The Overgrowth of Cadmium Sulphide on Conducting Polymers

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Modification of polyaniline by introduction of SO_3H groups produced high conductivities and induced nucleation of cadmium sulphide.

The potential application of conducting polymers in electronic devices has recently attracted considerable interest in their synthesis and physicochemical properties. Among conducting polymers, polyaniline exhibits high conductivity[1] and unusually good chemical stability, which suggests that this polymer may be used as photochromic material, as a protective film for photovoltaic elements and as a microelectronic element. Polyaniline is known to behave as a p-type semiconductor, therefore its possible use as a material for the development of new photovoltaic elements largely depends on the ability of deposition of metal sulphides, *e.g.* cadmium sulphide, on its surface. Recent investigations have shown that appropriate modification of the surface of polymeric substrates allows the occurrence of selective deposition of calcium carbonates[2,3] and calcium phosphates.[4,5] This Communication reports on the first successful results of modification of polyaniline polymeric substrates by the introduction of SO_3H groups. When the modified polymer was introduced in stable supersaturated cadmium sulphide solutions CdS was deposited. Since the deposition is believed to take place following nucleation in active sites offered by the groups introduced, a new possibility of constructing photovoltaic elements is envisaged, in which the layer of a classical p-type semiconductor is replaced by the modified polyaniline.

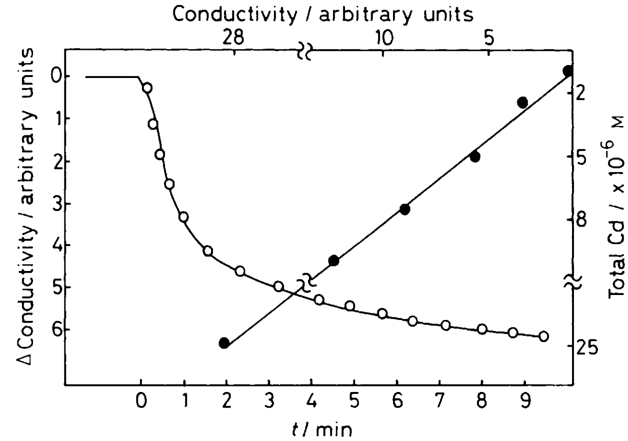

Figure 1. Deposition of cadmium sulphide on sulphonated polyaniline substrates. Variation in the conductivity of the supersaturated solution as a function of time (t) (○) and calibration line, obtained from the variation of the conductivity of the solution with supersaturation (●). Total cadmium = total sulphide, 25 °C, pH 2.0.

Polyaniline was prepared by polymerization with $KClO_3$ and $CuCl_2$ between 80 and 100 °C, followed by Soxhlet extraction for 36 h. This type of polymerization yielded polymers with conductivities ranging from 0.01 to 0.04 S cm^{-1}. Polyaniline polymerized in the presence of ammonium persulphate in an ice bath yielded conductivities ranging from 3 to 8 S cm^{-1}. The introduction of SO_3H groups was effected

Table 1. Effect of the introduction of SO_3H groups in polyaniline polymers.

Sample number	Conductivity of polyaniline/ S cm^{-1}	% Sulphonation	Conductivity of of sulphonated polyaniline/ S cm^{-1}
1	0.01	30	0.06
2	0.04	90	0.14
3	3	100	6
4	8	50	14
5	3	—	—
6	3	10	3
7	3	30	4
8	3	50	6

through the reaction of the NH groups of aniline with chlorosulphonic acid at approximately 5 °C. In all cases the sulphonated polymers exhibited the characteristic i.r. absorption band at 1335 cm^{-1}. Depending on the amount of chlorosulphonic acid used, various extents of polymer sulphonation were obtained. Sulphonation resulted in a dramatic increase of the polymer conductivity,[6] as may be seen in Table 1. The conductivity of the polymers increased up to a maximum value corresponding to 50% sulphonation. Further sulphonation had no effect on polymer conductivity.

Polyaniline polymers suspended in supersaturated cadmium sulphide solutions, prepared by mixing equal volumes of ammonium sulphide and cadmium nitrate solutions, did not react. It should be noted that the conditions were selected so that the resulting supersaturated solutions were stable. However, upon introduction of sulphonated polyaniline under the same conditions (25 °C, pH 2.0), precipitation of cadmium sulphide was induced, indicated by a change of the solution conductivity. The nature of the solid phase deposited was confirmed with i.r. and powder *X*-ray diffraction spectroscopy. The kinetics were determined by following the variation of supersaturation with time (Figure 1). The appropriate calibration curves of the solution conductivity as a function of supersaturation with respect to the depositing solid were used as a reference. The rates of cadmium sulphide deposition were proportional to the solution supersaturation, while short induction periods ranging between 60 and 200 s preceded the onset of the overgrowth process. The rates of precipitation varied linearly with the amount of the polymer suspended in the supersaturated solutions.

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