The Effect of Basicity of Dopant Anions on the Conductivity of Polypyrrole Films

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The conductivity of polypyrrole films doped with several kinds of carboxylate anions decreases with an increase in the basicity of the dopant anions.

It is well known that polypyrrole (PPy) films doped with electrolyte anions exhibit high conductivities owing to the contribution of polarons and bipolarons which are generated as charge compensators for the dopant anions.[1] Recently, considerable attention has been paid to factors which control the conductivity of the PPy films. Electrode potentials which control the dopant concentration of PPy films,[2] and the concentration[3] and the kind[4] of electrolyte anions used for film preparation influence the conductivity of PPy films. Furthermore, it has been reported that the film conductivity is varied by stretching of PPy films.[5] In our previous papers,[6] it was reported that the conductivity of PPy films doped with organic sulphonate derivatives decreases with an increase in the number of sulphonate groups on a dopant molecule. The result has been interpreted in terms of an electrostatic interaction between positive charge carriers in the polymer chains and the doped anions. Here we would like to report that the basicity of dopant anions has a remarkable effect on the conductivity of PPy films; the use of several kinds of carboxylate derivatives as dopants which cover pK_a values from -0.3 to 2.8 makes it possible to prepare PPy films having conductivity differences of almost three orders of magnitudes.

Polypyrrole films were prepared by anodic oxidation of 0.1 mol dm^{-3} pyrrole dissolved in water containing 0.01 mol dm^{-3} carboxylic acid.† The electrolyte solutions were adjusted to pH 6 with NaOH solution to ionize the included carboxylic acid, except for solutions containing maleic acid where solutions of pH 3 giving monovalent anions and of pH 7 giving dianions were prepared. The PPy films were deposited on indium tin oxide-coated glasses (ITO) with an electrolysis charge of 200 mC cm^{-2} under constant current conditions (0.2 mA cm^{-2}). Measurements of electrical conductivity of the prepared films were carried out by employing the four probe method after stripping the polymer film from the ITO electrode.

It was found that the pK_a value of carboxylic acids plays a decisive role in PPy film growth. If carboxylates whose conjugated acids have pK_a values greater than that of *p*-nitrobenzoic acid (pK_a = 3.40) were used as dopants, no appreciable film growth of PPy was observed. Soon after

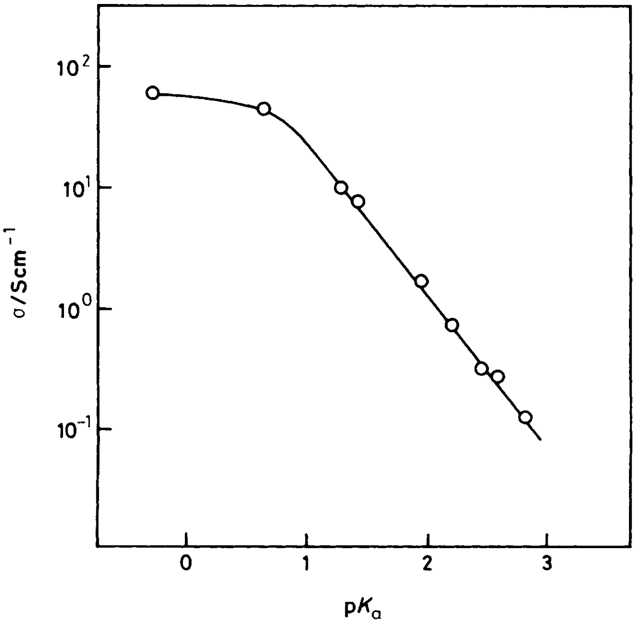

Figure 1. Relationship between the conductivity of polypyrrole films and pK_a values of conjugated acids used as dopant anions.

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† Carboxylic acids used in this study and their pK_a values: CF_3CO_2H -0.3, CCl_3CO_2H 0.64, $CHCl_2CO_2H$ 1.26, 2,4-dinitrobenzoic acid 1.42, maleic acid 1.93 and 6.59, *o*-nitrobenzoic acid 2.18, $CNCO_2H$ 2.43, monofluorobenzoic acid 2.59, 3,5-dinitrobenzoic acid 2.80, *p*-nitrobenzoic acid 3.40, $MeCO_2H$ 4.75.

beginning the constant current electrolysis of the pyrrole solutions, the electrode potential rose up to 2 V *vs.* standard calomel electrode (S.C.E.) or more, and simultaneously the PPy film growth apparently ceased. The PPy films obtained in those cases were too thin to be stripped from the substrate, and cyclic voltammetry of the film-coated electrode in 0.01 mol dm^{-3} $K_3Fe(CN)_6$ and 0.1 mol dm^{-3} Na_2SO_4 did not result in any appreciable redox waves. In the case of maleic acid, similar phenomena were observed when attempts were made to prepare PPy films in a solution of pH 7, but not so in a solution of pH 3.

When carboxylic acids having pK_a values smaller than 3,5-dinitrobenzoic acid (pK_a = 2.50) were used, PPy films could be prepared with an electrolysis charge of 200 mC cm^{-2}. Elemental analyses of PPy films prepared in these cases showed that the carboxylate anions were present in the films in the molar concentration of 0.3 ± 0.02 to pyrrole rings and that maleic acid was doped in the form of its monoanion. It is postulated that the degrees of ionization of PPy films prepared in this study are almost the same as those prepared in electrolyte solutions containing conventional inorganic anions such as ClO_4^-.[7]

Plots of the conductivity of the PPy films(σ) against pK_a values of the conjugated acids of the carboxylate anions doped in the films are shown in Figure 1. A PPy film doped with F_3CCOO^- exhibits the highest conductivity (60 S cm^{-1}) among the films prepared in the present study, and the film conductivity distinctly decreases with increasing the pK_a value, indicating that an increase in the basicity of dopant anions reduces the conductivity of PPy films. A linear relationship is established between pK_a and log σ for pK_a values >1, which can be formulated by $\log \sigma = -1.22\ pK_a + 2.50$. However, the dependence of the conductivity on pK_a is weak when pK_a values of the conjugated acids of dopant anions are <1.

The observed effects of the basicity of dopant anions on the conductivity of PPy films may be explained in terms of an interaction between positive charges in the polymer chains and the doped anions in the film. The interaction is thought to become stronger for carboxylic acids of higher pK_a, because when the conjugated anions are doped in PPy films they must have different affinities to positive charges in the polymer chains in the same way that they show different affinities to positively charged protons in water, depending on their pK_a values. The conductivity of PPy films decreases with an increase in electrostatic interaction between positive charges in polymer chains and doped anions as reported previously.[6] The absence of PPy film growth in the presence of a carboxylate whose conjugated pK_a is greater than the pK_a of *p*-nitrobenzoic acid can be explained by assuming that the electrostatic interaction is too strong for the deposited film to possess any appreciable conductivities. The finding that the very thin films prepared in such environments did not show any redox activity provides further indirect evidence for the insulating properties of PPy films prepared in this way. The deviation from the linear relationship between log σ and pK_a observed at pK_a values <1 seems to reflect that the interaction of positive charges with dopant anions is very weak below pK_a = 1, and that other factors determine the conductivity of PPy films. This assumption is supported by the fact that the conductivity of polypyrrole films doped with high acidic monovalent anions such as BF_4^- and ClO_4^- showed almost the same conductivity values of *ca.* 10^2 S cm^{-1}.[7]

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