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Well-defined Fluorinated Copolymers: Current Status and Future Perspectives

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CONSPECTUS: Well-defined fluoropolymers exhibit unique properties such as excellent oil and water repellency, satisfactory thermal stability, low refractive index, and low surface energy. The origin of these properties is attributed to the presence of strong electronegative and low polarizable Fluorine atom in the backbone of such polymers which leads to a strong C F bond (with a high bond dissociation energy of 485 kJ mol⁻¹). Due to these features, these polymers have found applications as functional coatings, thermoplastics, biomedical items, separators and binders for Li-ion batteries, fuel cell membranes, piezoelectric devices, high quality wires and cables, etc. Usually, fluoropolymers are synthesized by conventional radical (co)polymerization of fluoroalkenes which leads to the production of (co)polymers with ill-defined end group, uncontrolled molar mass, and high dispersity values. In the last two decades, significant developments of various reversible deactivation radical polymerization (RDRP) techniques have helped the design of macromolecular architectures (including block, graft, star, dendrimers) on demand. However, for relevant new applications, well-defined fluoropolymers with well-defined macromolecular architectures (e.g. block copolymers as thermoplastic elastomers and electroactive polymers or graft copolymers for fuel cell membranes) are required.

Several RDRP methods developed in the last couple of decades have paved the way for the synthesis of (co)polymers with well-defined molar mass, dispersity, chain end-functionality and

macromolecular architectures. Some of these RDRP techniques have been successfully employed for the synthesis of well-defined fluorinated copolymers. These techniques include iodine transfer polymerization (ITP), reversible addition fragmentation chain-transfer (RAFT) polymerization, organometallic mediated radical polymerization (OMRP) and to a lesser extent, Nitroxide-mediated polymerization (NMP). Impressive control of the molar mass parameters of the fluoropolymers synthesized via these techniques also encouraged the researchers to combine these techniques with other post-polymerization strategies leading to innovative novel polymeric materials.

Thus synthesized well-defined fluoropolymers exhibited a unique combination of properties (such as excellent weather resistance, high thermal/chemical/aging resistance, morphological versatility, low dielectric constant/flammability/refractive index). These led to application of such developed materials in various high-tech applications such as high performance elastomers, coatings for marine antifouling applications, fluorinated surfactants, fuel cell membranes and gel polymer electrolytes for Li-ion batteries.

Newer advances in the field of polymer synthesis tools/techniques are the need of the hour in order to synthesize more advanced fluorinated materials which may change the use of such polymers in engineering and biomedical fields in the current century. However, it should be kept in mind that success in this regard shall heavily depend on deeper understanding of polymerization process and structure-activity relationships.

1. INTRODUCTION

Well-defined fluoropolymers have achieved lot of interests from industry and academia as potential smart materials for various emerging applications.^{1,2} These types of polymers exhibit

unique combination of interesting properties such as low polarizability, strong electronegativity, low surface energy, excellent oil and water repellency, weather resistance, high thermal, chemical, aging, and weather resistances.³ For these reasons, these polymers are widely used in automobile industry, materials science, including as separator in lithium-ion batteries, UV-resistant coating materials and organic bulk heterojunction.³ However, fluorinated homopolymers suffer from a few drawbacks, including (i) high crystallinity (which leads to expensive processing), (ii) poor solubility in common organic solvents, (resulting in characterization limitations), and (iii) difficulty in crosslinking/functionalization. Incorporation of functional co-monomer(s) into the backbone of the fluorinated homopolymers might resolve these issues. Conventional radical (co)polymerization strategies are not capable to produce (co)polymers with controlled molar mass, low dispersity and high chain-end functionalities. The advent and significant development of various reversible deactivation radical polymerization (RDRP) methods have overcome these constraints, producing polymers with well-defined macromolecular architectures, predictable molar mass, and high chain-end fidelity.⁴ The specific objectives of this Account aims at discussing the synthesis of well-defined fluoropolymers with unique properties. This Account demonstrates the most compelling examples in the field of such specialty copolymers during the last decade, focusing on their synthesis, properties, and applications. First, the synthesis of such polymers using different RDRP methods will be highlighted, followed by a discussion on the relevant applications of the resulting materials. It is to be noted that this Account is not exhaustive and does not cover the entire domain of fluorinated (co)polymers. For further information, the readers may consult the recently published reviews or books in the field of fluoropolymers.^{3,5}

2. SEQUENCE CONTROL IN BIOPOLYMERS: LEARNING FROM NATURE

Sequence controlled bio(macro)molecules (such as nucleic acids and polypeptides) containing precisely defined monomer/repeat units maintains the variety, intricacy and flexibility of living organisms.^{1,2} Inspired by this, scientists have achieved some success in the preparation of lab-based synthetic macromolecules, as detailed in the recent reviews (Figure 1).^{1,2} With due consideration, this field has the potential to dominate the next decade of research in the area of advanced polymeric materials. However, important breakthrough in this research area is unlikely to happen without collaborative research from the active scientists.

Figure 1. Schematic representation of the main synthetic approaches toward sequence-defined and monodisperse macromolecules. IEG: iterative exponential growth (often also termed divergent/convergent approach); PG: protecting group. Reproduced with permission from reference 2. Copyright 2019 Wiley.

3. INTRODUCTION TO FLUOROPOLYMERS AND THEIR UNIQUE FEATURES

Fluoropolymers are niche polymers which exhibits some unique properties such as high thermal, chemical and weather repellent, excellent inertness to solvents/hydrocarbons/acids/alkalies, low flammability, low refractive index, and moisture absorption. These properties originate from high electronegativity, low polarizability, and small Van der Waals radius (1.32 Å) of fluorine atom and the presence of strong C-F bond (bond dissociation energy 485 kJ mol⁻¹). The first report of fluoropolymers dates back to 1934 when polychlorotrifluoroethylene, PCTFE, was synthesized.⁶ Subsequently, polytetrafluoroethylene was serendipitously produced by the DuPont Company in 1938.⁷ Despite their high price (which is due to the cost of purifying the gaseous monomers, to unusual processes of polymerization, and to the small scale of production), these polymers have found major developments in modern technologies, including automobile, building and petrochemical industries, and aeronautics (use of elastomers as seals, O-rings and gaskets).³

4. SEQUENCE REGULATION IN SYNTHETIC FLUOROPOLYMERS

Sequence regulation have emerged as one of the most promising field of research in fundamental and applied polymer science. This emerging area is a combination of classical polymer chemistry techniques with the tools from other domains such as biology, biochemistry, organic synthesis, engineering, and bioanalytics (Figure 2). The term “sequence-controlled polymers” (SCPs) was recently introduced to serve as a generic name for this kind of polymers. In the subsequent sections, the most compelling synthesis approaches of well-defined fluoropolymers will be discussed, covering a wide range of functionalized fluoromonomers with the functional group designed to target the necessary properties for the required applications.

Figure 2. The field of sequence-controlled polymers is at the crossroads between biology (red) and polymer science (blue). Reproduced with permission from reference 1. Copyright 2017 Wiley.

4.1. Synthesis via Reversible Deactivation Radical Polymerization (RDRP)

The following factors determine the success of a RDRP technique: (a) maintaining low “active” (macro) radical concentration compared to that of the “dormant” polymeric chains and (b) very fast and reversible exchange between living “active” and “dormant” radical species. In 1978, Tatemoto was the first actor to report RDRP technique while introducing the concept of *iodine transfer polymerization* (ITP) and the industrial production was implemented more than 25 years ago.⁸ Till date, various RDRP techniques have been reported (Figure 3), including nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), ITP, reversible addition-fragmentation chain transfer (RAFT) polymerization, organometallic-mediated radical polymerization (OMRP) and organo-hetero atom-mediated radical polymerization (Figure 3). Most of the fluorinated monomers (specially the olefinic ones) are gas at room temperature and specially designed reactors (high pressure autoclaves) are required to perform polymerization reactions involving these monomers. Different combinations of initiators, monomers, chain transfer agents (CTAs), solvents or surfactants have been employed to achieve the synthesis of

fluorinated SCPs. To keep the focus of this account, the following sections shall focus on the recent and exciting developments in the field of well-defined fluoropolymers since 2010, their properties and applications.

Figure 3. Strategies showing the types of reversible-deactivation radical polymerizations (RDRPs), their underlying mechanism and examples of their outcomes in terms of molar mass and functionality control, along with various architectures achieved through their uses. Reproduced with permission from reference ⁹. Copyright 2011 Taylor & Francis.

4.1.1. Synthesis via Iodine Transfer Polymerization (ITP)

Ameduri's group reported the synthesis of VDF and (substituted) styrene containing block copolymers via ITP.¹⁰ That technique was also achieved by Walkowiak-Kulikowska et al.¹¹ who prepared fluorinated α -methylstyrenes with styrene containing copolymers and by Lopez et al.¹² for the synthesis of original controlled chlorotrifluoroethylene-based fluorinated diblock copolymers. Subsequently, the same team investigated the kinetic and mechanistic aspects of the iodine transfer copolymerization of VDF with 2,3,3,3-tetrafluoro-1-propene and the subsequent functionalization of the resulting copolymers into ω -hydroxy fluorinated macromolecules.¹³ Interestingly, Asandei's team reported the photochemical ITP yielding original PVDF-*b*-poly(M) block copolymers.¹⁴⁻¹⁶ Then, Banerjee et al.¹⁷ synthesized ω - iodo and telechelic diiodo PVDF

and block copolymers thereof via ITP, initiated by an innovative persistent radical, perfluoro-3-ethyl-2,4-dimethyl-3-pentyl persistent radical being able to release a quite reactive $^{\circ}\text{CF}_3$ radical (Scheme 1). The thermal stability of the copolymers containing VDF and *tert*-butyl 2-trifluoromethacrylate (MAF-TBE) increased with molar mass of such copolymers.

Scheme 1. Synthesis of end functionalized iodo-PVDF and block copolymers thereof using perfluoro-3-ethyl-2,4-dimethyl-3-pentyl persistent radical. Reproduced with permission from reference ¹⁷. Copyright 2017 American Chemical Society.

Lee et al.¹⁸ obtained well-defined α,ω -diiodo-poly(VDF-*co*-HFP) copolymers of low dispersity (< 1.3) via ITP and subsequently incorporated ethylene units in it to produce a telechelic bis(hydroxyethyl)-poly(VDF-*co*-HFP). Inspired by the work reported by Percec et al.,¹⁹ Jaye and Sletten²⁰ copolymerized α,ω -diiodoperfluoroalkanes and telechelic dienes to produce high-molar mass alternating copolymers (>100 kDa) with up to 59 wt % fluorine content (Scheme 2) also inspired by He et al. who photopolymerized telechelic diallyl polyesters with the same diiodo-perfluoroalkenes.²¹ The former authors also demonstrated that the fluorous nature of the copolymer could be adjusted by incorporation of azides, thiols, and allyl functionalities via post-polymerization technique.

Scheme 2. Synthesis iodo-ene polymerization of 1,9-decadiene and diiodoperfluoroalkanes to yield alternating fluorinated copolymers. Reproduced with permission from reference ²⁰. Copyright 2019 American Chemical Society.

4.1.2. Synthesis via Reversible Addition Fragmentation Chain-Transfer (RAFT) Polymerization

RAFT polymerization has emerged as one of the most promising RDRP technique due to its applicability to polymerize a wide range of functional monomers bearing diverse functionalities. In the last ten years many studies on this topic have also been applied on fluorinated alkenes. In 2011, Kostov et al.²² produced poly(VDF-*co*-TFP) copolymers terminated by a xanthate function as the macroCTA to yield original poly(VDF-*co*-TFP)-*b*-oligo(VAc) block copolymers (where TFP and VAc stand for 3,3,3-trifluoropropene and vinyl acetate, respectively) for novel surfactants (see Section 6.3). Then, Girard et al.²³ also used that technique for the first VDF-based amphiphilic poly(VDF-*co*-PMVE)-*b*-poly(DMA) diblock copolymers (Scheme 3) (where DMA and PMVE stand for dimethylacrylamide and perfluoromethyl vinyl ether, respectively) as surfactants in supercritical CO₂ medium.

Scheme 3. Synthetic Procedure for the obtaining VDF-Based (co)polymers by RAFT/MADIX Polymerization (where tBPPI stands for *tert*-butylperoxypivalate). Reproduced with permission from reference ²³. Copyright 2012 American Chemical Society.

One year later and according to a similar strategy, Patil et al.²⁴ prepared copolymers containing VDF and *tert*-butyl 2-trifluoromethacrylate (MAF-TBE) in the presence of O-ethyl-S-(1-methyloxycarbonyl) ethyl xanthate as the CTA. The synthesized copolymers exhibited tunable surface properties. Interestingly, from the same strategy in miniemulsion, Arkema claimed the synthesis of PVDF latexes from poly(ethylene oxide)-xanthate,²⁵ while Chakrabarty and Singha described the synthesis of poly(fluoroacrylate)-based block copolymers with improved hydrophobicity.²⁶ Furthermore, Wang et al.²⁷ prepared fluorinated amphiphilic block copolymers containing CTFE and N-vinylpyrrolidone (NVP) initiated by ⁶⁰Co γ -ray irradiation in the presence of ethyl 2-(ethoxycarbonothioylthio) acetate. Such synthesized poly(CTFE-*co*-NVP)-*b*-poly(NVP) block copolymers exhibited good biocompatibility. Guerre et al.²⁸ reported the stepwise RAFT copolymerization of VDF and VAc to further produce amphiphilic PVDF-*b*-poly(vinyl alcohol) block copolymers, after hydrolysis. In addition, Banerjee et al.²⁹ prepared multiblock PVDF from a cyclic xanthate (Scheme 4) with potential applications in functional coating materials.

Scheme 4. Synthesis of multiblock (PVDF-XA)_n and copolymers thereof. Reproduced with permission from reference ²⁹. Copyright 2017 Royal Society of Chemistry.

Puts et al.³⁰ studied for the first time the RAFT/MADIX copolymerization of tetrafluoroethylene (TFE) with isobutyl vinyl ether producing controlled alternating poly(TFE-*alt*-iBuVE) copolymers with quite low dispersities. In addition, Jiang et al.³¹ described the LED light irradiation induced photo-organocatalyzed ambient temperature RAFT copolymerization of CTFE with various VEs to further obtain poly(CTFE-*alt*-VE)-*b*-PVA block copolymers with diverse functional side groups.

Furthermore, the combination of cationic and radical RAFT polymerizations was used by Guerre et al.³² who reported a facile strategy for the preparation unprecedented poly(vinyl ether)-*b*-PVDF block copolymers from a first cationic polymerization of vinyl ether controlled by a xanthate followed by radical RAFT of VDF (Scheme 5).

Scheme 5. Synthesis of PEVE-*b*-PVDF block copolymers *via* sequential cationic RAFT polymerization of ethyl vinyl ether (EVE) and radical RAFT polymerization of VDF. Reproduced with permission from reference ³². Copyright 2017 American Chemical Society.

Recently, Falireas et al.³³ reported the synthesis of dual pH/temperature responsive fluorinated block copolymers based on alternated poly(VAc-*alt*-2-trifluoromethacrylic acid) sequence and poly(DMA) and poly(N-isopropyl acrylamide) (PNIPAM) blocks (Scheme 6).

Scheme 6. Strategies to produce fluorinated diblock terpolymers by RAFT copolymerization: (a) preparation of alternating poly(MAF-TBE-*alt*-VAc) macroCTA; (b) hydrolysis of poly(MAF-TBE-*alt*-VAc) into poly(MAF-*alt*-VOH); (c) synthesis of Poly(MAF-TBE-*alt*-VAc)-*b*-PDMA, (d) obtaining of Poly(MAF-TBE-*alt*-VAc)-*b*-PNIPAM, (e) hydrolysis of Poly(MAF-TBE-*alt*-VAc)-*b*-PNIPAM into P(MAF-*alt*-VOH)-*b*-PNIPAM. Reproduced with permission from reference ³³. Copyright 2021 Royal Society of Chemistry.

More recently, the RAFT polymerization of trifluoroethylene in presence of xanthate was also successfully achieved with controlled molar masses and dispersities.³⁴

4.1.3. Synthesis via Organometallic Mediated Radical Polymerization (OMRP)

OMRP has emerged as an efficient technique for producing well-defined copolymers containing Vac. Alkyl-Co and bis(formylphenolato)cobalt(II)-mediated radical copolymerization of MAF-TBE with VAc, yielded alternating copolymers.³⁵ That strategy was also successfully used by Demarteau et al.³⁶ who synthesized statistic copolymers of predictable molar masses, based on 1H,1H,2H,2H-perfluorohexylethylene (PFHE) and VAc which could further be modified into poly(PFHE-*stat*-VAc)-*b*-oligo(VAc) block copolymers. The mild hydrolysis of VAc units led to the corresponding fluorinated amphiphilic poly(PFHE-*stat*-VOH)-*b*-oligo(VOH) copolymers (where VOH stands for vinyl alcohol). Banerjee et al.³⁷ reported for the first time the OMRP of VDF mediated by alkyl-Co complex producing well-defined PVDF and PVDF-*b*-PVAc block copolymers (Scheme 7). DFT calculations supported the efficient reactivation of both head and tail chain ends of the PVDF macroinitiator.

Initiation

Scheme 7. OMRP of VDF from an organocobalt complex bearing a few VAc units ($n = 4$). Reproduced with permission from reference ³⁷. Copyright 2018 Wiley.

Recently, the same group also prepared well-defined PVDF and then PVDF-*b*-PVAc block copolymers by OMRP using the combination of commercially available dialkyl peroxydicarbonate initiator and bis(acetylacetonato)cobalt(II).³⁸

4.1.4. Synthesis via Nitroxide-Mediated Polymerization (NMP)

Wang et al.³⁹ synthesized well-defined copolymers based on norbornene-lactone and pentafluorostyrene via NMP and showed its potential application for 193-nm photoresist materials. Then, alternating radical copolymerization of VAc with MAF-TBE was also reported using MAMA-SG1 mediated NMP (Scheme 8).⁴⁰

Scheme 8. Synthesis of alternating poly(VAc-*alt*-MAF-TBE) copolymers by NMP using MAMA-SG1. Reproduced with permission from reference ⁴⁰. Copyright 2016 American Chemical Society.

Tesch et al.⁴¹ prepared novel alternating copolymer based on 1,1,1,3,3,3-hexafluoroisopropyl acrylate (HFIPA) and [(6-trimethylsilyl)-hex-5-yn-1-yl]vinyl ether (THVE) via NMP. In 2020, Peltekoff et al.⁴² produced poly(pentafluorostyrene-*ran*-methyl methacrylate) copolymers via NMP to develop original dielectric polymers.

4.2. Synthesis via a Combination of ITP and “Click” Chemistry

Click chemistry is by far the most facile and selective chemical transformation which simplifies compound synthesis, providing faster discovery and optimization. The combination of click chemistry with ITP may allow preparation of a new generation of precisely tailored specialty PVDF and related copolymer membranes. Cai et al.⁴³ reported surface-functionalized and surface functionalizable PVDF membranes via ITP and click Chemistry. Beuermann and coworkers⁴⁴ first prepared PVDF-I macroinitiator via ITP in supercritical CO₂ and then converted the iodine extremity into azido function (PVDF-N₃) further being attached onto fullerenes *via* a post-polymerization modification. In addition, Loos et al.⁴⁵ recently investigated the structure-electroactive properties of PS-*b*-poly(VDF-*co*-TrFE)-*b*-PS and P2VP-*b*-poly(VDF-*co*-TrFE)-*b*-P2VP triblock copolymers (where 2VP and TrFE stand for 2-vinylpyridine and trifluoroethylene, respectively) synthesized via CuAAC click-coupling of telechelic bis(azide) terminated poly(VDF-*co*-TrFE) copolymers with ω -alkyne terminated P2VP or PS obtained by RAFT polymerization of 2VP or styrene.

5. PROPERTIES OF WELL-DEFINED FLUORO-POLYMERS

Well-defined fluoropolymers provide a unique combination of properties (such as excellent weather resistance, high thermal/chemical/aging resistance, morphological versatility, low

dielectric constant/flammability/refractive index/surface energy).⁶⁻⁸ In addition, these polymers exhibit high thermal stability (which depends on the properties of the comonomer) and tunable glass transition temperature (T_g). The reactivity and bulkiness of the comonomers directly influence the properties of the resulting fluorinated copolymers. It is well-established that hexafluoropropylene (HFP), or perfluoroalkyl vinyl ether (including perfluoro methyl vinyl ether, PMVE), used as comonomer with VDF, produced poly(VDF-*co*-HFP or PMVE) fluoroelastomers when the VDF mol% <82, having low T_g value with enhanced high-temperature resistance.⁴⁶ Besides many patents, the first article by Maccone et al.⁴⁷ reports the *pseudo* branching “living” radical copolymerization of HFP and VDF (with or without addition of tetrafluoroethylene as a termonomer), yielding fluoroelastomers in the presence of a iodoperfluorinated CTA in emulsion process. Actually, these fluorinated monomers are relatively difficult to handle because of their low boiling point (below -20 °C) and their low solubility in the water.⁴⁸

6. APPLICATIONS OF WELL-DEFINED FLUOROPOLYMERS

The applications of the well-defined fluoropolymers with precisely placed monomer sequences can be found in many high-tech applications. In this account, only a few important applications are supplied below.

6.1. High Performance Elastomers

Thermoplastic elastomers (TPEs) are composed of one thermoplastic or crystalline zone that can further enable physical crosslinking and one elastomeric (or amorphous) domain that (preferably) exhibits a low glass transition temperature (T_g).⁴⁹ Actually, fluorinated TPEs (FTPEs), produced by ITP and pioneered from late-70ies by the Daikin company⁵⁰, and followed

by DuPont (now Chemours) and Ausimont (now Solvay Specialty Polymers), have garnered some interest from both academia and industry. These specialty block copolymers are typically composed of a central soft block (low T_g) adjacent to thermoplastic sequences.⁴⁹⁻⁵¹ FTPEs have found applications as high resistance coatings, O-rings, and gaskets for the automotive and aerospace industries, and as biomedical items.⁵¹

6.2. Functional Coatings for Marine Antifouling Applications

Rusting is one of the most significant issues in the industrial world which decreased device/system performance and may also lead to system failure. To this end, Lopez et al.⁵² developed a 4-arm star PVDF bearing methacrylate end-functions and prepared crosslinked PVDF transparent coatings via fast photo crosslinking. These produced coating materials displayed excellent adhesion properties onto metal surfaces. Furthermore, their water contact angles and surface energies were tunable ranging from 80° and 32 mN.m⁻¹ (for photocured materials based on PVDF) to 120° and 8 mN.m⁻¹ (with networks containing perfluorooligoethers).

6.3. Fluorinated Surfactants

Kostov et al.²² synthesized original amphiphilic poly(VDF-*co*-3,3,3-trifluoropropene)-*b*-oligo(VOH) block cooligomers as potential non-persistent and non-bioaccumulative surfactants. These amphiphilic derivatives displayed low critical micellar concentrations (CMCs) and surface tensions (17 mN m⁻¹ for 0.5% of the cooligomer in water), comparable to those of commercially available perfluorooctanoic acid (PFOA). However, PFOA, as well as perfluorooctanesulfonic acid (PFOS) are persistent, poisonous, and bio-accumulative, and even suspected to be mutagenic because of their small size to enter into mammal and human cells and the high stability of the perfluorinated groups. These surfactants have been banned from 2015.⁵³ Thus,

such block cooligomers, bearing VDF and TFP hydrofluorinated moieties, can act as relevant potential alternatives to such toxic perfluoralkyl substances (PFASs).

6.4. Fuel Cell Membranes

Fuel cells are appealing electrochemical devices that supply a clean energy compared to traditional power sources, with higher efficiencies, a lower environmental expense, and sustainable fuels.⁵⁴ From 2017, the Toyota Company⁵⁵ has been manufacturing several thousand Mirai cars in Japan running on fuel cells, as well as other manufacturers such as Hyundai in South Korea. Based on the electrolyte used, several types of fuel cells exist, e.g. Phosphoric Acid Fuel Cells, Molten Carbonate Fuel Cell, Solid Oxide Fuel Cell, Solid Alkane Fuel Cell and Proton Exchange Membrane Fuel Cell.⁵⁶ For the last family, perfluorosulfonic acids (PFSA, such as commercially available Nafion®, Flemion®, and Aquivion®) are suitable electrolyte candidates to be used in fuel cells⁵⁵ because of their outstanding properties such as high proton conductivity, oxidative stability and durability.⁵⁶ However, they are expensive and show some methanol crossover. Hence, various alternatives of copolymers have been searched in the last three decades. One example deals with poly(VDF-*co*-CTFE)-*g*-PSSA graft copolymers, obtained by ATRP of styrene from the C-Cl cleavage of CTFE in poly(VDF-*co*-CTFE) copolymer (as recently confirmed in ATRP of styrene or divinylbenzene with poly(CTFE-*alt*-PLAVE where PLAVE stands for poly(lactic acid) vinyl ether⁵⁷), followed by sulfonation. Such graft copolymers exhibited relevant water uptake, conductivity, ionic exchange capacity, and effective proton mobility (Figure 4).⁵⁸

Figure 4. Plots of (a) water content (λ) vs IEC, (b) in-plane proton conductivity vs IEC, (c) effective proton mobility (μ_{eff}) (solid line) and analytical $[H^+]$ (dotted line) vs IEC, (d) μ_{eff} vs volume fraction of water (X_v) of poly(VDF-*co*-CTFE)-*g*-PSSA (full square symbols) and poly(VDF-*co*-HFP)-*b*-PSSA (empty circle symbols) proton conducting membranes. Reproduced with permission from reference ⁵⁸. Copyright 2007 American Chemical Society.

6.5. Gel Polymer Electrolyte for Li-ion Batteries

Well-defined fluoropolymers have recently shown some promise for their potential application as solid polymer electrolytes (SPEs) for Li-ion batteries (LIBs). The literature teaches that VDF containing (co)polymers have found applications in LIBs as polymer electrolytes, binders for electrodes or separators.⁵⁹ Apostolides et al.⁶⁰ reported that a 4-arm star amphiphilic polymer co-networks of PEO and PVDF could be involved in LIB application as SPEs (Figure 5). First,

PVDF stars were synthesized by using a tetraxanthate CTA through the RAFT polymerization of VDF, followed by a modification and a condensation with a POE tetra-arm, yielding original co-networks. Because of the presence of both the PVDF chains that supplied the electrochemical stability and POE moieties which favor the Lithium conductivity, these polymer gels acted as relevant SPE candidates and when doped with Li-salts, they exhibited high conductivities (ca. 2–4 mS.cm⁻¹).

Figure 5. Condensation Reaction between Tetraarm-PVDF terminated by Benzaldehyde functions (tetraPVDF-Bz) and a Tetraarm-PEG bearing benzoacylhydrazide end-groups (tetraPEG-BAH), yielding to solid polymer electrolytes (the inset is a picture of the resulting SPEs). Reproduced with permission from reference ⁶⁰. Copyright 2018 American Chemical Society.

4. CONCLUSIONS AND OUTLOOK

Well-defined fluoropolymers can lead to promising materials for their potential applications in emerging areas of engineering, energy, and biomedical science. In the last decade, with the development of different controlled polymerization techniques (or RDRP) and polymerization processes, this field has started to take some major steps forward both in terms of diversity of the

macromolecular architectures and versatility of the introduced functionalities. However, detailed understanding of the structure-activity relationship and kinetics (e.g. of copolymerization reactions) and mechanistic investigation of the polymerization process are required to design and synthesize such materials high-Tech applications. Again, it must be remembered that most fluorinated monomers are gases at room temperature and require specific designed high-pressure autoclaves to perform the polymerizations. Thus, in spite of significant progress in the industrial production of such polymers, more research is necessary to bridge the gap between lab-scale production and industrial pilot plants. As a matter of fact, techniques of RDRP have been able to supply original thermoplastic elastomers which maintain their properties for a wide range of temperatures thanks to their low T_g and high melting points. These are mainly block copolymers produced by ITP, regarded as the oldest strategy (since the late 70ies at the Daikin Company in Japan) and being the most convenient and industrialized technology. Other applications as polymer exchange membranes for fuel cells, coatings, new surfactants or SPEs for Li-ion batteries are growing. Still many studies are going on and it is expected that new strategies will also be invented, attracting the interests of many academic and industrial researchers in the coming decades.

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■ REFERENCES

- (1) Lutz, J. F. Defining the Field of Sequence- Controlled Polymers. *Macromol. Rapid Commun.* **2017**, *38*, 1700582/1-12.
- (2) Meier, M. A. R.; Barner-Kowollik, C. A New Class of Materials: Sequence- Defined Macromolecules and Their Emerging Applications. *Adv. Mater.* **2019**, *31*, 1806027/1-25.
- (3) Mohammad, S. A.; Shingdilwar, S.; Banerjee, S.; Ameduri, B. Macromolecular Engineering Approach for the Preparation of New Architectures from Fluorinated Olefins and their Applications. *Prog. Polym. Sci.* **2020**, *106*, 101255/1-60.
- (4) Scholten, P. B. V.; Moatsou, D.; Detrembleur, C.; Meier, M. A. R. Progress Toward Sustainable Reversible Deactivation Radical Polymerization. *Macromol. Rapid Commun.* **2020**, *41*, 2000266/1-24.
- (5) Ameduri, B.; Fomin, S.: Fascinating Fluoropolymers and Their Applications; Amsterdam: Elsevier Ltd; 2004, 494pp.
- (6) Boschet, F.; Ameduri, B. (Co)polymers of Chlorotrifluoroethylene: Synthesis, Properties, and Applications. *Chem. Rev.* **2014**, *114*, 927-980.
- (7) Puts, G. J.; Crouse, P.; Ameduri, B. M. Polytetrafluoroethylene: Synthesis and Characterization of the Original Extreme Polymer. *Chem. Rev.* **2019**, *119*, 1763-1805.

- (8) Tatemoto M, Nakagawa T. Segmented polymers containing fluorine and iodine and their production. US 1979/4158678 (assigned to Daikin KogyoCo., Ltd), 1979.
- (9) Shipp, D. A. Reversible-Deactivation Radical Polymerizations. *Polym. Rev.* **2011**, *51*, 99-103.
- (10) Laruelle, G.; Nicol, E.; Ameduri, B.; Tassin, J.-F.; Ajellal, N. Synthesis of Poly(Vinylidene Fluoride)-*b*-Poly(Styrene Sulfonate) Block Copolymers by Controlled Radical Polymerizations. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 3960-3969.
- (11) Walkowiak-Kulikowska, J.; Szwajca, A.; Boschet, F.; Gouverneur, V.; Ameduri, B. Iodine Transfer Copolymerization of Fluorinated α -Methylstyrenes with Styrene Using 1-Iodoperfluorohexane as the Chain Transfer Agent. *Macromolecules* **2014**, *47*, 8634-8644.
- (12) Lopez, G.; Thenappan, A.; Améduri, B. Synthesis of Chlorotrifluoroethylene-Based Block Copolymers by Iodine Transfer Polymerization. *ACS Macro Lett.* **2015**, *4*, 16-20.
- (13) Banerjee, S.; Zaghloul, S.; Alaaeddine, A.; Ameduri, B. Kinetic and Mechanistic Aspects of the Iodine Transfer Copolymerization of Vinylidene Fluoride with 2,3,3,3-Tetrafluoro-1-Propene And Functionalization into ω -Hydroxy Fluorinated Copolymers. *Polym. Chem.* **2016**, *7*, 6099-6109.
- (14) Asandei, A. D.; Adebolu, O. I.; Simpson, C. P. Mild-Temperature $\text{Mn}_2(\text{CO})_{10}$ -Photomediated Controlled Radical Polymerization of Vinylidene Fluoride and Synthesis of Well-Defined Poly(vinylidene fluoride) Block Copolymers. *J. Am. Chem. Soc.* **2012**, *134*, 6080-6083.
- (15) Asandei, A. D.; Adebolu, O. I.; Simpson, C. P.; Kim, J.-S. Visible- Light Hypervalent Iodide Carboxylate Photo(trifluoro)methylations and Controlled Radical Polymerization of Fluorinated Alkenes. *Angew. Chem. Int. Ed.* **2013**, *52*, 10027-10030.

- (16) Simpson, C. P.; Adebolu, O. I.; Kim, J.-S.; Vasu, V.; Asandei, A. D. Metal and Ligand Effects of Photoactive Transition Metal Carbonyls in the Iodine Degenerative Transfer Controlled Radical Polymerization and Block Copolymerization of Vinylidene Fluoride. *Macromolecules* **2015**, *48*, 6404-6420.
- (17) Banerjee, S.; Patil, Y.; Ono, T.; Ameduri, B. Synthesis of ω -Iodo and Telechelic Diiodo Vinylidene Fluoride-Based (Co)polymers by Iodine Transfer Polymerization Initiated by an Innovative Persistent Radical. *Macromolecules* **2017**, *50*, 203-214.
- (18) Lee, J.-h.; Lee, B.; Won, J.-w.; Kim, C.-h. Synthesis of Novel Telechelic Fluoropolyols based on Vinylidene Fluoride/Hexafluoropropylene Copolymers by Iodine Transfer Polymerization. *Macromol. Res.* **2017**, *25*, 1028-1034.
- (19) Percec, V.; Schlueter, D.; Ungar, G. Rational Design of a Hexagonal Columnar Mesophase in Telechelic Alternating Multicomponent Semifluorinated Polyethylene Oligomers. *Macromolecules* **1997**, *30*, 645-648.
- (20) Jaye, J. A.; Sletten, E. M. Modular and Processable Fluoropolymers Prepared via a Safe, Mild, Iodo–Ene Polymerization. *ACS Cent. Sci.* **2019**, *5*, 982-991.
- (21) He, E.; Tu, K.; Cheng, J.; Lu, H.; Zhang, L.; Cheng, Z.; Zhu, X. Multimesophase Transitions of Main-Chain Liquid Crystalline Copolymers with Strictly Alternating Fluorocarbon Chains. *Polym. Chem.* **2021**, *12*, 736-743.
- (22) Kostov, G.; Boschet, F.; Buller, J.; Badache, L.; Brandsadter, S.; Ameduri, B. First Amphiphilic Poly(vinylidene fluoride-co-3,3,3-trifluoropropene)-*b*-oligo(vinyl alcohol) Block Copolymers as Potential Nonpersistent Fluorosurfactants from Radical Polymerization Controlled by Xanthate. *Macromolecules* **2011**, *44*, 1841-1855.

- (23) Girard, E.; Marty, J.-D.; Ameduri, B.; Destarac, M. Direct Synthesis of Vinylidene Fluoride-Based Amphiphilic Diblock Copolymers by RAFT/MADIX Polymerization. *ACS Macro Lett.* **2012**, *1*, 270-274.
- (24) Patil, Y.; Ameduri, B. First RAFT/MADIX Radical Copolymerization of Tert-butyl 2-Trifluoromethacrylate with Vinylidene Fluoride controlled by Xanthate. *Polym. Chem.* **2013**, *4*, 2783-2799.
- (25) Devisme, S.; Kahn, A.; Fuentes-Exposito, M.; McKenna, T.; D'Agosto, F.; Lansalot, M.; Bonnet, A. Synthesis of Surfactant-Free Poly(vinylidene fluoride) Latexes via RAFT Emulsion Polymerization. US Patent, WO 2019/063445 A1 2019 (assigned to ARKEMA FRANCE).
- (26) Chakrabarty, A.; Singha, N. K. Tailor-made Polyfluoroacrylate and its Block Copolymer by RAFT Polymerization in Miniemulsion; Improved Hydrophobicity in the Core-Shell Block Copolymer. *J. Colloid Interface Sci.* **2013**, *408*, 66-74.
- (27) Wang, P.; Dai, J.; Liu, L.; Dong, Q.; Wang, H.; Bai, R. Synthesis and Properties of a Well-defined Copolymer of Chlorotrifluoroethylene and N-vinylpyrrolidone by Xanthate-Mediated Radical Copolymerization under ^{60}Co γ -ray irradiation. *Polym. Chem.* **2014**, *5*, 6358-6364.
- (28) Guerre, M.; Semsarilar, M.; Godiard, F.; Améduri, B.; Ladmiral, V. Polymerization-induced Self-Assembly of PVAC-*b*-PVDF Block Copolymers via RAFT Dispersion Polymerization of Vinylidene Fluoride in Dimethyl Carbonate. *Polym. Chem.* **2017**, *8*, 1477-1487.

- (29) Banerjee, S.; Patil, Y.; Gimello, O.; Ameduri, B. Well-defined Multiblock Poly(vinylidene fluoride) and Block Copolymers Thereof: A Missing Piece of the Architecture Puzzle. *Chem. Commun.* **2017**, 53, 10910-10913.
- (30) Puts, G.; Venner, V.; Améduri, B.; Crouse, P. Conventional and RAFT Copolymerization of Tetrafluoroethylene with Isobutyl Vinyl Ether. *Macromolecules* **2018**, 51, 6724-6739.
- (31) Jiang, K.; Han, S.; Ma, M.; Zhang, L.; Zhao, Y.; Chen, M. Photoorganocatalyzed Reversible-Deactivation Alternating Copolymerization of Chlorotrifluoroethylene and Vinyl Ethers under Ambient Conditions: Facile Access to Main-Chain Fluorinated Copolymers. *J. Am. Chem. Soc.* **2020**, 142, 7108-7115.
- (32) Guerre, M.; Uchiyama, M.; Folgado, E.; Semsarilar, M.; Améduri, B.; Satoh, K.; Kamigaito, M.; Ladmiral, V. Combination of Cationic and Radical RAFT Polymerizations: A Versatile Route to Well-Defined Poly(ethyl vinyl ether)-block-poly(vinylidene fluoride) Block Copolymers. *ACS Macro Lett.* **2017**, 6, 393-398.
- (33) Falireas, P. G.; Ladmiral, V.; Ameduri, B. Synthesis, Aqueous Solution Behavior and Self-Assembly of A Dual pH/Thermo-Responsive Fluorinated Diblock Terpolymer. *Polym. Chem.* **2021**, 12, 277–290.
- (34) Bouad, V.; PhD Dissertation, University of Montpellier, **2021**.
- (35) Banerjee, S.; Bellan, E.; Gayet, F.; Debuigne, A.; Detrembleur, C.; Poli, R.; Améduri, B.; Ladmiral, V. Bis(formylphenolato)cobalt(II)-Mediated Alternating Radical Copolymerization of *tert*-Butyl 2-Trifluoromethylacrylate with Vinyl Acetate. *Polymers* **2017**, 9, 702/1-11.

- (36) Demarteau, J.; Améduri, B.; Ladmiraal, V.; Mees, M. A.; Hoogenboom, R.; Debuigne, A.; Detrembleur, C. Controlled Synthesis of Fluorinated Copolymers via Cobalt-Mediated Radical Copolymerization of Perfluorohexylethylene and Vinyl Acetate. *Macromolecules* **2017**, *50*, 3750-3760.
- (37) Banerjee, S.; Ladmiraal, V.; Debuigne, A.; Detrembleur, C.; Poli, R.; Améduri, B. Organometallic-Mediated Radical Polymerization of Vinylidene Fluoride. *Angew. Chem. Int. Ed.* **2018**, *57*, 2934-2937.
- (38) Faliereas, P. G.; Ladmiraal, V.; Debuigne, A.; Detrembleur, C.; Poli, R.; Ameduri, B. Straightforward Synthesis of Well-Defined Poly(vinylidene fluoride) and Its Block Copolymers by Cobalt-Mediated Radical Polymerization. *Macromolecules* **2019**, *52*, 1266-1276.
- (39) Wang, Z. J.; Maric, M. Synthesis of Narrow Molecular Weight Distribution Norbornene-Lactone Functionalized Polymers by Nitroxide-Mediated Polymerization: Candidates for 193-nm Photoresist Materials. *Polymers* **2014**, *6*, 565-582.
- (40) Banerjee, S.; Domenichelli, I.; Ameduri, B. Nitroxide-Mediated Alternating Copolymerization of Vinyl Acetate with tert-Butyl-2-trifluoromethacrylate Using a SG1-Based Alkoxyamine. *ACS Macro Lett.* **2016**, *5*, 1232-1236.
- (41) Tesch, M.; Kudruk, S.; Letzel, M.; Studer, A. Orthogonal Click Postfunctionalization of Alternating Copolymers Prepared by Nitroxide-Mediated Polymerization. *Chem. Eur. J.* **2017**, *23*, 5915-5919.
- (42) Peltekoff, A. J.; Tousignant, M. N.; Hiller, V. E.; Melville, O. A.; Lessard, B. H. Controlled Synthesis of Poly(pentafluorostyrene-ran-methyl methacrylate) Copolymers by Nitroxide Mediated Polymerization and Their Use as Dielectric Layers in Organic Thin-film Transistors. *Polymers* **2020**, *12*, 1231/1-14.

- (43) Cai, T.; Neoh, K. G.; Kang, E. T. Poly(vinylidene fluoride) Graft Copolymer Membranes with “Clickable” Surfaces and Their Functionalization. *Macromolecules* **2011**, *44*, 4258-4268.
- (44) Vukićević, R.; Vukovic, I.; Stoyanov, H.; Korwitz, A.; Pospiech, D.; Kofod, G.; Loos, K.; Brinke, G. t.; Beuermann, S. Poly(vinylidene fluoride)-functionalized Single-Walled Carbon Nanotubes for the Preparation of Composites with Improved Conductivity. *Polym. Chem.* **2012**, *3*, 2261-2265.
- (45) Terzic, I.; Meereboer, N. L.; Acuautila, M.; Portale, G.; Loos, K. Electroactive Materials with Tunable Response Based on Block Copolymer Self-Assembly. *Nat. Commun.* **2019**, *10*, 601/1-21.
- (46) Otazaghine, B.; Sauguet, L.; Boucher, M.; Ameduri, B. Radical Copolymerization of Vinylidene Fluoride with Perfluoroalkylvinyl Ethers. *Eur. Polym. J.* **2005**, *41*, 1747-1756.
- (47) Maccone, P.; Apostolo, M.; Ajroldi, G. Molecular Weight Distribution of Fluorinated Polymers with Long Chain Branching. *Macromolecules* **2000**, *33*, 1656-1663.
- (48) Beuermann, S.; Imran-ul-Haq, M. Homogeneous Phase Polymerization of Vinylidene Fluoride in Supercritical CO₂: Surfactant Free Synthesis and Kinetics. *Macromol. Symp.* **2007**, *259*, 210-217.
- (49) Voorhaar, L.; Diaz, M. M.; Leroux, F.; Rogers, S.; Abakumov, A. M.; Van Tendeloo, G.; Van Assche, G.; Van Mele, B.; Hoogenboom, R. Supramolecular Thermoplastics and Thermoplastic Elastomer Materials with Self-Healing Ability based on Oligomeric Charged Triblock Copolymers. *NPG Asia Materials* **2017**, *9*, e385-e385.
- (50) M. Tatemoto and T. Shimizu, "Thermoplastic elastomers" In Modern Fluoropolymers; Scheirs, J., Ed.; Wiley: New York, 1997;. Chapter 30, pp 565–576

- (51) Ameduri, B.; Boutevin, B. Les Elastomères Thermoplastiques Fluorés: Synthèse, Propriétés et Applications. *l'Actualité Chimique*, Oct. Nov **2006**, 301-302.
- (52) Lopez, G.; Guerre, M.; Améduri, B.; Habas, J.-P.; Ladmiral, V. Photocrosslinked PVDF-based Star Polymer Coatings: An All-In-One Alternative to PVDF/PMMA Blends for Outdoor Applications. *Polym. Chem.* **2017**, 8, 3045-3049.
- (53) Glüge, J.; Scheringer, M.; Cousins, I. T.; DeWitt, J. C.; Goldenman, G.; Herzke, D.; Lohmann, R.; Ng, C. A.; Trier, X.; Wang, Z. An Overview of the uses of Per- and Polyfluoroalkyl Substances (PFAS). *Environ. Sci.: Processes Impacts* **2020**, 22, 2345-2373.
- (54) Kusoglu, A.; Weber, A. Z. New Insights into Perfluorinated Sulfonic-Acid Ionomers. *Chem. Rev.* **2017**, 117, 987-1104.
- (55) Tanaka Y. Development of the Mirai fuel cell vehicle. In: Sasaki K, Li HW, Hayashi A, Yamabe J, Ogura T, Lyth SM, editors. Hydrogen energy engineering, a Japanese perspective. Tokyo: Springer; 2016. chapter 34, p. 461-476.
- (56) Staffell, I.; Scamman, D.; Velazquez Abad, A.; Balcombe, P.; Dodds, P. E.; Ekins, P.; Shah, N.; Ward, K. R. The Role of Hydrogen and Fuel Cells in the Global Energy System. *Energy Environ. Sci.* **2019**, 12, 463-491.
- (57) Lee, J.; Lopez, G.; Améduri, B.; Seo, M. Synthesis of Heterograft Copolymers with a Semifluorinated Backbone by Combination of Grafting-through and Grafting-from Polymerizations. *Macromolecules* **2020**, 53, 2811-2821.
- (58) Tsang, E. M. W.; Zhang, Z.; Shi, Z.; Soboleva, T.; Holdcroft, S. Considerations of Macromolecular Structure in the Design of Proton Conducting Polymer Membranes: Graft versus Diblock Polyelectrolytes. *J. Am. Chem. Soc.* **2007**, 129, 15106-15107.

(59) Barbosa, J. C.; Dias, J. P.; Lanceros-Méndez, S.; Costa, C. M. Recent Advances in Poly(vinylidene fluoride) and Its Copolymers for Lithium-Ion Battery Separators. *Membranes* **2018**, *8*, 45/1-36.

(60) Apostolides, D. E.; Patrickios, C. S.; Sakai, T.; Guerre, M.; Lopez, G.; Améduri, B.; Ladmiral, V.; Simon, M.; Gradzielski, M.; Clemens, D.; Krumm, C.; Tiller, J. C.; Ernould, B.; Gohy, J.-F. Near-Model Amphiphilic Polymer Conetworks Based on Four-Arm Stars of Poly(vinylidene fluoride) and Poly(ethylene glycol): Synthesis and Characterization. *Macromolecules* **2018**, *51*, 2476-2488.

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Well-defined Fluorinated Copolymers: Current Status and Future Perspectives

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