Photoinduced Reorientation and Multiple Optical Data Storage in Photo-Cross-Linkable Liquid Crystalline Copolymer Films Using 405 nm Light

Nobuhiro Kawatsuki,*,† Kunihisa Kato,† Tomoko Shiraku,† Takeshi Tachibana,† and Hiroshi Ono‡

Department of Materials Science and Chemistry, Himeji Institute of Technology, University of Hyogo, 2167 Shosha Himeji, 671-2201 Japan, and Department of Electrical Engineering, Nagaoka University of Technology, 1603-1 Kamitomioka Nagaoka, 940-2188 Japan

Received January 17, 2006; Revised Manuscript Received March 1, 2006

ABSTRACT: New polymethacrylate liquid crystalline copolymers, which are comprised of photo-cross-linkable 4-(4-methoxycinnamoyloxy)biphenyl (MCB) and photosensitizing 4-nitrobiphenyl (NB) or 4-nitrophenyl (NP) side groups, were synthesized. The irradiation with linearly polarized (LP) 405 nm light was performed to investigate the photoinduced reorientation behavior of the thin films. On the basis of the polarization-preserved excited energy transfer from the photosensitizing groups to the MCB groups, a photoinduced optical anisotropy due to the axis-selective photoreaction of the MCB groups accompanied the photoreaction of the film. In all cases, annealing the film reversely amplified the photoinduced optical anisotropy and an in-plane order parameter greater than 0.7 was achieved for the NB-containing copolymer films. The axis-selectivity of the photoabsorption of the photosensitizing groups and the effective energy transfer played important roles in generating the large photoinduced optical anisotropy and the effective thermal enhancement. Finally, it was demonstrated that the orientation direction of the mesogenic side groups controlled the multiple optical information storage in a thin film.

1. Introduction

Since irradiating with linearly polarized (LP) light causes an anisotropic photoreaction on a photoreactive polymeric film, a lot of attention has been focused on the synthesis of photoreactive materials that generate large photoinduced optical anisotropies and possess efficient photoreactivities.[1−6] These materials are applicable to birefringent optical devices,[1−3,7−9] the photoalignment layer of liquid crystal displays,[3,4,10−15] optical memories, and holographic data storage devices.[1−3,16−21] The photoinduced optical anisotropy in a photoreactive film is due to the axis-selective photoreaction caused by Weigert's effect. Thus, a high axis selectivity of the photosensitive moiety is important for creating an efficient anisotropic photoreaction. Additionally, when a molecular reorientation accompanies the axis-selective photoreaction, a large optical anisotropy can be derived. Hence, various photoreactive materials have been synthesized, including azobenzene-containing polymers[3−5,22−25] and photo-cross-linkable polymers.[26−29] To apply reversible orientation control to optical memories and switches, numerous studies have examined azobenzene-containing polymeric films based on the axis-selective trans−cis−trans photoisomerization.[1−3,16−18,30−34] It has been determined that changing the polarization of the writing LP light beams can erase the photoinduced optical anisotropy. Furthermore, black and white images have been recorded on an azobenzene-containing liquid crystalline (LC) polymer using a color slide as a gray photomask.[1] Although the reorientation direction was identical, the photoinduced birefringence was varied according to the transparency of the mask. Alternatively, photo-cross-linkable materials, which have a high thermal stability due to the photo-cross-linked structure, have been investigated for passive optical device applications such as birefringent films for liquid crystal displays and polarization holographic gratings.[7,8,20,35−41]

During the course of our systematic study on thermally enhanced photoinduced molecular reorientation in photo-cross-linkable materials, it was determined that polymethacrylates with 4-(4-methoxycinnamoyloxy)biphenyl (MCB) side groups exhibit efficient in-plane molecular reorientations.[7,29,40] The LC nature of the material allows the axis-selective photoreaction of the MCB side groups to generate the photoinduced optical anisotropy of the film, while a subsequent thermal treatment enhances the molecular reorientation along the photo-cross-linked anchors parallel to the polarization direction (**E**) of LP light. Furthermore, doping with a small amount of a photosensitizer such as a benzophenone derivative or *p*-nitroaniline improves the photoreactivity of the material while maintaining the axis-selective photoreaction when LP 405 nm light is used.[42,43] In addition, the axis-selective photoabsorption of the photosensitizers followed by a polarization-preserved excited energy transfer from the excited photosensitizers to the MCB groups generates an anisotropic reaction. However, the thermally enhanced photoinduced in-plane order parameter is smaller than that generated in a film without photosensitizers exposed to LP 365 nm light. This is caused by the small photoinduced optical anisotropy of the film, which is due to the lower axis-selectivity of the photoabsorption of the photosensitizers and the insufficient polarization-preserved energy transfer from the excited photosensitizers to the MCB side groups.

For the axis-selective photo-cross-linking reaction of the MCB groups, exposure to LP light generates the photoinduced optical anisotropy of the film[29] and subsequent exposure to LP light with a different direction of **E** does not affect the orientation direction of the molecules, which reacted during the first irradiation. Therefore, plural exposures while changing the direction of **E** of LP light and subsequent annealing should vary the thermally amplified reorientation direction of the mesogenic

* To whom correspondence should be addressed. Telephone: +81-792-67-4886. Fax: +81-792-66-4885. E-mail: kawatuki@eng.u-hyogo.ac.jp.
† University of Hyogo.
‡ Nagaoka University of Technology.

10.1021/ma060117t CCC: $33.50
Published on Web 03/31/2006

groups in a film. This technique should lead to a new type of multiple optical storage system using polymeric films, which contain MCB side groups, plural LP light exposure, and analysis of the reorientation direction to decode the information.

The paper aims (1) to explore the highly efficient photoinduced reorientation based on the polarization energy transfer in photo-cross-linkable liquid crystalline copolymers with new photosensitizing groups and (2) to demonstrate a new type of multiple optical storage using the resultant polymeric films and 405 nm light. Thus, polymethacrylate LC copolymers, which are comprised of photo-cross-linkable MCB and photosensitizing 4-nitrobiphenyl (NB) or 4-nitrophenyl (NP) side groups, were synthesized and the photoinduced reorientation behaviors of these copolymer films were investigated using LP 405 nm light. The molecular orientation of the mesogenic and photosensitizing groups were estimated using polarization absorption spectroscopy, polarization FT-IR, and phosphorescent spectroscopy. All of the copolymer films generated photoinduced optical anisotropies, which thermally enhanced the cooperative reorientation of the mesogenic groups when the exposed films were annealed in the LC temperature range of the materials. Large photoinduced optical anisotropies and thermally enhanced in-plane orders were achieved for the copolymer films with NB groups. Finally, the first example of multiple optical data storage using LP 405 nm laser diode (LD) was demonstrated. This was achieved by controlling the orientation direction of the mesogenic groups in the recorded area using plural LD light exposures and by adjusting the polarization of the LD light.

2. Experimental Section

2.1. Materials. All starting materials were used as received from Tokyo Kasei Chemicals. The methacrylate monomer, which contained the MCB side group, was synthesized according to the literature.[29] The syntheses for the methacrylate monomers with NB or NP side groups are described in the Supporting Information. All (co)polymers were synthesized by a radical polymerization in a tetrahydrofuran (THF) solution using AIBN as the initiator. The copolymers were purified by reprecipitating several times from a chloroform solution to methanol and diethyl ether. The synthetic yield was between 30 and 70 wt %. The copolymerization ratio was controlled by adjusting the feed ratio and confirmed by ^{1}H NMR spectroscopy. Figure 1a and Table 1 summarize the chemical structure, copolymerization ratio, and molecular weight of synthesized (co)polymers.

2.2. Photoreaction. Thin copolymer films, which were approximately 0.2−0.3 μm thick, were prepared by spin-coating a methylene chloride solution of polymers (~2 w/w %) onto a quartz or CaF_2 substrate. The 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 with an intensity of 17 mW/cm^2. The photoreactivity of the films was estimated by monitoring the decreases in absorbances at 315 nm and 1635 cm^{-1} (C=C double bond of the cinnamoyl group) using UV and FT-IR spectroscopies, respectively. The photoproducts of the mesogenic group have been described in detail in the previous paper.[29] The 18 mW LP 405 nm LD, which had an exposure area of approximately 1.1 × 1.1 mm^2 and was roughly focused using a convex-plano focusing lens (f = 120 mm), was also used for the photoreactions.

2.3. Characterization. The ^{1}H NMR spectra were measured with a Bruckor DX-500 FT-NMR apparatus. The molecular weight of a (co)polymer was measured by GPC (Tosoh HLC-8020 GPC system with Tosoh TSKgel column; eluent, chloroform), which was calibrated using polystyrene standards. The thermal properties were examined using a polarization optical microscope (Olympus BHA-P) equipped with a Linkam TH600PM heating and cooling stage in addition to differential scanning calorimetry (DSC; Seiko-I SSC5200H) analysis at a heating and cooling rate of 10 °C/min. The polarization absorption spectra were measured with a Hitachi U-3010 spectrometer equipped with Glan-Taylor polarization prisms. The polarization FTIR spectra were recorded through a JASCO FTIR-410 system with a wire-grid polarizer. The photoinduced dichroism (DR) of the photoinduced optical anisotropy of a film is expressed as eq 1, where $A_{||}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to **E**, respectively.

$$\mathrm{DR} = \frac{A_{||} - A_{\perp}}{A_{||} + A_{\perp}} \tag{1}$$

The thermally enhanced molecular reorientation was conducted by annealing an exposed film in the LC temperature range of the copolymer for 5−10 min. The thermally enhanced in-plane order was evaluated using the order parameter, S, and is expressed as eq 2.

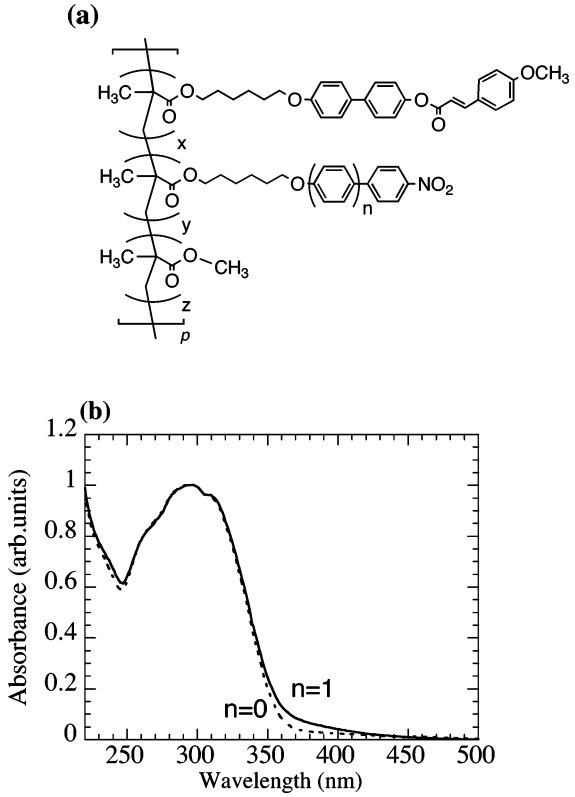

Figure 1. (a) Chemical structures of synthesized (co)polymers, **1**−**6**. (b) Absorption spectra of **1c** (thick line) and **2b** (dotted line) films on quartz substrates.

Table 1. Composition, Molecular Weight, and Thermal Properties of the Copolymers

		composition[a]			mol wt[c]			
PLC	n	x	y	z	PS[b]	$10^{-4}M_w$	M_w/M_n	thermal property[d] (°C)
1a	1	96.5	3.5	0	1.6	6.4	2.4	C 128 N 296 I
1b	1	94.3	5.7	0	2.6	5.3	2.8	C 128 N 301 I
1c	1	90.0	10.0	0	4.6	6.9	2.2	C 137 N 300 I
2a	0	94.1	5.9	0	1.8	9.8	2.2	G 91 N 297 I
2b	0	89.5	10.5	0	3.2	10.1	2.3	G 87 N 284 I
3a	1	0	3.0	97.0	6.3	2.3	2.3	G 78 I
3b	1	0	9.5	90.5	17.2	2.3	2.3	G 103 I
4	1	0	100	0		0.96	1.5	G 52 N 77 I
5	0	0	100	0		1.9	2.0	G 7 I
6		100	0	0		17.3	2.0	C 116 N 300 I

[a] Determined by ^{1}H NMR. Mole percent. [b] Weight percent of photosensitizer unit. [c] Determined by GPC. Polystyrene standards. [d] Determined by DSC. Second heating. Key: G, amorphous glass; C, crystalline; N, nematic; I, isotropic.

$$S = \frac{A_{||} - A_{\perp}}{A_{(\text{large})} + 2A_{(\text{small})}} \quad (2)$$

where $A_{(\text{large})}$ is the larger value of $A_{||}$ and $A_{\perp}$ and $A_{(\text{small})}$ is the smaller one. The birefringence of a reoriented film was measured at 633 nm by setting the reoriented film between two crossed polarizers. The Δnd value was calculated using eq 3.

$$I = I_0 \sin^2(2\theta) \sin^2\left(\frac{\pi \Delta n d}{\lambda}\right) \quad (3)$$

where the I is the transmittance, I_0 is the intensity of the prove beam, θ is the angle of the reoriented axis and polarizer film, λ is the wavelength, d is the film thickness, and Δn is the birefringence.

The phosphorescent spectra of the films were evaluated using a Hitachi F-4500 spectrometer and polarizer films under a nitrogen atmosphere at room temperature.

3. Results and Discussion

3.1. Synthesis and Thermal and Spectroscopic Properties of Copolymers. To prevent the photoabsorption of the NB or NP side groups, all the copolymers were synthesized by radical solution polymerization under dark conditions. For comparison, copolymers with MMA units (**3**) and methacrylate homopolymers, which contained photosensitizing moieties (**4** and **5**), were also synthesized. All the synthesized copolymers are soluble in common organic solvents such as chloroform, THF, and toluene. Table 1 summarizes the thermal properties of the copolymers. DSC scans of copolymers **1a**−**1c** exhibit a melting point (T_m) followed by a LC phase, while copolymers **2a** and **2b** exhibit a glass transition (T_g) followed by a LC phase. Polarization optical microscope observations for copolymers in series **1** and **2** display a nematic LC phase. Regardless of the composition, copolymers **1a**−**1c** have similar clearing temperatures (T_i). The high T_m and T_i of **1a**−**1c** are caused by the interaction between the MCB and NB groups in the solid state. On the other hand, the NP-containing comonomer units in **2a** and **2b** act as plasticizers that decrease T_m and T_i of the mesogenic MCB units.

Figure 1b shows the absorption spectra of **1c** and **2b** films. All the spin-coated films are transparent and amorphous in nature. Since the NB and NP groups have absorption bands in the longer wavelength region, the absorption spectra of the copolymers exhibit small absorptions near 405 nm.

3.2. Photoreaction and Photoinduced Optical Anisotropy of Copolymer Films. Irradiating copolymer films of **1** and **2** with LP 405 nm light causes the photoreaction of the MCB groups. However, homopolymer **6** is not photoreactive at 405 nm because it does not have an absorption band at 405 nm. We previously reported that a film of **6** doped with 0.5−9 wt % of a benzophenone derivative or *p*-nitroaniline displays a photoreactivity when exposed to 405 nm light due to the cinnamate derivatives, which are photosensitized by doping with the triplet photosensitizers (TPS).[42,43] Similarly, a photoreactivity is realized in copolymerized films of **1** and **2** with NB and NP groups when using 405 nm light since the NB and NP groups act like the TPS.[44,45] For these copolymers, the amount of the photosensitizer unit is less than 5 wt %. Figure 2 plots the degree of the photoreaction of the MCB groups as functions of LP 405 nm light exposure doses. It shows that the photoreactions for the copolymer **1** series are faster than those of the **2** series. The higher photoreactivities of films in series **1** are due to the large absorptions at 405 nm and effective photosensitizations of the NB groups. For both copolymer series, the photoreactions are faster and the maximum degree of the photoreaction is larger as the composition of the photosensitizers increases. Using the Perrin model to calculate the radius of the quenching sphere,[46,47]

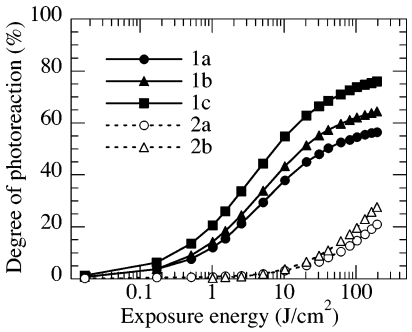

Figure 2. Degree of the photoreaction of the copolymer films as functions of the exposure energy for **1a** (closed circles), **1b** (closed triangles), **1c** (closed squares), **2a** (open circles), and **2b** (open triangles).

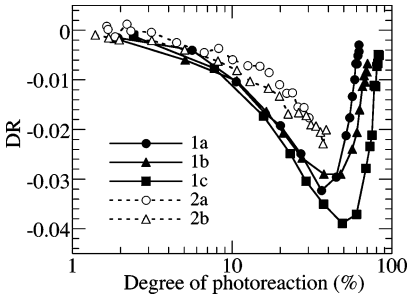

Figure 3. Photoinduced DR values at 315 nm of the copolymer films as functions of the degree of the photoreaction for **1a** (closed circles), **1b** (closed triangles), **1c** (closed squares), **2a** (open circles), and **2b** (open triangles).

R ($R = 6.5/[\text{A}]^{1/3}$, where [A] is the concentration of the acceptor), the R values of the copolymers are 16.2, 13.5, 11.0, 13.1, and 10.9 Å for **1a**, **1b**, **1c**, **2a**, and **2b**, respectively, when the assumed densities of the copolymer films are 1.0. Since an effective energy transfer occurs in the quenching sphere in a solid system, these values are reasonable for the photosensitizing reactions of the MCB groups. Hence, the photoreaction proceeds for all the copolymer films, especially for films with high photosensitizer concentrations.[46]

The MCB groups axis-selectively photoreact when using a LP light. Figure 3 plots the photoinduced DR values as functions of the degree of the photoreaction when films were exposed to LP 405 nm light. It reveals that the irradiation with LP 405 nm light generates a negative optical anisotropy ($A_{||} - A_{\perp} < 0$) for all the **1** and **2** copolymer films. A negative DR value indicates a polarization-axis-selective photo-cross-linking reaction of the MCB groups. The absolute DR values increase as the photoreaction proceeds when the degree of the photoreaction is less than 35−50 mol %, but decreases upon a further photoreaction. For **1a**−**1c**, the generated DR values are between −0.019 to −0.025 when the degree of the photoreaction is 20 mol %. These are the largest DR values among axis-selective photoreactions of the MCB side groups based on the polarization-preserved energy transfer using triplet photosensitizers excited with LP 405 nm light.[43] This implies that the NB group possesses an excellent axis-selectivity for both the photoexcitation and the polarization-preserved energy transfer to the MCB groups. On the other hand, the generated DR values for **2a** and **2b** are around −0.01− −0.015, respectively, which are similar to films of **6** doped with *p*-nitroaniline. The axis-selectivity of the NP moiety should be similar to the *p*-nitroaniline moiety due to the analogous chemical structure. A large transition moment of the NB group compared to the NP group contributes to the efficient axis-selection of the photoexcitation.[48] Additionally, the absolute DR values are larger as the composition of the photosensitizer increases for both copolymers if the degree of

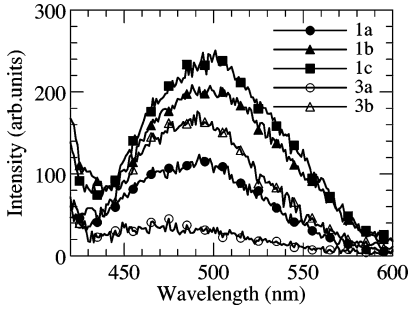

Figure 4. Photoluminescence spectra of **1a**, **1b**, **1c**, **3a**, and **3b** films. Films are 0.2 μm thick. Excitation wavelength is 405 nm.

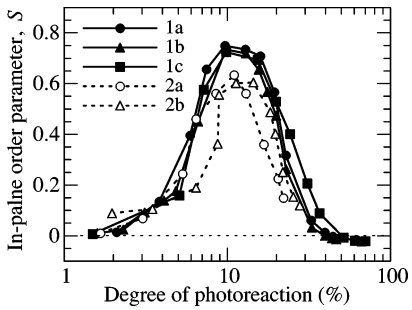

Figure 5. Thermally enhanced *S* values at 315 nm as functions of the degree of the photoreaction for **1a** (closed circles), **1b** (closed triangles), **1c** (closed squares), **2a** (open circles), and **2b** (open triangles). Annealing temperatures are 190 °C for **1a** and **1b**, 210 °C for **1c**, 160 °C for **2a**, and 180 °C for **2b**. Annealing time is 10 min.

the photoreaction is similar. The maximum DR value is obtained with a lower degree of the photoreaction and a low photosensitizer composition. The polarization-preserved energy transfer from the photoexcited sensitizers and the subsequent photoreaction of the MCB groups occur near the axis-selectively photoexcited photosensitizers within the quenching sphere.[43] Therefore, axis-selective photoreactions of the MCB groups, which are far from a photosensitizer, are difficult and lower the polarization-selectivity for the energy transfer as the composition of photosensitizer decreases.

Figure 4 indicates that films of **1** and **3** were luminiferous under 405 nm light irradiation due to the emission of the NB groups. The emission spectra of **1a**−**1c** films are similar and the emission intensity increases as the composition of the NB groups increases. The λ_{max} of the emissions for **1b** and **1c** are 495 nm, but that of **1a** is 490 nm. In contrast, λ_{max} of emission for **3b** is 491 nm, while that for **3a** is 473 nm and has a very small emission intensity. The red shifts in the emissions for films of **1a**−**1c** compared to **3a** film are due to the exciplexes between the NB and MCB groups, while the large emission intensities are derived from the larger amounts of exciplex formation. Similar red shifts due to exciplex formation have been reported for **6** and for poly(vinyl cinnamate) films doped with benzophenone derivatives.[43,49] For **3b**, the excimer formation, which is due to high concentration of the NB groups, may cause the red shift in the emission and the increased emission intensity. These results indicate that the interaction between the photoexcited NB and MCB groups form the exciplex, which is the origin of the polarization-preserved energy transfer.

3.3. Thermal Enhancement of Photoinduced Optical Anisotropy. The photoinduced optical anisotropies are reversely amplified when the exposed films of **1** and **2** are annealed in their LC temperature ranges. The reorientation direction of the mesogenic groups is parallel to **E**. Figure 5 plots the thermally enhanced order parameters of the copolymer films as functions of the degree of the photoreaction. The annealing temperatures

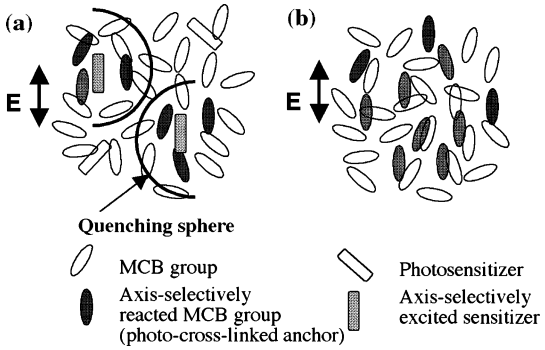

Figure 6. Schematic illustrations of the axis-selective photoreactions of (a) copolymer **1** and **2** films, and (b) the homopolymer film without photosensitizers.

were 190 °C for **1a** and **1b**, 210 °C for **1c**, 160 °C for **2a**, and 180 °C for **2b**. These thermally enhanced reorientations are due to the photo-cross-linked anchors parallel to **E** generated by the axis-selective photoreaction and the self-organization, which originate from the LC nature of the film.[29,50] The enhanced maximum *S* values of **1a**, **1b**, and **1c** films are between 0.73 and 0.75 and the generated Δn values are near 0.25, which are the highest *S* and Δn values for LC polymer films comprised of MCB groups based on a polarization-selective photosensitizing system using 405 nm light.[42,43] However, for films of **2**, the enhanced *S* values are approximately 0.55−0.64, which are similar to those of **6** doped with *p*-nitroaniline and benzophenone derivatives. The smaller *S* values for films of **2** are due to the smaller DR values compared to those of the copolymer **1** series. The high photoinduced DR values, which are initiated by the efficient axis-selective photoexcitation of the photosensitizer and polarization-preserved energy transfer, play an important role in the thermally enhanced high *S* values.

It is noteworthy that maximum *S* values for the copolymer films are obtained when the degree of photoreaction is between 7 and 15 mol %, which is less than the degree of photoreaction for homopolymer **6** using LP 365 nm light (∼20%). Figure 6 illustrates the axis-selective photoreaction. Figure 6a shows that the photo-cross-linked anchors for the thermally enhanced parallel reorientation for copolymers films of **1** and **2** are generated in the quenching spheres, while Figure 6b shows that the effective reorientation using the photo-cross-linked anchors of a homopolymer **6** film and LP 365 nm light is generated in the entire area. In this context, the degree of the photoreaction in the quenching sphere is similar to the case of the homopolymer without a photosensitizer, while the degree of photoreaction in the entire region is lower than that of the homopolymer. A small amount of the photo-cross-linked anchor, which is efficiently generated parallel to **E** in the quenching sphere, thermally reorients the surrounding mesogenic groups with a high reorientational order and the resulting domain reorients all the mesogenic groups according to the domino effect based on the LC nature of the film, especially for copolymer films of **1**.

Additionally, cooperative molecular reorientation for both the MCB and NB groups is observed due to the LC nature of both side groups. Figure 7 shows the polarization IR spectra of an oriented **1c** film. The differential spectrum reveals positive absorption bands for the C═C, Ph−O−C, and N═O vibrations, and negative ones for the C═O and C−H vibrations. The *S* values at 2942 (C−H), 1726 (C═O), 1631 (C═C), 1347 (N═O), and 1252 cm^{-1} (Ph−O−C) are −0.31, −0.11, 0.74, 0.58, and 0.63, respectively. These results indicate that both the MCB and NB groups, and alkylene spacers align parallel to **E**.

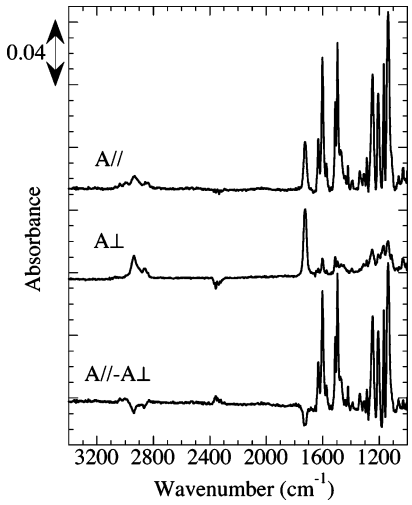

Figure 7. Polarization IR spectra of a reoriented **1c** film on CaF_2 substrate. Absorption parallel ($A_{\parallel}$), perpendicular ($A_{\perp}$) to **E** of LP 405 nm light, and differential spectrum, $A_{\parallel} - A_{\perp}$.

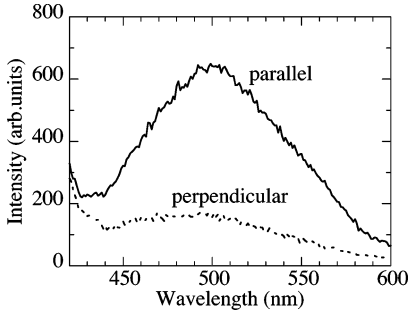

Figure 8. Polarization photoluminescence spectra of a reoriented **1c** film excited by nonpolarized 405 nm light. Film is 0.2 μm thick.

Furthermore, as shown in Figure 8, the polarization photoemission spectra of the reoriented **1c** film excited with nonpolarized 405 nm light support the cooperative molecular reorientation. It also reveals that λ_{max} for the emission parallel to the reorientation direction is 502 nm, while that for the emission perpendicular is around 480 nm. The DR for the emission intensity is 0.57. The red shift of λ_{max} is caused by the strong interaction between the MCB and NB groups after the cooperative reorientation.

3.4. Multiple Optical Data Storage Using LP 405 nm LD. Molecular reorientation in photoreactive materials is applicable to optical data storage systems.[1,2] Since the copolymer **1** films exhibit efficient molecular reorientation abilities and the key step is the axis-selective photo-cross-linking reaction of the MCB groups as described in the above section, plural exposures to LP light may independently record their axis-selective photo-cross-linked information. Thus, multiple optical data storage in a **1b** film was performed using multiexposures to LP 405 nm LD while controlling the polarization of the LD beam.

The photoinduced reorientation behavior of a 0.3 μm-thick **1b** film was initially probed using a LP LD beam. Figure 9a plots the thermally enhanced Δnd values of the films as a function of irradiation time and reveals that an induced Δnd greater than 60 nm is obtained when the exposure time is between 300 and 700 ms. In this case, the degree of the photoreaction is around 10 mol %, which implies that the reorientation behavior is similar to that obtained using LP 405 nm light. Next three types of LP LD beams with different polarization directions (LP1, LP2, and LP3, exposure time of 350 ms) were used to record the LD beams and to evaluate the

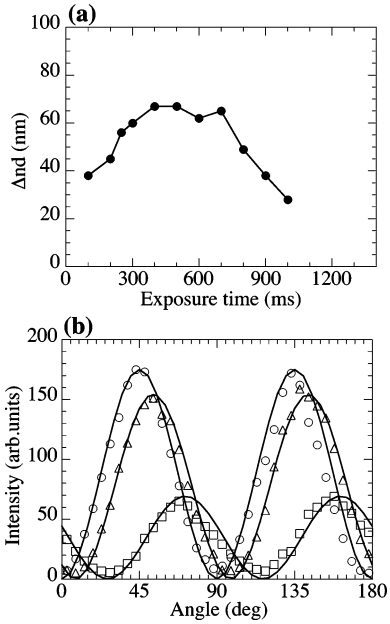

Figure 9. (a) Thermally enhanced birefringence (Δnd) values of **1b** films as a function of irradiation time of LP 405 nm LD. All the films are annealed at 190 °C for 5 min after irradiation. Δnd is measured at 633 nm. Film is 0.3 μm thick. (b) Transmittance intensity of the reoriented film exposed with three types of LP beams when the film is rotated between two crossed polarizers. **1b** films are exposed with LP1 (circle points), LP1 + LP2 (triangle points), and LP1 + LP3 (square points). All the irradiated films are annealed at 190 °C for 5 min.

thermally enhanced reorientation behavior under multiple LD exposure. The polarization directions of LP2 and LP3 beams were 15° and 50° against **E** of the LP1 beam, respectively. Then three different reoriented film were fabricated: the A-film was exposed to the LP1 beam, the B-film was exposed to the LP1 beam followed by LP2, and the C-film was exposed to the LP1 beam followed by LP3. To induce molecular reorientation, all the exposed films were annealed at 190 °C for 5 min. Figure 9b plots the transmittance intensity of the reoriented film set between two crossed polarizers as the film was rotated. It demonstrates that all the films are unixially oriented and the orientation directions are 0° for A-, 7.5° for B-, and 25° for C-films with respect to **E** of the LP1 beam. The reorientation direction for the B- and C-films is in the middle of the polarization angle of the two LP LD beams. Namely, the two directions of the photo-cross-linked anchors control the main reorientation direction of the film. The generated birefringence values are 61, 55, and 35 nm for the A-, B-, and C-films, respectively. The Δnd values for the B- and C-films are smaller than that of the A-film since irradiating with two types of LD beams is equal to using an ellipsoidal polarized light beam.[51] Although the exposure order is reversed, the molecular reorientation behaviors are similar. These results suggest that adjusting the polarization direction of the two LP light beams, which are exposed to the film, can control the orientation direction.

As summarized in Table 2, this phenomenon is successfully demonstrated since three LD light beams were used to control the reorientation direction for multiple information storage of seven kinds of data spots. The exposure time of each LD beam was 300 ms. Figure 10 shows photographs used to evaluate the reorientation direction of the recorded spots in a **1b** film with various film angles under a polarization optical microscope. It implies that the orientation direction coincides with the expected angle summarized in Table 2, which corresponds to the angle between the two beams when the spot is recorded with two LD

Table 2. Exposure Conditions and Expected Reorientation Angles of 1b Films Using Three Types of LD Beams

spot	LD beams (LP1, LP2, LP3)[a]	expected reorientation angle (deg)[b]
a	(1, 0, 0)	0
b	(1, 1, 0)	7.5
c	(0, 1, 0)	15
d	(1, 1, 1)	21.4
e	(1, 0, 1)	25
f	(0, 1, 1)	32.5
g	(0, 0, 1)	50

[a] The polarization directions of LP2 and LP3 beams are 15° and 50° against **E** of the LP1 beam, respectively. Key: on, 1; off, 0. Each LD beam is exposed for 300 ms. [b] Angle is the sum of LD beam polarization vectors.

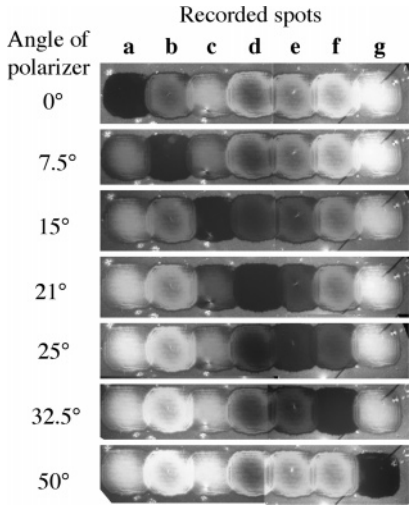

Figure 10. Polarization optical microscopy photographs of recorded spots in a 0.3 μm-thick **1b** film using three types of LP 405 nm LD with different polarization direction. Each spot corresponds to the information displayed in Table 2.

beams. The orientation direction of the recorded spot is 21° when irradiating with three LD beams (spot **d**). This value is close to the sum of the three LD beam polarization vectors. These results indicate that one recorded spot can include three kinds of information and analyzing the orientation direction can decode the stored information. Additionally, varying the intensity of the two LD beams can change the reorientation angle. Further detailed experiments to investigate these new types of recordings are currently underway.

4. Conclusion

Thermally enhanced photoinduced optical anisotropy with a sufficient reorientational order in new photo-cross-linkable LC copolymer films based on a polarization-axis-selective energy transfer was achieved using a LP 405 nm light. The energy transfer was attributed to the exciplex formation between an axis-selectively excited photosensitizer and the MCB groups. The resultant photoinduced optical anisotropy was reversely enhanced in a direction parallel to **E** of LP light. The generated DR value reached −0.025 when degree of the photoreaction was 20 mol %, and a thermally amplified *S* value of 0.75 was obtained for the copolymer, which had NB side groups as the photosensitizing group. To date, these are the largest DR and *S* values for the photoinduced reorientation in the photo-cross-linkable LC polymer films based on the polarization-preserved photosensitizing system. The axis-selectivity of the photosensitizer played an important role in generating the large photoinduced optical anisotropy of the film and the degree of thermal amplification depended on the photoinduced DR values. Since copolymer **1** films exhibited an efficient photosensitivity and photoinduced reorientation ability, plural LP 405 nm LD light exposures while changing the polarization of the LD light derived a new multiple optical data storage where the recorded information was decoded by analyzing the reorientation direction. Thus, it is anticipated that a photoinduced reorientation system using these copolymers is applicable as phase retarders for liquid crystal displays and in multiple optical data storage systems.

Acknowledgment. This work was partly supported by Grant-in-Aid for Scientific Research (S, No. 16105004, and B, No. 17350111) by Japan Society for the Promotion of Science, and Hayashi Telempu Co. Ltd.

Supporting Information Available: Text and scheme showing the synthesis of methacrylate monomer containing photosensitizing side groups. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Shibaev, V. P.; Kostromin, S. G.; Ivanov, S. A. *Polymers as Electroactive and Photooptical Media*; Shibaev, V. P., Ed.; Springer: Berlin, 1996; pp 37−110.
(2) (a) MacArdle, C. B. *Applied Photochromic Polymer Systems*; MacArdle, C. B., Ed.; Blackie: New York, 1991; pp 1−30. (b) Krongauz, V. *Applied Photochromic Polymer Systems*; MacArdle, C. B., Ed.; Blackie: New York, 1991; pp 121−173.
(3) Ichimura, K. *Chem. Rev.* **2000**, *100*, 1847−1873.
(4) O'Neill, M.; Kelly, S. M. *J. Phys. D: Appl. Phys.* **2000**, *33*, R67−R84.
(5) Natansohn, A.; Rochon, P. *Chem. Rev.* **2002**, *102*, 4139−4176.
(6) Kawata, S.; Kawata, Y. *Chem. Rev.* **2000**, *100*, 1777−1788.
(7) Kawatsuki, N.; Kawakami, T.; Yamamoto, T. *Adv. Mater.* **2001**, *13*, 1337−1339.
(8) (a) Kawatsuki, N.; Sakai, T.; An, M. X.; Hasegawa, T.; Yamamoto, T. *Proc. SPIE* **2001**, *4463*, 109−116. (b) Kawatsuki, N.; An, M. X.; Hasegawa, T.; Yamamoto, T.; Sakai, T. *Jpn. J. Appl. Phys.* **2002**, *41*, L198−L200.
(9) Wu, Y.; Natansohn, A.; Rochon, P. *Macromolecules* **2004**, *37*, 6801−6805.
(10) Schadt, M.; Seiberle, H.; Schuster, A.; Kelly, S. M. *Jpn. J. Appl. Phys.* **1995**, *34*, 3240−3249.
(11) Schadt, M.; Seiberle, H.; Schuster, A. *Nature (London)* **1996**, *381*, 212−215.
(12) Kawatsuki, N.; Matsuyoshi, K.; Hayashi, M.; Takatsuka, H.; Yamamoto, T. *Chem. Mater.* **2000**, *12*, 1549−1555.
(13) Gu, H.-W.; Xie, P.; Fu, P.-F.; Zhang, T.-Y.; Zhang, R.-B. *Adv. Funct. Mater.* **2005**, *15*, 125−130.
(14) Wilderbeek, H.-T. A.; Teunissen, J.-P.; Bastiaansen, C. W. M.; Broer, D. J. *Adv. Mater.* **2003**, *15*, 985−988.
(15) Lee, J.; Lee, J.-I.; Sung, S.-J.; Chu, H. Y.; Park, J.-K.; Shim, H.-K. *Macromol. Chem. Phys.* **2004**, *205*, 2245−2251.
(16) Ikeda, T. *J. Mater. Chem.* **2003**, *13*, 2037−2057.
(17) Todorv, T.; Nikolova, L.; Tomova, N. *Appl. Opt.* **1984**, *23*, 4309−4312.
(18) Wu, Y.; Natansohn, A.; Rochon, P. *Macromolecules* **2004**, *37*, 6090−6095.
(19) Häckel, M.; Kador, L.; Kropp, D.; Frenz, C.; Schmidt, H.-W. *Adv. Funct. Mater.* **2005**, *15*, 1722−1727.
(20) Kawatsuki, N.; Hasegawa, T.; Ono, H.; Tamoto, T. *Adv. Mater.* **2003**, *15*, 991−994.
(21) Nedelchev, L. L.; Matharu, A. S.; Hvilsted, S.; Ramanujam, P. S. *Appl. Opt.* **2003**, *42*, 5918−5927.
(22) (a) Wu, Y.; Demachi, Y.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Macromolecles* **1998**, *31*, 1104−1108. (b) Wu, Y.; Demachi, Y.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Macromolecles* **1998**, *31*, 4457−4463.
(23) Natansohn, A.; Rochon, P.; Gosselin, J.; Xie, S. *Macromolecules* **1992**, *25*, 2268−2273.
(24) (a) Fischer, T.; Läsker, L.; Czapla, S.; Rübner, J.; Stumpe, J. *Mol. Cryst. Liq. Cryst.* **1997**, *298*, 213−220. (b) Meier, J. G.; Ruhmann, R.; Stumpe, J. *Macromolecles* **2000**, *33*, 843−850.
(25) (a) Han. M.; Ichimura, K. *Macromolecles* **2001**, *34*, 90−98. (b) Han, M.; Morino, S.; Ichimura, K. *Macromolecles* **2000**, *33*, 6360−6370.

(26) (a) Kawatsuki, N.; Suehiro, C.; Yamamoto, T. *Macromolecules* **1998**, *31*, 5984−5990. (b) Kawatsuki, N.; Matsuyoshi, K.; Yamamoto, T. *Macromolecules* **2000**, *33*, 1698−1702.
(27) Kawatsuki, N.; Ono, H.; Takatsuka, H.; Yamamoto, T.; Sangen, O. *Macromolecules* **1997**, *30*, 6680−6682.
(28) Ichimura, K.; Akita, Y.; Akiyam, H.; Kudo, K.; Hayashi, Y. *Macromolecules* **1997**, *30*, 903−911.
(29) Kawatsuki, N.; Goto, K.; Kawakami, T.; Yamamoto, T. *Macromolecules* **2002**, *35*, 706−713.
(30) Anderle, K.; Birenheide, R.; Eich, M.; Wendorff, J. H. *Macromol. Chem. Phys.* **1989**, *10*, 477−483.
(31) (a) Shi, Y.; Steier, W. H.; Yu, L.; Chen, M.; Dalton, L. R. *Appl. Phys. Lett.* **1991**, *59*, 2935−2937. (b) Shi, Y.; Steier, W. H.; Yu, L.; Chen, M.; Dalton, L. R. *Appl. Phys. Lett.* **1991**, *58*, 1131−1133.
(32) Rochin, P.; Gosselin, J.; Natansohn, A.; Xie, S. *Appl. Phys. Lett.* **1992**, *60*, 4−5.
(33) Natansohn, A.; Rochon, P.; Pézolet, M.; Audet, P.; Brown, D.; To, S. *Macromolecules* **1994**, *27*, 2580−2585.
(34) Cimrová, V.; Neher, D.; Kostromine, S.; Bieringer, Th. *Macromolecules* **1999**, *32*, 8496−8503.
(35) Jackson, P. O.; O'Neill, M.; Duffy, W. L.; Hindmarsh, P.; Kelly, S. M.; Owen, G. J. *Chem. Mater.* **2001**, *13*, 694−703.
(36) Jain, S. C.; Kitzerow, H. S. *Appl. Phys. Lett.* **1994**, *64*, 2946−2948.
(37) Schadt, M.; Seiberle, H.; Schuster, A.; Kelly, S. M. *Jpn. J. Appl. Phys.* **1995**, *34*, L764−L767.
(38) Ichimura, K.; Kidowaki, M.; Akiyama, H.; Kudo, K. *Macromol. Rapid Commun.* **1996**, *17*, 545−551.
(39) Chang, J. Y.; Nam, S. W.; Hong, C. G.; Im, J.-H.; Kim, J.-H.; Han, M. J. *Adv. Mater.* **2001**, *13*, 1298−1301.
(40) Kawatsuki, N.; Fukumoto, H.; Takeuchi, O.; Furuso, N.; Yamamoto, T. *Polymer* **2004**, *45*, 2615−2621.
(41) Ono, H.; Emoto, A.; Kawatsuki, N.; Hasegawa, T. *Appl. Phys. Lett.* **2003**, *82*, 1359−1361.
(42) Kawatsuki, N.; An, M. X.; Matsuura, Y.; Sakai, T.; Takatsuka, T. *Liq. Cryst.* **2004**, *31*, 55−60.
(43) Kawatsuki, N.; Tachibana, T.; An, M. X.; Kato, K. *Macromolecules* **2005**, *38*, 3903−3908.
(44) Nakamura, K.; Kikuchi, S. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1977−1982.
(45) Tsuda, M. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 905−908.
(46) Turro, N. J. *Modern Molecular Photochemistry*; The Benjamin/Cummings Publishing Co.: Menlo Park, NJ, 1978.
(47) Ermolaev, V. L. *Soviet Phys., Dokl.* **1962**, *6*, 600−602.
(48) The transition moment of NB moiety, calculated by the MOPAC method, is 2.7, while that of NP moiety is 1.9.
(49) Furumi, S.; Ichimura, K. *Appl. Phys. Lett.* **2004**, *85*, 224−226.
(50) Kawatsuki, N.; Takatsuka, H.; Yamamoto, T.; Sangen, O. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1521−1526.
(51) Kawatsuki, N.; Takatsuka, H.; Yamamoto, T. *Appl. Phys. Lett.* **1999**, *75*, 1386-1388.

MA060117T