

Photodimerization of *trans*-Cinnamic Acid in a Bilayer of Dimethyldioctadecylammonium Bromide

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The photochemistry of *trans*-cinnamic acid (*trans*-1) was studied in a cast film of dimethyldioctadecylammonium bromide (2), deposited from aqueous dispersions as a crystalline solid by the spontaneous vaporization of water. UV irradiation of the cast film resulted in a highly selective formation of the *syn*-Head-to-Head dimer, suggesting a parallel orientation of *trans*-1 within a bilayer film. Analyses with X-ray diffraction, differential scanning calorimetry, and IR spectra revealed the formation of a bilayer structure of 2 in which the molecules of *trans*-1 are dissolved to interact with 2 of the polar head groups. The photoreactivity of *trans*-1 in the cast film was found to be dramatically suppressed by heating at 40–60 °C, which is attributed to an improvement in the crystallinity of the bilayer.

The photodimerization of various aromatic olefins in the crystalline state is a well-known topochemical reaction.^{1–4)} Many related studies concerning photodimerization in a variety of organized media, such as micelles, vesicles, air–water interface, and Langmuir–Blodgett multilayers, have been carried out.^{5–12)} In these heterogeneous systems, photoreactive moieties were incorporated into the amphiphilic backbone or as counter ions of amphiphiles; topochemical photodimerizations were achieved by changing the orientation of the organic molecular assemblies.

In previous literature,^{6,7)} we have reported that the irradiation of the salt of *trans*-cinnamic acid (*trans*-1) or 2-indenecarboxylic acid incorporated into self-assembled molecular aggregates results in a selective formation of Head-to-Head dimers (*syn*-HH and *anti*-HH), reflecting a selective orientation of substrates in the aggregates. In addition, the morphologies and structural rigidity of the molecular assemblies were demonstrated to affect the selectivity and efficiency of the photodimerization. For example, reversed micelles formed from *trans*-1 and dodecylamine in carbon tetrachloride produced a *syn*-HH dimer upon UV irradiation. However, the addition of small amounts of methyl alcohol caused a dramatic change in the major product to an *anti*-HH dimer. This clearly reflects the looseness of the ion-pair between *trans*-1 and dodecylamine.^{6c)} These findings show that the photodimerization reaction is extremely sensitive to the structure and rigidity of the molecular assemblies.

The crystal structures of some ammonium amphiphiles were found to consist of regularly stacking bilayers;^{13,14)} it has also been found that some aromatic molecules were incorporated into bilayers of host amphiphilic molecules in which guest aromatic molecules were arranged between the interdigitated host molecules.¹⁵⁾ These findings indicate that a bilayer can be used as a template for the topochemical photoreaction of guest molecules. Recently, it has been shown

that cast films prepared by drying an aqueous bilayer dispersion on a solid plate are characteristic of multibilayer structures with a macroscopic orientation,^{16–18)} and can be utilized as a template for preparing two-dimensional networks of organic¹⁹⁾ and inorganic polymers.²⁰⁾ In the present work, cast films prepared from an aqueous dispersion of dimethyldioctadecylammonium bromide (2)¹⁴⁾ including *trans*-1 were characterized by X-ray diffraction and differential scanning calorimetry (DSC). The photodimerization of *trans*-1 in molecular aggregates of 2 were studied in order to characterize the solubilization sites of the acid *trans*-1 in a bilayer of 2 (Chart 1). Topochemical photodimerization of *trans*-1 is discussed in relation to the incorporation and orientation of *trans*-1 in a bilayer of 2.

Results and Discussion

Irradiation of *trans*-Cinnamic Acid (*trans*-1) in the Cast Film of Dimethyldioctadecylammonium Bromide (2). An equimolar *trans*-cinnamic acid (*trans*-1) was added to a 2.5×10^{-2} mol dm⁻³ aqueous dispersion of dimethyldioctadecylammonium bromide (2), which produced

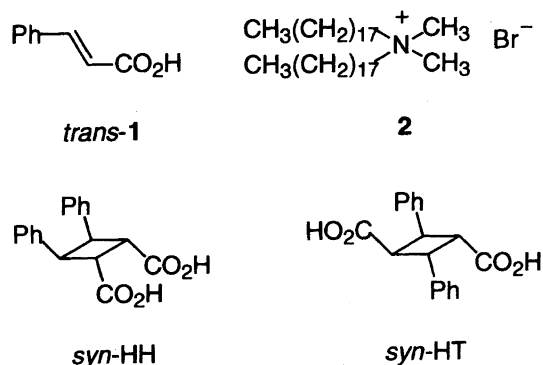


Chart 1.

a translucent crystalline film by drying after casting on glass slides. The photochemical reaction of *trans*-**1** was examined in order to investigate the features of the molecular packing of *trans*-cinnamic acid moieties in the cast film of **2**. UV irradiation of the film through a Pyrex filter (> 280 nm) resulted in the appearance of the *syn*-Head-to-Head dimer (*syn*-HH) and *cis*-isomer (*cis*-**1**) as shown in Fig. 1. Thus, 85.5% of the *syn*-HH dimer, 4.3% of the *syn*-Head-to-Tail dimer (*syn*-HT), and 15.6% of *cis*-**1** were included in the photolysate after 40 min of irradiation with a conversion of 45% of *trans*-**1**. It is interesting to note that the predominant photoproduct was found to be the *syn*-HH dimer, i.e., *syn*-HH/*cis* = 6–7 at any stage, irrespective of the irradiation times. In contrast, only *syn*-HT was observed in the photolysis of the α -form of crystal *trans*-**1** without **2**.^{1a)}

Table 1 summarizes the photoirradiation of *trans*-**1** in cast films of **2** at various ratios. In most cases, the major photoproduct was the *syn*-HH dimer. Interestingly, the selectivities of the *syn*-HH dimer were nearly constant at 70–80% for the various mixing ratios. This result corresponds to the formation of a composite bilayer, even at mixing ratios of *trans*-**1** to **2**, which are lower than unity. The predominant formation of the Head-to-Head dimer suggests that the molecules of

trans-**1** are arranged in a parallel orientation in the cast film of **2**.²¹⁾

Characterization of the Cast Film of **2** Including *trans*-**1**

1. The translucent crystalline films of various *trans*-**1** and **2** mixtures were investigated by DSC. Figure 2 shows DSC curves of mixtures of *trans*-**1** and **2** at various ratios; two endothermic peaks can be observed. The lower transition peak is sharp, and appeared constantly at 52 °C ($\Delta H = 16.3$ kcal mol⁻¹ based on **2**, Fig. 2f) while the higher peak is broad and gradually shifted from 72 to 52 °C. With the film of a component of **2** alone, a single endothermic peak was observed at 72 °C ($\Delta H = 21.3$ kcal mol⁻¹, Fig. 2a), which can be ascribed to the crystal-to-liquid crystal phase transition of the bilayer structure.²²⁾

It was at first expected that the peak newly observed at 52 °C could be attributed to a phase transition of a complex of *trans*-**1** and **2**, since this peak steadily increased with the addition of *trans*-**1** until suppression of the peak at 72 °C. The shift of the transition temperature from 72 to 52 °C is due to the incorporation of *trans*-**1** into the alkyl chain region of **2**. These observations strongly suggest that the molecules of *trans*-**1** and **2** form a composite self-assembly. However, the phase diagram obtained from the DSC curves upon heating of mixtures of *trans*-**1** and **2** in various composition ratios

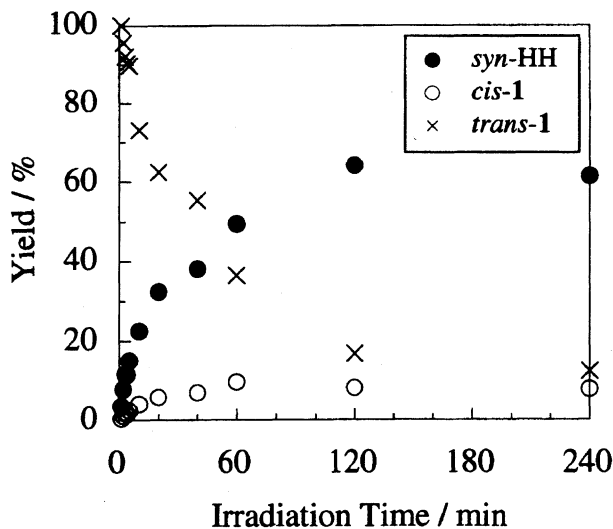


Fig. 1. Photoirradiation of *trans*-**1** in the cast film of **2** (1 : 1 mixed films); the formation of *syn*-HH and *cis*-**1**.

Table 1. Photoirradiation of *trans*-**1** in the Cast Films of **2** for the Various Mixing Ratios

Mixing ratios <i>trans</i> - 1 /2	Irradiation time/min	Conversion % ^{a)}	Selectivity/% ^{a)}		
			<i>cis</i> - 1	<i>syn</i> -HH	<i>syn</i> -HT
1	40	44.6	15.6	85.5	4.3
0.8	40	51.4	10.2	73.7	8.6
0.6	40	52.7	12.5	82.4	2.2
0.4	10	46.9	19.0	76.6	7.9
0.3	10	51.7	12.4	71.9	7.7
0.2	20	47.9	15.9	55.7	16.0

a) Irradiated with a 300 W medium-pressure Hg lamp, $\lambda > 280$ nm, under ambient atmosphere.

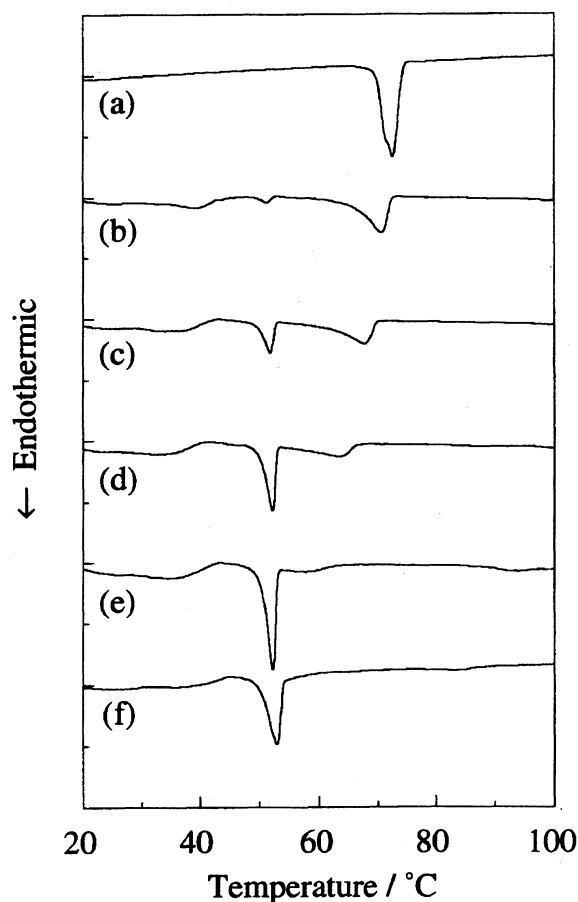


Fig. 2. DSC curves of the cast films of **2** including *trans*-**1** for the various mixing ratios; (a) **2** in crystal, *trans*-**1**/2 = (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8, and (f) 1.

indicates the formation of an eutectic mixture of *trans*-1 and 2, rather than a distinct complex, as can be seen in Fig. 3.

From the following results obtained from X-ray diffraction and IR spectral analyses, each component in the mixture was revealed to interact with each other, thus resulting in no segregation in the form of individual pure component. The translucent crystalline film of an equimolar mixture of *trans*-1 and 2 was investigated by X-ray diffraction. The 1 : 1 mixed films of *trans*-1 and 2 are characteristic of the high regularity of crystals which possess a series of peaks due to a spacing of $d = 30 \text{ \AA}$ up to the seventh order. On the other hand, the cast film of 2 exhibits a series of peaks due to a spacing of $d = 35 \text{ \AA}$ up to the tenth order. Both of the spacings were observed to be longer than the molecular length of 2, which is about $26 \text{ \AA}$ with the *trans* zigzag conformation of the alkyl chain, and which can be ascribed to the bilayer structure.

Surfactant molecules of 2 in a cast film are thought to be tilted 42° ($=\sin^{-1}(35/52)$) against the layer surface, assuming that the bilayer structure is formed without the interdigitation of the alkyl chains. The tilted structure is closely correlated to that in the single crystal of 2.^{14a)} The single crystal of ammonium salt 2 forms a bilayer structure where the molecules are tilted 45° in order to balance the cross-sections of the hydrophilic head group and hydrophobic alkyl chains. On the other hand, in the present films of 2, including *trans*-1, the spacing of the X-ray diffraction patterns was found to be smaller than that of the cast film of 2, implying a larger inclination of the molecules of 2 or an interdigitation of the alkyl chains of 2, as shown in Fig. 4.²³⁾ In any case, the results of the X-ray diffraction studies suggest the incorporation of *trans*-1 into a bilayer of 2, which resulted in the selective formation of the *syn*-HH dimer (Fig. 4 (d)).

The IR spectra provided further information about the molecular interaction of *trans*-1 with 2 in the cast film. The cast film exhibits the carboxylic acid C=O stretching vibration at 1705 cm^{-1} , which was found to be much higher than

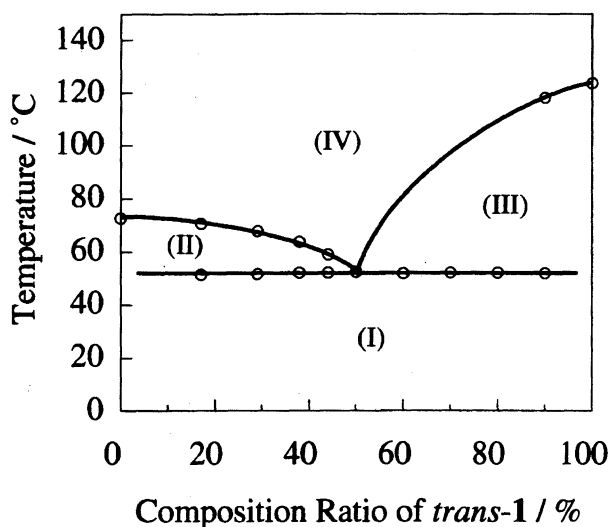


Fig. 3. Phase diagram of mixtures of *trans*-1 and 2 for the various composition ratios of *trans*-1: (I), *trans*-1+2; (II), 2+liquid; (III), *trans*-1+liquid; (IV), liquid.

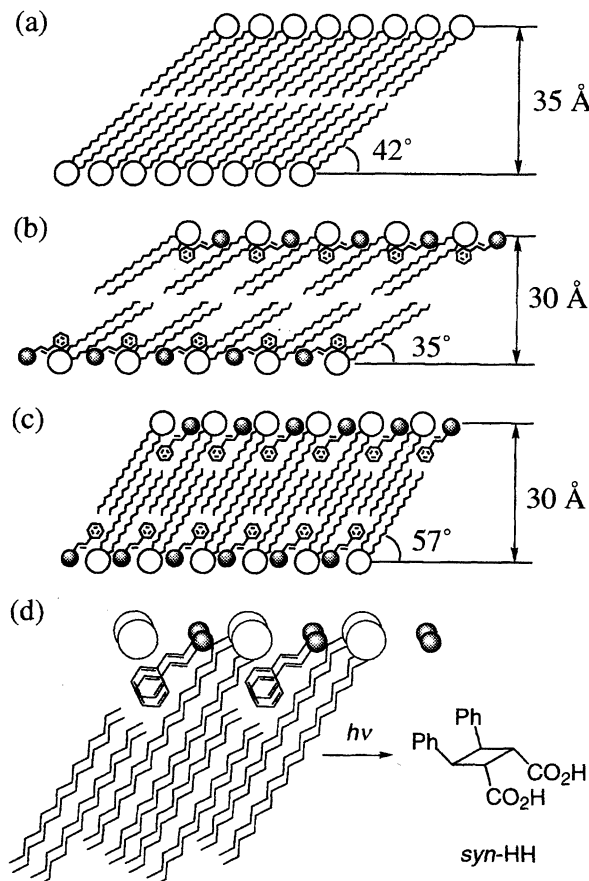


Fig. 4. A possible incorporation of *trans*-1 in the bilayer film of 2; (a) a film of single component 2, the mixture of *trans*-1 and 2 (b) without and (c) with interdigitation of the alkyl chains of 2, (d) formation of the *syn*-HH dimer in a bilayer film.

that of the α -form crystals *trans*-1 at 1684 cm^{-1} assigned to the dimeric structure due to hydrogen bonding between the carboxyl groups.²⁴⁾ The observed C=O stretching at 1705 cm^{-1} indicates the existence of an undissociated carboxylic acid. Moreover, the C=O stretching was quite different from those of the cinnamate ion possessing two carboxylic C=O absorptions at 1559 and 1410 cm^{-1} , asymmetric and symmetric, respectively. However, the *trans*-cinnamic acid moiety in the cast film may exist in environments different from those of the dimeric form of α -form crystals of *trans*-1. Toda et al.²⁵⁾ have reported on the formation of a 1 : 1 complex of phenols and alkylammonium halides through a hydrogen bond between the acidic OH group and halide ion. It can clearly be concluded that the *trans*-1 interacts with 2 in the cast film through hydrogen bonding between the OH group of *trans*-1 and Br^- of 2, although a definite stoichiometric complexation could not be observed with the mixture of *trans*-1 and 2 presumably because of the weak hydrogen bonding.

Effect of a Heat Treatment. The photochemical behavior of *trans*-1 in the cast film was investigated in order to study the effect of a heat treatment prior to photolysis. As a

heat-treatment method (method A), photolyses of 1 : 1 mixed films were carried out at a constant temperature in the range of 10–70 °C during irradiation. A dramatic change in the product selectivities could be observed at between 40–60 °C (Fig. 5a). The yields of the *syn*-HH dimer upon 1 h of irradiation drastically decreased upon increasing the temperature to over 40 °C, then leveled off and completely ceased above ca. 60 °C. Although this trend was accompanied by a significant increase in the formation of *cis*-1, most of *trans*-1 (above 80%) was recovered unchanged upon 1 h of irradiation. The sharp decrease in the formation of *syn*-HH seems to be related to a phase transition at 52 °C.

The reversibility of the molecular packing in the cast film was investigated by an alternative heat treatment (method B). Experiments were carried out using samples (1 : 1 mixed films) cooled down to ca. 20 °C after a preheat treatment in the range of around 20 to 80 °C for a few hours. The results showed a significant suppression of *syn*-HH formation by

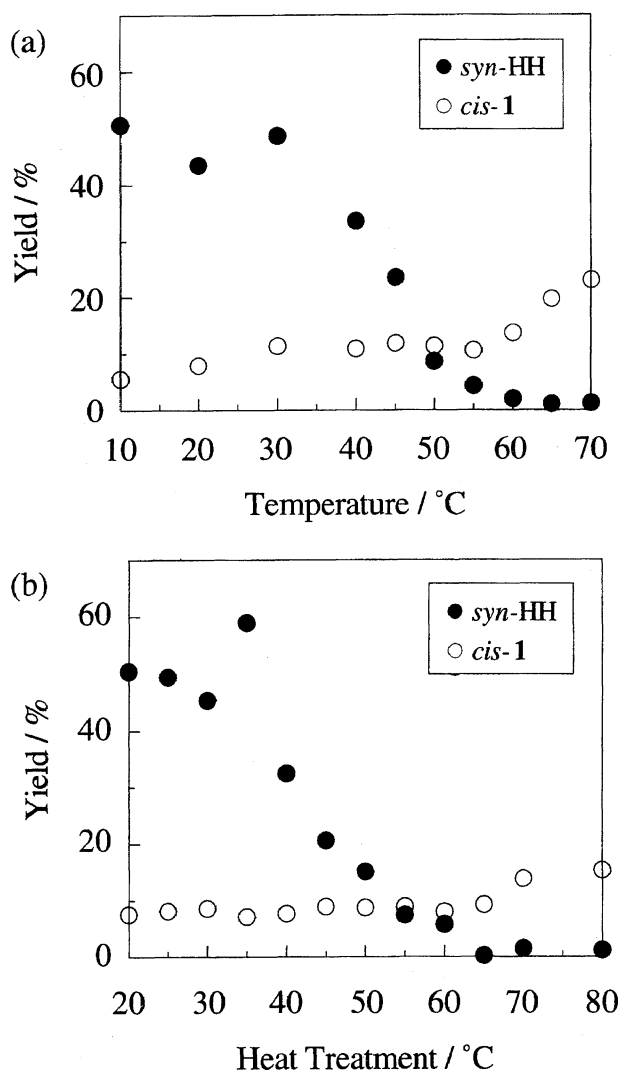


Fig. 5. Photoradiation of *trans*-1 in the cast film of 2 (1 : 1 mixed films) at various temperatures (a) and at 20 °C after heat treatment (b); the formation of *syn*-HH and *cis*-1 upon 1 h irradiation.

preheating at above 40 °C, as shown in Fig. 5b. This trend was similar to that under conditions carried out by method A. These observations clearly show that the photoreactivity of *trans*-1 is irreversible with regard to the heat treatment.

No practical change in the X-ray diffraction, DSC, and IR spectra could be observed in a study of the effect of heating at 80 °C on the spectroscopic nature of the cast film. These observations imply that the bilayer structure of the films is believed to be unchanged either before or after heat treatments, though their photoreactivities were distinctly different from each other. It was noticed, however, that a gradual change occurred in the crystallinity during heat treatments on the basis of DSC observations. A preheating effect was observed in a cast film in which the peak at 52 °C was increased and sharpened upon each subsequent heating at 80 °C. Thus, it could be seen that the enthalpy change ($\Delta H = 18.9 \text{ kcal mol}^{-1}$ based on 2) was increased in the preheated film more clearly than in the nonheated film ($\Delta H = 16.3 \text{ kcal mol}^{-1}$ based on 2). These observations suggest an improvement in the crystallinity caused by the phase transition of the bilayer. It has been reported that solid state reactions sometime demand a cavity in which the molecules to be reacted should be mobile.^{12a,26,27} Upon considering the present photodimerization, an improvement of the crystallinity may, in fact, suppress the mobility of the component molecules and cause a decrease in the photoreactivity. Another explanation for the suppression of photodimerization can be given by saying that the alignment of *trans*-1 in the bilayer, as shown in Fig. 4 (d), slightly changed and two adjacent molecules of *trans*-1 became separated by the molecules of 2. In order to clarify this point, the preparation of a single crystal for X-ray structural analysis was performed. Satisfactory crystals, however, have not yet been obtained.

In conclusion, the present composite films with a bilayer structure in the crystalline state were prepared from aqueous dispersions of *trans*-1 and 2, where the molecules of *trans*-1 are incorporated in the bilayer of 2 at any mixing ratios with less than unity of the ratio (*trans*-1/2). The hydrogen bonding and electrostatic interaction between the ammonium and carboxylic groups promote the incorporation of *trans*-1 into the film of 2, where *trans*-1 may be oriented parallel to the aggregated bilayer surfactant molecules. Thus, photoradiation of the films resulted in a selective formation of the *syn*-HH dimer. A heat treatment dramatically suppressed the photoreaction of *trans*-1 in the composite film, which is attributed to an improvement in the crystallinity caused by its phase transition.

Experimental

General. X-Ray diffraction patterns were obtained by the reflection method with an X-ray diffractometer (Rigaku Denki) and Ni-filtered Cu K α radiation. Differential scanning calorimetry was carried out using a Perkin-Elmer DSC7. The IR spectra were recorded on a JASCO FT/IR-300E. HPLC was recorded on a Shimadzu LC-10A with a CAPCELL PAK C18 UG120 S-3 μm , Shiseido Co., Ltd.

Materials. *trans*-Cinnamic acid (*trans*-1) and dimethyl-

dioctadecylammonium bromide (**2**) were purchased from Tokyo Kasei Co., Ltd. Olefin *trans*-**1** was recrystallized twice from benzene and **2** was used without any purification. The photodimers of *trans*-**1**, *syn*-HH, *anti*-HH, and *syn*-HT, were synthesized according to previous literature.^{1a,28)}

Preparation of Film of 2 Including *trans*-1. Aqueous dispersions of *trans*-**1** and **2** were prepared by sonication at 50–60 °C in an ultrasonic bath (BRANSON 5210) for several hours. For all samples, the concentration of **2** was held constant at 2.5×10^{-2} mol dm⁻³ and the ratios of *trans*-**1** to **2** were varied from 0.2 to 1. The obtained dispersions placed on Teflon® plates were dried in a desiccator at 20–25 °C for one day, affording translucent films. Then, photoirradiation and characterization of the samples were carried out with and without a heat treatment in a drying oven for 1 h.

Characterization of the Film of 2 Including *trans*-1. X-Ray diffraction was carried out in order to confirm the formation of the composite bilayer structure, comparing the mixture of *trans*-**1** and **2** with a single component of **2**. The phase-transition behavior of the films was investigated by DSC. The samples (3–4 mg) were sealed in aluminum pans and scanned from 20 to 100 °C at a rate of 1.0 °C min⁻¹ in a flow of N₂ gas. Interactions between the polar groups of *trans*-**1** and **2** were investigated by IR using the KBr method.

Irradiation of *trans*-1 in the Cast Film of 2. The cast film of *trans*-**1** and **2** was sandwiched between Pyrex-glass plates and was irradiated with a 300-W medium-pressure Hg lamp (> 280 nm) under an ambient atmosphere. Irradiation at a constant temperature was carried by sealing the sample in a Pyrex test tube in a thermostated water bath. The irradiated sample was dissolved in methyl alcohol, analyzed by HPLC, and detected at 225 nm using an eluent with the ratio of a phosphoric acid solution (3.0×10^{-2} mol dm⁻³): methyl alcohol = 55 : 50 (pH = 3.5); retention times/min, *trans*-**1**, 15; *cis*-**1**, 10; *syn*-HH, 45; *anti*-HH, 65; *syn* HT, 16.5.

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