

Synthesis and Characterization of Some Conducting Polymers and Their Complexed Compounds

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RESEARCH ARTICLE

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Abstract

The chemical co-polymerization of aniline with *o*-anthranilic acid (AA) to form copolymer films has been made in aqueous hydrochloric acid medium. Poly vinylcarbazole (PVK) was prepared by free radical mechanism. The copolymer (AA) and polymer (PVK) were reacted with KI respectively, to produce a complex compounds. Also, the complex of copolymer (AA) with NaOEt was prepared. The conductivity, IR spectra and the thermal gravimetric analysis of these polymers and their complexes were measured and discussed. It was found that, the specific electrical conductivity (σ) of the copolymer (AA) in presence of NaOEt increases with increase in temperature, whereas decreases with complex of copolymer (AA) +KI. The electrical properties of the PVK were enhanced upon reacting it with KI.

Keywords

complexes · aniline-co-anthranilic acid · Polyvinylcarbazole · Electrical properties

1 Introduction

Conducting polymers with a polyaromatic backbone have recently attracted a great deal of research attention, e.g. polypyrrole [1], polyaniline [2], polythiophene [3], polyphenylene [4]. In particular, polyaniline has been extensively studied for the possible use in commercial applications [5,6,7] in light-weight batteries, solar cell, electrochromic windows [8], biosensors [9], and antistatic materials [10]. Due to the difficult solubility of polyaniline in many solvents, we improve its solubility by co-polymerization of aniline with *o*-anthranilic acid (AA). This obtain co-polymer is soluble in aqueous alkaline solutions and in some organic solvents and it is easier to examine the physical properties of it. The chemical co-polymerization of aniline with *o*-anthranilic acid (AA) to form copolymer films has been made in aqueous hydrochloric acid medium. The copolymer films were monitored by using the quartz crystal microbalance (QCM) technique [11].

The FTIR and UV-visible spectra indicated that the anthranilic acid groups restrict the π -conjugation along the polymer chain. The electrical conductivity of the PAA copolymers decreases dramatically along the series from the polyaniline value of 5.2 S/cm to the poly (*o*-anthranilic acid) value of 10^{-8} S/cm. Poly (*o*-anthranilic acid) itself is fairly inactive, revealing little or no electrical conductivity and electrical activity [12]. The copolymers of aniline and *o*-anthranilic acid are soluble in *N*-methylpyrrolidone and dimethylsulfoxide when in the base form, but no mention is made of their solubility in aqueous solutions [13]. It has been shown that polyaniline with sulfonic acid groups on the benzene rings [14], or on the nitrogen atoms [15-18], are soluble in water and have conductivities between 0.1 and 10^{-9} S/cm depending on the level of substitution. Polyaniline with carboxyl groups are also expected to be soluble in aqueous alkaline solutions. Polyaniline (emeraldine base) could be prepared by chemical methods using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as an oxidant dissolved in 200 ml of HCl [19]. Vander Doncket et al. [20], constructed a solar cell using a thin film of poly-2-vinylpyridine enclosed between a sheet of platinum and platinum oxide. Poly-*N*-vinylcarbazole is as example for conducting and photo

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conducting polymers. Kloppfer [21], studied the photoconductivity of poly-*N*-vinylcarbazole. *N*-vinylcarbazole [22], is an inorganic compound used as a monomer in the production of poly(vinylcarbazole), a photoconductive polymer used in the photoreceptors of photocopiers [23]. Upon exposure to γ -irradiation, *N*-vinylcarbazole undergoes solid-state polymerisation [24]. A lot of interest in these polymers was caused by the discovery of photoconductivity in poly(*N*-vinylcarbazole) (PVK) by H. Hoegl [25]. In 1957, he has established that PVK sensitized with suitable electron acceptors showed high enough levels of photoconductivity to be useful in practical applications like electrophotography.

As a result of the following activities, IBM introduced its Copier I series in 1970, in which an organic photoconductor, the charge transfer complex of PVK with 2,4,7-trinitrofluorenone (TNF), was used for the first time [26]. The photoconductor was a 13 μm single-layer device. It was prepared by casting a tetrahydrofuran solution containing PVK and TNF onto an aluminium substrate [27]. The ongoing peak of interest in carbazole containing polymers is connected mostly with the discovery of polymeric light emitting diodes [28] and organic photorefractive materials [29]. Apart from electrophotographic photoreceptors [30], light-emitting diodes, and photorefractive materials carbazole containing polymers are studied as the components of photovoltaic devices [31]. Carbazole based compounds are attractive as photoconductors or charge-transporting materials. In this paper, aniline and co-anthranilic acid were polymerized in 1.2 M HCl aqueous solution using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as an oxidant and polyvinylcarbazole (PVK) was prepared by free radical mechanism. The electrical properties, thermal gravimetric analysis (TGA) and IR spectroscopy for the prepared polymers and their complexes with KI and NaOEt were determined.

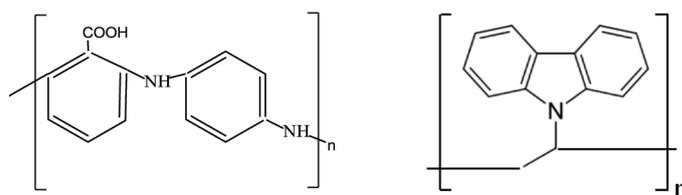
2 Methods

2.1 Preparation of Polyaniline-Co-o-Anthranilic Acid [12]

9.3 g (~9.1 ml) of aniline and 13.7 g of o-anthranilic acid were slowly added to 100 ml of 1.2 M HCl solution, containing 68 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ with constant stirring at room temperature. A dark green color developed immediately and the polymeric product precipitated from the solution. The polymer was collected by filtration, washed with 1.2 M HCl until the filtrate became colourless and then dried under vacuum at 20°C, till constant weight, structure [1].

2.2 Preparation of Polyaniline-Co-o-Anthranilic Acid complexes

0.5 mmol (~1.13g) of prepared copolymer dissolved in alkaline-water, 1 mmol (~0.167g) of KI dissolved in least amount of ethyl alcohol. KI solution was poured on the copolymer solution. The same procedure was made for NaOEt. 1 mmol



Structure. 1. (left), Structure. 2. (right)

(~0.068g) of NaOEt was dissolved in the least amount of ethyl alcohol and then poured on the copolymer solution. After evaporating the solvent, thin films of the complexes 1 cm diameter and 1 mm thickness were prepared.

2.3 Preparation of Polyvinylcarbazole and its complexes with KI [32]

0.1 mol (19.3 g) of vinylcarbazole was placed in a round bottomed 3-neck flask. 0.5 g of benzoylperoxide is dissolved in 100 ml acetonitrile and added to the flask which was heated at 70°C for 4 hours. The polymer was precipitated by methyl alcohol, washed with water and acetone and dried under vacuum, structure [2]. 1.6 g of KI dissolved in acetonitrile and added to 1.93 g of vinylcarbazole in 20 ml of toluene. A thin film of the polymer and the polymer with KI were prepared having 1 cm diameter and 1 mm thickness.

3 Methods of testing

The IR spectra were recorded by a Perkin-Elmer 1650 FTIR spectrophotometer using the KBr technique and the solvent used is toluene or chloroform. The I.R. Spectrum was carried out at wave length 500-3500 cm^{-1} and transmittance % from 40 – 90.

3.1 Thermogravimetric analysis (TGA)

All TGA spectra were recorded under a nitrogen atmosphere up to 1000°C using a programmed rate of 10°C/min.

3.2 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was obtained with a DSC-30 under N_2 atmosphere at a heating rate of 20°C/min.

3.3 Electrical conductivity measurements

The specimens were molding in thin films having 1 cm diameter and 1 mm thickness. After that, the specimens were annealed at temperature higher than 100°C for 48 hours with a dc field or 90 V applied across the specimen. This thermal forming process was important to improve the contact between the neighbouring particles. Silver electrodes were used for the specimens. Conductive silver points were applied to the faces of the specimens and then they were heated in a drying oven at 60°C for 10 hours. This type of electrodes was very satisfactory for measurements. This gave linear current voltage characteristics for weak electric fields.

To measure the temperature dependence of the specific electrical resistivity an electric cell consisting of two copper electrodes was used. The specimen was adjusted firmly between two copper electrodes. The specimens were heated from outside using non-inductive electrical oven. The temperature of the specimens was measured by a thermocouple temperature probe of the type TP-30 attached to a millivoltmeter. The electric circuit which was used for the measurements consisted of an electric source, the electric cell and a high impedance electrometer (a Keithley electrometer of the type 610C of sensitivity 10^{-14} ampere and a variable resistance.

4 Results and discussion

4.1 FTIR Fourier transforms infrared (FTIR) spectroscopy

IR Spectroscopy of aniline-o-anthranilic acid copolymer and its complexes with NaOEt [33] and KI are showed in Figure 1a-1c respectively. It is clear that a reaction is expected to take place between the copolymer with NaOEt and KI respectively. The bands at 3500 and 3441 cm^{-1} are due to NH stretching vibrations. The band at 1257 cm^{-1} is due to C-N tertiary aromatic vibrations. The OH bending and CO stretching vibrations are represented by the band 1050 cm^{-1} which is slightly tilted to the polymerization. The bands 2364 and 2265 cm^{-1} are for aryl nitriles while those at 1713 and 1637 cm^{-1} are for benzenoid compounds (benzoic acid derivatives). The carboxylate anion stretching vibrations is shown by the band 1394 cm^{-1} . The characteristic bands at $585\text{-}553\text{ cm}^{-1}$ are due to vibrations of p-disubstituted benzene Figure 1a-1c. From the IR Spectra of polyvinylcarbazole and its complexes with KI [33] as shown in Figure 2a-2b respectively, the band at 3410 cm^{-1} is for stretching vibration of amino (NH) group. Alkene monosubstituted (vinyl) vibrations is indicated by the band 3046 cm^{-1} . The bands between 1589 and 1626 cm^{-1} indicate the presence of amine salt. The C-H and $-\text{CH}_2-$ groups are shown by the presence of the bands 1480 and 1410 cm^{-1} . The bands at 1362 and 1319 cm^{-1} indicate the presence of C-NH- aromatic vibrations. Also the bands at 1147 and 1217 cm^{-1} are due to the C-N tertiary aromatic vibrations. Alkene disubstituted trans vibrations are shown by the bands $957\text{-}847\text{ cm}^{-1}$. The $(\text{CH}_2)_n$ vibrations are given by the bands $741\text{-}711\text{ cm}^{-1}$.

4.2 Thermal Properties (TGA & DSC)

The thermal stabilities of aniline-o-anthranilic acid copolymer complexes with NaOEt and KI are showed in Figures 3-4. Thermal gravimetric behaviour could be used as a proof of the copolymerization of aniline with anthranilic acid and reacted it with each sodium ethoxide and potassium iodide. The TGA thermo gram of the copolymer of aniline and anthranilic acid with KI, shows that, the first and the second degradation were occurred at the temperature ranging from 135 to 198°C , indicating that the compound lost 18% of its weight, which confirmed that there is no effect on the structure of the copolymer complex.

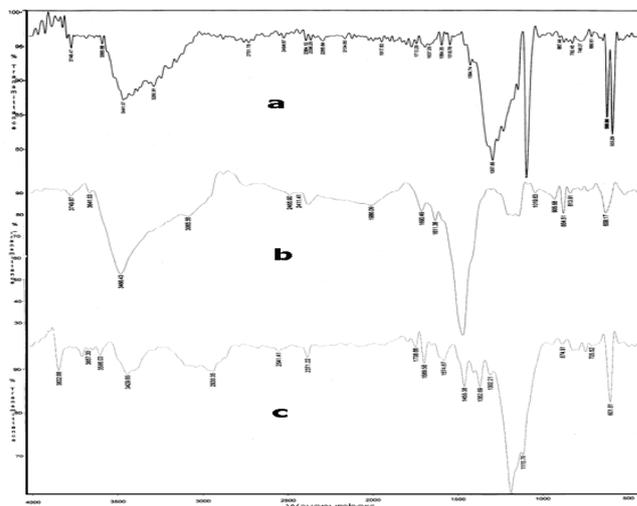


Fig. 1. IR spectroscopy of copolymer of (AA) and (a), copolymer of (AA)+NaOEt (b) and copolymer of (AA)+KI (c)

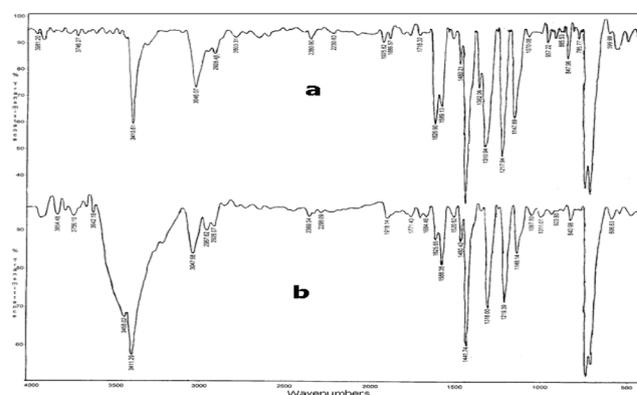


Fig. 2. IR spectroscopy of polymer (PVK) (a), and its complexes with KI (b)

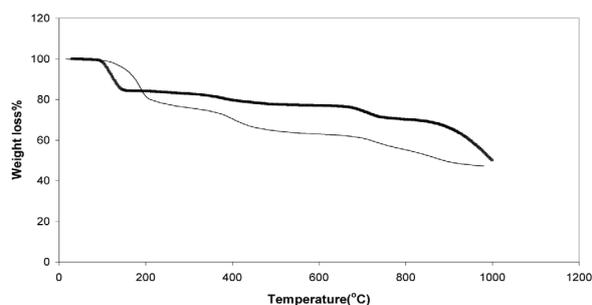


Fig. 3. TGA Thermo grams of Copolymer of (AA)+NaOEt (■) and with KI (○)

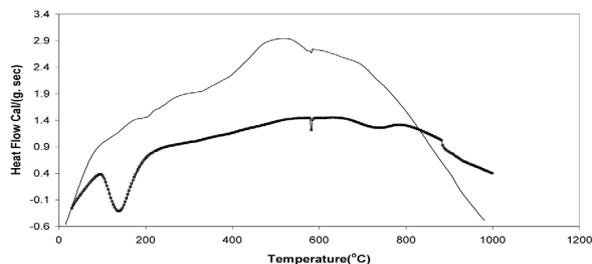


Fig. 4. DSC Thermo grams of Copolymer of (AA) + NaOEt (■) and with KI (○)

Therefore, it had high thermal stability till 640°C. But the stability of the copolymer decreased when it reacted with sodium ethoxide, where, the partial degradation occurred between 99 and 150°C. The thermal properties of the copolymer complexes were examined also by DSC. It was found that the copolymer of aniline and anthranilic acid with KI had more stability than the copolymer with sodium ethoxide, that had a large and sharp melting endothermic peak around 141°C and a glass transition T_g at 96°C as shown in Figure 4. The thermal degradation of polymer chain started above 1000°C, when the complex contained potassium iodide and this fact coincides with the results obtained by TGA. Also, the thermal stability of the Polyvinylcarbazole, and its complex with KI have been studied, Figures 5-6. The chains of PVK are stiff and the polymer has a glass transition temperature of 261°C which is among the highest known for vinyl polymers. PVK exhibits an excellent thermal stability up to at least 220°C. Unfortunately this property has never been fully utilised because of the extreme brittleness of the material. But, when was complexed with KI, it has thermal stability up to at least 520°C and a glass transition temperature of 666°C. It was clear from the results in TGA and DSC curves, that the thermal stability of PVK was improved at complexing it with KI.

4.3 Electrical conductivity

Compounds with semiconducting properties are characterized by specific electric conductivities between 10^{-12} and 10^{+2} $\text{ohm}^{-1} \cdot \text{cm}^{-1}$ and by a linear relation between $\log \rho$ and $1/T$. ρ is the specific electrical resistivity in $\text{ohm} \cdot \text{cm}$ and T is the absolute temperature. Applying these criteria, it can be show in Figure 7. The specific electrical conductivity σ of the copolymer aniline-o-anthranilic acid in presence of NaOEt, σ increases with increase of temperature. σ is $0.3 \text{ ohm}^{-1} \cdot \text{cm}^{-1}$ at 45°C and $0.55 \text{ ohm}^{-1} \cdot \text{cm}^{-1}$ at 75°C. When $\log \rho$ is traced vs. $10^3/T$, Figure 8 a linear relation is obtained. Where ρ is the specific electrical resistivity and T is the absolute temperature. This is the relation of semiconductors. When the complex is prepared from the copolymer and KI the specific electrical conductivity σ is traced vs. the temperature. σ decreases with increase in temperature, Figure 9 $\log \rho$ first increases with decrease in temperature. At temperature 30°C $\log \rho$ begins to decrease with decrease in temperature, i.e. there is an inversion in the slope and consequently in the activation energy for electrical conductivity, Figure 10. The relation between the electric current in ampere and voltage is linear and passes through the origin, Figures 11-12. This means that the mechanism of conductivity is electronic, i.e. the current passes through the overlapping of the electron d-orbital which forms extended conduction and valence bands [33]. The decrease in conductivity is due to two reasons. First, the strong intramolecular hydrogen bonding between the COO^- groups and the cationic radical nitrogen atoms that localized the movement of electrons in these structures. As a result, the conductivity is

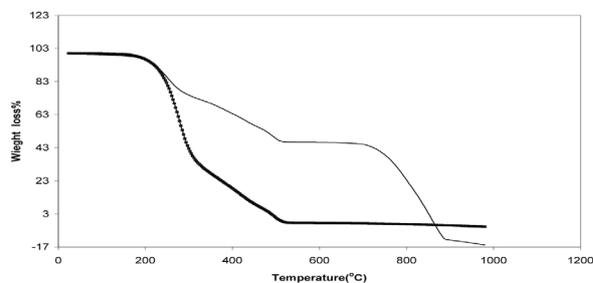


Fig. 5. TGA Thermo grams of polymer (PVK) (—■—) and with KI (-)

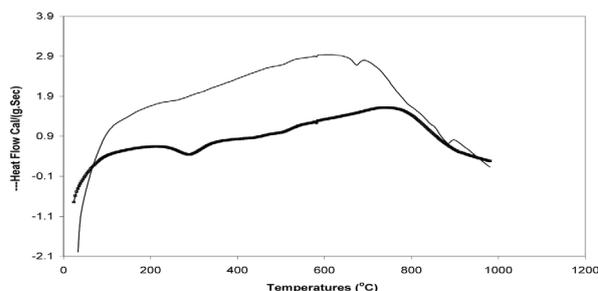


Fig. 6. DSC Thermo grams of polymer (PVK) (—■—) and with KI (-)

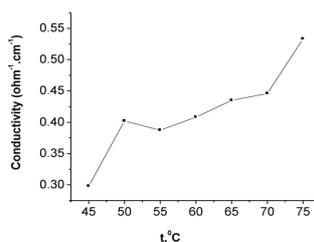


Fig. 7. σ vs. t , °C for copolymer of (AA) + NaOEt (left)

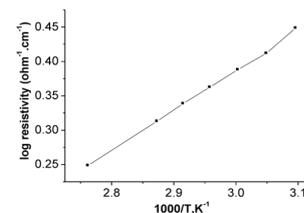


Fig. 8. $\log \rho$ vs. $10^3/T$, K^{-1} for copolymer of (AA) + NaOEt (right)

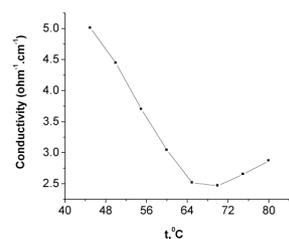


Fig. 9. σ vs. t , °C for copolymer of (AA) + KI (left)

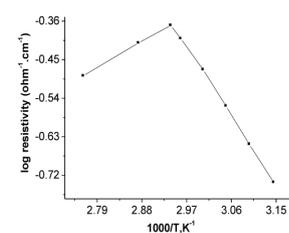


Fig. 10. $\log \rho$ vs. $10^3/T$, K^{-1} for copolymer of (AA) + KI (right)

adversely affected. Secondly, the steric effect of the carboxyl group is likely to disrupt the overlapping of orbitals, hence lowering the degree of conjugation, by forcing the aromatic rings out of plane relative to each other.

Carbazolyl groups easily forms relatively stable radical cations (holes). Some carbazole containing compounds exhibit relatively high charge carrier mobilities. Different substituents can be easily introduced into the carbazole ring; Carbazole containing compounds exhibit high thermal and photochemical

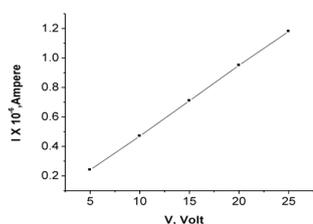


Fig. 11. I vs. V for copolymer of (AA)+NaOEt (left)

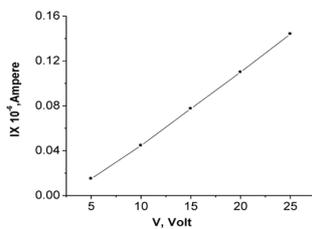


Fig. 12. I vs. V for copolymer of (AA)+KI (right)

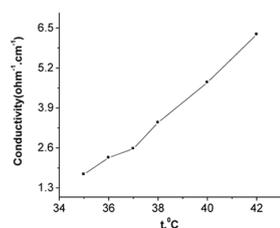


Fig. 13. σ vs. t , $^{\circ}\text{C}$ for (PKV) (left)

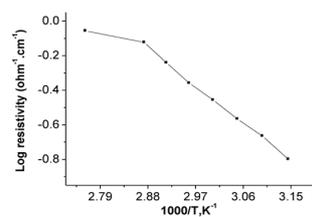


Fig. 14. $\log \rho$ vs. $10^3/T$, K^{-1} for (PKV) (right)

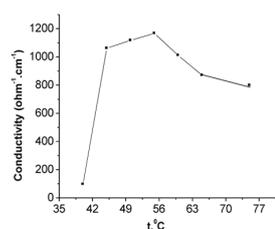


Fig. 15. σ vs. t , $^{\circ}\text{C}$ for (PKV) + KI (left)

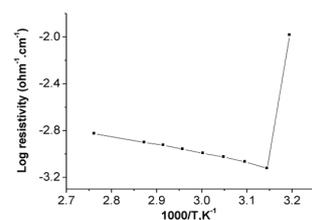


Fig. 16. $\log \rho$ vs. $10^3/T$, K^{-1} for (PKV) + KI (right)

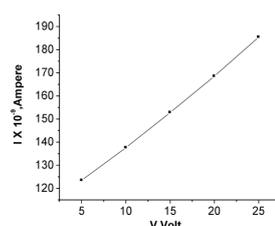


Fig. 17. I vs. V for (PKV) (left)

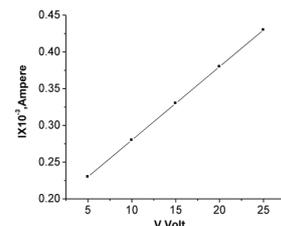


Fig. 18. I vs. V for (PKV) + KI (right)

stability; Carbazole is a cheap raw material readily available from coal–tar distillation. The plot of specific electrical conductivity of polyvinyl carbazole (PVK) vs. temperature in centigrade gives a straight line Figure 13. The specific electrical conductivity σ increases with increase in temperature.

$$\sigma = 3.5 \times 10^{-8} \text{ ohm}^{-1}.\text{cm}^{-1} \text{ at } 35^{\circ}\text{C}$$

$$\sigma = 4.3 \times 10^{-8} \text{ ohm}^{-1}.\text{cm}^{-1} \text{ at } 43^{\circ}\text{C}$$

The relation can be expressed by the equation: $\sigma_t = \sigma_o (1+kt)$, where k is constant. The complex of poly N-vinylcarbazole with KI was prepared to generate both charge carrier and mobility, that are substantially increased in the PVK complex compared to the PVK polymer. The plot of σ for the complex prepared from PVK with KI vs. temperature is shown in Figure 14 σ increases with increase in temperature. However above 55°C , σ decrease with further increase in temperature. These results were attributed to increasing in the bulkiness of the carbazole groups, and iodine atoms are severely restricted the mobility of the electrons in PVK complex. As a result, the numbers of the electron donors and electron acceptors and the movement (propagation) of the charged particles decrease. Figures 15 and 16 show the relation between $\log \rho$ and $10^3/T$, where ρ is the specific electrical resistivity and T is the absolute temperature. The plot of the electric current I vs. the voltage V is shown in Figures 17 and 18. It is a linear relation. The relation between $\log \rho$ vs. $10^3/T$ differs in the case of N-vinylcarbazole from that of the complex (the slope is different). The structure of the complexes of poly N-vinylcarbazole with KI and copolymer of aniline-o-anthranilic acid with each NaOEt and KI, can be predicted that:

The increase in the electrical conductivity in these complexes is due to [34]:

The improved intermolecular orbital overlap of the metal d-orbital and, The conjugation of the d-orbital of the metals with the π -electrons, thereby facilitating the conduction path through the metal atoms.

5 Conclusions

Two different polymer and their complexes with salts were prepared. The first was the Poly (aniline-co-o-anthranilic acid) (PAA) copolymers that were obtained from the chemical polymerization of aniline and o-anthranilic acid. The second, was the polyvinylcarbazole (PVK), which prepared by free radical mechanism. The electrical properties, thermal properties and IR spectroscopy for the prepared polymers and their complexes with KI and NaOEt were determined. It was found that, the specific electrical conductivity (σ), and the thermal stability for each of the copolymer aniline-o-anthranilic acid and the polyvinylcarbazole is enhanced by reacted each of them with KI than in with NaOEt or PVK only respectively. It is worthwhile to mention that there is a great possibility for NaOEt and KI to react with the COOH group of anthranilic acid to form sodium or potassium salts or with the NH group to form quaternary ammonium salts. However, above certain temperature, these groups are severely restricted the mobility of the electrons in polymers and their complexes. As a result, the numbers of the electron donors and electron acceptors and the movement (propagation) of the charged particles decrease and so, σ decrease with further increase in temperature. Finally, these compounds were found to obey the relations of semiconductors. The relation between $\log \rho$ and $10^3/T$ is linear and the specific electric conductivity σ is between 10^{-2} and $10^{-12} \text{ ohm}^{-1}.\text{cm}^{-1}$.

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