Electrical conductivity of halogen doped stabilized polyacrylonitrile

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The electrical properties of doped polyacetylene have recently attracted a great deal of attention[1,2]. Here, we report a similarly high electrical conductivity of halogen doped stabilized polyacrylonitrile (PAN) containing a system of conjugated C = N double bonds.

Stabilized PAN is widely used as a precursor for carbon fibres. Its stabilization is obtained by additional polymerization of the nitrile side groups, resulting in a ladder structure. The nitrile polymerization may be induced either by heating the polymer or by an initiator (see a review paper[3]). When the reaction is carried out in anaerobic conditions, the stabilized structure consists of a chain of C–C bonds and of a parallel chain of conjugated C = N double bonds. When stabilization takes place in aerobic (oxidative) atmosphere (where oxidation might occur in addition to the nitrile polymerization), some skeletal carbon atoms may be conjugated or take part in a fully delocalized condensed aromatic structure. This second reaction is demonstrated in *Figure* 1, where the proposed structure is the most likely chemical formula including the various chemical species. A fuller explanation is given in ref. 3.

The presence of the conjugated imine system is sufficient for the development of semiconducting properties in the stabilized PAN[3,4], and thus polymerization for that purpose may be conducted either in an inert or in an oxidative atmosphere. However, the C = C double bonds which form in the oxidative atmosphere increase conjugation and might improve the results.

Thus, regarding electrical conductivity, the in-air stabilized PAN may offer some advantages over polyacetylene by having an additional π system, and by the increased resonance due to the presence of the free electron pair on the nitrogen. Another benefit of PAN is its commercial availability in the form of fibres, the bulk doping of which is easier due to the relatively high surface to volume ratio. Also, the polymer chains are oriented along the fibre axis, and the drawing process carried out to improve conductivity in polyacetylene films[5], is unnecessary here.

The present study utilized commercial 'Courtelle' fast oxidizer fibre (Courtaulds Ltd) of 1.6 denier and a mean cross-sectional area of 1.5×10^{-10} m^2. (Some preliminary work, which is not reported here, was carried out with 'Acrilan' fibres stabilized as described in ref. 6). Stabilizations to different extents were carried out at 220°C in air. Doping was obtained by exposing the fibres to a bromine or an iodine atmosphere. Bromine was doped at room temperature, while iodine was doped either at 90°C with a highly stabilized (black) fibre, or at 220°C during stabilization. The bulk concentration of the dopant was determined by weighing the fibre after an ethanol wash for the removal of the surface layer. The distribution of the iodine over a fibre cross-section was detected by *SEM* probing. The electrical conductivity of a single fibre was measured using a aquadag contacts, and that of a fibre bundle using sputtered gold contacts. Bundles used included up to a hundred fibres as counted by an optical microscope.

Typical experimental results of conductivity vs. dopant concentration in a highly stabilized (black) PAN exhibit an increase up to a concentration of about 0.05 atom per repeating unit, thereafter the conductivity is independent of dopant concentration. It is possible that at this concentration, a transition from a semiconducting to a conducting state occurs, as reported for polyacetylene[1]. The doping time required for achieving the concentration corresponding with the conducting state conductivity was 20 min for bromine at room temperature and 120 min for iodine at 90°C. Typical conductivities of 1 and 10 $(\simeq \mathrm{cm})^{-1}$ were obtained with bromine and iodine, respectively.

Iodine doping was found to be more effective when carried out during the stabilization reaction. For this the fibre had to be heat treated for 3 h to obtain a stable structure, thereafter stabilization proceeded with simultaneous doping for 2 h at 220°C. This procedure resulted in a conductivity of 70 $(\Omega\,\mathrm{cm})^{-1}$, dropping by 20% after an ethanol wash, by 30% after 20 min at 60°C, and by 50% after 2 weeks in air at room temperature. Scanning electron microscopy of these fibres revealed that small iodine crystals on the fibre surface were easily removed by the ethanol wash. *SEM* probing showed that the iodine concentration across the fibre exhibited a gradient of 30% towards the centre.

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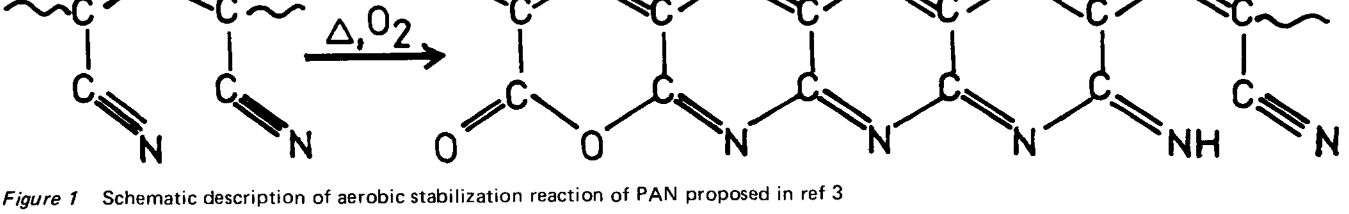

Figure 1 Schematic description of aerobic stabilization reaction of PAN proposed in ref 3

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The work reported above — although pointing out the potential properties of doped stabilized PAN — is still at a prelimary stage. More experiments, mostly involving the testing of other doping methods and of a range of different dopants are required to clarify the picture.

REFERENCES

1 Chiang, C. K., Fincher Jr., C. R., Park, Y. W., Heeger, A. J., Shirakawa, H., Louis, E. J., Gan, S. C. and MacDiarmid, A. G. *Phys. Rev. Lett.* 1977, **39**, 1098

2 Chiang, C. K., Park, Y. W., Heeger, A. J., Shirakawa, H., Louis, E. J. and MacDiarmid, A. G. *J. Chem. Phys.* 1978, **69**, 5098

3 Goodhew, P. J., Clarke, A. J. and Bailey, J. E. *Mater, Sci. Eng.* 1975, **17**, 3

4 Mark, H. *Israel J. Chem.* 1972, **10**, 407

5 Park, Y. W., Druy, M. A., Chiang, C. K., MacDiarmid, A. G., Heeger, A. J., Shirakawa, H. and Ikeda, S., to be published

6 Cohn, D., Marom, G. and Zilkha, A. *Eur. Polym. J.* 1976, **12**, 795