

UV Light Driven Morphological Changes in Lamella Films of a Poly(ethylene imine) Complex with 4-Dodecyloxycinnamic Acid

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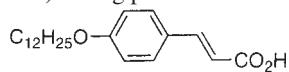
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A cast multilayer film of poly (ethylene imine) (**PEI**) complex involving 4-dodecyloxycinnamic acid (**C12OCin**) was found to show layer shrinkage along the *c*-axis on the glass plate under UV illumination at $\lambda > 300$ nm. The bilayer units in the stacked lamella film successively shifted from 4.7 to 4.2 nm in length, induced by the *E*-to-*Z* photoisomerization, indicating continuous changes in the layer distances. This shrinkage behavior shows a contrast to that observed in the case of an ion-pair film of dioctadecyldimethylammonium cinnamate (**DDAC**) which exhibits no intermediate layer distance during a similar photoinduced shrinkage of the film.

UV light responsive materials in organic supramolecular matrices are of special interest in the development of photofunctional devices.¹ It has been found that an equimolar mixture of ionic surfactants and photofunctional organic materials is able to form amphiphilic self-assembling oriented multilayer films which can generate 1 : 1 ion pairs on glass slides.²

Cinnamic acid is known to undergo efficient *E*-*Z* photoisomerization. In our previous studies of a series of self-assembling systems in dispersion,³⁻⁸ a 1 : 1 ion pair of dioctadecyldimethylammonium cinnamate (**DDAC**) has been investigated in the form of composite monolayer films on glass slides.⁹ In these self-assembling systems, *E*-to-*Z* photoisomerization was accompanied by a continuous change in the relative intensities of the diffraction peaks attributed to the changes observed in the lamella structure before and after isomerization. The photolyzed stacked film was, thus, found to be composed of a mixture of the initial and photolyzed layers. These morphological changes were found to originate the changes in the packing conformations and alignments of the olefinic moieties in the film. Along these lines, we have reported on the reversible transformation of the lamella structure of bis(*N*-methyl-4-octadecyloxy-stilbazolium) isophthalate thin films which could be induced by only a 10% conversion of the cyclodimer.¹⁰

Further study on the photoinduced morphological changes which could be seen in the cast film, poly(ethylene imine) [**PEI**, (CH_2CHNH_2)_n], was carried out to form a hydrogen-bonded complex with cinnamic acid and to observe the effect of the counterions on these photoinduced changes. In fact, stearic acid has been reported to form a characteristic layer structure with **PEI**.¹¹ In the present paper, we report on the lamella structural changes observed on the thin films of a 4-dodecyloxycinnamic acid (**C12OCin**) complex with poly(ethylene imine), (**PEI**, MW = 2×10^3) during photochemical reactions.



C12OCin

An equimolar solution of **C12OCin** and **PEI** in DMF(10 mM) resulted in the precipitation of a white powder after filtration and washing several times with deionized water followed by the addition of DMF and drying in vacuo.¹² The IR absorption spectra show that a complex made up of two components (**C12OCin** and **PEI**) can be characterized by the interactions between the carboxylic group of **C12OCin** and the imino group of **PEI** at the expense of a drastic weakening in the C=O stretching vibration of the associated two COOH groups at 1710 cm^{-1} . The broad absorption originating from the NH bending vibration and C=O absorption vibration, thus, appear at 1555 cm^{-1} , supporting the assumption that each **C12OCin** is linked to an imino group of **PEI** by an ionic or hydrogen-bond.¹²

A 0.3 mM solution of the resulting white powder (**C12OCin-PEI**) in CH_2Cl_2 was cast onto the silica glass slide with a turbid thin film of ca. $100\text{ }\mu\text{m}$ thickness. *E*-*Z* isomerization under UV irradiation through a Pyrex filter ($\lambda > 300$ nm) was carried out in the cinnamate moieties of **C12OCin-PEI**. Here, the only product which could be observed in the complex was (*Z*)-cinnamate. Figure 1 shows the plots of the *Z*-isomer content (%) against the irradiation time with light ($\lambda > 300$ nm). NMR analysis showed the formation of *Z*-isomers with a yield of 48% at the photostationary state (pss). This shows a sharp contrast to the case of the photolysis of a **C12OCin** film without **PEI**, where the head to head (HH) dimers (30%) were formed together with the *Z*-isomer (16%) after 3 h irradiation.¹³ The present film can, thus, be said to provide an environment for which the neighboring C=C bonds of the olefins (**C12OCin**) are separated by the **PEI** chains.

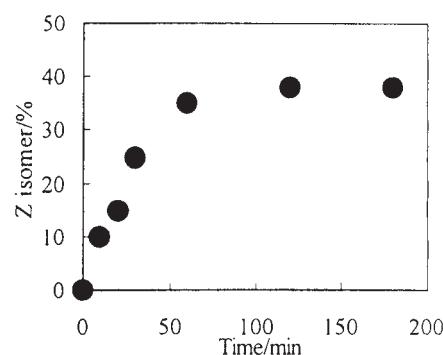


Figure 1. *E*-*Z* Photoisomerization of the **C12OCin-PEI** complex.

The lamella unit distance of the **C12OCin-PEI** film before UV irradiation was estimated to be 4.7 nm and continuously became smaller until it reached 4.2 nm at pss as the *E*-to-*Z* photoisomerization proceeded, as shown in Figure 2.^{14,15} Judging from the molecular length of 2.4 nm for **C12OCin**, the C12 alkyl

chain of the complex bilayer before irradiation was almost perpendicular to the layer surface. After UV irradiation, *E*-*Z* isomerization caused 0.5 nm shrinkage, since the length of the *Z*-isomer is smaller than that for the *E*-isomer.⁹ Thus, it can be said that the lamellar units changed in length as the photoisomerization proceeded, as shown in Scheme 1.

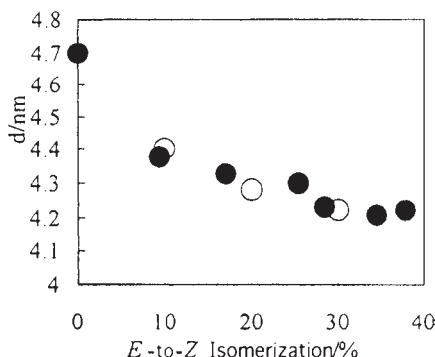
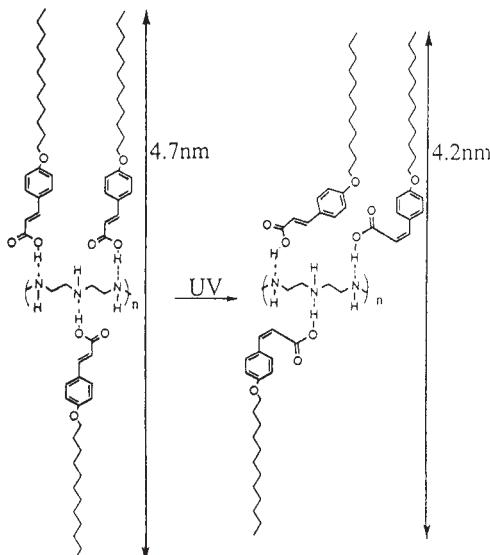


Figure 2. The plots of the **C12OCin-PEI** lamella unit (d) against the *E/Z* ratio (●). The open circle (○) denotes the lamella unit (d) for the cast films of a mixture of *E*- to *Z*-**C12OCin-PEI** with *E/Z* ratios of 90/10, 80/20, and 70/30.



Scheme 1. Structural changes observed in **C12OCin-PEI** by UV irradiation.

The continuous changes in the initial lamella unit (4.7 nm) to the final unit (4.2 nm) under UV irradiation are shown with closed circles in Figure 2. Figure 2 also shows the plots (open circles) for a number of mixed samples with *E/Z* ratios of 90/10, 80/20, and 30/70 for the **C12OCin** in the **C12OCin-PEI** films. A rather good overlap can be seen between the photolysate film and the mixture of the *E* and *Z* isomers, clearly indicating that the photoinduced layer shrinkage is attributed to the increase in the ratio of the *Z*-isomer homogeneously mixed within the entire film.

In contrast, the previously reported⁹ ion-pair, **DDAC**, is thought to be more rigid than **C12OCin-PEI** complex, and hence the molecular conformation is more immobile than for the **PEI** complex. In case of the ion pair **DDAC**, Figure 3 shows no

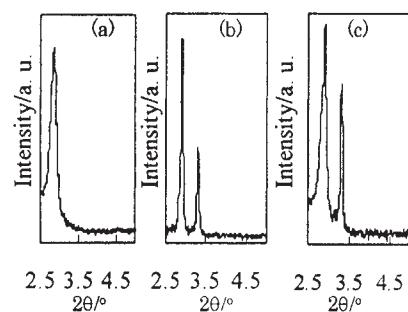


Figure 3. X-ray diffraction profiles of the 1 : 1 ion-pairs of DDAC: (a) before irradiation; (b) after irradiation of 6 hr (*E* : *Z* = 15 : 85) and (c) a film with an *E/Z* mixture of DDAC (*E* : *Z* = 15 : 85).

formation of an intermediate layer distance of the film during the *E*-*Z* photoisomerization process; (a) and (b) at *E/Z* ratios of 100 : 0 and 15 : 85, respectively. It was also observed that for the mixture of the *E* and *Z* isomers, the **C12Cin-PEI** morphology was starkly different from the intermediate state of the ion-pair **DDAC** during the photoisomerization process, as shown for (c) in Figure 3. Further study into the origin and mechanisms behind this reaction is now in progress.

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