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Recent advances in fluorinated polymers: synthesis and diverse applications

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Fluorinated polymers exhibit a unique combination of attributes, including chemical inertness, low surface energy, exceptional weather resistance, and intriguing electrical properties. This mini review provides an overview of recent advancements in the research of fluorinated polymers, highlighting the development of synthetic strategies for novel fluorinated polymers and their diverse applications in various fields. Traditional fluorinated polyolefins can be modified through chemical methods to produce functional materials. Copolymerization of fluorinated olefins with non-fluorinated monomers effectively addresses synthesis challenges, yielding main-chain fluoro-containing polymers with specific functional groups. Additionally, recent studies have revealed that free radical (co)polymerization of fluorinated (meth)acrylate monomers leads to new fluorinated polymers with enhanced solubility, processability, and structural diversity. Capitalizing on these new synthetic strategies, a range of fluorinated polymer materials has been developed for a multitude of applications, including flexible electrodes, alternating current (AC) electroluminescent devices, energy storage capacitors, triboelectric nanogenerators, and lithium batteries. With their customized structures and excellent properties, fluorinated polymers hold significant promise to uncover more potential applications in the era of flexible and wearable electronics.

fluorinated polymers, fluorinated monomers, flexible electronic device, lithium batteries, triboelectric nanogenerator

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1 Introduction

Traditional fluorinated polymers, especially the main-chain fluorinated polyolefins, possess remarkable properties such as thermal stability, chemical inertness, weather resistance, low surface energy, and distinctive electrical properties [1]. For example, polyvinylidene fluoride (PVDF) and its copolymer derivatives have been extensively utilized in many electrical devices as the preferred choice of polymer matrices [2,3]. These fluorinated polymers have been widely used in various fields, such as piezoelectric materials [4], energy storage capacitor [5], membranes for water treatment [6], and lithium batteries [7], due to their special ferroelectric properties and excellent chemical stability.

Despite of the exceptional properties of such traditional fluorinated polymers, one major limitation of PVDF-based materials is associated with the difficulty in synthesis and the lack of structural tunability, which restricts their applications in many scenarios. Thus, it is imperative to develop new fluorinated polymers with tunable structures and properties that can fill these gaps and meet the diverse material requirements towards different applications. For instance, with the recent surge in research on flexible electronic devices, novel fluorinated polymers have demonstrated extensive

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*Corresponding author (email: kanyue@scut.edu.cn) applications in flexible electrodes [8,9], owing to their unique ion-dipole interactions. Furthermore, their high dielectric constant and the electronegativity of fluorine atoms have made them important materials in emerging flexible cross-linked electroluminescent devices (ACEL) [10,11] and flexible triboelectric nanogenerators (TENG) [12].

In this mini review, we provide a brief overview of the design strategies and preparation methods of several novel fluorinated polymer systems that have been frequently employed in recent years. These methods encompass chemical modifications of traditional fluorinated polyolefins, copolymerization with non-fluorinated monomers, and the synthesis of novel side-chain fluorinated polymers using free radical (co)polymerization techniques (Figure 1). Next, we focus on several emerging applications of new fluorinated polymers, including substrates for flexible electrodes, dielectric light-emitting layers in ACEL devices, dielectric layers in energy storage capacitors, active layers in TENG, and solid-state electrolytes for lithium batteries. Lastly, we provide pespectives on the potential opportunities and challenges for future research in this direction.

2 Preparation strategies for new fluorinated polymers

2.1 Chemical modifications to traditional fluorinated polymers

The usability of traditional fluorinated polymers can be enhanced by proper chemical modifications, which alter the chemical structures by imparting reactive functional groups, adjusting molecular weight, or introducing crosslinking. These modifications can lead to improved mechanical performance, chemical stability, and electrical properties.

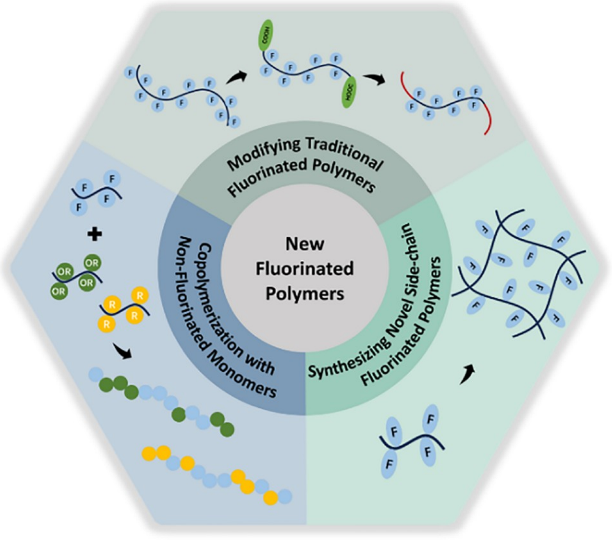

Figure 1 Schematic illustration of the design strategies for new fluorinated polymers (color online).

In the fields of ion-exchange membranes and water treatment, PVDF is an excellent polymer for use in aggressive environments and for the preparation of microporous hydrophobic membranes. To make it compatible with other functional polymers, chemical modification of PVDF is necessary [13,14]. For instance, Madaeni and Xu *et al.* [15] developed two different treatment methods based on the employment of an oxidative agent or a base to alter the miscibility of PVDF with other polymers to afford composites. Subsequent analysis *via* Fourier-transform infrared spectroscopy (FT-IR) revealed the degradation effects of these chemical agents on the PVDF structure. Notably, they observed unsymmetrical stretching vibrations peaks of carbon-carbon double bonds at 1,604 cm^{-1} and stretching vibrations peaks of hydroxide groups at 3,445/3,435 cm^{-1}, indicating successful chemical modification.

Recently, Hu and Li *et al.* [16] introduced the concept of "elastic ferroelectrics" and designed a precise "micro-crosslinking" method to establish a network structure in ferroelectric polymers. They chose poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) as the base material and utilized polyethylene glycol diamine (PEG-diamine) with soft and long chains as the crosslinking agent. Employing a low crosslinking density (1%–2%) imparted linear ferroelectric polymers with elasticity while maintaining a high degree of crystallinity. The study revealed that the crystalline phase of the crosslinked ferroelectric film was predominantly in the β-phase, uniformly dispersed within the polymer's crosslinked network. During stress, the network structure evenly dispersed external forces and bore more stress, preventing damage to the crystalline regions. This "micro-crosslinking" preparation approach proved to be an effective method for the elasticization of ferroelectrics, ingeniously achieving a strong match between ferroelectric properties and elasticity through simple chemical reactions, providing a novel pathway for the elasticization of ferroelectric materials.

Due to the lack of reactive sites, precise chemical modification of fluorinated polyolefins is not a trivial task. Qi *et al.* [17] performed oxidative degradation on high molecular weight fluorinated polymers to prepare low-molecular weight fluorinated polymers with terminal carboxylic acid groups (Figure 2a), which were subsequently cured with epoxy resin. Following this work, Bai *et al.* [18] conducted a reduction reaction on the carboxyl-terminated fluorinated polymers to synthesize a hydroxyl-terminated fluorinated polymer HO-P(VDF-*co*-HFP)-OH (LFH), which can be the starting material for synthesizing a library of fluorinated polyurethanes. In this case, the hard segments were formed by using 4,4′-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BDO), while the soft segments were composed of LFH and polytetrahydrofuran glycol (PTMG) (Figure 2b).

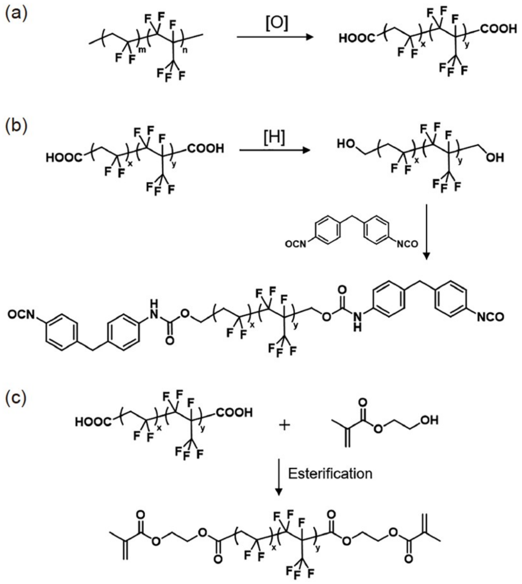

Figure 2 (a) Synthesis route of carboxyl-terminated low molecular weight fluoropolymers from commercial PVDF-HFP. (b) Synthesis route of a hydroxyl terminated low molecular weight fluoropolymer and a fluorinated polyurethane prepolymer. (c) Synthesis route of diacrylate-terminated fluorinated prepolymer.

Bai *et al.* [19] further developed a universal and simple method for synthesizing a series of novel photocrosslinkable fluorinated copolymer, which can be used as the precursor for constructing crosslinked polymeric network based on the PVDF-HFP backbone (Figure 2c). For example, rapid crosslinking of the diacrylated P(VDF-*co*-HFP) precursor was achieved through ultraviolet (UV) irradiation, resulting in a fluorinated elastomer network with excellent heat resistance, chemical resistance, and mechanical properties [19].

2.2 Copolymerization with non-fluorinated monomers

Fluorinated polyolefins, especially for the homopolymers, usually exhibit high crystallinity, which can pose challenges in terms of processability. To address this issue, copolymerization has emerged as an effective method for adjusting the crystallinity and solubility of fluorinated polyolefins while retaining their inherent advantages. Many commercial products are now produced by copolymerizing fluorinated monomers with other monomers. This approach not only offers control over the chemical structure but also allows for the manipulation of their physical properties.

In recent years, there have been many reports on new controlled polymerization methods for fluorinated olefins [20]. For instance, Chen *et al.* [1] introduced a reversible deactivation radical polymerization method for alternating copolymerization of chlorotrifluoroethylene (CTFE) and vinyl ethers using a organic photocatalyst under LED light exposure at room temperature and atmospheric pressure (Figure 3a).

The choice of photocatalysts and chain transfer agents was found to significantly impact the polymerization process [1]. For example, when a non-fluorinated photocatalyst was used, polymers with a broad dispersity (1.5–1.8) were obtained, due to the tendency toward self-assembly of the fluorinated copolymers during the copolymerization process [1]. To address this issue, a fluorinated photocatalyst (F-PTH) was employed, and the presence of the n-C8F17 substituent on F-PTH facilitated fluorine-fluorine interactions between photocatalyst and the growing polymer chains. This strategy enables the synthesis of alternating fluorinated copolymers with low dispersity and high chain-end fidelity. Besides fluorinated photocatalyst, fluorinated chain transfer agents (CTAs) also impact controlled chain-growth process for many fluoroalkenes [21]. For instance, in the copolymerization study of chlorotrifluoroethylene with vinyl esters/amides, significant emphasis was placed on optimizing the chemical structure of the substituent group on the CTA to obtain suitable redox activity. It is noteworthy that CTA with hexafluoroisopropyl substitution demonstrated superior control over the dispersion of vinyl acetate (VAc) and *N*-vinyl pyrrolidinone (NVP) compared with the CTA with trifluoroethyl substitution [21]. Furthermore, a perfluorohexylethyl substituted CTA provided improved conversion rates and reduced molecular weight distribution [21]. This highlights the enhancement of dispersion control achieved by increasing the fluorine atoms to attain sufficient hydrophobicity.

Chen *et al.* [22] also showcased a redox-relay pathway with a thermally activated delayed fluorescence (TADF) catalyst for controlled copolymerization of various fluoroalkenes under ambient conditions (Figure 3b). Importantly, this method enables the synthesis of a wide range of main-chain fluoropolymers with excellent selectivity, diverse sequences and topologies at low organocatalyst dosages (as low as 5 ppm). Specifically, they cleverly designed a fluorinated chain-transfer monomer (2-(vinyloxy)ethyl 2-(((2,2,2-trifluoroethoxy)carbonothioyl)thio)acetate) as an inimer. This allowed for the production of branched copolymers with good terminal fidelity.

Cheng and Zhang *et al.* [23] introduced an innovative polymerization technique called “step transfer-addition and radical-termination” (START) for the step-growth radical polymerization of α,ω-unconjugated dienes. It involves the alternating and efficient addition of α,ω-diiodoperfluoroalkane monomers onto α,ω-unconjugated dienes, resulting in the formation of perfluorocarbon-containing alternating copolymers. Importantly, this innovative approach not only advances the step-growth radical polymerization of α,ω-unconjugated dienes, but also offers high molecular weight perfluorocarbon-containing alternating copolymers. Subsequently, they employed this polymeriza-

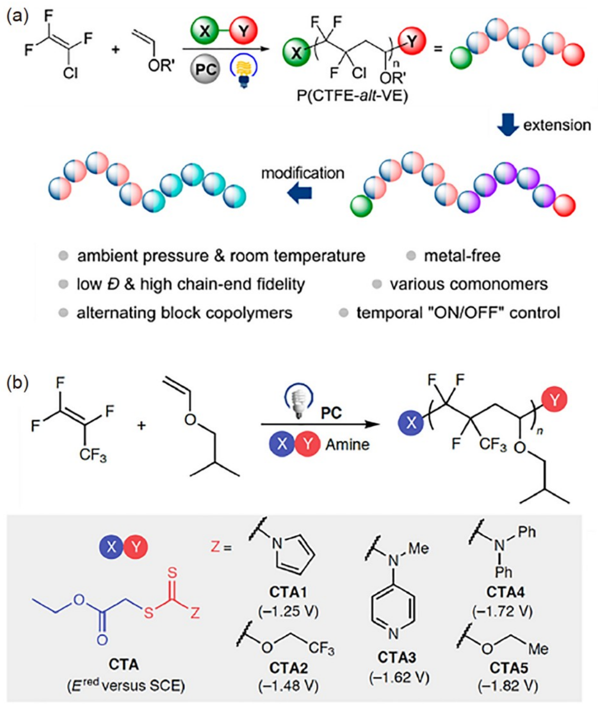

Figure 3 (a) Organic photocatalyzed reversible-deactivation radical alternating copolymerization of CTFE and vinyl ethers. Adapted with permission from Ref. [1]. Copyright 2020, American Chemical Society. (b) Photo-catalyzed copolymerization of hexafluoroprorylene and vinyl ethers. Adapted with permission from Ref. [22]. Copyright 2023, the author(s), under exclusive licence to Springer Nature Limited (color online).

tion method along with photocontrolled iodine-mediated reversible deactivation radical polymerization (RDRP) to synthesize a fluorinated macromolecular coupling agent [24]. Notably, this agent could be used to modify the surface of silica nanoparticles with high molecular weight fluorinated polymer brushes and for the fabrication of superhydrophobic cotton fibers, which holds great promise in the large-scale production of superhydrophobic materials [24].

The synthesis of fluorinated polymers by light-mediated controlled polymerization may face some difficulties due to the low reactivity and high stability of fluorinated monomers [25]. Fluorinated monomers are classified as less activated monomers, which require higher activation energy and stronger catalysts or initiators to undergo polymerization. Moreover, fluorinated monomers may have adverse effects on the catalysts or initiators, such as quenching the excited states, reducing the electron density, or increasing the steric hindrance. Therefore, more efficient and robust catalysts or initiators are needed to achieve high conversion and control of fluorinated monomers by lightmediated controlled polymerization. This raises questions about the scalability of such systems, as what proves to be an efficient photocatalyst or chain transfer agent in one publication may not perform as efficiently when applied to a different fluorinated monomer. For instance, a CTA that demonstrated good control in the copolymerization of chlorotrifluoroethylene and vinyl ethers might lead to poor vinyl ethers conversion rates when used in the copolymerization of perfluorinated vinyl ethers and vinyl ethers [1,20]. For researchers engaged in applied field studies, it is often challenging to predict the hydrophobicity, dielectric properties, mechanical characteristics, and other attributes of fluorinated polymers solely based on monomers. Instead, they often need to experiment with numerous combinations of monomers to identify suitable materials. If different monomers require distinct polymerization conditions, this introduces too many variables, making it challenging to compare the performance of different polymer materials. It also sig-nificantly increases the workload.

2.3 Synthesis of novel side-chain fluorinated polymers

Another general strategy towards novel fluorinated polymers is to introduce fluoro-containing side chain groups onto the polymeric backbone. Comparing with main-chain fluoropolymers, this strategy offers a much broader structural diversity for the selection of fluorinated monomers, such as the fluorinated acrylates and methacrylates that can be conveniently polymerized *via* the free radical polymerization mechanism. It is anticipated that the properties of the resulting homopolymers and copolymers are strongly influenced by the length of the fluorinated alkyl chains and the connecting groups (Figure 4a) [26,27]. Consideirng the solubility issue, monomers with shorter fluorinated side chains such as trifluoroethyl methacrylate (TFEMA), methyl trifluoroethyl methacrylate (MFEMA) [26,28], or monomers with incomplete fluorine substitution on the side chain such as hexafluorobutyl acrylate (HFBA) [9] are more commonly used.

Homopolymers of fluorinated acrylates and methacrylates can be prepared by mild solution polymerization using common free radical initiators such as azobisisobutyronitrile (AIBN) or benzoyl peroxide (BPO). When copolymerizing with a non-fluorinated acrylate/methacrylate comonomer, the composition of the resulting copolymer varies with different reaction conditions, resulting in a broad molecular weight distribution [29]. To tackle this challenge, new controlled living free radical polymerization methods have been developed in recent years to afford (co)polymers with narrow molecular weight distributions [25,30,31]. For example, Hawker *et al.* [25] reported an efficient photoinduced atom transfer radical polymerization (ATRP) method for semi-fluorinated acrylic ester and methyl methacrylate monomers (Figure 4b). The use of 2,2,2-trifluoroethanol as a solvent provides an optimal balance of the solubility of monomer, polymer, and catalyst, which eliminated adverse ester exchange side reactions during polymerization. The introduction of ppm levels of copper (II) bromide catalyst and Me_6TREN (TREN = tris(2-aminoethyl)amine) ligand allows

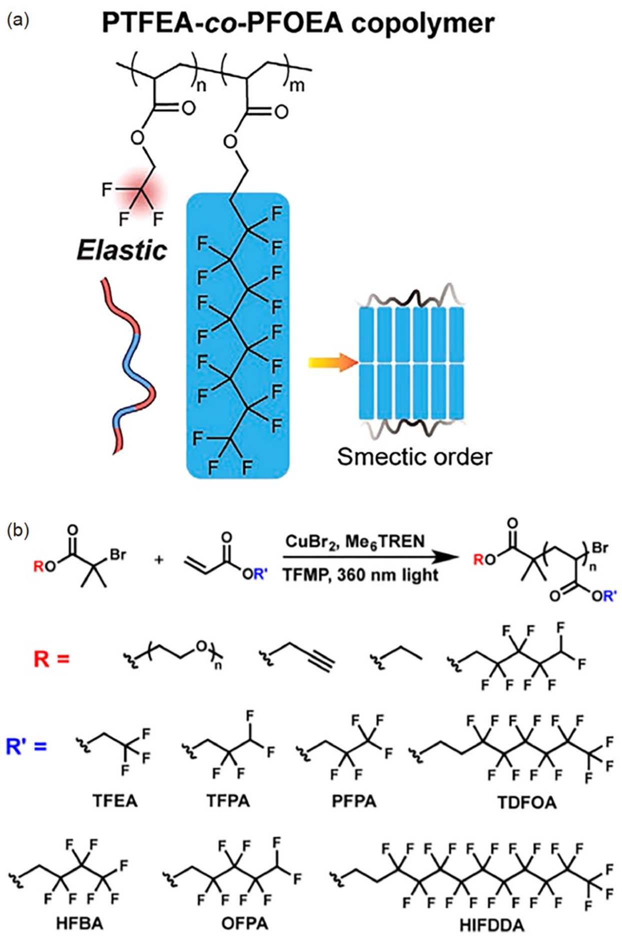

Figure 4 (a) Chemical structure of the PTFEA-*co*-PFOEA copolymer with the denoted smectic liquid crystalline packing of the long fluoroalkyl chains. Adapted with permission from Ref. [26]. 2023 Wiley-VCH GmbH. (b) Semi-fluorinated poly(acrylates) controllably polymerized. Adapted with permission from Ref. [25]. Copyright 2017, American Chemical Society (color online).

for efficient photo-induced ATRP of semifluorinated acrylate and methacrylate monomers containing 3–21 fluorine atoms on the side chain under controlled conditions using UV radiation. The resulting polymers exhibit narrow molecular weight distributions (~1.1) and high end-group fidelity even at conversion levels >95%. The success of this method critically hinges on the choice of an appropriate solvent. Using primary or secondary alcohols as the solvent can result in a variety of molecular weight distributions due to transesterification reactions involving the side chains of fluorinated acrylic ester monomers. Conversely, a tertiary alcohol solvent significantly suppressed the side reactions of transesterification for both the monomer (Figure 2b) and the resulting polymer (Figure 3b). This polymerization method enables the convenient preparation of semifluorinated polymers that were previously unavailable, which provides opportunities for the synthesis of customized fluorinated polymers in terms of their inherent, interfacial, and solution properties. Another important method for synthesis of semi-fluorinated polymers through photo RAFT polymerization was reported by Chen *et al*. [32]. This method is capable of producing a variety of perfluorinated polymers with narrow molecular weight distribution from semi-fluorinated thiocarbonates or perfluoroalkyl iodides. High “on/off” control and chain extension experiments further demonstrate the practicality and reliability of this approach. Furthermore, to stream-line the preparation of perfluorinated polymers, the authors have developed an scalable continuous-flow method. Importantly, the reaction time is only one-quarter of that required for control experiments under batch conditions, confirming the high efficiency of segmental copolymer synthesis under flow conditions.

3 Applications of novel fluorinated polymers

Although there have been many recent reports on novel polymerization methods for new fluorinated polymers, these studies often remain somewhat disconnected from the exploration of practical applications for the resulting polymer products. Due to the challenges associated with the controlled polymerization of different fluorinated monomers, the successful development of a new synthetic method is by itself an attractive and important goal. With the recent progress, these new methods enable the preparation of high molecular weight fluorinated polymers under conditions of high monomer conversion, and even the controlled polymerization of fluorinated monomers that are difficult to polymerize. These developments are aligned with the performance requirements of fluorinated polymer materials outlined in this paper, including exceptional processability, self-healing properties, proper mechanical strength, and high stretchability.

In this context, it is therefore our aim to provide an overview of some promising applications of new fluorinated polymers in this paper for bridging the gap. As to be discussed shortly, fluorinated polymers can serve both as functional components and structural components. For the former, some fluorinated polymers exhibit elastomeric characteristics, expanding their utility as fluoro-elastomers. Depending on the intended application, these fluorinated polymers can be processed into various forms, including films, fibers, and electrospun membranes. This also places demands on the processability of fluorinated polymers. Furthermore, when employed as structural components in combination with inorganic materials, their potential applications can be significantly broadened. For example, mixing fluorinated polymers with ionic liquids or electrolyte salts allows for the creation of gels or liquid-free ionic conductors, offering intriguing potential in various applications.

3.1 Flexible electrodes

Flexible electronic devices can closely conform to the skin, thus ensuring comfortable and accurate physiological monitoring and physical sensing applications. Soft and stretchable electrodes are an important component in achieving this function. In general, fluorinated polymers are not conductive due to the lack of conjugated structures. However, due to the excellent physical and chemical stability, superior mechanical properties, and the special ion-dipole interaction of fluorinated polymers, various conductive additives such as metal-based materials [33–35], carbon-based materials [35], ionic liquids [36,37], and salts [38] can be mixed with fluorinated polymers to prepare flexible electrodes.

Metal-polymer composite materials derived from metal nano/micro fillers and a polymeric network are a promising method for achieving both high conductivity and stretchability. Recent studies show that some fluorinated polymers can improve the performance stability and durability of metal-polymer materials and extend the applications [39,40]. For example, Someya *et al*. [33] reported a durable PVDF nanofiber-reinforced metal-elastomer composite material with high stability of conductivity upon cyclic stretching. As shown in Figure 5a, the introduction of PVDF nanofibers enhances toughness and inhibits crack propagation, and the filtering effect causes silver flakes to self-assemble and enrich on the top surface of the conductive layer. The resulting wrinkled electrode shows excellent cyclic durability, high conductivity, and high stretchability (up to 800%). By using this metal-polymer composite electrode, a wearable multimodal physiological sensing kit was demonstrated, which successfully monitored electrocardiogram, electromyogram, and motion in a continuous manner with no significant signal decay observed [33].

In contrast to electronically conductive materials such as metals, ionic conductive materials, such as ionic liquid gels and salt-elastomer composites, exhibit relatively low conductivity (10^{-3}–10^{-5} S cm^{-1}). However, the transparency and the maintenance of conductivity even under extremely high strain distinguish them from metal- and carbon-based conductive materials, which are useful for applications in flexible electronics. The fundamental design strategy of ionic conductive materials is to combine a polar and stretchable polymer with a mobile, highly ionized salt. Fluorinated polymers tend to exhibit typical ion-dipole interactions due to the large electronegativity of fluorine atoms, which forms strong dipoles along the C–F bonds. As a result, they demonstrate the characteristic ion-dipole interactions with many ions [42–45], which remain stable even under electrochemical conditions, as demonstrated by numerous gel electrolytes [46–49]. Therefore, the fluorinated polymer chains can be physically crosslinked through the ion-dipole interactions between the polymer chains and ionic salts.

Our group previously reported a multifunctional ionogel based on fluorinated polymers with excellent properties such

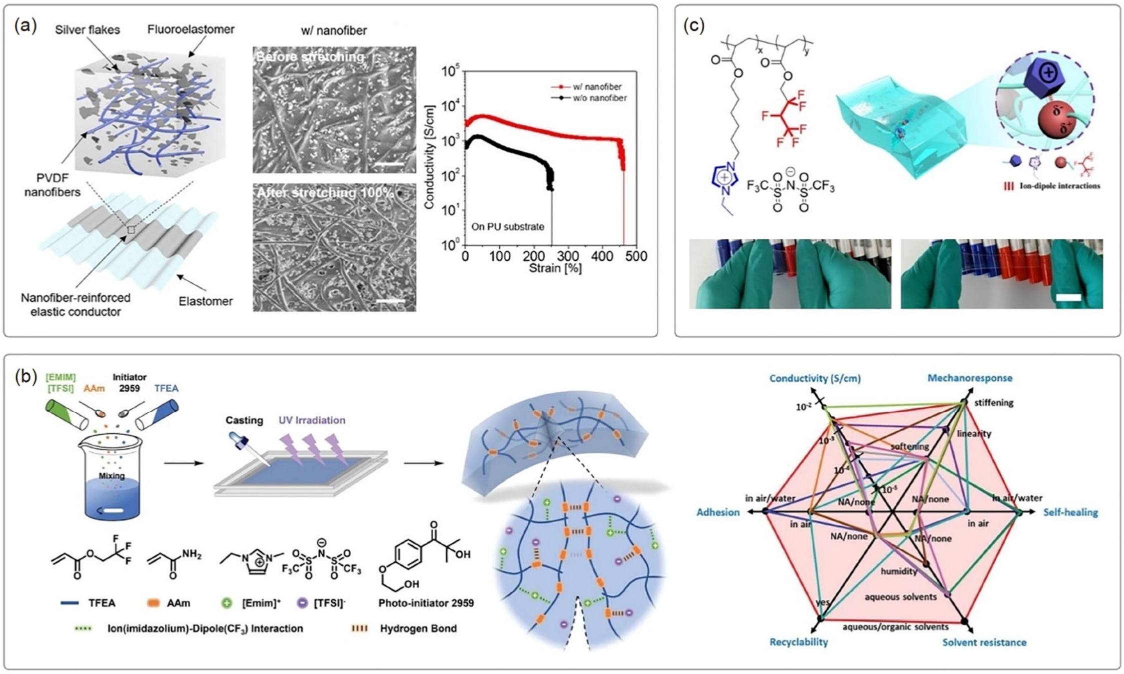

Figure 5 Fluorinated polymer-based flexible electrodes. (a) Schematic illustration of the PVDF nanofiber-reinforced metal-elastomer composite electrode. Such electrodes showed no obvious morphological change under 100% stretching. Scale bar: 10 μm. Reproduced with permission from Ref. [33]. Copyright 2019 American Chemical Society. (b) Schematic illustration and properties of an ionogel based on a fluorinated polymer network. Reproduced with permission from Ref. [37]. Copyright 2021 Wiley-VCH GmbH. (c) Structure of a fluorinated polyelectrolyte as a liquid-free self-healing ionic conductor, which shows high transparency and stretchability. Scale bar: 2 cm. Reproduced with permission from Ref. [41]. Copyright 2021 American Chemical Society (color online).

as transparency, high stretchability, solvent and temperature resistance, recyclability, high conductivity, underwater self-healing capability, and underwater adhesion (Figure 5b) [37]. The ionogel is prepared by one-step photo-induced polymerization of 2,2,2-trifluoroethyl acrylate (TFEA) and acrylamide in a hydrophobic ionic liquid. The trifluoromethyl groups provide abundant ion-dipole interactions, while acrylamide contributes to rich hydrogen bonding. These non-covalent interactions impart excellent mechanical strength, resilience, and rapid self-healing ability at room temperature. The fluorinated polymer matrix exhibits high water resistance and tolerance to various organic solvents, while demonstrating strong underwater adhesion on different substrates. Similarly, other examples of ionogels with fluorinated polymeric networks have also been reported recently by many other groups [50–53].

However, the presence of dispersed ionic liquids in ionogels may lead to leakage under deformation or fracture [54]. Therefore, in certain applications that demand high reliability, solid salts are as the conductive fillers to polymers, affording the so-called liquid-free ion-conductive elastomers [55]. In these systems, the ion-dipole interactions provided by the C–F dipoles of fluorinated polymers can similarly improve the miscibility and performance of the materials.

Another strategy to avoid liquid component in soft ionic conductors is to select a polymerizable ionic specie to prepare polyelectrolytes. For example, in a series work by Zhang *et al*. they initially selected the polymerizable ionic liquid 1-(6-acryloxyhexyl)-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide ([EIC6A][TFSI]) and *n*-butyl acrylate (*n*-BA) as the monomers for a free radical copolymerization [41]. The [EIC6A][TFSI] monomer has a long hydrocarbon spacer between the acrylate group and the imidazole group, leading to excellent ion conductivity. Additionally, when the acrylate group undergoes polymerization, the resulting polymeric electrolyte loses its liquid characteristics. In a subsequent study, when the copolymerization monomer changes from *n*-BA to HFBA, the resulting copolymer demonstrates intriguing autonomous self-healing capability, in addition to other desirable properties such as high optical transparency, ion conductivity, and mechanical stretchability (Figure 5c) [41]. The self-healing property is attributed to the ion-dipole interactions between the imidazole ions and the C–F dipoles from the HFBA monomer, allowing the ICEs to recover 96% of their original mechanical properties after 24 h of self-healing at room temperature. Such fluorinated polyelectrolytes can also be used for leakage-free flexbile electrodes.

3.2 ACEL devices

ACEL devices are composed of a luminescent layer sandwiched between two electrodes, and have attracted increasing attention for biomedical, aerospace, display, and information communication applications, owing to the low power consumption, easy preparation, and long operating life [56]. To achieve flexible or even stretchable ACEL devices, both flexible electrodes (Section 3.1) and high-performance flexible luminescent layers are essential. The stretchability of the luminescent layer can be achieved by embedding phosphorescent materials into soft elastomer matrices; while the demands for the luminescent layer's matrix in ACEL devices are more than that. ACEL devices are based on the principle of high-field electroluminescence, where electrons in the phosphorescent material are accelerated by a voltage exceeding the threshold. They then collide with the luminescent centers, exciting the transition of ground-state electrons to excited states. The excited electrons trapped below the conduction band in shallow donor levels combine with holes in the acceptor levels above the valence band, resulting in light emission through radiative recombination.

However, due to the low dielectric constant (κ) of the elastomers widely used in previous studies [8,57–59], ACEL devices typically require high AC electric fields to excite the luminescent centers, as well as high frequencies in the kHz range to achieve sufficient luminescence intensity. This inevitably requires complex external high frequency/high voltage AC power to drive ACEL devices. Such electrical operating conditions limit its widespread use in portable optoelectronic devices. Therefore, there is an urgent need to develop a dielectric layer with a high κ value. Kong *et al*. [60] reported a strategy for developing dielectric nanocomposites by filling $BaTiO_3$ nanoparticles into a polar PVDF-HFP elastomer. Such dielectric nanocomposites in the luminous layer can effectively concentrate the electric field onto the phosphor to enable low-voltage operation of the ACEL device, thus alleviating safety concerns for wearable applications (Figure 6a).

Aiming at tackling the limitation of intrinsically low κ values of the elastomer matrix, Tee *et al*. [11] proposed an ACEL device using an innovative high-κ transparent elastic dielectric material (Figure 6b). Such an elastomeric dielectric layer is based on PVDF-HFP, a traditional fluorinated polymer of high κ value. To further increase the maximum strain, a small amount of non-ionic fluorinated surfactant was added, which further imparts desirable self-healing property into the material. It is demonstrated that the resulting high-κ dielectric significantly reduces the required electric field, voltage, and frequency for achieving visible brightness under sunlight in ACEL devices. Additionally, this ACEL device exhibits repeatable, autonomous self-repairing optical performance after experiencing physical damage.

Subsequently, Wang *et al*. [61] developed a wearable, low-temperature-resistant, and self-powered electroluminescent (EL) system that integrates an organic hydrogel EL (OH-EL)

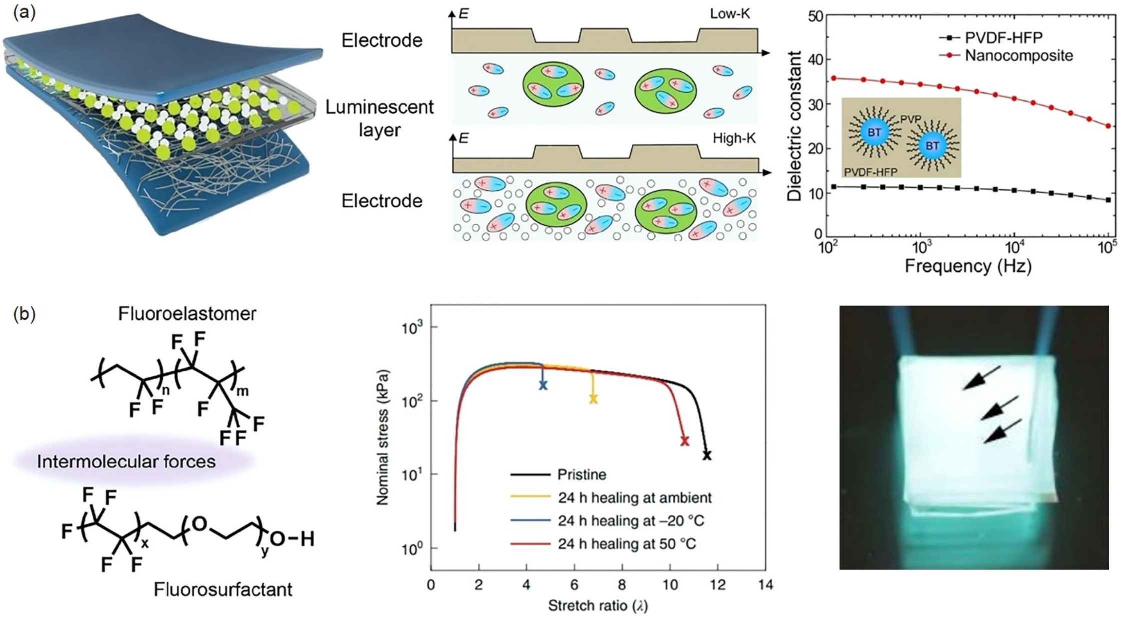

Figure 6 (a) Left: schematic illustration of a stretchable ACEL device. Middle: schematic image showing the influence of polarizability of dielectric matrix on the electric field distribution in the EL layer. Right: frequency-dependent dielectric constants of the nanocomposite and the pristine PVDF-HFP elastomer. Inset shows a schematic describing the composition of the nanocomposite embedded in a PVDF-HFP elastomer. Reproduced with permission from Ref. [60]. Copyright 2019 American Chemical Society. (b) Left: chemical structure of the PVDF-HFP based high-κ elastomer. Middle: self-healing behavior of the high-κ elastomer at ambient conditions. Right: photographs showing that the ACEL device can re-illuminate with no waiting time for healing after multiple punctures. Arrows show the scars from the punctures. Reproduced with permission from Ref. [11]. Copyright 2019, authors, under exclusive license to Springer Nature Limited (color online).

device with a single-electrode friction-based liquid electrolyte nanogenerator (LE-TENG) device. The OH-EL device, based on self-healing and highly conductive organic hydrogel electrodes, can be directly powered by the LE-TENG device. This work elegantly took advantage of the ZnS:Cu phosphor/PVDF-HFP elastomer system as the emitting layer and a TENG device for a self-powered optoelectronic device. The resulting stretchable OH-EL device displays bright and uniform light emission even under severe mechanical deformation such as 140% tensile strain, bending, rolling, and twisting. The optical performance shows excellent repeatability and durability after 2,000 continuous cycles.

One drawback of using PVDF-HFP materials in ACEL devices is their reliance on solution processing for fabrication. In contrast, fluorinated acrylic/methacrylic polymers can be polymerized without solvents, increasing flexibility, and reducing production costs. For instance, Liu *et al*. [10] developed a convenient method for manufacturing flexible electroluminescent devices and soft robots using three-dimensional (3D) printing *via* direct ink writing. They used a polymerizable fluorinated monomer, tridecafluorooctyl acrylate (TEAc), as a solvent in the electroluminescent and dielectric inks to dissolve PVDF-HFP and others. This eliminated the need for solvent evaporation and polymerized the monomers using UV light, forming high dielectric constant fluorinated polymers. This ink-based approach allows for on-demand creation of flexible and stretchable electroluminescent devices with great fidelity. The resulting 3D-printed devices exhibit attractive electroluminescent performance. They combined the ACEL device with a soft quadruped robot and sensing unit, creating adaptable artificial camouflage by displaying matching colors to the environment, laying a foundation for the next generation of soft camouflage.

3.3 Energy storage capacitor films

PVDF and its derivative copolymers, well-known for their high dielectric constant, are considered valuable ferroelectric materials for energy storage. However, fluorinated polymers have significant limitations in practical applications due to their high dielectric dissipation (10%), which severely restricts their use in fast charge and discharge scenarios within the frequency range of 100 kHz to 1 MHz. To overcome this, combining high dielectric constant nanoparticles with low loss ferroelectric polymers holds promise as a strategy to develop nanocomposites with high dielectric constant, strength, low loss, and comparable processability to polymer materials. In implementing this approach, appropriate surface modification of nanofillers becomes crucial in enhancing the performance of composite dielectric materials [62]. For instance, Jiang *et al*. [63] conducted surface-initiated RAFT polymerization to graft two fluorinated acrylate monomers onto the surface of $BaTiO_3$ nanoparticles with varying shell thicknesses or molecular structures. This surface modification aimed to improve the interface between the high dielectric constant $BaTiO_3$ nanoparticles and the ferroelectric polymer PVDF-HFP. The researchers then mixed the fluorinated polymer surface-modified $BaTiO_3$ nanoparticles with PVDF-HFP and evaluated the resulting nanocomposites' dielectric properties and energy storage capacity through broadband dielectric spectroscopy and electric displacement-electric field loop measurements. The findings demonstrated the successful achievement of nanocomposites with high energy density and low dielectric loss. Furthermore, the energy storage density of P(VDF-HFP)-based nanocomposites could be adjusted by modifying the structure and thickness of the fluorinated polymer shell [64]. This method holds wide applicability to various nanoparticles and polymer matrices, offering a novel approach to preparing polymer-based nanocomposites for the electronics and electrical industry.

3.4 TENG devices

With the advancement of flexible electronic devices, the need for renewable, battery-free, self-sustaining, and miniaturized power sources has become a focal point [65,66]. A promising option for achieving this goal is the TENGs, which convert mechanical energy into electrical energy. The friction layer, a crucial component of TENG, requires the selection of appropriate triboelectric materials to ensure high-performance.

Wang *et al*. [12] conducted a study on the mechanism of functional group types on the triboelectric properties of polymers. They chose a series of polymer films with similar carbon chains, but with different functional groups on the side chains. Among these functional groups, the fluorinated group on the carbon chain has the strongest ability to accept electrons, and its contact electrification performance is also the most outstanding. Moreover, it is revealed that increasing the density of fluorinated groups could also improve the charge density. This study highlights the general applicability of fluorinated polymers in TENG [12].

Kim *et al*. [67] have developed an efficient TENG device by focusing on two key aspects: the selection of proper materials and the introduction of surface micro/nanostructures (Figure 7). In this study, the team utilized poly (1H,1H,2H,2H-perfluorodecyl methacrylate) (PFDMA), a highly fluorinated methacrylate-based polymer, as the friction material. They employed the transfer printing technology to create a regularly arranged superhydrophobic micro/nanostructure on the surface of PFDMA while maintaining high transparency and transferability of the patterned PFDMA component.

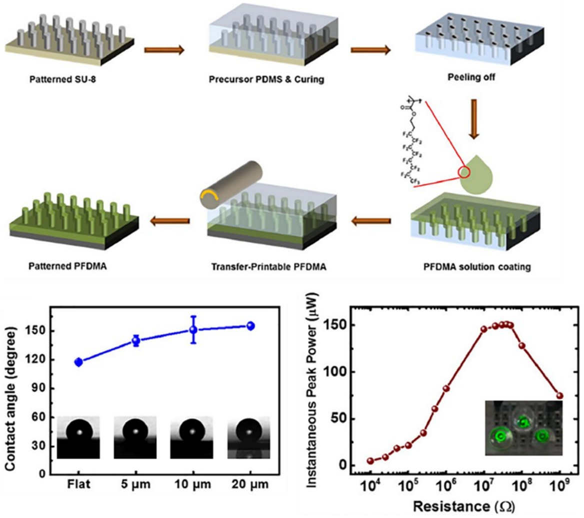

Figure 7 Fabrication of PFDMA-TENG based on transfer printing method. Wettability of PFDMA surface depending on height of PFDMA surface structure. Power output depending on external load resistance. Reproduced with permission from Ref. [67]. Copyright 2017 Elsevier Ltd. (color online).

The team conducted systematic tests to evaluate the frictional electric output performance of the PFDMA-based TENG. Their results demonstrated that the open circuit voltage (V_{OC}) and short circuit current (I_{CC}) of the TENG device increased with the height of the PFDMA surface microrod array. The optimal output voltage and current were found to be 68 V and 6.68 μA, respectively. The output power varied based on the external load resistance, reaching 150 μW when the load resistance was set at 500 MΩ. Furthermore, due to the low surface energy characteristics of fluorinated polymers, PFDMA exhibited exceptional hydrophobic properties. These findings indicate that PFDMA can be easily adjusted to regulate surface charge density and surface morphology, making it an excellent material for constructing TENG devices.

In a study by Li *et al*. [68], a self-healing fluorinated poly (urethane urea) was synthesized, which exhibited high mechanical strength, chemical stability, efficient healing ability, and outstanding triboelectric performance. This innovation leads to the development of a fully self-healing triboelectric nanogenerator (FSI-TENG) with a record output power density of 2.75 W m^{-2}, capable of reliable performance even under extreme conditions and after damage. Self-healing TENG devices have also been demonstrated by Jung *et al*. [69], using a versatile reactive block copolymer approach for imparting the self-healing behavior. By integrating ionic poly(hindered urea)-based covalent adaptive networks with pendant fluorinated species and ionic liquid, they achieve enhanced TENG outputs and over 90% recovery of triboelectric performance upon repairing damaged surfaces.

3.5 Solid polymer electrolyte

Solid polymer electrolytes (SPE) are regarded as attractive alternatives to conventional liquid electrolytes (LE) due to the high processability and highly tunable chemical functionality. This is particularly important to address hidden safety concerns associated with liquid electrolytes, such as the risk of leakage, combustion, and explosion caused by flammable organic liquids [70]. In comparison to the extensively studied polyethylene oxide (PEO) based SPE, fluorinated polymers offer advantages in terms of high-voltage stability, electrochemical stability, and non-flammability. Commercially available main-chain fluorinated polymers like PTFE, polychlorotrifluoroethylene (PCTFE), PVDF, and PVDF-HFP are important materials for high-voltage SPE application. However, their development is limited by challenges such as high crystallinity, weak ionic solubilization capability, low ionic conductivity, and low ion mobility [71].

To overcome these limitations, the exploration of novel fluorinated polymers is considered a promising avenue. Modifications to the traditional polyfluorinated polymeric backbone structures can effectively reduce crystallization and improve the efficiency of ion migration through the molecular chains. Furthermore, the alteration in polymer polarity and dielectric constant facilitates the dissociation of ion clusters, leading to enhanced performance [72]. For example, Huang *et al*. [73] reported the use of poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene) (P(VDF-TrFE-CTFE)) as the framework for ILs to prepare an iono-SPE material. As show in Figure 8a, this iono-SPE exhibited an exceptionally stable cycling performance for 1,500 h in symmetric cells at 0.1 mA cm^{-2} at room temperature. Moreover, the Li||LFP full cells demonstrated a steady capacity retention of 91.5% after 1,000 cycles at 1 C. The asymmetric fluorinated skeleton possesses a moderate local polarity (0.6–2.1 Debye) and a high dielectric constant (~40.2), which reduced the migration barrier for Li$^+$ ions from 0.35 to 0.25 eV, facilitating ion transport in various phases. The high dielectric constant created strong electronegative ends of dipoles, attracting Li$^+$ ions and promoting the dissociation of lithium salt. While the modulation of intrinsic properties of the fluorinated chain segments facilitated electrolyte stabilization, efficient ionic conductivity still heavily relied on the ionic liquid.

Whittaker *et al*. [74] demonstrated that perfluoropolyether fragment-terminated PEO block copolymers synthesized by macro-reversible addition-fragmentation chain-trasfer (RAFT) method possessed self-organizing nanostructures, achieving a stable solid-electrolyte interface (SEI) that inhibited sodium dendrite formation and enabled stable long-term cycling at high current density (0.5 mA cm^{-2}) for 1,000 h. The perfluoropolyether fragments were believed to facilitate uniform ion transport and deposition, stabilizing the electrode structure. Another approach, proposed by Chen *et al*. [75], involved molecular design and synthesis of fluorinated polymer electrolytes through organic photocatalyzed main-chain alternating copolymerization (Figure 8b). Such synthetic advantages of this method enable facile and on-demand access to main-chain fluoropolymers *via* the combination of photoredox catalysis and RAFT process. The obtained fluorinated polymer retained the chemical structural characteristics of PCTFE, but the alternating connection of two types of monomers resulted in a polymer chain without low crystallinity. When used as a solid-state electrolyte in high-voltage Li-ion batteries, this polymer effectively mitigated the formation of lithium dendrites and stabilized lithium deposition. It exhibited non-flammability, solid-state properties, chemical stability, and superior Li$^+$ ion transport with exceptional compatibility with the Li anode through the formation of a unique hexagonal solvation structure with Li$^+$ ions. Furthermore, it displayed significantly improved oxidative stability, expanding the overall electrochemical window to 5.3 V. In addition, some unconventional main-chain fluorinated monomers also have been explored for use in lithium metal batteries, such as perfluoro(propyl vinyl ether) (PFVE) and 1H,1H,11H,11H-perfluoro-3,6,9-trioxaundecane-1,11-diol (FTEG) [76,77]. Compared with conventional monomers, the above fluoro-oxygen fragment monomers exhibit chemical inertness, which can potentially mitigate lithium metal and electrolyte side reaction, form a long-term stable SEI interface, and optimize battery cycling performance.

However, as mentioned earlier, the synthesis of main-chain fluorinated polymers often requires rigorous processing of gaseous fluorinated ethylene monomers, making it challenging to obtain copolymers with non-fluorinated monomers. An alternative strategy is to explore simple methods for synthesizing end-functionalized or side-chain fluorinated polymer electrolytes. Acrylate- and methacrylate-based fluorinated monomers have been considered suitable alternatives, enabling the introduction of fluorine effects and dendrite suppression. Feasible polymerization methods have been used to develop new fluorinated SPEs using trifluoroethyl acrylate or hexafluorobutyl acrylate [78,79]. During repeated charge/discharge cycles, the active fluorinated side-chain segments can separate from the polymer, forming a stable LiF-rich SEI and stabilizing ion flow. For instance, Chen *et al*. [38] proposed the design of a bifunctional SPE in which the fluorinated segments are covalently linked to the polyether segments through photo-controlled free radical polymerization (Figure 8c). This fluorinated SPE provides a Li$^+$ transport window of up to approximately 5.0 V, forming Li-F interactions that enhance compatibility with the Li anode and suppress the growth of Li dendrites. The results demonstrate excellent cycling stability of this fluorinated SPE in Li||Li symmetric cells, even at a high current density of 0.2 mA cm^{-2}, with a working time exceeding 1,500 h. Moreover, full solid-state Li||LFP and Li||

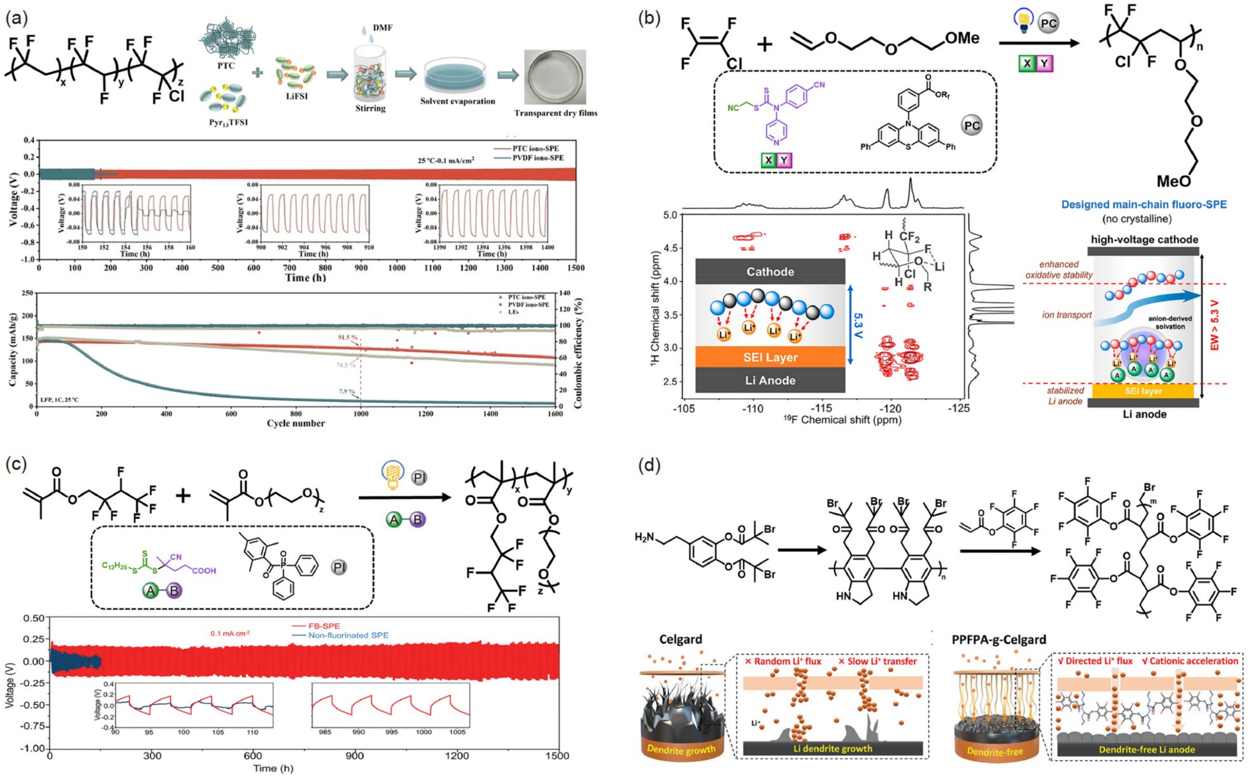

Figure 8 (a) High dielectric P(VDF-TrFE-CTFE) polymer for solid-state ionogel electrolytes. Reproduced with permission from Ref. [73]. Copyright 2023 John Wiley and Sons. (b) Weakly solvating main-chain fluoropolymer for ultrahigh stable Li anodes and high-voltage cathodes synergistically improve cycling stability. Reproduced with permission from Ref. [75]. Copyright 2021 American Chemical Society. (c) Novel fluorinated bifunctional copolymer for stable deposition and dendrite-free solid-state battery. Reproduced with permission from Ref. [38]. Copyright 2021 John Wiley and Sons. (d) Precise control over the directed transport of Li^+ ions *via* electronegative fluorinated polymer brush. Reproduced with permission from Ref. [80]. Copyright 2022 John Wiley and Sons (color online).

NCM batteries based on this bifunctional fluorinated SPE achieve stable cycling with an average coulombic efficiency of 99%. Additionally, perfluorophenyl acrylate polymers synthesized by ATRP method have also been reported to achieve stable ion deposition (Figure 8d) [80].

3.6 Other applications

Besides the above mentioned applications, fluorinated polymers have also been applied in many other scenarios. For instance, Lee *et al.* [81] utilized the hydrophobic fluorinated polymer poly(2,2,3,3,4,4,4-heptafluorobutyl acrylate) (EGC-1700) as the insulation and encapsulation layer for organic resistive random-access memory. This polymer demonstrated excellent resistance to various organic solvents and its compatible solvent, methyl nonafluorobutyl ether, can be used with most organic semiconductors. Hence, this flexible artificial synapse can be fabricated using solution processing techniques without the risk of dissolving the underlying semiconductor. Moreover, the amorphous fluorinated polymer exhibits low permeability to gases and moisture, making it suitable as a CF growth medium and encapsulation layer for organic transistors. Consequently, the developed flexible synapse exhibits high reliability and stability, maintaining a mobility of approximately 0.15 $cm^2\ V^{-1}\ s^{-1}$ and a threshold voltage drift of approximately 1.0 V, significantly lower than previously reported unencapsulated devices [82]. Additionally, the excellent insulating properties of the fluorinated polymer effectively suppress leakage current during device operation.

The demand for high-performance quantum dot light-emitting diodes (QLEDs) in wearable electronic applications has led to the development of flexible displays. However, the stability of quantum dot films and QLEDs in water/air environments remains a challenge, limiting their practical use. Researchers have explored ion-dipole interactions in non-liquid elastomers to prepare self-healing elastomer systems [9,83]. For instance, Wang *et al.* [9] utilized the ion-dipole interaction between perovskite quantum dots and fluorinated acrylic ester-based polymers to create a highly stable, stretchable, and self-healing polymer composite. This composite exhibited optical transparency, high mechanical strength, excellent stability in harsh environments, and self-healing capability under aqueous conditions. After immersion in various harsh environments for several months, the mechanical and optoelectronic properties remained stable, displaying a fracture stress of 1.8 MPa and stretchability up to 1,300% of its original length. Moreover, it could self-heal without external stimuli when damaged in these environments.

Chun *et al.* [84] demonstrated a durable and flexible InP@ZnSeS QLED encapsulated in a ultra-thin film of CYTOP, which is an amorphous fluoropolymer developed by Asahi Glass Company. The flexible green QLED encapsulated in CYTOP achieved a high external quantum efficiency (EQE) of 0.904% and a luminance of 1,593 cd m^{-2}, along with excellent waterproof performance. Even after immersing the flexible device in water for approximately 20 min, it continued to emit stable and strong light. The device maintained high luminance even under continuous tensile stress with a bending radius of 5 mm. This waterproof structure based on fluoropolymer represents a promising approach for wearable electronic applications.

4 Summary and outlook

In summary, this mini review has provided a comprehensive yet concise analysis of the preparation and applications of fluorinated polymers in various fields, including flexible electrodes, AC electroluminescent devices, energy storage capacitor films, triboelectric nanogenerators, lithium batteries, among others. Based on these recent studies, fluorinated polymers have shown great potential in these emerging applications due to their unique ion-dipole interaction, dielectric properties, physical and chemical stability, and compatibility with various fabrication teniques.

However, before these applications can be fully implemented, there are still challenges that need to be addressed. Traditional fluorinated polymers such as PVDF and PVDF-HFP, which are widely used in industries, often struggle to meet these demands. Although new types of fluorinated polymers based on fluorinated acrylate or methacrylate monomers can partially overcome these issues, these side-chain fluorinated polymers lose the beneficial fluorine atoms attached directly to the main chain, potentially leading to decreased physical and chemical stability and easy detachment of the fluorinated chain segments, which could affect the lifetime of devices.

Hence, it is suggested that future studies in this domain concentrate on selectively modifying conventional fluorinated olefin polymers using chemical approaches and exploring new polymerization techniques to produce innovative fluorinated homopolymers or copolymers. These materials are anticipated to surpass current limitations and exhibit exceptional processability, self-healing properties, sufficient mechanical strength, and high stretchability. Developing such novel fluorinated polymers will lay the groundwork for enhancing the performance and broadening the range of potential applications for fluorinated polymers. In addition, the development of large-scale production processes for new fluorinated polymers based on recently developed polymerization methods also deserves more attention. This aims to obtain commercially available fluorinated polymeric materials with low cost and stable quality for successful industrial implementation. In addition, the applications mentioned in this review are emerging, but there is still a considerable gap in achieving full industrialization. Therefore, in future studies, the availability of fluorinated polymers should be discussed from an industrial point of view.

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Conflict of interest The authors declare no conflict of interest.

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