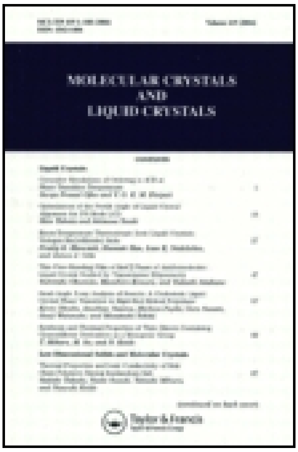

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Soft Actuators Based on Poly(3-alkyl thiophene) Films Upon Electrochemical Oxidation and Reduction

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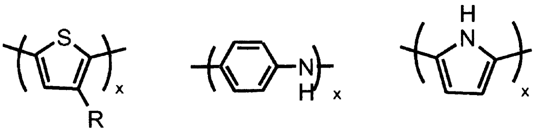
Expansion and contraction in poly(3-alkylthiophene), with alkyl = hexyl and dodecyl, films upon electrochemical oxidation and reduction are measured. The expansion of films is found to consist of two components, which are responding to electrochemical cycle and creeping. The expansion ratio and the creeping are discussed taking the morphology of films into consideration, and compared with the case of polyaniline and polypyrrole.

Keywords; Conducting polymers, Soft actuators, Polythiophene, Polyaniline, Polypyrrole, Electrochemistry

INTRODUCTION

Upon oxidization and reduction, the conducting polymers change physical properties as in the manner of swelling and contraction.[1-5] The change of dimension upon electrochemical cycle is called electrochemomechanical deformation, ECMD, which can be utilized as soft actuators. The mechanism of ECMD has been revealed[4-8] to be due to (1) insertion and extraction of bulky ions, (2) conformation



(a) (b) (c)

FIGURE 1 Chemical structures of (a) Poly(3-alkylthiophene), R=C_6H_{13}; PAT6, R=$C_{12}H_{25}$; PAT12, (b) Polyaniline and (c) polypyrrole.

change of structure resulted from delocalization of π-electrons and (3) electrostatic repulsion between like charges. It has been shown that actuators based on conducting polymers generate greater force than that of gel[9] and ion exchange resin[10]. However,the quantitative measurements for various conducting polymers have not been carried out sufficiently.

In this paper, behaviors of ECMD in poly(3-alkylthiophene), PAT shown in Figure1(a) film will be mentioned comparing with those of polyaniline, PAn[4-6] and polypyrroles, PPy[7] as shown in Figure 1 (b) and (c), respectively, with respect to the expansion/contraction ratio.

SAMPLE PREPARATION AND MEASUREMENTS OF ECMD

Poly(3-hexylthiophene) shown in Figure 1(a), where R=C_6H_{13} as define by PAT6 and poly(3-dodecylthiophene), R=$C_{12}H_{25}$ as PAT12 were purchased from Aldrich Chemical Co. Ltd. The PAT6 and PAT12, of which coupling are precisely controlled at 2,5 positions of thiophene ring, are named head-tail, HT-PAT. HT-PAT films are distinguished from the PAT prepared by conventional method[11] using $FeCl_3$, as defined non-regiocontrolled, NR-PAT. HT-PAT is rather straight, plane and rod-like structure compared with those of NR-PAT, which should be twisted, bent and coil-like structure. It is known that NR-PAT films are less crystalline and lower densities,[11] contrasting to the HT-PAT. PAT films are prepared by casting 5wt% chloroform solution on glass substrate. The thickness of films was approximately 50 μm. Au was deposited on one side of the films with the thickness of approximately 25 nm. PAn film was obtained chemical polymerization of monomers, followed by casting the N-methyl-2-pyrroridinone (NMP) solution.[5-6] PPy film[7] was prepared by an electrodeposition in an aqueous solution of NaCl. The PAn and PPy films were used without Au deposition because of their higher conductivity. The films were cut into rectangular strips with the typical dimension of 15 × 1 mm^2 and the weight was approximately 1 mg for the ECMD measurement.

The electrochemical cells and experimental setup have been described in elsewhere.[5-8] In the measurement of ECMD 0.2 M tetra-n-butylammonium tetrafluoroborate, TBABF$_4$/acetonitrile was used for PAT films as an electrolyte solution, an aqueous electrolyte of 1M HCl and 1M NaCl ware used for PAn and PPy, respectively. The scan rate of electrochemical cycle was 5 mV/s.

RESULTS AND DISCUSSION

Upper and lower curves in Figure 2 depict the typical cycle responses of the current and the expansion ratio of $\Delta l/l_0$ of ECMD in HT-PAT6 film, where $\Delta l = l\text{-}l_0$ and l_0 is the film length at the beginning and l is that at cycling. The upward direction of current and $\Delta l/l_0$ are the oxidization and the elongation of films, respectively. The ECMD of film consists of two components of responding to each redox cycle and creeping behavior. It is found that the PAT films easily break

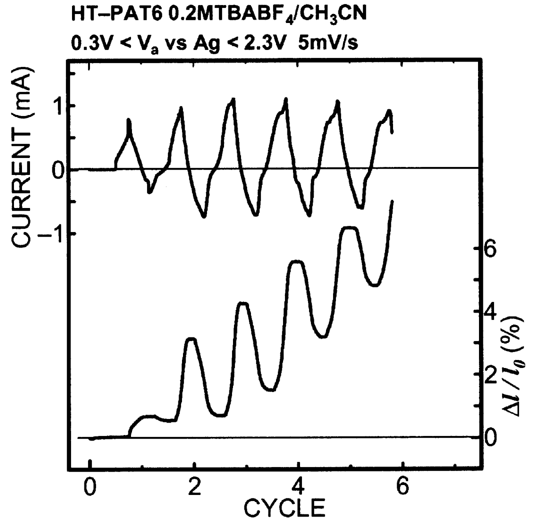


FIGURE 2 Cycle dependencies of current and expansion ratio, $\Delta l/l_0$ of (a) HT-PAT6 in an electrolyte solution of 0.2 M TBA BF4/acetonitle.

downned upon several cycles under the load strain of 0.2 MPa, which contrasts to the case of PAn and PPy which are stable for the load strain of 5MPa and more than several tens cycles[12]. NR-PAT6 showed a large creeping, compared with that of HT-PAT6, indicating that the coil-like structure of NR-PAT is easily expanded upon even weak load strain.

In order to analyze and compare the data obtained for various conducting polymers, the injected charge dependence of the stroke is evaluated. The electrochemical reaction of a conducting polymer (CP) for the monomer unit is shown by,[13]

$$CP - ye^- + yA^- \rightarrow CP^{+y}A^{-y}, \qquad (1)$$

where, y is the number of electrons withdrawn from the unit or degree of oxidation. The y is defined as $y = Mq/mF = QM/F$,
where M is molecular weight per monomer unit [g/mol], q is the amount of injecting electric charges [C], m is the weight of conducting polymer film employed [g], and F is Faraday constant. The amount of injected electric charge (q) is estimated by integrating the current. Q ($= q/m$) is the amount of injecting electric charges per unit weight of conducting polymer [C/g].

Curves in Figure 3 show the Q dependence of $\Delta l'/l_0$ for various PAT films, where $\Delta l'$ is the stroke or the change of film length from

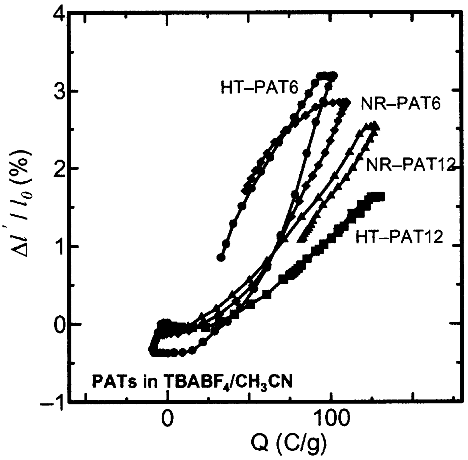


FIGURE 3 Characteristics of $\Delta l'/l_0$ vs. Q for various PAT films.

the oxidation of each cycle. It is noted that all curves did not return to their original position. For the horizontal axis this is due to the coulomb efficiency less than 100%, which depends on the level of oxidation and impurity in electrolyte solution, as well as due to the accumulation of charge in film. For the vertical axis, the creeping effect is responsible to this. It is known that the maximum stable oxidation is 0.07 per π-electron. From the data of Figure 3, y = 0.17 is obtained for PAT6 at Q=100 [C/g] which is the half of fully oxidized state. This fact suggests that the stroke of NR-PAT6 is expected to reach 6 % at full oxidation, regardless of creeping. On the other hand, PAT12 films at Q=130 [C/g], which corresponds to y=0.34 and fully oxidized level, shows $\Delta l'/l_0$ being 1.5~2.5 % including the creeping. The PAT6 films generally show larger stroke with smaller injected charge compared with that of PAT12. This results from that in PAT12 longer alkyl chain does not contribute to oxidation and expansion, whereas PAT6 with shorter alkyl chain is more compact and efficient to the expansion. On the other hand, for PAT6 a large hysterisis was observed in $\Delta l'/l_0$ vs Q curves, which is partially due to the large creeping effect and slow electrochemical reaction compared with those of PAT12 film.

The cyclic voltammogram and ECMD behavior in PAn and PPy

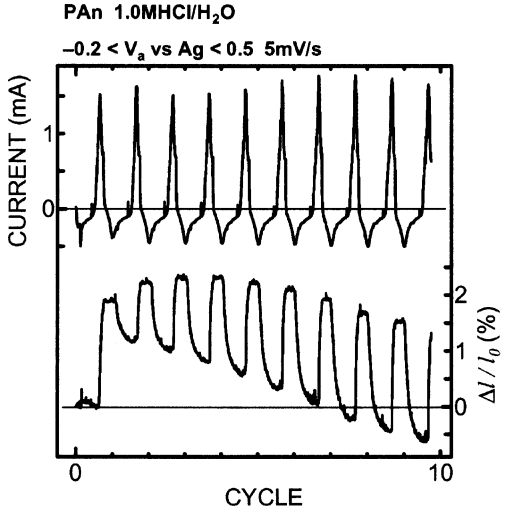


FIGURE 4 Cycle dependencies of current and expansion ratio, $\Delta l/l_0$ of PAn in the electrolyte solution of 1M HCl.

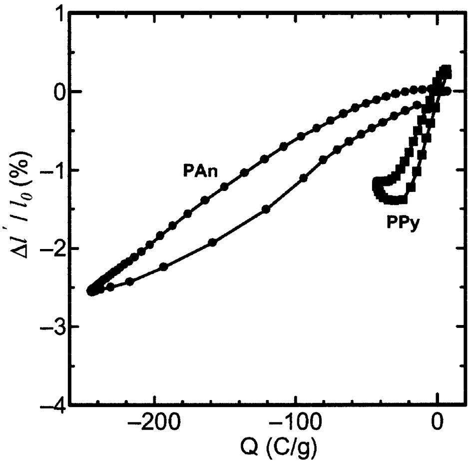


FIGURE 5 Characteristics of $\Delta l'/l_0$ vs. Q at 10th cycle for PAn in 1M HCl/H_2O and PPy in 1M NaCl/ H_2O.

films have been studied in our previous papers in detail.[5-8,12] Figure 4 shows a typical cycle dependence of current and $\Delta l/l_0$ responses in PAn,[12] demonstrating quite stable operation compared with that of PAT films. Namely, in PAT films operated in non-aqueous electrolyte,moisture and oxygen affect seriously on the electrochemical reaction. Small creeping effect observed in PAn is due to the high tensile strength originated from morphology and or entanglement of fibrils.

The $\Delta l'/l_0$ vs. Q curves at 10th cycle in PAn and PPy films are shown in Figure 5 to compare with the result of PAT films. The curves return back to the original coordinate, indicating the high coulomb efficiency and very small creeping effect for PAn and PPy. Since PAn and PPy films are obtained and stable at fully doped state, the fully doped state were employed as the starting material for electrochemical reaction, and placed at origin of the coordinate of $\Delta l'/l_0$ vs. Q plot. The electrochemical reduction of PAn and PPy films from the fully doped state is taking place by releasing anion or Cl^- ions from the film until use up of the available anion or the conductivity. At the maximum Q of −250 [C/g] for PAn, the degrees of reduction are estimated to be y = 0.24. The fact indicates that the largest expansion/contraction ratios are expected to be 4.4 % for PAn, when the maximum stable oxidation level of y = 0.42 is attained. It should be noted that the magnitude of expansion/contraction ratio of PPy film is much larger with respect to the Q in comparison with those of PAn and PAT. The saturation of stroke observed in PPy is not known at the present stage. At $Q = -50$[C/g], y of PPy is 0.04, which corresponds to only 14% of fully reduced state of y = 0.28, indicating that the largest stroke of more than 10 % is expected in PPy film upon the operation of full width of oxidation and reduction. In other words, the rate of expansion with respect to the Q is largest in PPy films, when the slops of $\Delta l'/l_0$ vs. Q curves are compared for the other polymers.

As a resultant, the expansion/contraction ratio of PAT films is found to be comparable to PAn and PmAn films. However, the tensile strength of PAT films is much smaller than that of PAn and PPy films. Also for the stable operation of PAT films in non-aqueous electrolyte, the sealing from oxygen and moisture is required to avoid the degradation of films.

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