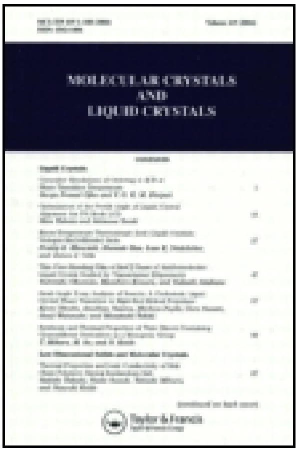

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Characterization of Pyrrole Copolymer Soft Actuators Prepared by Electrochemical Polymerization Pyrrole and Diethyl 3,4-pyrroledicarboxylate

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Characterization of Pyrrole Copolymer Soft Actuators Prepared by Electrochemical Polymerization Pyrrole and Diethyl 3,4-pyrroledicarboxylate

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Polypyrrole (PPy) actuators, which expand and contract by doping and dedoping ions in an electrolyte solution, have been reported to have a large strain under a large stress. However, many of these actuators exhibited notable electrochemical creep (swelling) after repeated electrochemical actuations. Here, actuator films were prepared by electrochemical polymerization of pyrrole and diethyl 3,4-pyrroledicarboxylate with different mol ratios. The actuating strain of the film actuators prepared from a solution of pyrrole and diethyl 3,4-pyrroledicarboxylate with 97:3 mol ratio showed significant reduction of the electrochemical creep with minimal reduction of the actuating strain.

Keywords: Soft actuator; creep; polypyrrole; diethyl 3; 4-pyrroledicarboxylate; LiTFSI

1. Introduction

Organic soft actuators made of conducting polymers such as polypyrrole (PPy) films are of special interest for application in microelectromechanical systems (MEMS) because they generate large electrochemical stresses between 3 and 5 MPa [1–5]. Their electrochemical strains were between 1 and 3%. Recently, it has been reported that some PPy actuators exhibit strains of more than 10% [6–13]. On the other hand, it should be noticed that these PPy actuators usually exhibited notable electrochemical creep (swelling) after repeated electrochemical actuations. The actuating strain corresponds to the dynamic length change of the actuator dependent on the repeated potential sweeps, while the electrochemical creep was defined to the continuous length change (swelling) during the actuation process. For precise positioning of the actuators, the electrochemical creep is the serious problem in the practical use and needs to be minimized. Tominaga *et al.* have recently reported that chemical cross-link in polypyrrole with di-pyrrole alkanes suppressed the creep, however, the actuating strain also decreased [14].

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We tried to modify polypyrrole by introducing pyrrole derivative units into the framework of polypyrrole and adjust its actuator performances. In this paper, actuator films were prepared from solutions with different mole ratios of pyrrole (Py) and diethyl 3,4-pyrroledicarboxylate. The behaviors of the actuating strain and the electrochemical creep of these films were compared.

2. Experimental Procedures

The molecular structures of monomers (pyrrole and diethyl 3,4-pyrroledicarboxylate) used here are illustrated in Fig. 1. The electrochemical polymerization of pyrrole and diethyl 3,4-pyrroledicarboxylate was carried out using a computer-controlled potentio-galvanostat (Hokuto Denko HZ-5000). A counter electrode (Ti), a reference electrode (Ag/AgCl), and a working electrode (Ti) were immersed into methyl benzoate solutions of 0.25 M of pyrrole and diethyl 3,4-pyrroledicarboxylate with 100:0, 97:3, 95:5, 93:7, 90:10 mol ratios and 0.2 M N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide, and the potential voltage was controlled to keep a constant current of 0.55 $mAcm^{-2}$ for 4h at 20°C between the counter electrode and the working electrode. The polymerization of the films using the solutions was successful. However, only black powders were deposited when using the solution containing more than 7 mol% of 3,4-pyrroledicarboxylate, implicating that too much introduction of diethyl 3,4-pyrroledicarboxylate units disturbed the fabrication of continuous copolymers films. The thickness of the prepared films was measured to be approximately 100 μm using a micrometer. The obtained films were peeled off from the electrode, rinsed with acetone, and dried in air. The PPy films were cut into 20×5 mm^2 strips to form the PPy actuators.

Fourier transform infrared (FT-IR) spectroscopic measurements were performed using Shimazu FT-IR 8900 with an attenuated total reflectance (ATR) method. The electrochemical profiles of the polymers were investigated using cyclic voltammogram (CV) method.

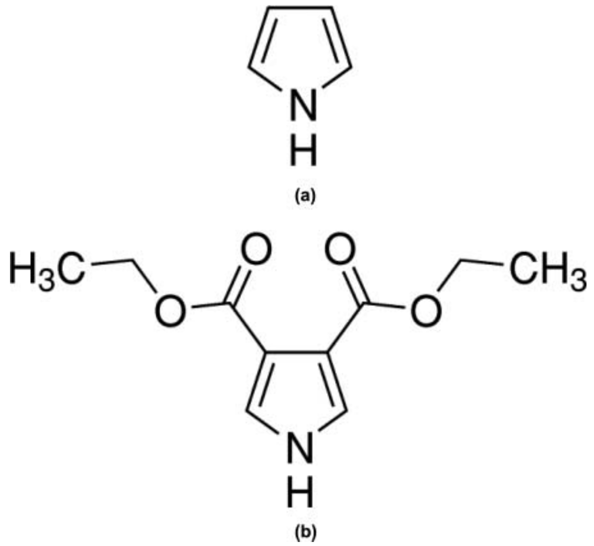

Figure 1. Molecular structures of (a) pyrrole and (b) diethyl 3,4-pyrroledicarboxylate.

Standard four probe method was used to measure the electrical conductivity at room temperature. The surface morphology of the deposited films were observed using a scanning electron microscope (SEM).

The actuator characterization system to measure the actuating strain and the electrochemical creep under a load stress was described elsewhere [13]. The PPy actuator was used as the working electrode in the 1 M LiTFSI aqueous electrolyte solutions. Both of the PPy actuator ends were clipped with two metal plates. The PPy actuator exhibited the expansion and contraction motions under an alternating potential with the triangular wave shape applied between the actuator films and the counter electrode. The potential voltage applied between the PPy actuator and the electrolyte solution was monitored using the Ag/AgCl reference electrode. The peak values of the potential voltage were -1 and +1 V, and the potential sweep rates were 10 mVs^{-1}. A load stress of 0.3 MPa was applied on the actuator films.

3. Results and Discussion

The FT-IR spectra of the electrochemically polymerized films are shown in Fig. 2. In case of the PPy film without containing diethyl 3,4-pyrroledicarboxylate units, the characteristic band for the pyrrole ring fundamental vibration appeared at 1558 cm^{-1}, and the C-H in-plane vibration and C-N stretching vibration appeared at 1276 and 1092 cm^{-1}, and 1164 cm^{-1}, respectively [15]. All of these peaks were also observed in the films of copolymers. While, the incorporation of diethyl 3,4-pyrroledicarboxylate units with electron-donating groups may have resulted in these band shifts towards lower wavenumbers.

The electrical conductivities of the PPy and the Py copolymers prepared from solutions with different mole ratios of pyrrole and diethyl 3,4-pyrroledicarboxylate were 12, 3.2 and 2.3 S/cm, respectively (summarized in Table 1). The conductivity usually depends on the chemical structure, molecular weight and the film morphology of polymers. These measured

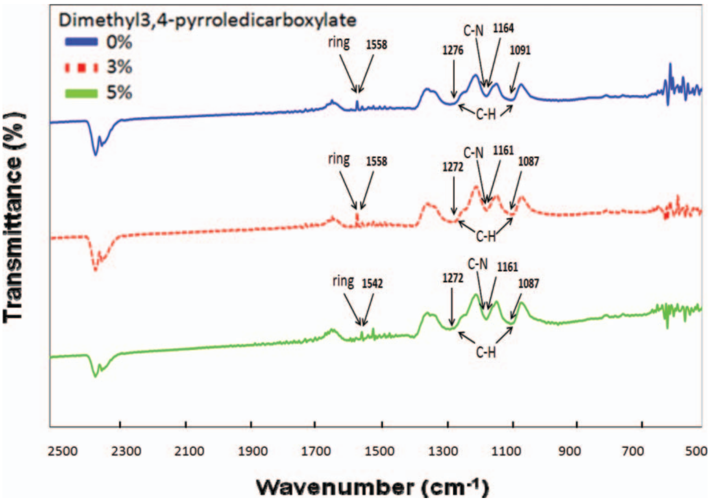

Figure 2. Comparison of FTIR spectra for the 3 films fabricated from pyrrole solutions containing 0, 3, and 5 mol% diethyl 3,4-pyrroledicarboxylate.

Table 1. Comparison of FT-IT peak positions and electrical conductivities for the films grown in pyrrole solutions containing 0, 3, and 5 mol% diethyl 3,4-pyrroledicarboxylate.

Concentration of diethyl 3,4-pyrroledicarboxylate	FT-IR peak positions (cm^{-1})			Electro conductivity (S/cm)
	Ring	C-H	C-N	
0% (PPy)	1558	1092, 1276	1164	12
3%	1558	1087, 1272	1161	3.2
5%	1542	1087, 1272	1161	2.3

results seem to suggest that the copolymers were different from PPy, and more diethyl 3,4-pyrroledicarboxylate units were incorporated into the PPy chains as the concentration of diethyl 3,4-pyrroledicarboxylate increased.

The electrochemical profiles for the PPy, Py copolymers are shown in Fig. 3, and these CV curves were measured in LiTFSI solutions with the potential sweep rate of 10 mVs^{-1}. The PPy and the Py copolymers denoted quasi-reversible profiles. Although oxidation and reduction onsets were not clearly seen, the Py copolymers showed different CV profiles from that of the PPy. These results indicate that the incorporation of diethyl 3,4-pyrroledicarboxylate units into the framework of PPy chains resulted in the weak change of electrochemical properties of PPy.

Figure 4 shows comparisons of the SEM images of the three films taken from the liquid-side and the electrode-side. The films were peeled off from the Ti working electrode after the polymerization was completed, and the electrode-side of the PPy/Py copolymer films means the surface of the PPy/Py copolymer films on the electrode side. Although the liquid-side surfaces of these films looked similar, the structures seen from the electrode sides were very different. The structures observed from the electrode-sides seem to reflect the internal porus and sponge-like structures in these films. The PPy film had very porus structures [Fig. 4 (a)], and these porus structures gradually disappeared as the increase of diethyl 3,4-pyrroledicarboxylate units in the Py copolymers [Fig. 4 (b), (c)]. Therefore,

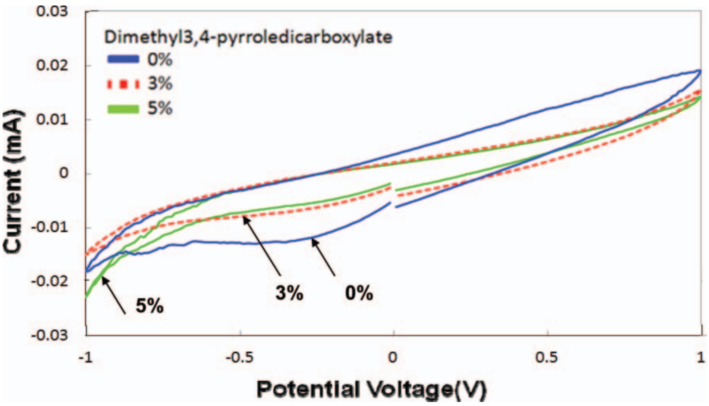

Figure 3. Cyclic voltammograms for PPy and Py copolymer films in LiTFSI solution with the potential sweep rate of 10 mVs^{-1}.

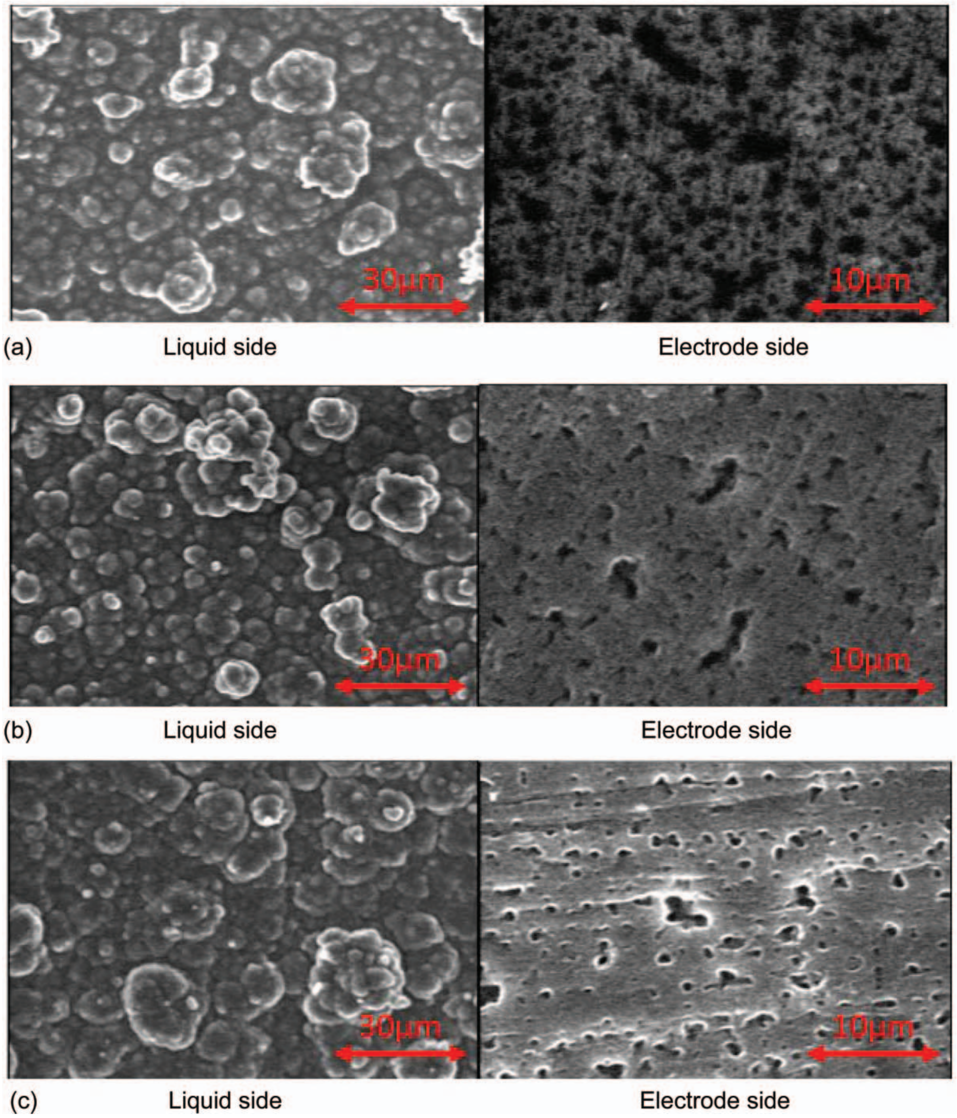

Figure 4. SEM micrographs for surface and electrode side of the films fabricated from solutions containing 0, 3, and 5 mol% diethyl 3,4-pyrroledicarboxylate, denoted as (a), (b), and (c), respectively.

it is interesting to know how the molecular structure change and the morphology change influence the soft actuator performances.

Figure 5 shows the time dependences of the strain of the actuators as measured by the displacement of the weight as a function of time under the load stress of 0.3 MPa. The strain was defined as the length change of the PPy/Py copolymers actuators divided by the length prior to deformation. No potential voltage was given for the first 30 s, and after that the repeated voltage sweeps with a period of 400 seconds at the potential sweep rate of 10 mVs^{-1} were applied to the PPy actuators. The characteristics of the actuators were measured in the aqueous solutions of LiTFSI.

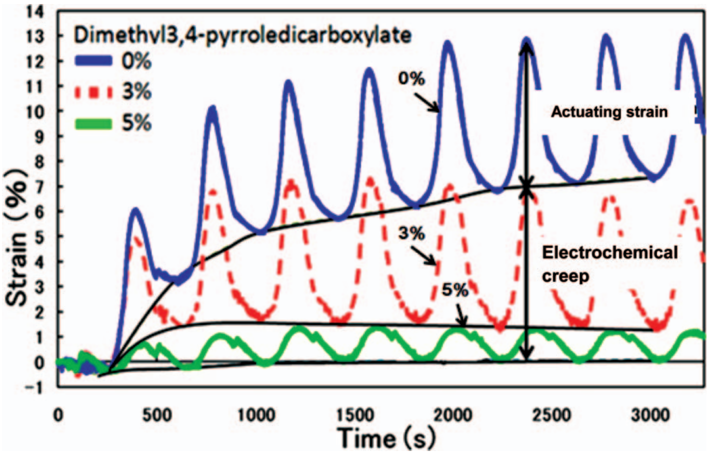

Figure 5. Relationships between the strain and time of actuators under repeated actuations in the LiTFSI aqueous solution with the potential sweep rate of 10 mVs^{-1}. The load stress during the actuation was 0.3 MPa. The actuators fabricated from pyrrole solutions containing 0, 3, and 5 mol% diethyl 3,4-pyrroledicarboxylate were compared.

The PPy actuator showed an actuating strain of 6%. However, the electrochemical creep increases to around 6.8% after 6 cycles of actuation. In contrast, the Py copolymer film, fabricated from pyrrole solution containing 3 mol% of diethyl 3,4-pyrroledicarboxylate showed an actuating strain of 5.4%, and the electrochemical creep dramatically reduced to 1.3%. The Py copolymer film, fabricated from pyrrole solution containing 5 mol% of diethyl 3,4-pyrroledicarboxylate showed a reduced actuating strain of approximately 1%, but the creep strain reduced to 0%. Table 1 compares the actuating strains and the electrochemical creep of the three PPy actuators. It should be noted that the previous method using the cross-linking of PPy actuators resulted in reductions of both the actuating strain and the electrochemical creep [14]. However, the Py copolymer film, fabricated from pyrrole solution containing 3 mol% of diethyl 3,4-pyrroledicarboxylate maintains the actuating strain while reducing the electrochemical creep dramatically. These results are summarized in Table 2.

Plausible explanations for the improved mechanical characteristics of the actuators have not yet been clear. However, the modification of PPy structures by adding suitable kinds of chemicals could lead to improved electrochemical creep for better positioning of PPy soft actuators.

Table 2. Comparison of actuating strains and electrochemical for the films grown in pyrrole solutions containing 0, 3, and 5 mol% diethyl 3,4-pyrroledicarboxylate.

Concentration of diethyl 3,4-pyrroledicarboxylate	Actuating strain		Electrochemical creep	
	2nd cycle	6th cycle	2nd cycle	6th cycle
0% (PPy)	6.9%	6.0%	3.2%	6.80%
3%	5.30%	5.4%	1.5%	1.3%
5%	1.0%	1.0%	0.0%	0.0%

4. Conclusion

PPy and its copolymer films were deposited using electroplymerization in the mixtures of pyrrole and diethyl 3,4-pyrroledicarboxylate. The actuation strain of the Py copolymer film actuator, fabricated from pyrrole solution containing 3 mol% of diethyl 3,4-pyrroledicarboxylate showed significant reduction of the electrochemical creep with minimal reduction of the actuating strain.

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