Photochemically Doped Polypyrrole

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Chemically prepared polypyrrole was treated with diphenyliodonium hexafluoroarsenate and upon u.v. irradiation a conductivity of $3 \times 10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ was attained.

We report here for the first time on the photochemical doping of polypyrrole. An elegant photochemical method of doping has been reported by Clarke *et al.*[1] for polyacetylene, which allows a particularly easy control of the doping level and thus of the desired conductivity in the illuminated areas of the polymer. Polypyrrole is a potential conducting polymer which has received considerable attention because it is comparatively easy to prepare and fairly stable.[2] Both electrochemical[3] and chemical routes[4] are known to give polypyrrole as a film. Using the electrochemical method polypyrrole was prepared on the surface of semiconductors to form a protective layer against corrosion in electrochemical solar cells.[5] Chemically prepared polypyrrole was found to have a similar surface structure as electrochemically prepared polypyrrole and has been made conductive up to $10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ by treatment with bromine, iodine, *etc.*[4]

The preparation of the polypyrrole film used in this investigation was based on the method of Salomon *et al.*[4] The photochemical dopant diphenyliodonium hexafluoroarsenate was prepared first in a direct coupling reaction of benzene with potassium iodate and then converted into the active salt as described by Crivello and Lam.[6] Doping was accomplished by immersing the polymer film in a 1 M solution of this salt in methylene dichloride and followed by irradiation with a mercury arc. The light beam passed through 10 cm of water and a 2 mm filter UG 11 (Schott) before reaching the sample. The sample was thus irradiated with the lines between 280 and 380 nm. The conductivity of the polymer was measured with a four-probe arrangement at different exposure times.

Curve 1 in Figure 1 shows the increase in conductivity of polypyrrole with exposure time. The conductivity approached a saturation value in the range 10^{-3}—$10^{-2}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ after the

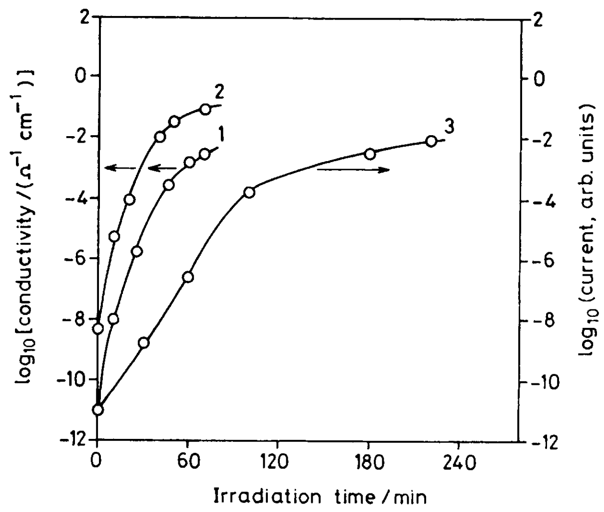

Figure 1. Dependence of conductivity on the time of irradiation (280—380 nm) for polymers impregnated with the active salt diphenyliodonium hexafluoroarsenate: 1, polypyrrole; 2, *trans*-$[CH]_x$; 3, polypyrrole (current).

sample had been irradiated for more than 60 min. Further irradiation and treatment with the active salt did not bring about any appreciable increase in this saturation value. We found that the conductivity slowly decreased when the doped film was stored for a few days in the dark. Curve 2 shows for comparison the results obtained with polyacetylene doped in the same way under an argon atmosphere. The saturation value of the conductivity obtained for this polymer was more than one order of magnitude higher than that for polypyrrole and close to the value reported by Clarke *et al.*[1] Curve 3 in Figure 1 represents the current in polypyrrole treated as above but measured with a two-electrode configuration. The contacts were made respectively with a stainless steel plate and a transparent gold film evaporated on a quartz plate. The latter served as a window for irradiation. The qualitative behaviour of the current in curve 3 is similar to that of the conductivity measured with the four-probe arrangement (curve 1). The gold contact deteriorated towards the end of the experiment, most probably owing to reaction with the acid that is formed in the photochemical doping process.[1,6]

The obvious attraction of photochemical doping is the easy establishment of a desired doping level within the accessible conductivity range. Thus, one can study the performance of a conductive polymer in a certain device at different doping levels ranging from insulating to almost metallic behaviour, as will be described elsewhere.

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