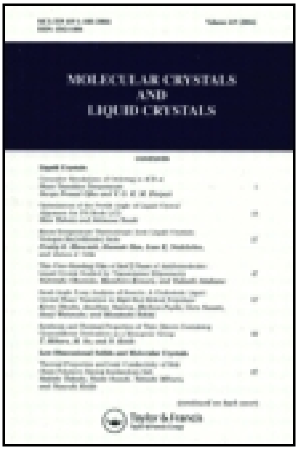

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Reversible UV Image Recording on a Photochromic Side Chain Liquid Crystalline Polymer

Lev M. Blinov [a b c], Riccardo Barberi [c], Gabriella Cipparrone [c], Mikhail V. Kozlovsky [a], Vladimir V. Lazarev [a c], Masanori Ozaki [b], Maria P. De Santo [c], Nicola Scaramuzza [c] & Katsumi Yoshino [b]

[a] Institute of Crystallography, Russian Academy of Sciences, 117333, Leninsky prosp. 59, Moscow, Russia

[b] Department of Electronic Engineering, Faculty of Engineering, Osaka University, 2-1 Yamada-Oka, Suita, Osaka, 565, Japan

[c] Istituto Nazionale di Fisica della Materia and Dipartimento di Fisica, Universitá della Calabria, 1-87036, Rende, Cs, Italy

Version of record first published: 24 Sep 2006

To cite this article: Lev M. Blinov, Riccardo Barberi, Gabriella Cipparrone, Mikhail V. Kozlovsky, Vladimir V. Lazarev, Masanori Ozaki, Maria P. De Santo, Nicola Scaramuzza & Katsumi Yoshino (2001): Reversible UV Image Recording on a Photochromic Side Chain Liquid Crystalline Polymer, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 355:1, 359-380

To link to this article: http://dx.doi.org/10.1080/10587250108023671

Mol. Cryst. Liq. Cryst., Vol. 355, pp. 359-380
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Reversible UV Image Recording on a Photochromic Side Chain Liquid Crystalline Polymer

LEV M. BLINOV[abc*], RICCARDO BARBERI[c],
GABRIELLA CIPPARRONE[c], MIKHAIL V. KOZLOVSKY[a],
VLADIMIR V. LAZAREV[ac], MASANORI OZAKI[b], MARIA P. DE SANTO[c],
NICOLA SCARAMUZZA[c] and KATSUMI YOSHINO[b]

[a]Institute of Crystallography, Russian Academy of Sciences, 117333, Leninsky prosp. 59, Moscow, Russia, [b]Department of Electronic Engineering, Faculty of Engineering, Osaka University, 2–1 Yamada-Oka, Suita, Osaka 565, Japan and [c]Istituto Nazionale di Fisica della Materia and Dipartimento di Fisica, Universitá della Calabria, I-87036, Rende (Cs), Italy

(Received October 18, 1999; In final form January 31, 2000)

Photochromism and photoinduced optical anisotropy have been studied for a chiral comb-like liquid crystalline copolymer containing azobenzene chromophores in its side chains. In a smectic glass phase of the polymer, upon irradiation by UV light, long living *cis-* isomers are observed. Spin coated films, irradiated by linearly polarized light manifest a photo-induced anisotropy, related to a strong stable dichroism, which is due to an enrichment and depletion of the chosen angular direction, correspondingly, with *trans-* and *cis-*isomers of azobenzene chromophores. These films are shown to be a novel medium for image recording, sensitive to UV light. In particular, a holographic grating may be recorded on top of a hidden UV image by interfering beams of visible Ar-laser light. Therefore, a stable holographic pattern of an image recorded by incoherent UV light is produced. It can be erased and recorded again.

Keywords: photoinduced anisotropy; liquid crystal polymer; UV image recording

PACS: 42.40.Ht; 78.20.Fm; 42.70.Ln

> "I knew Edgar Silinsh for 30 years. There were so many things discussed together in my Moscow kitchen: science, art, policy, national and psychological problems....quality of drinks. He was a great scientist and a wise man. I believe my co-authors would share my feelings if they knew him as closely as I did. We dedicate this work to memory of Prof. Edgar Silinsh"
>
> Lev Blinov

---

* Corresponding author, e-mail: lev@glasnet.ru

I. INTRODUCTION

Azobenzene derivatives are well known systems showing reversible transformations upon irradiation by UV and visible light [1]. Typically the absorption of an UV light quantum transforms an elongated rod-like molecular form (*trans* isomer of the azo-bridge) into a bent banana-like form (*cis* isomer). The transformations are accompanied by dramatic changes in the electronic spectra of the compounds (photochromism). Irradiation of the *cis*-form of the same compound by visible light causes a backward transformation of *cis*-isomers into the *trans* ones; this process is typically accompanied by thermal *cis-trans* transitions. The photochromism of azobenzene derivatives may be observed in both, dilute solutions and condensed phases, of azo-compounds. There have been reported various types of holographic photo-recording media based on the photochromic behavior of these materials [2–6].

During the last decade a number of studies were devoted to a photo-induced dichroism and to a related phenomenon, the photo-induced optical anisotropy in amorphous polymers and polymer liquid crystals with azo-dyes introduced as dopants, or chromophores chemically attached to a polymer chain [7–9]. In this case, linearly polarized light is used to induce the anisotropy, and the mechanism of the phenomenon is, presumably, based on a change in the azo-chromophore orientational distribution function after a sequence of *trans-cis-trans* photo-transitions. There were also reports on preparation of polar nonlinear optical materials by photo-electro-poling technique [10,11], and observation of giant photoinduced optical anisotropy in Langmuir- Blodgett films (LBFs) based on amphiphilic azo-dyes [12,13]. A recent review article [14] is devoted to this kind of phenomena, originating from the photo-induced molecular orientation in polymers, liquid crystals and LBFs.

Chiral systems have attracted special interest. There were studies of the influence of irradiation on the pitch of cholesteric liquid crystals [15,16] due to a change in the relative percentage of the *cis* and *trans* isomers and even observations of total unwinding of a cholesteric structure in a polymer liquid crystal [17] caused by photo-induced chromophore reorientation. Irradiation of the TGBA* phase of a methacrylic copolymer containing an azo-side chain was shown to induce phase transitions to the smectic A phase [18,19].

Recently there was synthesized an unusual liquid crystalline polymer with azobenzene chromophores attached to its main chain which manifests extremely long living *cis*-isomers both in dilute solutions and in solid films [20]. In a thin spin coated film, once excited by UV light (wavelength λ=300–400nm), they relax back to the *trans*- state on the scale of hours or even days at ambient conditions. At the same time, strong visible light in the 450–550nm range converts *cis*-isomers to their *trans*-counterparts during a few seconds. Since *cis*- and *trans*- isomers have different absorption spectra their photo-induced transformations must be accompanied by the corresponding changes in the refraction index. This phenomenon opens up a possibility for reversible recording optical images in the UV range with their subsequent developing by polarized visible light. In the present paper, we report on the relations between the photoinduced dichroism and the optical anisotropy, and demonstrate the development of a hidden UV image by both uniform illumination and by using a holographic technique.

II. EXPERIMENTAL

A. Materials

Substance

The chemical formula of the copolymer CP-40 is shown in Fig. 1. Its molecule contains azobenzene chromophores and chiral mesogenic groups in a 41: 59 molar ratio. The synthesis of the copolymer is briefly reported earlier [20]. Three characteristic bands are seen in the spectrum taken with a dilute chloroform solution, see Fig. 2: band M at 240nm belongs to the mesogenic group, band T at 350nm corresponds to the π-π^* electronic transition in the *trans* isomer of the azo-chromophore, and band N at 450nm corresponds to the n-π^* transition involving nitrogen atom orbitals.

Below 73°C the copolymer manifest a layered, smectic like structure, with a layer spacing of about 32Å, slightly decreasing with decreasing temperature. The layered phase, on cooling, is conserved in the glassy state at room temperature, Fig. 3. It is important to notice, that due to chirality of the substance, even rather thick polymer films are transparent and do not show any texture typical of the smectic A or C^*phases (probably, due to formation of a TGB phase with a short pitch [21]).

Films

Measurements of photochromism and optical anisotropy were made on thin and thick spin coated films. Thin (about 600nm) films were prepared from 2% (by weight) chloroform solution of the copolymer and deposited onto fused silica substrates with two subsequent speeds, 500rpm (10s) and 1700rpm (30s). Approximately 3μm thick films were cast onto a glass substrate from a 2% cyclohexanon solution.

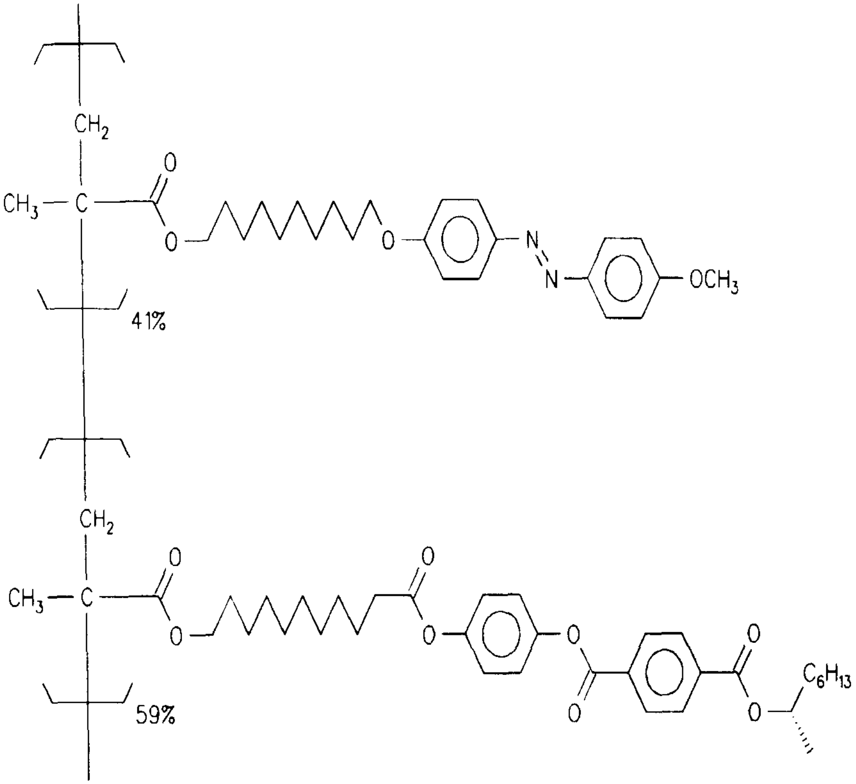

FIGURE 1 Chemical structure of the copolymer CP-40

The morphology of the films depends on their thickness and on the substrate used. We have imaged their surface by an Atomic Force Microscope (Autoprobe device by Park Scientific Instruments) in the "non-contact" AFM mode, where the probing tip moves along the surface at such a distance that no physical contact occurs and attractive long range van der Waals forces between a tip and a sample are measured [22]. Two images are shown in Fig. 4. The top one was taken for a 160nm thick spin coated film prepared from a 1% solution of the copolymer in dimethylformamide. It was deposited onto a glass substrate covered by an ultrathin polyimide layer and annealed at 200°C for 1h. One may see an unusual, quasi-periodic two-dimensional pattern consisting of small islands with characteristic dimensions about 0.3μm and the relief depth of about 250Å. We believe that this characteristic size is related to the pitch of the helix, in close analogy with the fingerprint cholesteric texture. Without a polyimide sublayer, the island structure is less pronounced, but may still be observed. Thick (3μm) cast films do not show such a texture at all, and their surface relief is rather shallow, about 50Å, see Fig. 4 (bottom).

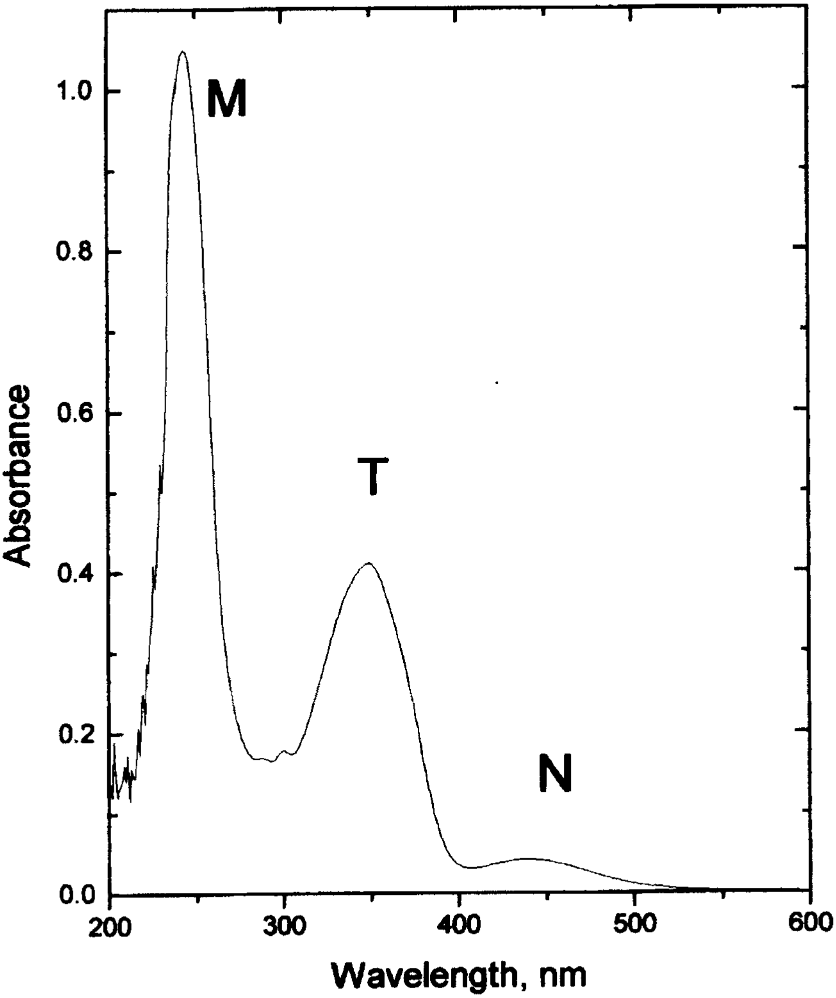

FIGURE 2 Absorption spectrum of CP-40 in 35mg/l chloroform solution [taken with a Cary-5E (Varian) spectrophotometer with pure chloroform in the reference beam]

B. Measurements

Photochromism

The photochromism measurements were carried out with a Hewlett-Packard Diode Array Spectrometer (Model HP 8452A). The spectrometer allowed to record a spectrum during 3s, therefore the kinetics of photo-isomerization could be studied. The irradiation of the samples was made directly in the spectrometer compartment, using a 100W metal-halide lamp IMH-160 (Sigma Koki) equipped with a fused silica light guide. To induce photoisomerization, a UVD filter was installed which transmitted about 20mW/cm^2 light power in the range 300–400nm. 1cm fused silica cells with chloroform solution of the copolymer were illuminated from their open top.

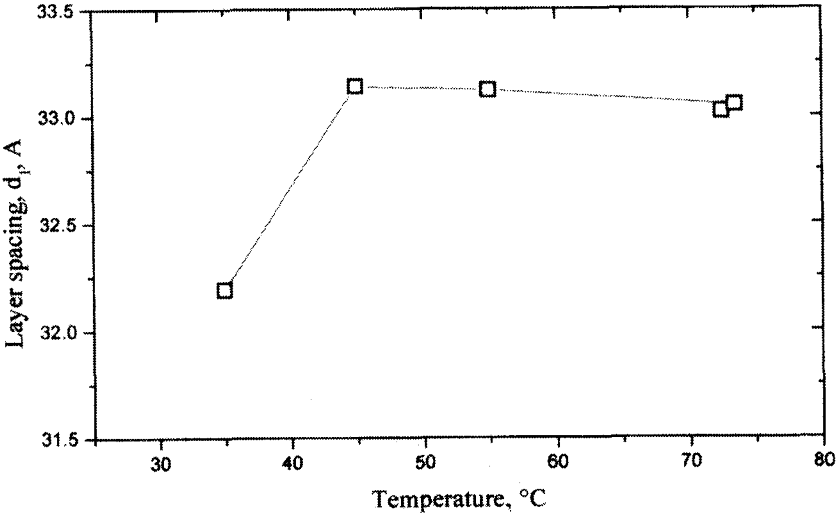

FIGURE 3 Temperature dependence of the layer spacing in a smectic structure (on cooling)

Photo-induced dichroism

The samples were installed at the spectrometer light emitting slit normal to the probing beam. Polarized absorption measurements were made with a Glan prism analyser installed at the light receiving slit of the spectrophotometer. The plane of incidence of the exciting light (UV or visible) was horizontal and the incidence angle α was about 60° with respect to the cell normal. A polarizing film was installed behind UV transmitting filter and allowed us to obtain both *s*- or *p*-polarized exciting beams (for details see ref. 20).

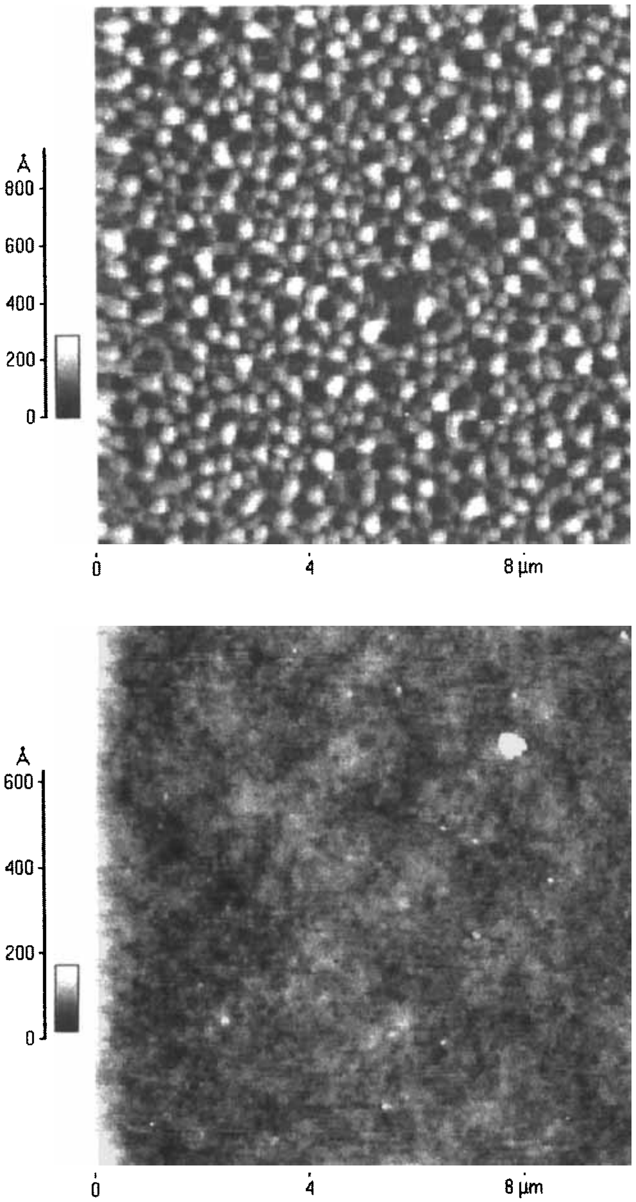

FIGURE 4 AFM 10x10 µm images of the surface of a 160nm thick film spin-coated on a polyimide sublayer (top) and of a 3µm film cast onto glass (bottom) (See Color Plate I at the back of this issue)

Photo-induced optical anisotropy

For measurements of the photo-induced phase retardation of a sample we use a modified ellipsometry technique described by Van Sprang [23]. The scheme of our set-up is shown in Fig. 5. A beam of a 8mW He-Ne laser is divided by a glass plate and a mirror into a signal and a reference beams. The signal beam is linearly polarized by polarizer P; it passes through a sample and λ/4 plate and is then chopped by a rotating analyzer (rotation frequency 50Hz). The reference beam is also polarized linearly in the same direction and chopped by the same rotating analyzer. Two identical silicon photodiodes (PDS and PDR) receive modulation signals and deliver them to the line input of a multimedia card of an IBM/PC computer. The card plays the role of a set of «virtual devices»: a digital oscilloscope, a lock-in amplifier and a recorder (for details see ref. 24). The technique allows the absolute measurement of the magnitude and sign of the phase retardation with accuracy better than 1°. It is used *in situ* during irradiation of films by polarized or unpolarized light of different spectral ranges, using a 300W Xe lamp and the optical filters. The pump beam formed an angle of 20° with respect to the probe, He-Ne laser beam.

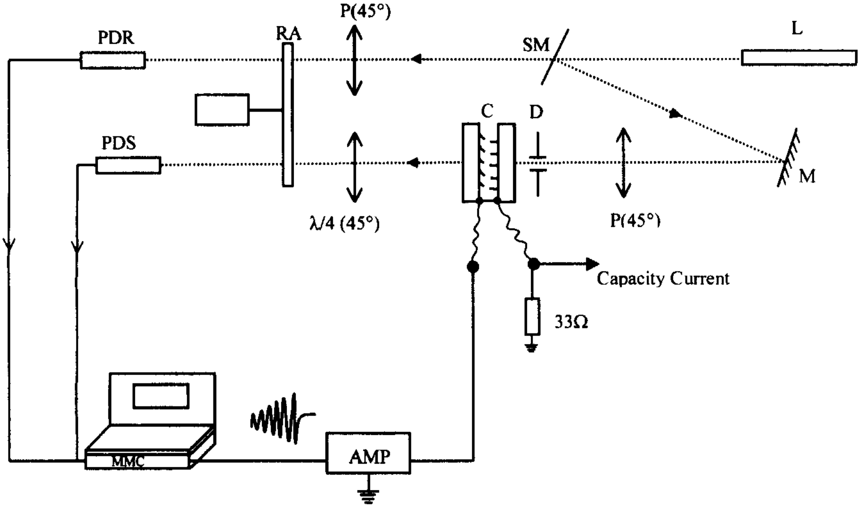

FIGURE 5 Experimental set-up for the light-induced optical retardation (and cell capacitance measurements). L: He-Ne laser; SM, M: mirrors; P-polarizers; D: diaphragm; C: liquid crystal cell; λ/4: λ/4-plate; RA: rotating analyzer; PDR and PDS: photodiodes in the reference and signal channels; MMC: multimedia card for an IBM/PC computer; AMP: amplifier

Holographic grating recording

The holographic gratings with period either 10 or 39μm were recorded and characterized with a pump and probe technique, described in more detail earlier [25]: an output beam of a writing Ar-ion laser (model Coherent T90) was split into two beams and sent to a sample at a small angle Θ≈ 2.8° or 0.8°. The two converging beams were either *s*- or p-polarized, that is their light electric vector was either perpendicular or parallel to the plane of light incidence on the sample. The illuminated spot at the sample was about 1.6mm in diameter. A probe (reading) beam of a He-Ne laser (λ_r=6328Å) with controlled polarization (either s or *p*) was sent onto the same spot perpendicularly to the film surface and detected by a Si photodiode behind the sample and a pinhole. The diffraction efficiency η of the grating was calculated as ratio I/I_0 where I_0 and I are the intensities of the incident light and of light in the 1st diffraction order.

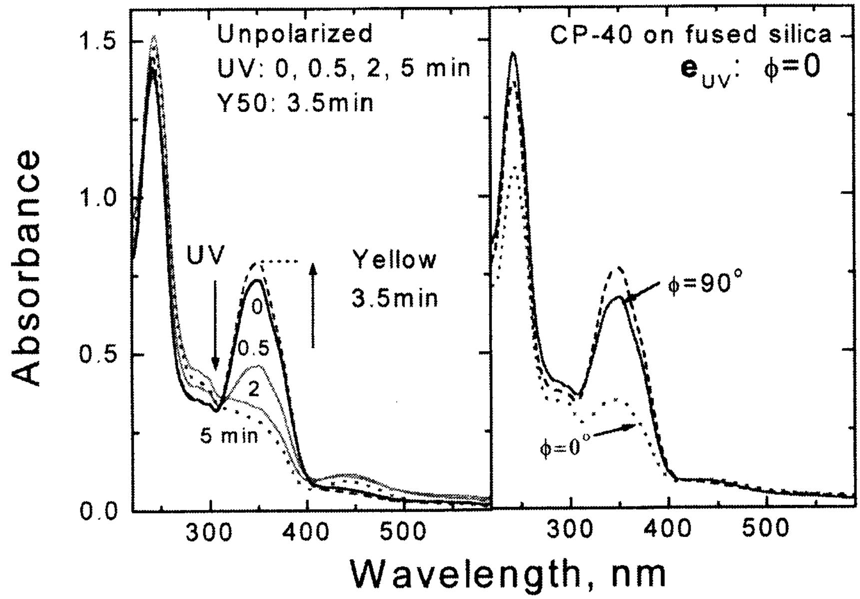

FIGURE 6 Photochromism of a 600nm thick spin coated film of CP-40. Left: the film is irradiated by unpolarized UV light (intensity 20mW/cm^2) for 0 (Solid line, virgin spectrum), 0.5, 2 and 5 min (*trans-cis* process) and then by yellow light for 3.5 min (with filter Y50 transmitting λ>500nm, *cis-trans* process, dashed line). Right: the film is irradiated by s-polarized UV light (intensity 3mW/cm^2) for 15min and the spectra are taken with s-polarized spectrometer light for the two azimuthal orientations of the film indicated in the Figure; the dashed line indicates the virgin spectrum

III. RESULTS AND DISCUSSION

A. Photochromism in solutions

Irradiation by UV light strongly suppresses the *trans*- band and increases absorption in the range of 250–300nm (π-π^* transitions in *cis*-isomers) and in the range 400–500nm, where a maximum at 442nm forms which corresponds to the n-π^* transitions in *cis*-isomers. The height of the maximum of the mesogen absorption at 250nm is almost insensitive to the *trans-cis* transitions in chromophores [20]. The *cis* -form of CP-40 is very stable: after the end of the UV irradiation, and waiting for 55 hours the *trans*-band was restored only to ca. 20–30% of the initial height, whereas it went back to 100% within 30s upon illumination with strong yellow light.

B. Photochromism of spin-coated films

The basic features of the spectral variation are the same as for chloroform solutions: on irradiation by unpolarized UV light, the *trans*-band at 348nm is suppressed, the *cis*-absorption (at 260–300nm) increases, the n-π^* band around 440nm forms, see Fig. 6 (left). The only difference is that now the mesogenic band is sensitive to the *trans-cis* transitions: upon irradiation, the absorption at 242nm increases by 5%. This phenomenon is related to a mesogen group reorientation[20]. The stability of the *cis* form in the glassy state of the copolymer is very high. In darkness, it takes more than 13 hours to convert only 20–30% of *cis* isomers back into its *trans* form. However, as shown in the same figure, on irradiation with strong yellow light the *trans* form is restored completely during 3–4min. The main features of the photochromism are also observed in a 3 μm thick film used further on for the image recording experiments, see Fig.7.

C. Polarized light-induced dichroism

It is essential that at room temperature the copolymer is in its optically isotropic, slightly scattering glassy state without any sign of preferable orientation. For example, a virgin, 600nm thick, spin coated film shows no dichroism. When it is irradiated by polarized UV light the angular distribution of *cis*-and *trans*-isomers becomes anisotropic: in the direction of the UV light electric vector $\mathbf{e}_{UV}$ there appears "a polarization hole" for the *trans* isomers and the same direction becomes almost solely populated by *cis*-isomers. Now the film is strongly dichroic, as can be seen in Fig. 6 (right). At an angular position ϕ=0, the film was

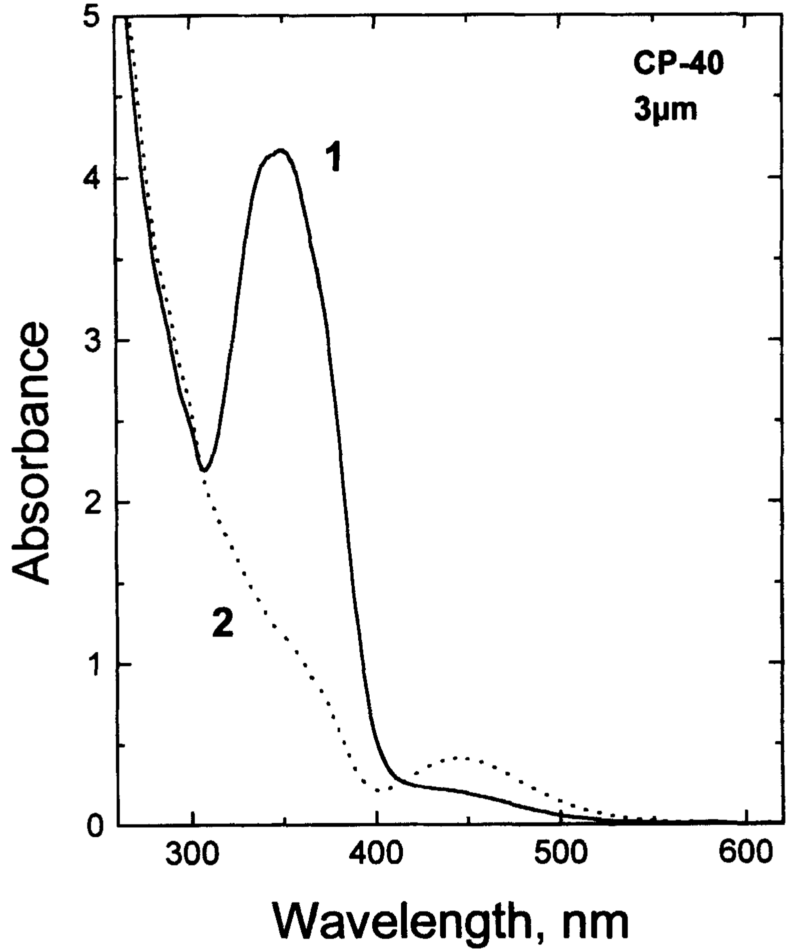

FIGURE 7 Virgin spectrum of a 3μm thick spin coated film of CP-40 (*trans*-form, solid line), and spectrum of the film irradiated by UV light for 5min with UV power density of 30mW/cm^2 (*cis*-form, dotted line)

irradiated by s-polarized UV light (intensity 3mW/cm^2) for 15min and then two polarization spectra were taken at two azimuthal orientations of the film, ϕ=0 and ϕ=90°. A stable dichroism was observed. What is of paramount importance, is a high stability of the new state: we have observed only a slight change in the dichroism for 6 days under ambient conditions. Light-induced dichroism may be obtained again by polarized UV light with an electric vector oriented at any arbitrary angle with respect to e_{UV}used for the first irradiation, see[20] for details.

D. Photo-induced optical anisotropy

Thin film

The evolution of the optical phase delay of a thin (600nm) film at the wavelength of a He-Ne laser was studied in a separate paper devoted to orientation of a nematic liquid crystal by copolymer CP-40. The film was subsequently irradiated by polarized UV and visible (green) light and the phase angle Φ between the ordinary and the extraordinary rays was measured [26].

Thick film

Since the diffraction grating efficiency is higher for thick films we made a detail investigation of the photo-induced optical anisotropy on a 3μm thick cast film. This film shows a small initial birefringence (phase delay $\Phi_0 \approx +2.1°$, optical anisotropy $\Delta n \approx 0.0012$). This anisotropy is almost 200 times less than the value typical of nematic and smectic mesophases and might be attributed to surface layers where the helical TGBA structure is distorted. On irradiation by rather strong, unpolarized visible filtered light (power density $P = 12 mW/cm^2$, $400 < \lambda < 500nm$) the birefringence changes only slightly. Such a change may be seen in the very beginning of the kinetic curve shown on the top of Fig. 8. The *s*-polarized visible light ($P = 5.3 mW/cm^2$) increases the phase delay up to $\Phi_{max} \approx +3.8°$ ($\Delta n \approx 0.0022$), the slow axis being directed perpendicular to the electric vector $\mathbf{e}_{vis}$ of the exciting light. After switching the visible light off the birefringent state remains stable. The *p*-polarised light reduces the anisotropy down to almost zero. With increasing light intensity the induced anisotropy even changes sign (finally, the axis is again perpendicular to $\mathbf{e}_{vis}$). A subsequent irradiation of the film with natural light restores the initial slightly birefringent state.

The irradiation of the film with a weak beam of the polarized UV light (power density $P = 0.08 mW/cm^2$, $300 < \lambda < 400nm$) gives rise to a similar effect, see Fig. 8 (bottom): s- and p-polarized beams create optical anisotropy of the opposite sign, $\Phi_{max} \approx +12.6°$ ($\Delta n \approx 0.0074$), $\Phi_{min} \approx -0.8°$, with the slow axis again perpendicular to $\mathbf{e}_{uv}$. The rate of the light induced birefringence is controlled by the intensity of the exciting light, the higher the intensity the faster the process.

Despite an apparent similarity of the two curves, the mechanism of the two phenomena is different. Before irradiation of the sample with UV light, the visible light absorbed by n-π band interacts with both types of the isomers and reorients azo-chromophores due to *repeated trans-cis-trans* isomerization without remarkable changes in the optical spectrum (for details see ref. 20). This is the process often used for information recording [3–9,27]. With UV light the situation is different, the s-polarization depletes the initial population of *trans*-isomers

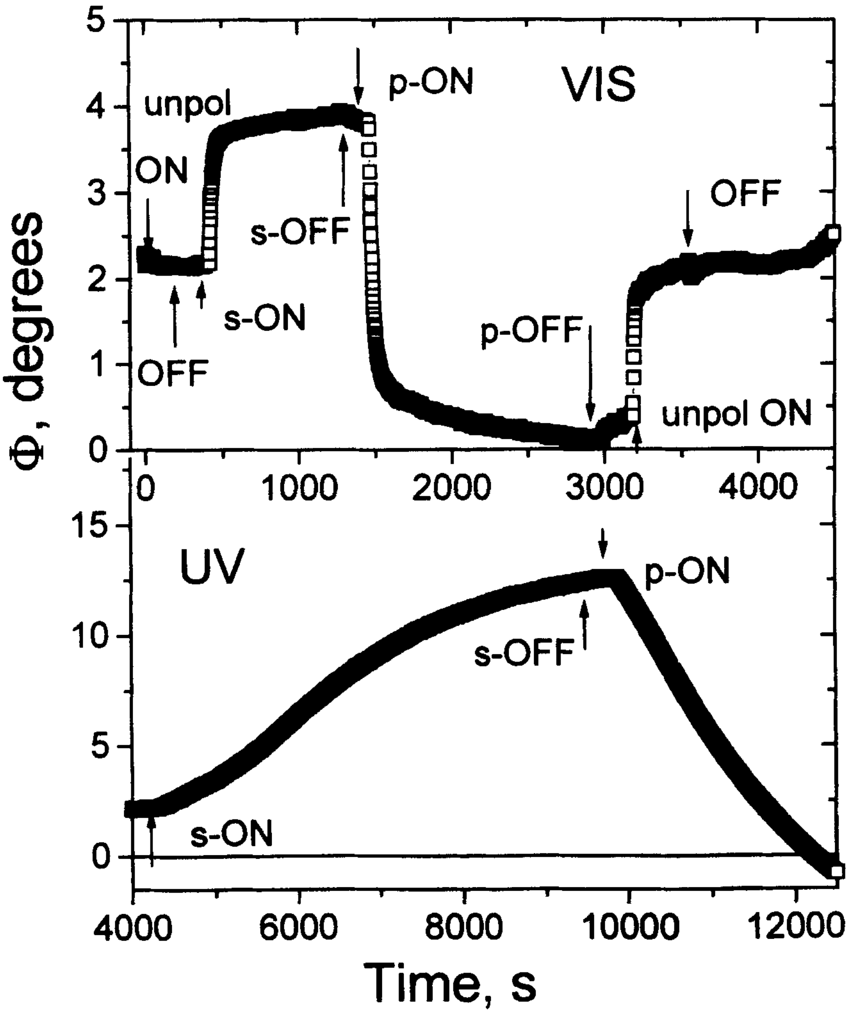

FIGURE 8 Evolution of the induced phase retardation upon irradiation of a 3μm thick film of CP-40 by solely visible or solely UV light beams. Top: irradiation with a beam of filtered visible ($400<\lambda<500$nm) light, with unpolarized (P=12mW/cm^2) and subsequently with s- and p-polarized (P=5mW/cm^2), and again unpolarized light. Bottom: irradiation with a weak beam of UV light (P=0.08mW/cm^2) and subsequently with s-polarized and p-polarized light

along the light electric vector and the slow axis follows the remaining *trans*- isomers in the perpendicular direction (because higher absorption causes a higher refraction index in the long wavelength part of the band). The depletion is proportional to $\cos^2\psi$ where ψ is an angle between the light electric vector $\mathbf{e}_{UV}$ and

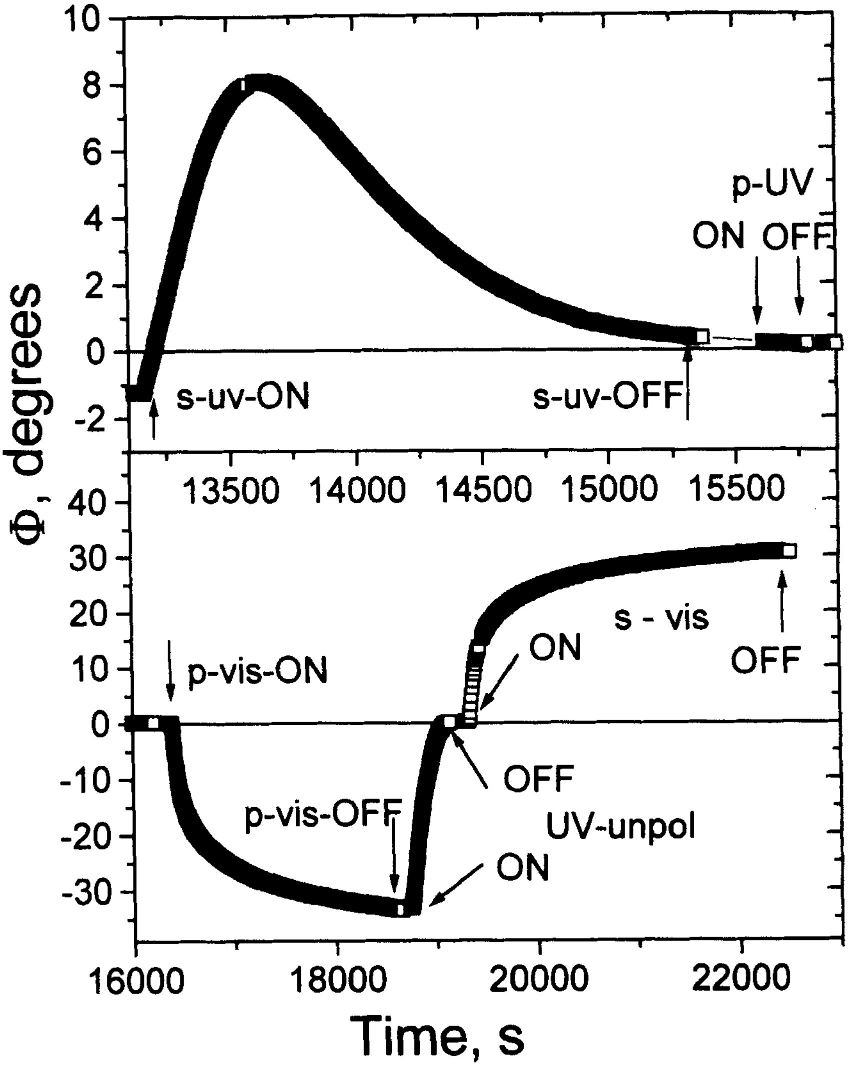

FIGURE 9 Evolution of the induced phase retardation upon combined irradiation of a 3μm thick film of CP-40 by UV and visible light. Top: irradiation with strong UV light (P=0.5mW/cm^2), with s-, and subsequently with p-polarized light. Bottom: irradiation with p-polarized visible light (400<λ<500nm, P=5mW/cm^2), unpolarized UV light (P=3.3mW/cm^2), and finally s-polarized visible light (400<λ<500nm, P=5mW/cm^2)

the transition dipole moment of the *trans*-isomer oscillator (coinciding with the azo-chromophore axis). A strong polarized UV light would convert all *trans*-isomers oscillators (not only those parallel to e_{UV} but even those oriented at ψ

angles close $\pi/2$) into their *cis*-counterparts and the optical anisotropy would decrease.

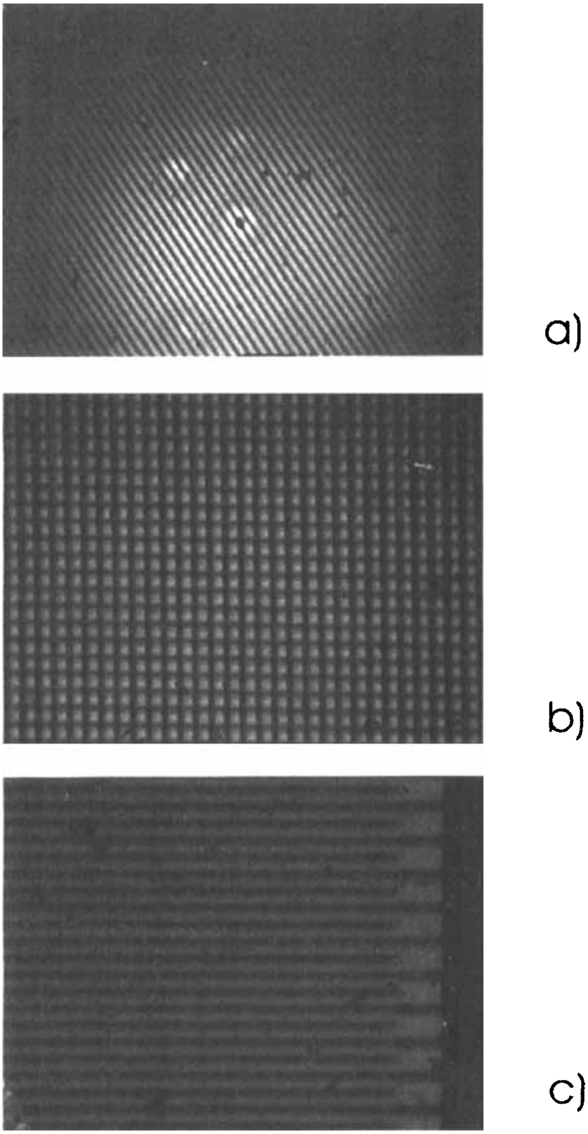

FIGURE 10 a) Image of a holographic grating recorded on a film uniformly irradiated by UV light (λ=514nm, two beams power 5mW, writing time 1s; grating period is 38μm). b) Holographic development (λ=458nm, each beam power 1.5mW, writing time 4s; grating period is 38μm) of an image of mask with period 40μm. c) Image of a mask recorded by unpolarized UV light and developed by polarized visible light (grating period is 400μm, see text) (See Color Plate II at the back of this issue)

The kinetic measurements shown in Fig. 9 were carried out to check this suggestion and to find the optimum regime for the UV image recording. The curve on the top of Fig. 9 shows the dependence of phase delay on irradiation of the film first by an s-polarized strong UV beam, then by a p-polarized one. As expected, a strong beam of any polarization suppress birefringence completely (after a short increase). This may be explained by complete (and reversible) reorientation of both the chromophores and mesogenic units along the light wave vector. In fact, after strong UV irradiation (even polarized) the copolymer is oriented homeotropically. This was verified by a special experiment. During the phase retardation measurements the normal to the sample was rotated of an angle ±20° off the direction of the probe beam. A considerable birefringence appeared, incompatible with existence of an isotropic phase which might, in principle, occur as a result of the UV irradiation.

After UV irradiation, the polarized visible light creates much stronger birefringence of the film than that observed for a film not treated by UV light. It is seen in Fig. 9 (bottom): the beginning of the curve corresponds to the end of the previous curve shown on the top, the film is not birefringent (for normal light incidence) after UV treatment. The irradiation of the film by p-polarized visible light results in a negative phase delay $\Delta\Phi \approx -32.5^\circ$ ($\Delta n \approx 0.045$), a subsequent irradiation with unpolarized UV light ($P=2\text{mW/cm}^2$) again eliminates birefringence and subsequent irradiation by s-polarized visible light induces positive birefringence $\Delta\Phi \approx +30.8^\circ$. The correspondent birefringence is almost 20 times higher, $\Delta n_{\text{ind}} \approx \pm 0.0185$, than that reached without UV treatment of the film, $\Delta n_{\text{ind}} \approx \pm 0.001$, see Fig. 8 (top). The sign of the birefringence is consistent with the new orientation of the *trans-* chromophores perpendicularly to the visible light electric vector. A similar phenomenon was also observed in Langmuir-Blodgett films [28]. Therefore the possibility to amplify the sensitivity of the material to visible light by previous UV irradiation is clearly demonstrated. To some extent, the phenomenon is similar to the "non-volatile holographic storage effect" observed recently in a doubly doped inorganic ferroelectric [29]. This is the basis for developing a hidden image, recorded by unpolarized UV light, by an uniform beam of polarized visible light (see below).

E. Recording of holographic gratings

At a wavelength of $\lambda=514\text{nm}$, it was only possible to record low contrast gratings on a virgin film using a power of the output Ar laser beam as high as $P=500\text{mW}$ and a writing time $t_{\text{w}}=2\text{s}$ (energy $E_{\text{w}}=1\text{J}$). On the contrary, on a film irradiated by UV light as explained above, the gratings are easily recorded with a power less than 10mW and $t_{\text{w}}=1\text{s}$ ($E_{\text{w}}=10\text{mJ}$). Therefore, with UV irradiation we gain, at least, a factor of 100 in sensitivity. In Fig. 10a, an image of such a grating is shown. Fig. 11 (left) shows the diffraction efficiency in the first diffraction order of gratings recorded with an *s*- polarized Ar-laser light (λ=514nm, *P*=10mW) as a function of the writing time. The grating efficiency is read out either by *s* (squares) or by *p*- (circles) polarized He-Ne laser. The maximum diffraction efficiency is reached within 3s, η_p(max)=0.27%; the same value is slightly higher (about 0.4%) when the grating is recorded with p-polarized Ar-laser beams.

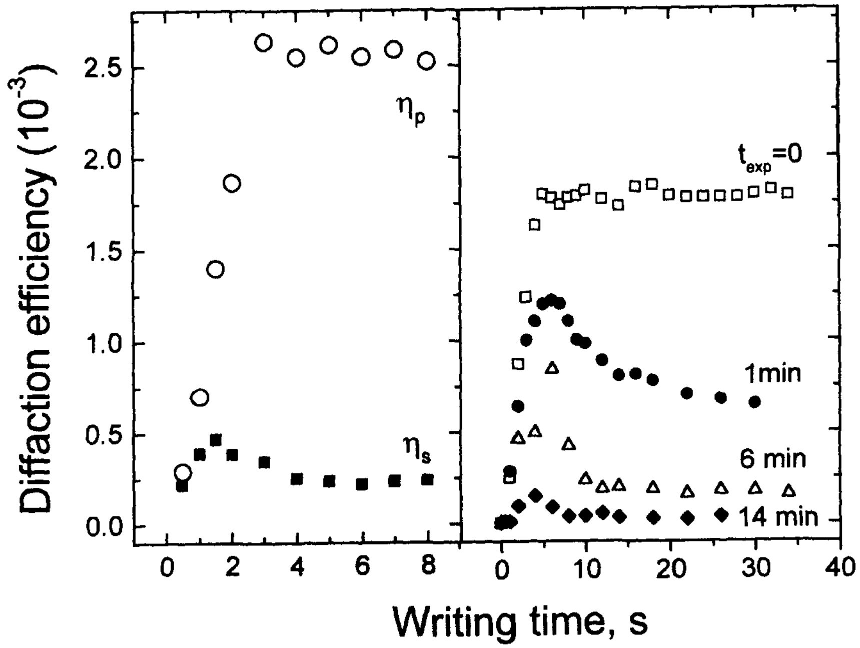

FIGURE 11 Diffraction efficiencies of 10μm gratings recorded with *s*- polarized writing beams as functions of writing time. Left: The gratings are read out either by *s*(squares) or p- (circles) polarized He-Ne laser. Ar-laser, two beams, total power was 5mW. Right: Grating diffraction efficiencies η_p for the *p*-polarized reading beam (Ar laser, two beams, total power =5mW, *s*-polarization). After the end of UV irradiating (t_{exp} =0) the film was exposed additionally to the light of an incandescent lamp, and gratings were recorded at the different exposition times t_{exp} shown at the curves

Under ambient conditions, a sensitivity of an UV irradiated film to the VIS writing beam completely degrades over about 10 hours (lifetime of *cis*-isomers). The process may be accelerated by additional exposition of the film to white light of an incandescent lamp (power density 2mW/cm^2 in the range 450–650nm) as shown in Fig. 11 (right). The curves of diffraction efficiency η_p of gratings recorded with *s*-polarized writing beams are displayed as functions of laser writing time t_w for different white light expositions t_{exp} = 0, 1, 6 and 14 min made *after* UV irradiation. Irradiation for half an hour is sufficient to suppress sensitivity by converting all *cis* isomers into their *trans-* counterparts. It is of great importance, however, that a grating, once recorded, remains stable for a much longer time (weeks under ambient conditions) even when all the *cis*-isomers are already converted into the *trans*-form. Even with additional illumination by visible light, which completely eliminates *cis*-isomers, the grating remains stable. For example, the diffraction efficiency of a control grating, recorded at t_{exp} =0 and then exposed for 14 min to 2mW/cm^2 visible light, is 50 times higher (η_p=0.17%) than the efficiency $\eta_p \approx 0.003\%$ of a newly recorded grating on the place exposed, at first, to the same visible light. This means, that the orientational state of the mesogenic groups and the chromophores memorises the recording process, probably due to a change in configuration of the backbone of the copolymer and a corresponding reorientation of the side chains responsible for the change in the refraction index. In any case, the stability of gratings is surprisingly high; however, they may be erased completely by repeated UV irradiation, (by newly created *cis*-isomers). Therefore, the whole recording process is characterised by fairly high sensitivity, grating stability and possible reversibility of recording.

F. UV image recording

An initially hidden UV image developed by incoherent light is shown in Fig. 10b. It was recorded as follows. a) The film was irradiated first by unpolarized filtered light ($400<\lambda<500$nm, exposition 10min, power density 50mW/cm^2) from a 300W Xenon lamp, in order to erase any remnant birefringence. b) Then the film was irradiated by unpolarized UV light ($300<\lambda<400$nm, exposition 10min, power density 3.3mW/cm^2) from the same lamp through a mask attached to the film. The mask with period 40μm consisted of a system of chromium interdigited electrodes on a fused silica substrate, the width of a finger was 20μm. After UV irradiation there was no grating observed under a microscope (with red filter), the film looked optically isotropic, i.e. black between crossed polarizers. c) Then the film was irradiated by polarized filtered light ($400<\lambda<500$nm, power density 5.3mW/cm^2) with direction of $\mathbf{e}_{vis}$ parallel to the chromium fingers. The grating appeared in 20s and was completely developed within 2 min. At each stage the optical anisotropy was monitored: after stage (a) the film was almost optically isotropic (quasi-planar, $\Phi \approx 2°$), after stage (b) it was optically isotropic (quasi-homeotropic, $\Phi < 0.5°$), and finally birefringent (between fingers $\Phi \approx 17°$, with the slow axis $\perp$ to the fingers). The grating shown in Fig. 10b strongly diffracts light of a He-Ne laser (5 orders of diffraction may be seen by the naked eye). The diffraction efficiencies in the first diffraction order are η_s =0.75% and

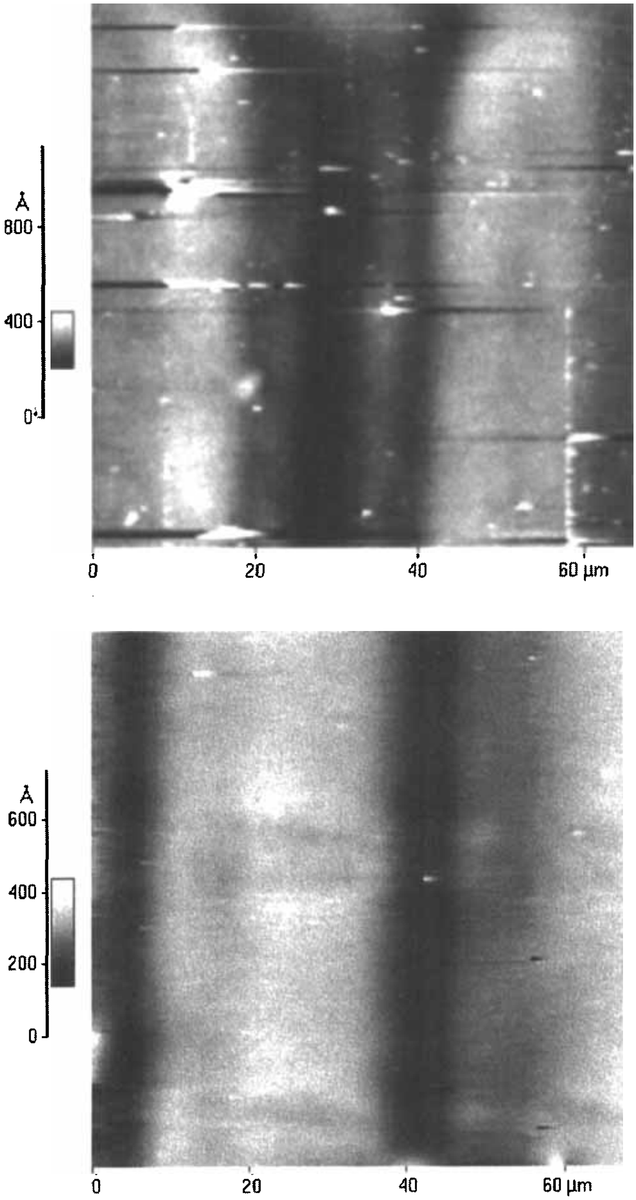

FIGURE 12 Two 80x80µm AFM images of the pattern shown in Fig. 10. Top: image of a T-type shadow of a chromium stripe at the right (black) edge of the picture shown in Fig. 10b. (note that AFM images are turned by 90° with respect to Fig. 10b) Bottom: image of the hologram shown in Fig. 10c. Laser fringes with period 38µm are vertical, faint shadows of the mask strips with period of 40µm are horizontal (See Color Plate III at the back of this issue)

η_p = 1.4%, for a laser beam polarized ∥ and ⊥ to the fingers (and $\mathbf{e}_{vis}$), respectively. The difference is consistent with the direction of the slow axis ⊥ to the fingers.

We made no special attempts to reach the maximum diffraction efficiency. However, the value η_p=1.4% is comparable with the best figures reported in literature for the polymer materials with reversible memory (e.g., 0.3% [6], 1% [30]). One should not forget, however, that in our case, the visible light was used only to develop an UV image (a possibility for UV holography).

The image, once recorded, is stable under ambient conditions for months. It cannot be erased even by very strong visible light, which eliminates all *cis-* isomers. The image, however, may easily be erased by unpolarized UV light. The subsequent irradiation with unpolarized visible light makes the same spot ready for new recording. We made several such cycles on the same spot without any traces of material degradation. This is consistent with observations[6] that the polymer films with azo-compounds may survive thousands *trans-cis-trans* photo-isomerisation cycles.

The hidden UV image of the mask may also be developed by interfering beams of the Ar-laser. Such an image is shown in Fig. 10c. The first two stages (*a* and *b*) were done as explained above. Then the hidden UV image of the mask was oriented in such a way that stripes of the image were parallel to the incidence (horizontal) plane of the laser beam. Correspondingly, the fringes of the holographic grating were in the vertical plane. A true holographic image in the form of a grid was developed within 4s at a laser wavelength λ=457.9nm with a total power of the two s-polarized beams of 3mW (energy about 12mJ). The maximum of the 1st order diffraction efficiency η_1 =1.2% corresponds to the *p*-polarization of the He-Ne laser and the beam diffracted along the vertical. As discussed above, the pattern does not degrade with time.

The formation of the image may, in principle, be accompanied by considerable changes in the surface topography and, consequently, by a change in optical path of the beam. To estimate this effect we made an AFM study of the surface relief. Fig. 12 shows two AFM images (80x80μm) of the pattern presented in Fig. 10. The first (top) image was taken of the area irradiated solely by UV light through the chromium mask. The dark (on the average) 20μm broad vertical band corresponds to the T-type shadow of a chromium stripe at the very right black edge of the picture shown in Fig. 10b. From Fig. 12 (top) it is clear, that, indeed, on the UV illuminated parts (two wide very bright bands), the thickness of the film is slightly increased with respect to the shadowed parts (dark). The depth of the relief is about 50Å at maximum.

On the bottom of Fig. 12, an AFM image of the hologram is shown (one cell of the grid displayed in Fig. 10c). Laser fringes with period 38μm are vertical; the bright bands correspond to the constructive interference (high light intensity), the dark bands to the destructive one. The relief is relatively deep, about 160 Å. On this background, much worse but still seen, are horizontal bands corresponding to shadows of the mask strips with a period of 40μm. Their relief measured along the vertical bright and dark bands (high and low laser intensity) is only about 40Å, close to that shown on the top of the same figure.

The profile of the relief for both laser and mask bands is not rectangular. For example, on the bottom image there were seen bright and dark sub-bands along the internal black band. In fact, UV light "sucks" some material out of the inner part of a shadow area and drags it close to the shadow edge. In any case the depth of the relief (maximum 15nm) is much smaller than the total thickness (3μm) of the film and does not significantly influence the total birefringence caused by the *trans-cis-trans* isomerization processes.

IV. CONCLUSION

Photochromism has been studied on a comb-like liquid crystalline copolymer with mesogenic units and azobenzene chromophores as its side chains. The copolymer possesses a smectic ordering in its glassy state, however, it remains optically isotropic. Upon short time irradiation by unpolarized UV light, long living (in darkness) *cis-* isomers are observed in spin-coated films. The isomers can easily be converted into their *trans* counterparts by short time green or yellow light irradiation.

Spin coated films of the copolymer manifest remarkable photo-induced optical anisotropy, which might be controlled by subsequent UV and visible light irradiation. The origin of the anisotropy is a strong dichroism, stable at least for many days and caused by a chromophore reorientation accompanied by a change in the angular distribution of the mesogenic groups and, to some extent, the main polymer chain. The dichroism occurs due to an enrichment and depletion of a chosen angular direction, correspondingly, with *trans-* and *cis*-isomers of the azobenzene chromophores.

These films are shown to be a novel medium for UV image recording. The principle of recording includes the formation of a hidden image, recorded by unpolarized UV light, and a second stage of image development by polarized blue or green light. The image may also be developed by interfering beams of linearly polarized Ar-laser light. Therefore a hologram of the UV image is formed which is stable, at least, for weeks, but may easily be erased by a second, uniform UV irradiation of the film and then rewritten again on the same spot.

Acknowledgements

L. Blinov thanks Prof. R. Bartolino for hospitality in Calabria University and Japanese Society for Promotion of Science for Fellowship in Osaka University. M. Kozlovsky thanks Prof. W. Haase for hospitality in TU Darmstadt where a part of the synthetic work on CP-40 has been done. The work has been carried out in framework of the Copernicus (grant no. IC15-CT96–0744) program and INFM "Progetto Sud"(Italy) and partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture (Japan) and Russian Fund for Basic Researches (grants N-99–02–16484, N98–02–17071).

References

(1) H. Durr ed. *Photochromism, Molecules and Systems*, (Elsevier, New York, 1990).
(2) M. Irie, Jpn. J. Appl. Phys. **28**, 215 (1989).
(3) T. Todorov, L. Nikolova, and N. Tomova, Appl. Optics **23**, 4309 (1984).
(4) M. Eich, J. H. Wendorf, Makromol. Chem. Rapid. Commun. **8**, 59 (1987).
(5) D. Y. Kim, S. K. Tripathy, Lian Li, and J. Kumar, Appl. Phys. Lett. **66**, 1166 (1995).
(6) J. J. A. Couture, Appl. Optics **30**, 2858 (1991).
(7) T. Fischer, L. Läsker, M. Rutloh, S. Czapla, J. Stumpe, Mol. Cryst. Liq. Cryst. **299**, 293 (1997).
(8) N. C. R. Holme, P. S. Ramanujam and S. Hvilsted, Appl. Opt. **35**, 4622 (1996).
(9) T. G. Pedersen and P. M. Johansen, Phys. Rev. Lett. **79**, 2470 (1997).
(10) Z. Sekkat and M. Dumont, Appl. Phys. **B54**, 486 (1992).
(11) L. M. Blinov, M. I. Barnik, T. Weyrauch, S. P. Palto, A. A. Tevosov, and W. Haase, Mol. Materials. **5**, 311 (1995).
(12) M. I. Barnik, V. M. Kozenkov, N. M. Shtykov, S. P. Palto and S. G. Yudin, J. Mol. Electr. **5**, 53 (1989).
(13) S. P. Palto, L. M. Blinov, S. G. Yudin, G. Grewer, M. Schönhoff and M. Lösche, Chem. Phys. Lett. **202**, 308 (1993).
(14) L. M. Blinov, J. Nonlinear Opt. Phys. and Materials **5**, 165 (1996).
(15) E. Sackman, J. Chem. Soc. Am. **93**, 7088 (1971).
(16) B. Schnuriger and J. Bourdon, J. Chem. Phys. **73**, 795 (1976).
(17) A. Petri, S. Kummer, H. Anneser, F. Feiner and C. Bräuchle, Ber. Busenges. Phys. Chem. **97**, 1281 (1993).
(18) M. V. Kozlovsky, V. P. Shibaev, A. I. Stakhanov, T. Weyrauch, and W. Haase, Liq. Cryst. **24**, 759 (1998).
(19) L. M. Blinov, M. V. Kozlovsky, G. Cipparrone. Chem. Phys. **245**, 473 (1999).
(20) L. M. Blinov, M. V. Kozlovsky, M. Ozaki, K. Skarp and K. Yoshino, J. Appl. Phys. **84**, 3860 (1998).
(21) E. Demikhov and M.V. Kozlovsky, Liq. Cryst. **18**, 911 (1995).
(22) L. M. Blinov, R. Barberi, G. Cipparrone, M. Iovane, A. Checco, V. V. Lazarev, and S. P Palto, *Liq. Cryst.* **26**, 427 (1999).
(23) H. A. Van Sprang, Mol. Cryst. Liq. Cryst. **199**, 19 (1991).
(24) S. Palto, R. Barberi, M. Iovane, V. V. Lazarev and L. M. Blinov, Mol. Materials **11**, 277 (1999).
(25) L. M. Blinov, G. Cipparrone and S. P. Palto, Int. J. Nonlin. Opt. Phys. **7**, 369 (1998).
(26) L. M. Blinov, R. Barberi, M. V. Kozlovsky, V. V. Lazarev, M.P. De Santo, J. Nonlinear Opt. Phys. and Materials, **49**, 1 (2000).
(27) C. Wang, H. Fei, Y. Yang, Z. Wei, Y. Qiu, Y. Chen, Opt. Commun. **159**, 58 (1999).
(28) J. Stumpe, T. Fischer, A. Ziegler, T. Geue, H. Menzel, Mol. Cryst. Liq. Cryst. **299**, 245 (1997).
(29) K. Buse, A. Adibili and D. Psaltis, Nature **393**, 665 (1998).
(30) M. Ivanov, T. Todorov, L. Nikolova, N. Tomova, V. Dragostinova, Appl. Phys. Lett. **66**, 2174 (1995).