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ELECTRICAL CONDUCTIVITY OF PYROLYZED POLYACRYLONITRILE†

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Using ultrapure samples of polyacrylonitrile (PAN) of 485,000 or 150,000 average molecular weight solution cast in dimethylformamide, the dc conductivity (σ) of pyrolyzed PAN (PANP) films has been studied for pyrolysis temperatures (T_p) of 280-435°C. Conductivity measurements made during pyrolysis indicate the onset of a dramatic increase in σ for T_p of 390-435°C. Conductivities as high as 5 $(\text{ohm-cm})^{-1}$ have been observed for $T_p < 435$°C. This situation contrasts sharply with previous literature which had indicated that σ increased uniformly and monotonically with T_p for 200°C < T_p < 900°C and that values of $\sigma > 1$ $(\text{ohm-cm})^{-1}$ were observed only for $T_p > 600$°C. Our results indicate that the maximum value of σ obtained is not a strong function of T_p (390°C < T_p < 435°C) or of molecular weight. However, the rate of increase of $\sigma(t)$ is strongly dependent on T_p in this range. After pyrolysis, repeated heating and cooling below T_p do not alter $\sigma(T)$. IR spectra show that the sudden increase in σ is correlated to the formation of conjugated C=C and C=N bonds. The shape of $\sigma(T)$ suggests that conduction is probably due to hopping.

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INTRODUCTION

It is well known that PAN can be made electrically conductive by pyrolysis - heat treatment in inert atmosphere - at temperatures up to 900°C.[1-7] The increase in conductivity has been attributed to thermal conversion of the PAN polymer chain (Figure 1(a)) first to a conjugated structure (Figure 1(b)), and eventually to a doubly conjugated ladder structure (Figure 1(c)) at temperatures from 200-600°C.[4,8-11] While this picture is undoubtedly an oversimplification,[4,12] IR spectra are consistent with the key features of this model as discussed briefly in the Experimental Results section. A more thorough examination of the structure of pyrolyzed PAN will be the subject of another report.[13]

The picture which emerges from the previous literature on the electrical conductivity of pyrolyzed PAN (PANP) for pyrolysis temperatures between 200 and 900°C is as follows[1-7]:

1. At any temperature below the pyrolysis temperature, the conductivity observed increases with the temperature at which the sample was pyrolyzed.
2. For a given sample pyrolyzed at some fixed temperature, the conductivity increases monotonically with measurement temperature up to the pyrolysis temperature.
3. Activation energy (see Experimental Results section) decreases monotonically with pyrolysis temperature.
4. High values of conductivity (>10° $(ohm\text{-}cm)^{-1}$) are observed only for pyrolysis temperatures above 600°C whereupon graphitization has probably begun.[14]

In this paper we present experimental results which significantly alter this picture. The electrical conductivity of PANP is more closely examined by measuring $\sigma(T)$ both during and after pyrolysis of PANP samples made from solution cast films of PAN of molecular weight 150,000 or 485,000. Conductivity data and associated IR spectra are presented and interpreted in order to provide a better understanding of the conduction behavior and mechanism in PAN.

EXPERIMENTAL TECHNIQUES

Sample Preparation

Ultrapure PAN powder of average molecular weight 485,000 (Scientific Polymer Products) prepared by free radical

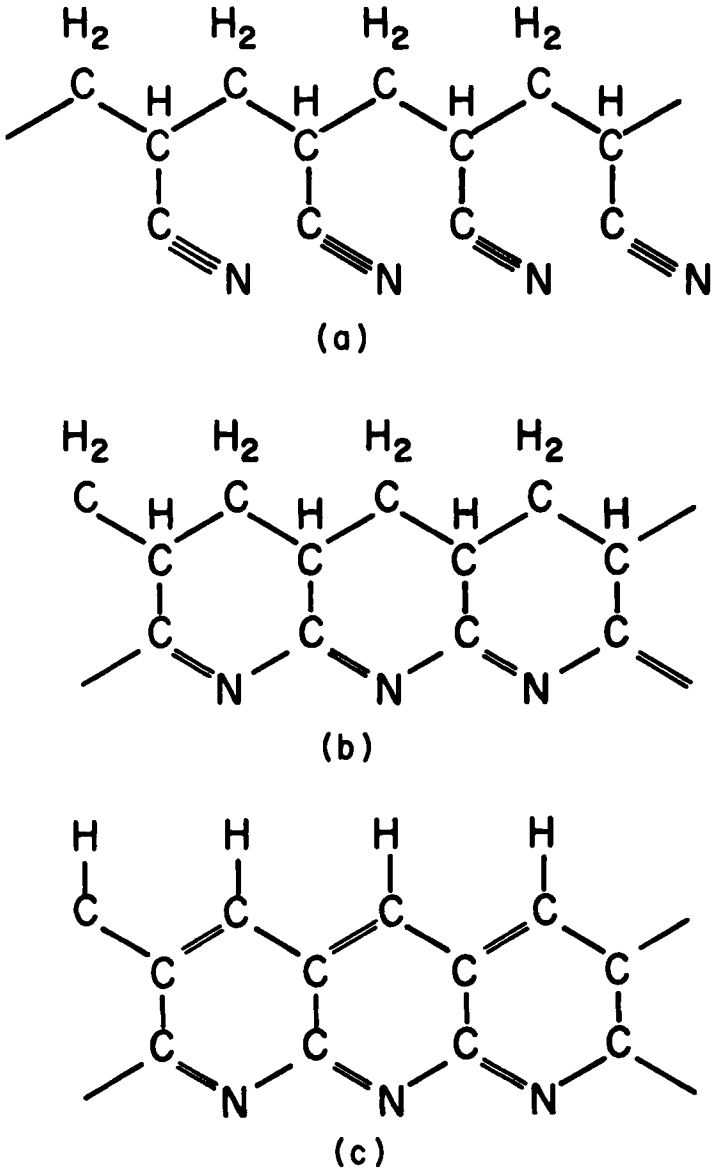

FIGURE 1 Structure of polyacrylonitrile
(a) before pyrolysis; (b) singly conjugated; and (c) doubly conjugated ladder

polymerization or of average molecular weight 150,000 (Polysciences, Inc.) prepared by emulsion and redox polymerization was first dissolved in dimethylformamide (DMF) by heating in a hot water bath. Then, thin films of uniform (∿10%) thickness were prepared on sample cells using a photoresist spinner (Headway Research Inc.). Each cell consists of a quartz substrate coated with two vacuum deposited gold electrodes (∿3000 Å) separated by a 2mm gap.

Pyrolysis and Electrical Conductivity Measurement Techniques

Each sample cell was clamped onto an isothermal copper block fitted with an electrical heating element and an N_2 gas cooling coil as shown in Figure 2. The system was evacuated to $\sim 10^{-5}$ torr. Samples were heated in vacuo at about 280°C for about three hours to drive off the DMF, and then cooled to about 200°C. They were then reheated to about 400°C and maintained at that temperature for various lengths of time, cooled and reheated. Sample temperature was monitored continuously by a chromal-alumel thermocouple mounted on a quartz plate located next to the sample cell on the isothermal block.

Electrical conductivity was measured continuously during heating and cooling by maintaining a constant dc voltage of 20 to 40 V across the 2mm gap between the gold electrodes of the sample cell with a constant voltage source (Power Design 5020). The contacts were found to be ohmic. Current was measured by an electrometer (Keithley 616) and recorded on a chart recorder with sample temperature. Film thickness (∿1000 Å) and profile were determined by a thickness monitor (Sloan Dektak Surface Profile Measuring System).

EXPERIMENTAL RESULTS

Infrared Spectra

In order to correlate the structural changes accompanying pyrolysis to the electrical conductivity of the PANP samples, IR spectra of samples pyrolyzed in vacuo were obtained using an IR spectrophotometer (Perkin Elmer 298). Figure 3(a) shows the IR spectrum of the 485,000 MW PAN powder at room temperature. Figure 3(b) is the spectrum of PAN film (8% PAN by weight) solution cast in DMF. The new absorption peaks at 1660 cm^{-1}, 1380 cm^{-1}, and 1090 cm^{-1} are attributed to the DMF. After heating for three hours at 277°C (Figure 3(c)) the disappearance of these peaks indicates removal of

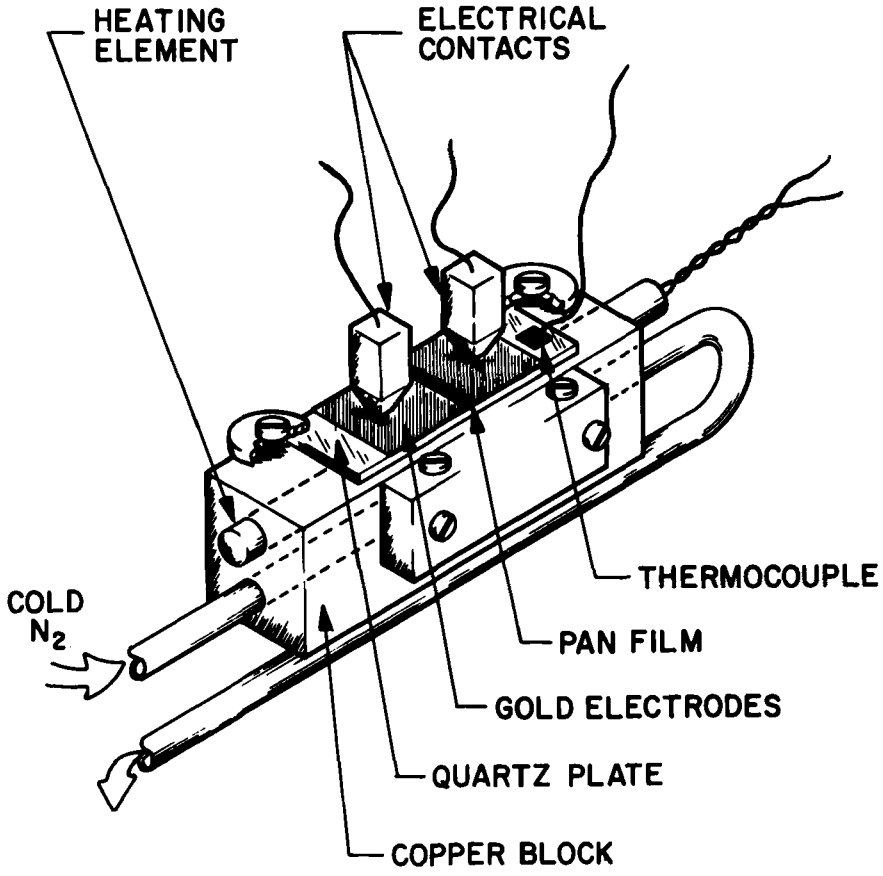

FIGURE 2 Apparatus for sample heating, cooling and electrical conductivity measurement

the DMF. At the same time, the peak at 2240 cm^{-1} assigned to the nitrile group (C≡N) has decreased while new peaks have formed at 1590 cm^{-1} and 1360 cm^{-1} indicating the onset of polymer chain conjugation through the formation of (C=C) and (C=N) bonds.[2]

In the IR spectrum obtained by heating PAN films for two hours at 440°C (Figure 3(d)), the C≡N absorption peak at 2240 cm^{-1} has disappeared completely while peaks in the 1300 and 1600 cm^{-1} range have broadened, suggesting the formation of conjugated carbon-carbon and carbon-nitrogen bonds at the expense of the nitrile group. This would be

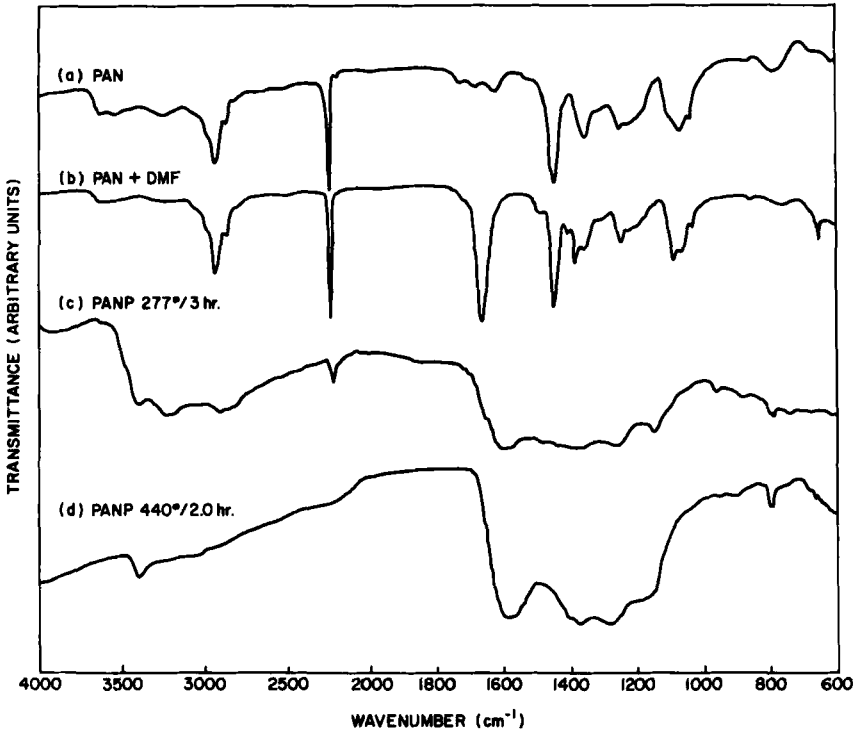

FIGURE 3 Infrared spectra of polyacrylonitrile (a) PAN powder; (b) PAN film solution cast in dimethylformamide; (c) PAN film pyrolyzed at 277°C for three hours and; (d) PAN film pyrolyzed at 440°C for two hours

expected to lead to semiconductive behavior analogous to polyacetylene. The N-H absorption peak at 3400 cm^{-1} has been attributed to the initiation stage of cyclization,[15] and diminishes upon further heating.[13]

Electrical Conductivity

Conductivities of PANP samples pyrolyzed at various temperatures have been measured as a function of time and temperature. Figure 4 contains conductivity vs temperature data for samples of PANP made from 485,000 or 150,000 MW PAN. Initially (Figure 4(d)), conductivities are low ($\sim 10^{-9}$ - 10^{-7} (ohm-cm^{-1})), rising monotonically for temperatures between approximately 200-300°C. Samples may be heated

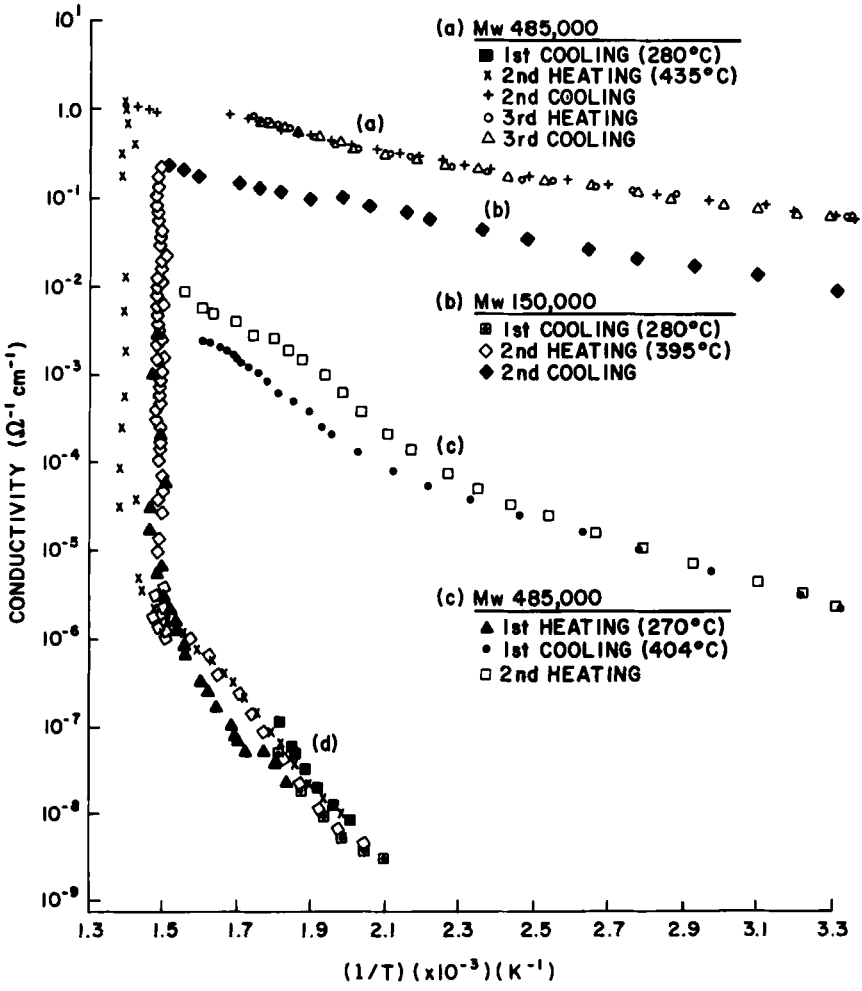

FIGURE 4 Electrical conductivity vs temperature of pyrolyzed PAN

to at least 300°C without altering the σ vs 1/T curve obtained during subsequent cooling or heating below this temperature. However, a qualitative change in the temperature dependence of the conductivity occurs once the pyrolysis temperature is raised above a critical value of approximately 390°C at which the conductivity is seen to rise dramatically

from 10^{-6} to 10° $(ohm\text{-}cm)^{-1}$. Previous reports on the conductivity of PANP did not note this behavior.[1-7]

Typical σ vs 1/T curves of samples heated above the critical temperature are shown in Figures 4(a), (b), and (c). Generally, conductivity is much higher than for the unpyrolyzed samples (Figure 4(d)) and decreases with decreasing temperature. The curves are slightly concave up and plotting $\ell n\sigma$ vs $T^{-1/4}$ yields a better linear fit,[13] indicative of hopping conduction.[16] Activation energy (slope of $\ell n\sigma$ vs 1/kT) decreases and $\sigma(T)$ increases as the conductivity at which cooling was begun increases. The $\sigma(T)$ curves are repeatable during subsequent heating or cooling below the pyrolysis temperature, particularly for the highest σ vs 1/T curve (Figure 4(a)), down to at least -100°C.[13]

The σ vs 1/T curves Figure 4(a), (b) and (c) strongly resemble those obtained previously for doped polyacetylene and PANP. For example, Figure 4(a) may be compared to that obtained for 0.017 mole percent iodine doped polyacetylene[17] or to that found for PAN pyrolyzed at about 650°C.[2]

While ultimate conductivity is weakly dependent on pyrolysis temperature above 390°C, the rate of increase of σ depends very strongly on pyrolysis temperature as seen in Figure 5. The samples of different molecular weight have fairly similar behavior on both Figures 4 and 5. Table 1 summarizes the data obtained from a number of samples, including activation energies determined from linear fits of $\ell n\sigma$ vs 1/T curves similar to those contained in Figure 4.

SUMMARY AND CONCLUSION

A dramatic increase in electrical conductivity from 10^{-6} $(ohm\text{-}cm)^{-1}$ to 10° $(ohm\text{-}cm)^{-1}$ has been found for polyacrylonitrile pyrolyzed above a critical temperature of $\sim$390°C. This phenomenon has not been previously reported. We have observed conductivities as high as 5 $(ohm\text{-}cm)^{-1}$ for pyrolysis temperatures below 435°C. The onset of high conductivity is correlated to changes in the IR spectrum of the material which have been attributed to conjugation of the polymer chain[2]. This would be expected to lead to semiconductive behavior. The $\sigma(T)$ curves resulting from pyrolysis are determined by the conductivity value at which cooling was begun. These curves are repeatable during subsequent heating and cooling below the pyrolysis temperature and resemble those obtained for doped polyacetylene.[17]

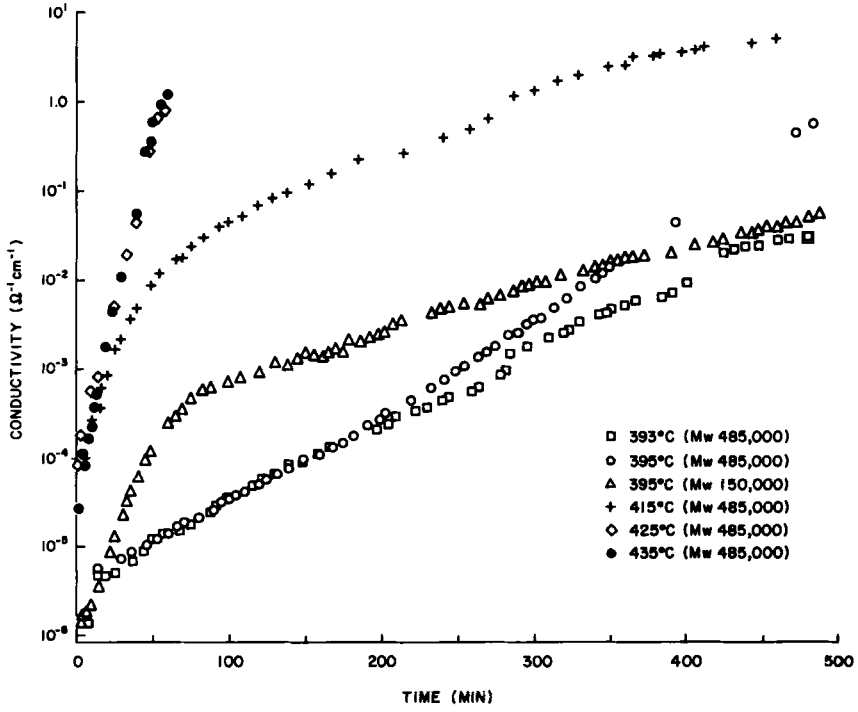

FIGURE 5 Electrical conductivity vs pyrolysis time of pyrolyzed PAN

TABLE 1 ELECTRICAL CONDUCTIVITY AND ACTIVATION ENERGY OF PYROLYZED POLYACRYLONITRILE

Molecular Weight (Mw)	Pyrolysis Temp. (°C)	Pyrolysis Time (min.)	Room Temp. σ $(ohm\text{-}cm)^{-1}$	Pyrolysis σ $(ohm\text{-}cm)^{-1}$	Activation Energy (eV)
485,000	415	458	2.2×10^{-1}	5.0	0.1
485,000	435	61	6.0×10^{-2}	1.04	0.1
485,000	425	80	2.3×10^{-1}	7×10^{-1}	0.1
485,000	393	877	2.1×10^{-3}	1.7×10^{-1}	0.2
150,000	395	617	8.6×10^{-2}	1.4×10^{-1}	0.2
485,000	404	33	2.2×10^{-6}	2.6×10^{-3}	0.4
485,000	280	180 - 230	-	-	1.0 - 1.9

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