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Use a Quantum Chemical to Study the Correlation between Intrinsic Viscosity of Polypropylene in three solvents and structure properties

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Abstract: Intrinsic viscosity of Polypropylene in different solvents were calculated by MP2 and B3LYP5 quantum chemical calculated methods at 6-31G(d) and 6-311G(d) levels of theory. Thecorrelation build up with help of the descriptors, total energy, Total free energy , Electrostatic interaction , Nuclear energy, Electronic energy, Dipole moment , Energy gap, HOMO and LUMO energies with Intrinsic viscosity depend on the nature of the variable as well as the method and the theoretical level used. All these values for descriptors have been calculated with help of MP2 and B3LYP5 methods to generate the correlation between Intrinsic viscosity of monomer under study and physicochemical properties. The best correlation depends onmethod and levels of theory was by MP2/6-31G(d) than B3LYB5/6-31G(d), while the correlation depends onMP2/ 6-311G(d) and B3LYB5/6-311G(d) methodbe close in results.

Keywords: Correlation,MP2 and B3LYP5, Intrinsic Viscosity[η],Polypropylene.

Introduction

Polypropylene (PP) is a typical thermoplastic with a number of desirable basic properties that make it a versatile material among thermoplastics. These properties coupled with its low specific gravity and low cost are the primary reason for its popularity as a commodity resin (1). Commercial polypropylene resins commonly are polymerized by conventional Ziegler–Natta catalyst systems and have a high molecular weight and a broad molecular weight distribution (MWD). The chemical structure of polypropylene is generally influenced by the kind of polymerization system used during its production. Because the MWD largely determines the rheological properties of polypropylene melts, this parameter must be controlled to improve the material response during processing and to achieve the diversity in polymer grades suitable for the different applications of polypropylene(2-5). Polypropylene is one of the most widely used polymers in the world because of the widespread availability and low cost of monomer, low manufacturing cost,and attractive polymer properties. These properties can be modified to be suitable for a wide variety of applications. Polypropylene can be processed by almost all commercial fabrication techniques. Approximately 30,000,000 ton was consumed worldwide in 2001(6). Polypropylene is an important commercial polymer with potential uses for producing package films, pipes, storage tanks, seat covers, monofilaments, ropes and also in washing machines(7).

Intrinsic viscosity of polymer in a solvent is of significant chemical and thermo-dynamical interest as well as of great practical importance. At low concentrations of polymer, the polymer chains are separated from each other, where each chain occupied a spherical volume of radiusRg. In this solution polymer–polymer interactions are smalland polymer coil volume is determined by polymer–solventthermodynamic interactions. The hydrodynamic volumeoccupied by a given polymer mass is the intrinsic viscosity,[η] which is a parameter that can be determined by dilutesolution viscosity measurements. Intrinsic viscosity probesthe interaction of molecular structure with the solution.There are many theories in polymer physics literature thatrelate intrinsic viscosity to molecular properties of polymerssuch as molecular properties, overlap concentration,and radius of gyration (8-11). The conformational properties of polymer chains are usually determined in dilute solutions of the polymers. Viscosity, light scattering, small-angle X-ray scattering, and osmotic pressure, are the main types of measurement performed in solutions. According to Biceraco, conformational properties play a key role in determining the properties of polymer solutions, and therefore, in both synthesis (i.e. polymerization in solution) and processing (i.e. solvent casting of thin films) (12).The aim of this study to the correlations between the experimental intrinsic viscosity and structure properties of Polypropylene polymer.

Experimental

The data set of intrinsic viscosity of Polypropylene in three solvents were collected from Bicerano (12).All calculation were carried out with the full geometry optimization of the monomer propylene Fig(1) that use in polymerization. Theoretical calculation were carried out at the MP2 and B3LYP5methods with theory level 6-31G(d) and6-311G(d) basis sets in the PCGAMESS program (13-14).

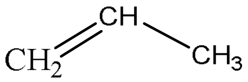

Fig1. Structure of Thepropylene

Results and Discussion

To study the correlation between intrinsic viscosity and quantum chemical parameters of polypropylene, values of total energy, total free energy, electrostatic interaction , nuclear energy, electronic energy, dipole moment, energy gap, HOMO and LUMO of polypropylene were calculated using B3LYP5 and MP2 methods in Benzene, Cyclohexane and Toluene .Results are given in Table 1,2,3and 4 respectively(15-16)..

Table 1. Calculated physico-chemical descriptors of propylene in three solvents, at B3LYP5/6-31G(d) method.

T.E a.u	D.M	ELEC.E . a.u	ELECTRO. INT a.u	DELTA G a.u	N.E a.u	HOMO eV	LUMO eV	GAP eV	EXP	solvent
-117.0678	0.3160	-156.036	-0.52	-73461.22	38.968	-9.608	4.759	14.367	160	Benzene
-117.4535	0.3460	-140.477	-0.93	-73461.6	23.409	-9.660	4.715	14.375	295	Cyclohexane
-117.0689	0.3513	-155.0247	-0.53	-73461.8	37.955	-9.728	4.884	14.612	182	Toluene

Table 2.Calculated physico-chemical descriptors of propylene in three solvents, at MP2/6-31G(d)method.

T.E a.u	D.M	ELEC .E . a.u	ELECTRO. INT a.u	ΔG Kcal/mol	N.E a.u	HOMO eV	LUMO eV	GAP eV	EXP	Solvents
-117.81726	0.389	-156.7859	-0.45	-73931.46	38.968	-6.680	0.590	7.270	160	Benzene
-117.81718	0.383	-159.6233	-0.40	-73931.41	41.806	-6.672	0.595	7.268	295	Cyclohexane
-117.81731	0.391	-155.3615	-0.48	-73931.49	37.544	-6.685	0.585	7.270	182	Toluene

Table 3. Calculated physico-chemical descriptors of polypropylene in threeSolvents, at B3LYP5/6-311G(d) method.

T.E a.u	D.M Debye	ELE.E . a.u	ELECTRO. INT a.u	DELTA G a.u	N.E a.u	HOMO eV	LUMO eV	GAP eV	EXP	solvents
-117.8468032	0.384235	-156.892383	-0.51	-73949.99	39.04558	-6.9797754	0.250	7.230	160	Benzene
-117.846714	0.378788	-159.7310458	-0.45	-73949.94	41.884332	-6.9716119	0.255	7.227	295	Cyclohexane
-117.8468497	0.387112	-155.4654684	-0.55	-73950.02	37.618619	-6.9852177	0.244	7.230	182	Toluene

Table 4. Calculated physico-chemical descriptors of polypropylene in three solvents, at MP2/6-311G(d) method.

T.E a.u	D.M Debye	ELE .E . a.u	ELECTRO . INT a.u	DELTA G a.u	N.E a.u	HOMO eV	LUMO eV	GAP eV	EXP	Solvent
-117.0919695	0.371367	-156.4284341	-0.54	-73476.33	39.33646	-9.83971	4.424606	14.26432	160	Benzene
-117.0918758	0.366258	-159.2737346	-0.47	-73476.27	42.18186	-9.83155	4.421885	14.25344	295	Cyclohexane
-117.0920184	0.373917	-155.0002799	-0.57	-73476.36	37.90826	-9.84244	4.424606	14.26704	182	Toluene

From the tables 5 and 6 those who represent the comparison between the values of the correlations between these variables and the intrinsic viscosity of the core using B3LYP5 and MP2 at levels 6-31G(d) and 6-311G(d) these relations depend on the nature of the variable as well as the method and the theoretical level used, Figures 1, 2, 3 and 4.

Table:5. Comparison between MP2 and B3LYP5.

Methods		Descriptors
B3LYP5/ 6-31G(d)	MP2/ 6-31G(d)	
R^2	R^2	
0.742	0.104	Total free energy in solvent
0.742	0.982	Electrostatic interaction
0.781	0.991	Nuclear energy
0.781	0.991	Electronic energy
0.773	0.977	Total energy
0.774	0.261	Dipole. moment
0.718	0.054	HOMO
0.606	0.340	LUMO
0.973	0.112	Energy gap

Table:6.Comparison between MP2 and B3LYP5.

Descriptors	Methods	
	MP2/ 6-311G(d)	B3LYP5/ 6-311G(d)
	R^2	R^2
Total free energy in solvent	0.781	0.742
Electrostatic interaction	0.811	0.716
Nuclear energy	0.781	0.780
Electronic energy	0.781	0.780
Total energy	0.772	0.773
Dipole .moment	0.782	0.770
HOMO	0.851	0.716
LUMO	0.976	0.608
Energy gap	0.887	0.976

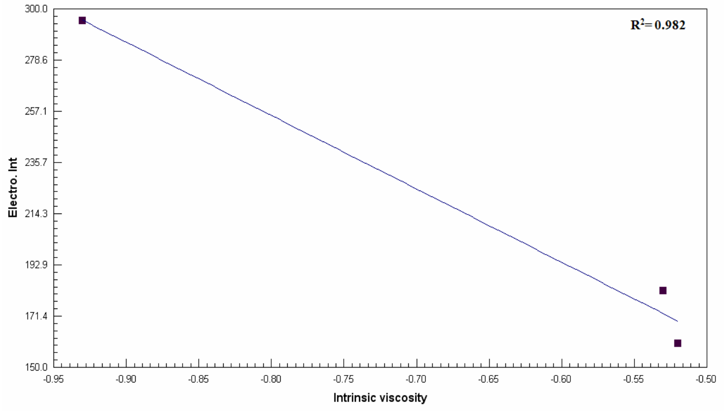

Fig.2. Correlation between Electrostatic interaction and intrinsic viscosity by MP2 /6-31G(d).

Fig (2), The variable electrostatic interaction has given the value of coefficient of regression 0.982 by using method MP2 and theoretical level 6-31G(d), while we note in the Fig (3) that the same variable given the value of 0.742 using the method B3LYP5 and theoretical level 6-311G(d) .

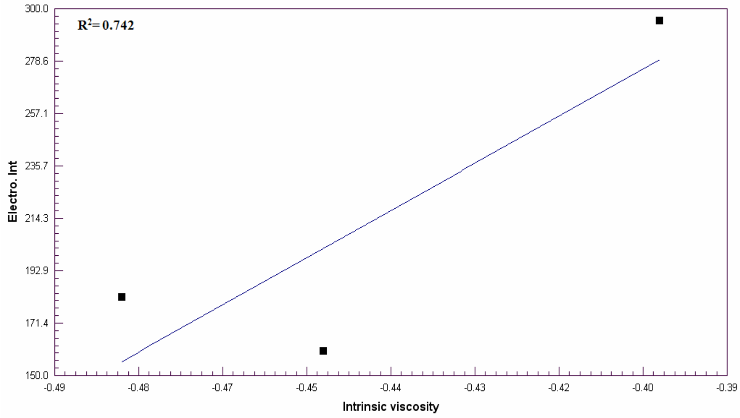

Fig.3.Correlation between Electrostatic interaction and intrinsic viscosity by B3LYP5/6-311G(d).

On the contrary, we note that in the case of variable Energy gap value in the case of regression coefficient method MP2 is 0.112Fig(4).

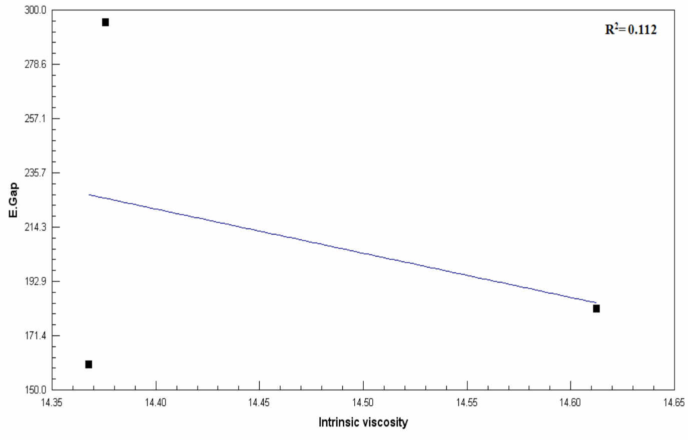

Fig.4.Correlation between E.Gap and intrinsic viscosity by MP2/ 6-31G(d).

Also the value of the regression coefficient is 0.973, fig(5)in the caseB3LYP5 method and at the sametheoretical level 6-31G(d).Either in the case of two variables Nuclear energy and Electronic energy we note accused have the same values of regression coefficient in the same method and theoretical level(15-16-17-18-1-20).

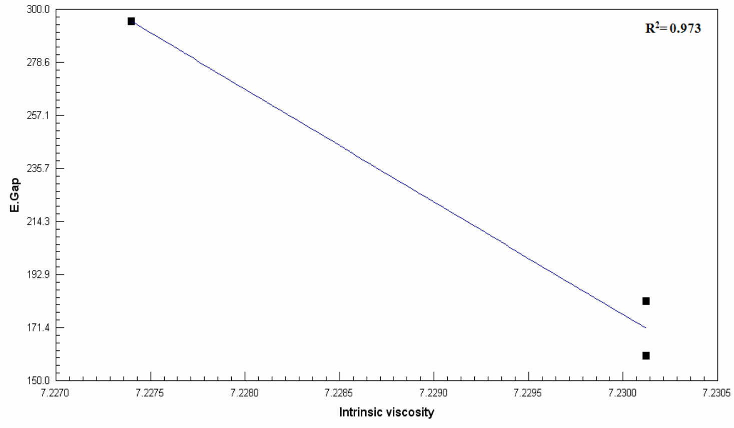

Fig.5. Correlation between E.Gap and intrinsic viscosity by B3LYP5/6-311G(d).

Conclusion

The quantum chemical calculations can be successfully used to find the best correlation between the various descriptors and intrinsic viscosity, depend on the nature of the variable as well as the method and the theoretical level used. The method adopted here for calculation density functional theory MP2/ B3LYP5 level of theory using the basis set 6-31G(d) and 6-311G(d), proved to be good to give the optimized geometry and minimized energy for the monomer under study.As well as the best correlation depends onmethod and levels of theory was by MP2/6-31G(d) than B3LYB5/6-31G(d), while the correlation depends onMP2/ 6-311G(d) and B3LYB5/6-311G(d) method be close in results.Also these theories levels suitable for studying influences of various descriptors on intrinsic viscosity and the structural properties as well as electronic properties of molecules studied.

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