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Review

Alignment modulation of azobenzene-containing liquid crystal systems by photochemical reactions

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Abstract

Recent progress in alignment modulation of azobenzene-containing liquid crystal systems by photochemical reactions has been reviewed by dividing the modulation methods into two types: phase transitions (order–disorder change) and change of liquid crystal directors (order–order change). First, photochemical phase transitions and alignment changes of liquid crystals in guest/host mixtures and polymers are summarized. Then, alignment control of liquid crystals by linearly polarized light and photoactive surface layers is discussed. Finally, recent applications of alignment change and photochemical phase transitions of liquid crystals in holographic technology and photomechanical effects are introduced. In addition, future possible applications for a variety of practical devices, such as display devices, optical switching and reversible optical image storage, are mentioned.
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Keywords: Liquid crystal; Azobenzene; Photoisomerization; Photochemical phase transition; Alignment change; Holography; Photomechanical effect

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1. Introduction

Liquid crystals (LCs) represent thermodynamically stable phases situated conceptually between an ordinary isotropic liquid and a crystalline solid. Due to simultaneously possessing the optical anisotropy of the crystal and the fluidity of the liquid, LCs show many unique properties, including self-organizing nature, fluidity with long-range order, cooperative motion, anisotropy in physical properties (optical, electrical and magnetic), and alignment change by external fields at surfaces and interfaces [1]. These properties have enabled LCs to be widely used in display technologies and various photonic applications, including optical storage, optical switching, optical computers and integrated optical devices for communication.

Controlling the LC alignment by external fields is the most important technology in various devices that use LCs as active media. For instance, in LC displays, LC materials placed in a cell are sandwiched between two electrodes, and electric fields are applied across the cell. Upon application of the voltage, LC molecules change their alignment from parallel (homogeneous alignment) to perpendicular (homeotropic alignment) with respect to the glass substrate (electrical Freedericksz transition). As a result, transmittance through a pair of crossed polarizers, with the LC cell placed between them, decreases due to loss of birefringence of the cell. In this way, bright–dark contrast is produced at each pixel, and two-dimensional images can be displayed in LC displays [1].

In this review, two types of alignment modulation of LCs induced by photochemical reactions are discussed: (1) phase transitions (order–disorder change); and (2) change of LC directors (order–order change) (Fig. 1). In both cases, a large change in refractive index can be induced. As Fig. 1A shows, linearly polarized light (LPL) with its electric vector oscillating in the vertical direction detects an extraordinary refractive index n_e when LC molecules are aligned vertically. A phase transition gives rise to a change in refractive index $n_e - n$,

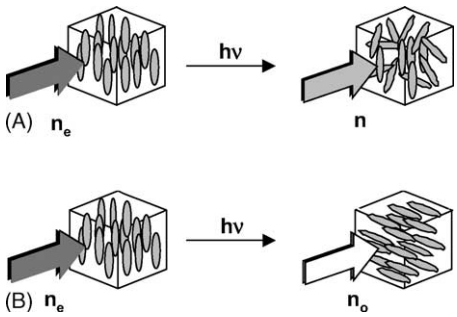


Fig. 1. Two types of alignment modulation of LCs induced by photochemical reactions: (A) phase transitions (order–disorder change); (B) change of LC directors (order–order change).

where n is the refractive index of an isotropic phase. As Fig. 1B shows, if the alignment of LC molecules is changed from the vertical state to the horizontal state, LPL will detect an ordinary refractive index n_o and a change in refractive index corresponding to birefringence, Δn ($= n_e - n_o$), of the LCs can be induced. The birefringence of LCs is usually quite large, so that changing the alignment of LC molecules by light produces a large change in the refractive index. The order of the refractive index is usually $n_e > n > n_o$; thereby, the change in the director gives rise to a larger change in refractive index than does the phase transition.

2. Photochemical phase transitions and alignment change of liquid crystals in guest/host mixtures

2.1. Photochemical phase transitions in azobenzene/nematic liquid crystal systems

As mentioned above, LC molecules exhibit good cooperative motion; thus, if a small portion of the LC molecules

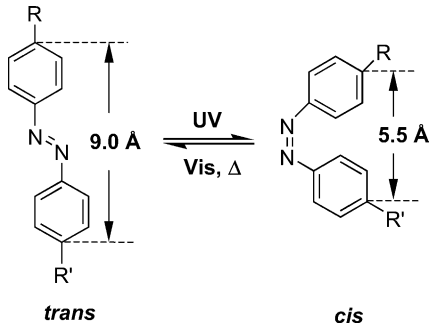


Fig. 2. Isomerization of azobenzene derivatives.

change their alignment in response to an external stimulus, the alignment of other LC molecules also changes (domino effect). It has been proposed that an amount of energy so small as to induce an alignment change of only 1 mol% of the LC molecules is enough to bring about an alignment change of the whole system [2].

It is well known that photochromic molecules such as azobenzenes can undergo a reversible photochemical reaction between two forms (Fig. 2). When a small number of photochromic molecules are incorporated into the LC molecules and the resulting guest/host mixtures are irradiated to cause photochemical reactions of the photochromic guest molecules, an LC-to-isotropic phase transition of the mixtures can be induced isothermally (Fig. 3A). This photochemically induced phase transition is called a photochemical phase transition and is reversible. The idea is very simple. The *trans* form of the azobenzene, with a rod-like shape,

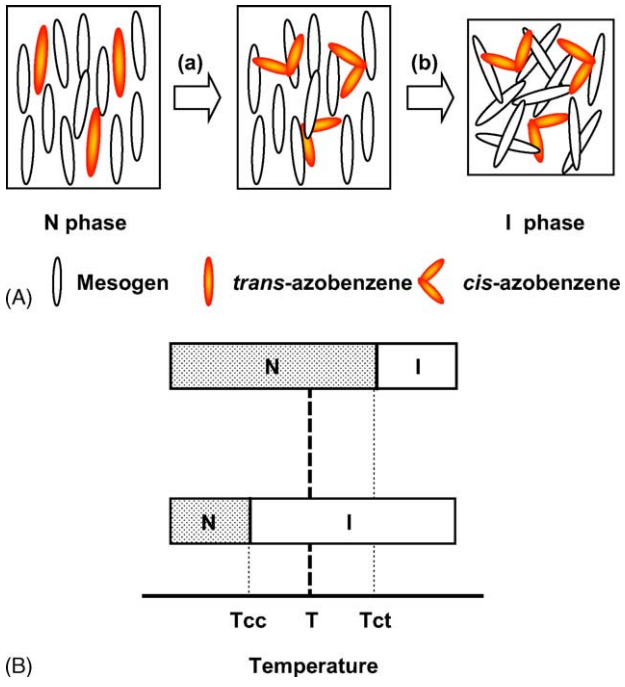


Fig. 3. (A) The process and (B) phase diagram of the photochemical phase transition of azobenzene/LC systems: (a) *trans–cis* photoisomerization; (b) orientational relaxation process; N, nematic; I, isotropic.

for instance, stabilizes the phase structure of the LC, while the bent *cis* form tends to destabilize the phase structure. As Fig. 3B shows, the LC-isotropic phase transition temperature T_c of the mixture with the *cis* form T_{cc} is much lower than that with the *trans* form T_{ct}. If the temperature of the sample T is set at a temperature between T_{ct} and T_{cc}, and the sample is irradiated to cause *trans–cis* photoisomerization of the azobenzene guest molecules, T_c decreases with the accumulation of the *cis* form. When T_c becomes lower than the irradiation temperature T, an LC-isotropic phase transition of the sample is induced. Photochemical reactions are usually reversible, and with *cis–trans* back-isomerization, the sample reverts to the initial LC phase.

The photochemical phase transition behavior of mixtures of azobenzenes and nematic LCs has been systematically explored. As expected from the phase diagram of the photochemical phase transition shown in Fig. 3B, ΔT ($= T_{ct} - T_{cc}$) is one of the most important parameters [3]. When the temperature of samples is set below T_{cc}, no phase transition is induced, even upon prolonged irradiation. On the contrary, if the temperature is set close to T_{ct}, the amount of *cis*-azobenzene needed to lower T_c below the irradiation temperature is small; thereby, the phase transition is induced very effectively [4]. Furthermore, interactions between guest molecules and host LCs are very important. Incorporation of a mesogenic moiety into photoresponsive guest molecules can lead to a strong interaction between the guest molecules and the host LCs. According to this idea, cyanobiphenyl moieties were attached at both ends of azobenzene molecules through alkyl spacers of various lengths, and the ability of the resulting azobenzene derivatives to induce a photochemical phase transition was investigated. A clear odd–even effect was observed in the alkyl spacers for the efficiency of azobenzene derivatives, which evidently results from a specific interaction between the guest azobenzenes and the host nematic LCs [5–7]. The interactions also depend on the structures of the host LCs. A series of LC molecules have been examined with respect to their susceptibility to undergo a photochemical phase transition [8,9].

The photochemical phase transition, and even the alignment change of LC systems, can be induced by the photochemical reactions of several other types of photochromic molecules, in addition to azobenzenes, for example, spiropyrans, fulgides and diarylethenes (Fig. 4). In this review, however, we focus on introducing the alignment modulation of azobenzene-containing LC systems, which has been investigated widely and deeply.

2.2. Alignment change in azobenzene/cholesteric liquid crystal systems

Cholesteric LCs show a unique property arising from their helical structure: the selective reflection of light. The selective reflection is observed only when the helix axis is normal to the cell surface. If the pitch of the helix of the cholesteric phase can be altered by light, all-optical control of the selec-

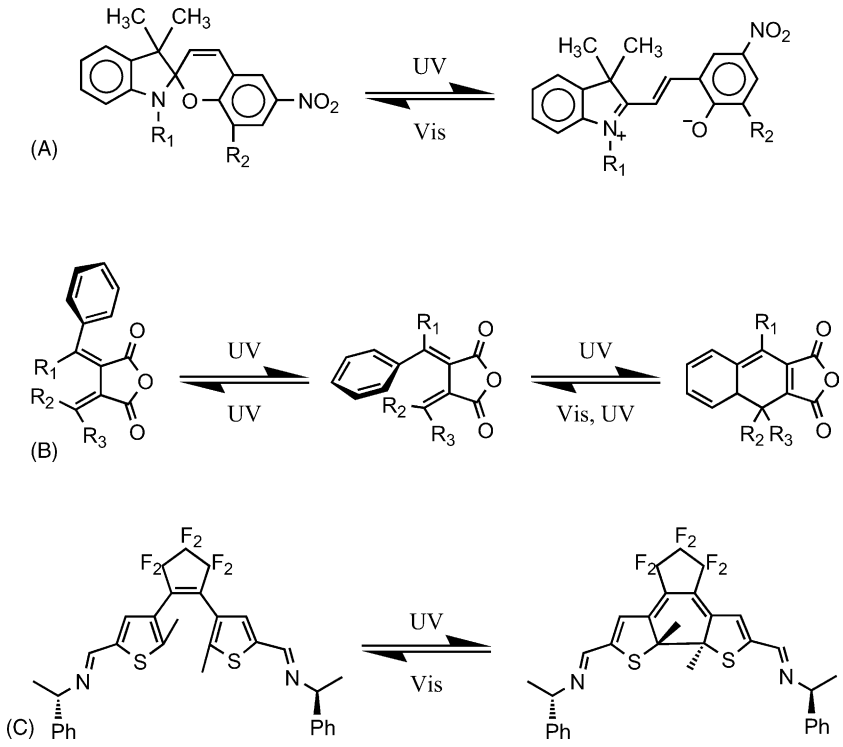


Fig. 4. Various photochromic molecules used to induce alignment change of LCs: (A) spiropyrans; (B) fulgides; (C) diarylethenes.

tive reflection becomes possible. Furthermore, as the helical pitch is very sensitive to temperature, pressure and impurities, the wavelength of the selective reflection is also strongly dependent on these factors. Cholesteric LCs are expected to be useful as active media for reflection-type displays. Particularly, if the wavelength of the selective reflection is in the visible region, these cholesteric materials would have great potential for full-color displays with extremely low energy consumption.

The first example of a change in alignment of cholesteric LCs by photochemical reactions was reported by Sackman [10]. He dispersed azobenzene compounds in cholesteric LCs and irradiated the mixtures to cause photoisomerization of the azobenzene molecules. He found that the pitch of the cholesteric LCs could be altered by this isomerization, which was confirmed by the change in the reflection wavelength.

Kreuzer and co-workers reported that the photoirradiation with linearly polarized light of a cyclic siloxane with cholesteric groups and an azobenzene moiety produced new reflection bands [11].

Lee et al. examined the change in the helical pitch of cholesteric LCs doped with a chiral azobenzene upon *trans–cis* photoisomerization. Doping of cyanobiphenyl nematic LCs with chiral dopants with strong helical twisting power produced cholesteric phases with reflection bands in the visible region. Photoirradiation of the cholesteric LC containing the chiral azobenzene resulted in a change in the helical pitch due to *trans–cis* isomerization of the chiral azobenzene, followed by the change in the reflection wavelength [12]. This change in the helical pitch was ascribed to a change of the phase transition temperature caused by the molecular shape change of the azobenzene guest molecule [12].

2.3. Alignment change in azobenzene/ferroelectric liquid crystal systems

Ferroelectric LCs exhibit spontaneous polarization P_s and show microsecond responses to a change in the applied electric field in a surface-stabilized state (*flip of polarization*) [13]. If a flip of the polarization of a ferroelectric LC in the surface-stabilized state can be induced by light in the presence of an applied electric field, one may obtain a photoresponse of the LC in the microsecond time region.

A mixture of an azobenzene and a ferroelectric LC (Fig. 5A), in which the concentration of the azobenzene guest was 3 mol%, was prepared and subjected to the surface-stabilized state in a very thin LC cell. The mixture was then irradiated with UV light at 366 nm to cause *trans–cis* photoisomerization of the azobenzene guest molecule. It was found that a threshold electric field (coercive force) for the polarization flip of the ferroelectric LC changed upon photoirradiation [14]. The ferroelectric LC in the surface-stabilized state showed hysteresis involving the applied electric field and the polarization [13]. It was observed that the hysteresis of the *trans*-azobenzene/ferroelectric LC mixture was different from that of the *cis*-azobenzene/ferroelectric LC. This effect of molecular shape on the coercive force is very similar to the different T_c values observed in the azobenzene/nematic LC mixtures described above. In the azobenzene/ferroelectric LC mixture, when the azobenzene is in the *trans* form, it does

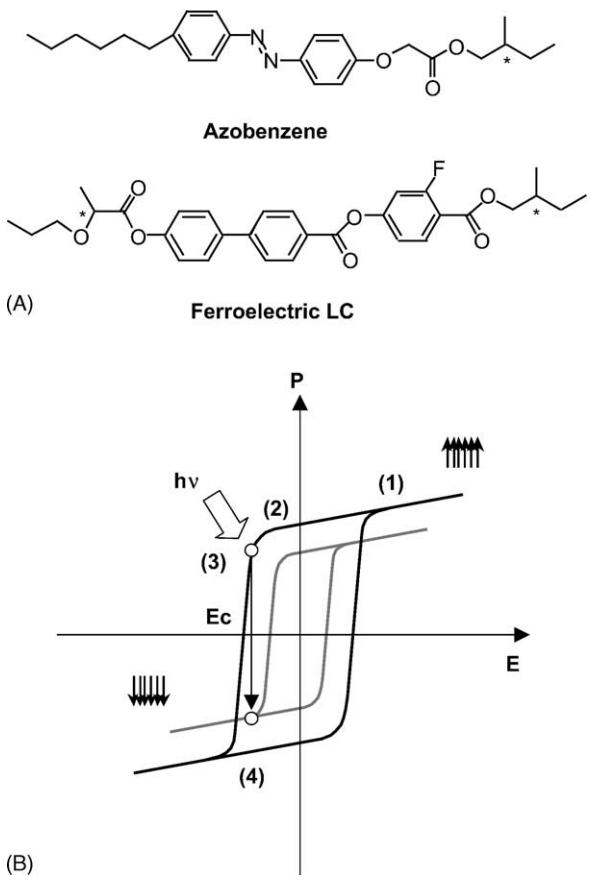


Fig. 5. (A) Chemical structures of an azobenzene and a ferroelectric LC; and (B) photochemical polarization flip in the ferroelectric LC.

not disorganize the phase structure of the chiral smectic C (SmC^*) phase of the ferroelectric LCs significantly. However, when the azobenzene is in the *cis* form, the phase structure of the SmC^* phase is seriously affected, and the threshold value for the polarization flip is much reduced.

With these properties, a new mode of optical switching of ferroelectric LCs (*photochemical flip of polarization of ferroelectric LCs*) has been proposed (Fig. 5B) [14,15]. (1) The polarization of a ferroelectric LC cell that contains a small number of azobenzene molecules is aligned along one direction by an electric field; (2) an opposite electric field is applied across the cell, which is small enough to keep the initial direction of polarization unchanged; (3) with this field as a bias, the LC cell is irradiated to cause photoisomerization of the azobenzene; then the hysteresis of the cell is changed; and (4) the threshold value for the polarization flip is lowered upon photoirradiation and becomes smaller than the bias voltage, which is certain to induce of polarization flip of the ferroelectric LCs. In other words, the bias voltage remains unchanged before and after photoirradiation; however, the threshold value for the polarization flip is reduced by *trans–cis* photoisomerization of the guest molecules. As a result, a polarization flip is induced at the irradiated sites, which leads to a change in alignment of the ferroelectric LCs. Ferroelectric LCs in the surface-stabilized state show bistability of polarization for the upward and downward directions with respect to the normal to the cell surface, and hence two alignments are stabilized. Furthermore, these two states remain unchanged even after the electric field is removed. Owing to these properties of ferroelectric LCs in the surface-stabilized state, once the polarization flip is induced upon photoirradiation, the direction of polarization is opposite between the irradiated and non-irradiated sites, and the alignment of the ferroelectric LCs is different between the two sites. These changes in polarization and alignment of the ferroelectric LCs produce an optical contrast between the irradiated and non-irradiated sites, and they remain unchanged (memory effect).

Time-resolved measurements of the alignment change of mesogens due to the polarization flip in azobenzene/ferroelectric LC mixtures were performed upon pulse irradiation. It was observed that a mixture composed of the azobenzene and the ferroelectric LC shown in Fig. 5A exhibited a polarization flip in 500 μs upon pulse irradiation with the third harmonic of a YAG laser (355 nm; fwhm, 10 ns) [14]. This is the first example of the induction of a polarization flip of ferroelectric LCs by photochemical reactions [14]. Since this first report, detailed studies have been performed on the polarization flip in photochromic guest/ferroelectric LC host systems, e.g., the effects of the structure of ferroelectric LC hosts [16,17], the structure of photochromic guests [18], temperature [19], bias voltage [15] and the change in P_s [19].

The photochemical polarization flip was also examined in antiferroelectric LCs. It was found that the polarization flip can be induced similarly in the azobenzene/antiferroelectric LC mixtures upon irradiation to cause *trans–cis* photoisomerization of the guest molecule (Fig. 6) [20].

Much attention has been paid to the molecular design of effective guest molecules to induce the photochemical polarization flip in ferroelectric LC systems. An azobenzene derivative with a chiral cyclic carbonate was designed on the basis of a large value of polarization, resulting from a chiral cyclic carbonate structure, and was examined as a chiral dopant to induce a SmC^* phase (Fig. 7A). In this system, the chiral dopant also acts as a photoresponsive molecule; thereby it is expected that a change in molecular shape of the

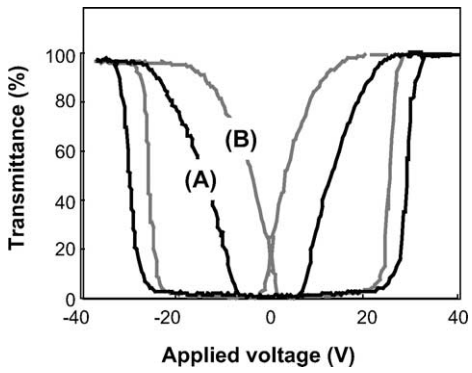


Fig. 6. Transmittance change in an antiferroelectric LC containing an azobenzene: (A) in the dark; (B) under photoirradiation.

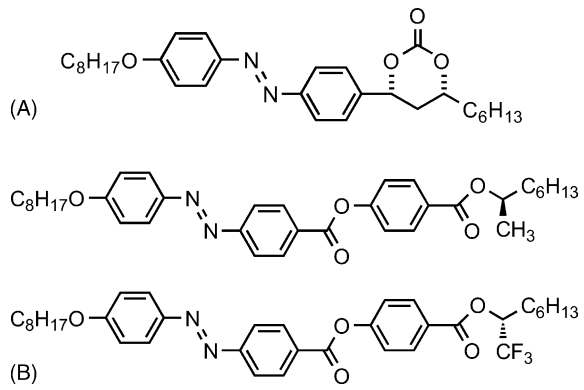


Fig. 7. (A) Photoactive chiral dopant; and (B) azobenzene antiferroelectric LCs.

dopant would significantly affect the phase structure of the SmC* phase, because the molecular shape of the dopant is crucial for the induction of the SmC* phase. It was observed that an azobenzene with a cyclic carbonate is quite effective in inducing the photochemical polarization flip of a ferroelectric LC mixture [21]. Furthermore, azobenzene derivatives that exhibit antiferroelectric properties were developed, and their photoresponsive behavior was examined (Fig. 7B). The photochemical polarization flip in these antiferroelectric LCs is induced very effectively [22], and a device fabricated with these antiferroelectric LCs was explored [23].

Yoshino and co-workers reported an elegant control of photoinduced layer alignment in ferroelectric LCs triggered by a doped azobenzene compound [24]. This layer alignment control is based on a chiral nematic-SmC* phase transition induced by photoisomerization of the guest azobenzene molecule. *Trans–cis* photoisomerization of the azobenzene guest in the SmC* phase resulted in a phase transition to the chiral nematic phase, and thermal *cis–trans* back-isomerization induced the formation of the SmC* phase again. The photochemical SmC*-chiral nematic-SmC* phase transition under an appropriate electric field makes it possible to control the smectic layer alignment in an elegant way.

2.4. Photochemical phase transitions of liquid crystals in polymer matrices

The photochemical phase transition in confined matrices gives rise to novel optical effects. Polymer/LC composite films, consisting of a polymer matrix and an LC component, can be converted from a light-scattering state to a transparent state by application of an external electric field. They need no polarizers to exhibit the scattering/transparent contrast and show high processability and flexibility because of the absence of substrates coated with an alignment layer, so that the polymer/LC composite films are now at the stage of practical use [25,26]. Although such polymer/LC composite films are usually prepared by emulsification and phase separation techniques, the resulting composites have a variety of morphological characteristics arising from differences in conditions and compositions in the sample preparation: nematic curvilinear aligned phase (NCAP) materials with an encapsulated LC structure [27,28], polymer-dispersed liquid crystals (PDLCs) with LC droplets dispersed in a polymer matrix by means of polymerization-induced or solvent-induced phase separation [29,30] polymer network liquid crystals (PNLCs) with micrometer scale LC domains [31] and polymer-stabilized liquid crystals (PSLCs) with a small amount of polymer network [32]. Many studies have been performed on electrically controllable polymer/LC composite films with such advantageous features as quick response to an electric field, high contrast, and a wide viewing angle, as well as reverse-mode and haze-free characteristics [33–37].

All-optically controllable polymer/LC composite films, which are driven by photon-mode processes in the absence of electric fields, have been achieved by means of photochemical phase transitions. Kawanishi et al. prepared polymer/LC composite films with a thickness of 2–3 μm from a mixture of a nematic LC and an azobenzene derivative dispersed in an aqueous solution of poly(vinyl alcohol) by the solvent-induced phase separation technique [38]. Although the composite films showed very low transmittance because of opacity of the composite film, they became transparent upon irradiation at 366 nm, resulting from a nematic-isotropic phase transition in LC droplets within the polymer matrix due to *trans–cis* photoisomerization of the azobenzene molecules. The recovery of the initial opaque state could be achieved by irradiation of visible light to cause *cis–trans* back-isomerization of the azobenzenes. In this system, the degree of change in transmittance was as low as 10–50%.

To improve the optical properties of the composite films, a ternary mixture of bifunctional acrylate monomers, nematic LCs, and azobenzene compounds was polymerized in a 10 μm gap cell under various conditions, and the optical properties of the resulting polymer/LC composite films were evaluated [39,40]. It was found that the transmittances of these composite films can be modulated in the range approximately from 0 to 100% as a result of photoirradiation that induces the photochemical phase transition (Fig. 8). Furthermore, by choosing network-forming materials and tuning the polymerization conditions, optical image storage and reverse-mode switching can also be achieved in the azobenzene-containing polymer network systems [41,42].

3. Photochemical phase transitions of polymers

3.1. Photochemical phase transitions in azobenzene/polymer liquid crystal systems

Polymers are high-performance materials with film-forming nature, high processability, easy fabrication characteristics, high corrosion resistance and low manufacturing costs. Polymer liquid crystals (PLCs) possess both properties of polymers and LCs and are currently regarded as promising photonic materials due to their advantageous properties.

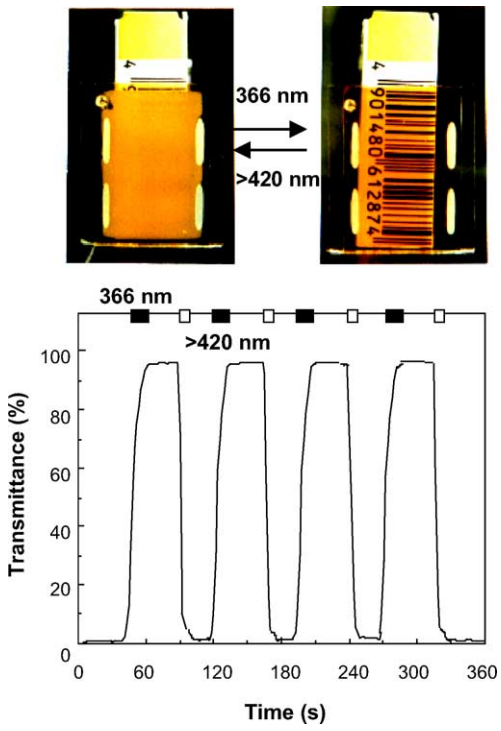


Fig. 8. Transmittance change of a polymer/LC composite film upon photoirradiation.

Wendorff and co-workers reported the first example of a photoresponse of PLCs: a holographic recording in PLCs. They successfully produced holograms in LC copolymers containing azobenzene moieties and mesogenic groups [43,44]. Ikeda et al. reported the first example of the photochemical phase transition in PLCs; they demonstrated that, upon photoirradiation to cause *trans–cis* isomerization of low-molecular-weight (LMW) azobenzene guests in PLC hosts, the mixture underwent a nematic-isotropic phase transition, and with *cis–trans* back-isomerization, the mixture reverted to the initial nematic phase as in LMW photochromic guest/LMWLC mixtures [45–47]. The first example of the photochemical phase transition was demonstrated in the LMW guest/PLC host systems; however, it soon became apparent that copolymers are superior to LMW guest/PLC host mixtures, because, in the LMW guest/PLC host mixtures, the solubility of the guest dye molecules in polymers is low and in some cases phase separation was observed when the concentration of the guest molecules was high. Thus, the dye-doped PLC systems were soon extended to copolymers, and a variety of copolymers containing azobenzene molecules and mesogens were prepared and examined for their photoresponsive behavior with respect to the photochemical phase transition [47–50].

One of the most important factors for the photonic applications of PLCs is how fast they respond to optical stimuli. In this respect, the response time of the photochemical phase transition has been explored in detail by means of refractive-index modulation by the photoinduced change in alignment of LCs. The response time was measured for the nematic-isotropic phase transition in azobenzene/LMWLC mixtures [51,52]. The sample was placed between a pair of crossed polarizers and irradiated with a single pulse of a YAG laser (third harmonic, 355 nm; pulse width, 10 ns fwhm) to induce *trans–cis* photoisomerization of the azobenzene guest molecule. The transmittance of probe light at 633 nm from a He–Ne laser was measured as a function of time. In the azobenzene/LMWLC mixtures, the nematic-isotropic phase transition occurred in 100 ms, as verified by the loss of birefringence of the sample [51]. The nematic-isotropic phase transitions in azobenzene/PLC systems were also found to take place in 50–200 ms in azobenzene-doped PLCs [53] and copolymers containing azobenzene moieties in the side chain [49].

3.2. Photochemical phase transitions of polymer azobenzene liquid crystals

Photochromic reactions are usually very fast, occurring on a timescale of picoseconds (ps). Thus, if an ultrafast laser with a pulse width of picoseconds is used as an excitation light source for the photochemical phase transition of guest/host systems, photochemical reactions of the photoactive molecules can be completed in ps, and the T_c of the system can be decreased below the irradiation temperature on this timescale. This means that immediately after pulse irradiation, a non-equilibrium state is produced, which is thermodynamically an isotropic phase in its equilibrium state in the phase diagram but shows optical anisotropy, because the orientational relaxation of the mesogens is not completed. Refractive-index modulation by means of alignment change of LCs depends strongly on this orientational relaxation of mesogens, which in fact is a rate-determining step in LC systems. LCs, especially PLCs, possess a high viscosity, so that the orientational relaxation of mesogens requires a relatively long time.

To overcome this difficulty, a new system has been developed, in which every mesogen in the LCs or PLC is provided with a photosensitive moiety [54–63]. It has been found that some azobenzene derivatives exhibit LC behavior in which the azobenzene moiety could play both roles, as a mesogen and a photosensitive moiety (Fig. 9). For instance, a PLC with side-chain azobenzene moieties (**PA6AB2** in Fig. 9) shows a very stable nematic phase between 45 °C, the glass transition temperature T_g of the polymer, and 150 °C [54–56]. These azobenzene LCs show an LC phase only when the azobenzene moieties are in the *trans* form, and they never show an LC phase at any temperature when all of the azobenzene moieties are in the *cis* form. In these azobenzene LCs, it was expected that photochemical phase transitions could be induced essentially on the same timescale as photochemical reactions of the photoactive moiety in each mesogen if the photochemical reactions of a large number of mesogens are induced simultaneously by means of a short laser pulse (Fig. 10) [54,55]. On the basis of this new concept, the photoresponses of azobenzene

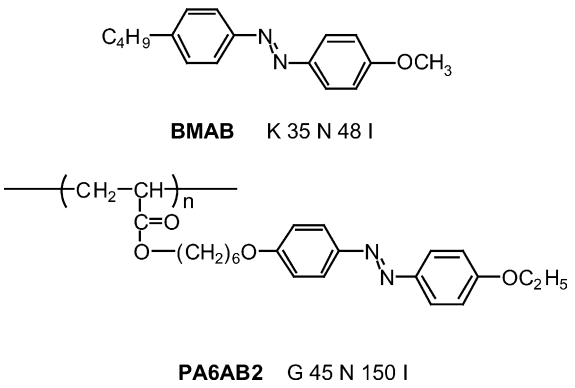


Fig. 9. Examples of azobenzene LCs: K, crystal; N, nematic; I, isotropic; G, glass.

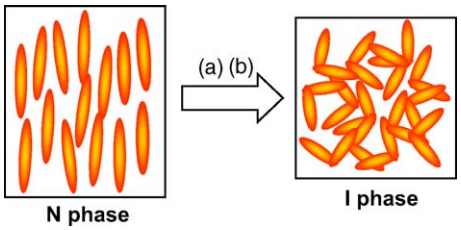


Fig. 10. Fast response by means of azobenzene LCs with a photosensitive moiety in every mesogen: (a) *trans–cis* photoisomerization; (b) orientational relaxation process.

LCs were examined with short laser pulses, and fast response of nematic-isotropic phase transitions in azobenzene LCs has been demonstrated. It was found that in polymer azobenzene LCs, the nematic-isotropic phase transition was induced in 200 ns under optimized conditions [56]. Fig. 11 shows a typical result observed for the polymer azobenzene LC [56]. This fast response of azobenzene LCs is an encouraging result from the viewpoint of applications of PLCs to photonic devices.

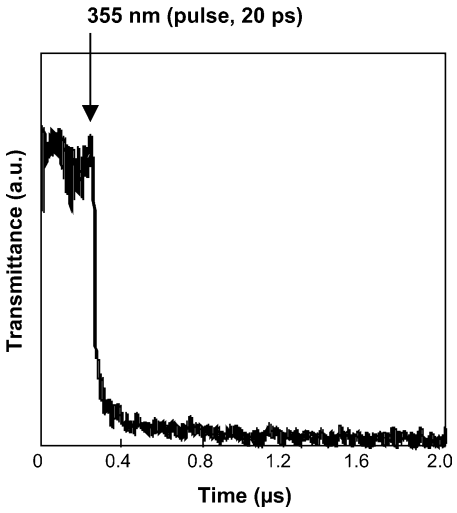


Fig. 11. Time-resolved measurement of the photochemical phase transition of a polymer azobenzene LC.

As described above, the temperature range in which the photochemical phase transition can be induced is limited in guest/host systems. In the temperature ranges above T_{ct} and below T_{cc}, no phase transition can be induced, even if the *trans–cis* photoisomerization of guest molecules is induced (Fig. 3B). In the polymer azobenzene LCs, the photochemical phase transition can be induced over an extremely wide temperature range (greater than 100 °C). This is an advantageous feature in terms of photonic materials and is characteristic to photochromic LCs in which every mesogen includes a photoactive moiety.

When photoirradiation ceases after the nematic-isotropic phase transition, the initial nematic phase is restored. This isotropic-nematic transition is composed of two processes: thermal *cis–trans* back-isomerization of the azobenzene moieties and reorientation of the mesogenic *trans*-azobenzenes. It was observed that the *cis–trans* back-isomerization is a rate-determining process [57]. It was also found that polymethacrylates with side-chain azobenzenes possessed higher T_g values than the corresponding polyacrylates with the same side-chain structures, while both polymer azobenzene LCs exhibited a similar photoresponse: they showed similar photochemical nematic-isotropic phase transition behavior. However, the recovery of the initial nematic phase was much slower in the polymethacrylate than in the polyacrylate, even though the thermal *cis–trans* back-isomerization took place at a similar rate. This is clearly due to the stiffness of the main chain of the polymethacrylate, which significantly affects the reorientation process of the *trans*-azobenzene mesogens after *cis–trans* back-isomerization [57]. On the basis of kinetic studies on the isotropic-nematic phase transition, polymer azobenzene LCs with both donor and acceptor moieties in the molecule, which were characterized by very fast *cis–trans* thermal back-isomerization, have been designed. With such donor–acceptor azobenzenes, a very fast recovery of the nematic phase was achieved, which was faster by one order of magnitude than that of conventional azobenzene LCs [57]. The effect of the spacer between the polymer main chain and the azobenzene chromophore on the photochemical phase transition behavior was explored in detail [58–60].

As another approach to a fast isotropic-nematic phase transition, the optical switching behavior of LMW and polymer azobenzene LCs has been explored by means of reflection-mode analysis (Fig. 12) [61]. On pulse irradiation, it is possible to switch the incident probe light reflected from the interface between LCs and a substrate, as a result of modulation of reflectivity arising from a photoinduced change in the refractive index of LC materials. In 4-butyl-4′-methoxyazobenzene (**BMAB**), the reflection-mode system gave a response similar to that observed in the usual transmission-mode systems; however, it gave a decay time of 1 ms, which was significantly shorter than that obtained in the transmission-mode systems. The molar extinction coefficients of the azobenzene moieties are very large ($>10^4$) at 355 nm, and hence the actinic light is absorbed entirely at the surface of the sample. Thus, *trans–cis* photoisomerization is also induced near

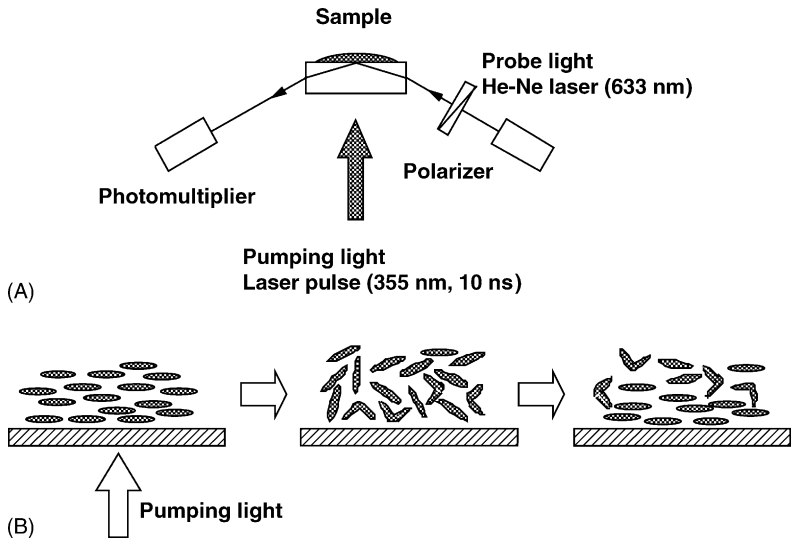


Fig. 12. (A) Reflection-mode optical switching of azobenzene LCs; and (B) its possible mechanism.

the surface, so that the nematic-isotropic phase transition occurs only in the surface region, leaving the bulk area intact as a nematic phase. In reflection-mode systems, the probe light can only penetrate the surface area, so that if molecules in the *cis* form produced at the surface by pulse irradiation diffuse into the bulk phase and are simultaneously replaced by molecules in the *trans* form from the bulk phase, recovery of the initial nematic phase can be achieved without involvement of the *cis–trans* back-isomerization process. Since diffusion and reorientation processes are much faster than the *cis–trans* back-isomerization, the reflection-mode optical switching has become much faster (Fig. 12) [62]. Such reflection-mode systems have another superior characteristic for optical switching: stability. Optical switching in the ordinary transmission-mode generally exhibits low fatigue resistance. However, the reflection-mode optical switching was found to be 10 times more fatigue-resistant than the conventional transmission-mode switching [63]. This fact suggests that optimization of this optical system for photoresponsive LCs may be an effective approach to realize more stable optical switching devices.

It has been demonstrated that polymer azobenzene LCs show a unique feature as optical image storage materials. In nematic glasses, polymer azobenzene LCs undergo a nematic-isotropic phase transition upon photoirradiation, while they never exhibit an isotropic-nematic phase transition. Fig. 13 shows photographs of a photomask and a binary test pattern recorded in the azobenzene LC films by pulse irradiation at 355 nm [54,55]. It is clear that the irradiated site becomes isotropic, as evidenced by the loss of birefringence under polarizing microscopic observation. The stored optical image has remained stable over a period of several years below T_g of the polymer. In the polymer films, it was observed that the thermal *cis–trans* back-isomerization took place in 24 h at room temperature. Although the *trans* form recovered completely, the isotropic glass induced at the irradiated

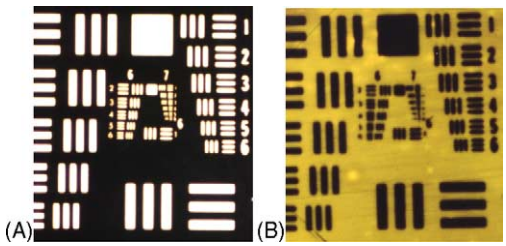
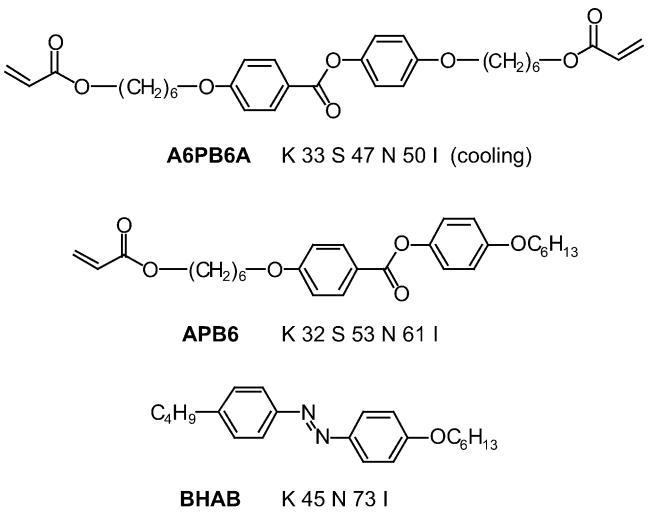


Fig. 13. Optical image storage in polymer azobenzene LC: (A) photomask; (B) stored image.

site still remained unchanged at room temperature even after several years [55]. These results suggest that below T_g the orientation of the mesogenic *trans*-azobenzenes becomes disordered through a thermal *cis–trans* back-isomerization process. This is because, even after the *trans* form recovers thermally, alignment of mesogens is hardly possible in the absence of segmental motions of the main chain of the polymer below T_g. Therefore, the polymer azobenzene LCs can be used as optical switching materials as well as optical image storage materials.

3.3. Photochemical phase transitions of crosslinked polymer liquid crystals

Crosslinking of polymer chains in PLCs gives a strong correlation among functional groups attached to the PLCs and results in anomalous behavior in response to external stimuli. Kurihara et al. prepared crosslinked PLC networks containing azobenzene molecules through polymerization of ternary mixtures of monofunctional, difunctional LC monomers and an LMW azobenzene LC (Fig. 14) and evaluated their photochemical phase transition behavior [64]. They demonstrated that the response time and the decay time were 1 and 100 μs, respectively (Fig. 14). This very fast response can be ascribed to the suppression of motion of mesogenic groups



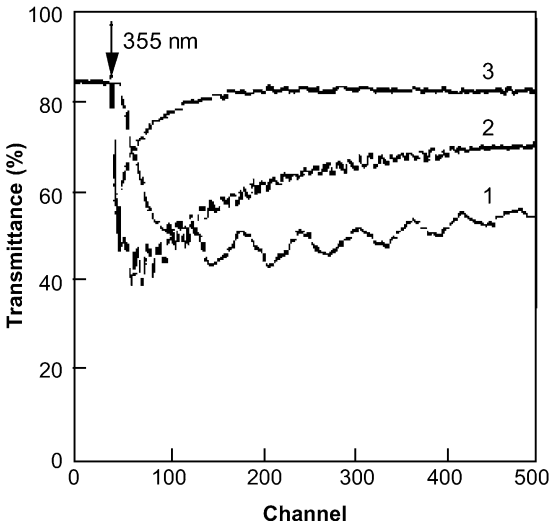


Fig. 14. Time-resolved measurements of transmittance changes in crosslinked polymer LC: (1) 10 ns ch21; (2) 50 ns ch21; (3) 1 ms ch21.

by crosslinking. In fact, non-crosslinked PLC analogs did not show such fast response. It has been concluded through intensive studies that the stabilization of an initial ordered state by crosslinking gives rise to a fast order–disorder transition, induced by a slight change in the orientational order of mesogens, and a fast disorder–order transition, due to relaxation of the strain generated upon photoisomerization of the azobenzene molecules [65,66].

4. Alignment control of liquid crystals by linearly polarized light

Light absorption to give excited states of molecules meets exclusive requirements involving the coincidence of the electric field vector of light with the direction of the transition moment of the molecule (photoselection). For instance, *trans*-azobenzenes exhibit π–π^* transition moments approximately parallel to the long molecular axis; thereby the *trans*-

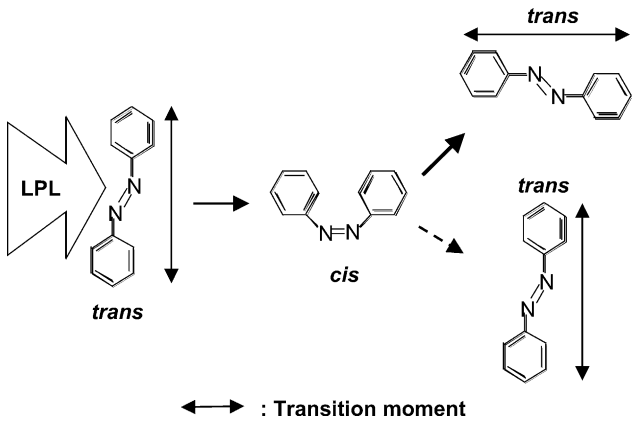


Fig. 15. Weigert effect in the alignment change of azobenzene molecules.

azobenzenes show angular-dependent absorption of LPL: *trans*-azobenzene molecules, with their transition moments parallel to the polarization direction of LPL, are activated very effectively to their excited states, followed by *trans–cis* isomerization, while molecules with their transition moments perpendicular to the polarization direction of the actinic light are inactive towards isomerization. After repetition of *trans–cis–trans* isomerization cycles, once *trans*-azobenzene molecules have fallen perpendicular to the polarization direction of the actinic light, they become inactive towards the incident radiation. This means that, at the end of the multiple cycles, there would be a net population of azobenzene molecules aligned perpendicular to the light polarization (Fig. 15). This is well known as the Weigert effect [67]. Since the first report by Weigert, there have been many studies published on this photoinduced anisotropy in the alignment of dye molecules. Among them, the work by Todorov et al., in which they showed the possibility of using a polymer containing azobenzene molecules as an optical recording medium, is a milestone in dye-doped optical systems [68]. Their system contained azo dyes, methyl red and methyl orange, dispersed in a poly(vinyl alcohol) matrix. When the dye-doped polymers were irradiated with a linearly polarized laser beam at 488 nm, the optical transmittance for light polarized along the polarization direction of the actinic light increased, while that for light perpendicular to the direction of the actinic light decreased. Optical dichroism was created in this way, owing to the anisotropic realignment of *trans*-azobenzene molecules. However, in this system, the stability of the induced anisotropy was low: it remained unchanged only for a very short period, even in the dark. This drawback was overcome by Natansohn et al., who developed amorphous azobenzene polymers, and by others [69–73]. They succeeded in inducing stable birefringence in amorphous polymers at ambient temperatures below T_g by attaching the azobenzene moieties to polymers through covalent bonds. The induced alignment can be erased thermally or photochemically and reinduced by irradiation with LPL.

Photoinduction of molecular alignment has been extended to copolymer LC systems possessing both mesogens and

azobenzene moieties in the side chains. Several studies clearly showed that non-photoactive mesogens could undergo reorientation concomitantly with azobenzene moieties above T_g due to their cooperative motion. On the other hand, various arguments were presented concerning reorientation behavior below T_g [74,75]. Recent work on the photoinduced alignment behavior of side-chain PLCs has revealed that dipole–dipole interaction affecting cooperative motion is crucial in the reorientation process [73].

Intensive studies indicate that the important factors for the reorientation process include the azobenzene composition [76], enthalpy changes during phase transitions [77], the sample morphology before irradiation [78,79], the intensity of the actinic LPL [80] and the spacer length of side-chains [81]. In addition, structural effects of azobenzene moieties on photoinduced alignment behavior have been explored systematically in a series of side-chain PLCs possessing different azobenzene moieties [82–84]. With an increase of the strength of donor and acceptor substituents at the 4- and 4′-positions of the azobenzene moieties, the possibility of alignment change in PLCs decreased due to slightly increased enthalpic stability of the LC phase and a significantly reduced concentration of *cis*-azobenzenes (i.e., an increased *cis–trans* thermal isomerization rate). However, high alignment efficiency was observed in a polyacrylate with strong donor–acceptor pairs in the azobenzene moiety and exhibiting low stability of the LC phase, since both the rate of *cis–trans* isomerization and the mobility of the mesogens are favorable for the alignment change. These results demonstrate that the photoalignment behavior can be optimized effectively by an appropriate choice of azobenzene units or polymer backbones.

One can control the alignment direction of azobenzene-containing polymers in a two-dimensional manner (in-plane) by changing the polarization direction of the linearly polarized actinic light. In the course of the in-plane alignment process, photoinduced biaxiality of azobenzene moieties was observed in LC and amorphous polymer films and in Langmuir–Blodgett films [69,85–87]. This phenomenon was interpreted in terms of the realignment of azobenzene moieties along the propagation direction of the actinic LPL (out-of-plane alignment) [69]. When the azobenzene moieties are aligned with the long molecular axis along the propagation direction of the actinic light, photoisomerization hardly occurs at all, because the propagation direction of light is always perpendicular to its electric field vector. In the case of unpolarized light, only the propagation direction is, in principle, perpendicular to the electric vector of the light. Thus, when unpolarized light is employed, it is expected that the azobenzene moieties become aligned only in the propagation direction of the actinic light. In fact, several results have been reported concerning the out-of-plane alignment behavior by using unpolarized light [88–91]. From the viewpoint of three-dimensional manipulation of molecules by light, promising results have been obtained for PLCs: by changing the incident direction of the actinic unpolarized light, one can control the alignment of azobenzene and mesogenic moieties in a three-dimensional fashion, precisely along the propagation direction of the actinic light, at room temperature (Fig. 16) [92,93]. Furthermore, it has also been confirmed that the induced three-dimensional alignment of molecules is very stable below T_g of the polymers. This result is expected to open a new methodology to manipulate molecules in a three-dimensional manner.

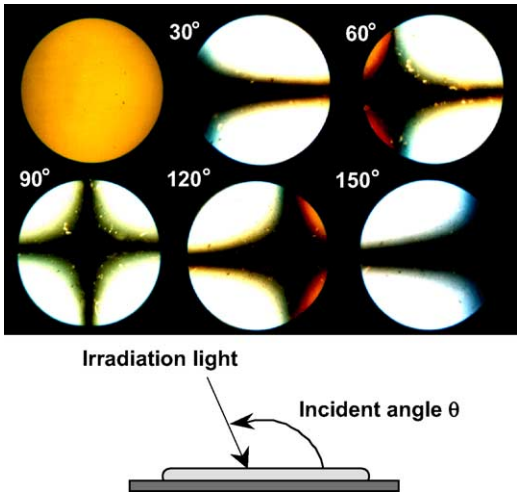


Fig. 16. Conoscopic observation of the alignment of azobenzene moieties as a function of the incident angle of the unpolarized actinic light.

5. Alignment change of liquid crystals by photoactive surface layers

The electric Freedericksz transition is the basic working mechanism of most LCDs today [94]. Homogeneous LC alignment is conventionally achieved by mechanically rubbing a polymer alignment layer coated on the substrates. If chemical and/or physical properties of the surface of substrates can be changed by external fields, LC alignment may be controlled by the substrate surface. Ichimura et al. employed azobenzene monolayers formed on glass substrates by silane coupling agents and demonstrated the possibility of the photoalignment of LCs using photoactive surface layers [95]. This basic concept of the photoalignment technique is illustrated in Fig. 17. In a cell filled with a nematic LC, made from the surface-treated substrates, the nematic LC shows a homeotropic alignment when azobenzenes immobilized on the substrates are in the *trans* form. Photoirradiation to cause *trans–cis* isomerization of azobenzenes enables repeatable changes in alignment from the homeotropic state to a planar state. Such photoactive surface layers are called “command surfaces” [95]. A similar photoalignment of LCs has been also reported for polymer films containing azobenzene moieties, and the effects of structure and density of azobenzene molecules on the photoalignment behavior have been explored systematically [96,97].

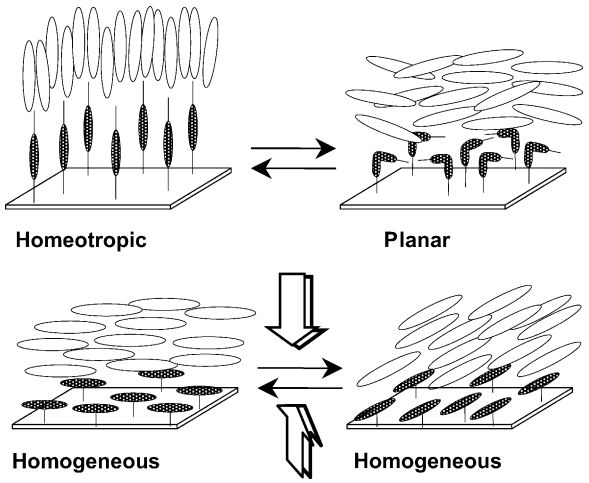


Fig. 17. Photoalignment of LCs by use of a "command surface".

Gibbons et al. employed a polyimide (PI) film doped with azobenzene molecules as a dichroic dye and found a similar phenomenon induced by LPL, showing that the direction of the homogeneous alignment of LC molecules can be established and altered by using polarized light [98]. A nematic LC cell fabricated from a substrate coated with a dye/PI mixture and a substrate coated only with PI, with the rubbing directions of both substrates mutually parallel, was exposed to LPL with the polarization parallel to the rubbing direction. It was found that the LC molecules at the irradiated dye-doped surface became aligned perpendicular to the polarization of the actinic light, whereas those at the undoped PI surface remained parallel to the rubbing direction, resulting in a twisted nematic structure within the irradiated region. The photoinduced alignment can be subsequently erased or rewritten by altering the polarization of the light. Furthermore, unidirectional alignment of LCs has been also achieved by a variety of materials with photoactive surfaces such as poly(vinyl alcohol) thin films containing a hydrophilic azo dye [99], glass substrates modified with azobenzene monolayers [100] and polymer azobenzene films [91,101]. Such photoalignment techniques using LPL are more favorable from the viewpoint of improvement of performance of existing LC devices and the development of novel LC devices with new functions, because the photoalignment process is free from the dust particles and static surface charges generated in the conventional rubbing process [102].

6. Holographic technology based on alignment change and photochemical phase transitions of liquid crystals

Holography is a unique technique that enables concomitant recording of phases and amplitudes of light waves. The most attractive feature of holography is that it can record and display a complete three-dimensional image of an object. In holography, the phase and amplitude of light waves are recorded by periodic alternation of the physical properties of the materials. Amplitude can be recorded in numerous photosensitive materials; however, they are usually insensitive to phase differences in various parts of the wave front. In 1947, Gabor invented a new method, introducing a background wave, generally referred to as a reference beam [103]. Interference between the reference beam and an object beam (the wave-front reflected by an object, the image of which is to be recorded) converts phase differences into amplitude ones, which can be recorded on photosensitive materials. Gabor coined the name "holography", meaning the "whole record", for his method because it contains all of the information necessary to reconstruct the object beam. The hologram can be played back by irradiation with a coherent beam identical to the reference beam, i.e., readout beam. On passing through the hologram, this beam acquires phase and amplitude modulations of the object beam, reconstructing the wave front that originally came from the object, the image of which was recorded. For holography, a coherent light source is the prerequisite component. The rapid progress of laser technology has enabled us to focus the greatest attention on holographic processes. Thus, holography is regarded as the most promising candidate for the storage of high-density information, as well as for recording three-dimensional objects. Furthermore, holographic storage allows information to be written and read simultaneously as parallel processes, resulting in an extremely high transmission rates.

Holograms are mainly classified into two types, according to the manner of recording of interference patterns [104,105]. One is an amplitude-type hologram, in which the interference pattern is recorded as a density variation in the recording medium. The other is a phase-type hologram, in which fringe patterns are recorded as a change in thickness or refractive index. Theoretically, the diffraction efficiency of phase-type holograms is always higher than that of amplitude-type holograms. Accordingly, most studies on holography are related to the phase-type holograms.

An ideal holographic material should possess simultaneously such properties as high diffraction efficiency, high sensitivity, high spatial resolution, high S/N ratio and erasability. For phase-type holograms with high diffraction efficiency, we need a large modulation either of the refractive index or of the thickness of the materials. In the development of nanotechnology, we may have to achieve phase-type holograms with high diffraction efficiency in thin films of nanometer thickness. With this in mind, we should develop holographic materials, in which a large modulation of refractive index is possible. In the application of holography to active recording devices, holograms should be erasable and rewritable on the nanosecond timescale.

As described above, LCs are ideal materials to induce a large change in refractive index. If one can induce an alignment change of LC molecules in a periodic fashion in accordance with interference patterns produced by overlapping two coherent beams, the object and the reference beams, in LC materials, one can obtain a large refractive-index modulation.

This is quite favorable in terms of high diffraction efficiency, since the diffraction efficiency is strongly related to the refractive-index modulation produced in the materials. Therefore, extensive studies have been performed concerning the formation of static and dynamic holographic gratings in LC materials: LMWLCs [106–127], LC/polymer composites [128–143], and PLCs [144–157].

In holographic gratings based on photochromism, azo dyes have been almost exclusively employed, mainly because the photoisomerization of azobenzenes facilitates alignment changes of LC molecules quite effectively, as mentioned above. Another advantage of using azobenzenes is their efficient reversibility in isomerization, which ensures static as well as dynamic control of grating formations. In fact, dynamic holography has been achieved in azo dye-doped nematic LCs [110,111]. In terms of the mobility of mesogens, LMWLCs are superior; however, it is often difficult to obtain holographic gratings with narrow fringe spacing (i.e., high resolution) and high stability because of the high mobility of mesogens. It is easy to imagine that PLCs, especially side-chain PLCs, are favorable from the viewpoint of stability of holographic gratings because of their restricted mobility of mesogens. Wendorff and co-workers showed for the first time that holographic gratings can be inscribed in PLCs composed of azobenzene monomers and mesogenic monomers [43,44,146].

Recently, the formation of phase-type holographic gratings by means of photochemical phase transitions has been demonstrated in side-chain PLCs containing azobenzene moieties and polymer azobenzene LCs [158–167]. Advantages of using photochemical phase transitions include a very fast formation and highly repeatable recording of holographic gratings, because photochemical phase transitions can be reversibly induced on the nanosecond timescale. In fact, it has been confirmed that holographic gratings were formed in polymer azobenzene LCs in ∼200 ns with a laser pulse (fwhm, 20 ps). It is worth mentioning that the magnitude of refractive-index modulation reached approximately 0.1 and phase-type gratings have been recorded in glassy ordered films. It was also demonstrated that surface-relief structures were formed on the surfaces of the polymers upon irradiation of two coherent laser beams, which are similar to those reported in amorphous azo polymers by Natansohn and co-workers [168] and Tripathy and co-workers [169] The gratings recorded in the LC phases of PLCs, with a thickness of 500 nm ∼ 1.2 μm, showed a high diffraction efficiency (32%), which is approximately the theoretical limit of the diffraction efficiency in the Raman-Nath regime. However, the surface modulation was small (∼10 nm). This means that the contribution of surface-relief structures to the overall diffraction efficiency is small, and the large enhancement of the diffraction efficiency is mainly due to spatial modulation of molecular alignment, resulting from the alternating arrangement of nematic and isotropic phases (Fig. 18). This system has been proved capable of holographic recording of three-dimensional objects with high resolution (Fig. 19).

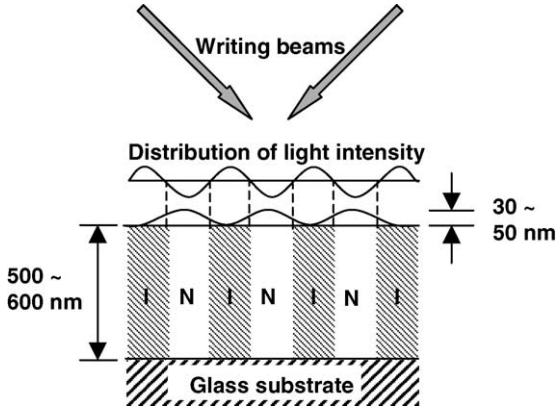


Fig. 18. Holographic grating formed in a polymer azobenzene LC film with an alternating arrangement of nematic and isotropic phases under the surface relief structure.

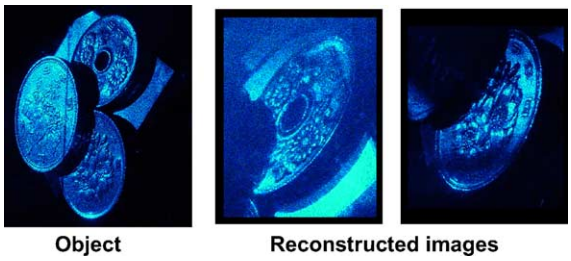


Fig. 19. Holographic recording of three-dimensional objects and reconstructed images.

7. Photomechanical effect of liquid crystal elastomers

7.1. Photoinduced contraction of liquid crystal elastomers

Photo-deformable “smart” materials that can undergo a shape or volume change in response to light have attracted much attention from researchers, because by using their deformations, one can directly convert light energy into mechanical power (photomechanical effect). Moreover, since their deformations driven by light require neither batteries nor controlling devices on the materials themselves, it should be simple to miniaturize such photo-deformable systems for potential applications in driving micromachines and nanomachines.

Upon photoisomerization, azobenzenes exhibit a large change in their molecular length: the distance between the 4- and 4′-carbons decreases from 9.0 Å (*trans*) to 5.5 Å (*cis*) (Fig. 2) [170]. Eisenbach reported that amorphous polymers crosslinked with azobenzenes contracted upon UV light irradiation, which causes *trans–cis* isomerization of the azobenzene chromophores, while it expanded by irradiation of visible light, which induces *cis–trans* isomerization. However, the observed contraction was very small (only 0.15–0.25%) [171].

In 1997, de Gennes et al. reported theoretical studies on the possibility of a large deformation of LC elastomers (LCEs)

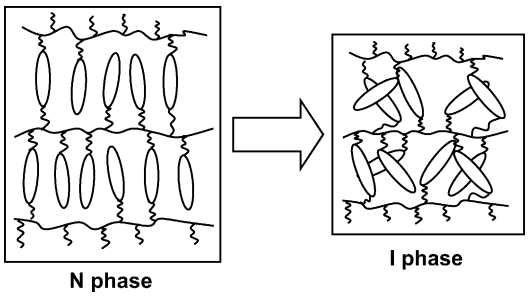


Fig. 20. Schematic illustration of a large deformation in LC elastomers caused by a subtle variation in microscopic ordering.

caused by a subtle variation in microscopic ordering (Fig. 20) [172] and subsequently several groups have experimentally demonstrated large deformations of LCEs induced by electric fields [173] or temperature [174–177]. Finkelmann et al. have reported a pioneering work on a photoinduced large contraction in azobenzene-containing LCEs arising from the photochemical phase transition behavior [178]. They synthesized mono-domain nematic LCEs containing a polysiloxane main chain and azobenzene chromophores in crosslinks (Fig. 21). When exposed to UV light at 365 nm, the elastomers contracted about 20%, caused by a decrease in order parameter due to the photochemical phase transition. After irradiation was switched off, the elastomers returned to the original state thermally due to *cis–trans* back-isomerization of the azobenzene units [178]. Subsequently, a range of such nematic LCEs containing different compositions and crosslinking topologies was studied in their response to UV light [179]. It was found that the magnitude of the photoinduced contraction was dependent on the proportion and the position of the azobenzene units in the crosslinked polymer network. In addition, the photomechanical effect was also observed in side-on nematic LCEs (Fig. 22) [180]. When exposed to UV light at 365 nm, the films contracted by up to 12–18%, and the extent of the contraction was found to be dependent on the intensity of the light used.

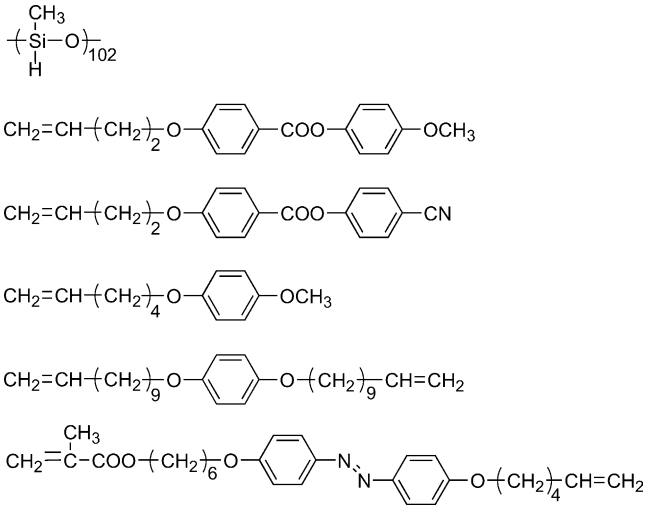


Fig. 21. Chemical structures of the compounds used for the synthesis of nematic LC elastomers.

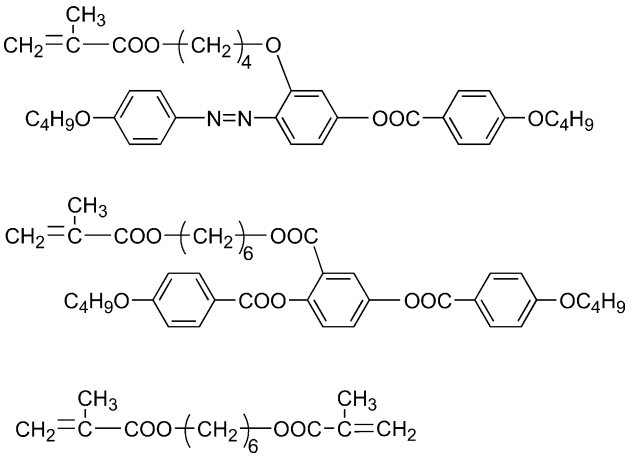


Fig. 22. Chemical structures of the monomers used for the synthesis of side-on nematic LC elastomers.

It is worth mentioning that these pieces of research provide a new mechanism for the photomechanical effect. However, there still remain several problems to be solved for practical application: the response time and the type of deformation.

7.2. Photoinduced bending of liquid crystal elastomers

As described in the previous sections, polymer azobenzene LCs show a very fast response in their phase transitions upon pulse irradiation. Therefore, it is expected that LCEs composed only of azobenzene mesogens undergo fast deformations. Furthermore, in these LCEs, due to the large extinction coefficients of the azobenzene moieties, the depth profile for absorption of photons can be controlled just by choosing suitable wavelengths of the actinic light.

The photoresponsive behavior of LCE films prepared by copolymerization of an LC monomer and a diacrylate, both containing an azobenzene moiety (Fig. 23), has been evaluated [181–183]. It was found that when exposed to unpolarized 366 nm light, the LCE films bent toward the irradiation

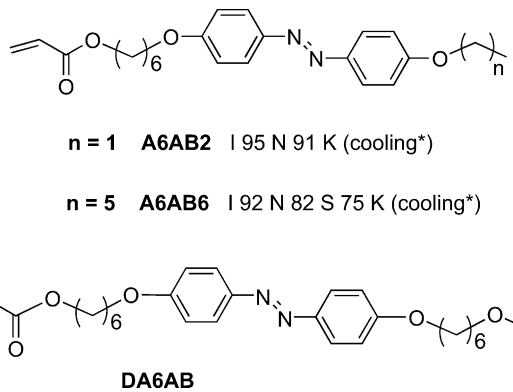


Fig. 23. Chemical structures of azobenzene LC monomers and a cross-linker containing an azobenzene moiety. *__A6AB2__ shows a monotropic nematic phase when cooled from an isotropic phase, and __A6AB6__ shows a monotropic smectic phase when cooled from a nematic phase.

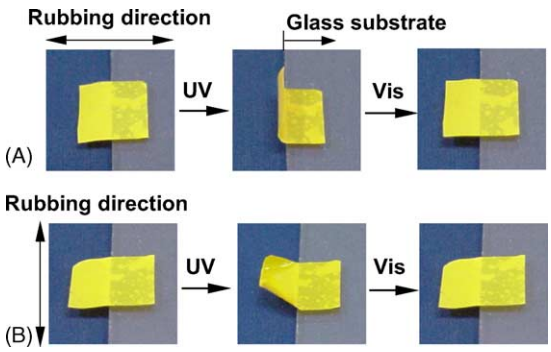


Fig. 24. Anisotropic bending and unbending behavior of oriented LC elastomer film. The rubbing direction was set (A) perpendicular and (B) parallel to one side of the glass substrate; film dimensions, 5 mm × 5 mm × 20 μm.

direction of the actinic light. Moreover, when the bent films were exposed to unpolarized visible light, unbending behavior was observed, and the bent films reverted completely to their initial flat states (Fig. 24). The bending and unbending behavior could be repeated by alternate irradiation of UV and visible light. It is interesting to note that the bending of the LCE films occurred anisotropically, only in the direction parallel to the rubbing direction of the alignment layers (Fig. 24). In comparison with the contraction mode, which is a two-dimensional action, the bending mode, a three-dimensional movement, should be advantageous for artificial hands and medical micro-robots that are capable of completing particular manipulations.

It has been described above that irradiation with UV light gives rise to *trans–cis* isomerization of the azobenzene moieties and even the LC-isotropic phase transition of the LC systems, both of which can bring about a volume contraction of the LCE films. However, the molar extinction coefficient of the azobenzene moieties at ∼360 nm is large ($>10^4$), and more than 99% of the incident photons are hence absorbed by the surface with a thickness less than 1 μm. Since the thickness of the LCE films used was always 10–20 μm, the volume contraction is generated only in the surface region, causing the bending toward the irradiation direction of the actinic light (Fig. 25). Furthermore, the azobenzene moieties are preferentially aligned along the rubbing direction, and the decreases in size and alignment order of azobenzene moieties are thus produced just along this direction, contributing to the anisotropic bending behavior.

The influence of temperature on the bending behavior was examined, and it was found that the bending could be induced only when the LCE films were heated to above T_g, because the relaxation of the polymer segments is necessary. It was also observed that the higher was the temperature, the faster was the bending, because the mobility of the polymer segments becomes larger [183]. Moreover, the study of the influence of light intensity on the bending behavior demonstrated that the bending time decreased with an increase of the light intensity, because actinic light with higher intensity produces a higher concentration of *cis*-azobenzene moieties [183]. In addition, it was observed that the bending time increased remarkably with the increment of the film thickness [183]. For LCE films with different crosslinking densities, it was observed that the maximum bending extent of the films increased with increasing crosslinking density, because a film with a higher crosslinking density showed a higher order parameter, and a larger volume contraction was thus generated at the film surface [184]. Moreover, the bending rates were also different for the films with different cross-linking densities, affected not only by the volume contraction at the film surface but also by the mobility of the polymer segments [184]. In addition, the photoresponsive behavior of the LCE films put in solvents was investigated. It was observed that only films swollen in good solvents such as toluene and chloroform could undergo the photoinduced bending due to the requirement of the cooperative movement of the polymer segments [182].

In the above studies, the azobenzene mesogens were preferentially aligned along one direction, and the actinic unpolarized light was a homogeneous external stimulus. In this case, the anisotropic bending is induced, whose direction is determined fully by the alignment direction of the azobenzene mesogens and cannot be freely varied. If poly-domain LCE films and LPL are used, what will happen? This great idea led to amazing bending and unbending behavior [185]. As Fig. 26 shows, a poly-domain LCE film was laid on a copper post fixed to a copper plate, and the hot stage under the plate was set to control the temperature of the film. Fig. 26A shows the film before light irradiation, and Fig. 26B shows how the film curls up after exposure to 366 nm LPL that has a polarization direction at zero degrees. The film bent toward the irradiation direction of the actinic light, with the bending occurring parallel to the direction of light polarization (white arrows). When the bent film was exposed to visible light at >540 nm, it completely reverted to its initial flat state.

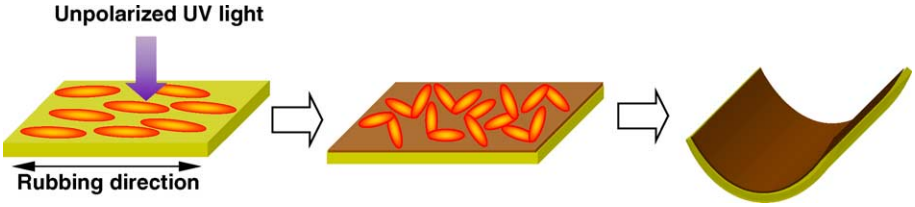


Fig. 25. Plausible mechanism of the anisotropic bending behavior of oriented LC elastomer film.

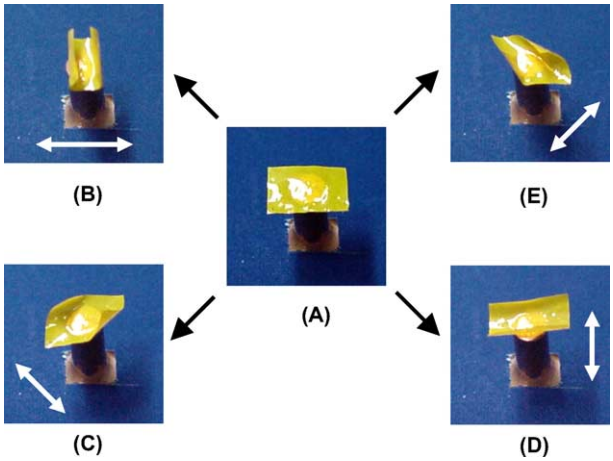


Fig. 26. Direction-controllable bending behavior of polydomain LC elastomer film upon irradiation of 366 nm LPL with different polarization directions indicated by the white arrows; film dimensions, 4.5 mm × 3 mm × 7 μm.

The effect on the film of altering the polarization direction of 366 nm LPL to −45, −90 and −135° is shown in Fig. 26C–E, respectively. It can be seen that the bending direction of the film moves anticlockwise by 45, 90 and 135°, respectively, keeping parallel to the direction of light polarization. The film could be restored from each bent state to its initial flat form by irradiation of visible light at >540 nm. The bending time for the four different directions was within 10 s, when the light intensity of 366 nm LPL was 3.5 mW/cm^2. After exposure to visible light at >540 nm (547 nm, 24.2 mW/cm^2; 577 nm, 26.8 mW/cm^2), the bent film reverted to the flat state in about 10 s. Moreover, the bending–unbending cycle of these four modes could be repeated without apparent fatigue. These results show that the bending direction of a single film can be precisely controlled by altering the polarization direction of the actinic UV LPL and that such a film can be bent repeatedly.

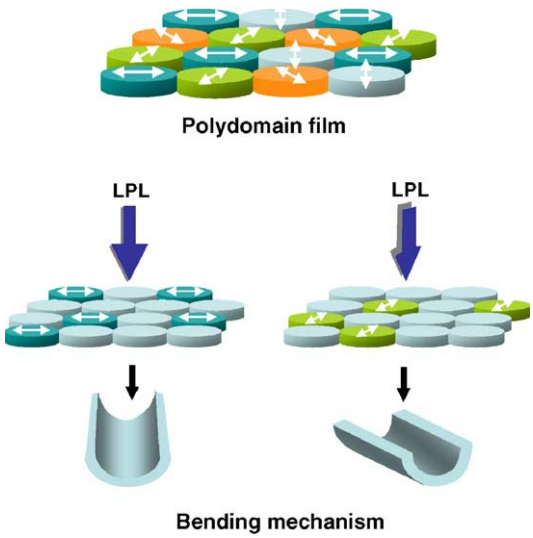


Fig. 27. Plausible mechanism of the direction-controllable bending behavior of polydomain LC elastomer film.

The poly-domain LCE film used here consisted of a large number of micro-size domains of azobenzene mesogens, in which the mesogens were aligned in one direction in each domain but macroscopically the direction of alignment was random (Fig. 27). Upon irradiation with UV LPL, selective absorption of light in a specific direction, light polarization, leads to *trans–cis* isomerization of azobenzene mesogens in specific domains where the azobenzenes mesogens are aligned along the direction of light polarization (Fig. 27). As a result, the subtle reduction in microscopic size and order of the mesogens gives rise to a substantial macroscopic volume contraction at the film surface and a bending of the whole film through the cooperative movement of the mesogens and the polymer segments.

This directed bending is a novel deformation mode that has not been reported in other photodeformable smart materials. The changeability of the bending direction and the repeatability of the bending behavior provide this new kind of smart material with potentiality for the development of high-speed actuators for microscale or nanoscale applications, for example, in micro-robots in medicine or optical micro-tweezers.

References

[1] G.W. Gray, in: D. Demus, J. Goodby, G.W. Gray, H.W. Spiess, V. Vill (Eds.), Handbook of Liquid Crystals, vol.1, Fundamentals, Wiley-VCH, Weinheim, 1998, Chapter 1.
[2] T. Ikeda, J. Mater. Chem. 13 (2003) 2037.
[3] C.H. Legge, G.R. Mitchell, J. Phys. D: Appl. Phys. 25 (1992) 492.
[4] S. Kurihara, T. Ikeda, S. Tazuke, Mol. Cryst. Liq. Cryst. 178 (1990) 117.
[5] T. Ikeda, T. Miyamoto, S. Kurihara, M. Tsukada, S. Tazuke, Mol. Cryst. Liq. Cryst. 182B (1990) 357.
[6] T. Ikeda, T. Miyamoto, S. Kurihara, M. Tsukada, S. Tazuke, Mol. Cryst. Liq. Cryst. 182B (1990) 373.
[7] T. Ikeda, T. Miyamoto, S. Kurihara, S. Tazuke, Mol. Cryst. Liq. Cryst. 188 (1990) 207.
[8] T. Ikeda, T. Miyamoto, S. Kurihara, S. Tazuke, Mol. Cryst. Liq. Cryst. 188 (1990) 223.
[9] T. Ikeda, T. Miyamoto, S. Kurihara, S. Tazuke, Mol. Cryst. Liq. Cryst. 188 (1990) 235.
[10] E. Sackmann, J. Am. Chem. Soc. 93 (1971) 7088.
[11] A. Petri, Ch. Bäuchle, H. Leigeber, A. Miller, H.-P.W. Weitzel, F.-K. Kreuzer, Liq. Cryst. 15 (1993) 113.
[12] H.-K. Lee, K. Doi, H. Harada, O. Tsutsumi, A. Kanazawa, T. Shiono, T. Ikeda, J. Phys. Chem. B 104 (2000) 7023.
[13] A. Fukuda, H. Takezoe, Structures and Properties of Ferroelectric Liquid Crystals, Corona, Tokyo, 1990.
[14] T. Ikeda, T. Sasaki, K. Ichimura, Nature 361 (1993) 428.
[15] T. Sasaki, T. Ikeda, K. Ichimura, J. Am. Chem. Soc. 116 (1994) 625.
[16] T. Sasaki, T. Ikeda, Ferroelectrics 149 (1993) 343.
[17] T. Sasaki, T. Ikeda, J. Phys. Chem. 99 (1995) 13002.
[18] T. Sasaki, T. Ikeda, J. Phys. Chem. 99 (1995) 13008.
[19] T. Sasaki, T. Ikeda, J. Phys. Chem. 99 (1995) 13013.
[20] T. Moriyama, J. Kajita, Y. Takanashi, K. Ishikawa, H. Takezoe, A. Fukuda, Jpn. J. Appl. Phys. 32 (1993) L589.

[21] M. Negishi, O. Tsutsumi, T. Ikeda, T. Hiyama, J. Kawamura, M. Aizawa, S. Takehara, Chem. Lett. (1996) 319.
[22] M. Negishi, K. Kanie, T. Ikeda, T. Hiyama, Chem. Lett. (1996) 583.
[23] K. Shirota, I. Yamaguchi, Jpn. J. Appl. Phys. 36 (1997) L1035.
[24] T. Matsui, K. Nakayama, M. Ozaki, K. Yoshino, Appl. Phys. Lett. 76 (2000) 1228.
[25] G.P. Montgomery Jr., G.W. Smith, N.A. Vaz, Liquid Crystalline and Mesomorphic Polymers, Springer-Verlag, New York, 1994.
[26] H. Kitzerow, Liq. Cryst. 16 (1994) 1.
[27] J.L. Fergason, SID Int. Symp. Digest Tech. Papers 16 (1985) 68.
[28] P.S. Drzaic, J. Appl. Phys. 60 (1986) 2142.
[29] J.L. West, Mol. Cryst. Liq. Cryst. 157 (1988) 427.
[30] J.W. Doane, N.A. Vaz, B.-G. Wu, S. Zumer, Appl. Phys. Lett. 48 (1986) 269.
[31] H. Takatsu, Kinouzairyou (Funct. Mater.) 15 (1995) 22.
[32] C.V. Rajaram, S.D. Hudson, Chem. Mater. 8 (1996) 2451.
[33] D.-K. Yang, L.-C. Chien, J.W. Doane, Appl. Phys. Lett. 60 (1992) 3102.
[34] P.P. Crooker, D.K. Yang, Appl. Phys. Lett. 57 (1990) 2529.
[35] R.A.M. Hikmet, H.M. Boots, M. Michielsen, J. Appl. Phys. 79 (1996) 8098.
[36] Y.-D. Ma, B.-G. Wu, G. Xu, Proc. SPIE 1257 (1990) 46.
[37] A.Y.-G. Fuh, C.-Y. Huang, C.-R. Sheu, G.-L. Lin, M.-S. Tsai, Jpn, J. Appl. Phys. 33 (1994) L870.
[38] Y. Kawanishi, T. Tamaki, K. Ichimura, J. Phys. D: Appl. Phys. 24 (1991) 782.
[39] H.-K. Lee, A. Kanazawa, T. Shiono, T. Ikeda, T. Fujisawa, M. Aizawa, B. Lee, Chem. Mater. 10 (1998) 1402.
[40] H.-K. Lee, A. Kanazawa, T. Shiono, T. Ikeda, T. Fujisawa, M. Aizawa, B. Lee, J. Appl. Phys. 86 (1999) 5927.
[41] S. Kurihara, K. Masumoto, T. Nonaka, Appl. Phys. Lett. 73 (1998) 160.
[42] H.-K. Lee, K. Doi, A. Kanazawa, T. Shiono, T. Ikeda, T. Fujisawa, M. Aizawa, B. Lee, Polymer 41 (2000) 1757.
[43] M. Eich, J.H. Wendorff, B. Reck, H. Ringsdorf, Makromol. Chem. Rapid Commun. 8 (1987) 59.
[44] M. Eich, J.H. Wendorff, Makromol. Chem. Rapid Commun. 8 (1987) 467.
[45] T. Ikeda, S. Horiuchi, D.B. Karanjit, S. Kurihara, S. Tazuke, Chem. Lett. (1988) 1679.
[46] T. Ikeda, S. Horiuchi, D.B. Karanjit, S. Kurihara, S. Tazuke, Macromolecules 23 (1990) 36.
[47] T. Ikeda, S. Horiuchi, D.B. Karanjit, S. Kurihara, S. Tazuke, Macromolecules 23 (1990) 42.
[48] T. Ikeda, S. Kurihara, D.B. Karanjit, S. Tazuke, Macromolecules 23 (1990) 3938.
[49] T. Sasaki, T. Ikeda, K. Ichimura, Macromolecules 25 (1992) 3807.
[50] O. Tsutsumi, Y. Demachi, A. Kanazawa, T. Shiono, T. Ikeda, Y. Nagase, J. Phys. Chem. 102 (1998) 2869.
[51] S. Kurihara, T. Ikeda, T. Sasaki, H.-B. Kim, S. Tazuke, J. Chem. Soc., Chem. Commun. (1990) 1751.
[52] S. Kurihara, T. Ikeda, T. Sasaki, H.-B. Kim, S. Tazuke, Mol. Cryst. Liq. Cryst. 195 (1991) 251.
[53] T. Ikeda, T. Sasaki, H.-B. Kim, J. Phys. Chem. 95 (1991) 509.
[54] T. Ikeda, O. Tsutsumi, Science 268 (1995) 1873.
[55] O. Tsutsumi, T. Shiono, T. Ikeda, G. Galli, J. Phys. Chem. B 101 (1997) 1332.
[56] T. Ikeda, Mol. Cryst. Liq. Cryst. 364 (2001) 187.
[57] O. Tsutsumi, T. Kitsunai, A. Kanazawa, T. Shiono, T. Ikeda, Macromolecules 31 (1998) 355.
[58] O. Tsutsumi, Y. Miyashita, S. Hirano, A. Shishido, A. Kanazawa, T. Shiono, T. Ikeda, Mol. Cryst. Liq. Cryst. 312 (1998) 33.
[59] A. Kanazawa, A. Shishido, M. Hasegawa, O. Tsutsumi, T. Shiono, T. Ikeda, Y. Nagase, E. Akiyama, Y. Takamura, Mol. Cryst. Liq. Cryst. 300 (1997) 201.
[60] A. Kanazawa, S. Hirano, A. Shishido, M. Hasegawa, O. Tsutsumi, T. Shiono, T. Ikeda, Y. Nagase, E. Akiyama, Y. Takamura, Liq. Cryst. 23 (1997) 293.
[61] A. Shishido, O. Tsutsumi, A. Kanazawa, T. Shiono, T. Ikeda, N. Tamai, J. Phys. Chem. B 101 (1997) 2806.
[62] A. Shishido, O. Tsutsumi, A. Kanazawa, T. Shiono, T. Ikeda, N. Tamai, J. Am. Chem. Soc. 119 (1997) 7791.
[63] A. Shishido, A. Kanazawa, T. Shiono, T. Ikeda, N. Tamai, J. Mater. Chem. 9 (1999) 2211.
[64] S. Kurihara, A. Sakamoto, T. Nonaka, Macromolecules 31 (1998) 4648.
[65] S. Kurihara, A. Sakamoto, D. Yoneyama, T. Nonaka, Macromolecules 32 (1999) 6493.
[66] S. Kurihara, D. Yoneyama, T. Nonaka, Chem. Mater. 13 (2001) 2807.
[67] T. Weigert, Verh. Phys. Ges. 21 (1919) 485.
[68] T. Todorov, N. Tomova, L. Nikolova, L. Opt. Commun. 47 (1983) 123.
[69] P. Rochon, J. Gosselin, A. Natansohn, S. Xie, Appl. Phys. Lett. 60 (1992) 4.
[70] M.S. Ho, A. Natansohn, P. Rochon, Macromolecules 28 (1995) 6124.
[71] O.K. Song, C.H. Wang, M.A. Pauley, Macromolecules 30 (1997) 6913.
[72] T. Buffeteau, A. Natansohn, P. Rochon, M. Pézolet, Macromolecules 29 (1996) 8783.
[73] A. Natansohn, P. Rochon, X. Meng, C. Barrett, T. Buffeteau, S. Bonenfant, M. Pézolet, Macromolecules 31 (1998) 1155.
[74] K. Anderle, R. Birenheide, M.J.A. Werner, J.H. Wendorff, Liq. Cryst. 9 (1991) 691.
[75] U. Wiesner, N. Reynolds, C. Roeffel, H.W. Spiess, Makromol. Chem. Rapid Commun. 12 (1991) 457.
[76] J. Stumpe, L. Läsker, Th. Fischer, M. Rutloh, S. Kostromin, R. Ruhmann, Thin Solid Film. 284 (1996) 252.
[77] Th. Fischer, L. Läsker, J. Stumpe, S. Kostromin, J. Photochem. Photobiol. A: Chem. 80 (1994) 453.
[78] L. Läsker, J. Stumpe, Th. Fischer, M. Rutloh, S. Kostromin, R. Ruhmann, Mol. Cryst. Liq. Cryst. 261 (1995) 371.
[79] L. Läsker, Th. Fischer, J. Stumpe, S. Kostromin, S. Ivanov, V.P. Shibaev, R. Ruhmann, Mol. Cryst. Liq. Cryst. 253 (1994) 1.
[80] Y. Wu, Y. Demachi, O. Tsutsumi, A. Kanazawa, T. Shiono, T. Ikeda, Macromolecules 31 (1998) 349.
[81] Y. Wu, Y. Demachi, O. Tsutsumi, A. Kanazawa, T. Shiono, T. Ikeda, Macromolecules 31 (1998) 1104.
[82] Y. Wu, Y. Demachi, O. Tsutsumi, A. Kanazawa, T. Shiono, T. Ikeda, Macromolecules 31 (1998) 4457.
[83] Y. Wu, Q. Zhang, A. Kanazawa, T. Shiono, T. Ikeda, Polymer 40 (1999) 4787.
[84] Y. Wu, Q. Zhang, A. Kanazawa, T. Shiono, T. Ikeda, Y. Nagase, Macromolecules 32 (1999) 3951.
[85] U. Wiesner, N. Reynolds, Ch. Boeffel, H.W. Spiess, Liq. Cryst. 11 (1992) 251.
[86] Th. Fischer, L. Läsker, S. Czapla, J. Rübner, J. Stumpe, Mol. Cryst. Liq. Cryst. 298 (1997) 213.
[87] M. Schönhoff, M. Mertesdorf, M. Lösche, J. Phys. Chem. 100 (1996) 7558.
[88] H.J. Haitjema, G.L. von Morgen, Y.Y. Tan, G. Challa, Macromolecules 27 (1994) 6201.
[89] F.H. Kreuzer, Ch. Bräuchle, A. Miller, A. Petri, in: V.P. Shibaev (Ed.), Polymers as Electrooptical and Photooptical Active Media, Springer, Berlin Heidelberg, 1996, Chapter 3.
[90] M. Pfaadt, C. Boeffel, H.W. Spiess, Acta Polymer 47 (1996) 35.
[91] K. Ichimura, S. Morino, H. Akiyama, Appl. Phys. Lett. 73 (1998) 921.
[92] Y. Wu, T. Ikeda, Q. Zhang, Adv. Mater. 11 (1999) 300.
[93] Y. Wu, J. Mamiya, A. Kanazawa, T. Shiono, T. Ikeda, Q. Zhang, Macromolecules 32 (1999) 8829.

[94] H. Gruler, G. Meier, Mol. Cryst. Liq. Cryst. 16 (1972) 299.
[95] K. Ichimura, Y. Suzuki, T. Seki, A. Hosoki, K. Aoki, Langmuir 4 (1988) 1214.
[96] K. Ichimura, Y. Suzuki, T. Seki, A. Kawanishi, K. Aoki, Makromol. Chem. Rapid Commun. 10 (1989) 5.
[97] T. Seki, M. Sakuragi, A. Kawanishi, T. Tamaki, R. Fukuda, K. Ichimura, Langmuir 9 (1993) 211.
[98] W.M. Gibbons, P.J. Shannon, S.T. Sun, B.J. Swetlin, Nature 351 (1991) 49.
[99] Y. Iimura, J. Kusano, S. Kobayashi, T. Aoyagi, T. Sugano, Jpn. J. Appl. Phys. 32 (Part 2) (1993) L93.
[100] K. Ichimura, Y. Hayashi, H. Akiyama, N. Ishizuki, Langmuir 9 (1993) 3298.
[101] K. Ichimura, H. Akiyama, N. Ishizuki, A. Kawanishi, Makromol. Chem. Rapid Commun. 14 (1993) 813.
[102] K. Ichimura, Chem. Rev. 100 (2000) 1847.
[103] D. Gabor, Nature 161 (1948) 777.
[104] R.J. Collier, C.B. Burckhardt, L.H. Lin, Optical Holography, Academic Press, New York, 1971.
[105] H.M. Smith, Holographic Recording Materials, Springer-Verlag, Berlin, 1977.
[106] I.C. Khoo, Y.R. Shen, Opt. Eng. 24 (1985) 579.
[107] R. Ortler, C. Brauchle, A. Miller, G. Riepl, Makromol. Chem. Rapid Commun. 10 (1989) 189.
[108] I.C. Khoo, R.G. Lindquist, R.R. Michael, R.J. Mansfield, P. Lopresti, J. Appl. Phys. 69 (1991) 3853.
[109] H.J. Eichler, G. Heppke, R. Macdonald, H. Schmid, Mol. Cryst. Liq. Cryst. 223 (1992) 159.
[110] A. Chen, D.J. Brady, Opt. Lett. 17 (1992) 441.
[111] A. Chen, D.J. Brady, Appl. Phys. Lett. 62 (1993) 2920.
[112] H.J. Eichler, R. Elschner, R. Macdonald, Mol. Cryst. Liq. Cryst. 250 (1994) 293.
[113] I.C. Khoo, H. Li, Y. Liang, Opt. Lett. 19 (1994) 1723.
[114] I.C. Khoo, Opt. Lett. 20 (1995) 2137.
[115] G.P. Wiederrecht, B.A. Yoon, M.R. Wasielewski, Science 270 (1995) 1794.
[116] J. Contzen, G. Heppke, D. Kitzerow, H. Schmid, Appl. Phys. B 63 (1996) 605.
[117] R. Elschner, R. Macdonald, Mol. Cryst. Liq. Cryst. 282 (1996) 107.
[118] S. Bartkiewicz, A. Januszko, A. Miniewixz, J. Parka, Pure Appl. Opt. 5 (1996) 799.
[119] F. Simoni, O. Francescangeli, Y. Reznikov, S. Slussarenko, Opt. Lett. 22 (1997) 549.
[120] S. Slussarenko, O. Francescangeli, F. Simoni, Y. Reznikov, Appl. Phys. Lett. 71 (1997) 3613.
[121] G.P. Wiederrecht, B.A. Yoon, W.A. Svec, M.R. Wasielewski, J. Am. Chem. Soc. 119 (1997) 3358.
[122] H. Ono, N. Kawatsuki, Appl. Phys. Lett. 71 (1997) 1162.
[123] I.C. Khoo, S. Slussarenko, B.D. Guenther, M.Y. Shih, P. Chen, W.V. Wood, Opt. Lett. 23 (1998) 253.
[124] G.P. Wiederrecht, M.R. Wasielewski, Appl. Phys. Lett. 74 (1999) 3459.
[125] G.P. Wiederrecht, M.P. Niemczyk, A. Svec, M.R. Wasielewski, Chem. Mater. 11 (1999) 1409.
[126] A. Stracke, J.H. Wendorff, D. Goldmann, D. Janietz, B. Stiller, Adv. Mater. 12 (2000) 282.
[127] T. Sasaki, A. Katsuragi, K. Ohno, J. Phys. Chem. B 106 (2002) 2520.
[128] F. Simoni, F. Bloisi, L. Vicari, Mol. Cryst. Liq. Cryst. 223 (1992) 169.
[129] V.P. Tondiglia, L.V. Natarajan, R.L. Sutherland, T.J. Bunning, W.W. Adams, Opt. Lett. 20 (1995) 1325.
[130] A.Y.G. Fuh, C.Y. Huang, M.S. Tsai, J.M. Chen, L.C. Chien, Jpn. J. Appl. Phys. 35 (1996) 630.
[131] H. Ono, N. Kawatsuki, Opt. Lett. 22 (1997) 1144.
[132] A. Golemme, B.L. Bolodin, B. Kippelen, N. Peyghambarian, Opt. Lett. 22 (1997) 1226.
[133] H. Ono, N. Kawatsuki, Jpn. J. Appl. Phys. 36 (1997) 6444.
[134] A.Y.G. Fuh, M.S. Tsai, T.C. Liu, L.C. Chien, Jpn. J. Appl. Phys. 36 (1997) 6839.
[135] A.Y.G. Fuh, T.C. Ko, M.S. Tsai, C.Y. Huang, L.C. Chien, J. Appl. Phys. 83 (1998) 679.
[136] G.P. Wiederrecht, M.R. Wasielewski, J. Am. Chem. Soc. 120 (1998) 3231.
[137] G. Cipparrone, A. Mazzulla, F. Simoni, Opt. Lett. 23 (1998) 1505.
[138] A. Golemme, B. Kippelen, N. Peyghambarian, Appl. Phys. Lett. 73 (1998) 2408.
[139] H. Ono, N. Kawatsuki, J. Appl. Phys. 85 (1999) 2482.
[140] H. Ono, T. Kawamura, N.M. Frias, K. Kitamura, N. Kawatsuki, H. Norisada, Adv. Mater. 12 (2000) 143.
[141] T. Ubukata, T. Seki, K. Ichimura, Adv. Mater. 12 (2000) 1675.
[142] N. Yoshimoto, S. Morino, M. Nakagawa, K. Ichimura, Opt. Lett. 27 (2002) 182.
[143] T. Sasaki, K. Ohno, Y. Nakazawa, Macromolecules 35 (2002) 4317.
[144] S. Hvilsted, F. Andruzzi, P.S. Ramanujam, Opt. Lett. 17 (1992) 1234.
[145] P.S. Ramanujam, S. Hvilsted, F. Andruzzi, Appl. Phys. Lett. 62 (1993) 1041.
[146] M. Eich, J.H. Wendorff, Mol. Cryst. Liq. Cryst. 243 (1994) 51.
[147] S. Hvilsted, F. Andruzzi, C. Kulinna, H.W. Siesler, P.S. Ramanujam, Macromolecules 28 (1995) 2172.
[148] N.C.R. Holme, P.S. Ramanujam, S. Hvilsted, Appl. Opt. 35 (1996) 4622.
[149] L. Nikolova, T. Todorov, M. Ivanov, F. Andruzzi, S. Hvilsted, P.S. Ramanujam, Appl. Opt. 35 (1996) 3835.
[150] P.S. Ramanujam, N.C.R. Holme, S. Hvilsted, Appl. Phys. Lett. 68 (1996) 1329.
[151] X. Wei, X.Z. Yan, D.R. Zhu, D. Mo, Z.X. Liang, W.Z. Lin, Appl. Phys. Lett. 68 (1996) 1913.
[152] N.C.R. Holme, L. Nikolova, P.S. Ramanujam, S. Hvilsted, Appl. Phys. Lett. 70 (1997) 1518.
[153] I. Naydenova, L. Nikolova, T. Todorov, N.C.R. Holme, P.S. Ramanujam, S. Hvilsted, J. Opt. Soc. Am. B 15 (1998) 1257.
[154] L. Andruzzi, A. Altomare, F. Ciardelli, R. Solaro, S. Hvilsted, P.S. Ramanujam, Macromolecules 32 (1999) 448.
[155] U. Pietsch, P. Rochon, A. Natansohn, Adv. Mater. 12 (2000) 1129.
[156] H.J. Eichler, S. Orlic, R. Schulz, J. Rübner, Opt. Lett. 26 (2001) 581.
[157] C. Sánchez, R. Alcalá, S. Hvilsted, P.S. Ramanujam, Appl. Phys. Lett. 78 (2001) 3944.
[158] M. Hasegawa, T. Yamamoto, A. Kanazawa, T. Shiono, T. Ikeda, Adv. Mater. 11 (1999) 675.
[159] M. Hasegawa, T. Yamamoto, A. Kanazawa, T. Shiono, T. Ikeda, Chem. Mater. 11 (1999) 2764.
[160] M. Hasegawa, T. Yamamoto, A. Kanazawa, T. Shiono, T. Ikeda, Y. Nagase, E. Akiyama, Y. Takamura, J. Mater. Chem. 9 (1999) 2765.
[161] T. Yamamoto, M. Hasagawa, A. Kanazawa, T. Shiono, T. Ikeda, J. Phys. Chem. B 103 (1999) 9873.
[162] T. Yamamoto, M. Hasagawa, A. Kanazawa, T. Shiono, T. Ikeda, J. Mater. Chem. 10 (2000) 337.
[163] T. Yamamoto, S. Yoneyama, O. Tsutsumi, A. Kanazawa, T. Shiono, T. Ikeda, J. Appl. Phys. 88 (2000) 2215.
[164] T. Yamamoto, A. Ohashi, S. Yoneyama, M. Hasegawa, O. Tsutsumi, A. Kanazawa, T. Shiono, T. Ikeda, J. Phys. Chem. B 105 (2001) 2308.
[165] S. Yoneyama, T. Yamamoto, M. Hasegawa, O. Tsutsumi, A. Kanazawa, T. Shiono, T. Ikeda, J. Mater. Chem. 11 (2001) 3008.
[166] S. Yoneyama, O. Tsutsumi, A. Kanazawa, T. Shiono, T. Ikeda, Mol. Cryst. Liq. Cryst. 368 (2001) 335.
[167] S. Yoneyama, T. Yamamoto, O. Tsutsumi, A. Kanazawa, T. Shiono, T. Ikeda, Macromolecules 35 (2002) 8751.

[168] P. Rochon, E. Batalla, A. Natansohn, Appl. Phys. Lett. 66 (1995) 136.
[169] D.Y. Kim, S.K. Tripathy, L. Li, J. Kumar, Appl. Phys. Lett. 66 (1995) 1166.
[170] M. Irie, Adv. Polym. Sci. 94 (1990) 27.
[171] C.D. Eisenbach, Polymer 21 (1980) 1175.
[172] P.-G. de Gennes, M. Hébert, R. Kant, Macromol. Symp. 113 (1997) 39.
[173] W. Lehmann, H. Skupin, C. Tolksdorf, E. Gebhard, R. Zentel, P. Krüger, M. Lösche, F. Kremer, Nature 410 (2001) 447.
[174] I. Kundler, H. Finkelmann, Macromol. Chem. Phys. 199 (1998) 677.
[175] H. Wermter, H. Finkelmann, Report No. 013, 2001 (unpublished) ( ).
[176] D.L. Thomsem III, P. Keller, J. Naciri, R. Pink, H. Jeon, D. Shenoy, B.R. Ratna, Macromolecules 34 (2001) 5868.
[177] J. Naciri, A. Srinivasan, H. Jeon, N. Nikolov, P. Keller, B.R. Ratna, Macromolecules 36 (2003) 8499.
[178] H. Finkelmann, E. Nishikawa, G.G. Pereira, M. Warner, Phys. Rev. Lett. 87 (2001) 15501.
[179] P.M. Hogan, A.R. Tajbakhsh, E.M. Terentjev, Phys. Rev. E 65 (2002) 041720.
[180] M.-H. Li, P. Keller, B. Li, X. Wang, M. Brunet, Adv. Mater. 15 (2003) 569.
[181] T. Ikeda, M. Nakano, Y. Yu, O. Tsutsumi, A. Kanazawa, Adv. Mater. 15 (2003) 201.
[182] M. Nakano, Y. Yu, O. Tsutsumi, A. Shishido, T. Shiono, T. Ikeda, Mol. Cryst. Liq. Cryst. 39 (2003) 1.
[183] Y. Yu, M. Nakano, T. Ikeda, Pure Appl. Chem. 76 (2004) 1435.
[184] Y. Yu, M. Nakano, A. Shishido, T. Shiono, T. Ikeda, Chem. Mater. 16 (2004) 1637.
[185] Y. Yu, M. Nakano, T. Ikeda, Nature 425 (2003) 145.