Macromolecules **2005,** *38,* 3903−3908 **3903**

Photoinduced Optical Anisotropy Based on Axis-Selective Triplet Energy Transfer and Thermally Enhanced Reorientation in a Photo-Cross-Linkable Liquid Crystalline Polymer Film

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Received December 22, 2004; Revised Manuscript Received February 15, 2005

ABSTRACT: An axis-selective photosensitized reaction of a photo-cross-linkable liquid crystalline polymer film doped with a triplet photosensitizer (TPS) based on axis-selective triplet energy transfer achieved a thermally enhanced molecular reorientation of the film using linearly polarized (LP) 405 nm light. Four types of TPS—4,4′-(*N*,*N*′-bis(diethylamino))benzophenone (DBP), 4-(*N*-diethylamino)benzophenone (BP), 5-nitroacenaphthene (AN), and *p*-nitroaniline (pNA)—were used to compare the efficiency of the axis selection of the energy transfer. In all cases, the photoreactivity of a film was generated when doping with less than 9 wt % of TPS. The quenching sphere played a role in the photoreactivity, while the photoinduced optical anisotropy depended on the type of TPS. The axis-selective photoexcitation of TPS and the polarization-preserved energy transfer to the photoreactive mesogenic groups dominated the photoinduced optical anisotropy as well as the thermal enhancement of the molecular reorientation.

1. Introduction

Since the optical property of a photoreactive film can be controlled by light exposure, a lot of attention is focused on synthesizing photoreactive polymers and their applications to optical devices.[1−6] Exposing to linearly polarized (LP) light generates an optical anisotropy of the photoreactive film through an anisotropic polarization-axis-selective photoreaction caused by the Weigert Effect.[3−5,7−16] If the axis-selective photoreaction is accompanied by a molecular reorientation, a large optical anisotropy can be created. Several types of materials for the photoinduced molecular reorientation have been investigated, including photopolymers that contain photoisomerized groups[3−7,11,12,17−26] and photo-cross-linkable groups.[8−10,27−31] Among them, numerous azobenzene-containing materials are investigated on the basis of an axis-selective trans−cis−trans photoisomerization.[17−26] Since the photoinduced reorientation of azobenzene groups can be optically or thermally erased, reversible optical memories and holographic devices and optical switches were investigated.[1−5,7,32−35]

Alternatively, the thermally enhanced photoinduced molecular reorientation in photo-cross-linkable materials, which are applicable to passive optical devices such as a phase retarder for liquid crystal displays, is investigated.[31,36,37] The reoriented molecular structure is thermally stable for photo-cross-linkable materials. We developed several types of liquid crystalline polymethacrylates with photo-cross-linkable mesogenic side groups, and a large optical anisotropy is generated by irradiating with linearly polarized ultraviolet (LPUV) light and subsequent annealing.[27−31] Among such materials, a polymethacrylate with 4-(4-methoxycinnamoyloxy)biphenyl (MCB) side groups (PMCB6M in Figure 1) exhibited an efficient in-plane molecular reorientation.[30,31] However, the exposure energy to obtain a large molecular reorientation of a PMCB6M film was greater than 1 J cm^{-2} at 365 nm light since the absorption coefficient at 365 nm is very small.[30]

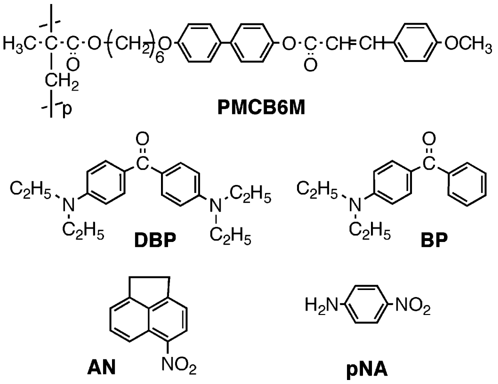

Figure 1. Photo-cross-linkable liquid crystalline polymer PMCB6M and triplet photosensitizers (TPSs) used in this study.

To improve the photosensitivity of photoreactive cinnamate derivatives, triplet photosensitizers (TPSs) are usually added to the material since TPSs absorb a longer wavelength of light than the absorption bands of the photoreactive groups.[38−40] For the axis-selective photoreaction of the photoreactive materials using LP light, a polarization-preserved energy transfer is required. There are few studies on the photosensitization reaction that maintains its polarization axis.[41,42] We reported that doping with a small amount of 4,4′-(*N*,*N*′-bis(diethylamino))benzophenone (DBP) as a TPS improved the photoreactivity of a PMCB6M film.[41] The photosensitivity at LP 365 nm light improved by 50 or more times, and annealing the exposed film at elevated temperatures led to an in-plane molecular reorientation similar to the case of a film without DBP. The exposed film exhibited a photoinduced optical anisotropy, which implied that the photosensitization reaction maintained the axis selectivity of the cinnamate group photoreaction, although the triplet energy transfer was generated through electron-exchange mechanism. Furumi and

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10.1021/ma047359i CCC: $30.25

Ichimura reported a similar polarization-selective photosensitization of a poly[methyl-4-(methacryloyloxy)-cinnamate] (PMCi) film doped with 33 mol % of Michler's ketone (MK) as a TPS.[42] They assumed that the collision complex between the polymer and MK created a polarization-preserved triplet energy transfer. However, the influence of the type of TPS on the photoinduced optical anisotropy and thermal enhancement of the molecular reorientation of PMCB6M and their mechanism via an axis-selective triplet energy transfer were not studied in detail.

In this paper, the photoinduced optical anisotropy and thermal enhancement of the molecular reorientation of a PMCB6M film doped with small amount of TPS using LP 405 nm light were investigated. All the photoreactions were based on the triplet energy transfer from the excited TPS to the photoreactive MCB groups. Four types of TPS—DBP, 4-(*N*-diethylamino)benzophenone (BP), 5-nitroacenaphthene (AN), and *p*-nitroaniline (pNA)—were used to clarify the influence of the chemical structure on the efficiency of the axis-selection for the energy transfer. The photoinduced optical anisotropy caused by the polarization-preserved triplet energy transfer and thermal enhancement of the molecular reorientation behavior of the film were estimated using polarization absorption spectroscopy. Finally, the phosphorescent spectra of TPS in the oriented PMCB6M film were measured to evaluate the excited state of the film.

2. Experimental Section

2.1. Materials. Photo-cross-linkable liquid crystalline polymer (PMCB6M) was synthesized according to the literature.[30] The number-average (M_n) and weight-average (M_w) molecular weight were 53 300 and 128 000, respectively. Poly(methyl methacrylate) (PMMA) was obtained by a radical polymerization using AIBN as the initiator ($M_n = 17\,500$, $M_w/M_n = 1.7$). TPSs were received from Tokyo Kasei Chemicals, and Figure 1 summarizes their chemical structure and abbreviations.

2.2. Photoreaction. A thin film of PMCB6M doped with 0.5−9 wt % of a photosensitizer was prepared by a spin-coating technique from a methylene chloride solution on 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 405 nm (fwhm = 10 nm) to obtain linearly polarized monochromic light. The light intensity was 17 mW/cm^2. The photoreactivity of the films was estimated by monitoring the decrease in absorbances at 315 nm and 1635 cm^{-1} (C=C double bond of the cinnamoyl group) in UV and FT-IR spectroscopies, respectively. The photoproducts of the mesogenic group are described in detail in the previous paper.[30]

2.3. Evaluation of Optical Property. The polarization absorption spectra were measured with a Hitachi U-3010 spectrometer equipped with Glan-Taylor polarization prisms. The photoinduced dichroism, ΔA, was determined by $\Delta A = A_{\parallel} - A_{\perp}$ using the absorbance at 315 nm, where $A_{\parallel}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to E, respectively. A dichroic ratio (DR) of the photoinduced optical anisotropy of the film is expressed as eq 1.

$$\mathrm{DR} = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + A_{\perp}} \qquad (1)$$

The thermally enhanced molecular reorientation was conducted by annealing the exposed film at 150 °C for 10 min. The thermally enhanced in-plane order was evaluated using the order parameter, S, at 315 nm and is expressed as eq 2.

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{(\mathrm{large})} + 2A_{(\mathrm{small})}} \qquad (2)$$

where $A_{(\mathrm{large})}$ is the larger of $A_{\parallel}$ and $A_{\perp}$, and $A_{(\mathrm{small})}$ is the smaller value.

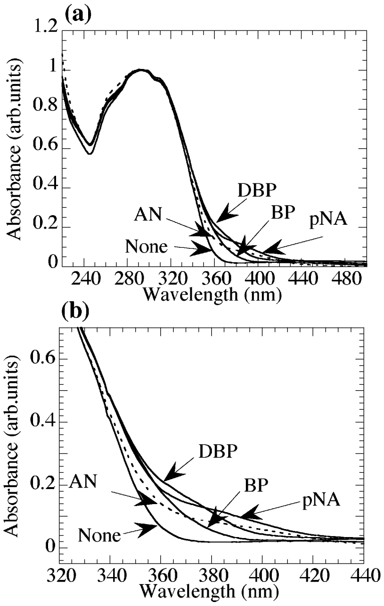

Figure 2. (a) Absorption spectra of PMCB6M film doped with 9 wt % of TPS on quartz substrate. (b) Closeup of (a).

2.4. Phosphorescent Spectra Measurement. The phosphorescent spectra of the film were evaluated using Hitachi F-2700 spectrometer and polarizer films under a nitrogen atmosphere at room temperature. PMCB6M films doped with 17 wt % of TPS were prepared by a spin-coating method. For comparison, PMMA films doped with TPS were used. TPS of DBP and BP were used for the phosphorescent measurement since the polymer films doped with these TPSs exhibited phosphorescent emission. The excitation wavelength was 405 nm, which does not excite the MCB groups. The sample film was set 40° to the incident exciting light beam to prevent the reflective light from entering the detector. The diffracted emitted light from the sample was measured. The p- and s-polarized excitation beams were used to evaluate the emission spectrum.

The emission from an oriented PMCB6M film doped with TPS was evaluated using a parallel sandwich cell (thickness = 12.5 μm) of PMCB6M doped with 17 wt % of DBP. Two oriented thin PMCB6M films ($S = 0.68$, thickness = 200 nm) on a quartz substrate, which were preoriented using LP 365 nm light, were used as the photoalignment layer.[43] The oriented cell was prepared by heating the DBP/PMCB6M mixture at 180 °C and then slowly cooled to room temperature. Mechanical alignment of the film was also performed upon cooling to amplify the orientation. The orientation was confirmed by a polarization optical microscope. The orientational order was approximately 0.15.

3. Results and Discussion

3.1. Photoreaction of TPS/PMCB6M Film with 405 nm Light.

All TPSs were uniformly dissolved in PMCB6M, and the spin-coated films were completely transparent. Figure 2 shows the UV−vis absorption spectrum for a PMCB6M film with 9 wt % of TPS. The small absorption bands around 405 nm are due to the absorption band of the TPS, as shown in Figure 2b.

When a PMCB6M film without TPS was exposed to 405 nm light, the photoreaction of mesogenic groups did not occur since PMCB6M does not have an absorption band at 405 nm, but the photoreaction proceeded for films doped with a TPS. This is due to the triplet energy transfer from the excited TPS to the methoxycinnamoyl group.[39,40] Figure 3a−d plots the degree of the photo-

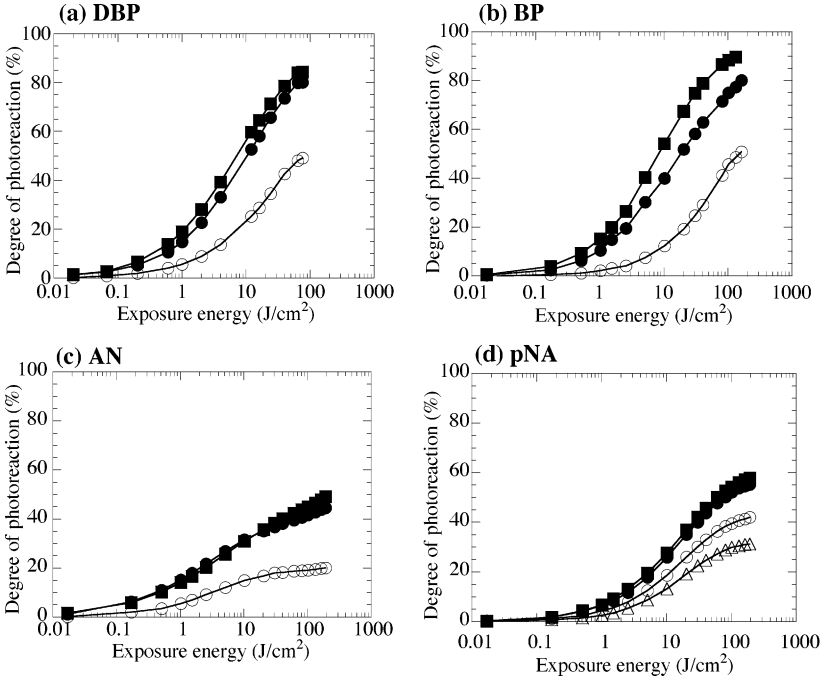

Figure 3. Degree of photoreaction of TPS/PMCB6M film as a function of exposure energy: (a) DBP, (b) BP, (c) AN, and (d) pNA. TPS content: 9 wt % (closed squares), 4.8 wt % (closed circles), 1 wt % (open circles), and 0.5 wt % (open triangles). Degree of the photoreaction was estimated by monitoring the decrease in absorbance at 315 nm in UV spectroscopy.

reaction for PMBC6M films that contain various TPS concentrations as a function of exposure doses with 405 nm light. It reveals that the photoreaction is faster for films doped with benzophenone derivatives (DBP and BP) than that of the other derivatives. The photosensitization efficiencies of DBP and BP are superior to AN and pNA. Furthermore, the photoreaction is faster as composition of TPS increases. For films doped with 1 wt % of DBP, BP, AN, and pNA and with 0.5 wt % of pNA, the photoreaction rate is much slower than those for other concentrations. Additionally, for AN and pNA, excessive exposure caused the TPS molecules to decompose, which resulted in a lower degree of the photoreaction as plotted in Figure 3c,d.

The photosensitized reaction of cinnamate derivatives originates from a triplet−triplet energy transfer, which is based on the electron exchange mechanism (Dexter mechanism), and the concentration of a TPS plays an important role in the probability of the energy transfer.[38] Since the photoexcited molecules and cinnamate groups must be close for an effective exchange interaction, the distance between the photosensitizer and the photoreactive group should be less than approximately 15 Å for the triplet−triplet energy transfer.[38,44] A useful relationship between the radius of the quenching sphere and the concentration of the acceptor is given by eq 3[38]

$$R = 6.5/[\mathrm{A}]^{1/3} \qquad (3)$$

where R is the radius of the quenching sphere and [A] is the concentration of the acceptor. This equation indicates that the energy transfer occurs when the acceptor molecules are located within the quenching sphere, R. Using this model, the calculated average distances among the TPS in the film are 20.7, 19.1, 17.6, and 19.6 Å for 1 wt % doping of DBP, BP, and AN and 0.5 wt % doping of pNA, respectively, when the assumed density of the TPS/polymer film is 1.0. These values are not close to the effective photosensitization of cinnamate molecules, which results in a lower degree of the photoreaction. In contrast, energy transfer in the entire area proceeds for films when the concentration of the TPS is larger than 4.8 wt %, where R is less than 15 Å.

3.2. Photoinduced Optical Anisotropy of TPS/PMCB6M Film. We reported that irradiating with LPUV light to a PMCB6M film generated a small negative optical anisotropy ($\Delta A < 0$) due to an axis-selective photoreaction of the cinnamoyl group.[30,31] To evaluate the influences of TPS on the photoinduced ΔA, a PMCB6M film doped with various content of TPS was exposed to LP 405 nm light. Figure 4a−d plots the photoinduced DR values of TPS/PMCB6M films as a function of the degree of the photoreaction. For all cases, a negative DR was generated when the photoreaction proceeded, but the magnitude of photoinduced DR values was greatly influenced by the type of TPS and its composition. Negative DR values indicate that the photoreaction proceeds faster parallel to **E** than perpendicular to **E**. Namely, the axis-selective photoexcitation of a TPS follows a polarization-preserved triplet energy transfer to a cinnamoyl group.

According to the Dexter mechanism, the overlap of the electron orbital of donor and acceptor is important for electron exchange, and the energy transfer originates from the π^* electron of the excited TPS through an exchange of the wave motion movement to the cinnamoyl group. Since the photoinduced optical anisotropy was negatively generated for the TPS/PMCB6M films as plotted in Figure 4, the direction of the electron orbital of the donor and acceptor may affect the axis selectivity of the energy transfer in the solid state. A triplet exciplex between TPS and a cinnamate group was observed in a composite film of PMCi and MK, which might play a role in the polarization-preserved triplet energy transfer.[42] A detailed discussion is described in section 3.4.

Additionally, Figure 4 shows that the photoinduced DR increases as the degree of the photoreaction increases. The generated negative DR values for films

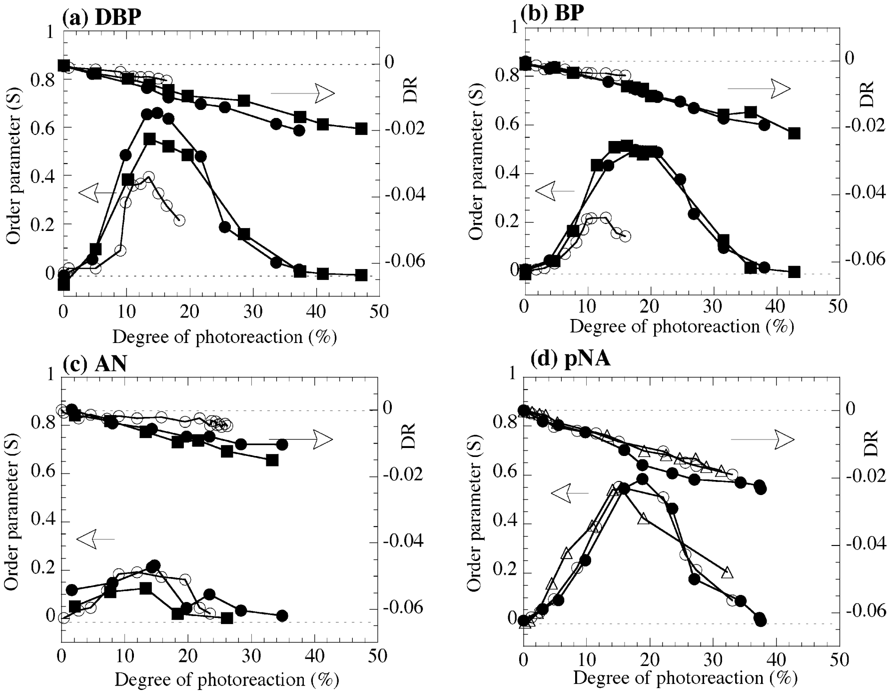

Figure 4. Photoinduced DR values and thermally enhanced order parameter *S* of TPS/PMCB6M films as a function of degree of the photoreaction: (a) DBP, (b) BP, (c) AN, and (d) pNA. TPS content: 9 wt % (closed squares), 4.8 wt % (closed circles), 1 wt % (open circles), and 0.5 wt % (open triangles).

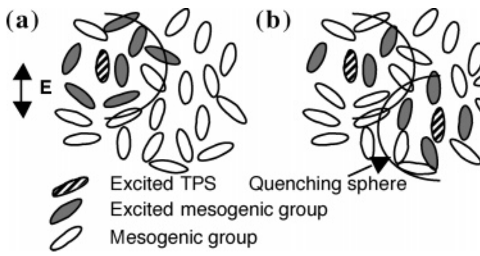

Figure 5. Schematic illustration of the influence of the quenching sphere on the triplet energy transfer from excited TPS to the photoreactive mesogenic groups using LP light: (a) low concentration of TPS, (b) high concentration of TPS.

doped with AN are smaller than that for films with DBP, BP, and pNA. When the degree of the photoreaction is 20 mol % for films with 4.8 wt % of TPS, the generated DR values are −0.012 (DBP), −0.010 (BP), −0.007 (AN), and −0.017 (pNA). These results indicate that the magnitude of photoinduced ΔA depends on the axis selectivity of both the photoexcitation of TPS and the energy transfer from the excited TPS to the cinnamoyl group. Furthermore, the DR values for films with 1 wt % of doping are much smaller than that for films with 4.8 and 9 wt % of doping.

Figure 5a,b shows schematic illustrations that explain these phenomena when the degrees of the photoreaction are similar. When the cinnamoyl moieties in mesogenic groups are far from TPS (as is the case for a low concentration of TPS; Figure 5a), the photoreaction of the mesogenic groups away with TPS by 15 Å or more hardly proceeds due to the lack of energy transfer, as described in the previous section. Furthermore, the extent of the polarization-preserved energy transfer from the axis-selectively excited TPS becomes lower as the distance between the TPS and the cinnamoyl group increases. In other words, excited energy will transfer to the cinnamoyl groups in the direction different from TPS, which results in small DR values, especially for 1 wt % doping of TPS. In contrast, as illustrated in Figure 5b, an efficient polarization-preserved energy transfer occurs when the distance between the excited TPS and cinnamoyl groups is within the quenching sphere since the amount of TPS excited parallel to **E** is large. However, for AN, the photoinduced DR values are much smaller than that of other films when the degrees of the photoreaction are similar. The DR values of BP are smaller than that of DBP, since the symmetry of a molecule is smaller. These results indicate that the form of a TPS molecule is an important factor for the axis selection of photoexcitation and the polarization-preserved triplet energy transfer. The photoexcited transition moment of the TPS molecule involves the axis selectivity of the photoexcitation of TPS.

3.3. Thermal Enhancement of Photoinduced Optical Anisotropy. We reported that the photoinduced negative optical anisotropy of a PMCB6M film without TPS is amplified in the same direction or reversely enhanced when the exposed film is annealed in the LC temperature range of the film. This thermally enhanced reorientation direction depends on the degree of the photoreaction.[30,31]

Figure 4a−d plots the thermally enhanced in-plane order parameter of TPS/PMCB6M films as a function of the degree of the photoreaction. In all cases, positive *S* values are obtained when the photoreaction proceeded, even though the degree of the photoreaction is 5 mol %. This means that the photoinduced negative optical anisotropy is reversely enhanced parallel to **E**. For a PMCB6M film without TPS, the photoinduced negative optical anisotropy is thermally enhanced in the same direction initially upon the photoreaction (the degree of the photoreaction is approximately 5 mol %), in which a small amount of photoproduct parallel to **E** plays a role in the thermal amplification of the photoinduced optical anisotropy.[30] However, thermal amplification of the negative optical anisotropy did not occur when the film contained TPS.

As explained in the previous section, the photoreaction of the mesogenic groups near the axis-selectively photoexcited TPS molecules effectively occurs, and the axis selectivity decreases as distance between the mesogenic groups and TPS increases, which results in small DR values compared to that of a film without TPS. Therefore, upon the initial photoreaction, since the axis-selective photoreaction only occurs near TPS, the average photoinduced optical anisotropy of the TPS/PMCB6M film is too small to thermally amplify its anisotropy. In contrast, when the photoreaction proceeds, the amount of the photo-cross-linked mesogenic groups parallel to **E** around TPS increases to thermally reorient other mesogenic groups along their direction similar to a PMCB6M film without TPS.[30] Additionally, the enhanced *S* values depends on type of the TPS and its concentration and the degree of the photoreaction.

For DBP and BP, the maximum *S* values, above 0.5, are obtained for films containing 4.8 wt % and more of TPS, when the degree of photoreaction is approximately 14−22 mol %. Larger *S* values for films doped with DBP than BP are due to larger DR values of DBP. In contrast, the maximum *S* values are less than 0.4 for films with 1 wt % of doping when the degree of photoreaction is about 10−14 mol %. For pNA, maximum *S* values are greater than 0.5 when the degree of the photoreaction is approximately 15−22 mol % when films contain 1 wt % and more of TPS. These *S* values are slightly smaller and the degree of the photoreaction required to attain the greatest *S* values is lower than that obtained for films without TPS exposing to LPUV light.[30] Since the reversion and enhancement of the molecular reorientation are attributed to the reorientation power of the photo-cross-linked mesogenic groups parallel to **E**, both the photoinduced optical anisotropy and the degree of the photoreaction play important roles in the thermally enhanced molecular reorientation. For films doped with TPS, the axis-selective photoreaction preferably occurs near TPS, and the resultant photoinduced DR values are smaller when the degree of the photoreaction is similar to films without TPS. [45] The smaller *S* values are due to the smaller photoinduced DR values. Furthermore, since the axis-selective photoreaction caused by the triplet energy transfer will generate nanoorder unevenness of the photoinduced optical anisotropy in the film, especially for low TPS concentration as illustrated in Figure 5, the amount of the photoreaction to attain the maximum *S* values becomes smaller to avoid the loss of the optical anisotropy near the TPS. For AN, the thermally enhanced *S* values are less than 0.25 for all cases. Small *S* values are due to the small DR values as described in section 3.2. Additionally, the *S* values decrease when the degree of the photoreaction becomes higher than 25 mol %. Although the DR values are large, the cross-linked structure prohibits the molecular motion.

3.4. Phosphorescent Study. To evaluate the triplet state of TPS/PMCB6M film, the phosphorescent spectrum was measured using DBP and BP. The excitation was carried out at 405 nm to excite the TPS molecules. For comparison, emission of a TPS/PMMA film was also measured. Film thickness was approximately 300 nm. Figure 6 shows the normalized phosphorescent spectra of PMCB6M and PMMA films doped with 17 wt % of DBP and BP, respectively. The emission of DBP-doped film was expanded because it was weaker than BP-doped film. The broad emission around 440−530 nm appears for PMCB6M film doped with DBP, while the λ_{max} of DBP/PMMA film is 438 nm. A red shift in the emission for a PMCB6M film doped with BP is also observed. The red shift of the emission spectra is due to the exciplex between TPS and MCB groups in the solid state.[38,46] The emission intensity of the exciplex was stronger than that in PMMA for both TPS. This might be because that the emission efficiency of the exciplex is higher than the TPS molecules in PMMA. A similar triplet exciplex was reported in PMCi film doped with MK.[42] The overlap of the electronic orbitals between the cinnamate and TPS plays a role in the exciplex emission. Therefore, the conformation between the TPS and MCB groups is important in the photosensitized reaction of a PMCB6M film.

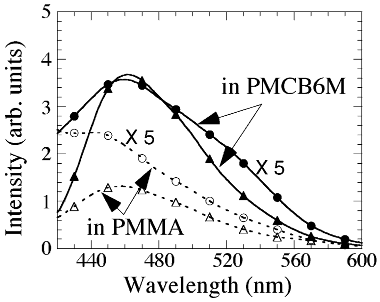

Figure 6. Phosphorescent spectra of TPS/PMCB6M (solid lines) and TPS/PMMA (dotted lines) films on quartz substrate. 17 wt % of TPS of DBP (circles) and BP (triangles) were doped in the polymer. Wavelength of excited light is 405 nm. Film thickness is normalized to be the same, and spectra of DBP doped films are expanded by 5.0.

To gain further insight into the triplet energy transfer, the emission spectra of an oriented PMCB6M film doped with DBP were evaluated. Both p- and s-polarized 405 nm light was used to measure the emission spectrum of an oriented PMCB6M film doped with 17 wt % of DBP (12.5 μm thickness cell). The schematic experimental setup is illustrated in Figure 7a. The sample cell was rotated by 90°, and the emission spectrum of each excitation polarized light was measured. Figure 7b shows the average spectrum when the orientation direction and the polarization of the excited beam are parallel or perpendicular. Since the TPS molecules are randomly doped in the oriented PMCB6M film, the triplet energy transfer occurs at interface between a mesogenic group and a TPS. As shown in Figure 7b, the exciplex emission is observed when the polarization of the excited beam is parallel to the orientation direction. In contrast, characteristics of the exciplex emission decrease when the excited beam is perpendicular to the orientation direction. These results suggest that interaction between the oriented MCB group and the DBP is larger when the transition moments of both molecules are parallel to each other since the DBP molecules, which are aligned parallel to the polarization of excitation light beam, are selectively excited. Therefore, the triplet energy transfer that preserves its direction preferentially occurs when the transition moments of TPS and the MCB group are parallel.

4. Conclusion

The photoinduced optical anisotropy and thermally enhanced molecular reorientation of photo-cross-linkable polymer liquid crystal film doped with small amount of TPS using LP 405 nm light were investigated on the basis of the axis-selective photoexcitation of TPS

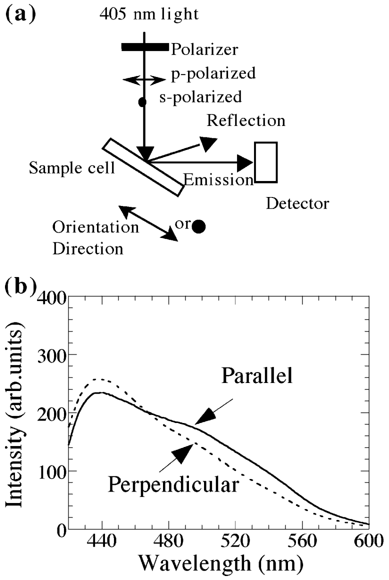

Figure 7. (a) Schematic illustration for the measurement of the emission of an oriented PMCB6M/DBP cell using polarized excitation light beams. (b) Phosphorescent spectra of a cell of an oriented PMCB6M doped with 17 wt % of DBP. The polarization of LP 405 nm light for the excitation is parallel (solid line) and perpendicular (dotted lines) to the orientation direction.

followed by polarization-preserved triplet energy transfer to the mesogenic groups. The photoreactivity and the photoinduced optical anisotropy were generated for all the films doped with TPS. Since the photosensitization was caused by the photoexcited TPS close to the photosensitive groups, the degree of the photoreaction and axis selectivity of the photosensitization decreased when less than 1 wt % of TPS was present. The shape and direction of the transition dipole moment of the TPS will be important factors for achieving a large photoinduced optical anisotropy. The reversion and thermally enhanced reorientation of the photoinduced optical anisotropy were generated in all cases, but the induced in-plane order depended on the photoinduced dichroism. A phosphorescent study of DBP and BP doped films suggested that the exciplex of the photoexcited TPS and the mesogenic groups and their direction controlled the polarization-preserved triplet energy transfer and the photoreaction. Since pNA and AN doped films did not show phosphorescence, exciplex formation was unclear for these TPS. The TPS/PMCB6M system would be applicable to the polarization optical memory using a LP 405 nm laser diode (blue-ray laser) since the large in-plane reorientational order greater than 0.5 was obtained when DBP, BP, and pNA were used as TPS. Further detailed theoretical and experimental studies on a mechanism of the axis-selective triplet energy transfer are underway.

Acknowledgment. This work was supported by Grant-Aids for Scientific Research from the Japan Society for the Promotion of Science No. 15550187.

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MA047359I