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MORPHOLOGY AND CONDUCTIVITY OF POLYPYRROLE CONTAINING HALOGEN COUNTER ANIONS

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Polypyrroles containing halogen anions as dopants were electrochemically prepared in aqueous solutions. Morphologies of the polypyrroles were found to depend on halogen anion species. The conductivities of the polypyrrole films were around 10 S/cm.

Polypyrrole films prepared by electrochemical oxidation of pyrrole contain counter anions incorporated from supporting electrolyte solutions. Obviously, the most important role of the counter anions is the neutralization of the partial cationic charge on skeletal pyrrole rings. The counter ion species, however, have been shown to influence the conductivity of polypyrrole films as well as their morphologies.[1,2) Polypyrroles with various kinds of anions, such as BF_4^-, ClO_4^-, AsF_6^-, and $CF_3SO_3^-$, have been prepared. No report has been appeared that claimed halogen anions, which are one of the simplest ions among various inorganic and organic anions, could be incorporated in polypyrrole films, except for the case of chemical oxidation of neutral polypyrrole. In this letter, we tried to examine the interrelation among counter anion species, morphologies and conductivities in the polypyrrole films which hold the simple monoatomic counter ions.

Inorganic salts which are insoluble in any non-aqueous solution can be employed, if the electrochemical polymerization proceeds in an aqueous pyrrole solution. The recent success on the preparation of several polypyrroles in aqueous solutions is encouraging.3,4) Then, we adopted lithium, sodium and potassium halides as supporting electrolytes. Polypyrrole chloride and polypyrrole bromide, which were dense and free-standing films and exhibited the conductivity of around 10 S/cm, were able to be prepared.

The electrochemical oxidation was performed in an aqueous solutions which contained pyrrole (0.2 M) and a supporting electrolyte (0.2 M). Platinum and indium-tin oxide (ITO) glass electrodes were used as counter and working electrodes, respectively. The applied potential between the electrodes was 2.0 V. When higher potential was applied, electrolysis of water could not be avoided. All the syntheses were carried out at room temperature (27 °C). The resulted polypyrroles were washed with distilled water and dried under vacuum. A scanning electron microscope was used for examining the morphology of the samples. The conductivities of the sample films were measured by the four-probe

Table 1. Conditions of synthesis, morphology and conductivity of polypyrroles

Supporting electrolytes	Currents $\mu A \cdot cm^{-2}$	Morphology of products	Thickness μm	Conductivity $S \cdot cm^{-1}$
LiCl	500	film	18	12.0
LiBr	550	film	10	5.6
LiI	700	powder	----	----
NaCl	500	film	20	14.0
NaBr	600	film	10	8.2
NaI	800	powder	----	----
KCl	500	film	12	12.0
KBr	450	film	20	10.0
KI	700	powder	----	----

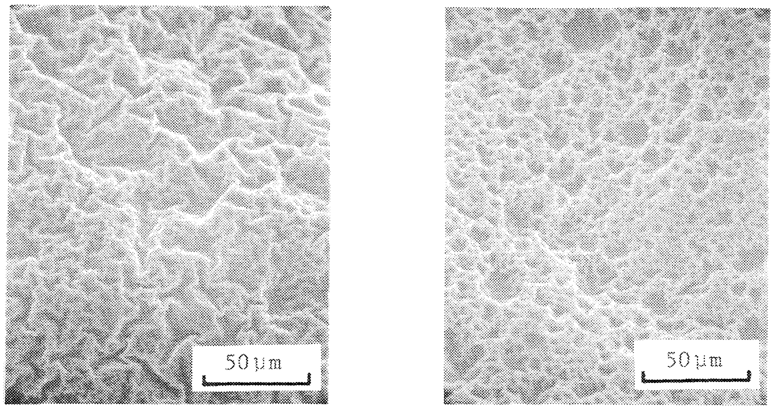
Table 2. The composition of polypyrroles prepared using sodium halides as supporting electrolytes

Supporting electrolytes	H	C	N	Anions / pyrrole unit
NaCl	3.40	(4.00)	1.00	0.67
NaBr	3.40	(4.00)	1.00	0.44
NaI	3.54	(4.00)	1.00	0.48

method under a vacuum of 10^{-2} Torr.

The supporting electrolytes used, the condition of electrochemical polymerization, morphologies of the products, and the conductivities at room temperature are listed in Table 1. Irrespective to anion and cation species, products were obtained on working electrodes. Specifically, the products were films that could be easily peeled off the ITO glass, when Cl or Br anions were adopted as counter ions. The growth of the polypyrrole films was found not to be affected by the cationic species of the supporting electrolytes, if the conditions of electrochemical oxidation, such as concentration of supporting electrolytes, current density, and temperature were fixed. In contrast, the anion species of the supporting electrolytes profoundly influenced the morphologies of the resulted polymers. Polypyrrole iodide could not be prepared in film forms. On the other hand, polypyrrole fluoride, disappointingly, was very difficult to prepare, for hydrogen fluoride generated by the electrochemical reaction corroded ITO electrodes.

In Table 2, the C:H:N ratio in the polypyrroles prepared by use of sodium halides for supporting electrolytes obtained from the results of elemental analyses were shown. The C:H:N ratio in Table 2 well corresponded to



(a) (b)

Fig.1. Scanning electron micrographs of polypyrrole films
(a) polypyrrole chloride, (b) polypyrrole bromide.

the composition of polypyrrole, 4:3:1, proving that polypyrroles were obtained. In Table 2, the contents of halogen anions (mole ion per mole pyrrole unit) estimated from the carbon contents and the residual weights in the elemental analyses were also shown. About one halogen ion per two pyrrole rings was found to be incorporated. These ratios were considerably higher than the cases of the polymers with ClO_4^- and BF_4^- counter ions in literatures.[1,2,5)] It is plausible that halogen anions are favorable to be incorporated in polymers during electrochemical polymerization due to their compactness.

The scanning micrographs of the polypyrrole films with Cl and Br anions are compared in Fig. 1. The sample of the polypyrrole chloride was non-porous, although wrinkles were observed. On the other hand, the sample of the polypyrrole bromide looked rather porous. Moreover, only powderly polymer adhered on working electrodes in the case of the polypyrrole iodide. From these observations, one finds the trend that the counter anions with high electron negativity lead to the production of dense and homogeneous polypyrrole films.

The conductivities of the polypyrrole films at room temperature were around 10 S/cm, and no trend between counter ion species and conductivity could be found. The temperature dependences of the conductivities of the polypyrrole chloride and the polypyrrole bromide prepared by using sodium salts for supporting electrolytes are shown in Fig. 2. The temperature dependency could be well described with the expression, $\sigma \propto \exp(a\,T^{-\frac{1}{4}})$. The $T^{-\frac{1}{4}}$ dependency of conductivity has been observed in several polypyrroles prepared in various conditions.[1,6,7)] Therefore, one should recognize that the electronic conduction in the polypyrroles prepared in this study does not differ from that in polypyrroles reported before, although small and simple counter ions were incorporated in polypyrroles.

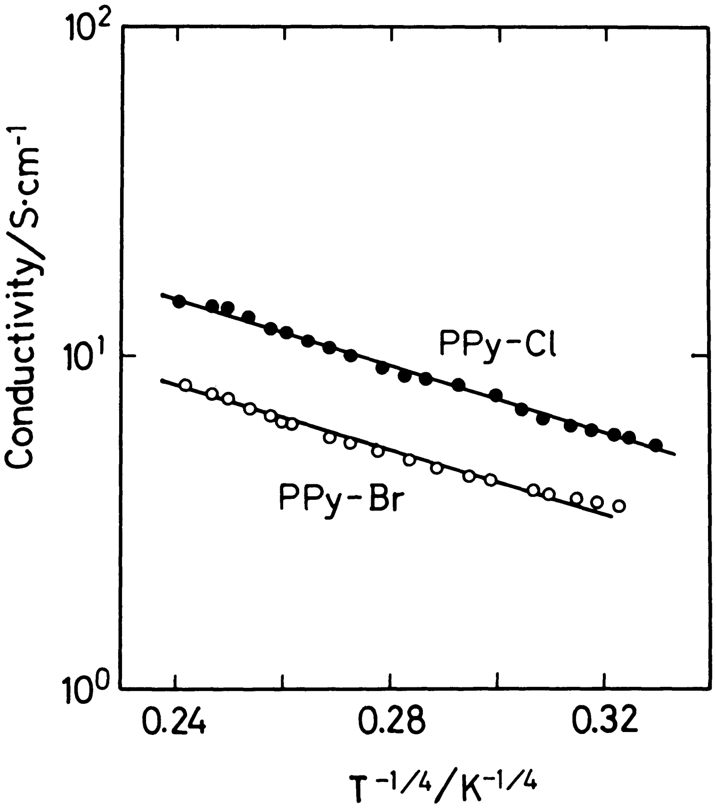


Fig.2. Temperature dependences of the conductivity in polypyrrole chloride (●) and polypyrrole bromide (○).

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