



Templated polypyrrole electro-polymerization: Self-assembled bundles of bilayer membranes of amphiphiles and their actuation behavior

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Received 16 January 2007; received in revised form 16 July 2007; accepted 23 July 2007

Available online 4 September 2007

Abstract

The electrochemical properties of conducting polymers are highly dependent on the microstructure. We report a method to produce specific microstructures of polypyrrole through electro-polymerization in the presence of the amphiphile *N*-{11-(2-hydroxyethyl)dimethylammonium)undecanoyl}-*N,N'*-dioctyl-L-glutamate, bromide, which forms supramolecular hydrogels with pyrrole in aqueous solution. These hydrogels were used as templates during polypyrrole electro-polymerization to give microstructures composed of the bundles of bilayer membranes. The highly porous nature of these films resulted in electrochemical properties superior to polypyrrole deposited under the same condition without use of an amphiphilic template. Analysis of the scan rate dependence on cyclic voltammogram reveals that the porous templated films facilitate fast diffusion of dopant ions. The actuation properties were also investigated in aqueous solutions containing sodium *p*-toluene sulfonate electrolyte. The strains displayed by the template polypyrrole films were twice those synthesized without the use of a template.

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Keywords: Polypyrrole; Self-assembly; Electro-polymerization; Actuation properties

1. Introduction

Actuator devices based upon electrochemical oxidation of conducting polymers such as polypyrrole (PPy), polythiophene, and polyaniline are attractive for many emerging applications, including medicine and robotics. It is well known that the electrochemical behavior and mechanical properties of the conducting polymers depend significantly on their chemical structure, the conditions by which they are synthesized, and their microstructure. Given that the microstructures of conducting polymers have a large influence on their electrochemical behavior [1], optimization of their properties ideally involves new methods to control this feature. There are a variety of routes to control the microstructures of conducting polymers. Of these, template-based polymerization using self-assembly

methods stands out as one of the most promising routes to control conducting polymer microstructures [2–9]. Previous template-based polymerization method and controlling conducting polymer microstructure have focused on producing films by chemical oxidation [9]. To produce actuators devices that can be electrochemically cycled it is important to produce free-standing films with optimal electroactivity. These films are best prepared by electrochemical deposition and hence the focuses of our efforts have been on extending template methods to produce freestanding with the mechanical and electrical properties needed to produce films for actuator applications.

Kunitake et al. has reported that bundles of bilayer membranes, which were composed of amphiphiles, could be utilized as an organizational element to create highly regioregular polymers [10,11] and specific polymer microstructures. An advantage of the amphiphilic templating methods is that high molecular weight materials can be organized and then the templates can be easily removed due to their comparatively low molecular weight and high solubility. In addition, it appears that

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The method is versatile and monomers need not have special substituents to be organized by the amphiphiles. In the case of pyrrole (Py), hydrogen bonding likely plays a role, however the monomer need not be elaborated further to produce a supramolecular hydrogel.

In this paper we report PPy electrochemically polymerized using self-assembled amphiphiles as a template in order to produce freestanding films and then compare the electrochemical behavior and the actuation properties of this microstructured material with typical PPy that is polymerized without template films.

Experiments

1. Reagents

Pyrrole was obtained from Aldrich and was purified before use by distillation. Sodium *p*-toluene sulfonate (*p*-TSNa) was obtained from Tokyo Kasei.

2. Synthesis of amphiphilic compounds

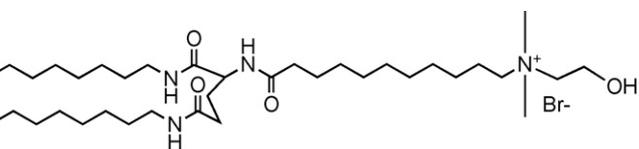
The amphiphile, *N*-{11-(2-hydroxyethyl)dimethylammonium)undecanoyl}-*N,N'*-dioctyl-L-glutamate, bromide (**1**) was synthesized by the method that is developed by Nakashima and Kimizuka et al. [11–13] The chemical structure of **1** is shown in Scheme 1.

3. Preparation and characterization of bundled bilayer membrane on ITO glass

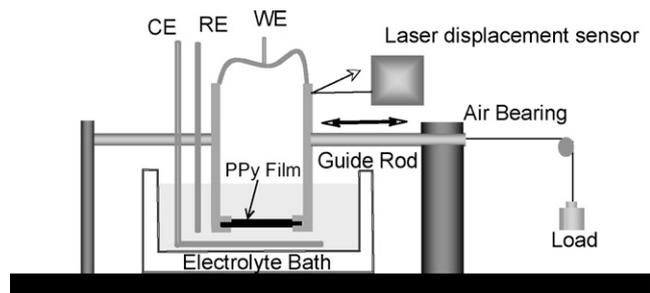
Amphiphile **1** dissolved in water and pyrrole was added to give a solution that was 26 mM in **1** and 0.741 M in Py. After sonification the mixture was cast on ITO glass and then stored under an argon atmosphere and dark for several days to produce dry membranes of assembled bilayer bundles on the ITO glass. This template on ITO glass was used as the working electrode during electro-polymerization.

4. Polymerization of polypyrrole in membranes of bundled bilayers (templated PPy)

Electro-polymerization of the Py was performed under constant potential conditions (0.8 V versus Ag/AgCl) on the functionalized ITO glass, with a stainless steel counter electrode and a Ag/AgCl reference electrode. The polymerization solution was an aqueous electrolyte with 0.2 M sodium *p*-toluene sulfonate (*p*-TSNa) and 0.3 M Py. All experiments were carried out



Scheme 1. Amphiphile **1** *N*-{11-(2-hydroxyethyl)dimethylammonium)undecanoyl}-*N,N'*-dioctyl-L-glutamate, bromide.



Scheme 2. Actuation testing apparatus.

at room temperature and the constant potential polymerizations were conducted for 20 min. The resulting PPy films (templated PPy) were then peeled off the ITO working electrodes, rinsed with water, and then subjected to sonification in water for several minutes in order to remove the amphiphile bundled bilayer membranes. For comparison purposes, PPy was polymerized under the same conditions on ITO that lacked the templating films of bundled bilayer membranes and we refer to this as typical PPy.

2.5. Electrochemical and actuation experiments

Cyclic voltammetry (CV) experiments were carried out with a potentiostat (Solartron SI 1287 and 1260). Scan rates from 10 mV/s to 500 mV/s were carried out in an aqueous solution containing 1.0 M *p*-TSNa. Actuation testing was performed by an in-house designed instrument as shown in Scheme 2. Free-standing polypyrrole films were clamped between Pt foils at both ends to establish both mechanical and electrical contacts. All actuation studies were performed in 1.0 M *p*-TSNa aqueous electrolyte. Forces of 0.3 MPa were applied to the films and the change of film length was monitored with laser displacement sensors, KEYENCE LB-1000. The applied potential was varied from -1.0 V versus Ag/AgCl to $+0.8$ V versus Ag/AgCl with a Solartron SI 1287 potentiostat.

3. Results and discussion

Nakashima and Kimizuka reported that aqueous solutions of **1** in conjunction with other chemical compounds can form fibrous aggregated structures by electrostatic, van der Waals interaction and hydrogen bonding, and that the observed morphology was characteristic of chiral bilayer membranes [13]. In some cases the compositions produced robust supramolecular hydrogels by self-assembly.

We expected that Py could be similarly self-assembled with **1** due to its hydrogen bonding properties. Amphiphile **1** was dissolved in water (26 mM) to produce a viscous liquid. This solution turned turbid immediately upon addition of Py suggesting that phase separation occurs. The phase diagram for this system is shown in Fig. 1. The solubility of Py in water is limited at room temperature to 5.8%. There is even more limited solubility for **1** and a maximum of 1.9% solutions are stable in water at room temperature. These single component phase considerations provide limits on the concentration ranges that could be investigated.

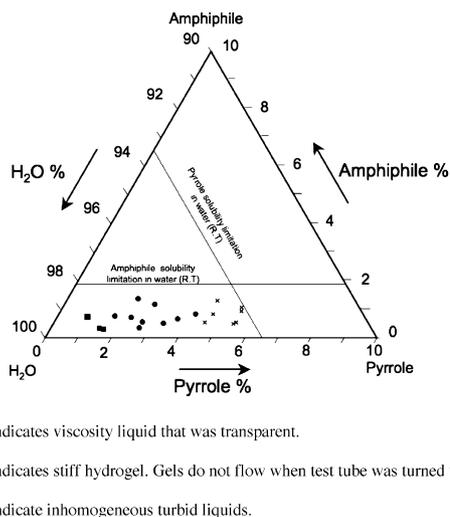


Fig. 1. Concentration dependence for hydrogel formation as a function of composition.

When the amount of Py added was between 2% and 4%, stiff hydrogels formed. Below 2% we observed persistent viscous liquids and with higher concentrations 4–4.8% inhomogeneous (turbid) liquids were produced. The stiff hydrogels showed a reversible gel to liquid phase transition. Differential scanning calorimetry revealed an endothermic peak at 48 °C. This reversible behavior indicates that the hydrogels have physical cross-links. Transmission electron microscope (TEM) analysis shown in Fig. 2 indicates the gels are fibrous aggregates with a minimum width of about several nanometers. Given the synergistic nature of **1** and Py to produce the gel state, it is assumed that the gel contains both materials. The hydrogels were cast on ITO glass and then kept in the dark under an argon atmosphere in order to avoid pyrrole oxidation while the self-assembly process developed. After several days, thin transparent films were

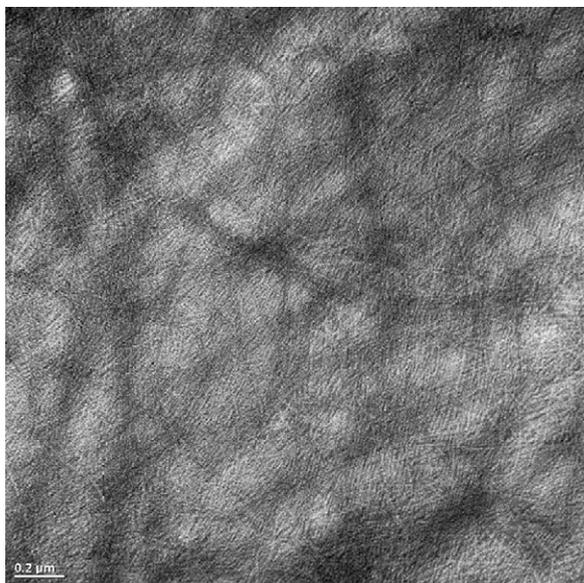


Fig. 2. Transmission electron microscope (TEM) image of dried hydrogels assembled from an aqueous solution of **1** and Py.

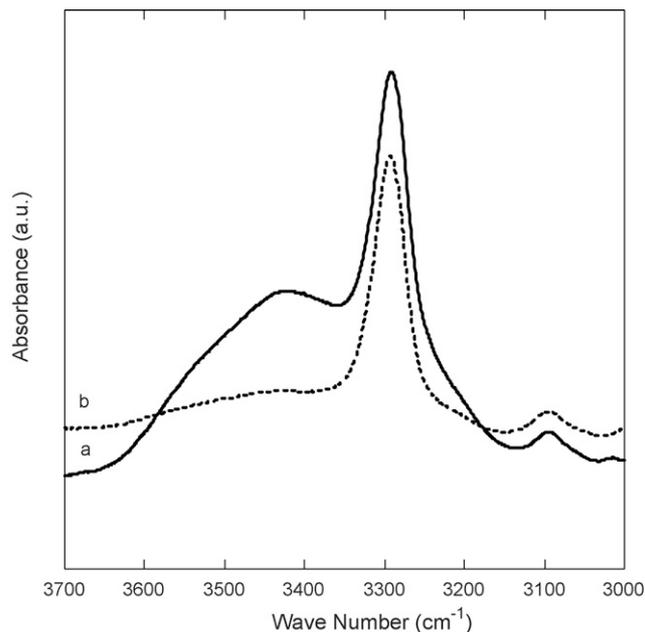


Fig. 3. FTIR spectra from 3700 cm^{-1} to 3000 cm^{-1} : (a) templated film, (b) amphiphiles.

formed on ITO glass. Films from aqueous solutions of **1** alone were structureless and the interaction of Py with **1** played a critical role in organizing the films on the ITO glass. To investigate the role of the Py in the assembly process as well as the interaction of the amide groups in **1**, FTIR spectra were obtained (Figs. 3 and 4). The intense band at 3300 cm^{-1} is characteristic of N–H groups associated with the secondary amides of **1**. In the case of the templated material, a new peak was observed at 3420 cm^{-1} . It seems likely that this is an N–H vibration of the Py or the amides in **1** that are disrupted from their hydrogen bonds.

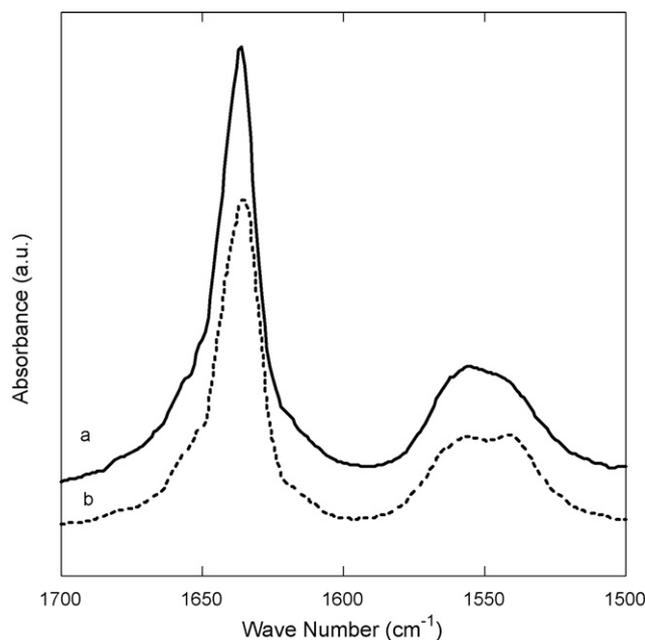


Fig. 4. FTIR spectra from 1700 cm^{-1} to 1500 cm^{-1} : (a) templated film, (b) amphiphile.

The strong band at 1635 cm^{-1} is characteristic of C=O groups associated with the secondary amides of **1**. This band shifted to a higher frequency in the templated material. The shift to higher energy in the template material indicates that the strong hydrogen bonding of molecules of **1** are disrupted in part by Py. From our FTIR investigation, it appears that Py are partially disrupting the hydrogen bonding of **1**, which is part of the driving force to form porous nanoassemblies [13], and it is likely that this interaction is playing an important role in the fibrous assembly process of the templated film.

The constant potential polymerization of the Py on the treated ITO proceeded via a nucleation of PPy, which appeared as black points on the surface immediately when the polymerization potential was applied. These black points expanded to cover the entire surface and created a continuous film over the 10 min of polymerization. Freestanding PPy films were peeled off ITO glass, rinsed and then sonicated in water to remove **1**. The obtained freestanding film thickness was about $25\text{ }\mu\text{m}$ and its peak tensile strength was 8 MPa.

Scanning electron microscope (SEM) images of the templated PPy (Fig. 5) are very different from typical PPy, which was polymerized on untreated ITO. The templated PPy dis-

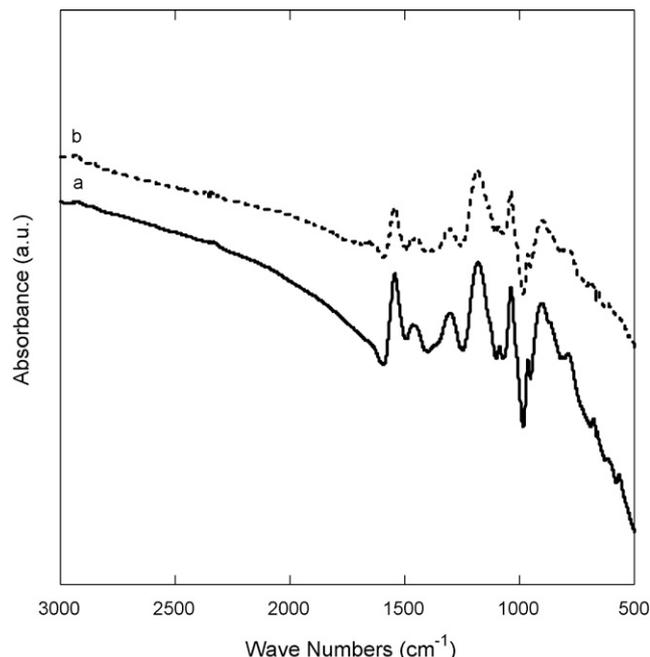


Fig. 6. FTIR spectra for (a) templated PPy and (b) typical PPy.

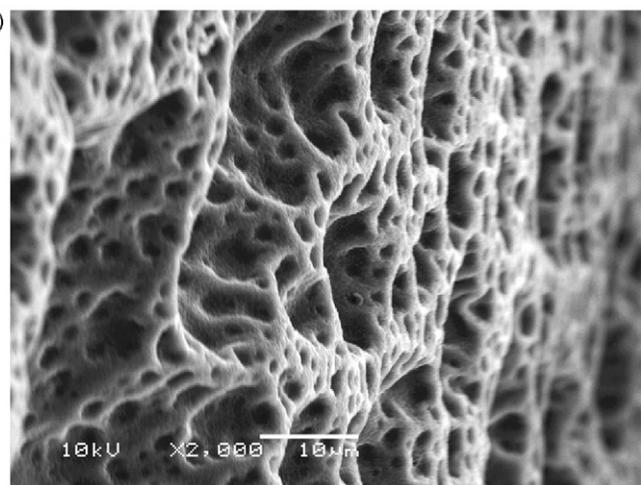
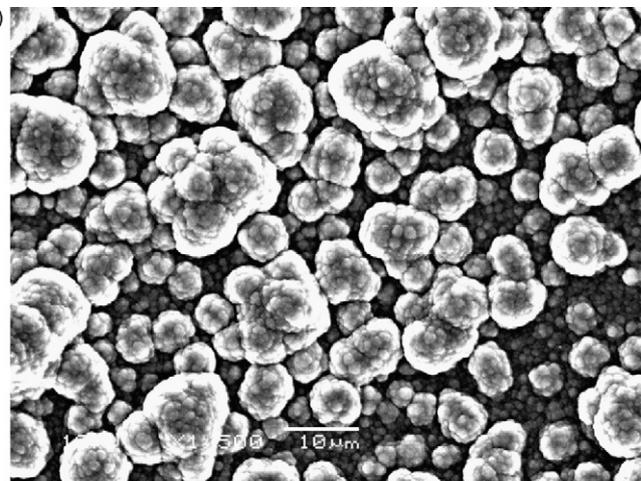


Fig. 5. SEM images of (a) typical polypyrrole and that of (b) templated polypyrrole.

plays specific porous microstructures and a network structure that resembles natural tissue. There is both Py initially bound in the template as well as some dissolved in the electrolyte. The FTIR spectra of the templated PPy and typical PPy are almost the same as shown in Fig. 6. The characteristic peaks of PPy about 1530 cm^{-1} and 1450 cm^{-1} are assigned the fundamental stretching vibration of pyrrole rings and about 1170 cm^{-1} and 900 cm^{-1} are the stretching vibration of doped PPy [9].

We propose that the Py in the template may be involved in the initiation of the polymerization and that continued growth to give a mechanically stable film is accomplished by mass transport limited polymerization of the PPy from the electrolyte solution.

Cyclic voltammetry (CV) measurements were performed in aqueous *p*-TSNa and representative cycles of the templated PPy and typical PPy are shown in Fig. 7. When the CVs for both materials are recorded between 1.0 V versus Ag/AgCl and -1.0 V versus Ag/AgCl at the scan rate of 10 mV/s , the oxidation and reduction peak currents were observed at approximately -0.1 V versus Ag/AgCl and -0.5 V versus Ag/AgCl, respectively, indicating that the electrochemical doping/undoping were chemically reversible. The current associated with the templated PPy was higher than typical PPy peak current, indicating that either a larger amount of templated PPy was deposited and/or that the templated PPy displayed superior electroactivity. To evaluate the electroactivity further we determined the size of the peak currents versus scan rate relationship as shown in Figs. 8 and 9. The results reveal that the dopant diffusion characteristics against the current are linear with the square root of the scan rate, thereby indicating diffusion-limited behavior. From the slopes of the lines in Figs. 8 and 9, the dopant ion diffusion speed is fastest in the case of templated PPy. It seems likely that faster movement of the dopant is facilitated by the porous microstructures of templated PPy. We are undertaking further

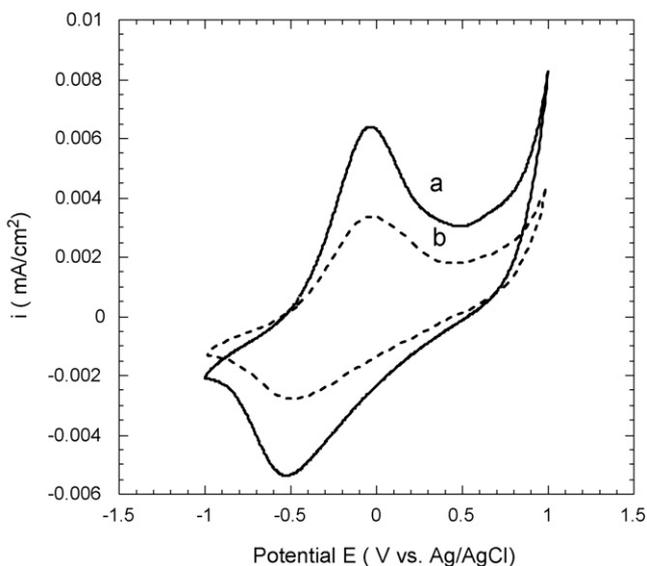


Fig. 7. Cyclic voltammograms for (a) templated PPy and (b) typical PPy grown under identical circumstances.

studies to establish the relationship between nanostructure and electrochemical properties that will be published at a later date.

There were large differences between the actuation behavior of templated and typical PPy in aqueous 1.0 mol/l *p*-TSNa electrolytes. Fig. 10 depicts the actuation behavior with a square wave applied potential cycled between -1.0 V versus Ag/AgCl and $+0.8$ V versus Ag/AgCl with a dwell time of 50 s at each potential. As shown in Fig. 10, both forms of PPy were in an expanded state when they are in a neutral uncharged state and contracted with oxidation contracts. The actuation behavior in *p*-TSNa aqueous electrolyte is the opposite observed with NaPF₆ and this result suggests that sodium ion movement during redox reaction creates the actuation behavior. The templated PPy displays a comparatively larger strain than typical PPy and the experimental data shows that the strain over 4% in templated

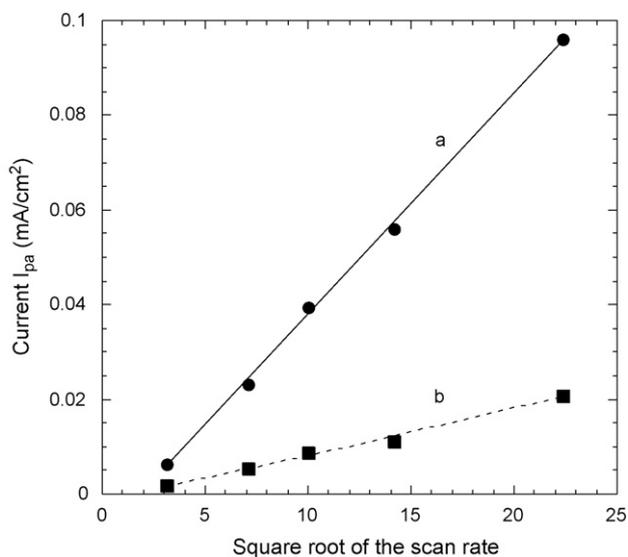


Fig. 8. Anodic peak height (I_{pa}) vs. square root of the scan rate. The line marked as 'a' is for templated PPy and that labeled 'b' is for typical PPy.

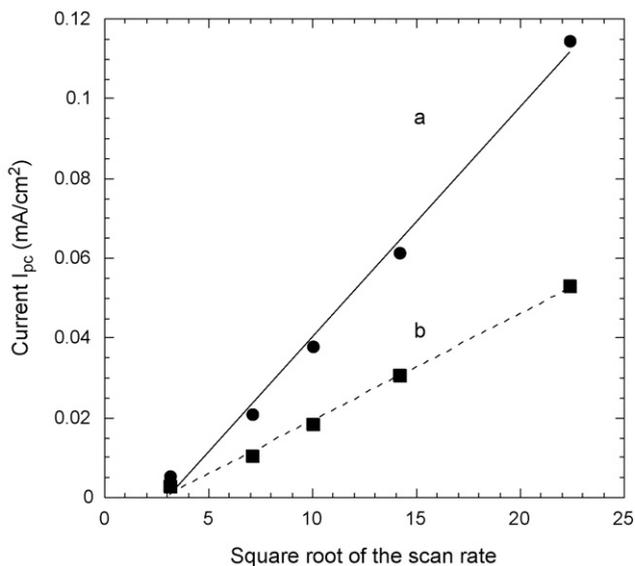


Fig. 9. Cathodic peak height (I_{pc}) vs. square root of the scan rate. The line marked as 'a' is the response of template PPy and line 'b' is the data for typical PPy.

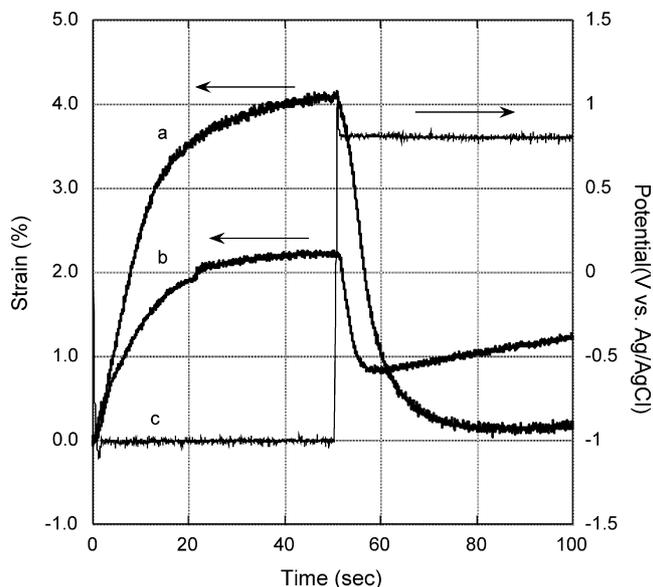


Fig. 10. Comparative actuation behavior of templated PPy and typical PPy in aqueous 1.0 M *p*-TSNa electrolyte. The line marked as 'a' is the strain behavior of template PPy, line 'b' is the data for typical PPy and line 'c' is the applied potential.

PPy was twice as large as that of typical PPy. We believe that the larger strain in the templated PPy is related to its higher electroactivity and the improved diffusion of the dopant ions into the films.

4. Conclusions

Amphiphile **1** in aqueous solutions assembled into supramolecular hydrogels with added Py. These hydrogels were robust structures that could be dried and then used as a template to direct the electrochemical synthesis of PPy. CV measurements of templated PPy displayed superior electroactivity and ion dif-

sion when compared to PPy films synthesized under the same conditions that only lack the template. It was also found that the templated PPy displays a two-fold higher strain in actuation experiments than typical PPy. This study establishes that structured films such as those produced in templated PPy are useful to improve the performance of conducting polymers in actuator applications. We expect similar improvements can be made in capacitors as well.

Acknowledgements

We would like to acknowledge Prof. Kimizuka and Dr. Takashima who were in Kyushu University for synthesis of hydrophilic compounds. This work was supported in part by the Office of Naval Research. We are also grateful for discussions with the Swager research group at the Massachusetts Institute of Technology.

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