Photochemical Switching of Ferroelectric Liquid Crystals Using a Photoswitchable Chiral Dopant

Makoto Negishi, Osamu Tsutsumi, Tomiki Ikeda,* Tamejiro Hiyama,* Joji Kawamura,† Masao Aizawa,† and Sadao Takehara††
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226
†*Central Research Laboratories, Dainippon Ink & Chemicals Inc., 631 Sakado, Sakura, Chiba 285*
††*Dainippon Ink & Chemicals Inc., 4472-1 Komuro, Inamachi, Kita-adachi-gun, Saitama 362*

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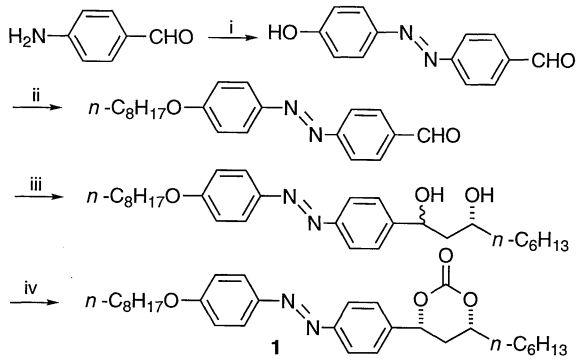
Fast optical switching (response time 90 μs) was achieved of ferroelectric liquid crystals doped with a photoresponsive chiral dopant having an azobenzene moiety.

Ferroelectric liquid crystals (FLCs), when aligned properly, can be used for switching controlled by electric field.[1] This switching principle applies also to the system consisting of host smectic C (SmC) LCs and a chiral dopant which is responsive for FLC properties.[2] Recently, rapid switching of FLCs by light has been disclosed.[3] We assumed that a chiral dopant having a photoresponsive functional group also might induce the photochemical switching. Herein we report the synthesis of a photochromic chiral dopant containing an azobenzene moiety, the FLC behavior of a mixture of the chiral dopant and host LCs, and the photochemical switching of the mixture.

As the chiral dopant, we chose a cyclic carbonate, because an optical active *syn* carbonate is shown to induce large spontaneous polarization (Ps).[4] Thus, we designed photoresponsive chiral dopant **1** containing an optical active *syn* carbonate moiety. Synthetic procedures of **1** are shown in Scheme 1. Thus prepared **1** was recrystallized to obtain the compound of >99% e.e. A sample **2** containing 1 wt% of **1** and 99 wt% of a host LC[5] was injected into a 2 μm gap glass cell equipped with ITO electrodes and coated by polyimide. This mixture showed phase transition temperatures of Cr 4 SmC* 61 SmA 74 Iso, Ps of 3.34 nC/cm^2 that was fairly large as we expected, and tilt angle of 16° at 43 °C.



i: (1) $NaNO_3$, aq HCl, Me_2CO, -15°C; (2)C_6H_5OH, NaOH, Me_2CO, -15 °C, 47% yield
ii: K_2CO_3, *n*-$C_8H_{17}I$, DMF, r.t., 54% yield
iii: (*R*)-1,2-epoxyoctane, Li, (4-*t*-$BuC_6H_4)_2$, THF, -90 °C, 28% yield
iv: $(Cl_3CO)_2CO$, Et_3N, THF, r.t., 45% yield

Scheme 1. Synthesis of the chiral dopant **1**.

The setup used for the measurement of optical behaviors is illustrated in Figure 1. The sample was placed between two crossed polarizers, and the temperature was controlled by a thermostat. The phase transition caused by the photoisomerization of the chiral dopant was observed by measuring the transmittance of He-Ne laser (633 nm) through the crossed polarizers.[6] In the steady-state measurement, the sample was photoirradiated with Hg lamp (366 nm) upon applying alternating voltage. For the time-resolved measurement, the sample was photoirradiated with YAG laser (the third harmonic, 355 nm; pulse width, 10 ns FWHM) with direct voltage being applied.

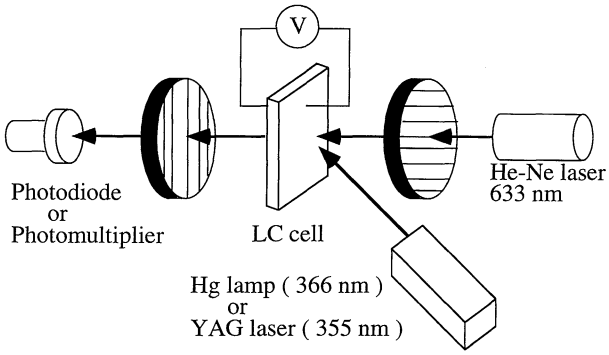


Figure 1. The setup used for optical measurements.

The optical hysteresis loop of the sample mixture is shown in Figure 2. Before irradiation, namely when –N=N– moiety of **1** was *trans*, the sample mixture exhibited FLC behavior. Upon irradiation (366 nm), however, the transmittance did not follow the change of the applied voltages, probably because the chiral dopant isomerized to *cis* form and the sample mixture was not SmC* anymore. In fact, the phase was assigned as SmA.[7]

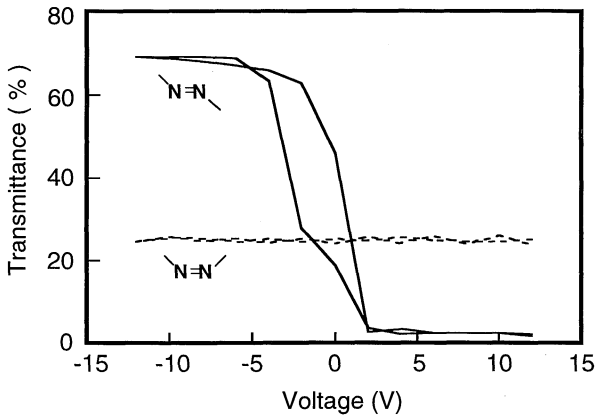


Figure 2. Optical hysteresis of **2** at 43 °C.

Figure 3 demonstrates the change of transmittance on photoirradiation at 43 °C obtained by the steady-state measurement. The sample irradiated did not respond to the applied alternating voltage, since *trans*→*cis* isomerization caused the SmC*→SmA phase transition. When irradiation was ceased, transmittance remained constant for a while, and after about 300 s induction period, realignment to SmC* was observed.

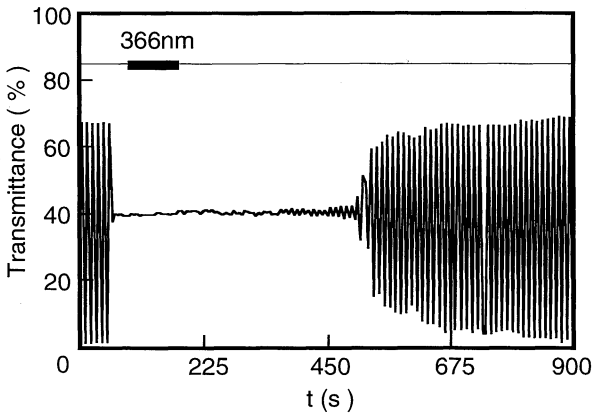


Figure 3. Change in transmittance on photoirradiation of **2** at 43 °C.

Time-resolved measurement at 45 °C revealed that *trans*→*cis* photoisomerization of the chiral dopant caused disappearance of the SmC* phase effectively and the phase transition took place in 90 μs (Figure 4).

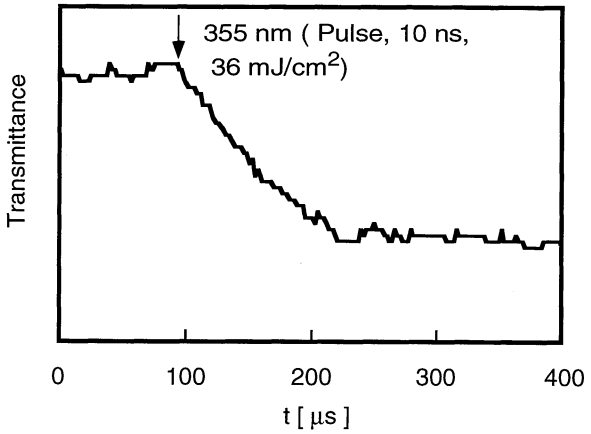


Figure 4. Time-resolved measurements for optical switching at 45 °C.

The relationship of the applied voltage and the response time is shown in Figure 5. The fast response was observed when the applied voltage was low. In particular, when the sample was irradiated without applied voltage, it exhibited a response time of 90 μs.

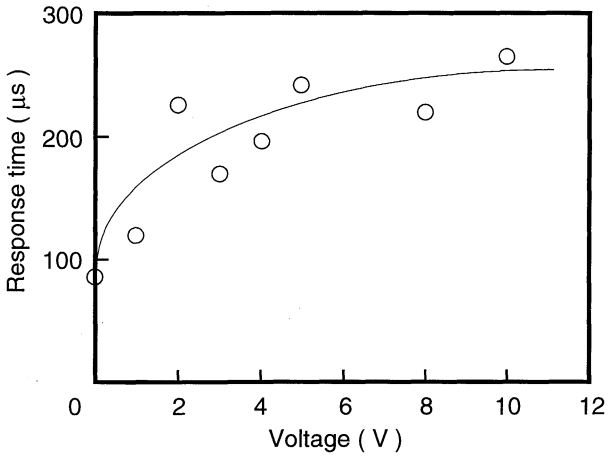


Figure 5. Applied voltage vs response time of **2** at 45 °C.

In conclusion, *trans*→*cis* photoisomerization of the chiral dopant **1** effectively caused change of SmC* into SmA, and thermal *cis*→*trans* back isomerization restored SmC*. The sample upon irradiation without any applied voltage responded extremely quickly with the response time of 90 μs, the fastest photochemical response to date.

References and Notes

1 N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.*, **36**, 899 (1980).

2 a) T. Kusumoto, T. Hiyama, and S. Takehara, *Dyestuffs and Chemicals,* **38**, 57 (1993); b) T. Kusumoto and T. Hiyama, *Dyestuffs and Chemicals,* **40**, 227 (1995); c) T. Kusumoto, T. Hiyama, S. Takehara, and S. Shoji, *Yuki Gosei Kagaku Kai Shi,* **49**, 475 (1991); d) T. Kusumoto, T. Hiyama, and S. Takehara, *Nippon Kagaku Kyokai Shi,* **12**, 1401 (1992).

3 a) T. Ikeda, T. Sasaki, and K. Ichimura, *Nature,* **361**, 428 (1993); b) T. Sasaki, T. Ikeda, and K. Ichimura, *J. Am. Chem. Soc.*, **116**, 625 (1994); c) T. Moriyama, J. Kajita, Y. Takanishi, K. Ishikawa, H. Takeze, and A. Fukuda, *Jpn. J. Appl. Phys.* **32**, L589 (1993).

4 T. Kusumoto, K. Sato, K. Ogino, T. Hiyama, S. Takehara, M. Osawa, and K. Nakamura, *Liquid Cryst.*, **14**, 727 (1993).

5 The host LC was racemic 2-[4-(6-methyl-1-octyloxy)phenyl]-5-octylpyrimidine. The phase transition temperatures were Cr 3 SmC 47.6 SmA 58.2 Iso.

6 Before photoirradiation, FLCs were always aligned by applied voltage, and the polarizers were adjusted so that the transmittance of the probe light become zero.

7 Phase assignment is based on the microscope observation of the texture as well as the insensitive behavior to applied voltage.