Self-Assembled Supramolecular Films Derived from Marine Deoxyribonucleic Acid (DNA)−Cationic Surfactant Complexes: Large-Scale Preparation and Optical and Thermal Properties

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Series of polyelectrolyte−surfactant complexes, DNA−cationic surfactant complexes (cetyltrimethylammonium, cetylpyridinium, and cetylbenzyldimethylammonium), and their self-assembled bulk film materials were prepared on a large scale. Circular dichroism (CD) analysis indicated that the right-handed double helix structure of DNA was retained in these bulk film materials. TGA analysis suggested that 4 molecules of water were required to retain the B-type conformation of the DNA helix in the self-assembled bulk film materials. In addition, it revealed that DNA and the DNA−surfactant complex film materials were thermostable up to as high as 180 °C. Thermodynamical analysis indicated that these film materials were thermo-extensive over a temperature range from 100 to 148 °C. The DNA conformation in the supramolecular complex films can be reversibly tuned by changing the environmental humidity. Film formation was found to occur by self-assembly and self-organization with evaporation of solvent molecules. Various functional dyes such as laser dye, NLO dye, and photochromic dye could easily be incorporated in the self-assembled supramolecular complex films as adducts. Studies of the induced CD spectra demonstrated that 4[4-(dimethylamino)styryl]-1-dococylpyridinium (DMASDPB) could orient on the chiral nanotemplates of DNA in the self-assembled films. UV−vis analysis indicated that these film materials have high transparency from 300 to about 1000 nm. These self-assembled functional-dye-containing DNA−surfactant complex materials, with good processability for multilayer integration into large-area devices, will have promising applications in molecular optical and molecular optoelectronic fields.

Introduction

It has been shown that the 1:1 stoichiometric combination of an anionic polyelectrolyte with a cationic surfactant leads to spontaneous formation of highly organized assemblies.[1−3] The self-assembled bulk materials exhibit interesting properties such as thermotropic liquid-crystalline behavior, which results from long-range organization on a mesoscopic length scale. Also, DNA, which is an anionic polyelectrolyte, could be quantitatively precipitated with cationic surfactants in water.[4−6] The method of precipitating various types of DNA by cationic surfactants has been applied to DNA extraction, concentration, and counting.[7−9] It was suggested that DNA could be recovered in a native state to form DNA−cationic surfactant complexes with 12-, 14-, and 16-carbon alkyltrimethylammonium bromides.[9] Recently, the physicochemical properties and conformational changes of single-chain DNA−cationic surfactant complexes in mixtures of ethanol−water and low-polarity organic solvents were systematically studied by the Yoshikawa and Sergeyev groups.[10−14] No doubt, these studies are very important for understanding the

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mechanisms of cell transfection and gene therapy. Furthermore, Okahata reported that the complex of DNA with a specially designed and synthesized cationic amphiphile, DNA−*N*,*N*,*N*-trimethyl-*N*-(3,6,9,12-tetraoxadocosyl)ammonium (TTOA), was soluble in most polar organic solvents and that a helical DNA−TTOA complex film was obtained by a solvent casting method.[15] This study pointed out that the DNA−cation complex film is not only important for life science but also for material science, as the unique chemical structure of DNA can be applied in electron transfer, the formation of rodlike liquid crystals, and so on. However, the TTOA required a complicated synthesis process.

Our intention was to find a simpler method for preparing high-quality films of DNA−cationic surfactant complexes. We think that such film materials are also promising for applications to molecular optics and molecular optoelectronics based on following well-known facts. First, the $\pi-\pi$ stacking structure of the nucleobase pairs of DNA not only forms a tunnel ready for electron transfer, but also gives the film materials high optical transparency. Second, some fluorescent dyes can easily be intercalated or inserted in the helices, resulting in greatly enhanced fluorescence intensity. Third, it has been clear that intercalation and insertion is a relatively nonspecific interaction that involves insertion of all or part of the ligand between adjacent base pairs and insertion of all or part of the ligand in a minor groove. However, the film materials prepared from DNA or inorganic salts of DNA are too water-sensitive and have insufficient mechanical strength for the fabrication of optical and optoelectronic devices.

Based on this expected application, we focused on the design of novel DNA−surfactant complex film materials in which the length of the alkyl group and the size and chemical structure of the group substituted on the ammonium head were varied. The $CH_3(CH_2)_{15}$ cationic surfactants and their derivatives offer a convenient framework for construction of such a species. Here, cetyltrimethylammonium (CTMA), cetylpyridinium (CP), and benzyldimethylcetylammonium (BDMA) were used to constitute DNA−surfactant complex film materials. These surfactants were selected for the following reasons: Cationic surfactants having longer (>16) alkyl chains are water-insoluble, and chains shorter than C_{16} might induce poor mechanical property of the materials. Second, DNA complexes made with longer alkyl chains might damage the double helix structure of DNA as the strong association and aggregation among alkyl chains might break the hydrogen bonds of the nucleobase pairs. The third reason is that these surfactants are commercially available. Syntheses of all of the complexes were carried out by using salmon DNA, because salmon DNA is also commercially available on a large scale from salmon sperm.

We found that slow evaporation of an ethanol solution of the DNA−surfactant complex resulted in the formation of self-assembled supramolecular complex films. Our investigation indicated that the self-assembled films are highly transparent and exhibit both excellent thermal stability and chemical stability. The self-standing films of DNA−CTMA, DNA−CBDA, and DNA−CP complexes could easily be applied to optical and optoelectronic materials by doping with functional dyes, such as laser, nonlinear optical (NLO), electroluminescence, and photochroism dyes. The solid film matrix of the DNA−surfactant complex contains a significant amount of nanosize free volume such as minor grooves, major grooves, spaces between base pairs, and micelles of surfactants.

This paper mainly describes the formation, optical absorption, CD absorption spectroscopy, and thermal analyses of self-assembled film materials of DNA−surfactant complexes. A typical NLO organic dye, 4-[4-(dimethylamino)styryl]-1-dococylpyridinium bromide (DMASDPB), is used as the incorporating dye.

Experimental Section

Materials. CTMA chloride (95%), CP chloride (95%), BDMA chloride, fiberlike DNA sodium salts [salmon sperm, $M_w = 2 \times 10^6$, ca. 3077 base pairs (bp)], DMASDPB, and ethanol (99.5%) were purchased from Aldrich and used without further purification.

Preparation of DNA−Surfactant Complexes. Fiberlike NaDNA was dissolved in distilled water (6.5 g/L, 10 mM in base pairs), followed by shaking incubation overnight at 20 °C. One liter of the aqueous NaDNA solution was added to 1 L of aqueous solution of CTMA chloride (6.8 g/L, 20 mM). A 1:1 stoichiometric combination led to the spontaneous formation of the DNA−CTMA complex precipitate. The precipitate was collected by filtration, washed with distilled water, and then dried in a vacuum at 37 °C. A white powder (11.15 g) was obtained as a yield of about 95%. Powders of DNA−CP and DNA−BDMA were synthesized by the same procedure in similar yields. These DNA−surfactant complexes are very stable at ambient temperature and under atmosphere at a humidity 45%, but they are sensitive to moist atmosphere, which can lead to sticky films. These DNA−surfactant complexes were stored in a desiccator. If the powder sample was placed under a moist atmosphere (above a humidity of 50%) for some time, it had to be dried before being used to prepare the films.

Preparation of Films. Three kinds of DNA−surfactant complexes (at a humidity of about 45%) from CTMA, CP, and BDMA were separately dissolved in ethanol (99.5%) in a concentration range from 5 to 50 mM bp^{-1}, and the mixtures were slowly stirred for 1 day at room temperature to obtain transparent solutions. After being stirred, the mixed solution was allowed to stand for one night so that air bubbles would be removed from the solution and high-quality optical films would be obtained. The transparent solutions were placed on Teflon culture plates so that free-standing films could be obtained. A closed drying apparatus was used to slowly evaporate the ethanol at 37 °C. The drying apparatus was a closed chamber or a desiccator that was connected to a cold trap for ethanol recovery. The speed of formation of the films was controlled by the temperature difference between the drying ap-

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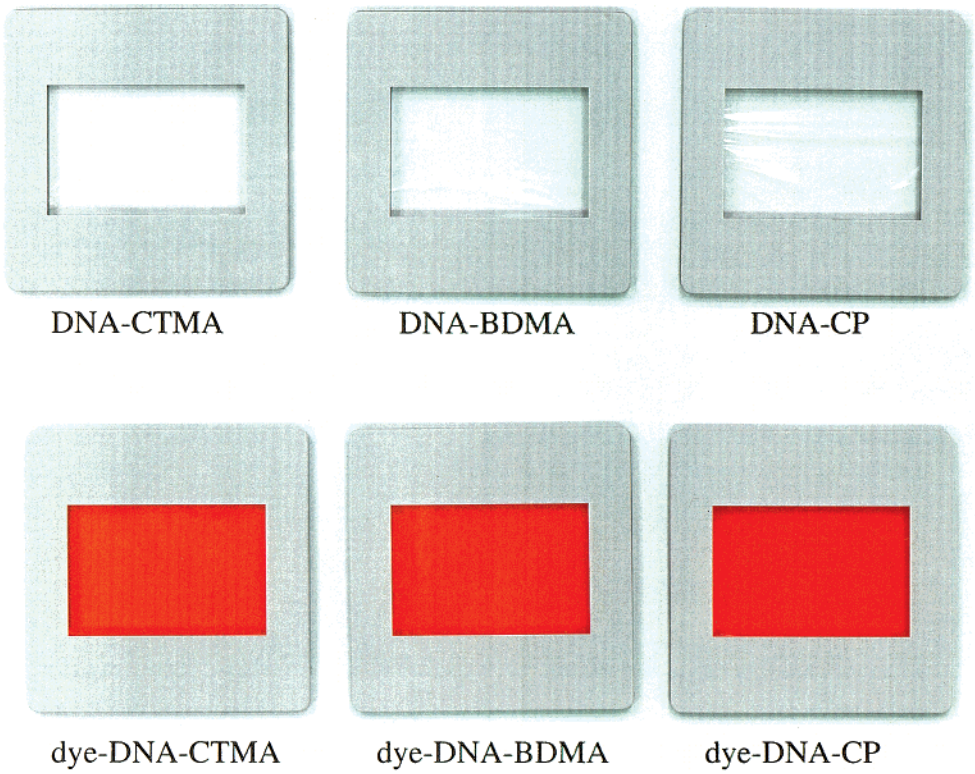

Figure 1. Photographs of DNA−surfactant complex films and functional-dye-doped DNA−surfactant complex films.

paratus and the cold trap. The thickness of the self-standing films could be freely tuned from a few microns to a few millimeters by changing the concentration and casting thickness of the DNA−surfactant solutions. The area of the films was determined by the area of the Teflon culture plate. Thin or superthin films also could easily be prepared on a solid matrix such as a quartz plate, ITO/glass slide, mica surface, or Pt electrode surface by spin coating of 5−20 mM DNA−surfactant ethanol solutions or by the insertion−absorption−drying method.

Preparation of Functional-Dye-Doped DNA−Surfactant Complex Films. A weighed dye or a dye solution was directly added to the DNA−surfactant ethanol solution. The molar ratio of the dye to the DNA−surfactant complex was determined by observing the maximum point of fluorescence enhancement when the DNA was titrated into the dye solution. The rest of the procedure was similar to that described above.

Instrumentation. Optical absorption spectra were recorded with a Shimadu UV-2400 spectrophotometer. CD absorption spectra were measured on a Jasco J-720 spectropolarimeter using a 1-cm quartz cell. X-ray diffraction patterns were recorded using DIP2000 X-ray generator (Rigaku, Tokyo, Japan) with a power of 1.2 kW. TGA analysis and dynamic mechanical spectroscopy (DM) of the film materials were performed with TG-DTA 6200 and DMS6100 instruments (Seiko Instruments). For DM measurements, the instrument was in the temperature/frequency sweeping mode with an applied frequency of 0.05−1 Hz. Storage (E') and loss (E'') moduli of the film materials were measured, and tan δ was derived from the two moduli. The polymer film thicknesses were determined with a micrometer, which could read to 0.001 mm.

Results and Discussion

Formation of Films. When an ethanol solution of the DNA−surfactant complex was cast on a Teflon culture plate, ethanol at the air−solution interface immediately evaporated. The preferential evaporation of ethanol caused enrichment of the cationic surfactant and DNA anion. Because the alkyl chains of the cationic surfactant molecules automatically oriented toward air and aggregated with each other, orientation of the DNA chain was induced. The rodlike DNA helices were oriented perpendicular to the alkyl chain of the cation because of electrostatic attraction and thermodynamical stability. A two-dimensional template was formed in this way. Thus, a Langmuir−Blodget-like monolayer formed on the solution surface. Second and third layers formed following the formation of the template because of both electrostatic forces between the DNA and the cationic surfactant and aggregation among alkyl chains with accompanying ethanol evaporation. Through further evaporation of ethanol, the concentration of cationic surfactant created micelles inside the growing film. The self-organization of the micelles promoted continuous self-assembly of DNA into DNA−surfactant liquid-crystal-like mesophases. The obtained self-standing films exhibited very transparent morphologies, as shown in Figure 1. Such a self-assembly phenomenon has two causes. First, being oriented, the cationic surfactant molecules occupy less space than they would if randomly organized does; this might reduce the tension. Second, with the formation of the oriented structure of the alkyl chains pointing toward the air, a template effect might occur. The C_{16} alkyl-chain-containing cationic surfactant in this case not only promotes assembly but also provided the necessary counterion for electrostatic attractive forces and maintains the conformation of the

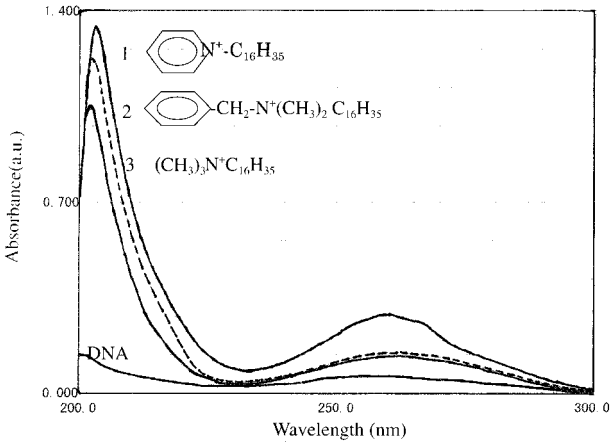

Figure 2. UV−vis spectra of 25 μM DNA and DNA−surfactant (CTMA, BDMA, and CP) complexes in ethanol solution.

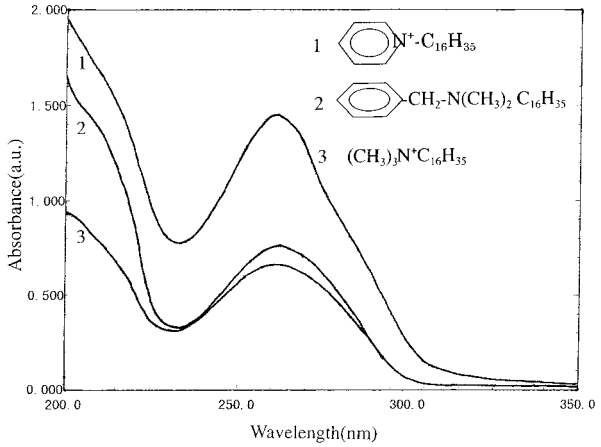

Figure 3. UV−vis spectra of DNA−CTMA, DNA−BDMA, and DNA−CP films (thickness = 5 μm).

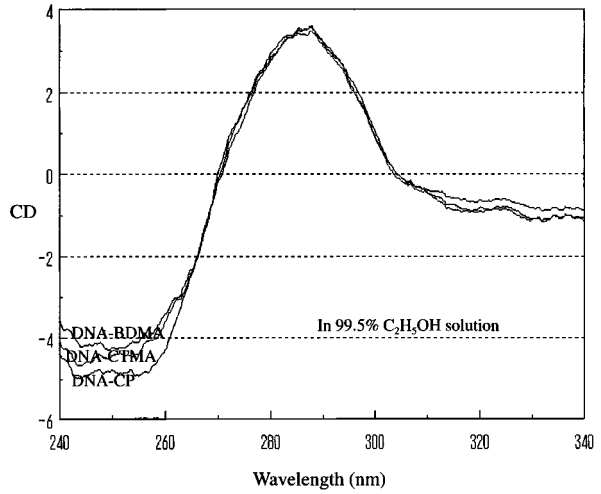

Figure 4. CD spectra of 40 μM DNA−surfactant (CTMA, BDMA, and CP) complexes in ethanol solution.

DNA strands. The degree of homogeneity of the films depends strongly on the evaporation speed of the solvent. It is likely to be monocrystal growth. For many functional dyes (such as NLO, laser, EL, and photochromism dyes), dye-incorporated DNA−surfactant films were also fabricated from the self-assembled films by the slow evaporation technique. Hydrophobic but ethanol-soluble functional dye molecules could be distributed into the film in at least four areas, namely, the minor and major grooves of the DNA stands, the hydrophobic spaces between base pairs, and the micelle interiors, upon ethanol evaporation.

Optical Characteristics. *UV Absorption.* The UV absorption of DNA is an important property for determining whether $\pi-\pi$ stacking of nucleobases occurs. The DNA double helix in aqueous solution has a specific absorption band from 220 to 300 nm and a λ_{max} at 260 nm. Figure 2 shows the UV−visible spectra of 25 μM DNA−CTMA, DNA−DBMA, and DNA−CP ethanol solutions. For comparison, the UV absorption spectrum of a 25 μM aqueous DNA solution is also shown in Figure 2. It is clear that the peaks at 202, 202.4, and 203.2 nm can be assigned to the absorptions of the three kinds of ammonium headgroups. The three kinds of DNA−surfactant complexes have the same absorption λ_{max} at 260 nm, which was assigned as the characteristic absorption of the nucleobases in DNA. However, it seems that the absorption coefficient was not the same as for the DNA in aqueous solution. The absorption coefficient became larger for all of the DNA−surfactant complexes compared with that of DNA aqueous solution. This indicated changes in the $\pi-\pi$ stacking structure of the DNA strands to some degree. Presumably, damage to the double helix of the DNA strands in the complexes cannot occur to a significant degree in this case. For these DNA−surfactant complex films (Figure 3), the same absorption λ_{max} at 260 nm was observed, which indicates that the chemical structure of DNA in these films is the same as that of DNA in solution. Also in the film states, the UV absorption coefficient for the DNA−CP complex film seems to be larger than those for the other DNA−surfactant complex films. This means that the $\pi-\pi$ stacking structure of the base pairs in the DNA−CP complex film was different from that in the DNA−CTMA and DNA−BDMA complex films to some degree. All of these films were transparent in a range from 350 to 1000 nm.

CD Absorption. CD analysis is one of the most useful techniques for probing the conformation of DNA in aqueous solution, as well as in gels, films, and fibers. To investigate the effects of the structure of the headgroup of the cationic surfactant on the double helix structure, three kinds of DNA−surfactant complexes were investigated. Figures 4 and 5 show the CD spectra of the three kinds of DNA−surfactant complexes in 99.5% ethanol solution and in the film states, respectively. All of the complexes either in ethanol solution or in film state show sharply conservative CD signals: a positive Cotton effect at about 285 nm and a negative Cotton effect at about 245 nm, similar to those of native DNA in an aqueous solution, which indicates the B-form conformation of the DNA strands. Thus, the DNA−surfactant complexes retained double helical B-form structure even in 99.5% ethanol, similar to the native DNA structure in aqueous solution. The CD spectra of the three kinds of complexes in both solution and solid state were similar to that of the B-form of DNA strands. This result indicates that these cationic surfactants can protect the conformation of the DNA double strands from change in ethanol solution and in films. To investigate the effects of water on the DNA conforma-

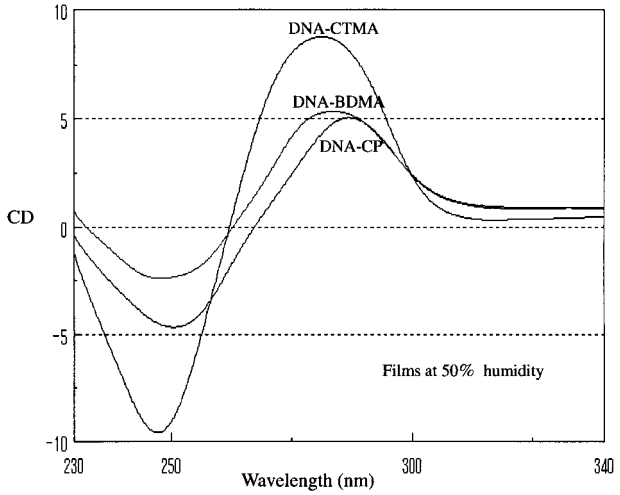

Figure 5. CD spectra of DNA−surfactant (CTMA, BDMA, and CP) complex films (thickness = 5 μm) at 50% humidity.

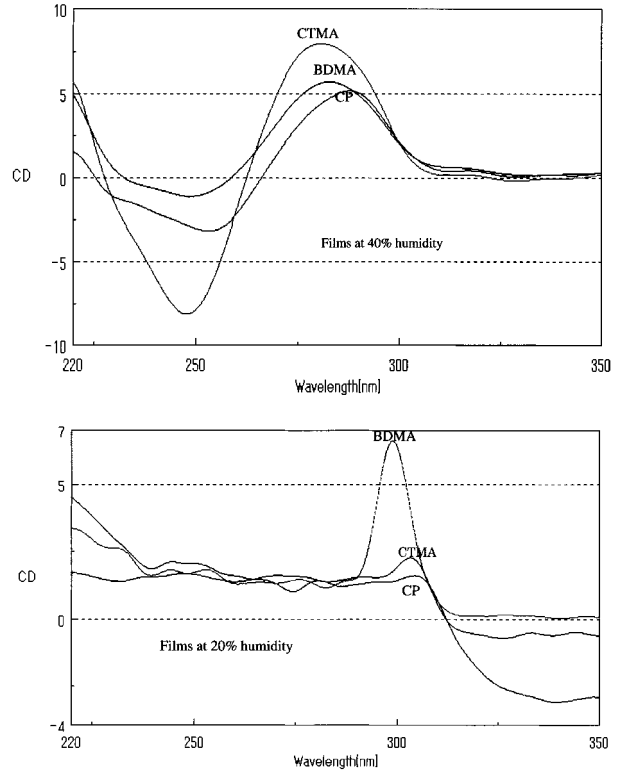

Figure 6. CD spectra of DNA−surfactant (CTMA, BDMA, and CP) complex films (thickness = 5 μm) at 40 and 20% humidities.

tion, CD spectra for the three kinds of complexes at 40 and 20% humidity were investigated, as shown in Figure 6. It is clear that the DNA conformation was gradually changed from B type to A, Z, and Z types for DNA−BDMA, DNA−CTMA, and DNA−CP, respectively, because the decrease in humidity induced volatilization of the binding water. Although it is said that water molecules are important in retaining the B-form helix of DNA, the question is, how many water molecules are needed to retain the B-type conformation of DNA. We suggest that a few water molecules that were bound when the DNA−surfactant complexes were synthesized are required. Analysis of the TGA thermograms indicates that this is about 4 molecules of water per base pair in these complexes.

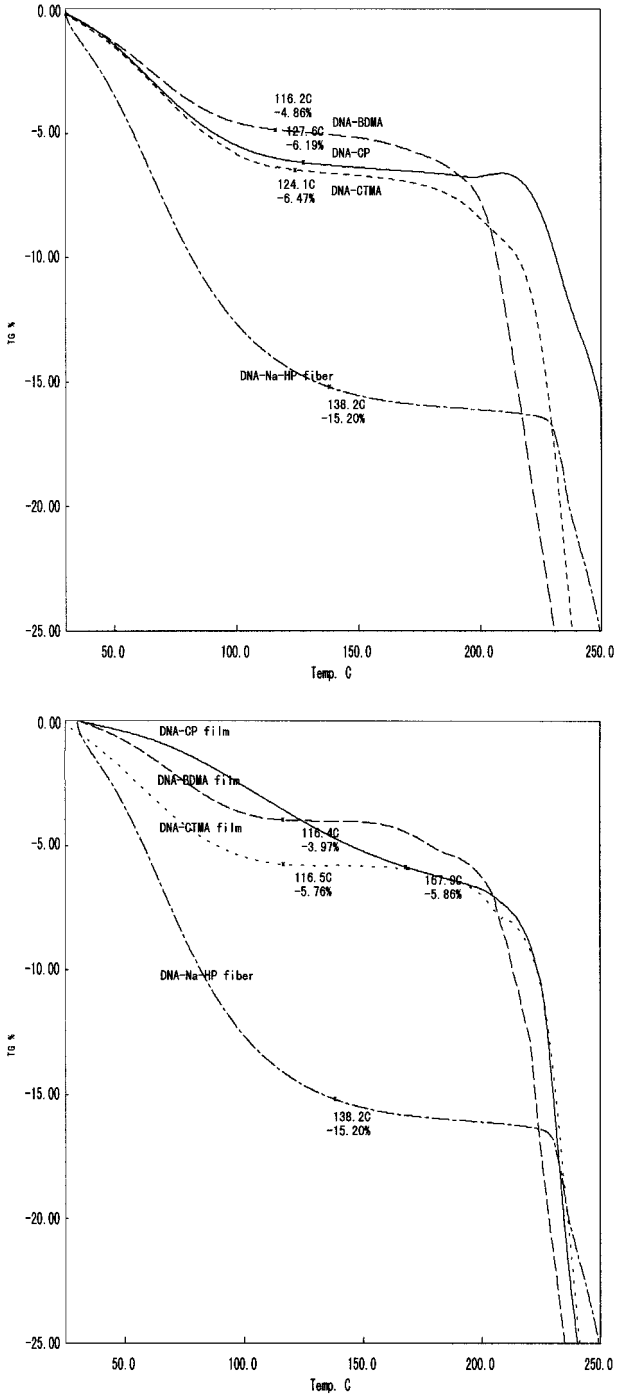

Figure 7. Thermograms of DNA, DNA−CTMA, DNA−BDMA, DNA−CP: (a) synthesized powders and (b) films.

Thermostability. *TGA Analysis.* To evaluate the thermostability of these films and the water percent in the DNA and DNA−surfactant complex powders and films, TGA thermograms were recorded, as exhibited in Figure 7a and b. Surprisingly, fiberlike NaDNA is thermostable up to 220 °C, and the complex powders and films were stable up to 200 °C, comparable to the result for DNA fibers. There is an initial weight loss of 4−7% for the three kinds of complexes and about 15% for fiberlike NaDNA, at 25−140 °C, because of volatilization of the binding water, with accompanying changes in the conformation of the DNA and the structure of the micelles for the DNA−CTMA, DNA−BDMA and DNA−CP complexes, as shown in Figure 6. The second

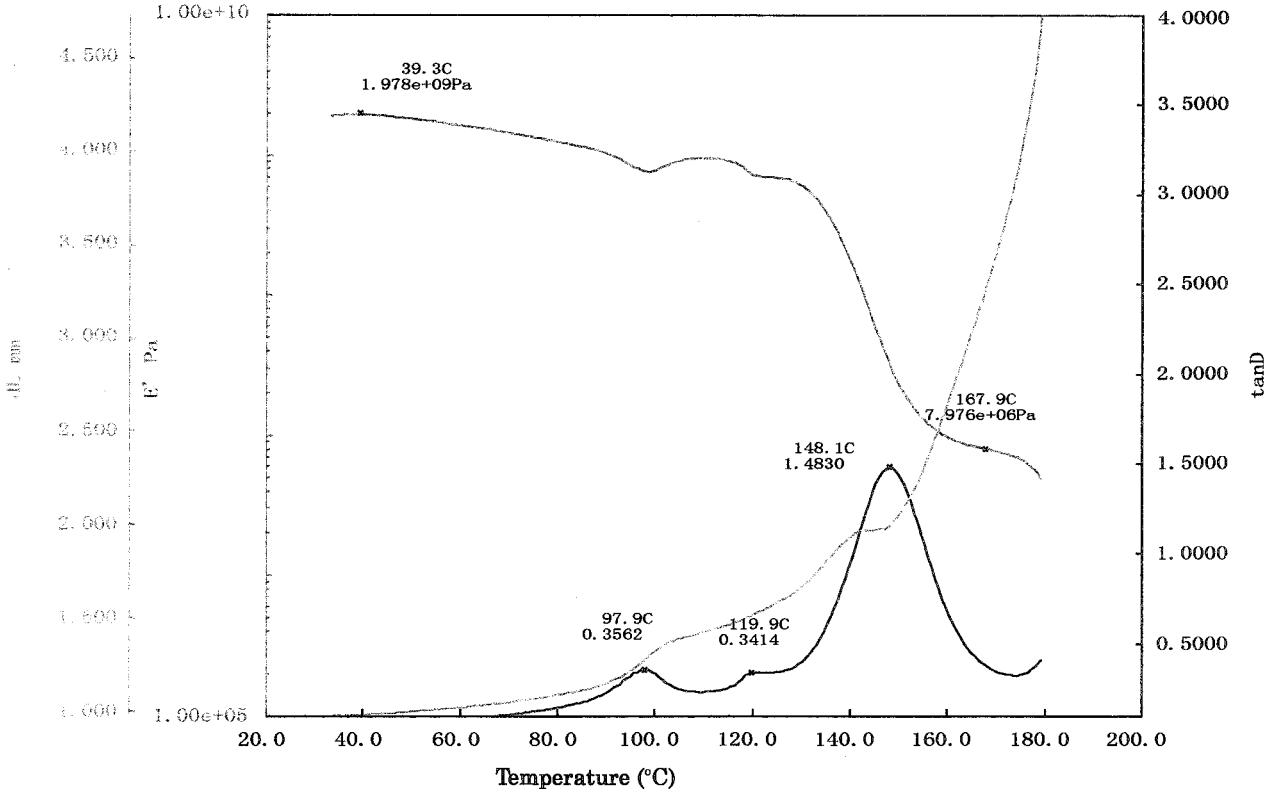

Figure 8. Dynamic mechanical analysis of the DNA−CTMA film at an applied frequency of 1.0 s^{-1}.

weight-loss step is due to the degradation of the complex backbone, with the maximum rate occurring between 180 and 250 °C. The DNA−CP film shows a unique water-loss property compared to the DNA−CTMA and DNA−BDMA films. Water molecules bound in the complex backbone seem to be not easily evaporated, which might be due to increasing interactions between the water molecules and the headgroup (pyridinium) of the complex. On the other hand, DNA−BDMA seems to show lower weight percent of binding water, about 4%, than the others. In fact, if the weight-loss percentages were changed to water molecules lost per base pair, it would be 4 molecules of water per base pair for the three kinds of complexes but 6 molecules of water per base pair for fiberlike NaDNA.

Thermodynamic Mechanical Analysis. The dynamic mechanical behavior of DNA−surfactant complexes was investigated using the DNA−CTMA film cast from ethanol, as shown in Figure 8. It is apparent that the dynamic mechanical thermogram includes three peaks. The first peak, at about 100 °C, is in surprisingly good agreement with the value of the terminal temperature of the first weight-loss step determined by TGA for this sample. This means that the evaporation of binding water was accompanied by changes in the conformations of the DNA strands, when compared with the TGA thermograms. The second peak at 119.9 °C can be ascribed to the melting of surfactant micelles. The third peak, at 148 °C, corresponds to a glass transition. This result suggests that these complexes can be thermoextensive in the temperature range from 100 to 148 °C because the film was largely elongated in that range. It is also anticipated that these films will find useful applications as high-strength materials and as molecular-reinforcing agents in nanocomposites.

Structure of Cast Films. To clarify the microscopic structure of the DNA−complex films, X-ray diffraction measurements were performed. Figures 9 and 10 present X-ray diffraction patterns and analysis results, respectively, for the DNA−CTMA and DNA−CP films. When the incident beam was perpendicular to the film plane, one sharp circular reflection peak in the small-angle region with a spacing of about 40 Å was observed, which corresponds to the diameter of the DNA−surfactant complexes. This value is smaller than the previously published result for the crystal structure of DNA−CTMA.[10,11] This result suggests that these films have a more compacted stacking structure. In addition to this diffraction peak, another small reflection peak with a spacing of about 4 Å was also observed in the wide-angle region. When the beam was exposed parallel to the film edge, in addition to a sharp circular reflection peak in the small-angle region with a spacing of about 40 Å , a stronger hemicircular reflection peak with about a 4-Å spacing was observed. From the symmetric shape of the diffraction peak, it becomes clear that the alkyl tails of the cationic surfactant were packed in a lamellar structure. This indicates that the structure of the DNA−surfactant films was anisotropic in two dimensions. The other kinds of DNA−surfactant complex films also had the same packing structure as the DNA−CTMA and DNA−CP complex films.

Another study on measurement of the anisotropic refractive index by using "the prism coupling method"[16] indicated the anisotropy of these self-assembled films in two dimensions, finding $N_{\text{film thicknees}} = 1.497$ and $N_{\text{film face}} = 1.534$ (to be published in another paper).

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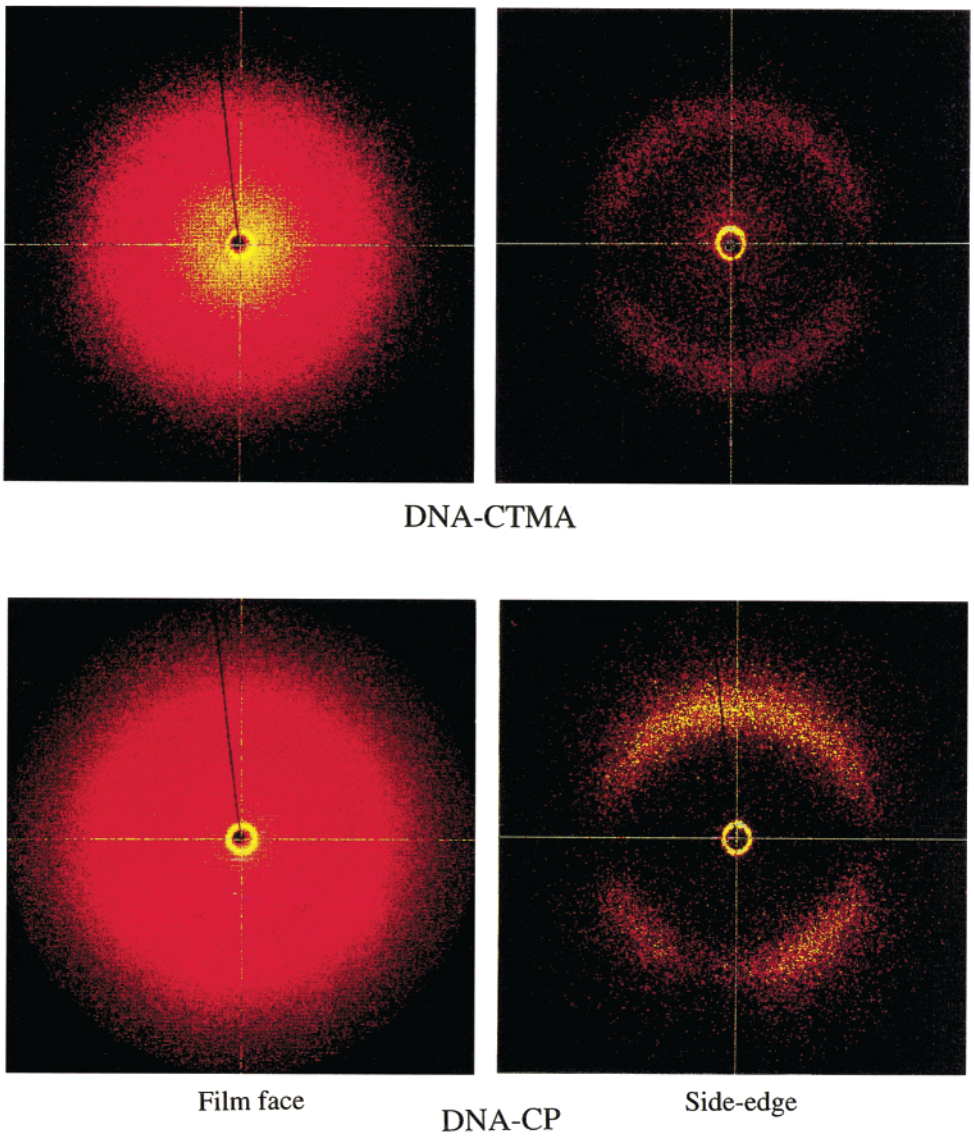

Figure 9. X-ray scattering photographs of DNA−CTMA and DNA−CP films. Film face: the incident beam was perpendicular to the film plane, Side-edge: the incident beam was parallel to the side-edge.

A Proposed Structural Model for DNA−Surfactant Complex Films. Based on previous experimental results and the model proposed by Ghirlando et al.,[10] a formation mechanism for the chiral lamellar structure of these DNA−surfactant complex films was suggested and is illustrated in Figure 11. According to the mechanism proposed, the LB (Langmuir−Blodgett) monolayer of cationic surfactant acts as a template, which provides chiral DNA anions with a fixed direction. Then, the chiral DNA provides the cationic surfactant with a given spatial conformation that determines the next stacking. Because the alkyl chains were oriented perpendicular to film plane, the chiral DNA helices were oriented in the direction parallel to the film plane.

Optical Properties of Dye-Doped DNA−Surfactant Complex Films. Cyanines and other intercalators were extensively used to probe the conformation of DNA helix through the measurement of induced CD spectra.[17−23] To examine the double helix structure of DNA in these complex solutions and films, the induced CD spectra of a hemicyanine NLO dye, DMASDPB, were investigated. We first found that the binding of the achiral DMASDPB to the right-handed double helix of DNA induced a weak, positive CD band in the absorption spectra of the dye for the three kinds of the DNA−surfactant complex in ethanol solution. This is demonstrated in Figure 12, which shows the formation of a partial orientation structure along the DNA double helices. A surprising result was obtained upon measurement of the induced CD spectra for the NLO dye incorporated into the three kinds of self-organized DNA−surfactant films, as shown in Figure 13. Each of the self-organized films shows a strong biphasic signal centered at about 500 nm. This is attributed to the

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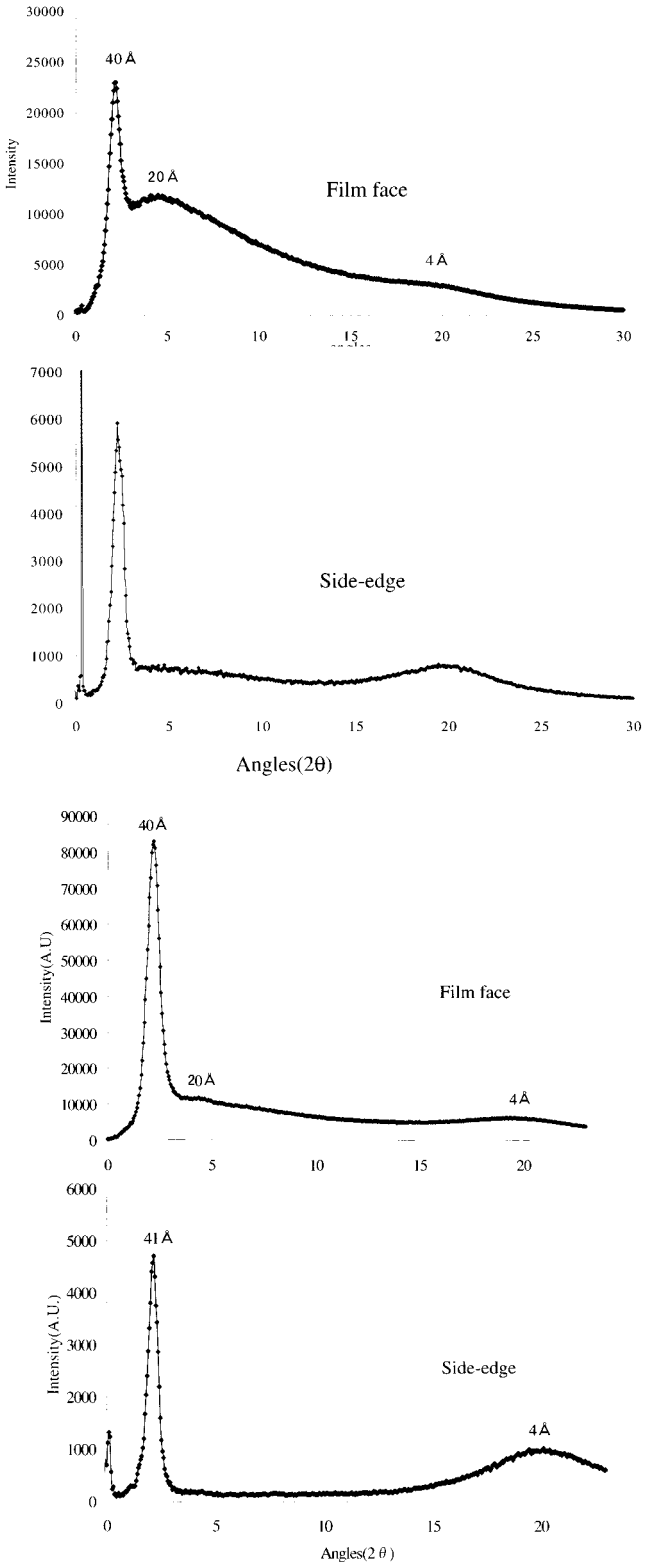

Figure 10. X-ray scattering analyses of (a) DNA−CTMA and (b) DNA−CP films.

formation of a full orientation structure along the chiral DNA double helices. Furthermore, the dye molecules not only display directional binding to the DNA helix, but also play a role for the cross-linking of DNA strands with the cationic surfactants. In these films, the cationic aromatic head of the amphiphilic hemicyanine dye inserted into the chiral cavity of DNA strands leads to the induced CD spectrum. The alkyl tail extends toward the aggregated cationic surfactant micelles. Therefore,

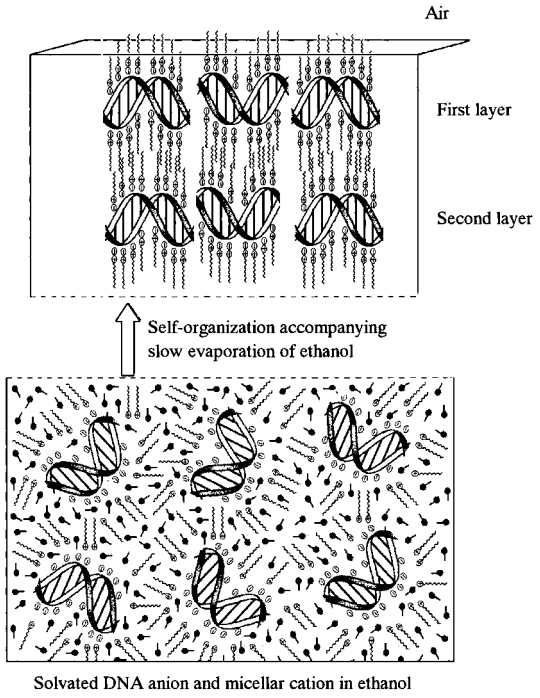

Figure 11. Idealized model for self-assembly process of DNA−surfactant cation complexes.

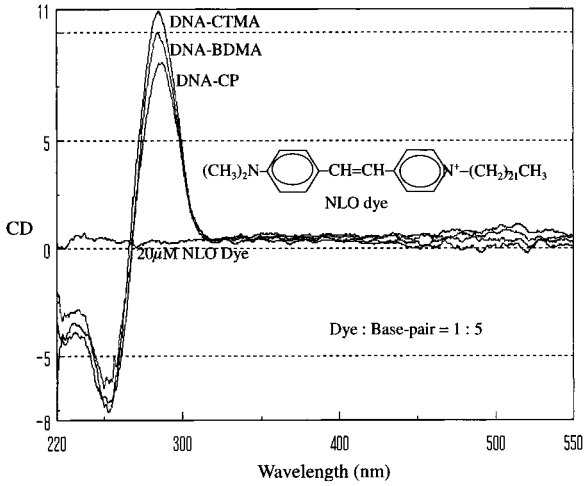

Figure 12. CD spectra of DMASDPB−DNA−surfactant complexes in ethanol solution (all solutions contain 20 μM DMASDPB and 140 μM DNA−surfactant cation).

the L-type structure of dye molecule might be formed to match with DNA strand and the alkyl chain of the surfactant, which is likely the structure in the LB film of these hemicyanine dyes.[24] The cross-linking effect was remarkable in retaining the higher-order structure of the DNA−surfactant complexes.

Summary

A simple method for the large-scale preparation of double helical DNA−surfactant films was proposed from the ethanol solution of dry stoichiometric DNA−surfactant complexes by controlled evaporation of the solvent. Optical analytical methods confirmed that the double-helical structure of DNA was retained after film forma-

(24) Zong, Y.; Qin, J.; Liu, D.; Xu, Y.; Liu, Y.; Zhu, D.; Yu, A.; Zhao, X. *Nonlinear Opt.* **1998**, *19*, 227−238.

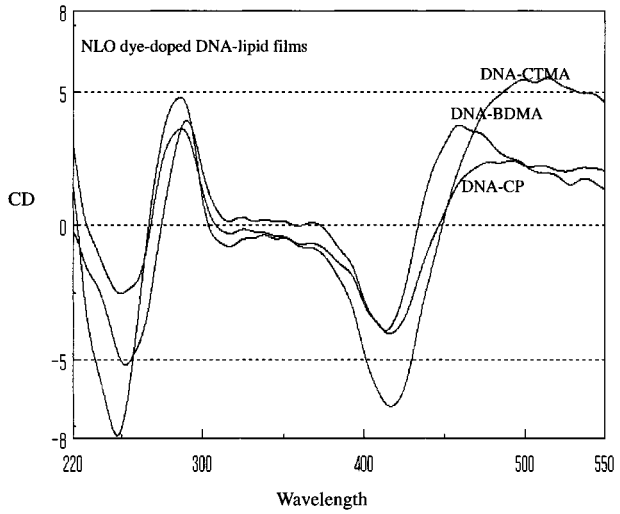

Figure 13. CD spectra of DMASDPB−DNA−surfactant complex films (molar ratio of dye to nucleobase pair =1:10).

tion from the organic solvent. Thermoanalysis combined with CD analysis indicated that the DNA conformation could be controlled by varying the environmental humidity. A study of the induced CD of a functional dye molecule, DMASDPB, revealed that functional dye molecules could be incorporated into the anisotropic DNA−surfactant films and, moreover, that the dye molecules were oriented in the films.

These self-organized films exhibit optical transparency and thermostability. The DNA−surfactant complex films are not only important for research of biophysics and biochemistry, but are also very promising as optical and optoelectronic materials. More detailed reports on optical and optoelectronic applications are published elsewhere.[25−28]

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