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Tailoring Fluorinated Electroactive Polymers Toward Specific Applications

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Abstract

Fluorinated Electroactive Polymers (FEPs) are emerging as one of the most prominent classes of insulating materials found in organic electronic devices. Despite their broad application, those materials have fixed electronic properties that are difficult to be tuned in order to achieve optimal performance in different applications. This mini-review highlights the need for tailoring the electronic properties of FEPs and explores the different approaches our group has proposed as solutions to such problem. Those include strategies to obtain stable dielectric properties and thus stable OFET performance over a broad range of temperature, as well as strategies to make FEPs directly compatible with photolithography, which is the most widely used fabrication technique by the semiconductor industry. Last, a general strategy to introduce different functional groups on FEPs is presented, allowing the introduction of altogether new properties to those polymers.

Keywords

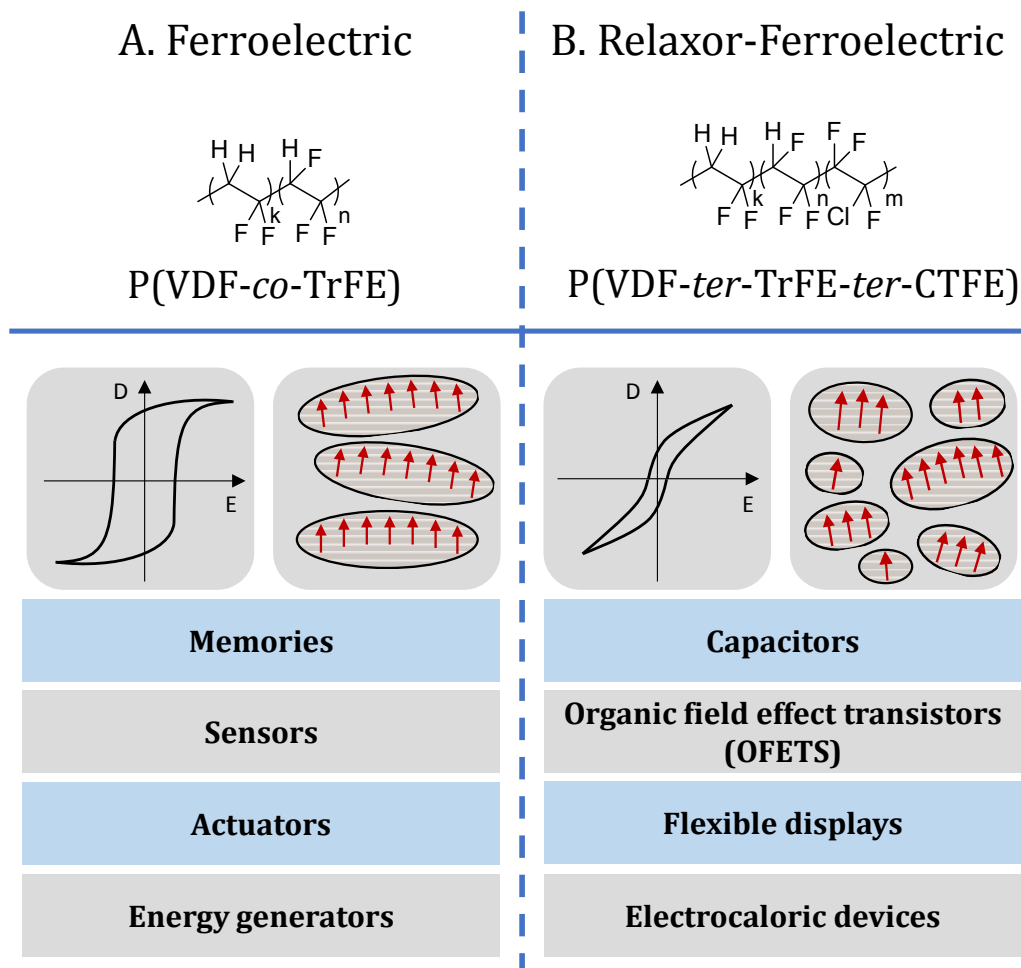Fluorinated Electroactive Polymers, Dielectric, Ferroelectric, Relaxor-ferroelectric, Photolithography, OFET

Introduction

With electronic devices playing an increasingly important role in our everyday lives, organic electronics have the potential to be one of the cornerstone technologies that can make those devices available to more and more people while waiving many of the constraints imposed by silicon. Those include the lack of flexibility, stretchability and conformability, combined with high production costs [1]. One class of polymeric materials which find different applications in organic electronics, is that of Fluorinated Electroactive Polymers (FEPs), most commonly encountered as poly(vinylidene fluoride) (PVDF) and its copolymers. Those materials are electric insulators at core but can have many other very interesting properties such as ferroelectricity [2], piezoelectricity [3], pyroelectricity [4] combined with exceptional mechanical and thermal stability. From an application standpoint, FEPs are encountered in some of the highest-end fingerprint sensors on the market. Their application though is not limited to that, as they are encountered in a plethora of devices that have not yet reached the

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mainstream markets including capacitors, memories [5,6], sensors [7,8], actuators [8,9], organic field effect transistors (OFETs) [10] and electrocaloric cooling devices [11,12] amongst many others.

While the fundamental properties of FEPs (e.g. piezoelectricity, high dielectric constant, mechanical durability, chemical stability) play a vital role across the whole range of applications in electronics, each application requires a slightly different combination of properties or even altogether new properties that do not exist in the original fluoropolymers in order ensure optimal device performance. This very need motivated the work of our group in the field, which is summarized in this mini-review.

The electronic properties of FEPs derive from the difference in electronegativity between the carbon and the fluorine atoms which leads to the formation of permanent electric dipoles along their polymer chains. Since those polymers are often semicrystalline in nature, the dipoles can organize in domains of different sizes [13]. Polymers whose dipoles organize in large domains are called ferroelectrics, with the most prominent and best studied example of this group being the copolymer P(VDF-*co*-TrFE) which is a statistical copolymer of vinylidene fluoride and trifluoroethylene (Figure 1A). The exceptional ferroelectric properties of those polymers derive from the addition of the trifluoroethylene (TrFE) group [3], which forces the polymer to crystallize in the most polar orientation (all-trans) [14]. In the case where the dipoles of the polymer organize in smaller nano-sized domains in the crystalline matrix, the polymer is called a relaxor-ferroelectric. Relaxor-ferroelectrics, with main representative of this group being the P(VDF-*ter*-TrFE-*ter*-CTFE) [15], which is a statistical terpolymer of vinylidene fluoride, trifluoroethylene and chlorotrifluoroethylene (Figure 1B), are materials of very high dielectric constant (good insulators of electricity). An overview of the most common ferroelectric and relaxor-ferroelectric polymers, their electroactive behavior as well as some of their key applications in electronics is presented in Figure 1.

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A. Ferroelectric

P(VDF-*co*-TrFE)

B. Relaxor-Ferroelectric

P(VDF-*ter*-TrFE-*ter*-CTFE)

A. Ferroelectric	B. Relaxor-Ferroelectric
Memories	**Capacitors**
Sensors	**Organic field effect transistors (OFETS)**
Actuators	**Flexible displays**
Energy generators	**Electrocaloric devices**

Figure 1. Schematic representation of (A) ferroelectrics and (B) relaxor-ferroelectrics demonstrating the differences in domain size, ferroelectric character and application in electronics.

Stabilizing the dielectric performance at different temperatures

Since the scope of application of those polymers is so broad, the need emerges for tailoring the properties of FEPs to specific applications, beyond the crude distinction between ferroelectrics and relaxor-ferroelectrics [16]. One illustration of this, is relaxor-ferroelectric polymers which can be used either in temperature sensors or organic field effect transistors acting as pixel drivers on flexible displays. The two applications require opposingly different temperature dependence of the dielectric constant, as temperature sensors take advantage of the change of electronic properties as a function of temperature in order to produce different signals, while pixel drivers have to ensure similar performance across a broad temperature range. Therefore, while in the case of sensors, the resolution increases by increasing the temperature variation of the dielectric constant, high variation would make a flexible display unusable as it would only be able to operate in a very narrow temperature window. To tackle the latter problem, our group has developed an approach where blending P(VDF-*co*-TrFE) and P(VDF-*ter*-TrFE-*ter*-CTFE) leads to almost no variability of dielectric properties over a wide range of temperature [17]. Similar blending approaches have been previously employed for the enhancement of various properties of FEPs, such as ferroelectricity [18], breakdown strength [19], energy density [20] or even electrocaloric cooling potential [21]. This fluoropolymer blend was then used as gate dielectric in OFETs, leading to stable operation over a large temperature range (20°C-80°C) as described in Figure 2. The temperature dependence of the dielectric properties before and after blending is

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presented in Figure 2a, b, while the temperature dependence of transistor operation before and after blending is presented in Figure 2e, f respectively.
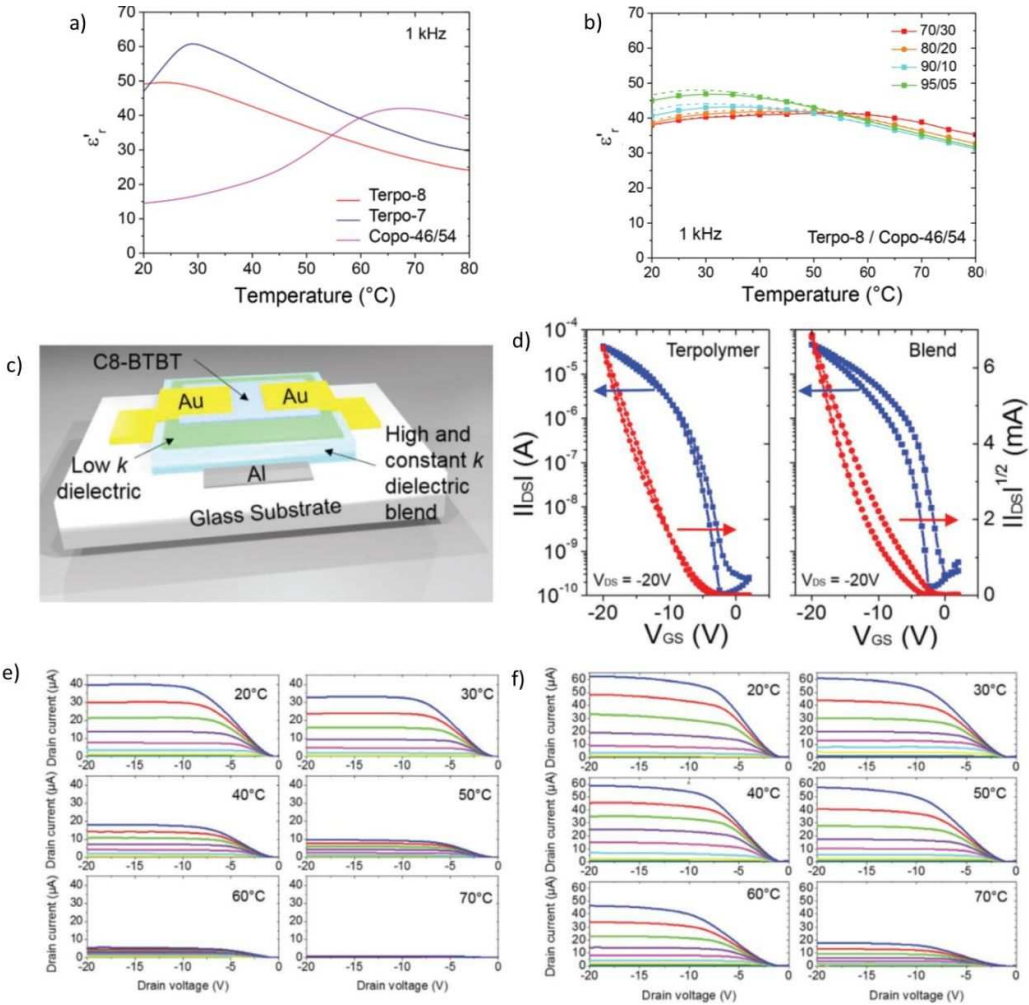

Figure 2. a), b) Dielectric spectroscopy at 1kHz of a) P(VDF-co-TrFE) copolymer compared to P(VDF-ter-TrFE-ter-CTFE) terpolymers b) comparison of terpolymer copolymer blends. c) Schematic representation of OFET architecture. d) Transfer characteristics in saturation regime (VDS = −20 V) of OFET with either) terpolymer or terpolymer-copolymer blend as gate dielectric layer. e) output characteristics at different operating temperature of OFETs with terpolymer and f) with the blend system showing improved thermal stability. Reproduced with permission from [17]. Copyright (2020)

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Making FEPs directly compatible with photolithography

Another factor limiting the realization potential of FEPs is their limited compatibility with photolithography, which is the method of choice for the fabrication of electronics by the semiconductor industry. This process is based on the premise that once a material which is called a photoresist gets exposed to UV light, its solubility to a certain solvent system will change. That way, selective exposure to UV light allows for the transferring of a pattern, from a so called "photolithographic mask" to a polymeric layer. However, since FEPs do not possess these "photoresist" like properties, their integration in a photolithographic process requires a rather lengthy six step approach as described in the upper part of Scheme 1. That involves the deposition of an additional photoresist layer on top of the FEP, which allows for the pattern to be transferred initially on the photoresist layer and finally on the FEP. However, if one material could combine the desired electronic and the photoresist properties [22,23], the required number of steps for such process could be reduced in half as described in the lower part of Scheme 1. That would lead to a drastic cost reduction of electronics utilizing such materials.
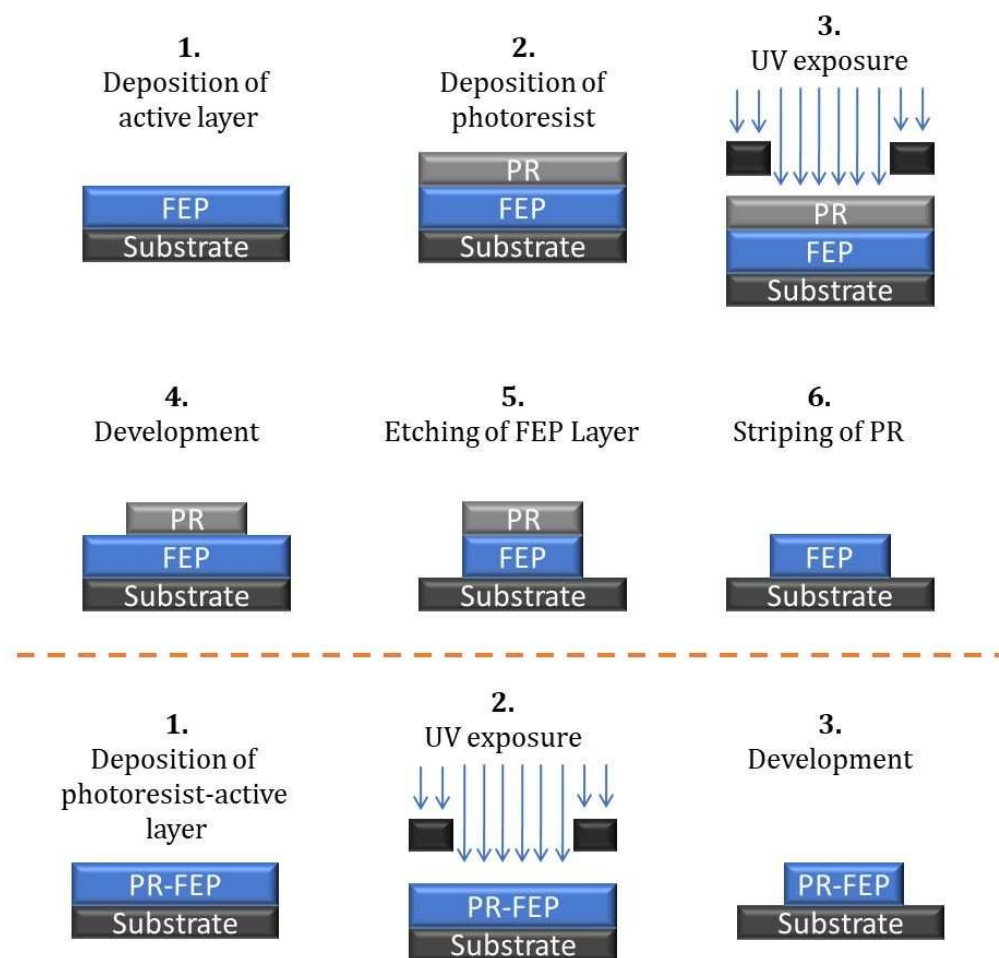

Scheme 1. Six-step photolithographic patterning protocol of a FEP using a commercial photoresist (top) and three-step photolithographic patterning protocol of a FEP-photoresist material (bottom).

Photo-patternable FEPs: The Azido Approach

The dominant approach reported in literature that manages to combine the electroactive and photoresist properties involves the addition of a bis-azide photoinitiator to a solution of the polymer. That way, photopatternability was induced to the resulting films, making them cross-linkable upon exposure to UV light [24,25]. Despite the success of this approach, the high costs associated with the used azides drastically limited its potential for the production of electronics at scale. For that reason, an attempt was made by our group to directly graft the photosensitive azido group on the fluoropolymer backbone [26]. That was achieved by simply treating the P(VDF-*ter*-TrFE-*ter*-CTFE) terpolymer with sodium azide and thus substituting the chlorine groups of the -CTFE termonomer with the azido groups as described in Scheme 2.
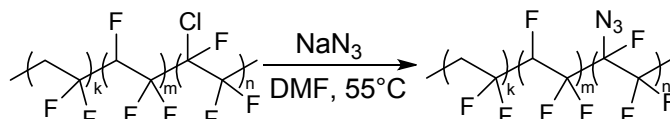
Scheme 2. Grafting Reaction of the azido group on the P(VDF-ter-TrFE-ter-CTFE) Terpolymer. Reproduced with permission from [26] . Copyright (2020)

The resulting polymers were integrated in a photolithographic process, where after carefully tuning of a variety of parameters excellent quality patterned films were obtained (Figure 3) at a UV dose below 2 J/cm^2, while exhibiting very low surface roughness (Figure 3b), which is especially important for applications such as OFETs. The cross-linked films maintained a high dielectric constant (k=21 at RT, 1 kHz), which was nevertheless slightly reduced compared to the dielectric constant of the pristine terpolymer (k= 34 at RT, 1 kHz).
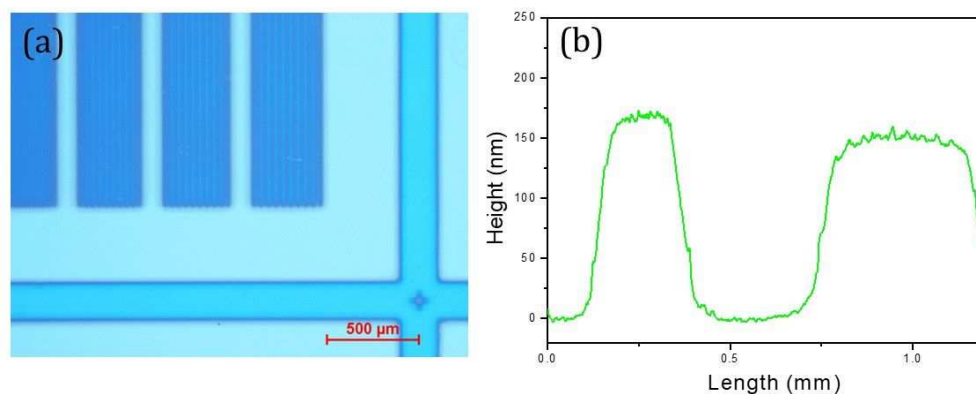

Figure 3. (a) Azido-grafted P(VDF-ter-TrFE-ter-CTFE) on silicon substrate patterned through a single photolithographic step. (b) Measurement of the film roughness using mechanical profilometer. Reproduced with permission from [21]. Copyright (2020)

Williamson Etherification: A General Approach

Although the azidation method mentioned above was successful in introducing photosensitive groups on the fluoropolymer backbone, some drawbacks inherent in this approach limit its potential. First, this method is specific in introducing azido groups on the fluoropolymer and allows for no flexibility in terms of the grafted group. Therefore, properties such as UV absorption, stability and others cannot effectively be tuned. Second, the azidation and the subsequent cross-linking appear to have a slightly negative impact on the electroactive

properties. We therefore started exploring alternatives that could allow for some more freedom when it comes to the grafted group, while solving the issues created by the previous approach.

In that quest, we began looking for a much more general methodology that could allow us to graft photosensitive groups, as well as any other kind of functional groups on the fluoropolymer's backbone. In order to create such approach, the property of the -CTFE repeating unit to give products of substitution reactions was again leveraged. The difference though was that this time, the nucleophile was a deprotonated phenol which could in turn bear different kinds of functional groups on its phenolic ring. This general reaction is presented in Scheme 3, where the phenol is first deprotonated in the presence of a base and then filtered and added into a solution of the fluoropolymer giving the substitution product.
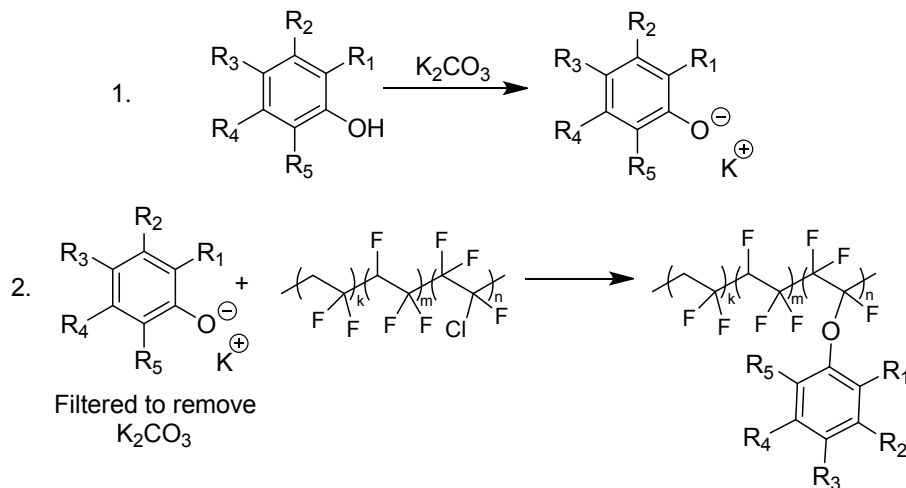

Scheme 3. Two step etherification reaction of functionalized phenols on P(VDF-ter-TrFE-ter-CTFE). First the phenol is deprotonated with the use of a base and subsequently filtered in a solution of the polymer, where the substitution and thus the grafting occur. Reproduced with permission from [27]. Copyright (2020)

Two different photoinitiator derivatives were grafted on the fluoropolymer's backbone using this methodology. Both molecules, shown in Scheme 4 are similar to the azido groups in the sense that they create free radicals upon UV exposure and those free radicals can react with a plethora of moieties including -C-H, -C-F, -C-C- etc. and thus effectively cross-link the polymers.
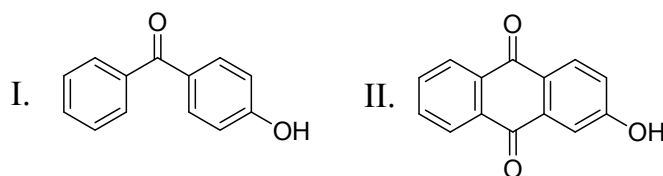
Scheme 4. Chemical structures of 4-hydroxy benzophenone (I) and 2-hydroxy anthraquinone (II). Reproduced with permission from [27]. Copyright (2020)

The two groups were different though in the way those free radicals were created. Both benzophenone and anthraquinone groups, when exposed to UV light reversibly create free radicals (Scheme 5B, C). On the other hand, the azido groups create free radicals in a non-reversible manner by expelling nitrogen (Scheme 5A). Therefore, polymers bearing either benzophenone or anthraquinone groups enjoy far superior stability than their azido containing counterparts.
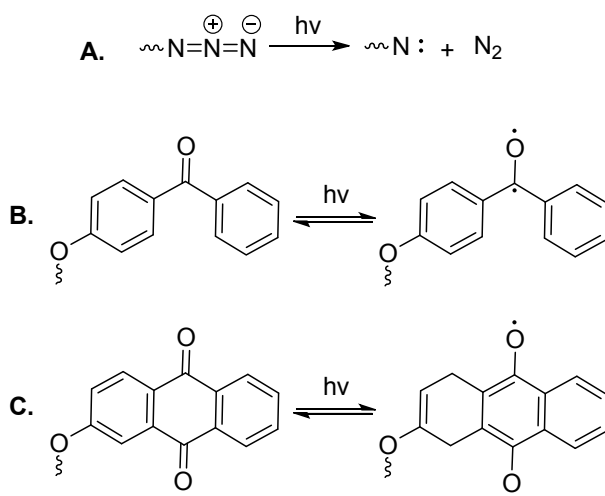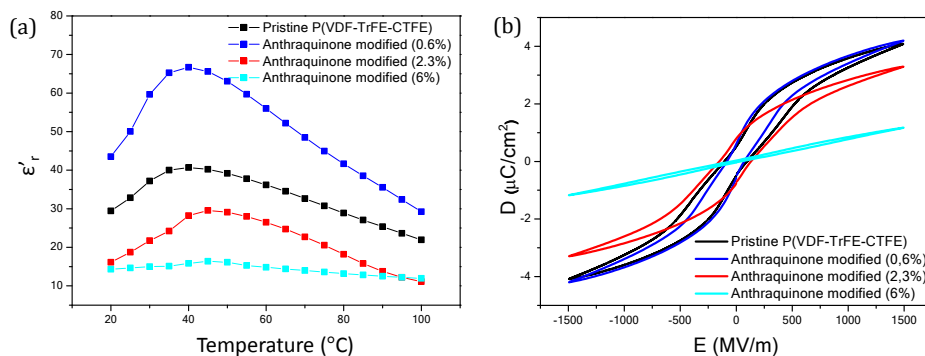
Scheme 5. Free radical creation upon exposure to UV light for polymers containing azido groups (A) as well as benzophenone (B) and anthraquinone (C) moieties.

Another drawback of the azido approach was the deterioration of both ferroelectric and dielectric properties as mentioned previously. Contrarily to that, some of the FEPs grafted with those new photoinitiators showed an improvement both in dielectric and ferroelectric properties. Namely, when the grafted content was very low, both dielectric (Figure 4a) and ferroelectric (Figure 4b) properties were enhanced, while higher photoinitiator contents led to a deterioration of properties as shown in Figure 4. This augmentation of electroactive performance at low photoinitiator contents is mainly due to the introduction of double bonds on the polymer backbone as a side product of the functionalization reaction. Their impact on the electroactive properties has been shown to be pretty drastic with as much as 60% permittivity enhancement being achieved by double bonds alone [12].

Figure 4. (a) Real part of the relative permittivity (1kHz) as a function of temperature for P(VDF-ter-TrFE-ter-CTFE) functionalized with different contents of anthraquinone. (b) Ferroelectric testing at room temperature of P(VDF-ter-TrFE-ter-CTFE) functionalized with different contents of anthraquinone. Reproduced with permission from [27]. Copyright (2020)

Therefore, a general method to graft almost any functional group and thus induce a variety of different functionalities on FEPs was provided by this approach. At the same time by fine-tuning the photoinitiator grafted content, the electroactive properties can not only be retained but even enhanced compared to the pristine polymers.

Conclusions and perspectives

To sum up, this mini-review highlights the need for tailoring the properties of Fluorinated Electroactive polymers depending on the targeted application. That includes the effect of temperature on the dielectric performance as well as the introduction of altogether new properties on FEPs such as photo-patternability. Stable operation in a broad temperature range was achieved by a simple blending approach, leading to almost no variation of dielectric performance in a temperature range from 20°C to 70°C. On the other hand, two different grafting approaches were presented for the introduction of photo-patternability. First, an approach involving the grafting of azido groups was explored, which made the polymers photo-patternable. Then, a much more general grafting approach was developed, involving an etherification reaction and allowing for the grafting of a plethora of functional groups. Thus, not only photo-patternability was induced in FEPs, but at the same time, enhancement of their electroactive performance was made possible. Interestingly, the latter approach is not limited to the grafting of photo-sensitive groups on FEPs but it can also be used as a general tool to graft a plethora of functional groups in order to tailor the final properties of FEPs to specific applications.

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Author contributions

All authors have given approval to the final version of the manuscript.

Aknowledgements

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