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Research Article

Electronic Properties of Poly(N-vinylcarbazole) Using semi-empirical oligomer extrapolation approximations

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Abstract: Poly(N-vinylcarbazole) has been widely used in polymer light emitting diodes due to its unique electronic properties. The electronic properties of Poly(N-vinylcarbazole) were examined using the Semi-Empirical Zerner Modified Intermediate Neglect of Differential Overlap (ZINDO) oligomer extrapolation method. In this calculation, the electronic properties of Poly(N-vinylcarbazole) were extracted from oligomer electronic properties. We identified a tendency for oligomers with large HOMO-LUMO gaps in the form of linear regression as function of reciprocal of monomeric units. The increasing number of monomers induce the interaction between energy levels of each monomer which boardening the energy levels. The localized molecular orbital and vibration spectra of the basic unit of polymer Poly(N-vinylcarbazole) also has been investigated.

Keywords: Poly(N-vinylcarbazole), ZINDO, extrapolation method, polymer electronic structure, oligomer

1. Introduction

The structure of a polymer based on carbazole can be thought of either as having carbazole as the backbone polymer or the pendent group. Poly(N-vinylcarbazole) (PVK) is a non-conjugated polymer which has carbazole as the pendent group. PVK films, are the interest around the carbazole polymeric system. PVK can be synthesized by radically, ionically or thermally polymerization of N-vinylcarbazole [1]. PVK can also be synthesized using N-epoxypropyl-carbazole [2]. PVK has been used as electrophotography in Xerox Cooperation [3]. This is because carbazole-based compounds are interesting for use as photoconductors because they have very high charge carrier mobilities and easily produce relatively stable radical cations [4]. PVK has presented high photochemical stability high charge mobility [4]. PVK also has the potential to enable the rational design and optimization of high performance organic photoactive polymers, oligomers, and low-molar mass organic glasses [5].

PVK is one of the semiconducting polymers for electroluminescent devices. In polymer light emitting diode (pLED), PVK has been used as hole transport layer which makes the electronic device becomes more efficient. Furthermore, PVK-based devices show good electrical properties and thermal stabilities. These are due to the PVK contains carbazole group which relatively has stable radical cations and high hole mobility [6]. Single layer PVK-based polymer light emitting diode (pLED) shows the maximum emission at blue region [7]. PVK acts as a matrix for luminophores in WLEDs, which can be fluorescent or phosphorescent. When an electric current is applied to the device, the luminophores generate light by recombining excited electrons and holes. Due to the presence of several energy levels in the polymer, the light emitted by the luminophores is subsequently absorbed by the PVK matrix, which re-emits the absorbed light as a broad white emission [4, 8]. The emission spectra of PVK strongly depends upon the emission of sample history and modification such blending, alternation of monomer and grafting [9,

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10]. Therefore, there is a need to study the electronic properties of PVK.

In this framework of studies by theoretical methods, we envisaged a study of the effects of oligomer of vinylcarbazole on the electronic properties of PVK. Calculating the molecular orbitals of the monomer, dimers, and oligomer of a polymer can provide insight into the electronic characteristics of the entire polymer. In order to find the energy gap of PVK, a series of oligomer of vinylcarbazole has been investigated. In this work we use ZINDO/S-CI (Zerner's Intermediate Neglect of Differential Overlap — Spectroscopic version with Configuration Interactions) to observe the electronic properties of PVK.

2. Computational Method

The MS Visualizer Material Studio® was utilized in the construction of the molecular structures of PVK and its oligomer. Figure 1 shows the molecular structure of vinylcarbazole. The molecular geometry of carbazole oligomer is

denotes as PVKn, where n is the number of monomers. The structure of the oligomer has been drawn by defining the head atom and the tail atom on the molecular structure. After that, the oligomer was constructed by specifying the chain length and orientation in the appropriate order. After the required atomic arrangement of the molecule was sketched out, geometry optimizations were carried out. In order to achieve a configuration of a molecule that is stable, the optimization of its geometry is a core component of the quantum chemistry computation process[11]. The ground-state geometry of each oligomer has been determined by a full optimization of its structural parameters. The molecule is stable when it has the minimum amount of local energy. Geometry optimization has been carried out using PM3 parameter, Pulay convergence scheme with SCF tolerance is medium. This computation will provide a stable geometry parameter for PVKn oligomer and polymer.

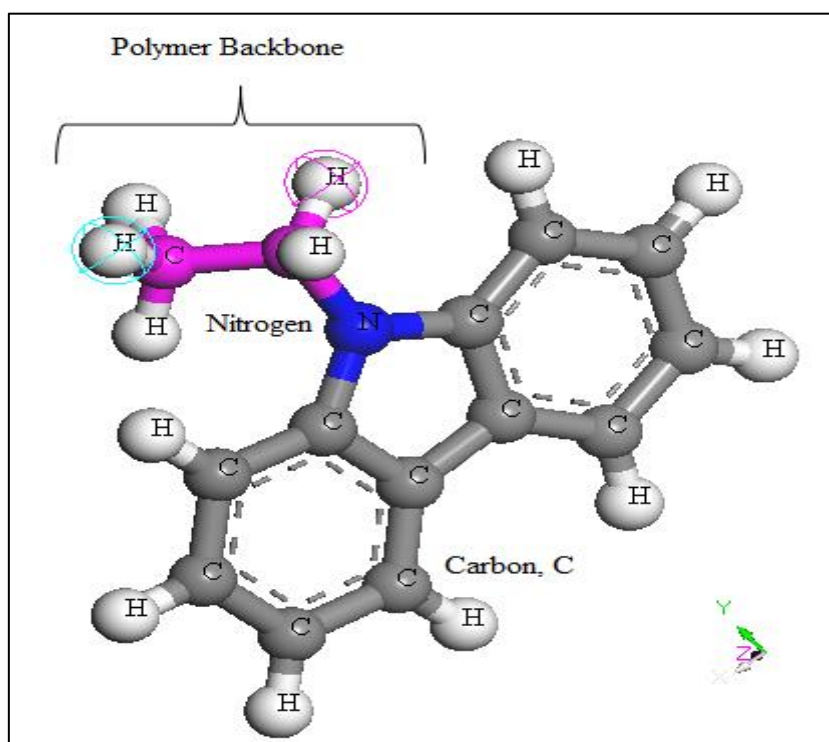


Figure 1. Molecular structure of monomer vinylcarbazole by using MS Visualizer Material Studio®

The electronic computation and transition energy of PVKn were determined using the Zerner modification intermediate neglect of differential Overlap (ZINDO) calculation based on the

geometry optimization[12]. The empirical model used is INDO/1. Electron repulsion integral ($\gamma_{\mu\nu}$) uses Nishimoto-Magata approximation [13]. All computations were carried out using the VAMP

Material Studio Program package. A single Configuration Interaction (CIS) approach was utilised to allow permutations of electronic excitation in each orbital. The Perkin and Stewart technique was used to compute SCF.

The energy gap was determined using the HOMO-LUMO gap. Then, for polymer, we apply the well-known experimental reciprocal rule. This method has the special benefit of providing the convergence behaviour of oligomer structural and electrical characteristics. The plot of HOMO-LUMO of the energy gap was determined using linear extrapolation as a function of $1/n$. The dispersion band-structure diagrams were extrapolated from the eigen value from each oligomer to predict the dispersion band diagram of the polymer chain. For IR vibration spectra simulations and localized orbital, the package VAMP Material Studio Program package was used. The IR vibration spectra simulations and localized orbital was perform using NDDO scheme with PM3 as parameter. All calculations are based on molecules isolated in vacuum.

3. Results and discussion

3.1. Electronic Properties of PVK

Carbazole consist of two benzene rings attach one nitrogen atom in cyclic carbon. In analysing the dependence of the HOMO-LUMO gaps of oligomers, we identified a tendency for oligomers with larger HOMO-LUMO gaps in the form of linear regression:

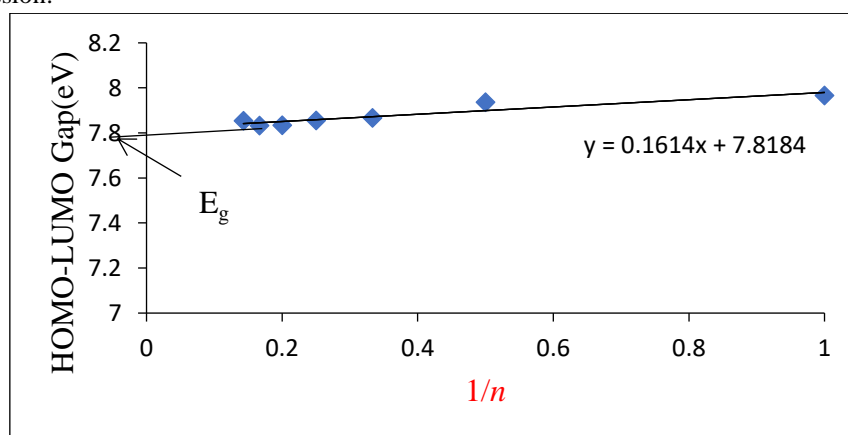


Figure 2. HOMO-LUMO gap as function of reciprocal number of oligomer n for PVK

The discrete energy level (eigen value) of molecular orbitals for PVK $_n$, are shown in Figure 3. There is a correlation between the energy levels

$$E_g(1/n) = a + b/n \quad (1)$$

where n is the number of monomers, a is the energy gap at $n \rightarrow \infty$ and b is the gradient of linear equation. Figure 2 shows a plot of HOMO-LUMO gap as function $1/n$. The regression r^2 value for figure 2 is 0.980. As the number of oligomers increases, the excitation energy oscillator strength shift towards high transition energy. This shifting might be due to the increment of oligomer number changes the molecular geometry and heat formation which affected the chromophore and bond length in the molecule[14]. The extrapolation at $n \rightarrow \infty$ at intersects at y-axis gives the value of energy gap of PVK which is 7.818 eV. PVK is non-conjugated polymer is based on C - C backbone which has large gap between filled and empty state. This is because of the small shift in the overlap integral, which has an effect on the energy levels in the vacancy orbital when it is in either the filled or empty state [15]. The substitutions of carbazole in C - C backbone has reduced the energy gap. In figure 2 also reveal that the HOMO-LUMO energy gap correlated with substitutional of carbazole group which can change electronic properties as the whole molecules. It's possible that the substitution carbazole has altered the electron donor or acceptor in the complete molecule, which has led to a reduction in the amount of molecular overlap as a result [16].

of the oligomer and the energy levels of the polymeric system. The interaction between the energy levels of each monomer happens more

frequently as the number of monomers in the system grows. When there are more oligomers, the

discrete energy levels become higher and begin to overlap.

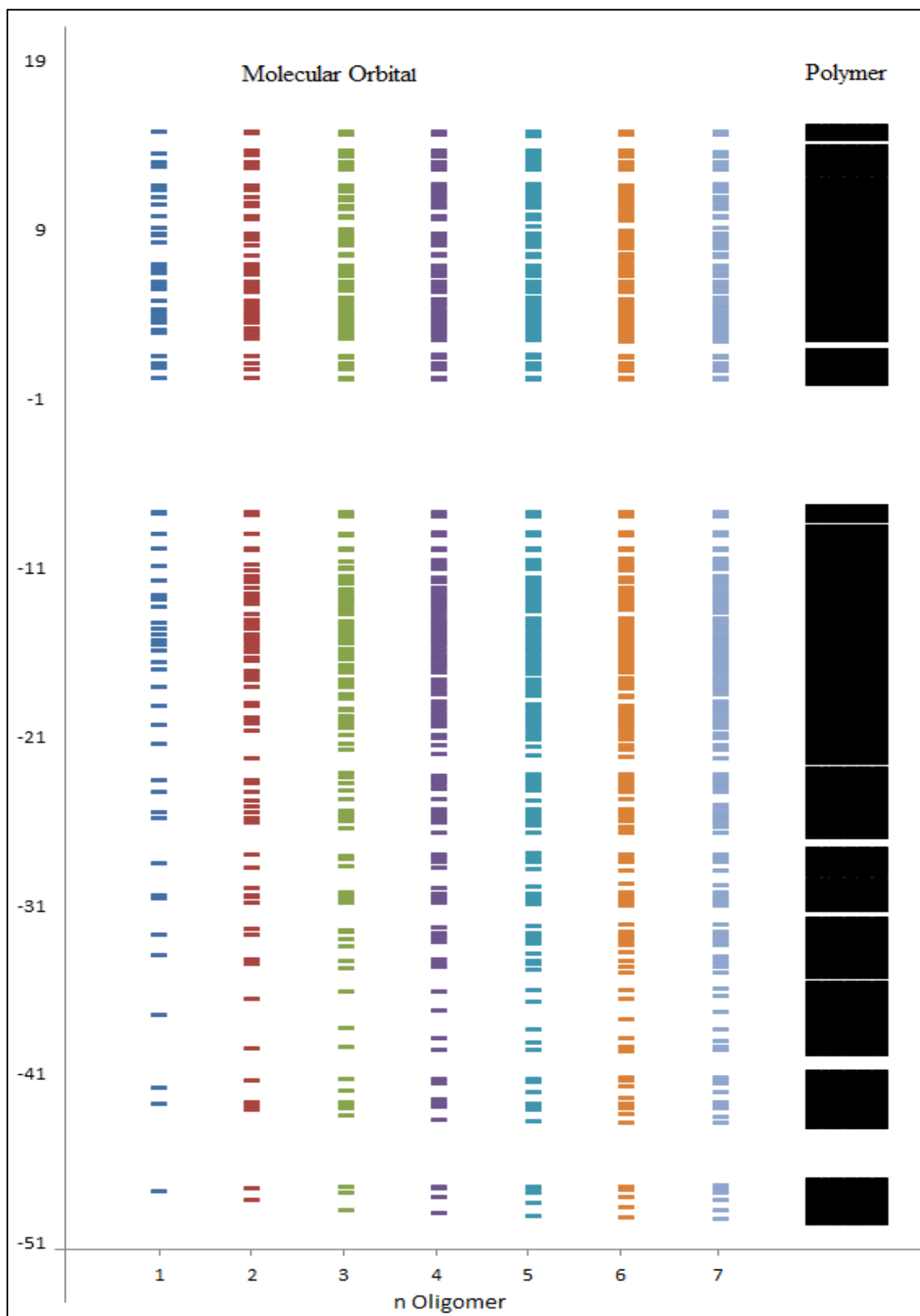


Figure 3: Eigen value of oligomer of carbazole for PVK band formation

This happens when there are more oligomers. These energy levels are perturbed, and a splintering effect is produced across the entirety of the oligomers and the polymer. Then, the amounts of energy will increase and begin to board to create a band. It is plausible that the broadening of energy levels is

caused by a combination of factors, including the hyper conjugation effect, changes in wavefunction, changes in the speed of electrons and nuclides in periodic systems, and spin molecular orbital coupling [17, 18].

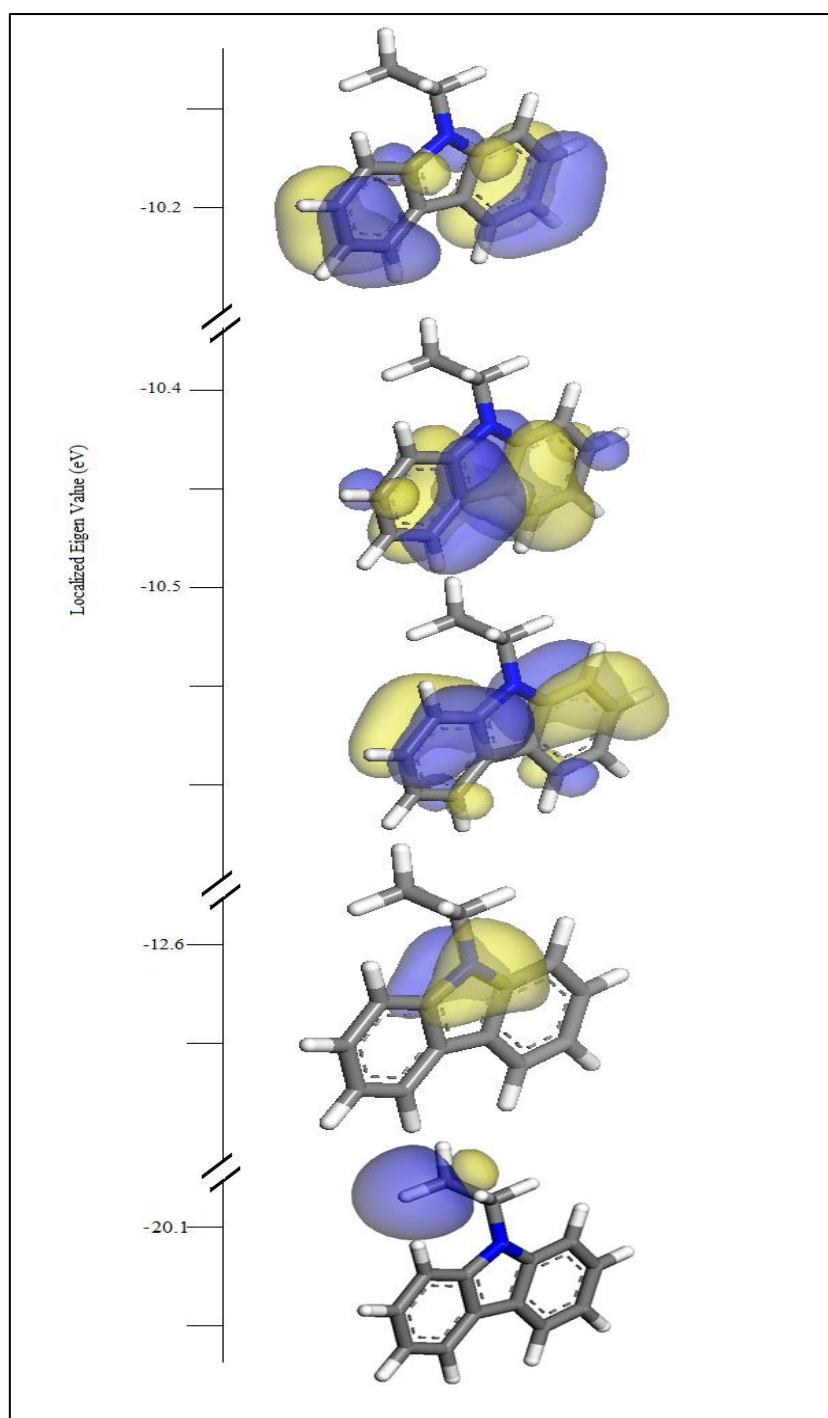


Figure 4: Localized orbital of Vinylcarbazole

In oligomer extrapolation approximations, the molecular orbital consists of discrete energy levels. These energy levels occupied by electron gives arrive electron distribution to the bonding and antibonding molecular orbital. When a molecule interacts with other molecules, such as in the situation of an oligomer molecule, the overlapping of HOMO and/or LUMO between surrounding molecule monomers as unit cells creates a continuous energy band that is referred to as bandwidth. The bandwidth is a measurement of delocalization of polymer because of the effect crystal potential in solid. Figure 3 demonstrates that the electronic states are distributed in such a way that there is a greater abundance of higher energy than lower energy, and this illustrates further characteristics of the band structure of PVK. Since PVK, are non-conjugated polymers which lack of π -electron on polymer backbone, the bandwidth of this polymer associated with σ -electron which is responsible for the formation of strong covalent bonds and a high HOMO-LUMO energy gap.

Localized orbital of vinylcarbazole.

Figure 4 shows the highest 5 localized orbital for vinylcarbazole at -10.245, -10.472, -10.516, -12.759 and -20.157eV. For the three highest localized orbitals, they spun over aromatic benzene rings. Since vinylcarbazole has two benzene rings which bridge at nitrogen and carbon atom, the calculation shows that these localized orbitals have two same eigen values. This indicates that the contribution of electron in both benzene rings is equivalent for the left and right benzene rings. According to Neissen, localized orbitals in benzene are contributed by electrons from C-C σ and π -bonding and C-H σ -bonding [19]. For -12.749eV, the electron density at that orbital residues on the nitrogen atom is surrounded by carbon atom. The calculation reveals that the polymer backbone of

PVK consists of C-H and C-C localized orbitals occur at fifth eigen value of -20.157eV.

FTIR Calculation

The calculated vibration frequency of PVK is presented graphically in Figure 5. Five significant vibration frequencies have been chosen for vibration assignment using PM3 calculation. The highest vibration intensity at 771 cm^{-1} (106.49 km/mol) is the aromatic benzene ring deformation followed by 1531 cm^{-1} (103.67 km/mol) which is due to C-C=C stretching mode in benzene ring. Comparing these results with MINDO calculation which have been done by Dewar and Thiel [20], the C-C=C is located at 1689 cm^{-1} . In the polymer backbone, the vibration frequency at 1348 cm^{-1} is attributed to the CH vinyl group. While the vibration frequency at 3070 cm^{-1} is due to C-H asymmetric stretching mode. This frequency is comparable with the experimental work done by Alias, Zabidi, Harun, Yahya and Ali [21] which have also observed the vibration at 3060 cm^{-1} . However, other workers i.e Dewar and Ford [22] reported using MINDO calculation that the vibration frequency occurs at 3507 cm^{-1} . Another important vibration assignment for carbazole molecule is the CN stretching frame work that has been calculated at 1270 cm^{-1} (7.9 km/mol). Table 1 shows the calculated vibration assignments using PM3 calculation for PVK.

As shown in Figure 5, most vibrations discrete and concentrate in the range of 913-1177 cm^{-1} which correspond to the assignment of twisting CH₂ and asymmetric stretching mode of skeleton bending C - C - C backbone [23]. The vibrations in the range of 1041-1229 cm^{-1} which correspond to the CF and CF₂ stretching mode. Another important vibration frequency occurs at 890 cm^{-1} which corresponds to CF₂ asymmetric stretching mode.

Table 1: Calculated Vibration Assignments and Intensity Using PM3 Calculation For PVK

Assignments	Vibration Frequency (cm^{-1})	Intensity (km/mol)
C - H asymmetric stretching	3070	41.94
Benzene C - C = C stretching	1531	103.67
CH vinyl	1348	61.72
CN stretching frame work	1270	7.9
aromatic benzene ring deformation	771	103.67

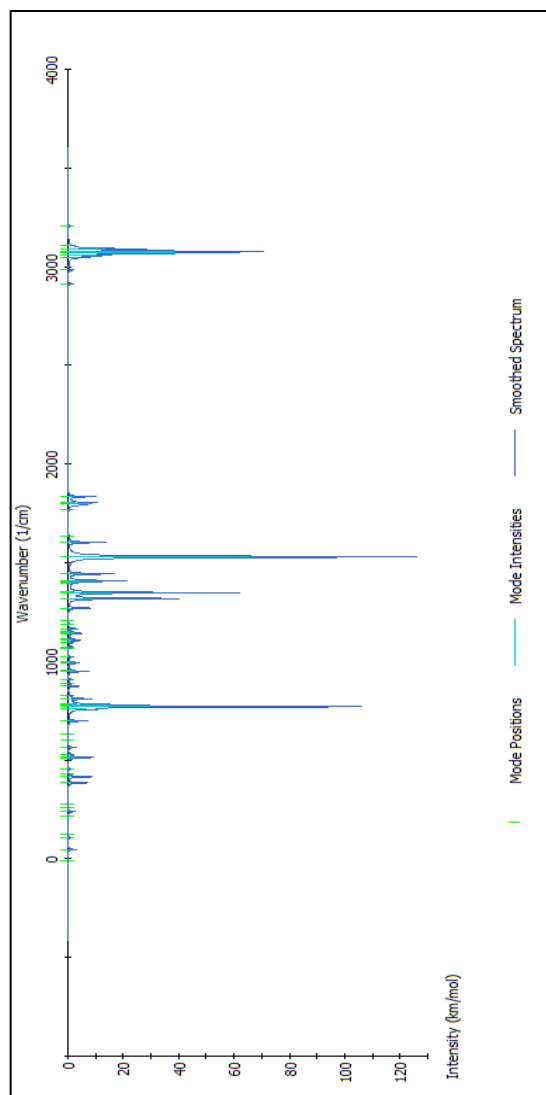


Figure 5: The graphical vibration spectra of PVK

4. Conclusions

The electronic properties of PVK were calculated using a semi-empirical extrapolation technique. The HOMO-LUMO of PVK was calculated. The energy gap for PVK is 7.818 eV. All oligomers did not show any specific changes in excitation transition as the oligomer number increased. The band formation, which is correlated with the energy levels of the oligomer and the energy levels of the polymeric system, has also been reported. Four of the highest localised orbital energies have been successfully shown. The calculated vibration assignments and intensity using PM3 have also been demonstrated.

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