Biointerface Research in Applied Chemistry

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Original Research Article
Open Access Journal

Molecular modeling analyses for polyvinylidene X (X=F, Cl, Br and I)

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ABSTRACT

Polyvinylidene (PVDF) substituted with different halogens (F, Cl, Br and I) has been studied theoretically by performing some semi-empirical calculations at PM3 to obtain some physical parameters and improve the electronic properties. As a result of substitution bond length increases from 1.1083 Å to 1.9921 Å; bond angels decreased from 105.5120° to95.3750°; total dipole moment is increased from 0.0013 to 9.8242 Debye and the energy gap is decreased from 14.2929 to 6.1591eV. In addition, ESP results are indicated that the electro-negativity of the studied model molecules is increased upon substitution. The change in these calculated physical parameters reflects the reactivity of PVD.

Keywords: *PVD, geometrical parameters, TDM and HOMO/LUMO band gaps.*

1. INTRODUCTION

Poly(vinylidene fluoride) (PVDF) is a semicrystalline polymer which exhibits excellent mechanical strength, high chemical resistance and thermal stability these in turn reflect an excellent aging resistance [1-4]. It could be formed as a result of these properties as membranes which dedicates it for many applications [5-8]. Au-decorated SWNT/PVDF membrane was produced with electrospinning according to its low infrared emissivity to act as infrared stealth uniforms [9]. Molecular modeling with different levels of theory was extensively used to elucidate the properties of natural as well as synthetic polymers [10-13]. Molecular modeling at AM1, PM3, PM5, B88-PW91, B88-LYP, D-VWN calculations used for the complexes between acetone or ethyl acetate and vinylidene fluoride tetramer. The overall aim is to understand the solubility and H-bonding of poly(vinylidene fluoride) copolymers in carbonyl liquids, results were compared with experiment data [14]. Molecular modeling compared with experimental data elucidates the electronic and spectroscopic properties of PVDX where X is F,

Cl and Br [15]. Molecular Dynamics MD simulations, is applied to investigate the properties of PVDF/POSS system to investigate the miscibility, morphology, crystallization, piezoelectricity, mechanical properties and erosion effects [16-19]. It is stated that, some properties of PVDF could be achieved throughout MD simulations including improvements in PVDF as well as understanding the erosion effect of PVDF clusters [20-21]. Rather modeling based on quantum mechanical approach and/or molecular dynamics approach there are mathematical modeling which is conducted to investigate certain behavior. Such class of computational work could be also utilized to model the behaviors of PVDF [22-23]. In our previous work we apply a different level of theory to study both natural and synthetic polymers and understand their behavior including structural, physical, chemical and vibrational characteristics [24-29]. In this study the semi-empirical calculations at PM3 is utilized to study the physical parameters and the electronic properties of PVDX where X is F, Cl, Br and I.

2. MATERIALS AND METHODS

Calculation Details.

The structural models of Polyvinylidene fluoride, Polyvinylidene chloride, Polyvinylidene bromide and finally Polyvinylidene iodide are supposed to study the change in reactivity of Polyvinylidene as a result of substitution with halides (F, Cl, Br and I). The studied structures are undergoeing to optimization by performing some calculations using semi-empirical theory at the

PM3 level using the restricted Hartree–Fock (RHF) procedure. All calculations were carried out using GAUSSIAN09 [30] program at Spectroscopy Department, National Research Centre, Egypt. Geometrical parameters as (bond length, bond angles), total dipole moment, band gap energies (HOMO/LUMO) and molecular electrostatic potentials are calculated for all models under study.

3. RESULTS

The proposed structures of all model molecules are subjected to optimization to study the change in bond length and bond angles of Polyvinylidene (PVD) as a consequence of

substitution with halides (F, Cl, Br and I). Fourteen units of vinylidene are supposed to be a model molecular presenting PVD structure and similarly for PVDF, PVDCl, PVDBr and PVDI as

indicated in figure 1. The interactions occurred between are described in terms of bond length, bond angles, total dipole moment as well as HOMO/LUMO band gap energies. Table 1 illustrates the change in both geometrical parameters (bond length and angles) where the bond length increases with increasing atomic number (ongoing downwards) that is increased from 1.10829 A° to 1.36347, 1.77247, 1.90159 and 1.99208 Å and from 1.10829 Å to 1.36124, 1.77247, 1.90159 and 1.99208Å for the two side chain bonds meanwhile, the angles changed from 105.5120° to 102.0120°, 106.7820°, 95.547° and 95.375° for PVD, PVDF, PVDCl, PVDBr and PVDI respectively.
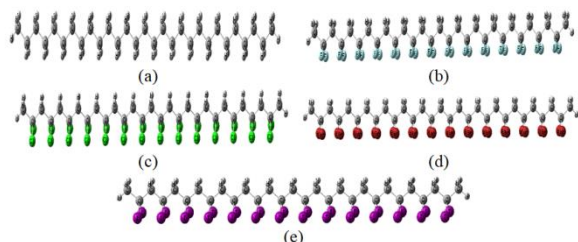

Figure 1. Geometrical structures of (a) PVD, (b) PVDF, (C) PVDCl, (d) PVDBr and (e) PVDI calculated at PM3 level of semi-empirical theory.

Table 1. The calculated optimized geometries (bond length as angstrom Å and bond angels as degree) of PVD and its substitutions (F, Cl, Br and I) at PM3 level of semi-empirical theory.

Structure	Bond length(Å)		Bond angel(deg.)
	L_{5-15}	L_{5-14}	
PVD	1.1083	1.1083	105.5120
PVDF	1.3635	1.3612	102.0120
PVDCl	1.7725	1.7725	106.7820
PVDBr	1.9016	1.9016	95.5470
PVDI	1.9921	1.9921	95.3750

More importantly, the calculated band structures (both total dipole moment and the molecular orbital energies) of PVD, PVDF, PVDCl, PVDBr and PVDI showed that the electronic properties of PVD are enhanced strongly as a result of substitution. Table 2 presents the effect of halogens up on PVD where, the total dipole moment increases from 0.0013 Debye to 9.8242, 6.1350, 5.6645 and 6.1233 Debye for PVD, PVDF, PVDCl, PVDBr and PVDI respectively which means that PVD is approximately stable and considered an indicator for increasing the reactivity of PVD due to substitution. However, the band gaps are narrowed when PVD is substituted by F, Cl, Br and I. As shown in figure 2, the band gap energies decreases strongly with increasing the atomic number for the studied halogens where it decreases from 14.2929 eV to 13.1013, 9.8707, 7.8791and 6.1591 eV.

Finally, the molecular electrostatic potentials (ESP) are discussed briefly to give a further explanation of the properties of the studied models. The calculated ESPs are displayed in figures 3 and 4 as total surface area and as contour action respectively. It is clear that there is a change in the distribution of charges around each model and there is an increase in the electro-negativity which is an

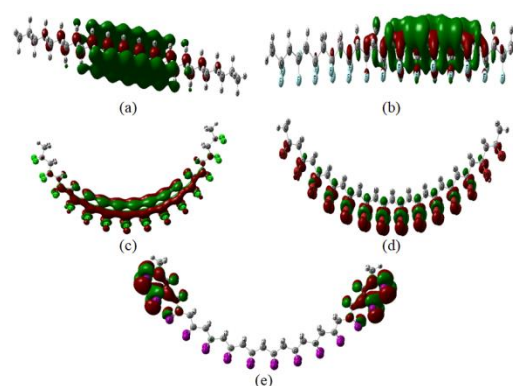indication of increasing the reactivity of the structures under study.

Figure 2. HOMO/LUMO band gap energies of (a) PVD, (b) PVDF, (C) PVDCl, (d) PVDBr and (e) PVDI calculated at PM3 level of semi-empirical theory.

Table 2. The calculated TDM as Debye and HOMO/LUMO band gaps as eV of PVD and its substitutions (F, Cl, Br and I) at PM3 level of semi-empirical theory.

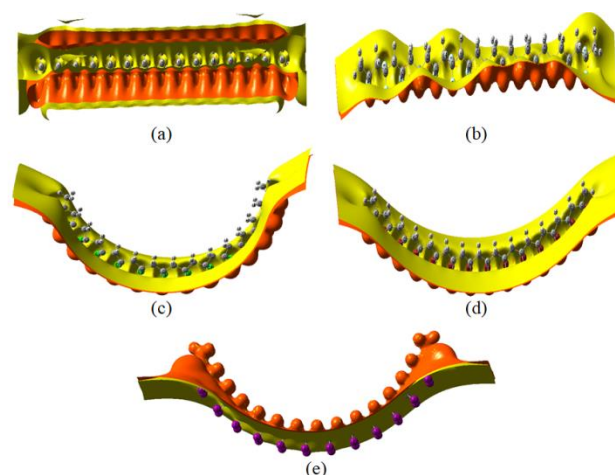| Structure	TDM	ΔE
PVD	0.0013	14.2929
PVDF	9.8242	13.1013
PVDCl	6.1350	9.8707
PVDBr	5.6645	7.8791
PVDI	6.1233	6.1591

Figure 3. PM3 level of semi-empirical theory calculated ESPs for (a) PVD, (b) PVDF, (C) PVDCl, (d) PVDBr and (e) PVDI as total surface area.
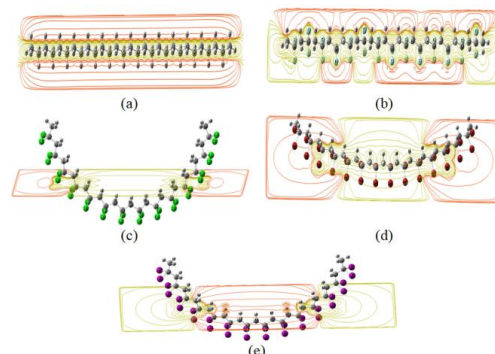

Figure 4. PM3 level of semi-empirical theory calculated ESPs for (a) PVD, (b) PVDF, (C) PVDCl, (d) PVDBr and (e) PVDI as contour action

These findings confirm the early investigations which stated that, physical properties such as total dipole moment, HOMO/LUMO band gap beside ESP are reflecting the reactivity of a given compound [31-34]. As total dipole moment increases while HOMO/LUMO decreases the compound became reactive.

On the other hand SEP maps the active sites for the studied compound. Finally one can conclude that, DFT as well as other computational level of theories continue to be useful tool of research for investigating the different properties of many systems and molecules [35-39].

4. CONCLUSIONS

Model molecules presenting PVD, PVDF, PVDCl, PVDBr and PVDI are subjected to optimization at PM3 through performing semi-empirical quantum mechanical calculations. As a result of substitution of PVD with F, Cl, Br and I, there is a noticeable change in the geometrical parameters where the bond lengths increased but the most angles are decreased. Most notably, PVDI has the largest bond length in comparison with other studied models and also it possesses the lowest angle. On the other hand, the results indicated ongoing downwards from F to I, that the

electronic properties are strongly improved and PVD decorated with iodide atom can be chosen as the best halogen to improve PVD properties as TDM value has increased significantly and equals 6.1233 Debye for PVDI while the HOMO/LUMO energy becomes 6.1591eV and this is considered a significant improvement in the electronic properties. Furthermore, ESP study indicated that the reactivity of PVD increases greatly due to decoration as the electro-negativity increases highly.

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