

Preparation of Polyaniline and Studying Its Electrical Conductivity

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ABSTRACT: Polyaniline was prepared by chemical methods. Its electrical conductivity was measured. The electrical conductivity of polyaniline salt and polyaniline base were compared with composites prepared by the hot press of polyaniline base with KBr, $\text{Co}(\text{CH}_3\text{COO})_2$, and picric acid. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1658–1665, 2000

Key words: polyaniline; specific resistivity, electrical conductivity, activation energy

INTRODUCTION

Conjugated polymers are the new class of materials used for fabrication of solid-state devices.^{1–10} Comparison of semiconducting polymers with conventional semiconductors is not straightforward and simple. Electrical conduction in polymers may arise due to a variety of phenomena operating in polymers that may differ from the ones in conventional semiconductors. However, the resultant electronic effects in the polymeric semiconductors appear to be similar to those in inorganic ones. Most of the semiconducting polymers, polypyrrole, polyaniline, and polythiophene, are prepared by electrochemical and chemical methods. In the case of electrochemical methods of preparation, the polymer films are formed on the conducting electrode (usually an indium tin oxide-coated glass of the electrochemical cell). The aim of this work was to add dopants to polyaniline (emeraldine base) to obtain materials that have semiconducting properties or to increase the electric conductivity of the emeraldine base.

Polyaniline (emeraldine base) was prepared by chemical methods.¹¹ Polyaniline exists in four different forms. The three other forms are prepared by other methods.² These four structurally transformed forms of polyaniline are achieved through the protonation and doping of the base form. These forms have a wide range of electrical conductivity, from insulating to conducting. Conductivity of the order of 10 S/cm can be obtained for the conducting forms.^{2,3}

In this work, polyaniline salt was prepared from which polyaniline (emeraldine base) was obtained. The electrical conductivity of polyaniline, of polyaniline salt, and of the composites prepared by the hot press of polyaniline with KBr, $\text{Co}(\text{CH}_3\text{COO})_2$, and picric acid were measured.

PREPARATION OF POLYANILINE¹¹

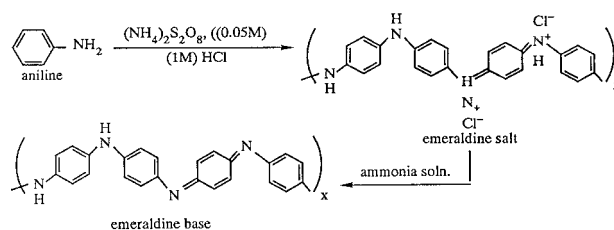
Polyaniline is usually prepared by redox polymerization of aniline using ammonium perdisulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, as an oxidant. Distilled aniline (0.2M) was dissolved in 300 mL of a precooled HCl (1.0M) solution maintained at 0.5°C. A calculated amount of ammonium perdisulfate (0.5M) dissolved in 200 mL of HCl (1M), precooled to 0–5°C, was added to the above solution. The dark green

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precipitate resulting from this reaction was washed with HCl (1M) until the green color disappeared. This precipitate was further extracted with tetrahydrofuran and dried to yield emeraldine salt. Emeraldine base can be obtained by heating emeraldine salt with an ammonia solution. The powder so obtained can be used for device fabrication such as in photovoltaics, photo-

cells, electrochromic and memory devices, battery electrode application, and civil, military, photonic, and optoelectronics applications and communications¹¹: Polymerization of aniline using ammonium perdisulphate as catalyst to yield emeraldine salt from which emeraldine base was obtained by treating the salt with ammonia solu. is expressed by the following equation:



Various additives such as KBr, $\text{Co}(\text{CH}_3\text{COO})_2$, and picric acid were added to the emeraldine base in different proportions using the hot-press method. The electrical conductivity of the pellets so obtained was measured.

PHYSICAL MEASUREMENT

Samples of the emeraldine salt, emeraldine base, and the composites prepared from the emeraldine base with different additives were prepared by pressing into pellets in a special vacuum mold. The pressure was 3770 kg/cm^2 . This pressure was sufficient to give compact specimens. After molding, the specimens were annealed at 115°C for

48 h with a dc field of 90 V applied across the specimen. This thermal forming process was important to remove residual voids, improve the contact between the neighboring particles, and to orient the molecules with the axis of the specimen. The circuit which was used for the measurements consists of an electric source, the cell, a high impedance electrometer (a Keithly electrometer of type 610 C of sensitivity 10^{-14} amperes), and a variable resistance. The temperature of the specimen was measured by a thermocouple temperature probe of the type TP-30 attached to a millivoltmeter. The specimen was heated from outside using a noninductive electrical oven.

When the relation of $\log \rho$ versus $1/T$ is linear, it obeys the Arrhenius equation

Table I Activation Energy Calculated for Each Compound

Compound	Activation Energy (kcal/mol)	Activation Energy (eV)	
1	90% polyaniline + 10% KBr	8	0.343
2	85% polyaniline + 15% KBr	5.74	0.246
3	75% polyaniline + 25% KBr	4.596	0.197
4	50% polyaniline + 50% KBr	0.45	0.02
5	90% polyaniline + 10% picric acid	38.8	1.663
6	75% polyaniline + 25% picric acid	15.05	0.645
7	50% polyaniline + 50% picric acid	6.533	0.28
8	80% polyaniline + 15% picric acid	8.015	0.229
9	90% polyaniline + 10% cobalt acetate	5.366	0.230
10	85% polyaniline + 15% cobalt acetate	18.66	0.8
11	75% polyaniline + 25% cobalt acetate	4.596	0.197
12	50% polyaniline + 50% cobalt acetate	0.0295	0.0134
13	Polyaniline	7.77	0.333
14	Polyaniline salt	2.5	0.109

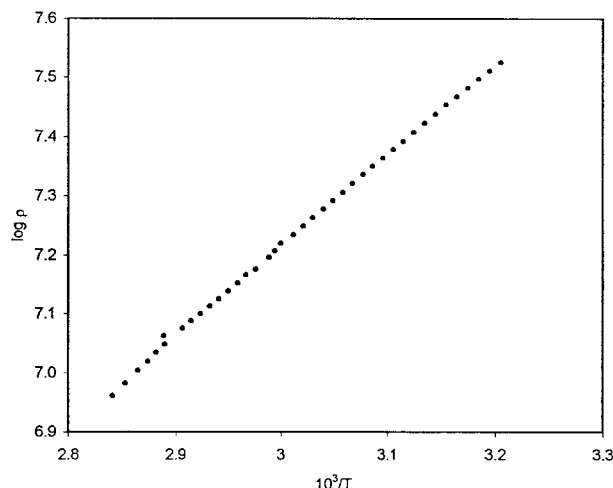


Figure 1 Variation of specific resistivity with T^{-1} for polyaniline.

$$\log \rho = \log \rho_0 - \frac{Ea}{RT}$$

ρ is the specific electric resistivity in Ω cm. Ea is the activation energy for electrical conductivity and R is the gas constant which is approximately equal to 2 cal $\text{deg}^{-1} \text{mol}^{-1}$.

From Table I, it is noticed that compounds 4 and 12 have the lowest activation energy, meaning that little energy is required for excitation of this compound in order that it can behave as a semiconductor, for example, in the case of KBr, it forms a complex with polyaniline. This complex is easily ionized when an electric current passes through the specimen. The electric conductivity of the material increases. This increase in electric conductivity is directly proportional to the increase in the concentration of KBr. The increase in electric conductivity was accompanied by a subsequent decrease in the activation energy.

RESULTS AND DISCUSSION

The relation between the specific electric resistivity, ρ , and $1/T$ is linear (Fig. 1), where T is the absolute temperature, ρ is $3.2 \times 10^6 \Omega$ cm at $t \approx 40^\circ\text{C}$, and ρ is $7.9 \times 10^5 \Omega$ cm at $t = 87^\circ\text{C}$. Accordingly, this material is a semiconductor, since compounds with semiconducting properties are characterized by specific electric resistivity between 10^{12} and $10^2 \Omega$ cm and by a linear relation between $\log \rho$ and $1/T$.¹²

Figure 2 shows the variation of the specific electric resistivity, ρ , with $1/T$ for polyaniline salt

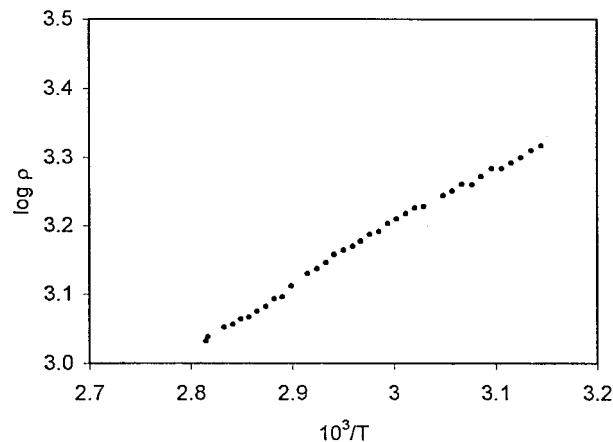


Figure 2 Variation of specific resistivity with T^{-1} for polyaniline salt.

(emeraldine salt). It is also a linear relation. However, this material possesses higher electric conductivity, since $\rho = 2.24 \times 10^2 \Omega$ cm at 40°C and $\rho = 11 \times 10 \Omega$ cm at 87°C (Fig. 3), indicating that the electric conductivity of this material approaches that of conductive materials as the temperature increases. This fact is due to ionization of emeraldine salt at higher temperature to emeraldine base carrying positive charges and chloride ions carrying negative charges,¹¹ that is, emeraldine salt:

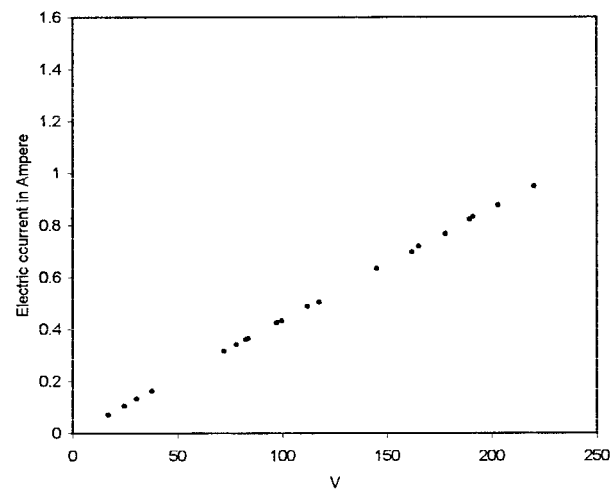
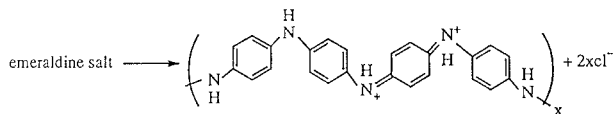


Figure 3 Variation of current with voltage for polyaniline salt.

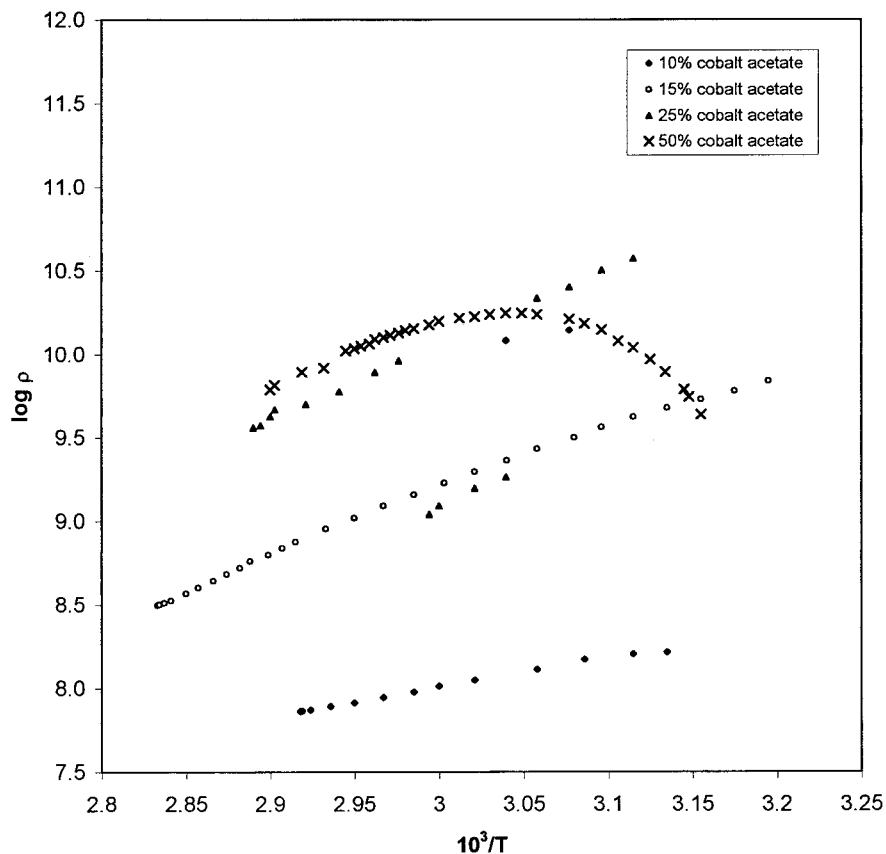
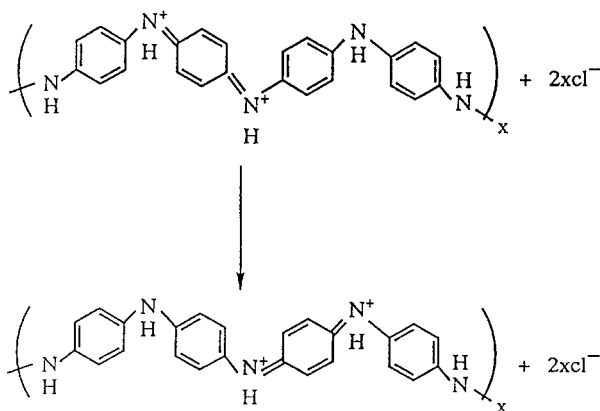


Figure 4 Variation of specific resistivity with T^{-1} at different cobalt acetate concentrations.

When an electric current passes through the material, these charges become mobile, leading to increased conductivity.¹³ The existence of a potential gradient assists in the generation, separation, and migration of the charged carrier species produced by heat or light activation:



The polarons and bipolarons are mobile and under the influence of an electric field can move along the polymer chain, from one chain to an-

other and from one granule to another, exactly in the manner electrons and holes do in inorganics.

In the case of composites of polyaniline with cobalt acetate, the specific electric resistivity ρ was lower when the dopant was 10% by weight (Fig. 4):

$$\rho = 10^8 \text{ } \Omega \text{ cm at } 50^\circ\text{C}$$

and

$$\rho = 5.6 \times 10^6 \text{ } \Omega \text{ cm at } 72^\circ\text{C}$$

When the concentration of the dopant was 15%, ρ increases. This can be explained by that cobalt acetate could be easily ionized by heat and due to the passage of electric current when its concentration was low. Hence, cobalt could be linked to the nitrogen atoms of polyaniline to form quaternary ammonium salts.

When cobalt acetate was 15 wt %,

$$\rho = 6.3 \times 10^8 \text{ } \Omega \text{ cm at } 40^\circ\text{C}$$

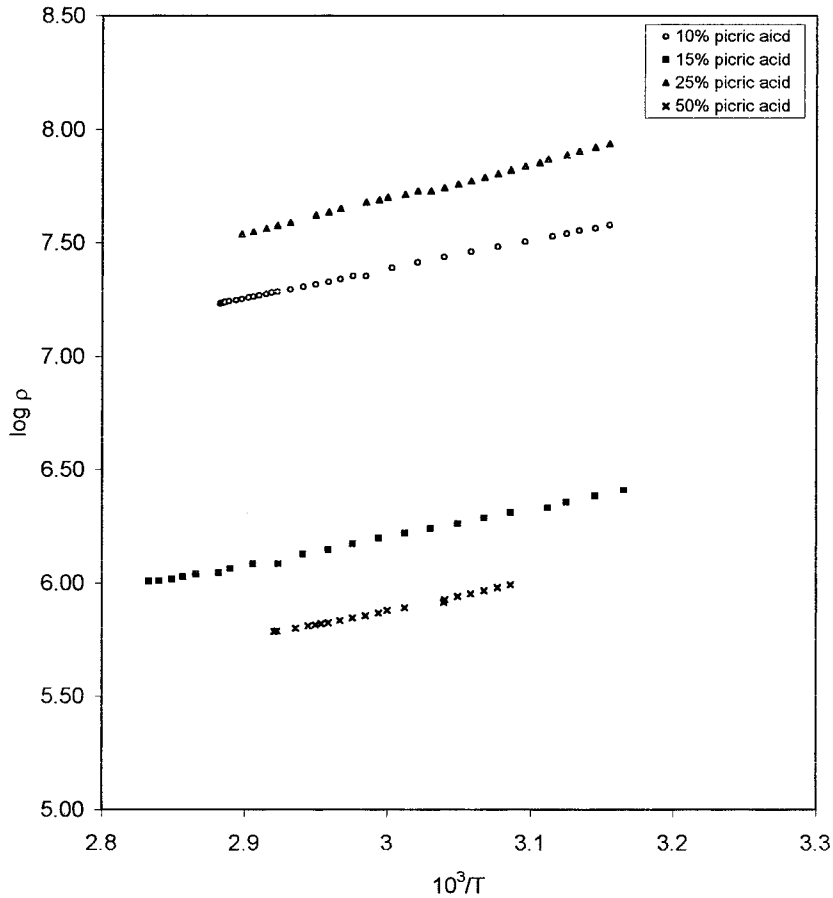


Figure 5 Variation of specific resistivity with T^{-1} at different picric acid concentrations.

and

$$\rho = 2.5 \times 10^7 \Omega \text{ cm at } 87^\circ\text{C}$$

The variation of ρ with $1/T$ when the concentration of cobalt acetate was 25 wt % was

$$\rho = 5 \times 10^9 \Omega \text{ cm at } 40^\circ\text{C}$$

and

$$\rho = 3.9 \times 10^7 \Omega \text{ cm at } 72^\circ\text{C}.$$

Log ρ versus $1/T$ is also linear. When cobalt acetate was 50 wt %, it was found that the first part of the curve obeys the relation of the semiconductors. The second part of the curve obeys the relation of the metals, which is $\Delta\rho/\rho_0 = \alpha\Delta T$; α is the temperature coefficient of the resistance. This relation means that ρ decreases with decrease of the

temperature. However, in both cases, ρ is much greater than that of the metals:

$$\rho = 6.3 \times 10^8 \Omega \text{ cm at } 72^\circ\text{C}$$

$$\rho = 1.6 \times 10^9 \Omega \text{ cm at } 60^\circ\text{C}$$

and

$$\rho = 3.98 \times 10^8 \Omega \text{ cm at } 45^\circ\text{C}$$

In all the above-mentioned cases, the relation between the electric current in amperes and the voltage were linear (Figs. 3, 7, 8, and 9) meaning that the relation between the current and voltage is ohmic.

When picric acid was used as the dopant, ρ first decreases with increase of the concentration of picric acid from 10 to 15 wt %; then it again

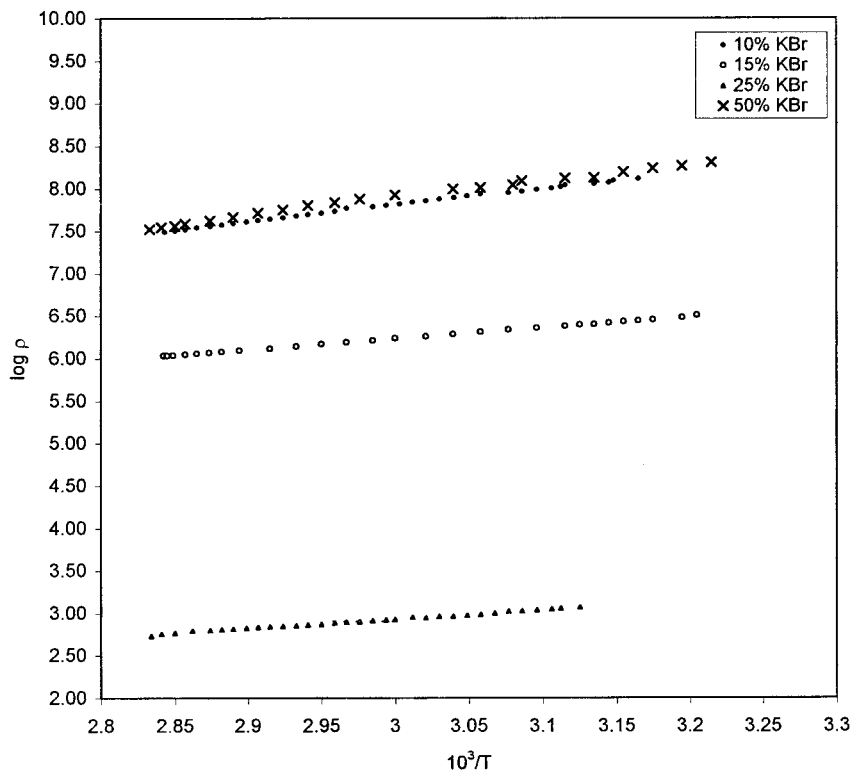


Figure 6 Variation of specific resistivity with T^{-1} at different KBr concentrations.

increases when the concentration of picric acid increases from 25 to 50 wt % (Fig. 5). The lowest value of ρ was at temperature 84°C when the picric acid concentration was 15 wt %. This can be

explained by the fact that the highest ionization of picric acid occurs when its concentration is 15 wt %. We can say also that a sort of percolation occurs at this concentration.

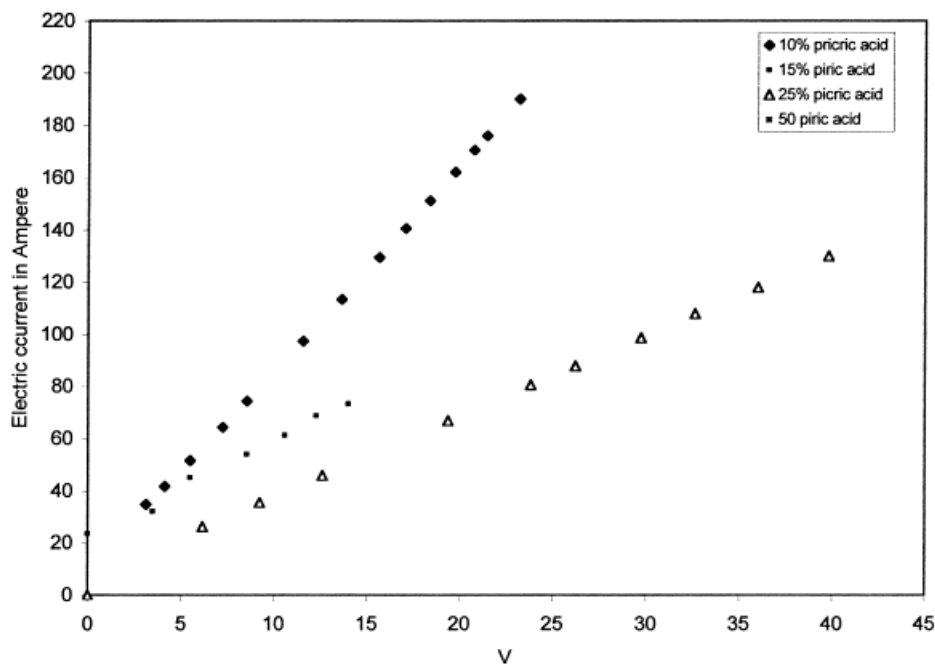


Figure 7 Variation of current with voltage for PVA with picric acid.

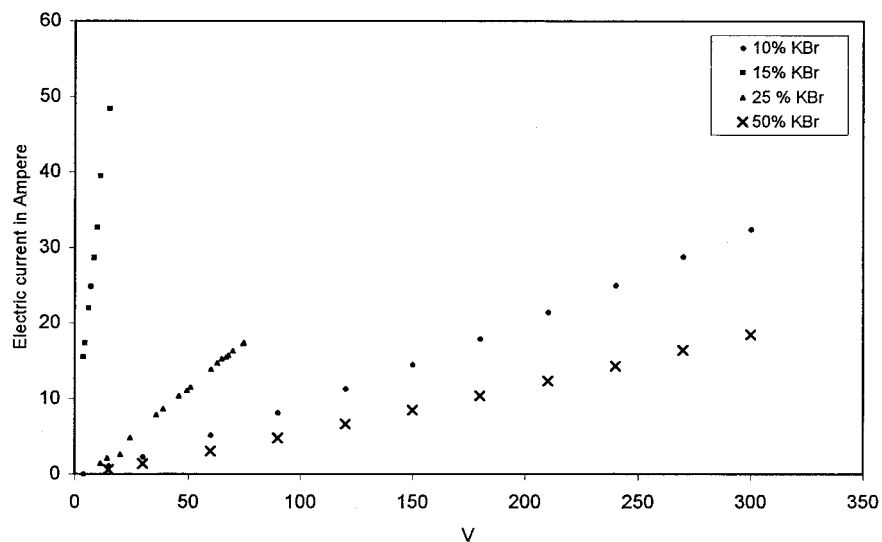


Figure 8 Variation of current with voltage for PVA with KBr.

$\rho = 8.9 \times 10^4 \Omega \text{ cm}$ at 84°C and the highest value of ρ was when the concentration of picric acid was 50%, and at a temperature = 45° , $\rho = 8.9 \times 10^6 \Omega \text{ cm}$ at 45° . All the relations between $\log \rho$ and $1/T$ are linear.

Most probably, picric acid forms complexes with polyaniline like that between pyridine and picric acid.

Figure 6 gives the relation between $\log \rho$ and $1/T$ for polyaniline using different concentrations of KBr as dopant. The highest electrical conduc-

tivity was observed when KBr concentration was 25 wt %.

$$\rho = 6.99 \times 10 \Omega \text{ cm at } 75^\circ\text{C}$$

and

$$\rho = 10^3 \Omega \text{ cm at } 45^\circ\text{C}$$

Variation of $\log \rho$ with $1/T$ for various composites of polyaniline with potassium bromide

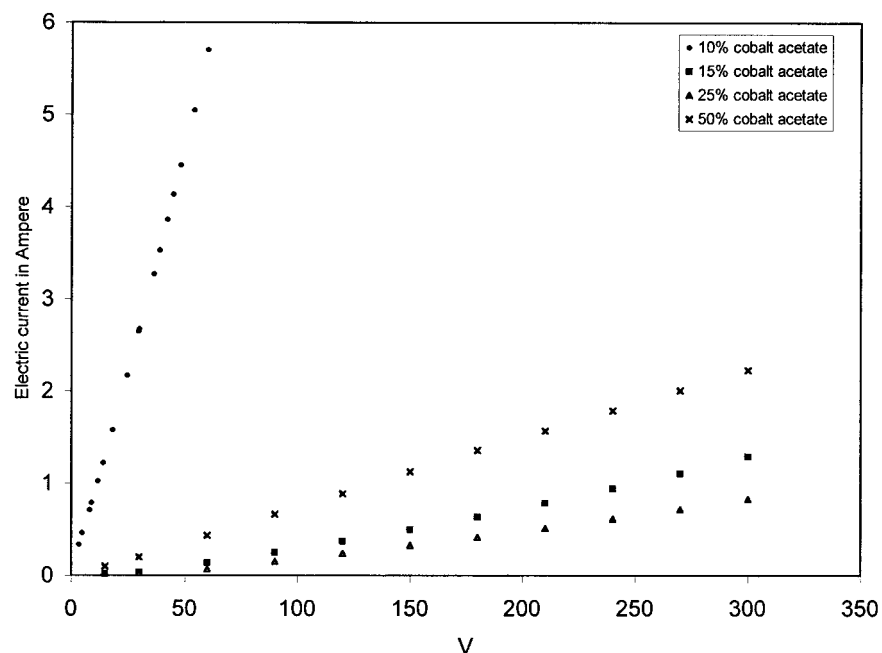


Figure 9 Variation of current with voltage for PVA with cobalt acetate.

are also linear at different concentrations of KBr (Fig. 6).

From the above-mentioned discussion, it is seen that all compounds are semiconductors. The highest electric conductivity was found in the case of emeraldine salt. If the number of quinoid structures were increased by using a more powerful oxidant as a catalyst, for example, potassium perchlorate, higher electric conductivity would be expected because the number of polarons in each polymer chain would increase.

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