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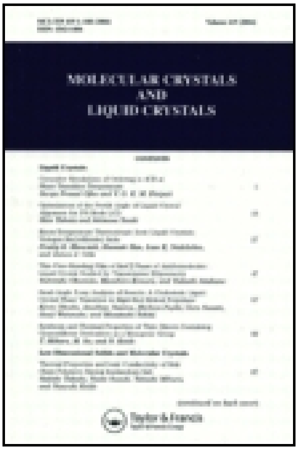

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Photochromic Diarylethenes for Optical Data Storage Media

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PHOTOCHROMIC DIARYLETHENES FOR OPTICAL DATA STORAGE MEDIA

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Abstract A new type of photochromic compounds, diarylethene derivatives, has been developed for optical data storage media. The photochromic dye - polymer media had read-out stability more than 10^6 times, and write/erase cycles could be repeated 3 X 10^3 times without loss of performance.

INTRODUCTION

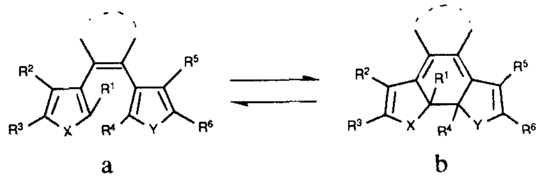
Although magnetic recording presently dominates mass memories, it is being challenged on several fronts by optical recording. Optical recording utilizes focused laser light to effect some optical property change in the recording media which can subsequently be read back by the laser. By far inorganic media, which use magneto-optic effect or phase change as the basis of optical recording, have been extensively studied. These media are based on a heat-mode optical recording method. Photon energy of the laser is once converted to heat energy on the recording media and used for the recording. In order utilize the versatile function of light fully, a photon-mode recording method and media should be explored. Photon-mode recording will be advantageous in the sense of resolution, speed of writing, and multiplex recording capability. One of the candidates for the photon-mode erasable recording media is organic photochromic materials.

Photochromism is defined as a reversible transformation in a chemical species between two forms having different absorption spectra by photoirradiation. Although much efforts have been paid, the photochromic materials still await the practical application. The limitation is due to the lack of suitable compounds which fulfill the requirements for the reversible recording media. The requirements for the use are as follows:

1) Archival storage capability (thermal stability)

2) Low fatigue (can be cycled many times without of loss of performance)
3) High sensitivity at diode laser wavelengths and rapid response
4) Non-destructive read-out capability.

We recently developed a new type of fatigue resistant and thermally stable photochromic compounds, diarylethenes with heterocyclic rings.[1,2,4-11]



For the practical application other properties, 3) and 4), are also equally required. In this paper, we report on our approach to gain access to a photochromic dye - polymer media which fulfill all of these requirements simultaneously.

THERMAL STABILITY

The most important property which photochromic compounds should have for optical data storage media is thermal stability of both isomers. In order come up with a guiding principle for the thermal stability, we first carried out a theoretical study of 1,3,5-hexatriene to cyclohexadiene type photochromic reactions.[2] The state correlation diagrams were calculated by semiempirical MNDO method.[3] From the diagrams it was concluded that the thermal stability of both isomers of the diarylethene type photochromic compounds is attained by introducing aryl groups, which have low aromatic stabilization energy, such as furan or thiophene rings.

The theoretical prediction was confirmed by the synthesis of diarylethenes with various types of aryl groups shown in Fig. 1. The stability was depended on the type of aryl groups. When the aryl groups were furan or thiophene rings, which have low aromatic stabilization energy, the closed ring forms were thermally stable. They did not show any decay of the absorption intensity even at 80°C for more than 12 h. On the other hand, photo-generated closed-ring forms of diarylethenes with phenyl or indole rings were thermally unstable.

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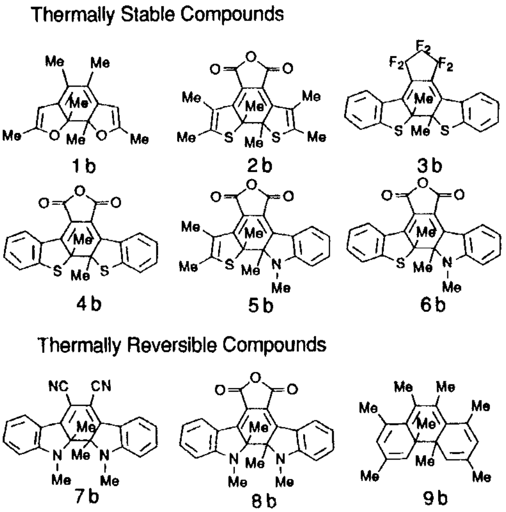
Thermally Stable Compounds

Thermally Reversible Compounds

FIGURE 1 Thermal stability of photogenerated closed-ring forms of diarylethenes with various types of aryl groups.

The closed-ring forms returned to the open-ring forms in the dark at 80°C. The different behavior in the thermal stability between diarylethenes with furan or thiophene rings and phenyl or indole rings agrees well with the theoretical prediction that the thermal stability depends on the aromatic stabilization energy of the aryl groups.

It is worthwhile to note that the closed-ring forms of 5b and 6b were found to be thermally irreversible but photochemically reversible. The result indicates that the closed-ring forms of non-symmetric diarylethenes are thermally stable when at least one of the heterocyclic rings has low aromatic stabilization energy.

FATIGUE RESISTANT PROPERTY

Photochromic reactions are always attended by rearrangement of chemical bonds. During the bond rearrangement undesirable side reactions take place to some extent. This limits the cycles of photochromic reactions. The difficulty to obtain fatigue resistant photochromic compounds can be easily understood by a simple calculation. We assumed the following reaction scheme, in which a side reaction to produce B' is involved in the forward process.

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$$B' \xleftarrow{\Phi_s} A \rightleftarrows B$$

Even under the conditions that the side reaction quantum yield, Φ_s, is as low as 0.001 and B perfectly converts to A, 63 % of the initial concentration of A will decompose after 1,000 times colouration/decolouration cycles. The quantum yield should be less than 0.0001 to repeat the cycles more than 10,000 times.

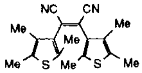
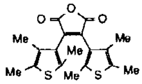
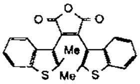
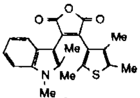
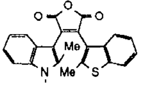
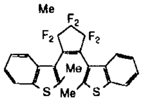
Fatigue resistant property of diarylethenes with various types of aryl groups was measured to search for fatigue free molecular structures. Table 1 summarizes the result of repeatable cycle numbers. The number indicates the cycle number when the coloured intensity decreases to 80 % of the first cycle. For the symmetric diarylethenes, the repeatable cycle number was limited to less than 480 times even in the absence of air so far the compounds had thiophene rings. When the thiophene rings were replaced with benzothiophene rings, the number remarkably increased. Non-symmetric diarylethenes with an indole ring on one end had a good fatigue resistant property. 2-(1,2-Dimethyl-3-indolyl)-3-(2,4,5-trimethyl-3-thienyl)maleic anhydride 5a for example, kept the adequate photochromic property even after the cycles of 8.7×10^3. Diarylperfluorocyclopentene derivatives, such as 1,2-bis(2-methyl-benzothiophen-3-yl)perfluoropentene 3a showed an excellent fatigue resistant property even in the presence of air.

SENSITIVITY AT LONGER WAVELENGTHS

From the view point of practical application the photochromic compounds should have the sensitivity in the region of wavelengths 650 - 830 nm. In order to obtain compounds which have sensitivity at longer wavelengths, symmetric diarylethenes with various heterocyclic rings have been synthesized.[4,6,7,10] Among the compounds the closed-ring form of 2,3-bis(1,2-dimethyl-3-indolyl)maleic anhydride 8b had the longest absorption maximum at 620 nm. It was, however, thermally unstable and returned to the open-ring form in the dark. In an attempt to get a thermally stable photochromic compounds having the absorption band at longer wavelengths we synthesized unsymmetrically substituted non-symmetric diarylethenes having an indole ring on one end and a thiophene or a benzothiophene ring on the other end.

A compound having an indole ring on one end and a thiophene ring

TABLE I Fatigue resistant property

Compd	Repeatable Cycle Number	
	in air	under vacuum
	10	—
	70	480
	3.7×10^3	1.0×10^4
	—	8.7×10^3
	—	$>1.1 \times 10^4$
	$>1.3 \times 10^4$	—

on the other end 5a underwent a photochromic reaction to produce a closed-ring form with absorption maximum at 578 nm. Replacing a thiophene ring of symmetric bis(2,4,5-trimethyl-3-thienyl)maleic anhydride 2a with an indole ring caused a bathochromic shift of the closed-ring form as much as 45 nm. The photogenerated closed-ring form was stable, and maintained a constant absorption intensity for more than 12 h at 80°C. The maximum, however, was shorter than that of 8b.

To shift the maximum further to longer wavelengths, we introduced an electron donating group into the indole ring and an electron withdrawing group into the thiophene ring. The closed-ring forms of 2,3-diarylmaleic anhydride with a 5-methoxyindole ring on one end and a thiophene ring on the other end 10b had the maximum at 611 nm in hexane, while the derivative with an indole ring and a 5-cyanothiophene ring 11b at 626 nm. The maxima were still shorter than 650 nm.

Finally, we synthesized 2-(5-methoxy-3-indolyl)-3-(2,4-dimethyl-5-cyano-3-thienyl)maleic anhydride 12a. The absorption maximum of the closed-ring form was observed at 680 nm and the edge was extended to 860 nm, as shown in Fig. 2. Table II summarizes the absorption maxima of the derivatives.

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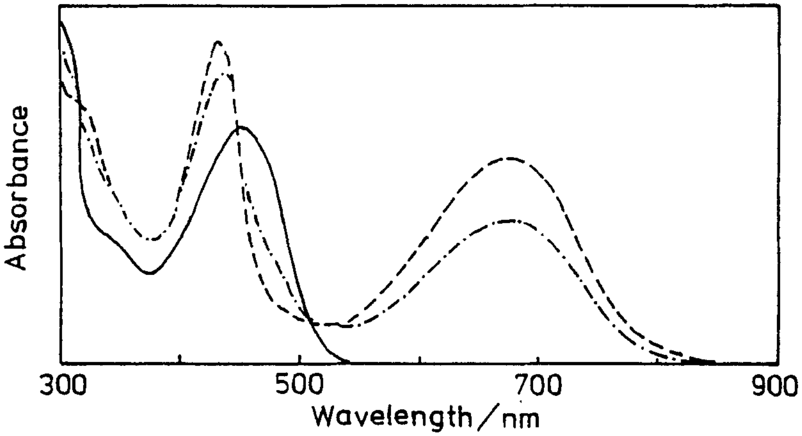
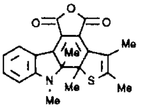
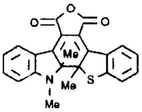
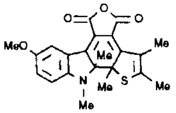
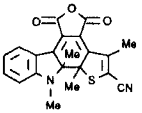
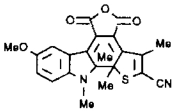


FIGURE 2 Absorption spectra of 12a(—), 12b(···) and the spectrum at the photostationary state under irradiation with 490 nm light in hexane.

TABLE II Absorption maxima of non-symmetric diarylethenes

Structure		λmax	Conversion, %
	5b	578 nm	70
	6b	583 nm	66
	10b	611 nm	71
	11b	626 nm	78
	12b	680 nm	70

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NON-DESTRUCTIVE READ-OUT CAPABILITY

A remaining problem to be solved for the application to optical recording is a non-destructive read-out. Photochromic media have not read-out stability. Even very weak light can induce the reactions in proportion to the number of photons absorbed by the media. Therefore, after many times read-out the memory is destroyed. A property that is desired to avoid the destructive read-out problem is a gated photochemical reactivity. The gated reactivity means the property that irradiation with any wavelength causes no reaction, while a photoreaction occurs when another external stimulation, such as heating or light of another wavelength, is present. We tried to construct a reaction system, in which the photochemical reactions is suppressed at room temperature, while it occurs at higher temperature.

A large medium dependence of 2-(2-methoxybenzothiophen-3-yl)-3-(1,2-dimethyl-3-indolyl)maleic anhydride 13a was used for controlling the reactivity by heating.[11] When 13a was dispersed in polystyrene, the compound was photochemically inactive at room temperature. The photocyclization reaction was not observed even by prolonged irradiation with 490 nm light. On the other hand, the compound became photochemically active when the polymer film was heated above 60 °C. The reactivity change is ascribable to the decrease in dielectric constant of the polymer medium and the increase in medium mobility at higher temperature.

The gated photochemical reactivity made it possible to read the memory many times without destruction. Write/read processes were carried out as follows. A high intensity 477 nm laser was used for writing. The laser heated the medium above 60 °C and enabled the compound to undergo photochemical ring-closure reaction, which induced a reflection decrease at 633 nm. The reflection change was read with two lasers, 633 nm and 477 nm lasers, as shown in Fig. 3. The 633 nm laser was used for controlling the temperature of the medium. The temperature at the recorded area was increased by absorption of the laser light and the 477 nm laser induced the photochemical ring-closure reaction. The erased area, on the other hand, was not heated by the laser, because the area had not absorption band at 633 nm. Photochemical reaction was not induced by the 477 nm laser.

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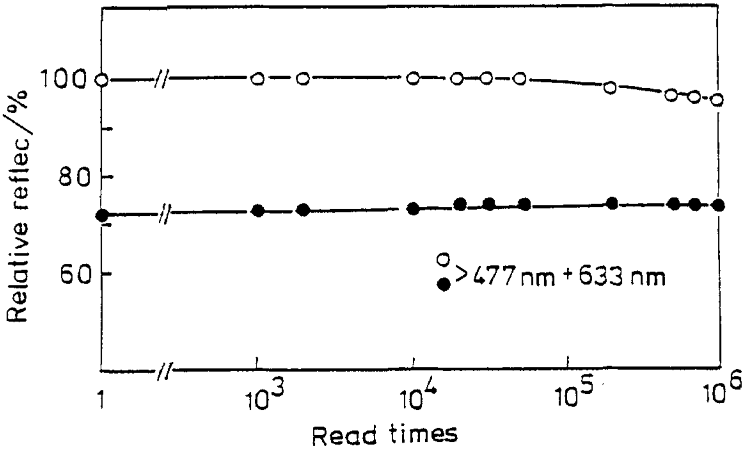

FIGURE 3 Changes of reflection of polystyrene film containing 13a after many times read-out with two lasers, 0.13 mw 477 nm and 0.05 mw 633 nm lasers.

The temperature difference between the two areas kept the reflection values almost constant even after 10^6 times read-out. The medium had read-out stability and write/read/erase cycles could be repeated 3 x 10^3 times without loss of performance.

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