Available online at www.sciencedirect.com

ScienceDirect

Synthetic Metals 157 (2007) 733–738

SYNTHETIC METALS

www.elsevier.com/locate/synmet

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

Kazuhiro Kagawa[a,*], Pu Qian[a], Akihisa Tanaka[a], Timothy M. Swager[b]

[a] *Honda R&D Co. Ltd., Fundamental Technology Research Center, 1-4-1 Chuo Wako-shi,*
Saitama 351-0193, Japan
[b] *Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue,*
Cambridge, MA 02139, USA

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-hydroxyethyldimethylammonium)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.

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 freestanding 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

---

* Corresponding author. Tel.: +81 48 462 5191; fax: +81 48 462 5330.
E-mail address: kazuhiro.kagawa@f.rd.honda.co.jp (K. Kagawa).

0379-6779/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.synthmet.2007.07.011

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.

2. Experiments

2.1. Reagents

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

2.2. Synthesis of amphiphilic compounds

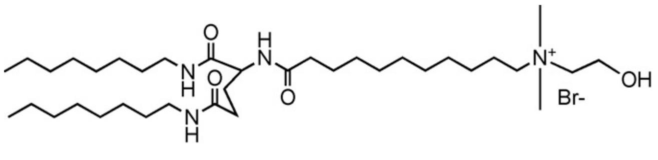
The amphiphile, *N*-{11-(2-hydroxyethyldimethylammonium)undecanoyl}-*N*,*N*′-dioctyl-L-glutamate, bromide (**1**) was synthesized by the method that is developed by Nakashima and Kimizuka et al. [11–13] The chemical structure of **1** is shown in Scheme 1.

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

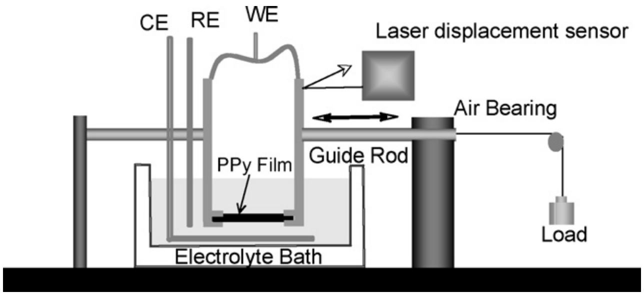
Amphiphile **1** dissolved in water and pyrrole was added to give a solution that was 26 mM in **1** and 0.741 M in Py. After sonification the mixture was cast on ITO glass and then stored in an argon atmosphere and dark for several days to produce dry membranes of assembled bilayer bundles on the ITO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

2.4. 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 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.



Scheme 1. Amphiphile **1** *N*-{11-(2-hydroxyethyldimethylammonium)undecanoyl}-*N*,*N*′-dioctyl-L-glutamate, bromide.



Scheme 2. Actuation testing apparatus.

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. Freestanding 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.