A Quantum Chemical to Study the Correlation between Density of Some Polymers (Amorphous and Crystalline) and Structure Properties

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Abstract

Physico-chemical parameters of monomer were calculated by MP2 quantum chemical calculated methods. The correlation builds up with the help of the descriptors, Total energy, Electrophil, Hardness, Electronegative, Dipole moment, Energy gap, HOMO and LUMO energies. All these values for descriptors have been calculated with the help of a MP2 method using the basis set 6-31G(d) to generate the correlation between density of polymers under study and physicochemical properties. In case Amorphous the best value of R^2 for the linearity correlate was 0.985 with total energy. While in case crystalline the best value of R^2 for the linearity correlate was 0.982 with LUMO which indicate that these descriptors Total Energy and LUMO play an important role in effect on density properties of polymers in both cases (Amorphous and Crystalline) which allow chemists to elucidate and to understand how molecular structure influences properties.

Keywords: Quantum Chemical, Polymer(Amorphous, Crystalline), Structural Properties.

Introduction

Polymers can be divided into two groups morphologically: amorphous polymers and crystalline polymers. Amorphous polymers lack sufficient regularity in packing of the chains to produce the sharp x-ray diffraction pattern characteristic of highly crystalline polymers. The term crystalline polymer is actually a misnomer since no polymer is 100% crystalline, containing both crystalline domains and amorphous domains. Therefore, a more correct yet seldom used designation is ‘‘semi crystalline’’ polymer. The polymer chains are packed together more efficiently and tightly in the crystalline region than in the amorphous region, consequently the density of the crystalline region ρc will typically be larger than that of the corresponding amorphous region ra. For this reason, the density of a polymer increases with its degree of crystallinity xc. The ratio ρc / ρa can vary considerably from polymer to polymer from the average value of 1.13 g/cm [1,2]. In typical cases, the rc and ra of a polymer will generally differ up to 15% [3]. Polymers with unsubstituted monomeric units, such as poly(ethylene) and nylon-6,6, show the largest difference between ρc and ρa. These chains crystallize in an all-trans conformation with particularly tight packing of the chains. In contrast, helix-forming polymers with large substituents, such as isotactic poly(styrene), pack less efficiently in the crystalline state thus $\rho c - \rho a$ is correspondingly smaller. For semicrystalline polymers, van Krevelen [2] gives the approximate relationship $\rho sc=\rho a = 1 + 0{:}13xc$, where ρsc is the density of the (semi-) crystalline polymer. The bulk density ρ of polymer solids is influenced strongly by the elemental composition and, to a certain degree, by the packing arrangement of chains and side groups. A polymer chain must exhibit an ordered, regular structure to allow efficient packing into the crystal lattice. Consequently, a stereo regular polymer is more likely to be crystalline and possess a higher density than the corresponding stereo irregular polymer [4].

Theoretical foundation for modern chemistry was laid more than 70 years ago at this time it becomes possible, in principle, to use this for understanding how electrons, atoms, and molecules interact. Theoretical calculation methods are helpful tools for elucidating structure and behavior of molecules , atoms and electrons. Quantum chemical molecular descriptors used to establish the relationship between structural characteristics of molecule and its properties the mathematical methods can be used[5-8].

The aim of this work is to theoretically calculate of the physico-chemical descriptors and correlate them with the experimental density with some monomers (Amorphous and Crystalline).

Experimental

The data set of density of polymers was collected from Rfe [9]. All calculation was carried out with the full geometry optimization of the Ethylene, Isobutylene, Propylene, Vinyl chloride and Vinylidene chloride. Theoretical calculation was carried out at the MP2 method using the basis set 6-31G(d) in the PCGAMESS program[10].

Results and Discussion

The global minimum energy obtained by the MP2 structure optimization obtained by calculation (the global minimum energy) of monomers (Amorphous and Crystalline). The total energy(the global minimum energy) and the system properties such as HOMO and LUMO energies ,energy gap(ΔE), Dipole moment, hardness(η), electronegetivity(X), electrophilicity(ω) of the compounds are presented in table l&2; it can be seen that have almost different energies and thus comparable instabilities. To study the correlation between density and quantum chemical parameters of monomers (Amorphous and Crystalline). the values of correlation coefficients R2 of the density of polymers

(Amorphous and Crystalline) for compounds understudy are different depends on the effect quantum chemical descriptors on the density of polymers in both cases(Amorphous and Crystalline).

Table 1. Calculated physico-chemical parameters of monomers by MP2 method using the basis set 6-31G(d) Amorphous.

Monomer	^{1}**Exp**	**HOMO**	**X**	η	ω	**LUMO**	ΔE	**D. M**	**T. E**
Ethylene	0.85	-0.3715	0.0955	0.276	0.01652	0.1805	0.552	8.80E-05	-78.0312
Isobutylene	0.915	-0.3371	0.07675	0.26036	0.011311	0.1836	0.5207	0.42789	-156.1059
Propylene	0.85	-0.3505	0.08675	0.26375	0.014265	0.177	0.5275	0.269967	-117.0671
VC	1.41	-0.3678	0.10575	0.26205	0.021337	0.1563	0.5241	1.592414	-536.9326
VDC	1.77	-0.3727	0.1173	0.2554	0.02691	0.1381	0.5108	1.495074	-995.8254

Table 2. Calculated physico-chemical parameters of monomers by MP2 method using the basis set 6- 31G(d) Crystallin.

Monomer	^{2}Exp	HOMO	X	η	ω	LUMO	ΔE	D. M	T. E
Ethylene	1	-0.3715	0.0955	0.276	0.01652	0.1805	0.552	8.80E-05	-78.0312
Isobutylene	0.94	-0.3371	0.07675	0.26036	0.011311	0.1836	0.5207	0.42789	-156.1059
Propylene	0.94	-0.3505	0.08675	0.26375	0.014265	0.177	0.5275	0.269967	-117.0671
VC	1.52	-0.3678	0.10575	0.26205	0.021337	0.1563	0.5241	1.592414	-536.9326
VDC	1.96	-0.3727	0.1173	0.2554	0.02691	0.1381	0.5108	1.495074	-995.8254

Definition of Descriptors Used in This Study1Exp= Experimental data of Amorphous, 2Exp= Experimental data of Crystalline, T.E= Total Energy(in Hartree), D.M= Dipole Moment in Debyes, η= Global hardness, X= Electronegative(in eV) ω= Electrophilicity(in eV), HOMO= The Energy of Highest Occupied Molecular Orbital (in eV), LUMO= The Energy of lowest Unoccupied Molecular Orbital (in eV), ΔE= Energy. GAP=Different between HOMO and LUMO is energy gaps in eV. VDC= Vinylidene chloride. VC= Vinyl Chloride.

The linearity correlates between the density of polymer in case amorphous with the parameters LUMO give a very good correlation coefficient R2 value of 0.967, Fig (1), while the density of polymer in case crystalline the excellent correlation coefficient R2 value of 0.982, Fig(2). In both cases (Amorphous and Crystalline) which indicate that the parameter LUMO play an important role in effect on the density properties of polymers.

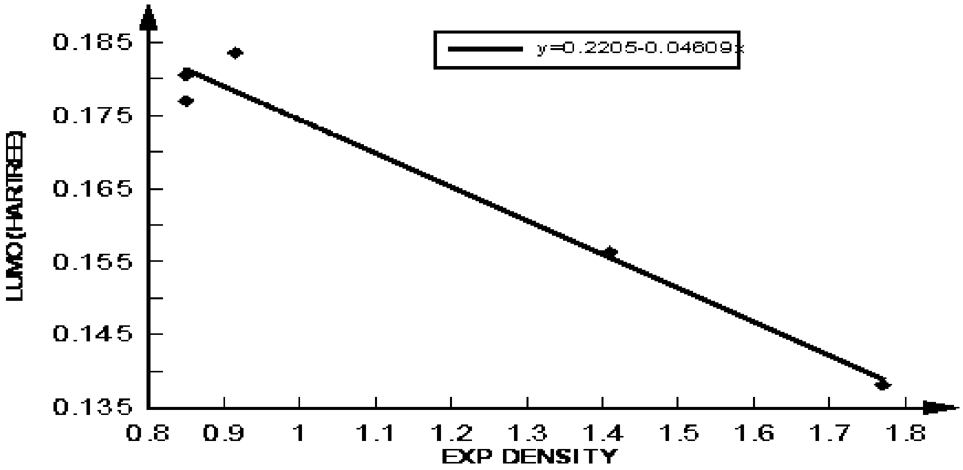

Fig 1. Correlation between experimental density of amorphous monomers and LUMO R^2= 0.967.

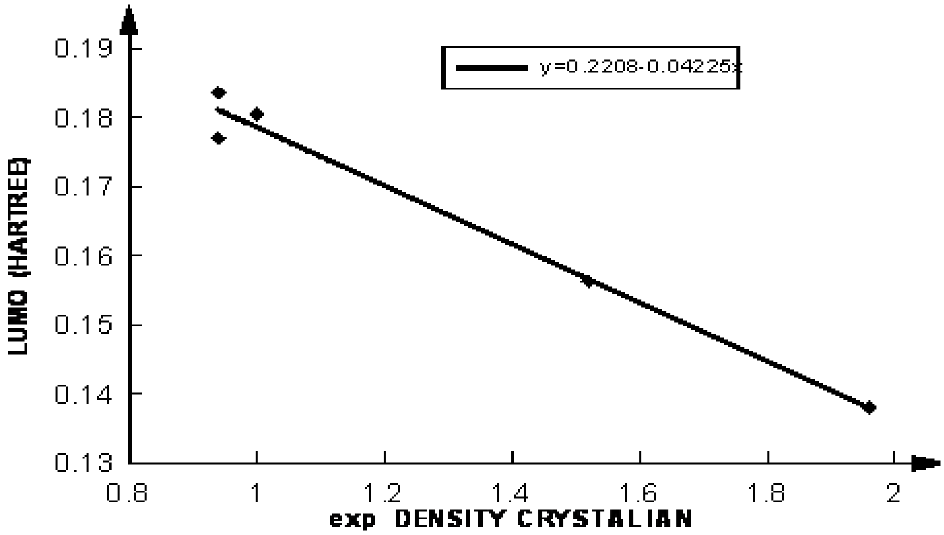

Fig 2. Correlation between experimental density of crystalline monomers and LUMO, R^2 =0.982.

While in figures (3&4), it can see the value of the total energy it influences by good linearity correlate with the density properties of polymers in both cases (Amorphous and Crystalline) with value of correlation coefficients, R2=0.979 & 0.985 respectively. On the other hand in figures (5&6) we notice the the value of Electrophilicity is a good correlationship with the experimental value of the density properties of polymers in the case crystalline with value of correlation coefficients, R2=0.932 compared with the case amorphous with value of correlation coefficients, R2=0.872. According to the correlation coefficients the density properties of polymers effected by the parameter electrophilicity in case crystalline more than amorphous[11-17].

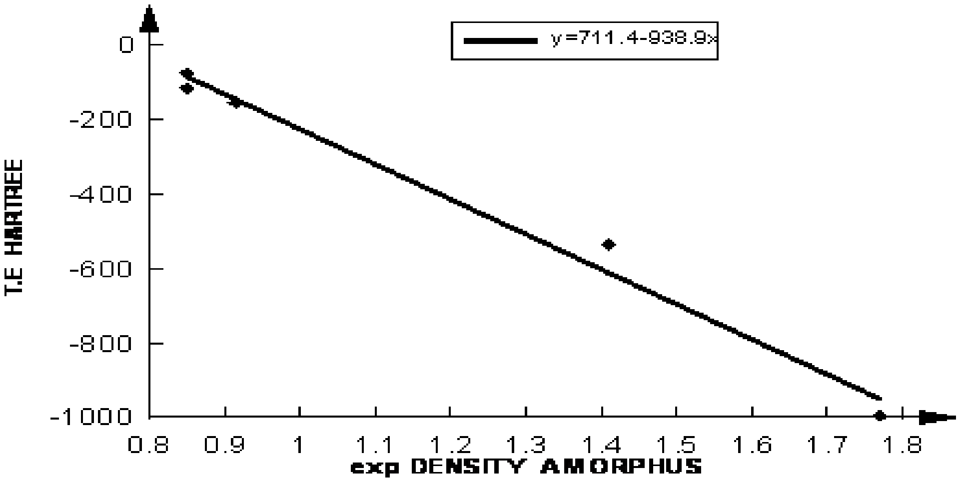

Fig 3. Correlation between experimental density of amorphous monomers and T.E, R^2= 0.979.

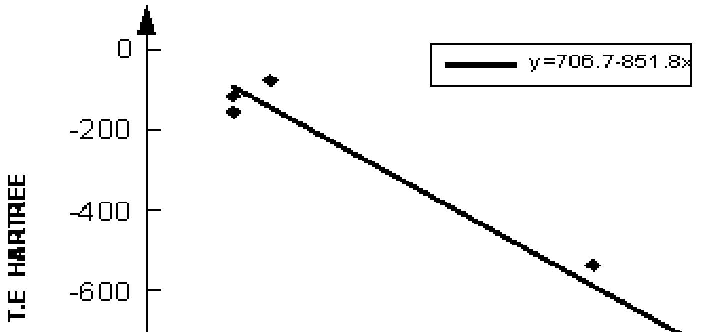

Fig 4.

Correlation between experimental density of crystalline monomers and T.E, R^2= 0.985.

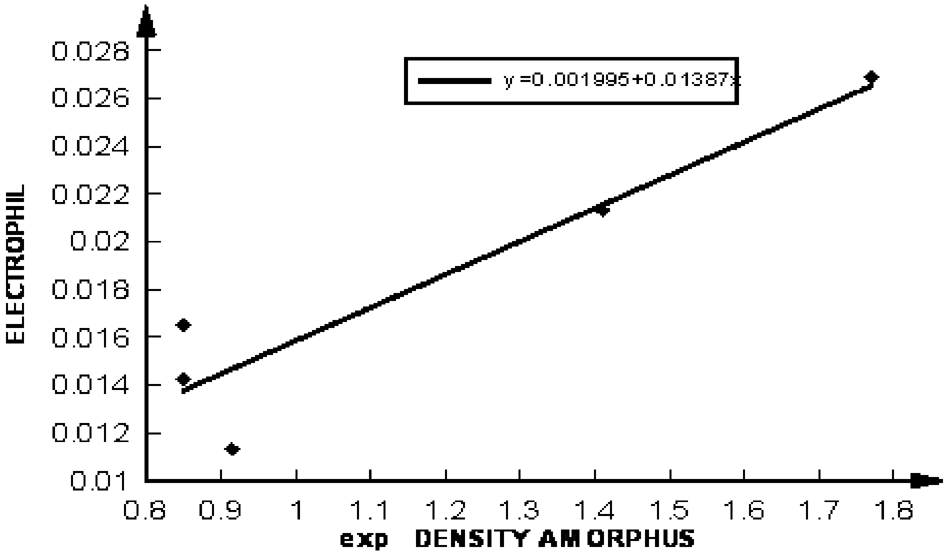

Fig 5. Correlation between experimental density of amorphous monomers and electrophilicity
R^2 =0.872.

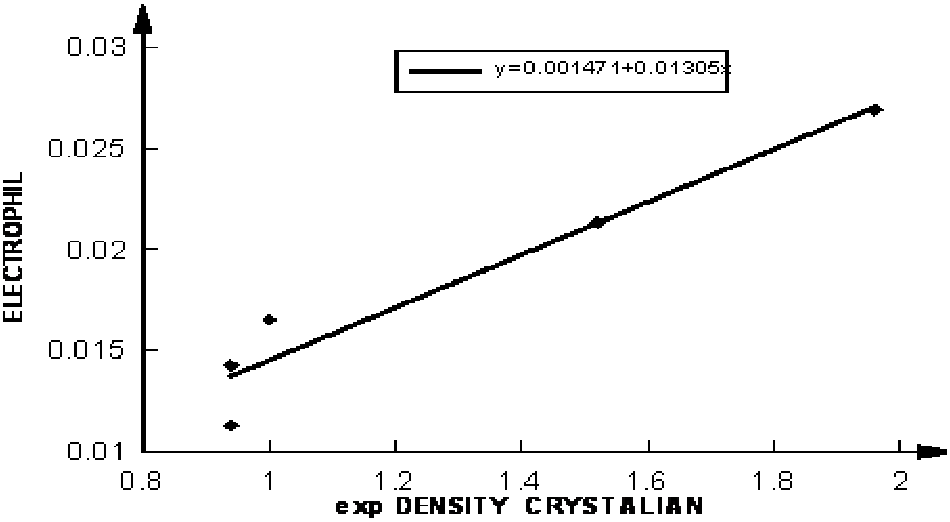

Fig 6.

Correlation between experimental density of crystalline monomers and Electrophilicity
R^2 =0.932.

Table 3, Shown the comparison between descriptors and the density properties of polymers in both cases (Amorphous and Crystalline), it can be seen in Table 3, From this table the descriptors HOMO, Energy Gap, Hardness, gave poor correlation coefficient R2 values comparable with the other descriptors.

Table: 3. Comparison between amorphous and crystalline

Descriptors	Correlation Coefficient R^2	
	Amorphous	Crystalline
HOMO	0.324	0.416
LUMO	0.967	0.982
Energy Gap	0.447	0.361
D.M	0.853	0.792
T.E	0.985	0.979
Electronegative	0. 778	0.854
Hardness	0.448	0.361
Electrophil	0.872	0.932

Conclusion

The experimental and the theoretical investigations of this compound have been performed successfully by using quantum chemical calculations. The computation analysis of these compounds by MP2 method using the basis set 6-31G(d) is used to find the best correlation between the various descriptors and density properties of polymers in both cases (Amorphous and Crystalline), The method adopted here for calculation MP2 using the basis set 6-31G(d), proved to be good to give the optimized geometry and minimized energy for the monomers under study. From all the results(In case Amorphous), The values of R2 for the linearity correlate was in the range 0.324-0.985. It found that the density properties of polymers it influences by the excellent linearity correlate with the descriptor total energy with the value of R2= 0.985, while the poor linearity correlate with HOMO, with value of R2=0.324. As well as (In case Crystalline) The values of R2 for the linearity correlate was in the range 0.361-0.982. The density properties of polymers it influences by the excellent linearity correlate with LUMO with the value of R2= 0.982. On the other hand the poor linearity correlate with the descriptors Hardness & Energy Gap , with value of R2=0.361& 0.361 respectively. From these values which indicate that these descriptors Total Energy and LUMO play an important role in effect on density properties of polymers in both cases (Amorphous and Crystalline) which allow chemists to elucidate and to understand how molecular structure influences properties.

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كيمياء الكم لدراسة العلاقة بين كثافة البوليمرات (المتبلورة . والغير المتبلورة) وخواصها التركيبية

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الخلاصة :

تم في هذه الدراسة حساب المتغيرات الكيميائي الفيزيائية للمونمرات باستخدام كيمياء الكم وبطريقة MP2 وباستخدام المستوى النظري 6-31G(d) ...لايجاد وتكوين العلاقة بين الموصوفات التالية

Total energy, Electrophil, Hardness, Electronegative, Dipole moment, Energy gap, HOMO and LUMO energies وكثافة البوليمرات في كلتا الحالتين (المتبلورة . والغير المتبلورة) ...وبينت الدراسة بأن افضل قيمه عالية ل($R^2=0.985$) للعلاقة الخطية مع الطاقة الكلية total energy..بينما في الحالة البلورية كانت افضل قيمه عالية ل($R^2=0.982$) للعلاقة الخطية مع طاقة االمدار الجزيئية LUMO. والتي اكدت بأن هذه المتغيرات الطاقة الكلية Total Energy و طاقة االمدار الجزيئية LUMO لها دور كبيرا في التاثير على خواص الكثافة للبوليمرات في كلتا الحالتين، والتي تساعد الكيميائي على فهم ومعرفة ودراسة تأثير التركيب الجزيئي على الخواص المركبات