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Effect of electric field on the structure and piezoelectric properties of poly(vinylidene fluoride) studied by density functional theory

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ABSTRACT

The geometry and piezoelectric properties of chain in PVDF under different electric fields are studied by density functional theory (DFT). The simulation gives optimized geometry of PVDF of α chain and β chain, with rotation angle around ±50° and arbitrary angle between 175° and 185° respectively. The energy barrier is about 16.16 kJ/mol in the chain transition from α chain to β chain, and the one of reverse transition is about 6.24 kJ/mol. The positive electric decreases the energies of α chain and β chain. There would be a critical positive electric field inducing the transition from α chain to β chain. Positive electric field increases dipole moment of the β chain and has few effects on mean molecular polarizibility. It is found that the change of geometry increases dipole moment and the change of electronic properties decrease dipole moment under positive electric field and the geometry plays an important role.

1. Introduction

Recently, poly (vinylidene fluoride) (PVDF) and its copolymers have been well studied because of their outstanding piezoelectricity and ferroelectricity [1–6]. The breakthrough came in the year of 1969. Kawai [1] discovered the strong piezoelectric effect in PVDF. Within the last decades, Bergman [2] and Wada [3] had found its pyroelectricity, and soon typical ferroelectric hysteresis loop were also found. Compared with conventional piezoelectric ceramic, PVDF has many unique features, such as excellent mechanical behavior, light weight, large strain without structure fatigue, corrosion resistance and easy forming. Many of them have been applied as sensor, transducer, actuator, and underwater acoustic transducer [4].

The fascinating characteristic of PVDF is polymorphism [4,5,7–9]. Presently, four crystalline forms of PVDF are known: β, α, γ and δ. β PVDF exhibits excellent electrical properties such as high piezoelectric constant and dielectric constant in these phases [10]. The chain in β PVDF has an all-trans (planar zigzag) conformation (TTT). Its C—F bond and C—H bond are polar, so the per monomer unit possesses a dipole moment (2.0D) perpendicular to the carbon backbones [11,12]. Additionally, in this crystal, all chains are oriented essentially parallel to the direction of dipoles, so the β PVDF has the highest spontaneous polarization in all the phases [8]. However the chain in α PVDF has a trans-gauche-trans-gauche′ conformation (TGTG') [4]. Its dipole moment of per monomer unit orients two directions: parallel (1.2D) and perpendicular (1.02D) to the carbon backbones [11], and the value is smaller than that in β PVDF. In α crystal, all chains are arranged anti-parallel, so α PVDF is non-polar. In these phases, α PVDF is the stable phase [13]. Transition between these phases may occur by mechanical or electrical treatments.

There are many literatures about the β PVDF fabrication. Generally, it is obtained by the transformation from α PVDF. For example, it can be prepared by simultaneous stretching and the static electric field poling [14,15], or firstly obtaining non-polar β PVDF by stretching α PVDF and then poling it [16]. Thus it can been seen that stretching and poling are critical processes in β PVDF fabrication. So it is important to investigate the effect of electric field on β PVDF. And the first step is to investigate the chain in PVDF.

In order to reveal the effect of electric field on the structure and electrical properties of β PVDF and the transformation between phases, many aspects must be taken into account including the cause of the stability in α PVDF, the energy barrier, the possibility of the transition between different phases, the effect of different electric field on the geometry and the dependence of property with according geometry etc. There have been some studies about these aspects in different simulation methods. Based on the energy-minimization method, Zhu et al. discussed the effect of electric field on intermolecular spacing, and confirmed that the origin of piezoelectricity in β PVDF is dimensional effect [17]. Wang et al. studied the internal rotation of chain in PVDF, effects of chain

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Table 1
The electronic Hamiltonian settings involved in the convergence tests.

Quality	Functional	SCF tolerance (Hartree)	Core treatment	Basis set	Orbital cutoff (Å)
Coarse	GGA-PBE	1×10^{-4}	All electron	DN	3.0 Å
Medium	GGA-PBE	1×10^{-5}	All electron	DND	3.3 Å
Customized	GGA-PBE	1×10^{-6}	All electron	DNP	3.7 Å

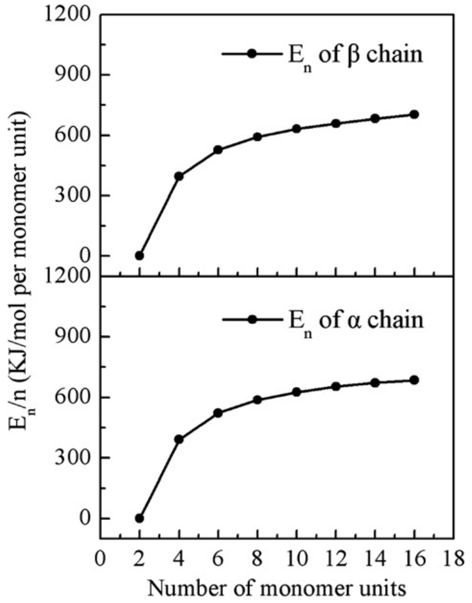

Fig. 1. Energy of per monomer unit of the chain in α and β PVDF vs. chain lengths.

length and defects on the piezoelectric properties and vibration spectra by density functional theory at B3PW91/6-31G (d) level [13]. Romas et al. used a self-consistent quantum molecular dynamics method to study the effect of electric field and reorientation on both α and β PVDF [18].

Although there have been a lot of theory studies about various properties in PVDF, few attentions are focused to the mechanism of the effect of electric field on the geometry of chain in PVDF and the piezoelectric properties. In this work, by the density functional theory, we attempted to study the effect of electric field on the geometry of chain in PVDF, and to discuss the piezoelectric properties with corresponding geometry. In addition, we investigated the possibility of phase transition from α PVDF of β PVDF in the view of energy.

2. Modeling

All of the calculations were carried out by DMol3 code package in Material Studio (MS) modeling 4.0. The chains in PVDF with different torsions and lengths were modeled in Materials Visualizer. Geometry optimization employed the density functional theory (DFT) method provided by DMol3 for two times, the first step with the "coarse" quality, the second one with the "customized" quality, which was based on the result of the first step. The electronic properties also employed the density functional theory (DFT) method provided by DMol3 with the "medium" quality. The electronic settings involved in the tests are shown in Table 1. The geometry optimization and electronic properties including density of state (DOS), dipole moment and Mulliken charge were obtained at Perdew-Burke-Ernzerh (PBE) of generalized gradient approximation (GGA) for the exchange correlation potentials, with the spin unrestricted approach. The molecular polarizability was obtained by semiempirical quantum mechanics method provided by VAMP code package.

The chains in α and β PVDF with different lengths were optimized according to methods stated above. The α chain and β chain containing 2-16 monomer units were examined, as shown in Fig. 1. It is found that both the energies converge to a nearly constant value in 10 monomer units. So the studies below are all carried out with the chain containing 10 monomer units. All average bond lengths and bond angles are determined by final optimized geometry. As shown in Table 2, the result of the geometry parameters agrees well with others' results from experiment and simulation. In this paper, the orientation of dipole moments from negative fluoride atoms to positive hydrogen atoms is supposed to be positive, and the electric field is defined as positive when it has the same direction with the dipole moment. All carbon atoms at the two ends of the chain are capped with hydrogen atoms.

3. Results and discussion

3.1. *Internal rotation and energy barrier*

In the present work, we study the internal rotation of the chain in PVDF with two monomer units. In theory [2], the chain in α PVDF has a trans-gauche-trans-gauche′ (TGTG') conformation, and its rotation angle is 60°. The chain in β PVDF has an all-trans (planar zigzag) conformation, and the rotation angle is 180°. Our results are a little different from these conformations. As shown in Fig. 2, the rotation angle of α chain is around ±50°, and in β chain there is a transition state in the path of internal rotation between 175° and 185° with very small energy barrier of around 0.11KJ/mol as shown in the inset which is even smaller than diatomic molecular zero point vibratory energy. So we indicate that the rotation angle of β chain is not a certain value but also an arbitrary angle between 175° and 185°. These results agree well with the values of ±55° and around 180° obtained by Wang et al. [13]. We also find that there is another saddle point in 0°, whereas the conformation with 0° torsion has not found in experiment now. This can be explained that the chain with 0° torsion can get across the energy barrier of 1.3KJ/mol (this barrier is very small, even smaller than diatomic molecular zero point vibratory energy) easily, and transforms to a much more stable state: α chain. So we think this saddle point is

Table 2
Parameters of bond lengths and bond angles of the chain in β PVDF.

Angle	δ (degree)	theory δ′ (degree)	Experiment δ″ (degree)	Bond	A (Å)	a′ (Å)	Experiment a″ (Å)
H–C–H	108°	116°	112°	C–C	1.53	1.52	1.54
C–C–C	117°	118°	112.5°	C–H	1.10	1.08	1.09
F–C–F	107°	110°	108°	C–F	1.38	1.35	1.40

* the values of δ and a are obtained in this work.
** the values of δ′ and a′ are from theory reference [17].
*** the values of δ″ and a″ are from theory reference [19].

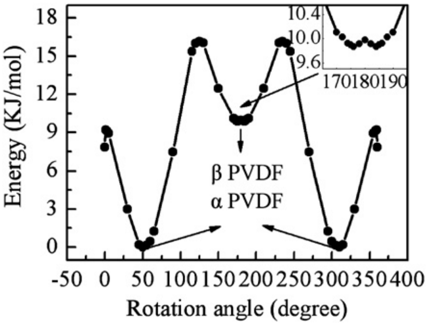

Fig. 2. Internal rotation energy curve of the chain in PVDF with two monomer units.

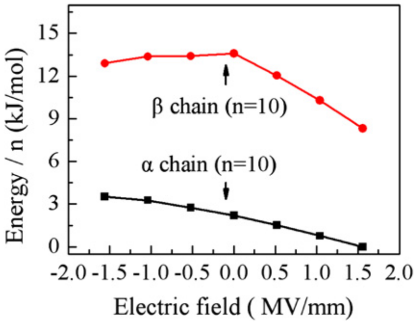

Fig. 4. Energy of per monomer unit of the chain in α and β PVDF with 10 monomer units vs. electric fields.Å.

not a stable state, and there is no corresponding conformation in experiment.

The energy barrier is important for the possibility of transition between different phases. So the energy barrier is also investigated, and the results are shown in Fig. 2. In the two monomer units PVDF chain, the energy barrier is about 16.16 kJ/mol in the chain transition from α PVDF to β PVDF, and the one of reverse transition is about 6.24 kJ/mol. This result also agrees well with the values of 16.3KJ/mol and 8.2KJ/mol obtained by Wang et al. [13].

3.2. *The effect of electric field on the energy of the chain in PVDF*

Firstly, we study the effect of electric field on the internal rotation and energy barrier of the chain in PVDF with two monomer units, and the results are shown in Fig. 3. It can be seen that under the positive electric field of 1.56 MV/mm, the internal rotation energy curve is similar with that under zero electric field, with around ±60° rotation angle of α chain and a transition state in the path of internal rotation between 176° and 184° with small energy barrier of around 0.11KJ/mol in β chain. While It also can be seen that under the negative electric field of −1.56 MV/mm, the figure of rotation angle is large different from the others, especially the rotation angle of β chain. The rotation angle of β chain is an arbitrary angle between 130° and 230° and in this extent there is a little larger energy barrier of 1.3KJ/mol than the others. Besides, it can be seen that under the electric field of −1.56 MV/mm, 0 MV/mm and 1.56 MV/mm, the energy barrier is about 22.98KJ/mol, 16.17KJ/mol and 10.18KJ/mol in the chain transition from α PVDF to β PVDF, respectively, and around 4.23KJ/mol, 6.25KJ/mol and 8.39KJ/mol in the chain transition from β PVDF to α PVDF, respectively. So we can conclude that under the positive electric field, the β chain can be transited from α chain much more easily than those under the zero and negative electric field because of the lowest energy barrier from α chain to β chain in these conditions. While under the positive electric field, the β chain is much more stable than those under the zero and negative electric field because of the largest energy barrier from β chain to α chain in these conditions.

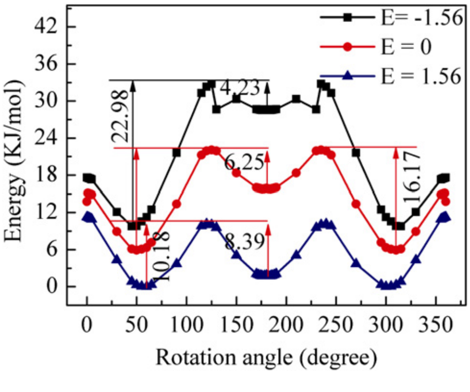

Fig. 3. Internal rotation energy curve of the chain in PVDF with two monomer units under the electric field of −1.56 MV/mm, 0 MV/mm and 1.56 MV/mm.

Considering the effect of chain lengths on the energy of the chain in PVDF, then we study the effect of electric field on the energy of α and β chain with ten-monomer-units respectively, and the results are shown in Fig. 4. It can be seen that the energy of α chain decreases with increasing electric field from −1.56 MV/mm to 1.56 MV/mm. The energy of β chain decreases with increasing positive electric field and negative electric field, while the energy under the positive electric field decreases much more sharply than the one under the negative electric field. And the decline of the curve of α chain is much slower than that of β chain under a positive electric field. So a positive electric field can decrease the energy of β chain more effectively. Moreover, as shown in Fig. 5, individual chains are parallel in β PVDF crystal while anti-parallel in α PVDF crystal. Based on above two points, we can make an analysis of the effect of electric field on the energy in α PVDF crystal and β PVDF crystal respectively. For researching this issue, we discuss the interaction between chains in crystal, and then the single chain in crystal under electric field. The interaction between chains is represented by the difference value between half of the energy of two chains and the energy of single chain. So we build two chains with 2 monomer units in accordance with the crystal structure, as shown in Fig. 6. By calculation, we get the difference value between the energies of per monomer unit of single chain under 0 MV/mm and 1.56 MV/mm is 6.98 kJ/mol, and the one of interaction between two chains under 0 MV/mm and 1.56 MV/mm is 0.82 kJ/mol. The effect of electric field on the energy of interaction between chains is much smaller than that on the energy of single chain. So we ignored the interaction of chains within the crystal when discussing PVDF under electric fields, and just make an analysis about the effect of electric field on the energy of single chain. According to the description of Fig. 4, when a positive electric field is applied to β PVDF crystal, the energy of chain (c) and chain (d) (in Fig. 5) decreases together. So we conclude that a positive electric field decreases the energy of β PVDF crystal largely. While the same positive electric field is applied to α PVDF crystal, it is

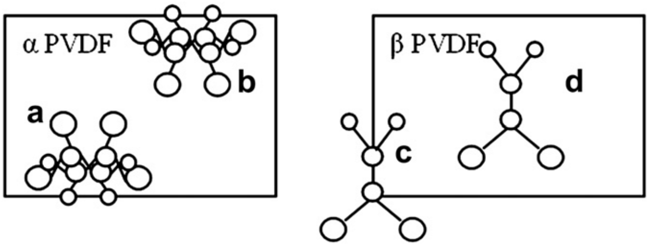

Fig. 5. The sketch maps of α and β PVDF crystal.

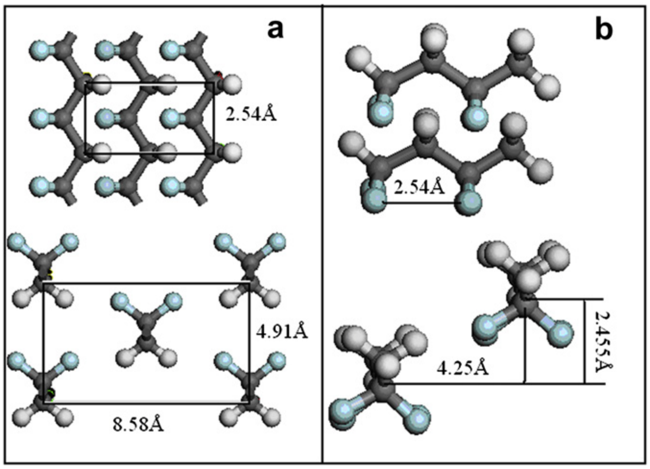

Fig. 6. (a) Models of two β chains with 2 monomer units (b) Sketch map of β PVDF crystal.

equivalent to apply a positive electric field to chain (b) but a negative electric field to chain (a) because of the anti-parallel collocation in α PVDF crystal, as shown in Fig. 5. So the energy of chain (b) in Fig. 5 decreases and chain (a) in Fig. 5 increases. So we conclude that a positive electric field has little impact on the energy of α PVDF crystal. Based on explanation above, we infer that when a strong electric field is applied, the energy of β PVDF crystal will be probably lower than that of α PVDF crystal. So β PVDF crystal will achieve preferentially under a strong positive electric field. And there would be a critical electric field between α PVDF crystal and β PVDF crystal transition. This conclusion is consistent with the results reported by P.D. Southgate [20], in which α phase PVDF (6 μm) by poling on the corona point changes of 10 kV can transform to an approximately β phase. D.K. Das Gupta and K. Doughty [21] also got the similar results from the experiment that the changes in molecular conformation of 16 μm thick films of PVDF due to corona charging source at voltages of up to 6 kV at room temperature is observed. The poling electric field in the experiment is lower than that in this paper, but it is reasonable. Because in the experiment the impurity, defect and dimension all can make the poling electric field decrease heavily.

3.3. The effect of electric field on the geometry of the chain in β PVDF

We also investigate the impact of electric field on the geometry of the chain in β PVDF with ten-monomer-units. As shown in Fig. 7 (a) and (b) are the theoretical ideal chains in β PVDF with a classical planar zigzag conformation in cross direction and longitudinal direction respectively, (c) and (d) are the optimized geometries of chain without electric field. It can be seen that the chain is bent in cross direction and distorted in longitudinal direction compared with the theoretical chain. This difference of geometry, especially for long chain, can be explained by the steric effect and Coulomb repulsion as follows. The volume and charge of F atom is larger than H atom, so the repulsion between F atoms is larger than those of H atoms. The chain gets balanced through increasing the distance between F atoms and decreasing the distance between H atoms. It results in bend in cross direction and distortion in longitudinal direction. When a positive electric field is applied to β chain, the optimized geometry can be seen in (e) and (f). The chain becomes slightly straight, and the torsion eases obviously. It also can be found that F atoms and H atoms are arranged more centralized. This result can be attributed to the orientation of the chain with the positive electric field. The repulsion between F—F atoms along the direction of the chain is weakened. So the chain becomes straight and less distorted.

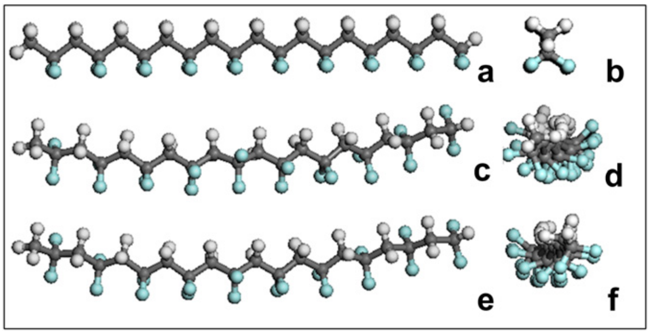

Fig. 7. Geometry of the β chain with 10 monomer units: (a) and (b) are the theoretical ideal chains, (c) and (d) are the optimized chains, (e) and (f) are the optimized chains under the positive electric field of 1.56 MV/mm; (a), (c) and (e) are in cross direction, (b), (d) and (f) are in longitudinal direction.

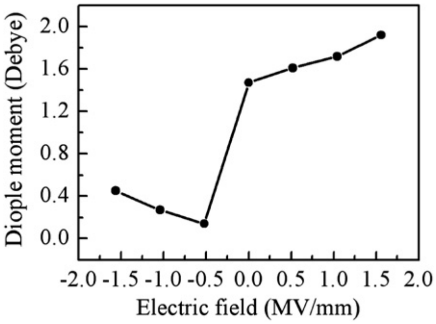

Fig. 8. Dipole moment of the β chain with 10 monomer units vs. electric fields.

3.4. The effect of electric field on dipole moment and molecular polarizability

According to the geometry of β chain with different electric fields, we studied the effect of electric field on dipole moment of β chain. As shown in Fig. 7 (a) and (b), the dipole moment of the theoretical ideal chain originates from the dipole moment of C—F bonds and C—H bonds, and its direction is vertical to the horizontal direction. While as shown in Fig. 7 (c) and (d), final optimized chain is bent and distorted. In this situation, the horizontal component of the dipole moment of C—F and C—H bonds are totally counteractive with each other, and the longitudinal component are less than those of theoretical ideal chain. The total dipole moment, which is equal to the longitudinal component, decreases compared with the

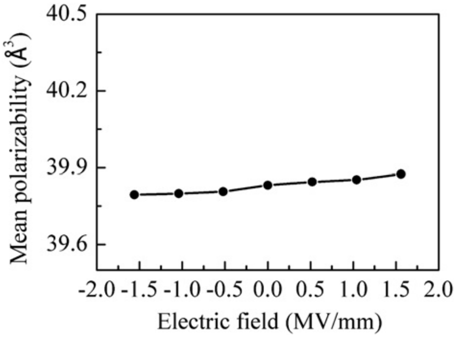

Fig. 9. The molecular mean polarizability of the β chain with 10 monomer units vs. electric fields.

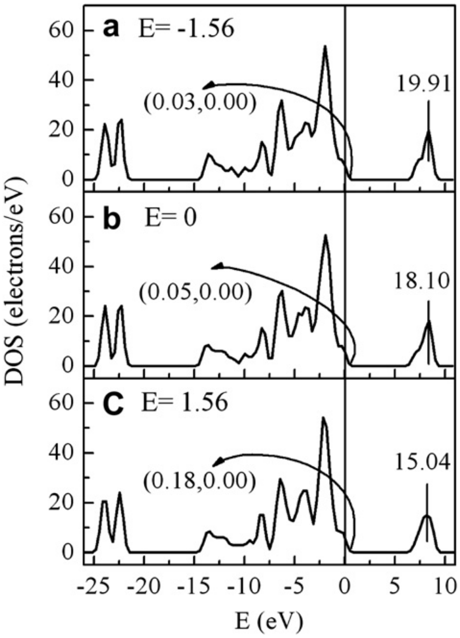

Fig. 10. Total density of state of the β chain with 10 monomer units under different electric fields: (a) −1.56 MV/mm, (b) 0 MV/mm, (c) 1.56 MV/mm.

ideal chain's dipole moment. It can be illustrated from Fig. 7 (e) and (f) that when a positive electric field is applied to the chain, the chain becomes straighter and less distorted than those of chains in Fig. 7 (c) and (d). So the longitudinal component becomes large, which results in the increase of the total dipole moment of the chain. Based analysis above, it is indicated that the dipole moment of β chain would increase with a positive electric field.

Besides, we calculate the dependence of dipole moment with different electric fields to validate our conjecture above. The calculated dipole moment of the β chain without electric field per monomer (1.5Debye) is found to be in good agreement with other studies [22,23]. And in Fig. 8, we can see that the negative electric field nearly makes the dipole moment of the chain disappear, while the positive electric field augments its dipole moment. So we can conclude that the dipole moment increases with the increase of the positive electric field. This result agrees well with our conjecture.

In Fig. 9, the dependence of molecular mean polarizabilities under different electric fields is shown. It is found that the molecular mean polarizabilities increase slightly with the electric field increasing. But the electric field dose not seems to produce a significant effect on the molecular mean polarizability. And the value of the molecular mean polarizability is from 39.79 to 39.88 $\mathring{A}^3$.

3.5. The effect of electric field on the density of state (DOS) and Mulliken charge of the chain in β PVDF

For further investigation about the effect of electric field on dipole moment of the chain in β PVDF, we study the electronic structures. Total density of state (TDOS) under the electric field of −1.56 MV/mm, 0 MV/mm and 1.56 MV/mm are shown in Fig. 10. It can be seen that the value of energy gap is 5.00 eV, 4.66 eV, and 4.66 eV corresponding to −1.56 MV/mm, 0 MV/mm and 1.56 MV/mm, respectively. So we conclude that the insulating property of the chain under the negative electric field is better than others. It also can be seen that from −1.56 MV/mm to 1.56 MV/mm the whole valence bands move towards the Fermi energy, which leads to more electrons appear around Fermi face under the electric field of 1.56 MV/mm. But the difference of these data isn't obvious enough to study the change of dipole moment. So we examined the partial density of state (PDOS) and the results are displayed in Fig. 11. It shows that the lower valence band of TDOS is composed predominantly of F-2s, and the upper valence bands are composed predominantly of F-2p in the energy range from about −3.30 eV to 0.60 eV. The upper valence band also consists of F-2p in the energy range from −7.30 eV to −3.28 eV, which shows a hybridization character with C_F-2p, and H-1s in the energy range from −14.60 eV to −7.27 eV, which shows a hybridization character with C_H-2s.

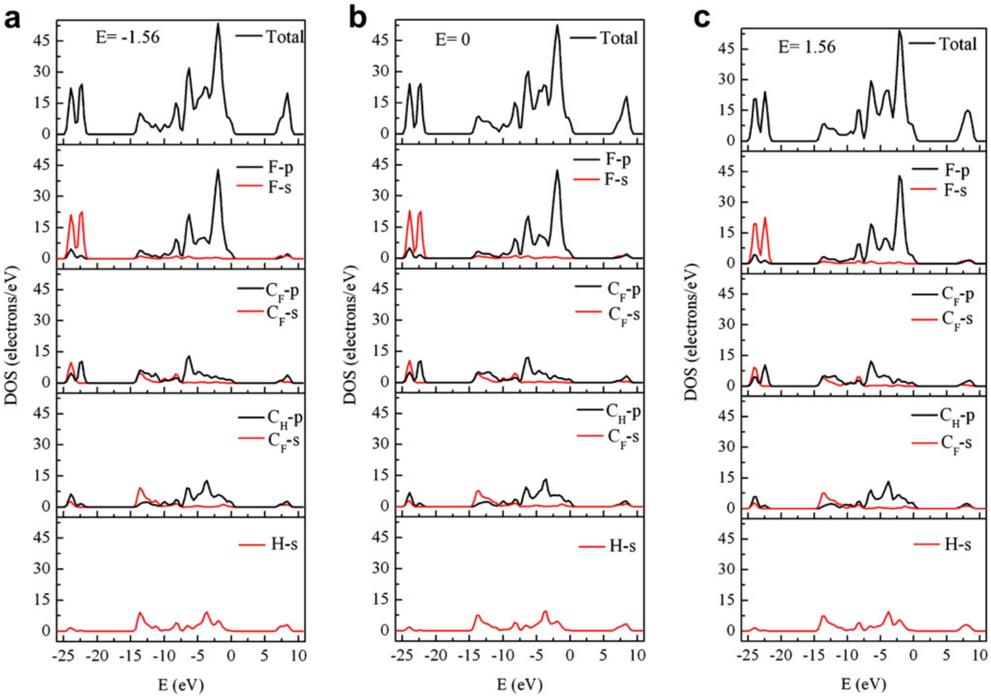

Fig. 11. Partial density of state of the β chain with 10 monomer units under different electric fields: (a) −1.56 MV/mm, (b) 0 MV/mm, (c) 1.56 MV/mm.

Table 3
Values of the strongest hybridization peak of different atom states of the β chain in Fig. 11 under different electric fields.

Atom state	Values of hybridization peaks under *E*		
	$E = -1.56$ MV/mm	$E = 0$ MV/mm.	$E = 1.56$ MV/mm
F-2p	21.30	20.20	19.32
C_F-2p	13.04	12.12	12.06
Difference between F-2p and C_F-2p	8.26	8.08	7.26
H-1s	9.17	7.61	7.57
C_H-2s	9.40	7.40	7.32
Difference between H-1s and C_H-2s	0.23	0.21	0.25

E- represents electric field; CF- represents the C atom bonded with F atom; CH - represents the C atom bonded with H atom.

As we mentioned above, the dipole moment of the chain originates from the dipole moment of C—F bonds and C—H bonds. So the value of dipole moment is determined by the polarity of bonds. The most efficient way to improve the polarity of the bond is to enhance the difference of electronegativity of the atoms attaching to a polar bond, and the difference of electronegativity of the atoms is visually represented by the difference of the strength of hybridization peaks. The values of the strongest hybridization peak of F-2p, C_F-2p, H-1s and C_H-2s under different electric fields are shown in Table 3. It is found that the strongest hybridization peaks under the negative electric field are all higher than those under zero electric field and the positive electric field, which suggesting that C—F bonds and C—H bonds under the negative electric field are stronger than those of others. The stronger the hybridization is, the more stable the chain is. But this is opposite to our investigation that the energy of the chain with a positive electric field is the lowest in part 3. 2. Besides, it also can be seen in Table 3 that the difference between hybridization peaks of atom states engaged in bonding under the negative electric field are still larger than others, which would result in the enhancement of the polarity of the polar bonds. So the dipole moment of the chain under the negative electric field would increase, which is different from our previous study that the dipole moment of the chain under the negative electric field is the smallest in part 3. 4. This is an interesting feature.

In order to characterize the difference of electronegativity of the atoms exactly, we integrate the PDOS curve of atom states (concluding F-2s, F-2p, CF-2s, CF-2p, H-1s, CH-2s, CH-2p) in their respective hybridization region of both valence bands to get the number of electrons engaged in bonding. The values are shown in Table 4. It can be seen that the number of electrons of F atoms engaged in bonding under the negative electric field are much more than those under zero and positive electric field, while those of CF atoms are much less under the negative electric field than others. The difference between the numbers of electrons of F and CF atoms engaged in bonding under the negative electric field are larger than others. Although the difference between the numbers of electrons of H and CH atoms engaged in bonding are smaller under the negative electric field than others, they don't lead the predominance compared with those between F and CF atoms. So the dipole moment increases. This conclusion is the same to the result from Table 3.

Table 4
Integral values of hybridization peaks of different atom states of the β chain in Fig. 11 under different electric fields.

Atom state	Integral values of hybridization peaks under *E*		
	$E = -1.56$ MV/mm	$E = 0$ MV/mm	$E = 1.56$ MV/mm
F-2p	79.35	77.97	77.93
C_F-2p	43.72	44.05	44.37
Difference between F-2p and C_F-2p	35.63	33.92	33.56
H-1s	32.26	31.51	30.51
C_H-2s	62.75	62.98	62.78
Difference between H-1s and C_H-2s	30.49	31.47	32.27

E- represents electric field; CF- represents the C atom bonded with F atom; CH - represents the C atom bonded with H atom.

Table 5
Mulliken charge of the atoms of β chain under different electric fields.

Atom	Mulliken charges with different E (e/Å^3)		
	$E = -1.56$ MV/mm	$E = 0$ MV/mm	$E = 1.56$ MV/mm
F	−0.319	−0.316	−0.321
C_F	0.641	0.637	0.632
C_H	−0.444	−0.437	−0.437
H	0.200	0.196	0.200

E- represents electric field; CF- represents the C atom bonded with F atom; CH - represents the C atom bonded with H atom.

For further investigation about the electronegativity of atoms, we calculated the Mulliken charges of each atom of the β chain under different electric fields. The values are shown in Table 5. It can be seen that the absolute value of the Mulliken charge of C_H and C_F under the negative electric field are 0.007 e/Å^3 and 0.004 e/Å^3 respectively bigger than that under the zero electric field and 0.007 e/Å^3 and 0.009 e/Å^3 than that respectively under the positive electric field. Although the absolute value of Mulliken charge of F under the negative electric field are 0.002 e/Å^3 smaller than that under the positive electric field, the difference is very small compared with the difference between C_F. So we consider that the difference value of Mulliken charge of F plays an slightly important role on the change of dipole moment and those of C_H and C_F play an predominant role.

As we know, the dipole moment is the product of absolute value of the charge and distance between atoms. We examined the bond lengths and found there are few changes. So we can infer that the increase of the absolute value of charge can make the dipole moment increase. It agrees well with our analysis above in this part.

3.6. Who play an important role in the change of dipole moment of the chain in β PVDF under the positive electric field?

According discussion above, under the negative electric field, the dipole moment of the β chain with 10 monomer units would increase. But it is obviously opposite to the analysis in the part 3.4. So we can make a conjecture that under a positive electric field the dipole moment of β chain with ten monomer units would be affected by two points: one is the normalization of the geometry and the other is the change of electronic properties. In this case, the normalization of the geometry will enhance the dipole moment while the electronic properties will weaken the dipole moment. But the geometry leads dominant role in the change of dipole moment. More details about how these two factors affect on the change of dipole moment will be further studied in next step.

4. Conclusions

We used the density functional theory (DFT) to calculate the geometry and piezoelectric properties under different electric fields. The following are conclusions and remarks derived from our theoretical calculations.

(1) The rotation angle of α chain is around ±50° and that of β chain is an arbitrary angle between 175° and 185°. In the chain with

two monomer units, the energy barrier is about 16.16 kJ/mol in the chain transition from α PVDF to β PVDF, and the one of reverse transition is about 6.24 kJ/mol.

(2) β chain can be prepared more easily under the positive electric field and it can be much more stable. The positive electric field can decrease the energy of both α chain and β chain. And the energy of β chain decreases more effectively than that of α chain. There would be a critical electric field between α PVDF and β PVDF.

(3) The positive electric field can make the β chain slightly straight, and the torsion eases obviously compared with the chain without electric field.

(4) The positive electric field can increase the dipole moment of β chain. Both the negative and positive electric fields do not seem to produce a significant effect on the molecular polarizability.

(5) The positive electric field weakens the dipole moment of β chain through investigating electronic properties (TDOS, PDOS and Mulliken charge). That is opposite to the conclusion in part 3. 4.

(6) Under the positive electric field, dipole moment is affected both by the geometry and electronic electrons. They have the opposite effect on the dipole moment and the geometry plays an important role.

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