane after Al₂O₃ doping [86]. The resultant composite membranes with an optimum content (10% w/w) showed significantly reduced methanol permeability than either pure PVDF-*g*-PSSA or Nafion. Divinylbenzene (DVB) and bis(vinyl phenyl) ethane (BVPE) were used to cross-link the PVDF-*g*-PSSA membranes and improve the mechanical and swelling properties [87].

Table 1

Despite the promising results of radiation-induced radicals towards the synthesis of PVDF-graft copolymers, we believe that in the coming decades the impact of controlled/living methods will further enrich the PVDF-based graft copolymer portfolio [88] with a plethora of novel materials with unique properties.

3.1.4. Grafting by controlled/living polymerization method

As previously mentioned, the progress in control radical polymerization has made it possible to synthesize graft fluoropolymers with a controlled chain length and end group

fidelity[89]. Albeit the controlled cleavage of carbon-fluoride bond is not an easy task, vinyl monomers such as methacrylates were successfully grafted on PVDF or PVDF-*co*-PTrFE *via* the direct C-F backbone bond activation.

In 2002, Mayes' group first demonstrated the direct grafting of poly(ethylene glycol methacrylate) (PEGMA) from parent PVDF (**Scheme 6**), inspired by the work of Matjaszewski and Möller groups on the ATRP of St and butyl acrylate using the bromopropionyloxy groups of poly(2-(2-bromopropionyloxy) ethyl acrylate) as initiators [90]. The secondary fluorine of PVDF initiated the oligomerization of EGMA (only nine monomeric units) giving rise to PVDF-*g*-PEGMA amphiphilic copolymer [91]. At the same study, authors grafted *tert*-butyl methacrylate (*tert*-BuMA) onto PVDF stem and by subsequent hydrolysis enabled the synthesis of another amphiphilic graft copolymer PVDF-*g*-PMAA [91]. In the following publication, the same group confirmed the "living" nature of ATRP process *via* kinetic studies of MMA grafting from PVDF backbone [92]. By adopting the above-mentioned single-step method, Kim *et al* prepared proton-conducting graft copolymer electrolytes of PVDF-*g*-PSPMA (where SPMA: sulfopropyl methacrylate) and (PVDF-*g*-PSSA) [93]. The authors claimed exceptional thermal stability even at 350 °C for both copolymers, with proton conductivity values of 0.015 S/cm and 0.007 S/cm, respectively.

Scheme 6.

After these pioneer works, Chen [94] and Nandi [95] groups studied the grafting of relatively more reactive monomers such as 2-(dimethylamino) ethyl methacrylate (DMAEMA). In more details, the first group applied the ATRP initiation of DMEMA and (ethylene glycol) monomethacrylate (EGMA) from secondary fluorinated sites of PVDF enabling the surface polymerization from PVDF coated films [94]. Kinetic studies showed a linear increase in the graft concentration with time showing the "living" character of the polymerization. Formation of block copolymer by subsequent addition of St further confirmed the control chain growth. At the same period, Liu, Chen *et al.* carried out the grafting of MMA and EGMA monomers on PVDF by hydroxylation and esterification with 2-bromoisobutyrate bromide to introduce ATRP initiating sites along the backbone [96]. Kinetic studies and water contact angle measurements of the copolymer films indicated that the tethered bromide groups enabled the controlled grafting and the significant increase of film coverage by the hydrophilic brushes. From mechanism point

of view, Nandi group presented a more in-depth study on how the grafting density increases upon increasing the polymerization time up to 36% (w/w) conversion with respect to the monomer [95]. Additional mechanical tests led to the conclusion that the storage modulus of graft copolymers decreases compared to the pristine PVDF precursor due to the decrease of crystallinity but giving rise to supergluing polymeric material.

During the last decade, PEGylated or PEG-based PVDF membranes *via* either free or controlled/living polymerization grafting of EGMA were also fabricated. Blending of this type of graft copolymers with PVDF has been used by many groups to enhance hydrophilicity and fouling resistance of PVDF membranes [97-100]. A sophisticated comparison of grafting EGMA monomer either by surface-initiated ATRP or plasma-induced graft-polymerization was described by Quemener's group [101]. The brush-like PEGMA of the former membrane (controlled) showed less water absorbency than the network-like PEGMA membrane (uncontrolled) of the latter one. On the other hand, the brush-like structure led to lower protein absorption and better antifouling as indicated by filtration test with bovine serum albumen (BSA) solution.

For the same application purpose, NIPAAAM constitutes another widely used monomer that grafted onto PVDF parent chain drawing much attention in environmental stimuli-responsive membranes. After phase inversion treatment in aqueous solution, PVDF-*g*-PNIPAAAM materials showed significant response in water flux under temperature changes the reason authors gave the nick-name "smart" membranes to these materials [102]. Additionally, porosimetry measurements on similar membranes were conducted by Chen's group concluding that pore size of the copolymer membranes increases with the increase of the volume fraction of the grafted PNIPAAAM [103]. More recently, similarly prepared membranes were evaluated before and after the NIPAAAM grafting, indicating dramatic increase of hydrophilicity and change in porous structure from sponge-like structure to continuous channels as revealed from AFM and SEM images [104]. Unlike acrylate or acrylamide based monomers, the methacrylate ones are more efficient in grafting by ATRP from PVDF backbone. They form relatively stable free radical centers during initiation or propagation step. The reason that ATRP grafting onto PVDF backbone proceeds satisfactorily is the modest reactivity of this monomer group due to its non-interactive nature [88].

Nandi's group first reported that ATRP grafting on PVDF backbone proceeds more efficiently with *n*-butyl methacrylate (*n*-BMA) in comparison to the rest acrylate and acrylamide monomers in terms of yield and graft length [105]. The grafting of *n*-BMA onto PVDF backbone was carried out by using a Cu⁺/bipyridine-based catalyst system in NMP at 90 °C. The authors proved their claims utilizing ¹⁹F NMR, which indicated that 100% grafting occurs on the H-H defect sites of the PVDF chain. This is because the H-H defects have more significant steric strain than that of H-T bonds due to the larger atomic radius of fluorine ($r_F=1.35 \text{ \AA}$) compared to that of hydrogen ($r_H=1.25 \text{ \AA}$). On the other side, under similar reaction conditions, the grafting of monomers such as DMAEMA and GMA from PVDF macroinitiator yields much lower conversions. For instance, ATRP of GMA using a copper/4,4'-dimethyl-2,2'-dipyridyl as catalytic system in a highly polar solvent (ethylene carbonate) yield only 34% conversion [106]. Additional attempts using DMF and NMP as polymerization medium showed no polymerization, a phenomenon, which is attributed to the thermal polymerization of GMA as authors assumed.

In order to keep the properties of PVDF backbone intact during the grafting, it is of utmost importance the implement of highly controlled conditions and "livingness" of radical sites. However, this is not possible through the direct breakage of stable (C-F) bond, which results in lower initiation rate compared to the rate of propagation. The radical center stability along PVDF backbone after (C-F) bond cleavage is lower than the stabilization of produced macroradicals. This mismatch of reactivity leads to poor initiation efficiency while is reduced even more when the radical center produced from monomer molecules that are much less stable as in the case of acrylates or acrylamides. Even for these monomers where the grafting onto PVDF backbone has been confirmed, the reported conversions are significantly low (15-40 %) [91, 94, 95, 105]. To avoid the drawback of low conversion and to succeed higher molecular weight grafting of non-acrylate monomers, some other groups tried to activate fluorinated backbones by initiators bearing C-I, C-Br, and C-Cl active sites. For instance, Zhang and Russel reported the grafting of PS and poly(*tert*-butyl acrylate) (PtBA) from the fluorinated backbone of poly(VDF-*co*-CTFE)) random copolymer *via* ATRP [107] (**Scheme 7**). The PCTFE section of poly(VDF-*co*-CTFE) bears pendant secondary halogen atoms that are capable of initiating graft polymerization of St or *tert*-butyl acrylate. Starting by model reactions of oligomer units of CTFE, the authors indicated that grafting density, as well as the distribution of grafts, solely depends on the density and distribution of CTFE units in the parent fluoropolymers. Subsequent

hydrolysis of PtBA grafts of poly[(VDF-*co*-CTFE)-*g*-PtBA] copolymer resulted in amphiphilic graft copolymers with polyacrylic acid (PAAc) side chains. The authors mentioned the potential applications of these graft polymers as pH-sensitive membranes. The abovementioned synthetic route triggered the fabrication of several functional graft copolymers due to their well-oriented film formation.

By replacing the PAAc to PSSA as grafting chains, Kim *et al.* studied the microphase separated structure of poly[(VDF-*co*-CTFE)-*g*-PSSA] (**Scheme 7**) [108]. After the conversion of chloride to azide groups, UV irradiation was applied in order to crosslink the polymer electrolyte membrane. The crosslinked membranes showed significantly reduced water uptake while proton conductivity was slightly affected compared to the uncrosslinked membrane. Also, poly(VDF-*co*-CTFE)-*g*-POEM graft copolymer was used as a template film for the selective localization of silver NPs *via* the in situ reductions of AgCF₃SO₃ precursor under UV irradiation [109]. The selectivity of silver NPs confinement into POEM domains was explained as a result of NPs coordinative interaction with the polar ether oxygens of POEM moiety.

Scheme 7.

PtBA was also grafted onto poly(VDF-*co*-TrFE) film by using surface-initiated ATRP method while the produced polymer brushes were converted to poly(acrylic acid sodium salt) after hydrolysis [110]. Ameduri's group discovered the efficient St grafting *via* the cleavage of C-Br bond along PVDF backbone obtained by copolymerization of VDF with 8-bromo-1H,1H,2H-perfluorooct-1-ene (BDFO) [111]. The bromide anchored group of BDFO units served as macroinitiator for the grafting of St in a typical ATRP process using different temperature, ligand and solvent amount. Kinetic studies {ln([St]₀/[St]) *vs* time} indicated linear dependency which essentially confirmed that ATRP grafting was carried out in a controlled manner to produce PVDF-*g*-PS copolymer. Till 2016, none of the involved studies had clarified the exact mechanism of C-F cleavage during the ATRP grafting of tBA and St monomer onto poly(VDF-*co*-TrFE) backbone. Takahara *et al.* proved with detailed spectroscopic results (¹H and ¹⁹F NMR) that all grafted chains were covalently bonded exclusively by the fluorine abstraction from the CFH group in TrFE units of the backbone [112].

In a more recent work, Nandi *et al.* grafted various polyacrylamide and polymethacrylate derivatives along PVDF backbone by anchoring initiating sites even more reactive than fluorine by adopting a two-step process of i) atom transfer radical coupling (**Scheme 6**) and ii) ATRP [113] (**Scheme 8**). The transformation of radical sites involves the replacement of one fluorine atom of -CF₂ units of PVDF backbone with 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl(4-hydroxy-TEMPO). Subsequent esterification with 2-bromopropionyl bromide or 2-chloropropionyl chloride enabled the synthesis of macroinitiator which has been used for the grafting of MMA, *tert*-BMA either DMAEMA respectively. The higher graft conversion and length of grafting blocks of these model polymers compared to those initiated from ATRP of typical secondary fluorinated sites revealed significant impact in thermal and stress-strain measurements as mentioned by the authors.

Scheme 8.

One of a very few works that involves a non-ATRP grafting method without any preactivation step published by Lienafa *et al* [114] used nitroxide-mediated polymerization in order to emanate PS grafts from PVDF backbone (**Scheme 9**). The low molecular weight of PVDF stem was synthesized by using 1-iodoperfluorohexane as a CTA while the synthesized stem was functionalized with 2,2-diphenyl-3-phenylimino-2,3-dihydroindol-1-yloxy nitroxide (DPAIO) in NMP solution.

Scheme 9.

Then PVDF-*g*-DPAIO was used as a macroinitiator for the styrene grafting. The authors highlighted the potential of nitroxide radicals under mild conditions for the synthesis of PVDF-*g*-PS graft copolymers. They also proved that grafting occurred from methylenic protons of tail-to-tail addition defects as revealed from the corresponding decrease of percentage (by ¹H-NMR spectroscopy).

Table 2

3.2. Star Polymers

Star polymers are branched polymers with chemically same or different arms, emanating from a single junction. These polymers can be synthesized *via* controlled/living polymerization techniques using two well-established strategies: core-first and arm-first or coupling-onto approaches. Various polymerization methods that include anionic, ring-opening metathesis polymerization, ATRP, nitroxide-mediated living radical polymerization have been used for the synthesis of star polymers. However only few of these (RAFT, ITP) are applicable for the synthesis of PVDF-based star polymers [115]. Star polymers exhibit different properties compared to their linear analogs, e.g. lower hydrodynamic volume allowing them to be used as viscosity modifiers in lubricants while their multiple arms aid to improve flocculation and adhesion [116]. Star polymers also used as interfacial stabilizing agents, drug/gene delivery, imaging, nanoreactor/catalysis, ink printing, adhesion, and coating. Although star polymers imbued with PVDF arms are particularly interesting, their synthesis is challenging the reason there are only three examples reported in the literature.

The first report of PVDF-based stars comes from Ameduri and coworkers [117]. As shown in **Scheme 10**, a 4-arm star PVDF was synthesized by RAFT method controlled by a tetraxanthate, followed by reaction with hexylamine and 3-(acryloyloxy)-2-hydroxypropyl methacrylate in a one-pot process to afford a 4-arm star PVDF end-capped with photocrosslinkable methacrylate moieties. The resultant 4-arm star PVDF tetramethacrylate can be photocrosslinked using the photoinitiator (Darocur® 1173) under UV light. This photocrosslinked PVDF star polymer exhibited an appealing alternative to PVDF/PMMA blends for transparent coatings in outdoor applications (*Discussed in details in Applications Section 4*).

Scheme 10.

Patrickios and coworkers [118] used such above strategy to synthesize 4-arm star PVDF terminated by tetrabenzaldehyde (tetraPVDF-Bz) in a three-step procedure: (i) RAFT polymerization of VDF using the tetraxanthate CTA to produce tetraPVDF-XA (where XA is the xanthate terminal groups), (ii) end-group modification using a one-pot aminolysis/thia Michael addition to obtain tetraPVDF-OH and (iii) esterification of the terminal hydroxyl end-groups with 4-formylbenzoic acid (**Scheme 11**). Later, they prepared amphiphilic polymer conetworks (APCN) by mixing tetraPVDF-Bz and 4-arm star PEG end-functionalized with

benzacylhydrazide (tetraPEG-BAH) in glacial acetic acid (**Scheme 12**). In this work, the authors studied the equilibrium swelling behavior of the APCN in various solvents and concentrations by small-angle neutron scattering which indicated phase separation at the nanoscale. Finally, they conclude this work with potential applications in drug delivery, tissue engineering, low adsorption coatings, and phase transfer catalysis (*Discussed in details in Applications Section 4*).

Scheme 11.

Scheme 12.

Lin and coworker [119] synthesized 21-arm star-like amphiphilic block copolymer composed of PAAc and PVDF blocks by a combination of ATRP, “click” reaction and hydrolysis step. As shown in **Scheme 13**, β -cyclodextrin, a cyclic oligosaccharide possessing 21 hydroxyl groups was esterified by reacting with 2-bromoisobutyryl bromide, yielding 21-arm star-like initiating sites. Subsequently, ATRP of *tert*-butyl acrylate (*t*BA) was performed to achieve star-like poly(*tert*-butyl acrylate) (PtBA) and then Br groups were transformed into N₃ to produce PtBA-N₃. On the other hand, alkyne-terminated PVDF was obtained by the nucleophilic substitution of the hydroxyl-capped PVDF using propargyl bromide (**Scheme 13**). Finally, the “click” reaction between PtBA-N₃ and alkyne terminated PVDF formed the star-like PtBA-*b*-PVDF diblock copolymer. The *tert*-butyl ester groups of PtBA in PtBA-*b*-PVDF star BCP were readily hydrolyzed and yielded amphiphilic star-like PAAc-*b*-PVDF BCP (**Scheme 13**). As next step, the PAAc-*b*-PVDF diblock star copolymers were used as a platform for the *in-situ* generation of BaTiO₃ nanoparticles by dissolving it in a mixture of solvents (DMF + benzyl alcohol), appropriate amount of BaCl₂·2H₂O, TiCl₄ precursor and sodium hydroxide (**Scheme 13**). The PAAc moieties of star diblock copolymers provide a strong coordination interaction between their –COOH groups and BaTiO₃ metal precursors. Despite the high number of required steps, the proposed methodology is effective for the decoration of inorganic nanoparticles with polymeric surfaces preventing their aggregation and increasing their dispersibility into nanocomposite blends.

Scheme 13.

3.3. Miktoarm Star Polymers

Miktoarm stars (sometimes called asymmetric star, heteroarm star polymers) are branched polymers with chemically different arms emanating from a single branching point, created by the combination of various linking and polymerization techniques. This simple nonlinear structure makes stars ideal candidate for studying the solution and bulk properties of branched polymer systems [120]. The properties of these systems can be adjusted by modifying the number of arms and their corresponding molecular characteristics, as well as through polymer composition [116]. The latter can be properly manipulated to introduce properties like lipophilicity and biocompatibility [121-123]. Miktoarm stars are a synthetically challenging class of polymers. Multiple synthetic strategies, orthogonality, and combination of different polymerization methods are typically necessary for the synthesis of these polymers, regardless of the specific type of desired miktoarm star polymer (A_2B , ABC , AB_2C_2 , A_2B_2 , $(AB)_2C_2$, etc.). In recent years, considerable advances in synthetic strategies, self-assembly, and applications have developed, making scientific community to become increasingly aware of miktoarm star polymers [124]. Although, the synthesis of novel materials by combining the special characteristics of miktoarm and PVDF is an appealing target, nevertheless, only one work was reported until now.

Rodionov *et al* synthesized PVDF-based miktoarm star polymers $(AB)_2C_2$ -type (where A: PS, B: PVDF, C: PEG) by combining ATRP, ITP and CuACC techniques [125]. As shown in **Scheme 14**, the synthesis involves: (i) preparation and use of diazido-dibromo initiator for the ATRP of St leading to $(PS-Br)_2(N_3)_2$, (ii) conversion of terminal benzylic Br into I groups through a nucleophilic substitution reaction, which serve as an ITP macrotransfer agent, (iii) ITP of VDF, yielding the azide functionalized $(PVDF-b-PS)_2$ diblock copolymer, and (iv) “click” reaction with alkyne-terminated PEG to yield the final amphiphilic $(PVDF-b-PS)_2(PEG)_2$ 4-miktoarm star copolymer. Spectroscopy (1H - and ^{19}F -NMR, FTIR) as well as SEC characterization confirmed the successful formation of the PVDF-based 4-miktoarm star copolymer. Furthermore, the authors investigated the self-assembly in selective solvents, bulk and surface by dynamic light scattering, transmission electron microscopy and atomic force microscopy. Finally, the authors considered the potential application of this amphiphilic miktoarm star polymer for the encapsulation and transfer of hydrophobic molecules in aqueous

media (*Discussed in details in Applications Section 4*). To date, this is the only work on PVDF-based miktoarm star polymers by following a relatively easy way toward its synthesis.

Scheme 14.

3.4. Dendrimers

Dendrimers are perfectly defined hyperbranched polymers with tunable multivalent surfaces that can find applications in supramolecular chemistry, catalysis, biomedical, drug/gene delivery, etc. [126-129]. Dendrimers are nano-sized, branching symmetric molecules with well-defined homogeneous and monodisperse structure that has a typically symmetric core [130]. The structure of dendrimer molecules begins with a central atom or group of atoms (core) through the branches of other atoms called ‘dendrons’ which grow by using a variety of chemical reactions [131]. Due to their molecular architecture, dendrimers show some significantly improved physical and chemical properties when compared to traditional linear polymers. For example, in solution, the linear chains exhibit flexible coils while dendrimers form a tightly packed ball. This has a great impact on their rheological properties. For example, their viscosity is lower than that of linear polymers [132].

A rapid increase of interest in the chemistry of dendrimers has been noticed since the first discovery by Frechet and Tomalia in the early 1980s [133, 134]. Despite three decades since the discovery of dendrimers, the association of dendrimers and PVDF has appeared in only two publications. Caminade and coworkers synthesized the first PVDF-based dendrimers *via* CuAAC [135]. From the synthetic aspect (as shown in **Scheme 15**), first alkyne containing phosphorous dendrimer was prepared from a dendrimer bearing $[P(S)Cl_2]_6$ end-groups and propargyloxyphenol in the presence of cesium carbonate. Along with, the azide-functionalized PVDF was synthesized by RAFT polymerization using azide-bearing xanthate. Finally, “click” reaction between multialkyne-dendrimer and N_3 -PVDF produced PVDF dendrimer in the presence of copper iodide and diisopropylethylamine. The surface properties of this dendrimers displayed a higher hydrophobicity than both of its precursors. This well-defined PVDF-based dendrimers belongs to a first generation of polyphosphorhydrazone dendrimer demonstrating the increase of PVDF crystallinity and hydrophobicity of the corresponding film.

Scheme 15.

Very recently, Ouali and coworkers [136] synthesized pyrene-tagged PVDF-dendrons through “click” chemistry by reacting azide-functionalized PVDF with peripheral acetylenic functions of dendron possessing a pyrene core and 10 PVDF chains (**Scheme 16**). Then, the resultant PVDF-dendrimer was non-covalently coated on the graphene surface of cobalt magnetic nanoparticles (MNPs) (**Figure 2**). This work showed the preparation and characterization of new dissymmetric dendrimers bearing ten PVDF branches and one flexible arm ended by a pyrene moiety able to interact with the graphene surface (**Figure 2**). The tagged MNPs by PVDF dendrimer may constitute key building blocks for the dispersion of nanoparticles in the PVDF matrix to produce highly attractive nanocomposites targeting applications in the growing fields of printed and flexible electronics, binders for lithium ion batteries, and additives for coatings.

Scheme 16.

Figure 2.

4. Applications

PVDF-based linear building blocks are known for extensive use in a wide range of products including aeronautics/aerospace, building construction, petrochemicals, automotives, chemical engineering, textile treatment, electrical/electronic devices and other specialty applications. In spite of their high market value, these polymers have met major development in modern technologies. As for the whole class of fluoropolymers and PVDF-based linear BCPs, commercial applications of PVDF-based complex structure materials reflect their specific synergy (besides the structure) of properties arising from PVDF and the combined polymer moiety. The complex macromolecules based on PVDF can be involved in many applications such as membranes, gel polymer electrolytes (GPEs), high performance thermoplastic elastomers, piezo, pyro and ferroelectric and biomedical materials.

a) Graft polymers

From an industrial point of view, graft copolymers with the general form Poly(VDF-*g*-X) (where X is the grafting monomer) have received the highest attention. Some of the most representative examples and according to the targeting applications are classified as follows:

i) **Fluorothermoplastic elastomers (FTPE):** Under the trademark of Cefral Soft®, Central Co. commercialized a tough-resilient material by the PVDF grafting onto a fully fluorinated terpolymer consisting of VDF, chlorotrifluoroethylene and an olefinic peroxy carbonate (e.g., *tert*-butylperoxyallyl carbonate, TBPAC) with a $T_g = 170$ °C [137]. A slightly different version of a fully fluorinated graft copolymer such as P[(CTFE-*co*-VDF)-*g*-PVDF], was also commercialized by Central Glass company resulting in a thermoplastic elastomer of significantly lower T_g (-21°C) [138]. Although FTPEs are more expensive than the typical neoprene or nitrile rubber elastomers, their higher heat and chemical resistance categorize them in the class of materials suitable in extreme environments such as aerospace applications, protection coatings in electronics and high durability O-rings and gaskets.

ii) **Additives for antifouling membrane technology:** Graft copolymers consisting of crystalline (i.e., rigid) stem are expected to be a very good candidate for the development of well-organized porous assemblies. Poly(VDF-*g*-M) (M corresponds to a hydrophilic monomer) has shown improvement to the antifouling properties and can be used as an additive for the fabrication of membranes as an alternative treatment in water and wastewater management [139]. For this purpose, the grafting of hydrophilic acrylate polymers *via* ATRP process is of critical importance for the preparation of defect-free and high performance ultrafiltration membranes [140]. Over the last decade, many groups studied the filtration performance based on both hydrophilic and oleophobic surface properties and evaluated them as an additive material to PVDF membranes. After hydrolysis of poly(*tert*-butyl acrylate) (PtBA) grafts, the resulted P(VDF-*co*-CTFE)-*g*-PMAAc membrane was esterified with perfluoroalkyl PEG surfactant [141]. PVDF-*g*-PEGMA copolymers are also important candidate materials of antifouling membranes for several type of waste processes (chemical, biochemical, and pharmaceutical industries) [142]. The surface “PEGylation” of PVDF blended membranes by the addition of PVDF-*g*-PEGMA in order to increase hydrophilicity and antifouling resistance has been demonstrated in several previous studies. For instance, Hashim *et al.* prepared PVDF membranes by adding to PVDF homopolymer, a mixture of PVDF-*g*-PEGMA and unreacted PEGMA coming from the ATRP method that was used for the synthesis of graft copolymer [97].

Although, the authors highlighted the low number of required steps and the higher pure water flux in comparison with the pristine PVDF ($116 \text{ L/m}^2 \cdot \text{h}^{-1}$), a few years later, Crittenden's and Chen's group succeeded at least one order of magnitude higher pure water flux ($5170 \text{ L/m}^2 \cdot \text{h}^{-1}$) for their own PVDF/PVDF-*g*-PEGMA blends [98]. In this case, authors noticed a defect-free pillar-like structure by properly varying the PVDF/PVDF-*g*-PEGMA/solvent ratio. More recently, the same group investigated the formation mechanism of the aforementioned pillar-like structures by a series of experiments where solvent and additive were varied [99]. They claimed that 1-methyl-2-pyrrolidinone and PVDF-*g*-PEGMA must coexist in the membrane casting solutions to obtain these special "pillar-like" structures, while the proposed by the authors membranes reached the pure water reflux value of $2173 \text{ L/m}^2/\text{h}$. In the same work, the authors concluded that more residual PEGMA in the casting solution can facilitate more the migration of PEGMA segments to PVDF-*g*-PEGMA along the membrane surface. For the same kind of mixtures, Crittenden's and Chen's group managed to manipulate the membrane pore size by directly controlling the reaction time of ATRP process to obtain a better membrane flux performance [100].

iii) **Proton conducting/exchange (PEM):** Membranes of PVDF-*g*-PSSA with high proton conductivity and low methanol permeability are able to compete the traditional perfluorosulfonate membranes, such as Nafion [93, 143]. Holdcroft's group explained the importance of macromolecular architecture on the crucial properties, such as proton conductivity and mobility [144]. Interestingly, graft copolymers yielded membranes of higher ionic content compared to that of diblock copolymers without excessive swelling of membrane. The comparison of these two model polymers revealed also significant differences in the ionic transport resistance. The *in*-plane and *through*-plane conductivities of the diblock copolymer were different while the graft membranes showed similar values for both planes (anisotropy =0.95). A thorough study on PVDF-*g*-PSSA graft copolymers for PEMs applications showed the strong dependence of morphology and consequently ionic conductivity from other compositional parameters, such as graft and backbone length, graft density and degree of sulfonation of the copolymers [145, 146].

iv) **Lithium ion battery (LIB):** PVDF has already dominated the Li-ion battery industry serving as binder for the manufacture of both anode and cathode electrodes [147]. The major properties of PVDF for such applications are the mechanical stability, good adhesion to the current collectors, electrochemical stability over a wide potential range and chemical stability

against a wide range of lithium organic electrolytes. Furthermore, the electron withdrawing nature of the C-F bond promotes the dissolution and conduction of Li^+ ions thus enabling the use of PVDF and its copolymers as gel polymer electrolytes. As previously mentioned, Liu *et al.* observed a remarkable value of ionic conductivity (1.6×10^{-3} at 30°C) and a wide potential range of electrochemical stability of a PVDF-based graft copolymer [148]. Nhos' group reported the increase of ionic conductivity up to 2.5 mS/cm (at room temperature) upon increasing the styrene grafting degree and simultaneous decrease of crystallinity degree for PVDF-*g*-PS membranes [149]. Recently, Hsu *et al.* studied the blends of PVDF-*g*-polyacrylonitrile (PAN) with PEO as additive polymer for the preparation of gel-polymer electrolyte in LIBs [150]. These polymer electrolytes showed an impressive electrochemical stability up to 5.0 V , while maintaining a high thermal stability. The latter property is of high importance for the automotive industry due to the current safety concerns arising from the high flammability and toxicity of the organic liquid electrolytes. There are many examples where the risk of fire and explosion is high when the service temperature of the batteries is critically high or any electrolyte leaks occurs [151]. In this direction, a gel polymer electrolyte network consisted of fire-resistant PVDF copolymers is more favorable for high safety batteries. Also, the electrolyte leakage can be minimized by using PEO as polymer electrolyte [152]. Although, PEO assists the Li^+ transport, several limitations arise by its poor chemical stability, solubility and high crystallinity. To mediate the crystallinity and enhance chemical stability, the blending of PVDF with PEO has been applied for these applications [153, 154]. Based on its high ionic conductivity, PAN utilized as a compatibilizer between PVDF and PEO by the form of PAN grafts along PVDF backbone giving rise to conductive gel-polymer electrolyte [150, 155].

v) **Dielectric materials** have been also reported from PVDF-based graft copolymers as high energy density pulse discharge capacitors [156]. Zhu's group grafted low dielectric loss styrene grafts onto PVDF-*co*-PCTFE backbone to modify the ferroelectric properties of PVDF crystals. After PVDF crystallization-induced microphase separation of the segments, PS side chains segregated as peripheral domains surrounding the PVDF lamellar crystals. A fast discharge speed and low dielectric loss behavior was attributed to this nanoscale confinement as the authors proposed [157]. Instead of low polar PS grafts, poly(ethyl methacrylate) (PEMA) and PMMA were also grafted onto PVDF-based stem in order to study the effect of crystal domains confinement by the grafting in energy loss. For the case of [(PVDF-*co*-TrFE)-*g*-PEMA], it was

noticed an enhanced discharged energy density but a lower energy loss compared to the ungrafted films [158]. In the latter case, the rigid PMMA side chains induced improved breakdown strength and high energy storage capacity U_e [159]. With these two contributions, the authors helped in deeply understating the dielectric transition mechanism (from typical ferro- to either linear dielectric or anti-ferroelectric). Zhu continued to investigate the effect of crystal orientation on the ferroelectric property by grafting PS chains onto PVDF-*ter*-TrFE-*ter*-CTFE, which can be proved advantageous in high energy density and low dielectric loss applications [160].

b) Star

From roofs to doors, PVDF-based coatings protect and enhance various metal products. As mentioned above, Ameduri and coworkers [117] reported photocrosslinked PVDF-based star polymer for the outdoor coating applications [161-163] (**Scheme 10**). They measured the adhesion properties of the 4-arm PVDF star by placing coating films to metallic substrates. For reference, coating made from the commercially available PVDF (Solef®) was found to be completely removed from the metal substrate, whereas the crosslinked 4-arm star PVDF coating displayed significantly better adhesion properties. The photocrosslinked coating made from the 4-arm star PVDF clearly exhibits enhanced adhesion properties. The authors also examined the surface energy and water contact angle of the coatings which clearly indicated low surface energy (ranged between PMMA and PVDF homopolymers) and higher water contact angle (compared to that of pure PVDF). Beyond these measurements, coatings made from the 4-arm star PVDF and a PVDF/PMMA blend were also compared to commercial PVDF (Solef®) by typical “scratch” test. This fast, versatile and original photocrosslinking process represents an attractive alternative to PVDF/PMMA blends for outdoor coating application.

In another example, Patrickios *et.al* demonstrated the use of PVDF-based 4-arm star APCN (**Scheme 11 and Scheme 12**) as GPEs [118]. They prepared GPEs using the APCN and a mixture of two ionic liquid electrolytes. These gels exhibited superior mechanical properties, did not flow and easily cut into disks. These properties allow the GPEs to be easily handled during cell assembly. Furthermore, the GPE disks maintained their shape without collapsing at higher temperatures at which ionic conductivities were measured. Mechanical testing indicated that GPE samples could tolerate maximum strain without breaking. No liquids were released from the gel matrix three months after sample preparation. In addition, these GPEs showed good

electrochemical stability and competitive ion conductivities (up to 4 mS/cm at 80 °C) while the authors claimed that these materials can be useful for coating and drug delivery.

Lin and coworkers developed stable ferroelectric nanocomposite nanoreactors using 21-arm star-like PAAc-*b*-PVDF diblock copolymer (**Scheme 13**) and they claimed potential applications in energy conversion and storage, catalysis, electronics, nanotechnology, and biotechnology [119]. These nanocomposites displayed superior long-term stability, high dielectric constant and low dielectric loss. In addition, the ferroelectric tetragonal structure occurred when the star PAAc-*b*-PVDF diblock copolymer used as platform for the formation of metal oxide nanoparticles, which is a desired structure in lithium ion batteries.

c) Miktoarm star

Rodionov *et.al* [125] considered the application of PVDF-based miktoarm star polymer (**Scheme 14**) for the transport of hydrophobic molecules in water. The water insoluble model dye such as Nile Red (NR) was chosen for this investigation and it was easily incorporated into a hydrophobic environment of PVDF-miktoarm star polymer. Its insertion was easily detected by the coloration of the solution and by fluorescence spectroscopy. In water, NR is insoluble and non-fluorescent, however, pink micellar solutions readily obtained when solid NR powder is added in an aqueous dispersion of a 1 wt% of miktoarm star polymer. As a proof, the authors tested the NR solubility in a 1 wt% aqueous solution of PEG which resulted in colorless solutions and no fluorescence. The fluorescence emission spectrum of NR in miktoarm star polymer exhibited a λ_{max} at 604 nm, suggesting a polarity of the aqueous solution containing NR in miktoarm star polymer comparable to that of dichloromethane and other polar solvents. The authors hypothesize that some of the dye molecules was linked to hydrophilic and lipophilic blocks, while others penetrate through hydrophobic PVDF domains. Hence, PVDF-miktoarm stars may be suitable candidates for transferring hydrophobic drugs.

d) Dendrimers

Folgado *et al.* [135] prepared PVDF-based dendrimers (**Scheme 15**) with increased crystallinity and much higher hydrophobicity of the PVDF films. Due to these characteristics, potential applications such as coatings, surface modifiers or additives for nanocomposites is also possible. The same teams [136] reported pyrene-tagged dendritic PVDF (**Figure 2** and **Scheme 16**) MNPs for coating applications. These MNP dendrimers were also shown a thermo-

responsive behavior, which allow their future use as hybrid thermo-responsive nanocomposites for high-tech applications.

5. Conclusions and Future outlook

The design of CMAs creates a substantial platform in modern polymer chemistry and provides the opportunity to generate a broad range of materials with tunable properties. Among them, fluorinated and especially PVDF CMAs have received significant attention due to their ability to enhance physico-chemical and electric properties in comparison with their linear and homopolymer counterparts.

As a versatile polymer with outstanding properties, PVDF had an intriguing evolution over the last four decades. Initially, PVDF was mostly synthesized as copolymer with other fluorinated polymer (CTFE, HFP, etc.) while later on as linear or grafted block and more recently by the form of other CMAs including, miktoarm star, star, branched and dendrimers. The previous decade was the time of the advent for many “control radical” polymerization methods that efficiently combined with the pre-existed radiation treatment. This combination led to many remarkable contributions with the most prominent being that of graft copolymers with PVDF as a backbone.

Instead, recent advances in the last decade in organic and polymer chemistry have forged a useful “toolbox” (“click”-chemistry, ATRC) for more applicable and versatile structures making them more attractive for high-tech applications. It is evident that the formation of PVDF-based CMAs *via* grafting has already build up a field with a plethora of graft copolymers while star, miktoarm and dendrimers is still rare. A modest number of PVDF-based CMA has been achieved so far on a fundamental level while the focus of polymer scientists is shifting toward applications such as additives for second generation antifouling membranes, Li-ion batteries and dielectric materials whereas the drug-delivery is still in ‘infant’ state.

As to concern the progressive research on PVDF-based complex architectures, we expect that novel pathways towards these fluorinated complex macromolecules will be developed in the near future. From our point of view, the following directions that deserve attention are: (i) the development of new initiators, chain transfer agents in order to combine free and controlled/living VDF polymerization methods with other “living” techniques; (ii) super hydrophobic membranes combining PVDF with other hydrophobic polymers such as

polydimethylsiloxane for membrane distillation is an upcoming field. For the moment, all relative attempts are limited to PVDF blends and poly(VDF-*co*-CTFE) copolymer without involving any CMA of covalently attached moieties. (iii) the design of more complex structures with induced internal morphologies such as Janus shape membranes, (iv) the opening of new interdisciplinary application fields especially in nanotechnology, micro-device technology, biology, supramolecular chemistry, or single-molecule science. Thus, one can conclude that the design of PVDF-based CMAs has potential to be a promising pathway to generate new materials with unique properties and will certainly play a significant role in the future of polymer science.

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