PVDF-based dielectric polymers and their applications in electronic materials

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Abstract: The attractive dielectric poly(vinylidene fluoride) (PVDF) and its copolymers are well confirmed possessing the highest electroactive response including dielectric constant, piezoelectric and ferroelectric effects, which have increasingly wide range of applications such as in energy transfer, energy generation and storage, monitoring and control, and include the development of capacitors, sensors, actuators and so on. In this study, by clarifying the reliability of dielectric performances on their crystal phase structure of various PVDF polymers, the different physical and chemical fabricating ways to achieve different forms of PVDF samples such as linear polymers, ferroelectrics, and relaxor ferroelectrics were identified and quantified. In addition, many recent advances in the PVDF-based polymer dielectrics and some developed applications of these polymers are presented, which gives a reference in academic and engineering area to select an appropriate PVDF series dielectric polymer.

1 Introduction

Conventionally, the systematic investigation of fluorinated polymers started with the invention of poly(tetrafluoroethylene) (PTFE) by Roy Plunkett in DuPont Co. by 1930s [1–3]. From then on, fluoropolymers have received considerable attention in polymer engineering area for various states such as thermoplastics, elastomers, plastomers, and thermoplastic elastomers. Nowadays, these plastics are produced by several companies in the United States, Europe, Japan, China, India, and Russia [2, 3].

It is commonly believed that the F atom possesses the low polarisability and the strongest electronegativity, it can bond to C atom and form the strong C–F bond (485 kJ/mol) and thereby displays a unique combination of relevant properties [4]. For the strong covalent bond, fluoropolymers exhibit unique mechanical, chemical, and electrical characters including excellent inertness to solvents, to hydrocarbons, to acids, and to alkalis, high thermal, chemical, aging, and weather resistance, relative high dielectric constants and so on [5, 6]. According to the number of substituents of C–F bond on the olefin series polymers, the fluoropolymers are divided into two classes, including perfluorinated and partially fluorinated polymers, as shown in Fig. 1 [7]. The most famous PTFE is perfluorinated polymers which have been used all over the world. Comparatively, poly(vinylidene fluoride) (PVDF) belongs to partially fluorinated fluoropolymer containing hydrogen (H) or other atoms (e.g. chlorine) in addition to fluorine and carbon. Recently, partially fluorinated fluoropolymers gained increased application prospect in various engineering aspects [8, 9].

Among the various fluoropolymers, PVDF is the research focus which can provide special electrical properties and has highly valuable applications in electronics and electrical devices as insulation, sensors, energy harvesting devices, actuators, and front-end processor (FEP) in data communications [7]. In this paper, we mainly discuss the dependence of electrical properties of PVDF-based fluoropolymers on its condensed state structures. By introducing the dielectric response mechanisms of dielectric polymer, the PVDF-based dielectrics would be proposed involving the molecular chains, crystalline properties, and conformations PVDF-based homopolymers. Together with related thermal processing, the different sorts of PVDF-based homopolymers including relaxor ferroelectrics, normal ferroelectric and linear dielectrics are clarified. Moreover, the prospects of their application in various devices prospect. Our goal is to provide a reference of how to fabricate PVDF-based dielectrics and develop their potential applications in electronics and electrical engineering areas [10, 11].

2 PVDF homopolymer dielectrics

2.1 Principles of dielectric response in PVDF-based homopolymers

PVDF-based homopolymers are the famous dielectric materials and also called dielectric macromolecules, consisting of a long molecular skeleton constructed by monomers vinylidene fluoride (VDF). Generally, the backbone of PVDF polymers is predominantly carbon atoms substituted with H and F alternatively [12, 13]. Therefore, the dielectric properties of PVDF polymers depend on not only their backbones but also the pendant functional groups C–F. Similar to the other solid dielectrics, PVDF-based dielectric polymers have five different polarisations, originating from the dielectric response of electrons, atoms, ions, dipoles, and space charges or interfaces. As shown in Fig. 2 [15], electronic polarisation is due to the opposite displacement of positive nuclear and negative electrons within the same atoms C, F, and H, which can response with the ultra-high frequency of 1016 Hz. Atomic
Dielectric properties of PVDF-based homopolymers

2.2 Dielectric properties of PVDF-based homopolymers

2.2.1 Synthesis of PVDF: The first report of synthesis of PVDF from VDF monomer could be traced to 1948 by Ford T. A. in the USA [17]. Later, the patent was assigned to Dupont Co. which proposed that VDF monomer was polymerised by using a peroxide initiator in water at 50–150°C and 30 MPa. From that on, a number of methods including emulsion, suspension, solution, and bulk were presented to produce the functional PVDF from the VDF with ethylene and halogenated ethylene monomers [18]. As the polymerisation technical was completely improved, the commercial PVDF was appeared in engineering area in 1960 [19]. The main manufacturing process of PVDF was by emulsion polymerisation or suspension processes from VDF assisted with a stable fluorinated surfactant and an initiator such as peroxide or persulfate. In the circumstance of ranges from 10 to 150°C at the pressure of 1 MPa or higher, and in the presence of an appropriate dispersant such as hydroxyl cellulose, the PVDF products could be obtained in solvents initiated by free-radical initiators [20].

Nowadays, commercial PVDF resins have been fabricated into a wide range of shapes including pipes, pump assemblies, sheets, films, tanks, membranes, foams, tubes and so on. PVDF films with a thickness range from 1 to 175 μm depending on its various application areas. For example, the PVDF film with the thickness of 20 μm has been well used in electronic apparatus.

2.2.2 Crystal phases of PVDF: PVDF is a semi-crystalline partially fluorinated fluoropolymers whose crystallinity is ranging from 35 to 70% depending on the polymerisation method and polymer fabrication process [21]. Besides, the –CF2– and –CH3– has a head (–CF2–) to tail (–CH3) addition dominates configuration (–CF2–CH2–CF2–CH2–) along with various molecular weight, molecular weight distribution, the amount of chain irregularity, side chains, and crystalline regime. Moreover, occasional reversed head-to-head or tail-to-tail additions may result in defects depending on the polymerisation conditions, particularly temperature [22]. With an aid of 1H NMR (nuclear magnetic resonance) and other techniques such as atomic force microscope (AFM) and Fourier transform infrared spectroscopy (FTIR), the number of defects could be expressed. As shown in Fig. 3, the main peaks at 2.9 and 2.4 ppm refer to the head-to-tail (–CF2–CH2–CF2–) and head-to-head (–CF2–CH2–CH2–CF2–), respectively. Generally, PVDF obtaining from emulsion polymerisation produces more likely result in head-to-head defects, which does not follow by a tail-to-tail configuration in suspension polymerisation [24, 25].

Besides the defects in the normal configuration in PVDF, it has several polymorphs, including four known chain conformations and a fifth suggested one. Commercial PVDF block or thick films possess a mixture phase including four types of crystal phases in its crystalline region [4, 14, 17, 26]. The most common crystalline phase is α (density of 1.92 g/cm3). The α phase of PVDF occurs in a trans-gauche-trans-gauche (TGTG) configuration. This formation is not a helical or a planar zigzag but their combination. Either a series of G or TG would represent a purely helical structure [27, 28]. It is formed both during polymerisation and during cooling of the molten polymer. The α phase has a pack in a unit cell with a = 4.96 Å, b = 9.64 Å, c = 4.62 Å, and all angles 90°. In this crystal confirmation, one-unit cell shows no polarity since the alternate chains are packed with their dipole components normal to c in an anti-parallel fashion although each TGTG segment possesses a net dipole moment. Comparatively, the β phase is the most attraction conformation possessing the largest polarity, in which the molecules are in an all-trans conformation (or a statistically distorted version thereof) and are packed in an orthorhombic unit cell with a = 8.58 Å, b = 4.91 Å, and c = 2.56 Å. The β crystal phase of PVDF forms a planar zigzag, or TT, where T represents a trans bond that remains in the same plane as the carbon backbone [27]. The β crystalline form has a density of 1.97 g/cm3 and is less favoured than α form, and it is obtained when PVDF is mechanically deformed, e.g. stretched, near its melting point. It has an all-trans chain conformation, positioning the fluorine atoms on one side and hydrogen atoms on the other side of the chain.

The third kind of phase of PVDF is called γ phase, which shows the same a (b) cell base with a phase. However, the repeated length of the c-axis is twice of the a phase. Moreover, the γ phase shows a medium polarity for a conformation of T3G7T′G′. The γ crystals are less usual and are obtained from ultra-high molecular weight PVDF [29, 30]. The fourth phase δ is not well expressed which is generated by the distortion of one of the other crystalline forms.
Amorphous PVDF has a theoretical density of 1.68 g/cm³, suggesting that a typical part with a density of 1.75–1.78 has a crystallinity of 40% [32, 33]. PVDF is soluble in polar solvents such as esters, acetonitrile, N,N-dimethylformamide and some organic solvents. PVDF has a high dielectric constant of 10–15 and a low dielectric loss of 0.02–0.05 at frequencies of 1 MHz [8]. PVDF has a dielectric constant of about 10 at frequencies of 1 MHz and a dielectric loss of about 0.04 at frequencies of 1 MHz. PVDF has a high dielectric constant, high dielectric strength, good dielectric stability, high breakdown strength, high dielectric loss, and a high energy density of 200 J/cm³. PVDF has a high dielectric constant, high dielectric strength, high dielectric loss, high energy density, good thermal stability, high stability to ultraviolet and higher energy radiation, and good chemical resistance to most chemicals and solvents. It is not hygroscopic and absorbs <0.05% of water at room temperature. The properties of PVDF homopolymers and copolymers are dependent on the chemical composition of the polymer, molecular weight, and molecular architecture [41]. Some of the important properties of PVDF homopolymers and copolymers are a function of the crystalline content and type of crystalline structure, both of which are affected by the processing methods and conditions [9], which has been illustrated in Fig. 4. The most attractive characters of PVDF and its polymers are their unique dielectric performances under various electrical fields. Commonly, the researchers concerned the electrical properties of PVDF including two aspects, i.e. large piezoelectric applying in the electrical-mechanical transforming device and high energy density using high-pulse capacitors.

To clear understanding the dependence of crystal phase on their dielectric, ferroelectric, and energy storage properties, the dielectric response of three phases PVDF of α, β, and γ as a function of frequency is presented in Fig. 6 [42]. The dielectric permittivity of three films is reduced as the frequency increases, and α-PVDF possesses a higher permittivity than β- and γ-PVDF. Besides dielectric constant, α-PVDF also shows a larger dielectric loss than β-PVDF and γ-PVDF at low frequency (ranging from 100 Hz to 1 kHz). When the testing frequency is increased to 1 kHz, β-PVDF has a large dielectric loss. At above 1 MHz, the dielectric loss of α-PVDF and γ-PVDF increases apparently because of the dielectric relaxation. Otherwise, the dielectric loss of β-PVDF is relatively low for β relaxation and molecular motion in the interface between the crystal region and amorphous region. Consequently, dielectric properties of PVDF are mostly related to their crystal structures which influence the polarity, the proportion of polar region, and the freedom of molecular chains in the polar region.

The dielectric response under low electric field could not reflect the overall polarisation mechanism of PVDF because the dipole movement under high electric field is the critical factors to determine the dielectric performance. Thus, we provide the displacement versus electrical field loops (D–E loops) of PVDF
with various crystal phases which are used to illustrate their potential applications in electrical engineering and electronic devices clearly. Fig. 7 compares the bipolar D–E loops of PVDF with three different crystal phases of α, β, and γ under the alternating current at 10 Hz. Under the electric field of 150 MV/m, β-PVDF shows a typical character of normal ferroelectric with a high remnant polarisation in the rectangle shaped D–E loop for its all-trans conformation. In contrast, the D–E loops of α- and γ-PVDF are quite close, and they have a smaller remnant polarisation under the high electric field of 200 MV/m. Moreover, the remnant polarisation of γ-PVDF is slightly higher than that of α-PVDF, which may be attributed to the T2G conformation of γ-PVDF possesses relative higher polarity than that of TGTG in α-PVDF. Meanwhile, for the high polarity of TTTT (or GGGG) conformation, β-PVDF has the larger maximum displacement than α- and γ-PVDF under the same electric field [34, 42].

Through the comparison of the dielectric properties under low and high electric fields of different PVDF, the researchers found that these polymers can meet the various applications. For example, α- and γ-PVDF with high dielectric constant may be used as the energy storage related areas where the large remnant polarisation is not welcome. In contrast, β-PVDF agrees fairly well with the demands of the piezoelectric device where the remnant polarisation rather than the high dielectric constant is the most concerns.

Currently, PVDF series ferroelectric and piezoelectric materials have been well developed in energy transformation apparatus including crystal oscillators, transducers in telephone speakers, headphones, sonar arrays, mechanical actuators and so on. If the extra pressure is applied to a well polarised β-PVDF film under appropriate circumstances, a voltage can be generated. The signal including the information of the pressure could be caught and processed. Indeed, the early piezoelectric transducers were developed at the beginning of the 20th century, notably by Langevin, and immediately found application in detecting the sound waves emanating from submerged submarines. It was believed that the piezoelectricity in β-PVDF is usually explained in terms of ‘a dipole model’. As a semi-crystalline polymer, the crystalline phase in β-PVDF compose of two major contributions of antiparallel chain and parallel chains where the dipoles align. Under a service electric field, the polymer chains align themselves in the field by rotating the dipoles around the axis. The net polarisation occurred is responsible for the piezoelectric effect in PVDF [44].

As discussed in Fig. 4, the pure PVDF with various crystal phases are obtained from different physical fabricating methods. However, the most attractive scenery is that PVDF polymers have been copolymerised with other monomers including chlorotrifluoroethylene (CTFE), hexafluoropropylene (HFP), trifluoroethylene (TrFE), tetrafluoroethylene (TFE) and so on. The introducing these units to PVDF chains will not only change the configuration but also modify the condensed state structures of these fluoropolymers. As shown in Fig. 8 [45], in the crystal phase of PVDF, the interchain distance is defined as \( l_1 \). When comonomer TrFE is introduced, the interchain distance in PVDF is pre-expanded by the large functional group \( l_2 > l_1 \), where \( l_2 \) is the interchain distances in (PVDF-TrFE) crystals. Subsequently, the larger third comonomers such as chlorotrifluoroethylene (CFE) and CTFE can be incorporated into the isomorphic crystalline structure. For a (PVDF-TrFE-X) terpolymer \((X = CFE \text{ or } CTFE)\), the interchain distance of PVDF-TrFE crystals is further expanded by the comonomer \( X \), namely, \( l_3 \) or \( l_4 > l_2 \), where \( l_3 \) and \( l_4 \) are the interchain distances in the (PVDF-TrFE-X) terpolymer crystals \((l_3 \text{ for } CFE \text{ and } l_4 \text{ for } CTFE)\). Due to the expansion of interchain distance and pinning from the larger third comonomers (shown in Fig. 8), the α-crystal phase of PVDF may convert into β or γ phase, which will further affect the dielectric properties of these fluoropolymers. In the following section, we will express the rations of condensed state structure and dielectric performance of different fabricated PVDF co-(αr)-polymers.

3 PVDF homopolymer dielectrics and their applications

3.1 Linear polymers

A linear dielectric polymer is a special material whose polarisation expresses a linear relationship with the electric field. In linear polymers, the dielectric constant is invariably with the change of field, frequency, and even temperature [46–54]. Linear dielectrics with low energy loss are playing dominant roles in the modern electric power system for their significant advantages, such as the low energy loss, high breakdown strength, high impedance, a wide operating temperature range and low cost. Currently, biaxially-oriented polypropylene (BOPP) is believed still one of the few available polymers in capacitors [55]. Nevertheless, more and more scientists were not satisfied with the relatively small dielectric constant (~2.2) and low discharging energy density of BOPP. Spontaneously, PVDF-based dielectrics have attracted considerable attention for their relatively larger dielectric constant (~12) than that of BOPP. Moreover, PVDF-based dielectrics possess high electric breakdown electric field (500 MV/m). Therefore, these homopolymers are expected to be the best choice of capacitors coordinate materials with high dielectric response coupled with electric field independent properties [56]. However, because of the strong C–F bond, most of the PVDF-based homopolymers show the characters of the non-linear dielectric constant with the frequency or temperature unless it is completely fabricated. Recently, it was found, at ambient temperature, a poly(tetrafluoroethylene–hexafluoropropylene) (P(TFE–HFP)) films, thin films showed linear dielectric behaviour as BOPP by hot-pressing followed by uniaxially stretching [57]. The insertion of hexafluoropropylene (HFP) monomer causes a decrease in \( T_m \) so that P(TFE–HFP) may melt at high temperatures and is easily processed. As shown in Fig. 9, the relatively low content of HFP monomer helps maintain the majority of the crystalline phase in P(TFE–HFP) with a relatively high degree of crystallinity of 61.6%. That is estimated from the differential scanning calorimetry (DSC) results by the equation \( \gamma = \Delta H_f/\Delta H_{f_p} \), where \( \Delta H_f \) and \( \Delta H_{f_p} \) refer to the enthalpy for fusion of P(TFE–HFP) and PTFE with 100% crystallinity, respectively.

After a high electric field of 750 MV/m applying on the P(TFE– HFP) film, the discharge energy density of the sample increased to

**Fig. 7** D–E loops of PVDF with different crystalline phase

A Comparing of D–E loops of α-, β- and γ-PVDF [34, 42, 43]

**Fig. 8** Schematic representation of weak versus strong physical pinning in the crystal of PVDF based co-(αr)-polymers [45]
achieved in BOPP at 650 MV/m. As shown in Fig. 10, both of PSAN, can be improved accordingly. Recently, there have many kinds of literature related to the fabricating methods and the potential applications of PSAN in energy storage areas [48, 62–66].

P(TFE–HFP) and BOPP show relatively low energy loss or high discharge efficiency. And yet similar to most of the piezoelectric properties of this kind of copolymers, and some application examples on sensors, actuators, and energy harvesting devices and so on were presented accordingly.

### 3.2 PVDF-based ferroelectric polymers

The pvdf-based polymer has not been well developed to the application in energy storage because their high dielectric loss both in low and high electric fields. Otherwise, since it was noted by Fukada and Takashita [72], PVDF-based homopolymers were given considerable attention as a normal ferroelectrics for their favourable piezoelectricity ($\beta$-PVDF is well confirmed possessing a high piezoelectric value ($d_{31}$ and $d_{33} = -20$ pC/N)) and large electromechanical coupling effect (0.30). Currently, some commercial $\beta$-PVDF films produced by Daikin Co. (Japan), Piezotech Co. (France) and MEAS Co. (USA) and so on, have been used as the sensors to measure the abrupt vibration, ultrasound, and some circumstances including acceleration and pressure measurements [73].

In Section 3.2, the physical fabricating methods and crystal properties of $\beta$-PVDF have been well depicted. Here we will introduce some chemical grafting ways to improve the ferroelectric and piezoelectric properties of this kind of polymers, and some application examples on sensors, actuators, and energy harvesting devices and so on were presented accordingly.

### 3.2.1 Fabrication of PVDF-based ferroelectric polymers: Copolymerised P(VDF-TrFE):

Several years after the discovery of the piezoelectric property of $\beta$-PVDF, Ohigashi group introduced a certain proportion of new monomers such as TrFE into PVDF molecular chains for fabricating the TTTT conformation [74–76]. Without mechanical stretching, the target P(VDF-TrFE) possesses a high crystallinity and the spontaneous $\beta$ phase with TrFE content ranging from 20 to 50 mol% [77–80]. When TrFE monomer content is reduced to below 20 mol%, P(VDF-TrFE) shows mixed phases of $\alpha$, $\beta$, and $\gamma$ [78]. As a normal ferroelectrics, $\beta$ phase P(VDF-TrFE)s have a special phase transition point, i.e. Curie temperature ($T_c$), and the value of $T_c$ is mostly depending on the TrFE molar content besides the processing conditions of the sample. Above $T_c$, ferroelectric P(VDF-TrFE) is converted into paraelectric phase showing no more ferroelectric characters. Therefore, $T_c$ is the very determined factor to the operating temperature range of the copolymers, and the research on ferroelectric properties is mainly focusing on the samples below $T_c$.

As early as 1990, Koga et al. [80] described $T_c$ and phase transition processes of various P(VDF-TrFE)s and found that these copolymers with TrFE from 20 to 65 mol% have $T_c$ ranging from about 37 to 90°C. The condition dependence of ferroelectric phase in various TrFE molar contents the P(VDF-TrFE) is presented in Fig. 11 as well. Even so, after a high electric polarising, the mixture crystalline phases in P(VDF-TrFF) with a low TrFE content would show the phase transition from low polar $\alpha$ and $\gamma$ to a high polar $\beta$ phase which favours the ferroelectric and piezoelectric properties of this kind of copolymer.

Besides TrFE molar content, thermal processing at various temperatures has been proved to have a significant influence on the ferroelectric properties of P(VDF-TrFE) films by altering the crystalline structures. For example, we compared the $D$–$E$ loops of three processing P(VDF–TrFE) 70/30 mol% sample from melting followed by 140°C annealing (A0), room temperature cooling.
stacked lamellar crystal grain size, which could provide sufficient hydrogenated P(VDF-co-TrFE) samples are effectively improved by hot polarisation. As a result, the electric field of 60 MV/m (C0), and ice water quenching (Q0), respectively, as presented in Fig. 12. The annealed films (A0) possess larger crystallinity and stacked lamellar crystal grain size, which could provide sufficient time for the dipoles aligning. The ferroelectric domains deriving from crystal region in all the samples are effectively improved by hot polarisation. A result, the remnant polarisations ($P_r$) and coercive electric field ($E_c$) of the corresponding films are improved at a low frequency due to the response of dipoles in crystal phase (see Fig. 13), and the largest piezoelectric constant in the longitudinal thickness mode ($d_{33} = -25$ pC/N) is obtained in the annealed copolymer film. The results illustrate that improving the crystal structure of P(VDF-TrFE) is an effective way to realise high ferroelectric and piezoelectric properties, which provides broadly applied scenery for this kind of copolymer in piezoelectric components [81, 82].

Hydrogenised P(VDF-co-TrFE): Although the favourable ferroelectric property of the traditional P(VDF-TrFE) has drawn considerable attention for the increased applications in energy transferring and harvesting devices. However, people recently noted that the difficult synthesis conditions prevent them from the application in wider areas. Most importantly, for the inconvenience of TrFE as comonomers, such as high price resulting from poor sources, the poor controllability of the copolymer composition due to varied reactivity ratios of different monomers, and the hazard and difficulty during the transportation and storage of TrFE monomer, the production of copolymerised P(VDF-TrFE) was largely restricted for the high cost [4].

In order to solve the scarce TrFE monomer in the synthesis of traditional P(VDF-TrFE), a post-polymerisation method was proposed to obtain P(VDF-CTFE-TrFE) from commercial P(VDF-CTFE) [83]. It has been noted that head-to-head VDF-TrFE ($\text{CH}_2=\text{CF}_2-\text{CFH}-\text{CH}_2=\text{CF}_2$) in these "reduced" P(VDF-TrFE) copolymers is in the majority, which is rather different from the head-to-tail VDF-TrFE ($\text{CH}_2=\text{CF}_2-\text{CFH}-\text{CF}_2-\text{CH}_2=\text{CF}_2$) connection produced from direct radical copolymerisation of VDF with TrFE, as shown in Figs. 14 and 15 [83]. Although this strategy to synthesise P(VDF-TrFE) copolymers requires one more step than the direct radical copolymerisation of VDF with TrFE, it has the significant advantage of without using hazardous and expensive TrFE monomer (dangerous to transport and store). Lu et al. also noted that the ferroelectric fluoropolymers exhibited high dielectric constants of over 100 at the optimum composition. At the same time, Zhang et al. presented a hydrogenated P(VDF-co-TrFE) from P(VDF-CTFE) with varied CTFE content, where the Cl atom has been completely replaced by the H atoms [62, 84]. And they found that the $T_c$ could be adjusted by the volume of the introduction of TrFE monomer. More recently, the hydrogenation process of P(VDF-co-TrFE) has been well improved, and a further environmentally friendly and controllable P(VDF-CTFE) hydrogenation route named atom transfer chain reaction was reported by Zhang’s group [23, 85]. In an effort to avoid the use and production of high toxic chemical (such as tributyltin hydride and tributyltin chloride). And some other reductive metal bearing reagents have been patented for the hydrogenation of P(VDF-CTFE) as well [86]. Unfortunately, metal salts or complexes have to be utilised in all the above catalysts, which would significantly harm the dielectric and ferroelectric properties and limit the application of the resultant polymers in many fields. In this year, a hydrosilane ((Me$_3$Si)$_3$SiH) catalyst system with no metal specie has been reported for the hydrogenation of P(VDF-CTFE) in a controlled radical chain transfer reaction process by Zhang et al. [87], as illustrated in Fig. 16. Moreover, as indicated in Fig. 15, VDF and TrFE units are also mostly in the head–head connection in the hydrogenated copolymer, which is responsible for the significant difference in the thermal and dielectric properties of the direct-copolymer and hydrogenised copolymer.

The comparing of $D$-$E$ loops of traditional copolymerised P(VDF-co-TrFE) (H0) and hydrogenated P(VDF-co-TrFE) (H0) in Fig. 17 illustrated that the improved crystallinity and increased crystal domains are the main contributions to the remnant and saturated polarisation of the hydrogenised copolymer, which exhibits a positive influence on its ferro- and piezoelectric properties. That could partially eliminate the negative effect on its electric properties induced by the reduced polarity of polymer chain owing to H–H connection of VDF and TrFE [88, 89]. In addition, Fig. 18 compares the $D$-$E$ loops of various hydrogenated P(VDF-co-TrFE). Due to the improving of regularity.
The ferroelectric performance of P(VDF-TFE) copolymers was obtained under an applied electric field of 300 MV/m, and it is considered a convenient synthetic strategy and wealth of the sensors and generators areas. Considering the conformational change between the trans (low temperature) and gauche (high temperature) phases of P(VDF-TFE), the evidence for the presence of paraelectric phase transition could be obtained below melting point 91–93.

Lovinger et al. [94, 95] found the evidence for the presence or the absence of ferroelectric transitions and, in the former case, attempting to elucidate their nature and their relevance to homopolymeric PVDF. They found that the merits of using TFE rather than TrFE are clear and impressive. PTFE is subject to neither tauticity nor rigidity defects, and its conformation (variable with temperature, but always a slightly twisted helix) is distinctly different from those of β-PVDF and P(VDF-TrFE). Importantly, TFE monomers do not inject new chemical species into the copolymer chain since the –CF2– group is already present in PVDF. Therefore, as Lando and Doll pointed out [96], the resulting copolymer macromolecules can be viewed essentially as PVDF chains with an increased content of head-to-head but not tail-to-tail defects.

Structural changes occurring in the ferroelectric phase transitions of P(VDF-TFE) copolymers with VDF contents of 0–80 mol% have been investigated by Tashiro et al. [97]. It was confirmed that the conformational change between the trans and gauche phases of P(VDF-TFE) 81/19 mol% copolymer occurs in the temperature region close to the melting point with thermal hysteresis. As TFE is increased to 25 mol%, the copolymer shows a similar transition between the low and high temperature phases but via the disordered cooled phase, which is similar to P(VDF-TrFE) 65/35 mol%. As the TFE further decreases, the transition becomes more diffuse and trans-gauche conformational change occurs gradually over a wide temperature region with almost no detectable hysteresis. The transition of P(VDF-TFE) copolymers with TFE molar contents of 60–80% corresponds to that of P(VDF-TrFE) copolymers with lower VDF content. As the TFE content increases, the low temperature phase is stabilised more due to the effect of the TFE monomeric units [98].

More recently, Kochervinski et al. [99] reported the ferroelectric behaviour of typical P(VDF-TFE)/94/6 mol% copolymers, which is found that the copolymer looks like a linear dielectric whose permittivity nonlinearly increases with the amplitude of the alternating field in low fields, as shown in Fig. 19. This behaviour is related to the preferential orientation of the dipole moment of the chain along the normal to the surface and to the monocryystal-structure formation. As the electrical field increases to 95 MV/m, the copolymer appears double hysteresis loops (DHLs), showing the characters of the anti-ferroelectricity. When the applied field reaches 125 MV/m, a normal D–E loops of ferroelectric could be obtained in the P(VDF-TFE) 94/6 mol% copolymer and the remnant displacement is 85 mC/cm2 which is a favourable value for PVDF-based ferroelectricity.

3.2.2 Applications of PVDF-based ferroelectric polymers: PVDF, in its β-phase, exhibits strong and stable piezoelectric and pyroelectric activities, which means mechanical energy can be converted into electrical energy and vice versa. It also has attracted much interest as a next-generation piezoelectric and pyroelectric material because of its light weight, flexibility, low power consumption, and non-toxicity [100]. Thermal transducers employing a thin pyroelectric film of PVDF can be designed to provide fast response time [101]. The piezoelectric and pyroelectric properties of thin films enable fabrication of multifunctional sensors for a number of practical applications such as shock impact and pressure sensors, biomedical, acoustic, tactile sensors, active vibration control, and structural health monitoring of civil and aerospace structures [102].

Stefan et al. showed a PVDF the sensor with ultra-high sensitivity and ultra-short response time, as shown in Fig. 20. The flexible capacitive pressure sensor can be made cheaply over a large area of the microstructured film of the biocompatible elastomer polydimethylsiloxane [103].

Fig. 21 presents a fabricated nanostructured film with graphene electrodes using PVDF and ZnO, where the film is only 80 μm thick (about 15% of the human epidermal thickness) and is a highly sensitive and ultra-fast response time, as shown in Fig. 20. The flexible capacitive pressure sensor can be made cheaply over a large area of the microstructured film of the biocompatible elastomer polydimethylsiloxane [103].

Fig. 21 presents a fabricated nanostructured film with graphene electrodes using PVDF and ZnO, where the film is only 80 μm thick (about 15% of the human epidermal thickness) and is a highly sensitive and ultra-fast response time, as shown in Fig. 20. The flexible capacitive pressure sensor can be made cheaply over a large area of the microstructured film of the biocompatible elastomer polydimethylsiloxane [103].
A sensitive mixed-function measurement sensor that can be used to measure both pressure and temperature. The working principle of this sensor is to monitor the pressure change through the piezoelectric resistance of the material, infer the temperature according to the signal recovery time [100]. Moreover, Vinh Nguyen et al. designed and fabricated a low-cost, high-fidelity system consisting of a thin film PVDF piezoelectric strain and rosette and data logging electronics to monitor the dynamics and torques in single-point cutting processes [104].

Because traditional batteries not only need to be frequently replaced but also the abandoned battery without professional treatment will cause environmental pollution. Energy harvesting technology is a promising technology that can replace traditional batteries. Piezoelectric energy harvesting devices possess the merits of manufacturing process compatibility, simple structure, and high conversion efficiency. Recently, the ferroelectric PVDF-based polymer was reported to have a potential application in the energy harvesting area including low-power wireless sensor networks and the Internet of things. Li et al. exhibit a bi-resonant structure based on a piezoelectric β-PVDF energy harvester consisting of two cantilevers with resonant frequencies of 15 and 22 Hz. As the acceleration increases, the vibration amplitudes of the two cantilever structures increase and collisions occur, resulting in a strong mechanical coupling between the two subsystems [105]. Moreover, Manisha et al. introduced the methodology and experimentation of harvesting exhaled air energy by PVDF film, as shown in Fig. 22, which shows that it is promising to acquire the voltage arising from the exhaled air [106] providing the variation of the energy harvested with different physical parameters and gender were observed.

Besides the application of β-PVDF polymer, by coupling the pyroelectric and piezoelectric effect of PVDF with the shape memory of TiNiCu alloy recently, a novel flexible composite thermal energy harvester was developed. This harvester combines the superior flexibility of PVDF with the large temperature induction strain of shape memory alloy to harvest small, quasi-static temperature variations [107]. Moreover, some literature concerned the application of P(VDF-TrFE)-based nanoparticles in energy harvesting technology, which provide a reference of PVDF-based ferroelectrics using in prospective regions [108].

More recently, some researchers reported the application of PVDF-based homopolymers in actuator because this area reflected in the demand for small piezoelectric devices of low cost, low power, and the manufacture of high quality micrometre-sized patterns on a variety of substrates. Feng et al. [109] presented a high performance flexible magnetically controllable actuator based on magneto active elastomer and PVDF composite film. Based on this kind of actuator, a magnetically controllable tentacle is developed, which grasp, transport, and release could object by switching the supplied current. Also, by airbrush and ink-jet printing methods, PEDOT-PSS films were deposited on PVDF, where the coated PVDF sheets are claimed to be capable of using as an actuator [110].

Furthermore, PVDF-based ferroelectrics were also reported using as memory units because PVDF has a shape memory effect. Raja et al. [111] prepared a polymer blend based on polyurethane (PU) and PVDF filled pristine or modified multi-walled carbon nanotubes by melt blending technology and expressed their mechanical, dynamic mechanical and electroactive shape memory properties.

### 3.3 PVDF-based anti-ferroelectrics

The anti-ferroelectric is actually a ferroelectric behaviour which shows the DHLs, as shown in Fig. 23. The anti-ferroelectric polymer is proposed to obtain a large discharging energy density...
Therefore, the anti-ferroelectric phenomenon has drawn a lot of applications, a convenient strategy is to solve the practical problem et al. PXMA).

3.3.1 PVDF and P(VDF-TrFE) ferroelectrics: The anti-ferroelectric like behaviour under high electric field together with the remnant displacement reduced to a very low value or zero. Therefore, the anti-ferroelectric phenomenon has drawn a lot of attention in the energy storage area.

3.3.1 PVDF and P(VDF-TrFE) ferroelectrics: The anti-ferroelectric behaviour of PVDF was firstly reported by Furukawa et al. [112] for β-PVDF at temperatures below −60 °C, which was confirmed by the two peaks in current versus time curves. They explained that the dipoles in PVDF appear to switch back to their original direction, resulting in a minimum displacement at zero electric field.

Fig. 23 Schematic illustration of a Normal ferroelectric b Anti-ferroelectric-like c Paraelectric behaviours of the high temperature PE phase in P(VDF-TrFE) under different poling frequencies (f) [26]

Fig. 24 Schematic models of polarisation mechanisms for a PVDF b P(VDF-TrFE)-g-PS. Note that after PVDF crystallisation, the grafted PS side chains form a nanoscale interfacial layer around the ferroelectric crystal [26]

with the remnant displacement reduced to a very low value or zero. Therefore, the anti-ferroelectric phenomenon has drawn a lot of attention in the energy storage area.

3.3.2 P(VDF-CTFE)-g-PS: Besides, Zhu’s group has utilised a novel concept of confinement effect to modify the ferroelectric property of PVDF crystals. Specifically, they have grafted low loss PS side chains onto the P(VDF-CTFE) copolymer main chain [118]. After crystallisation-induced micro-phase separation, PS has been segregated to the crystal periphery, forming a dielectric confinement layer around the PVDF lamellar crystals. Their purpose is to confine the ferroelectric relaxation by weakening the coupling among adjacent ferroelectric domains, low polar PS has been introduced in the P(VDF-CTFE) and P(VDF-TrFE-CTFE) as side chains to form micro-insulator layers surrounding the ferroelectric domains [21, 119]. As a result, the long distance coupling among ferroelectric crystals (or domains) has been interrupted and the less space charge has been induced in the polymer matrix. A fast discharge speed and low loss have finally achieved in these ferroelectric dielectric films.

Due to the low polarity of the PS-rich layer at the amorphous–crystalline interface, the compensation polarisation is substantially decreased resulting in a novel confined ferroelectric behaviour in the grafted copolymers to purposely reduce $P_{\text{comp}}$ and limit domain growth upon repeated poling, as shown in Fig. 24. Most interestingly, drawing P(VDF-TrFE-CTFE)-g-PS bearing 14 wt% of PS segment uniaxial results into the ferroelectric transition from linear dielectrics to ferroelectrics with a DHL, which is closely dependent on the extension ratio. Compared with the DHLs observed in PVDF-based normal ferroelectrics under a low electric field in a very narrow range and within limited polarising circles, DHLs are found to be well maintained under a relatively high electrical field in the stretched P(VDF-TrFE-CTFE)-g-PS films. However, when the extension ratio is 450%, the discharging is obtained as only 2.5 J/cm$^3$ under 150 MV/m together with discharging efficiency ~30% in the grafted polymer films mainly due to the quickly vanishing of the DHLs behaviour under the elevated electric field. Therefore, fabricating a polymer with an anti-ferroelectric like behaviour under high electric field together with high breakdown strength should be a desirable way to achieve high discharging energy density in metallised capacitors.

3.3.3 P(VDF-TrFE-CTFE)-g-PXMA: Zhang et al. recently reported another non-crystal polymer as side chains to form micro-insulator layers surrounding the ferroelectric domains and to realise the anti-ferroelectric properties of P(VDF-TrFE-CTFE)-g-PXMA, and X represents M (methyl), E (ethyl) and so on [120–122]. It is found that grafting different poly(methacrylic ester)s (PXMA)s onto P(VDF-TrFE-CTFE) may provide an excellent compatibility of PXMA with the main chains and could effectively impede the crystallisation of P(VDF-TrFE-CTFE). The D-E hysteresis behaviours of P(VDF-TrFE-CTFE) clearly showed that the grafted P(VDF-TrFE-CTFE)-g-PXMA tuned from typical ferroelectric to either anti-ferroelectric or linear dielectric by facilely depending on the types and amount of XMA monomers onto it as shown in Fig. 25.

Taking the normal ferroelectric P(VDF-TrFE) (80/20) for an instance, which is easy to form large size and high polar β-phase crystal. In electro polarisation, the presence of electrostatic forces between orientation areas may have a strong coupling effect.
Therefore, after the electric field is removed, the polar grains are not able to return to the original position, a reverse electric field $E_r$ must be applied to make the polarisation return to zero. As a result, $D–E$ loops are shown as a rectangular shape. By inserting defects chemically or physically into the polymer chains may turn the normal ferroelectric performance of the P(VDF-TrFE) into the relaxor ferroelectrics. By grafting PXMA onto the side chain of PVDF-based copolymers, the normal and the relaxor ferroelectric behaviour of PVDF copolymers could be transferred into anti-ferroelectric like dielectrics characterised with DHLs and even linear dielectrics. The depressed ferroelectric relaxation and the transition from normal ferroelectric to anti-ferroelectric or linear dielectric are responsible for its significantly decreased electrical energy discharging loss, well maintained energy density.

The outstanding confining and decoupling effects of PXMA side chains on the disorientation of the high polar crystal domains and the transition from normal ferroelectric to anti-ferroelectric or linear dielectric are responsible for its significantly decreased electrical energy discharging loss, well maintained energy density. A low energy loss of 16.6% and relatively high discharging energy density of 19.3 J/cm³ under an electric field of 675 MV/m was achieved in this literature. Among all the investigated three types of PXMA, PMMA exhibits the strongest confinement onto the ferroelectric performance of the P(VDF-TrFE) for its highest polarity, modulus at ambient temperature and $T_g$.

Zhang’s group also reported the synthetic process of P(VDF-TrFE-CTFE)-g-PMMA [122–124], as shown in Fig. 26. They further found that uniaxial stretching has been conducted onto a family of solution cast P(VDF-TrFE-CTFE)-g-PMMA films bearing different PMMA content. The dependence of the crystalline, dielectric and ferroelectric properties of the films with varied PMMA content on the extension ratio has been carefully investigated. Thanks to the strong confinement of PMMA side chains and orientation induced ferroelectric phase transition, DHLs behaviour of P(VDF-TrFE-CTFE)-g-PMMA with 24 wt% of PMMA and an extension ratio of 300% could be well maintained up to 675 MV/m and the highest discharging energy density is obtained as 23.3 J/cm³.

3.4 PVDF-based relaxor ferroelectric polymers

3.4.1 Fabrication of PVDF-based relaxor ferroelectric polymers: Although all-trans $\beta$ phase P(VDF-TrFE) copolymer shows a high piezoelectric value ($d_{31/33} = 15–30 \text{pC/N}$) [77], the response of the dipoles to the electric field is very low at ambient temperature due to the high energy barrier of switching the dipole direction [125, 126]. To solve the problem, many researchers proposed a series physical and chemical fabricating method in an attempt to break up the large crystal grains as well as improve the dipoles responses to the low electric force. In this case, the normal ferroelectric PVDF based homopolymers were transformed to the relaxor ferroelectricity, which is expected to possess a large electro-strictive effect. Consequently, the low sensitivity to the external stimulus of ferroelectric materials confines its wide application in the electro-strictive device.

Early in 1998, it was found that by introducing defects via high electron irradiation of the P(VDF-TrFE), the copolymer is converted from a normal ferroelectric to a relaxor ferroelectric, as shown in Fig. 27 [127, 128]. The remnant polarisation of P(VDF-TrFE) is finally eliminated, and the dielectric temperature spectrum shows typical ferroelectric relaxor behaviour. In this process, the conformation of molecular chains in P(VDF-TrFE) has a change from the disordered TGTG and $T_g$ to the all trans $TTTT$, leading to the observed large electro-strictive strain coupled with relatively high modulus (>0.3 GPa). This irradiation process makes the P(VDF-TrFE) suitable as a structural component in addition to the electroactive functions (actuators and sensors).

Furthermore, by chemical introducing CFE and CTFE to P(VDF-TrFE), the ferroelectric polymers could be fabricated into a relaxor ferroelectric terpolymers. Piézotech Co. (France) synthesised P(VDF-TrFE-CFE) and P(VDF-TrFE-CTFE) via the suspension process from the normal ferroelectric PVDF polymer by employing proper defect modifications which eliminate the detrimental effects associated with a normal first-order F-P transition while maintaining high material responses [129–131]. The introduction of the third monomers of CFE and CTFE into the VDF chain is expected to interrupt the ferroelectric domains, thereby reducing their size [131]. Similar to the irradiated P(VDF-TrFE), random defect introduction broadens the ferroelectric transition and reduces the ferroelectric-paraelectric transition temperature. The random incorporation of the bulky third monomer into P(VDF-TrFE) chains results in a conformation change from the $TTTT$ conformation to TGTG or $T_g$ conformations [132, 133]. The reduction of the normal ferroelectric phase will further lead to a relaxor ferroelectric with electromechanical strain >7% (also called electro-strictive strain) and an elastic energy density of 0.7 J/cm³ under electrical field up to 150 MV/m [134].

These relaxor-ferroelectric terpolymers P(VDF-TrFE-CFE) and P(VDF-TrFE-CTFE) exhibit a room temperature dielectric constant $\varepsilon > 5 \times 10^9$, as shown in Fig. 27 [129–131]. It should be borne in mind that the amount of CFE or CTFE added to the P(VDF-TrFE)
Temperature and melting temperature of terpolymers would shift to chain. As a result, the terpolymer possesses a high dielectric constant at room temperature. For example, the dielectric constant of the terpolymer is about 30 at 1 kHz, and tan δ is <0.15, whereas that of the corresponding copolymer is 15. Compared with P(VDF-TrFE), the coercive field (Eₘ) of terpolymers is decreased from 60 to 20 MV/m under 100 MV/m. It is found that, when the HFP content increases to 2.5 mol%, P(VDF-TrFE-HFP) (62/38/2.5 mol %), Pₑₑₚₚ of P(VDF-TrFE-HFP) (62/38/2.5 mol%) decreases to ~5.0 μC/cm² in comparison to ~10.0 μC/cm² for P(VDF-TrFE) (65/35 mol%) near 100 MV/m applied field [135].

More recently, we synthesised P(VDF-TrFE) containing internal instauration (P(VDF-TrFE-DB)) via controlled hydrogenation of P(VDF-TrFE-CTFE) terpolymer (Fig. 24) and investigated its dielectric properties. As shown in Figs. 29 and 30, the double bonds (CF=CH) in P(VDF-TrFE) are playing the same steric kink role as the Cl atom in the CTFE unit in P(VDF-TrFE-CTFE) terpolymer, which turn the normal ferroelectric behaviour of P(VDF-TrFE) into relaxor ferroelectric properties by tailoring the highly polar β phase crystal domain in the long sequence into smaller pieces. As a result, the coercive field (Eₘ) and remnant polarisation (Pₑₑₚₚ) of P(VDF-TrFE-DB) are both decreased. After uniaxial stretching of the cross linked film, Pₑₑₚₚ can further reduce to 2.5 μC/cm² at 300 MV/m. Therefore, a relatively high energy density of 17.5 J/cm³ and a low energy loss of 8.0 J/cm³ (about 32% of overall energy charged) compared to the most promising P(VDF-TrFE-CTFE) (about 50% of overall energy charged) are obtained in the stretched P(VDF-TrFE) at 575 MV/m.

Based on that, we further synthesised a P(VDF-TrFE) containing inner CH=CH bonds via Cu(0) mediated single electron transfer radical elimination (SET-RE) process directly from P(VDF-TrFE) copolymer (Fig. 31) [136]. The introduction of CH=CH bonds into P(VDF-TrFE) leads to a reduced crystallinity but a slightly elevated F-P transition temperature, as shown in Fig. 31, which is expected using in the electro-strictive area. This copolymer was found to show excellent anti-ferroelectric like behaviours under the high electric field. However, after treated at an elevated temperature, the normal ferroelectric profiles are finely recovered for the cleavage of CH=CH bonds.

### 3.4.2 Applications of PVDF-based relaxor ferroelectric polymers

Thanks to their actuation abilities, high flexibility, low cost, conformability and process ability of fluoride-based electro active terpolymers (EAPs), such as P(VDF–TrFE–CFE), P(VDF–TrFE–CTFE), and P(VDF–TrFE–HFP) are promising candidate materials for electromechanical actuator applications due to their excellent electromechanical performances. In particular, electro-strictive polymers have been of significant interest in the scientific community [137–140]. There are various origins of electrostriction, such as dielectric or ionic nature, and many works have been devoted to enhancing the electromechanical response of these materials [141–144]. Still, due to their high strain capabilities, such devices feature promising application potentials, for instance as microvalves and pumps or in the fields of robotics, biomedical engineering (artificial muscles and minimally intrusive surgery) and shape control [145–148].

A typical using of PVDF-based relaxor ferroelectrics was shown in Fig. 32 as the schematic drawing of this micro-pump with diffuser and nozzle (valueless pump), which utilises non-symmetric flow characteristics of the diffuser and nozzle. The flow rate can reach 25 μl/m for a 2 mm size pump at 60 Hz. The flow rate increases linearly with the frequency (f < f₀). At higher frequencies (above the resonance frequency f₀), the flow rate decreases with frequency. The fluid used to be methanol. Besides, a lot of unimorph actuators using electro-strictive polymers have been realised. Nevertheless, the high strain change and the high elastic energy density of the terpolymer can lead to a high motion of a based terpolymer unimorph. Two layers of terpolymer (45 mm in length, 10 mm in width and 20 μm in thickness) have been bonded together. When the active layer is subjected to the action of an electric field the electro-strictive layer extends in length and the free extremity of the unimorph will follow a curved trajectory as we can see in Fig. 33 [149].
that influence of introduced DEHP on the electro-strictive response of the terpolymer could be well expressed by Maxwell stresses calculated from Young modulus and tuneable dielectric permittivity (ε). And by defining the relationship of Young modulus and tuneable dielectric permittivity FOM = m/Y, they compared the using area of PVDF-based EAP materials in all electro-strictive materials, as shown in Fig. 34 [147].

It is clear that the plasticised terpolymers out performed all of the considered materials (constant FOM being depicted as dashed lines), including relaxor ferroelectric ceramics, by several orders of magnitude [150].

4 Conclusions

PVDF-based homopolymers with various dielectric properties have been discussed including the properties, characterisation, and preparation of PVDF membranes with different morphs, methods of promotion and transformation in the solid state. The dielectric properties are increasingly important in a wide range of applications such as in energy generation and storage, monitoring and control, and include the development of sensors and actuators, separator and filtration membranes and smart scaffolds, among others. For many of these applications the polymer should be in one of its crystal phases. This part presents the developments and summarises the main characteristics of the crystal phases of PVDF and its copolymers, indicates the different processing strategies as well as the way in which the phase content is identified and quantified. The main purpose of this work is to provide a platform of this kind of polymers for various applications. And more important, their outstanding electrical characteristics among polymers, are still at the base of a dynamic, fruitful and interesting research field that will certainly support some of the most challenging applications of the near future.

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6 References


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