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Amplified Image Recording in Liquid Crystal Media by Means of Photochemically Triggered Phase Transition

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Over 100 times amplified image recording was achieved by means of reading out nematic isotropic phase transition of liquid crystal induced by partial trans→cis photoisomerization of a small amount(up to 5 mol%) of 4-butyl-4'-methoxyazobenzene mixed with 4-cyano-4'-n-pentylbiphenyl.

Recent development in optical image recording systems to take over conventional electromagnetic systems arose interest in seeking for highly sensitive, reversible, and tough photochromic systems both in academic and industrial circles. While the present optical memories are read-only media or write-once media, the technology is expected to grow from direct read after writing (DRAW) to erasable DRAW(EDRAW) system.[1] Although the heat-mode recording could be reversible, the best reversible image recording system will be the use of photochromic compounds. A broad definition of photochromic compounds is a class of compounds which induce any reversible property changes as a result of reversible photoreactions. To aim at practically usable materials, present photochromic systems are subject to a number of drawbacks such as low photosensitivity, poor reversibility, poor stability, limited wavelength region of sensitivity and so forth.

We are focussing our effort to improve sensitivity and have demonstrated a noble concept of photochemically triggered physical amplification.[2,3] Information provided in a form of photoreaction in molecular aggregate systems is amplified and stored as physical changes in molecular aggregation. The definition of amplification is as follows. When a signal in the form of transmitted light is provided, the sensitivity is decided by the signal-to-noise(S/N) ratio. Since the signal is received by a photomultiplier or a pin photodiode, larger the optical density change per unit input photoenergy higher the S/N ratio and consequently the sensitivity is higher. When we can achieve improved sensitivity, we name the process **amplification.** Highly sensitive read-out is possible by various methods other than direct measurement of color change. The monitor signal change is non-linearly related to the amount of photoreaction, particularly in the case of phase transition. We examined photochemically triggered-micelle formation, change in vesicle size and shape and change in induced circular dichroism, all of which exhibited amplified

photoresponse with respect to the amount of photoreaction induced. However, phase transitions in these systems are not very sharp and consequently, amplification is not phenomenal.

We found that tremendous image amplification was possible by means of photoreaction in liquid crystals to induce phase transition and to be read out optically through crossed polarizers. The use of photoreactive liquid crystal systems to imaging devices is not unprecedented. As early as 1971, Sackmann showed for the first time the photochemical change of pitch in cholesteric liquid crystals.[4] Since then, high contrast photoimage with nematic liquid crystals,[5] photoimaging under biased potential,[6] cholesteric compound tagged with azobenzene,[7,8] and so forth have been reported. None of them, however, described the concept of image amplification.

4-Cyano-4'-n-pentylbiphenyl(I) which formed nematic liquid crystals was doped with 4-butyl-4'-methoxyazobenzene(II) and placed in a thin layer glass cell after rubbing treatment. The sample was irradiated at 355 nm to conduct trans → cis photoisomerization of II. Phase transition induced by the photoisomerization was followed by monitoring at 633 nm(a He-Ne laser) via two crossed polarizers, the sample being placed between them. The strongest monitor signal was obtained when the angle of the monitor light to the cell was 45°. The results are shown in Fig. 1. While photoisomerization proceeds nearly linearly with reaction time, the change in monitor signal intensity is drastic.

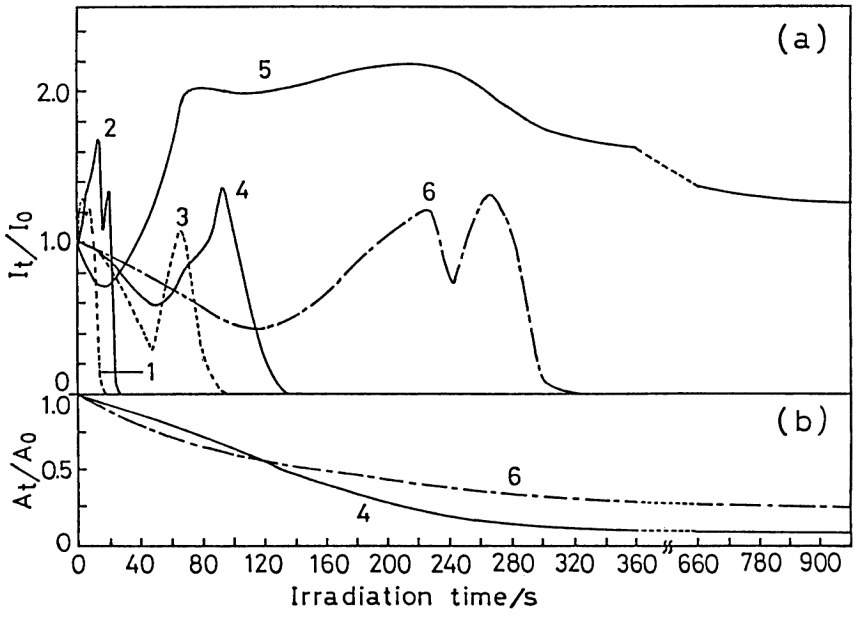

Fig. 1. Read-out intensity change(a) and absorbance change(b) owing to trans → cis photoisomerization of azobenzene group in liquid crystals.
1. II:4.9 mol%, 34 °C. 2. II;3.0 mol%, 34 °C.
3. II:4.9 mol%, 30 °C. 4. II:3.0 mol%, 30 °C.
5. II:1.2 mol%, 30 °C. 6. azobenzene:3.0 mol%, 30 °C.

The change in monitor light intensity is due to change in birefringence. When a small fraction of II is photoisomerized, the total system becomes isotropic abruptly so that the polarized monitor light is shut off completely by the crossed polarizers. The change in monitor light intensity is complicated but quite reporoducible. However we have no interpretation for the initial rise of signal. With increasing the ratio of II/I, the system becomes more and more sensitive. Comparing the rate of photo-reaction(A_t/A_0 vs. t) with the corresponding change of monitor signal(I_t/I_0 vs. t)at its maximum, more than 100 times amplification was demonstrated. If azobenzene was used instead of II, the non-linear read out is also possible but the sudden change of I_t/I_0 appears after photoisomerization is nearly completed(compare 4 and 6 in Fig.1).

To erase the image, the photoirraddiation is switched to 525 nm to induce cis - trans isomerization(Fig. 2). While the photoreaction proceeds independent of chromophore concentration, recovery of ordering in liquid crystals depends on concentration. The slow recovery of liquid crystalline state is due to weak absorbance of the cis form of II at 525 nm. Although there is a certain time lag between photoreaction and recovery of liquid crystalline state, their recovery is complete indicating the physical amplification process is reversible.

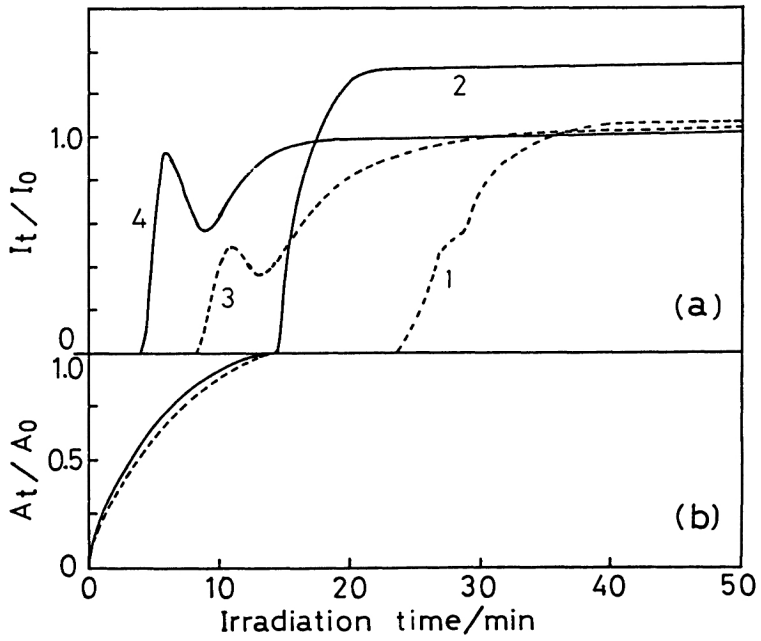

Fig. 2. Reverse phase transition induced by cis → trans photoisomerization of II(a) and recovery of absorbance(b).
The numbers are same as those in Fig. 1.

Transformation of trans azobenzene to the cis form brings about bending of the molecule. When the functional group is incorporated in molecular aggregates, the cis isomer tends to destabilize the molecular aggregates. This phenomenon has been demonstrated for micelles, vesicles and membrane.[2,3] Melting point depression phenomena brought about by photochromism in liquid crystals were reported by

several researchers.[5,6] The present amplified recording seems to be based on nematic - isotropic phase transition. Observation by polarized microscope showed drastic change of molecular ordering to isotropic state at a certain degree of the photoisomerization. The critical point at which the phase transition occurs depends on the concentration and shape of photochromic compound, the nature of host liquid crystal system, and temperature. The nematic/isotropic phase transition temperatures(T_{NI}) of the samples in Fig. 1 are as follows; 1,3: 36.7 °C, 2,4: 35.6 °C, 5: 35.0 °C, 6: 32.4 °C. Apparently, the effect of photoisomerization of II on T_{NI} is much stronger than that of azobenzene. Analysis of these critical factors is a future problem. A clear thing is that the system is more sensitive if photoirradiation is conducted at temperature below but very close to the phase transition temperature of the initial system. In principle, innumerable combinations of liquid crystal with photochromic compounds will exhibit the phenomenon of photochemically triggered physical amplification of photo-responsiveness.

Besides the amplified photoresponsiveness, additional merits are envisaged. Firstly, the recording and the read out wavelength are largely different so that fading of image during read out is prevented. Secondly, as a bonus of amplified read out, photochemical conversion is reduced to a minimum amount. This will greatly prevent the fatigue of reversible photochromism and will extend the lifetime of the imaging material. On the other hand, the drawbacks are as follows. Firstly, since liquid crystalline materials are viscous but in anyway fluid, long term stability of image will be difficult. Secondly, temperature dependence of photoresponsiveness will also be a serious restriction. These difficulties may be overcome by the combination of photon-mode and heat-mode recording. Namely, moderate laser heating and simultaneous photoreaction will enable the use of liquid crystalline system having a high phase transition temperature and then a high amplification will be possible without sacrificing image stability.

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