Control of the Dopant-Exchange Process in Polypyrrole by a Magnetic Field

Iwao Mogi
Institute for Materials Research, Tohoku University, Katahira, Sendai 980-77

(Received September 22, 1995)

The effect of high magnetic fields on the dopant-exchange (DE) process in p-toluenesulfonate-doped polypyrrole (PPy/TsO$^-$) was investigated in a LiClO$_4$ aqueous solution by means of cyclic voltammetry. It was found that the magnetic field accelerates the DE process in the PPy/TsO$^-$ film polymerized in the absence of magnetic field and that the DE process hardly proceed in the PPy/TsO$^-$ film polymerized in the magnetic field of 12 T.

Organic conducting polymers are of great potential interest in connection with a neural element because they exhibit fractal growth,[1,2] the learning effect[3] and the electrical plasticity .[4,5] Iseki *et al.* reported that a p-toluenesulfonate-doped polypyrrole (PPy/TsO$^-$) film shows electrically plastic behavior, which is gradual activation of the film in a dopant-exchange (DE) process during redox cycles in electrolytic solutions containing spherical anions (*e.g.* NO$_3^-$, ClO$_4^-$ and BF$_4^-$).[5] The PPy/TsO$^-$ film has an anisotropic molecular organization, where the planes of aromatic rings lie preferentially parallel to the electrode surface, while the spherical-anion-doped PPy film has an isotropic organization.[6,7] The DE process between TsO$^-$ and the spherical anions is thus considered to cause the considerable change in the film morphology.[8] On the other hand, it is well known that most organic polymers have so large anisotropy in a diamagnetic susceptibility that they are subject to the diamagnetic orientation, resulting in the morphological changes, in magnetic fields.[9] Considering these facts, we have tried to control the plastic behavior in the DE process of the PPy/TsO$^-$ film by the magnetic field.

The electrochemical measurements were performed at 20 °C with an electrochemical analyzer BAS-100B/W. The electrode system consisted of a platinum disk (ϕ1.6 mm) as a working electrode, a Ag/AgCl electrode as a reference one and a platinum plate as a counter electrode. The PPy/TsO$^-$ film was prepared on the platinum disk electrode by electrochemical polymerization[10] (1.0 C cm^{-2}) at a constant potential (1.0 V) in a 0.1 M (1M=1mol dm^{-3}) pyrrole aqueous solution containing 0.1 M TsONa as a supporting electrolyte. In order to examine the plastic behavior of the DE process, we measured the cyclic voltammogram (CV) of this film in a 0.1 M LiClO$_4$ aqueous solution in a potential range of -0.5 ~ 0.5 V, where gradual current increase is clearly observed with repeating redox cycle. The undoping process in the PPy/TsO$^-$ film occurs at -0.5 ~ -0.6 V,[8] hence the more negative potential sweep leads to rapid saturation of the current within 10 cycles. On the other hand, the repeating potential sweep of -0.3 ~ 0.5 V results in only slight current increase caused by the spontaneous DE process. The CV's were measured just after the immersion of the film in the LiClO$_4$ solution to eliminate the influence of the spontaneous DE process.

The magnetic field generated by a Bitter magnet was applied perpendicularly to the surface of the working electrode and parallel to the faradaic current to eliminate the magnetohydrodynamic effect as described.[11]

We set out to investigate the magnetic field effect on the DE process of the PPy/TsO$^-$ film prepared in the absence of magnetic field. Figure 1 shows the CV's (30 cycles) of the film measured in (a) 0 T and (b) 12 T. Both doping (anodic) and undoping (cathodic) currents increase with repeating potential sweep, and the PPy film undergoes the doping and undoping processes of ClO$_4^-$ instead of TsO$^-$. Figure 2 shows the plots of the anodic current at 0.084 V in the CV's in 0 T and 12 T as a function of the cycle number. It is clearly seen that the magnetic field increases the doping current at the initial stages of the DE process (in the first 15 cycles), and such a effect is enhanced with increasing magnetic field (see the inset in Figure 2). This result indicates that the magnetic field facilitates the morphological changes of the PPy film and accelerates the DE process.

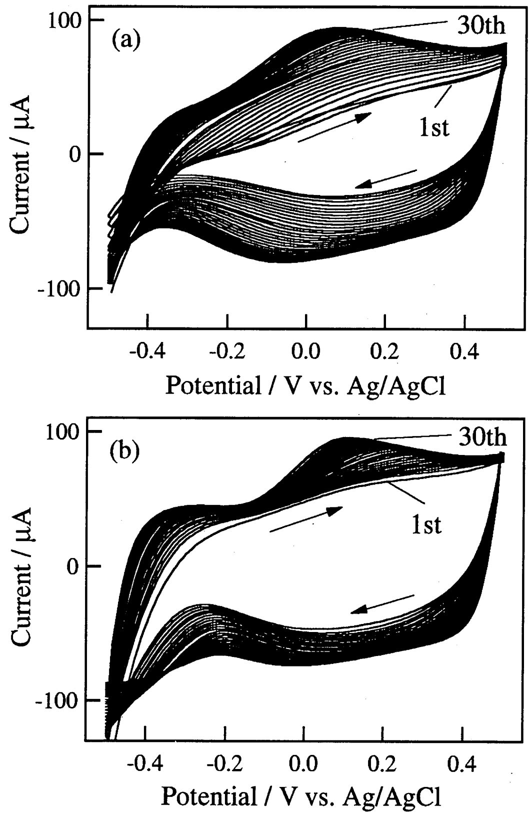

Figure 1. Cyclic voltammograms of the PPy/TsO$^-$ film measured in (a) 0 T and (b) 12 T. The film was prepared in 0 T. The CV's were measured for 30 cycles in a 0.1 M LiClO$_4$ aqueous solution after keeping the potential at -0.5 V for 2 s. The potential sweep rate was 50 mV s^{-1}, and arrows represent the sweep direction.

As mentioned above, in the PPy/TsO$^-$ film the planes of aromatic rings lie preferentially parallel to the electrode surface and the dopant molecules lie between the PPy layers.[7] On the other hand, the aromatic ring is most stable at the orientation parallel to the magnetic field because of the large diamagnetic susceptibility perpendicular to the ring plate.[9] In the present experiment the magnetic field is applied perpendicularly to the electrode surface, it is thus speculated that the magnetic field

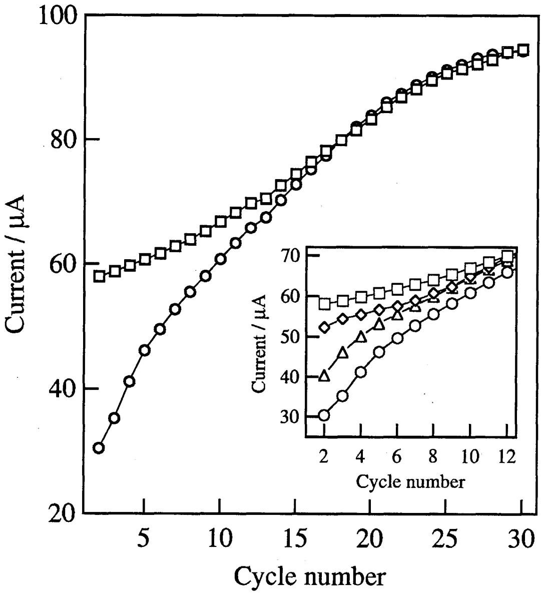

Figure 2. Plots of the doping (anodic) current at 0.084 V in 0 T (circle) and 12 T (square) as a function of the cycle number in the CV's in Figure 1. The inset shows similar plots for the first 12 cycles in 0 T (circle), 1 T (triangle), 6 T (rhombus) and 12 T (square).

degrades the anisotropic organization of the PPy/TsO$^-$ film, resulting in the acceleration of the DE process.

Our previous paper[12] showed that the magnetic field induces the oriented polymerization of pyrrole owing to the diamagnetic effect, resulting in the drastic morphological change from an open-ramified fractal pattern in 0 T to a closed pattern in 0.5 T. We examined the DE process of the PPy/TsO$^-$ film prepared in the magnetic field of 12 T. The CV's (the 30th cycle) of the films prepared with and without magnetic fields are shown in Figure 3(a), where the CV's were measured in the absence of magnetic field. Figure 3(b) shows the plots of the doping current at 0.084 V in both CV's as a function of the cycle number. It is obviously seen that the PPy/TsO$^-$ film prepared in 12 T shows only slight current increase, being considered to be so rigid that the dopant anions cannot migrate within the film. Such suppression of the plastic behavior was observed in the PPy/TsO$^-$ film prepared in the magnetic fields higher than 1 T.

In summary, we have shown two opposite effects of the magnetic field on the DE process in the PPy/TsO$^-$ film; one is the acceleration, and the other is the suppression. Both effects seem to arise from the diamagnetic orientation of the aromatic rings, but the detailed mechanism is a future subject. The feasibility of such control of the plastic behavior is essential for the development of an intelligent molecular device.

We thank the stuff of the High Field Laboratory of Tohoku University for operating the magnet. This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Area (no.236) from the Ministry of Education, Science and Culture.

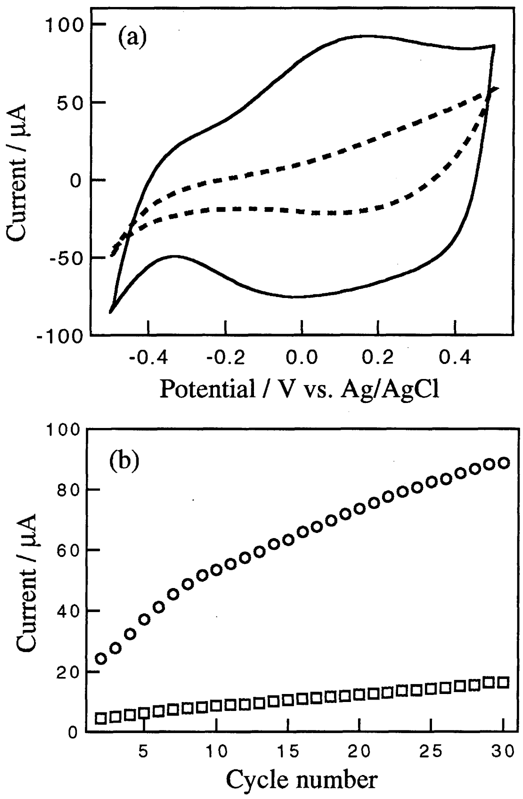

Figure 3. (a) Cyclic voltammograms (the 30th cycle) of the PPy/TsO$^-$ films prepared in 0 T (solid) and 12 T (dotted). The CV's were measured in 0 T with the potential sweep rate of 50 mV s^{-1} in a 0.1 M $LiClO_4$ aqueous solution after keeping the potential at -0.5 V for 2 s. (b) Plots of the doping (anodic) current at 0.084 V of the PPy/TsO$^-$ films prepared in 0 T (circle) and in 12 T (square) as a function of the cycle number.

References and Notes

1 J. H. Kaufman, C. K. Baker, A. I. Nazzal, M. Flickner, O. R. Melroy, and A. Kapitulnik, *Phys. Rev. Lett.*, **56**, 1932 (1986).

2 M. Fujii, and K. Yoshino, *Jpn. J. Appl. Phys.*, **27**, L457 (1988).

3 K. Yoshino, T. Kuwabara, and T. Kawai, *Jpn. J. Appl. Phys.*, **29**, L995 (1990).

4 M. Iseki, K. Saito, M. Ikematsu, Y. Sugiyama, K. Kuhara, and A. Mizukami, *J. Electroanal. Chem.*, **358**, 221 (1993).

5 M. Iseki, K. Saito, M. Ikematsu, Y. Sugiyama, K. Kuhara, and A. Mizukami, *Mat. Sci. Eng.*, **C1**, 107 (1994).

6 G. R. Mitchell, F. J. Davis and C. H. Legge, *Synth. Met.*, **26**, 247 (1988).

7 G. R. Mitchell, F. J. Davis, R. Cywinski, and W. S. Howells, *J. Phys. C: Solid State Phys.*, **21**, L411 (1988).

8 M. Iseki, K. Saito, K. Kuhara, and A. Mizukami, *Synth. Met.*, **40**, 117 (1991).

9 G. Maret, and K. Dransfeld, *Strong and Ultrastrong Magnetic Fields and Their Applications* (ed by F. Herlach, Springer-Verlag, Berlin Heidelberg, 1985) 143.

10 R. A. Bull, F. F. Fan, and A. J. Bard, *J. Electrochem. Soc.*, **129**, 1009 (1982).

11 I. Mogi, *Denki Kagaku*, **62**, 1295 (1994).

12 I. Mogi, and M. Kamiko, *J. Crystal Growth*, (in press).