Optical Switching and Image Storage by Means of Azobenzene Liquid-Crystal Films

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Liquid crystals are promising materials for optical switching and image storage because of their high resolution and sensitivity. Azobenzene liquid crystals (LCs) have been developed, in which azobenzene moieties play roles as both mesogens and photosensitive chromophores. Azobenzene LC films showed a nematic phase in trans isomers and no LC phase in cis isomers. Trans-cis photoisomerization of azobenzene with a laser pulse resulted in a nematic-to-isotropic phase transition with a rapid optical response of 200 microseconds.

Nematic liquid crystals (NLCs) are now used extensively as active media in liquid-crystal display (LCD) devices because of their quick response to a change in electric field. Although their viscosity is low compared with other LC materials such as smectic LCs, their response times (typically milliseconds) are still not satisfactory for use in animation and large-area LCD. Ferroelectric liquid crystals (FLCs), which exhibit a chiral smectic C phase, respond toward the electric field on a time scale of microseconds because of the presence of spontaneous polarization, but their cell fabrication requires a cell gap smaller than 2 μm and no short-circuiting of the two electrodes. This requirement has made exploitation of FLCs in display devices difficult, and NLCs still predominate.

Photochromic molecules change their molecular shape upon photoirradiation, and this property has been used extensively to control the orientation of LCs by light (*1*–*9*). For instance, the trans form of azobenzene derivatives is rod-like, which stabilizes the LC phase, whereas the cis form is bent and destabilizes the LC phase when it is present. Therefore, the trans-cis photoisomerization of azobenzenes in the LC phases can cause disorganization of the phase structure. This property has formed the basis of the photon-mode response of FLCs (*8*).

Isothermal phase transitions of LCs can be induced reversibly by photochemical reaction of photochromic molecules dispersed in the LC phase at concentrations of 1 to 5 mole percent (mol%). Time-resolved measurements have shown that the photochemical nematic-to-isotropic phase transition occurs on a time scale of 50 to 200 ms for nematic hosts of low molecular weight and polymeric LCs (*5*, *6*). Propagation of this perturbation due to the trans-cis isomerization of a small amount of the photosensitive molecules may need a relatively long time in the LC systems.

Photoisomerization of photochromic molecules is a fast process: Transient absorption spectroscopy shows that the trans-cis photoisomerization of azobenzene derivatives is completed within 10 ns (*5*). Some azobenzene derivatives (trans form) exhibit a nematic phase, whereas their isomers (cis form) show no LC phase. If a large fraction (ideally, all molecules) of the LC azobenzene molecules (trans form) in the nematic phase could be isomerized to the cis form simultaneously by means of a short laser pulse, the disappearance of the LC phase could take place in principle on the same time scale as the trans-cis photoisomerization, because the cis forms show no LC phase. We report a photochemical response of very thin films of photochromic LCs (~200 nm) composed of photosensitive azobenzenes. Because the trans-cis photoisomerization is a fast process, the nematic-to-isotropic phase transition of the azobenzene LC films took place in 200 μs both for low molecular weight and polymeric LCs.

We synthesized three azobenzene derivatives that exhibited the nematic phase in the trans form [BMAB, 8AB8, and PA6AB2 (*10*); Fig. 1] and prepared thin films of these azobenzenes by casting dilute solutions (~10^{-3} mol/liter in chloroform) on glass plates that had been coated with poly(vinyl alcohol) and then removing the solvent. The surface of the poly(vinyl alcohol) layer was rubbed before the casting of the solution to align the LC molecules (rubbing treatment). The thickness of the LC films was estimated to be ~200 nm by absorption spectroscopy on the basis of the molar extinction coefficients of the azobenzene moieties. Annealing of the LC films at temperatures corresponding to the nematic phase yielded a well-aligned monodomain of the nematic phase as confirmed by polarizing microscopy. The films became dark when viewed with the rubbing direction parallel to one of the crossed polarizers, and the transmitted light intensity was highest when the rubbing direction was 45° with respect to the polarizers. Photoirradiation was performed with a 500-W high-pressure Hg lamp, and the 366-nm line was isolated by a combination of glass filters. Time-resolved measurements were performed with a yttrium-aluminum-garnet–Nd (YAG-Nd) laser as a light source [the third harmonic at 355 nm, 10 ns full width at half maximum (FWHM)]. The change in transmittance of a probe light at 633 nm (a He-Ne laser) through a pair of crossed polarizers, with the thin LC film between them, was measured with a photomultiplier as a function of time after a single-pulse irradiation of the laser.

Irradiation of the LC films in the nematic phase at 366 nm, which brings about the trans-cis photoisomerization of the azobenzene moieties, caused an isothermal nematic-to-isotropic phase transition of the films, as shown in Fig. 2, for PA6AB2. The nematic phase was recovered when photoirradiation ceased, because thermal cis-trans back-isomerization took place. The cis-trans back-isomerization proceeded even at room temperature, but it took place quite effectively at >100°C. Irradiation of the LC films (BMAB and 8AB8) in the nematic state by means of the laser pulse (70 mJ/cm^2) brought about the nematic-to-isotropic phase transition in 200 μs. Furthermore, the corresponding phase transition of the polymeric LC film (PA6AB2) was also induced in 200 μs at 140° and 23°C, as demonstrated in Fig. 3 for the behavior at 23°C. This polymer shows a glass transition temperature (T_g) at 45°C, so that the nematic-to-isotropic phase transition could be induced in 200 μs even below T_g by a single-pulse irradiation of the laser. This response was faster by at least

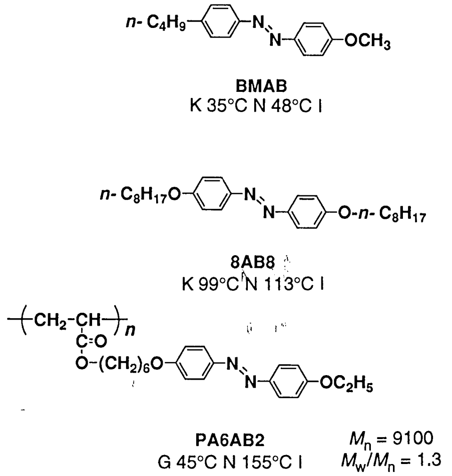

Fig. 1. Structures and phase-transition temperatures of three azobenzene liquid crystals. Abbreviations: K, crystal; N, nematic; I, isotropic; G, glass; M_n, number-average molecular weight; and M_w, weight-average molecular weight.

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two orders of magnitude than the response of polymeric NLCs previously reported (*5*, *6*). We examined whether a heat-mode process was involved in the phase transition by irradiating the LC films with a high-power infrared laser pulse at 1064 nm (YAG-Nd) laser, fundamental; 1 J/cm^2, 10 ns FWHM). No phase transition was induced in any sample by this process.

The polymeric azobenzene LC films have two advantages. First, they show a much wider temperature range for the nematic phase, and so a wide temperature range is available for optical switching. Second, they have a T_g, so that they can function as image storage materials when they are operated at temperatures below T_g. For instance, the stability of the induced isotropic phase was quite high when the irradiated sample was kept below T_g. Figure 4 shows a photograph of the stored image in the polymeric LC film obtained by the use of the standard photomask: the thin film of PA6AB2 was covered with the photomask (Fig. 4A) and irradiated with a single pulse of the YAG laser, the third harmonic at 355 nm and 23°C, and was kept at the same temperature in the dark. The stored image remained unchanged after 8 months (Fig. 4B). Even at 23°C PA6AB2 showed cis-to-trans thermal back-isomerization, which was nearly completed in 24 hours, but the isotropic phase induced at the irradiated site remained unchanged even after 8 months.

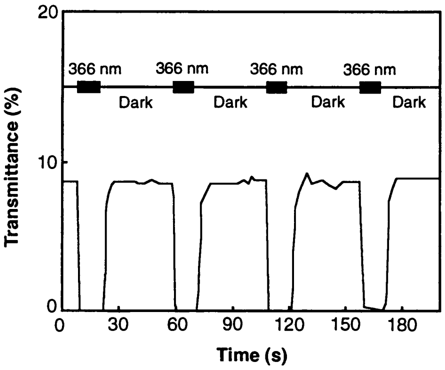

Fig. 2. Photochemical nematic-to-isotropic phase transition and thermal isotropic-to-nematic transition of PA6AB2. Photoirradiation was performed at 366 nm. The transmitted light intensity of the He-Ne laser (633 nm) through crossed polarizers, with the thin LC film between them, was measured with a photodiode.

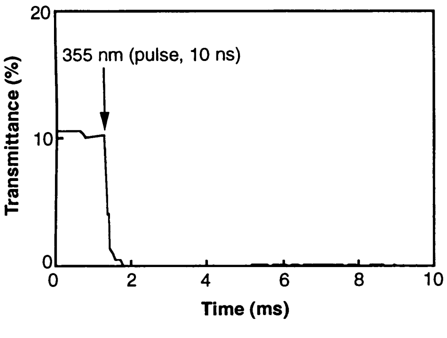

Fig. 3. Time-resolved measurements of the photochemical nematic-to-isotropic phase transition in PA6AB2 at 23°C. Pulse source: YAG laser, 10 ns FWHM at 355 nm. The change in transmittance of the He-Ne laser through the crossed polarizers, with the thin LC film between them, was measured with a photomultiplier as a function of time after a single-pulse irradiation of the laser.

Trans-azobenzene shows an absorption at ~360 nm due to the π-π* transition, and its transition moment lies along the molecular long axis of the azobenzene moiety. Therefore, order parameters of azobenzene dyes can be evaluated by the ultraviolet dichroism at the absorption band of the π-π* transition. The order parameter determined by the polarized absorption spectra was 0.45 before photoirradiation. The polymeric LC film was irradiated at 23°C to cause the trans-cis isomerization, and this film was kept at the same temperature in the dark for 1 week to ensure that the trans form was restored. After the trans-cis-trans cycles, the order parameter was 0.05, which indicates that the orientation of the trans form became random. To restore the nematic phase, it is necessary to raise the temperature of the irradiated sample above T_g to enable the *trans*-azobenzene mesogens to reorient so as to align with the segmental motion of the main chain of the polymer, as shown in Fig. 5. This characteristic is quite favorable to the use of this polymeric LC film as an image storage material: the image can be stored stably below the T_g of the polymer for a long period, and the image can be erased just by raising the temperature of the material above T_g.

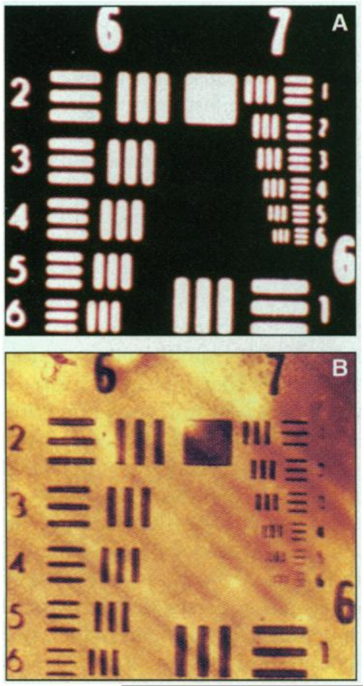

Fig. 4. Stored image in a polymeric NLC. The thin film of PA6AB2 was covered with a photomask (**A**) and irradiated with a single pulse of the YAG laser, the third harmonic at 355 nm, at 23°C (below the T_g). The image, after storage for 8 months, is shown in (**B**).

Intensive studies have been performed to determine the mechanism of photoisomerization of azobenzene derivatives (inversion or rotation mechanism), and it is now accepted that photoisomerization of azobenzenes occurs mainly through an inversion mechanism (*11*, *12*). This mecha-

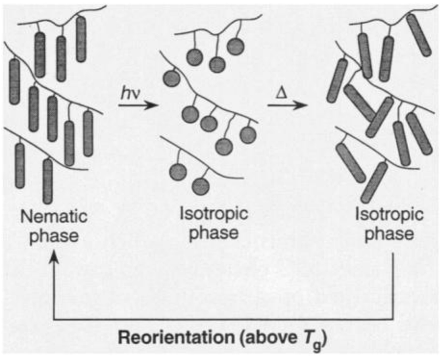

Fig. 5. Orientation of *trans*-azobenzene mesogens after the trans-cis-trans cycles. The orientation of the *trans*-azobenzene mesogens is random after the thermal cis-to-trans back-isomerization, and this random orientation is fixed below the T_g of the polymer. The nematic phase can be restored if the temperature is raised above T_g.

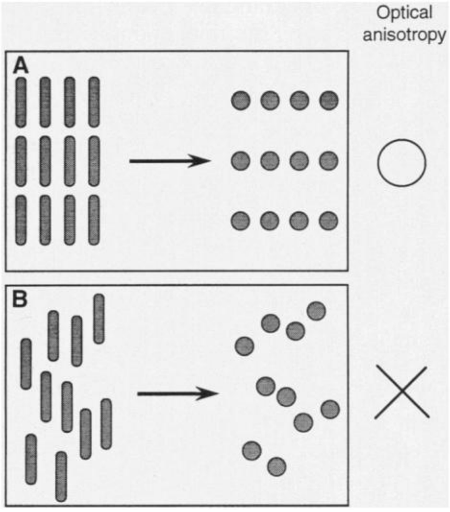

Fig. 6. Schematic illustration for the loss of optical anisotropy. In crystals (**A**), optical anisotropy still remains after the anisotropy in the shape of each molecule vanishes because the center of gravity of each molecule is aligned regularly. However, in NLCs (**B**), the optical anisotropy disappears when the anisotropy in the shape of each molecule is eliminated because in NLCs the optical anisotropy arises only from the anisotropy in molecular shape (rod-like shape).

nism requires a much smaller sweep volume for isomerization than the rotation mechanism, so that the azobenzene derivatives undergo isomerization in relatively rigid matrices such as polymer matrices below T_g, depending on the spatial and temporal distribution of the free volume in the polymer (*13–15*). Below T_g, segmental movement of the main chain of the polymers is frozen; however, movement of side chains is allowed to some extent.

In a system in which the center of gravity of each molecule is aligned regularly, as in crystals, optical anisotropy still remains active even after the anisotropy in the shape of each molecule vanishes (Fig. 6A). On the other hand, in NLCs optical anisotropy arises only from the anisotropy in the molecular shape (rod-like shape); the center of gravity of each molecule is random. Therefore, in the NLCs the optical anisotropy disappears if the anisotropy in the shape of each molecule is eliminated by trans-cis isomerization (Fig. 6B). This behavior provides the basis of the microsecond response time observed for the polymeric NLC film in the present study.

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Observation of Shoemaker-Levy Impacts by the Galileo Photopolarimeter Radiometer

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The Galileo Photopolarimeter Radiometer experiment made direct photometric observations at 678 and 945 nanometers of several comet Shoemaker-Levy 9 fragments impacting with Jupiter. Initial flashes occurred at (fragment G) 18 July 1994 07:33:32, (H) 18 July 19:31:58, (L) 19 July 22:16:48, and (Q1) 20 July 20:13:52 [equivalent universal time coordinated (UTC) observed at Earth], with relative peak 945-nanometer brightnesses of 0.87, 0.67, 1.00, and 0.42, respectively. The light curves show a 2-second rise to maximum, a 10-second plateau, and an accelerating falloff. The Q1 event, observed at both wavelengths, yielded a color temperature of more than 10,000 kelvin at its peak.

The impact of comet Shoemaker-Levy 9 (SL9) into Jupiter in July 1994 stimulated an unparalleled set of astronomical observations. The instrument complement of the Galileo spacecraft, on its way to a December 1995 orbit insertion at Jupiter, observed the impact events directly from a vantage point above the dawn terminator. A number of Earth-based observers have reported detection of impact-related phenomena at times preceding those from Galileo, in spite of the impacts occurring behind the limb of Jupiter as viewed from Earth. Correlation of these disparate data sets should lead to a model of how those singular events took place. We report here observations by the Photopolarimeter Radiometer (PPR) (*1*), a single–field-of-view instrument that uses a rotating filter wheel covering wavelengths in the visible and near infrared for photometric and polarimetric remote sensing of Jupiter's atmosphere and satellites.

For the SL9 observations, the PPR was used as a high-speed photometer, maximizing the likelihood of observing the radiation associated with the impact events, given the considerable uncertainty about their magnitude, timing, and duration (*2*). Consequently, single-filter measurements with a 0.23-s sample time were used for most of the observed impacts.

Among the available wavelengths, we selected 678 and 945 nm (with bandwidths of 9 and 11 nm, respectively). Most events were observed at 945 nm alone, to allow detection of thermal emission from a rapidly rising fireball, which at some 3000 K (*3*, *4*) would be cooler than the entry meteor flash. For fragment Q1, however, measurements alternated between 678 and 945 nm, with a sample period of 1.26 s at either wavelength.

For impact events B, H, L, Q1, and S, the PPR 2.5-mrad field of view was centered on Jupiter's 0.6-mrad disk (*5*), and the data were buffered in the spacecraft computer memory and read out within 1 day (*6*). For the C, G, and R events, the PPR was set up to record data on tape simultaneously with the infrared and ultraviolet spectrometer measurements (*7*).

Detection of an impact event by the PPR depended on (i) the time of the actual impact relative to a fixed observing interval, defined in mid-June, (ii) the brightness of the impact, and (iii) the amount of stored data that could be returned within the available downlink communication time. Among the set of memory-buffered observations, definite signals were found for H, L, and Q1 (*8*) (Figs. 1 and 2). These events were all much shorter than the observed time span (Table 1). The 1σ noise level at 945 nm for all observations was 1.2 data numbers (DN) after averaging the two polarization channel signals together without smoothing (*2*). This is about 0.5% of the integrated brightness of Jupiter at 945 nm.

All of the events detected rose to maximum signal within 2 s, at which time there was a sudden slope change at the peak intensity. All of the 945-nm measurements had a similar shape, with about a 10-s plateau before falloff. The maximum duration of detected light was 35 s for the impact of fragment L. Data returned from the G impact, although sampled less frequently, show the same general behavior as the others (Fig. 3). There was a suggestion of secondary flashes in the 3 min following the main G flash. However, examination of the two PPR channels shows a lack of correlated signals during this period, and it is unlikely that these peaks are real. It should be pointed out that there is no structure in the G, H, or L data indicating the detection of separate meteor and fireball phases, except perhaps for the slope change.

The 678-nm signal for Q1 decayed faster (Fig. 4) (*9*). The brightness curve extracted from the time-drift images of impact K at 890 nm by the Solid State Imaging (SSI) instrument on Galileo (*10*) shows a similar shape and a duration comparable to our 945-nm data for G, H, and L. The SSI sequence of images for impact W at 559 nm show a rise and fall within about 5 s, which is similar

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