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Theoretical study of isomerization and polymerization in polyethylene terephthalate

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Abstract

Using ab initio DFT (Density Functional Theory) investigation, an attempt was made to gain insight into some physical properties ofpolyethylene terephthalate (PET) including polymerization (repeating monomer units) and *cis-trans* isomerization at 298 K. DFT calculations were performed at Becke's three parameter functional and Lee–Yang–Parr functional (B3LYP) level of calculation with 6-31+G(d,p) basis set. Geometry optimization of a series of conformations was employed to greatly increase the global energy minimum for each molecule. Molecular structure calculations yielded several thermochemical parameters,including the magnitude and direction of the dipole moment, electron densities, total electronic energy at 0 K, enthalpy, Gibbs free energy at 298 K of the investigated polymer, and its conformers. Both the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) energy gaps were also represented.
Keywords: Isomerizations; PET; Polymeization; DFT; Conformers.

1. Introduction

Polyethylene terephthalate (PET) is a well-known engineering polymer used in the creation of fibers, films, tapes, and bottles, as well as in the moulding of powders and the production of composite materials. Amorphous and unoriented PET has little economic value due to poor mechanical properties, increased gas penetration, decreased dimensional stability, and increased extensibility [1-3]. PET's physical and mechanical properties can be greatly enhanced by crystallization and orientation [2,3]. On the other hand, the rate of crystallization, the degree of crystallinity, and the degree of orientation can all be altered to affect microstructure

[2,3]. PET's qualities have long been influenced by its crystallinity, and scientists have known this for years.

To the best of our knowledge, PET is a significant commercial commodity, with one of the biggest tonnages of any polymer product on the planet. It is a rigid, stiff, robust, and dimensionally stable substance with a low water absorption rate that is utilized in the manufacture of synthetic fibers, textiles, and fabrics [4,5]. For many years, synthetic fibers were marketed under some of the most well-known commercial names, including Dacron, Trevira, and Terylene. Although PET fabrics have a more synthetic feel than natural fibers such as cotton, linen, and hemp, they do have the advantage of

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greater crease and wrinkle resistance. However, PET is frequently blended with natural fibers to create a product that combines the benefits of both fibers.

Interestingly, PET has steadily taken over the carbonated soft drink and bottled water bottle markets due to its lightweight, durable, and clear properties when aligned amorphous as well as its superior oxygen and carbon dioxide barrier capabilities [6-8]. For the same reasons, it's also been used in food containers and packaging. Since more PET bottles and containers are being recycled, many of the early concerns regarding the use of such a costly material as PET have subsided, which explains why global PET consumption is increasing [6-8].

Other applications for thermally stabilized biaxially oriented PET films include capacitors, graphics, and film bases, among others [6-8]. Using high tensile fiber and PET together could have substantial uses in the military industry for body protection. PET has been widely used in recent years in the manufacture of fiber reinforced composites.

In order to sustain material features during processing, rapid analytical techniques for measuring crystallinity and fiber orientation were essential for the polymer's commercialization. For defining PET's crystallinity and orientation, numerous infrared spectroscopic techniques have been used. However, many limitations have been identified [9–17], not the least of which is how to assign the molecular characteristics of PET's vibrational spectrum's absorption bands and where they belong in the crystal and amorphous regions.In the literature, PET has been extensively investigated in different theoretical and experimental studies [18-27].

Generally, quantum chemical computations have made molecular modeling an extremely useful toolfor studying molecular and vibrational characteristics. When it comes to vibrational frequency assignments and complicated organic system bonding and structural properties, density functional theory (DFT) and the Becke3–Lee–Yang–Parr (B3LYP) technique are the most accurate tools [28-31]. In this work, we will use quantum chemistry as an alternative tool to investigate PET thermochemical properties, including polymerization (repeating monomer units), and *cis-trans* isomerization at 298 K. Also, we will analyze electronic properties based on the van der Waals dispersion-corrected density functional theory calculations.

2. Experimental

Our quantum chemical computations were performed by the hybrid generalized gradient approximation B3LYP method (Becke's three-parameter exchange functional and the correlation functional from Lee, Yang, and Parr) [32] and 6-31+G(d,p) [33] with the Gaussian 09 software package [34], in addition to CHEMCRAFT [35] used for visualization of the results. The dispersion corrections for the non-bonding van der Waals interactions were included using Grimme's DFT-D3 method [36] to avoid double-counting of electron correlation effects. The density of states [37] for the models was obtained using Gaussian smearing of Kohn–Sham orbital energies.

We calculated the optimized geometries of a series of conformations as shown in Figure 1. Also, we calculated many physical parameters such as thermo-chemistry, overall dipole moment, HOMO/LUMO Bandgap, ionization energies, electronic affinity, chemical potential, global electrophilicity index, global hardness, softness, and denisty of states at the same theory level.

3. Results and discussions
3.1. Geometry optimization

PET is typically manufactured using ethylene glycol (EG) and either terephthalic acid or dimethyl terephthalate (TPA dimethyl ester) [38]. Bis(hydroxyethyl) terephthalate (BHET) is the product of both reactions, which are carried out at temperatures between 240 and 260°C and pressures ranging from 300 to 500 kPa for reaction 1 and 140 to 220°C and 100 kPa for reaction 2 [38]. Following the first reaction, the molecular weight is required in two or three phases of polymerization.

At 250–280 °C and 2–3 kPa, BHET transesterification displaces EG as the first step in polymerization [38]. To produce polymers, the oligomers are then polycondensed at 270–280 °C and 50–100 kPa [38]. To get a higher molecular weight, the polymer must be put through a third step of solid state polymerization at temperatures between 200°C and 240°C under pressure of 100kPa [38]. At this point, it is appropriate for applications that do not require high molecular weight chains. After the raw polymer is manufactured, it can be extruded, injected, or blown into the required shape [38].

This work investigated different PET conformers and initial monomers at 298 K and 1 bar pressure. In Figure 1, we display the optimized

structures at B3lyp/6-31+g(d,p) for ethylene glycol monomer, dimethyl terephthalic acid ester monomer, and methanol byproduct. Also, different PET models with chain configurations were donated as: PET1, PET2, PET3, PET4, PET5, PET6, PET7, PET8, PET9, PET10, PET11 PET12, PET13, PET14, PET15, PET16 were introduced.

PET1 and PET2 were the first two isomers with no repeating units of ethylene glycol or TPA dimethyl ester. EG repeating units were introduced in PET3 and PET4 isomers. Then, three isomers with

TPA repeating unit monomers were donated as PET5, PET6, and PET7. Also, PET8, PET9, and PET10 conformers were shown, including the addition of 2 repeating units, one of ethylene glycol and one of TPA ester. Furthuremore, PET11, PET12, and PET13 conformers were designed, including the addition of 3 repeating units of ethylene glycol and two TPA ester. Finally, PET14, PET15, and PET16 conformers were designed including the addition of 3 repeating units of ethylene glycol and three of TPA ester.

(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)

(i)

(j)
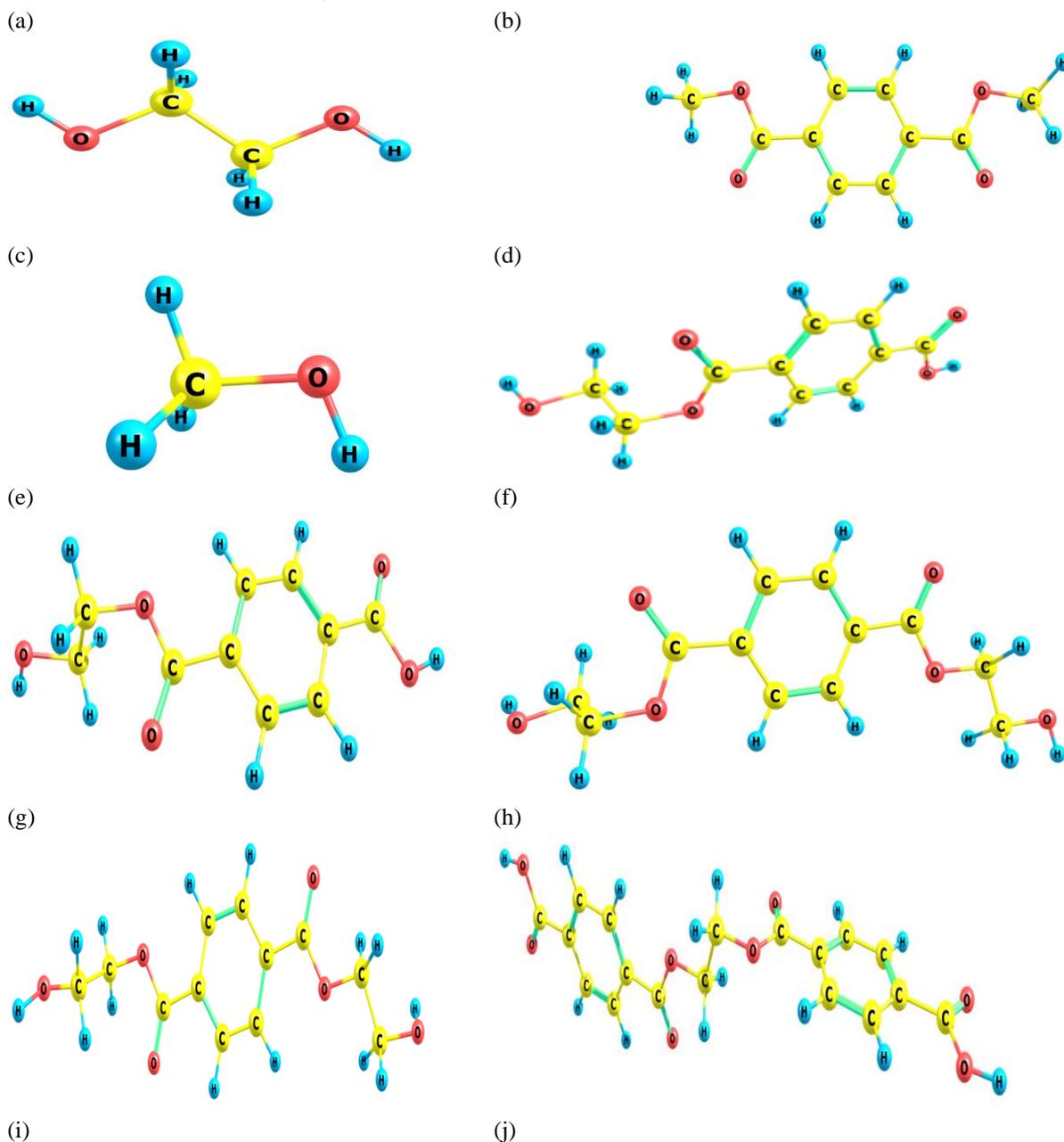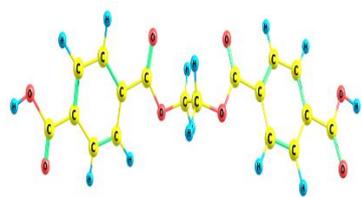
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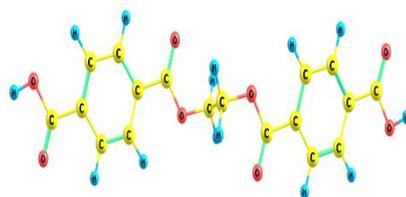
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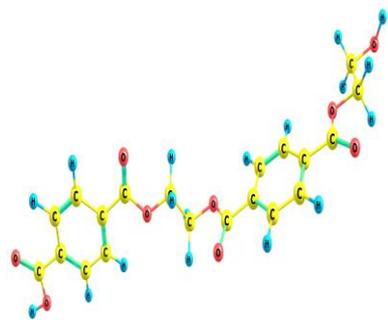
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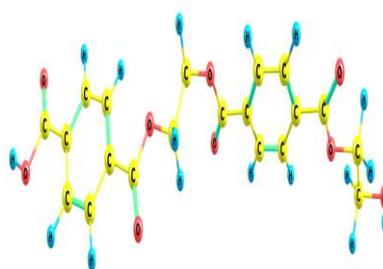
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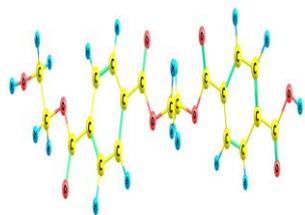
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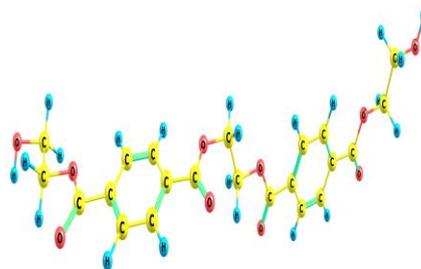
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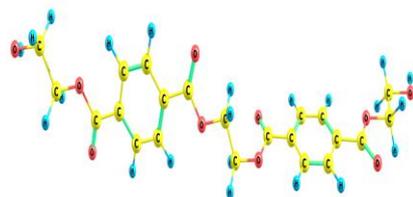
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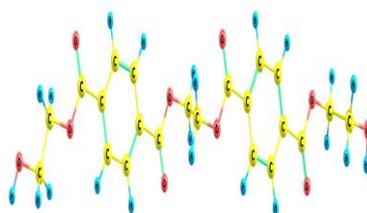
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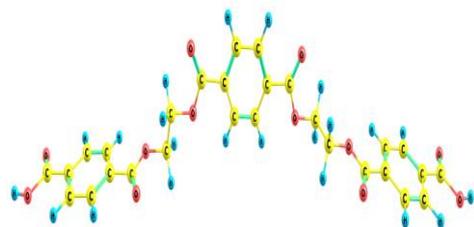
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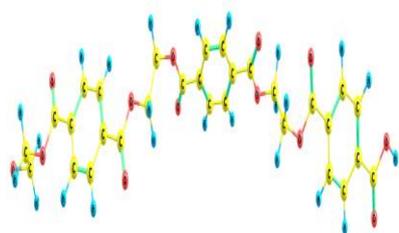
Fig 1.Optimized geometry at B3lyp/6-31+g(d,p): (a) Ethylene glycol monomer, (b) Dimethyl terephthalic acid ester monomer, (c) methanol byproduct, (d) PET1 (e) PET2, (f) PET3, (g) PET4 (h) PET5, (I) PET6, (J) PET7, (K) PET8, (l) PET9, (m) PET10, (n) PET11 (o) PET12, (P) PET13, (Q) PET14, (r) PET15, (s) PET16

3.2. Thermo-chemistry and related physical insights

Many calculated thermo-chemical parameters are donated in Table 1, including total energy (HF), zero-point vibrational energy (E_0) at 0K, thermal energy (E_{298}), thermal enthalpy (H_{298}) and Gibbs free energy (G_{298}) for all species involved in this study at room temperature in atomic units (a.u).

In Table 2, total dipole moment (Debye), HOMO-LUMO energy gap (eV), changes in energies, enthalpies and Gibbs free energies in 298 K in Kcal/mol, for polymer conformers are introduced at B3lyp/6-31+g(d,p). There are two kinds of molecular orbitals in Fermi-molecular orbitals (FMOs): HOMOs, which are the most occupied, and LUMOs, which are the least occupied. These orbitals provide information about the chemical activity of the researched conformers. Because the ease with which electrons can be lost (HOMO) and gained (LUMO) is a measure of this easiness. The values of band gap energies range approximately from 5.0-5.2 eV.

When two charges are separated, a dipole moment occurs. Dipole moments are caused by changes in electronegativity and can occur in covalent bonds between atoms. Bigger differences in electronegativity and more polarity equate to a larger dipole moment. For all polymer conformers, the computed dipole moments vary from zero to 4.6 Debyethat means relatively low chemical activity in general for all PET conformers at 298 K and 1 bar pressure.

According to dipole moments values, PET 1 in *cis* form is more polar and more reactive than its isomer PET2 in *trans* form, where PET3 in *cis* form is highly reactive at 4.4 debye in comparison with PET4, its isomer (*trans* form, 0.33 debye). Also, PET5 with 4.35 debye is highly reactive in comparison with its *trans* form isomers (PET6, 0.04 Debye and zero for PET7), where PET8 has 3.36 debye in comparison with its other isomers of 1.7 and 1.3 for PET9 and PET10, respectively. Comparable dipole moments values for PET11, PET12, and PET13 are 4.61, 3.12, and 3.0 debye, respectively. Finally, 3.19, 0.28, and 1.48 debye are the dipole moments for PET14 (*cis* form, more polar and more reactive), PET15, and PET16 (*trans* forms), respectively.

Table 1. Energies (a.u) of monomers, byproduct and polymer conformers at B3lyp/6-31+g(d,p).

Species	Total energy	E_0	E_{298}	H_{298}	G_{298}
Ethylene glycol	-230.219	-230.185	-230.186	-230.19	-230.277
TPA dimethyl ester	-609.359	-609.312	-609.313	-609.32	-609.45
Methanol	-115.706	-115.679	-115.680	-115.683	-115.73
PET1	-763.151	-763.093	-763.094	-763.108	-763.3
PET2	-763.151	-763.093	-763.094	-763.108	-763.3
PET3	-916.943	-916.874	-916.875	-916.89	-917.15
PET4	-916.943	-916.874	-916.875	-916.893	-917.15
PET5	-1296.082	-1296.0	-1296.001	-1296.024	-1296.3
PET6	-1296.081	-1295.999	-1296.0007	-1296.023	-1296.3
PET7	-1296.082	-1296.001	-1296.002	-1296.025	-1296.3
PET8	-1449.8745	-1449.78	-1449.7827	-1449.809	-1450.169
PET9	-1449.874	-1449.782	-1449.783	-1449.810	-1450.17
PET10	-1449.874	-1449.781	-1449.782	-1449.809	-1450.168
PET11	-1603.6669	-1603.562	-1603.563	-1603.595	-1604.016
PET12	-1603.667	-1603.563	-1603.564	-1603.595	-1604.016
PET13	-1603.666	-1603.564	-1603.565	-1603.596	-1604.017
PET14	-1982.806	-1982.689	-1982.69	-1982.726	-1983.19
PET15	-1982.806	-1982.689	-1982.690	-1982.726	-1983.19
PET16	-2136.5961	-2136.46	-2136.4705	-2136.5108	-2137.038

Table 2. Total dipole moment (Debye), HOMO-LUMO energy gap (eV), changes in energies , enthalpies and Gibbs free energies in 298 K in Kcal/mol, for polymer conformers at B3lyp/6-31+g(d,p).

Species	E_g(eV)	ΔE_{298}	ΔH_{298}	ΔG_{298}	Dipole moment
PET1	5.17	-39.279	-39.276	-39.275	2.75
PET2	5.16	-39.278	-39.275	-39.274	1.53
PET3	5.2	-193.056	-193.056	-193.071	4.4
PET4	5.19	-193.055	-193.053	-193.070	0.33
PET5	5.11	-572.182	-572.182	-572.209	4.35
PET6	5.15	-572.181	-572.186	-572.207	0.046
PET7	5.13	-572.183	-572.185	-572.208	0
PET8	5.17	-725.964	-725.964	-726.001	3.36
PET9	5.14	-725.965	-725.965	-726.002	1.73
PET10	5.11	-725.968	-725.969	-726.003	1.38
PET11	5.1	-879.743	-879.746	-879.797	4.61
PET12	5.17	-879.744	-879.743	-879.795	3.12
PET13	5.12	-879.745	-879.744	-879.794	3.0
PET14	5.089	-1258.85	-1258.87	-1258.93	3.19
PET15	5.105	-1258.87	-1258.90	-1258.91	0.28
PET16	5.064	-1412.66	-1412.67	-1412.72	1.48

Table 3. Ionization energy (eV), electron affinity (eV), global hardness (eV), electronic chemical potential (eV), global electrophilicity index (eV) and finally softness (eV -1) for polymer conformers at B3lyp/6-31+g(d,p).

Species	Ionization energies	Electronic affinity	Global hardness	Electronic chemical potential	Global electrophilicity index	Softness
PET1	7.668	2.496	2.586	-5.082	4.994	0.386
PET2	7.657	2.496	2.580	-5.077	4.994	0.387
PET3	7.588	2.380	2.604	-4.984	4.770	0.383
PET4	7.614	2.423	2.595	-5.019	4.853	0.385
PET5	7.7185	2.608	2.555	-5.163	5.217	0.391
PET6	7.714	2.569	2.572	-5.141	5.138	0.388
PET7	7.723	2.591	2.565	-5.157	5.182	0.389
PET8	7.715	2.540	2.587	-5.127	5.081	0.386
PET9	7.665	2.528	2.568	-5.096	5.056	0.389
PET10	7.672	2.557	2.557	-5.114	5.115	0.391
PET11	7.635	2.529	2.552	-5.082	5.058	0.391
PET12	7.648	2.481	2.583	-5.065	4.964	0.387
PET13	7.642	2.518	2.561	-5.080	5.038	0.390
PET14	7.702	2.613	2.544	-5.157	5.227	0.39
PET15	7.705	2.600	2.552	-5.153	5.201	0.391
PET16	7.635	2.571	2.532	-5.103	5.142	0.394

On the other hand, according to the energies calculated atroom temperature, the spontaneous nature of the polymerization reaction has been illustrated, especially with increasing repeating units. The arrangement can be mentioned from high spontaneous to low spontaneous reaction as PET16 of approx. -1412.6 Kcal/mol then -1258.8Kcal/mol for PET14 and PET15 conformers then (~ -879.743) Kcal/mol for PET11-13 conformers and around -725.965 Kcal/mol for PET8-10 conformers then approx. -572.186 Kcal/mol for PET5, PET6, and PET7 then (~-193.056) Kcal/mol ~~were~~ for PET3 and PET4 and finally around -39.275 Kcal/mol for PET 1 and PET2

According to the molecular orbital theory, using FMOs energies, the ionization energy (I) and electron affinity (A) can be expressed by as I = -EHOMO and A = -ELUMO. Also, theglobal hardness (ŋ) and electronic chemical potential (μ) are given by ŋ = 1/2(ELUMO–EHOMO) and μ= 1/2(ELUMO+ EHOMO). The global electrophilicity index is ψ = μ² /2ŋ and softness is ζ = 1/ŋ [39,40]. All these resultsare listed for polymer conformers at B3lyp/6-31+g(d,p) in Table 3.

Figure 2 shows the calculated density of state (DOS) spectrum for some polymer conformers donated as: PET1, PET3, PET7, PET10, PET13, and PET16, respectively, to rationalize the observed changes in the band region at the same level of theory. The band gaps were not affected by increasing the repeating units.For all polymer conformers, the computed band gap energies were (~5.0-5.2 eV) at 298 K and 1 bar pressure.

(a)

(b)

(c)

(d)

(e)

(f)

Fig 2.Total density of states spectrum at B3lyp/6-31+g(d,p): (a) PET1, (b)PET3, (c) PET7, (d) PET10, (e) PET13, and (f) PET16 at B3LYP/6-31+G(d,p)

4. Conclusions.

An attempt was made to obtain some physical features of polyethylene terephthalate (PET) using ab initio DFT (Density Functional Theory) study, including polymerization (repeating monomer units) and *cis-trans* isomerization at 298 K. Each molecule's global energy minimum was achieved through geometry optimization of a sequence of conformations. The magnitude and direction of the dipole moment, ionization energies, electronic affinity, chemical potential, global electrophilicity index, global hardness, softness and denisty of states, total electronic energy at 0 K, enthalpy,the HOMO and LUMO energy gaps, and the free Gibbs energy of the examined polymer and its conformers were all derived using molecular structure simulations. *Cis* form polymers are more symmetrical, more polar, and more reactive. These are the reasons for their ease of crystallization and polymerizatio in comparison with *trans* forms. More spontaneouspolymerizations were noticed withincreasing repeating units of conformers. Less dipole moments of *trans* forms make them more stable. All results were at room temperature.

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