

Highlight Review

Photoalignment and Photoinduced Molecular Reorientation of Photosensitive Materials

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Abstract

Photosensitive materials for photoalignment of liquid crystals (LCs) and photoinduced molecular reorientation are described, especially focusing on azobenzene-containing materials and photocrosslinkable polymers. All the materials generate photoinduced optical anisotropy by means of linearly polarized (LP) light exposure. The large optical anisotropy is induced when the axis-selective photoreaction is accompanied by molecular reorientation.

◆ Introduction

Due to practical applications of the alignment layer of functional materials such as low-molecular-weight liquid crystals (LCs), photoalignment and photoinduced molecular reorientation of photosensitive films have received much attention.^{1–3} Additionally, these films have been investigated for molecularly oriented birefringent devices due to the absence of mechanical damage, absence of electric charge, and patterning ability.^{1–3} Photoinduced optical and physical anisotropies can be generated in a photoreactive polymeric film by light exposure because the photoreaction changes the inherent refractive index of the molecules. Irradiating with linearly polarized (LP) light causes the photosensitive molecules parallel to the polarization (**E**) of LP light (*y* axis) to preferentially photoreact (Figure 1). This axis-selective photoreaction leads to optical anisotropy (birefringence) between the *y* axis and *xz* plane if the photoreaction changes the inherent refractive indices of the molecules.

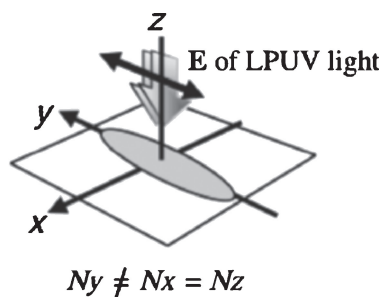


Figure 1. Schematic illustration of axis-selective photoreaction.

To obtain uniaxial alignment of LCs on thin polymeric films, the LC photoalignment layer should exhibit optical or physical anisotropy. Under this circumstance, a large molecular orientation of the film is unnecessary. The anisotropic interaction between the photoalignment layer and LC molecules induces uniaxially oriented LC molecules.¹ Because the axis-selective photoreaction induces a small change in the refractive index of the photoalignment layer,⁴ a thick film is necessary for optically anisotropic devices such as a birefringent film. Consequently, a large optical anisotropy in the photoreacted film is generated when molecular reorientation occurs during an anisotropic photoreaction.³

Various types of materials that undergo an axis-selective photoreaction to generate photoinduced optical anisotropy have been investigated, including azobenzene-containing polymers^{2,5–7} and photocrosslinkable polymers.^{1,3,4} For the azobenzene molecules, axis-selective photoisomerization is generated when the film is irradiated with linearly polarized (LP) light (Figure 2a). Similarly, irradiating with LP ultraviolet (LPUV) light induces both axis-selective [2 + 2] photo/cycloaddition (photocrosslinking) reaction and photoisomerization for cinnamic ester derivatives (Figure 2b). Low-molecular LC molecules easily align on these anisotropically photoreacted films. When an axis-selective photoreaction occurs without generating molecular reorientation, the photoinduced birefringence (Δn) is less than 0.01.⁴ An anisotropic photoreaction combined with molecular motion may generate a large optical anisotropy ($\Delta n > 0.1$). This review describes recent progress on photoreactive materials for LC photoalignment technology that can generate photoinduced molecular reorientation with a large optical anisotropy.

◆ Photoalignment for Liquid Crystals

Photoalignment control of LCs on azobenzene molecules was initially developed by Ichimura's group using an azobenzene LB monolayer.⁸ They investigated the control between the in-plane and out-of-plane LC alignment based on trans-cis photoisomerization.^{8,9} The control of the in-plane LC alignment direction has been achieved via an axis-selective photoreaction in photosensitive materials using LP light.¹⁰ Many materials have been developed as the photoalignment layer to align not only LCs but also other functional materials such as dichroic dyes,^{11,12} electroluminescent materials,^{13–15} mesoporous silica,^{16,17} and conducting materials.^{18–20}

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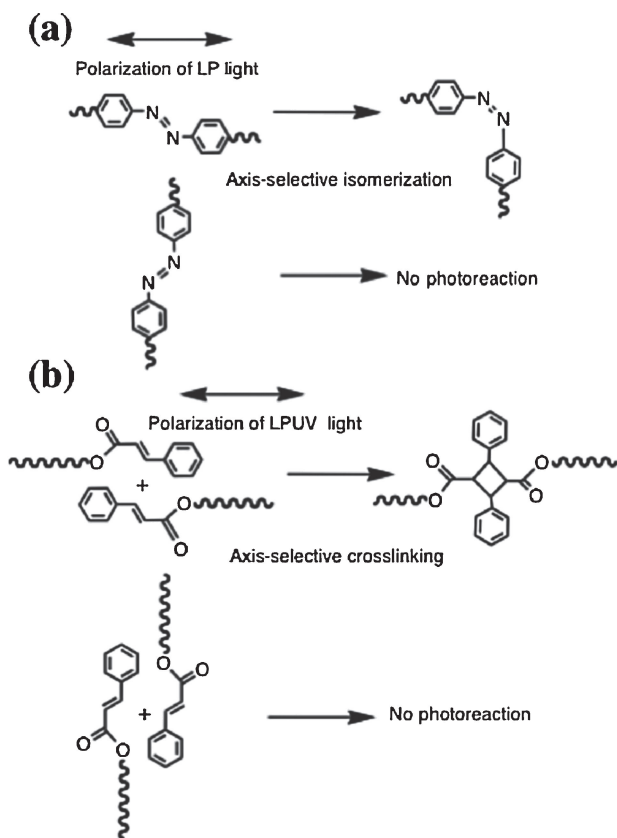


Figure 2. Axis-selective photoreaction of (a) azobenzene and (b) cinnamate moieties.

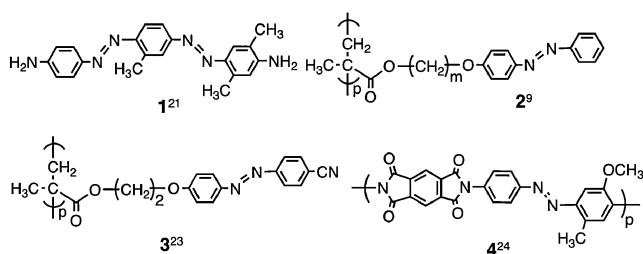


Figure 3. Azobenzene derivatives for the LC photoalignment.

Because LC molecules preferentially interact with *trans*-azobenzene, LCs align parallel to the direction of the *trans*-azobenzene molecules. Numerous azobenzene-containing materials can control the in-plane LC alignment (Figure 3). In many cases, LCs align perpendicular to the polarization of LP light when the photoalignment azobenzene-containing layer is exposed to LP light.^{1,10} Gibbons et al. investigated a polyimide film doped with azobenzene **1** as the LC alignment layer and demonstrated the photoregulation of the LC alignment direction.^{21,22} Polymethacrylates with azobenzene side groups such as **2** and **3** are also useful for homogeneous LC alignment. **3** exhibits a high thermal stability up to 280 °C due to its high glass-transition temperature.²³ Photopatterning dichroic dye molecules onto the photoalignment azobenzene-containing layer can fabricate a polarizer film.¹¹ Azobenzene-containing polyimide **4** shows a high orientation order by irradiating with LP

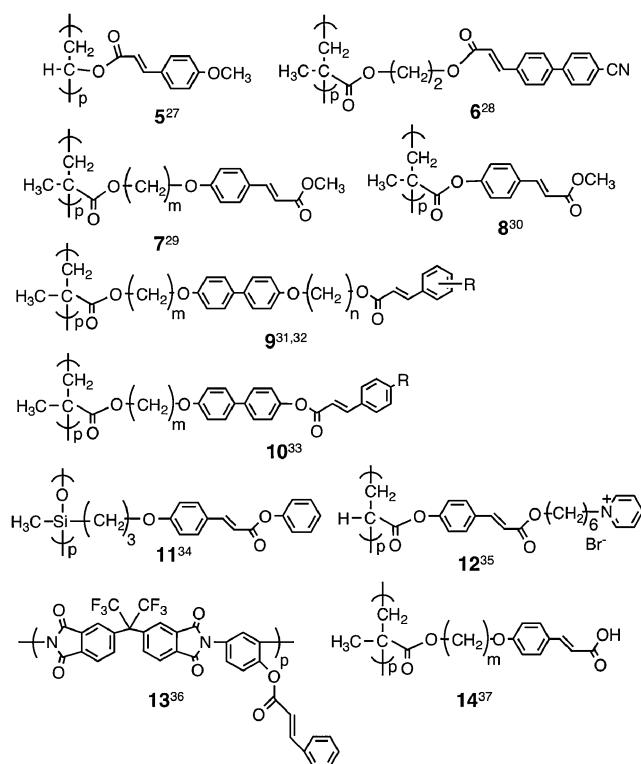


Figure 4. Cinnamate-containing polymers for the LC photoalignment.

light²⁴ and can align various types of functional materials such as fullerene derivatives and pentacene for organic electroluminescent and semiconductor applications, respectively.^{14,18,25}

Many photocrosslinkable materials, including cinnamate, coumarin, calcone, stilbene, styrylpyridine, phenylacetylene, and anthracene groups, have been synthesized as photoreactive moieties for LC photoalignment.^{26–36} Figure 4 summarizes photoreactive polymers containing cinnamate groups for the LC alignment layer. Schadt et al. initially reported LC photoalignment on poly(vinyl cinnamate) (PVCi) derivative **5** based on axis-selective photocrosslinking caused by LPUV light.²⁶ Commercially available PVCi has also been utilized in LC photoalignment technology.^{37–39} These materials focus on the anisotropic photoreaction of the cinnamate moieties to investigate the LC photoalignment behavior. Polyimide with cinnamate side groups **13** has been synthesized to improve thermal stability.³⁵ Additionally, polymethacrylates with cinnamic acid side groups **14** act as the LC photoalignment layer.³⁶

Similar to the case with an azobenzene photoalignment layer, the LC alignment direction in PVCi is perpendicular to **E** of LPUV. In contrast, for **8**, **9**, and **10**, the LC alignment direction can be controlled both parallel and perpendicular to the polarization of LPUV light by adjusting the degree of the photoreaction in the film.^{29–32} LC alignment on the photoalignment layer parallel to **E** is important to generate the tilt angle formation of the aligned LCs when three-dimensional anisotropy in the photoalignment layer is induced via slantwise p-polarized LPUV light exposure.³⁰

Various factors determine the orientation direction of LCs in axis-selective photoreacted polymeric films with cinnamate

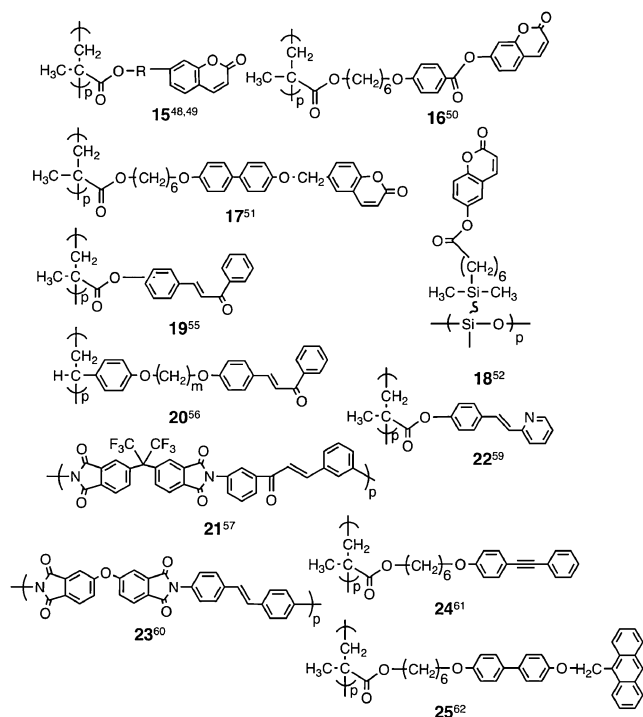


Figure 5. Photocrosslinkable polymers containing coumarin, calcene, styrylpyridine, stilbene, diphenylacetylene, and anthracene groups for photoalignment of LCs.

groups. When the photoreacted moieties align perpendicular to **E** and preferentially interact with LCs as indicated by Schadt et al.,²⁶ the LC alignment direction is perpendicular to **E** because LCs align along the photoreacted moieties. Additionally, when the photoproducts reduce the interaction with LCs, LCs align along the remaining cinnamate direction, resulting in perpendicular LC alignment. In contrast, when the direction of the photoreacted moieties is parallel to **E** and the photoproducts preferentially interact with LCs, parallel LC alignment to **E** is achieved.³⁰ Ichimura et al. have systematically studied the axis-selective photoreaction of polymethacrylates with cinnamate side groups and clarified the influence of the distribution of [2 + 2] photocycloaddition and photoisomerized photoproducts on the LC photoalignment behavior.²⁸ Furthermore, in **9** and **10**, which exhibit LC characteristics, the biphenyl mesogenic moieties play an important role in determining the LC alignment direction after the axis-selective photoreaction.^{30–32}

For the PVCi photoalignment layer, the azimuthal-anchoring energy is much lower than that for a rubbed polyimide LC alignment film.⁴⁰ The molecularly oriented photoalignment layer based on photoreactive liquid-crystalline polymeric film **10** is reported to improve the azimuthal-anchoring energy due to the improved interaction between the LCs and oriented mesogenic side groups in the alignment layer.⁴¹ Furthermore, polarization-selective photosensitization of cinnamate-containing polymeric films has been explored to improve the photosensitivity.^{42–46}

Figure 5 shows photocrosslinkable polymers other than cinnamates for the photoalignment of LCs. The axis-selective [2 + 2] photocrosslinking of coumarin-containing polymeric films such as **15–18** have been investigated.^{47–51} Because coumarin derivatives only undergo a [2 + 2] photocycloaddition

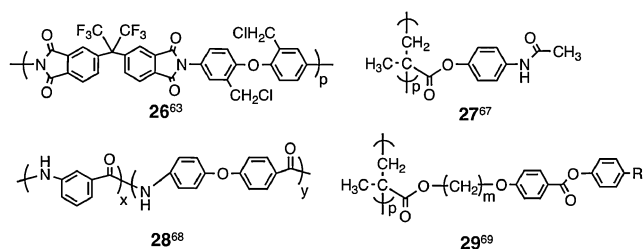


Figure 6. Polyimide, polymers with amide groups, and liquid crystalline polymethacrylate with benzoate side groups for photoalignment of LCs.

reaction, the photocrosslinked products determine the LC alignment direction. Schadt et al. have fabricated a multidomain LC cell using **15** by means of patterned slantwise LPUV light exposure where the LC alignment direction is parallel to **E**.⁴⁷ Additionally, the influences of the type of photoproduct of thin coumarin-containing polymethacrylate film on the LC alignment behavior have been investigated.^{48,49} Whether parallel or perpendicular LC alignment is observed depends on the distribution of *head-to-head* crosslinked and *head-to-tail* crosslinked products.^{48,49} Chen et al. have systematically investigated alignment control of LCs using photoluminescent materials with several types of photoalignment coumarin-containing polymeric films.^{52,53} Calcene-containing polymers **19–21** have also been employed as the LC alignment layer.^{54–56} Kimura et al. synthesized **20**, which exhibits a large azimuthal-anchoring energy with a high photoreactivity.⁵⁵ They have also proposed a new LPUV light exposing method to achieve pretilt formation of the LC orientation.⁵⁷ Other photocrosslinkable polymers containing styrylpyridine **22**,⁵⁸ stilbene **23**,⁵⁹ diphenylacetylene **24**,⁶⁰ and anthracene **25**⁶¹ groups also exhibit axis-selective photocrosslinking and act as photoalignment layers in LCs.

Other photosensitive polymers have also been synthesized as the LC photoalignment layer (Figure 6). The axis-selective photodegradation of a thin polyimide film such as **26** is applicable to the LC photoalignment.⁶² Conventional polyimides for the rubbed LC alignment layer are also useful for LC photoalignment.⁶³ Pretilt angle control of LC alignment is attained by slantwise LPUV light exposure to a polyimide film with side groups.^{64,65} Polymethacrylate with amide side groups **27** and polyamide **28** are also active for the LC photoalignment.^{66,67} Furthermore, liquid-crystalline polymer **29** shows an axis-selective photo-Fries rearrangement of the benzoate side groups followed by thermally amplified molecular reorientation, and the resultant film has an LC alignment ability.⁶⁸ In this case, the LC alignment direction depends on the exposure energy and type of end substituent groups.

◆ Photoinduced Molecular Orientation

Photosensitive polymeric films can generate a large optical anisotropy when the axis-selective photoreaction is accompanied by molecular reorientation. For azobenzene-containing polymeric films, a reversible photoinduced molecular reorientation has been reported. This reorientation is applicable to rewritable optical and holographic memories.^{5,6,9,69–72} Passive optical elements can be created using photocrosslinkable polymers with thermally enhanced molecular reorientation.^{3,73–75}

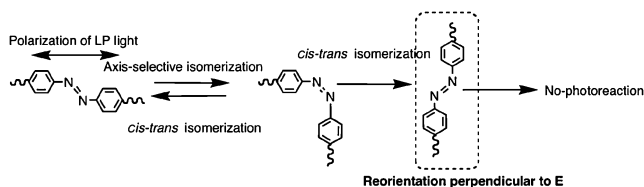


Figure 7. Photoinduced reorientation of the azobenzene moieties through axis-selective *trans*–*cis* photoisomerization and *cis*–*trans* back-isomerization.

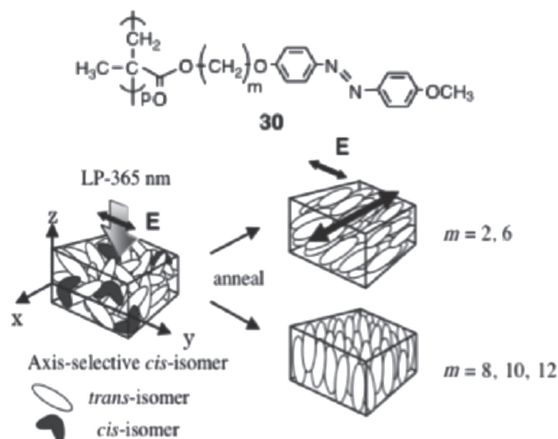


Figure 8. Model illustrating the thermally enhanced in-plane and out-of-plane reorientation of 30 films generated by irradiating with LP-365-nm light and annealing.

When the axis-selective *trans*–*cis* photoisomerization reaction in azobenzene molecules is combined with *cis*–*trans* back-isomerization simultaneously, a versatile photoinduced molecular orientation of the azobenzene groups is generated (Figure 7).⁹ In this case, the *cis*–*trans* back-photoisomerization thermally or photochemically does not absorb the incident LP light, resulting in reorientation perpendicular to **E**. Therefore, the wavelength of the LP light and reaction temperature for the photoinduced molecular reorientation are important due to the different thermal stability and *trans*/*cis* isomer ratio at the photostationary state upon irradiation.^{76–79} This phenomenon is observed in both amorphous and liquid-crystalline polymers with azobenzene side groups.^{80–84} Cooperative molecular reorientation can be generated in a copolymer containing azobenzene and nonphotosensitive side groups when the copolymer exhibits liquid-crystalline characteristics.^{85–89} There are some review articles about the photoinduced molecular reorientation behavior of azobenzene-containing polymeric films.^{5,6,9,90} Additionally, thermal enhancement of the photoinduced optical anisotropy of the liquid-crystalline azobenzene-containing polymethacrylates has been observed.^{91,92} For example, polymethacrylate with 4-methoxyazobenzene side groups **30** displays thermally enhanced in-plane or out-of-plane molecular reorientation, depending on the length of the alkylene spacer and the amount of the axis-selectively formed *cis* isomers, as illustrated in Figure 8.^{76,92} Furthermore, Seki et al. have investigated the control of the microphase separation direction in diblock copolymers containing azobenzene groups by adjusting the polarization of the exposed LP light.⁹⁰

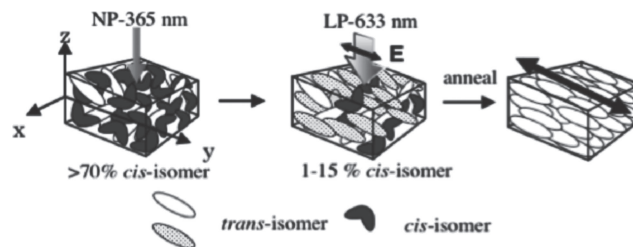


Figure 9. Model illustrating the thermally enhanced in-plane and out-of-plane reorientations of 30 films generated by irradiating with NP-365-nm light and subsequently irradiating with LP-633-nm light and annealing.

Several groups have investigated photoinduced reorientation parallel to **E** of azobenzene-containing polymeric films.^{93–96} This technique uses nonpolarized ultraviolet (NPUV) light combined with longer wavelength LP light where the *trans*-azobenzene groups are almost off-resonant. Namely, molecular reorientation is based on an axis-selective photoreaction of the *cis* isomers, which are prepared by exposure to NPUV light in advance. Kempe et al. have reported the photoinduced reorientation of polymeric films with 4-cyanoazobenzene side groups using linearly polarized (LP) 633-nm light combined with pre-exposure to NPUV light to create a photostationary state of the *cis* isomers prior to irradiating with 633-nm light.^{93,94} As shown in Figure 9, the thermally enhanced reorientation of **30** using LP-633-nm light has achieved an in-plane reorientational order greater than 0.8.^{95,97} In this case, the orientation behavior is independent of the alkylene spacer length.

Thermally enhanced photoinduced molecular reorientation in photocrosslinkable liquid-crystalline polymers with cinnamate and cinnamic acid side groups has been reported.^{32,36,98–101} Because cinnamate derivatives are transparent in the visible region, they are useful for display applications.^{73–75} When a photocrosslinkable liquid-crystalline polymeric film is irradiated with LPUV light, axis-selective photocrosslinking is induced. In this situation, photoinduced optical anisotropy of the film is small because molecular reorientation does not occur. If the axis-selectively formed products act as impurities in the film, a thermal treatment at the liquid-crystalline temperature range of the film generates reorientation perpendicular to **E** of LPUV light due to the greater liquid-crystalline properties in this direction (route A in Figure 10). This is similar to the thermal enhancement of azobenzene-containing polymers that form the axis-selective *cis* isomer upon irradiating with LP light (Figure 8). In contrast, thermally enhanced reorientation parallel to **E** is generated when the axis-selectively formed photocrosslinked products act as photocrosslinked anchors to thermally reorient non photoreacted mesogenic side groups parallel to them (route B in Figure 10).³²

Several photocrosslinkable liquid-crystalline polymers have been developed to generate in-plane photoinduced molecular orientation with a large orientational order (Figure 11). In all cases, a very small optical anisotropy is generated after the axis-selective photoreaction ($S < 0.1$, $\Delta n < 0.01$), while annealing in the liquid-crystalline temperature range of the film reverts the optical anisotropy ($S > 0.5$, $\Delta n > 0.15$), resulting in the molecular reorientation parallel to **E**. Polymethacrylates with tolane mesogenic groups **32** and **33** exhibit a large photoinduced

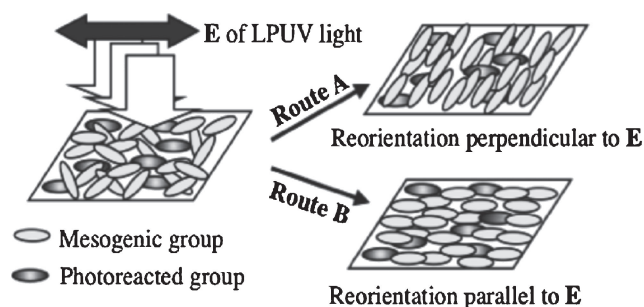


Figure 10. Schematic illustration of thermally enhanced molecular reorientation in a photocrosslinkable liquid-crystalline polymeric film.

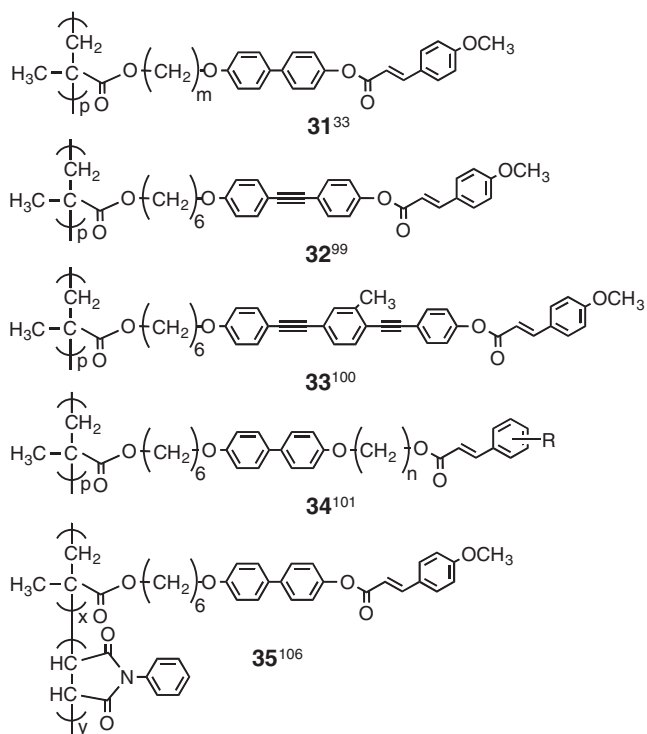


Figure 11. Photocrosslinkable liquid crystalline polymers exhibiting a thermally enhanced photoinduced molecular orientation.

birefringence due to the large inherent birefringence of the tolane moieties.^{98–100,102,103} For **34**, an effective photoinduced molecular reorientation is observed when $n = 3$, but the reorientation order is small when $n = 2$.¹⁰¹ The linearity between biphenyl and cinnamate end groups plays an important role for sufficient molecular reorientation.¹⁰⁴ Table 1 summarizes thermally enhanced molecular reorientation order and direction and generated birefringence of photocrosslinkable liquid-crystalline polymeric films. Generally, polymers containing mesogenic side groups with cinnamate end groups demonstrate molecular reorientation parallel to **E**. However, the reorientation for cinnamic acid side groups **14** is perpendicular to **E**.³⁶ Additionally, for **35**, adjusting the degree of the photoreaction controls the reorientation direction both perpendicular and parallel to **E**. Furthermore, cooperative molecular reorientation and control of

Table 1. Reorientation direction, in-plane order parameter and birefringence of photocrosslinkable liquid-crystalline polymers

| Polymer | Direction ^a | S^b | Δn^c |
|-----------------------|------------------------|-------|--------------|
| 31 ($m = 6$) | | 0.7 | 0.24 |
| 32 ($n = 3$) | | 0.6 | 0.18 |
| 33 | | 0.7 | 0.27 |
| 34 | | 0.65 | 0.34 |
| 14 | ⊥ | 0.7 | 0.15 |

^a|| and ⊥ denote reorientation parallel and perpendicular to **E** of LPUV light, respectively. ^bReorientational in-plane order parameter. ^cBirefringence at 633 nm.

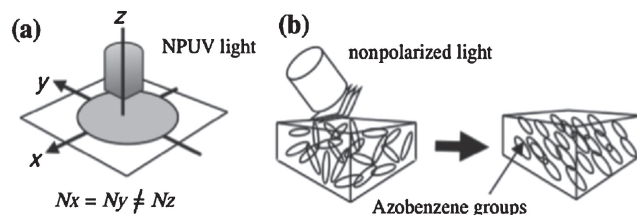


Figure 12. (a) Schematic illustration of the direction-selective photoreaction using nonpolarized light. (b) Schematic illustration of slantwise molecular reorientation in azobenzene-containing polymeric film with nonpolarized light.

the generated birefringence have been realized by copolymerization using comonomers with nonphotosensitive side groups, which is similar to the case for azobenzene-containing copolymers.^{105–107}

◆ Three-dimensional Orientation

For photosensitive materials that exhibit molecular reorientation perpendicular to **E**, out-of-plane reorientation may occur because molecules aligned along the z axis are inactive. For example, the in-plane and the out-of-plane reorientation behavior of **30** upon irradiating with various wavelengths of LP light has been investigated; the photoreactivities of the trans and cis isomers depend on the wavelength of light.^{76,78} Both the wavelength of LP light and the substituents on the azobenzene groups play important roles in the three-dimensional (3D) molecular reorientation direction.^{76–78}

Furthermore, nonpolarized (NP) light exposure to the azobenzene-containing polymeric films generates out-of-plane reorientation.^{108,109} Because the “direction-selective photoreaction” in the xy plane preferentially occurs via NP light exposure (Figure 12a), photoinduced optical anisotropy with molecular reorientation between the xy plane and z axis can be generated. Therefore, azobenzene molecules are reoriented according to the incident NP light direction (Figure 12b).^{109,110}

In contrast, photocrosslinkable materials exhibiting reorientation parallel to **E** generate the three-dimensional molecular reorientation via slantwise p-polarized LP light exposure (Figure 13a).^{73,74} For example, Figure 13b plots the angular dependence of the retardation of a **31** ($m = 6$) film exposed to slantwise LP light (45° with p-polarization) and subsequent annealing.⁷³ Retardation varies between 47 and 118 nm when the incident angle is changed, and the mesogenic groups are aligned in a hybrid manner because the minimum retardation is not zero.

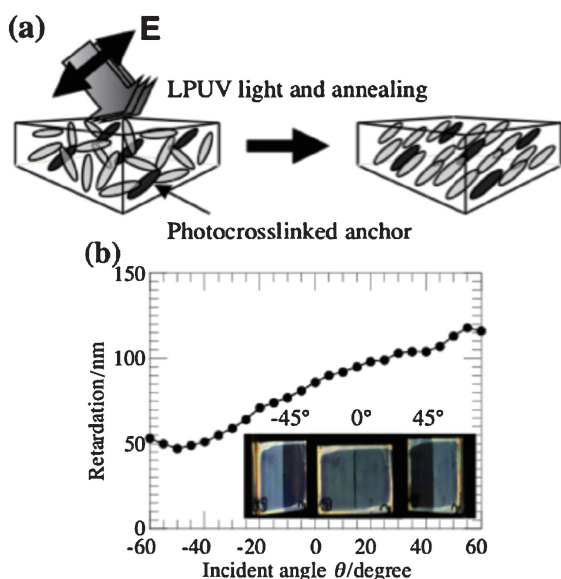


Figure 13. (a) Schematic illustration of slantwise molecular reorientation in a photocrosslinkable polymeric film with p-polarized LPUV light. (b) Angular dependence of the retardation of a 30 ($m = 6$) film (with thickness of $0.48 \mu\text{m}$) fabricated by exposing to LPUV light for 2.25 J cm^{-2} at a 45° irradiation angle and subsequent annealing at 150°C for 30 min. Inset shows photographs of the transmittance of a patterned film as examined between crossed polarizers when viewed at -45° , 0° , and 45° with respect to the surface normal.

This film is suitable for the optical compensation to improve the viewing angle in TN-LCDs.

◆ Outlook

Photoalignment materials have many advantages for the fabrication of molecularly oriented functional devices. Azobenzene-containing materials and photocrosslinkable polymers have been developed based on axis-selective photoisomerization and photocrosslinking. Both materials have realized practical applications. Various azobenzene-containing polymers are used in high-density holographic memory. The photoinduced molecular reorientation technique should be useful for next-generation holography, including polarization information. Additionally, the thermal stability of the photoalignment layer may be improved by introducing polymers exhibiting high T_g , such as a polyimide structure. Such films will be useful for anisotropic organic electric devices. Moreover, molecularly orientable materials should be applicable to display applications, including a patterned retarder film for 3D displays, because the molecularly oriented structure can be easily fabricated.

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