



Effects of ion implantation doping accompanying heat treatment on the electrical properties for pristine and poly(acrylonitrile)

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Shehdeh Jodeh¹

Abstract

Heat treatment of polyacrylonitrile (PAN) leads to products with semiconductor to metal-like conductivities. The electrical properties of these materials are further modified by ion implantation. It is noted that the conductivity ($\sim 10^{-7} (\Omega \text{ cm})^{-1}$) of heat-treated PAN at 435 °C (PAN435) increases upon ion implantation with arsenic reaching a maximum value of $1.4 \times 10^{-1} (\Omega \text{ cm})^{-1}$ at a dose of 5×10^{16} ion cm^{-2} and energy of 200 keV. On the other hand, ion implantation of the more conducting heat treated PAN at 750 °C (PAN750) leads to a decrease in the electrical conductivity of the material. The data also indicate that the decrease in conductivity observed after implantation of PAN750 is due to the breakup of the graphite-like extended electronic states. The temperature dependence of conductivity provided further information on the structures of the pyrolyzed and of the ion-implanted samples. Whereas the conductivity temperature behavior of PAN750 is consistent with the Cohen–Jortner model for transport in inhomogeneous and disordered solids, the ion-implanted sample (PAN750I) displays a behavior which can be described most adequately in terms of a variable range-hopping conduction mechanism.

Keywords

Implantation, polyacrylonitrile, conductivity, thermal

Introduction

Organic polymers with a semiconductor or a metal-like conductivity may be obtained using three distinct methods; namely, chemical doping of polymers having structures containing some degree of π -electron conjugation, pyrolysis at high temperature, and ion implantation. Chemically doped polymers are the most widely studied class of conducting polymers. A large number of experimental and theoretical investigations have been devoted to the elucidation of their electronic properties.¹ New concepts such as neutral and charged solitons,² polaron, and bipolarons,³ have been proposed to account for the conduction mechanism in doped polymers.

Pertaining to the pyrolyzed polymers, however, efforts seem to have been concentrated on searching for new, high-performance materials exhibiting favorable fabrication, solubility, environmental, and thermal characteristics. Products with such characteristics having conductivities exceeding $10^2 (\Omega \text{ cm})^{-1}$ have been reported for some pyrolyzed polymers and ceramics.^{4–6} Polyacrylonitrile (PAN) has been extensively used as a precursor material for high

performance carbon fibers.⁷ The conductivity of PAN fibers pyrolyzed at 1200 °C reaches a value of $2 \times 10^2 (\Omega \text{ cm})^{-1}$, even though the original PAN contains no conjugated π -bonds. In order to obtain the PAN carbon fibers, heat treatment in an oxidative atmosphere at a temperature around 240 °C is needed to achieve a thermally stabilized structure. This is followed by pyrolysis at a higher heat treatment temperature (HTT) in an inert gas atmosphere which causes dehydrogenation and denitrogenation. At first a ladder-like π -conjugation structure grows, and then intermolecular crosslinking takes place to develop a plane-like structure.⁸

¹ Department of Chemistry, An-Najah National University, Nablus, Palestine

Corresponding Author:

Shehdeh Jodeh, Department of Chemistry, P. O. Box 7, An-Najah National University, Nablus, Palestine
Email: sjodeh@najah.edu

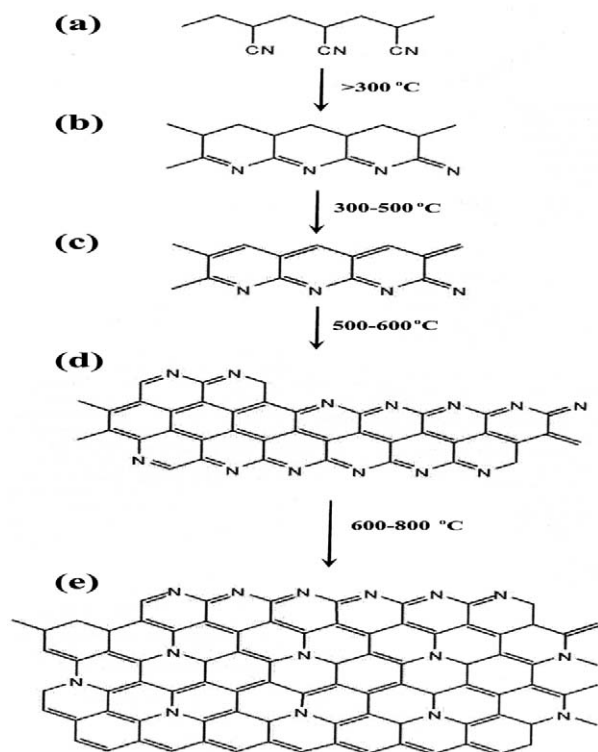


Figure 1. A possible scheme of the structural evolution in heat-treated PAN. Charged carriers are designated by a dot.

Thermal treatment of PAN at temperatures up to 900 °C in an inert atmosphere or under a vacuum without the initial stabilization step also leads to a high conductivity, the value of which depends on the HTT.⁹ The increase in conductivity has been attributed to the thermal conversion of the PAN chain first to a conjugated polyimine structure and eventually to a doubly conjugated ladder structure at temperatures ranging from 200 to 600 °C. The scheme for the development of the two-dimensional structure in the course of the pyrolysis of PAN is depicted in Figure 1.

Huang and Young studied the relationship between structure and mechanical properties of both polyacrylonitrile (PAN) and pitch-based carbon fibres.¹⁰ In their studies using Raman spectroscopy, they found that Raman band shift per unit strain, for both PAN and mesophase pitch-based fibres, increase linearly with Young's modulus of the fibres. Their study showed there is a profound skin-core difference in PAN-based fibres, with more highly oriented and greater crystallinity in the skin region, and less crystallinity in the core.

Although doping by ion implantation has not been applied to polymers until recently, current findings have shown that conductivity values as high as $10 (\Omega \text{ cm})^{-1}$ can be obtained in certain polymers using this technique.¹¹ Wnek et al., compared the properties of products obtained from pyrolysis and from ion implantation of polymeric and carbon films and concluded that these two different modes

of energy deposition have similar effects on these materials. In a previous study, the author focused on the chemical structural characterization of pyrolyzed and subsequently ion-implanted poly(acrylonitrile).¹² In that study, infrared (IR), Auger electron spectroscopy (AES) and x-ray photon spectroscopy (XPS) of pristine, pyrolyzed and ion-implanted poly(acrylonitrile) samples was used to correlate the structural changes accompanying pyrolysis and implantation. In the present study the investigation focused on the correlation of structural changes on electrical properties after pyrolysis at different high temperatures and implantation of thin films of poly(acrylonitrile).

Experimental

Polyacrylonitrile (PAN) was obtained from the Aldrich Chemical Company. It was purified by dissolution in *N,N*-dimethylformamide (DMF) at 80 °C and reprecipitation with distilled water. The purified material was then dried at 80 °C in a vacuum oven for a period of 72 h. Thin films of PAN were prepared by spin-coating from a solution of purified PAN in DMF. The samples used in the conductivity measurements were fabricated by spin-coating onto a 1 μm film of thermally grown SiO₂ on a silicon substrate.

In the pyrolysis experiments, the deposited PAN films were dried in a vacuum oven at room temperature for a period of 48 hours. They were then moved to a tubular furnace (2 inches in diameter) and placed under a dynamic vacuum of 1×10^{-6} torr for 4 h at room temperature. To evaporate the residual solvent, the temperature of the tube was raised to 80 °C and maintained at that level for a period of 15 to 20 h. This was followed by additional heating at 200 °C for a period not exceeding 3 h. After complete removal of the solvent, the samples were pyrolyzed under vacuum at the desired temperature. The selected pyrolysis temperatures were 350, 435, 550, 650, and 750 °C and the corresponding samples were labelled as PAN350, PAN435, PAN550, PAN650, and PAN750 in order to designate their respective pyrolysis temperatures.

Additional sets of pyrolyzed PAN were prepared and were ion implanted with arsenic at an energy level ranging between 50 and 200 keV and at doses of 5×10^{14} to 5×10^{16} ion cm⁻². In this case the concentration of arsenic will be less than 0.6 ppb (50 ppb in drinking water) which is still safe and environmentally friendly. However, it was found that PAN-based conducting polymers are better absorbers for the removal of As (III) ions from aqueous solutions than other polymers.

The implantation was performed at room temperature with the ion beam directed normal to the film surface. The ion beam current density was less than 1 mA cm⁻² in order to minimize target heating. The depth distribution of the ions was determined by Auger spectroscopy as a function of argon sputtering time. A typical result is presented in

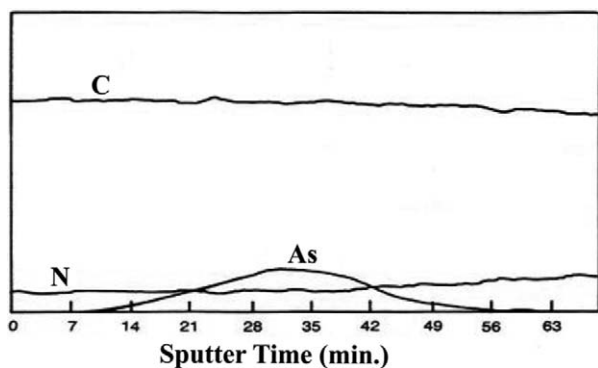


Figure 2. Auger depth profile of arsenic implanted PAN435. Sputtering rate is 65 \AA min^{-1} .

Figure 2, for a PAN435 sample implanted with arsenic at 200 keV and $1 \times 10^{16} \text{ ion cm}^{-2}$, based on analysis of the 376 eV arsenic Auger transition. A crude estimate of the sputtering rate for the polymer was made by comparison with the sputtering rate of a chemically grown Ta_2O_5 layer. The results of Figure 2 show a Gaussian profile, as expected from the LSS theory,¹³ and the measured ion penetration depth ($R_p \sim 2200 \text{ \AA}$) is in good agreement with the theoretical value. For convenience the ion-implanted samples have been labelled with a letter I preceded by the temperature at which the sample was pyrolyzed before implantation, e.g., PAN435I represents a sample pyrolyzed at 435 °C then ion implanted.

The electrical resistance of the films was measured using a four-point probe for samples of low resistivity and a two-point probe for samples of high resistivity. The electrical contacts to the films were made from a silver-epoxy compound. The current-voltage characteristics of both the pyrolyzed and the ion-implanted samples displayed ohmic behavior. The temperature dependence of the DC conductivity for PAN750 and for PAN750I was measured using a four-point probe. The resistance measurements were carried out at temperatures between 10 and 300 K for PAN750. However, due to the very high sample resistance of PAN750I at low temperatures, measurements were possible only at temperatures higher than 50 K. The pyrolyzed and the ion-implanted PAN samples were characterized using ATR-FTIR spectrometry, Electron spectroscopy for chemical analysis (ESCA or XPS) and Auger electron spectroscopy (AES). The FTIR spectra were obtained by internal reflectance with a 60° germanium crystal using a Nicolet 5 DXB FTIR spectrometer. The ESCA and the AES spectra were recorded using a Perkin-Elmer model 549 ESCA/SAM electron spectrometer. Depth profile analyses for the ion implanted samples were performed by sputtering with a 2 keV argon ion beam.

Results and discussion

The room temperature DC conductivity of pyrolyzed PAN as a function of HTT is given in Figure 3 and Table 1.

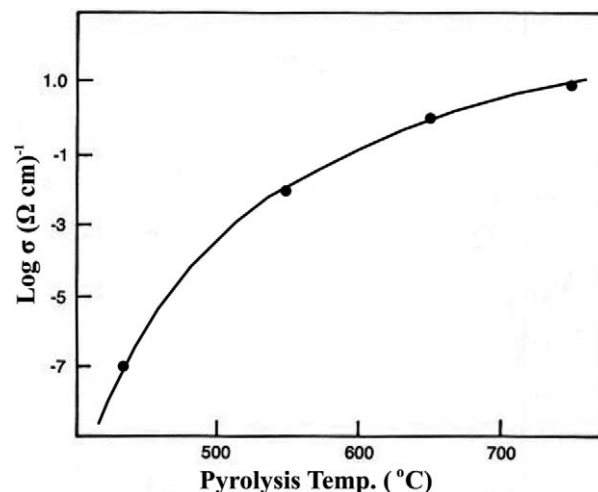


Figure 3. The effect of heat treatment temperatures on the electrical conductivity of PAN.

Table 1. Conductivities of pyrolyzed and ion-implanted PAN.

Sample	Ion energy (keV)	Ion dose (ion cm^{-2})	Conductivity ($(\Omega \text{ cm})^{-1}$)
PAN435	—	—	1.34×10^{-7}
PAN550	—	—	9.50×10^{-3}
PAN650	—	—	8.00×10^{-1}
PAN750	—	—	6.70×100
PAN435I	50	5×10^{15}	4.65×10^{-4}
PAN435I	100	5×10^{15}	2.70×10^{-3}
PAN435I	150	5×10^{15}	8.70×10^{-3}
PAN435I	200	5×10^{15}	1.10×10^{-2}
PAN435I	200	5×10^{14}	1.67×10^{-5}
PAN435I	200	5×10^{15}	2.50×10^{-5}
PAN435I	200	5×10^{16}	2.63×10^{-2}
PAN435I	200	5×10^{16}	1.40×10^{-1}
PAN550I	200	5×10^{15}	4.10×10^{-3}
PAN550I	200	5×10^{15}	1.51×10^{-2}
PAN550I	200	5×10^{16}	3.20×10^{-1}
PAN750I	200	5×10^{15}	3.00×100
PAN750I	200	5×10^{15}	1.10×100
PAN750I	200	5×10^{16}	3.70×10^{-1}

A dramatic increase of more than seven orders of magnitude in the conductivity of PAN was obtained by pyrolysis at 435 °C. Above 435 °C, the conductivity gradually increased to a measured value of $6.7 (\Omega \text{ cm})^{-1}$ at a pyrolysis temperature of 750 °C.

These values are in agreement with those reported in the literature with one exception. Toeh et al. have reported a conductivity of $5 (\Omega \text{ cm})^{-1}$ for PAN samples pyrolyzed at temperatures below 435 °C which is in contradiction with the present measured value of only $10^{-7} (\Omega \text{ cm})^{-1}$. These authors suggested that the high conductivity value is associated with the quasi-one dimensional polyconjugated hetero aromatic chain system (Figure 1(c)) formed upon pyrolysis of PAN at or below 435 °C. However, a

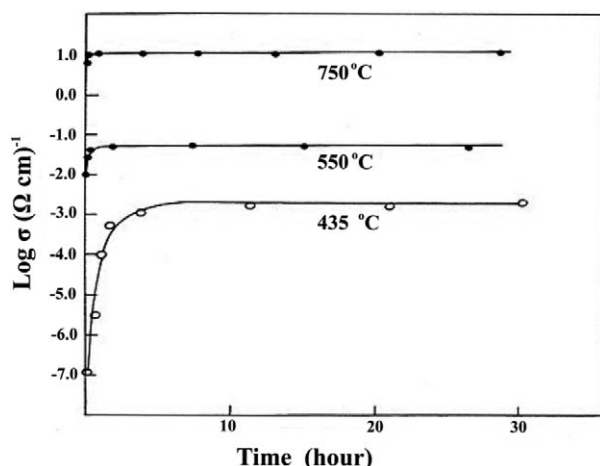


Figure 4. The conductivity of pyrolyzed PAN as a function of the time of exposure to iodine vapor.

calculation of the electronic band structure of such a system by the valence effective Hamiltonian method showed a band gap of the order of 3 eV. This value is too high to account for the conductivity value of $5 (\Omega \text{ cm})^{-1}$ reported.¹⁴

The electrical properties of polymers with a molecular structure containing some degree of π -electron conjugation can be modified by chemical doping with appropriate electron-donating or electron-accepting reagents. Chemical doping leads to changes in the π -electron density of the polymer through the formation of charge-transfer complexes.

Reagents, which are commonly used electron-acceptors (oxidants) include I_2 , Br_2 , and AsF_5 . Figure 4 shows the conductivity of pyrolyzed PAN as a function of the time of exposure to I_2 vapor at room temperature.

In the case of PAN435, the conductivity increases by a factor of four orders of magnitude within the first hour of exposure. This was followed by a more gradual increase up to a value of $2 \times 10^{-3} (\Omega \text{ cm})^{-1}$ with longer times. When the iodine-doped sample was placed under vacuum, its conductivity decreased to a value of $8 \times 10^{-5} (\Omega \text{ cm})^{-1}$ indicating that part of the iodine is loosely bound to the pyrolyzed material. As the pyrolysis temperature was increased, the iodine became less effective in increasing the conductivity as shown for samples pyrolyzed at 550 and 750 °C.

The reduced iodine reactivity of samples pyrolyzed at temperatures higher than 435 °C may be explained in terms of the formation of a graphite-like structure at these temperatures. Such a structure would require stronger oxidizing agents than the iodine. Antimony pentachloride (SbCl_5) is a strong oxidizing agent usually used in graphite intercalation. Exposure of PAN550 and PAN750 to SbCl_5 vapor at room temperature did not alter their conductivity.

Rikukawa and Rubner studied the influence that various doping treatments have on the molecular structure and

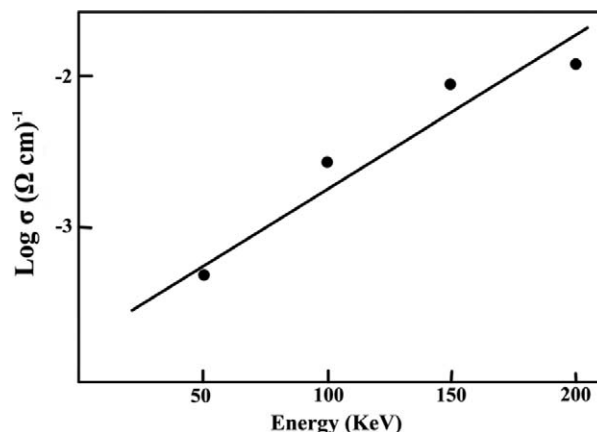


Figure 5. Conductivity–ion energy relationship in arsenic implanted PAN435.

organization of mixed Langmuir–Blodgett films comprised of poly(3-hexylthiophene) and deuterated stearic acid was investigated using reflection-absorption infrared spectroscopy. The molecular organization and electrical properties of these films were found to depend strongly on the type of dopant used and its method of introduction. When doped from solution with NOPF_6 and SbCl_5 , the original molecular organization of the multilayer film was significantly disrupted and the deuterated stearic acid molecules were extracted into the doping solution. In some cases, this extraction process produced uniform thin films of poly(3-hexylthiophene) with conductivities comparable to free-standing films. Gas-phase doping with I_2 and SbCl_5 , on the other hand, could be accomplished without significantly altering the molecular morphology of the film.¹⁵

The heterogeneous two-phase nature of the multilayer films in this case resulted in lower conductivities. Arsenic ion implantation in PAN435, PAN550, and PAN750 was conducted for the purpose of investigating the ion implantation-induced electrical and structural property modifications of pyrolysis products having different chemical structures. The choice of arsenic was motivated primarily because of its large ionic mass.

To establish a useful ion energy range, PAN435 was implanted with arsenic ions at energies between 50 and 200 keV. The data in Figure 5 indicate that the higher-energy As ions were more effective in increasing the conductivity of PAN435. Hence, to obtain the maximum possible conductivities, the ion energy was set at 200 keV for the remaining implantation experiments.

Figure 6(a) shows plots of the conductivity as a function of ion dose for PAN samples pyrolyzed at 435, 550, and 750 °C. It is clear that there is a material dependence in the conductivity–dose relationship. The data of PAN435 displayed a typical dependence normally observed for ion-irradiated polymers.¹⁶ There was a rapid increase in the conductivity of the material at doses lower than $5 \times 10^{15} \text{ ion cm}^{-2}$. At higher doses the material exhibited

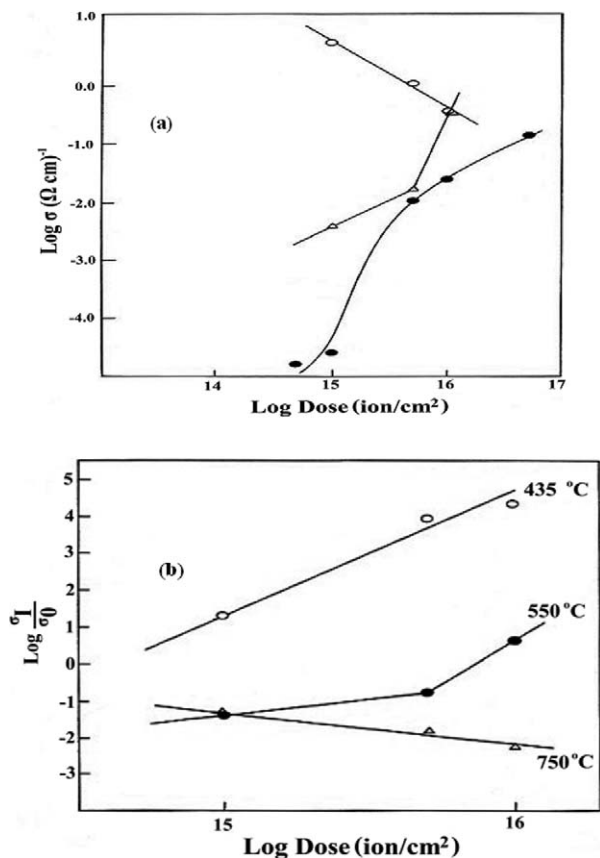


Figure 6. Conductivity–dose dependence in arsenic implanted (200 keV) PAN435 (●), PAN550 (Δ), PAN750 (○) (a). The ratio of conductivity (σ_1/σ_0) as a function of dose in arsenic-implanted–pyrolyzed PAN (b).

only modest increases in conductivity indicative of the onset of saturation. The most striking observation from the data in Figure 6(a) is the fact that the conductivities of PAN550 and PAN750 decreased upon implantation with arsenic at a dose of 1×10^{15} ion cm^{-2} (Table 1).

At doses above 1×10^{15} ion cm^{-2} the decrease in conductivity of PAN750 is continuous and is linearly proportional to the applied dose. On the other hand, the initial drop in the conductivity of PAN550 at 1×10^{15} ion cm^{-2} is followed first by a moderate and then by a more rapid increase in magnitude at higher doses (Figure 6(a)).

This unusual behavior of the conductivity–dose relationship is more apparent when the data in Figure 6(a) are plotted in terms of the normalized function, σ_1/σ_0 , where σ_1 and σ_0 are the conductivities of the polymer samples after and before arsenic implantation, respectively (Figure 6(b)).

A decrease in the conductivity after implantation is indicated by a negative $\log \sigma_1/\sigma_0$ value. The data clearly show that for a constant ion energy and a constant ion dose, the change in the conductivity (in magnitude and direction) is dependent upon its value before implantation and consequently upon the chemical structure of the corresponding pyrolyzed product. It is shown that heat treatment of PAN

at 435 °C leads to the formation of a heteroaromatic fused ring structure. The low conductivity value, 10^{-7} ($\Omega \text{ cm}^{-1}$), and the high energy band gap (3 eV) associated with such a structure are due primarily to the presence of nitrogen atoms in the aromatic rings. Earlier in the discussion a correlation was established between the depletion of the nitrogen atoms and the formation of extended delocalized graphite-like structure. The presence of nitrogen atoms in such a structure seems to inhibit the formation of extended-delocalized electronic states. In other words, the nitrogen atom does not favor a strong π -orbital overlap resulting in reduced carrier mobility and a low conductivity value. This interpretation is corroborated by a calculation of the carbon fiber electronic structure which showed that nitrogen atoms situated inside the fiber pattern lead to localized electronic states.

In the present study it has also been shown that ion implantation of PAN435 increases its conductivity by more than six orders of magnitude. The increase in conductivity can be attributed to either enhanced carrier mobility or increased carrier density. Wasserman et al., have reported that the magnitude of the thermo power in arsenic-implanted (1×10^{16} ion cm^{-2}) PAN is very small (3 mV K^{-1}), consistent with a large concentration of low mobility carriers ($\mu \leq 10^{-3}$ $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).¹⁶ However, the corresponding conductivity value (10^{-3} ($\Omega \text{ cm}^{-1}$)) is two orders of magnitude lower than that obtained in the author's laboratory for PAN435 implanted under similar conditions (Table 1). These observations suggest that the high conductivity of ion-implanted PAN435 (compared with ion-implanted PAN) is due to both increased carrier density and increased carrier mobility. The enhancement in the carrier mobility can be correlated with implantation-induced structural transformation in the material.

Upon ion implantation, a large number of free radical, and ionic species are produced along the ion track. These reactive intermediates undergo significant rearrangements followed by intra- and inter-molecular crosslinking. The final product of the various complex reactions could be envisaged as composed of a completely three-dimensional, randomly crosslinking carbon network of polynuclear aromatic units. The electrical conductivity data show that such a structure is more conductive than the one-dimensional heterocyclic aromatic fused ring structure proposed for PAN435. To explain the increase in resistivity of PAN750 following ion implantation, it is suggested that the interaction of the energetic ion with this material produces a more 'defective' polyconjugated π -electron system. Although the carrier density increases upon implantation, the mobility of these carriers is significantly reduced by virtue of the defective nature of the produced polyconjugated structure.¹⁶ It is further suggested that the structure of PAN550 before implantation consists of an extended polyconjugated graphite-like conducting configuration and of a significant proportion of a less conducting

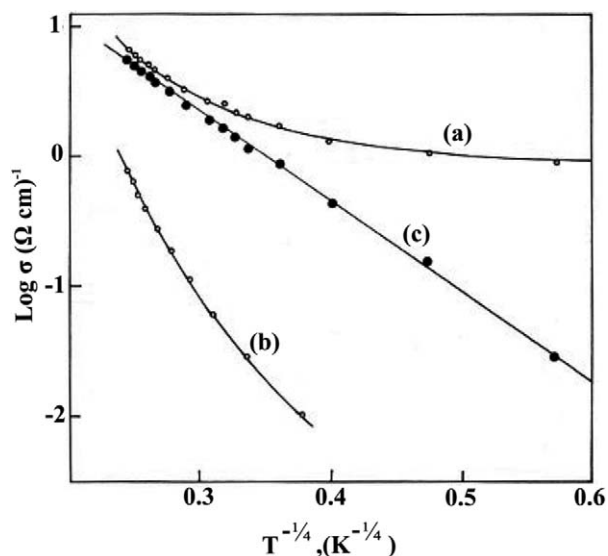


Figure 7. The temperature-dependence of conductivity for PAN750 ((a) and (c)) and PAN750I (b).

heteroaromatic-fused ring structure (Figure 1(d)). The initial decrease (Table 1) in the conductivity of PAN550 upon implantation at a dose of 1×10^{15} ion cm^{-2} can then be explained in terms of ion-induced conversion of the conducting polyconjugated pattern into a disordered, more defective and slightly less conducting system. In other words, this low ion implantation dose is sufficient to distort the π -electron configuration of the polyconjugated system but not high enough to transform the remaining structure (heterocyclic) into that state (polyconjugated but defective state). However as the applied dose increased, the total structure was gradually converted into the more conducting disordered polyconjugated network structure. The equal conductivity values obtained for ion-implanted PAN550 and PAN750 at a dose of 1×10^{16} ion cm^{-2} provide evidence in support of this conclusion. It shows that at a sufficiently high ion dose the resulting structures are fundamentally similar in all the pyrolyzed samples irrespective of the pyrolysis temperature. Obviously, for PAN435 the dose required to bring about such transformations is necessarily higher than those needed to cause the same transformations in PAN550 and PAN750. This is because the material is carbonized first in addition to a subsequent rearrangement of the carbon atoms to produce the final structure.

The behavior of conductivity as a function of temperature provided additional evidence for the difference in the structures between the pyrolyzed and the ionimplanted PAN samples. The conductivity of PAN750 and of PAN750I (1×10^{16} ion cm^{-2}) plotted as a function of $T^{-1/4}$ is given in Figure 7.

The conductivity of PAN750 exhibits a temperature-independent characteristic at low temperatures. The estimated value of the temperature-independent conductivity (0.89 ($\Omega \text{ cm})^{-1}$) was subtracted from the conductivity

data of Figure 7(a), and the results are plotted as a function of $T^{-1/4}$ in Figure 7(b). Thus, the total conductivity of PAN750 can be closely approximated by an equation of the form:

$$\sigma = \sigma_m + \sigma_T = \sigma_m + \sigma_1 \exp \left[-(T_0/T)^{1/4} \right]$$

where σ_m is the temperature-independent conductivity and $\sigma_1 \exp \left[-(T_0/T)^{1/4} \right]$ is the temperature-dependent conductivity derived for a variable range hopping conduction mechanism.¹⁷

The existence of a temperature-independent conductivity at low temperatures is thought to involve an irreversible disorder-induced nonmetal-metal transition. Two models have been proposed for such transitions in disordered solids. The Anderson-Mott transition model applies to microscopically homogeneous solids.¹⁸ It states that in elemental materials, the positional disorder of the atoms induces Anderson localization of the electronic energy states at the edge of the energy bands.¹⁹ A transition takes place when the nature of the states at and near the Fermi levels changes from localized to extended forms. On the other hand, Cohen and Jortner assume that near such a transition there must appear long-range fluctuations of potential, density, etc., in the material.²⁰

It can then no longer be considered as homogeneous. Hence, the material may undergo locally an Anderson-Mott transition, which brings part into the metallic state, whereas the other parts stay in the nonmetal insulating state. The transition occurs when the volume fraction of conducting regions reaches a critical value. This is in agreement with percolation theory.¹¹

The temperature-conductivity behavior of PAN750 is consistent with the Cohen-Jortner model for transport in inhomogeneous regions of disordered matter. The microscopic inhomogeneities in pyrolyzed PAN are caused by growing aromatic carbon rings within a more disordered amorphous carbon matrix at pyrolysis temperatures higher than 700 °C. These structural inhomogeneities also cause inhomogeneities in the electronic structure. From electronic conduction considerations, PAN750 has metallic domains in a nonmetallic amorphous carbon medium. These metallic domains are the results of local development of aromatic fused carbon rings, which form a graphite-like network with a strong π -orbital overlap. In other words, pyrolysis of PAN at 750 °C produces a material with a heterogeneous structure consisting of two conducting paths: one is a metallic channel with extended electronic states for which the conductivity has no temperature dependence (Figure 7(a), at low temperatures) and the other is a disordered system in which the electron conduction is by a variable range hopping mechanism, $\sigma \propto T^{-1/4}$, (Figure 7(c)). A different conductivity-temperature behavior is displayed by PAN750I (Figure 7(b)) indicating an ion implantation-induced structural transforms in PAN750. Of particular

importance is the absence of temperature-independent conductivity, which clearly suggests a significant reduction in the volume fraction of the extended electronic states (the metal-like regions) in the material. This observation together with the noted decrease in the room temperature conductivity by two orders of magnitude demonstrates that ion implantation of pyrolyzed PAN results in a breakup of the regions of the polyconjugated graphite-like structure. The volume concentration of these highly conducting regions and hence their connectivity, decreases when the sample is exposed to ion irradiation. In this case, the conduction is via a variable range hopping between the conducting regions or between the localized and the extended states. The fact that the conductivity–temperature dependence in terms of $\log \sigma \alpha T^{-1/4}$ is not exactly a straight line relationship (Figure 7(b)) suggests the existence of other contributing mechanisms. It should be stated that the data did not follow simple thermal excitation dependence, $\log \sigma \alpha T^{-1/4}$, nor did it follow the functional form for a thermally activated one-dimensional hopping conduction mechanism, $\log \sigma \alpha T^{-1/2}$.^{21,22} This is unlike the recent finding of Wasserman et al.,¹⁶ that the conductivity of pristine PAN implanted with arsenic under similar conditions exhibited a temperature dependence of the form $\log \sigma \alpha T^{-1/2}$. Thus, it appears that, although the products of ion implantation of pristine PAN and of pyrolyzed PAN may be superficially similar, their electrical properties are different.

Conclusion

The results of this investigation show that highly conducting and environmentally stable thin film materials can be obtained by pyrolysis and ion implantation of PAN. Pyrolyzed PAN may prove useful as a resistor material in microelectronics and hybrid microcircuit design. The very high temperature stability of PAN750 makes it attractive for such applications, particularly in devices now being developed which will operate continuously at temperatures above 300 °C. The author's efforts are currently focused on the fabrication of a p–n junction diode from pyrolyzed and chemically doped PAN.

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