Conductive Polymers

Helical Superstructure of Conductive Polymers as Created by Electrochemical Polymerization by Using Synthetic Lipid Assemblies as a Template**

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Poly(ethylenedioxythiophene) (poly(EDOT)) and poly(pyrrole) are conductive polymers easily obtained by electrochemical polymerization or chemical synthesis of the corresponding monomers.[1] In spite of the convenience of the preparation method and the cheapness of the monomers, the applications have been rather limited.[1–3] This limitation is due to the difficulty in the structural control arising from their hardness and low solubility. So far, several attempts have been made to overcome this difficulty: for example, deposition of monomers in the oriented environments such as LB membranes,[4] surfactant aggregates,[5,6] liquid crystals,[7] or self-assembly of chemically modified monomers.[8,9] It is known, however, that in these systems the prediction of the resultant superstructures and the fine tuning of the molecular assemblies are nearly impossible.

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 ("templating sol–gel reaction"), by which one can control the morphology of inorganic compounds and create various new superstructural inorganic materials.[10–18] The driving force operating in this templating sol–gel reaction is considered to be electrostatic and/or hydrogen-bonding interactions between silica nanoparticles and organic assemblies acting as templates.[16] Thus, it occurred to us that the morphology of these conductive polymers would be also controllable by applying the concept of the templating method to the electrochemical polymerization process: that is, as oxidative polymerization of these monomers produces cationic intermediates, the anionic assemblies should act as a potential template owing to the

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mutual electrostatic attractive force. More recently, we found that [60]fullerene encapsulated in *p*-sulfonatocalix[8]arene and J aggregates of 5,10,15,20-tetrakis(4-sulfonatophenyl)-porphyrin are readily deposited on the indium–tin oxide (ITO) electrode by electrochemical polymerization of these monomers.[19] Observation by SEM established that the resulting conductive polymeric assemblies have superstructures similar to those of the original organic templates. This finding prompted us to apply this concept to some anionic organic template that bears a helical superstructure. Here, we synthesized amphiphile **2** from **1**, which is already known as a helix-forming amphiphile (Scheme 1).[20] We confirmed from the TEM and SEM images (prepared from [**2**] = 0.3 mM, 10% MeOH aqueous solution) that **2** forms a fibrous structure with a left-handed helical motif (see Supporting Information). Oxidative polymerization of EDOT and pyrrole was carried out by using this helical superstructure as a template. Interestingly, we have found that electrochemical polymerization results in polymeric superstructures such as a helical-tape superstructure. This is the first example of a helical superstructure that is composed of conductive polymers designed by a templating method.

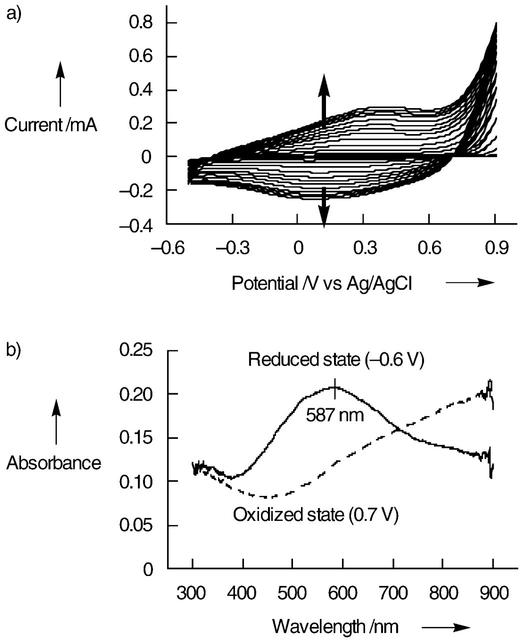
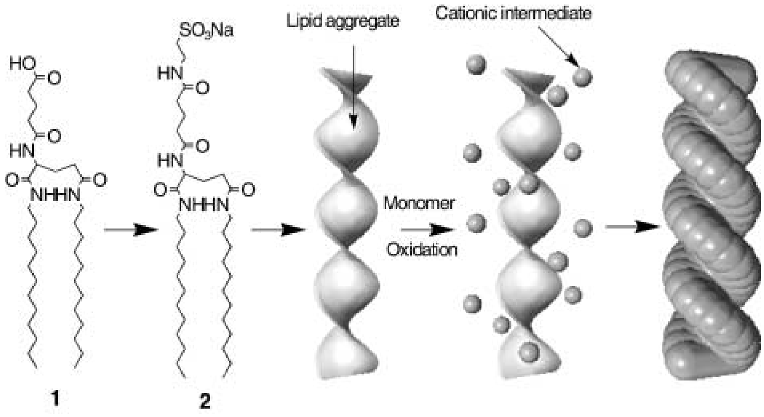


Figure 1. a) Cyclic voltammograms for EDOT obtained on an ITO electrode and b) UV/Vis absorption spectra of a poly(EDOT) film at reduced (——) and oxidized (-----) states electrodeposited on an ITO electrode from a tamplating method.

Compound **2** (2.1 mg, 2.9 μmol) EDOT (13 mg, 92 μmol) and $NaClO_4$ (61 mg, 0.5 mmol) of were dissolved in a 10% MeOH aqueous solution (10 mL). The cell consisted of an ITO electrode as the working electrode (working area = 2.2 cm^2), a Pt counter electrode, and an Ag/AgCl reference electrode. The redox cycle was repeated in a voltage range of –0.5–0.9 V (versus Ag/AgCl) with a scan rate of 0.05 $V s^{-1}$ at 25 °C. In the electrochemical polymerization, the value of electric current increased during the successive potential sweeping in the presence of **2** (Figure 1 a). The oxidized and reduced states of an obtained poly(EDOT) film deposited on ITO electrode was characterized by UV/Vis spectroscopy. The oxidized state showed a weak absorption band in the visible region and a strong absorption band in the near-IR region, whereas the reduced state showed a broad absorption band at 587 nm because of the π–π* electronic transition (Figure 1 b). The cyclic voltammetry (CV) waves and UV/Vis spectral change were very similar to those reported for the EDOT/SDS (anionic micelle; SDS = sodium dodecyl sulphate) system.[21] This result indicates that the poly(EDOT)·amphiphile composite film is deposited on the ITO electrode. After the electrode had been washed, we carried out a further five redox cycles in 50 mM $NaClO_4$ aqueous solution in the absence of EDOT and **2**.



Scheme 1. Structure of a synthetic lipid **1** and **2** bearing an L-glutamic segment and schematic illustration of a templating oxidative polymerization.

The attenuated total reflection (ATR) IR spectra of the modified ITO electrode were measured (see Supporting Information). One can recognize a new peak at 1641 cm^{-1} (shown by an arrow mark), which is not present in the film of poly(EDOT) obtained in the absence of **2**. This result shows that **2** is deposited on the poly(EDOT) film. Figure 2 shows the SEM images of this composite film.

Electrochemical polymerization of EDOT in the presence of **2** results in a left-handed helical superstructure. In contrast, the same treatment in the absence of **2** results in a film with a smooth surface covered by pebblelike masses (see Supporting Information). As evidenced from a

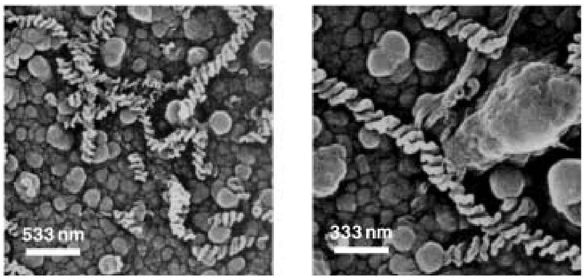


Figure 2. SEM images of poly(EDOT)·**2** composite film obtained by a templating method.

TEM image of the poly(EDOT)·**2** composite prepared by chemical oxidation with ammonium peroxodisulfate (APS) (Figure 3), this poly(EDOT) has a tubular structure, which indicates that the lipid fiber acts as a template.[22]

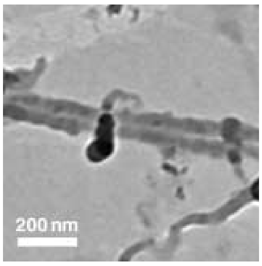


Figure 3. TEM image of poly(EDOT)·**2** composite prepared by chemical oxidation with APS.

Pt coated interdigitated microelectrodes were used for in situ conductance measurements[23,24] of the poly(EDOT)·**2** composites. The polymers were electrosynthesized under the same conditions as those used for the ITO electrode. As shown in AFM images of poly(EDOT)·**2** composites electrochemically deposited on interdigitated microelectrodes (Figure 4). The bridge between two electrodes is attained only by helical fibers. It is also seen from Figure 4 that poly(EDOT) dots generated without the presence of template are adsorbed onto the surface of the microelectrodes, but do not bridge the two electrodes.

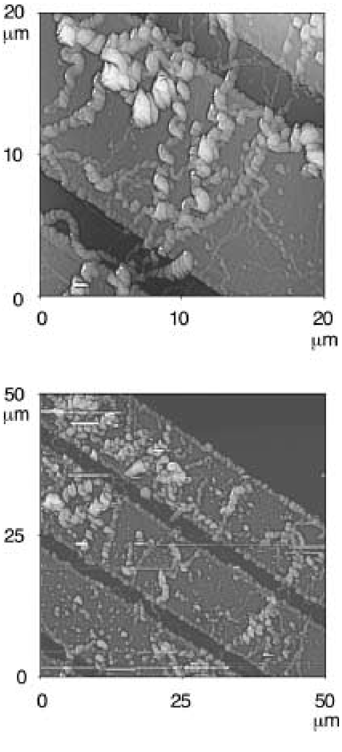


Figure 4. AFM images of poly(EDOT)·**2** composites electrochemically deposited on interdigitated microelectrodes by a templating method.

The conductance measurement of the poly(EDOT) polymer was carried out in 50 mm $NaClO_4$ aqueous solution. The conductivity was estimated by holding one Pt line at fixed potential, Vg, versus Ag/AgCl and the other at Vg+20 mV. The potential difference between the electrodes results in a current flow (drain current). The drain current was scarcely observed under −0.5 V, then increased above −0.5 V, and reached a plateau at +0.1 V (Figure 5).[25] This result is similar to that reported in reference[24] and indicates that the observed conductivity is due to the poly(EDOT)·**2** fiber composites.

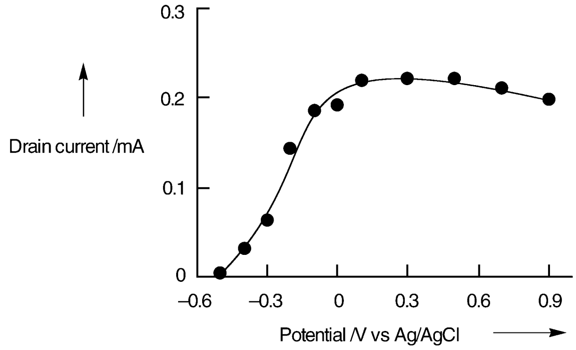


Figure 5. Drain current vs gate voltage (Vg) plot for poly(EDOT)·**2** composite.

It occurred to us that electrochemical polymerization of pyrrole, the mechanism of which is basically similar to that of 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. The electrochemical polymerization was carried out with [pyrrole] = 14 mm, [$NaClO_4$] = 50 mm, and [**2**] = 0.3 mm. After 60 redox cycles (between −0.50 and 0.8 V versus Ag/AgCl) in the polymerization solution and five redox cycles in the 50 mm $NaClO_4$ solution (for washing the electrode in the absence of pyrrole and **2**), the poly(pyrrole) film was observed by SEM. In the SEM studies (Figure 6a), one can see a left-handed helical superstructure similar to that observed for the poly(EDOT)·**2** composites.[26] As shown in a TEM image of poly(pyrrole)·**2** composites prepared by chemical oxidation with APS (Figure 6b), this poly(pyrrole) has a hollow structure with a helical motif, indicating that the lipid fiber acts as a template.[22]

In conclusion, this study demonstrates, 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 synthetic lipid assemblies as a template. Therefore, one may regard this process as a novel templating of anionic templates to oxidizable monomers through electrochemical polymerization. Until now, it was believed that in the electrochemical polymerization of these monomers, the easiness in the preparation method is an

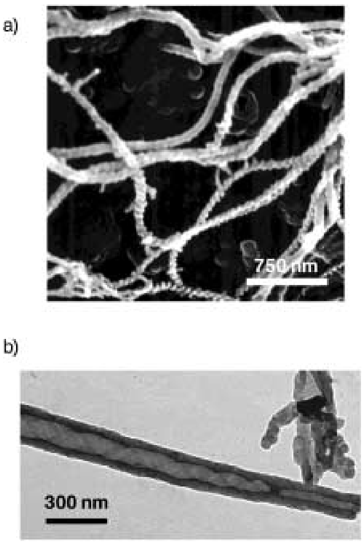


Figure 6. a) SEM image of poly(pyrrole)·**2** composite film electropolymerized on an ITO electrode and b) TEM image of poly(pyrrole)·**2** composite prepared by chemical oxidation with APS.

advantage, whereas the difficulty in the morphology control is a serious disadvantage. This disadvantage, which has outweighed the benefits, has hampered the broad application of these conductive polymers as functional materials. Therefore, we now believe that as this problem of morphology control has been solved (at least partially) and this study will stimulate further use 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.

Experimental Section

The synthesis of **1** was reported previously.[20]

The synthesis of **2**: **1** (0.15 g, 0.25 mmol) and a few drops of triethylamine were added to DMF (10 mL). Benzotriazol-1-yloxytris(dimethylamino)phosphonium hexafluorophosphate (BOP) reagent (0.22 g, 0.5 mmol, 2.0 equiv) was added and the resultant reaction mixture was allowed to react for a few minutes. 2-Aminoethanesulfonic acid (63 mg, 0.5 mmol, 2 equiv) was dissolved into 50% DMF aqueous solution containing a few drops of triethylamine and this solution was subsequently added to the reaction mixture. This mixture was stirred for one day at room temperature and then evaporated under reduced pressure. The residue was dissolved into water and an excess of octyltrimethylammonium bromide was added. The ion-paired product of lipid·octyltrimethylammonium was extracted with CH_2Cl_2 and the organic layer was separated and dried over Na_2SO_4. An addition of a solution of $NaClO_4$ in MeCN into the organic layer resulted in a white precipitate. The precipitate was recovered by filtration and washed with CH_2Cl_2 and MeCN in that order. This operation gave the white solid **2** (100 mg, 55%): mp decomposed at 230 °C; ^{1}H NMR (600 MHz, [D$_6$]DMSO): $\delta = 0.85$ (t, 6H, $J = 6.72$ Hz), 1.20–1.28 (br d, 36H), 1.30–1.40 (br d, 4H), 1.62–1.81 (m, 4H), 1.99 (t, 2H, $J = 7.07$ Hz), 2.05–2.14 (m, 4H), 2.53–2.61 (m, 2H), 2.92–3.01 (br d, 4H), 3.24–3.30 (m, 2H), 4.11–4.15 (m, 1H), 7.77–7.80 (m, 2H), 7.85 (t, 1H, $J = 5.64$ Hz), 8.02 ppm (d, 1H, $J = 7.92$ Hz); IR (ATR): $\tilde{\nu}_{max} = 1639, 1177, 1060\ cm^{-1}$; MALDI-TOF MS found m/z 726([M+H]$^+$), 748([M+Na]$^+$); calcd for $C_{36}H_{69}N_4O_7SNa$ m/z 726([M+H]$^+$), 748([M+Na]$^+$).

Pyrrole (Tokyo Kasei Kogyo) was used after distillaion. Ethylenedioxythiophene (Aldrich), and Sodium perchlorate (Tokyo Kasei Kogyo) were used as received. CV experiments were performed with a one-compartment, three-electrode electrochemical cell driven by an electrochemical analyzer (Autolab PGSTAT12 potentiostat/galvanostat) in aqueous solution containing supporting electrolyte ($NaClO_4$, 50 mM) and 10% MeOH. The oxidative polymerization of ethylenedioxythiophene was carried out in a CV cell with an ITO electrode as the working electrode, a Pt counter electrode and an Ag/AgCl reference electrode. The redox was repeated in a voltage range of −0.5–0.9 V (versus Ag/AgCl) with scan rate 0.05 mV s^{-1} at 25 °C. The oxidative polymerization of pyrrole was carried out in a CV cell by using an ITO electrode as the working electrode, a Pt counter electrode and an Ag/AgCl reference electrode. The redox was repeated in a voltage range of −0.5–0.8 V (versus Ag/AgCl) with scan rate 0.05 V s^{-1} at 25 °C. After polymerization, five redox cycles in the corresponding range were performed in 50 mM $NaClO_4$ aqueous solution to wash the film. Conductivity measurements were carried out Autolab PGSTAT12 with BIPOT bipotentiostat. Atomic force microscopy (AFM) studies were carried out on a Topometrix TMX-2100 (noncontact mode). SEM studies were carried out on a Hitachi S-5000. Transmission electron microscopy TEM studies were carried out on a JEOL JEM-2010. ATR IR spectra were recorded with a PerkinElmer Spectrum One.

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[1] D. T. McQuade, A. E. Pullen, T. M. Swager, *Chem. Rev.* **2000**, *100*, 2537–2574.
[2] E. Pringsheim, E. Terpetschnig, S. A. Piletsky, O. S. Wolfbeis, *Adv. Mater.* **1999**, *11*, 865–868.
[3] E. Shoji, M. S. Freund, *J. Am. Chem. Soc.* **2001**, *123*, 3383–3384.
[4] T. Iyoda, M. Ando, T. Kaneko, A. Ohtani, T. Shimizu, K. Honda, *Langmuir* **1987**, *3*, 1169–1170.
[5] W. Wernet, M. Monkenbusch, G. Wegner, *Macromol. Rapid Commun.* **1984**, *5*, 157–164.
[6] a) M. Kanungo, A. Kumar, A. Q. Contractor, *J. Electroanal. Chem.* **2002**, *528*, 46–56; b) Z. Zhong, M. Wan, *Synth. Met.* **2002**, *128*, 83–89; c) Z. Zhong, M. Wan, *Adv. Mater.* **2002**, *14*, 1314–1317; d) L. Qu, G. Shi, *Chem. Commun.* **2003**, 206–207; e) Z. Wei, M. Wan, T. Lin, L. Dai, *Adv. Mater.* **2003**, *15*, 136–139.
[7] J. F. Hulvat, S. I. Stupp, *Angew. Chem.* **2003**, *115*, 802–805; *Angew. Chem. Int. Ed.* **2003**, *42*, 778–781.
[8] J. H. Georger, A. Singh, R. R. Price, J. M. Schnur, P. Yager, P. E. Schoen, *J. Am. Chem. Soc.* **1987**, *109*, 6169–6175.
[9] a) M. Ikegame, K. Tajima, T. Aida, *Angew. Chem.* **2003**, *115*, 2204–2207; *Angew. Chem. Int. Ed.* **2003**, *42*, 2154–2157; b) G. Li, S. Bhosale, T. Wang, Y. Zhang, H. Zhu, J. H. Fuhrhop, *Angew. Chem.* **2003**, *115*, 3948–3951; *Angew. Chem. Int. Ed.* **2003**, *42*, 3818–3821.
[10] a) J. H. Jung, Y. Ono, K. Hanabusa, S. Shinkai, *J. Am. Chem. Soc.* **2000**, *122*, 5008–5009; b) J. H. Jung, Y. Ono, K. Sakurai, M. Sano, S. Shinkai, *J. Am. Chem. Soc.* **2000**, *122*, 8648–8653; c) Y. Ono, K. Nakashima, M. Sano, J. Hojo, S. Shinkai, *J. Mater. Chem.* **2001**, *11*, 2412–2419.
[11] S. Kobayashi, N. Hamasaki, M. Suzuki, M. Kimura, H. Shirai, K. Hanabusa, *J. Am. Chem. Soc.* **2002**, *124*, 6550–6551, and references therein.

[12] A. M. Seddon, H. M. Patel, S. L. Burkett, S. Mann, *Angew. Chem.* **2002**, *114*, 3114 – 3117; *Angew. Chem. Int. Ed.* **2002**, *41*, 2988 – 2991, and references therein.

[13] K. Katagiri, R. Hamasaki, K. Ariga, J. Kikuchi, *J. Am. Chem. Soc.* **2002**, *124*, 7892 – 7893.

[14] J. H. Jung, S. Shinkai, T. Shimizu, *Nano Lett.* **2002**, *2*, 17 – 20.

[15] K. Sugiyasu, S. Tamaru, M. Takeuchi, D. Berthier, I. Huc, R. Oda, S. Shinkai, *Chem. Commun.* **2002**, 1212 – 1213.

[16] For recent reviews see a) G. J. de A. A. Soler-Illia, C. Sanchez, B. Lebean, J. Patorin, *Chem. Rev.* **2002**, *102*, 4093 – 4138; b) K. J. C. van Bommel, A. Friggeri, S. Shinkai, *Angew. Chem.* **2003**, *115*, 1010 – 1030; *Angew. Chem. Int. Ed.* **2003**, *42*, 980 – 999.

[17] a) Y. Ono, K. Nakashima, M. Sano, Y. Kanekiyo, K. Inoue, J. Hojo, S. Shinkai, *Chem. Commun.* **1998**, 1477 – 1478; b) J. H. Jung, Y. Ono, S. Shinkai, *Chem. Eur. J.* **2000**, *6*, 4552 – 4557.

[18] The helical structure of CdS has been also created; E. D. Sone, E. R. Zubarev, S. I. Stupp, *Angew. Chem.* **2002**, *114*, 1781 – 1785; *Angew. Chem. Int. Ed.* **2002**, *41*, 1705 – 1709.

[19] a) T. Hatano, M. Takeuchi, A. Ikeda, S. Shinkai, *Chem. Commun.* **2003**, 342 – 343; b) T. Hatano, M. Takeuchi, A. Ikeda, S. Shinkai, *Chem. Lett.* **2003**, 314 – 315; c) T. Hatano, M. Takeuchi, A. Ikeda, S. Shinkai, *Org. Lett.* **2003**, *5*, 1395 – 1398.

[20] For compound **1** see H. Hachisako, Y. Murata, H. Ihara, *J. Chem. Soc. Perkin Trans. 2* **1999**, 2569 – 2577. For the helical structure of lipid molecules see N. Nakashima, S. Asakuma, T. Kunitake, *J. Am. Chem. Soc.* **1985**, *107*, 509 – 510.

[21] N. Sakmeche, S. Aeiyah, J. J. Aaron, M. Jouini, L. C. Lacroix, P. C. Lacaze, *Langmuir* **1999**, *15*, 2566 – 2574.

[22] TEM pictures were taken without staining treatment. Therefore, the observed contrast is due to the formation of conductive polymers.

[23] G. Schiavon, S. Sitran, G. Zotti, *Synth. Met.* **1989**, *32*, 209 – 217.

[24] K. Krishnamoorthy, A. V. Ambade, S. P. Mishra, M. Kanungo, A. Q. Contractor, A. Kumar, *Polymer* **2002**, *43*, 6465 – 6470.

[25] Since the interdigitated microelectrode gaps were not filled with helical fibers, it was difficult to transfer the observed drain current to conductance.

[26] In the electrochemical polymerization, the value of electric current increased during the successive potential sweeping in the presence of **2** (see Supporting Information).