Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Thermally enhanced photoinduced molecular reorientation in a photo-crosslinkable polymer liquid crystal based on polarization triplet energy transfer

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To cite this Article Kawatsuki Corresponding author, Nobuhiro , An, Ming-Xing , Matsuura, Yasushi , Sakai, Takeya and Takatsuka, Hirofumi(2004) 'Thermally enhanced photoinduced molecular reorientation in a photo-crosslinkable polymer liquid crystal based on polarization triplet energy transfer', Liquid Crystals, 31: 1, 55 — 60

To link to this Article: DOI: 10.1080/02678290310001628537

URL: http://dx.doi.org/10.1080/02678290310001628537

Liquid Crystals, Vol. 31, No. 1, January 2004, 55–60

Thermally enhanced photoinduced molecular reorientation in a photo-crosslinkable polymer liquid crystal based on polarization triplet energy transfer

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(*Received 26 March 2003; in final form 15 July 2003; accepted 20 August 2003*)

Polarization-selective photosensitization and molecular reorientation in photo-crosslinkable polymer liquid crystal (PMCB6M) films, based on polarization-selective triplet energy transfer using LP-365 nm and LP-405 nm light with different photosensitizers, are described. A dramatic improvement in the photoreactivity of the film was observed with a small amount of photosensitizer; and a high degree of molecular reorientation and slantwise reorientation were generated when annealing the resulting films at elevated temperatures. The efficiency of reorientation depended on the photoinduced dichroism of the film.

1. Introduction

Molecular orientation in photosensitive polymer films has received much attention because the photoinduced optical anisotropy can be used in numerous applications, such as optical memory, optical switching and birefringent devices [1, 2]. In order to achieve molecular orientation, a variety of different photoreactive materials have been investigated, including azobenzene-containing polymers, which can reversibly control optical anisotropy, and photo-crosslinkable polymers, which thermally stabilize the molecular orientation [3–7].

In our systematic study of photo-crosslinkable polymer liquid crystals (PPLCs), irradiation with linearly polarized ultraviolet (LPUV) light generated films with optical anisotropy based on an axis-selective photoreaction and subsequent annealing, which enhanced the molecular reorientation parallel to the polarization direction (**E**) of the LPUV light [8–12]. In addition, slantwise molecular reorientation was achieved using oblique LPUV light exposure [10, 11]. Among such materials, a polymethacrylate with 4-(4-methoxycinnamoyloxy)biphenyl side groups—PMCB6M in figure 1 (*a*)—exhibited an efficient in-plane molecular orientation, and the resulting film has application potential as a phase retarder in liquid crystal displays [11, 12]. The exposure energy required for the reorientation, however, is much greater than used for conventional photoresists. Therefore, for commercial considerations in the fabrication of birefringent films of this material, the exposure energy must be reduced.

In general, photosensitizers are often used to improve the photosensitivity of photoreactive materials [13], and the photosensitization of cinnamate derivatives has been studied in many aspects of organic photochemistry [13, 14]. It is well known that the photosensitization involves a triplet energy transfer from the photoexcited photosensitizer to the acceptor groups, and that the photosensitizer absorbs a longer wavelength light compared with the absorption bands of the photoreactive groups [13–16]. If both the photosensitizer and the acceptor groups exhibit polarization-selective photoexcitation, then the triplet energy may be transferred from the excited photosensitizer to the photoreactive group selectively. Furumi applied this concept to the polarization-selective photosensitization of a poly[methyl-4-(methacryloyloxy)cinnamate] film doped with 33 mol% of a bis-4,4′-dimethylaminobenzophenone by irradiating with LP-365 nm light and the resulting thin film was applied as an alignment layer for low molar mass liquid crystals [17]. To obtain an

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Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2004 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290310001628537

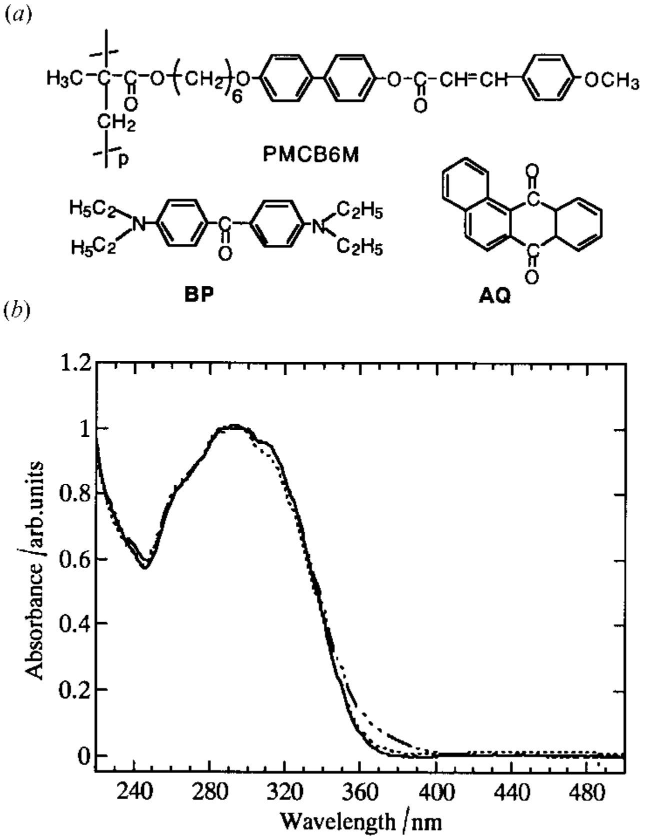


Figure 1. (*a*) Chemical structures of PMCB6M, **BP** and **AQ**. (*b*) Absorption spectra of PMCB6M (solid line), PMCB6M with 4 wt% of **BP** (solid-dotted line), and PMCB6M with 4 wt% of **AQ** (dotted line).

efficient degree of photoreaction in the solid state, a large amount of the photosensitizer is required in the material, since the distance between the donor and acceptor for the triplet energy transfer is less than 15 Å [13]. Doping with a large amount of the photosensitizer, however, will cause colour changes in the visible region since conventional photosensitizers partially absorb visible light [14–16] and thus, this approach is unsuitable for display devices.

In this paper, we describe an axis-selective photoreaction of a PMCB6M film doped with a small amount of photosensitizer (less than 8 mol%), which is based on polarization-selective triplet energy transfer, and thermal enhancement of the molecular reorientation. Two different photosensitizers, bis-4,4′-diethylaminobenzophenone (**BP**) and 1,2-benzoanthraquinone (**AQ**), were used with LP-365 nm and LP-405 nm light, respectively. A significant improvement in the photoreactivity was achieved, but the axis-selectivity and efficiency of thermal enhancement of the photoinduced optical anisotropy were dependent on the photosensitizer and the wavelength of irradiating LP light.

2. Experimental

2.1. *Materials*

PMCB6M ($M_n = 145\,000$, $M_w/M_n = 1.9$) was synthesized according to the previous method [12]. It exhibits a nematic phase between 116 and 312°C. **BP** and **AQ** were used as received from Aldrich; see figure 1 (*a*).

2.2. *Photoreaction and characterization*

A thin film of PMCB6M with 2–4 wt% of photosensitizer was prepared by spin-coating from a methylene chloride solution onto a quartz substrate, which resulted in a 200 nm thick film. Photoreactions were performed using an ultrahigh pressure Hg lamp equipped with Gran–Taylor polarizing prisms and an interference filter at 365 nm and 405 nm (FWHM = 10 nm) to obtain linearly polarized monochromic light. The light intensity was 34 mW cm^{-2} (365 nm), and 16 mW cm^{-2} (405 nm). The photoreactivity of the films was estimated by monitoring the decrease in absorption at 315 nm, and at 1635 cm^{-1} the FTIR spectrum (C–C double bond of the cinnamoyl group). Details of the photoproducts of the mesogenic group are described in a previous paper [12]. The photoinduced dichroism, ΔA, was determined by $\Delta A = A_{//} - A_{\perp}$ using the absorbance at 315 nm, where $A_{//}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to **E**, respectively. Annealing the exposed film at 150°C for 10 min resulted in molecular reorientation. The in-plane order was evaluated using the order parameter, S, at 315 nm and is defined as

$$S = \frac{A_{//} - A_{\perp}}{A_{(\text{large})} - 2A_{(\text{small})}} \tag{1}$$

where $A_{(\text{large})}$ is the larger of $A_{//}$ and $A_{\perp}$ and $A_{(\text{small})}$ is the smaller value.

3. Results and discussion

3.1. *Photoreaction and photoinduced optical anisotropy*

Figure 1 (*b*) shows the absorption spectra of a PMCB6M film and PMCB6M with either 4 wt% **BP** or **AQ**, where the molar content of **BP** and **AQ** to the mesogenic groups was 6.2% and 7.7%, respectively. Figure 1 (*b*) reveals a very small increase in absorption around 380 nm and 420 nm, which are the absorption bands of **BP** and **AQ**, respectively. Differential scanning calorimetry (DSC) scans indicated that these samples have a single melting point and a clearing temperature around 310°C. The melting point decreased slightly and the melting peak of the photosensitizer (**BP** at 95°C, **AQ** at 170°C) was not observed when the polymer was doped with a photosensitizer. Polarizing optical microscopy revealed the same textures and similar liquid crystalline temperature ranges. (Partial degradation of the polymer was observed above 300°C.) In addition, all the films were completely transparent and did not exhibit phase separation after storing for one year at room temperature, suggesting that the photosensitizers are completely dissolved in the PMCB6M.

To evaluate the axis-selective photoreaction of the mesogenic groups, the films were irradiated with LP-light. Figure 2 plots the degree of the photoreaction and photoinduced ΔA as a function of exposure energy. For LP-365 nm light, figure 2 (*a*) the photoreaction without a photosensitizer is very slow because the PMCB6M absorbance at 365 nm is very small ($\varepsilon < 0.1\ \mu m^{-1}$). The photoreaction rate increased dramatically for films containing **BP**. For example, to achieve 20 mol% of the photoreaction, the required exposure energy for a film with 4 wt% of **BP** was about 100 mJ cm^{-2}, while that for a film without a photosensitizer was 4 000 mJ cm^{-2}. Additionally, all cases generated a small negative ΔA, which implies that the photoreaction of the mesogenic side groups is axis-selective. The polarization-selective triplet energy transfer from the excited photosensitizers caused the photoreaction to be accelerated and ΔA is due to the polarization-selective triplet energy transfer as shown in figure 3. Exposing the film without a photosensitizer to LP-405 nm light did not change the properties because PMCB6M does not absorb 405 nm light, figure 2 (*b*). The photoreaction proceeded when the film contained **AQ** and generated a small negative ΔA. The photoreaction was attributed to the triplet energy transfer from the polarization-selectively photoexcited **AQ**, although the degree of photoreaction was saturated at less than 50% regardless of the irradiation time. This may be due to the limited distance of the triplet energy transfer and the use of insufficient photosensitizer.

Figure 2 indicates that the photosensitizer influenced the magnitude of the photoinduced negative ΔA. The generated $|\Delta A|$ for PMCB6M/**BP** was smaller than that without **BP** when an equivalent number of the

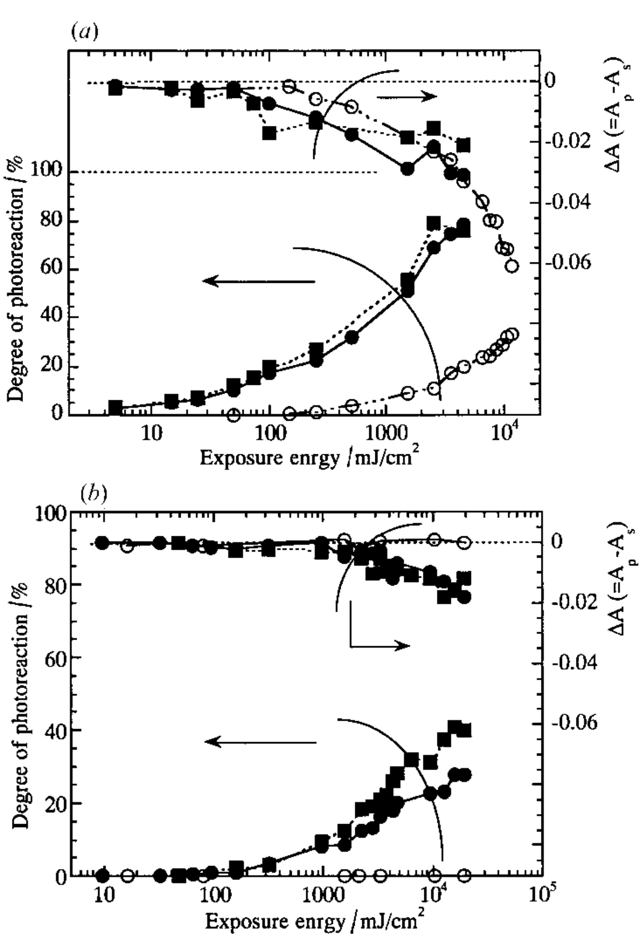
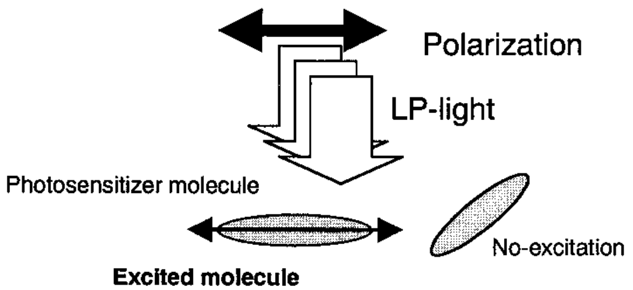


Figure 2. Degree of photoreaction and the photoinduced optical anisotropy (ΔA) of PMCB6M films without photosensitizer (open circles), with 2 wt% (closed circles), and 4 wt% of photosensitizer (closed squares) as a function of exposure energy. (*a*) PMCB6M/**BP** system exposed to LP-365 nm light; (*b*) PMCB6M/**AQ** system exposed to LP-405 nm light.

(*a*) ***Polarization-selective photoexcitation***



(*b*) ***Polarization-selective triplet energy transfer***

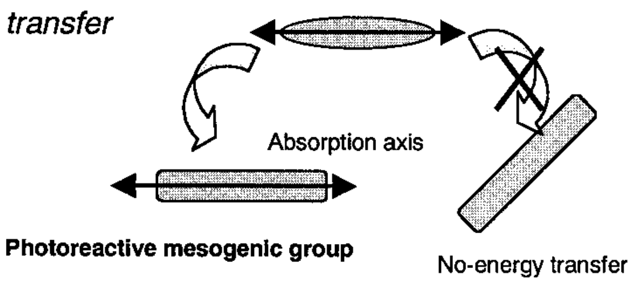


Figure 3. Schematic illustration of polarization-selective triplet energy transfer and photoreaction.

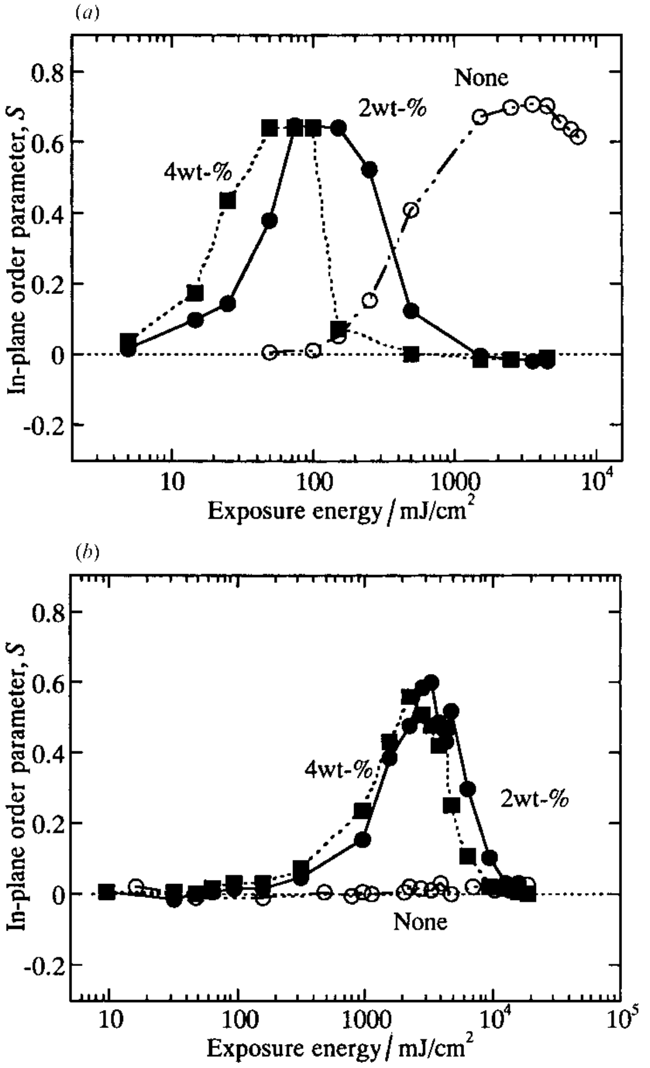


Figure 4. Comparison of the order parameter S of PMCB6M films without photosensitizer (open circles), with 2 wt% (closed circles), and 4 wt% of photosensitizer (closed squares) as a function of the exposure energy. (*a*) PMCB6M/**BP** system exposed to LP-365 nm light; (*b*) PMCB6M/**AQ** system exposed to LP-405 nm light.

mesogenic groups photoreacted. For the PMCB6M/**AQ**, $|\Delta A|$ was much smaller than for the other systems. When the degree of the photoreaction was approximately 15%, the generated $|\Delta A|$ was 0.022, 0.01 and less than 0.003 for the film without photosensitizers, 2 wt% **BP**, and 2 wt% **AQ**, respectively. The axis-selectivity of both (a) the polarization-selective photoexcitation of the photosensitizer and (b) polarization-selective triplet energy transfer from the excited photosensitizer to the mesogenic groups in PMCB6M, played an important role in the effective photoinduced dichroism, because the triplet energy transfer from the excited photosensitizer occurs by an electron exchange mechanism [13].

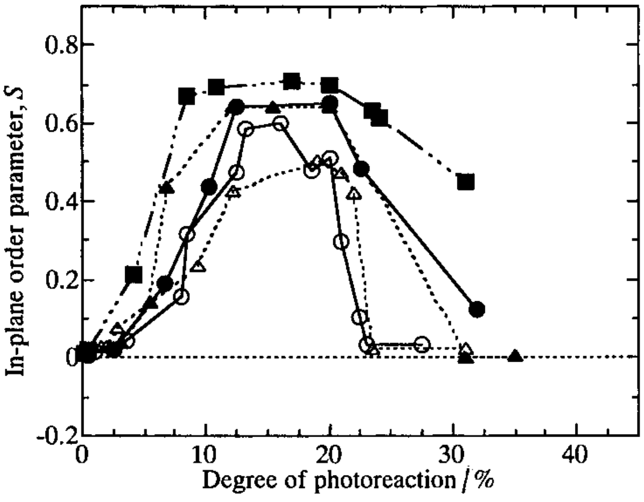


Figure 5. Comparison of the order parameter S of PMCB6M films without photosensitizer (closed squares) with 2 wt% of **BP** (closed circles), 4 wt% of **BP** (closed triangles), 2 wt% of **AQ** (open circles) and 4 wt% of **AQ** (open triangles), as a function of the degree of the photoreaction.

Due to its distorted chemical structure, the axis-selectivity of the triplet energy transfer from **AQ** was inferior to that of the **BP** system. In order to quantify the polarization-selectivity of the triplet energy transfer, further theoretical and experimental investigations are necessary.

3.2. *Thermally enhanced reorientation*

It is known that when the exposed film is annealed at elevated temperatures the thermal enhancement of the photoinduced reorientation of the mesogenic groups of PMCB6M is parallel to **E** [11, 12, 18]. The photo-crosslinked mesogenic groups parallel to **E** act as the 'command in bulk' and lead to the reorientation of the mesogenic groups due to the liquid crystalline nature of the film. Films were exposed to LP light and subsequently annealed in order to investigate the influence of the photosensitizer on thermally enhanced reorientation. Figure 4 (*a*) plots the induced S values as a function of the exposure dose of LP-365 nm light and shows large positive S values around 0.70 for the film with no photosensitizer after annealing, when the exposure energy was between 1 600 and 4 000 mJ cm^{-2}. In contrast, the required irradiation energy was 70 mJ cm^{-2} for 2 wt%, and 50 mJ cm^{-2} for 4 wt% doping of **BP**. The maximum S value was slightly smaller ($\sim$0.65) than that without doping, which is attributed to the smaller photoinduced $|\Delta A|$ for films doped with **BP** as described already. Figure 5 plots the S values obtained as a function of the degree of photoreaction, showing that the largest S values are achieved when the degree of photoreaction is in the range 12–20%. However, for films doped with **BP**, the S values decreased abruptly when the degree of photoreaction was greater than 25%. These results suggest that a similar amount of the photoreacted mesogenic groups generate an efficient reorientation of the mesogenic groups, although the small $|\Delta A|$ of PMCB6M/**BP** and the high degree of photoreaction cannot induce reorientation.

As shown in figure 4 (*b*) no molecular reorientation was observed with LP-405 nm light for films without the photosensitizer, but the orientational order was thermally enhanced when the film contained **AQ**. Positive S values of 0.59 and 0.53 were obtained when the exposure energy was 2 800 mJ cm^{-2} for 2 wt%, and 2 200 mJ cm^{-2} for 4 wt% doping of **AQ**; but the S values were smaller than for films without the photosensitizer and doped with **BP**. As shown in figure 5 the degree of the photoreaction required for large S values is in a limited range compared with the other conditions. This was due to small $|\Delta A|$ for the PMCB6M/**AQ** system. The table summarizes the birefringence of the films and required exposure energy for each system. The difference in the photoinduced optical anisotropy caused coplanar reorientation, which can control the in-plane ellipsoid of the refractive index of the film [11, 19].

3.3. *Slantwise molecular orientation*

Slantwise molecular reorientation of a PMCB6M/**BP** film was performed using oblique LP-365 nm light. Since the reorientation direction is adjusted by the photoreacted mesogenic groups this technique provides molecular reorientation with the desired orientational angle [10, 11]. Figure 6 (*a*) illustrates the irradiation diagram. The sample birefringent film was prepared by exposing to p-polarized 365 nm light of 68 mJ cm^{-2} at an incident angle of 45°, followed by annealing at 150°C. For comparison, 4 000 mJ cm^{-2} doses were required to fabricate a film without **BP** using the same method. Figure 6 (*b*) plots the angular dependent UV absorbance at 315 nm as a function of the incident angle θ of the p and s-polarized beams. It reveals that the absorption of a p-polarized beam is higher when the incident angle of the probe light is positive and becomes smaller on decreasing the incident angle for both films. This indicates that the orientation characteristics of the mesogenic groups are similar. Thus, the photoexcitation of the **BP** and the triplet energy transfer can occur three-dimensionally when irradiating with oblique LPUV light.

Table. Birefringence and exposure energy of the PMCB6M films.

Sens[a]	Content/ wt%	Exposure condition[b]/ mJ cm^{-2} nm^{-1}	Birefringence[c]
None	—	4000/365	0.24
BP	2	68/365	0.22
BP	4	51/365	0.21
AQ	2	2880/405	0.17
AQ	4	2240/405	0.16

[a] photosensitizer.
[b] exposure energy and wavelength.
[c] Measured at 632.8 nm.

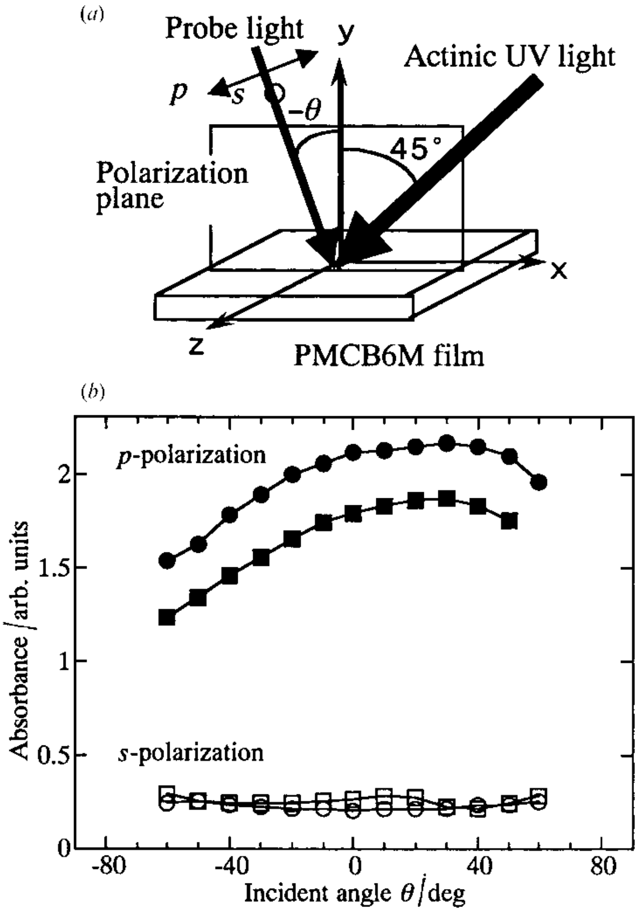


Figure 6. (*a*) Schematic illustration of the measurement of slantwise orientation and the angle θ of a probe monitoring light. The xy-plane is the polarization plane of the LPUV light beam. (*b*) Angle-dependent UV absorbance at 315 nm of PMCB6M films without photosensitizer (circles) and with 4 wt% of **BP** (squares).

4. Conclusions

Polarization-selective photosensitization in PMCB6M films was successfully achieved based on polarization-selective triplet energy transfer using LP-365 nm and LP-405 nm light with different photosensitizers. A small amount of photosensitizer (less than 4 wt%) effectively improved the axis-selective photoreaction, which is attributable to the polarization-selective triplet energy transfer mechanism. Annealing at elevated temperatures enhanced the molecular reorientation, and slantwise reorientation was feasible with oblique LP-light exposure similar to the PMCB6M film without a photosensitizer. The efficiency of the in-plane reorientation order depended on the ΔA obtained. This system will improve the potential for fabricating birefringent films using photoreactive polymers and will serve as new photochemistry for polarization energy transfer. Further studies on the detailed mechanism and on the influence of the photosensitizers and the wavelength of the LP light on the energy transfer are in progress.

This work was partly supported by a Grant-in-Aid for Scientific Research from the JSPS of the Japanese Government.

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