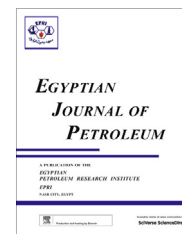




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FULL LENGTH ARTICLE

Comparison between the electrical properties of polyphenylacetylene and polyaminotriazole



M. Yahia Abed, Azza M. Mazrouaa, Zizi Abdeen *, A. Ashery, Rasha G. Abdelaziz

Egyptian Petroleum Research Institute (EPRI), Nasr-City, Cairo, Egypt

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KEYWORDS

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Abstract The electrical properties of a polymer containing aromatic rings were compared with those of polyheterocyclic compound. Each segment of the polyheterocyclic compound contains three nitrogen atoms. Both polymers were prepared at the laboratory. It was found that the specific electrical conductivity of polyphenylacetylene is higher than that of polyaminotriazole. $\log \rho$ vs. $10^3/T$ was traced for both compounds, where ρ is the specific electrical resistivity and T is the absolute temperature. Complexes of each compound with KI were prepared. The electrical properties of these complexes were studied. The microstructure of both compounds was determined by FTIR spectroscopy.

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1. Introduction

Conjugated polymers were found to have electrical properties similar to those of semiconductors and accordingly they were used for solar cells and other electronic devices [1,2] and fabrication of solid-state devices [3–12]. The conductivity in conjugated double bond polymers was believed to depend on the overlapping of electrons of the π orbitals which form extended conduction and valence bands [13]. Examples of conjugated

double bond polymers are polyphenylacetylene, polyaminotriazole, polyaniline, polypyrrole and polyacetylene. Conductivity of the order 10 S/cm can be obtained for the conducting forms [4,5]. Polyphenylacetylene could be polymerized by free radical mechanism [14]. It was also prepared by catalytic polymerization in the presence of Rh (I) complex [15,16]. Since the initial discovery of polyacetylene in (1977), conducting polymers which were p-or n- doped, were prepared either chemically or electrochemically [17,18]. Various $WOCl_4$ and $MoCl_5$ catalysts were used in the polymerization of phenylacetylene. It was found that titanocene derivatives could polymerize phenyl acetylene [19,20] with the aid of triethylaluminium.

In this work phenylacetylene was polymerized by free radical mechanism [14] using benzoyl peroxide as initiator. Polyaminotriazole was prepared from oxalic acid and hydrazine hydrate or from urea and formalin [21]. The electrical properties of these polymers were studied. The electrical properties of the polymers before and after reaction with C_2H_5ONa and KI were also studied.

* Corresponding author.

E-mail address: ziziabdeen@yahoo.com (Z. Abdeen).

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2. Materials and methods

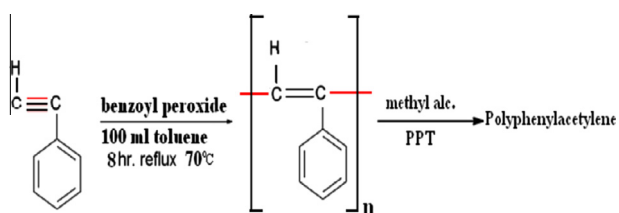
2.1. Materials

- Phenyl acetylene was supplied from BDH M.W: 102.13, b.p.142–144 °C, density: 0.967 g/ml at 25 °C. It was distilled under vacuum, in the presence of nitrogen.
- Benzoyl peroxide (C₆H₅CO)₂O₂ supplied from Aldrich M.W.: 242.23, m.p. after drying: 102–105 °C, recrystallized from ether.
- Formaldehyde HCHO solution stabilized with 10% methanol supplied from Fluka
- M.W.: 30.03 g/mol, 1L = 1.09 kg, b.p.: 96–98 °C, Flash point: 62 °C. Commercial formalin is aqueous solution containing 37–40% W/V of formaldehyde.
- Urea:H₂NCONH₂, supplied from BDH M.W.:60.06 g/mol, m.p.: 132–135 °C, crystalline extra pure.
- Oxalic acid (COOH)₂·2H₂O supplied from Nil Company Cairo, Egypt. Crystallized from water as colorless crystals with two molecules of water of crystallization, m.p. of the hydrate: 101.5 °C.
- Hydrazine hydrate: H₂N·NH₂·H₂O M.W.: 32.05 g/mol, *d*₂₀⁴⁰:1.029, Fp: 204 °F (95 °C), Hydrazine content 55%.
- Conc. ammonia solution 33% Wt. per ml at 20 ° = 0.8860 g.

2.2. Methods

2.2.1. Preparation of polyphenylacetylene [15]

51 g of phenylacetylene, after distillation was placed in a 3-neck round bottomed flask equipped with a reflux condenser. 0.5 g of benzoyl peroxide was added together with 100 ml toluene. The flask was heated at 70 °C for 8 h. Polyphenylacetylene was precipitated with methyl alcohol. The polymer was washed with distilled water, alcohol and acetone and dried in vacuum desiccators. Pellets of the polymer having 1 cm diameter and 1 mm thickness were prepared. The specific electrical conductivity of the polymer was determined using Keithley electrometer at temperature ranging from 30 to 120 °C. Because the polymer and its complexes are insoluble in any solvent, complexes of the polymer with EtONa and KI were prepared by pressing a sample of the polymer with EtONa and KI respectively at a ratio of 50:50 by weight. The specific electrical conductivities of the complexes formed were also determined.

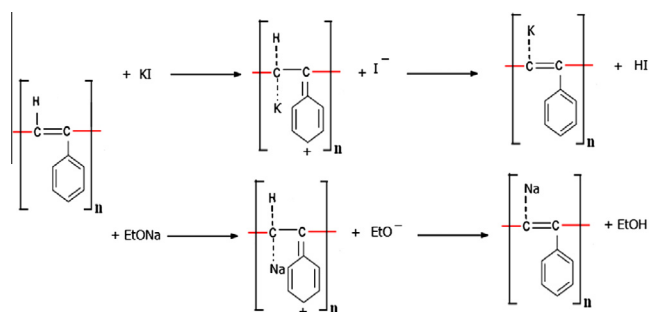


Phenylacetylene

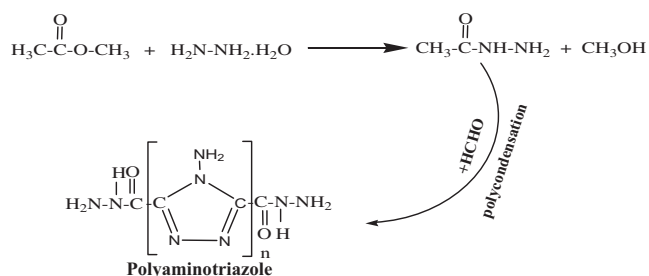
Reactions mechanism for formation of Polyphenylacetylene Complexes with KI and EtONa:

2.2.2. Preparation of polyaminotriazole [22,23]

50 ml of hydrazine hydrate was added to 50 g of methyl acetate. The mixture was heated gently under reflux for 15 min.

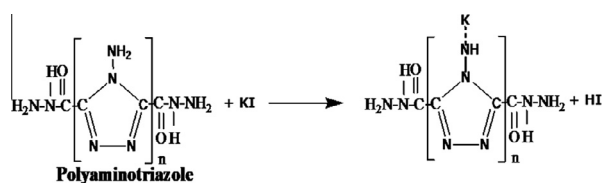


Absolute ethanol was added just enough to produce a clear solution. The total mixture was refluxed for a further 2–3 h. Ethyl alcohol was distilled off. After cooling, the hydrazide produced was polycondensed in the presence of 1 g of p-toluenesulfonic acid, 6 ml conc. H₂SO₄ and 100 ml formalin. The polyaminotriazole produced was precipitated by methyl alcohol, washed with water, alcohol and dried.



The same reaction can be made using 63 g oxalic acid, 50 ml hydrazine hydrate. 1 g of p-toluene-sulfonic acid and 13.3 ml conc. H₂SO₄, dihydrazide is produced and after refluxing, the polyaminotriazole is formed. It was precipitated by methyl alcohol, washed with water and alcohol and dried in vacuum desiccators. Because of the polymer and its complexes are insoluble in any solvent, they were plated, having 1 cm diameter and 1 mm thickness. The specific electrical conductivities of the polymer and its complexes were determined and the structure of polyaminotriazole [22,23] was investigated by IR measurement.

Formation of Polyaminotriazole Complexes with KI:



3. Physical measurements

3.1. FTIR spectroscopy

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 wavelength 500–3500 cm⁻¹ and transmittance % from 40 to 90.

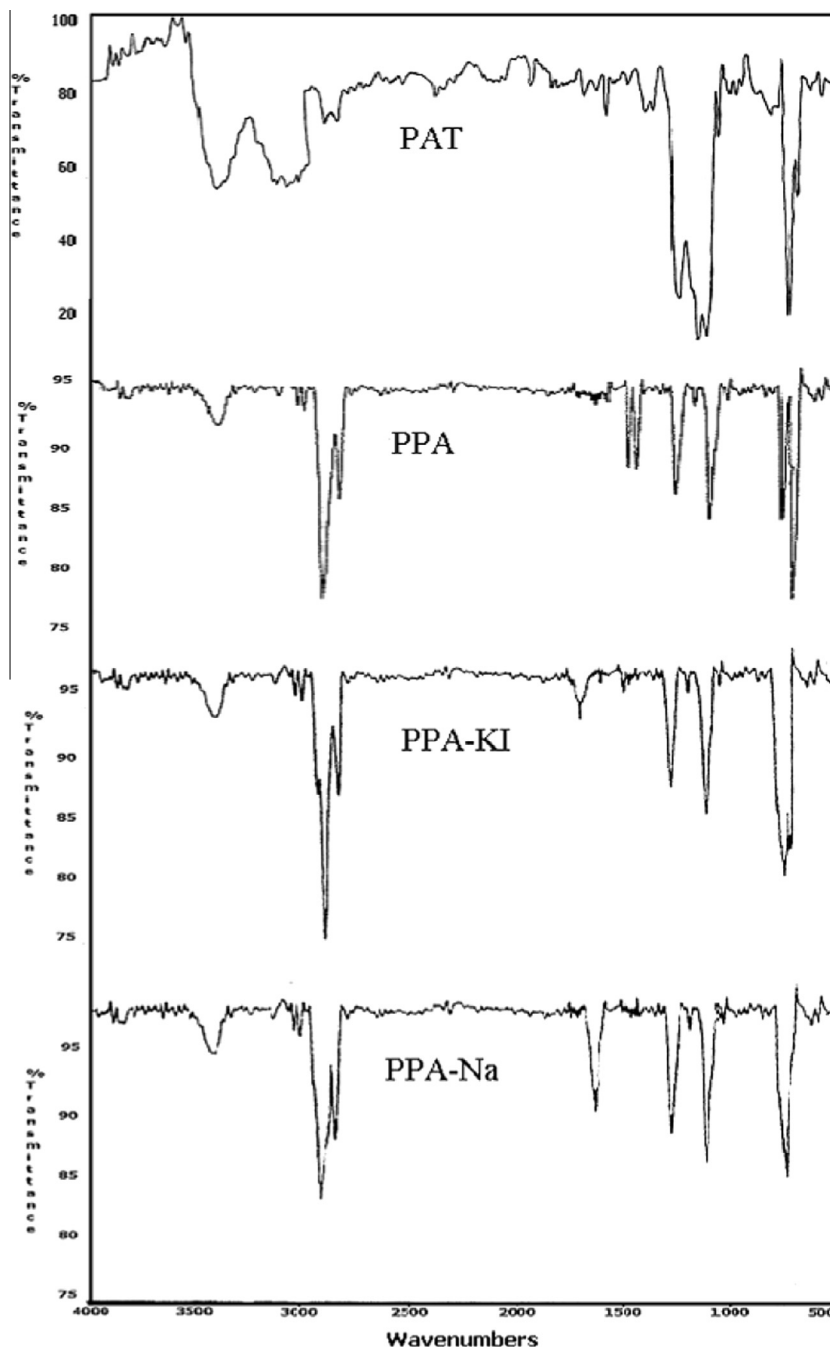


Figure 1 IR spectrum for PAT, PPA, PPA doped with KI and PPA doped with NaOC_2H_5 .

3.2. Electrical conductivity measurements

A sample of the polymer or the polymer complexes was prepared either as a thin film 1 cm diameter and 1 mm thickness, or it was pressed into pellets 1 mm thickness 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 or 90 V applied across the specimen. This thermal forming process was to improve the contact between the neighboring particles and to orient the molecules with the axis of the specimen. Silver electrodes were used for the specimens. Conducting silver point

was applied to the faces of the specimens and then they were heated in a drying oven at 60°C for 10 h. This type of electrodes was very satisfactory for the measurements. This gave linear current voltage characteristics for weak electric fields. To measure the temperature dependence of the specific resistivity an electric cell consisting of two copper electrodes was used. The specimen was adjusted firmly between the two copper plates of the electrodes. The specimen was heated from outside using a non-inductive electrical oven. The temperature of the specimen was measured by a thermocouple temperature probe of the type TP-30 attached to a milli voltmeter. The electric circuit which was used for the measurements consists of an electric

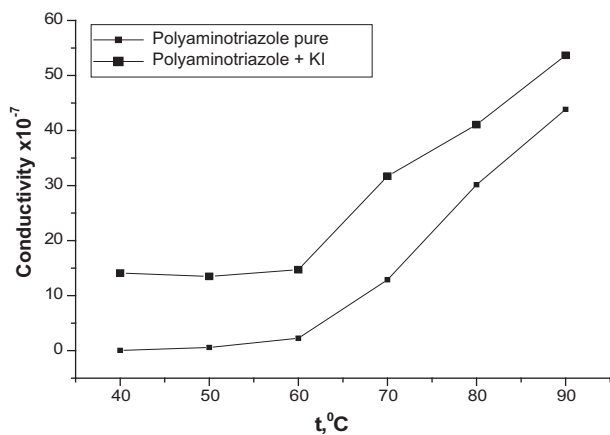


Figure 2 Conductivity vs. temperature of polyaminotriazole and with KI.

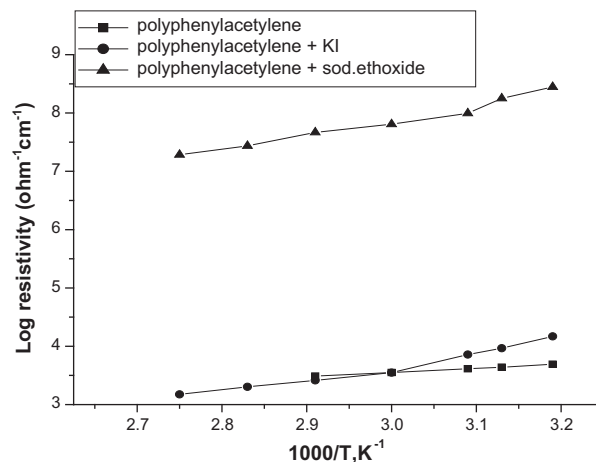


Figure 5 Log resistivity vs. $1000/T$ of polyphenylacetylene and its complexes with KI and NaOEt.

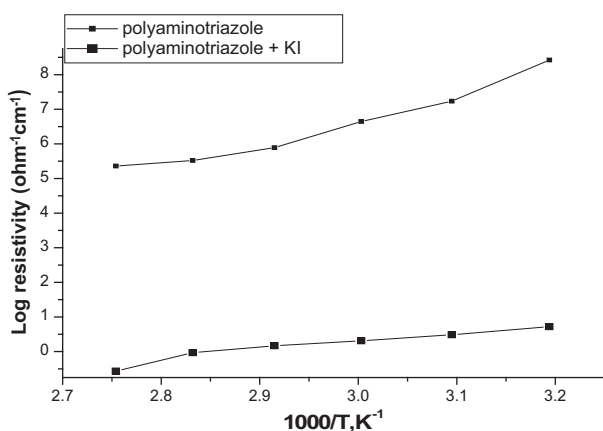


Figure 3 Log resistivity vs. $1000/T$ of polyaminotriazole and with KI.

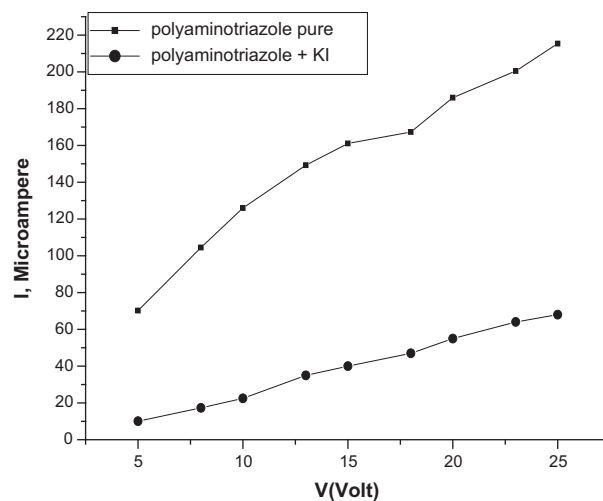


Figure 6 $I&V$ for polyaminotriazole and its complexes with KI.

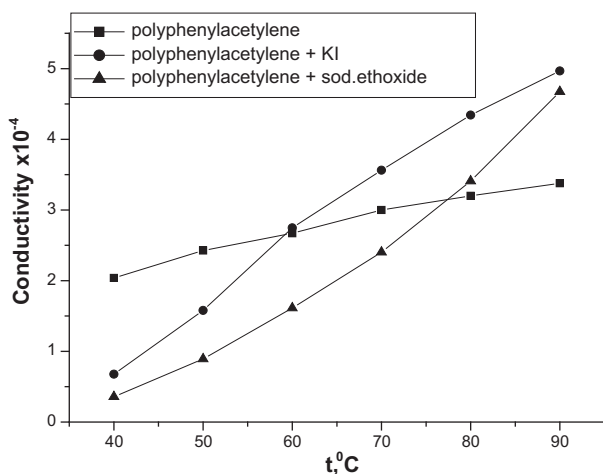


Figure 4 Conductivity vs temperature of polyphenylacetylene and its complexes with KI and NaOEt.

source, the cell, high impedance electrometer (A Keithley electrometer of the type 610C and sensitivity 10^{-14} A) and a variable resistance.

4. Results and discussion

4.1. FTIR spectroscopy [24–26]

For the spectrum of (PAT) a large band appears at $1149\text{--}1050$ and 1000 cm^{-1} which are due to CO stretching and OH bending vibration. The medium band at 3421 cm^{-1} is due to NH stretching vibrations while the wide bands at 3129 , 3095 , 3014 and 2957 cm^{-1} stretching vibrations are due to the presence of imines. C–N vibrations are shown by the bands $1315\text{--}1278\text{ cm}^{-1}$. Stretching vibrations at $2795\text{--}2346\text{ cm}^{-1}$ indicate the presence of aldehyde group that are confirmed with the presence of a weak band of CO group at 1740 cm^{-1} and C–H stretching vibration at 2795 and 2957 cm^{-1} . These are attributed to the presence of some traces of formalin solvent used in the preparation process. The small bands at 1883 and 1623 cm^{-1} are due to the group $C=N$. A small band at 1623 cm^{-1} stretching vibrations is due to the presence of the group $-N=N-$ Fig. (1, PAT). The group $-N=C=N-$ is at 2346 cm^{-1} stretching vibrations and the band at 1511 cm^{-1}

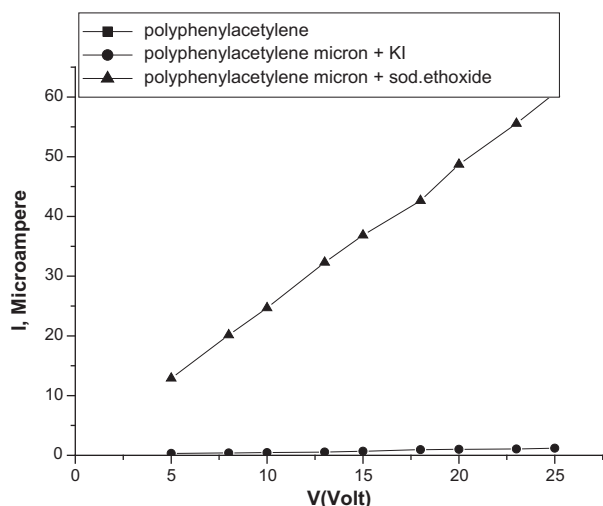


Figure 7 I & V for polyphenylacetylene and its complexes with KI and NaOEt.

vibrations indicates the presence of amide groups. In the case of polyphenylacetylene, Fig. (1, PPA), it is clear that there is a band at $\sim 1600\text{ cm}^{-1}$ in the spectra of compounds (1, PPA-KI) and (1, PPA-Na) which is absent in the spectrum of compound (1, PPA). This is most probably due to the reaction of the acetylenic groups of the polymer with the compounds KI and NaOEt. However in the case of the reaction between the polymer and NaOEt the band near 1600 cm^{-1} is highly greater than in the case of the polymer with KI. The reactions of the polymer with compounds KI and NaOEt lead to the formation of quinoid structures in the polymer chain and that the ability of the benzene ring to form quinoid structure is greater in the case of NaOEt.

4.2. Electrical conductivity measurements

In the case of polyaminotriazole pure and the complex polyaminotriazole with KI, Figs. (2, 3), shows the relation between σ and t , where σ is the specific electrical conductivity in $\Omega^{-1}\text{ cm}^{-1}$ and t is the temperature in centigrade. It is a relation of two straight lines, (two lines with different slopes).

From the relation it is clear that:

$$\sigma_t = \sigma_0(1 + \alpha t) \quad (\text{A})$$

where σ_0 is the specific electrical conductivity at $t = 0$ and α is the temperature coefficient for electrical conductivity. Also it is found that the relation $\log \rho$ vs. $10^3/T$ is almost linear. From the values of the electrical conductivities and the linear relation between $\log \rho$ and $10^3/T$, it is predicted that these materials have the same properties as those of semiconductors.

The relation of $\log \rho$ vs. $10^3/T$ for the same complex is also almost linear and valid at temperature between 40 and 90 °C. The linear relation in the case of $\log \rho$ vs. $10^3/T$ for polyaminotriazole (PAT) and its complex with KI means that:

$$\log \rho = \log \rho_0 + \Delta E/kT \quad (\text{B})$$

where ρ is the specific electrical resistivity and T is the absolute temperature, ΔE is the activation energy for electrical conductivity, k is Boltzmann constant and ρ_0 is constant and is the specific electrical resistivity at $t = \infty$. In the case of

polyphenylacetylene (PPA), σ vs. t and $\log \rho$ vs. $10^3/T$ shown in Figs. (4, 5) obey the relations (A) and (B). However in the case of (PPA) and its complexes with KI and NaOEt, σ increases by 10^2 order of magnitude than in the case of (PAT) and its complex with KI. These results could be attributed to sterical hindrance due to the presence of large groups in the polyheterocyclic compound, despite the polarity of these groups that are capable of orientation in an electric field; this restricts the rotation of the large polyaminotriazole molecule. But, (PPA) and its complexes with KI and NaOEt, shows with increasing the temperature, the increase in the mobility of ionic and ionic complexes bodies that takes place as a result of the excitation by heat. Accordingly, (PPA) complexes with KI and NaOEt have higher electrical conductivity than (PPA) pure. Thus the value of σ in S/cm for the above mentioned compounds is nearly 10^{-4} S/cm , i.e. these values are in the range of semiconductors. The relation between the current in ampere I and the voltage V for PAT complex with KI is linear and passes through the origin (an Ohmic relation) Fig. (6), which means that the mechanism of the reaction is electronic. Also for (PPA) complexes with KI and NaOEt, the relation between I and V is linear and passes through the origin (an Ohmic relation) Fig. (7). The conductivity of (PPA) with KI is higher than that of PPA with NaOEt.

5. Conclusion

From the studies of the electrical properties of the polymers after reaction with $\text{C}_2\text{H}_5\text{ONa}$ and KI, it was found that the relation between I and V is linear and passes through the origin (an Ohmic relation). In the case of polyphenylacetylene (PPA) and its complexes with KI and NaOEt, σ increases by 10^2 order of magnitude than in the case of polyaminotriazole (PAT) and its complex with KI. (PPA) complexes with KI and NaOEt have higher electrical conductivity than (PPA) alone. The values of the electrical conductivities and the linear relation between $\log \rho$ and $10^3/T$, predicted that these materials have the same properties as those of semiconductors.

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