

New Morphology-controlled Poly(aniline) Synthesis Using Anionic Porphyrin Aggregate as a Template

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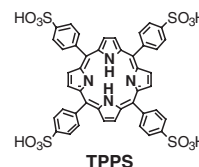
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It was found that 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (TPPS), which is known to aggregate in a one-dimensional direction in water, acted as a template for electrochemical polymerization of aniline on ITO electrode. Examinations using cyclic voltammetry (CV) and UV-vis spectroscopy established that J-aggregated TPPS molecules were entrapped in the resultant poly(aniline). Scanning electron microscopy (SEM) observation established that poly(aniline) grew up to a nanosized rod-like structure, reflecting the aggregation structure of TPPS. It is a very novel and important finding that poly(aniline), which has been believed to result in only "rigid" film, can be morphologically controlled using a "template method".

Poly(aniline) is a conductive polymer easily obtained by electrochemical polymerization of aniline.¹ In spite of the convenient method of preparation and cheapness of the monomer, the application have been rather limited.¹⁻³ One reason for the limited application is the serious disadvantage related to the difficulty in controlling the morphology in the polymerization process; If poly(aniline) is once formed, it is very rigid and scarcely soluble in any solvent. Recently, we and others have explored a method to transcribe a variety of organic superstructures into inorganic materials by the 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 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.⁴⁻⁹ Thus, it occurred to us that the film structure of poly(aniline) would be also controllable, applying the template method to the electrochemical polymerization process: As aniline is protonated at acidic condition, the anionic assemblies should act as the appropriate template because of the mutual electrostatic interaction. In fact, 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 precedence, in which the organic superstructure acting as the template is strictly compared with that of the resultant polymer to clarify whether or not the fine transcription is really induced. Here, we employed the assembly of an anionic porphyrin (TPPS) as a template, because the porphyrin tends to aggregate in a one-dimensional direction and the aggregate structure is well characterized by microscopic methods.^{12,13} We here report, for the first time, that electrochemical polymerization of aniline results in a novel rod-like structure due to the template effect of

the one-dimensionally-stacked TPPS aggregate.



An aqueous solution containing aniline sulfate (5.0 mmol dm^{-3}), H_2SO_4 (50 mmol dm^{-3}), and Na_2SO_4 (50 mmol dm^{-3}) was subjected to electrochemical polymerization in the absence and the presence of TPPS ($0.11 \text{ mmol dm}^{-3}$). 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 $-0.2 \sim 1.1 \text{ V}$ (vs. Ag/AgCl) with a scan rate of 0.1 Vs^{-1} at 25°C . Three redox peaks at $E_{\text{ox}}/E_{\text{red}} = 0.2/0.0$, $0.5/0.35$, and $0.65/0.5 \text{ V}$ (vs. Ag/AgCl) increase during the successive potential sweeping in the presence of TPPS, corresponding to the growth of an electroactive polymer film on the ITO electrode. Figure 1 shows the UV-vis absorption spectra of the film at potentials from 0 to 0.8 V (vs. Ag/AgCl) electropolymerized after 120 cycles on the ITO electrode. One can clearly recognize an exciton-coupling band (491 nm) as well as the Soret band (426 nm) and Q bands ($660\text{--}730 \text{ nm}$), indicating that TPPS is deposited in this thin film layer.¹⁴ To obtain unambiguous evidence that this thin film is made from poly(aniline), the UV-vis absorption spectra were measured under the various voltages (Figure 1). As expected, the absorbance at visible wavelength region increases with an increase of the applied voltage, which is a characteristic property of the poly(aniline) film.¹⁵ The foregoing findings consistently support the view that oxidative polymerization of aniline on the ITO electrode proceeds under the electrostatic interaction with anionic TPPS aggregates to form a poly(aniline)/TPPS composite film.

To obtain a visual image of this composite film, we took the SEM pictures (Figure 2). As shown in Figure 2d, electrochemical polymerization of aniline results in a film with the

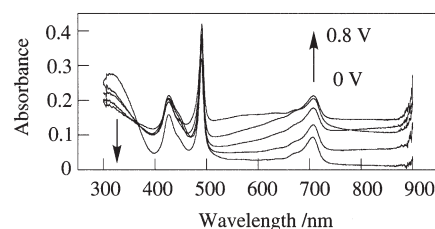


Figure 1. UV-vis absorption spectra of poly(aniline) film in $50 \text{ mmol dm}^{-3} \text{ H}_2\text{SO}_4$ at potentials from 0 to 0.8 V electropolymerized after 120 cycles in a voltage range of $-0.2 \sim 1.1 \text{ V}$.

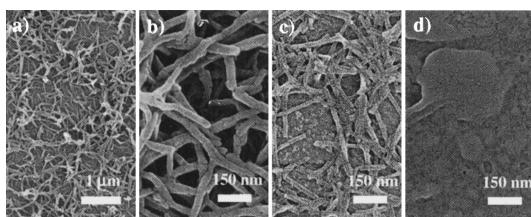


Figure 2. SEM images of poly(aniline) films electropolymerized after various cycles: a) and b) 120 cycles in the presence of TPPS, c) 30 cycles in the presence of TPPS, d) 120 cycles in the absence of TPPS.

smooth surface in the absence of TPPS. In contrast, the same treatment in the presence of TPPS (after 120 cycles) affords a rod-like structure with 200–1000 nm length and 30–50 nm diameter (Figures 2a and 2b). When the redox treatment was stopped after 30 cycles, the resultant nanorods are “thinner” (with 20–40 nm diameter: Figure 2c) than those obtained after 120 cycles (Figure 2b). This morphological difference implies that the nanorods are adsorbed onto the ITO electrode surface in its incipient stage and then grow up to “fat” nanorods on the surface.

Next, we estimated the influence of the TPPS concentration on the CV and the morphology. Figure 3 shows the CV charts after 120 cycles. As expected, two peaks at 0.2/0.0 and 0.65/0.5 V (vs. Ag/AgCl) increase with increasing TPPS concentration. As these redox peaks are not observed either for TPPS or for aniline itself, one may assign them to the redox reactions of TPPS/poly(aniline) complex. As shown in Figure 4a, TPPS is scarcely entrapped at 0.011 mmol dm⁻³ even after 120 cycles. At this condition, the CV pattern in Figure 3 is basically same as that of aniline oxidation. With increasing the TPPS concentration, the peaks assignable to the TPPS/poly(aniline) complex increase and the typical UV–vis absorption spectrum is observed at [TPPS] = 0.11 mmol dm⁻³ (Figures 4b and 4c). The SEM images obtained after 120 cycles at various TPPS concentrations are shown in

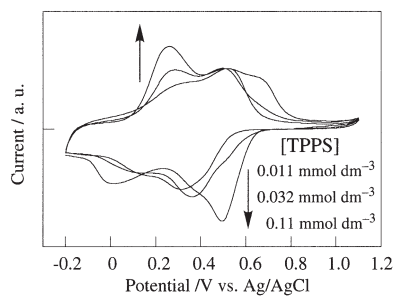


Figure 3. Cyclic voltammograms of poly(aniline) films electropolymerized at various concentrations of TPPS normalized at 0.5 V.

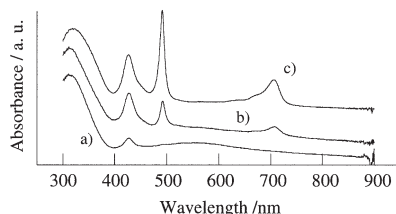


Figure 4. UV–vis absorption spectra of poly(aniline) films electropolymerized at various concentrations of TPPS in 50 mmol dm⁻³ H₂SO₄: a) 0.011 mmol dm⁻³, b) 0.032 mmol dm⁻³, c) 0.11 mmol dm⁻³.

Figure 5. As long as the aniline concentration is kept constant, the size of the nanorods is not so different among Figures 5a–5c. However, the “density” of the nanorods was significantly dependent on the TPPS concentration: The network becomes more crowded with the increase in the TPPS concentration. This is raised as further evidence that the TPPS aggregates act as a template for the nanorods formation by electrochemical polymerization of aniline.

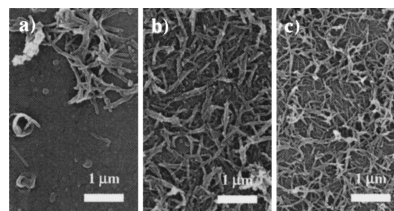


Figure 5. SEM images of poly(aniline) films electropolymerized after 120 cycles at various concentrations of TPPS: a) 0.011 mmol dm⁻³, b) 0.032 mmol dm⁻³, c) 0.11 mmol dm⁻³. the flat background is the poly(aniline) film formed without the template effect.

In conclusion, the present study has demonstrated, for the first time to the best of our knowledge, that the morphology of poly(aniline) 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 poly(aniline) through electrochemical polymerization. So far, it has been believed that the difficulty in the structure control is a serious demerit in electrochemical polymerization of aniline in spite of its easiness of preparation. This demerit has hampered the broad applications of poly(aniline) as functional materials. The present study would solve the demerit (at least partially) and stimulate further utilization of poly(aniline) as new functional materials. We now consider that in principle, the various polymeric superstructures can be created from poly(aniline) as long as the appropriate “anionic” assemblies suitable for the template exist.

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