

Density Functional Theory calculations of the ferroelectric poly(vinylidene fluoride-chlorotrifluoroethylene) copolymer, compared to those of poly(vinylidene fluoride)

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ABSTRACT

The quantum mechanics calculations of the energetics and structures corresponding to the different representatives structural conformations of poly(vinylidene fluoride-trifluoroethylene) and poly(vinylidene fluoride-chlorotrifluoroethylene) copolymers show that the all-trans, Tp conformation, is energetically stabilized even with a chlorine substituent. The changes in the molecular arrangement associated to Tp or TGa conformations lead to significant changes in shape and electrical-chemical properties. A larger dipole moment and a orientational charge polarization were obtained for the all-trans Tp molecular structure even with a sort chlorine contamination. According to the computed results, the Curie transition temperature should be smaller in P(VDF-CTFE) than in PVDF. The fluorine NMR spectra were calculated for the different representative systems. The B3LYP functional and the 6311+G(d,p) bases set were used with the Gaussian program for carrying out the calculations.

Keywords: quantum chemical study, PVDF, P(VDF-CTFE), electronic properties.

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(vinylidene 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 and 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 or β -phase. 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. Considerable effort has been devoted to understand the structure-property relationships [4-15] but the mechanism and the phase stability and phase transitions are not yet completely elucidated. Quantum mechanics calculations can provide valuable information about the polarity and conformational energy states (also related to the Curie temperature) for several polymer compositions. The present contribution is focused on studying the conformations of VDF-VDF and VDF-CTFE comonomer, their energy states, energy transitions and dipole moment, which are in turn related to their electrical properties. Results are compared to those obtained for pure PVDF representative models, in a previous study.

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) [16] whereas the Kohn-Sham orbitals are represented by a triple- ζ

numerical with double polarized functions (d,p) plus one diffuse basis set; implemented in the Gaussian 03 code [17]. The electrostatic potential method was used for the charge calculation (ESP) [18]. 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 using the Bery algorithm. The Threshold convergence criterion was 10^{-6} hartrees for the energy, 0.000450 for the Maximum Force and 0.001800 for the Maximum Displacement. Two different phases were calculated for the copolymer (VDF-CTFE), namely, T_p , TG_a and are compared with the PVDF pure in T_p phase. T indicates trans and G means gauche conformation and the subindexes p and a correspond to polar phases with parallel dipoles and nonpolar phases with antiparallel dipole moments, respectively (vide Figure 1).

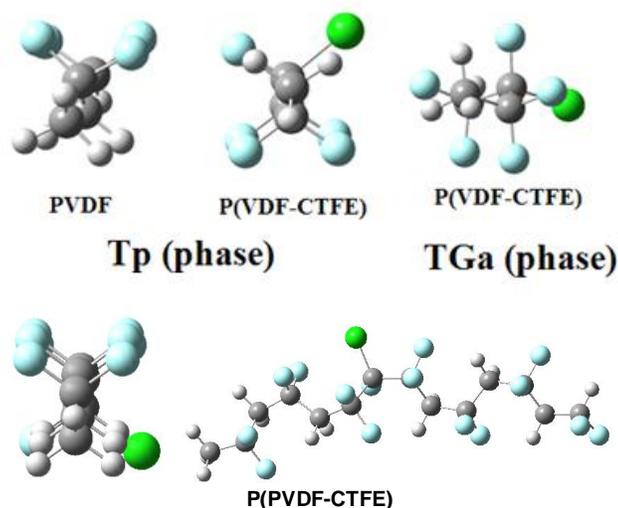


Figure 1. Structural representation of the two different polymer building blocks: VDF, and VDF-CTFE (one hydrogen atom is substituted by a chlorine atom and other hydrogen atom is substituted by fluorine atom, if compared to VDF-VDF conformers. T_p and TG_a are related with the different phases formed. Fluorine atoms are in blue, carbon atoms are in grey, chlorine atom is in green and hydrogen atoms are in white.

3 RESULTS AND DISCUSSION

In order to understand the differences among the chemical and electrical properties of PVDF with respect to the P(VDF-CTFE) materials, we have been performed the torsion of the dihedral angle of representative two monomer units, vide Figure 2. Following the dihedral angle torsion of the G -to- T geometry transformation, the potential energy surface (PES) gives the relative energies and structural changes among them. Figure 2 shows that the TG_a , TG_p and T_p are stable geometric conformations for all the materials, because all of them are situated at minimum

positions within the PES. We shall bear in mind that the molecular energy computed in this simplified model is far away from that of the real crystal (formed by large domains); nevertheless, computing simulations are consistent with available experimental observations [19]. According to Figure 2, it is possible to observe that for all the materials, the TG phases are energetically more stable than the T_p phase, and that the (VDF-VDF)-PES profile shows a symmetric curve distribution; which is mostly due to the symmetric disposition of fluorine substituents. For the (VDF-CTFE)-PES case, this even distribution is lost, because the addition of substituents to the VDF, such as fluorine and chlorine.

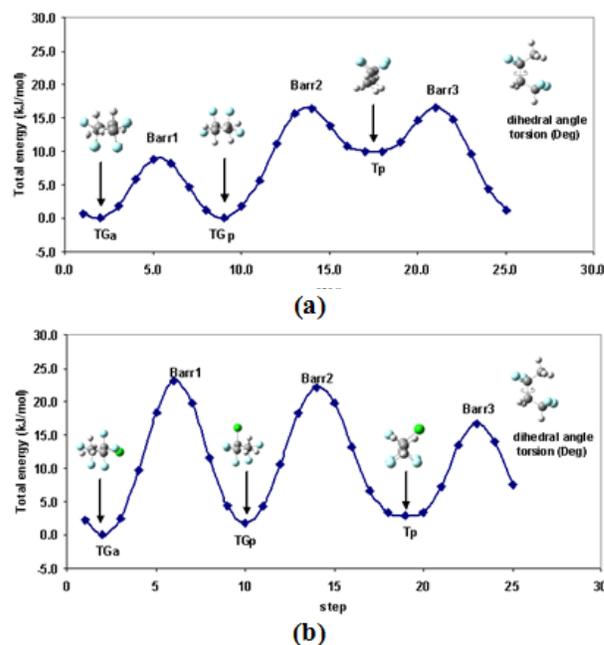


Figure 2. Graphical representation of the PES for the dihedral angle torsion showed on the right side of the picture. This graph displays the energy associated to the different model structural conformations, TG_a , TG_p and T_p of the different materials: (a) VDF and (b) VDF-CTFE.

According to Figure 2, to reach the T_p conformation requires an energy supply for all the three cases. *Barrier 2 (Barr2)* indicates the amount of energy required to reach T_p from TG_p ; approximately 4 kcal/mol for PVDF and 4.9 kcal/mol for VDF-CTFE. For the VDF-VDF case, the order of the energy difference is in agreement with that reported elsewhere [19]. On the other hand, *Barrier 1 (Barr1)* indicates the amount of energy required to reach T_p from TG_a being around 3.93, 2.01, and 3.99 kcal/mol following the same order mentioned before. Now, *Barrier 3* represents the amount of energy required to reach TG_p from TG_a being around 2.09, 3.05, 3.5 kcal/mol, keeping the same ordering. Based on the computed results, the energy barrier for converting the TG_a into the TG_p structural conformation is half of the energy required to

reach the T_p structural conformation for the VDF-VDF material, as it can be observed in Figure 2, while for the VDF-CTFE increases there is no significant difference. The analysis of the energy differences among the different structural phases involves looking at the minima points along the PES for the different materials conformations, as follows. For VDF-VDF, TGa and TGp have a similar energy level (vide Figure 2), while the energy difference between them and the T_p conformer is about 2.3 kcal/mol. Analyzing the graphical representation in Figure 2 again, but now for VDF-CTFE, all the conformations, namely, TGa, TGp and T_p have a similar energy level, with less than 1 kcal/mol difference among them. This result mean, that for VDF-CTFE, the T_p conformation becomes almost as stable as the TGa or TGp phases, although the rotational energy barrier for reaching the T_p conformation is larger than for the other systems; but once the energetic barrier may be overcome, a stable structure is obtained. These structural conformations are related with a corresponding phase in the crystal. For the PES in Figure 2 only two monomer units, i. e., $n_r=4$, where n is the total number of carbon atoms in the structure, the computed results indicate that the dipole moment of the T_p conformation is always higher than the rest of the structural conformations (TGa and TGp), for example, for VDF-VDF, the T_p phase is about 4.68 D, while for VDF-CTFE is 2.54 D. The TGa phase in VDF-VDF has a value of 2.37 and for VDF-CTFE is 1.65 D. When the a representative model for PVDF and copolymer P(VDF-CTFE), namely PVDF and P(VDF-CTFE), chain is enlarged (85% of VDF and 15% of CTFE), as presented in Figure 3, the dipole moment keeps a similar behavior as in the two monomer units calculations. In this case, for the PVDF in a T_p phase is 12.6 D, for the P(VDF-CTFE) in TGa phase is about 8.95 D and for P(VDF-CTFE) in T_p phase is 11.32 D. On the other hand, the dipole moment becomes stronger as the chain length increases.

Analyzing the ESP charge distribution for the above mentioned three cases, first, the charge polarization of PVDF was obtained for the T_p conformation (vide Figure 3a), where positive and negative ESP charges arrange in the T_p conformation. The quantum mechanics calculations of the ESP charge distribution indicate (Figure 3a) that the electrical charges are perfectly ordered at the outside part of the molecule, being one side positive and the other negative. For the P(VDF-CTFE) cases, in which a chlorine atom is present in the structure, a charge polarization is also obtained outside the molecule, exhibiting a negative charge where fluorine atoms are present, contrary to results obtained when only two monomers were taken into account, where there is an alternate charge distribution, being negative at fluorine and chlorine atoms positions and positive at hydrogen atoms positions. When the chain is enlarged, the charge polarization of the T_p phase splits, vide Figure 3c. The TGa conformational system for P(VDF-CTFE) with a 85% of VDF and 15% of CTFE composition, do not show a charge

polarization or the same split charge distribution (vide Figure 3b), as it is expected.

Hence, the strong dipole and the charge polarization of the T_p system are characteristic of a ferroelectric material; they together act to form an electric dipole moment even in the absence of an external electrical field, as experimentally observed. This behavior is the result of a change in the phase structure. Moreover, the simple molecular model in Figure 1 shows that the energy barriers among the different structural conformations are not too high to stop switching among them with a relatively low energy supply, vide Figure 2.

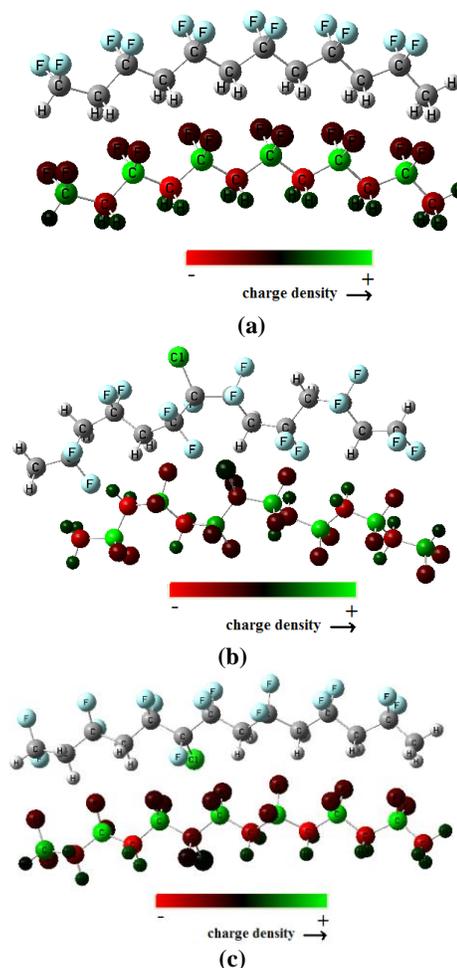


Figure 3. Geometrical and schematic ESP charge distribution for representative models of the different materials, namely, (a) PVDF T_p phase; (b) P(VDF-CTFE) TGa phase (c) P(VDF-CTFE) T_p phase. We considered a 85% VDF and 15% CTFE for the namely, P(VDF-CTFE) molar composition. Negative charge values are depicted in red, positive charge values are in dark green and the larger positive charges are depicted in light green.

The P(VDF-CTFE) system, containing chlorine, a sort of contamination, with a molar composition of 85% VDF and 15% CTFE, studied here, does not has a strongly effect over the charge polarization of the T_p phase, if compared to PVDF. However, according to the vibrational frequencies

obtained for both phases, T_p and T_{Ga} , the presence of the chlorine atom in the P(VDF-CTFE) structure gives not too much flexibility to the neighboring chain. In fact, since chlorine is heavier than fluorine or hydrogen atoms, it anchors the molecule and restricts the mechanic movement. This special factor may provide distinct properties to the copolymer, with respect to the PVDF system.

The ^{19}F NMR spectra of the different systems studied are presented in Figure 4. PVDF in T_p phase shows only two signals, whereas P(VDF-CTFE) in both, T_{Ga} and T_p phases, exhibits three more signals, as a consequence of the chemical composition change and the electronic environment change produced by the chlorine atom. A stronger chemical shift was obtained for the (VDF-CTFE)- T_p conformation with respect to P(VDF-CTFE)- T_{Ga} and PVDF- T_p .

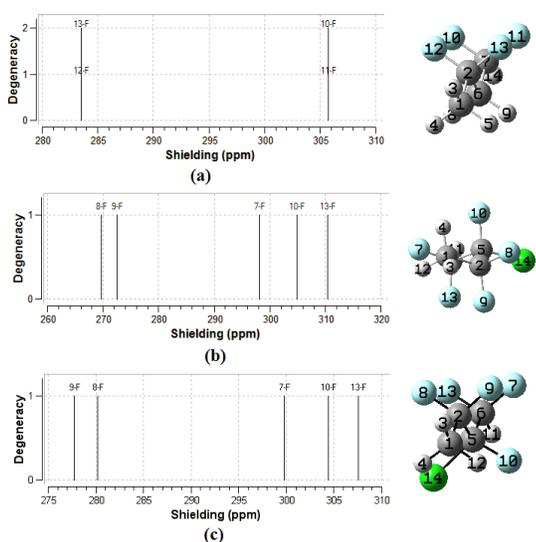


Figure 4. ^{19}F NMR Spectrum of the (a) VDF-VDF in T_p phase, (b) VDF-CTFE in T_{Ga} phase and (c) VDF-CTFE in T_p phase.

4 CONCLUSIONS

The quantum mechanics calculations of the energetics and structures corresponding to the different structural conformations of PVDF-VDF and VDF-CTFE dimmer show that the T_p conformation is energetically stabilized even with the introduction of a chlorine substituent. The changes in the molecular arrangement associated to T_p or T_{Ga} conformations lead to significant changes in shape and electrical-chemical properties. A larger dipole moment and orientational charge polarization were obtained for the all-trans T_p molecular structure even with a sort chlorine contamination. According to the computed results, the Curie transition temperature should be smaller for P(VDF-CTFE) than for PVDF. The interphase 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 or electrical energy storage device, such as, stationary power generators or capacitors, due to the strong charge polarization of the T_p phase.

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