Chemical Reactivity Behavior of Polyethylene and Polyacetylene Depending on Number of Unit via Global Reactivity Parameters and Some Spectral Results

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ABSTRACT

Polymers are composed of a large number of repeating units, forming a chain. In the present study, the chemical reactivity or stabilities of polyethylene and polyacetylene polymer molecules were investigated depending on the number of unit (n) via global reactivity parameters and some spectral results, In this context, after the geometry optimizations of the molecules were carried out at B3LYP/6–311++G(d,p) level, their global reactivity parameters such as E_{HOMO}, E_{LUMO}, energy gap between E_{LUMO} and E_{HOMO}, ionization potential, electron affinity, electronegativity, chemical potential, hardness, softness, electrophilicity and nucleophilicity, and their spectral results such as IR, ^{1}H NMR and ^{13}C NMR have been calculated and, commented. It was seen that their activities increase with the increasing number of unit (n) but, become nearly constant after n=10 for polyethylene and, after n=18 for polyacetylene. The bigger unit number for polyacetylene was attributed to that it is an unsaturated molecule. In addition we have concluded that these obtained unit numbers are theoretically enough to investigate the chemical properties of these polymers.

Keywords: Polymer, Number of unit, Global Parameters, Spectrum, DFT

I. INTRODUCTION

Polymers are long chain molecules with properties dominated by their chain behavior. Their physical properties are strongly dependent on the size or length of the polymer chain. For example, as chain length is increased, melting and boiling temperatures increase. There are both naturally occurring and synthetic polymers. Among naturally occurring polymers are proteins, starches, cellulose, and latex. Synthetic polymers are produced commercially on a very large scale and they have a wide range of properties and uses. The materials commonly called plastics are all synthetic polymers. Polyethylene is perhaps the simplest polymer, composed of a chain of repeating CH_2 units. It is produced by the addition polymerization of ethylene, $CH_2=CH_2$. The discovery of high electrical conductivity of this polymer led to intense interest in the use of organic compounds in microelectronics (organic semiconductors). This discovery was recognized by the Nobel Prize in Chemistry in 2000 [1]. Polyacetylene is an alkene molecule and so, consists some characteristics of *unsaturated* carbon–carbon bonds. It is rather stiff molecule since the activation energy for closure of such structures is too high. The chain molecule has to contain more than two hydrogen atoms to dispose of at least one sp^2 hybridized carbon atom. Since polyacetylene is chemically unstable, a huge amount of synthetic work has been carried out to produce

conducting organic polymers with better stability and property tailored for specific applications [2–4].

In this study the molecular reactivity or stability of polyethylene and polyacetylene polymer molecules was investigated and, commented via analysis of frontier molecular orbitals (FMO) and some spectral results.

II. METHODS AND MATERIAL

The geometric optimizations were done by using density functional theory (DFT) method which has almost been the most accurate approach applied to so large-size systems to get important insights and accurate predictions. All quantum chemical calculations were performed using Gaussian-09 software package [5] and Gauss-View molecular visualization program [6] on the personal computer. For the geometry optimizations, B3LYP/6–311++G (d,p) level were used. The obtained linear optimized structures of polyethylene and polyacetylene given in Fig.1 were used in the calculations of global reactivity parameters and spectra. The trans-isomer of polyacetylene was taken into account since it is more stable than its cis-isomer. The IR and NMR spectra were calculated at the B3LYP/6–311++G (d, p) and at HF/6-31 G (d) levels, respectively. In the NMR spectra tetramethylsilane (TMS) was used as reference molecule.
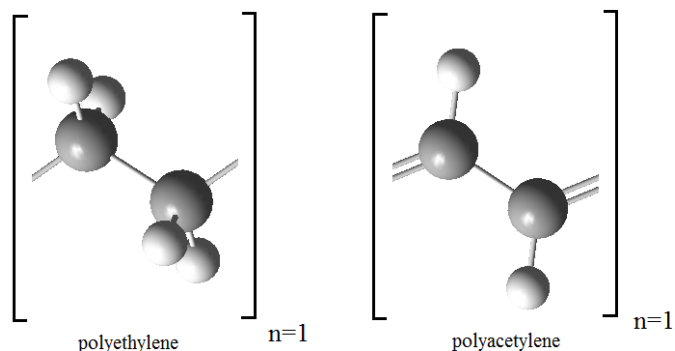

Figure 1: Calculated optimized structures of polyethylene and polyacetylene

In the conceptual density functional theory, chemical reactivity indices such as electronegativity (χ), chemical hardness (η) and chemical potential (μ) are defined as derivatives of the electronic energy (E) with respect to number of electrons (N) at a constant external potential V(r). Within the framework of this theory, mentioned chemical properties are given as:

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{V(r)}$$

and

$$\eta = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{v(r)} = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{V(r)}$$

[7, 8]. According to Koopmans's theorem [9], the negative of the highest occupied molecular orbital energy and the negative of the lowest unoccupied molecular orbital energy correspond to ionization energy (I) and electron affinity (A), respectively (-E_{HOMO}= I and -E_{LUMO} =A). As a result of this theorem, chemical potential and chemical hardness can be expressed as:

$$\chi = -\mu = \frac{I + A}{2}$$

$$\eta = \frac{I - A}{2},$$

respectively [10]. The global softness (S) is defined as the inverse of the global hardness and, given as:

$$S = \frac{1}{\eta} = -\left(\frac{\partial N}{\partial \mu}\right)_{v(r)}$$

[11]. The global electrophilicity index (w) introduced by Parr [12] is given by

$$w = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta}.$$

			TABLE I								
			GLOBAL REACTIVITY PARAMETERS FOR POLYETHYLENE								

n	E_{HOMO}	E_{LUMO}	Energy gap (ΔE)	Ionization Potential (I)	Electron Affinity (A)	Chemical Potential (μ)	Electron egativity (χ)	Hardness (η)	Softness (S)	Electro-philicity Index (ω)	Nucleo-philicity Index (ε)
1	-0.34599	-0.00585	0.34014	0.34599	0.00585	-0.17592	0.17592	0.17007	5.87993	0.09098	10,99143
2	-0.32480	-0.00616	0.31864	0.32480	0.00616	-0.16548	0.16548	0.15932	6.27667	0.08593	11,63738
3	-0.31335	-0.00691	0.30644	0.31335	0.00691	-0.16013	0.16013	0.15322	6.52656	0.08367	11,95172
4	-0.30510	-0.00740	0.29770	0.30510	0.00740	-0.15625	0.15625	0.14885	6.71817	0.08200	12,19512
5	-0.29977	-0.00772	0.29205	0.29977	0.00772	-0.15374	0.15374	0.14602	6.84814	0.08093	12,35636
6	-0.29626	-0.00794	0.28832	0.29626	0.00794	-0.15210	0.15210	0.14416	6.93673	0.08230	12,15067
7	-0.29380	-0.00810	0.28570	0.29380	0.00810	-0.15095	0.15095	0.14285	7.00035	0.07975	12,53918
8	-0.29199	-0.00822	0.28377	0.29199	0.00822	-0.15010	0.15010	0.14188	7.04820	0.07939	12,59604
9	-0.29063	-0.00832	0.28231	0.29063	0.00832	-0.14947	0.14947	0.14115	7.08466	0.07914	12,63584
10	-0.28957	-0.00839	0.28118	0.28957	0.00839	-0.14898	0.14898	0.14059	7.11288	0.07893	12,66945
11	-0.28879	-0.00845	0.28034	0.28879	0.00845	-0.14862	0.14862	0.14017	7.13419	0.07878	12,69358
12	-0.28809	-0.00850	0.27959	0.28809	0.00850	-0.14829	0.14829	0.13979	7.15358	0.07865	12,71456

Nucleophilicity (▯) is the inverse of the global electrophilicity index [13] and, given as:

$$\varepsilon = \frac{1}{w} \quad .$$

III. RESULTS AND DISCUSSION

The computed quantum chemical properties such as E_{HOMO}, E_{LUMO}, energy gap between E_{HOMO} and E_{LUMO} energy levels (ΔE), ionization potential (I), electron affinity (A), chemical potential (μ), electronegativity (χ), hardness (η), softness (S), electrophilicity (ω) and nucleophilicity (▯) depending on the number of unit (n) of the title molecules are given in Tables 1-2. For some of them the variation graphics can be seen in Figs. 2-3.
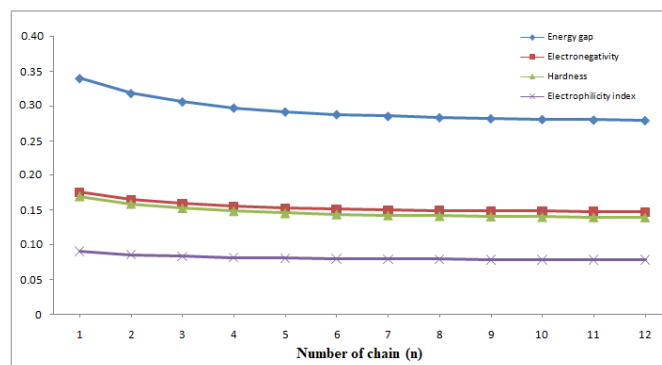

Figure 2 : Variation graphics of some geometrical parameters depending on number of chain for polyethylene

TABLE 2
GLOBAL REACTIVITY PARAMETERS FOR PoLYACETYLENE

| n	E$_{HOMO}$	E$_{LUMO}$	Energy gap (ΔE)	Ionization Potential (I)	Electron Affinity (A)	Chemical Potential (μ)	Electron egativity (χ)	Hardness (η)	Softness (S)	Electro-philicity Index (ω)	Nucleo-philicity Index (ε)
1	-0.28151	-0.01081	0.27070	0.28151	0.01081	-0.14616	0.14616	0.13535	7.38825	0.07891	12,67267
2	-0.24320	-0.04267	0.20053	0.24320	0.04267	-0.14293	0.14293	0.10026	9.97406	0.10188	9,815469
3	-0.22322	-0.06124	0.16198	0.22322	0.06124	-0.14223	0.14223	0.08099	12.34720	0.12488	8,007687
4	-0.21083	-0.07309	0.13774	0.21083	0.07309	-0.14196	0.14196	0.06887	14.52011	0.14630	6,83527
5	-0.20239	-0.08126	0.12113	0.20239	0.08126	-0.14182	0.14182	0.06056	16.51118	0.16605	6,022282
6	-0.19624	-0.08722	0.10902	0.19624	0.08722	-0.14173	0.14173	0.05451	18.34525	0.18425	5,427408
7	-0.19157	-0.09175	0.09982	0.19157	0.09175	-0.14166	0.14166	0.04991	20.03606	0.20103	4,974382
8	-0.18790	-0.09529	0.09261	0.18790	0.09529	-0.14159	0.14159	0.04630	21.59593	0.21649	4,619151
9	-0.18495	-0.09813	0.08682	0.18495	0.09813	-0.14154	0.14154	0.04341	23.03616	0.23074	4,333882
10	-0.18253	-0.10046	0.08207	0.18253	0.10046	-0.14149	0.14149	0.04103	24.36944	0.24396	4,099033
11	-0.18052	-0.10239	0.07813	0.18052	0.10239	-0.14145	0.14145	0.03906	25.60163	0.25612	3,90442
12	-0.17882	-0.10402	0.07480	0.17882	0.10402	-0.14142	0.14142	0.03740	26.73796	0.26737	3,740135
13	-0.17736	-0.10541	0.07195	0.17736	0.10541	-0.14138	0.14138	0.03597	27.80094	0.27784	3,599194
14	-0.17610	-0.10661	0.06949	0.17610	0.10661	-0.14135	0.14135	0.03474	28.78526	0.28756	3,477535
15	-0.17500	-0.10767	0.06733	0.17500	0.10767	-0.14133	0.14133	0.03366	29.70885	0.29670	3,370408
16	-0.17406	-0.10855	0.06551	0.17406	0.10855	-0.14130	0.14130	0.03275	30.53435	0.30481	3,280732
17	-0.17322	-0.10935	0.06387	0.17322	0.10935	-0.14128	0.14128	0.03193	31.31850	0.31255	3,199488
18	-0.17248	-0.11005	0.06243	0.17248	0.11005	-0.14126	0.14126	0.03121	32.04101	0.31967	3,128226
19	-0.17181	-0.11067	0.06114	0.17181	0.11067	-0.14124	0.14124	0.03057	32.71180	0.32627	3,064946
20	-0.17122	-0.11123	0.05999	0.17122	0.11123	-0.14122	0.14122	0.02999	33.34444	0.33249	3,007609
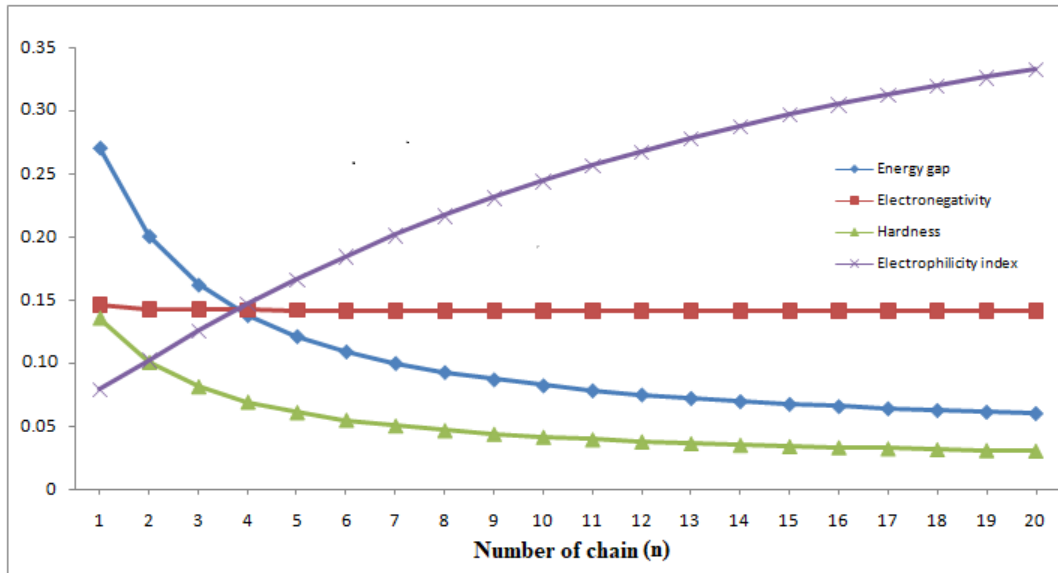
Figure 3: Variation graphics of some geometrical parameters depending on number of unit for polyethylene
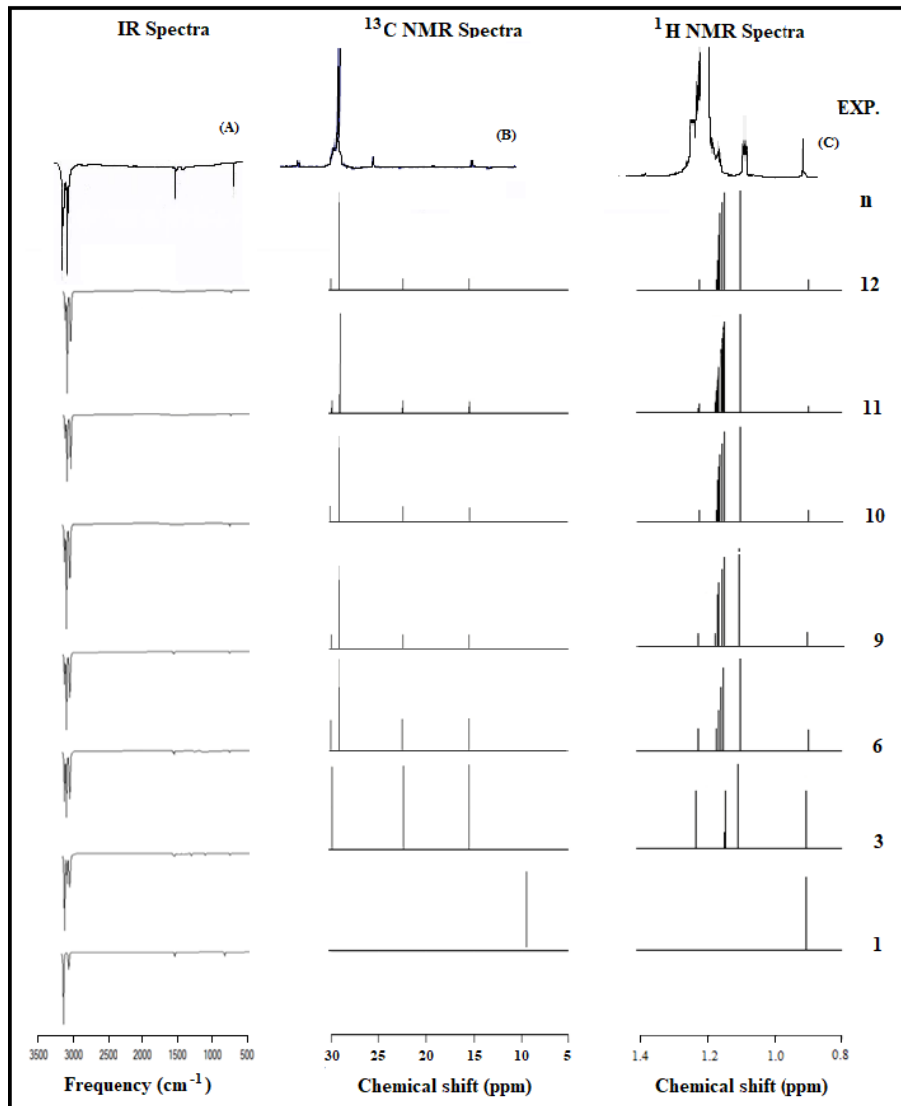

Figure 4: Theoretical spectra of polyethylene depending on number of chain with together experimental ones (A) [14], (B) [15] and (C) [16]
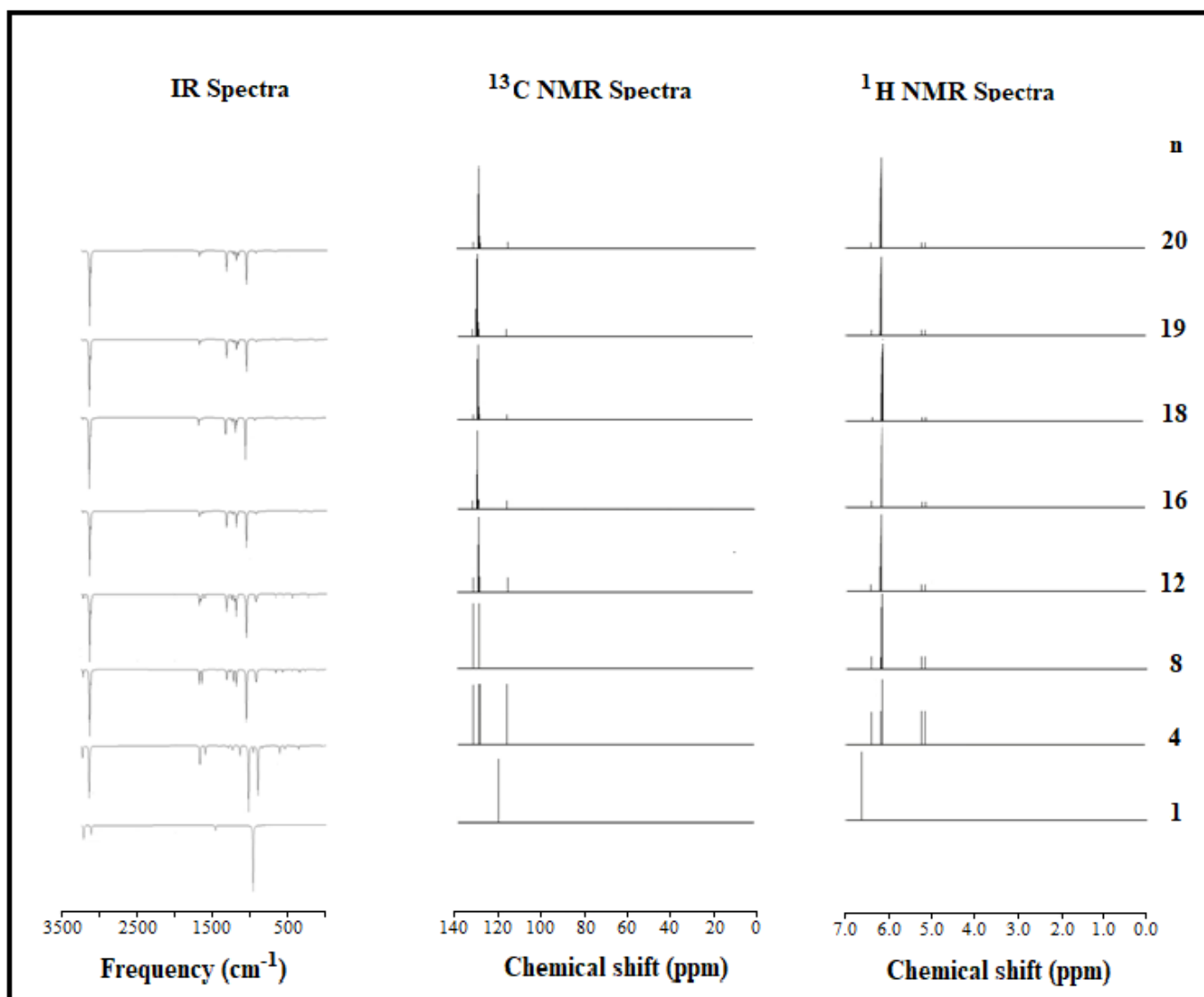
Figure 5: Theoretical spectra of polyacetylene depending on number of unit

HOMO energy is associated with the electron donating ability of a molecule while LUMO energy is an indicator of its electron accepting ability. ΔE is an important parameter as a function of reactivity of a molecule. Hardness is a measure of the molecule's ability to be polarized while softness is indicative of its ability to accept electron. Hardness and softness provide information about the reactive behavior of a molecule. So, a molecule with a low-energy gap is called as a soft molecule which is more polarizable and, generally associated with a high chemical reactivity and low kinetic stability, but vice versa is called as a hard molecule [11]. The results indicated in Tables 1-2, and the graphics in Figs. 2-3 show that while the number of unit (n) increase ΔE decreases, namely the chemical activities of the title molecules increase with the increasing number of unit. Similarly, their softness increases or their hardness decreases. But as seen from the figures they become nearly constant at n=10 for polyethylene, and at n=18 for polyacetylene. So, we mention that these unit numbers are enough to investigate the chemical properties of these polymers since all the quantum chemical properties become almost constant at bigger numbers than these. The obtained bigger unit number (n=18) for polyacetylene can be attributed to its being an unsaturated molecule. The above comments are also supported by the calculated IR and NMR spectra

of the molecules (Figs. 4-5). We see from the figures that the theoretical spectra stay nearly same at the bigger numbers of unit than n=10 for polyethylene and n=18 for polyacetylene and, these spectra of polyethylene are also very similar to the experimental ones given in the upper section of Fig.4 which are obtained from the literature [14-16].

Electronegativity is an important parameter in terms of the prediction and comparison of activity efficiencies of a molecule. It is the tendency of a molecule to attract electron. As seen from Tables 1-2 or Figs.2-3 the electronegativity of molecules decreases with increasing chain number and, becomes nearly constant at n=3 for the both molecules. According to Sanderson's electronegativity equalization principle [17], the electron transfer between two systems continues until their electronegativity values become equal to each other. Ionization energy is a fundamental descriptor of the chemical reactivity of atoms and molecules. High ionization energy indicates high stability and chemical inertness, and small ionization energy indicates high reactivity of molecules [18]. As seen for the tables the ionization energies decrease with increasing unit number, and they become nearly constant at bigger numbers than n=10 for polyethylene and, than n=18 for polyacetylene as we mentioned before. The electrophilicity index (w) indicates the tendency of a molecule to accept electron. Nucleophilicity (Ꙩ) is physically its inverse (1/w). As seen from Fig.3 the electrophilicity index value for polyacetylene increases with the increasing number of unit. This can be attributed to its increasing appetite to accept an electron because of an unsaturated molecule.

IV. CONCLUSION

The chemical reactivity or stability of the title polymer molecules depending on the number of unit were investigated via global reactivity parameters and some spectral results. The geometry optimizations of the molecules were carried out by DFT (B3LYP) /6–311++ G (d, p) method. It was seen that their activities increase with increasing unit number. Their global reactivity parameters and, IR and NMR spectra become nearly constant after n=10 for polyethylene and after n=18 for polyacetylene (since it is an unsaturated molecule). So, we have concluded that these found unit numbers are enough to investigate the chemical properties of these polymers.

V. REFERENCES

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