Piezoelectricity in β-phase PVDF crystals: A molecular simulation study

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ABSTRACT

Based on the energy-minimization method in molecular simulation, the origin of piezoelectricity in β-phase PVDF crystals was investigated. Simulation results indicated that under the action of a constant applied voltage, PVDF crystal would be stretched or compressed, dependent on the orientation of dipoles and the polarity of the applied voltage. Our simulation confirmed that piezoelectricity in polymers would be mostly attributed to the dimensional effect. Piezoelectric coefficient calculated from our model was well consistent with experimental data, which showed the credibility of this model.

1. Introduction

In 1969, Kawai [1] discovered strong piezoelectricity in poly(vinylidene fluoride) (PVDF, as abbreviated); in 1971, Bergman [2] and Wada [3] found its pyroelectricity; and soon typical ferroelectric hysteresis loops were also found from the direct polarization measurements using the standard Sawyer-Tower circuit [4]. All these discoveries in PVDF family have been regarded as the milestone in organic transducers [5].

Before the discovery of organic ferroelectrics, it is usually believed that piezoelectricity and ferroelectricity are characteristics of crystals and ceramics, and the related mechanism has been intensively studied. However, polymers are mostly semi-crystalline with coexistence of crystalline phase and amorphous phase, so ferroelectricity and piezoelectricity of polymers are inevitably different from those of inorganic materials. Studies on these polymers have elicited great interest because of their potential applications to transducers, sensors, actuators, and potential ultra-high-density data storage.

A widely accepted mechanism, called a dimensional effect, has been put forward to explain the piezoelectricity and pyroelectricity in polymers, and this mechanism assumes that piezoelectric and pyroelectric activities arise from macroscopic dimensional changes when a sample is deformed, while the moment of constituent molecular dipoles is kept constant. Theoretical considerations by

Broadhurst et al. [6] and Wada and Hayakawa [7] have shown that macroscopic dimensional changes played an important role in the piezoelectric activity of drawn and poled PVDF. Furukawa et al. [8] had examined the contribution of the dimensional effect to the piezoelectricity in VDF/TrFE copolymers by experimental measurements and theoretical calculations.

In our previous work [9], we introduced the molecular simulation method to the study of ferroelectricity in PVDF and illuminated the effect of trapped charges on ferroelectric switching process in polymers. In this paper by the molecular simulation method we attempted to study the origin of piezoelectricity in β-phase PVDF crystals.

2. Modeling

2.1. Structural parameters of β-phase PVDF

PVDF polymers have four phases: α, β, γ, δ [10]. In this paper β-phase PVDF is simulated, which has the highest spontaneous polarization in all these four phases [11]. In β-phase PVDF, an all-trans conformation induces the alignment of the CH_2CF_2 in zigzag plane and perpendicular to the chain axis (see Fig. 1). All chains arrange in a quasi-hexagonal-symmetry structure (Fig. 1a). Molecular dipoles associated with positive hydrogen and negative fluoride atoms are entirely aligned in one direction to generate the largest spontaneous polarization. The lattice constants of such a quasi-hexagonal-symmetry unit cell are $a = 0.850$ nm, $b = 0.491$ nm, and $c = 0.256$ nm [12]. The other structural parameters (bond length

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Fig. 1. Structure of β-phase PVDF.

Table 2
Parameters of van der Waals potential for β-phase PVDF [14]

Atomic pair	A	B	C
C–C	14976.0	3.0900	640.80
H–H	2649.6	3.7400	27.36
F–F	135782.0	4.5461	106.12
C–H	4320.0	3.4150	138.24
C–F	45094.0	3.8181	260.77
H–F	12300.0	4.1431	53.88

2.2. Model and force field for our simulation

In this paper we assume that the molecular chains in β-PVDF crystals are rigid and neglect the influence of chain torsion on potential energy. The model used in our simulation is shown in Fig. 2. This model includes a PVDF crystal consisting of 5×10 molecular chains with quasi-hexagonal symmetry. Each chain is structured by twenty CH_2CF_2 repeat units. The directions of a, b, c vectors are also indicated in Fig. 2. The electric field (voltage) is set along b axis. Two charge layers in planes are constructed to simulate this applied electric field (or voltage), both of which are parallel to the ac plane. The top and the bottom layers were set with the same charge density, but with opposite polarity. In this paper the applied electric field (voltage) is defined as positive when the top layer is set with a positive charge density. The orientation of dipoles, from negative fluoride atoms to positive hydrogen atoms, was set upward.

In this model, we assume that it is not the dipole moment but the intermolecular spacing in PVDF crystal that changes along b axis direction when the electric field (voltage) (simulated by two charge layers) is applied. For a certain applied field (voltage), we keep the dipole moment constant and change the value of lattice constant b and plot the dependence on b increment ($\Delta b = b - b_0$) of total potential (W_{total}) in PVDF crystal, consisting of van der Waals potential between molecular chains, interatomic Coulomb potential and electrostatic potential between PVDF crystal and the applied field. We regard the corresponding state, in which the new lattice constant b minimizes the total potential, as the new stable state for a certain applied field or voltage, the corresponding new lattice constant b was marked as b_{stable}, and the dif-

Table 1
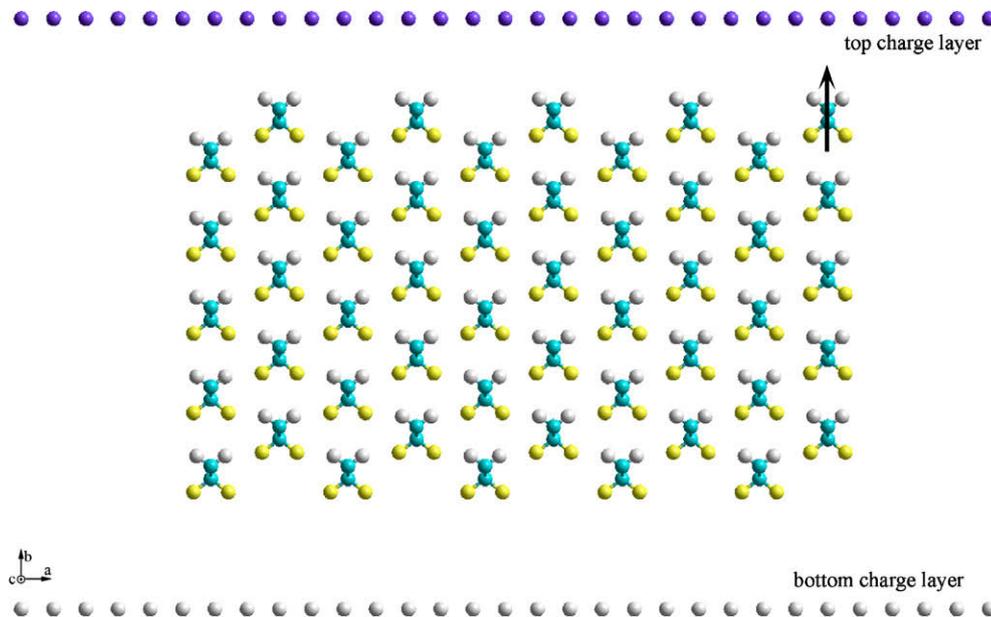Parameters of bond length and angle of β-phase PVDF [13]

Bond angle/degree		Bond length/nm	
H–C–H	116.4161	C–C	0.15242
C–C–C	117.8	C–H	0.10789
F–C–F	109.5665	C–F	0.13457

and angle) are listed in Table 1. The partial atomic charges for β-phase PVDF are directly quoted from Byutner's calculated values [14]: $Q_H = 0.1807$, $Q_F = -0.2266$, $Q_{CH} = -0.5202$, $Q_{CF} = 0.6120$, where the subscript H and F represent hydrogen atoms and fluorine atoms, and the subscript CH and CF represent the carbon atoms bonded with hydrogen atoms and the carbon atoms bonded with fluorine atoms, respectively.

Fig. 2. Model for the simulation of piezoelectricity in β-phase PVDF.