Photopolymerization of amphiphilic diolefins in mono- and multilayers

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Photoreactive thin films were prepared from amphiphilic diolefins using the Langmuir–Blodgett technique and their photoreaction was investigated. *p*-Phenylenediacrylic acid (*P*-PDA) monoesters having long-chain alkyl ester residues were found to form stable monolayers on $CdCl_2/KHCO_3$ aqueous solution and they were transferred onto a substrate with Z-type deposition. The u.v. and fluorescence spectra of the multilayers showed that *p*-PDA monoester molecules are arranged side by side with the stacking of aromatic rings. The linear relationship observed between absorbance and the number of the layers supports the successful formation of multilayers. On irradiation, double bonds reacted to form cyclobutane rings and the subsequent cycloaddition led to the formation of oligomers and then polymers.

(Keywords: long-chain monoalkyl esters of *p*-phenylenediacrylic acid; monolayers; multilayers; photoreaction)

INTRODUCTION

For many potential applications, Langmuir–Blodgett multilayer has received a considerable amount of attention by virtue of their unique combination of properties such as defined structure and controllable, homogeneous thinness of a few nanometers. In addition, in mono- and multilayers the molecular arrangement, molecular orientation and the distance of functional groups may be controlled. Polymerization of several amphiphilic compounds having functional groups has been investigated in these systems[1–3]. For example, Tieke and his coworkers[2] have studied topochemical polymerization of amiphiphilic diacetylenes in multilayers and obtained ultra-thin highly ordered polymers. We have studied the crystalline state photopolymerization of rigid rod-like olefinic compounds[4] which undergo topochemical polymerization in a similar way to diacetylene.

It is of interest to apply this reaction in multilayers and to build-up photoreactive thin films which may be useful as photoresists for microlithography. For this purpose amphiphilic diolefins, a series of long-chain alkyl monoesters of *p*-phenylenediacrylic acid (*p*-PDA) were prepared[5]. They are liquid crystalline and some of these crystals show photoreactivity. In this work, preparation of mono- and multilayers using these compounds has been carried out and their properties have been revealed. The photoreaction in these films also has been investigated and described with reference to the molecular arrangement.

EXPERIMENTAL

Preparation of monomers

p-PDA monoesters of the general structure ($HOOCCH{=}CHC_6H_4CH{=}CHCOOC_nH_{2n+1}$), were prepared as described below.

Monoheptyl p-*phenylenediacrylate* (p-*PDAmC*$_n$). Diheptyl *p*-phenylenediacrylate (5 mmol) was dissolved in heptyl alcohol (40 ml). Sodium heptyloxide (5 mmol) was added to this solution and the reaction mixture was heated at 70–80°C for 1 h. After heating for a few minutes, white precipitate appeared. It was collected by filtration and washed with ether and ethyl alcohol to remove heptyl alcohol. In this way, sodium salt of *p*-PDAmC$_7$ was obtained. It was dispersed in water and converted into *p*-PDAmC$_7$ by adding dilute hydrochloric acid solution; yield: 60%. Crude *p*-PDAmC$_7$ was recrystallized from acetone to remove a small amount of *p*-PDA which was formed as by-product. Further purification was achieved by recrystallization from benzene several times. *p*-PDAmC$_7$ crystals showed a mesophase between 185–193°C.

^{1}H n.m.r.: δ (DMSO-d$_6$, ppm) 0.9(3H, 5, CH_3), 1.2–1.7(10H, m, CH_2), 4.2(2H, t, OCH_2), 6.6, 6.7(2H, d, $=CH$), 7.6, 7.7(2H, d, $CH=$), 7.8(4H, m, ArH). Elemental analysis: found, C, 72.43%; H, 8.14%; calculated for $C_{19}H_{24}O_4$ (MW 316.4); C, 72.12%; H, 7.65%.

Monodecyl *p*-phenylenediacrylate (*p*-PDAmC$_{10}$) was prepared from didecyl *p*-phenylenediacrylate in the same way as *p*-PDAmC$_7$. Yield: 60%. *p*-PDAmC$_{10}$ crystals showed a mesophase between 178–184°C. Elemental analysis: found, C, 73.52%; H, 8.90%; calculated for $C_{22}H_{30}O_4$ (MW 358.5), C, 73.71%; H, 8.44%.

Monododecyl p-*phenylenediacrylate* (p-*PDAmC*$_{12}$). Didodecyl *p*-phenylenediacrylate (5 mmol) was dissolved in dehydrated dioxane (20 ml) by warming. To this solution sodium dodecanoate (5 mmol) was added. The reaction mixture was heated for 1 h at 70–80°C. During this period white precipitate appeared gradually. It was collected by filtration and washed with ether to remove dodecyl alcohol. Sodium salt of *p*-PDAmC$_{12}$ obtained in this way was dispersed in water and acidified dilute

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hydrochloric acid to give *p*-PDAmC$_{12}$. Yield: 55%. Crude *p*-PDAmC$_{12}$ was recrystallized from acetone or benzene several times. *p*-PDAmC$_{12}$ crystals showed a mesophase between 170–182°C.

^{1}H n.m.r.: δ (DMSO-d$_6$, ppm) 0.9(3H, t, CH$_3$), 1.2–1.7(20H, m, CH$_3$), 4.15(2H, t, OCH$_2$), 6.55, 6.65(2H, d, =CH), 7.6, 7.7(2H, d, CH=), 7.8(4H, m. ArH). Elemental analysis: found, C, 73.92%; H, 8.69%; calculated for $C_{24}H_{34}O_4$ (MW 386.5); C, 74.57%; H, 8.87%.

Monotetradecyl *p*-phenylenediacrylate (*p*-PDAmC$_{14}$) was prepared in the same way as *p*-PDAmC$_{12}$ using dehydrated hexane instead of dioxane. Yield: 40%. Crude *p*-PDAmC$_{14}$ was recrystallized from acetone or benzene several times. *p*-PDAmC$_{14}$ crystals showed a mesophase between 164–178°C.

Elemental analysis: found, C, 75.23%, H, 9.23%; calculated for $C_{26}H_{38}O_4$ (MW 414.6), C, 75.32%; H, 9.24%.

Monooctadecyl *p*-phenylenediacrylate (*p*-PDAmC$_{18}$) was prepared in the same way as *p*-PDAmC$_{12}$. *p*-PDAmC$_{18}$ crystals showed a mesophase between 162–176°C.

^{1}H n.m.r.: δ (DMSO-d$_6$) 0.9(3H, t, CH$_3$), 1.3–1.7(32H, m, CH$_2$) 4.2(2H, t, OCH$_2$), 6.5, 6.6(2H, d, =CH), 7.6, 7.68(2H, d, CH=), 7.7(4H, m, ArH). Elemental analysis: found, C, 76.85%; H, 10.85%; calculated for $C_{30}H_{46}O_4$ (MW 470.7), 76.85%, H, 9.85%.

Preparation of mono- and multilayers. A commercially available film balance (MGW-Lauda) was used as the trough. *p*-PDA monoesters were dissolved in chloroform (Merck, Uvasol) at the concentration of 4–10 mg of *p*-PDA monoester per 10 ml of chloroform. *p*-PDA monoester was spread on a subphase consisting either of redistilled water or 10^{-3} M CdCl$_2$/10^{-5} M KHCO$_3$ aqueous solution and the surface pressure–area isotherms were measured at 20–22°C. The monolayers were transferred onto either a glass or a quartz plate by the Langmuir–Blodgett technique at a surface pressure of 20–30 dyne/dm. Substrates were dipped at a speed of 5 mm/min.

Photoreaction. Photoreaction of monolayers at an air–water interface was carried out as follows. A monolayer was formed by compressing up to 20 dyne/cm and it was irradiated through a Pyrex glass by a 400 W high pressure mercury lamp, which was placed 25 cm from the monolayer surface. Photo-irradiation was carried out at constant surface pressure or at constant monolayer area. Changes in the monolayer on irradiation were monitored by either movement of a barrier or measuring surface pressure. The reaction process was also followed by measuring u.v. or i.r. spectra. To measure a u.v. spectrum, a monolayer was transferred onto a quartz plate by the Langmuir–Blodgett method and its spectrum was measured by a u.v. spectrometer. In order to identify a photoproduct, the irradiated monolayer was collected from the surface of the subphase after compression and it was dried in a desiccator.

The photoreaction of multilayers was carried out by irradiating with either a 500 W Xenon lamp or a spectro-irradiator (Jasco CRM-FA) consisting of a 2000 W Xenon lamp and a grating monochrometer. The photoreaction process was monitored in the same way as described in the photoreaction of the monolayer at an air–water interface.

Measurement. U.v. spectra were recorded with a Shimadzu UV-220 spectrophotometer. Fluorescence spectra were measured by using a Hitachi MPF 2A fluorescence spectrometer. ^{1}H n.m.r. spectra were recorded with a Nicolet NT360 spectromer. DMSO-d$_6$ was used as a solvent. G.p.c. (Shimadzu LC-5A) was used for estimation of molecular weights of irradiated films. A sample was dissolved in tetrahydrofuran and it was also used as an eluent.

RESULTS AND DISCUSSION

Monomers

Five *p*-PDA monoesters having long-chain alkyl ester residues were prepared by partial hydrolysis of the corresponding *p*-PDA dialkyl esters. The yield of these *p*-PDA monoesters was in the range of 40–60% except for *p*-PDAmC$_{18}$. The yield of *p*-PDAmC$_{18}$ was poor (less than 10%) because of the difficulty in preparing sodium alkoxide of octadecyl alcohol. There are two points to be mentioned concerning preparation of these compounds. First, to prevent exchange of ester residues of *p*-PDA dialkyl ester, the same alcohol as the ester residue of *p*-PDA dialkyl ester must be used as a reaction medium. For example, diheptyl *p*-phenylenediacrylate was dissolved in heptyl alcohol and treated with sodium heptyl oxide. In the case of longer-chain alcohols such as dodecyl, tetradecyl, and octadecyl alcohol which are solid at room temperature, dehydrated hexane was added to the alcohol in order to decrease the viscosity of the reaction medium. The second point is the molar ratio of sodium alkoxide and *p*-PDA dialkyl ester. In the preparation of *p*-PDAmC$_7$ and *p*-PDAmC$_{10}$, it is preferable to use an equimolar of sodium alkoxide and *p*-PDA alkyl ester. These sodium alkoxides are reactive and excess sodium alkoxide causes the formation of *p*-PDA which makes *p*-PDA monoester difficult to purify. However, in the case of sodium alkoxide which is not so reactive, an excess of sodium alkoxide must be used and the heating time should be extended by 2–3 h. The purity of these compounds was checked by g.p.c.. These monoesters were confirmed to be *trans–trans* configuration by ^{1}H n.m.r. and i.r. spectrum. *p*-PDA monoesters showed the absorption maximum at 318 nm in solution and they show a broad peak from 280–320 nm in the solid state. Three *p*-PDA monoesters (*p*-PDAmC$_7$, *p*-PDAmC$_{10}$, *p*-PDAmC$_{12}$) are photoreactive in the crystalline state, while other esters (*p*-PDAmC$_{14}$, *p*-PDAmC$_{18}$) are photostable[6]. All of these esters show liquid crystalline behaviour and a smectic phase was observed.

Surface pressure–area isotherms for p*-PDA monoesters*

The surface pressure–area isotherms for these monoesters measured at CdCl$_2$/KHCO$_3$ aqueous solution, are shown in *Figure 1*. Three compounds showed the presence of condensed phase and collapsed at around 50 dyne/cm. The molecular area for each ester is as follows: *p*-PDAmC$_{10}$, 23 Å^2; *p*-PDAmC$_{12}$, 24 Å^2; *p*-PDAmC$_{14}$, 27 Å^2. These values are close to the reported value (28.7 Å^2) for long-chain acid molecule[7], an end group of which is —CH=CHCOOH and suggest the tight packing of these molecules in a monolayer. The surface pressure–area isotherms for *p*-PDAmC$_{18}$ were obtained both on distilled water and CdCl$_2$/KHCO$_3$

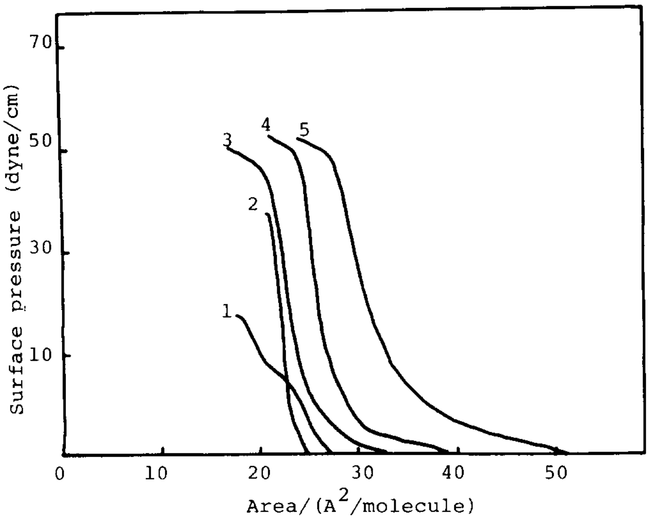

Figure 1 Surface pressure–area isotherms for *p*-PDA monoesters. Curve 1, *p*-PDAmC$_7$; curve 2, *p*-PDAmC$_{10}$; curve 3, *p*-PDAmC$_{12}$; curve 4, *p*-PDAmC$_{14}$; curve 5, *p*-PDAmC$_{18}$

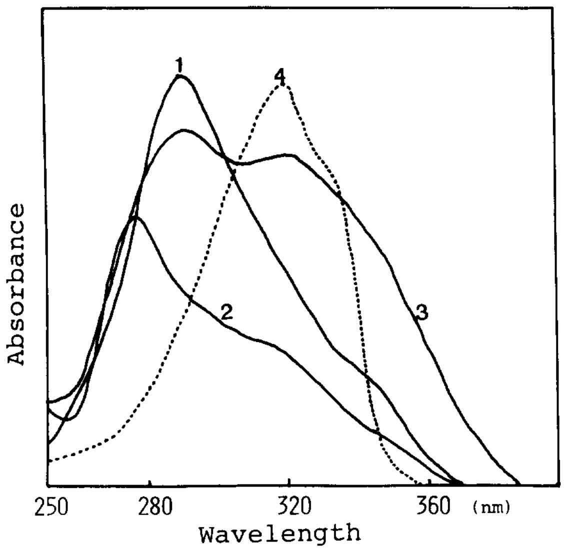

Figure 2 U.v. absorption spectra of *p*-PDA monoesters. Curve 1; *p*-PDAmC$_{12}$ multilayer; curve 2, *p*-PDAmC$_{14}$ multilayer; curve 3, *p*-PDAmC$_{18}$ multilayer; curve 4, *p*-PDAmC$_{12}$ in chloroform solution

aqueous solution. The isotherms were somewhat expanded and the molecular area was 34 Å^2 suggesting more loose packing of *p*-PDAmC$_{18}$ molecules. The surface pressure isotherms for *p*-PDAmC$_7$ were not stable and the reproducibility was poor. Except for *p*-PDAmC$_7$, these monolayers could be transferred onto a substrate by the Langmuir–Blodgett method. The monolayer transfer was observed only on the upward strokes with Z-type deposition.

Properties of mono- and multilayers

I.r. spectrum of the monolayer formed at an air–water interface showed the absorption peak at 1520 cm^{-1} due to the formation of cadmium salt of carboxylic acid. It was shown that by e.s.c.a. measurement of the multilayers that two molecules of *p*-PDA monoesters share one molecule of cadmium, forming cadmium salt (O:Cd:C = 11.7:1:46.1). The u.v. spectra of multilayers of *p*-PDA monoesters, which were prepared at surface pressure 20 dyne/cm, are shown in *Figure 2* together with that of the solution. In both mono- and multilayers, the absorption peak was observed at 290 nm with a shoulder peak at 350 nm, while in the solution it was observed at 318 nm. The difference between these spectra is due to the different molecular arrangement of each state. In the mono- and multilayers, molecules must be arranged side by side. This arrangement causes the interaction of excitons, which makes two excited states, resulting in two absorption peaks; one allowed at a higher energy and the other forbidden at a lower energy[8]. The fluorescence spectrum of the *p*-PDAmC$_{12}$ multilayer also supports this molecular arrangement[12]. The emission maxi-mum shifted to a longer wavelength (420 nm) compared with that of the solution (370 nm). The same u.v. and fluorescence spectra were observed for *p*-PDAmC$_{10}$ and *p*-PDAmC$_{14}$ multilayers. These spectral data indicate that the molecules in the multilayers are arranged side by side with the stacking of aromatic rings to form the excimer. The same excimer emission was observed in the fluorescence spectrum of 4-(*β*-methoxy carbonyl vinyl)-*α*-cyanocinnamate[9], for which such molecular arrangement (B-type of Stevens classification) was confirmed by X-ray crystal structure analysis[10]. The u.v. spectrum of the *p*-PDAmC$_{18}$ multilayer (*Figure 2*) is different from those of other three though excimer emission was observed. It has two peaks at 290 nm and 320 nm suggesting that exciton interaction is not so strong compared with that of other multilayers. The spectral data and the larger molecular area (34 Å^2) indicate the *p*-PDAmC$_{18}$ molecules are more loosely packed in the multilayer compared with the other three compounds. It should be mentioned that the molecular arrangement of *p*-PDA monoester multilayer is different from that of crystal in which two *p*-PDA monoesters are paired by hydrogen bonding and the pairing units are displaced to form a parallel plane-to-plane stack[11], i.e., the similar to Y-type film. It was observed in the *p*-PDAmC$_{12}$, and *p*-PDAmC$_{14}$ multilayer that there was a linear relationship between the absorbance at their absorption maxima and the number of layers suggesting the successful formation of multilayer (*Figure 3*).

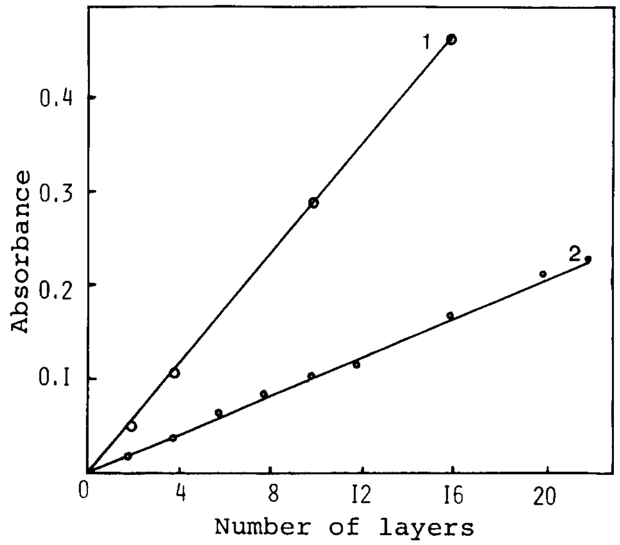

Figure 3 The relationship between absorption and number of layers. Curve 1; *p*-PDAmC$_{12}$ multilayer; curve 2, *p*-PDAmC$_{14}$ multilayer

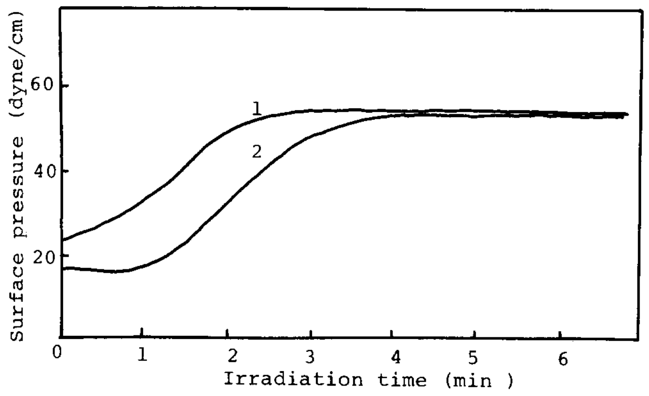

Figure 4 Change in surface pressure of monolayers on irradiation. Curve 1, p-PDAmC$_{12}$ monolayer; curve 2, p-PDAmC$_{14}$ monolayer

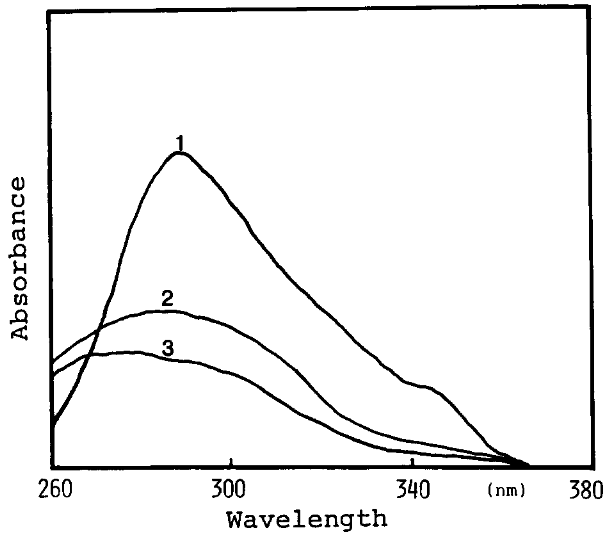

Figure 5 Change of u.v. spectrum of p-PDAmC$_{12}$ monolayer on irradiation; irradiation time (min): 1:0, 2:2, 3:5

Photoreaction in monolayers formed at an air/water interface

On irradiation of p-PDAmC$_{12}$ monolayer under the constant surface pressure (20 dyne/cm), a barrier moved resulting in increase in the area of a monolayer. This suggests the increase of surface pressure by photoreaction of p-PDAmC$_{12}$ molecules. In the case of p-PDAmC$_{12}$, the monolayer area increased by 20% after 1 min of irradiation and p-PDAmC$_{14}$ 5% after 4 min of irradiation. Photo-irradiation under the constant monolayer area caused an increase in surface pressure as shown in *Figure 4*[12].

On irradiation of p-PDAmC$_{12}$ monolayer a remarkable increase in surface pressure was observed. The surface pressure reached 50 dyne/cm after 3 min of irradiation and it did not increase further. In the case of p-PDAmC$_{14}$ monolayer, the increase in surface pressure was slower than that of p-PDAmC$_{12}$ monolayer, but surface pressure also nearly reached 50 dyne/cm. On irradiation the u.v. absorption peak of p-PDAmC$_{12}$ monolayer decreased gradually and almost disappeared after 5 min of irradiation as shown in *Figure 5*. The i.r. spectrum of this irradiated monolayer showed the disappearance of the absorption peak at 1640 cm^{-1} (ν c=c, aliphatic) and 980 cm^{-1} (δ c=c, trans CH=CH) and the shift of the absorption peak of carbonyl group to a higher frequency. These spectral data and expansion of monolayers on irradiation suggest the disappearance of double bonds by cycloaddition to form cyclobutane rings. The results of g.p.c. analysis of the p-PDAmC$_{12}$ monolayer irradiated for 1 min showed that it consisted of dimers, trimers, tetramers and a small amount of unreacted monomers. With increase in reaction time, the amount of large molecular weight product increased and that of monomers decreased. After 10 min of irradiation, most parts of the irradiated monolayer became insoluble in terahydrofuran and only small amounts (less than 3%) of dimers and monomers were detected by g.p.c.. The insoluble product may be due to the formation of high molecular weight polymers. The same spectral and molecular weight changes were observed in the irradiated p-PDAmC$_{14}$ and p-PDAmC$_{18}$ monolayers. It should be noted that p-PDAmC$_{14}$ and p-PDAmC$_{18}$ which are photostable in the crystalline state became photoreactive by forming their monolayers. Judging from properties of photoproducts and behaviour of monolayers on irradiation, it is reasonable to conclude that photoreaction in monolayers proceeded by cycloaddition of double bonds to form a cyclobutane ring yielding polymer via oligomers.

Photoreaction in multilayers

On irradiation of the multilayers prepared from p-PDAmC$_{12}$ and p-PDAmC$_{14}$ with monochromatic light (289 nm), the u.v. absorption peak decreased gradually as shown in *Figure 6* and the absorption maxima were observed at 295 nm. These spectral changes indicate that conjugation through double bonds disappeared by photoreaction and cinnamoyl groups were formed in the products. The molecular weight of p-PDAmC$_{12}$ multilayer irradiated for 3 min showed that it consisted of oligomers. After prolonged irradiation, the multilayer became insoluble in ordinary organic solvents. These results suggest that cycloaddition of double bonds occurred to form cyclobutane rings as it did in the monolayer, giving oligomers and finally polymers. There is another piece of indirect evidence for the formation of

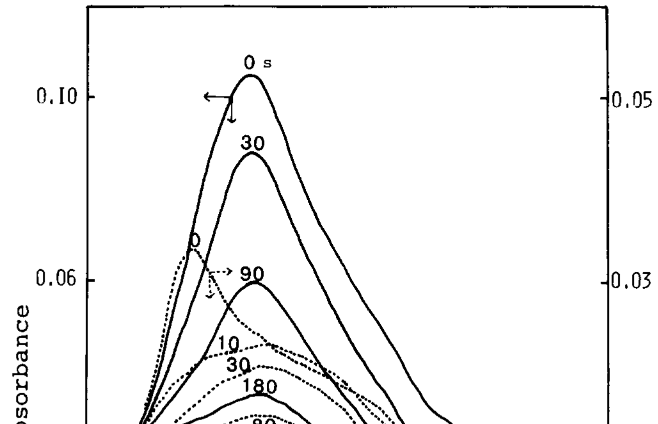

Figure 6 Change of u.v. spectra of multilayers on irradiation. ——, p-PDAmC$_{12}$; ----, p-PDAmC$_{14}$

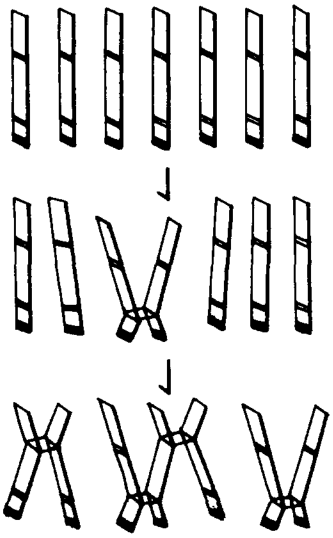

Figure 7 Schematic representation of photoreaction of *p*-PDA monoester in the multilayer

cyclobutane rings in the multilayers. That is, the spectral changes due to the cyclobutane ring cleavage were observed in the irradiated films[5,13].

In summary, the reaction process in multilayers is described in *Figure 7*. In a monolayer, reaction also proceeded essentially in the same way. *p*-PDA monoester molecules are arranged side by side with the stacking of aromatic rings. On irradiation, double bonds in the stack react to form cyclobutane rings with mirror symmetry. Molecular movement caused by the formation of cyclobutane rings breaks down the regular arrangement of surrounding monomers and causes the subsequent random cycloaddition to give oligomers and then polymers. Thus, new photoreactive thin films were prepared from amphiphilic diolefins having long-chain alkyl ester residues using the Langmuir–Blodgett technique.

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