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Research Article

Theoretical and Experimental Study of the Amphiphilic Block Copolymer poly (4-chloromethylstyrene) -b-poly (ethylene oxide)

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Abstract
In recent years, the significant evolution in the computer field and the progress made in quantum chemistry [1-3] calculation methods make it possible to give a good prediction and a good description of the electronic properties of a given entity. These circumstances favor a more common use of these tools in different fields of chemistry for the comparison of experimental and calculated results, as well as a better understanding of the reaction mechanisms.

For this we combine two methods: the theory and the experimental on the amphiphilic copolymers which constitute currently a particular class, which arouses a lot of interest as well in the field of the fundamental research as in the industrial field, in particular the pharmaceutical field where they are more particularly used in the vectorization of active principles because of their ability to encapsulate, transport and release some non-water soluble molecules.

Our work will be divided into two parts: the experimental part which consists of preparing a block amphiphilic copolymer with a well-defined structure that can adopt micelle type morphologies poly (4-chloromethylstyrene) -b-poly (ethylene oxide) and analyzes by the different structural analysis techniques: nuclear magnetic resonance (^{1}HNMR, ^{13}CNMR), absorption spectroscopy (IR) and gel permeation chromatography (GPC), SEM.

The theoretical part: or we have studied by the theory of the functional density DFT synthetic amphiphilic copolymer poly (4-chloromethylstyrene) -b-poly (ethylene oxide). Using three different bases B3LYP, 6-31G and 6-31G ** for minimizing energy and choosing the best base. The results were also developed by theoretical analysis of 1H NMR, 13C NMR, and IR spectra.

Keywords
Amphiphilic Copolymers, Micelle, 4-Chloromethylstyrene, Quantum Chemistry, DFT.

Declaration of Conflicting Interest
The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Introduction:
The development of original materials with new properties or improved properties opening the way to new applications is an essential axis of research in the field of polymers and the development of increasingly complex macromolecular architectures is motivated by the need to produce new nanostructured materials to lead to the preparation of model systems with specific properties.

Amphiphilic copolymers constitute a particular class which arouses a great deal of interest [1-4] both in the field of fundamental research and in the industrial field, in particular the pharmaceutical field [5-7] where they are more particularly used in vectorization. active ingredients due to their capacity to encapsulate, transport and release certain water-insoluble molecules. These amphiphilic copolymers can also be used in the medical field [8], especially in the optical field [9-11] where they are used as thin films for optical glasses [12-17].

Our work will be divided into two parts:

An experimental part which consists in preparing an amphiphilic block copolymer with a well-defined structure, poly (4-chloromethylstyrene) –b-poly (ethylene oxide).

The synthesis methodology that we used is the direct route, it allowed us to obtain a block copolymer of well-defined architecture, of variable nature and composition. . This method consists in deactivating a macrocation obtained by acid initiation of the first block of the block copolymer with a functional polymer.

We have obviously characterized this block copolymer by structural analysis techniques, such as infrared FTIR spectroscopy, 1H NMR and 13C NMR nuclear magnetic resonance.

In the second part this is a theoretical part: where we used quantum chemistry [18,19] which allows the study of phenomena by means of calculations on computers. This is of great interest for determining reaction mechanisms since quantum chemistry can then be used to model short-lived intermediates or even transition states. Thus, quantum chemistry provides information about molecules that are difficult and sometimes impossible to study experimentally. The theory, through the intermediary of the DFT [20,21] makes it possible to overcome the experimental shortcomings (molecular geometry, structural parameters, polymerization path and electronic structure ...).

We have treated the study by different methods of quantum chemistry such as: the theory of the functional density of DFT, Hartree Fock [22,24] on the amphiphilic copolymer synthesized poly (4-chloromethylstyrene) –b-poly (oxide d 'ethylene). Using three different bases B3LYP, 6-31G and 6-31G ** to minimize energy and choose the best base. We have also developed the results found by theoretical analysis of 1H NMR, 13C NMR, and IR spectrum.

Experimental part:

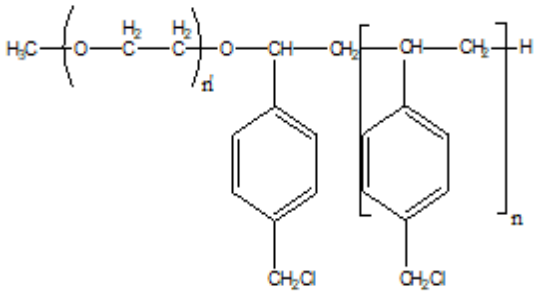
1-Synthesis and characterization of the poly (4-chloromethylstyrene) -b-poly (ethylene oxide) block amphiphilic copolymer:

The synthesis of the amphiphilic block copolymer of poly (4-chloromethylstyrene) -b-poly (ethylene oxide) was carried out from the initiation of 4-chloromethylstyrene by sulfiric acid H_2SO_4 in solution in chloroform. followed, respectively, of a deactivation of the macrocation obtained by poly (ethylene oxide) (PEO) which is a biocompatible polymer and a hydrophilic polyether, it is because of its excellent affinity to water that the PEO is widely used in the preparation of the copolymer.

Using the direct method of disabling a macrocation we have thus tried to prepare this amphiphilic block copolymers.

The amphiphilic block copolymer obtained was precipitated in cyclohexane cold and then dried under vacuum.

Scheme 1: the scheme of the structure of the amphiphilic copolymer of poly (4-chloromethylstyrene-b-poly (ethylene oxide)



2-characterization of the product obtained:

The product obtained according to experiment was characterized by infrared absorption spectroscopy, nuclear magnetic resonance (1H NMR and 13 C NMR), and gel permeation chromatography (GPC).

2-1-Analysis by IR absorption spectroscopy:

FT-IR spectra were obtained on a Nicolat Avatar 320FT-IR spectrometer, 32 scans at a resolution of 1cm-1 were collected with a KBr disk at room tempm erature in the range of 4000 - 500 cm^{-1} (Algeria). (Figure.1). FT-IR (cast film): 2920,6cm^{-1} (γ CH), 1423cm^{-1} (d CH), and 754 cm^{-1} (γ C-Cl) , 1105,9 cm^{-1}

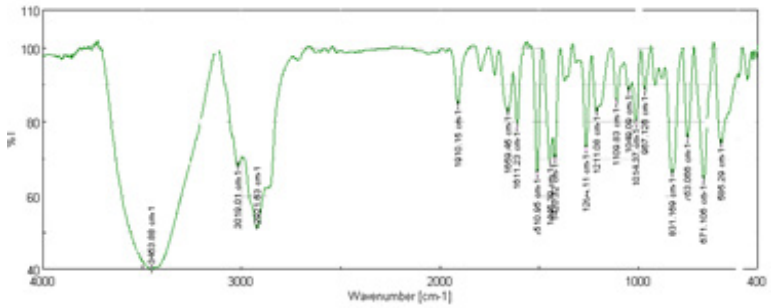


Figure 1: FTIR of the amphiphilic block copolymer obtained in CCl_4

2-2-^{1}H NMR Analysis:

The sample was characterized by 1H NMR. The results obtained confirmed that this is indeed the expected structure and the product obtained corresponds well to poly (4-chloromethylstyrene) -b-poly (ethylene oxide).

^{1}H NMR (CDCl3): d = 3.7ppm (CHCH2), 2.0ppm (CH2CH2C-O), 1.7ppm (CH2CH) and 1.1 ppm (CCH3) , 7.26ppm (CH benzene), 2.05ppm(CH2Cl).(figure.2)

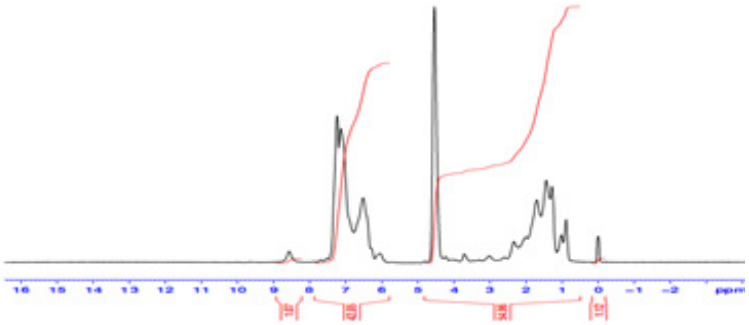


Figure 2: ^{1}H NMR of amphiphilic block copolymer obtained in $CDCl_3$

1-2-3- ^{13}C NMR Analysis:

Sample N1 was subjected to ^{13}CNMR analysis (Figure 3). The results obtained indicate the presence of characteristic signals for poly (ethylene oxide) and poly (4-chloromethylstyrene).

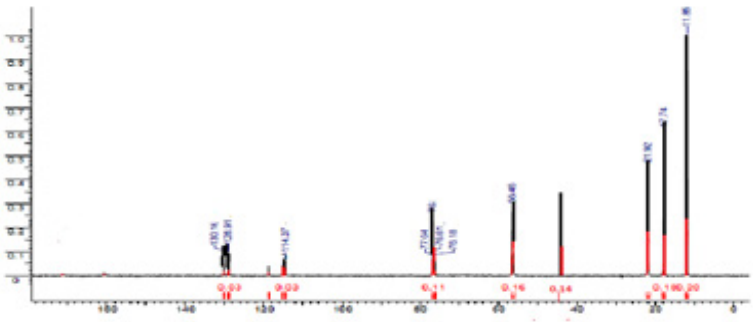


Figure 3: ^{13}C NMR spectrum of poly (4-chloromethylstyrene) -b-poly (ethylene oxide) in $CDCl_3$

1-2-4-Analysis by GPC:

Tablel: Number and weight average molar masses as well as the polydispersity index of the amphiphilic block copolymer obtained during experiment N1.

Expérience	Mn	Mw	Ip	L'éluant	Standard
N1	2097	1959	1,070	THF	polystyrène

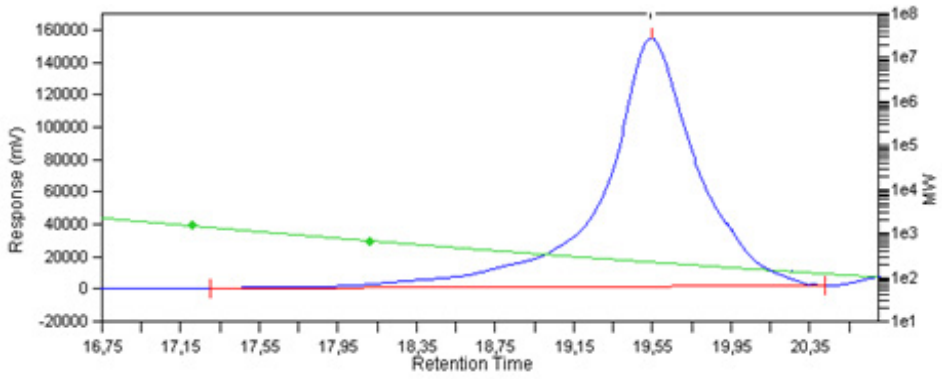


Figure 4: GPC Chromatography of poly (4-chloromethylstyrene) -b-poly (ethylene oxide) in THF

Given the presence of a hydrophilic-hydrophobic balance in the block copolymer wich prepared, we tried to exploit this character amphiphatic to study the tensioactives properties.

The measures were made by the technique of ring on a tensiometer «CSC-Du NOUY». This equipment is operated in a range of 0 at 90dyne/cm with a precision 0,05dyne/cm at 25°C. The ring is used for measurements have a diameter 60mm,and there is from platine.

Micelle formation by the water-soluble fraction of PEO/VBC block copolymers was investigated at 25°C in water at 5 mg/ml concentration. We used a tensiometer method to determined a critical micellaire concentration.

The measures of the tension relative superficial in the aqueous solution of copolymer block show that there is a reduction in the tension superficial of the water.

We were able to, determined a micellaire critical concentration wich equal 0,593mg/ml(Figure.5).

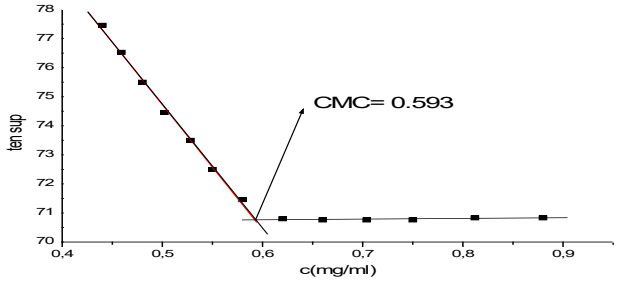


Figure 5: Variation of the equilibrium surface tension with poly(VBC-b-EO) copolymer in water solution

These tensioactive properties allow us to conclude that this copolymer establish a new class of tensioactive no-ionic.

II-Theoretical part :

In recent years, the significant evolution in the computer field and the progress made in quantum chemistry calculation methods make it possible to give a good prediction and a good description of the electronic properties of a given entity. These circumstances favor a more common use of these tools in different fields of chemistry for the comparison of experimental and calculated results, as well as a better understanding of the reaction mechanisms.

II-Methods and materials:

The discussion that we will engage to validate the method is based on the use of the Gaussian software and its gaussview graphical side to model the molecule calculates it was launched with the correlation exchange functional B3LYP and the Gaussian base 6-31G * * or 6-31G (p, d). The latter has the same denomination, where the set of functions p added to the hydrogens and the set of functions d added to the other heavy atoms is well defined.

In the first instance the theoretical calculation was made with two hartree fock and DFT methods using the functional B3LYP (Becke Lee-Yang-Parr) and two different basic ones the 6-31G, and the 6-31G ** for the latter.

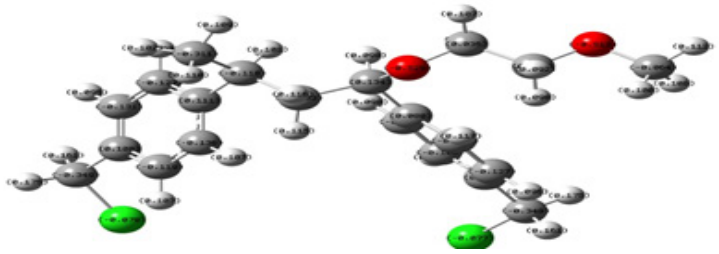
II-1-Comparison of the best valid method for energy:

The ab initio calculations from the Hartree Fock (and post Hartree Fock) method and those from the DFT functional theory have been chosen. These two approaches differ in solving the Schrödinger equation. Table II.1 shows the energy values calculated by the two methods chosen.

Table II.1: represents the different energy values calculated by the two methods H-F and DFT on the synthesized copolymer.

HF (6-31G dp)	DFT (6-31G dp)
-1879,09895996 a.u	-1886,76577112 a.u

From these results it is concluded that the DFT method is a better validated approach with lower energy.



Representation of the copolymer structure optimize by DFT with B3LYP, 6-311G **

II-2-Electronic study:

We applied the most valid method "DFT ++": Table II.2 shows the purely theoretical parameters of the dipole moment (DM), the energy of the boundary orbitals, HOMO, LUMO and the energy gap.

dipole moment	3.2984 debye
Homo	-0.03142 a.u
Lumo	-0.24206 a.u
GAP	0.21064 a.u

Table II. 2: Represents the values of the dipole moment (DM), the energy of the boundary orbitals, HOMO, LUMO and the energy gap.

II-2-1-Orbital boundaries HOMO -LUMO:

Frontier orbitals are two types of particular molecular orbitals (OM): the HOMO orbital (or HOMO), HO (High Occupied) which is the highest energy molecular orbital occupied by at least one electron, and the orbital LUMO (acronym for lowest unoccupied molecular orbital), BV (for Low Vacant) which is the lowest orbital energy not occupied by an electron. We performed a qualitative study of the boundary orbitals of copolymer geometry by the DFT method at B3LYP / 6-31G ** level. Figure II.2 is the representation of the HOMO and LUMO boundary orbitals for the different isomers

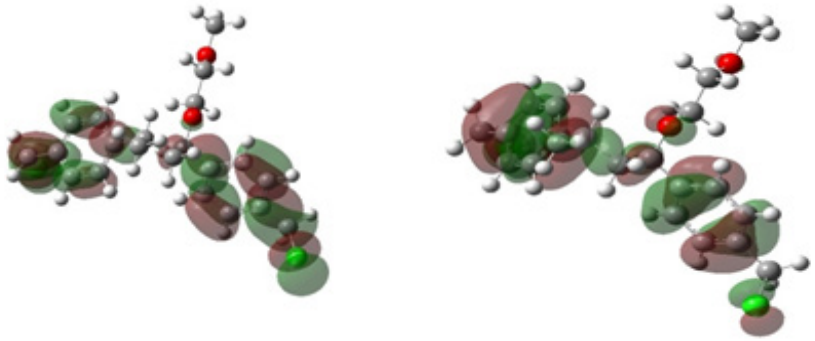


Figure II.2: HOMO and LUMO 2D MESP images

II-3-1-Theoretical Study of the Infra-Red Spectrum of Synthesized Amphiphilic Copolymer

Examination of the theoretical IR spectrum (Figure4) of the synthesized amphiphilic copolymer allowed us to identify the main characteristic bands. Table 4 groups together the main characteristic bands of the synthesized amphiphilic copolymer.

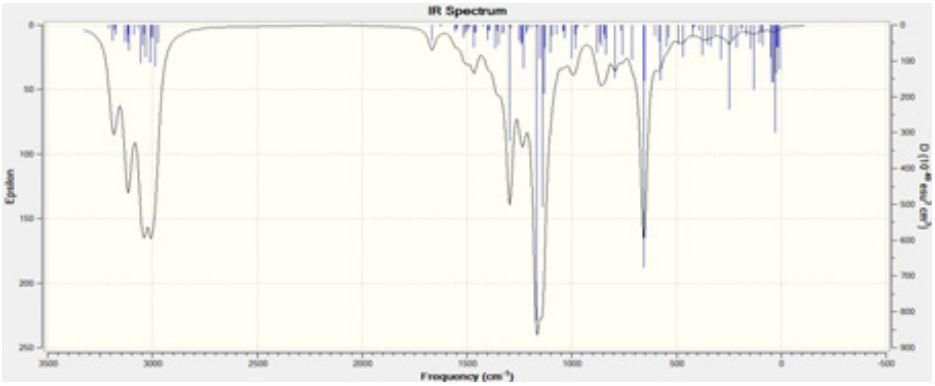


Table II.4: The main IR bands characteristic of the synthesized amphiphilic copolymer

II-3-2-Theoritical Study of NMR of amphiphilic block copolymer obtained :

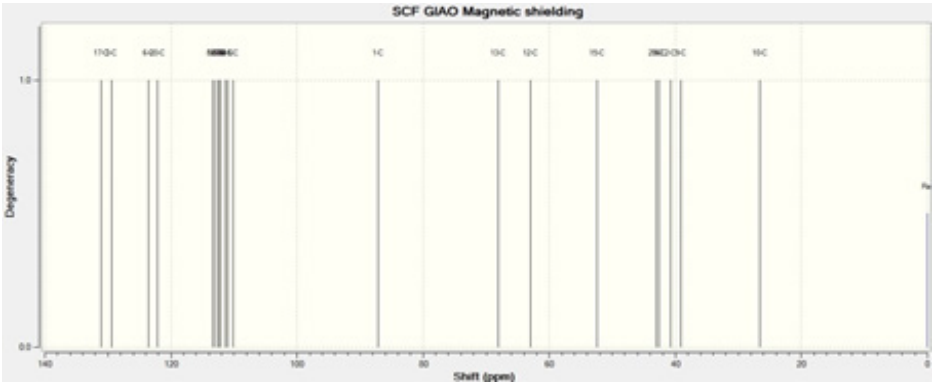


Figure II.5 : ^{13}C NMR theoretical spectrum of poly (4-chloromethylstyrene) -b-poly (ethylene oxide) in $CDCl_3$

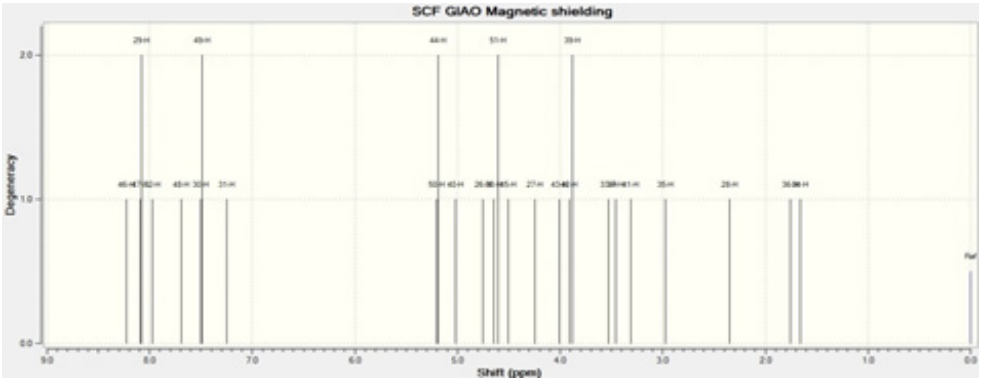


Figure II.6 : ^{1}H NMR spectrum of poly (4-chloromethylstyrene) -b-poly (ethylene oxide) in $CDCl_3$

Conclusion:

The general objective of this essentially fundamental work is to bring new knowledge on the behavior of amphiphilic block copolymers in experimental rather than theoretical terms. Thus, our study focused, on the one hand, on the synthesis and characterization of amphipathic block copolymer and their physicochemical properties in aqueous solution. And on the other hand, used quantum chemistry as a theoretical tool, or we used the ab initio method: the DFT which is able to accurately determine geometric molecular properties, binding energies and different types of spectrum for molecules as complex as coordination compounds.

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