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ELECTRICAL CONDUCTIVITY OF DOPED POLYACRYLONITRILE (PAN)

H. Teoh*, D. MacInnes, Jr.** and P.D. Metz

Solar and Renewables Division, Building 701, Brookhaven National Laboratory, Upton, NY 11973, U.S.A.

Abstract - The electrical conductivity and optical absorption spectra of halogen doped PAN have been investigated. When films of PAN previously heated in vacuum to 280°C are exposed to bromine or iodine vapor the conductivity rises suddenly. The conductivity is reduced by pumping off the vapor, but upon subsequent reheating the conductivity increases dramatically, with a transition occurring at about 270°C. Undoped samples were previously reported to undergo a similar transition above 390°C. All samples obey \( \sigma \propto T^{-1/4} \), which suggests a mechanism by hopping to 3 dimensions. The optical and infrared absorption spectra of doped PAN are compared to those previously reported for the undoped material. The stability of doped PAN in air is also discussed.

I. INTRODUCTION - It is well known that polyacrylonitrile (PAN), ordinarily an insulator, can be made electrically conductive by pyrolysis (heat treatment in an inert atmosphere). The increase in conductivity has been attributed to the thermal conversion of the PAN polymer chain (Fig. 1(a)) first to a singly conjugated ladder (Fig. 1(b)), and then to a doubly conjugated ladder structure (Fig. 1(c)) [1-9]. In this work, the electrical conductivity, optical absorption and the infrared spectra of PAN doped with bromine and iodine are presented. The stability of doped PAN exposed to air is also examined.

II. EXPERIMENTAL METHODS - Thin films of polyacrylonitrile were prepared from PAN powder of average molecular weight 150,000 dissolved in dimethylformamide using a photoresist spinner. Before doping, samples were pyrolyzed in vacuo (~10⁻⁵ Torr) at about 280°C for 1-2 hours and then cooled to room temperature. Doping was accomplished by exposing the preheated PAN films to bromine or iodine vapor at...
Upon exposure to the halogen vapors, the preheated films darkened and became far more electrically conductive. Unpyrolyzed PAN films did not exhibit these changes. Upon pumping off the dopant vapor, the film color lightened to almost its original color and the conductivity decreased considerably. Subsequent heating was found to increase the conductivity with a sharp transition occurring at about 2700°C.

Electrical conductivity measurements, using a 2 probe technique described in greater detail elsewhere [8], were made continuously during pyrolysis and doping. To correlate the structural changes accompanying pyrolysis and doping of the PAN samples, IR spectra of the films used in the conductivity measurements were obtained using a Perkin Elmer 298 infrared spectrophotometer. The optical absorption spectrum of each sample was also measured using a Cary 17 spectrophotometer.

III. EXPERIMENTAL RESULTS

The structural changes accompanying the pyrolysis of PAN [1-9] are indicated in Figure 1. While this picture is undoubtedly an oversimplification, the IR spectra shown in Figure 2 are consistent with this model. The IR spectrum [10] of untreated PAN shown in Figure 2(d) indicates the presence of the following structures: C=N (2240 cm\(^{-1}\)), C-H (2930, 1445 cm\(^{-1}\)), C-H (2885, 1335 cm\(^{-1}\)) and aliphatic C-C (1070 cm\(^{-1}\)). As shown in Figures 2(a), 2(b), and 2(c), the IR spectra of PAN films pyrolyzed at about 2800°C indicate an almost complete loss of these absorption peaks, while new absorption frequencies including C=N (1605, 1260 cm\(^{-1}\)) and C=C (1610, 800 cm\(^{-1}\)) are observed.

There are definite differences between the IR spectrum of pyrolyzed PAN and those of PAN doped with Br\(_2\) or I\(_2\). The IR spectra of halogen doped PAN shown in Figures 2(b) and 2(c) both show a strong absorption at 1150 cm\(^{-1}\) (cyclic C-C) not present for the undoped pyrolyzed PAN shown in Figure 2(a). In addition, the spectra of the doped polymers display more pronounced absorption at 1260 cm\(^{-1}\) (C=N), 800 cm\(^{-1}\) (C=C), and 1380 cm\(^{-1}\) (aromatic C-C and C-H) than the undoped pyrolyzed PAN. They best fit a structure in which some of the nitrile groups have cyclized with some loss of hydrogen to give a conjugated top chain and polyaromatic system along part of the chain (Figure 1b and 1c). In short, the IR spectra of doped PAN show closer agreement to the idealized conjugated structures shown in Figures 1(b) and 1(c) than those samples which were pyrolyzed but not exposed to halogen vapor.

Figures 3 and 4 present the electrical conductivity of PAN doped with Br\(_2\) and I\(_2\) as a function of temperature. Previously reported data on PAN pyrolyzed at 395°C is superimposed for comparison. All samples exhibit initially low electrical conductivity (<10\(^{-3}\) ohm\(^{-1}\) cm\(^{-1}\)), increasing monotonically with temperature, with a sharp transition in conductivity [8,9] observed above a threshold temperature. However, a higher electrical conductivity at all temperatures has been observed for doped samples, with the transition occurring at a lower temperature (<270°C) than for pure PAN (<390°C). Doped PAN, heated above the critical temperature of 270°C displays a dramatic rise in conductivity from 10\(^{-6}\) to 10\(^{6}\) ohm\(^{-1}\) cm\(^{-1}\). In the case of I\(_2\) doped PAN, an initial decrease in conductivity was observed when heated beyond 270°C followed by a sharp increase in the electrical conductivity as shown in Figure 4. A previous report on the electrical properties of halogen doped PAN did not note this behavior [11].

In general, the plots of \(\ln\sigma\) vs \(1/T\) shown in Figures 3 and 4 are not linear. As shown in Figure 5, however, plotting \(\ln\sigma\) vs \(T^{-1/4}\) gives a better linear fit, suggesting three dimensional variable range hopping as the conduction mechanism [12].

The stability of the doped PAN has also been investigated by examining the variation of electrical conductivity with time after exposure to air. As shown in
Figure 6, the conductivity of Br$_2$ doped PAN drops instantly by about two orders of magnitude upon exposure to air. Following the initial drop, the conductivity decreases slowly with time, reaching an equilibrium value over a period of several months. The electrical conductivity measured after five months of exposure was still within an order of magnitude of the value after the initial exposure, indicating a stable structure.

Figure 7 presents the optical absorption spectra of PAN films pyrolyzed and doped as indicated. The optical absorption spectra of halogen doped PAN are qualitatively similar to those of pure PAN pyrolyzed at higher temperatures. This is in agreement with the IR spectra and electrical conductivity measurements, suggesting that halogen doping facilitates cyclization of PAN at lower temperatures than is otherwise possible.

IV. CONCLUSIONS

The dramatic increase in electrical conductivity for pyrolyzed polyacrylonitrile reported previously [8] is also observed in halogen doped PAN, but at lower temperatures. The changes in the conductivity are correlated to the changes in the IR and optical absorption spectra which indicate conjugation of the polymer chain. Finally, the halogen treated polymer forms a stable structure maintaining a high electrical conductivity even when exposed to air for long periods.

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REFERENCES

[1] Brennan (W.D.), Brophy (J.J.) and Schonhovn (H.), Organic Semiconductors; Proc. Inter-Industry Conf., Brophy (J.J.) and Buttery (J.W.), Eds., 1962, 159.
FIG. 1. - Structure of polyacrylonitrile (a) before pyrolysis, (b) singly conjugated; and (c) doubly conjugated ladder.

FIG. 2. - Infrared spectra of polyacrylonitrile (a) film pyrolyzed at 280°C, (b) Br₂ doped film reheated to 273°C, (c) I₂ doped film reheated to 280°C; and (d) unheated powder.

FIG. 3. - Electrical conductivity of PAN films treated as indicated vs 1/T.

FIG. 4. - Electrical conductivity of PAN films treated as indicated vs 1/T.
FIG. 5. - Electrical conductivity of PAN films treated as indicated vs $T^{-1/4}$.

FIG. 6. - Electrical conductivity of Br$_2$ doped PAN film exposed to air.

FIG. 7. - Optical absorption spectra of PAN films treated as indicated.