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New Properties and Applications of Polyvinylidene-Based Ferroelectric Polymer

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Abstract

There are different kinds of novel properties and applications of polyvinylidene difluoride (PVDF)-based ferroelectric polymer films. Several issues associated with the structure, properties, and applications of PVDF-based ferroelectric polymer films are discussed. The main achievements of the research include high electric tunability of relaxor ferroelectric Langmuir–Blodgett (LB) terpolymer films, the creep process of the domain switching in poly(vinylidene fluoride-trifluoroethylene) ferroelectric thin films, transition from relaxor to ferroelectric-like phase in poly(vinylidene fluoride-trifluoroethylene -chlorofluoroethylene) terpolymer ultrathin films, abnormal polarization switching of relaxor terpolymer films at low temperatures, huge electrocaloric effect in LB ferroelectric polymer thin films, self-polarization in ultrathin LB polymer films, enhanced dielectric and ferroelectric properties in artificial polymer multilayers, and transition of polarization switching from extrinsic to intrinsic in ultrathin PVDF homopolymer films.

In addition, the recent progresses of PVDF-based ferroelectric polymer films are connected with potential applications.

Keywords: Poly(vinylidene fluoride), Langmuir–Blodgett technique, Ferroelectric polymer, Ferroelectric relaxor

1. Introduction

Polyvinylidene difluoride (PVDF), consisting of $(-\text{CF}_2-\text{CH}_2-)_n$, with a carbon chain and hydrogen and fluorine atom on the two sides of carbon, respectively, is not a new synthe-

sized material, which has been found in 50 years ago. In the beginning, PVDF was studied for its high dielectric permittivity and for the diversity of crystalline-phase types. About 10 or 15 years later, piezoelectricity and ferroelectricity properties were found in PVDF materials [1–6].

As it is known, PVDF was found in possession of four or more crystalline-phase types. It consists of the α -phase, β -phase, γ -phase, and σ -phase. Phase types are related to various molecular configurations. In these different phase types, the β -phase is of polar form and the α -phase is of antipolar form; the molecular configuration is shown in Fig. 1. The antipolar form α -phase PVDF can be transformed to the β -phase polar form by rapid cooling from the melting or stretching along the carbon chain [1,2,5].

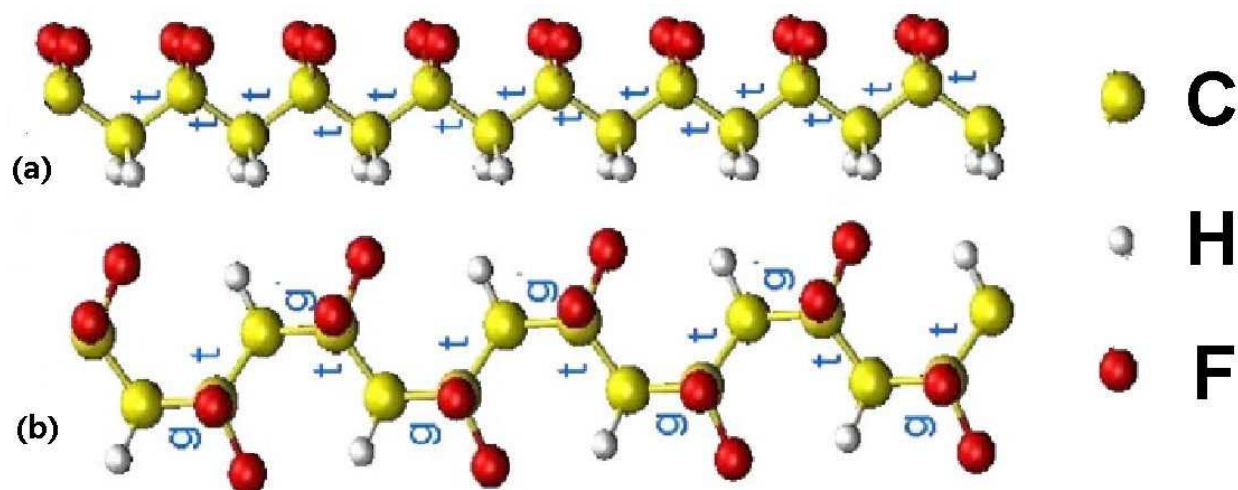


Figure 1. The typical molecular configuration of PVDF (a) α -phase, (b) β -phase

The other two types of PVDF phases derive from the β -phase and α -phase. Recently, it has been proved that the σ -phase PVDF is also a polar form. When the poly(trifluoroethylene) is added into the PVDF, a new type of copolymer P(VDF-TrFE), consisting of $-((-\text{CF}_2-\text{CH}_2)_x-(\text{CF}_2-\text{CHF}-)_{1-x})_n-$ chains, is achieved. The copolymers with 50 % or less trifluoroethylene (TrFE) are ferroelectric, though with reduced polarization and transition temperatures, because some of the hydrogen atoms are replaced with fluorine, reducing the net dipole moment polymer chains [5]. The β -phase P(VDF-TrFE) with ferroelectricity can be obtained easily, so the copolymer has been studied widely and popularly.

The terpolymer derived from the P(VDF-TrFE) is the ferroelectric relaxor polymer P(VDF-TrFE-CFE), which adds chlorofluoroethylene into the P(VDF-TrFE) copolymer. PVDF-based polymer films possess many special properties: dielectric, ferroelectric, piezoelectric, pyroelectric properties and so on. Based on these properties, these films can be used as transducers, ferroelectric memory, gate of transistor, and uncooled infrared sensor. In the following paragraph, some special properties and potential applications of PVDF-based polymer films will be introduced.

2. Method

There are several methods for preparing the PVDF-based films, for instance, spin coating, wire bar method, and Langmuir–Blodgett (LB) technique [7–9]. The mostly used film preparing method is spin coating, which is widely used for preparing the films with thickness larger than 30 nm. It is very difficult to get the ultrathin PVDF-based films based on spin coating and other normal methods. The LB method can be used to prepare the ultrathin two-dimensional ferroelectrics. In this chapter, the films of PVDF-based films mostly fabricated using LB technology. In 1995, S. P. Palto, L. M. Blinov, and V. M. Fridkin et al. began studies of ultrathin ferroelectric LB films of P(VDF-TrFE) copolymers with trifluoroethylene, P(VDF-TrFE) [9]. In 2007, J.L. Wang et al. prepared the ultrathin P(VDF-TrFE-CFE) terpolymer LB films [8]. Recently, we achieved the ultrathin PVDF homopolymer films with good ferroelectric performance. The detail of preparing the PVDF-based polymer films by LB technique is described as follows. The typical characteristic of the LB method is one monolayer (ML) at a time by repeatedly dipping a substrate into a liquid subphase coated with a monolayer of the desired polymer. The PVDF-based polymer should be firstly dissolved in dimethylformamide to form a dilute solution 0.01–0.05 wt%. The liquid subphase is ultrapure water with 18 M Ω /m. After the PVDF-based polymer solution is dropped into the water, about 30 min later, the PVDF-based polymer molecule chain will be floating on the surface of the water (as shown in Fig. 2a). In this case, the films are not uniform. The next step is pressing the bar of the LB technique until the surface pressure is up to 5 mN/m or less (as described in Fig. 2b). In this processing, if the surface is too large, the film on the water surface will collapse. The final step is shown in Fig. 2c, dipping the substrate horizontally on the surface of the water covered with monolayer PVDF molecule. Then raising the substrate slowly, one monolayer of PVDF ultrathin film is achieved. Repeating this process, the different thicknesses of PVDF-based film will be produced.

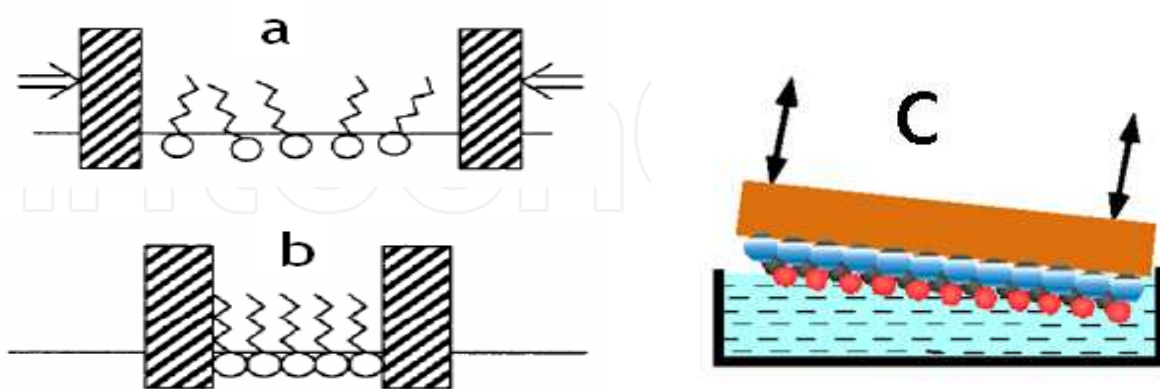


Figure 2. The horizontal transfer of LB technique: (a) and (b) the processing of the LB films; (c) transferring the PVDF-based film to the substrate

PVDF-based polymer films possess many special properties, for example, dielectric, ferroelectric, piezoelectric, and pyroelectric properties and so on. Based on these properties, the films

can be used for preparing the transducers, ferroelectric memory, gate of transistor, and uncooled infrared sensor. In the following paragraph, some special properties and applications will be introduced.

3. Dielectric tunability properties of PVDF-based polymer

The dielectric tunability of the PVDF has been studied by Lu et al. in 2008; the huge tunability can be reached in the P(VDF-TrFE) copolymer films, but in the P(VDF-TrFE-CFE) relaxor terpolymer films, the tunability is lower than the copolymer's [10]. For the traditional way of the relaxor ferroelectrics, the electric tunabilities are very large. Since the film thickness is controlled on a molecule level, ferroelectric LB polymer films have shown some exceptional properties, such as excellent crystallinity, two-dimensional ferroelectricity, surprising giant breakdown voltage, etc.; it is expected that terpolymer films derived from the LB technology can provide a special microstructure to study the origin of the excellent properties of relaxor ferroelectric terpolymers. High-quality ultrathin films of both ferroelectric P(VDF-TrFE) and relaxor ferroelectric P(VDF-TrFE-CFE) have been successfully fabricated by using the LB technique.

The P(VDF-TrFE-CFE) shows a typical relaxor from temperature dependences of the dielectric constant and dielectric loss versus frequency, as it is shown in Fig. 3.

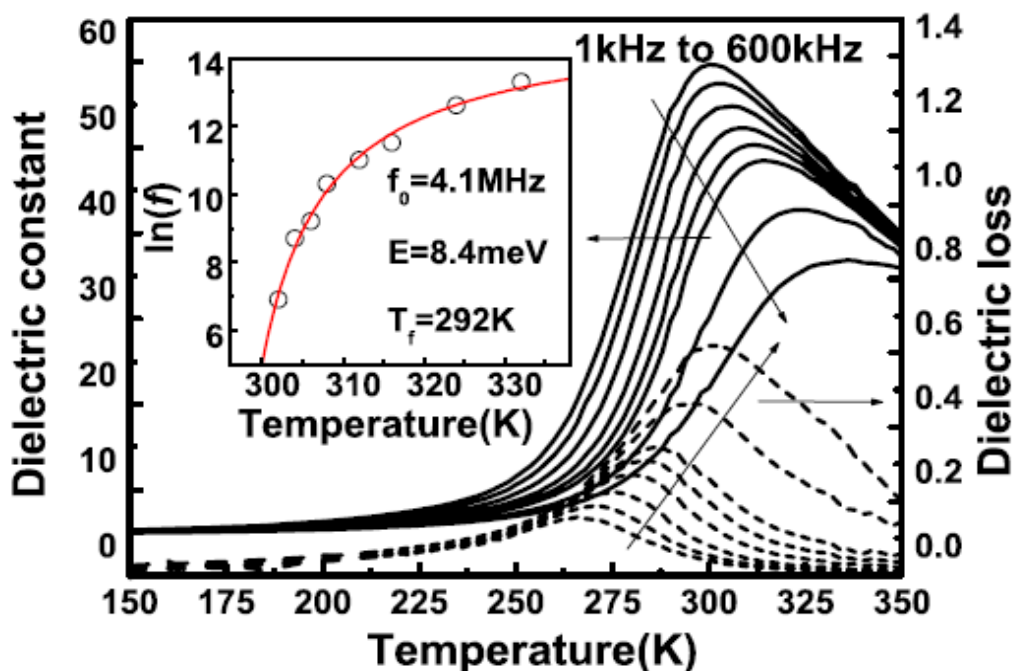


Figure 3. The dielectric constant and dielectric loss of P(VDF-TrFE-CFE) LB films as a function of temperature. The inset is the peak temperature of dielectric constant T_m as a function of $\ln(f)$ and the parameters fitted with the Vogel–Fulcher relation

A tunability of 80 % at 240 MV/m was obtained in P(VDF-TrFE-CFE) terpolymer LB films (shown in Fig. 4), which is due to the highly ordered molecules and the high breakdown electric field.

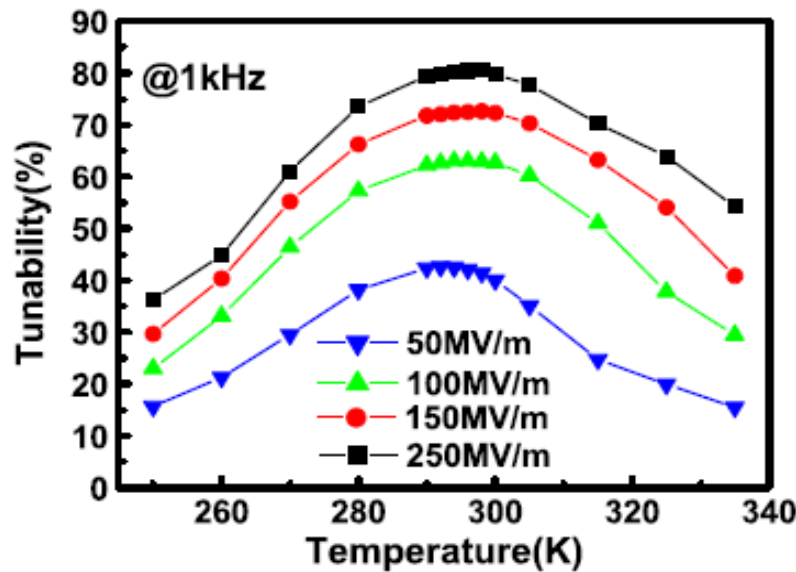


Figure 4. The tunability as a function of temperature for P(VDF-TrFE-CFE) LB films measured at 1 kHz, under the dc electric fields of 50, 100, 150, and 250 MV/m, respectively

What are the reasons for the large tunability in our terpolymer LB films? In our opinion, they should be associated with the special microstructure of the terpolymer LB films. It is known to us that LB polymers demonstrate some exceptional features such as good crystallinity and highly planar ordered and close parallel packing of the molecules.

4. Huge electrocaloric effect in LB ferroelectric polymer thin films

Recently, the huge electrocaloric effect (ECE) resulting from changes in the entropy and temperature of a material under an applied electric field has attracted the attention of researchers to ferroelectric materials [11,12]. The ECE occurs in both ferroelectric and paraelectric phases and is found to be larger in the paraelectric phase just above the ferroelectric–paraelectric phase transition [13].

In a working cycle-based ECE, the working material contacts the load and absorbs entropy from it. Then the material is isolated from the load and an electric field is applied. With an increase in the electric field, the polarization and temperature of the working material increase under adiabatic condition. The material is then placed in thermal contact with the heat sink and transfers the entropy absorbed from the load to the heat sink. Then the material is isolated from the heat sink. As the applied field is reduced, the temperature of the material decreases

back to the temperature of the cooling load. Thus, the larger the ECE of the working material, the better the efficiency of cooling.

We present a detailed investigation of the ECE of P(VDF-TrFE) and P(VDF-TrFE-CFE) films grown by the LB technique on technologically desirable aluminized flexible polyimide substrates. Our results clearly show a large ECE, as the variations of adiabatic temperature ΔT of P(VDF-TrFE) films (at 390 K under 300 MVm^{-1}) and P(VDF-TrFE-CFE) films (at 350 K under 350 MVm^{-1}) are 21 K (shown in Fig. 5).

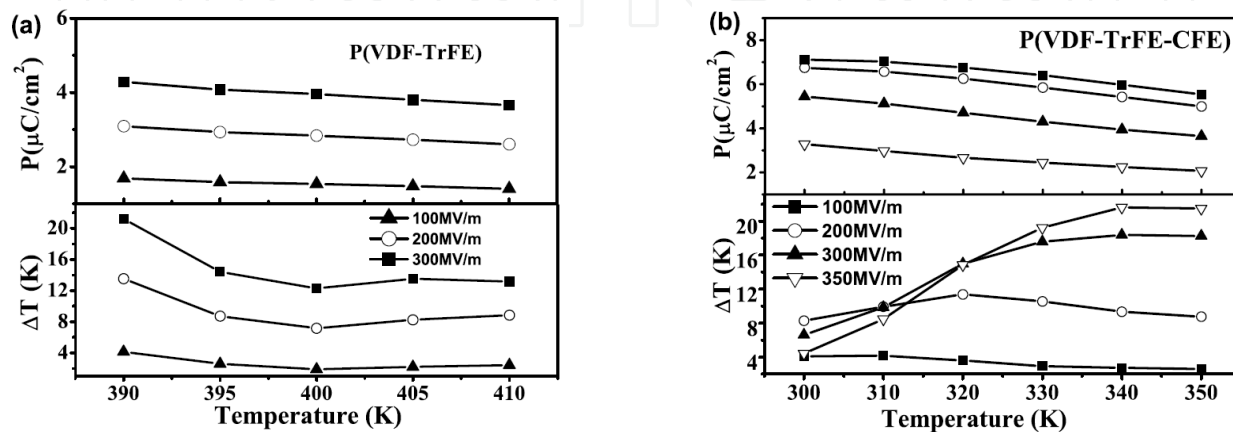


Figure 5. Polarizations from P - E loops and adiabatic temperature change ΔT versus temperature in different electric fields for (a) P(VDF-TrFE) films and (b) P(VDF-TrFE-CFE) films

Especially for P(VDF-TrFE-CFE) terpolymer films, the peak of ΔT is close to room temperature. Considering their practical availability, ferroelectric PVDF-based polymers are potentially applicable for refrigeration by ECE. Professor J. F. Scott has pointed out that PVDF-based polymers are the most promising commercial material due to their large temperature cooling per volt and to their scalability in size and shape [14].

5. Ferroelectric-like phase transition in P(VDF-TrFE-CFE) terpolymer ultrathin films

P(VDF-TrFE-CFE) terpolymer has attracted considerable attention for its fruitful properties and related potential application. Investigations have shown that the all-trans ($TTTT$) polar conformations have been converted into shorter all-trans conformations or polar nano-domains by the induced defect modifications [15]. Further studies verify that there coexist various molecular conformations in the terpolymer, such as trans-gauche ($TGTG$), and less polar $TTTG$ conformations, and the $TTTG$ is the dominant one responsible for the relaxor nature. Klein et al. found that the crystallization conditions can also impact the microstructures and the ferroelectric properties [16]. We have observed that the electric fields can change the length of the conformation.

The temperature dependence of the complex permittivity for the terpolymer films measured at 1 kHz in the heating process is shown in Fig. 6. For the film with 10 nm, the temperature of permittivity maximum T_m is at 308 K, which is consistent with the bulk terpolymer or thick films. Note that T_m increases with the decreasing thickness, and it is up to 360 K for the film with one transferred layer, which is even higher than the Curie temperature T_c of the copolymers with the same composition.

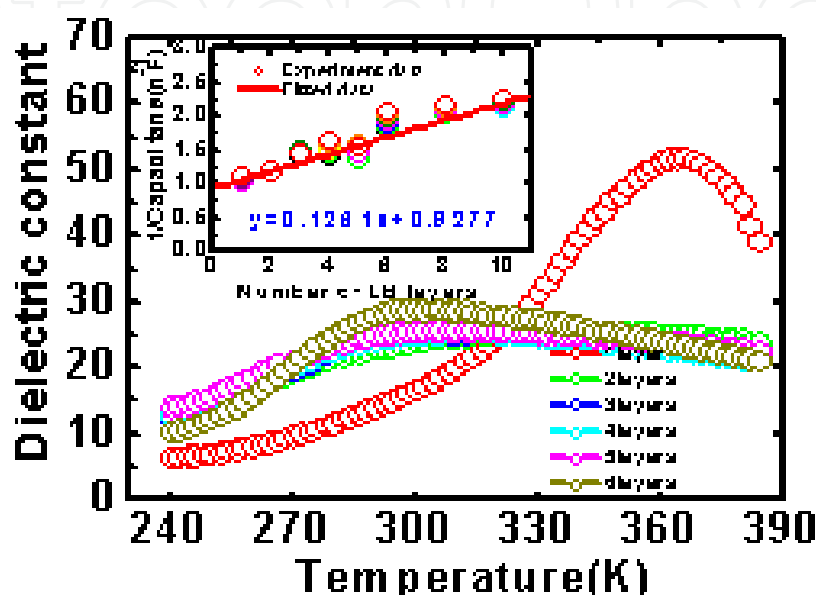


Figure 6. The dielectric constant of different thickness terpolymer films as a function of temperature of at 1 kHz

The coercive voltage is 1.2 V, which is also in accord with the polarization versus electric field (P - E) loop and C - V curve. In addition, the temperature dependence of the C - V curves for the terpolymer film with one monolayer is measured and shown in Fig. 7. The butterfly-shape feature disappears as the temperature is higher than 360 K, indicating a transition from ferroelectric-like to paraelectric phase. This is in accord with the temperature dependence of the capacitance.

A hypothesis can be deduced from the above results that all-trans-like molecular conformations form in the ultrathin terpolymer films. As mentioned earlier, the dominant conformation in P(VDF-TrFE-CFE) terpolymer is the less polar $TTTG$ conformation. It has been reported that the polar phase or ferroelectric-like phase can be induced by controlling the kinetic factors of the annealing process of terpolymer because the crystal structure is determined by both thermodynamics and kinetics. As it is known, the large PVDF dipoles can induce mirror charges on conducting substrates, thus forming an extrinsic vertical electric field on the substrate [17]. Here, it is considered that the terpolymer dipoles are also large enough to induce mirror charges on the conducting Al electrodes, which then can lead to a vertical electric field. Under such high vertical electric field, the less polar conformations are converted into higher polar conformations.

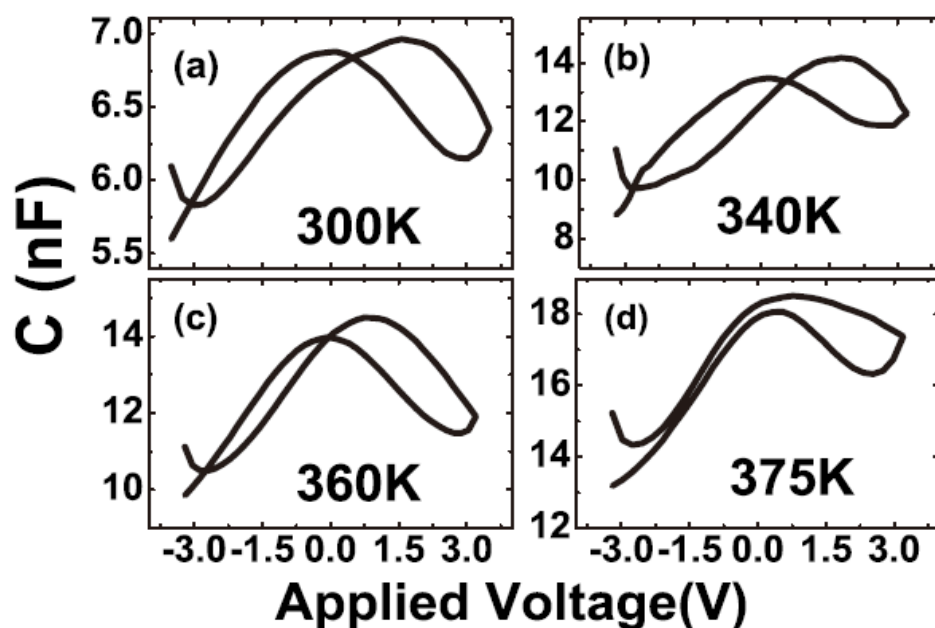


Figure 7. The temperature dependence of C-V curve at 10 kHz for one transferred layer terpolymer film. (a) 300 K, (b) 340 K, (c) 360 K, and (d) 375 K

The ferroelectric-like phase transition is observed in the P(VDF-TrFE-CFE) terpolymer films as the thickness is lower than 3 nm. The ferroelectric-like features are considered to result from the induced electric field due to the mirror charges in the electrodes.

6. Abnormal polarization switching of relaxor terpolymer films at low temperature

The temperature dependences of the dielectric and ferroelectric properties of terpolymer films produced using the LB method were systematically investigated, with an emphasis on the nature of the ferroelectricity at low temperatures [18].

The change of remanent polarization (P_r) with temperature is not sharp, and a broad peak at around 265 K is seen for $\partial P_r / \partial T$ (Fig. 8(a)).

A broad peak at ~270 K is displayed in the plot of $\partial D / \partial E_{E=0}$ versus T (Fig. 8(b)). The coercive field (E_c) increases slowly with decreasing temperature to ~265 K, below which it increases rapidly (Fig. 8(c)). This verifies that a ferroelectric phase transition occurs at ~270 K in the P(VDF-TrFE-CFE) films. The P_r value of the P(VDF-TrFE-CFE) film is smaller than that of the P(VDF-TrFE) film, and the magnitude of the P_r of the P(VDF-TrFE-CFE) film is still smaller than that of the film's saturation polarization (P_s) (Fig. 8(d)).

This suggests that some less-polar molecular conformations (TTTG') still affect the polarization switching. A deviation from Merz's law was observed in the relationship between the coercive

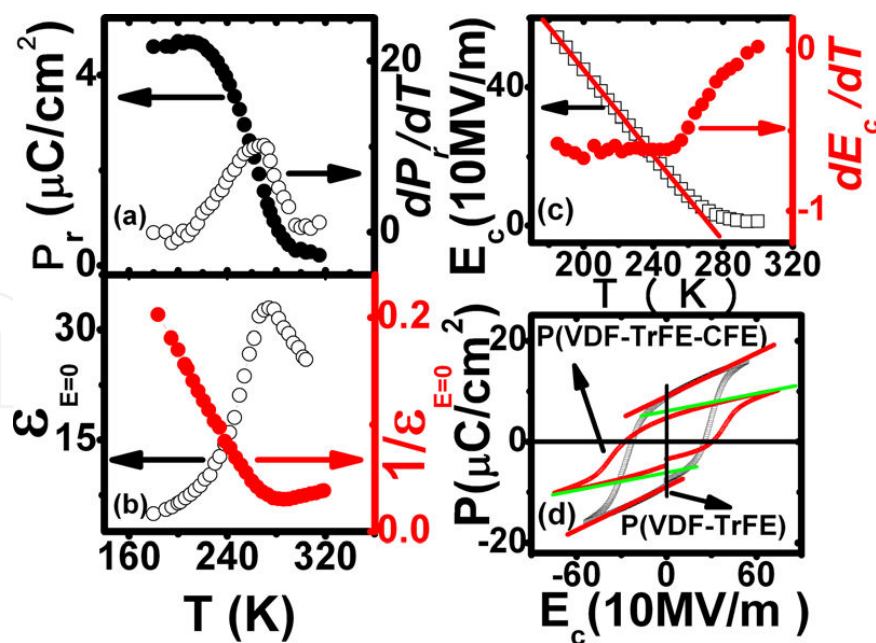


Figure 8. Temperature dependence of (a) P_r (left), $\partial P_r/\partial T$ (right); (b) E_c (left), $1/\partial D/\partial E_{E=0}$ (right); and (c) E_c derived from P - E loop at zero P_r (left), $\partial E_c/\partial T$ (right). (d) P - E loops of $P(\text{VDF-TrFE-CFE})$ and $P(\text{VDF-TrFE})$ films at 210 K and 100 Hz

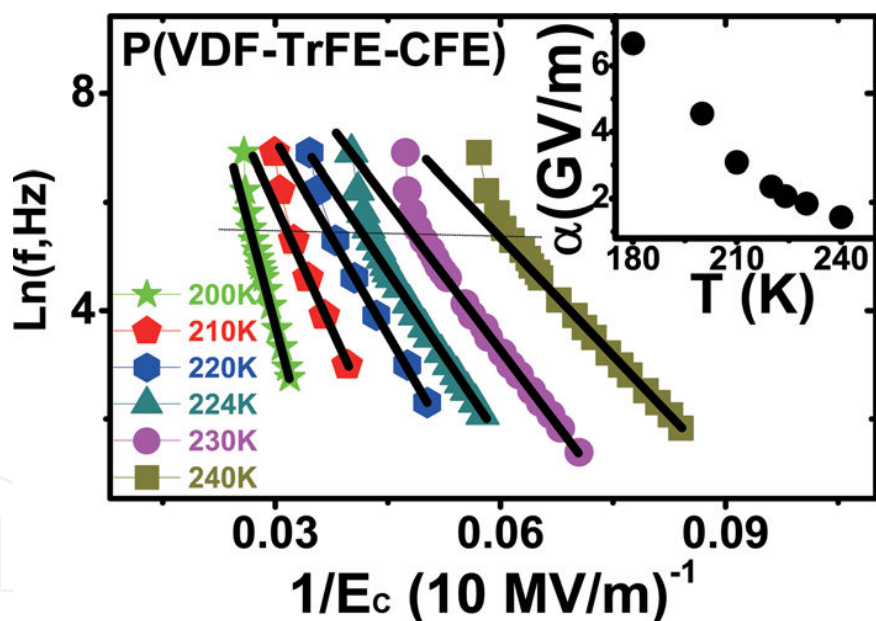


Figure 9. Relationship between $1/E_c$ and $\ln f$ for relaxor $P(\text{VDF-TrFE-CFE})$ terpolymer films

field and the frequency (Fig. 9). The deviation from Merz's law at high frequency further evidences the presence of $TTTG'$ conformations in the ferroelectric state.

The relaxor $P(\text{VDF-TrFE-CFE})$ terpolymer, the CFE monomer is introduced into the ferroelectric $P(\text{VDF-TrFE})$ copolymer as a defect, leading to all-trans polar conformations being converted into less-polar conformations, i.e., $TTTG'$, which are considered to be nanometer-sized all-trans conformations. The dynamics of the $TTTG'$ conformations of $P(\text{VDF-TrFE-CFE})$

films under electric fields or on cooling demonstrate a behavior different from that of the polar nanoregions (PNRs) of the $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) system [19]. The weak intermolecular interactions impede the development of some $TTTG'$ conformations into all-trans ones along the direction perpendicular to the molecular chains, so these $TTTG'$ conformations can largely retain their dynamics. This may be responsible for both the relaxor nature of the $\text{P}(\text{VDF-TrFE-CFE})$ terpolymer and the difference between its P_r and P_s values, even in its ferroelectric state.

The temperature dependences of the ferroelectricity of $\text{P}(\text{VDF-TrFE-CFE})$ terpolymer films were systemically investigated. Both the polarization current ($\partial P_r/\partial T$) and the dielectric response derived from the P - E loop at zero field, suggesting that a ferroelectric phase transition occurs at 270 K. Distinct differences were observed in the $\text{P}(\text{VDF-TrFE-CFE})$ terpolymer films compared with perovskite relaxors, e.g., a broad peak in the $\partial P_r/\partial T$ curve, deviation from Merz's law at high frequency, and a smaller activation field [20]. These differences are considered to be caused by the existence of the less-polar $TTTG$ conformation in the ferroelectric state.

7. The creep process of the domain switching in $\text{P}(\text{VDF-TrFE})$ ferroelectric thin films

The polarization switching behavior in poly(vinylidene fluoride-trifluoroethylene) $\text{P}(\text{VDF-TrFE})$ (70/30 mol%) thin films was investigated using a pulse transient current method [21]. The dependence of the domain switching current on the coercive electric field was derived. The current in the plateau region increases with the capacitor areas, whereas t_w is basically constant (Fig. 10(a)), while the current density is independent of the capacitor areas (Fig. 10(b)). This indicates that the charging current around the coercive field is limited by domain switching instead of the series resistor in the measurement circuit. Thus, it can reflect directly the speed of domain switching. The relationship between switching current and the electric field across the film fits well to the creep model with $\mu=0.5$ (Fig. 11). The exact dynamical exponent μ was found to be 0.5011, and resultant parameters $d_i=2$ and $n=1$, respectively. (An interface is characterized by its dimension d_i ($d_i=1$ for a line or 2 for a surface) and can move in n transverse directions.) The result implies that the two-dimensional domain walls propagate along one transverse direction.

Considering the derived parameters $d_i=2$ and $n=1$ in the present study, a model was proposed for the polarization switching process in a crystalline lamella of the $\text{P}(\text{VDF-TrFE})$. Firstly, 180° rotation of dipolar appears along a single-chain molecule; secondly, intermolecular expansion of chain rotations along external applied electric field with the switched molecular chains as the center because of the minimization of the depolarization energy; thirdly, domain walls with $d_i=2$ appeared at both sides of the switched dipolar plane. The domain wall, assumed to have a shape like a thin slab, propagates slowly, corresponding to $n=1$, till the completion of the domain switching in the lamellae

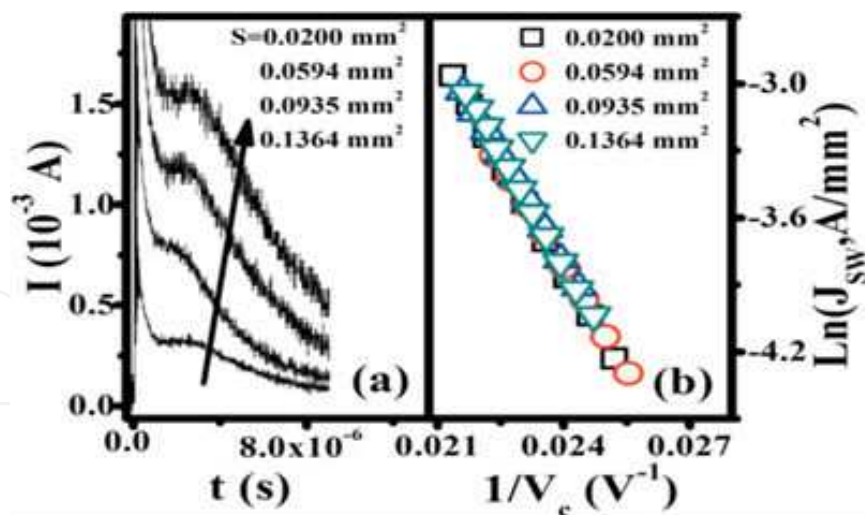


Figure 10. The variation of transient current with different capacitor areas under $V_a = 40$ V, $R_L = 1$ K Ω . (b) J_{sw} dependence of V_c with different capacitor areas for P(VDF-TrFE) film

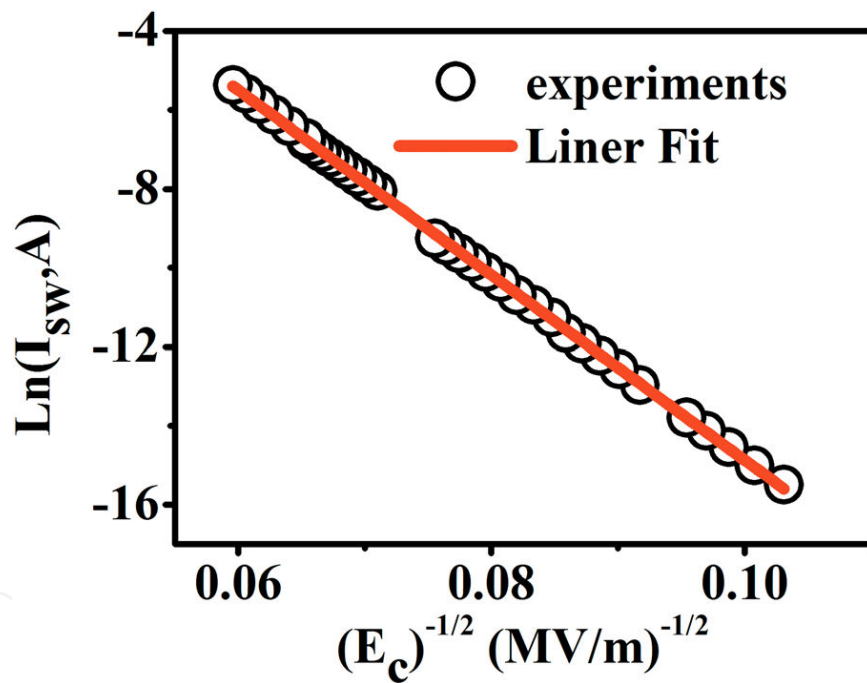


Figure 11. Dependence of domain switching current on the reciprocal of the square root of E_c .

8. Self-polarization in ultrathin LB polymer films

Ultrathin copolymer films of P(VDF-TrFE) were deposited on Al-coated polyimide substrates, by the LB method. A top Al electrode was evaporated onto the polymer film to form an Al/polymer/Al structured infrared detector. The pyroelectric voltage response of the detector under various polarizing processes was characterized. The detector with only one transferred polymer layer exhibited a preferential polarization direction. This was considered to result

from the self-polarization of the ultrathin polymer film [22]. It was due to the preferred alignment of the dipoles on the Al substrates. This process can be applied for designing stable fast-response infrared detectors.

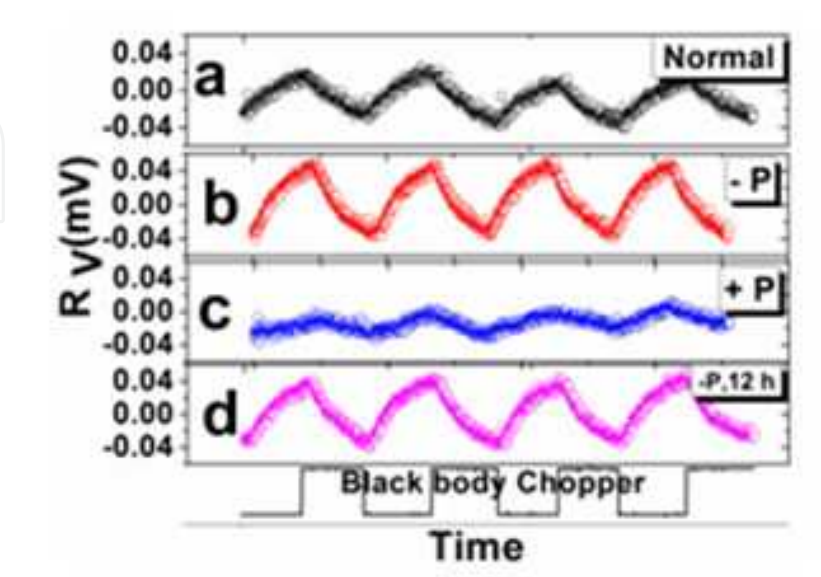


Figure 12. Pyroelectric voltage of the device under infrared radiation (a) before poling, (b) after poling at -1 V, (c) after poling at +1 V, and (d) 12 h after poling at -1 V

The fresh unpolarized device shows an appreciable pyroelectric voltage response, suggesting a preferential polarization. Upon polarizing the device at -1 V, the voltage response increases by a factor of 2, compared with the fresh device. Upon polarizing at +1 V, the voltage response decreases, in comparison with the fresh device. The applied 1 V is higher than the coercive electric field of the P(VDF-TrFE) ultrathin film with only 1 ML, reported in our previous investigation. Thus, the pyroelectric voltage responses under different polarizing directions should exhibit a 180° phase difference, but no such phase difference is observed in Fig. 12. This may be due to the back switching of domains, after removal of the positive poling voltage. It also suggests that the preferential polarization of the fresh device is aligned from the bottom electrode to the surface of the P(VDF-TrFE) film. The unpolarized detector exhibited a preferential voltage response.

This was considered to result from the self-polarization of the ultrathin P(VDF-TrFE) polymer film, due to the preferred alignment of the dipoles on the Al substrates. This result can be used to fabricate fast-response room temperature infrared detectors.

9. Electronic transport property in ferroelectric polymer films

The leakage current mechanism of ferroelectric copolymer of P(VDF-TrFE) prepared by LB was investigated in the temperature range from 100 K to 350 K. The electron as the dominant

injected carrier was observed in the ferroelectric copolymer films. The transport mechanisms in copolymer strongly depend on the temperature and applied voltage. From 100 K to 200 K, Schottky emission dominates the conduction. With the increase of temperature, the Frenkel–Poole emission instead of the Schottky emission conducts the carrier transport. When the temperature gets to 260 K, the leakage current becomes independent of temperature, and the space charge limited current conduction was observed [23].

The P(VDF-TrFE) film shows a saturated hysteresis loop with a remanent polarization (P_r) of $\sim 6.8 \mu\text{C}/\text{cm}^2$ and saturation polarization (P_s) of $\sim 11 \mu\text{C}/\text{cm}^2$, respectively, which indicates good ferroelectricity. It was previously reported that the electron affinity of β -P(VDF-TrFE) was about 4 eV, based on a density functional theory study [24]. The work function value of Au and Al metals are 5.1 eV and 4.1 eV [25], respectively.

The conduction through the lowest unoccupied molecular level (LUMO) of P(VDF-TrFE) and the leakage current is controlled either by the interface energy barrier that exists between the Fermi level of the metal and the LUMO level of the polymer or by the bulk-controlled mechanics such as Frenkel–Poole emission and space-charge-limited current (SCLC) conduction [26,27]. The schematic diagram of the band structure of the P(VDF-TrFE) and the work functions of Au and Al are presented in the figure. The temperature dependence of the I-V behaviors from 100 K to 350 K was measured, and the temperature dependence of the current density under voltage 5 V (about 70 MV/m) is presented in Fig. 13. It can be seen that the current density increased with the temperature, increasing from 100 K to 260 K, but it is nearly independent of temperature as the temperature is higher than 260 K.

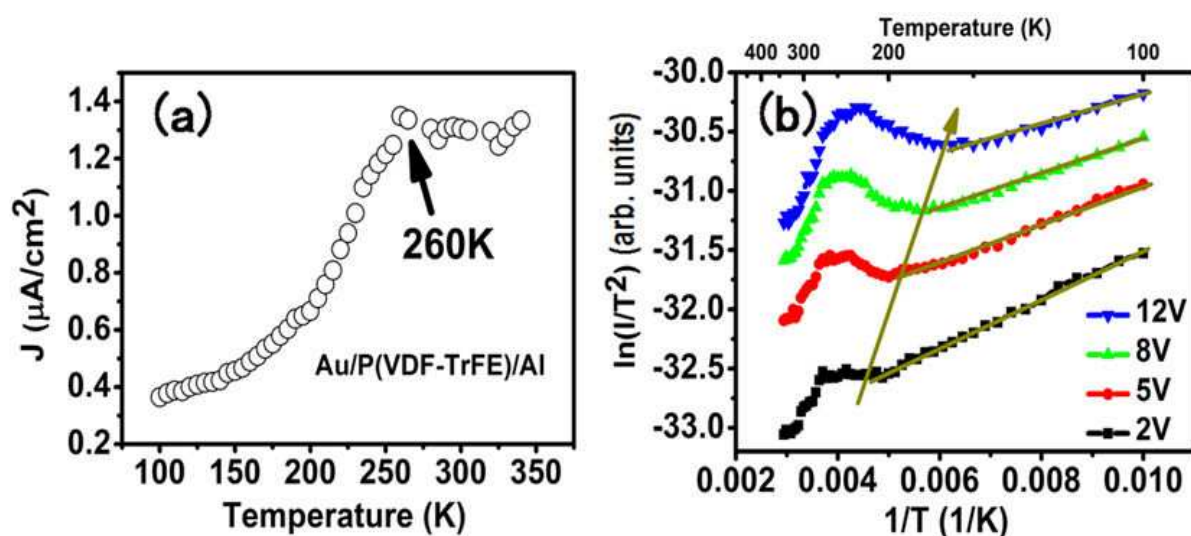


Figure 13. Temperature dependence of the current for P(VDF-TrFE) film under 5 V. (b) $\ln(I/T^2)$ vs. $1/T$ plots at different voltages. The direction of the arrow indicates a reducing temperature for increased voltage

The electric conduction of the ferroelectric P(VDF-TrFE) copolymer films has been comprehensively investigated. It is found that the electrons are the dominant injected carriers in the P(VDF-TrFE) films, and the charge injection occurs either at the polymer/electrode interface

or in the bulk polymer films. Various transport mechanisms are observed in the P(VDF-TrFE) films, which are influenced by both temperature and applied voltage.

Schottky emission and Frenkel–Poole emission are found to be the dominant transport mechanism in the temperature range from 100 K to 200 K and the range from 200 K to 260 K, respectively. Space-charge-limited current conduction is the main transport mechanism as the temperature is higher than 260 K.

10. Enhanced electric properties in the artificial polymer multilayers

Multilayers consisting of alternative ferroelectric P(VDF-TrFE) copolymer and relaxor P(VDF-TrFE-CFE) terpolymer with different periodicities in thickness were prepared. A superlattice-like structure is shown in the polymer multilayer as the periodic thickness is lower than a critical value. The dielectric constant of the multilayer with a small periodic thickness is two times higher than that of the P(VDF-TrFE) copolymer over a temperature range between 300 K and 350 K. The multilayer also shows a good ferroelectricity in the same temperature range. The enhanced electrical properties of the multilayers are due to the long-range ferroelectric coupling [28,29].

Organic ferroelectric polymers have recently attracted much attention for their potential applications in flexible electronic devices, such as display, solar cell, information storage, and so on [30–32]. However, compared with its inorganic counterpart, organic ferroelectric polymer has some drawbacks, e.g., the lower dielectric constant and electric polarization, which is an obstacle for their practical applications. It is well known that many artificial superlattices (SL) and multilayers (ML) based on perovskite ferroelectrics show some amazing properties [33–35].

High-quality ultrathin films of both ferroelectric P(VDF-TrFE) and relaxor ferroelectric P(VDF-TrFE-CFE) have been successfully fabricated using the LB technique, which provide precise control of the film thickness in molecular scale. In the present study, periodic multilayers composed of alternating ferroelectric P(VDF-TrFE, 70/30) layer and relaxor ferroelectric P(VDF-TrFE-CFE, 56.2/36.3/7.5) layer were fabricated.

Figure 14 shows the XRD patterns of the multilayers with different periodicities. Two diffraction peaks were observed in the multilayer structure of (15/15)₂, i.e., $2\theta = 18.57$ and 19.97 , which are assigned to the typical (110,200) reflection of the P(VDF-TrFE-CFE) and (110,200) reflection of P(VDF-TrFE), respectively. Compared with the pure P(VDF-TrFE-CFE) and P(VDF-TrFE), there is no shift in the (110,200) peaks for the (15/15)₂ multilayer, suggesting that both the terpolymer and copolymer components in the multilayer keep their original phase structure. When the periodic thickness is decreased to five transfer layers, a shift is observed in both the diffraction peaks. Simultaneously, the intensity of the diffraction peak associated with the pure terpolymers becomes weaker.

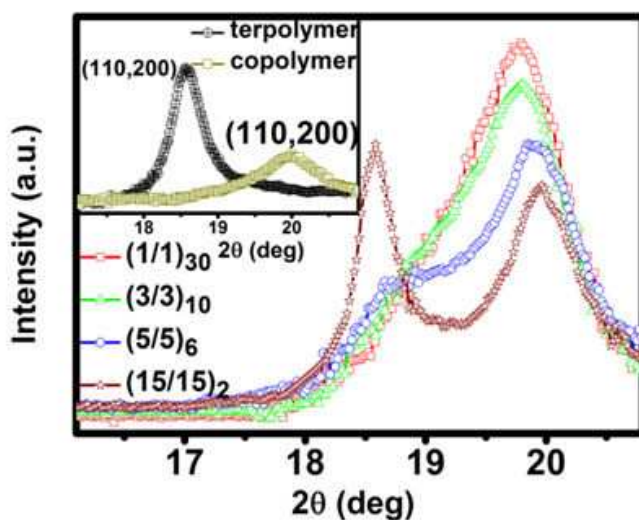


Figure 14. The XRD patterns of the multilayers with various periodicities. The inset shows the XRD patterns of copolymer and terpolymer

The temperature dependence of the dielectric constant of the multilayer structures on the heating process is shown in Fig. 15. Dielectric constant calculated with a series capacitor model of the individual copolymer and terpolymer is also shown in Fig. 15. It can be seen that the temperature dependence of the dielectric constant for the multilayer with the transfer number m larger than 10 is analogous to that of the series model, which shows a platform between 300 K and 360 K. This suggests that these multilayers with thick interlayer are just a combination of individual copolymer and terpolymer components.

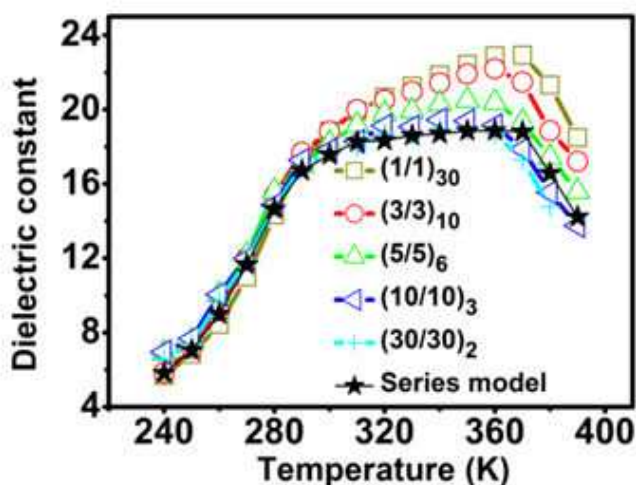


Figure 15. The dielectric constant of multilayers with different periodicities and the calculated dielectric constant using series model as a function of temperature

The P - E hysteresis loops for the multilayers as well as the pure copolymer and terpolymer films are shown in Fig. 16. The $(1/1)_{30}$ multilayer structure displays a good ferroelectricity with

a remanent polarization (P_r) of $\sim 5.2 \mu\text{C}/\text{cm}^2$, which is just a little smaller than that of pure P(VDF-TrFE) thin films. The temperature dependence of the P_r of the multilayers with various periodic thicknesses is summarized in the inset of Fig. 3.

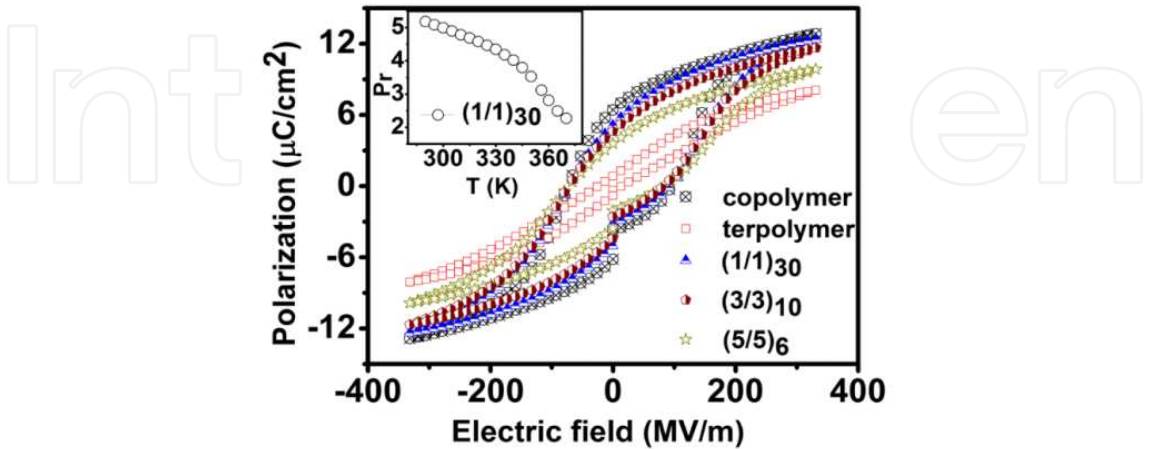


Figure 16. P - E hysteresis loops of the multilayers with different periodicities, pure copolymer and terpolymer films at 1 kHz. The inset shows P_r of (1/1)₃₀ multilayer as a function of temperature

The piezoelectric properties of the copolymer P(VDF-TrFE) and terpolymer P(VDF-TrFE-CFE) multilayers are presented in Fig. 17.

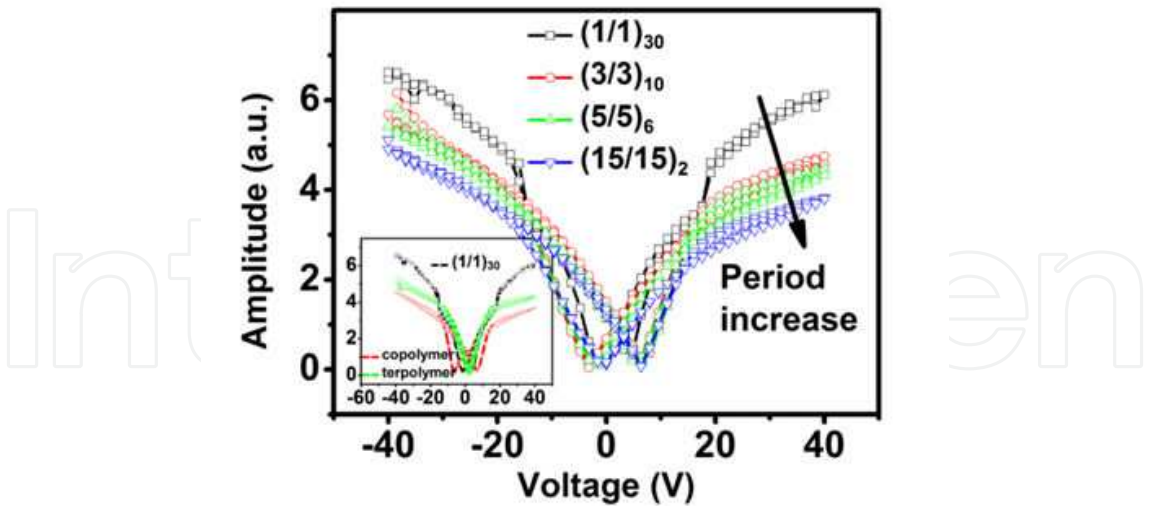


Figure 17. The piezoelectric response curves of multilayers with different periodicities. The inset compares the piezoelectric response curves of the (1/1)₃₀ multilayer, P(VDF-TrFE) and P(VDF-TrFE-CFE) homogenous films

The piezoelectricity of the samples was measured by piezoresponse force microscopy (PFM). To increase the degree of accuracy and allow meaningful comparison of the piezoresponses of the samples, measurements were made at ten different locations for all samples and then

averaged. The piezoelectric coefficient d_{33} for various multilayer structures are listed in Fig. 19. The d_{33} of the pure copolymer and terpolymer are 41 pC/N and 52 pC/N, respectively, which is close to the reported value for the copolymer (49 pC/N) and equal to that observed for the terpolymer. Interestingly, an enhanced piezoelectric response of 81.6 pC/N is observed for the (1/1)₃₀ multilayers, which is nearly 57 % larger than the pure terpolymer. As the periodic thickness increases, the piezoelectric response of the multilayers decreases dramatically.

In summary, the multilayers composed of alternating P(VDF-TrFE) copolymer and P(VDF-TrFE-CFE) terpolymer layers have been prepared, and their crystal structure and dielectric and ferroelectric properties have been studied. The multilayers with a periodic thickness of ~3 nm shows a superlattice-like crystal structure, high dielectric constant, good ferroelectricity, and piezoelectricity over a wide temperature range from 300 K to 350 K. The long-range ferroelectric coupling is considered to be dominant for multilayers with a smaller periodic interlayer.

11. Polarization switching properties of PVDF homopolymer films

PVDF homopolymer thin films have been prepared by the Langmuir–Blodgett technique, and their electrical properties have comprehensively been studied [36]. The PVDF homopolymer films show better ferroelectricity with higher polarization and higher breakdown electric field than that of P(VDF-TrFE) copolymer films.

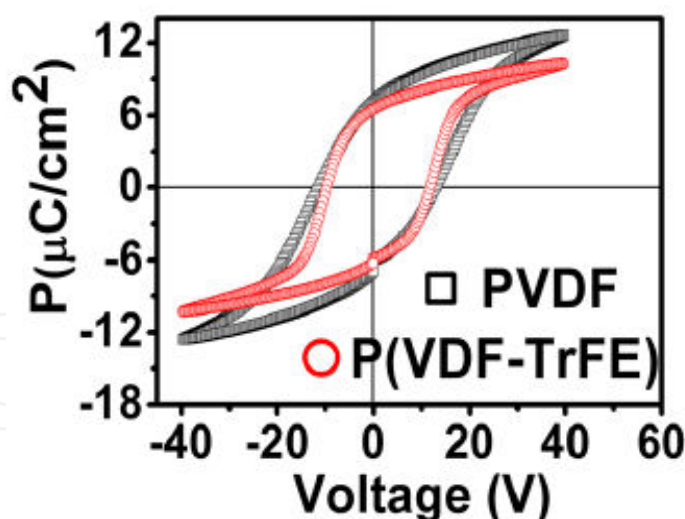


Figure 18. *P-E* loops of PVDF and P(VDF-TrFE) copolymer LB films

The phase image of the piezoresponse shows a polarization switching in the PVDF homopolymer films, suggesting a typical ferroelectric feature. The ferroelectric *P-E* loops of the PVDF homopolymer and P(VDF-TrFE) films are shown in Fig. 18. The well *P-E* hysteresis loop of the PVDF films also confirms its ferroelectricity. It can also be seen that both the P_r and E_c of the PVDF LB films are higher than that of P(VDF-TrFE) LB films. In addition, the breakdown

voltage of the PVDF LB films is found to be above 50 V, whereas the breakdown voltage of the P(VDF-TrFE) LB films is only 40 V.

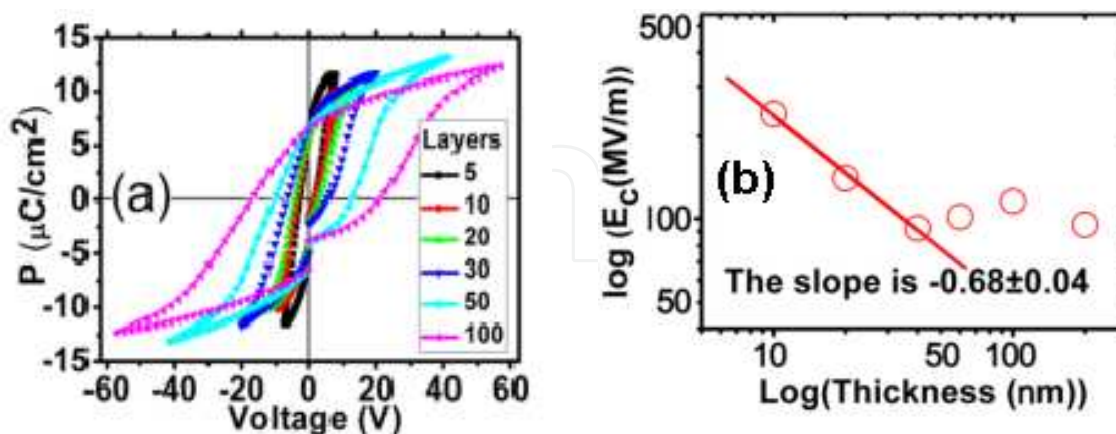


Figure 19. (a) The P - E loops of the PVDF homopolymer LB films with 10 to 200 transferred layers. (b) $\log E_c$ vs. \log thickness of the PVDF homopolymer LB films

In this study, the film thickness dependence of the E_c of the PVDF homopolymer LB films is investigated. Figure 19(a) shows the P - E loops of the PVDF homopolymer LB films with various transferred layers. Note that the E_c is basically constant between 200 nm and 44 nm but dramatically increases with the thickness decreasing in the range from 45 nm to 11 nm (Fig. 19(b)). Thus, the switching in the thicker thickness range is attributed to be extrinsic. Further investigation on the thickness dependence of the E_c of our PVDF homopolymer films in the thinner thickness range, i.e., from 45 nm to 11 nm, reveals that the relationship basically complies with the semi-empirical scaling law of the Janovec-Kay-Dunn (JKD) scaling, suggesting that the switching is neither extrinsic nor intrinsic in this range.

12. Conclusion

PVDF-based ferroelectric polymers have been studied for many years, and widely used in many electronic devices, for example, transducers, actuators, switches, and infrared sensors. Nonetheless, there are lots of novel properties that need to be explored. In this chapter, the LB method has been used for preparing ultrathin films of PVDF-based films. In addition, many special characteristics of these films have been generalized. These special properties include high tunability, huge electrocaloric effect, polarization switching, self-polarization, and enhanced electric properties in the artificial polymer multilayers. Besides these properties and potential applications, ferroelectric polymers possess many other advantages for applications. The advantages of this type of ferroelectric polymers include low cost, ease and flexibility of fabrication in different kinds of thin film forms, and resistance to degradation caused by strain. PVDF-based polymers are also more readily altered to conform to complex device requirements imposed by the environment, size, shape, physical

flexibility, reliability, durability, and other constraints. PVDF-based films can be easily patterned for integrated electronic applications.

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