

Studies on computational chemistry and complexation behavior between Poly(styrene-co-methacrylic acid) and Poly(styrene-co-4-vinylpyridine)

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Abstract

Computational approaches plays a dynamic role in the variety of modules for quantum mechanical (QM) and molecular mechanical (MM) simulations by Gaussian®09 software. In this work complexation behavior has been investigated between different composition of poly styrene-co-methacrylic acid (SMA) and poly styrene-co-4-vinylpyridine (S4VP). Polymer-polymer complexations performed by semi-empirical methods are DFT (B3LYP,RHF) levels of theory via 6-31G* basis set. Quantitative interaction analyzed by different techniques such as optimization of conformers, binding energy of blend polymers through Hartree-Fock (HF), hydrogen non-polar bond distance, spectrum of IR/UV-Vis spectroscopy at MM & QM model, and the excitation energy at quantum mechanical level change into wavelength contains a number of absorption bands (200, 261.17, 250, 300, 350 nm). In this research an impact on miscibility complexation was also observed in polymers blend system followed by hydrogen-bonding SMA and S4VP (QM = 6.40, MM = 17.25). This research further confirmed the Hydrogen-bonding connections between carboxylic and pyridine clusters in different areas (MM = 3200cm^{-1} , QM = 3400cm^{-1}) by a qualitative analysis through IR. Furthermore it is observed that QM methods provide distinct data as compared to MM methods, however it is worth mentioning that QM methods produce more reliable data of different properties of the system.

Keywords: Computational approaches, Quantum and molecular mechanical, Gaussian® 09 software, Complexation behavior.

1.Introduction

Miscibility enhancement approach is well explained by the development of hydrogen-bonding interactions in mixture of various polymers. Many miscible polymer blends are reported in the previous literature [1-3]. Customized characteristics and complexations are observed between different polymers prepared by blending two polymers or copolymers, and it further helped in monitoring the interactions occurred in the mixtures of components [4]. Mixture of two polymers or copolymers contain donor and acceptor protons [5]. Enhancement of miscibility for sufficient densities of interacting species is usually developed by the specific interactions within disparate components of a mix [6]. In recent years, there has been great interest in the advanced methods of processing of polymers with its widespread applications and polymers complexation evaluated by numerous investigators [2-4, 7]. Complexation behaviors were reported in the various polymer-polymer complexes such as poly vinylpyridine/poly *n*-alkylitaconates, poly 2-hydroxypropyl methacrylate/poly *N,N*-dimethylacrylamide, poly styrene-*co*-vinylphenol/polystyrene-*co*-4-vinylpyridine, and poly vinylphenol/poly *N,N*-dimethylacrylamide [3]. Nonradiative energy transfer fluorospectroscopy, laser light scattering, viscometry, FTIR and various other methods were frequently used for polymer-polymer complexation behavior studies [2,3,8]. During the last several years computational chemistry becomes a very popular and novel discipline in computing powers to understand chemical reactions and complexation behaviors of different chemical and biological systems numerically by applying fundamental laws of physics [1, 3]. Computational-theoretical modelling software often based on empirical information and becomes a powerful mean for predicting unknown properties and suggesting experiments [9]. In the present work miscibility enhancement in polymers blend system of SMA and S4VP interaction induced by employing hydrogen bonding technique of DFT under B3LYP/6-31G* approach. Moreover, Co-polymers 3D structures, energy of optimization and spectrum results were summarized by using Gaussian® 09 software as computational application.

1. Materials and Methods

The experiment has been accomplished for the quantitative study of complexation behavior between two different co-polymers structures such as Poly(styrene-*co*-4-vinylpyridine)/S4VP and Poly(styrene-*co*-methacrylic acid)/SMA by Gaussian® 09 3D software. It is a powerful computational device and a versatile molecular editor for predicting many properties of molecules, energies simulation and reactions using techniques based on quantum, molecular and statistical mechanics. The Opt of SMA and S4VP by the model SP and hybrid calculations in which molecular geometries were optimized by using semi-empirical (DFT) techniques. The Methods is followed by B3LYP and RHF on the basis set of 6-31G* level. During Opt of QM job take more time and form many conformers of polymer. The energy change during a chemical reaction were obtained after the complete SP and pooled Opt calculate the ΔE_{bind} by HF determination in terms of Kcal/mol in Equation 2. This experiment elaborates the conformation of mixture co-polymers in a hybrid methods on the basis of non-polar interaction of binding forces distance between SMA and S4VP by the hydrogen bonding interaction of benzene ring and methane H bond. Though, three dimensions represent the bond angle, bond distance and the Hartree-Fock energy values. This research expressed, firstly the vibrational frequency of IR spectrum of single/blend co-polymers to visualize the results by the hybrid methods of RB3LYP/RHF in 6-31G* at a singlet determination. Secondly, QM method in ultraviolet-visible spectra of combined Opt of blend polymers by DFT techniques gave the excitation of energy which converts into the wavelength by oscillator strength. The excitation energy at quantum mechanical level change into wavelength involves a number of absorption bands. The Peaks are observed in hybrid levels typically under UV/Visible spectra zone designed as ϵ vs. λ . Equation 5 represents the molar absorptivity analyzed by Gaussian band shape equation which determines the different wavelengths for QM by ultraviolet-visible range.

2. Results and Discussion

The computational methodologies are used for simulation of complexation behavior between different polymers blends such as poly(styrene-co-4-vinylpyridine)/(S4VP) and poly(styrene-co-methacrylic acid)/(SMA) with intermolecular interactions of their components [3]. The quantum mechanical simulation of co-polymers chemical networks, molecular dynamics and mechanics are based on classical force fields techniques. Gaussian® software delivers a range of molecular mechanics (MM) and quantum mechanics (QM) modules calculations. This software further describes the overall progress and manageability of completely distributed applications, as well as capable of predicting many properties of molecules [10]. These applications are mostly based on solving Schrodinger's equation to calculate the probability of finding electron.

3.1 Geometry Optimization (Opt) of S4VP and SMA

Gaussian® can calculate three dimensional (3D) structure Opts (minimizations) with both MM/QM methods and find the molecular structure coordination that represent a potential energy minimum and also determine the enforced structural changes in a molecule. In the present work, Opt of polymers S4VP and SMA energy is calculated by density functional theory (DFT) techniques is similar to the Hartree-Fock (HF). Opt of structures in semi-empirical methods of energy calculations output followed by RB3LYP and RHF/6-31G* in basis set of singlet determination of dipole moment (Figure 1 and 2).

Table 1. Single point and pooled Opts of S4VP and SMA in hybrid calculation

SP = Single point energy Opt of poly(styrene-co-methacrylic acid)/SMA, poly(styrene-co-4-vinylpyridine)/S4VP & pooled Opt S4VP + SMA is reported in DFT techniques by MM and QM methods.

Summary	S4VP		SMA		SMA & S4VP	
	QM	MM	QM	MM	QM	MM
Calculation type	SP	SP	SP	SP	FOPT	FOPT
Calculation method	RB3LYP	RHF	RB3LYP	RHF	RB3LYP	RHF
Basis set	6-31G	6-31G	6-31G	6-31G	6-31G	6-31G
E(RB+HF-LYP)	-1029.4674 a.u	-1022.3102 a.u	-1010.2548 a.u	-964.3960 a.u	-2039.7227 a.u	-1986.7062 a.u
Dipole moment	3.1534 Debye	3.2406 Debye	1.5949 Debye	1.8923 Debye	1.6839 Debye	4.9772 Debye
Job CPU time	4 mint, 2.6 sec	1 mint, 21.2 sec	4 mint, 11.0 sec	1mint,35.0 sec	1 day,7 hour,16 mint, 28.5 sec	5 hour, 35 mint, 39.7 sec

The molecular structure found to be an Opt of S4VP containing 4-vinylpyridine (Figure 1) and SMA containing methacrylic acid (Figure 2) in a hybrid base calculations which was co-related with Bennour et al., 2005. In pooled opt polymers by a singlet spins of SMA & S4VP for MM method have 31 conformers compare to the QM which is contain 92 conformations, this job takes more time of Opt (Figure 3). The single point energy (SP) and approximate energy in pooled opt of co-polymers based on DFT or semi-empirical methods in hybrid calculations presented in a table-1.

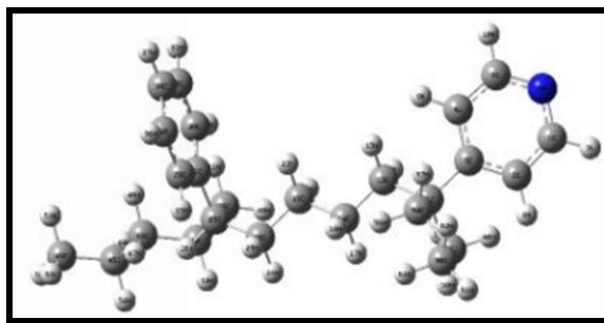


Figure 1: Opt of poly(styrene-co-4-vinylpyridine)/S4VP

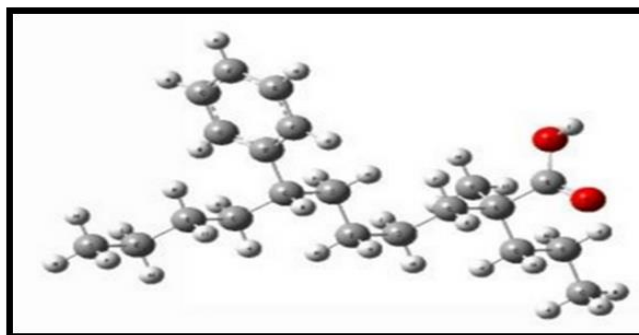


Figure 2: Opt of poly(styrene-co-methacrylic acid)/SMA

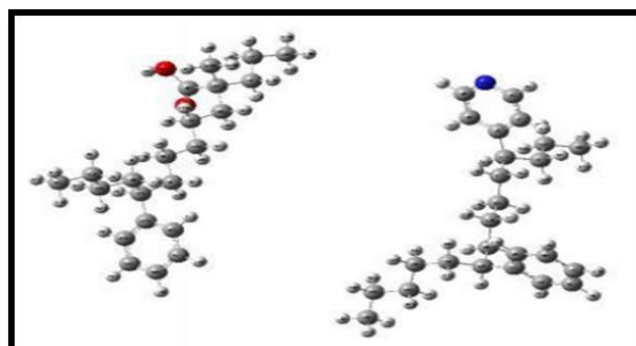


Figure 3: Pooled Opt of poly (styrene-co-methacrylicacid)/SMA and poly (styrene-co-4-vinylpyridine)/S4VP

2.2 Binding Energy Calculation (ΔE_{bind})

Binding energy calculations provide complete information of a system along with the interactions between different components and its chemical composition. Collective determinations of various non-covalent interactions, for instance hydrogen bonding, electrostatic, hydrophobic, cation- π , π - π interactions and steric complementarity can be used to understand the binding and selectivity in binding mechanisms [12]. The Structures were fully optimized using the density equation ΔE_{bind} for the calculation of polymers SMA & S4VP. The dissimilarity among the energy variations in free ligand, complex and ion were explained by,

$$\Delta E_{bind} = E_{complex} - (E_{ion} + E_{Ligand}) \quad \text{Eq. (1)}$$

So we can estimate the energy according to Optimization of polymers SMA & S4VP by the formula of change in energy Eq. 1 such as,

$$\Delta E_{bind} = E(S4VP + SMA) - SP(E_1) + SP(E_2) \quad \text{Eq. (2)}$$

The Opt, frequency, and SP calculation of the complexes in polymers were carried out with the interaction of energies for ground and excited states in QM/MM based methods in Eq. 2. Molecules are most stable when their energy is low

estimated according to Hartree-Fock (HF) energy determination (E_h) = 2625.49962 KJ/mol or 627.509 Kcal/mol listed in Table-2 [13]. Many simulations are summarized in numerous different means to calculate binding energies, binding free energies or relative binding free energies after the complete Opt of structure [11].

Table 2. $SP(E_1)$ = Single point energy Opt of poly(styrene-co-methacrylic acid)/SMA, $SP(E_2)$ = single point energy Opt of poly(styrene-co-4-vinylpyridine)/S4VP, E_{Opt} = Total energy Opt of S4VP & SMA, and ΔE = Change in Energy or BE.

SMA S4VP	& SP(E ₁)	SP(E ₂)	(E ₁ +E ₂)	ΔE_{bind}		
MM	-964.3960 a.u	-1022.3102 a.u	-1986.7062 a.u	0.0000 a.u	-0.1208 Kcal/mol	-0.0289 Kcal/mol
QM	-1010.2548 a.u	-1029.4674 a.u	-2039.7227 a.u	-0.0044 a.u	-11.6310 Kcal/mol	-2.7799 Kcal/mol

3.3 Structural Confirmation of Polymers

There are four carbon-hydrogen single covalent bonds (nonpolar covalent bonds) in methane molecule and due to equal sharing of electrons it signifies the no charge separation (dipole moment). Whereas the benzene is non-polar (non-covalent bond) and it's highly structural energetic symmetry is comparably stronger than a typical hydrogen bond. So that the non-polar bond distance/length between the two blend co-polymers (SMA & S4VP) interaction of CH_3 and C_6H_6 due to high structural symmetry hydrogen bonding interface in QM = 6.40 and MM = 17.25 methods (Figure 4).

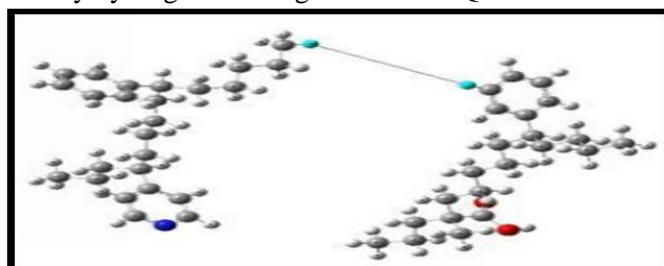


Figure 4: Bond length of optimized blend structure of SMA & S4VP

Data related to the contact between co-polymers obtained at QM level methods is lower than MM based methods, it is also pertinent to mention that later produce less reliable data shown in Figure 4 and 5.

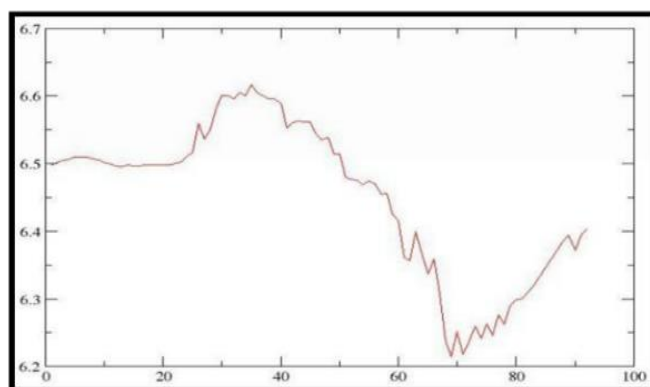


Figure 5: Spectrum of optimized blend co-polymers

3.4 Vibrational Frequency (IR)

The research performed a vibrational analysis in hybrid calculation of co-polymers (SMA & S4VP), then chose vibrational spectrum to visualize the results by the methods of RB3LYP and RHF in 6-31G* at a singlet determination. Spectrums of all the vibrational frequencies are simulated by infrared (IR) spectra in which dipole moment 4.9772 Debye. The vibration analysis calculation should be performed after Opt in polymers of configuration interactions to predict frequencies and intensities of spectrum in a hybrid models due to specific interactions rise from hydrogen bonding among the pyridine groups of the S4VP (Figure 1) and the carboxylic groups of the SMA (Figure 2) in the most exciting areas [1,3].

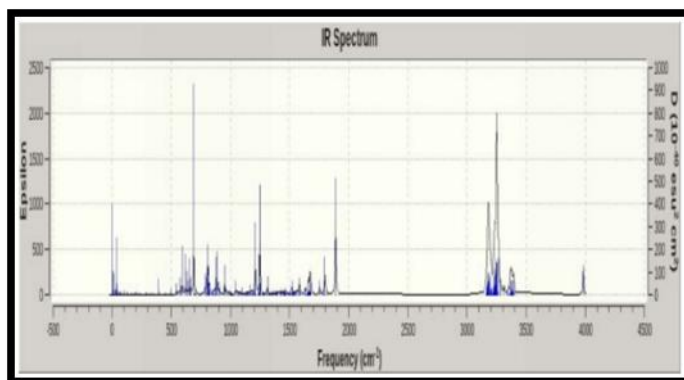


Figure 6: MM, IR spectra of SMA & S4VP different ratios of their blends at 3300 cm^{-1} region

The interactions of study was carried out in the carbonyl region of SMA and S4VP in which the S4VP is transparent and Gaussian spectral curve-fitting technique were used for the determination of carbonyl bands fractions of relative areas [3]. The quantitative analysis of inter polymer relations that arise with the SMA/S4VP chiefly obtained from the peaks 3200 cm^{-1} observed in a region of QM (Figure 7) and 3300 cm^{-1} for MM (Figure 6) frequencies. The hybrid specific interactions that occurred between two constituents of blend co-polymers were observed in a regions in MM is 3200 cm^{-1} and QM is 3400 cm^{-1} in IR spectra, in which styrene groups absorbed in the same region (Figure 8). This type of calculation carrying force constants and the simulations of vibrational frequencies IR and Raman spectra with different interaction of molecular work were also evaluated by several researchers [1-2, 6, 14-15].

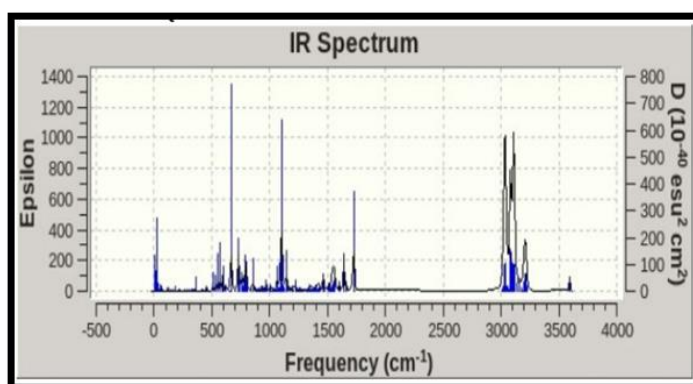


Figure 7: QM, IR spectra of SMA & S4VP different ratios of their blends at 3200 cm^{-1} region

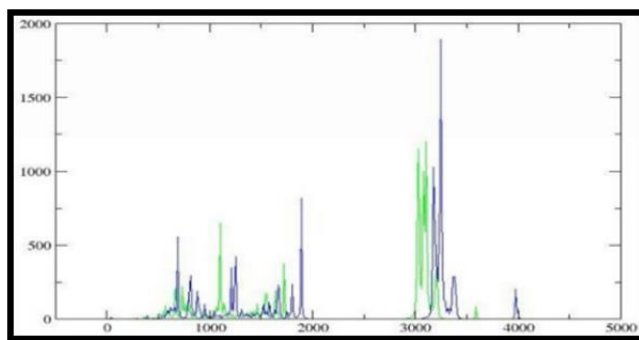


Figure 8: Hybrid, IR spectra of SMA & S4VP different ratios of their blends at 3200-3400 cm^{-1} region

3.5 UV-Visible Spectra

Gaussian® software can determine the simulation of vibrationally electronic spectra described by three basic parameters (position, intensity and width), which can be used for the estimation of fundamental transition characteristics as well as quantitative analysis [16]. The study of QM method by UV-visible spectra of pooled Opt interaction of co-polymers SMA & S4VP (Figure 1 and 2) analyzed the electron excitations in the Methods of time-dependent DFT singlet configuration [17]. In quantitative work performed, a blend of co-polymers single point excitation energy is 261.17 observed which then convert into the wavelength by the oscillator strength (f) 0.007, while using RTD-B3LYP-FC/6-31G* methodology. This also gives a restricted Hartree-Fock energy/E(RHF) -2039.72265653 a.u, in which dipole moment is 1.6839 Debye (Figure 10). UV-visible spectra have much smaller number of bands and much broader bandwidth as compare to vibrational spectra. Different band shapes of ultraviolet-visible spectra are also documented under the conditions of high resolutions and high signal-to-noise. The quantitative analyses are discussed only in terms of UV-Vis spectroscopy they can be easily used in all branches of molecular spectroscopy [18]. Therefore several studies revealed that ultraviolet-visible spectroscopy and elemental investigation used for the determination of styrene matters in complexation behavior of copolymers [3].

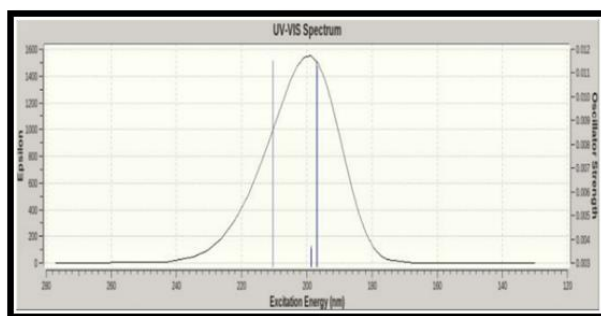


Figure 9: MM method UV-Vis spectra of blends SMA & S4VP of different excitation energy 198-210 nm region.

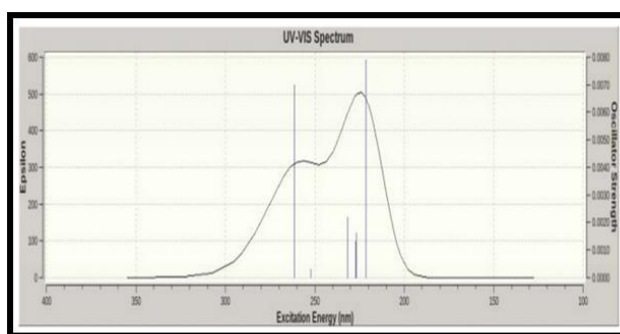


Figure 10: QM method UV-Vis spectra of blend SMA & S4VP of different excitation energy 150-300 nm region.

The experiment has been performed by Gaussian® software, and excitation energies and oscillator strength for each excited state were evaluated by QM calculations (Figure 10). Generally, absorption spectrum consists of a number of absorption bands plot of the molar extinction coefficient (ϵ) versus the excitation energy/wavelength (λ) in nm. The Gaussian band shape equation represent Equation 3 [16, 18-19].

$$\epsilon(\tilde{\nu}) = \epsilon_i^{max} \exp \left[- \left(\frac{\tilde{\nu} - \tilde{\nu}_i}{\sigma} \right)^2 \right] \quad \text{Eq. (3)}$$

$$\epsilon_i(\tilde{\nu}) = \frac{\sqrt{\pi} e^2 N}{1000 \ln(10) \cdot c^2 m_e \sigma} f_i \exp \left[- \left(\frac{\tilde{\nu} - \tilde{\nu}_i}{\sigma} \right)^2 \right] \quad \text{Eq. (4)}$$

Where, i subscript states the electronic excitation of interest in which the charge on the electron (e) 4.803204×10^{-10} esu, mass (m_e) 9.10938×10^{-31} g, Avogadro's number (N) $6.02214199 \times 10^{23}$, the speed of light (c) $29979245800.0 \text{ cm} \cdot \text{s}^{-1}$ and Planck's constant (h) $6.62606876 \times 10^{-27}$, these are the constant terms represent in Equation 4. Only one peak was observed at MM level (Figure 9) whereas two peaks were visible at QM level (Figure 10) in which excitations energy is convert into a wavelength, applying a value of 0.4 eV for the standard deviation $\sigma = 0.4 \text{ eV} = 1/3099.6 \text{ nm}^{-1} = 10^{-7}/3099.6 \text{ cm}^{-1}$ we will find the result from Equation 5.

$$\epsilon_i(\lambda) = 1.3062974 \times 10^8 \frac{0.007}{10^7/3099.6} \exp \left[- \left(\frac{1/\lambda - 1/\lambda_i}{1/3099.6} \right)^2 \right]$$

Eq. (5)

Excitation energy in nm (red) λ_1 is 261.17, oscillator strength corresponding to the electronic excitation (blue) f_i is 0.007 and the wavelength is 150 nm, subsequently calculating the data ranging from 150 nm to 300 nm from Eq. 1 are listed in table-3 (Figure 10).

Table 3. Wavelengths for molar absorptivity in QM level.

Wavelength (λ) nm	Molar absorptivity $\epsilon_i(\lambda)$ $\text{L mol}^{-1} \text{cm}^{-1}$
200	5.3728×10^{-4}
261.17	7.11632×10^{-32}
250	0.2139×10^3
300	0.02676×10^3
350	0.032517

3. Conclusion

Computational chemistry methods were applied to study miscibility complexation of SMA and S4VP polymers blend system. Complexation behavior was use for the determination of potential inter molecular interactions among different polymer chains. Furthermore, IR calculations used for the qualitative evaluation of co-polymers provide insightful information which needs further investigation. Moreover, it is also witnessed that QM methods provided distinct data compared to MM methods. Although, it is worth mentioning that QM methods produces more reliable data of different properties of the system.

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