Superstructural Poly(pyrrole) Assemblies Created by a DNA Templating Method

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ABSTRACT: It was found that DNAs can act as attractive templates for oxidative polymerization of pyrrole and result in novel higher-order superstructures composed of the DNA padding and the conjugate polymer outer layer. Furthermore, the resultant DNA/poly(pyrrole) composite can be deposited on an ITO electrode. The TEM and SEM observations have shown that oxidative polymerization creates a variety of superstructural poly(pyrrole) assemblies such as nanosized rodlike, circular, or supercoiled structures, reflecting the higher-order conformations of DNAs acting as the templates. The findings establish that the morphology of the conjugate polymer assemblies are controllable by a change in the DNA morphology used as their templates. The deposition of DNAs onto the ITO electrode was characterized by (1) ATR IR absorption bands assignable to DNA, (2) XPS binding energy of the phosphate group assignable to DNAs, and (3) binding of ethidium bromide (EB) to DNAs as detected by UV−vis spectroscopy and confocal laser scanning microscope (CLSM). The further detailed examination of the SEM pictures has established that the composite consists of a fibrous structure or its bundled structure, depending on the polymerization conditions. Interestingly, the ITO electrode modified by the DNA/poly(pyrrole) composite showed the CV responsiveness to DNA intercalators, indicating a potential to apply this system to a new amperometric DNA-based sensor.

Introduction

To design and create functional materials in a nanosized level is the major research target in the field of nanotechnology. When we extend diversity of such functional materials and immobilize such newly developed materials, a fabrication technique based on a template method seems to be most attractive and most convenient.

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.[1−7] In particular, when superstructures of molecular assemblies constructed from low-molecular-weight gelators in the gel phase[8] are used as templates and sol−gel polycondensation of tetraethoxysilane is applied to their fabrication, the organic template architectures are scrupulously transcribed into the silica.[1] The primary driving force operating in this sol−gel transcription is considered to be an electrostatic interaction between "anionic" silica nanoparticles and "cationic" organic assemblies acting as templates.[1−7] This concept suggests a new templating system in which anion/cation combination is inversed: that is, "anionic" superstructures would be also useful as templates and could be transcribed into some "cationic" polymer-forming materials. Thus, it occurred to us that the morphology of poly(pyrrole) would be controllable, applying this template method to its electrochemical polymerization process:[9] as oxidative polymerization of pyrrole produces "cationic" intermediates, the "anionic" assemblies should act as an appropriate template due to the mutual electrostatic attractive force. Poly(pyrrole) is a well-known conjugate polymer easily obtained by oxidative polymerization of pyrrole.[9] Despite the convenience of the preparation method and the cheapness of the monomer, however, the applications have been rather limited. One major reason is the serious drawback related to the difficulty in controlling the morphology in the polymerization process. Such a few examples have been reported, in which the presence of anionic micelles affects the resultant poly(aniline) morphology.[10,11] To the best of our knowledge, however, there was no clear systematic concept for such a transcription method, until we proposed this idea as a general concept, that the morphology of the template superstructures is strictly compared with that of the resultant polymer superstructures in order to clarify whether the fine transcription is really attained though oxidative polymerization. So far, we have demonstrated that a [60]-fullerene-*p*-sulfonatocalix[8]arene complex (low-molecular-weight compound), a self-assembled 5,10,-15,20-tetrakis(4-sulfonatophenyl)porphyrin (molecular assembly), a SDS−single-walled carbon nanotubes composite (supramolecular complex), a DNAs−single-walled carbon nanotubes composite (supramolecular complex), and synthetic lipids bearing an L-glutamic segment (helical superstructure) are useful as templates to transcribe their specific superstructures into the conjugate polymers.[12] Here, we noticed that a polymeric template which is not yet applied to this system but would be the most suitable and attractive candidate for the template is a "polynucleotide". It is known that DNAs exhibit various unique higher-order structures, so that they should act as fascinating templates to create novel poly(pyrrole)-based superstructures.[13] However, DNAs are highly water-soluble and biochemically

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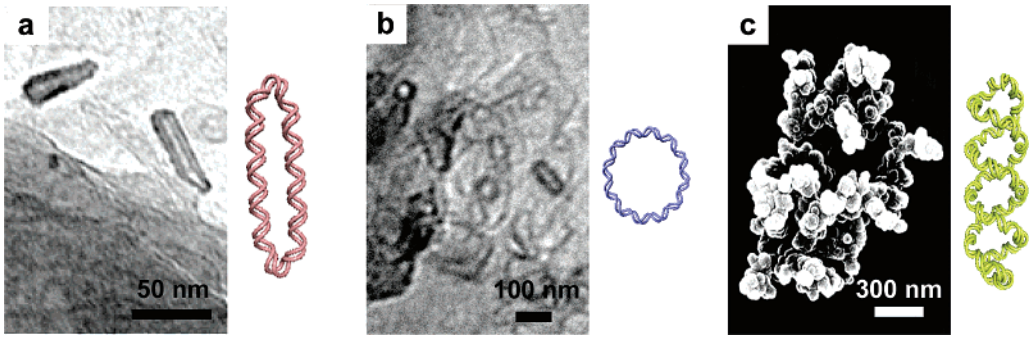

Figure 1. TEM and SEM images of DNA/poly(pyrrole) composites with the higher-order conformation: (a) rodlike, (b) circular, and (c) supercoiled structure.

unstable. To use DNAs as templates, we have to overcome these drawbacks.[14] We thus employed a few DNAs as templates and carried out oxidative polymerization of pyrrole by chemical and electrochemical methods. We here found that when plasmid DNA is used as a template, the higher-order DNA structures are not only immobilized in the poly(pyrrole) matrix but also create novel superstructures consisting of poly(pyrrole) aggregates.[15] Furthermore, we have report that salmon tests DNA is deposited on an ITO electrode as a stable composite with a poly(pyrrole) film, and the resultant modified electrode is useful as a sensor for intercalators and side-binders of DNA. This is the first example that a variety of higher-order DNA conformers are successfully transcribed into conjugated polymers, which are shown to be utilizable as a novel functional materials, that is, a new DNAs-based sensor.

Results and Discussion

Chemical Polymerization of Pyrrole Using Plasmid DNA Conformers as Templates and Poly(pyrrole) Assembly Morphologies as Observed by TEM and SEM. The chemical oxidation of pyrrole (60 mM) in the absence and the presence of ColE1 plasmid DNA (11 μg mL^{-1}) was carried out by the reaction with ammonium peroxodisulfate (APS, 10 mM) for 20 min at 25 °C. It is well-known that plasmid DNA adopts a supercoiled structure in the solution containing the appropriate concentration of salt. To observe the inner and outer structures of the poly(pyrrole) assembly, the polymer structure was examined by TEM and SEM. Figure 1a shows a TEM image of the obtained poly(pyrrole) assembly. One can regard that dark parts reflect poly(pyrrole) and bright parts reflect plasmid DNA because the TEM picture of Figure 1a was taken without any staining treatment. As can be seen from Figure 1a, one can recognize the rodlike structures in this TEM image. Furthermore, it is clearly seen that the hollow with ca. 10 nm diameter exists inside the rodlike polymeric architecture. The diameter and the length (ca. 50−300 nm) of the hollow are well consistent with those of plasmid DNA in solution. These findings unambiguously confirm the view that the plasmid DNA works as a template for formation of the rodlike polymeric structures.

It is known that relaxation of the supercoiled DNA structure finally gives the circular form. This fact further stimulated us to utilize the circular DNA structure as a template for oxidative polymerization because one can create a new circular-shaped poly(pyrrole) assembly. Topoisomerase I is an enzyme that can relax the supercoiled structure. The relaxation process by topoisomerase I is known to proceed almost quantitatively under the physiological mild conditions. Accordingly, we first incubated plasmid DNA with topoisomerase I for 1 h at 37 °C under the appropriate reaction conditions (see Experimental Section). Then, the chemical oxidation of pyrrole was carried out by the reaction with APS. Figure 1b shows a TEM image of the DNA/poly(pyrrole) composite thus obtained. As evidenced from Figure 1b, this poly(pyrrole) has a circular structure with ca. 30−100 nm diameters, indicating that the circular plasmid DNA acts as a template for the oxidative polymerization. Furthermore, these images indicate that a single plasmid molecule of 6700 base pairs (assuming a circular structure composed of a double-stranded chain, ca. 700 nm diameter) condenses into a single toroid of ca. 100 nm diameter, when measured from center-to-center. This discrepancy in the diameters is reasonably explained as such that the higher-order DNA coiling is induced by the presence of cationic species, such as APS and poly(pyrrole) in the present system. It is known that the increase in the salt concentration changes the DNA conformation into the tightly coiled structure.[15] A SEM image of the DNA/poly(pyrrole) composite prepared by chemical oxidation with APS under the high ionic concentration (50 mM LiCl) resulted in a supercoiled polymer structure (Figure 1c). The result indicates that the tightly supercoiled plasmid DNA produced by the influence of LiCl addition acted as a template.

The foregoing findings based on the TEM and SEM observations consistently support the view that the conformationally isomerized DNA susperstructures are successfully transcribed into the assemblies of poly(pyrrole) polymers.

Fabrication of Salmon Tests DNA by Electrochemical Polymerization of Pyrrole. One may expect that the similar fabrication would be possible by electrochemical polymerization of pyrrole. Thus, electrochemical polymerization of pyrrole (60 mM) in the presence of DNA was carried out in a CV cell in a voltage range of 0−0.8 V (vs Ag/AgCl) with a scan rate of 50 mV s^{-1} at 25 °C (scan cycle: 30 cycles) under the similar conditions as those used for chemical polymerization (LiCl, 50 mM). To conduct electrochemical polymerization cleanly, one must maintain the salt concentration relatively high. Under these experimental conditions, it is difficult to handle plasmid DNA, the conformation of which is sensitive to the salt concentration. Thus, we here used salmon tests DNA which is easier to handle than plasmid DNA. With the increase in the scanning cycle the magnitude of the CV redox waves increased, indicating that the poly(pyrrole) film

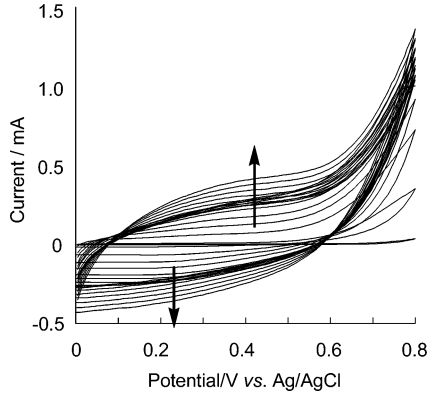

Figure 2. Cyclic voltammograms for pyrrole oxidation in the presence of salmon tests DNA obtained on an ITO electrode; [pyrrole] = 60 mM, [LiCl] = 50 mM, 25 °C, sweep rate 50 mV s^{-1}.

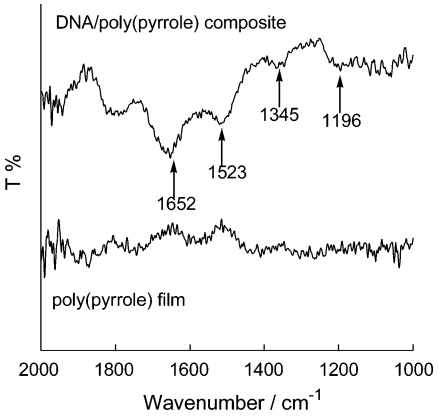

Figure 3. ATR IR spectra of the poly(pyrrole) film and the DNA/poly(pyrrole) composite film.

is constructed on the ITO electrode surface (Figure 2). When this electrochemical polymerization was carried out in 100 vol % aqueous solution, the resultant film tended to peel off from the ITO electrode. We thus tested 10, 20, and 30 vol % ethanol solutions. With the increase in the ethanol concentration the cohesiveness between the film and the electrode was improved, but the increment of the redox peak wave per one redox cycle became smaller. We thus chose the 10 vol % ethanol solution which gave the moderate peak increase and resulted in the stable poly(pyrrole) film on the ITO electrode. The CV pattern is similar to that obtained from electrochemical polymerization of pyrrole itself under the same reaction conditions. The results indicate that the composite film comprised of salmon tests DNA and poly(pyrrole) is deposited on the ITO electrode.

To obtained evidence that these poly(pyrrole) films are composed of the DNA as a template, we measured the ATR IR spectra because DNAs have a characteristic vibration peak of the phosphate group. The ATR IR spectra of the DNA/poly(pyrrole) composite and poly(pyrrole) itself are compared as shown in Figure 3. In the spectrum of the DNA/poly(pyrrole) composite, several new peaks assignable to DNA are observable: that is, 1652 cm^{-1} (C=O in the thymine), 1523 cm^{-1} (ring in the cytosine), 1345 cm^{-1} (C−N stretching), and 1196 cm^{-1} (PO_2^-).[17] These peaks are not found in the poly(pyrrole) film.

Furthermore, to confirm the deposition of DNA in the poly(pyrrole) film, we carried out XPS analysis (Figure 4). For comparison, we prepared a DNA film by casting

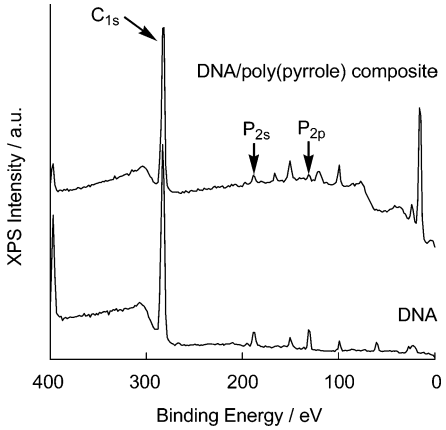

Figure 4. XPS spectra of DNA and DNA/poly(pyrrole) obtained by chemical polymerization.

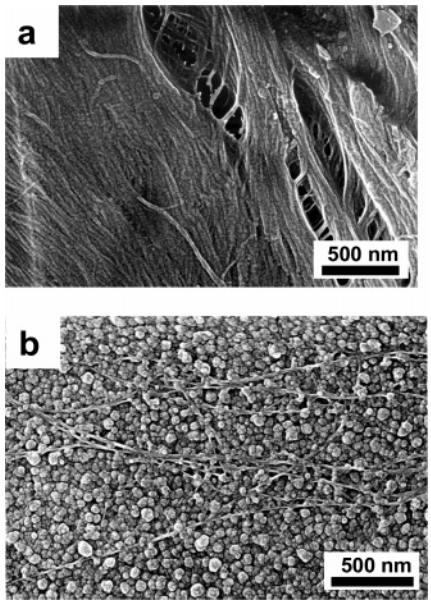

Figure 5. SEM images of the surface of DNA/poly(pyrrole) composite film.

the DNA solution by a spin-coat method. The XPS spectra exhibit the peaks of C and P elements arising from the DNA film and the DNA/poly(pyrrole) composite film. The most intense peak of the XPS spectra at 285 eV is due to aromatic and alphatic carbons coupled to carbons of the same type.[18] Using the intensity of this carbon peak, the C/P ratio for the DNA/poly(pyrrole) composite film was estimated to be C: 90.06 and P: 2.49 (the remainder is Si and other atoms arising from the ITO electrode). On the other hand, the C/P ratio for the DNA film was estimated to be C: 79.63 and P: 4.71. As a result of the XPS measurements, therefore, one can propose that the DNA/poly(pyrrole) composite is formed from three pyrrole units per one phosphate group of DNA.

Surface Morphology as Observed by SEM and Confocal Laser Scanning Micrograph (CLSM). Figure 5 shows SEM images of the ITO electrode surface covered by the DNA/poly(pyrrole) composite film. When the concentration of DNA was very high (100 μg mL^{-1}), the sheetlike aggregate structure composed of fine fibrils was observed (Figure 5a). When the concentration was moderately lowered (11 μg mL^{-1}), the fibrous structures (as shown in Figure 5b) appeared on the pebble-like background of the poly(pyrrole) film. We identified that

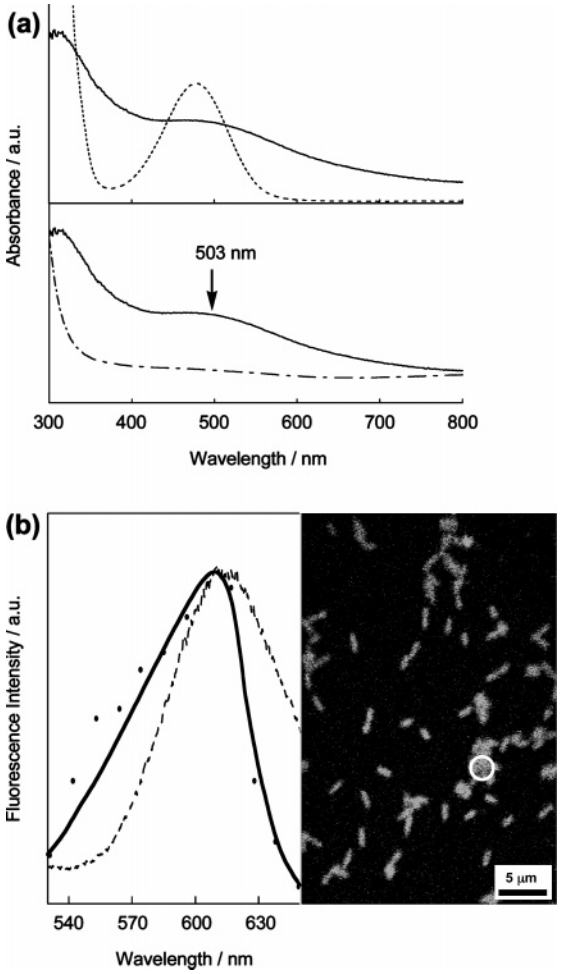

Figure 6. (a) UV−vis absorption spectra of the DNA/poly(pyrrole) composite film, (– · –) before immersion, (—) after immersion in an EB solution (50 mM) and rinse with water; (b) CLSM image of the poly(pyrrole)plasmid DNA composite film binding EB and its fluorescence spectrum obtained by exciting the white open spot at 470 nm; only EB solution (· · ·).

the thickness of polymer increases with the increase in the scan cycle:[12c] that is, the morphology of polymer does not depend on the thickness of polymer. In the present system, the same change in morphology (200 cycles) was observed under the condition of Figure 5a (see Supporting Information Figure S1).

To obtain evidence that these fibrous aggregates consist of the DNA/poly(pyrrole) composite, we measured the UV−vis absorption spectra as well as the fluorescence spectra by CLSM. The modified ITO electrode was immersed in an aqueous solution containing ethidium bromide (EB, 50 mM), a typical DNA intercalator for 64 h at 25 °C. Then, the electrode was rinsed for 30 min by distilled water. As shown in Figure 6a, a new absorption maximum appeared at 503 nm, which is assignable to EB. This absorption peak intensity was not decreased even though the electrode was further washed. This EB-stained electrode was submitted to the CLSM observation (Figure 6b). When the white open spot was photoexcited at 470 nm, the corresponding fluorescence spectrum gave a fluorescence maximum at around 610 nm ascribable to emission from EB (Figure 6b). The finding indicates that these fibers include the EB-binding DNA. Furthermore, we confirmed that the fibrous structures as observed by SEM (Figure 5) also show a typical fluorescence color of EB in the CLSM

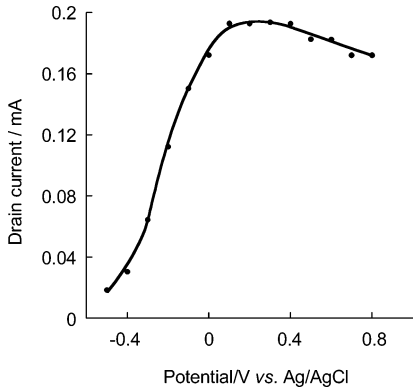

Figure 7. Drain current vs gate voltage (Vg) plot for the DNA/poly(pyrrole) composite.

image. These spectral characteristics were not observed at all for the poly(pyrrole)-modified ITO electrode prepared under the same conditions but in the absence of DNA. In addition, when the poly(pyrrole)-modified ITO electrode was immersed in aqueous DNA solution (100 μg mL^{-1}) for 64 h at 25 °C and then rinsed with water for 30 min, adsorption of EB to this modified electrode was not detected at all. The results clearly establish that the poly(pyrrole) surface has no specific affinity with DNA and cannot bind DNA or preserve it from the water rinse. It is undoubted, therefore, that these fibrous structures are constructed by DNA and poly(pyrrole). One can propose, therefore, that the DNA is deposited on the electrode as a poly(pyrrole) composite through the electrochemical polymerization process and responsible for the binding of EB to this modified electrode.

In Situ Conductivity of the DNA/Poly(pyrrole) Composite. Using the electrochemical polymerization, the DNA/poly(pyrrole) composite was prepared on the Pt-coated interdigitated microelectrode under the same conditions as those for the ITO electrode. The conductance measurements of the composite film were carried out in 50 mM $NaClO_4$ aqueous solution at 25 °C. The conductivity was estimated, as reported previously,[12e] by holding one platinum line at fixed potential Vg vs Ag/AgCl and the other at Vg +20 mV. The potential difference between the electrodes results in a drain current. The in situ conductivity, which could be measured up to 0.8 V, gives a linear increase up to 0.1 V of the potential followed by an expanded plateau of conductivity (Figure 7). This result is basically similar to that reported in the reference of Zotti et al.,[19] indicating that the obtained conductivity is due to the DNA/poly(pyrrole) composite.

Application of the Electrode Modified by the DNAs/Poly(pyrrole) Composite as a DNA-Based Sensor. As demonstrated above, it has become obvious that EB is bound to DNA included in the poly(pyrrole) film and does not leak out of the film by the simple rinsing treatment. This type of composite bearing a cascade communication function may be applicable as a "DNA-based sensor" to analytes which interact with the DNA. In fact, Contractor et al.[20] deposited antibiotics on the electrode by electrochemical polymerization of 3,4-ethlyenedioxythiophene and succeeded in detecting the antigen−antibiotic interaction. As a preliminary study, we here applied the ITO electrode modified by the salmon tests DNA/poly(pyrrole) composite as a DNA-based sensor. Figure 8 shows the CV diagrams in the absence and the presence of EB. It is seen from

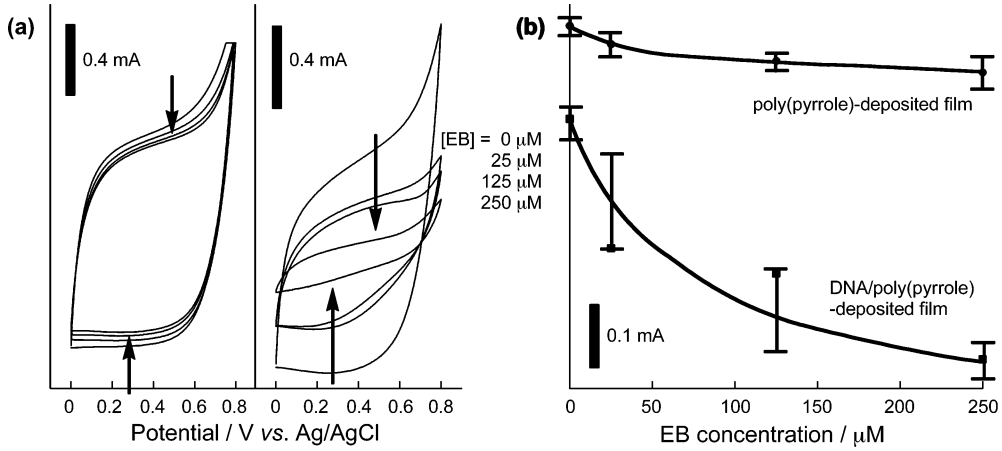

Figure 8. (a) CV of the poly(pyrrole)-deposited film (left) and the DNA/poly(pyrrole)-deposited film (right): in aqueous 50 mM LiCl by the fifth scan in the range of 0−0.8 V vs Ag/AgCl; sweep rate 50 mV s^{-1}, [EB] = 0, 25, 125, and 250 μM. (b) Variation of oxidation current as a function of EB concentration: at a constant potential E = 0.4 V vs Ag/AgCl.

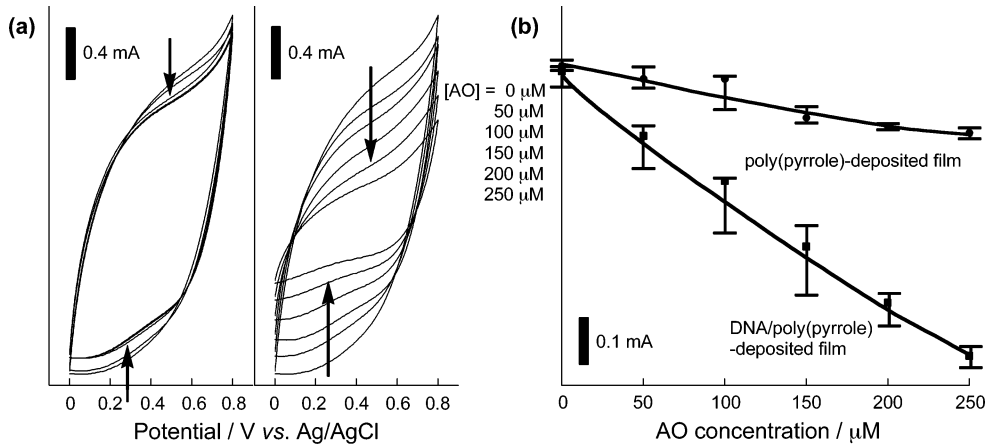

Figure 9. (a) CV of the poly(pyrrole)-deposited film (left) and the DNA/poly(pyrrole)-deposited film (right): in aqueous 50 mM LiCl by the fifth scan in the range of 0−0.8 V vs Ag/AgCl; sweep rate 50 mV s^{-1}, [AO] = 0, 50, 100, 150, 200, and 250 μM. (b) Variation of oxidation current as a function of AO concentration: at a constant potential E = 0.4 V vs Ag/AgCl.

Figure 8a that the CV redox waves in the poly(pyrrole) film are scarcely affected by added EB. In contrast, those in the DNA/poly(pyrrole) composited film changes with the increase in the EB concentration (Figure 8a). The difference supports the view that bound EB changes the conformation of DNA, which affects the conductivity of the poly(pyrrole) film.

The shape of the voltammograms shows that a potential exists around 0.4 V vs Ag/AgCl, where the oxidation potential in Figure 8a is accompanied by a large variation of the electrode oxidation current intensity, allowing an amperometric analysis of the hybridization. When applying a potential of 0.4 V vs Ag/AgCl to the electrode, the variation of the electrode oxidation current plotted as a function of the EB concentration is almost negligible for the poly(pyrrole)-deposited film (Figure 8b). On the other hand, the current in the DNA/poly(pyrrole)-deposited electrode decreases continuously as a function of the EB target concentration in solution. As shown in Figure 8b, the electric current for the DNA/poly(pyrrole) composite film has the dynamic range of ca. 0.3 mA.

This electrochemical behavior was further examined to analyze other DNA-interactive compounds. Figure 9 shows the CV diagrams in the absence and the presence of acridine orange (AO). It is seen that the CV redox waves are very similar to those in Figure 8a. As in the case of Figure 8b, Figure 9b displays the decrease in the amperometric peaks observed upon increasing the intercalator concentration on the 0−250 μM range. It is undoubted, therefore, that the DNA/poly(pyrrole)-deposited film responds to the concentration change in AO. The results suggest, together with those in Figure 8b, the view that this modified electrode system is useful as an amperometric sensor toward such guest molecules that interact with DNA.

The concentration of dye molecules such as EB and AO can be easily estimated by spectroscopic methods. However, to sense those compounds that do not show such absorption or fluorescence properties is more difficult. Figure 10 compares the response of the deposited film to spermine by the CV diagram. It took 5 min until the CV diagram was stabilized after addition of spermine. As expected, the poly(pyrrole)-deposited film does not respond to this molecule. In contrast, the current for the DNA/poly(pyrrole)-deposited film decreases with increasing spermine concentration, indicating that the interaction has occurred between spermine and DNA. The finding implies that the electrochemical response of poly(pyrrole) is affected by the DNA−spermine interaction in the electrolytic medium. It is worthy to mention that spermine, which is difficult to sense because of the lack of a chromophoric group, can be quantitively detected by this method.

These results confirm that the DNA/poly(pyrrole)-deposited film is able to specifically recognize interca-

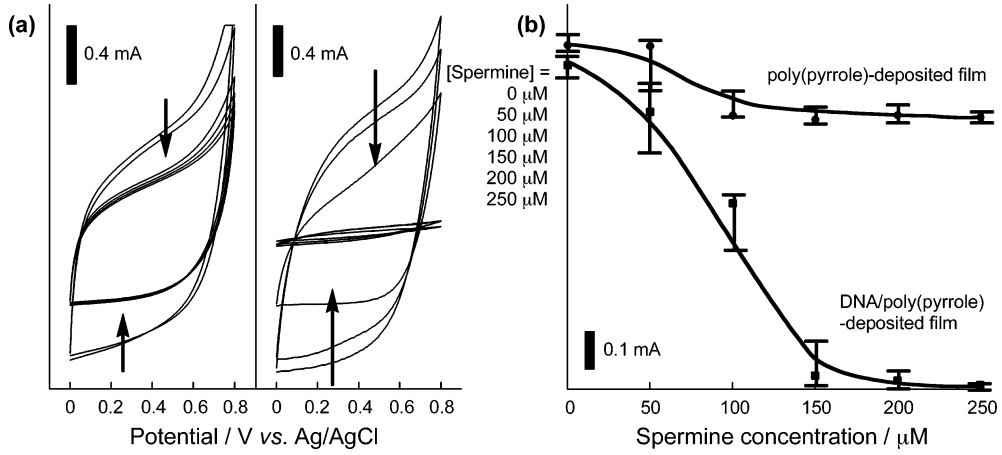

Figure 10. (a) CV of the poly(pyrrole)-deposited film (left) and the DNA/poly(pyrrole)-deposited film (right): in aqueous 50 mM LiCl by the fifth scan in the range of 0−0.8 V vs. Ag/AgCl; sweep rate 50 mV s^{-1}, [spermine] = 0, 50, 100, 150, 200, and 250 μM. (b) Variation of oxidation current as a function of spermine concentration: at a constant potential E = 0.4 V vs Ag/AgCl.

lators and side-binders of DNA in an aqueous medium, and this recognition event is transduced as a molecular signal to the wrapping conjugate polymer film, which is eventually sent to the supporting electrode as an electrochemical signal.

Conclusion

In conclusion, the present study has demonstrated, for the first time to the best of our knowledge, that the morphology of the poly(pyrrole) film obtained by chemical and electrochemical polymerization of pyrrole can be controlled by using DNAs as templates. One may regard, therefore, that this is a novel and general transcription process of anionic templates to oxidizable monomers through oxidative polymerization. So far, it has been believed that in oxidative polymerization of pyrrole the easiness in the preparation method is a merit whereas the difficulty in the morphological control is a serious demerit. The convenience of the fabrication method and the easiness of the morphology control as attained in this system suggest a new potential toward the broad applications of these conjugate polymers as functional materials. In fact, the DNA/poly(pyrrole) film prepared by electrochemical polymerization could interact with DNA-binding compounds, such as EB, AO, spermine, etc. One can propose, therefore, that the DNA/poly(pyrrole) film composite has a potential utility as a sensor for biochemical materials. We now believe that this is the first step to functionalize the recognition ability of DNA on the conjugate polymer.

Experimental Section

Materials. ColE1 plasmid DNA and salmon tests DNA (for hybridization) were purchased from Wako Pure Chemical Industries, Ltd. These DNAs were used without further purification. Pyrrole (Tokyo Kasei Kogyo Co.) was used after distillation. Lithium chloride (LiCl, Kishida Co.), sodium perchlorate ($NaClO_4$, Wako Pure Chemical Industries, Ltd.), ethidium bromide (EB, Wako Pure Chemical Industries, Ltd.), acridine orange (AO, Wako Pure Chemical Industries, Ltd.), spermine (Wako Pure Chemical Industries, Ltd.), and triethylene glycol (TEG, Tokyo Kasei Kogyo Co.) were used as purchased. DNA topoisomerase I (Takara Bio Inc., Japan) was used as received. Ultrapure water from a Millipore purification system was used for the preparation of the solutions in all the experiments described. Ethanol used as a solvent was purchased from Aldrich.

Electrochemical Polymerization. Cyclic voltammometry (CV) experiments were performed using a one-compartment, three-electrode electrochemical cell driven by an electrochemical analyzer (BAS 100B) in aqueous solution containing supporting electrolyte (LiCl, 50 mM) and 10 vol % ethanol. The oxidative polymerization of pyrrole was carried out in a CV cell 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 0−0.8 V (vs Ag/AgCl) with a scan rate of 50 mV s^{-1} at 25 °C. After polymerization five redox cycles in a corresponding range were performed in 50 mM LiCl aqueous solution to wash the film. The typical concentrations employed for electrochemical oxidation are as follows: [pyrrole] = 60 mM, [LiCl] = 50 mM, [ColE1 plasmid DNA] = 11 μg mL^{-1}, and [salmon tests DNA] = 100 μg mL^{-1} (scan cycles: 50 cycles).

Apparatus for Spectroscopic Measurements. UV−vis spectra were measured on a Shimadzu UV-2500 PC spectrophotometer. ATR IR spectra were recorded with a Perkin-Elmer Spectrum One. XPS spectra were measured on a Physical Electronics PHI 5800 ESCA system.

TEM Observations. The obtained solution by chemical oxidation was dropped on a carbon-coated copper grid (200 mesh). The solution was dried by a vacuum pump for 1 day. TEM pictures were taken without any staining treatment. TEM (accelerating voltage: 125 kV) studies were carried out on a JEOL JEM-2010.

SEM Observations. SEM was used for observing the morphology of the films. The prepared film was cutted by a glass cutter. The film was dried by a vacuum pump for 1 day. The obtained film was shielded with platin for 30 s and examined with a Hitachi S-5500. The accelerating voltage of SEM was 25.0 kV, and the emission current was 10 μA.

CLSM Measurements of Films. CLSM was used for taking the fluorescence spectra. The film was sandwiched by cover glasses and fixed by an adhesive. CLSM studies were carried out on a BIO-RAD Radiance 2000 AGR3. Excitation wavelength was 470 nm (argon laser with a reflector turrnet).

In Situ Conductance Measurements. Conductivity measurements were carried out in 50 mM $NaClO_4$ aqueous solution by an Autolab PGSTAT12 with BIPOT bipotentiostat. The conductivity was estimated by holding one Pt line at fixed potential Vg vs Ag/AgCl and the other at Vg +20 mV.

Electrochemical Measurements. Recognition properties toward EB, AO, and spermine were performed with a three-electrode configuration in aqueous solution containing supporting electrolyte (LiCl, 50 mM) by CV. The modified ITO electrode was used as the working electrode, the counter electrode being a platinum wire. An Ag/AgCl electrode was used as the reference electrode. The scan rate was 50 mV s^{-1}. All measurements were carried out under argon at 25 °C.

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Supporting Information Available: SEM image of the surface of the DNA/poly(pyrrole) composite film (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For recent reviews, see: (a) van Bommel, K. J. C.; Friggeri, A.; Shinkai, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 980. (b) Cölfen, H.; Mann, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 2350. (c) Soler-Illia, G. J. A. A.; Sanchez, C.; Lebeau, B.; Patarin, J. *Chem. Rev.* **2002**, *102*, 4093. (d) Sanchez, C.; Soler-Illia, G. J. A. A.; Ribot, F.; Lalot, T.; Mayer, C. R.; Cabuil, V. *Chem. Mater.* **2001**, *13*, 3061. (e) Soler-Illia, G. J. A. A.; Sanchez, C.; Lebeau, B.; Patarin, J. *Chem. Rev.* **2002**, *102*, 4093.

(2) (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.

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

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

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

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

(7) (a) Sugiyasu, K.; Tamaru, S.; Takeuchi, M.; Berthier, D.; Huc, I.; Oda, R.; Shinkai, S. *Chem. Commun.* **2002**, 1212. (b) Numata, M.; Sugiyasu, K.; Hasegawa, T.; Shinkai, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 3279.

(8) For recent reviews on low-molecular-weight gels, see: (a) Terech, P.; Weiss, R. G. *Chem. Rev.* **1997**, *97*, 3133. (b) Melendez, R. E.; Carr, A. J.; Linton, B. R.; Hamilton, A. D. *Struct. Bonding (Berlin)* **2000**, 31. (c) Gronwald, O.; Shinkai, S. *Chem.—Eur. J.* **2001**, *7*, 4329. (d) Gronwald, O.; Snip, E.; Shinkai, S. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 148. (e) van Esch, J.; Schoonbeek, F.; de Loos, M.; Kooijman, H.; Veen, E. M.; Kellogg, R. M.; Feringa, B. L. In *Supramolecular Science, Where It Is and Where It Is Going*; Ungaro, R., Dalcanale, E., Eds.; Kluwer: Dordrecht, The Netherlands, 1999; p 233.

(9) For recent reviews and references on electrochemical polymerization, see: (a) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537. (b) Pringsheim, E.; Terpetschnig, E.; Piletsky, S. A.; Wolfbeis, O. S. *Adv. Mater.* **1999**, *11*, 865. (c) Shoji, E.; Freund, M. S. *J. Am. Chem. Soc.* **2001**, *123*, 3383.

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

(11) (a) Zhang, Z.; Wan, M. *Synth. Met.* **2002**, *128*, 83. (b) Wei, Z.; Wan, M. *Adv. Mater.* **2002**, *14*, 1314.

(12) (a) Hatano, T.; Takeuchi, M.; Ikeda, A.; Shinkai, S. *Chem. Commun.* **2003**, 342. (b) Hatano, T.; Takeuchi, M.; Ikeda, A.; Shinkai, S. *Chem. Lett.* **2003**, *32*, 314. (c) Hatano, T.; Takeuchi, M.; Ikeda, A.; Shinkai, S. *Org. Lett.* **2003**, *5*, 1395. (d) Hatano, T.; Bae, A.-H.; Sugiyasu, K.; Fujita, N.; Takeuchi, M.; Shinkai, S. *Org. Biomol. Chem.* **2003**, *1*, 2343. (e) Hatano, T.; Bae, A.-H.; Takeuchi, M.; Fujita, N.; Kaneko, K.; Ihara, H.; Takafuji, M.; Shinkai, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 465. (f) Bae, A.-H.; Hatano, T.; Nakashima, N.; Murakami, H.; Shinkai, S. *Org. Biomol. Chem.* **2004**, *2*, 1139. (g) Shinkai, S.; Takeuchi, M.; Bae, A.-H. *Supramol. Chem.* **2005**, *17*, 181.

(13) Davis, S. A.; Burkett, S. L.; Mendelson, N. H.; Mann, S. *Nature (London)* **1997**, *385*, 420.

(14) (a) Mirkin, C. A.; Letsinger, R. L.; R. C. Mucic, J. J. Storhoff, *Nature (London)* **1996**, *382*, 607. (b) Mucic, R. C.; Storhoff, J. J.; Mirkin, C. A.; Letsinger, R. L. *J. Am. Chem. Soc.* **1998**, *120*, 12674. (c) Alivisatos, P.; Johnsson, K. P.; Peng, X.; Wilson, T. E.; Loweth, C. J.; Bruchez, M. P.; Schults, P. G. *Nature (London)* **1996**, *382*, 609. (d) Tanaka, K.; Okahata, Y. *J. Am. Chem. Soc.* **1996**, *118*, 10679. (e) Okahata, Y.; Kobayashi, T.; Tanaka, K.; Shimomura, M. *J. Am. Chem. Soc.* **1998**, *120*, 6165. (f) Kawabe, Y.; Wang, L.; Horinouchi, S.; Ogata, N. *Adv. Mater.* **2000**, *12*, 1281. (g) Yamada, M.; Kato, K.; Nomizu, M.; Sakairi, N.; Ohkawa, K.; Yamamoto, H.; Nishi, N. *Chem.—Eur. J.* **2002**, *8*, 1407.

(15) Bae, A.-H.; Hatano, T.; Numata, M.; Shinkai, S. *Chem. Lett.* **2004**, *436* (preliminary communication).

(16) (a) Fang, Y.; Hoh, J. H. *Nucleic Acids Res.* **1998**, *26*, 588. (b) Dunlap, D. D.; Maggi, A.; Soria, M. R.; Monaco, L. *Nucleic Acids Res.* **1997**, *25*, 3095. (c) Golan, R.; Pietrasanta, L. I.; Hsieh, W.; Hansma, H. G. *Biochemistry* **1999**, *38*, 14069.

(17) (a) Mondragon-Sanchez, J. A.; Liquier, J.; Gryaznov, S. M.; Taillandier, E. *J. Mol. Struct.* **2003**, *661*, 183. (b) Petrovykh, D. Y.; Kimura-Suda, H.; Whitman, L. J.; Tarlov, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 5219.

(18) Tran, L. D.; Pio, B.; Pham, M. C.; Ledoan, T.; Angiari, C.; Dao, L. H.; Teston, F. *Synth. Met.* **2003**, *139*, 251.

(19) Zotti, G.; Zecchin, S.; Schiavon, G.; Vercelli, B.; Berlin, A.; Dalcanale, E.; Groenendaal, L. B. *Chem. Mater.* **2003**, *15*, 4642.

(20) Kanungo, M.; Srivastava, D. N.; Kumar, A.; Contractor, A. Q. *Chem. Commun.* **2002**, 680.

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