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THERMAL TRANSFORMATION OF LOCAL TO EXTENDED ELECTRONIC STATES IN POLYACRYLONITRILE

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Abstract - The electronic structure of pyrolyzed polyacrylonitrile treated at pyrolysis temperatures of 200 - 600°C has been studied by electron energy loss spectroscopy.

The insulating polymer polyacrylonitrile (PAN) can be transformed to a highly conducting material by pyrolysis, i.e. thermal treatment in inert atmosphere. The model /1,2/ for the structural changes accompanying the increase in conductivity is shown in Fig. 1. At pyrolysis temperatures $T_p \approx 200 - 300°C$ PAN is converted to a single conjugated structure (Fig. 1b) and becomes a semiconductor with a conductivity ($\sigma$) between $10^{-7}$ and $10^{-3}$ S/cm and an activation energy of $\approx 1.5$ eV. At higher pyrolysis temperatures the single conjugated structure is transformed to a doubly conjugated ladder structure (Fig. 1c) resulting in a highly conducting state with $\sigma \approx 1$ S/cm and a low activation energy of about 0.2 eV. At still higher temperatures graphite-like layer molecules are formed. At temperatures near 1000°C "graphitization" occurs as most non-carbon atoms are driven out of the material. Spectroscopic investigations of the electronic structure have not unequivocally verified this model, however. For example, optical spectra have been interpreted in terms of the formation of certain chemical groups /3,4,5/ but cannot determine the extent to which these states are localized in narrow bands or delocalized into nearly-free-electron-like band states with high mobility. One technique for doing this is electron energy loss spectroscopy (ELS) where the momentum dependence of electronic excitations can make this distinction. In this contribution we report on the investigation to identify the thermally induced transition from local to extended electronic states in PAN.

About 1000 Å thick films were prepared by casting thin films on glass slides from a dilute solution in dimethylformamide and then removing the samples from the glass. All heat treatments were carried out at constant temperature for periods of 18-20 hours in a vacuum of $10^{-9}$ torr. The ELS spectra were measured at room temperature. After introduction into the vacuum system, samples were never exposed to air since the heat treated samples were activated with air altering the energy loss spectra. Data were recorded on a 170-keV electron energy loss spectrometer with an energy resolution of 0.1 eV and a variable momentum resolution chosen between 0.03 and 0.16 Å⁻¹ for beam currents of 1 to 5 na. ELS spectra at small momentum transfer in the region of valence excitations and at zero momentum transfer in the region of carbon K-shell excitation for different pyrolysis temperatures are shown in Figs. 2 and 3, respectively. Fig. 4 gives the momentum dependence of the valence excitations for PAN pyrolyzed at $T_p = 400°C$, showing the characteristic difference between narrow and wide band states.

For pyrolysis temperatures $T_p < 200°C$ there is weak absorption in the valence region below $\approx 8$ eV as seen in Fig. 2, typical for a system having no double bond $\pi$.
In Fig. 3 we observe for small $T_p$ a very sharp peak at 286.7 eV due to excitations into the antibonding triple bond $\pi$ state. For $T_p > 200^\circ$C we observe a strong change in the ELS spectra due to structural changes similar to those expected from Fig. 1. In the core level spectra the triple bond peak is reduced and a new peak appears at 285.1 eV. This latter feature occurs near the energy expected for linear conjugated bonds as in polyacetylene /6/ or for rings as in polystyrene /7/. In the valence spectrum for $T_p = 300^\circ$C, strong peaks at 3.6 eV and at 6.4 eV appear. For samples heated to $400^\circ$C both peaks shift by a small amount to lower energies. In Fig. 4, the momentum dependence of the two excitations is shown. The 3.3 eV peak shows essentially no dispersion while the 6.4 eV peak shows a strong dispersion. In pure carbon conjugated systems as in polyacetylene /6/ or polydiacetylene /9/ strong positive dispersion of $\pi$ electron excitations is observed. One way to explain the independence of the 3.3 eV peak of the momentum transfer is to relate this peak with excitations of $\pi$ electrons in small linear C-N conjugated sequences. Small isolated units imply narrow energy bands and in narrow energy band states no dispersion is expected. The peak at 6.4 eV can be associated with the formation of conjugated rings /7/. Electrons in these states are more tightly bound than those in conjugated C-N chains and will not affect the conductivity for pyrolysis temperatures $T_p = 200-400^\circ$C. The strong dispersion of the peak at 6.4 eV shown in Fig. 4 implies delocalized states in longer ring structures. In fact, the dispersion of the 6.4 eV peak is quadratic in momentum with the same dispersion coefficient as for the $\pi$ plasmon in graphite. This implies that the electronic structure of the long ring structures which might resemble polypyrindinopyridine (Fig. 1c) is similar to graphite.

The experimental results for $T_p=200-400^\circ$C should also be compared with recent bandstructure calculations /10,11/ on nitrogen containing conjugated polymers. These calculations show that there is no clear separation of $\sigma$ and $\pi$ bands as in pure carbon conjugated systems. In some nitrogen containing polymers, the $\sigma$ nitrogen "lone pair" band is close to the top of the valence band. In general, the width of these $\sigma$ bands is smaller than that of the $\pi$ bands, indicating a stronger localization of these $\sigma$ electrons compared to the $\pi$ electrons. Thus the peak at 3.3 eV having no dispersion might also be explained by an excitation of localized $\sigma$ electrons. Then, the peak at 6.4 eV showing strong dispersion is ascribed to excitation of delocalized $\pi$-electrons. For the structure shown in Fig. 1b no bandstructure
calculation exists and thus no detailed comparison is possible. For polypyrudinopyridine (Fig. 1c) the bandstructure calculations \cite{12} show large bonding and antibonding $\pi$ and $\sigma$ bands just below and above a predicted band gap of the order of 3 eV. Thus, in our spectra we should observe peaks immediately above 3 eV having strong dispersion in contradiction with our experimental findings. In summary, the existing bandstructure calculations do not allow to associate the observed spectra for $T_p = 200-400^\circ C$ to one definite chemical structure.

Between $T_p = 400^\circ C$ and $450^\circ C$ there is a second important change of the valence spectra. The absorption threshold is shifted to about 0.5 eV suggesting a reduced activation energy. The 3.3 eV peak disappears and a new broad structure at about 2 eV is formed. Also the peak near 6 eV is considerably broadened. Both peaks show a dispersion in momentum space. Also the core level peaks broaden noticeably. When the sample is heated to $600^\circ C$ the energy loss spectra are very similar to those of graphite: The core level spectrum shows a broad peak at 285.5 eV dominating the absorption edge, although a small amount of unconverted material remains. The onset of absorption is below 0.4 eV. The observed shoulder at 2 eV is close to the observed shoulder in graphite at about 1.5 eV which is known to be due to interband transitions \cite{12}. The main $\pi$ electron peak near 6 eV is slightly lower than the $\pi$ plasmon in graphite at 7 eV. The close similarity of our spectra for $T_p=600^\circ C$ to those of graphite is explained by the formation of larger and longer ring structures at pyrolysis temperatures above $450^\circ C$.

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