

## Poly(1-*n*-octadecylpyrrole) Films with ‘Needle’-like Morphology

Hu YAN,<sup>†,††</sup> Yutaka HATTORI, Junichi FUJISATO, and Naoki TOSHIMA<sup>†</sup>

Department of Materials Science and Environmental Engineering, Tokyo University of Science, Yamaguchi,  
1-1-1 Daigaku-dori, SanyoOnoda-shi 756-0884, Japan

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Electrochemical polymerization can provide conductive polymer films with various morphologies according to the reaction conditions. Therefore, the electrochemical polymerization was extensively studied using various kinds of monomers.<sup>1</sup> Recently conductive polymers with unique shapes or their films with unique morphologies attract much attention due to their unique physical properties.<sup>2,3</sup> Polypyrrole microtubes form during such electrochemical polymerization.<sup>4</sup> The formed microtubes show unique properties, such as incandescence and extremely high thermal stability of the tube-shape.<sup>5</sup> Very recently, poly(alkylpyrrole) films with unique morphology were synthesized using a two-electrode electrochemical cell.<sup>6–8</sup> The polymer films show super water-repellency,<sup>6,7</sup> and those coated with fluorinated compound by a facile way have very high oil-repellency.<sup>8</sup> The excellent liquid-repellency is simply caused by the ‘needle’-like morphology or fractal structure of the film surface.<sup>7</sup> The films have been mainly studied from the viewpoint of the liquid-repellency and its relevant properties. Poly(alkylpyrrole), however, can be considered as a kind of conductive polymers based on the nature of the molecular structure. Herein we report the synthesis of the polymer films using a three-electrode electrochemical cell, focusing on the optimum applied potential against reference electrode, Ag/AgCl. We also report electrochemical and electrical properties of thus-synthesized polymer films, and discuss the formation process of the ‘needle’-like morphology.

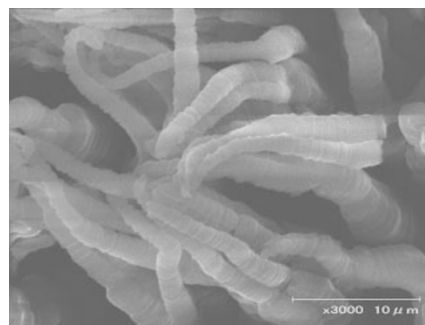
The poly(1-*n*-octadecylpyrrole) films were synthesized using three-electrode setup, in which indium-tin oxide (ITO) glass, platinum net, and Ag/AgCl were used as a working, counter, and reference electrode, respectively. The typical synthetic procedure was as follows: An acetonitrile solution of 1-*n*-octadecylpyrrole (5 mmol dm<sup>-3</sup>) and sodium *p*-toluenesulfonate (0.5 mmol dm<sup>-3</sup>) was electrochemically polymerized in a three-electrode cell at 9,000 mV vs. Ag/AgCl for 1 h. The polymer films were washed with acetonitrile and distilled water, and finally dried in vacuum overnight. The dried films were used for scanning electron microscopic (SEM), cyclic voltagramic (CV), and electrical conductivity measurements.

SEM images of the films were obtained after gold-sputtering. CV curves were recorded using the films as a working electrode in an acetonitrile solution of sodium *p*-toluenesulfonate (0.5 mmol dm<sup>-3</sup>). Electrical conductivity of the films was

measured by a conventional four-point technique.

The poly(1-*n*-octadecylpyrrole) films were previously synthesized in a two-electrode cell.<sup>6</sup> The films were extensively studied in terms of water or oil-repellencies.<sup>6–8</sup> The surface structures of the films have mathematically fractal dimension of 2.2, based on analysis by a box-counting method.<sup>6,7</sup> Such kind of solid surfaces with fractal structure interestingly influenced the cell cultures, which may provide potential biological applications.<sup>9</sup>

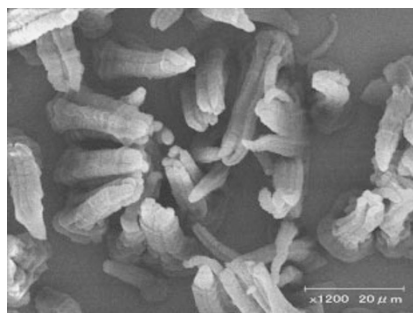
One can easily consider this polymer as a kind of conductive polymers simply because the polymer chains are the same with that of well-known conductive polymer of polypyrrole. In the present work the poly(1-*n*-octadecylpyrrole) films were synthesized in a three-electrode electrochemical cell. The synthesis was conducted by various applied potentials. No polymer film was formed by an applied potential of 800 mV vs. Ag/AgCl, by which polypyrrole microtubes were formed.<sup>4,5</sup> Polymer films were formed in the range of 5,000–7,000 mV vs. Ag/AgCl, but with relatively smooth morphology. From the applied potential of 8,000 mV vs. Ag/AgCl, polymer films with rough morphology were formed. The polymer films with ‘needle’-like morphology formed at an applied potential of 9,000 mV vs. Ag/AgCl, as shown in Figure 1. For comparison, the synthesis of the polymer films was performed in a two-electrode cell according to the procedure previously reported.<sup>6</sup> Almost the same polymer films were formed at an applied voltage of 22.5 V, as shown in Figure 2. Accordingly, it is rea-



**Figure 1.** SEM image of poly(1-*n*-octadecylpyrrole) film synthesized by the setup of three electrodes.

<sup>†</sup>To whom correspondence should be addressed (Tel: +81-836-88-4561, Fax: +81-836-88-4567, E-mail: yanhu@ed.yama.tus.ac.jp or toshima@ed.yama.tus.ac.jp).

<sup>††</sup>Present Address: Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, 4-4-37 Takada, Kofu 400-8511, Japan



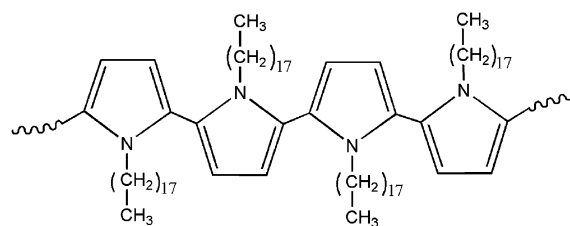
**Figure 2.** SEM image of poly(1-*n*-octadecylpyrrole) film synthesized by the setup of two electrodes.

sonable that the electrochemical condition of the applied potential, *i.e.*, 9,000 mV *vs.* Ag/AgCl, correspond to that of the applied voltage, *i.e.*, 22.5 V by which the fractal poly(1-*n*-octadecylpyrrole) films were synthesized and were extensively studied from a viewpoint of liquid-repellency.<sup>6–8</sup>

CV measurements were conducted using the poly(1-*n*-octadecylpyrrole) films in the acetonitrile solution of sodium *p*-toluenesulfonate. No clear redox waves were observed in CV curves. Usually clear redox waves appear in a range of –500–500 mV *vs.* Ag/AgCl, due to oxidation and reduction of polymer chains.<sup>1</sup> In the present work no redox waves were observed in so wide range of –3,000–3,000 mV *vs.* Ag/AgCl, indicating that the polymer films are electrochemically inactive, or in other words, very stable to the electrochemical oxidation and reduction. Usually *N*-substituted pyrroles have higher oxidation potential in electrochemical polymerization.<sup>1</sup> Therefore, the electrochemical inactivity of such polymer films are easily understandable.

On the other hand, the films showed electrical conductivity of *ca.*  $1 \times 10^{-5} \text{ S cm}^{-1}$  which was measured by the four-point technique. The conductivity is five or six orders of magnitude lower than those of polypyrrole films or microtubes.<sup>1,4,5</sup> Result of elemental analysis showed that the polymer chains in the films may be oxidized at the very high applied potential because the lower ratio of C or H to N.<sup>10</sup> Sulphur and nitrogen elements originate from the *p*-toluenesulfonate anions and pyrrole rings of the polymer films, respectively. The ratio of S/N corresponds to doping ratio. The doping ratio (S/N) of the polymer also was calculated to be 0.1 based on the result of the elemental analysis.<sup>10</sup> Usually the highly conductive polypyrrole films have a doping ratio of *ca.* 0.3.<sup>1</sup> Therefore, it can be considered that the oxidation of main chains and the lower doping ratio are partly reasons of the low conductivity.

The poly(1-*n*-octadecylpyrrole) films, synthesized in a two-electrode cell, were previously analyzed by Raman spectroscopic and X-ray photoelectron spectroscopic (XPS) measurements.<sup>7,8</sup> The films showed Raman band at  $980 \text{ cm}^{-1}$  due to pyrrole rings with radical cations,<sup>7</sup> similarly in the case of polypyrrole films or microtubes.<sup>5,11</sup> Based on the Raman band, it is considered that the polymer films have electrical carriers by *p*-toluenesulfonate-doping. Furthermore, the XPS analysis showed high ratio of sulphur to nitrogen (S/N), *ca.* 0.5.<sup>8</sup> These indicate that the doping ratio of surface may be much different from that of inner part of the film. The difference of the doping ratio in the two methods also may originate from the difference of the electrochemical condition since the applied potential (9,000 mV *vs.* Ag/AgCl) may not exactly correspond to the applied voltage (22.5 V).



**Figure 3.** Bulk octadecyl side-groups on the poly(1-*n*-octadecylpyrrole) main chains.

It is considered that the low conductivity of the present polymer films, even though having considerably high doping ratio, is attributed to the molecular structure, *i.e.*, substitution by a bulky side group (Figure 3). It is also considerable that the low conductivity comes from defects and impurities of the film which are possibly induced by oxidation of monomer and solvent at very high applied potential (out of potential window of acetonitrile). It is plausible that the bulky octadecyl side groups hinder the conjugation among pyrrole rings of the polymer main chains, resulting in shorter conjugation which may induce strong localization of electrical carries on the polymer chains. The shorter conjugation or strong carrier localization, and defects and impurities of the film may result in the poor electrical conductivity.<sup>12</sup> It is considered that the low conductivity could need so high applied potential 9,000 mV *vs.* Ag/AgCl for formation of the films, especially the protruding parts of the films whose higher density of electric charge makes the electrochemical polymerization preferable, finally resulting in the 'needle'-like morphology.

In conclusion poly(1-*n*-octadecylpyrrole) films with 'needle'-like morphology were synthesized electrochemically at high applied potential of 9,000 mV *vs.* Ag/AgCl. The poly(1-*n*-octadecylpyrrole) films were electrochemically inactive, and showed poor electrical conductivity, *ca.*  $1 \times 10^{-5} \text{ S cm}^{-1}$ . The experimental results suggest a formation mechanism of the films in which the protruding parts with higher charge density on films preferably grow, resulting in the 'needle'-like morphology.

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10. a) Elemental analysis: C, 76.66%; N, 4.13%; H, 10.90%; S, 0.6%. b) S/N: 0.1. c) Based on the S/N ratio of 0.1,  $\text{C}_{22}\text{N}_1\text{H}_{39}$  (calcd.);  $\text{C}_{21.0}\text{N}_1\text{H}_{36.0}$  found for main chains in Figure 3.
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