Magnetic Field Effects on the Dopant-Exchange Process in Polypyrrole

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The electrochemical dopant-exchange (DE) process of *p*-toluenesulfonate-doped polypyrrole (PPy/TsO$^-$) was studied in LiClO$_4$ and LiBF$_4$ aqueous solutions under high magnetic fields of up to 12 T. The application of magnetic fields to the redox process of the PPy/TsO$^-$ film or to the electropolymerization process shifts the undoping potential of the TsO$^-$ ion to a positive or negative side, respectively. As a result, the magnetic fields allow control of the plastic behavior in the DE process of the PPy/TsO$^-$ film. These results are discussed in connection with the effect of the diamagnetic orientation.

Organic conducting polymers are of great potential interest from the point of view of the application to a neural element or an intelligent molecular device because they exhibit fractal growth,[1,2] the learning effect[3] and the electrical plasticity.[4,5] Doping and undoping processes in the conducting polymers, accompanied by large morphological changes, proceed gradually by repeating redox cycles. Yoshino et al. showed that the doping process of poly(3-alkylthiophene) is activated by repeating the doping–undoping process and implied that such a phenomenon can be related with the learning of the neural elements.[3] Iseki et al. reported that a *p*-toluenesulfonate-doped polypyrrole (PPy/TsO$^-$) film shows gradual activation in a dopant-exchange (DE) process during redox cycles in electrolytic solutions containing spherical anions (e.g. NO$_3^-$, ClO$_4^-$, and BF$_4^-$), and indicating some applications to devices simulating the synaptic plasticity.[5] The PPy/TsO$^-$ film has an anisotropic molecular organization, where the planes of aromatic rings lie preferentially parallel to an 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 involve considerable changes in the film morphology.[8]

It is well-known that most organic polymers have such a large anisotropy in diamagnetic susceptibility that they are subject to the diamagnetic orientation, resulting in the morphological changes, in magnetic fields.[9—12] Considering these facts, we made an attempt to control the plastic behavior in the DE process of the PPy/TsO$^-$ film by the magnetic field. In our previous paper[13] we reported the preliminary results of acceleration and retardation of the DE process by the magnetic fields. In this paper we show the magnetic field effects on the undoping process of the PPy/TsO$^-$ film and discuss the reasons why the magnetic fields are capable of controlling the plastic behavior in the DE process.

Experimental

All chemicals were of guaranteed reagent grade. The electrochemical measurements were done using an electrochemical analyzer BAS-100B/W which was composed of a potentiostat, a function generator, and a personal computer. The electrode system consisted of a platinum disk (ϕ 1.6 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 electropolymerization[14] (1.0 C cm^{-2}) at a constant potential (1.0 V) in a 0.1 M (1 M=1 mol dm^{-3}) pyrrole aqueous solution containing 0.1 M TsONa as a supporting electrolyte. A cyclic voltammogram (CV) of the PPy/TsO$^-$ film was measured in 0.1 M electrolytic aqueous solution (LiClO$_4$, LiBF$_4$, and TsONa) with a potential sweep rate of 50 mV s^{-1}.

The magnetic fields were generated by a water-cooled electromagnet (the Bitter solenoid) in the High Field Laboratory of Tohoku University, which can produce up to 15 T in a 82 mm bore with the maximum current of 21 kA.[15] The electrochemical cell was placed at the center of the magnet as shown in Fig. 1, and the temperature within the magnet was controlled at 20±0.1 °C by using a water-circulating thermoregulator. The magnetic field was applied perpendicularly to the surface of the working electrode and parallel to the faradaic current to eliminate the magnetohydrodynamic effect.[16]

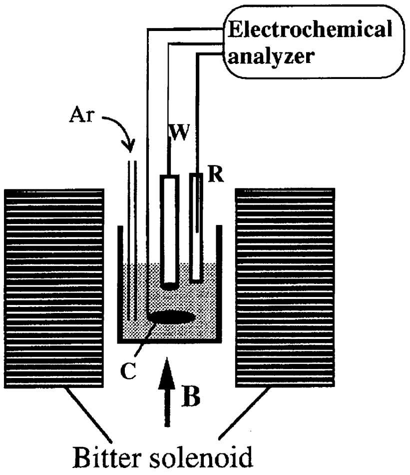

Fig. 1. Experimental setup of the electrochemical cell in the water-cooled electromagnet (Bitter-solenoid). W; a working electrode, R; a reference electrode, C; a counter electrode and B; a magnetic field.

Results and Discussion

Acceleration of the DE Process. We set out to examine the magnetic field effect on the DE process of the PPy/TsO$^-$ film electropolymerized in the absence of a magnetic field. In order to examine the plastic behavior of the DE process, we measured the CV of this film in a 0.1 M $LiClO_4$ aqueous solution in a potential range of −0.5—0.5 V, where a gradual current increase is clearly observed with repeating redox cycles. The undoping process in the PPy/TsO$^-$ film occurs at −0.6—−0.7 V,[17] hence the more negative potential sweep leads to rapid saturation of the current. On the other hand, the repeating potential sweep of −0.3—0.5 V results in only a slight current increase caused by the spontaneous DE process. The CV's were measured just after the immersion of the film into the $LiClO_4$ solution to eliminate the influence of the spontaneous DE process. Figure 2 shows the CV's (30 cycles) of the PPy/TsO$^-$ 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 3(a) 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 that such an effect is enhanced with increasing magnetic field (see Fig. 3(b)). This result shows that the magnetic field accelerates the DE process.

The first step of the DE process in the PPy/TsO$^-$ film is the undoping of the TsO$^-$ ions. We examined the magnetic field effect on the undoping process by measuring CV's over

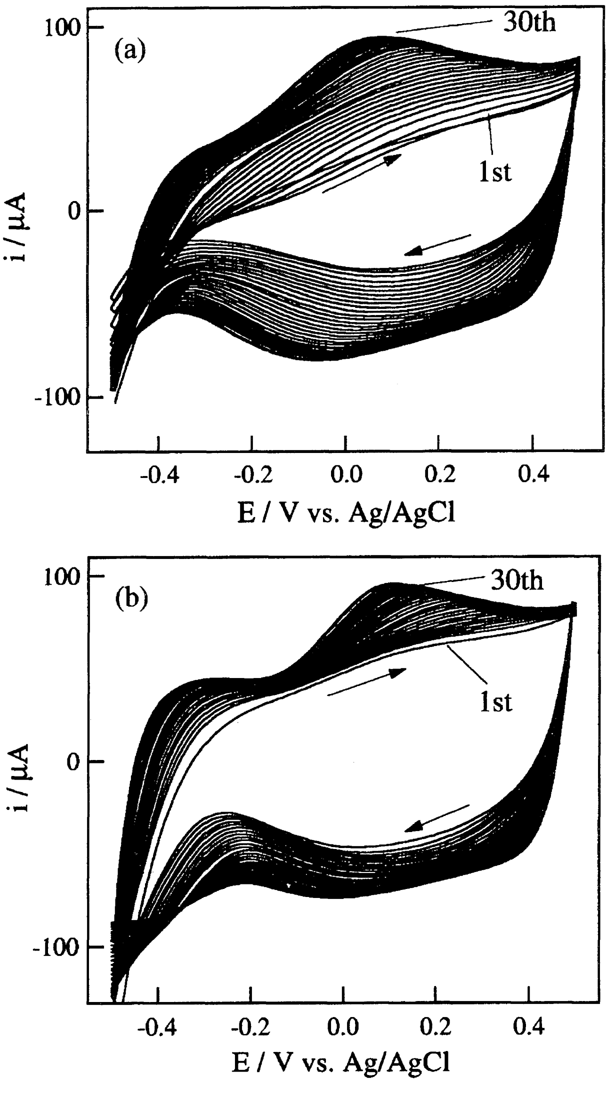

Fig. 2. Cyclic voltammograms of the PPy/TsO$^-$ film in a 0.1 M $LiClO_4$ aqueous solution in (a) 0 T and (b) 12 T. The film was electropolymerized in the absence of a magnetic field. The CV's were measured for 30 cycles after keeping the potential at −0.5 V for 2 s. The potential sweep rate was 50 mV s^{-1}, and arrows represent the sweep direction.

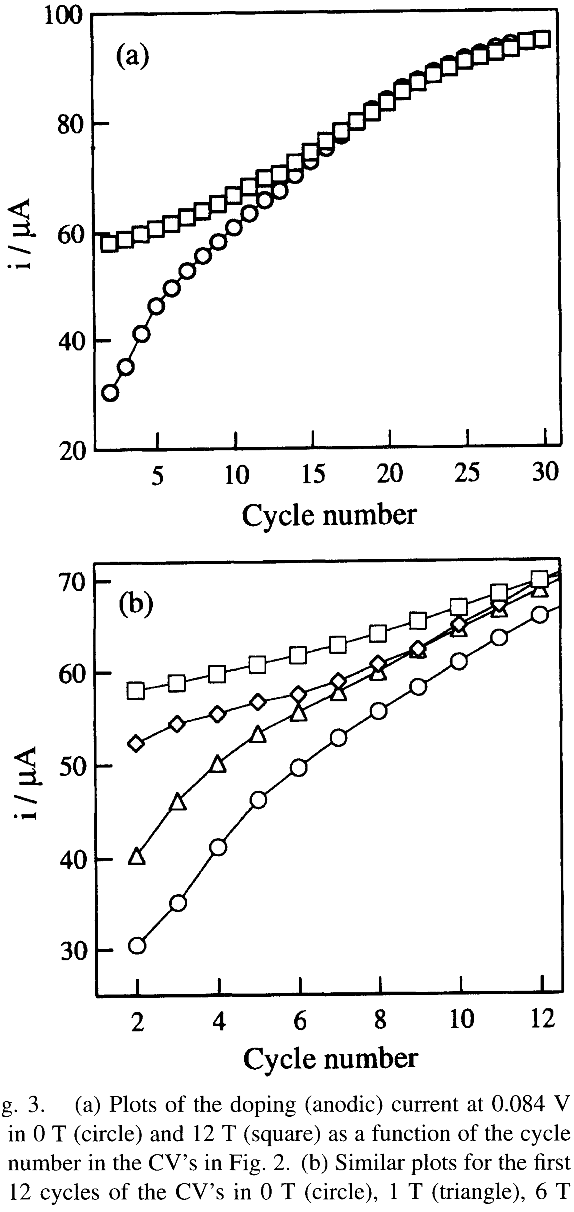

Fig. 3. (a) Plots of the doping (anodic) current at 0.084 V in 0 T (circle) and 12 T (square) as a function of the cycle number in the CV's in Fig. 2. (b) Similar plots for the first 12 cycles of the CV's in 0 T (circle), 1 T (triangle), 6 T (rhombus), and 12 T (square).

the more negative potential range of −0.9—0.5 V. Figure 4 shows the CV's (5 cycles) of the PPy/TsO$^-$ film in the 0.1 M $LiClO_4$ aqueous solution measured in (a) 0 T and (b) 12 T. A cathodic peak at ca. −0.7 V in the first cycle corresponds to the undoping of the TsO$^-$ ion.[17] While this peak lies around −0.7 V with repeating redox cycle in 0 T, it drastically shifts to more positive potentials at the first 3 cycles in 12 T (see Fig. 5). The shift of the peak potential surprisingly goes up to ca. 200 mV at the 3rd cycle, and the peak potential E_{pc} is −0.48 V at the 3rd—5th cycles. This results demonstrates that the magnetic field facilitates the undoping process of the TsO$^-$ ions.

The PPy/TsO$^-$ film has an anisotropic organization with the layered structure of PPy, in which the planes of aromatic rings lie preferentially parallel to the electrode surface and the dopant molecules lie between the PPy layers.[6] 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.[9,18] In the present experiment

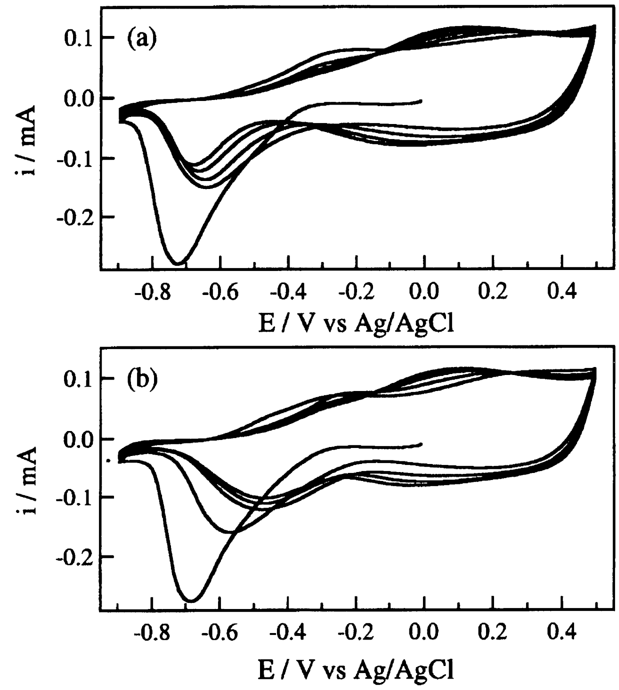

Fig. 4. Cyclic voltammograms of the PPy/TsO$^-$ film in a 0.1 M $LiClO_4$ aqueous solution in (a) 0 T and (b) 12 T. The film was electropolymerized in the absence of a magnetic field. The CV's were measured for 5 cycles with the potential sweep rate was 50 mV s^{-1}.

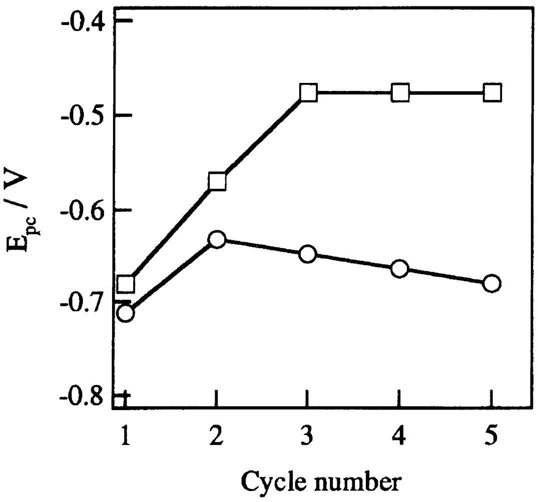

Fig. 5. Plots of the cathodic peak potential E_{pc} in 0 T (circle) and 12 T (square) against the cycle number in the CV's in Fig. 4.

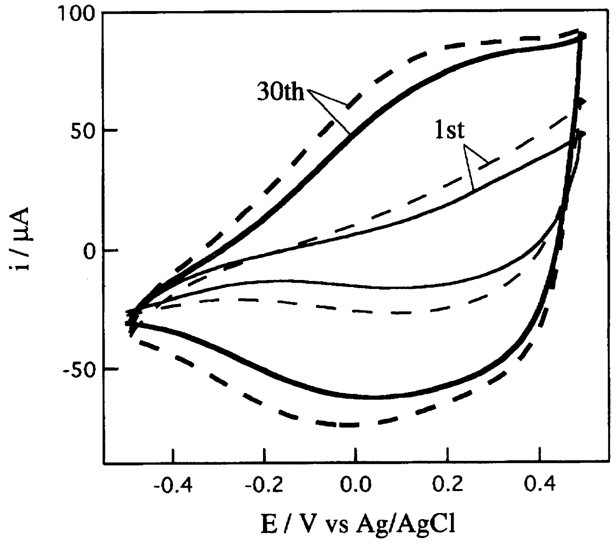

Fig. 6. Cyclic voltammograms (the 1st and the 30th cycles) of the PPy/TsO$^-$ film in a 0.1 M $LiBF_4$ aqueous solution in 0 T (solid) and 12 T (dashed). The film was electropolymerized in the absence of a magnetic field. The CV's were measured for 30 cycles with the potential sweep rate was 50 mV s^{-1} after keeping the potential at −0.5 V for 2 s.

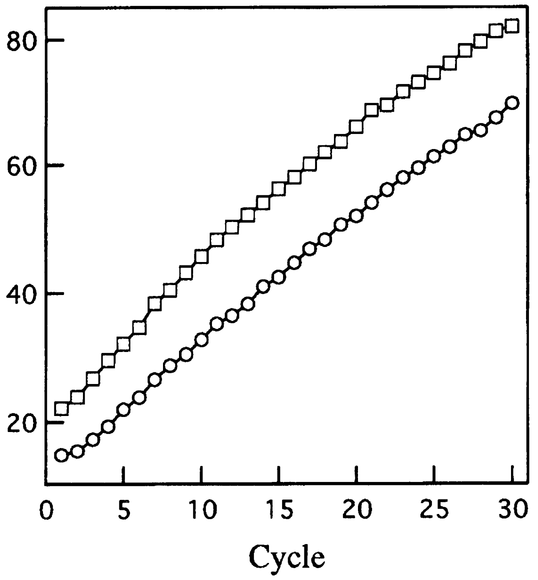

Fig. 7. Plots of the doping (anodic) current at 0.156 V in 0 T (circle) and 12 T (square) as a function of the cycle number in the CV's in Fig. 6.

the magnetic field is applied perpendicularly to the electrode surface. We thus speculate that the magnetic field degrades the anisotropic organization of the PPy/TsO$^-$ film during the repetition of the redox cycles, resulting in the facilitation of the undoping process. In the experiments to investigate the plastic behavior in the DE process, the potential sweep range is −0.5—0.5 V (Fig. 2). It is obvious that, in this potential range, the undoping proceeds slowly in 0 T and proceeds rapidly in 12 T (see Figs. 4 and 5). Consequently, the acceleration of the DE process by the magnetic fields is attributed to the facilitation of the undoping process.

We examined the magnetic field effect on the DE process in the solution containing another spherical anion. Figure 6 shows the CV's (the 1st and the 30th cycles) of the PPy/TsO$^-$ film in a 0.1 M $LiBF_4$ aqueous solution with and without the magnetic field of 12 T. The doping currents of the BF_4^- ion at 0.156 V are plotted in Fig. 7. A current increase is clearly seen over the whole cycles, indicating that in this system the magnetic field also accelerates the DE process. This result implies that the acceleration of the DE process by the magnetic fields occurs in the case that the DE process changes the film morphology from the anisotropic layered structure into the isotropic structure.

Retardation of the DE Process. We have tried to investigate the DE process of the PPy/TsO$^-$ film magneto-electropolymerized (electropolymerized in the magnetic field) in 12 T. The CV's (the 30th cycle) of the films electropolymerized with and without the magnetic field are shown in Fig. 8, where the CV's were measured in the absence of a magnetic field in 0.1 M $LiClO_4$ (Fig. 8(a)) and 0.1 M $LiBF_4$ (Fig. 8(b)) solutions. Figure 9 shows the plots of the doping currents in both CV's as a function of the cycle number. The PPy/TsO$^-$ film magneto-electropolymerized in 12 T shows only a slight current increase in both solutions, losing the plastic behavior. Such retardation of the DE process was also observed in the PPy/TsO$^-$ film magneto-electropolymerized in the fields higher than 1 T.

We examined the undoping potential of the magneto-electropolymerized PPy/TsO$^-$ films in a 0.1 M TsONa solution

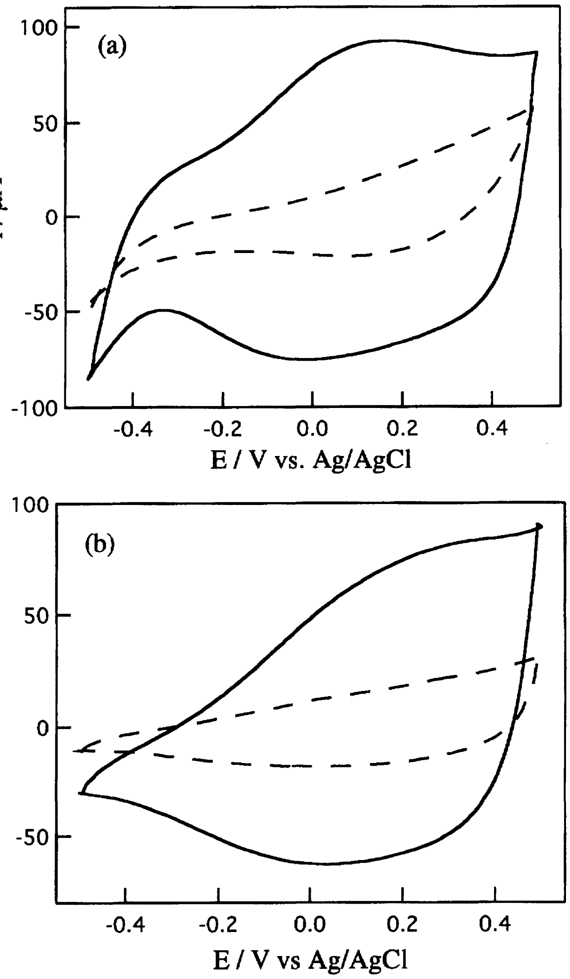

Fig. 8. Cyclic voltammograms (the 30th cycle) of the PPy/TsO$^-$ film electropolymerized in 0 T (solid line) and 12 T (dashed line). The CV's were measured in the absence of a magnetic field in a 0.1 M (a) $LiClO_4$ or (b) $LiBF_4$ aqueous solution with the potential sweep rate of 50 mV s^{-1} after keeping the potential at −0.5 V for 2 s.

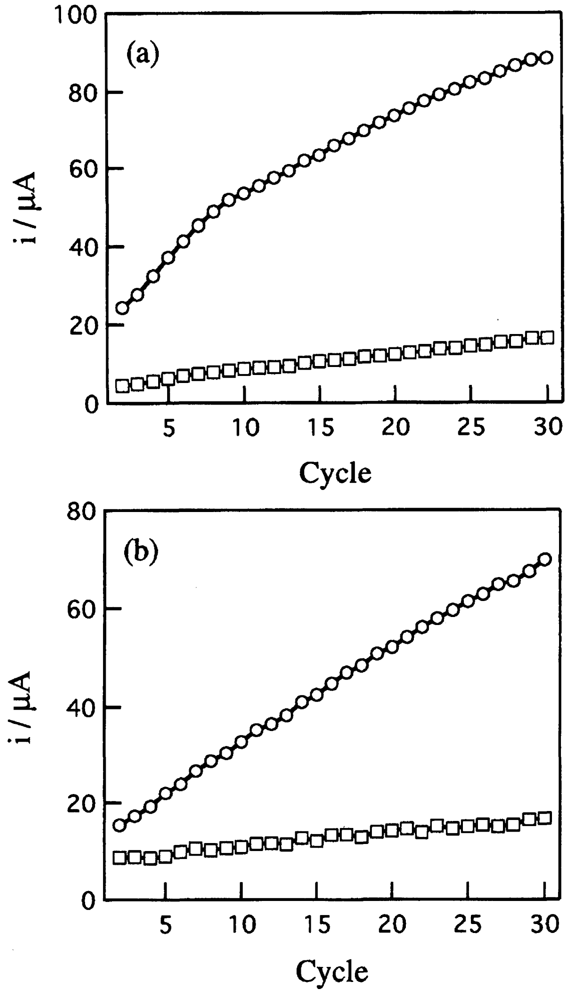

Fig. 9. Plots of the doping (anodic) currents of (a) the ClO_4^- ion (at 0.084 V) and (b) the BF_4^- ion (at 0.156 V) in the 0 T-film (circle) and the 12 T-film (square) as a function of the cycle number in the CV's in Fig. 8.

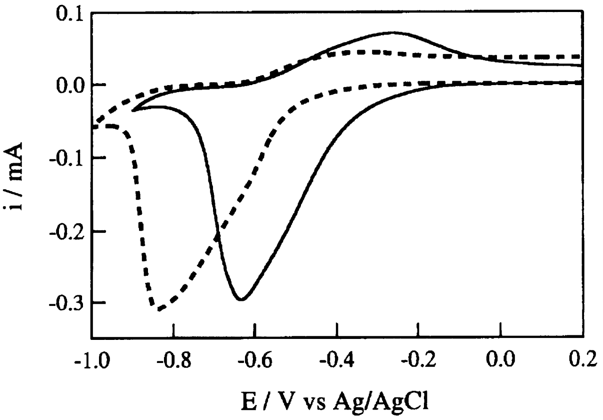

Fig. 10. Cyclic voltammograms of the PPy/TsO$^-$ film electropolymerized in 0 T (solid) and 12 T (dashed). The CV's were measured in a 0.1 M TsONa aqueous solution with a potential sweep rate of 50 mV s^{-1} in the absence of a magnetic field.

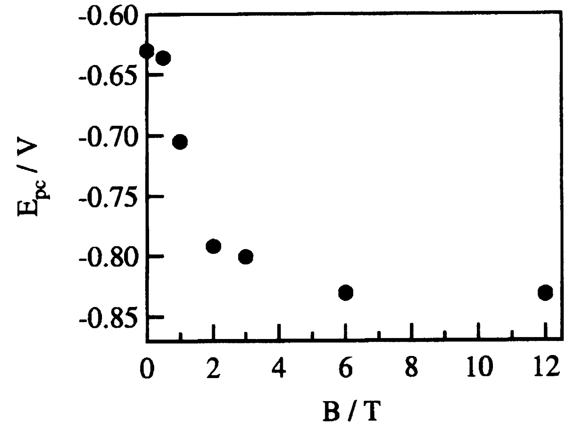

Fig. 11. Cathodic peak potential E_{pc} in the CV's of the PPy/TsO$^-$ films versus the magnetic field B in which the films were electropolymerized.

in the absence of a magnetic field. Figure 10 shows the CV's of the PPy/TsO$^-$ films electropolymerized in 0 T and 12 T. A characteristic reduction peak at −0.63 V in the 0 T-film, corresponding to the undoping of the TsO$^-$ ion,[17] lies at the more negative potential of −0.83 V in the 12 T-film. The undoping peak potentials E_{pc} of the magneto-electropolymerized films are plotted as a function of the magnetic field B in Fig. 11. The peak potential drastically changes around 1 T, and the potential shift surprisingly goes up to −200 mV for the 6 T- and 12 T-films. We made a similar experiment on a PPy/ClO$_4^-$ film, which has an isotropic structure. No remarkable change was observed in the CV's of the magneto-electropolymerized PPy/ClO$_4^-$ films.

Our previous paper[19] showed that magnetic fields drastically change the growth morphology of electropolymerized PPy/TsO$^-$ in a quasi two-dimensional space. PPy/TsO$^-$ grows into a diffusion-controlled fractal pattern in 0 T and a kinetic-controlled closed pattern in 0.5 T. The micrograph of the latter showed that the organization of the polymer is dense aggregates of needle-like branches, resulting from the diamagnetic orientation of the aromatic planes. The magneto-electropolymerized PPy/TsO$^-$ film is thus considered to be so rigid that the higher energy is necessary for the migration of the dopant anions within the film, resulting in the negative shift of the undoping peak potential. The fact that the magneto-electropolymerized PPy/ClO$_4^-$ films exhibit no remarkable change in the CV's indicates that the influence of the diamagnetic orientation is most effective on the polymers with the anisotropic layered structure, like the PPy/TsO$^-$ film.

As regards the DE process in the magneto-electropolymerized PPy/TsO$^-$ films, the retardation occurs in both LiClO$_4$ and LiBF$_4$ solutions and appears to be almost independent of exchange anions in the electrolytic solutions. In the potential sweep range of −0.5—0.5 V (Fig. 8), the undoping of the TsO$^-$ ion easily proceeds in the 0 T-film, while it hardly proceeds at all in the 12 T-film (see Fig. 10). Hence, the negative shift of the undoping potential of the TsO$^-$ ion leads to the retardation of the DE process in the magneto-electropolymerized films.

Conclusion

We have shown two opposite effects of the magnetic field on the DE process in the PPy/TsO$^-$ film; the acceleration by the magnetic fields and the retardation by the magneto-electropolymerization. These effects has been proven to arise from the positive and negative shifts of the undoping potential of the TsO$^-$ ion, respectively, and can be attributed to the diamagnetic orientation of the polymer. The feasibility of control of the plastic behavior or the learning effect is essential for the application to intelligent molecular devices.

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