

Adsorption-Induced Chemomechanical Behavior of Polypyrrole Films

HIDENORI OKUZAKI, TOSHIO KUNUGI

Department of Applied Chemistry and Biotechnology, Faculty of Engineering, Yamanashi University, 4-3-11 Takeda, Kofu 400, Japan

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ABSTRACT: We have discovered that electrochemically synthesized polypyrrole films undergo quick and intensive bending in ambient air without the use of heat, ions, or an electric field. The principle of motion was based on a reversible van der Waals adsorption of water or polar organic molecules onto the film, which distinguished it from other systems owing to electrochemical doping and undoping. The motion of film largely depended on the kind of adsorbate used: water vapor molecules caused rapid bending of the film to the opposite side. In contrast, when polar organic molecules were used as an adsorbate, the bending of film occurred to the same side, namely, the direction of bending was just opposite to that observed for water vapor. On the basis of this phenomenon, we have devised a novel actuator which moves by a spontaneous rotation. Further, an experimental "polypyrrole engine" has been made, which used a polypyrrole belt as working substance and adsorbate as fuel. When water and iodomethane were used as the adsorbates, the belt rotated at a speed of 22 cm min⁻¹. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 383–388, 1997

Key words: polypyrrole film; chemomechanical system; adsorption; bending; actuator

INTRODUCTION

An isothermal system transducing the chemical energy directly into a mechanical work by the use of polymeric material is called a "mechanochemical"^{1,2} or "chemomechanical"³ system, which underlies the motility of all living organisms. Polymeric gels have attracted considerable attention for this system because a gel can change its size and shape in response to environmental stimuli.^{1–12} One of the authors has previously reported on a polymeric gel with an electrically driven worm-like motility.^{13,14} The motility lies in a molecular assembly reaction between surfactant molecules and the polymeric gel, where the electric field con-

trols the direction and equilibrium of the surfactant binding.^{15,16} Baughman et al.¹⁷ have proposed electrochemical actuating devices using conducting polymers.^{18–21} The dimensional changes of the conducting polymers occur after electrochemical donor or acceptor doping and undoping.^{22–24} However, these devices work only in a solution or in a swollen state.

Very recently, we have reported on an electrochemically synthesized polypyrrole film with quick and intensive bending motion in ambient air without using heat, ions, or an electric field.^{25,26} This article is a further detailed study of the chemomechanical behavior of polypyrrole films. The results demonstrate that the mechanism of motion is associated with a reversible van der Waals adsorption of various substances in the vapor state. The speed and direction of bending largely depend on the adsorbate used. Further, we have devised novel actuators capable of trans-

Correspondence to: T. Kunugi.

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ducing a chemical free energy change of adsorption directly into a continuous rotation.

EXPERIMENTAL

Materials

Pyrrole (Wako Chem. Co., Ltd.) as a monomer was purified by distillation before use. Tetraethylammonium perchlorate, used as an electrolyte, was commercially available (Kanto Chem. Co., Ltd.) and used without further purification. Propylene carbonate and iodomethane (Kanto Chem. Co., Ltd.) were used as received.

Preparation of Polypyrrole Films

Free-standing polypyrrole films containing perchlorate (PPy/ClO₄) were electrochemically synthesized by the anodic oxidation of pyrrole²⁷: pyrrole monomer and tetraethylammonium perchlorate were dissolved in propylene carbonate containing 1 vol % of water in concentrations of 0.06 and 0.05 mol L⁻¹, respectively. A constant current (0.125 mA cm⁻²) was applied through a platinum plate (50 mm long, 20 mm wide, and 0.1 mm thick) as an anode and aluminum foil 10 times in area as a cathode with a potentiostat/galvanostat HA-301 (Hokuto Denko Co., Ltd.). Polymerization was carried out for 12 h at -20°C. After polymerization, the polypyrrole film was peeled from the platinum electrode, soaked in a large amount of propylene carbonate for 1 h, and then dried overnight in a vacuum. Elementary analysis of the film obtained gives a composition of C_{4.18}H_{4.02}N_{0.84}(ClO₄)_{0.34}. Young's modulus and the tensile strength of the film are 0.61 GPa and 34 MPa, respectively.

Measurements

The apparatus for the measurement of the chemomechanical behavior of the polypyrrole film is schematically shown in Figure 1. The polypyrrole film was 25 mm long, 5 mm wide, 30 μm thick, and 3.6 mg by weight and was suspended from a chuck made of stainless steel. When a tissue containing an adsorbate is brought to a distance of 2 mm from one side of the film, the film bends. The extent of bending was evaluated by measuring a geometrical change of the film at its free end with a laser displacementmeter LB-300 (Keyence Co., Ltd.). The relative humidity and the

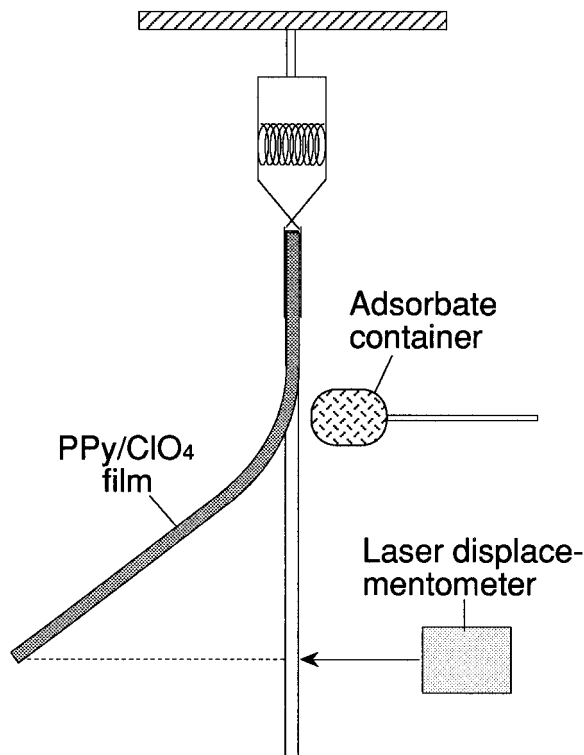


Figure 1 Apparatus for the measurement of the chemomechanical behavior of polypyrrole films.

temperature in the vicinity of the film were measured with a portable hygrometer MC-P (Panametrics Japan Co., Ltd.) which was located at a distance of 1 mm from the film surface. The electrical conductivity of the film was measured by a normal four-probe method with a VOAC-7512 digital multimeter (Iwatsu Co., Ltd.). The four copper wires were attached with silver paste onto the gold plates (5 mm long, 1 mm wide, and 0.1 μm thick) evaporated on the polypyrrole film (16 mm long, 5 mm wide, and 30 μm thick). The mechanical stress generated by the bending was measured with a strain gauge (T7-8-120, Orientech Co., Ltd.) fixed to the bottom end of the film. The amount of adsorption was measured by the use of a quartz crystal microbalance (QCM) technique.²⁸ The pyrrole was polymerized on a gold electrode evaporated on the AT-cut quartz crystal plate (Wakabayashi Co., Ltd.). The polymerization was carried out for 30 min at -20°C. After polymerization, the QCM covered with PPy/ClO₄ was soaked in propylene carbonate and then dried in a vacuum overnight. The frequency change was monitored with a universal counter (SC-7202, Iwatsu Co., Ltd.), and the amount of adsorption was calculated as

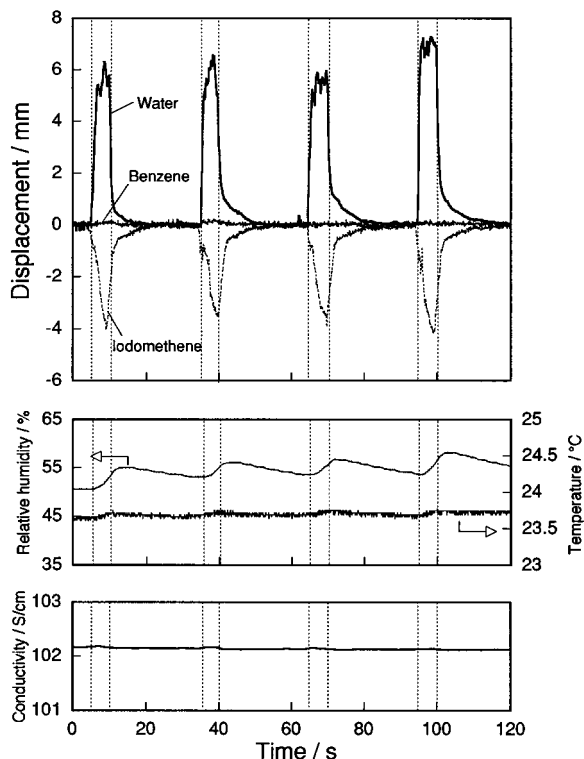


Figure 2 Time profiles of the displacement, the relative humidity, the temperature, and the electrical conductivity. The tissue containing adsorbate was brought to a distance of 2 mm from one side of the film at periods of 5–10, 35–40, 65–70, and 95–100 s.

$$\Delta m = -(10^6/2.26) \times (\Delta F/F_0^2) \quad (1)$$

where, Δm is the amount of adsorption (g cm^{-2}), ΔF is the resonance frequency change (Hz), and F_0 is the fundamental frequency of the QCM (9 MHz). All measurements were carried out under thermostatic conditions (temperature, 25°C; relative humidity, 47%).

RESULTS AND DISCUSSION

Chemomechanical Behaviors

Figure 2 shows time profiles of the displacement, the relative humidity, the temperature, and the electrical conductivity. The displacement represents a geometrical change of the film at its free end. When a tissue containing water is brought to a distance of 2 mm from the film surface, (1) the film bends to the opposite side, (2) the displacement reaches 6–7 mm within 1–2 s, (3) the speeds of bending and recovery attain 5.6 and 4.9 mm s^{-1} , respectively, (4) the relative humidity

changes by 2–4%, (5) there is no notable change in the temperature, and (6) the electrical conductivity is constant about 102.2 S cm^{-1} during the experimental period. After the film was exposed to ambient air for several months, no notable mass change of the film was measured and the chemomechanical behavior was completely reproducible.

It should be noted that the bending occurs before a measurable rise in the relative humidity and that the peaks of bending appear several seconds before those of the relative humidity measured. This fact demonstrates that the response of the polypyrrole film is much faster than that of the hygrometer.

When the tissue containing a polar organic solvent such as alcohol, aldehyde, ketone, amine, or monohaloalkane is brought to a distance of 2 mm from the film surface, the bending occurs to the same side, namely, the direction of the bending is just opposite to that observed for water vapor. Among the polar organic molecules, iodomethane or *N,N'*-dimethylformamide causes the most quick and intensive bending. On the other hand, involatile, aromatic, or nonpolar organic molecules could not induce bending. The chemomechanical response to various kinds of adsorbates is summarized in Table I. Further, we have examined other polymeric films made of polyaniline, polythiophene, polyolefines, polyamides, polyesters, polyethers, polystyrene, and polycarbonate, but they did not bend. The quick bending and recovery motion was observed only for the polypyrrole films.

Pei et al.¹⁹ have investigated that bipolymer strips made of a polypyrrole layer bound together with a polyethylene support layer bend under an electric field. The motion is based on the electrochemical doping and undoping of the polypyrrole in an aqueous solution. They found that when dodecylbenzenesulfonate is used as a dopant, the

Table I Chemomechanical Response of the PPy/CIO₄ Film to Various Adsorbates

| Response | Adsorbate |
|------------------------------|--|
| Bending to the opposite side | Water, organic or inorganic aqueous solutions |
| Bending to the same side | Alcohols, ketones, aldehydes, amines, ethers, nitrils, monohaloalkanes |
| No response | Alkanes, alkenes, aromatic and involatile compounds |

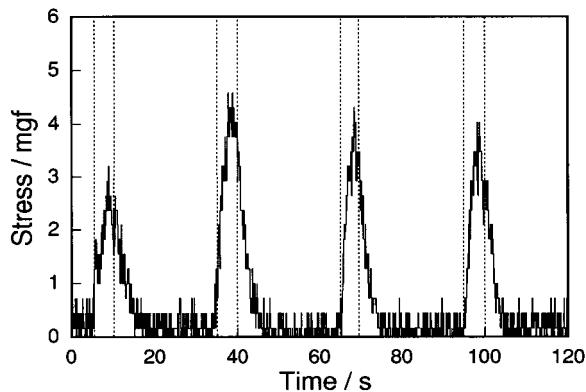


Figure 3 Time profile of the stress generated in the film.

strip bends at a maximum speed of 0.5 mm s^{-1} . Compared with this system, the polypyrrole film in our system bends one order of magnitude faster in ambient air without the use of ions or an electric field.

If the bottom end of the film is fixed with a strain gauge, the film generates a mechanical stress due to the bending. Figure 3 shows a time profile of the stress generated when the tissue containing water is brought to a distance of 2 mm from the film surface. The stress appears repeatedly by approaching the tissue, and the value attains 4.6 mgf, which is 1.5 times its own weight.

Mechanism

Figure 4 shows time profiles of the amount of adsorption for various adsorbates measured by use of the QCM technique. The dry weight of the PPy/ ClO_4 polymerized on the QCM was estimated to be $72 \mu\text{g cm}^{-2}$ from eq. (1). By exposing the QCM to ambient air, the weight immediately increases and attains an equilibrium amount of adsorption of $2.9 \mu\text{g cm}^{-2}$ within 3 min. Then, if the tissue containing water is brought to a distance of 2 mm from the PPy/ ClO_4 surface, further adsorption of water occurs and the value attains $4.6 \mu\text{g cm}^{-2}$ within 5 s. If the tissue is removed, the water molecules rapidly desorb and the value recovers to the original level. One can see that the adsorption and desorption of water molecules coincide well with the bending and recovery of the film, as shown in Figure 2. This fact indicates that the mechanism of motion is based on a reversible van der Waals adsorption of water vapor molecules onto one side of the film, causing the film surface to expand. If a bending curve of the film fits with

a part of a circle, the degree of expansion of the film surface (γ) can be calculated as^{12,21}

$$\gamma(\%) = 100d\theta/L \quad (2)$$

where d and L are the thickness and initial length of the portion of film at the bending occurs, respectively. The degree of bending θ (rad) is defined as the angle between two tangents of arcs at both ends of the portion of film at the bending occurs. From this equation, the maximum expansion of the film is estimated to be about 0.3%. Kaneto²¹ has demonstrated that a polyaniline tape bends in a hydrochloric acid aqueous solution. The bending is caused by the electrochemical doping and undoping of polyaniline. The degree of expansion of the tape by the proton doping is about 1%. Shiga et al.⁷ have investigated that copolymeric gels made of poly(vinyl alcohol) and poly(sodium acrylate) undergo bending under an electric field. They found that the degree of expansion of the gel due to swelling is about 20%. Thus, the expansion of polypyrrole solid film is one or two orders of magnitude smaller than those of the swollen gels. In other words, such a small expansion of the film caused by the adsorption of water vapor molecules via weak interactions can induce a large bending of the film. This nature of the film has led us to make a chemomechanical system with a quick bending and recovery motion.

When the tissue containing iodomethane is

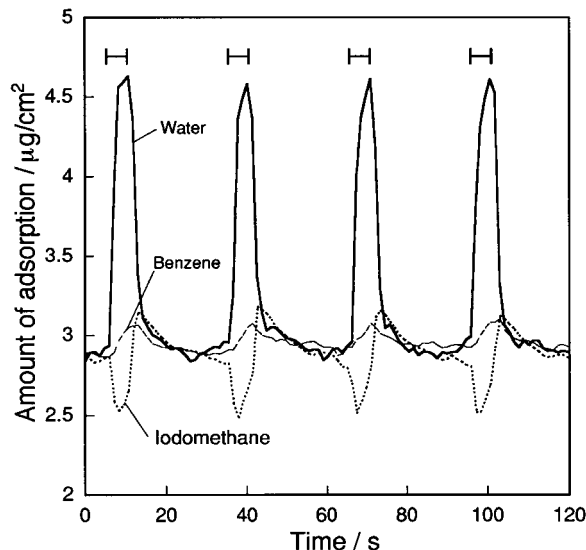


Figure 4 Time profiles of the amount of adsorption onto PPy/ ClO_4 for various adsorbates measured by the QCM technique.

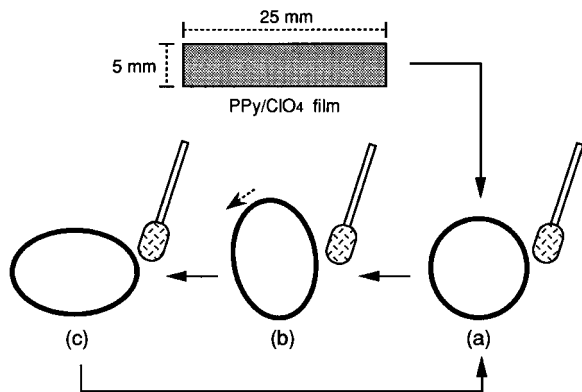


Figure 5 Schematic diagram of the strategy of the rotary actuator.

brought to a distance of 2 mm from the QCM, the amount of adsorption at first decreases and then increases. This indicates that the iodomethane molecules adsorb onto the PPy/ClO₄ by the replacement of the water molecules equilibrated adsorbed in ambient air. Thus, the bending of the film to the opposite direction can be explained by a contraction of the film surface. On the other hand, the amount of adsorption of benzene within 5 s is one order of magnitude smaller than that of water vapor, and the film does not bend.

Application to Chemomechanical Actuators

Rotary Actuator

By using the bending of polypyrrole film, we have devised a "rotary actuator" which moves by a spontaneous rotation. A schematic diagram of the strategy is shown in Figure 5. When a tissue containing adsorbate is brought to a ring made of polypyrrole film (a), the curvature of the ring decreases and the ring is deformed in an elliptical shape (b). By moving a center of gravity, the ring rotates by 90° to the opposite direction (c). The rotation successively brings a new surface of the ring, and the ring moves with a continuous rotation. When iodomethane is used as an adsorbate, the ring moves by the spontaneous rotation at an average speed of 15 cm min⁻¹.

Polypyrrole Engine

Figure 6 shows the schematic construction of an experimental "polypyrrole engine." A closed belt made of polypyrrole film is wound around two pulleys. When a tissue containing water (C) is set below the pulley A and one containing polar or-

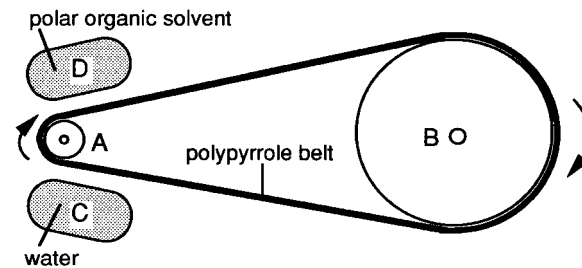


Figure 6 Schematic construction of the polypyrrole engine. Radius: pulley A, 1 mm; pulley B, 5 mm; wheel base, 20 mm. C, tissue containing water; D, tissue containing polar organic solvent.

ganic solvent (D) is set above the same pulley at a distance of 2 mm, the curvature of the belt increases near C but decreases near D. A net rotary moment acts on the pulleys and causes a clockwise rotation. The rotation brings a new surface of the belt to C and D, thereby enabling continuous rotation. The speed of the rotation would depend on the dimensions of the film, the ratio of the radius of the pulleys, and the adsorbate used. We have found that when water and iodomethane are used as the adsorbates, the polypyrrole belt rotates at a speed of 22 cm min⁻¹, corresponding to the rotation of pulley B at 6–7 rpm. The rotation continues until the adsorbates are completely vaporized. Replacing the tissue containing water by a finger caused similar deformation of the belt, and the photograph of the apparatus is shown in Figure 7.

This system has the following advantages: (1) the mechanism and construction are quite simple and easy, (2) it operates in ambient air, (3) it provides a combination of sensor and actuator, (4) a high reproducibility and reliability of motion can be obtained because of no incidental chemical reactions, (5) the mechanical and electrical prop-

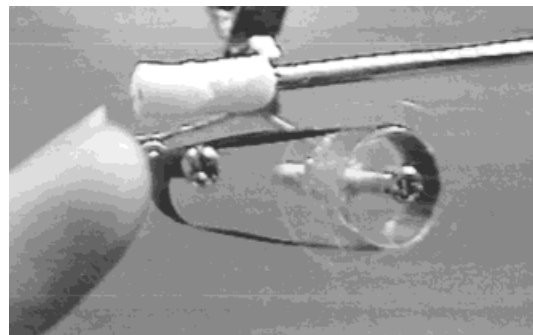


Figure 7 Photograph (side view) of the polypyrrole engine.

erties of the film can be improved by drawing,²⁷ and (6) it can be applied to the electric devices by use of the electroconductivity of the film. This kind of moving device can provide a "silent" and "flexible" power source and can be used as a new type of molecular engine or artificial muscle in which the chemical free energy change of adsorption is directly transduced into the mechanical work.

CONCLUSIONS

The electrochemically synthesized polypyrrole films underwent quick and intensive bending in ambient air without the use of heat, ions, or an electric field. The principle of motion was based on a reversible van der Waals adsorption of water or polar organic molecules in the vapor state, and the motion of film largely depended on the adsorbate used. On the basis of this phenomenon, we have devised novel actuators capable of transducing a chemical free energy change of adsorption directly into a continuous rotation. It was found that when iodomethane was used as the adsorbate, the rotary actuator moved by a spontaneous rotation at a speed of 15 cm min⁻¹. Further, the experimental polypyrrole engine was devised. When water and iodomethane were used as the adsorbates, the polypyrrole belt rotated at a speed of 22 cm min⁻¹.

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