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Great improvement of polypyrrole films prepared electrochemically from aqueous solutions by adding nonaphenol polyethyleneoxy (10) ether

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We report the effect of adding nonaphenol polyethyleneoxy (10) ether (OP_{10}) into the electropolymerization solution of pyrrole on the tensile strength and structure of the as-prepared polypyrrole (PPy) films. The tensile strength of the PPy film prepared from TsONa aqueous solution with OP_{10} [PPy(TsO^-, OP_{10})] reaches 127 MPa, which is much stronger than that of the film from usual aqueous solution without OP_{10} [PPy(TsO^-), 27.8 MPa]. The results of elemental analysis indicate that the amount of excess oxygen in PPy(TsO^-, OP_{10}) decreased obviously, compared with that in PPy(TsO^-). The morphology and structure of PPy(TsO^-, OP_{10}) and PPy(TsO^-) were also compared by SEM and X-ray diffraction spectroscopy. © 1997 Elsevier Science Ltd.

(Keywords: polypyrrole; electrochemical polymerization; tensile strength)

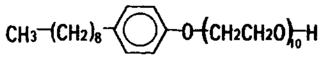
Introduction

Conducting polymers have attracted a great deal of attention in the last two decades, since they show interesting properties to scientists and potential applications in many ways[1–11], such as molecular devices, electrochromic display, secondary batteries and artificial muscle. Among them, polypyrrole (PPy) is the most attractive for its ease of preparation, good stability in air and high conductivity. Electrochemical polymerization of pyrrole in an electrolyte solution is the main method to prepare PPy films[12–17]. Some organic solvents and water can be used as the solvents of the solutions. Obviously, the aqueous solution is more advantageous than the organic solution from the viewpoint of environmental preservation. Moreover, more salts can dissolve in water so that a wider range of salts can be selected as the supporting electrolyte in the solutions.

For the application of PPy, much effort has been devoted to the preparation of the conducting PPy films with high strength and good flexibility[14,18–22]. The properties of the as-prepared PPy films are very sensitive to the polymerization conditions[18,19,23–26], such as electrolyte anions, solvents and temperature, etc. The effect of the electrolyte anions is the most important to the preparation of PPy films. It was found that the conductivity and tensile strength of the PPy films produced from the solutions with anionic surfactants, such as tosylate, as supporting electrolyte are much better than that of the films from the solutions with inorganic salts as supporting electrolyte. The positive effect of the surfactant anions may come from the effect of the surfactants or from the anions. To check the influence of the surfactants on the electropolymerization of pyrrole, we study in this paper the effect of adding the nonionic surfactants OP_{10}, etc. in the aqueous solutions on the pyrrole polymerization.

Experimental

PPy films were electrochemically prepared in the aqueous solutions containing 1 mol l^{-1} sodium *p*-toluene sulfonate (TsONa) and 0.1 mol l^{-1} pyrrole with or without adding nonaphenol polyethyleneoxy (10) ether (OP_{10}):



The pH value of the solutions was adjusted to 2 by adding *p*-toluenesulfonic acid (TsOH). Pyrrole was distilled and preserved in the inert gas atmosphere prior to use. Two stainless steel plates were used as working electrode (anode) and counter electrode (cathode). The electropolymerization of pyrrole was performed at −5°C on the anode under a constant current of 0.5 mA cm^{-2} for 90 min. The thickness of the films is *ca.* 20 μm.

The tensile strength of the film was measured at 15°C using Instron 1122 universal testing instrument at the stretching rate of 1 mm min^{-1}. The SEM photographs of the cross-section of the PPy film were taken by Hitachi S-530 scanning electron microscope. The cross-section was created by fracturing the film after cooling in liquid nitrogen. X-ray diffraction spectra were measured using a Dmax-2400 X-ray multicrystal powder diffractometer with $CuK\alpha_1$ radiation.

Results and discussion

After polymerization of pyrrole in TsONa aqueous solution by adding 0.1 mol l^{-1} OP_{10} for 90 min, a black PPy film [PPy(TsO^-, OP_{10})] was formed on the anode. The film is very smooth and shiny with metallic lustre, and it is extremely flexible. For comparison, the PPy(TsO^-) film was obtained under the same conditions from usual aqueous solution without adding OP_{10}.

The tensile strength of the PPy(TsO^-, OP_{10}) and PPy(TsO^-) films was studied by stretching the films. The

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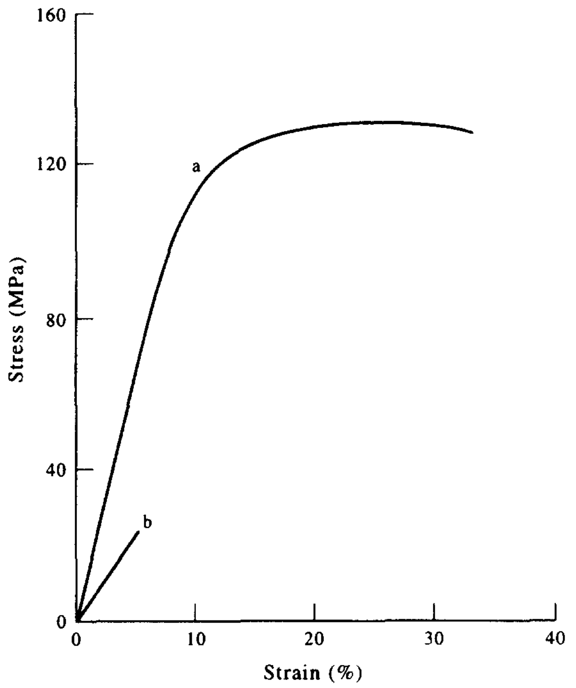

Figure 1 The stress–strain behaviour of (a) PPy(TsO^-, OP_{10}) film and (b) PPy(TsO^-) film

stress–strain behaviour of both films are shown in *Figure 1*. The stretching process of the PPy(TsO^-, OP_{10}) film can be divided into two stages. In the first stage, the curve shows elastic behaviour, i.e. the stress increases with the increase of the strain of the film. Then a yield point appears and the process develops to the second stage where the curve shows plastic feature. The stress almost remains unchanged until the film fractures, although the strain of the film continues to increase. The elongation at the break is 33%. The tensile strength of the film is 127 MPa, which is stronger than most common polymer materials such as polyethylene and polytetrafluoroethylene[27]. Only elastic behaviour was observed on the stress–strain behaviour of the PPy (TsO^-) film (see *Figure 1b*). Its tensile strength is only 27.8 MPa and its elongation at the break is only 4–5%. Therefore, it can be concluded that the tensile strength and elongation of the PPy film are greatly improved by adding OP_{10} into the polymerization solution.

The conductivity of the PPy(TsO^-, OP_{10}) film is *ca.* 50 S cm^{-1}, which is a little lower than that of the PPy(TsO^-) film.

The chemical composition of the PPy(TsO^-, OP_{10}) and PPy(TsO^-) films was determined by elemental analysis, as shown in *Table 1*. The elemental ratio of C, H, N and S in PPy is directly taken from the results of the elemental analysis, and that of O is calculated according to the chemical composition balance. The content of C and H in PPy(TsO^-, OP_{10}) is a little higher, and that of N, S and O is a little lower than that in PPy(TsO^-). The slightly higher C : N ratio in PPy(TsO^-, OP_{10}) indicates that a little of OP_{10} may have mixed into the polymer. The C : N ratio in the PPy chain should be 4/1. If the excess amount of carbon is considered as the contribution from the mixed OP_{10}, the stoichiometry of PPy(TsO^-, OP_{10}) is $C_{4.00}H_{2.70}N_{1.00}(TsO)_{0.34}(OP_{10})_{0.02}O_{0.15}$. In comparison, the stoichiometry of PPy(TsO^-) is $C_{4.16}H_{3.49}N_{1.00}(TsO)_{0.34}O_{0.44}$. Obviously, both polymers have the same doping degree of the counter anions TsO^-, indicating that adding OP_{10} into aqueous solution does not vary the doping level of the as-prepared PPy films. Interestingly, the amount of excess oxygen in PPy(TsO^-, OP_{10}) is lower than that in PPy(TsO^-). The excess oxygen in PPy[14,24,26,28] may come from the overoxidation of the PPy chains and the adsorption of oxygen in air. The decrease of the excess oxygen in PPy(TsO^-, OP_{10}) indicates that the overoxidation was partly avoided during the electropolymerization of pyrrole in the solutions with OP_{10}.

Table 1 The results of the elemental analysis of the PPy films

	Elemental ratio (%)				
Sample	C	H	N	S	O
PPy(TsO^-)	59.04	4.42	10.35	8.40	17.79
PPy(TsO^-, OP_{10})	59.95	4.57	10.21	7.93	17.34

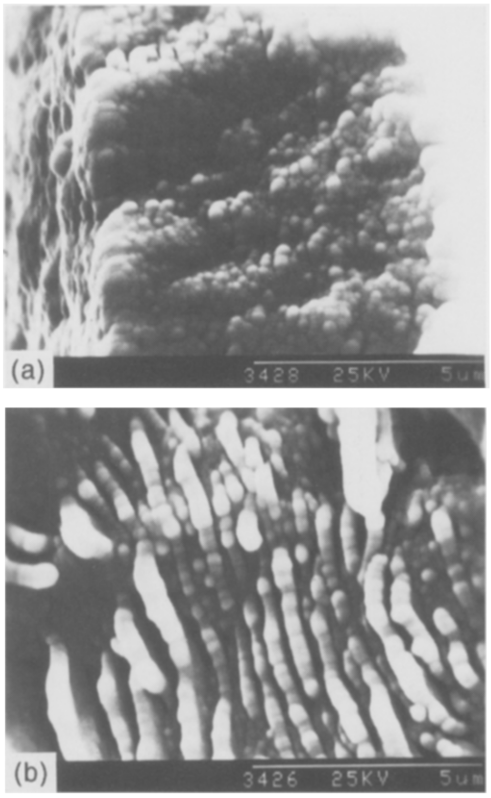

Figure 2 Scanning electron micrographs of the cross-section of (a) PPy(TsO^-, OP_{10}) film and (b) PPy(TsO^-) film

In order to investigate the mechanism of the excess oxygen reduction, the polymerization potential was measured during the galvanostatic electropolymerization in the electrolyte solution with and without OP_{10}. At the polymerization conditions with the current density of 0.5 mA cm^{-2}, the potential in the solution without OP_{10} is 0.65–0.68 V vs. SCE, while the potential in the solution with OP_{10} is 0.66–0.69 V vs. SCE. The latter is a little higher than the former, which indicates that the reduction of the excess oxygen in PPy(TsO^-, OP_{10}) is not from the effect of the polymerization potential, since the higher potential could cause more overoxidation. Probably, the surfactant changed the interface structure between the anode and the electrolyte solution[29,30], where the electropolymerization takes place. The water

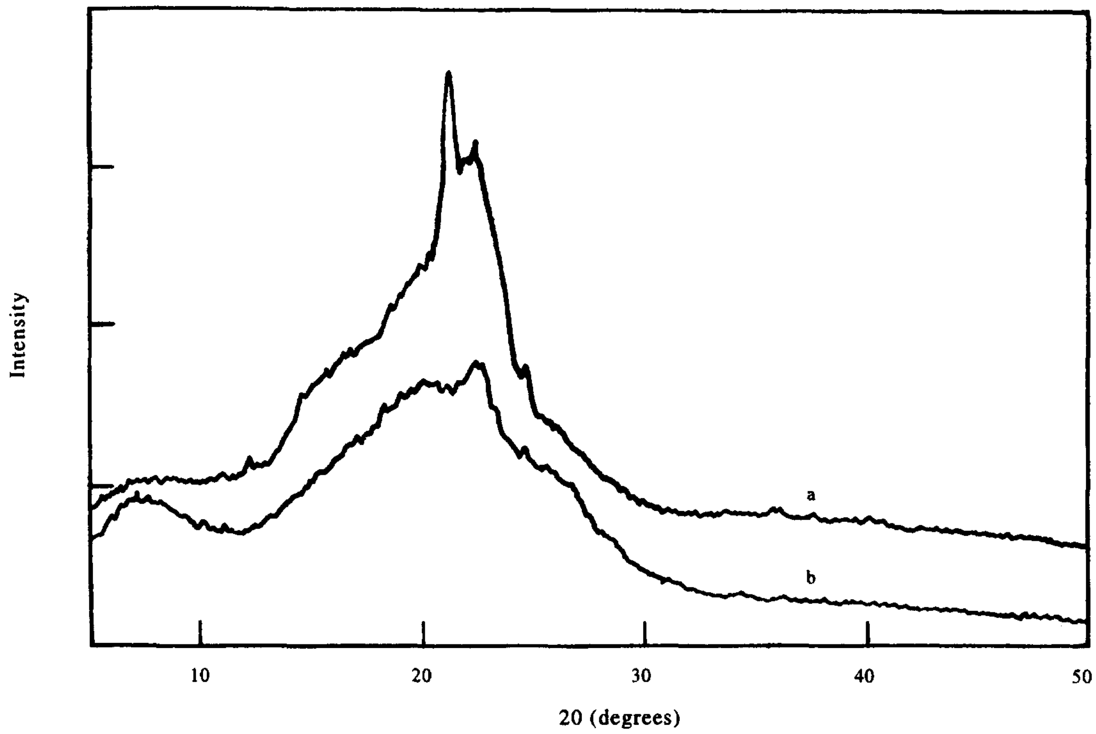

Figure 3 X-ray diffraction spectra of (a) PPy(TsO^-, OP_{10}) film and (b) PPy(TsO^-) film

molecules in the interface may be replaced by the OP_{10} molecules for the solutions with OP_{10}, so that the oxidation of water into oxygen, which causes the overoxidation of PPy chain, could be avoided during the anodic polymerization.

The SEM photographs of the cross-section of the two films are shown in *Figure 2*. A layered structure can be clearly seen for the PPy(TsO^-) film. It is not clear for the PPy(TsO^-, OP_{10}) film. *Figure 3* show the X-ray diffraction patterns of the two films. Two broad peaks exist in the X-ray diffraction pattern of PPy(TsO^-), one at $2\theta = 7.1°$ and another at $2\theta = 22.4°$, corresponding to the distance of 12.4 Å and 3.9 Å, which agrees with the results of Warren and Anderson[13]. The peak at $2\theta = 7.1°$ flattens and two sharp peaks at $2\theta = 21.3°$ and 22.4°, which correspond to the *d* values of 4.16 and 3.96 Å respectively, are observed in the X-ray diffraction spectra of PPy(TsO^-, OP_{10}) film. Wynne and Street assigned the peak at $2\theta = 22.4°$ to the scattering from PPy chain at the interplanar spacing in the PPy(TsO^-)[31]. The appearance of the sharp peaks in PPy(TsO^-, OP_{10}) implies that the PPy chains in the PPy(TsO^-, OP_{10}) film has more ordered arrangement than those in the PPy(TsO^-) film.

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