ORGANIC LETTERS

2003
Vol. 5, No. 9
1395−1398

Nano-Rod Structure of Poly(ethylenedioxythiophene) and Poly(pyrrole) As Created by Electrochemical Polymerization Using Anionic Porphyrin Aggregates as Template

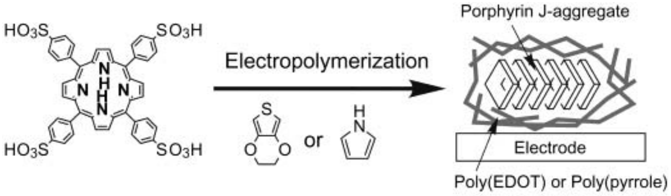
Tsukasa Hatano,[†] Masayuki Takeuchi,[†] Atsushi Ikeda,[‡,§] and Seiji Shinkai*,[†]

Department of Chemistry and Biochemistry, Graduate School of Engineering,
Kyushu University, Fukuoka 812-8581, Japan, Graduate School of Materials Science,
Nara Institute of Science and Technology, Ikoma, Nara 630-0101, Japan, and
PRESTO, Japan Science and Technology Corporation, Ikoma, Nara 630-0101, Japan

seijitcm@mbox.nc.kyushu-u.ac.jp

Received December 26, 2002

ABSTRACT



It was found that a one-dimensional rodlike structure of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (TPPS) in water acts as a powerful template for electrochemical polymerization of ethylenedioxathiophene (EDOT) and pyrrole on an ITO electrode. Examination using CV and UV–vis spectroscopic examinations established that J-aggregated TPPS molecules are entrapped in the resultant poly(EDOT) and poly(pyrrole) films. SEM observation established that these monomers are electrochemically oxidized to grow up to a nanosized rodlike structure, reflecting the aggregation structure of TPPS.

Poly(EDOT) and poly(pyrrole) are conductive polymers easily obtained by electrochemical polymerization of the corresponding monomers.[1] Despite convenience of the preparation method and cheapness of the monomer, the applications have been rather limited.[1−3] One reason for the limited applications is the serious drawback related to the difficulty in controlling the morphology in the polymerization process: if the polymers are once formed, they are very rigid and scarcely soluble in any solvent. Recently, we and others have explored a new method to transcribe a variety of organic superstructures into inorganic materials by a sol−gel reaction of metal alkoxides (“sol−gel transcription”), by which one can control the morphology of inorganic compounds and create various new superstructural inorganic materials.[4−9] The

---

[†] Kyushu University.

[‡] Nara Institute of Science and Technology.

[§] Japan Science and Technology Corporation.

(1) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537.

(2) Pringsheim E.; Terpetschnig E.; Piletsky, S. A.; Wolfbeis, O. S. *Adv. Mater.* **1999**, *11*, 865.

(3) Shoji, E.; Freund, M. S. *J. Am. Chem. Soc.* **2001**, *123*, 3383.

(4) (a) Jung, J. H.; Ono, Y.; Hanabusa, K.; Shinkai, S. *J. Am. Chem. Soc.* **2000**, *122*, 5008. (b) Jung, J. H.; Ono, Y.; Sakurai, K.; Sano, M.; Shinkai, S. *J. Am. Chem. Soc.* **2000**, *122*, 8648. (c) Ono, Y.; Nakashima, K.; Sano, M.; Hojo, J.; Shinkai, S. *J. Mater. Chem.* **2001**, *11*, 2412.

(5) Kobayashi, S.; Hamasaki, N.; Suzuki, M.; Kimura, M.; Shirai, H.; Hanabusa, K. *J. Am. Chem. Soc.* **2002**, *124*, 6550 and reference cited therein.

(6) Seddon, A. M.; Patel, H. M.; Burkett, S. L.; Mann, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2988.

10.1021/ol027558r CCC: $25.00

driving force operating in this sol−gel transcription is considered to be electrostatic and/or hydrogen-bonding interactions between silica nanoparticles and organic assemblies acting as templates. Thus, it occurred to us that the morphology of these polymers would be also controllable, applying the template method to the electrochemical polymerization process: as oxidative polymerization of these monomers produces cationic intermediates, the anionic assemblies should act as the appropriate template as a result of the mutual electrostatic attractive force. A few examples, in which the presence of anionic micelles affects the resultant poly(aniline) morphology, have been reported.[10,11] To the best of our knowledge, however, there is no precedent for such a system that the morphology of the superstructures acting as the template is strictly compared with that of the resultant polymers in order to clarify whether the fine transcription is really realized. Here, we employed the assembly of anionic porphyrin (TPPS) as a template, because porphyrins tend to aggregate into a one-dimensional rodlike structure, which has been well-characterized by microscopic methods.[12,13] We here report, for the first time, that electrochemical polymerization of EDOT or pyrrole results in a novel rodlike polymer structure as a result of the template effect of the one-dimensionally stacked TPPS aggregate.

A triethylene glycol (0.1 mL) containing EDOT (10 mg) was mixed with water (10 mL) under sonication. To this solution were added TPPS (1.0 mg) and LiCl (21 mg). The resultant solution was used for subsequent electrochemical experiments; the final concentrations were [EDOT] = 7.1 mM, [LiCl] = 50 mM, and [TPPS] = 0.11 mM. We measured the UV−vis absorption spectra of this solution. The absorption maximum appears at 490 nm, and the Soret band shifts to a longer wavelength. These findings indicate that TPPS J-aggregate exists in the present system. The cell consisted of an ITO electrode as the working electrode, a Pt counter electrode, and a Ag/AgCl reference electrode. The redox was repeated in a voltage range of 0−1.0 V (vs Ag/AgCl) with a scan rate of 0.05 V s^{-1} at 25 °C. In CV, the value of electric current increased during the successive potential sweeping in the presence of TPPS. The CV waves are similar to those reported for the EDOT/SDS (anionic micelle) system.[14] The result indicates that the poly(EDOT) film is deposited on the ITO electrode.

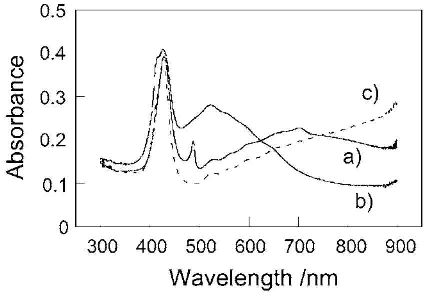


Figure 1. UV−vis absorption spectra for (a) poly(EDOT) film, (b) at the reduced state, and (c) at the reoxdized state.

To obtain evidence that the TPPS aggregates are immobilized in this film, we measured the UV−vis absorption spectra of the modified ITO electrode. As shown in spectrum a in Figure 1, one can clearly recognize an exciton-coupling band (489 nm) as well as a Soret band (429 nm). Since the Soret band is red-shifted by 17 nm in comparison to that in dilute aqueous solution, one can conclude that the J-aggregates of TPPS are immobilized in this film.[15] When this film was reduced to −0.6 V (vs Ag/AgCl) on the ITO electrode, a broad absorption band assignable to reduced poly(EDOT) appeared at around 520 nm.[14] Very interestingly, the Soret band remained unaffected while the exciton-coupling band disappeared (spectrum b). When the film was reoxidized to +0.8 V (vs Ag/AgCl), the exciton-coupling band was recognized only very weakly (spectrum c). The findings indicate that the J-aggregates of TPPS are maintained by the electrostatic interaction with the cationic sites in poly(EDOT); however, once the cationic sites are erased by electrochemical reduction, it becomes energetically difficult to maintain this stereoregular aggregation structure.

To obtain a visual image of this composite film, we took the SEM images (Figure 2). As shown in Figure 2d, electrochemical polymerization of EDOT (without TPPS) results in a film with the relatively smooth surface covered by pebble-like masses. In contrast, the same treatment in the

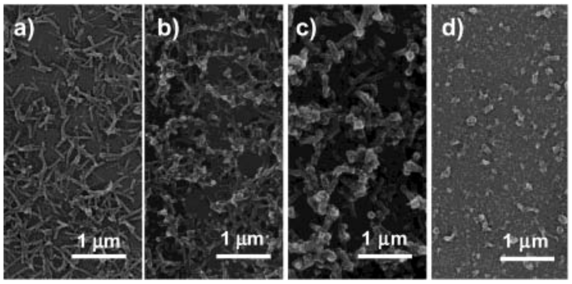


Figure 2. Scanning electron micrographs of poly(EDOT) films: (a) after 10 cycles in the presence of TPPS, (b) after 30 cycles in the presence of TPPS, (c) after 60 cycles in the presence of TPPS, (d) after 10 cycles in the absence of TPPS.

---

(7) Katagiri, K.; Hamasaki, R.; Ariga, K.; Kikuchi, J. *J. Am. Chem. Soc*. **2002**, *124*, 7892.

(8) Jung, J. H.; Shinkai, S.; Shimizu, T. *Nano Lett*. **2002**, *2*, 17.

(9) Sugiyasu, K.; Tamaru, S.; Takeuchi, M.; Berthier, D.; Huc, I.; Oda, R.; Shinkai, S. *Chem. Commun*. **2002**, 1212.

(10) Kanungo, M.; Kumar, A.; Contractor, A. Q. *J. Electroanal. Chem*. **2002**, *528*, 46.

(11) Zhong Z.; Wan, M. *Synth. Met*. **2002**, *128*, 83; *Adv. Mater*. **2002**, *14*, 1314.

(12) (a) Kimura, M.; Shiba, T.; Yamazaki, M.; Hanabusa, K.; Shirai, H.; Kobayashi, N. *J. Am. Chem. Soc*. **2001**, *123*, 5636. (b) Tamaru, S.; Takeuchi, M.; Sano, M.; Shinkai, S. *Angew. Chem., Int. Ed*. **2002**, *41*, 853.

(13) Miura, A.; Yanagawa, Y.; Tamai, N. *J. Microsc*. **2001**, *202*, 401.

(14) Sakmeche, N.; Aeiyah, S.; Aaron, J. J.; Jouini, M.; Lacroix, J. C.; Lacaze, P. C. *Langmuir* **1999**, *15*, 2566.

(15) (a) Ariga, K.; Lvov, Y.; Kunitake, T *J. Am. Chem. Soc*. **1997**, *119*, 2224. (b) Imahori, H.; Norieda, H.; Nishimura, Y.; Yamazaki, I.; Higuchi, K.; Kato, N.; Motohiro, T.; Yamada, H.; Tamaki, K.; Arimura; M.; Sakata, Y *J. Phys. Chem. B* **2000**, *104*, 1253.

presence of TPPS (after 10−60 cycles) results in a rodlike structure with 300−500 nm length and 30−50 nm diameter (Figure 2a−c).[16] It is also seen from these images that both the density and the size of the nano-rods increase with the increase in the redox cycle. This implies that the incipient nano-rods are successively adsorbed onto the ITO electrode surface and then grow up to “fat” nano-rods on the surface.

Next, we estimated the influence of the scan rate on the absorption spectra of the immobilized TPPS aggregates and the poly(EDOT) morphology. As shown in Figure 3, the intensity of the Soret band was scarcely affected by the scan rate. On the other band, the exciton-coupling band, an indication of the TPPS J-aggregates,[15] was observed only for the spectra obtained at the high scan rates. Presumably, the aggregation mode in solution[17] is entrapped as it is only when the scan rate is fast enough, whereas the J-aggregates can reorganize to some less ordered structure in the film layer when the scan rate is slow (Figure 4).

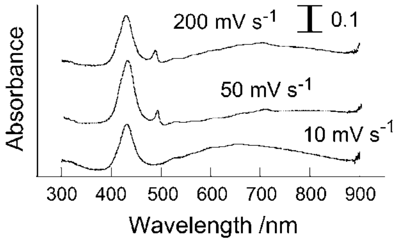


Figure 3. UV−vis absorption spectra of poly(EDOT) films electropolymerized at various scan rates.

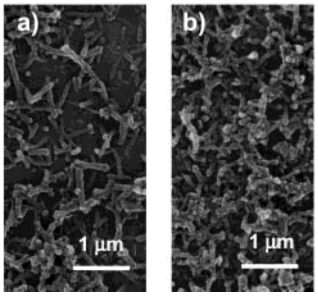


Figure 4. Scanning electron micrographs of poly(EDOT) films electropolymerized at each scan rate: (a) 10, (b) 200 mV s^{-1}.

We used 5,10,15,20-tetrakis(*N*-methylpyridinium-4-yl)-21*H*,23*H*-porphine tetrakis(*p*-tolenesulfonate) (TMPyP) instead of TPPS; however, SEM and UV−vis measurements showed that the surface is the same as that obtained in the absence of TPPS. These results indicate that the electrostatic interaction between anionic template and oxdized monomer is very important.

Here, it occurred to us that electrochemical polymerization of pyrrole, the mechanism of which is basically similar to that of poly(EDOT), would also proceed under the template effect. The poly(pyrrole) film is more rigid than the poly-(EDOT) film, and if it is once formed, it is scarcely soluble in any solvent. This means that the morphology-controlled poly(pyrrole) synthesis is highly significant. Figure 5 shows a UV−vis absorption spectrum of the poly(pyrrole) film obtained on the ITO electrode after 40 cycles in a voltage range of −0.2 to 0.8 V (vs Ag/AgCl) in the presence of pyrrole (15 mM), TPPS (0.11 mM), LiCl (50 mM), and triethylene glycol (1 wt %). One can clearly recognize a Soret band at 426 nm and an exciton-coupling band at 488 nm. Since the Soret band is red-shifted by 14 nm in comparison to that in dilute aqueous solution, one may regard that TPPS also adopts the J-aggregate in the poly(pyrrole) film. The SEM image is shown in Figure 6a and b; as expected, the poly(pyrrole) film consists of nano-rods with 300−500 nm length and 50−80 nm diameter. This morphology is entirely different from that obtained in the absence of TPPS, which features a very smooth surface (Figure 6c).

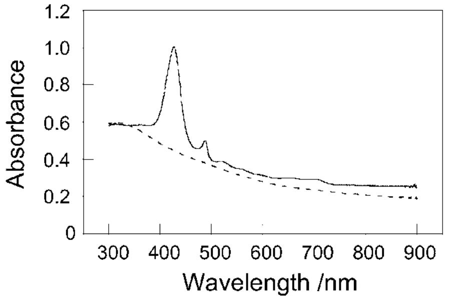


Figure 5. UV−vis absorption spectra of (—) TPPS-deposited film and (- - -) poly(pyrrole) film.

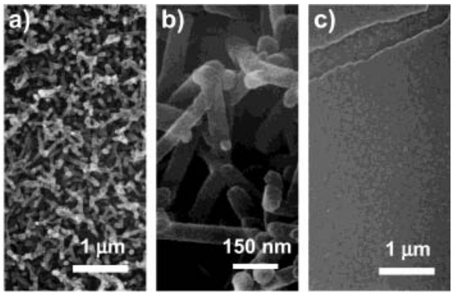


Figure 6. Scanning electron micrographs of poly(pyrrole) films: (a and b) after 40 cycles in the presence of TPPS, (c) after 200 cycles in the absence of TPPS.

---

(16) The aqueous solution of TPPS (0.10 mM) was extended on mica and observed with AFM. We could find long fibers with 1 μm length and ca. 3 nm height.

(17) (a) Rubires, R.; Farrera, J. A.; Ribo, J. M. *Chem. Eur. J.* **2001**, *7*, 436. (b) Kano, K.; Fukuda, K.; Wakami, H.; Nishiyabu, R.; Pasternack, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 7494.

In conclusion, the present study has demonstrated, for the first time to the best of our knowledge, that the morphology of the poly(EDOT) and poly(pyrrole) films obtained by electrochemical polymerization of EDOT and pyrrole, respectively, can be controlled by using anionic TPPS aggregates as a template. One may regard, therefore, that this is a novel transcription process of anionic templates to oxidizable monomers through electrochemical polymerization.[18] So far, it has been believed that in electrochemical polymerization of these monomers, the easiness in the preparation method is a merit, whereas the difficulty in the morphology control is a serious demerit. This demerit, possibly bigger than the merit so far, has hampered the broad applications of these conductive polymers as functional materials. We now believe, therefore, that as this demerit has been solved (at least partially), the present study would stimulate further utilization of these polymers as new functional materials. We now consider that in principle, the various polymeric superstructures can be created from poly(EDOT) and poly(pyrrole) as long as the appropriate "anionic" assemblies suitable for the template exist.

Supporting Information Available: UV−vis absorption spectrum of TPPS J-aggregate in the polymerization solution; AFM images of TPPS aggregates on mica; structure of TMPyP; UV−vis absorption spectra for poly(EDOT) films in the presence of TMPyP; and scanning electron micrographs of poly(EDOT) film electropolymerized in the presence of TMPyP. This material is available free of charge via the Internet at http://pubs.acs.org.

OL027558R

---

(18) We are applying this concept (to use polyanionic materials as templates) to other related systems. Most of them act as good templates, and these results will be subsequently published as full papers.