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Langmuir, **2002**, 18 (4), 1165-1170 • DOI: 10.1021/la010683b • Publication Date (Web): 22 January 2002

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Self-Assembled Thin Solid Films of Diocetadecyldimethylammonium Cinnamate Lamella Units That Control the Photostationary State of *E–Z* Photoisomerizations

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Received May 7, 2001. In Final Form: November 8, 2001

UV illumination of dioctadecyldimethylammonium cinnamates (C18 *trans*-cin and C18 *cis*-cin) was found to result in the *E–Z* photoisomerization of the cinnamate moieties in self-assembling multilamella films. In the present case, a common photostationary state (pss), which can usually be observed in solution, was not seen in the photolysis of the self-assembled material films of C18 *trans*-cin and C18 *cis*-cin having a bimolecular (bilayer)-unit lamellar structure. Both the *E*- and *Z*-isomers are difficult to isomerize and exhibit different *E/Z* ratios, 73:27 and 10:90, respectively, even under prolonged UV irradiation. However, the same *E/Z* ratio (15:85) could be attained at the pss from either isomer in a monolayer-unit structure. The *E/Z* ratios were found to change abruptly upon heat treatment at around 55 °C before photoisomerization, implying a thermal structural change in the films. Analysis of X-ray diffraction, differential scanning calorimetry, and polarized IR and UV–vis spectroscopic investigations have indicated that the solid films have a characteristic multilamellar structure consisting of bilayer units when they are cast on the silica glass without heat treatment above 55 °C. Moreover, the solid films preheated to 80 °C were composed of an interdigitated monolayer unit having a loose packing structure. This result is in contrast to the bilayer-unit structure of the solid films where *E–Z* photoisomerization of both isomers is suppressed.

Introduction

Amphiphilic compounds are known to form various self-assembling aggregates, including not only micelles, lamellae, and vesicles in water but also stacked lamellar membranes on solid surfaces. Such self-assembling properties are important factors in controlling the photochemical reaction processes of the incorporated guest molecules by regulating their interactions with the media as well as with the aggregated structures. By application to photofunctional materials, such morphological changes in lamellar solid films can be induced by the photochemical transformations of the incorporated guest molecules.¹ The photofunctional properties of such solid films are significant when considering their potential to the development of photonic devices such as nonlinear optical systems^{2–4} and photon-mode memory storage systems^{5–7} and in

applications using the magnetic susceptibility effect.^{8–10} In previous work, we reported the [2 + 2] photocyclodimerization of cinnamic acid incorporated in solid films of dioctadecyldimethylammonium bromide (DODAB) and focused on the effects of the phase transition on the cyclodimerization efficiency.¹¹ The photochemistry was found to change dramatically with the change from cyclodimerization to *E–Z* photoisomerization with heat treatment above 52 °C, which is the phase-transition temperature of the DODAB films before and during photolysis. The self-assembled structure of a DODAB solid film in the absence of organic guest molecules has been reported by Kunitake et al.^{12–14} by means of X-ray diffraction (XRD) analysis and electron microscopy and by a more conclusive single-crystal technique.^{15–18} However, the structure of single crystals of DODAB with

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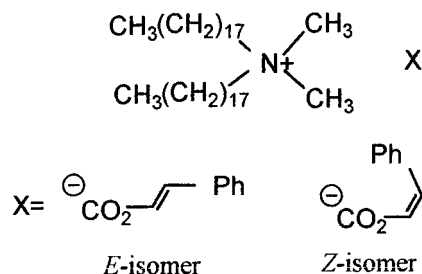
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Chart 1. C18 *trans*-cin and C18 *cis*-cin

incorporated cinnamic acid has not been elucidated. As an alternative method, a study of the 1D electron density distribution could be applied to the characterization of the self-assembled stacking structure of the solid films along the *c*-axis by means of small-angle X-ray diffraction investigations.¹⁹ In this contribution, we report on the *E*–*Z* photoisomerization of solid films made of 1:1 ion pairs of dioctadecyldimethylammonium/cinnamate ions (C18 *trans*-cin) on glass slides and discuss the relationship between the photoreactivities and conformational structures of the films using X-ray diffraction analysis and polarized spectroscopic techniques (see Chart 1).^{20–25}

Experimental Section

Preparation of Dioctadecyldimethylammonium Cinnamate. A. C18 *trans*-cin. (*E*)-Cinnamic acid and DODAB of extra-pure grade were purchased from Tokyo Kasei Co., Ltd. and were recrystallized once each from benzene and acetic acid. An aqueous solution (20 mL) of 0.3 g of sodium cinnamate was mixed with an equal amount of DODAB in dichloromethane (30 mL), and the organic layer was separated from the mixture, washed several times in water, dried over Na_2SO_4 , and condensed in vacuo to produce a white powder (0.5 g). This compound was found to be dioctadecyldimethylammonium cinnamate (C18 *trans*-cin) from ^1H NMR: δ 0.87 (t, 6 H), 1.26 (m, 60 H), 1.69 (m, 4 H), 3.43 (m, 10 H), 6.60 (d, 1 H), 7.23 (m, 3 H), 7.31 (d, 1 H), 7.62 (m, 3 H).

B. C18 *cis*-cin. Allocinnamic acid (*Z*-isomer) was prepared according to a previously reported method.²⁶ A methanol solution (400 mL) of 20 g of cinnamic acid (*E*-isomer) was irradiated for 2 days with a 300 W high-pressure mercury lamp ($\lambda > 300$ nm). The photolyzed mixture was concentrated in vacuo to give the crude *Z*-isomers, which could be separated from the unchanged *E*-isomers because of the difference in water solubility between the two. The *Z*-isomers were recrystallized from hexane with a yield of 0.2 g (2%), and the ion pairs of the *Z*-isomers (C18 *cis*-cin) were then prepared in a manner similar to that of C18 *trans*-cin.

Preparation of Cast Films. Five mL of 2.5×10^{-2} mol dm^{-3} C18 *trans*-cin in aqueous solution was spread onto a silica glass slide (50 mm \times 50 mm) to obtain a translucent colorless film after drying at ambient temperature. Heat treatment of the deposited film was carried out on a metal plate at 80 °C for a few hours, followed by cooling to 20 °C.

Measurements. Differential thermal analysis was carried out with a Perkin-Elmer differential scanning calorimeter, model DSC 7. X-ray diffraction analysis was carried out with a RINT 2000 diffractometer (Rigaku), using $\text{Cu K}\alpha$ radiation, operating

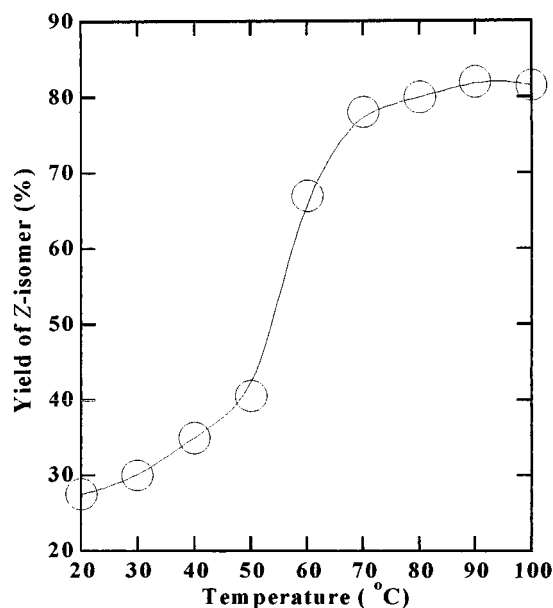


Figure 1. Yields of the *Z*-isomers against the preheating temperature of the C18 *trans*-cin lamellar solid films before UV irradiation for 200 min.

at 40 kV (applied voltage) and 40 mA (applied current). The polarized UV–vis and IR absorption spectra were recorded on a JASCO V-550 spectrophotometer with a JASCO polarizer unit attachment (model RSH-452) and JASCO V-300 or V-500 spectrophotometer. HPLC was performed on a Shimadzu LC-10A liquid chromatograph equipped with a CAPCELLPAK column, C18 UG120 S-3 μm (Shiseido Co., Ltd.), using a mixture of a phosphoric acid (3.0×10^{-2} mol dm^{-3}) and methanol (50:50 v/v) with pH = 3.5 as the eluent. The retention times of the *E*- and *Z*-isomer products were 15 and 10 min, respectively.

Irradiation of the C18 *trans*-Cin and C18 *cis*-Cin Films. The films (20 mm \times 20 mm \times 1 μm) were covered by a 5 mm-thick Pyrex glass plate and irradiated with a 300 W medium-pressure Hg lamp ($\lambda > 280$ nm) at an ambient temperature of 20 °C. The photolyzed films were dissolved in 5 mL of methanol and then analyzed by HPLC at 225 nm.

Results and Discussion

UV Irradiation of the C18 *trans*-Cin Films. The cinnamate moieties of C18 *trans*-cin and C18 *cis*-cin were subject to *E*–*Z* photoisomerizations by UV irradiation through a Pyrex filter ($\lambda > 280$ nm). Figure 1 shows the yields of the *Z*-isomers in the photostationary state (pss) against the temperature at which the films were treated for 30 min before irradiation. When the preheated C18 *trans*-cin films were exposed to UV light, only *E*–*Z* isomerizations could be observed, without any formation of cinnamate cyclodimers. The yields of the *Z*-isomers rapidly increased with an increase in the heat treatment temperature above 55 °C and reached ca. 85% at 80 °C; however, the yields were rather low (~27%) when the films were treated at $T < 30$ °C. This abrupt change clearly indicates that a conformational structural transformation in the films occurs with heat treatment temperatures > 55 °C.

Figure 2 shows the *E*–*Z* photoisomerization profile against the irradiation time in the photolysis ($\lambda > 280$ nm) of the solid films of C18 *trans*-cin and C18 *cis*-cin that were preheated to 80 °C. The pss of the *E*/*Z* ratios was smoothly attained within 150 min for both the preheated and nonheated solid films of the C18 *trans*-cin and C18 *cis*-cin ion pairs. However, the *E*/*Z* ratios of C18 *trans*-cin (73/27) and C18 *cis*-cin (10/90) at the pss were quite different from each other. These results are in sharp

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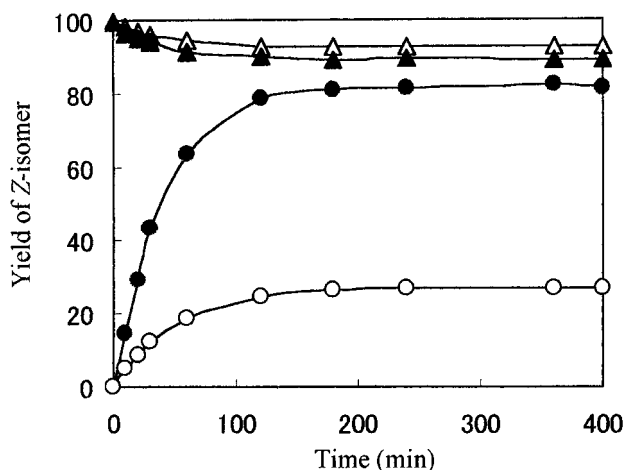


Figure 2. Dependence of irradiation time on the yield of the Z-isomers. Preheated C18 *trans*-cin (●); C18 *cis*-cin (▲); prepared C18 *trans*-cin (○); C18 *cis*-cin (△).

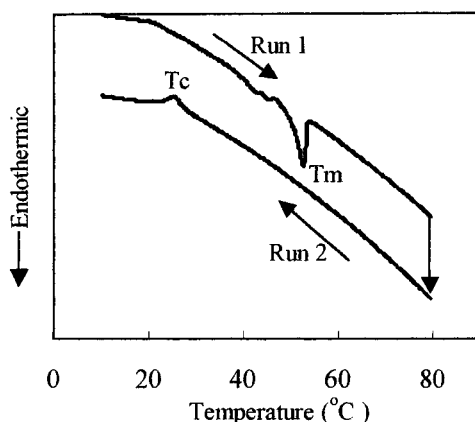


Figure 3. DSC analysis of C18 *trans*-cin.

contrast to those of the preheated samples before UV irradiation, where the *E/Z* ratios of the *trans* and *cis* isomers at the pss were almost identical (i.e., 15/85).

The *E–Z* photoisomerization of olefins has been extensively studied under various conditions.^{27–31} On the basis of these studies, solid or viscous matrixes have been shown to affect the isomerization efficiencies, and the effect is especially prominent in the case of an increase in the molecular volume of the transition state between the *E*- and *Z*-isomers. We have found from our work that nonheated solid films may suppress the isomerization because of the rigidity of the reaction spaces.

Differential Scanning Calorimetry (DSC). DSC analysis of the C18 *trans*-cin films is shown in Figure 3. An endothermic peak (T_m) appeared at 55 °C when the temperature was increased from 10 to 80 °C (run 1), implying that the lamellar structures in the solid films undergo a phase transition. When the 80 °C films were cooled at a rate of 1 °C/min, a reverse exothermic peak could not be reproduced until 55 °C, although an endothermic peak was observed near 25 °C. Furthermore, the endo- (T_m) and exothermic peaks (T_c) were observed repeatedly at 55 and 25 °C, respectively.

X-ray Diffraction Analysis. Figure 4 shows the X-ray diffraction patterns of the solid films of C18 *trans*-cin and C18 *cis*-cin before and after the above-mentioned heat treatment. A series of sharp diffraction (001) peaks were observed, indicating that these films have a lamellar stacked structure along the *c*-axis. As seen in Figure 4a, the lamellae have a repetitious and highly ordered structure with intervals of 3.6 nm in the diffraction patterns of the C18 *trans*-cin. A series of higher-order diffraction peaks located between the first and eighth peaks are shown in the inset of Figure 4a. The d_{001} values of the preheated C18 *trans*-cin films (Figure 4b) were estimated to be 3.1 nm smaller than those of the nonheated films (3.6 nm).

When the preheated C18 *trans*-cin films were irradiated with UV light, the d_{001} values decreased while the intensities of the X-ray diffraction signals were constant. The resulting X-ray diffraction peaks correspond to those of the C18 *cis*-cin lamellar films (Figure 4d), and the *E–Z* photoisomerization of the cinnamate components induced no collapse of the definitive conformation of the lamellar structure.

To observe the changes in the structural regularity of the solid films of C18 *trans*-cin at the phase-transition temperature of 55 °C, studies of the XRD spectral changes were carried out under heat treatment from 25 to 80 °C. Figure 5 shows that the (001) diffraction-peak intensity decreases abruptly above 55 °C without the appearance of any new diffraction peaks, indicating that the structure of the cast film changes from bilayer to amorphous above 55 °C. Cooling of the amorphous film at a rate of 1 °C/min caused new diffraction peaks resulting from another structure (repetition unit = 3.1 nm) to appear. This structure changed gradually and was eventually transformed into the original bilayer lamellar structure after standing at ambient temperature (ca. 25 °C) for a week; therefore, this new structure was found to be metastable.

Electron Density Distribution. The electron density distributions along the *c*-axis in the lamellar-structured solid films have been successfully estimated from a series of the integrated intensities of the (001) diffraction peaks. Figure 6 shows the electron density distribution profiles of the unit layer of the lamellae evaluated from the X-ray diffraction patterns of both the C18 *trans*-cin and C18 *cis*-cin films, where the phases have been chosen to satisfy the conditions of the regions occupied by the hydrocarbon chains, which are almost flat and have relatively low electron density. The prepared samples of C18 *trans*-cin exhibited zero electron density distribution at the lamellar center (Figure 6a), which is indicative of a bilayer stacking structure of the solid films of C18 *trans*-cin because the electron density exhibits a dip at the center of the lamellar unit. Figure 6b, however, shows electron density at the center of the unit layers of the samples preheated to 80 °C.¹⁹ On the basis of these characteristics, we find that the lamellar structure of the C18 *trans*-cin films changes from an interdigitated monolayer to a bilayer-unit lamellar structure at the phase-transition temperature (ca. 55 °C). It is noteworthy that the electron density distribution can be determined from C18 *cis*-cin formed upon UV irradiation; however, the interdigitated lamellar structure did not change during *E–Z* photoisomerization, although the lamellar spaces shortened, as shown in Figure 6c.

Polarized Spectroscopic Measurements. The orientation of the components (the cinnamate and surfactant ammonium ions) in the solid films was determined by measuring the polarized absorption spectra of the molecular self-assembled films in UV–vis and IR regions.^{20–25} UV and IR spectroscopic absorbances are proportionally

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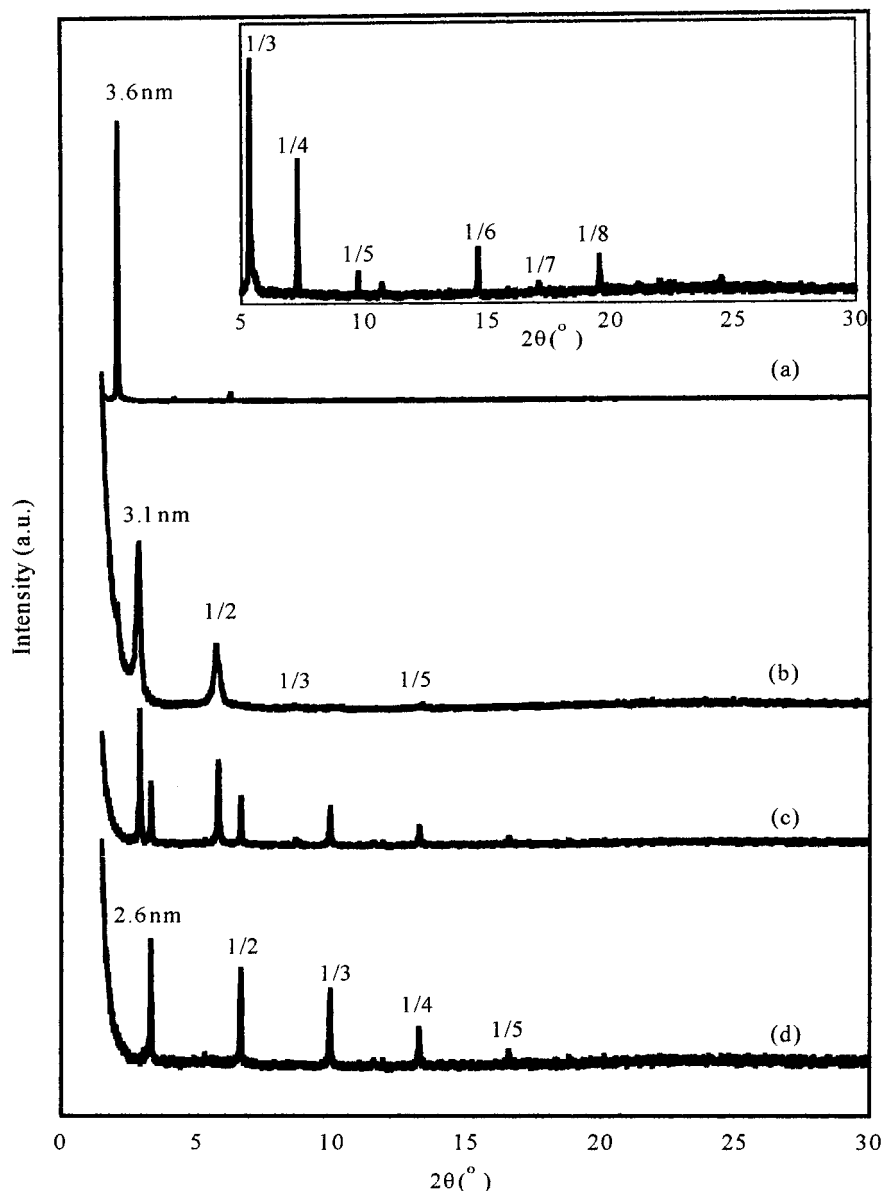


Figure 4. X-ray diffraction patterns of the C18 *trans*-*cis* lamellar films. (a) Without heat treatment above 50 °C. (b) After heat treatment at 80 °C. (c) After irradiation of sample (b) for 200 min. (d) C18 *cis*-*cis* lamellar films after heat treatment at 80 °C.

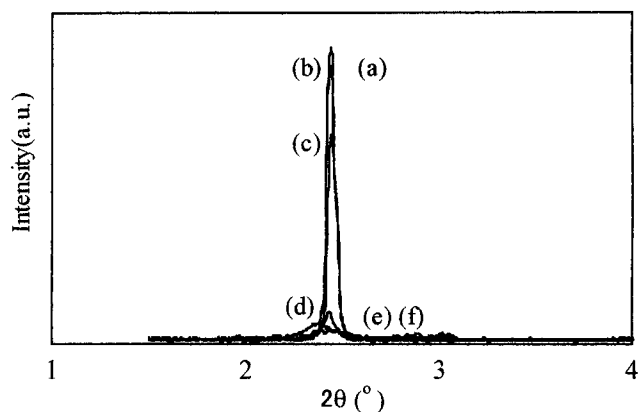


Figure 5. Effect of heat-treatment temperature on the regularity of C18 *trans*-*cis* films at (a) 20, (b) 40, (c) 50, (d) 60, (e) 70, and (f) 80 °C.

dependent on the squared optical transition moments of the components, which can be obtained from irradiation at the appropriate incident wavelength and from the transition moments. Here, the optical transition moments

are closely related to the average values of the molecular dipole moments in the electric field of the incident light. When the organic components are regularly organized within the films, their absorption intensities change with changes in the angles between the incident light and changes in the optical transition moment. Thus, the angle dependence of the absorption intensities can be evaluated from the analysis with polarized incident light.

Figure 7 shows a schematic illustration of the measurements obtained by such UV and IR polarized absorbance spectroscopy. The absorbance ratio R_{yx} of perpendicularly polarized incident light is given by eq 1, where A_x and A_y denote the absorption intensities for the vertically and horizontally polarized incident light beams, respectively.^{24,25}

$$R_{yx} = \frac{A_y}{A_x} = \frac{\{2[\sin^2 \theta + \sin^2 \alpha(3 \cos^2 \theta - 1)] - (3 \sin^2 \alpha - 1)(3 \cos^2 \theta - 1) \sin^2 \gamma\}}{\{2 \sin^2 \theta + (2 - 3 \sin^2 \theta) \sin^2 \gamma\}} \quad (1)$$

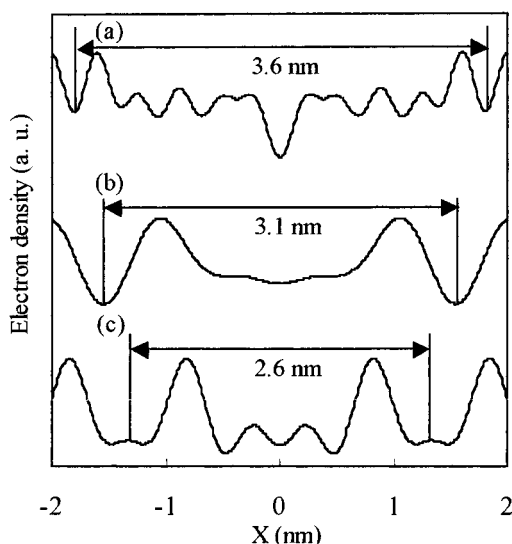


Figure 6. Electron density distribution of C18 *trans*-cin lamellar films (a) as prepared, (b) after heat treatment, and (c) C18 *cis*-cin lamellar films after preheating treatment at 80 °C.

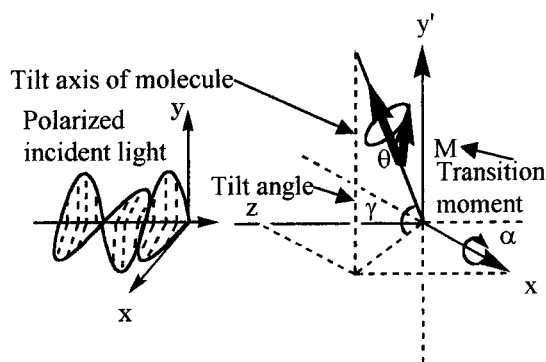


Figure 7. Scheme of polarized spectroscopic measurements.

θ , α , and γ represent the angle of the molecular axis against the optical transition moment, the rotation angle of the substrate for the x axis, and the tilt angle of the molecular axis against the normal line of the glass slide surface, respectively. The cast films were found to possess an optical anisotropy that was due to the alignment of the organic molecules because the R_{yx} value changes as α changes. The values of γ were estimated from eq 1. θ values measured from UV (265 nm) and IR (2915 cm^{-1}) spectroscopy were attributed to the π - π^* transition of the cinnamate group and to C-H stretching vibration in *trans*-polymethylene, respectively. In the case of the polymethylene C-H stretch, θ was 90° because the vibration at 2915 cm^{-1} is perpendicular to the polymethylene chain. In the case of cinnamate ions, θ was determined to be 0° by analysis of the MO calculations of PM3 and ZINDO.³²⁻³⁵

For the measurement of γ of polymethylene in the surfactant, the R_{yx} ratio was calculated from the 2915 cm^{-1} absorbance against α , as shown in Figure 8. Both of the R_{yx} values of the nonheated and preheated films at 80 °C were plotted against α . γ values calculated from eq 1 are compiled in Table 1. γ values of the component polymethylene chains in the nonheated films were some-

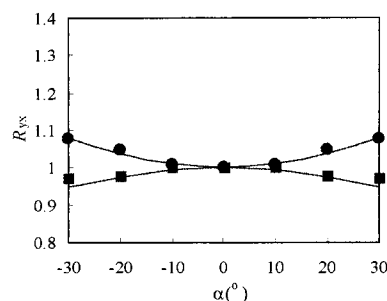


Figure 8. Relationship between R_{yx} at 2915 cm^{-1} and α of the C18 *trans*-cin films on the SiO_2 solid glass as prepared (■) and with preheating treatment (●).

Table 1.

sample	γ polymethylene	γ cinnamate
nonpreheated	58 ± 5	51 ± 5
preheated ^a	49 ± 3	59 ± 3

^a The samples were heated to 80 °C for 2 h and then cooled to ambient temperature (~ 20 °C).

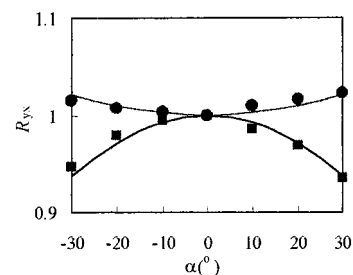


Figure 9. Relationship between R_{yx} at 265 nm and α of the C18 *trans*-cin films on the SiO_2 solid glass as prepared (■) and with preheating treatment (●).

what larger than those of the preheated samples, suggesting that the surfactant chain had a larger inclination in the nonheated samples than in the preheated samples.

In a similar manner, the plots of R_{yx} against α are shown for the cinnamate within the C18 *trans*-cin films and were obtained from the 265 nm absorption maximum, as shown in Figure 9. The γ values for the cinnamic moieties are also included in Table 1. A substantial difference in the γ values between the cinnamic moieties of the nonheated and the preheated samples is observed. The tilt angles are interesting because they were found to be inversely dependent on the preheating treatment of the solid films.

Structural Elucidation of the C18 *trans*-Cin Films. Okuyama et al.¹⁷ have determined that the crystal structure of dioctadecyldimethylammonium bromide (DODAB), the surfactant component of C18 *trans*-cin, consists of bimolecular layers stacked regularly along the c -axis, with hydrocarbon chains of $\gamma = 45^\circ$ against the bilayer surface. The thin solid film of DODAB cast on a glass slide is assumed to possess a lamellar structure very similar to that of the above-mentioned single crystal, as indicated by its XRD pattern.

An attempt to make single crystals of the C18 *trans*-cin ion pair to use for structural characterization was not possible. As an alternative approach to characterize the lamellar structure of the C18 *trans*-cin film, the tilt angles, lamellar unit length, and the electron density distribution of the hybrid films were clarified, as shown in Figure 10. A lamellar unit distance of 3.6 nm, determined from XRD analysis, was coincident with that of 3.6 nm estimated from the tilted C18 *trans*-cin bilayer in the nonheated film (Figure 10a) when the lengths of the cinnamate and dioctadecyldimethylammonium ions are 0.8 and 2.4 nm,

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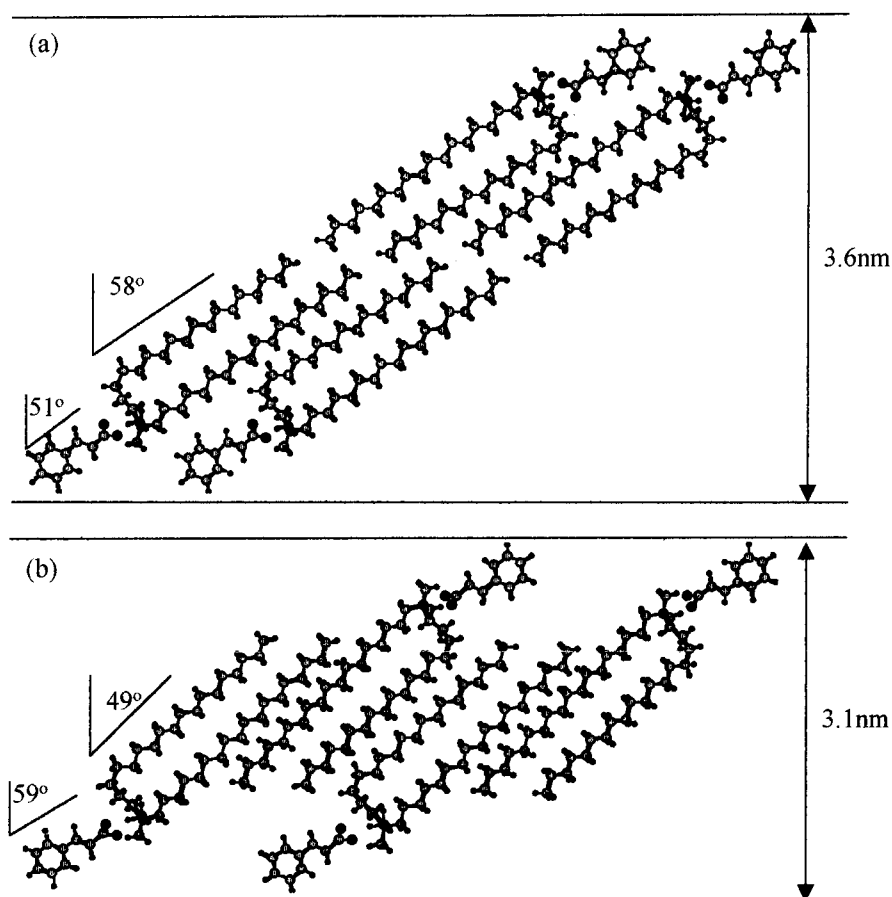


Figure 10. Model of the unit lamellar structures showing the bisection of C18 *trans*-cin (a) as prepared and (b) with preheating treatment at 80 °C.

respectively. However, the interdigitated monolayer with perfect overlap of the ion-pair molecules had a lamellar unit length of 2.6 nm. This value is not coincident with the value (3.1 nm) from XRD analysis.

Figure 10b shows an incomplete interdigitated picture in which the monolayer unit was drawn so as to fit the unit lamella of length 3.1 nm. The cinnamate groups are bulkier and more tilted than DODAB and thus cause the ion pair to be loosely packed and the monolayer to be incompletely interdigitated. Hence, DSC analysis showed that the introduction of the cinnamate ion as a counterion of DODAB converted the stable bilayer unit into a metastable monolayer-unit lamellar structure.

***E–Z* Photoisomerization in the Lamellar Structures.** Because the dioctadecyldimethylammonium ions form a bilayer-unit lamellar structure in the nonheated solid films of C18 *trans*-cin, the cinnamate components can be rigidly packed in the bilayer-unit lamellar structure, in contrast to the case of the incompletely interdigitated layers. Indeed, UV irradiation of the C18 *trans*-cin bilayer solid films resulted in the inefficient formation of *Z*-isomers with a yield of 27% at the pss. This yield is presumably due to the spatial restriction for the *E–Z* isomerization because the *E*-isomers dwell in rather firmly packed lamellar units. In addition, no photodimers were observed, presumably because the larger inclination of the cinnamate against the normal line of the lamellar surface, thus minimizing the overlap of the electronic interactions with the neighboring olefins, which is an important interaction for dimerization.

In the case of the film preheated to 80 °C and then cooled to 25 °C, we concluded that the dioctadecyldimethylammonium ions were self-assembled as incom-

pletely interdigitated monolayers, as shown by X-ray diffraction electron density estimations and by polarized spectroscopic investigations (Figure 10b). The interdigitated monolayers of the DODAB surfactant provide sufficient space for the isomerizations of the cinnamate moieties to occur. Thus, the cinnamate anions are mobile within this space; consequently, *E–Z* isomerization is favorable. The space filling may also explain the different reactivities of the *E*-isomers in the mono- and bilayer-unit assemblies.

Conclusions

Thin solid films of dioctadecyldimethylammonium cinnamate (C18 *trans*-cin) were studied in detail by Fourier 1D electron density distributions derived from X-ray diffraction patterns and polarized-light IR and UV–vis spectroscopic analyses. These investigations clearly indicate that preheating samples above 55 °C may convert the bilayer units to incompletely interdigitated monolayer units in the lamellar structure of the solid films. Under UV irradiation, the nonheated films show a different pss in the *E–Z* photoisomerization process; however, the preheated films had identical pss values (15:85) for both isomers. We conclude that the differences in the photo-activities between the nonheated and preheated films are due to the differences in the reaction spaces accommodating the cinnamate ions.

Acknowledgment. This work was supported in part by the Grant-in-Aid for Scientific Research of the Ministry of Education, Science, Sports, and Culture. We thank the Ministry for its support.

LA010683B