A Functionalized Polypyrrole Film prepared by Chemical Polymerization at a Vapour–Liquid Interface

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Thin conducting polypyrrole films doped with negatively-charged functional molecules were prepared by chemical polymerization of pyrrole at a vapour–liquid interface.

We report here that hybridization of a thin conducting polypyrrole (PPy) film with a negatively-charged functional molecule was carried out by polymerization of pyrrole at a vapour–liquid interface. Recently, several approaches to hybridization of PPy with a functional and/or supporting material have been attempted in order to endow the parent PPy with new properties.[1] Particularly, anodic doping by electrochemical polymerization of pyrrole is of interest as a simple and rapid method of hybridization at a PPy electrode/film with an anion.[2] Chemical hybridization of PPy film with a functionalized anion has not been reported previously, since a homogeneous and free-standing PPy film is not easily obtained by chemical polymerization[3] compared with electrochemical polymerization. However, chemical polymerization is a useful method of preparing conducting polymers, because it is achieved without electrodes and supporting electrolytes.

Preparation of a free-standing PPy film by chemical polymerization at a liquid–liquid or vapour–liquid interface has been reported.[4] We attempted to hybridize PPy with an anion by chemical polymerization at a vapour–liquid interface. On anodic doping by the anion in the electrochemical polymerization of pyrrole in water containing both a supporting electrolyte anion and the anionic dopant, the dopant is partly incorporated in the PPy matrix, even if the concentration of anionic dopant is lower than that of the supporting electrolyte anion.[5] We considered that the dopant anion should be incorporated in the PPy matrix on chemical polymerization of pyrrole in water containing both oxidant and dopant anions, in a similar way to the anodic doping process. Thin PPy films were obtained when pyrrole saturated vapour (25 °C) was brought into contact with a $Fe(NO_3)_3$ (0.05 M) aqueous solution containing an anionic dye {*e.g.*, Zn-tetrakis(sulphonatophenyl)porphyrin complex ($ZnTPPS_4$; 1×10^{-3} M), Fe-tris(bathophenanthroline disulphonic) acid complex [$Fe(BPS)_3$; 7×10^{-4} M], and indigo carmine (2×10^{-3} M)} for few minutes, respectively. The PPy films grew at the vapour–liquid interface. Figure 1 shows visible absorption spectra of the PPy films obtained. The characteristic absorption bands of the dyes appeared with the original absorption spectrum of PPy. These spectra are similar to those of anion doped PPy prepared by electrochemical polymerization.[5] Table 1 gives properties of the PPy films prepared by contact of pyrrole saturated vapour (25 °C) with a $Fe(NO_3)_3$ (0.05 M) aqueous solution containing various large anions; {anionic dyes, anionic poly-1-electrolytes [*e.g.*, sodium poly(styrene-4-sulphonate) (PSSNa; 0.004 M), potassium poly(vinyl sulphate) (PVSK; 0.004 M)], and an anionic surface-active agent (sodium decane-1-sulphonate; 0.004 M)} for 2 h. The homogeneous and free-standing PPy film (3—39 μm thickness) was obtained at the vapour–liquid interface. The conductivity of the PPy film was 0.1—10 S cm^{-1}, which was comparable with PPy film prepared by electrochemical polymerization in water.[6] The dopant anion incorporated in the PPy film was not soaked out. From elemental analysis it was shown that an appreciable amount of sulphur (corresponding to the sulphonate or sulphate groups in the dopant) was incorporated into the PPy films. The dopant ratio (*f*), the ratio of sulphonate or sulphate to a single pyrrole unit, was 0.018—0.087. These observations suggest that the large anions were incorporated in the PPy matrix as dopants. This incorporation of dopant probably results from the attractive electrostatic force between the positively-charged PPy and the negatively-charged dopant, as in the anodic doping process. The oxidant anion, NO_3^-, was also incorporated in the PPy matrix. Therefore, the oxidant anion and dopant anion coexist in the PPy matrix. The incorporation of large anions in the PPy films on chemical polymerization at the vapour–liquid interface is a useful hybridization procedure for PPy.

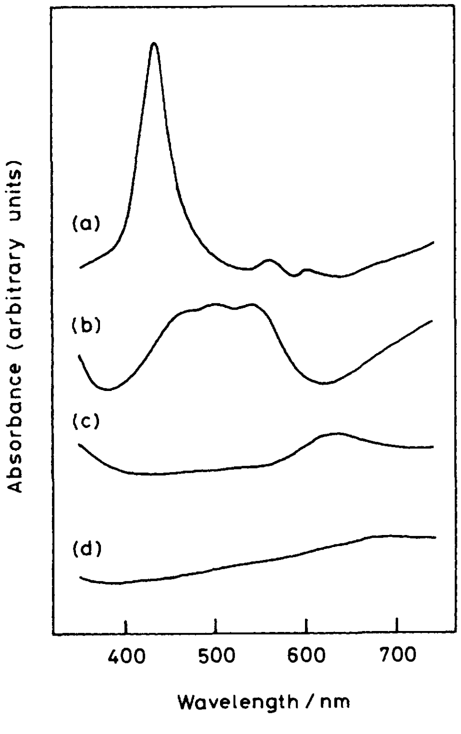

Figure 1. Visible absorption spectra of thin PPy films prepared by contact of pyrrole saturated vapour (25 °C) with $Fe(NO_3)_3$ (0.05 M, 20 cm^3) aqueous solutions containing dyes [(a) $ZnTPPS_4$; (b) $Fe(BPS)_3$; (c) indigo carmine; (d) none].

Table 1. Properties of PPy films doped with negatively-charged functional molecules.

Dopant anion	Film thickness/ μm	Conductivity/ S cm^{-1}	*f*
$ZnTPPS_4$	18	1.5	0.022
$Fe(BPS)_3$	18	5.3	0.058
Indigo carmine	3	0.1	0.018
PSSNa	10	3.1	0.086
PVSK	39	0.6	0.021
Sodium decane-1-sulphonate	25	6.1	0.087

This study provides a novel method of functionalizing PPy film through hybridization of PPy with a large functionalized anion by chemical polymerization at a vapour–liquid interface.

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