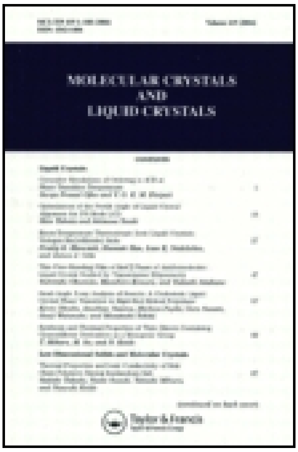

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006.

To cite this article: Yang-Kyoo Han , Dong-Yu Kim & Young Ha Kim (1994): Application of Side Chain Liquid Crystalline Polymers Containing Azo Dye Unit to Optical Information Recording Materials, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 254:1, 445-453

To link to this article: http://dx.doi.org/10.1080/10587259408036092

Mol. Cryst. Liq. Cryst. 1994, Vol. 254, pp. 445–453
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Printed in the United States of America

APPLICATION OF SIDE CHAIN LIQUID CRYSTALLINE POLYMERS CONTAINING AZO DYE UNIT TO OPTICAL INFORMATION RECORDING MATERIALS

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(Received: February 7, 1994)

Abstract Novel side chain liquid crystalline poly(malonic ester)s with two symmetrical mesogens containing azobenzene unit were found to be excellent as reversible optical information recording media for data storage and retrieval through a trans-cis isomerization of the azobenzene units by ultra-violet (UV) irradiation and thermal process. The sensitivity of information recording was dependent not only on the thickness of the polymeric thin film used but on the intensity of writing beam. The resolution of the information stored in liquid crystalline phase became better as UV irradiation time was increased and it was stable for over one year at room temperature.

INTRODUCTION

In recent years there have been increasing interest in the synthesis of a variety of thermotropic side chain liquid crystalline (LC) polymers with unusual anisotropic optical and electrical properties useful for electronic applications.[1,2] Furthermore, since they show a strong potential as information recording media of thermo-recording and holographic optical data storage systems, many researchers are focusing their efforts on the development of erasable optical media for data storage and retrieval by using side chain LC polymers with azo dye groups sensitive to the light.[3,4]

A laser beam addressed display, so-called thermo-recording process[5,6], is based on the thermo-optic effect of LC molecules: With irradiating a writing beam with high power intensity onto a preoriented transparent film of a LC polymer, a phase transition from LC (nematic or smectic) state to isotropic one occurs by a local optical heating. The resulting macroscopic unoriented light scattering spots give rise to a dark image pattern due to the change of refractive index during a read-out process. High power laser light (over 100 watt), however, is required for enhancing the sensitivity of information recording.

On the other hand, holographic ditial data storage technique, which was developed by Eich and Wendorff[7,8], produces an optical image excellent in resolution (high signal to noise ratio). This is attributed to the optical birefringence resulting from a photoisomerization of azobenzene moiety by a polarized laser. However, this method also requires preorientation of the LC polymers employed as optical media, before a write-in process, utilizing a special electro-optical cell equipped with two transparent conductive glasses (ITO glass). Such a process has a considerable difficulty in processibility from an industrial point of view. In order to overcome several disadvantages about preorientation and recording sensitivity, Ikeda et al.[9,10] have demonstrated photochemically induced isothermal phase transitions in polymer liquid crystals containing azo dye mesogens.

In the previous paper we have reported synthesis and characterization of new thermotropic side chain LC poly(malonic ester)s with two symmetrical mesogenic groups containing azobenzene unit, and also examined the effect of the length of spacer on LC behavior.[11] The present work describes the results of their applications to reversible optical information storage through a trans-cis isomerization of azobenzene group by UV irradiation and thermal process.

EXPERIMENTAL

As optical recording media, novel side chain LC poly(malonic ester)s were used. They were prepared according to the reported procedure[11] shown in Figure 1. Four kinds of new thermotropic LC malonic ester compounds were first synthesized by refluxing in ethyl acetate for 24 h malonyl dichloride and mesogenic alcohols with different ethyleneoxy spacer length linked to azobenzene group. They were then condensed with 1,6-dibromohexane in dimethyl sulfoxide in the presence of sodium hydride at 100°C for 24 h to give poly(malonic ester)s with two symmetrical azo dye mesogens.

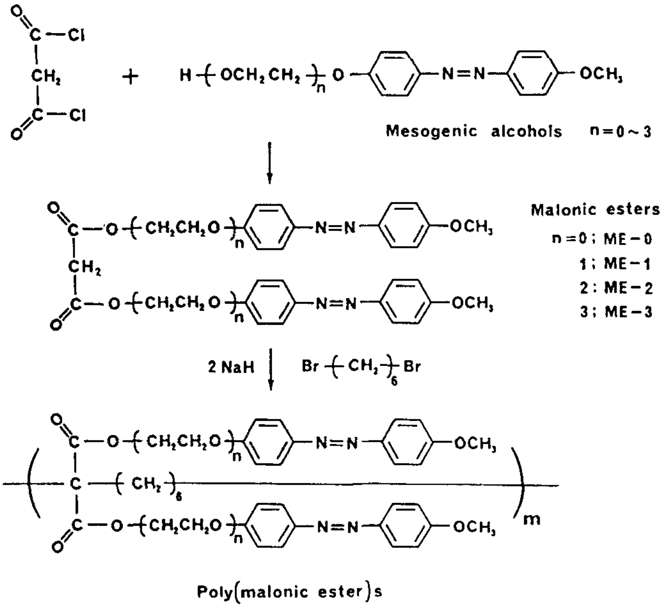

Figure 1. Synthetic route of poly(malonic ester)s

Trans-cis photoisomerization of azobenzene was carried out by the irradiation of UV (λ_{max} = 365 nm), which was selected into the wavelength between 310 and 430 nm through an optical glass filter (Kenko B-370), with a 500 W high-pressure mercury lamp (Ushio UI-501C). For example, a chloroform solution of the polymer (30 mg/L) in a 1 cm quartz cell was illuminated for a given period of time and then the UV absoprtion of the solution was measured immediately with a Shimadzu UV-240 spectrophotometer.

Thin film was cast from the polymer solution (4 wt%) in dioxane onto glass plate for 60 seconds using a spin coater with 2000 rpm and then removing the solvent under reduced pressure. The film was annealed within the range of phase transition temperature at which LC phase appears. The resulting film with a monodomain texture was irradiated by UV through a photomask for a desired time to obtain image patterns. LC behavior and birefringent texture of the film were observed by a polarizing microscope (Zeiss-Ultra) equipped with a hot stage.

RESULTS AND DISCUSSION

LC Behavior of Polymer Thin Film

In our preceding paper all the prepared malonic ester derivatives and polymers were observed to show nematic schlieren textures only on a cooling cycle (monotropic) by means of optical polarizing microscopy.[11]

Unlike powdery polymers, however, solvent-induced thin films obtained from poly(malonic ester)s exhibited enantiotropic behavior in which mesophase appears on both heating and cooling cycles. It appears to be due to the interaction between the solvent, dioxane, and the ethyleneoxy flexible spacer, which results in the orientation of the polymer chains. This is supported by the fact that the films were oriented to radial direction when cast by a spin coater.

The phase transition temperatures of polymeric thin films are summarized in Table I, where numerical values denote the number of ethyleneoxy spacer group. On a heating cycle, the phase transitions of polymer-2 and 3 to LC state appeared at 70 and 50°C, respectively, and their isotropization temperatures were 100 and 74°C. On the other hand, the phase transition temperatures observed on a cooling cycle were consistent with those of the powdery polymers reported. In contrast, it was difficult to prepare the film from low molecular weight polymer-1 and polymer-0 could not be synthesized because of the insolubility of the corresponding malonic ester compound (ME-0) in most solvents. Therefore, only the two thin films prepared from polymer-2 and 3 were used as optical data storage materials.

Table I. Phase transition temperatures of polymer thin films

Polymer	Heating (°C)	Cooling (°C)
Polymer-2	k 70 n 100 i	i 83 n 54 k
Polymer-3	k 50 n 74 i	i 56 n 35 k

Photoisomerization of Azobenzene

UV absorption spectrum was measured to investigate a photo-induced trans-cis isomerization of azobenzene incorporated into poly(malonic ester)s. Figure 2 and 3 show the absorption bands of the solution and film of polymer-2 before and after UV irradiation. As shown in Figure 2, the absorbance at 356 nm due to the stable trans conformation of azobenzene decreased rapidly as the irradiation time was increased from 5 to 80 seconds. On the contrary, new absorption band around 450 nm resulting from the cis form increased gradually with increasing the exposure time. Especially, Figure 2 displays an isosbestic point at which the absorbances of two different conformational species are equal. This indicates a typical photo-chemical reaction. Consequently, photoisomerization of azo dye (about 80% after 80 s) is found to occur very quickly in the polymer solution although the intensity of illuminated UV (I = 1 mW/cm^2 at λ_{max}) is very low.

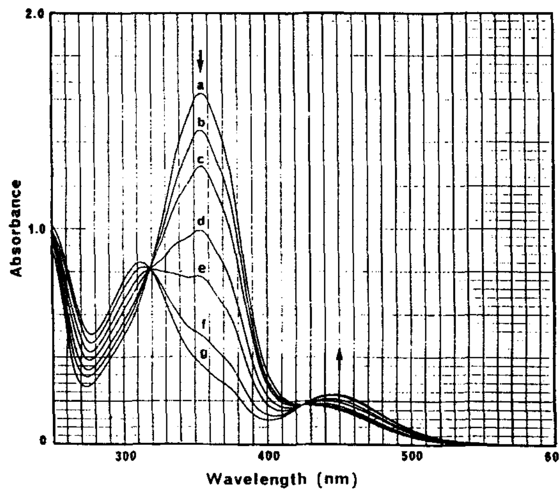

Figure 2. UV absorption spectra of Polymer-2 before and after UV irradiation: (a) before irradiation; (b) 5 s; (c) 10 s; (d) 20 s; (e) 30 s; (f) 50 s; (g) 80 s.

In the case of the film, however, the illumination time and intensity (I = 20 mW/cm^2 at λ_{max}) of UV for photoisomerization of azobenzene should be much longer and greater than those of the solution because of low mobility of polymer chains, as given in Figure 3. The general trend how UV absorption changes on irradiation is very similar to the results obtained for the solution except for slower trans-cis conformational change.[12]

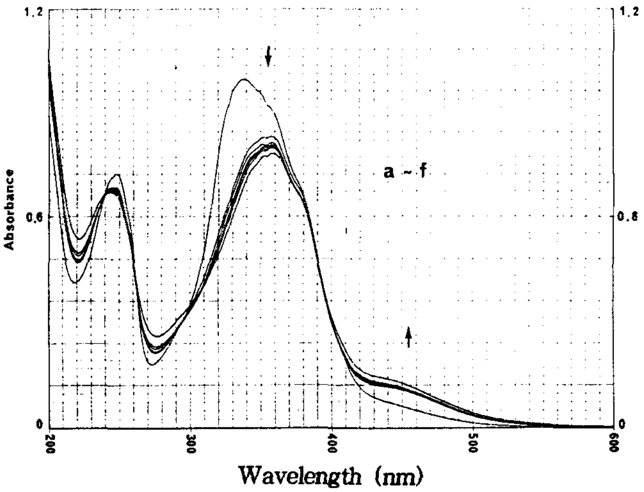

Figure 3. UV absorption spectra of the thin film from Polymer-2 before and after UV irradiation: (a) before irradiation; (b) 2 min; (c) 5 min; (d) 10 min; (e) 15 min; (f) 30 min.

Application as Information Storage Materials

Based on the above mentioned results, we examined the possibility of the application of these thermotropic side chain LC poly(malonic ester)s to reversible optical information recording media through a trans-cis isomerization of azo dye by UV irradiation and thermal process.

Writing precess for optical data storage is as follows. The polymeric thin film (about 8 μm) was prepared as described in Experimental section. The film from polymer-2 was heated up to 75°C with a scan rate of 10°C/min (65°C in the case of polymer-3) to show a LC phase and then annealed for 30 min in order to develop a monodomain texture as given in Figure 4. The resulting film was immediately quenched below glass transition temperature (Tg) at which mesophase was frozen. A photomask with a line width from 50 to 2 μm (<--), which is shown in Figure 5, was directly placed on the polymer film and UV with a intensity of 20 mW/cm^2 was irradiated onto the sample for a given period of time at room temperature. In order to store an image pattern, the illuminated film was finally cooled below Tg.

We have examined the influence of UV irradiation time (2 to 15 min) on the sensitivity of information recording and the resolution of image pattern. The sensitivity increased as the thickness of the film employed was decreased. The resolution of the stored image pattern was improved with increase in the exposure time of UV, and a clear pattern with a

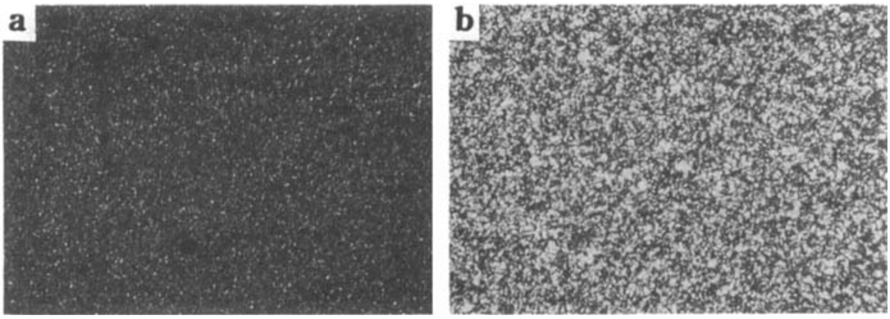

Figure 4. Monodomain textures of polymer-2 (a: 100X) and polymer-3 (b: 160X) developed at 75 and 65°C, respectively. See Color Plate V.

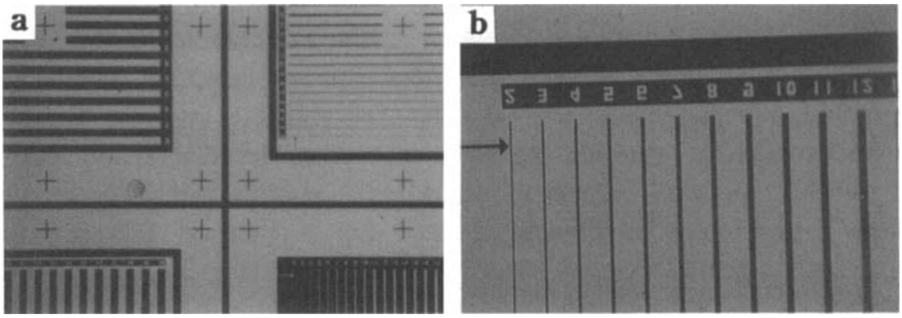

Figure 5. Image pattern of photomask: (a) 25X; (b) 100X. See Color Plate VI.

minimum line width of 2 μm (<--) was obtained when exposed over 10 min. In addition, both sensitivity and resolution were proportional to the intensity of UV irradiated. Figure 6 shows a representative photographs of the image patterns stored in the LC phase of polymer-3 after UV irradiation for 10 min. In these photographs, a dark pattern results from the phase change from LC to isotropic state induced by a trans-cis isomerization of azobenzene.[7,10] The stored image was very stable for over one year at room temperature. However, the resolution was not so high as expected because of the thread-like textures remaining in nematic LC phase unexposed to UV, which results in a low signal to noise ratio during a read-out process.

The stored information can be read by a optical polarizing

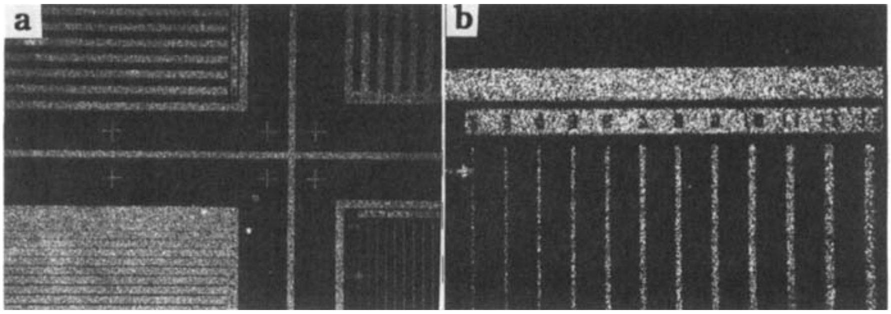

Figure 6. Image pattern stored in the thin film of polymer-3 after UV irradiation for 10 min: (a) 25X; (b) 100X. See Color Plate VII.

microscope. A maximum contrast of image pattern was observed when the angle of two-crossed polarizers of optical polarizing microscope was 45° relative to the orientation direction of the LC polymer chains aligned during annealing. The recorded data also can be erased by heating over the melting temperature of the polymer used and it is possible to rewrite the information by repeating the write-in process described previously.

Lately, we were successful to develop another technique in which optical data storage is directly induced by a polarized UV without a preorientation for information recording. Detailed results will be published elsewhere in the near future.

ACKNOWLEGEMENT

This work was supported by the Korea Institute of Science and Technology Grant BSE1047-3827-6.

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