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Accounts

Photochemical Modulation of Alignment in Liquid Crystals

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Liquid crystals (LCs) show an anisotropic nature in various aspects of optical and electronic properties. This anisotropy enables LC materials to be used as active media in display devices. Birefringence, an anisotropy in optical properties of LCs, is especially useful from the viewpoint of changing refractive indices of LC materials. If alignment of LCs can be changed by light, a large change in refractive index can be induced by light. This is the principle of LC photonics, in which optical signals are processed with the aid of LC materials. In this article, various approaches are described to change the alignment of the LC molecules: 1) photochemically induced phase transition of LCs by photochromic reactions is an order to disorder transition and can be brought about in a time scale of micro- to nanosecond; 2) reorientation of LC molecules by means of linearly polarized light is a change in alignment of LC molecules that occurs within the LC phases and induces a large change in refractive index, but needs more time. Applications of LC systems as photonic materials are also discussed.

We will soon have an information society where a huge amount of information is exchanged simultaneously all over the world through optical fiber networks. We will need optical elements that have such functions as switching, storage, interconnection, and computing of optical signals transported through optical fibers. To process optical data, it is most effective to modulate refractive indices of the optical elements. Especially, refractive-index modulation by light as a stimulus is regarded as a final goal for optical data processing in the information society. We will need optical elements that can change their refractive index as much and as fast as possible upon photoirradiation.

Liquid crystals (LCs) show unique and excellent properties such as 1) a self-organizing nature in a certain temperature range with fluidity and long-range order; 2) a cooperative effect; 3) anisotropy in refractive index (birefringence); 4) alignment change by external fields at surfaces and interfaces. These properties will lead to the unique feature of LCs: a large change in refractive index can be obtained by changing the alignment of LCs. This property of LCs is very useful for refractive-index modulation, which in turn is quite favorable for optical date processing, because as described above to change the refractive index of materials or devices by external fields is the most effective way to control optical signals. The LC materials can be used not only in LC displays (LCDs) but also in various photonic applications, such as optical storage, optical switching, optical display, and optical computing.

Two types of photoinduced alignment changes of LC molecules would be possible: 1) change in director of LCs in LC phases; 2) change in phases (phase transition) as shown in Fig. 1. In both cases, a large change in the refractive index is obtained; however, the former will be preferable in view of the larger change in the refractive index. In the case where one employs linearly polarized light as probe light and the polarization of the probe light is parallel to the director of LCs, the probe light detects n_e (extraordinary refractive index). If the director of LCs is changed perpendicular to the initial direction by another light as a stimulus, the probe light will then detect n_o (ordinary refractive index). This will lead to a change in the refractive index corresponding to birefringence ($\Delta n = n_e - n_o$). LCs possess large values of

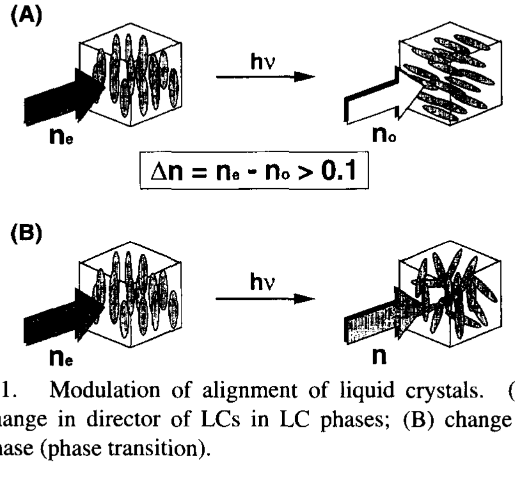


Fig. 1. Modulation of alignment of liquid crystals. (A) change in director of LCs in LC phases; (B) change in phase (phase transition).

Δn ($\Delta n > 0.1$), so we can obtain such large changes in the refractive index by the photoinduced alignment change of LCs (Fig. 1A). If the refractive index of the isotropic phase of LCs is denoted by n, the order of the refractive index is usually $n_o < n < n_e$. Then we can still have a large change in the refractive index by inducing the LC to isotropic phase transition of LC materials by light (Fig. 1B).

1. Change in Alignment of Liquid Crystals by Photochemical Processes

1-1. Photochemical Phase Transition in Guest/Host Systems. Due to the cooperative effect, only a small amount of photoresponsive molecules dispersed in LC systems, which change their molecular shape on photoexcitation, can induce changes in the alignment of entire LC systems. Many photochromic compounds have been used as a photosensitive guest molecule such as azobenzenes, stilbenes, spiropyrans, and fulgides. Advantages of these photochromic compounds as a photoresponsive molecule are as follows:

1) they undergo a change in molecular shape, which in most cases results in changes in other properties of the molecules such as polarity and molar volume;

2) most photochromic reactions are reversible and two isomers can usually be interchanged effectively by light with different wavelengths, so that the alignment of LCs can be altered reversibly by light with different wavelengths;

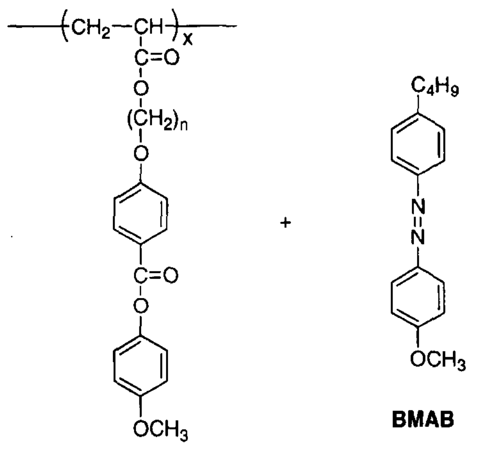
3) photochromic reactions are in most cases very fast; they occur in a time region of picoseconds, which may enable very fast changes in alignment of LCs.

The first example of inducing the change in alignment of LCs by photochromic reactions was reported by Sackmann in 1971, who discovered the change in pitch of cholesteric LCs on photoirradiation to cause *trans–cis* isomerization of azobenzene dispersed in cholesteric LCs, which was evidenced by the change in a reflection wavelength.[1] Since then, many studies have been performed on the photoinduced change in alignment of LCs, focusing mainly on a photochemically induced phase transition of LCs: smectic (Sm)–cholesteric (Ch) phase transition[2] and nematic (N)–isotropic (I) phase transition[3,4] induced by photoisomerization of azobenzenes dispersed in LCs; N–I phase transition induced by photochemical reactions of spiropyrans;[5] change in pitch of Ch LCs caused by photoisomerization of fulgides;[6] helix inversion in Ch LCs induced by photoisomerization of bithiopiranilidene.[7]

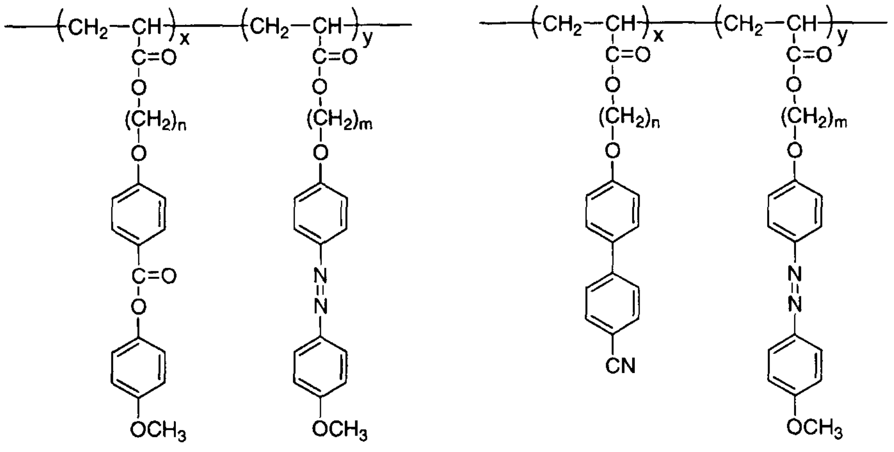
The photochemically induced phase transition (**photochemical phase transition**) of LCs in the guest/host systems is interpreted as the following sequence of events.[8] A small amount of photochromic compounds such as azobenzene dispersed in nematic LCs (NLCs) change the phase structure of the NLCs by photochemical reactions of the photochromic guest molecules. The *trans* form of azobenzene has a rod-like shape, which stabilizes the phase structure of NLCs; however, its isomer, the *cis* form, is bent and tends to destabilize the phase structure of NLCs. So the N to I phase transition temperature, T_{NI}, of the *cis*-azobenzene/NLC mixture is much lower than that of the *trans*-azobenzene/NLC mixture. This phenomenon resembles depression of freezing point caused by a small amount of impurity. In this case, an impurity (*cis* form) is produced on photoirradiation. The depression of freezing point is a colligative property of materials: decrease in temperature does not depend on the structure of impurity, but it is dependent on the concentration of the impurity. However, the photochemically induced decrease in T_{NI} strongly depends on the structure of guest molecules. For instance, two types of azobenzenes were used as a guest molecule, and T_{NI} of the mixtures of azobenzene/4-cyano-4′-pentylbiphenyl (5CB) was measured before and after *trans–cis* photoisomerization. It was found that 4-butyl-4′-methoxyazobenzene (BMAB)/5CB mixture showed a much larger value of ΔT ($= T_{\mathrm{NI}}(trans) - T_{\mathrm{NI}}(cis)$) than nonsubstituted azobenzene/5CB mixture. If an NLC sample containing an azobenzene guest is set at temperature between T_{NI} (*trans*) and T_{NI} (*cis*), and irradiated to cause *trans–cis* isomerization of the azobenzene guest molecules, N to I phase transition of the sample is induced isothermally. Before photoirradiation, when the guest molecule is in the *trans* form, the sample shows an N phase because temperature of the sample is below T_{NI} (*trans*). On *trans–cis* photoisomerization, the concentration of the *cis* form in the sample increases and concomitantly T_{NI} of the mixture decreases, and when T_{NI} is lowered below irradiation temperature, N to I phase transition is induced. Namely, when the concentration of the *cis* form exceeds a threshold value in the phase diagram of the *cis*-azobenzene/NLC system, the mixture shows an I phase at the irradiation temperature. Since the *trans–cis* photoisomerization is reversible, this process is also reversible; with *cis* to *trans* back-isomerization either photochemically or thermally, the initial N phase is restored. This is the mechanism proposed for the photochemical phase transition of NLCs in the guest/host systems. The photochemical phase transition of NLCs in the guest/host systems has been explored extensively: Topics include effects of temperature of the sample, effects of structure of guest molecules, effects of concentration of the guest molecules, and effects of structure of host LCs on the photochemical phase transition behaviors.[9–14]

1-2. Photochemical Phase Transition in Polymer Liquid Crystals. Polymer liquid crystals (PLCs) are high performance materials that show properties of both polymers and LCs. PLCs are currently recognized as a promising material for optical data processing due to a film-forming nature and high birefringence observed in an ultrathin film of PLCs.

The first example of photoresponsive PLCs was reported by Wendorff et al. on holographic recording in PLCs. They successfully produced holograms in LC copolymers containing azobenzene moieties by irradiation of two coherent beams from an Ar^+ laser.[15,16] The first report of the photochemical phase transition of guest/PLC host systems was done by the authors' group.[17–19] It was found that the BMAB/PLC mixture shown in Fig. 2 underwent N–I phase transition on photoirradiation to cause *trans–cis* isomerization of the guest BMAB molecule as in photochromic guest/low-molecular-weight (LMW) LC systems. The dye-



Guest / host system



Copolymers

Fig. 2. Structure of polymer liquid crystals for photochemical phase transition.

doped PLC systems were then extended to copolymer systems on which detailed studies were performed (Fig. 2).[19—22]

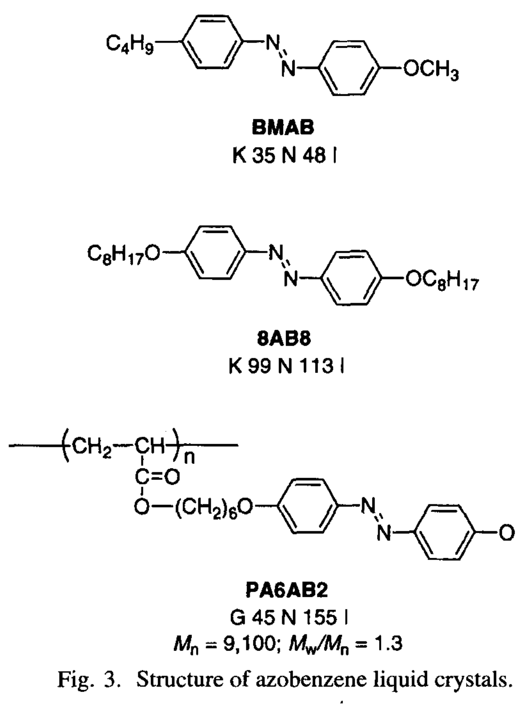
Response times were measured for N–I phase transition in azobenzene/LMWLC systems.[23,24] A thermostated sample composed of an azobenzene guest and an NLC host was placed between a pair of crossed polarizers and irradiated with the third harmonic of a YAG laser at 355 nm (10 ns fwhm) to bring about the *trans–cis* photoisomerization of the azobenzene guest molecules; transmittance of probe light at 633 nm from a He–Ne laser was measured as a function of time. In the azobenzene/LMWLC systems, N–I phase transition (as proved by loss of birefringence of the LC sample) occurred in 100 ms.[23] The response time for azobenzene/PLC systems was also examined and it was observed that the N–I phase transition took place in 50—200 ms in azobenzene-doped PLCs[25] and copolymer LCs containing side-chain azobenzene moieties.[21]

2. Novel Approach to Fast Response of Liquid Crystals by Photochemical Processes

It is very difficult to obtain fast responses in guest/NLC host systems. As mentioned above, most photochromic reactions are very fast, occurring in a time region of picoseconds. Therefore, if ultrafast lasers with a pulse width of picoseconds or nanoseconds are used as an excitation light source for the photochemical phase transition of guest/host systems, photochemical reactions of the guest molecules can be completed in picoseconds or nanoseconds, and T_{NI} of the system can also be lowered below the irradiation temperature in these time regions. This means that immediately after pulse irradiation a nonequilibrium state appears which is thermodynamically isotropic in its equilibrium state but shows birefringence due to nonrelaxation of mesogens. From this state, relaxation of mesogens takes place to their equilibrium state, an I state. The change in refractive index of samples depends on this relaxation process; the relaxation of mesogens is a rate-determining step in the refractive-index modulation.

LCs possess a high viscosity, so that relaxation of alignment of LCs takes a relatively long time.

Furthermore, the temperature range to induce the photochemical phase transition of NLCs in the guest/host systems is limited. In the temperature range above T_{NI} of the *trans*-azobenzene/NLC mixture and below T_{NI} of the *cis*-azobenzene/NLC mixture, phase transition can not be induced even if the *trans–cis* photoisomerization of the guest molecules is brought about. To obtain a faster response and a wider temperature range for the photochemical phase transition, a new system has been developed in which every mesogen is provided with a photosensitive moiety. Through extensive studies on the photochemical change in alignment of LCs, in which a large number of azobenzene derivatives were used as guest molecules, it was realized that some azobenzene derivatives show LC phases; the azobenzene moiety plays roles of both a mesogen and a photosensitive molecule (Fig. 3). For instance, BMAB shows an N phase between 35 and 48 °C, and 4, 4′ -dioctyloxyazobenzene (8AB8) exhibits the N phase around 100 °C. Furthermore, polyacrylate with side-chain azobenzene moieties (PA6AB2 in Fig. 3) shows a very stable N phase between 45 °C, which is the glass transition temperature (T_g) of this polymer, and 155 °C. These azobenzene LCs show the liquid-crystalline phase only when the azobenzene moiety is in the *trans* form. They show no liquid-crystalline phase at any temperature when the azobenzene moiety is in the *cis* form. In these azobenzene LC systems, it is expected that phase transition can be induced basically on the same time scale as the photochemical reactions of the photoresponsive moiety in each mesogen if the photochemical reactions of a large number of mesogens are caused simultaneously by the use of a short laser pulse (Fig. 4).[26] On the basis of this new concept, the photoresponse of azobenzene LCs was examined with the laser pulse, and it was revealed that N to I phase transition was induced in 200 μs.[26,27] This fast response in the microsecond time region has been shown for the first time in NLCs. From the viewpoint of applications of LCs to photonic devices, such fast response is quite favorable.


BMAB
K 35 N 48 I

8AB8
K 99 N 113 I

PA6AB2
G 45 N 155 I
M_n = 9,100; M_w/M_n = 1.3

Fig. 3. Structure of azobenzene liquid crystals.

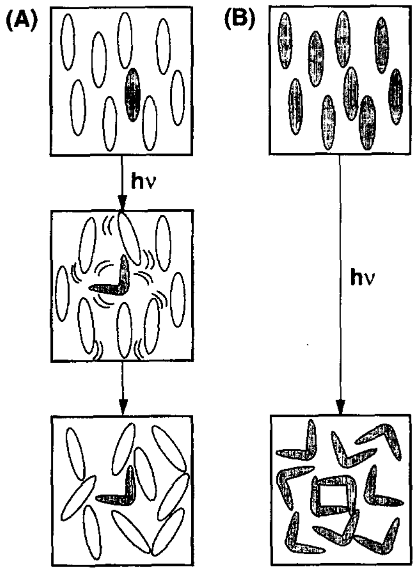


Fig. 4. Novel concept for fast response of azobenzene liquid crystals. (A) guest/host systems; (B) azobenzene liquid crystals.

In general, the response time of PLCs is longer than that of LMWLCs, since in PLCs mobility of mesogens is highly restricted by main chains of the polymer. In the photochemical phase transition behavior of azobenzene LCs, however, no difference in response was observed between polymer and LMWLCs. It is worth mentioning that the polymer azobenzene LCs show a similar 200-μs response even below T_g.[26,27] Figure 5 shows typical results observed for PA6AB2. In the polymer azobenzene LCs, the photochemical phase transition can be induced in an extremely wide temperature range over 150 °C. This advantageous feature as photonic materials is specific for the azobenzene LCs because in the guest/host systems the temperature range to induce the photochemical phase transition is about 20 °C. A relationship between the structure of polymer azobenzene LCs and the photochemical phase transition behavior has been explored extensively to develop high-performance photonic materials. It was revealed that the structure of the polymer backbone as well as the spacer of the side-chain component are crucial factors for the photoresponse of PLCs.[28—31]

Since the photochemical phase transition accompanies a large change in refractive index of materials, the polymer azobenzene LCs may be potential candidates for all-optical switching materials and dynamic holographic materials. In these applications, it is necessary to induce rapidly not only the N–I phase transition but also the I–N phase transition (recovery of N phase). After photoirradiation of the polymer azobenzene LC films (N–I phase transition), when irradiation has ceased, the initial N phase can be restored because of thermal *cis–trans* back-isomerization. To accelerate the thermal

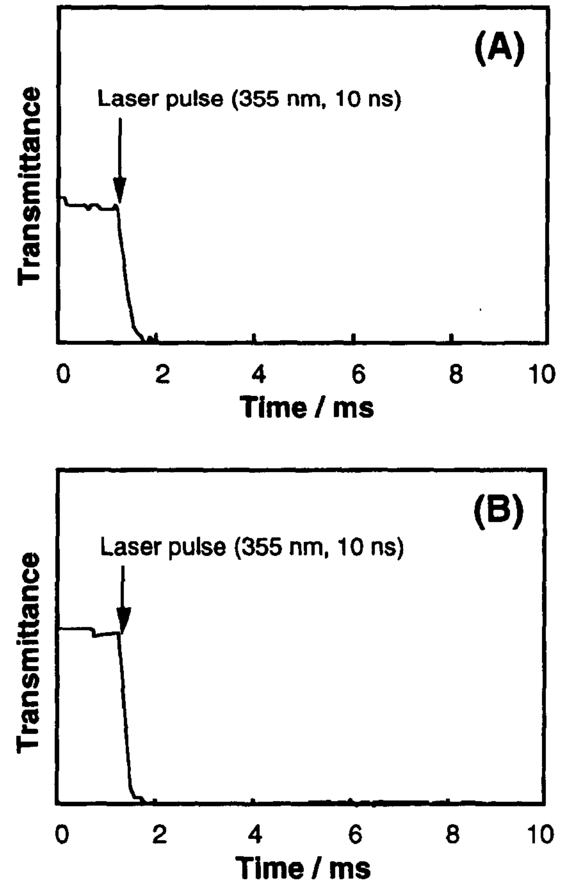


Fig. 5. Time-resolved measurements of the photochemical phase transition of the polymer azobenzene liquid crystal. (A) at 140 °C; (B) at R.T.

recovery of the LC phase, the mechanism of the I–N phase transition has been investigated in detail. The recovery consists of two processes: thermal *cis–trans* back-isomerization of the azobenzene moieties and reorientation of the mesogenic *trans*-azobenzenes. It was found that *cis–trans* back-isomerization is a rate-determining process.[27] On the basis of the results of the kinetic studies on the I–N phase transition, new polymer azobenzene LCs were designed, which have both donor and acceptor moieties in a molecule and are characterized by very fast *cis–trans* thermal back-isomerization. With such donor-acceptor azobenzenes, a very fast recovery of the N phase (800 ms) was achieved (Fig. 6).[28] This response is faster by one order of magnitude than that of the conventional azobenzene LCs.

As another approach to fast I–N phase transition, the optical switching behavior of LMW and polymer azobenzene LCs has been explored by means of reflection-mode analysis (Fig. 7).[32] The incident probe light reflected from the interface between the LC and the substrate can be switched upon laser-pulse irradiation, resulting from modulation of reflectivity due to the photoinduced change in the refractive index of the LC materials. In BMAB, the reflection-mode system gave a response time of 100 μs, which was very similar to that observed in the usual transmission-mode analysis, and a decay time of 1 ms, which was significantly shorter than that obtained in the transmission-mode analysis (Fig. 8). The molar extinction coefficients of the azobenzene moieties are very large (approximately 10^4) at 355 nm, and hence pumping light is absorbed entirely at the surface of the sample. Then, the *trans–cis* photoisomerization is also induced near the surface. Consequently, the N–I phase transition occurs only in the surface, leaving the bulk area intact as an N phase. In the reflection-mode analysis, the probe light can penetrate only in the surface area, so if molecules in the *cis* form produced at the surface by photoirradiation diffuse into the bulk phase and simultaneously molecules in the *trans* form in the bulk phase replace them, recovery of the initial N phase can be achieved without the slow *cis–trans* back-isomerization process. Since the diffusion and the reorientation processes are much faster than the *cis–trans* back-isomerization process, optical switching has become much faster in the reflection-mode observation (Fig. 8).[33] This reflection-mode switching shows another superior character for optical switching. In the practical use of the optical switching devices containing organic dyes as functional components, stability is one of the most important prerequisites. The ordinary transmission-mode optical switching generally exhibits low fatigue resistance. With the aim of developing high fatigue-resistant optical switching systems, a detailed optical switching behavior of azobenzene LCs was explored by means of the reflection-mode observation. The reflection-mode optical switching was found to be repeated over 15000 cycles, which is 10 times as stable as that obtained

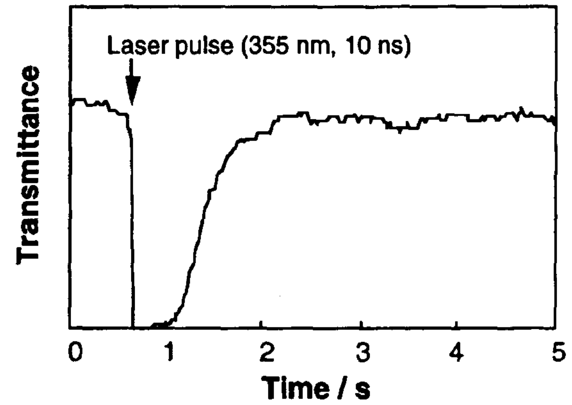


Fig. 6. Time-resolved measurements for recovery of the initial nematic phase in the "push-pull" polymer azobenzene liquid crystal at 135 °C.

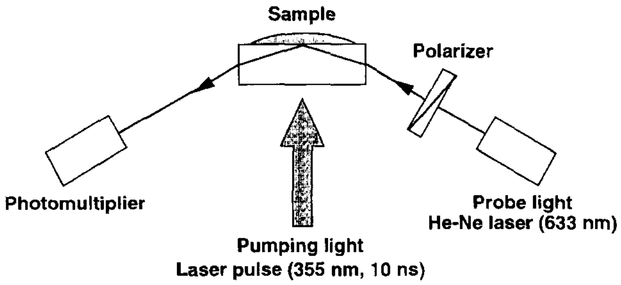


Fig. 7. Reflection-mode optical switching of azobenzene liquid crystals.

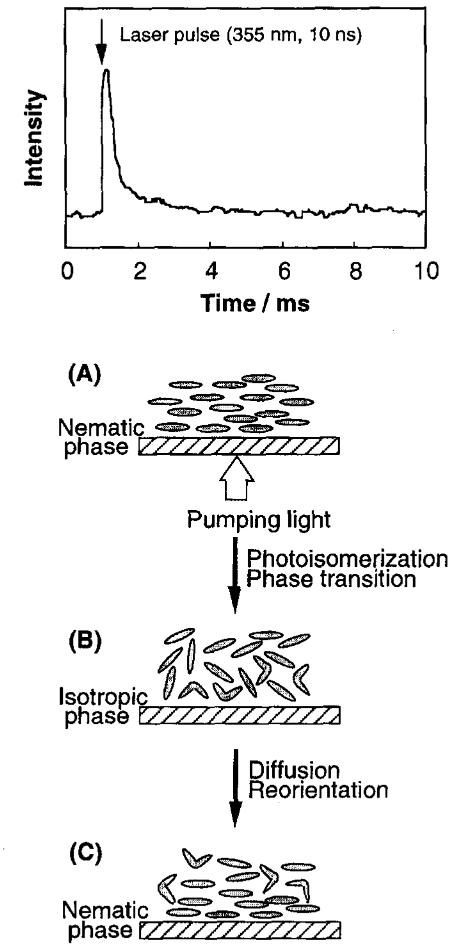


Fig. 8. Time-resolved measurements of the reflection-mode optical switching and the possible mechanism.

in the transmission-mode switching.[34] This fact suggests that the optimization of the optical system for photoresponsive LCs may be an effective approach to realize more fatigue-resistant optical switching devices.

A unique feature of polymer azobenzene LCs as optical image storage materials has been demonstrated. In the solid-state azobenzene LC films retaining an N phase structure below T_g (i.e., nematic glass), only the N–I phase transition is induced and the I–N phase transition never occurs. Figure 9 shows the photographs of the photomask and the binary test pattern recorded in the azobenzene LC films by pulse irradiation at 355 nm.[26,27] Pulse irradiation was performed at room temperature below T_g, and it was found that the irradiated site became isotropic as observed dark with the polarizing microscope. The stored optical image has been kept stable over two years. 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 was recovered nearly completely, the isotropic glass induced at the irradiated site below T_g still remained unchanged at room temperature even after two years.[27] These results imply that below T_g the orientation of the mesogenic *trans*-azobenzenes becomes disordered through thermal *cis–trans* back-isomerization. Even though the *trans* form was recovered thermally, orientation of the mesogens could not be attained in the absence of segmental motion of the main chain of the polymer below T_g. Consequently, the polymer azobenzene LCs can be used as optical switching materials above T_g and as optical image storage materials below T_g.

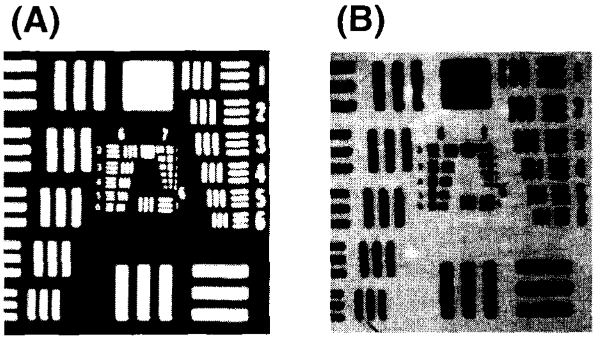


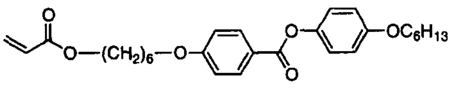
Fig. 9. Optical image storage in the polymer azobenzene liquid crystal. (A) photomask; (B) stored image.

In addition, more recently, an interesting approach to the fast response of photoresponsive LCs has been reported. Crosslinked PLC networks containing azobenzene molecules were prepared through polymerization of ternary mixtures of monofunctional and difunctional LC monomers as well as a LMW azobenzene LC, as shown in Fig. 10, and their photoresponsive behavior was evaluated by monitoring the change in intensity of the probe light transmitted through a pair of crossed polarizers, with the sample film showing birefringence between them, on pulse irradiation at 355 nm.[35] As shown in Fig. 10, the response time and the decay time were 1 and 100 μs, respectively. This very fast response seems to be ascribed to the suppression of motion of the mesogenic groups by crosslinking. In fact, the non-crosslinked PLC analogs showed no such fast response. Through the intensive studies, it has been concluded that the stabilization of an initial ordered state by crosslinking leads to a fast order-disorder transition, which is induced by a slight change in the orientational order of mesogens, and a fast disorder–order transition, which is due to relaxation of the strain generated by the photoisomerization of the azobenzene molecules on irradiation.

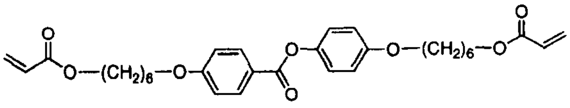
3. Novel Concept for Alignment Change of Liquid Crystals by Photochemical Processes

To obtain a fast photoresponse of LCs, a new guest/host system was developed in which ferroelectric LCs (FLCs) were used as host LCs. FLCs possess spontaneous polarization (P_S) and show microsecond responses to the change in the applied electric field (flip of polarization) in a surface-stabilized state.[36] If a flip of polarization of FLC molecules in the surface-stabilized state can be induced by light in the presence of an applied electric field, a photoresponse in the microsecond time region might be achieved.

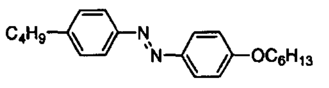
A mixture of an azobenzene derivative and FLC (Fig. 11), in which the concentration of the azobenzene guest was 3 mol%, was prepared and subjected to the surface-stabilized state in a very thin LC cell. Then the mixture was irradiated



APB6
K 32 S 53 N 61 I



A6PB6A
K 33 S 47 N 50 I (cooling)



BHAB
K 45 N 73 I

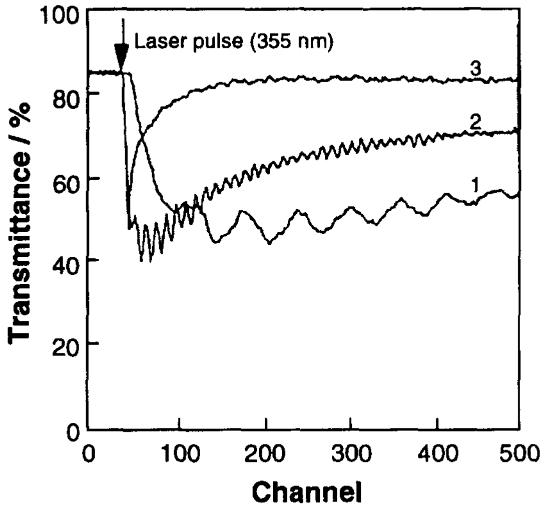
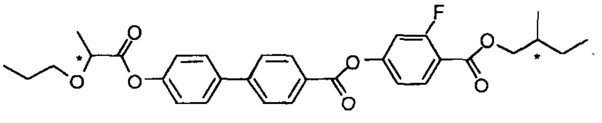
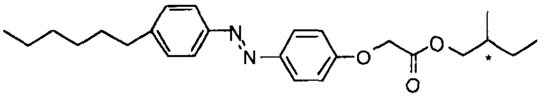


Fig. 10. Time-resolved measurements of change in transmittance of the crosslinked polymer network. 1, 10 ns/ch; 2, 50 ns/ch; 3, 1 μs/ch.



FLC



Azobenzene

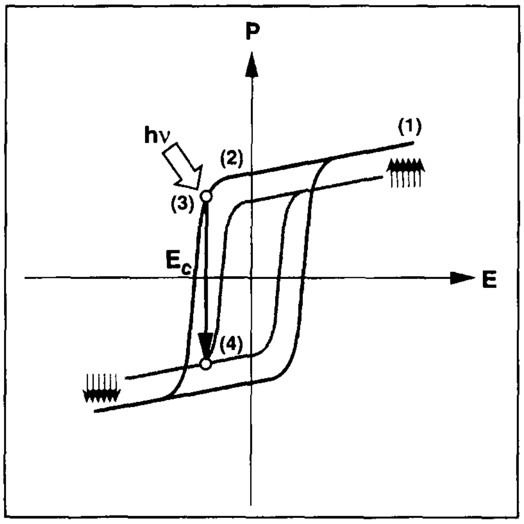


Fig. 11. Photochemical flip of polarization in ferroelectric liquid crystals.

with light at 366 nm to cause *trans–cis* photoisomerization of the azobenzene guest molecule. It was found that a threshold electric field for the flip of polarization (coercive force; E_c in Fig. 11) of FLC was changed on photoirradiation.[37] FLC in the surface-stabilized state shows hysteresis between applied electric field and polarization.[36] It was observed that hysteresis of the mixture with the azobenzene guest molecule in a *trans* form was different from that of the mixture with the azobenzene in a *cis* form. It is already described in **1-1** that in the azobenzene guest/NLC mixtures T_{NI} (*trans*) is different from T_{NI} (*cis*), and this difference arises mainly from the molecular shape of the guest molecule. In the azobenzene guest/FLC host systems, the change in the threshold value for the flip of polarization between the mixture with a *trans* azobenzene and that with a *cis* azobenzene is also similarly interpreted in terms of a change in the molecular shape of the guest molecule. When the azobenzene guest is in a *trans* form, the rod-shaped azobenzene molecules do not disorganize the phase structure of chiral smectic C (SmC*) phase of FLCs to any great extent, and the mixture shows a similar threshold value of the electric field to that without the guest molecule for the flip of polarization. However, when the azobenzene is in a *cis* form, due to the bent shape of the guest molecules, the phase structure of SmC* phase is significantly disorganized and the threshold value for the flip of polarization is much reduced. On the basis of these experimental observations, a new mode of photoresponse of FLC (**photochemical flip of polarization of FLC**) was proposed (Fig. 11).[37,38] (1) Polarization of the FLC cell containing a small amount of azobenzene guest molecules is aligned into one direction by an electric field; (2) an opposite electric field is applied across the FLC cell, which is small enough to retain the initial direction of polarization unchanged; (3) with this opposite electric field as a bias, the FLC cell is irradiated to cause *trans–cis* photoisomerization of the azobenzene guest molecule, then the hysteresis of the cell is changed; (4) the threshold value for the flip of polarization of the FLC cell is lowered on photoirradiation and becomes smaller than the bias voltage, which induces a flip of polarization of FLC molecules. Namely, the bias voltage remains unchanged before and after photoirradiation; however, the threshold value for the flip of polarization of FLC cell is reduced by *trans–cis* photoisomerization of the guest molecules. As a result, a flip of polarization is induced at irradiated sites, which leads to a change in alignment of FLC molecules (**photochemical flip of polarization of FLC**). FLC molecules in a surface-stabilized state show bistability of polarization with upward and downward directions with respect to normal to the cell surface and hence two alignments of FLC molecules are stabilized. Furthermore, these two states remain unchanged even after the electric field is removed. Owing to these properties of FLC in the surface-stabilized state, once the flip of polarization is induced on photoirradiation, the direction of polarization is opposite between the irradiated site and unirradiated site, and the alignment of FLC molecules is different between the two sites. These changes in polarization and alignment of FLCs produce an optical contrast between the irradiated and unirradiated sites, and they are kept unchanged (memory effect). Time-resolved measurements of change in alignment of mesogens due to the flip of polarization in the azobenzene guest/FLC host mixtures were performed on pulse irradiation. It was observed that the mixture composed of the azobenzene and FLC shown in Fig. 11 showed the flip of polarization in 500 μs on pulse irradiation with the third harmonic of a YAG laser (fwhm, 10 ns).[37] This is the first example of inducing the flip of polarization of FLC by a photochemical reaction.[37] Since this first report, detailed studies have been performed on the flip of polarization in the photochromic guest/FLC host systems: topics include effects of structure of FLC hosts,[39,40] structure of photochromic guests,[41] temperature,[42] bias voltage,[38] and change in *P*s.[42]

The photochemical flip of polarization was immediately extended to antiferroelectric LCs (AFLCs), and it was revealed that in the azobenzene guest/AFLC host systems, the flip of polarization could be induced photochemically and effectively as shown in Fig. 12.[43] Novel photochromic molecules to induce the flip of polarization effectively have been developed and molecular design on the basis of large *P*s due to chiral cyclic carbonates has been found to be quite effective. An azobenzene dopant containing chiral cyclic carbonate was synthesized and used as a chiral dopant to induce the SmC* phase (Fig. 13). In this system, the photosensitive azobenzene acts as a chiral dopant, which is essential for the dopant/host LC mixtures to exhibit the SmC* phase, and therefore the change in molecular shape of the dopant is expected to affect significantly the phase structure of the mixture. It was observed that in this system the flip of polarization was induced in 90 μs on pulse irradiation.[44] Furthermore, a very interesting photoresponsive molecule has been developed, which possesses both a photochromic nature and an antiferroelectric property (Fig. 13). The photoresponsive property of this AFLC molecule has been extensively investigated.[45] The flip of polarization in AFLCs is very effective and reliable, so devices based on this mechanism have been explored.[46]

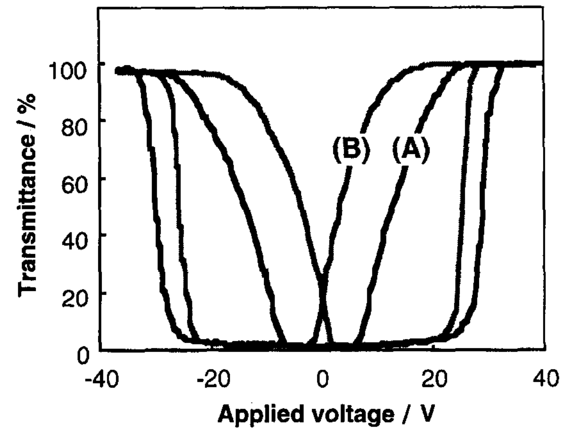
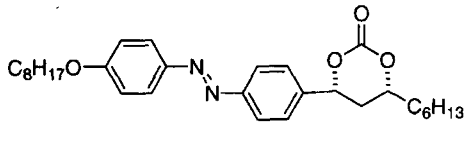
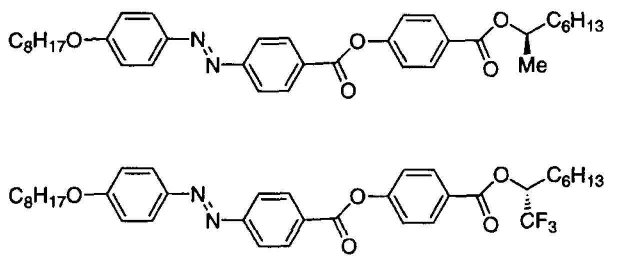


Fig. 12. Change in transmittance of antiferroelectric liquid crystal containing an azobenzene. (A) in the dark; (B) under photoirradiation.



Azobenzene dopant



Azobenzene antiferroelectric liquid crystal

Fig. 13. Structure of azobenzene dopant and azobenzene antiferroelectric liquid crystal.

Thioindigo shows two isomers with parallel (*cis* form) and antiparallel (*trans* form) arrangement of carbonyl groups attached to α-carbons of the double bond, and the two isomers exhibit distinct dipole moments. The *cis* form shows a high dipole moment due to parallel arrangement of the carbonyl moiety, while in the *trans* isomer antiparallel dipole moments associated with the carbonyl moieties are cancelled out, giving a very small overall dipole moment. Another feature of thioindigo as a photoresponsive molecule is a small change in molecular shape on isomerization. Thus the thioindigo derivatives are classified as a novel class of guest molecules in guest/FLC host systems because they possess a dipole-moment-tunable nature without significant changes in the molecular shape.[47,48] By using this unique feature of thioindigo, optical modulation of *P*s of FLCs has been achieved. Photoirradiation (> 505 nm) to cause *trans–cis* isomerization resulted in 1.5-fold enhancement of the *P*s, which is due to the increase of dipole moments of the guest thioindigo molecules (Fig. 14).

4. Photochemical Alignment of Liquid Crystals by Linearly Polarized Light

The nature of light is simply represented by electromagnetic waves with oscillating electric dipoles. The key idea in

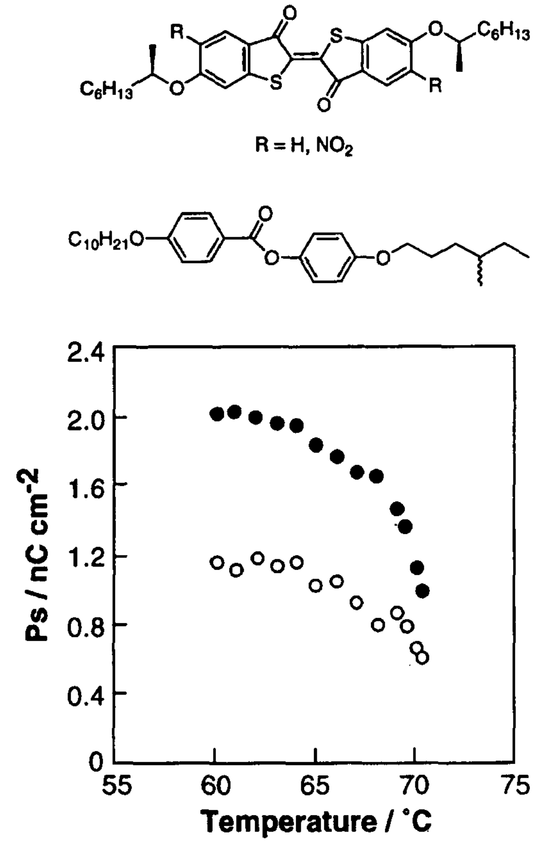


Fig. 14. Spontaneous polarization as a function of temperature. (●) *cis* isomer of thioindigo; (○) *trans* isomer of thioindigo.

understanding the interaction of light with molecules is that electrons may be set into motion by the oscillating electric field of light. The major force operating on the electrons of a molecule in consequence of the passing lightwave is that due to the undulating electric field. Light absorption to give excited molecules is achieved under exclusive requirements including the coincidence of the electric field vector of light with the direction of a transition moment of the corresponding ground state chromophores.

In the case of the *trans*-azobenzene moiety, light is absorbed when the electric field vector of radiation is not perpendicular to the transition moment of the azobenzene moiety. The *trans* form possesses the π–π^* transition moments approximately parallel to the molecular long axis. Light is considered to be "linearly polarized" when it contains waves that only fluctuate in one specific plane. Thus, it can be concluded that the *trans*-azobenzene moieties exhibit angular-dependent absorption (photoselection) of the linearly polarized light. The *trans*-azobenzene molecules with the transition moment parallel to the polarization direction of light are activated to undergo *trans–cis* isomerization, while the molecules with the transition moment perpendicular to the polarization direction are inactive for isomerization. After each isomerization cycle, the azobenzene moieties may have a different orientation, because the *trans* and *cis* isomers show different molecular shapes and the isomerization causes a perturbation on the molecular environment. Once the azobenzene moieties have fallen perpendicular to the polarization direction of the irradiation light after repetition of the *trans–cis–trans* isomerization cycles, they become inactive. At the end of the multi-cycles, there will be a net population of azobenzene groups aligned in the direction perpendicular to the light polarization. Taking the advantage of the photoselection of azobenzene moieties, the possibility of using a polymer system containing azobenzene molecules as optical recording medium was first suggested in 1983 with azo dyes (Methyl Red and Methyl Orange) dispersed in a polymer matrix (poly(vinyl alcohol)).[49] When the dye-doped polymer film was irradiated with a linearly polarized laser beam at 488 nm, transmittance of light polarized parallel to the polarization direction of the writing light increased and that perpendicular to the polarization of the writing light decreased. Optical dichroism was induced because of the anisotropic rearrangement of *trans*-azobenzenes. However, the induced anisotropy could only be maintained for a short time even in the dark. This shortcoming was overcome by Natansohn and co-workers, who developed amorphous azobenzene polymers, and by other groups.[50—54] They used polymers with side-chain azobenzene moieties and achieved stable birefringence at room temperature below T_g. The induced birefringence could be erased thermally or photochemically and re-induced on irradiation of linearly polarized light.

Since these reports on amorphous polymers, the photoinduced molecular alignment has been extended to copolymer LCs having both mesogens and azobenzene moieties in the side chain. Several studies on the photoinduced reorientation behavior showed that non-photoactive mesogens could undergo reorientation together with azobenzene moieties above T_g. This was explained in terms of the cooperative motion of the neighboring groups due to the similar shape of the rigid groups. On the other hand, different arguments were presented on the reorientation behavior below T_g. Anderle et al. reported that only reorientation of azobenzene moieties was induced below T_g and that the orientational director of mesogens was unchanged.[55] In contrast, even below T_g, the cooperative motion of mesogens resulting from the reorientation of azobenzene moieties was observed by Wiesner et al.[56] Recent works on the photoinduced alignment behavior of side-chain PLCs have revealed that the dipole–dipole interaction affecting cooperative motion is a more important effect in the reorientation process.[54]

Evaluation of the photoinduced alignment behavior of various PLCs with side-chain azobenzene moieties has revealed that the important factors for the reorientation process are azobenzene contents,[57] enthalpy change in the phase transition,[58] morphology of the sample before irradiation,[59,60] intensity of linearly polarized light as an incident light,[61] and spacer length of the side chain.[62] On the other hand, the structural effect of azobenzene moieties on the photoinduced alignment behavior was investigated systematically for a series of side-chain PLCs containing different azobenzene moieties and interesting results were obtained (Fig. 15).[63—65] With an increase in the strength of a donor and an acceptor

polymer	R^1	Z	R^2	x : y
MACB-AB6	CH_3	O	C_2H_5	94 : 6
MACB-CNAB6	CH_3	O	CN	93 : 7
MACB-NAB6	CH_3	O	NO_2	93 : 7
MACB-ABA6	CH_3	N-CH_3	NO_2	95 : 5
ACB-ABA6	H	N-CH_3	NO_2	95 : 5

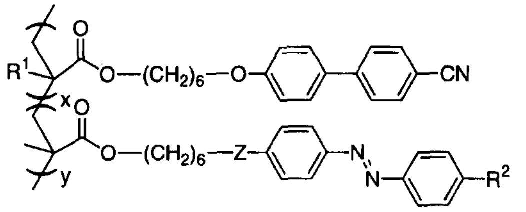


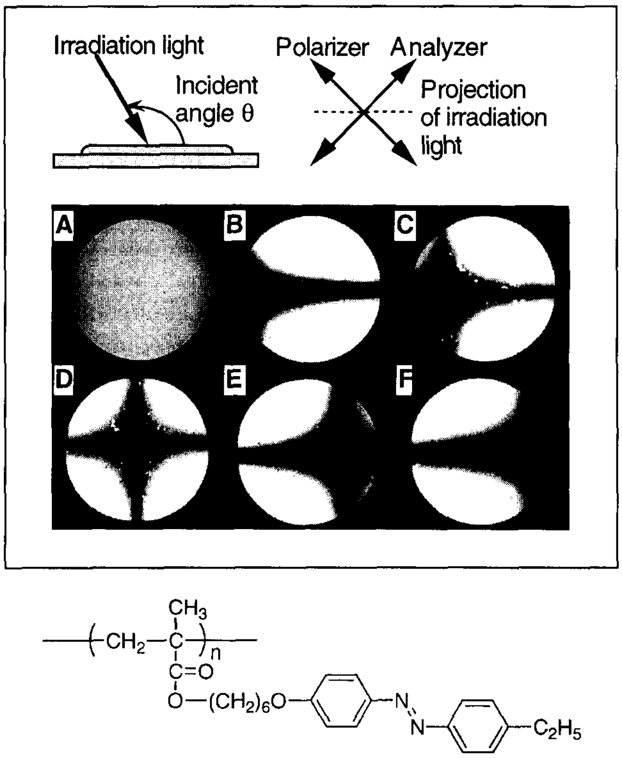
Fig. 15. Polymer liquid crystals containing various azobenzene moieties.

at 4 and 4′ positions of the azobenzene groups, the possibility of the alignment change in the PLCs having the same methacrylic backbone decreased due to the slightly increased enthalpic stability of the mesophase and the significantly decreased concentration of the *cis*-azobenzene (i.e., increased *cis–trans* isomerization rate). However, a high alignment efficiency was observed in ACB–ABA6, which is polyacrylate having strong donor–acceptor pairs in the azobenzene moiety and showing low stability of mesophase, since both the rate of *cis–trans* isomerization and the mobility of mesogens are favorable for alignment change. These results demonstrate that the photoalignment behavior can be regulated by the choice of azobenzene units or polymer backbones.

The azobenzene-containing polymer systems described above can control the alignment direction two-dimensionally by changing the polarization direction of the irradiation light. During the in-plane alignment process, photoinduced biaxiality of azobenzene moieties was observed in liquid-crystalline and amorphous polymer films as well as Langmuir–Blodgett film.[50,66—68] This phenomenon was interpreted in terms of realignment of the azobenzene moieties along the propagation direction of the irradiation light, i.e., the existence of out-of-plane alignment was demonstrated.[50] When the azobenzene moieties are aligned with the molecular long axis along the propagation direction of the irradiation light, little photoisomerization takes place, since 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 field vector of the unpolarized light. Thus, when unpolarized light is used, it is expected that the azobenzene moieties become aligned only in the propagation direction of the irradiation light. In fact, several studies have reported the out-of-plane alignment behavior by the use of unpolarized light.[69—72] Recently, an attractive result was shown in polymer azobenzene LCs, in which by changing incident direction of the irradiation light, three-dimensional manipulation of PLCs was brought about effectively at room temperature, which is about 70° below T_g of the polymer (Fig. 16).[73,74] This result is expected to open a new way for high-density data storage since information can be stored as a change in the three-dimensional alignment direction of the azobenzene moieties. The stored information may be read in a nondestructive way with light outside the absorption band of the azobenzene moieties in terms of the difference in transmittance.

5. Manipulation of Alignment of Liquid Crystals by Photoactive Surface Layers

Control of alignment of LCs is important for their optical and optoelectrical applications such as LCDs and LC spatial light modulators (LC-SLMs). The homogeneous LC alignment is conventionally achieved by rubbing mechanically a polymer alignment layer coated on the substrates. If it is possible that the chemical and/or physical properties of the surface of substrates can be changed by an external field, the LC alignment may be controlled by change in the surface property of substrates. Recently, control of the LC alignment by light is a hot topic. Ichimura and co-workers employed azobenzene monolayers, which were formed on



PMAB6
G 95 S 118 I
$M_n = 19{,}000$; $M_w/M_n = 2.1$

Fig. 16. Conoscopic observation of the alignment of the azobenzene mesogens as a function of the change in the incident angle. From A to F: before irradiation, after irradiation at the incident angle of 30°, 60°, 90°, 120°, and 150°, respectively.

glass substrates by silane coupling agents, and showed the possibility of photoalignment of LCs using the photoactive surface layers. The basic concept of this photoalignment is illustrated in Fig. 17. In the cell filled with an NLC, which is made from the surface-treated substrates, the NLC molecules show a homeotropic alignment when the azobenzene immobilized on the substrates is in the *trans* form. Photoirradiation to cause *trans–cis* isomerization of azobenzenes enables a repeatable change in alignment from a homeotropic to a planar state. Such photoactive surface layers are called the "Command surface".[75] 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.[76,77]

A closely related phenomenon induced by linearly polarized light was found independently by Gibbons et al., who employed a polyimide (PI) film doped with azobenzene molecules as a dichroic dye and showed that the direction of the homogeneous alignment of LC molecules could be controlled using polarized light.[78] An NLC 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 linearly polarized light with polarization parallel to the rubbing direction. It was revealed that LC molecules at the irradiated dye-doped surface became aligned perpendicular to the polarization of 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 could be subsequently erased or rewritten by altering the polarization of 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,[79] glass substrates modified with azobenzene monolayers (Fig. 17),[80] polymer azobenzene films,[72,81] and poly(vinyl cinnamate) with a photodimerizable property.[82] Such photoalignment methods using linearly polarized light are more favorable from the viewpoints of the improvement of the performance of existing LC devices and the development of novel LC devices with a new function. This is because the photoalignment process is free from dust particles and static surface charges which are generated in the conventional rubbing process.

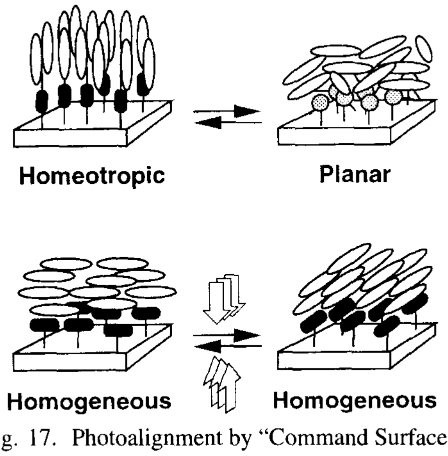


Fig. 17. Photoalignment by "Command Surface".

A unique LC alignment method based on a novel principle has been reported: the dynamic and static control of LCs by means of photoresponsive PIs as an alignment layer. The most significant characteristic of this system is the absence of any photochemical reactions to control alignment of LCs. The optical switching of NLCs was achieved with the photosensitive PI containing a benzophenone moiety as an alignment layer (Fig. 18).[83] The LC cells with a gap of 5 μm, in which substrates were coated with the PI films and then rubbed, were fabricated to evaluate the optical response of 5CB. Figure 18 shows the change in transmittance as a function of the applied voltage (DC) for the sample cell. It is clear that the threshold voltage, at which change in LC alignment occurs, is quite different between the irradiated and unirradiated conditions. It was found that photoirradiation at 366 nm resulted in an immediate change in the transmittance when

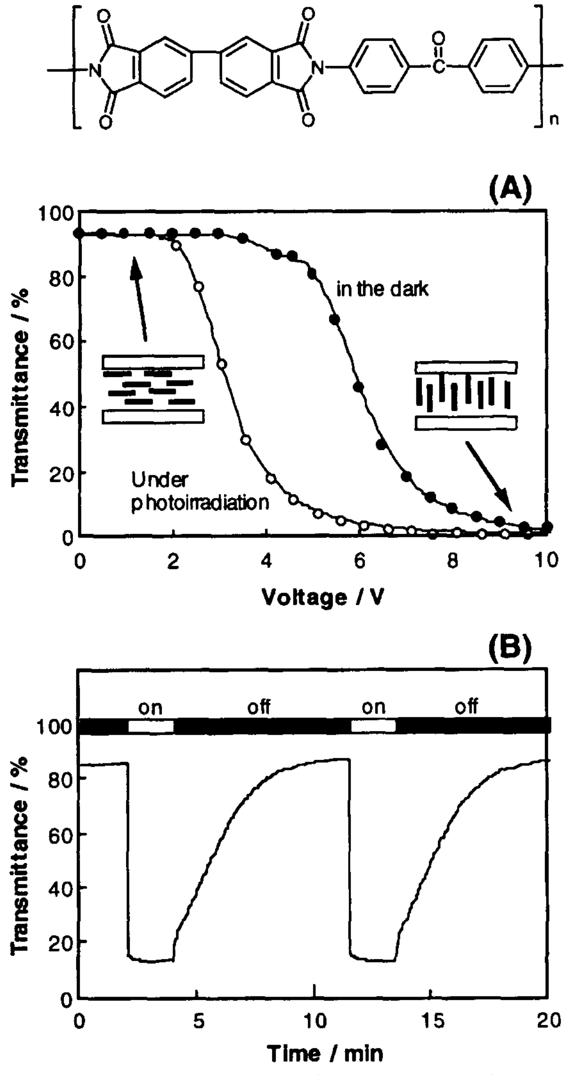


Fig. 18. *T–V* profile of the cell with the photosensitive PI as an alignment layer (A) and optical switching behavior (B). 5CB was used as an NLC.

a bias voltage of 4.5 V was applied across the cell (Fig. 18). Since the transmittance recovered when photoirradiation was ceased, it was assumed that the optical switching observed is based on the alignment change between a homogeneous state and a homeotropic state. Although the switching mechanism is not well understood at the present stage, formation of intra- or intermolecular charge transfer complexes in the surface area of PI films by photoirradiation (i.e., change in the polarity) seems to participate in the optical switching.

The photoresponsive PI films have also been applied to photoalignment (nonrubbing alignment) for LC devices. As early as in 1995, Hasegawa and co-workers realized homogeneous alignment of NLCs by anisotropic photodegradation of PIs exposed to linearly polarized UV light of short wavelengths (254, 257, or 313 nm).[84] However, this method is accompanied by chemical reactions, resulting in deterioration of the thermal stability of PIs due to serious destruction of backbone structures. Recently, aromatic PIs exposed to linearly polarized UV light of a long wavelength (366 nm) were reported to show a high efficiency of photoalignment without any significant change in their chemical structures.[85—87] To evaluate alignment ability, the PI film formed on the glass substrate was irradiated with linearly polarized light at 366 nm and an LC cell with a gap of 5 μm was assembled with two pieces of the exposed PI-coated substrates, and then 5CB was filled into the cell. As is seen in Fig. 19, the transmittance of probe light through crossed polarizers, with the unexposed cell between them, displayed no distinct angular dependence. In contrast, a maximum and a minimum of the transmittance appeared regularly at every 90° interval for the exposed cell. It is obvious that a unidirectional homogeneous alignment of 5CB was successfully induced with the photoresponsive PI film. The degree of uniformity of LC alignment was strongly affected by the structure of PIs, and it has been demonstrated that an aromatic PI with a diphenyl ether diamine unit is more favorable as a photoalignment film in terms of photosensitivity and chemical stability.

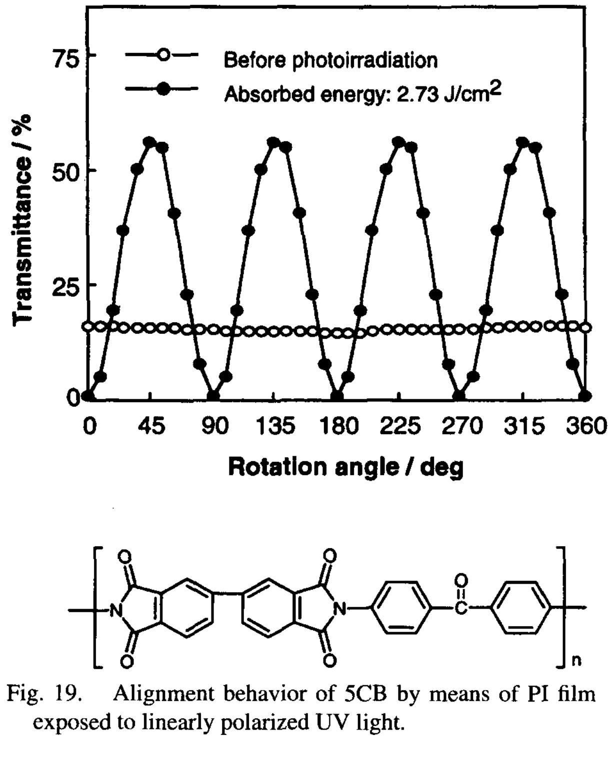


Fig. 19. Alignment behavior of 5CB by means of PI film exposed to linearly polarized UV light.

6. Modulation of Lightwave with Polymer/Liquid-Crystal Composite Films

The photoresponsive LC systems described in the preceding sections are very useful for refractive-index modulation by light; however, the loss of optical efficiency in LC devices is unavoidable due to the use of a pair of crossed polarizers. This problem can be overcome by modifying the morphology of materials. Polymer/LC composite films, consisting of polymer matrices and LC components, can be transformed from a light-scattering state to a transparent state by application of an external electric field. They set the LC devices free from polarizers and possess a 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 a stage of practical use.[88,89]

Although such polymer/LC composite films are usually prepared by emulsification and phase separation methods, the resulting composites have a variety of morphologies owing to different conditions and compositions in the preparation. The polymer/LC composite films are classified into four main types: nematic curvilinear aligned phase (NCAP) materials with an encapsulated LC structure,[90,91] polymer-dispersed liquid crystals (PDLCs) with LC droplets dispersed in a polymer matrix by means of polymerization-induced or solvent-induced phase separation,[92,93] polymer network liquid crystals (PNLCs) with micrometer-sized LC domains,[94] and polymer-stabilized liquid crystals (PSLCs) with a small amount of polymer network.[95] At present, to develop more functionalized LC devices, intensive studies have been performed on electrically switchable polymer/LC composite films with advantageous features such as a fast response to an electric field, a high contrast, and a wide viewing angle as well as reverse-mode and haze-free characteristics.[96—100]

With respect to photonic applications of the polymer/LC composite films, a projection light valve was reported by Takizawa et al.[101] This is an SLM to display large images on a screen by projecting an image created on a small valve, whose schematic illustration is shown in Fig. 20. The PDLC-SLM consists of two main components: a PDLC layer that modulates the probe light, and a photoconductive layer ($Bi_{12}SiO_{20}$) that detects the stimulus light. In the initial state, some voltage is applied as a bias to the two layers. On irradiation of the stimulus light, resistance of the photoconductive layer decreases. The voltage, therefore, is applied mainly to the PDLC layer. Increase in the voltage on the PDLC layer brings about unidirectional alignment of LC droplets. Consequently, the probe light reflected at the dielectric mirror can be modulated due to transformation between the light-scattering state and the transparent state in the PDLC layer. A high contrast ratio of 178 : 1, a response time of 14 ms, and a decay time of 15 ms have been achieved.

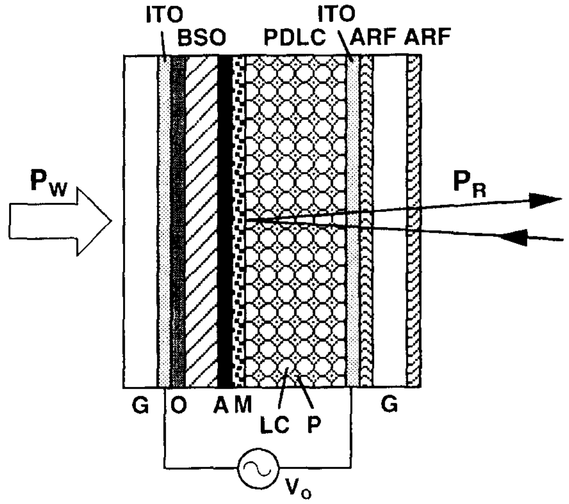


Fig. 20. PDLC-SLM. LC, liquid crystal droplet; M, dielectric mirror; A, light absorption layer; BSO, photoconductive layer; O, optical cement; P_W, writing beam; P_R, reading beam.

Light addressing and optical image recording by means of polymer/LC composite films showing an electric-field-frequency-dependent optical property have been reported by Kajiyama et al.[102] A composite film, which consists of a side-chain PLC with polysiloxane backbones and LMWLCs shown in Fig. 21, shows a remarkable light scattering state on application of a low-frequency electric field, while it is highly transparent on application of a high-frequency electric field. This composite is inactive to light because the LC component used has no photoresponsiveness by itself. An azobenzene derivative was then added into the composite film as a photoresponsive molecule. The threshold frequency, defined as the critical frequency at which the composite films change from a transparent state to a turbid one, was found to be altered by irradiation as an external stimulus. The threshold frequency in the composites containing the *trans*-azobenzene, f_c, was smaller than that in the composites with *cis*-azobenzene, f_{cs} (Fig. 21). The transmittance of the composites can be therefore switched by stimulation in the presence of an electric field with frequency of f_d which is between f_c and f_{cs} as shown in Fig. 21. Since both transparent and turbid states of the composite films are stably memorized even after removal of electric fields, they can be applied to rewritable optical image recording media. In addition, a similar phenomenon can be induced by laser irradiation, leading to the formation of both positive and negative images due to a heat-mode process.[103]

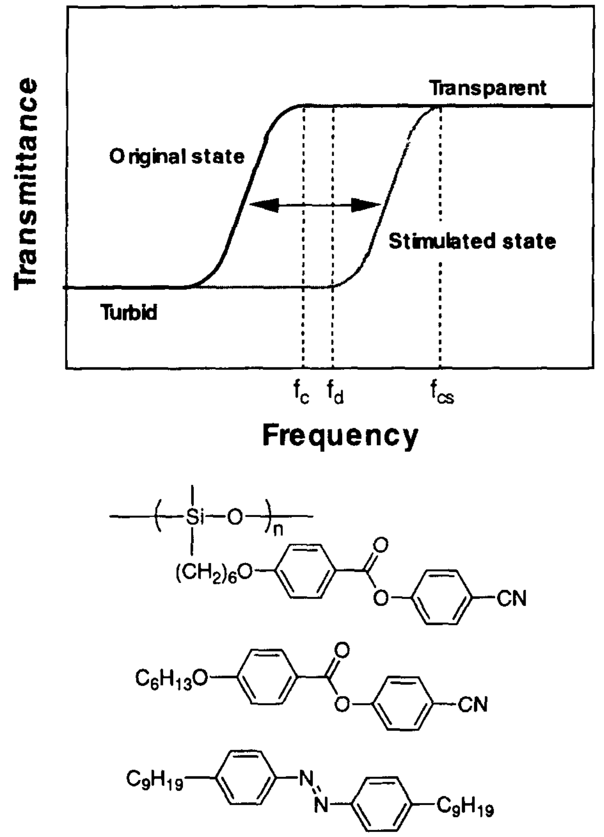


Fig. 21. Frequency dependence of transmittance of the composite film.

All-optically controllable polymer/LC composite films, which are driven by photon-mode processes in the absence of an electric field, have been achieved by means of the photochemical phase transition. Kawanishi et al. prepared polymer/LC composite films with thickness of 2—3 μm from a mixture of an NLC and an azobenzene derivative dispersed in an aqueous solution of poly(vinyl alcohol) by the solvent-induced phase separation method.[104] Although the composite films showed very low transmittance because of opacity of the composite film, they became transparent on irradiation at 366 nm resulting from N–I phase transition in the LC droplets within the polymer matrix owing 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 the change in the transmittance was as low as 10—50 %. With the aim of construction of novel photoresponsive polymer/LC composite systems possessing a superior optical property, a ternary mixture of bifunctional acrylate monomers, NLCs, and azobenzene compounds was polymerized in a 10-μm-gap cell and an optical property of the resulting polymer networks was systematically evaluated.[105,106] It was found that the transmittance of these composites can be modulated in the range approximately from 0 to 100% on photoirradiation to cause the photochemical phase transition (Fig. 22). Furthermore, by choosing network-forming materials and polymerization conditions, optical image storage and reverse-mode switching could be also achieved in the azobenzene-containing polymer network systems.[107,108]

As a unique feature of polymer/LC composite films, a second harmonic generation (SHG) property has been reported as one of the nonlinear optical effects. For the SHG, the key requirement is the presence of noncentrosymmetric (polar) order. In the molecule-based systems, materials exhibit an SHG activity only when the noncentrosymmet-

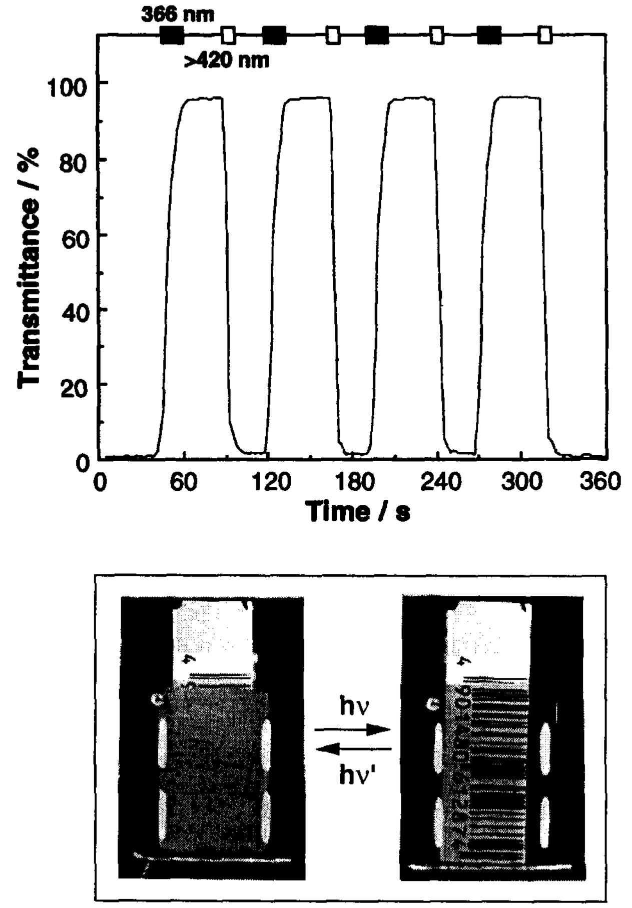


Fig. 22. Reversible change in transmittance of the composite film.

ric molecules are incorporated into a noncentrosymmetric macroscopic structure. Achievement of such a macroscopic ordering (i.e., dipolar alignment), however, is a formidable task, since permanent electric dipoles of noncentrosymmetric molecules tend to pair in opposite directions to give rise to a centrosymmetric macroscopic structure. Although an NLC molecule itself usually possesses dipole moments parallel to the molecular long axis, which is due to the noncentrosymmetric molecular shape, no SHG can be observed in the N phases because of cancellation of the dipolar vectors. The surface and interface of substances invariably show a noncentrosymmetric nature. This implies that the SHG is generated from the surface or interface region of substances. In the polymer/LC composite films, there are numerous interfaces since micrometer-sized LC droplets are dispersed in a polymer matrix. This structural characteristic leads LCs to wavelength-controllable materials. Several studies have been done so far on the SHG behavior of the composite films.[109,110]

7. Holography as a Future Technology in Photonics

7-1. Distinct Image-Recording and -Displaying Technique. Holography is an image-recording process which is essentially different from other processes: Both the phase and amplitude of lightwaves that intersect at the recording medium are recorded. The most attractive feature is that holography can record and display completely three-dimensional images of objects. In holography, the phase and amplitude of lightwaves are modulated by periodic alternation of various physical properties of the medium. Therefore, holography can be developed for photonic applications. The amplitude can be recorded by any of numerous photosensitive materials; many of these materials, however, are insensitive to phase differences between various parts of the wavefront. In 1948, to overcome this, Gabor introduced a background wave, generally referred to as the reference beam.[111] Interference between the reference beam and the object beam (the wavefront reflected by the object whose image is to be recorded) converts the phase differences into amplitude differences, which can be recorded by photosensitive materials. Gabor gave the name "holography" to this record, meaning the whole record, because it contains all information necessary to reconstruct the object beam. The hologram can be "played back" by illumination with a beam of coherent light identical with the reference beam (i.e., readout beam). On passing through the hologram, this beam acquires the phase and amplitude modulations of the object beam, reconstructing the wavefront that originally came from the object whose image was recorded. For the holography, coherent light sources are prerequisite optical components. On the basis of progress in laser technologies as well as change in a social situation, the greatest attention is being focused on the holographic process, since the information packing density can be considerably increased by using this unique storage method in the form of the interference pattern. Therefore, holography is expected to be the most promising candidate for storage of high-density information as well as recording three-dimensional objects. Moreover, holographic storage permits information to be written and read simultaneously as parallel processes, resulting in a extremely high transmission rate.

Holograms are classified into two main types according to the recording manner of the interference pattern.[112,113] One is an amplitude-type hologram. The interference pattern is recorded by a density variation of the recorded medium, and thus the amplitude of the illuminating wave is modulated. The other is a phase-type hologram. The fringe pattern is recorded as a change in thickness or refractive index and accordingly the phase of the illuminating wave is modulated. In terms of diffraction efficiency, it is well known that the theoretically-calculated diffraction efficiency of the phase-type holograms is always higher than that of the amplitude-type holograms. Therefore, most studies on holography are associated with the phase-type holograms.

In an early stage of researches on the holography, silver halide emulsions and dichromated gelatins were widely used as holographic materials. These materials, however, have some drawbacks such as a need of post-treatment based on the wet-process, low exposure sensitivity, and a high-gain noise in the holograms. Organic materials, especially polymer materials, for holographic recording have been investigated for many years because they show great facility in molecular design and good mechanical properties in comparison with inorganic materials.[113] Recent trends in the holographic recording materials include photorefractive materials,[114—118] thermoplastics,[119—121] photochromic compounds,[122—134] and ordinary photopolymers.[135—140] All of these materials can form the phase-type holograms and possess some advantages, but also some limitations. For instance, photorefractive materials are erasable and have unique nonlinear optical properties, but have only moderate diffraction efficiency and possess relatively low stability of stored information; thermoplastics have relatively high exposure sensitivity and are erasable, but have only moderate diffraction efficiency and a high scattering noise; photochromic compounds have high resolution and high exposure sensitivity and are erasable, but have relatively low diffraction efficiency; finally, photopolymers have excellent diffraction efficiency and noise properties, but are not erasable and require post-treatments. For the holographic recording, therefore, it is preferable that materials should possess simultaneously a number of specific characteristics such as high diffraction efficiency, high spatial resolution, and high S/N ratio. To construct the phase-type holograms with high diffraction efficiency, large modulation either of refractive index or of thickness of recording materials is required. In application of the holographic technique to active recording devices, holograms should be erasable and rewritable. Furthermore, for dynamic holography, by which it would be possible to reconstruct 3-D moving objects, rapid response in both processes of formation and disappearance of the holograms would be requisite for materials.

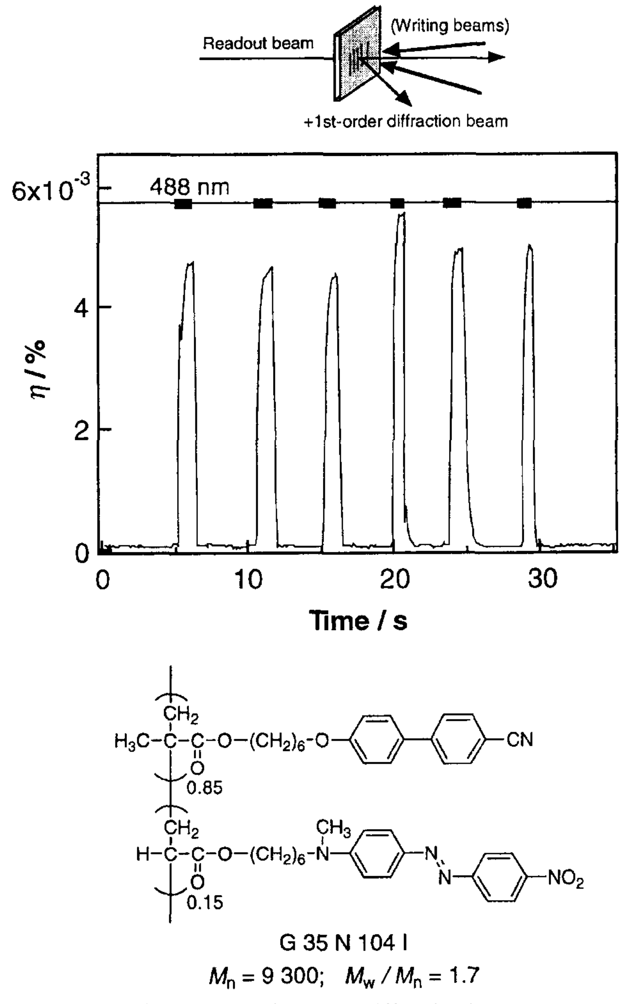


Fig. 23. Switching behavior of the diffraction beam by turning on and off the writing beams.

7-2. Liquid-Crystalline Materials in Holography. As described above, LC materials have large optical anisotropy resulting from self-assembly characteristics and provide additional features such as an ability to respond to applied external fields. These features are quite favorable from the viewpoint of formation of rewritable phase-type holograms as well as realization of dynamic holography. In the past decade, with the aim of 2-D or 3-D image recording, many extensive studies have been performed on the refractive-index-modulated holographic grating using LC materials which are LMWLCs,[78,141—158] PDLCs,[159—167] and PLCs.[15,16,168—180] The holographic gratings are basically formed by photorefractive effect or photochromism. In the gratings based on the photorefractive effect, Khoo et al. have obtained high diffraction efficiency of 30% at low writing-beam intensity of 40 μW cm^{-2} in a LMWLC system.[152] Ono and Kawatsuki have also revealed that the periodic modulation of LC alignment induced by the spatial charge distribution leads to a relatively large change in the refractive index ($\Delta n = 3.6 \times 10^{-3}$) in a LMWLC cell coated with photoconductive layers.[153] Furthermore, the photorefractive rise time as short as 40 ms was obtained in a LMWLC containing donor and acceptor molecules in which photoinduced electron transfer reactions occur effectively,[146] and the memory effect of photorefractive

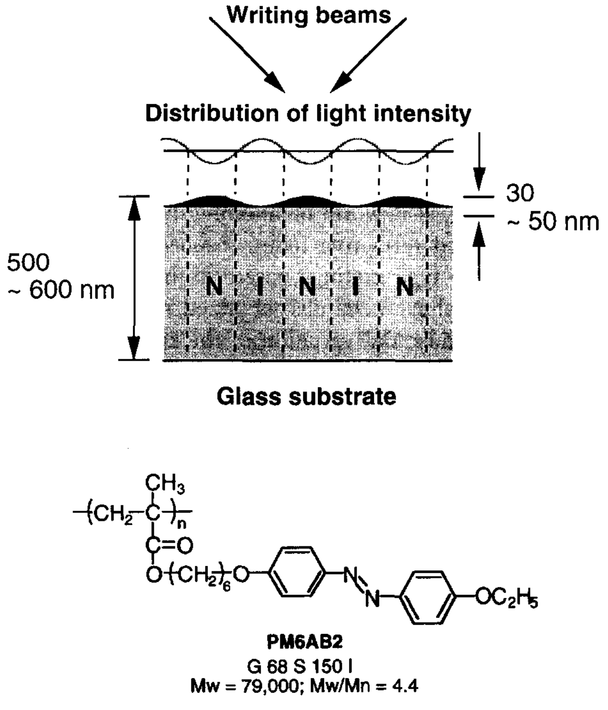


Fig. 24. Plausible structure of the holographic diffraction grating, in which the alternate arrangement of N and I phases is present under the relief structure.

gratings was observed in a PDLC.[160]

On the other hand, the grating formation by photochromism has been achieved in LC materials containing azobenzene derivatives as a photochromic molecule. It is expected that such systems will enable dynamic and/or effective control of formation of the gratings. This is because the photoisomerization of azobenzene molecules leads to a very fast change in alignment of LCs, resulting in a large change in the refractive index as mentioned above. In fact, dynamic holography has been realized in the dye-doped NLCs.[141,142] Although the grating formation is mainly due to the realignment of LCs in the bright region of interference patterns, the change in refractive index based on N–I phase transition seems to participate in the grating formation.[141] In LMWLCs, however, it is often difficult to obtain a holographic grating showing a narrow fringe spacing (i.e., high resolution) and high stability because of the high mobility of LC molecules. It is easy to imagine that side-chain PLCs may be one of the most promising materials in holography, because they possess not only high viscosity due to polymer structure but also superior LC properties in which flexible side-chain spacers play a crucial role to decouple the motion of the polymer backbone from that of the aligned mesogens. Wendorff et al. have shown for the first time that a holographic recording can be built into PLCs containing azobenzene moieties in the side chain as mentioned above.[15,16,168—170] This holographic image storage seems to originate from periodically photoinduced LC alignment by linearly polarized writing beams.

Recently, formation of the phase-type holograms by means of the photochemical phase transition has been attempted in side-chain PLCs containing azobenzene moieties at various temperatures at which sample films are in LC phases or in a solid state retaining an LC structure.[181—185] A typical result on dynamic gratings is shown in Fig. 23.[181,182] The holographic diffraction in an N phase was observed repeatedly by turning on and off the writing beams. In this system, the formation and disappearance of the grating, showing a narrow fringe spacing of 1.4 μm, were achieved within about 150 and 190 ms, respectively. It is worth mentioning that the magnitude of the modulated refractive index reached to 0.08. Furthermore, phase-type gratings based on the photochemical phase transition have been also obtained in glassy ordered films.[184,185] A sinusoidal variation of thickness of the films (surface-relief structure) was confirmed to be generated by irradiation of two interfering beams, which is similar to the results obtained in azobenzene-containing amorphous polymers reported by Natansohn et al. The gratings recorded in the ordered sample with thickness of about 500 nm showed high diffraction efficiency of approximately 28%; however, the surface modulation was slight (33—53 nm). Through theoretical calculation of the degree of surface modulation, it was revealed that the gratings can not be characterized only as conventional surface-relief gratings. These results have demonstrated that the large enhancement of the diffraction efficiency is mainly governed by spatial modulation of molecular alignment resulting from alternate arrangement of N and I phases (Fig. 24).[184,185] The grating formation, therefore, is associated with the photochemical phase transition of azobenzene-containing PLCs. Additionally, this system has enabled holographic recording of 2-D or 3-D objects with high resolution.[185]

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