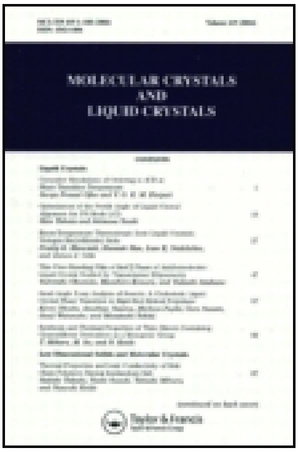

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Polarization Photochromsm of Polymer Thin Films and Its Applications

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To cite this article: Kunihiroichimura (1997): Polarization Photochromsm of Polymer Thin Films and Its Applications, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 298:1, 221-226

To link to this article: http://dx.doi.org/10.1080/10587259708036164

*Mol. Cryst. Liq. Cryst.*, 1997, Vol. 298, pp. 221-226
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# POLARIZATION PHOTOCHROMISM OF POLYMER THIN FILMS AND ITS APPLICATIONS

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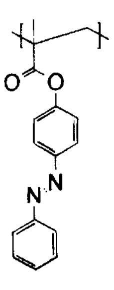
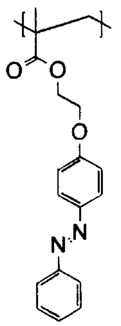
Abstract Linearly polarized light irradiation of films of polymethacrylates with azobenzene side chains induces dichroism and is applicable to the alignment photocontrol of thermotropic and lyotropic nematic liquid crystals and to the preparation of optical polarizers consisting of anisotropic dye films.

## INTRODUCTION

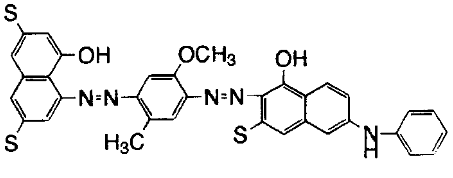
Our endeavors have been focused on revealing the structure/function relationship of "command surfaces" which display the surface-assisted alignment regulation of thermotropic nematic liquid crystal (LC) by photochromic molecules tethered from a topmost surface of silica substrate plates.[1] When actinic light for surface photochromism is linearly polarized, bulk LC molecules orient uniaxially to form homogeneous alignment.[1b] The efficiency of alignment photocontrol is markedly influenced by molecular structures of photochromic molecules. The linearly-polarized-light (LPL)-induced LC alignment regulation is also performed by photochromic reaction of spin-cast thin films of polymers with azobenzene side chains.[2,3] In contrast to command surfaces prepared by surface silylation of silica plates,[1b] there seems to be no restrictive effect of the chemical structures of photochromic units attached to polymer



pMAz



pMC2Az



C. I. Direct Blue 67

backbones on the LPL-induced alignment regulation; even thin films of a simple polymer, poly(4-phenylazophenyl methacrylate) (pMAz), causes homogeneous alignment upon LPL irradiation.[2] Furthermore, we found recently a novel phenomenon triggered by LPL-irradiated films of pMAz; the same polymer films are able to produce anisotropic dye molecular films by casting an aqueous solution of a water-soluble dye (C. I. Direct Blue 67).[4] This paper deals with polarization photochromism of polymers with azobenzene side chains and its application to the LC alignment photocontrol and the production of optically anisotropic dye films, stressing on remarkable amplification of LPL-induced dichroism of polymer films based on self-assemble of mesophasic molecules.[5]

## PHOTOINDUCED DICHROISM

Two homopolymers, pMAz and pMC2Az, have been employed here. Because the latter gave better results for the LC alignment, some behavior of films of pMC2Az upon LPL exposure was examined. Films of the polymer ($Mw=1.5 \times 10^{-5}$, $Tg=88°C$) were subjected to irradiation with monochromatic LPL at 365 nm and 436 nm, respectively. Fig. 1 shows dichroic ratios (DR) defined as $(A_{\perp} - A_{//})/(A_{\perp} + A_{//})$ as a function of exposure energies of LPL where $A_{\perp}$ and $A_{//}$ are absorbances at $\lambda_{max}$ during LPL irradiation using polarized probe light with electric vectors perpendicular and parallel to that of actinic light, respectively.

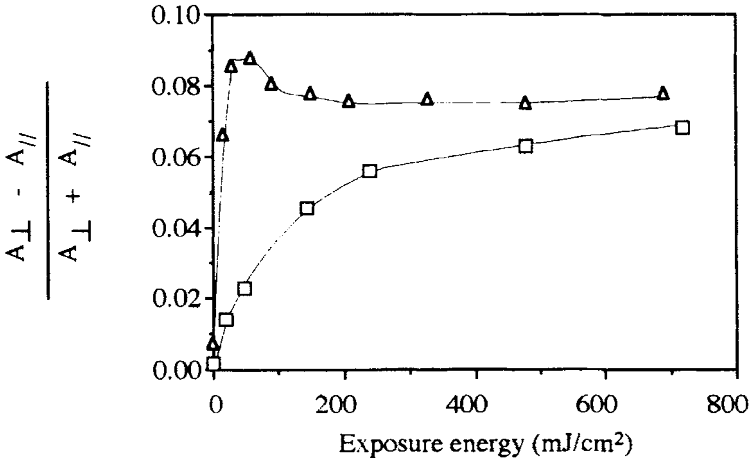


FIGURE. 1 Dichroic ratios of LPL-irradiated pMC2Az films as a function of exposure energy of 365 nm (-△-) and 436 nm (-□-), respectively.

The results are summarized as follows. First, upon irradiation with polarized 365 nm light, DR leveled off at an exposure energy of about 200 mJ cm$^{-2}$ through a maximum value centered at around 50 mJ cm$^{-2}$. Second, no maximum of DR appeared for polarized 436 nm irradiation and a gradual increase in dichroism takes place even after the saturation of cis-isomer formation. The facts are reasonably interpreted in terms of the involvement of two subsequent processes; the axis-selective, destructive photoisomerization and the molecular reorientation.

## PHOTOCONTROL OF LIQUID CRYSTAL ALIGNMENT

Our previous work showed that homogeneous alignment of nematic liquid crystals is achieved by LPL irradiation of pMAz thin films.[2] Problems arose from this polymer since the photoinduced homogeneous alignment is deteriorated even in the dark probably owing to the penetration of LC molecules into polymeric films to cause the thermal randomization of photo-oriented azobenzene chromophores.[2] On the contrary, it was found that very stable homogeneous alignment is obtained by using thin films of pMC2Az. The LC alignment photocontrol was carried out according to our previous work.[2,3] A substrate glass plate was covered with a spin-cast film of the polymer and exposed to LPL. A hybrid cell was fabricated subsequently by placing a nematic LC, NPC-02 ($T_{NI}=35$℃), containing a 1 wt% of a dichroic dye between the photoirradiated plate and a glass plate treated with lecithin in advance for homeotropic alignment. Photoinduced LC alignment was determined by monitoring the orientational direction of the guest dye using linearly polarized He-Ne laser beam (633 nm) as probe light.

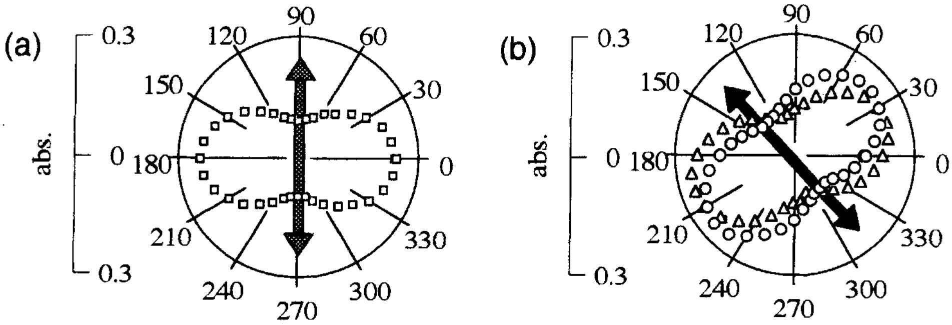


FIGURE 2 Polar diagrams of a dye-doped LC cell monitored with a He-Ne laser beam. LPL-irradiation at 436 nm was made (a) before (-□-; 100 mJ cm$^{-2}$-exposure) and (b) after cell assembly (-△-; 300 mJ cm$^{-2}$-exposure, -○-; 2000 mJ cm$^{-2}$-exposure).

Homogeneous alignment was generated readily by the irradiation of a film with polarized 436 nm light at an exposure energy of 100 mJ cm$^{-2}$ or less, as illustrated in Fig. 2. The uniaxial orientation was altered by re-illumination of a cell with LPL after changing the polarization plane of the light. The LC reorientation in a cell required an exposure energy much larger than that before the cell assembly. This implies strongly that LPL-induced reorientation of azobenzene units occurs much slowly when a polymer film is in contact with an LC layer. As discussed in our papers,[3,6] it is very likely that the effect of the presence of LC molecules on the rate of photoinduced reorientation is due to the formation of supramolecular aggregates consisting of LC molecules and surface azobenzene groups at an interface.

LC alignment control was influenced remarkably by heat treatment of a film before LPL irradiation. A polymer film pre-baked at 100°C for 1 hr resulted in homeotropic orientation of LC, in a sharp contrast to the fact that parallel alignment was induced by a film of the same polymer without heat treatment. A pre-baked film needed much larger exposure energy (> 1000mJ cm$^{-2}$) of polarized 436 nm light for the generation of homogeneous alignment. Very interestingly, irradiation of a pre-baked film with polarized 365 nm light reduced considerably an exposure energy required for homogeneous alignment.

Thin films of pMC2Az gave a homogeneous alignment with excellent optical quality without any defect such as disclination lines and with good storage stability below $T_{NI}$. An LC cell coated with a polymer film showed also a high resolution power; 2 μm lines and spaces were resolved

## FORMATION OF OPTICALLY ANISOTROPIC DYE MOLECULAR FILMS

We reported recently that LPL-irradiation of a film of pMAz provides a way to optically anisotropic formation of dye molecular films which are applicable to optical polarizers.[4] The preparation is carried out as follows. A spin-cast film of the polymer is exposed to LPL, followed by spreading an aqueous solution of a water-soluble dye (C. I. Direct Blue) to form a dye film. It was suggested, based on observation with atomic force microscopy and scanning electronic microscopy, that the dye films are composed of fine fibrous materials which are probably supramolecular aggregates of the dye.[7] The comparison of a visible absorption spectrum in a dilute aqueous solution with that of a dye film confirmed that dye molecules aggregate in a film state.

Under certain preparation conditions, dye films possess many spindle-shaped craters which are a few μm in width and *ca.* 50 nm in depth.[7] Furthermore, polarized optical microscopic observation revealed that the orientation of dye films are not fully uniform and consist of many domains of uniaxially aligned dyes with variant orientational direction.[4] In order to determine the optical anisotropy of dye films in a microscopic scale, polarized microscopic absorption spectra were taken with a minimum measuring area of 1 μm. As given in Fig. 3 as typical examples, polarized spectra of the inside of a crater show essentially no dichroism with lower absorbances. On the other hand, dye molecules at an outside of a crater display a very high dichroism, supporting the implication that a dye film comprises highly oriented supramolecules.

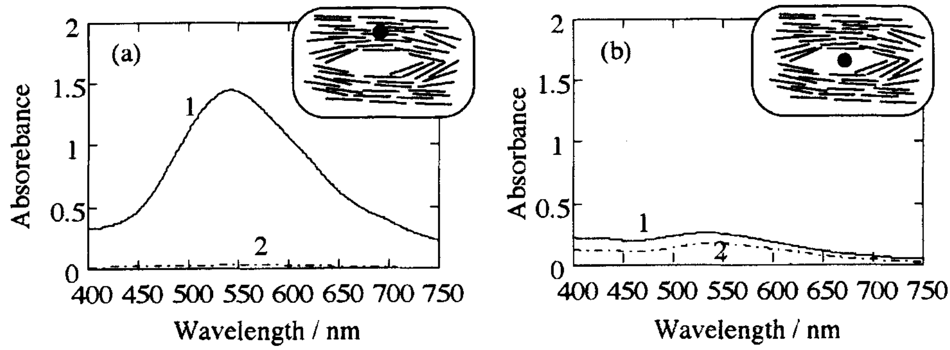


FIGURE 3 Polarized microscopic absorption spectra (1; parallel probing, 2; perpendicular probing) of a dye film with a circular area of 1 μm diameter (a) at the outside of a crater and (b) at the inside of the crater.

Some water-soluble dyes form lyotropic phases in concentrated solutions. This fact has led us to observe an anisotropic texture of a highly concentrated solution of the dye. A cell filled with a dye solution showed a schlieren texture which disappeared at *ca.* 50℃ and was recovered by cooling down, indicating that a dye solution is lyotropic. In order to examine the possibility that the orientational direction of dye molecules in a lyotropic phase is regulated by command surfaces, an inside of an empty cell was covered with a pMAz film which was subjected to LPL irradiation, followed by filling with a concentrated dye solution. It was found out that even the alignment of the lyotropic LC is regulated by the polymer surface. This is the first example for the regulation of alignment of lyotropic LC by a photochemical way. It should be stressed here the following. Whereas the alignment regulation of thermotropic LCs involves *molecule-to-molecule* interactions between surface azobenzene residues and LC molecules at a boundary region, orientational photocontrol of a lyotropic LC arises from *molecule-to-*

*supramolecule* interactions at an interface. This may open a new way to orientational regulation of organic molecules by command surfaces.

## CONCLUSION

1 LPL-irradiation of thin films of polymers with azobenzene side chains induces dichroism as a result of axis-selective, destructive photoisomerization, followed by photoinduced reorientation of azo-chromophores.

2 Films of pMC2Az exposed to LPL generate homogeneous alignment of a nematic LC with excellent optical quality and storage stability. Exposure energies for homogeneous alignment are dependent on the wavelength of actinic light, pre-baking of polymer films and whether a polymer surface is in contact with an LC layer.

3 Optically anisotropic dye molecular films are formed on LPL-irradiated films of azobenzene polymers. A following reorientation mechanism of dye molecules has been proposed. The water-soluble dye forms a lyotropic LC phase in a concentrated aqueous solutions, and the alignment of the supramolecular dye aggregates is regulated by photoaligned azo-chromophores of the polymer film and frozen-in by dryness to give rise to dichroic dye molecular films.

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