DFT Study of the ferroelectric properties for PVDF

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ABSTRACT

A theoretical study of poly(vinylidene fluoride), PVDF, which exhibits piezoelectricity effect, is presented. By Density Functional Theory (DFT) calculations, some of the properties of this material have been obtained. Among those properties, hardness, capacitance, dipolar moment and energy associated to the structural changes. The B3LYP functional and 6311+G(d,p) bases set were used with a Gaussian program. Five length chain molecules were studied, $H-(CH_2-CF_2)_x-H$, where x=1,2,3,4 and 6 for the four different PVDF conformations, namely, $I=T_p$, $II=TG_a$, $III=TG_p$ and $IV=T_3G$, where T means trans and G means gauche

Keywords: Theoretical study, PVDF, hardness, nanoscale capacitance.

1 INTRODUCTION

Poly(vinylidene fluoride)-based polymers have been the focus of extensive research work due to their unique electrical properties: ferroelectric, piezoelectric and electro-acoustic properties. Common dielectric materials may become polarized under an applied electrical field, whereas ferroelectric materials may become spontaneously polarized. Piezoelectric materials can transform a mechanical movement into an electric signal and vice versa. On the other hand, electro-acoustic materials can transform an acoustic wave into an electric signal and vice versa. Several inorganic compounds are ferroelectric while poly(vinilydene fluoride), PVDF, is the only ferroelectric organic polymer known. Because of their light weight and easy processing and handling, PVDF-based polymers have potential application in several new-technology electronics such as in sensors, transducers, energy storage devices, communications or microphones [1]. Some applications currently under development include artificial muscles and harnessing energy from sea waves. However, only one of the four different PVDF conformations exhibits ferroelectric behavior, the all-trans conformation. The all-trans, all-T, conformation has a highly polarized backbone. The ferroelectric properties of PVDF can be enhanced by the introduction of trifluoroethylene, TrFE, as comonomer. P(VDF-TrFE)

copolymers exhibit ferroelectric properties at TrFE contents between 50 and 85 mole percent [2]. At a specific temperature, the Curie temperature, P(VDF-TrFE) copolymers show a conformational and phase transformation, from ferroelectric to paraelectric. The Curie temperature depends on the copolymer composition and at this temperature the PVDF-based materials show some of the highest dielectric constants of any organic polymer, resulting from large crystalline polar domains. However, for energy storage applications, as in capacitors, is more convenient a relatively high dielectric constant at room temperature and a smaller remnant polarization [3], that can be accomplished by reducing the crystal domain size through high energy radiation or by the introduction of a third monomer, such as chlorotrifluoroethylene. Quantum mechanics calculations can provide valuable information about the polarity and conformational energy states (related to the Curie temperature) for several polymer compositions. The present contribution is focused in studying the variation in polarity, quantum capacitance and chemical hardness of a growing PVDF chain.

2 METHODOLOGY

The electronic structure study includes all-electrons within the Kohn-Sham implementation of the Density Functional Theory (DFT). The level of theory used in this work corresponds to the non-local hybrid functional developed by Becke, Lee-Yang-Parr (B3LYP) [4] whereas the Kohn-Sham orbitals are represented by a triple-ζ numerical with double polarized (d,p) plus a one diffuse basis set; implemented in the Gaussian 03 program [5]. The electrostatic potential method was used for charge calculation (ESP) [6]. The Electrostatic Potential (ESP) charge calculation algorithm was chosen because it has no basis set dependence. Geometry optimization calculations were carried out for all the involved systems. Five different length chain molecules were studied, $H-(CH_2-CF_2)_x-H$, where x=1,2,4,6 for the four different PVDF conformations, namely, $I=T_p$, $II=TG_a$, $III=TG_p$ and $IV=T_3G$, vide Fig. 1. T means all-T, TG indicates TGTG' and T_3G means TTTGTTG', where T indicate trans and G means gauche conformation and the subindexes p or a correspond to polar phases with parallel dipoles and

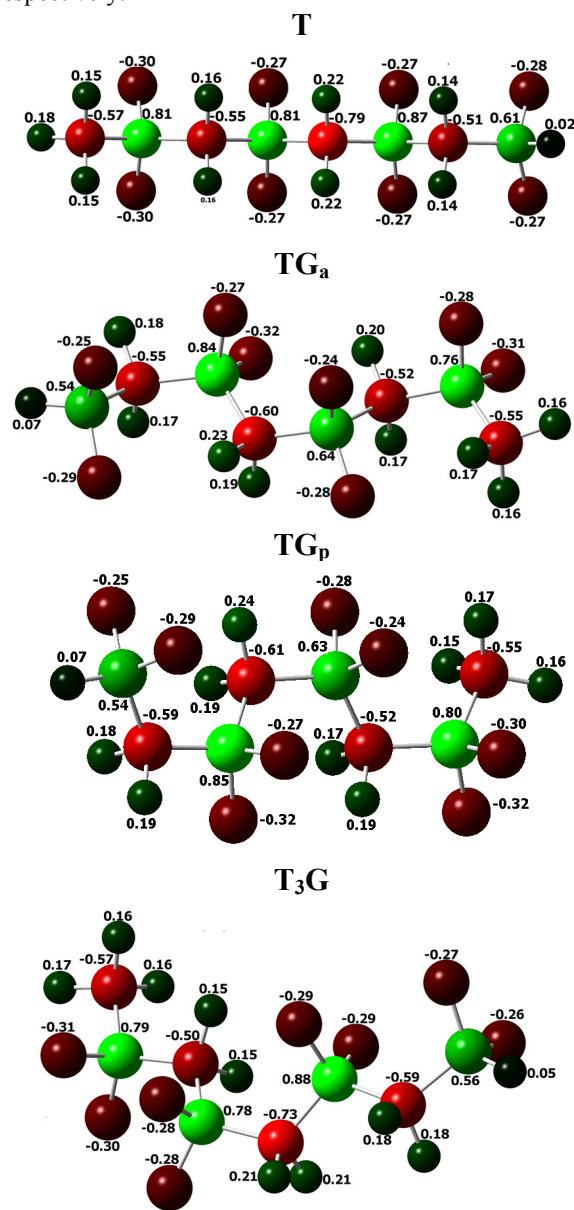nonpol ar phases with antiparallel dipole moments, respectively.

T

TG$_a$

TG$_p$

T$_3$G

Fig. 1. ESP charge representation for T$_p$, TG$_a$, and for T$_3$G. Negative charge value in Red, positive charge value in dark green and light green a larger positive charge

3 THEORETICAL BACKGROUND

Electronegativity[7] (χ), and hardness[8] (η), for an N-electron system with total energy E, are defined as follows:

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{\upsilon(\vec{r})} \quad (1)$$

$$\eta = (1/2)\left(\frac{\partial^2 E}{\partial N^2}\right)_{\upsilon(\vec{r})} = (1/2)\left(\frac{\partial \mu}{\partial N}\right)_{\upsilon(\vec{r})} \quad (2)$$

where μ and $\upsilon(\vec{r})$ are chemical and external potentials, respectively. The global softness (S) is the following inverse of hardness [9],

$$S = \frac{1}{2\eta} = \left(\frac{\partial N}{\partial \mu}\right)_{\upsilon(\vec{r})} \quad (3)$$

Using finite difference approximation for the small change in the number of the particles, we can approximate the μ, η, and S as

$$\mu = -\left(\frac{IP + EA}{2}\right) \quad (4)$$

$$\eta = \frac{IP - EA}{2} \quad (5)$$

$$S = \frac{1}{IP - EA} \quad (6)$$

By means of Koopmans [10] theorem for close-shell, -IP can be directly related with the HOMO eigenvalue energy and EA to the LUMO eigenvalue energy. On the other hand, making use of the hardness global descriptor, it is possible to take a simpler alternative of direct approach for connecting the dimensions of quantum systems and their energetics. This approach takes advantage of the principles of electrostatics and a developing body of evidence that atoms and molecules behave much like macroscopic spherical capacitors, with their specific shapes and capacities. It has been demonstrated by Ellenbogen et al [11] that quantum capacitances of nonspherical, rodlike molecular wires vary or "scale" according to a linear law much like that obeyed by classical spherical capacitors. This linear isoperimetric [12] scaling law for the capacitances leads to a simple formula that relates a molecule´s difficult-to-calculate electron affinity (EA) directly to its ionization potential (IP) and its spatial dimensions. Therefore, following Iafrate et al. [13], as well as Gazquez and Ortiz [14] and Perdew [15], the capacitance of an atom or molecules may be evaluated as

$$C_I = \frac{1}{(IP - EA)} \quad (7)$$

So the capacitance has length $\boldsymbol{L}$ dependence. $\boldsymbol{L}$ is length of the chain (number of carbon atoms).

4 RESULTS AND DISCUSSION

Trying to understand the electrochemical properties of the PVDF material, we performed the torsion

of the dihedral angle of two units was done, vide Fig. 2. Scanning the dihedral angle torsion for the G -to- T transformation along the potential surface gives the relative energies and structural changes among them. Fig. 2 shows that the TGa, TGp and Tp are stable geometric conformations because all of them are situated in minimum positions within the surface potential. In this case the TG´s phases are energetically more stable than the Tp phase. According to the schematic picture, to reach the Tp conformation requires larger energy supply. Barr2 from TGp to Tp has a value of 4 kcal/mol and the energy difference between them is about 2.35 kcal/mol. The energy barrier for converting TG_a into TG_p structural conformation is about 2.1 kcal/mol, according to the computed results; it means half of the energy required to reach the Tp structural conformation, as observed in the Fig.2. Therefore, even if the Tp conformation has a higher energy level with respect to TG conformations, once the energetic barrier could be jumped a stable structure is obtained. These structural conformations are directly related with its corresponding a phase in the crystal.
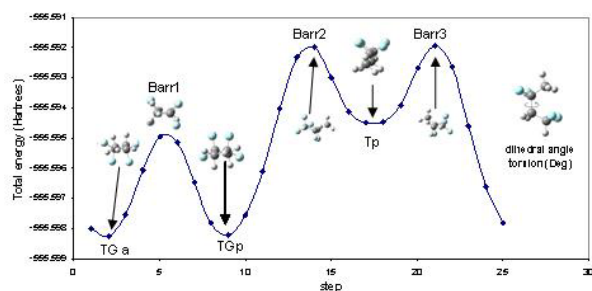

Figure 2. Graphical representation of the surface potential energy for the dihedral angle torsion showed in the right side of the picture. The Graphic displays the energy obtained for the different structural conformations, namely, TG_a, TG_p and T_p.

We shall bear in mind that, the molecular energy computed in this simple model is far away from the real crystal, but the simulations are consistent with available experimental observations [16].
Now, analyzing the differences among the different structural changes obtained along the potential surface scanning, in Fig. 2, Table 1 shows some electronic properties and their resulting parameters. Pointing only at two units, i. e., n_f=4, where n is the total number of carbon atoms involved in that structure, the computed result shows that Tp conformation the dipole moment increase is in average about 40% higher than the rest of the structural conformations (TGa, TGp and T3G). A graphical picture of the dipole moment is presented in Figure 2. Here, we observe in blue the dipole tendency for the transformation, in green the TG (a or p) tendency and the orange color line corresponds to the T_3G phase tendency. In general, the

picture shows that the dipole moment increases as the length of the carbon chain increase. The Tp structural conformation shows the larger increment in the dipole moment. The TG structural conformation shows an intermediate increment whereas the T_3G conformational phase has the lowest one. The dipole moment increment for Tp is about 40% stronger with respect to the TG´s conformations and 55% stronger with respect to the T_3G. It means that the structural arrangement of the Tp phase promotes an increment in the polarity of the system. As a consequence of this, a charge polarization is also obtained, as can be seen in Fig. 1, where positive and negative charges for Tp are perfectly ordered at the outside part of the Tp molecule. The same split charge distribution is not obtained for the TG´s and T_3G conformational systems. Hence, dipole increment and charge polarization in a T_p system are characteristics for a ferroelectric material, they together act to form an electric dipole moment even in the absence of an external field, as has been demonstrated here. This behavior takes place as a result of a change in the phase structure. Additionally, from Fig. 2, the simple molecular model shows that the barriers among the different structural conformations are not too high to switch among them with a relatively low energy supply, All these additive properties present in the Tp structure model may produce a ferroelectric material when the system size grows up to a polymer crystal.

According to obtained results presented so far, the models representation give a good description of the systems, therefore some additional information could be presented making use of the chemical descriptors development by the DFT scheme. So, the hardness and the C_I indexes remained almost invariable through the growing of the molecular system, vide Table 1. These values indicate that the invariability and the similar order of magnitude contribute to the switching facility between different structural conformations, the hardness, η, is inversely related to the quantum capacitances, C_I.
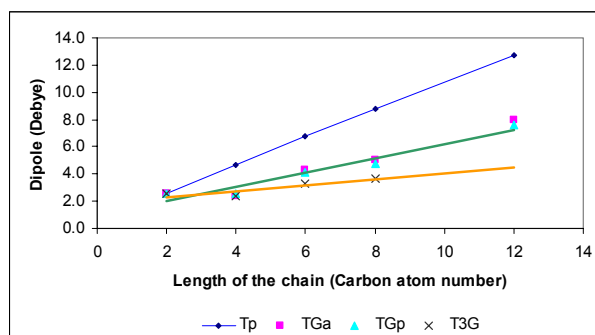

Figure 3. Dipole tendency (in Debye) for different PVDF structural conformations. In Blue Tp structural phase, in green shows the tendency for TG_a, TG_p and in orange the tendency for T_3G conformation.

No. of C Atoms n_r	Length L (Å)	- I P HOMO (eV)	A E LUMO (eV)	η (eV)	C_I (eV)$^{-1}$	Dipole (Debye)
Tp						
2	3.30	-9.631	0.084	4.773	0.105	2.518
4	5.62	-9.239	-0.328	4.783	0.105	4.679
6	8.17	-9.076	-0.578	4.827	0.104	6.743
8	10.68	-8.995	-0.746	4.870	0.103	8.764
12	15.63	-8.927	-0.950	4.939	0.101	12.693
TGa						
2	3.30	-9.631	0.084	4.773	0.105	2.518
4	5.25	-9.568	-0.187	4.878	0.103	2.374
6	7.62	-9.474	-0.366	4.920	0.102	4.290
8	9.86	-9.405	-0.456	4.930	0.101	5.038
12	14.43	-9.302	-0.579	4.941	0.101	7.965
TGp						
2	3.30	-9.631	0.084	4.773	0.105	2.518
4	5.26	-9.556	-0.070	4.813	0.104	2.550
6	7.62	-9.484	-0.479	4.982	0.100	4.075
8	9.86	-9.415	-0.572	4.994	0.100	4.733
12	14.43	-9.308	-0.703	5.005	0.100	7.567
T3G						
2	3.30	-9.631	0.084	4.773	0.105	2.518
4	5.26	-9.570	-0.187	4.879	0.102	2.361
6	6.75	-9.380	-0.486	4.933	0.101	3.319
8	9.90	-9.194	-0.562	4.878	0.103	3.641

Table 1. Energetic values and polar moment for the different PVDF structural conformations. Comparison of the hardness and molecular capacitances results. Quantum capacitances (C_I) from DFT calculations

5 CONCLUSION

The quantum mechanics calculations of the energetics and structures corresponding to the different PVDF structural conformations show that the Tp configuration is energetically stabilized. The changes in the molecular conformation associated to Tp, TGa or TGp and T_3G lead to significant shape changes and electrochemical properties. A larger dipole moment and orientational charge polarization was obtained for the Tp molecular structure, which could be obtained by cooperative motion of the neighboring groups through large-scale T-G conformational changes. The dipole increment and charge polarization in the T_p system are characteristics of a ferroelectric material, they together act to form an electric dipole moment even in the absence of an external field. The molecular model shows that the energy barriers among the different structural conformations are not too high allowing to switch among them with a relatively low energy supply. The interface mobility among the different conformations is an important property for actuators. All these additive properties of the T_p structure model may produce a ferroelectric material when the system size scales up to a polymer crystal.

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