

Density Functional Theory Simulation of PVDF Transition in Electric Field Polarization

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Abstract—The molecular model of PVDF is established by the calculation method of density functional theory(DFT). A process of applying an electric field of different magnitude to PVDF to cause a phase transition was simulated. The transformation of the molecular chain of PVDF molecules under the electric field strength below 0.05Ha was studied in detail. It is found that the main role in the transformation process is the transformation of the carbon skeleton. Then we calculated the dipole moment and average molecular polarizability of the PVDF molecular chain under different structures. The results showed the dipole moment increases from 7.6Debye to 9.9Debye with the structure of α PVDF to β PVDF, the mean polarizability also increased from 39.5 to 40.3. These calculations provide theoretical calculations for the study of PVDF and demonstrate the effect of electric field polarization on the production of β PVDF.

Keywords—DFT; PVDF; polarization

I. INTRODUCTION

Due to its special structure, Polyvinylidene fluoride(PVDF) has excellent piezoelectric properties. PVDF has five crystal forms, namely α , β , γ , δ , ϵ [1,2]. β phase has outstanding piezoelectric properties in these structures. The α phase can be converted into a polar β phase by mechanical stretching[3], polarization[4], etc, and then the β PVDF applied to the desired device for application[5]. Nowadays, the most common way to convert the PVDF of the α phase structure into the β phase is the stretching method and the electrode method. Compared with the electrode method, the stretching method is simple and practical, and it is a common method for industrial production and commercial film formation. But the disadvantages such as its transformation low degree and difficulty in control, the electrode polarization method is more efficient[6]. The electrodeposition method is widely used in the laboratory stage, and the conversion efficiency can be almost 100%, but the disadvantage is high cost. And pay attention to the problem of electric field breakdown, ensure that the voltage is not too large, and prevent the film from penetrating.

II. SIMULATION METHODS

The research on PVDF is not only a lot of experiments to explore, in order to save the experiment consumption and save

time, after the computer matures, the research on simulation calculation is especially prominent, and the accuracy and credibility of the calculation simulation are more and more. It has been recognized by a large number of research scholars[6,7]. The theoretical calculation of the applied simulation predicts and theoretically proves the performance of the material, which has become an important road in the current research approach. In this paper, the molecular calculation method of density functional theory is used to simulate the electrical properties of PVDF piezoelectric film. The structure of PVDF is analyzed from the atomic point of view, which proves the particularity of PVDF structure. And prove the cause of its piezoelectricity; further deep analysis at the electron angle, research and study the essential factors of piezoelectricity. DFT(density functional theory) is the E_0 and other properties of the calculation system starting from. In 1965, Kohn and Sham gave a method for constructing energy from electron density, it is Kohn-Sham equation[8]:

$$E_v[\rho] = -\frac{1}{2} \sum_i \langle \theta_i^{KS} | \nabla_i^2 | \theta_i^{KS} \rangle - \sum_\alpha Z_\alpha \int \frac{\sum_i |\theta_i^{KS}|^2}{r_{i\alpha}} d\vec{r} + \frac{1}{2} \iint \frac{\sum_i |\theta_i^{KS}(1)|^2 \rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + E_{xc}[\rho] \quad (1)$$

The first term on the right side of the equation is the kinetic energy of electrons, the second term is the attraction of electrons and electrons, and the third term is the Coulomb interaction of charges. The fourth item $E_{xc}[\rho]$ is exchange related energy. ρ is the electron density in the energy

formula. $\rho = \sum_{i=1}^N |\theta_i^{KS}|^2$, θ_i^{KS} is the K-S track. Based on the theory, after the atomic model is established, the electric field is polarized, and the atomic model after polarization is structurally analyzed and the piezoelectric constants of each structure are calculated.

In order to phase-transform PVDF by electrodeposition method, we theoretically calculate and analyze the process of electrode polarization by establishing PVDF atom model[9]. The electrical performance index under different structures is calculated. First, PVDF is an organic polymer, the C-C-C-C bond has a dihedral angle of 60° , and an atomic model of α -phase PVDF of ten repeating units is established, and the COMPASS force field is applied thereto, using local density approximation (LDA, Local Density Approximation)[10]. Generalized Gradient Approximation (GGA) for structural optimization[11].

The total potential of the COMPASS force field can be written as the sum of the energy of the bond form and the non-bond form. The bond form also includes the diagonal and non-diagonal cross-coupling form[8].

$$\begin{aligned}
 E_{pot} = & \sum_b [k_2(b-b_0)^2 + k_3(b-b_0)^3 + k_4(b-b_0)^4] \\
 & + \sum_\theta [k_2(\theta-\theta_0)^2 + k_3(\theta-\theta_0)^3 + k_4(\theta-\theta_0)^4] \\
 & + \sum_\phi [k_1(1-\cos\phi) + k_2(1-\cos 2\phi) + k_3(1-\cos 3\phi)] \\
 & + \sum_x k_2 \chi^2 + \sum_{b,b'} k(b-b_0)(b'-b'_0) \\
 & + \sum_{b,\theta} k(b-b_0)(\theta-\theta_0) + \sum_{b,\phi} (b-b_0)(k_1 \cos\phi + k_2 \cos 2\phi + k_3 \cos 3\phi) \\
 & + \sum_{\theta,\phi} (\theta-\theta_0)(k_1 \cos\phi + k_2 \cos 2\phi + k_3 \cos 3\phi) \\
 & + \sum_{b,\theta} k(\theta-\theta_0)(\theta'-\theta'_0) + \sum_{\theta,\theta'} k(\theta-\theta_0)(\theta'-\theta'_0) \cos\phi
 \end{aligned} \quad (2)$$

For non-key forms, the electrostatic interactions described by the Coulomb terms are expressed as:

$$E_{clc} = \sum_{i>j} \frac{q_i q_j}{r_{ij}} \quad (3)$$

The interaction described by the van der Waals term is expressed as:

$$E_{vdw} = \sum E_{ij} \left[2 \left(\frac{r_{ij}^0}{r_{ij}} \right)^9 - 3 \left(\frac{r_{ij}^0}{r_{ij}} \right)^6 \right] \quad (4)$$

The electron density gradient function satisfies the following functional equation:

$$E_{XC}^{GGA} [\rho^\alpha, \rho^\beta] = \int f [\rho^\alpha(\vec{r}), \rho^\beta(\vec{r}), \nabla \rho^\alpha(\vec{r}), \nabla \rho^\beta(\vec{r})] d\vec{r} \quad (5)$$

The general formula of the density on which the kinetic energy is based is:

$$\tau_i(\vec{r}) = \sum_i^{\text{occup}} \frac{1}{2} |\nabla \psi_i(\vec{r})|^2 \quad (6)$$

The suitable force field and optimization method are the first guarantee to ensure the correctness of the established model. Secondly, after selecting a series of parameters such as cutoff energy and cutoff distance, the model is optimized to obtain the standard model of the optimized structure. The calculation provides the basis of the model[12]. Applying different electrostatic fields to the established α -phase model, simulating the phase transformation process. As the applied electric field strength increases, the α phase begins to transform into the β phase structure. But when the electric field is too large, the bond between the models it is broken by the electric field force[13]. Electric field polarization is an important factor in the transformation of α PVDF to β PVDF. By applying electric field forces of different sizes, the molecular structure of PVDF will change accordingly. It is necessary to discuss the performance of the molecular structure morphology after the transition. In this article, the process of phase change in electric field polarization is carefully studied. And calculated the energy, structure, polarization state, etc. that occurred during the transformation process.

The models shown in Figure 1 are created separately. Established a model of two structures of PVDF, (a) and (b) are the α PVDF, (c) and (d) are the β PVDF, the light gray atoms are H atoms, the dark gray atoms are C atoms, and the light blue atoms represent F atoms. Observing the molecular model from different angles, in order to understand the accuracy of the atomic model more accurately, we have carried out detailed calculations on the information such as the bond length and corner angle of the atom. List a series of parameters of α PVDF in Table 1. Through the comparison of these data, you can get an accurate model structure. The chain in α PVDF has a trans-gauche-trans-gauche' conformation (TGTC'), all chains are arranged anti-parallel. Different force fields and optimization methods will result in different parameters of the atomic structure, but this does not affect the accuracy of the model.

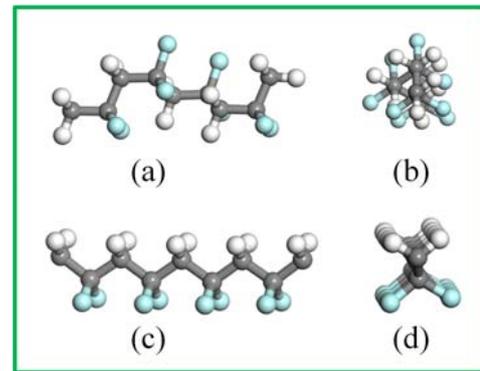


FIGURE 1. THESE ARE THE A PHASE AND B PHASE PVDF MODEL DIAGRAM.(A) AND (B) ARE THE HORIZONTAL AND VERTICAL STRUCTURAL DIAGRAMS OF A PVDF, RESPECTIVELY. (C) AND (D) ARE THE STRUCTURE DIAGRAM OF DIFFERENT POSITIONS OF β PVDF.

TABLE I. BOND LENGTH, BOND ANGLE AND TORSION ANGLE OF A-PVDF

	Optimized values(Å and °)		Values from X-ray diffraction[14]
	Before	Later	
Bond length			
C1-C4=C2-C3	1.542	1.531	1.54
C2-F1=C2-F2	1.491	1.391	1.34
C1-H1=C1-H2	1.141	1.099	1.09
Bond angle			
C2-C3-C4	112.105	116.901	116.50
C1-C4-F4	107.659	108.662	109.00
Torsion angle			
C1-C2-C3-C4	174.536	179.440	179.00

β PVDF is established for the purpose of the later contrast transformation. First establish an accurate standard model structure, and then observe the difference between the transformed model and the standard model. The chain in β PVDF has an all-trans (planar zigzag) conformation(TTTT). Its C-F bond and C-H bond are polar, such a polar structure is the focus of many research scholars.

Theoretically, the dihedral angle between carbon and carbon in the α phase structure is 60° , and the dihedral angle between the carbon-carbon bonds in the β phase structure is 180° . Due to the interaction between atoms and the interaction between molecules, whether it is the simulated optimized model or the actual real structure, the angle is not exactly an integer. The process of the α phase structure in the transition to the β phase is the twisting of the carbon-carbon bond and the ordered arrangement of the hydrogen atom and the fluorine atom. There is a transition state δ phase during the transition from α phase structure to β phase. Based on this theoretical basis, we established the schematic diagram of the atom as shown in figure 1. A series of basic parameters such as bond length and bond Angle were measured. Local density approximation (LDA, Local Density Approximation) and Generalized Gradient Approximation (GGA) used to optimize the structure of α -PVDF and β -PVDF. The basic parameters before and after optimization of the two structures are listed in table 1 and table 2. In order to ensure the correctness of the established model, it is also compared with the data in the literature and experiments, and listed in the table. Apply an electric field to α -PVDF, this field strength are 0.01Ha, 0.02Ha, 0.03Ha, 0.04Ha, 0.05Ha, respectively, and then observe the molecular structure of the atoms under different electric fields.

TABLE II. BOND LENGTH, BOND ANGLE AND TORSION ANGLE OF B-PVDF

	Optimized values(Å and °)		Literature Data[13-15]
	Before	Later	
Bond length			
C1-C4=C2-C3	1.512	1.515	1.53
C2-F1=C2-F2	1.364	1.380	1.38
C1-H1=C1-H2	1.102	1.101	1.10
Bond angle			
C2-C3-C4	116.831	116.900	117.00
C1-C4-F4	109.586	109.483	107.00
Torsion angle			
C1-C2-C3-C4	179.663	179.120	179.00

III. RESULTS AND DISCUSSION

The process of electric field polarization transformation of PVDF is studied in detail. Observing the transformation of molecular structure under different electric fields by applying different magnitudes of electric field to α phase PVDF. A series of structural parameters such as bond length and bond angle under different electric fields are calculated. Through calculation and comparison, in the process of electric field polarization, the bond length between atoms does not change significantly(such as C-C,C-H,C-F,etc),but the torsion angle of carbon-carbon bond has a significant change, as the electric field increases, the torsion angle also increases. The torsion angle and the magnitude of the applied electric field are plotted in Figure 2.Through the structural change diagram, the α phase to β phase transition can also be clearly and intuitively seen.

During the process of electric field polarization, it was found that during the phase transition, the hydrogen atom and the fluorine atom were only changed in position, but the distance from the carbon atom did not change. In other words, the bond lengths of the C-H and C-F keys have not changed. A substantial role in the transformation process is the twist of the C-C bond. For the change of the torsion angle of the C-C bond, we have made further research to theoretically calculate the energy barrier change between α phase and β phase.

A. Polarization Transformation

Applying an electric field in the positive X direction to α PVDF, its polarization direction is the positive X direction. Because the α PVDF has a TGTG' conformation, so if α PVDF wants to convert to β phase, after applying the electric field in the positive direction of X, the hydrogen atoms need to rotate to the right, and the fluorine atoms all rotate to the left.

As shown in Fig.2, as the electric field is polarized, the hydrogen atoms rotate in the direction of the electric field and the fluorine atoms rotate against the electric field. In order to observe the process of PVDF phase transition more clearly, the structure under different electric fields is also listed in the picture. It can be found that when the applied electric field strength is about 0.04H, α phase will all be converted to β phase. When 0.05Ha, it is found that the structure is still complete β phase, but the molecular structure is destroyed and the atomic bond is broken. This is because the electric field is too strong, beyond the range that the atomic bond can withstand.

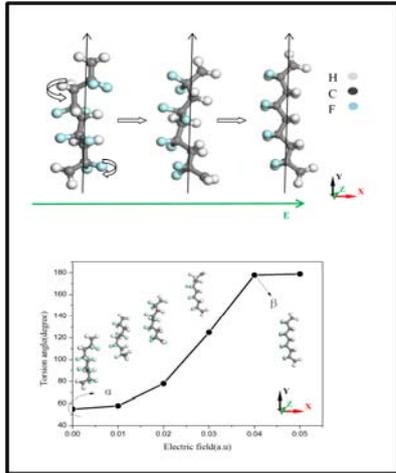


FIGURE II. ELECTRIC FIELD POLARIZATION STRUCTURE TRANSITION DIAGRAM

B. Torsional and Phase Transition

For the transformation process from α PVDF to β PVDF, before we found out that C-C-C-C twisting plays a major role. In the following calculations, we calculated the relationship between the internal rotation angle and the energy barrier, and studied the internal rotation energy of the carbon bond during the transformation. The result is shown in Figure 3.

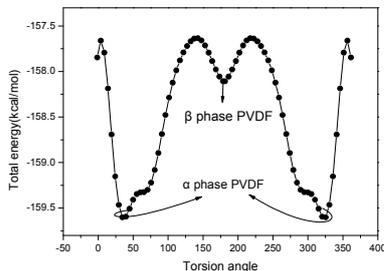


FIGURE III. INTERNAL ROTATION ENERGY CURVE OF THE CHAIN IN PVDF

There are two distinct troughs between 0° and 180° . From the lowest energy principle, it can be concluded that these two extreme points are stable phase structures. The extreme point existing around 40° is the α phase, and the extreme point existing around 180° is the β phase structure. Calculate the energy difference between the two troughs to determine the energy change of the α phase to the β phase in 6.27 kJ/mol. The calculation result mentioned in the literature of Weijia Wang[13] is 6.24 kJ/mol. The method of generalized gradient approximation adopted by Weijia Wang is the same as this paper. The energy difference between the α phase and the β phase is obtained by calculating the energy barrier size during the conversion process. It is proved that the α phase is converted into the β phase.

C. Moment of Dipole

Based on this theoretical basis, we establish different models for carbon-carbon bonds between 60° and 180° as structural models under different electric fields. The electrical properties of each model are tested to obtain the relationship between the model and the average polarizability and dipole moment under different carbon-carbon bond states. We can be seen from the results of the calculation (figure.4), as the structure of C-C-C changes, the dipole moment and the molecular polarizability of the molecule increase. The dipole moment is about 7.7 Debye at α structure, with structural changes the size of the dipole moment is similar to linear growth. During the transition from the α PVDF to β PVDF structure, the dipole moment is increased by approximately 2.3 Debye. Although the value does not change much, but from the perspective of the atom, the change is sufficient [16]. It is precisely because of the change of the dipole moment that the piezoelectric properties of PVDF are changed.

In addition to the calculation of the dipole, we also simulated the average molecular polarizability. As the torsion angle increases, the average molecular polarizability also increases, with a value of around 40. This is similar to the value calculated in the literature published by Weijia Wang [13] on the polymer, which can determine the accuracy of the settlement. The mean molecular polarizability also increased from 39.5 to 40.3.

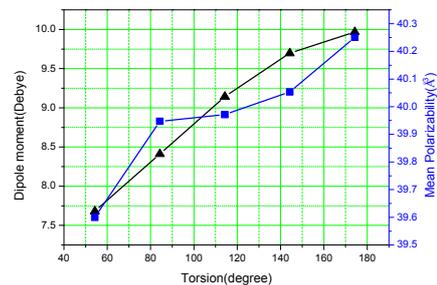


FIGURE IV. DIPOLE MOMENT AND AVERAGE MOLECULAR POLARIZABILITY UNDER DIFFERENT STRUCTURES

IV. CONCLUSIONS

Whether it is dipole moment or molecular polarizability, both are representations of PVDF has been Polarized.

This paper theoretically calculates and studies the causes of piezoelectric properties of PVDF from a molecular perspective. We have carefully studied the transition process under different electric field strengths. If the electric field strength is higher than 0.04 Ha, the molecular chain will be destroyed under strong electric field. During the transformation process, we found that the main role of PVDF phase change is that the carbon skeleton is transformed, and the hydrogen and fluorine atoms are arranged in an orderly manner. Then we calculated the dipole and polarizability of PVDF molecular chains under different structures. Microstructure determines macro performance. Our calculations provide some theoretical

calculations for the study of PVDF piezoelectric properties, and some research has been done on the application of PVDF electrical properties.

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REFERENCES

- [1] Lovinger, Andrew J, "Ferroelectric Polymers." *Science* 220.4602(1983):1115-1121.
- [2] Karasawa, Naoki, and W. A. I. Goddard . "Force fields, structures, and properties of poly(vinylidene fluoride) crystals." *Macromolecules* 25.26(1992):7268-7281.
- [3] Sencadas, V., R. Gregorio , and S. Lanceros-Mendez . " α to β Phase Transformation and Microstructural Changes of PVDF Films Induced by Uniaxial Stretch." *Journal of Macromolecular Science, Part B* 48.3(2009):514-525.
- [4] Davis G T , Mckinney J E , Broadhurst M G , et al. Electric - field - induced phase changes in poly(vinylidene fluoride)[J]. *Journal of Applied Physics*, 1978, 49(10):4998-0.
- [5] Bystrov, V. S . Molecular modeling and molecular dynamics simulation of the polarization switching phenomena in the ferroelectric polymers PVDF at the nanoscale[J]. *Physica B: Condensed Matter*, 2014, 432:21-25.
- [6] Zhu G D, Zeng Z G , Zhang L , et al. Piezoelectricity in β -phase PVDF crystals: A molecular simulation study[J]. *Computational Materials Science*, 2008, 44(2):224-229.
- [7] Ramos M , Correia H M G , S. Lanceros-Méndez. Atomistic modelling of processes involved in poling of PVDF[J]. *Computational Materials Science*, 2005, 33(1-3):0-236.
- [8] Tuckerman M. *Statistical mechanics and molecular simulations*[J]. Oxford University Press Oxford, 2010.
- [9] Bystrov V S, Bystrova N K , Paramonova E V , et al. First principle calculations of molecular polarization switching in P(VDF-TrFE) ferroelectric thin Langmuir-Blodgett films[J]. *Journal of Physics: Condensed Matter*, 2007, 19(45):456210.
- [10] Mann C , Yang Q K , Fuchs F , et al. Quantum Cascade lasers for the Mid-Infrared Spectral Range: Devices and Applications[J]. *Advances in Solid State Physics*, 2003, 43:351-368.
- [11] Perdew J P , Burke K, Ernzerhof M . Generalized Gradient Approximation Made Simple[J]. *Physical Review Letters*, 1996, 77(18):3865-3868.
- [12] Duan C G , Mei W N, Hardy J R , et al. Comparison of the theoretical and experimental band structure of poly(vinylidene fluoride) crystal[J]. *Europhysics Letters (EPL)*, 2003, 61(1):81-87.
- [13] Wang Z Y , Fan H Q, Su K H , et al. Structure and piezoelectric properties of poly(vinylidene fluoride) studied by density functional theory[J]. *Polymer*, 2006, 47(23):7988-7996
- [14] Hasegawa R, Takahashi Y , Chatani Y , et al. Crystal Structures of Three Crystalline Forms of Poly(vinylidene fluoride)[J]. *Polymer Journal*, 1972, 3(5):600-610.
- [15] Zhu G D, Zhang J H , Luo X Y , et al. Microscopic characterization of polarization fatigue in ferroelectric vinylidene fluoride and trifluoroethylene copolymer films[J]. *Organic Electronics*, 2009, 10(5):753-760.
- [16] Duan C G, Mei W N , Yin W G , et al. Simulations of ferroelectric polymer film polarization: The role of dipole interactions[J]. *Physical Review B*, 2004, 69(23):235106.