Some Physical Properties of Vinylpyridine Carbon-Black Composites

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Samples of 2-Vinylpyridine oligomer and polymer were prepared by chemical method. The polymer and the oligomer were hot-pressed with different wt% of C-black. The molecular weights of the oligomer and polymer were measured. The electrical conductivity of the polymer-C-black and the oligomer-C- black composites were measured in the temperature range from 303 to 353 K as a function of carbon content. The results have been discussed and compared with those of the oligomer and the polymer–CH_3I complex. It was found that the activation energy for different samples decreased with increasing C-black percentage. The diffused reflectance of polymer C-black, oligomer-C-black composites and oligomer-CH_3I, polymer-CH_3I complex was measured at room temperature in the wavelength range from 500 to 1800 nm. The analysis of optical absorption spectra revealed the existence of two indirect transitions. It is found that the optical energy gaps of these samples decrease with increasing C-black percentages.

Introduction:

Polymer materials in pure state are electrical insulators. However they are filled with specific additives, such as metallic powders [1] metallic fibers [2], carbon black [3,4], ionic conductive polymers [5,6], and intrinsically conductive polymeric powder (polypyrrole) [7,8]. Carbon black has long been used as reinforcing ingredient in polymer composites [9]. Among the various uses of conducting carbon polymer composites are materials for electromagnetic shield [10], conducting discs for information storage [11], and antistatic materials [10]. The conductivity of polyvinyl pyridine, for example, increases by many orders of magnitude on complexation with transition metals Co; Pt and Pd. Initially composites based on polymers, along with some conductive filler were prepared to achieve these objectives [12]. Some mechanisms of electrical conduction in filled composites have been reported [4]. In the case of metal filled systems, Frenkel proposed the electron tunneling theory to describe the contact resistance between two metallic bodies [9]. In the case of carbon black-filled - composites, Sheng Sichel, and Gittleman have shown that tunneling activated by thermal fluctuation of the electric potential is the dominant mechanism under certain conditions [4].

The objective of the present work is to prepare 2-vinylpyridine oligomer and poly-2-vinylpyridine, which was hot, pressed with different carbon black content. Also to investigate the electrical and optical properties of polymer-C-black and oligomer-C-black composites and compare these results with those oligomer and polymer-CH_3I complexes.

2.Experimental:
2.1 Preparation
Preparation of P 2VP:

52.5 g (0.5 mol.) ~ 54 ml. of 2VP was dissolved in 200 ml. Chloroform in a 500 ml. round bottomed flask equipped with a refluxing condenser. 0.5 g of benzoyl peroxide was added. The flask was heated at 60°C for 4 hours. The polymer was separated by adding n-hexane then it was washed with alcohol and dried in air oven at 100 °C.

Composites of P2VP with C-Black:

1 g of P2VP was hot pressed with 5 %, 10 %, 17 % and 33 % of thermal C-black at 3770 kg / cm^2 and 70 °C. Accordingly pellets of 2VP oligomer with C-black and P2VP with C-black were prepared.

P2VP - CH$_3$I complex

20 ml of CH$_3$I was added to 10 ml of a saturated solution of P2VP in chloroform and it was slightly warm. A precipitate of P2VP-CH$_3$I complex was formed. Pellets of the polymer complex were prepared. The samples were mixed thoroughly in a porcelain ball mill (dry mixing) and sieved completely by
200-mesh sieve. Compressing the powder in a cylindrical block made compact discs, approximately 2 mm thickness and approximate 2 cm diameter and also the polymer- CH$_3$I complexes were molded under pressure of 10^4Pa.

2.2 Electrical Measurements:

The pellets were adjusted tightly between two copper electrodes of an electric cell. The electric circuit used for the measurement, consists of an electric source, the cell, a high impedance electrometer (A Keithley electrometer of the type 610 C of sensitivity 10^{14} A) and a variable resistance. The specific electrical resistivity of the sample was measured by means of the electrometer at different temperatures. A thermocouple temperature probe of the type TP-30 attached to a mill voltmeter, measured the temperature of the specimen.

2.3 Optical Measurements:

The samples of the oligomer, polymer-C-black and also the polymer–CH$_3$I complex were too thick for transmission experiment in the spectrum range (500-1800 nm) therefore, the optical properties were studied in diffused reflection only. Diffused reflectance measurements, in the range from 500 to 1800 nm, were carried out using PMO111 spectrophotometer, which was fitted with an integrated sphere diffused reflectance attachment type RA3.
The Kubelka and Munk function [13].

$$K/S = (1-R)^2/ 2R$$

has been used as a measure of absorption by powder samples, where K and S are the absorption and scattering coefficients respectively. The energy coordinate of the drop of the linear decrease in the absorption curve, i.e. in the highest energy side, has been taken as measure of the forbidden gap [14].

3. Results and Discussion:
3.1. Electrical Conductivity:

A polymer composite could change from an insulator to a semiconductor over a very narrow range of filler concentration. At low filler concentration the composite remains an effective insulator. At a critical volume concentration the conductivity of the composite starts to increase sharply to a level at which the

composite can conduct electricity. Additional increase in the filler content had a much smaller effect. The temperature dependence of the electrical resistivity ρ of P-2VP and 2VP oligomer in the temperature range 300 K up to 353 K is shown in Fig. (1) while Fig. (2) represents this relation for P2VP with 5, 10, and 17 wt % carbon black content in the same temperature range. It is clear from this figure that, the relation is a linear one. The resistivity for P2VP samples with 5, 10 and 17wt % C-black has the same behavior. It increases with decreasing temperature, but the increase is slow at low C-black content (5 wt%) and   above   5wt   % C-black the resistivity decreases sharply. The linearity of log ρ against 1/T in the case of P2VP with 5, 10, &17 C-black wt % indicates that ρ in this region exhibits activated behavior accordance to the relation

$$\sigma = \sigma_0 \exp (-\Delta E / KT)$$

where ΔE is the conductivity activation energy, K is the Boltzmann constant and σ_o is the pre-exponential factor includes the charge carrier mobility and density of state. From Fig. (1) it is found that for pure P2VP sample the relation is not linear but there are two different behaviors, which indicate that there are two types of conduction mechanisms that contribute to the conductivity. At low temperature the resistivity increases by increasing the temperature while at high temperature the resistivity decreased with temperature. This decrease of resistivity may be due to the increase of the mobility in this range.

Fig. (3) represents the relation between ρ and 1/T for 2VP oligomer with 5, 10 and 17 wt% carbon black content. From this figure it is found that the oligomer samples with different wt% of carbon black have the same behavior like the P2VP but have smaller resistivity. However, the activation energy for electric conductivity is lower in the case of P2VP with C - black than in the case of 2VP oligomer with C- black. Table (1) summarizes the value of activation energy for these samples.

Table (1): The values of activation energy for the samples.

Composites	Activation energy
2VP Oligomer + 5 wt % C -Black	0.46 eV = 10.7 Kcal / mol
P2VP + 5 wt% C - Black	0.17 eV = 3.9 K cal / mol
2VP Oligomer + 10wt% C - Black	0.2 0 eV = 4.7 K cal /mol
P2VP + 10 wt% C - Black	0.11 eV = 2.6 Kcal / mol
2VP Oligomer + 17 wt% C -Black	0.19 eV = 4.4 Kcal /mol
P2VP + 17 C - Black	0.86 eV = 8.3 Kcal / mol

In the case of P2VP- CH_3I and 2VP oligomer- CH_3I complexes, the specific resistivity were found to have the values,

$$\rho = 1.0 \times 10^8 \ \Omega \ cm \qquad at \quad 242 \ K$$
$$\rho = 0.4 \times 10^9 \ \Omega \ cm \qquad at \quad 303 \ K$$
$$\rho = 4.2 \times 10^8 \ \Omega \ cm \qquad at \quad 242 \ K$$
$$\rho = 0.48 \times 10^9 \ \Omega \ cm \qquad at \quad 303 \ K$$

To explain the behavior of the curves in Fig. (1, 2 and 3), we suggested that electronic charge must hop between carbon- black particles, and that the gaps between C-black particles actually control the conductivity rather the C-black itself [4]. Further evidence that hoping process transports charge comes from temperature dependence of the conductivity of P2VP and 2VP oligomer C-black composites at high temperature.
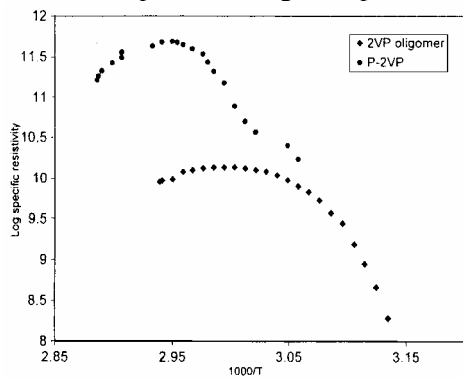
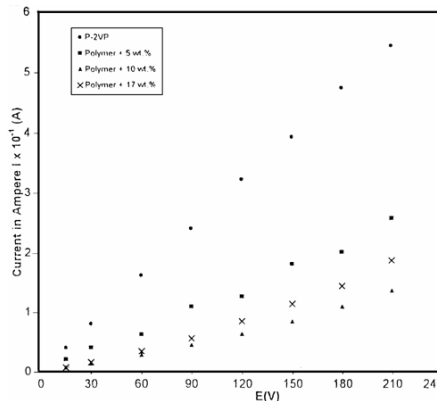**Fig. (1):** Variation of specific resistivity for P-2VP and 2VP oligomer vs 1000/T.

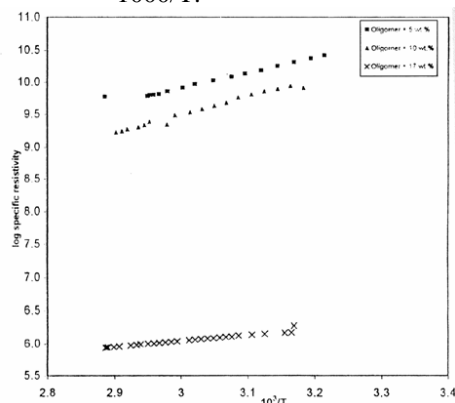**Fig. (2):** Variation of specific resistivity for poly-2-vinyle pyridine vs. T^{-1}.

Fig. (3): Variation of specific resistivity for 2-vinyl pyridine oligomer with different C-black concentrations.
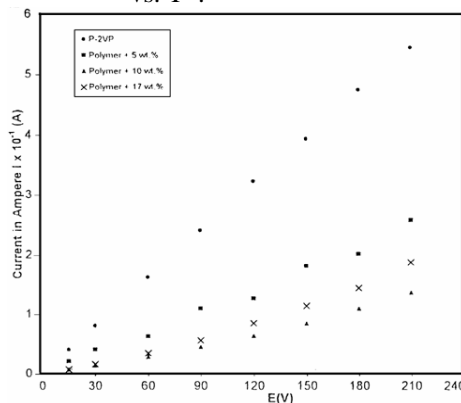

Fig.(4): Variation of current with voltage for poly-vinyl pyridine and for the polymer with different C-black concentrations.

Fig. (4) and (5) show the plot of electric current I and the voltage V for P2VP and 2VP oligomer with different C-black content 0, 5, 10, and 17 wt %. It is clear from these figures that the current increases with increasing the voltage.
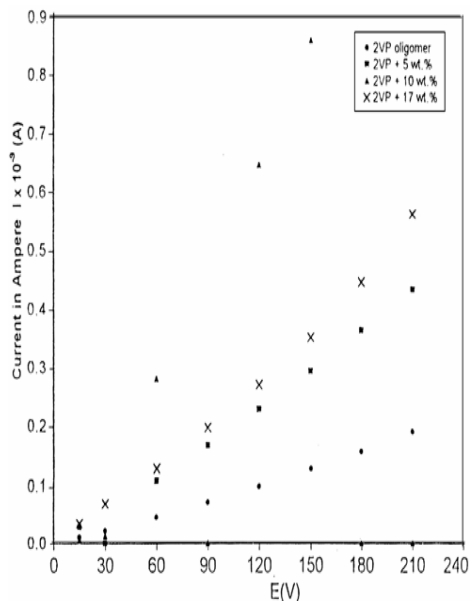

Fig. (5): Variation of current with voltage for 2-vinyl pyridine oligomer and for 2VP oligomer with different C-black concentrations.
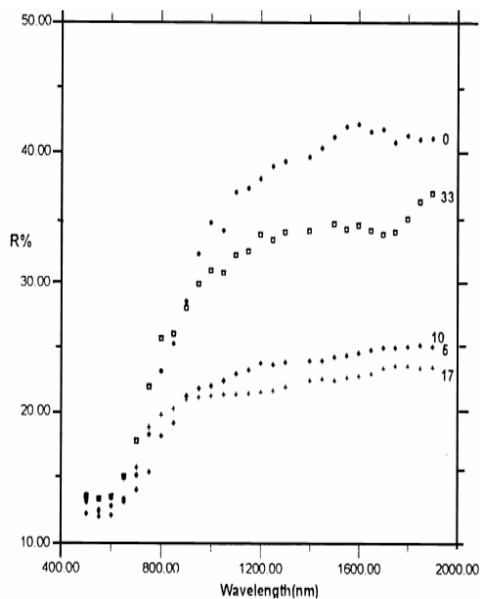
Fig. (6): Reflectance R vs. wavelength for P2VP with 0, 5, 10, 17 & 33 C-black wt%.

3.2- Optical Properties

The diffused reflectance R was measured at room temperature as a function of wavelength (nm) in the range from 500 nm to 1800 nm. The spectra in the band gap region are shown in Fig. (6) for P2VP with 0, 5, 10, 17 and 33-wt% C-black. Fig. (7) represents the plot of reflectance(R) versus the wavelength for 2VP oligomer with 0, 5, 10, 17 and 33 wt % C-black, while Fig. (8) represents this relation for polymer- CH_3I and oligomer-CH_3I complexes. The absorption variation (K/S) dependence of photon energy (hν) eV at room temperature for P2VP with 0, 5, 10, 17 and 33 wt % C-black is shown in Fig. (9) and for 2VP oligomer with 0, 5, 10, 17 and 33 wt% C-black is shown in Fig. (10). The plot of photon energy (hν) eV against (K/S) for 2VP oligomer- CH_3I oligomer and P2VP- CH_3I complexes is represented in Fig. (11). From Fig. (9, 10 and 11), it is found that, there are two indirect transitions for all samples. These curves show that the energy gap, which is the highest point of the linear parts in the absorption curve, varies with the C-black wt% for different samples.
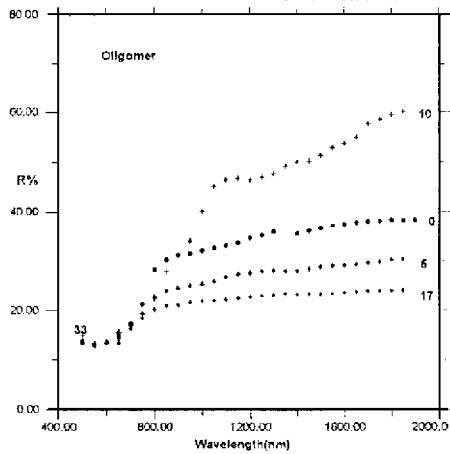
Fig.(7): Reflectance R vs. wavelength for 2VP oligomer with 0, 5, 10, 17 & 33 C-black wt%.
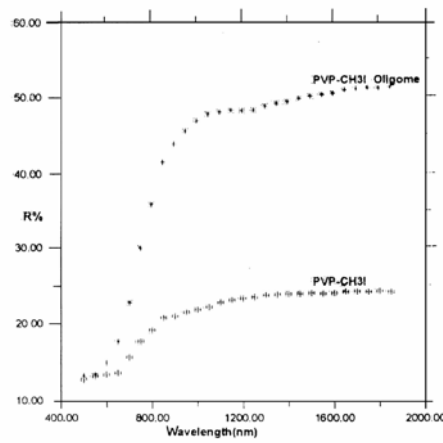
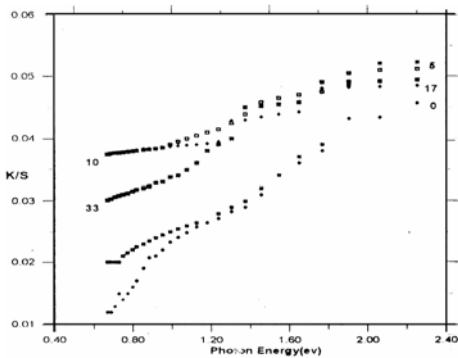**Fig.(8):** Reflectance R vs. wavelength for polymer & oligomer–CH31 complex.

Fig. (9): Absorption spectra of P2VP with 0, 5, 10, 17 & 33 wt% C-black.
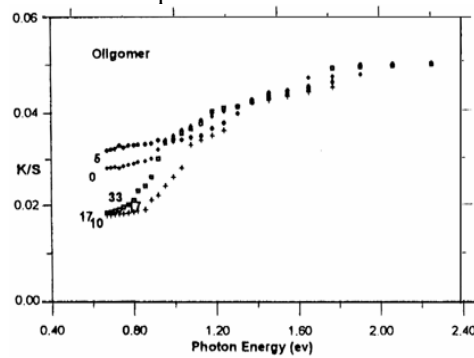
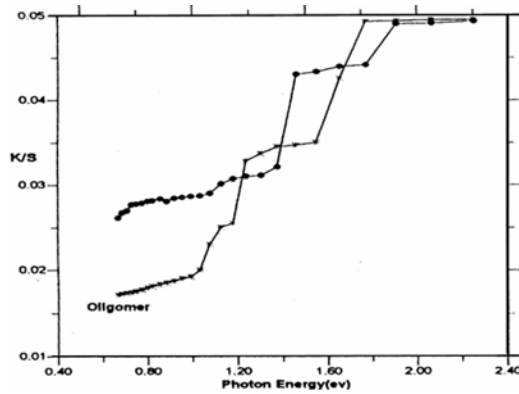**Fig.(10):** Absorption spectra of 2VP with 0, 5, 10, 17 & 33 wt% C-black.

Fig. (11): Absorption spectra of 2VP oligomer-CH31 & P2VP-CH31 complex.

Fig. (12a and b) and (13a and b) represent the relation between the energy gap (hv) and the C-black wt% for P2VP and 2VP oligomer. From these figures, it is clear that the energy gaps for all samples decreased with increasing C-black wt% from 5wt % to 17wt% and become constant after that i.e. at 33wt%. Curves (a) and (b) in these figures represent the two energy gaps for the two indirect transitions. This behavior may explain the fact that the C-black (wt%) increased the disorder of these materials [15]. The increasing degree of disorder causes the band tail to increase, which according to the electronic structure of amorphous materials, will lead to a decrease of the estimated optical gap [16].
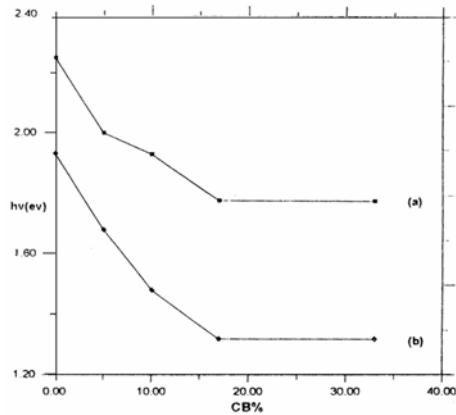
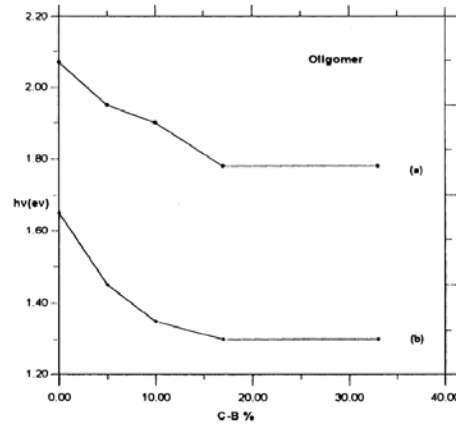**Fig. (12):** Energy gap (ev) vs. C-black wt% for P2VP oligomer.   **Fig. (13):** Energy gap (ev) vs. C-black wt% for 2VP oligomer.

Table (2) summarizes the results of the energy gaps for two optical transitions of poly-2-vinylepyridine, 2-vinylpyridine oligomer and poly-2-vinylpyridine-CH_3I complex. It is clear from Table (2) that the energy gaps for the polymer complex are greater than that for the polymer composites with C-black.

Table (2): Energy gaps data for P2VP, 2VP oligomer, P2VP-CH_3I & 2VP oligomer-CH_3I.

Samples	C–Black (wt%)	Eg1(eV)	Eg 2 (eV)
P2VP	0	2.25	1.93
	5	2.09	1.68
	10	1.93	1.48
	17	1.78	1.32
	3	1.78	1.32
2VP oligomer	0	2.07	1.65
	5	1.95	1.40
	10	1.9	1.35
	17	1.78	1.30
	33	1.78	1.30
P2VP CH_3I	-	1.95	1.45
2VP CH_3I	-	1.85	1.35

The structure of P2VP–CH$_3$I is
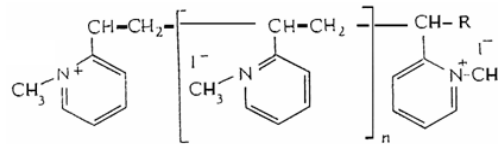
Molecular Weight Distribution of the Polymer

The average molecular weight (M$_n$) and molecular weight distribution (MWD) of the polymer were determined by means of Gel permeation Chromatography (GPC) using a high-pressure-GPC equipment (Waters) consisting of a high pressure pump type (600 E Multisolvent Delivery System) three ultra steerages chromatographic columns connected in series, and deferential refract meter (type M2410) as a detector. Fig. (14) represented the average molecular weight (M$_n$) and molecular weight distribution (M$_w$) of the polymer.

GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		149998	37163	314686	72984	1104259		2.47763		

GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		168	185	120	207	23		1.101905		
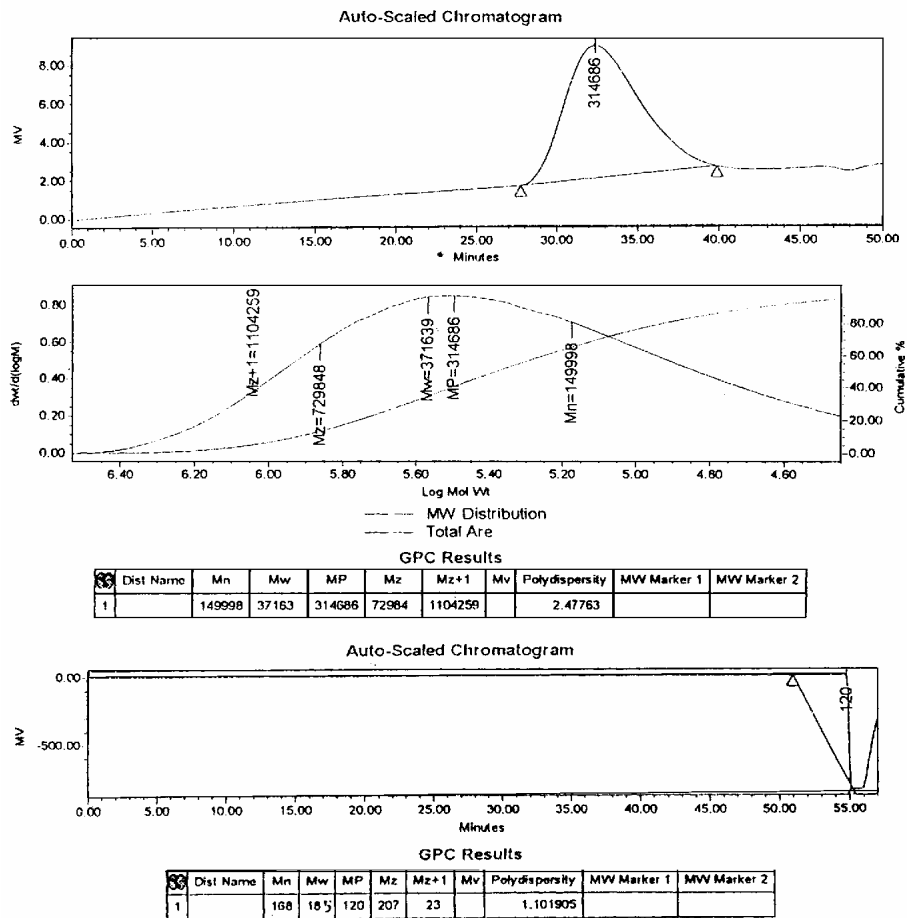
Fig.(14): The molecular weight distribution of polymer.

M_n of the	2VP oligomer	=	168	g /mol
M_w of the	2VP oligomer	=	185	g/mol.
M_n of the	P2VP	=	149998	g/mol.
M_w of the	P2VP	=	371639	g/mol.

4. Conclusion:

2-vinylpyridine oligomer and polymer were prepared and hot pressed with different wt% of C-black. The molecular weights of the oligomer and polymer were measured. The electrical conductivity of the 2-vinylpyridine oligomer and polymer with 0, 5, 10, and 17 carbon-black content were measured in the temperature range from 300 K up to 353 K, as a function of carbon black content. The conductivity of all samples increased with increasing temperature and this behavior was explained by suggesting that the electronic charge must hop between carbon black particles and that the gaps between carbon black partials actually control the conductivity rather than the C-black itself. The diffused reflectance of these samples was measured at room temperature in the wavelength range from 500 nm to 1800 nm. The energy gaps of these different samples were then deduced as well as the positions and the numbers of the indirect transitions, which were found to be dependent on the C-black wt%. The energy gap for the polymer complex is greater than that for the polymer composites with 17-wt% C-black. The decrease of the energy gaps indicates that C-black wt% increases the disorder of these materials. The increasing of the disorder causes the band tail to increase, which according to the electronic structure of amorphous materials, will lead to a decrease of the estimated optical gap.

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