Photoinduced anisotropy and polarization holography on UV exposure in films of N-benzylideneaniline in PMMA matrix

Detelina ILIEVA[1], Lian NEDELCHEV[2*]

[1]Varna Medical University, 55 Marin Drinov St., 9002 Varna, Bulgaria

[2]Institute of Optical Materials and Technology, Bulgarian Academy of Sciences,
 Acad. G. Bonchev St., bl. 109., P.O. Box 95, 1113 Sofia, Bulgaria

*Corresponding author: lian@iomt.bas.bg

In this paper, we present a study of the photoinduced processes in films of N-benzylideneaniline incorporated in a polymethylmethacrylate (PMMA) matrix both by spectrophotometric and holographic methods. Photodichroism of the order of $\Delta D = 0.15$ is induced in the films by polarized UV light at room temperature. We are also able to record stable holographic gratings in these materials for the first time to the best of our knowledge.

Keywords: photoinduced anisotropy, polarization holography, UV recording, polarization diffraction grating, N-benzylideneanilines.

1. Introduction

Polarization holography has been a field of intensive research during the last three decades since TODOROV *et al*. [1] established in 1984 the possibility to record high--efficient polarization diffraction gratings in azobenzene materials. In contrast to conventional holography, where the intensity and phase of an object beam are recorded using a second beam as a reference, in polarization holography also the polarization state is recorded on a suitable medium [2].

Numerous materials have been studied by researchers all over the world oriented towards different applications – understanding the mechanism of the recording [3, 4], formation of surface relief structures [5–11] and chiral structures [12–16], recording polarization holographic gratings and optical elements with specific polarization properties [17–21] and last but not least – for reversible optical storage of information [4, 22–26].

In most of these studies though the wavelength of the recording laser is from the visible part of the spectrum, usually at 488 nm or 514 nm. This is related with

the sensitivity of the materials used, mainly azo-dyes or azopolymers. On the other hand, it is well known that reducing the wavelength allows the density and capacity of optical storage media to be increased. Therefore, we focus our attention in this paper on investigating materials with absorbance in the UV, which at the same time have structure similar to the azobenzene compounds, namely the N-benzylideneanilines.

N-benzylideneanilines (NBA) are imines-type compounds. They have two aromatic rings linked by a –C=N– bridge. Just like the azobenzenes and stilbenes they have two isomeric forms: *trans*-NBA and *cis*-NBA. They absorb in the UV region of the spectrum with the absorption extending into the visible region. The photoinduced processes and, in particular, the *trans–cis* photoisomerization play an important role in the investigations on N-benzylideneaniline structure [27–33]. It has been established that on exposure to UV light NBA undergoes *cis–trans* isomerization about the carbon–nitrogen bond with the *trans* isomer being stable in the dark, yielding the *cis* isomer on exposure to light. The kinetic properties of this process have been studied and the lifetime of the *cis* isomer was estimated to be of the order of 1 sec at room temperature [27, 28]. Hence NBA is representative of a group of compounds which can apparently undergo *trans–cis–trans* isomerization and as a result, reorient perpendicularly to the polarization of the exciting light. Therefore, these materials are possible candidates for polarization holographic storage.

The main objective of this paper is to study the photoinduced processes, in particular, the photoinduced anisotropy in N-benzylideneaniline incorporated in a polymethylmethacrylate (PMMA) matrix. We are looking for optical storage materials sensitive to UV light and transparent in the visible range. It is expected that anisotropy can be induced in these materials due to the difference in the optical properties of the *trans* isomer in different directions. As a result, we demonstrate the possibility to record a stable holographic grating in NBA by UV laser at 257 nm.

2. Materials and methods

The material used in our study is N-benzylideneaniline incorporated in a polymethylmethacrylate matrix (NBA/PMMA). The chemical structure of the NBA is given in Fig. 1.

The N-benzylideneaniline may isomerize by –C=N– bond torsion (Θ) and by a mechanism that involves the inversion of the CNC bond angle (ϕ) at one of the nitrogen atoms via a semi-linear transition state [30, 33]. In our experiments,
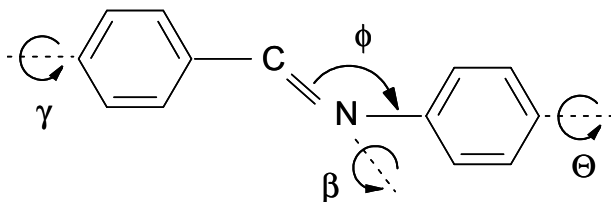

Fig. 1. Chemical structure of the N-benzylideneaniline (NBA).

the N-benzylideneaniline was added to a solution of polymethylmethacrylate (5%) in chloroform. The NBA concentration with respect to the PMMA is 1:1 wt%. The samples were dried for one week at room temperatures for elimination of residual solvent. Films with thickness about 0.5 µm were obtained by solution casting onto clean quartz substrates for the spectrophotometric investigation and onto glass plates for the holographic experiments.
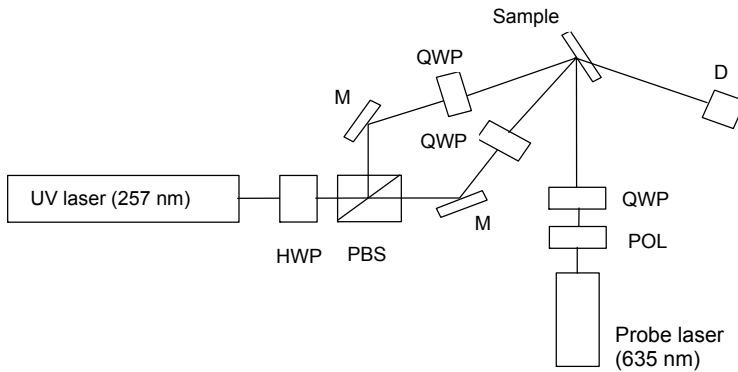

Fig. 2. Optical set-up for the holographic experiments. PBS – polarization beam splitter, HWP – $\lambda/2$ plate, QWP – $\lambda/4$ plates, M – mirrors, POL – linear polarizer, D – photodetector.

Linearly polarized light from a high pressure mercury lamp (HBO 200 with $\lambda_{max} \approx 365$ nm) was used to induce isomerization in the NBA/PMMA films. The light intensity at the surface of the samples was 0.05 mW/cm^2. The illumination was done directly with the lamp. The polarization of the beam was at 45° with respect to the horizontal. The spectral measurements were carried out with a Cary 5E (UV Vis NIR) spectrophotometer. For the holographic experiments a frequency doubled Ar$^+$ laser was used with wavelength $\lambda = 257$ nm. The optical set-up in this case is shown in Fig. 2. Using a half-wave plate (HWP) followed by a polarization beam splitter allows us to control and equalize the intensity of the two beams. Introducing the quarter-wave plates (QWP) in the optical scheme varies the polarizations of the recording beams from linear to circular.

3. Experimental results

In Figure 3, we compare the absorption spectra of films of N-benzylideneaniline incorporated in a polymethylmethacrylate matrix (NBA/PMMA) before and after a 2-hour exposure directly with mercury lamp with light intensity 0.05 mW/cm^2. Both non-irradiated and irradiated films are measured through polarizer oriented parallelly and perpendicularly to the exciting light polarization direction. For the non-irradiated films the two measurements coincide and are equal to D_0 – the optical density before illumination. The absorption maximum is about 255 nm. The corresponding optical densities after the exposure differ and are denoted as D_{par} and D_{ort}.
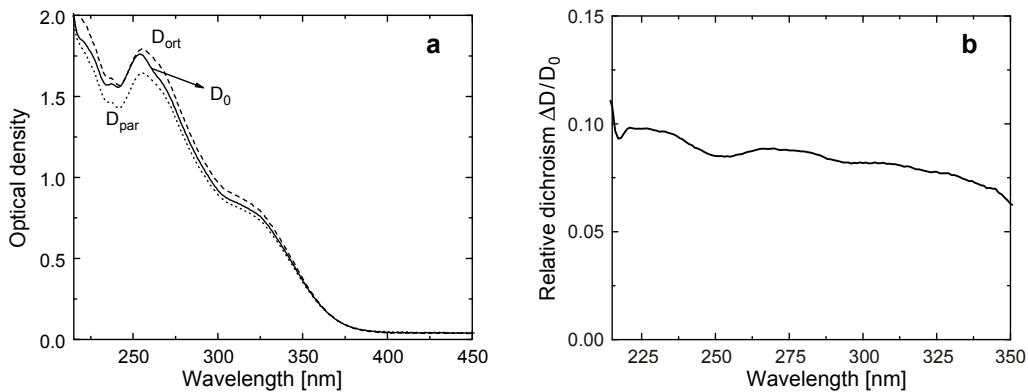
Fig. 3. Photoinduced changes in the absorption of the NBA/PMMA film. D_0 – the optical density before the illumination, D_{ort} and D_{par} – the polarized spectra after 2 h exposure with mercury lamp, $I = 0.05$ mW/cm^2 (**a**); relative change of the optical density: $(D_{ort} – D_{par})/D_0 = \Delta D/D_0$ (**b**).

Most significant changes are seen in the maximum of the absorption spectrum in NBA/PMMA films, mainly of the *trans*-band. The maximal photoinduced dichroism of the sample was $\Delta D = D_{ort} – D_{par} = 0.15$, which coincides with the absorbance maximum of the *trans*-molecules (about 255 nm). The relative dichroism is also shown in Fig. 3**b** and as seen, it does not vary significantly over the entire absorbance band. The effect is also stable in time – we did not observe considerable changes in the photoinduced dichroism ΔD in a NBA/PMMA films during one month following the exposure.

Along with the dichroism, birefringence is induced in the samples on illumination with polarized light from the mercury lamp. Using a He-Ne laser we measured the photoinduced birefringence (Δn) at $\lambda = 633$ nm, outside the absorption band. For the NBA/PMMA films we obtained $\Delta n = 3 \times 10^{-4}$. This value is small because the illumination was done with relatively low light intensity.

Further we investigated the possibility for holographic storage in the NBA/PMMA films using a frequency doubled Ar$^+$ laser at 257 nm. As shown in Fig. 2, the laser beam was split in two beams with orthogonal linear polarizations by a polarization beam splitter. In some of the experiments each of the beams passed through QWP and their polarizations were converted to circular. The half-angle between the recording beams was 8° (corresponding to a grating with 540 lines/mm).

Depending on the recording polarizations, two types of experiments were conducted: *i*) with two waves with the same polarization (leading to modulation only of the intensity of the interference light field) and *ii*) with two beams with orthogonal polarizations (leading to modulation of the polarization only, but not the intensity of the interference light field). The total light intensity in all these cases was approximately 160 mW/cm^2. The recorded holographic gratings were probed by a red laser beam. In Figure 4, the time evolution of the diffraction efficiency in the +1 order of these two gratings is shown. As seen from the figure, the maximum efficiency of
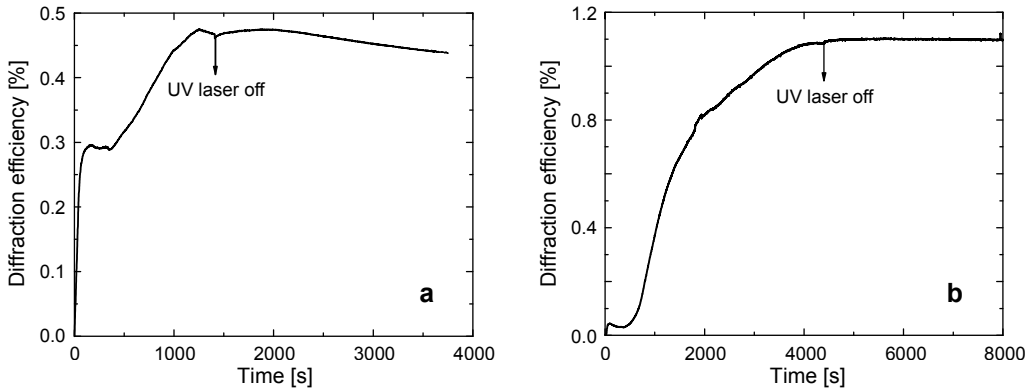
Fig. 4. Time evolution of the diffraction efficiency of the holographic grating recorded in NBA/PMMA films by a frequency doubled Ar$^+$ laser, $\lambda = 257$ nm, $I = 160$ mW/cm^2 with two beams with: the same circular polarizations (**a**) and orthogonal linear (s-p) polarizations (**b**).

the polarization grating (about 1.1%) is more than two times higher than the efficiency of the intensity grating (0.47%). They are stable for a long time after the exciting light is switched off.

4. Discussion

In this paper, we present the results from the spectral investigation of the photoinduced anisotropy in films of N-benzylideneaniline incorporated in a polymethylmethacrylate matrix. Following the exposure to polarized UV light, significant dichroism was induced in the absorbance maximum (the main *trans*-band) and though being smaller is also noticeable in the region of the *cis*-band (about 235 nm and 315 nm). MAEDA and FISCHER [31] also investigated UV irradiation of solution of the *trans*-isomers at reduced temperature. This resulted in extensive (80%–90%) conversion of the *trans*--isomers into *cis*-isomers. The process was found to be reversible both thermally and photochemically. In this case, the *cis*-isomers were stable only at low temperatures (less than –80 °C).

As seen in Fig. 3, the observed changes in the absorption in our experiments are anisotropic if the illumination is done with polarized UV light at wavelengths absorbed by both *trans*- and *cis*-isomers. It is well known that the *cis* molecules are not stable at room temperature and the *cis*–*trans* isomerization is very rapid [31–33]. Hence, it might not be necessary to use an optical-pumping scheme to reorient the molecules back to *trans* state and one can use the strong π–π* transition at 310 nm for the absorption and reorientation [33]. After the exposure the absolute value of the optical density for light polarized orthogonally to the exciting light polariza-tion (D_{ort}) increases mainly in the *trans*-band region (Fig. 3**a**). Therefore, we believe that the *trans*-isomers are reoriented into directions perpendicular to the exciting light polarization, similarly to the photoprocesses in azobenzene and stilbene molecules.

The absorption spectra after the illumination remain stable in darkness or on exposure to normal daylight. There are not detectable changes in them during the following month.

We have also recorded for the first time stable holographic gratings in NBA/PMMA films. In order to compare conventional holographic recording (where only the intensity of the light field is modulated) to pure polarization recording (where only the polarization is modulated), we used different combinations of polarizations of the recording beams. Initially, we recorded a set of conventional holographic gratings – with parallel linear polarizations (s-s and p-p) and with circular polarizations with the same handedness. They showed similar behavior and close maximal values of the diffraction efficiency, the one recorded with same circular polarizations showing the highest efficiency. Afterwards we recorded a sequence of pure polarization gratings, again with similar dynamics and highest value of the diffraction efficiency for the case of orthogonal linear (s-p) polarizations. In this case we have also measured the polarization of the first order diffraction beam and established that it has polarization orthogonal to the zero order beam.

The conclusion is that the diffraction efficiency of the gratings recorded by modulation of the polarization of the interference pattern (Fig. 4**b**) is higher than the efficiency of the ones recorded by modulation of only the intensity of the field (Fig. 4**a**) and therefore these materials are more sensitive to polarization recording than to conventional holographic recording. Most probably the diffraction at 633 nm can be further increased by modifying the chemical structure of the photosensitive compound or alternatively increasing the intensity of the recording beams.

The shape of the curves in Fig. 4 can be attributed to the presence of "fast" and "slow" processes as observed in azopolymers [34], where the growth of birefringence is described by biexponential functions. The "slow" process may also have certain exposure threshold and is activated after the "fast" one has achieved saturation.

We believe that the NBA/PMMA films could be used for fabrication of optical elements in the visible range.

5. Conclusions

In summary, we have obtained considerable photoinduced dichroism in the absorption spectra of PMMA films containing N-benzylideneaniline on illumination with polarized UV light. We believe that the exposure leads to reorientation of the *trans*-isomers into direction perpendicular to the exciting light polarization in a way similar to the azobenzene and stilbene compounds. We have also recorded stable holographic gratings in these films and showed that the diffraction efficiency of the polarization gratings is higher than of the intensity ones.

References

[1] TODOROV T., NIKOLOVA L., TOMOVA N., *Polarization holography. 1: A new high-efficiency organic material with reversible photoinduced birefringence*, Applied Optics **23**(23), 1984, pp. 4309–4312.

[2] NIKOLOVA L., RAMANUJAM P.S., *Polarization Holography*, Cambridge University Press, Cambridge, 2009.

[3] EICH M., WENDORFF J.H., *Erasable holograms in polymeric liquid-crystals*, Die Makromolekulare Chemie, Rapid Communications **8**(9), 1987, pp. 467–471.

[4] NATANSOHN A., ROCHON P., GOSSELIN J., XIE S., *Azo polymers for reversible optical storage. 1. Poly[4'-[[2-(acryloyloxy)ethyl]ethylamino]-4-nitroazobenzene]*, Macromolecules **25**(8), 1992, pp. 2268–2273.

[5] KIM D.Y., LI L., JIANG X.L., SHIVSHANKAR V., KUMAR J., TRIPATHY S.K., *Polarized laser induced holographic surface relief gratings on polymer films*, Macromolecules **28**(26), 1995, pp. 8835–8839.

[6] BARRETT C.J., NATANSOHN A.L., ROCHON P.L., *Mechanism of optically inscribed high-efficiency diffraction gratings in azo polymer films*, Journal of Physical Chemistry **100**(21), 1996, pp. 8836–8842.

[7] LEFIN P., FIORINI C., NUNZI J.-M., *Anisotropy of the photoinduced translation diffusion of azo-dyes*, Optical Materials **9**(1–4), 1998, pp. 323–328.

[8] VISWANATHAN N.K., DONG YU KIM, SHAOPING BIAN, WILLIAMS J., WEI LIU, LIAN LI, SAMUELSON L., KUMAR J., TRIPATHY S.K., *Surface relief structures on azo polymer films*, Journal of Materials Chemistry **9**(9), 1999, pp. 1941–1955.

[9] NATANSOHN A., ROCHON P., *Photoinduced motions in azo-containing polymers*, Chemical Reviews **102**(11), 2002, pp. 4139–4175.

[10] JINGLI ZHOU, JIANJUN YANG, YAN KE, JING SHEN, QIJIN ZHANG, KEYI WANG, *Fabrication of polarization grating and surface relief grating in crosslinked and non-crosslinking azopolymer by polarization holography method*, Optical Materials **30**(12), 2008, pp. 1787–1795.

[11] XIAOLIN WANG, JIANJUN YIN, XIAOGONG WANG, *Epoxy-based polymers functionalized with bisazo chromophores: Synthesis, characterization and photoresponsive behavior*, Polymer **52**(15), 2011, pp. 3344–3356.

[12] NIKOLOVA L., NEDELCHEV L., TODOROV T., PETROVA Tz., TOMOVA N., DRAGOSTINOVA V., RAMANUJAM P.S., HVILSTED S., *Self-induced light polarization rotation in azobenzene-containing polymers*, Applied Physics Letters **77**(5), 2000, pp. 657–659.

[13] NEDELCHEV L., NIKOLOVA L., TODOROV T., PETROVA T., TOMOVA N., DRAGOSTINOVA V., RAMANUJAM P.S., HVILSTED S., *Light propagation through photoinduced chiral structures in azobenzene-containing polymers*, Journal of Optics A – Pure and Applied Optics **3**(4), 2001, pp. 304–310.

[14] IFTIME G., LABARTHET F.L., NATANSOHN A., ROCHON P., *Control of chirality of an azobenzene liquid crystalline polymer with circularly polarized light*, Journal of the American Chemical Society **122**(51), 2000, pp. 12646–12650.

[15] YAGER K.G., BARRETT C.J., *Novel photo-switching using azobenzene functional materials*, Journal of Photochemistry and Photobiology A: Chemistry **182**(3), 2006, pp. 250–261.

[16] HAO JIANG, XIU-JUAN PAN, ZHANG-YUAN LEI, GANG ZOU, QI-JIN ZHANG, KE-YI WANG, *Photocontrol of chiroptical properties of polydiacetylene carrying azobenzene in the side chain*, Chemical Physics Letters **500**(1–3), 2010, pp. 100–103.

[17] NIKOLOVA L., TODOROV T., IVANOV M., ANDRUZZI F., HVILSTED S., RAMANUJAM P.S., *Polarization holographic gratings in side-chain azobenzene polyesters with linear and circular photoanisotropy*, Applied Optics **35**(20), 1996, pp. 3835–3840.

[18] Nedelchev L., Todorov T., Nikolova L., Petrova Tz., Tomova N., Dragostinova V., *Characteristics of high-efficient polarization holographic gratings*, Proceedings of SPIE **4397**, 2001, pp. 338–342.

[19] Martinez-Ponce G., Petrova T., Tomova N., Dragostinova V., Todorov T., Nikolova L., *Bifocal-polarization holographic lens*, Optics Letters **29**(9), 2004, pp. 1001–1003.

[20] Ramanujam P.S., Dam-Hansen C., Berg R.H., Hvilsted S., Nikolova L., *Polarisation-sensitive optical elements in azobenzene polyesters and peptides*, Optics and Lasers in Engineering **44**(9), 2006, pp. 912–925.

[21] Kawatsuki N., Kondo M., Okada M., Matsui S., Ono H., Emoto A., *Surface relief formation in photo-cross-linkable polymer/benzophenone composite films using 325 nm laser*, Japanese Journal of Applied Physics **49**, 2010, article 080207.

[22] Hvilsted S., Andruzzi F., Kulinna C., Siesler H.W., Ramanujam P.S., *Novel side-chain liquid crystalline polyester architecture for reversible optical storage*, Macromolecules **28**(7), 1995, pp. 2172–2183.

[23] Rasmussen P.H., Ramanujam P.S., Hvilsted S., Berg R.H., *A remarkably efficient azobenzene peptide for holographic information storage*, Journal of the American Chemical Society **121**(20), 1999, pp. 4738–4743.

[24] Ramanujam P.S., Hvilsted S., Ujhelyi F., Koppa P., Lörincz E., Erdei G., Szarvas G., *Physics and technology of optical storage in polymer thin films*, Synthetic Metals **124**(1), 2001, pp. 145–150.

[25] Nedelchev L., Matharu A.S., Hvilsted S., Ramanujam P.S., *Photoinduced anisotropy in a family of amorphous azobenzene polyesters for optical storage*, Applied Optics **42**(29), 2003, pp. 5918–5927.

[26] Audorff H., Kreger K., Walker R., Haarer D., Kador L., Schmidt H.-W., *Holographic gratings and data storage in azobenzene-containing block copolymers and molecular glasses*, Advances in Polymer Science **228**, 2010, pp. 59–121.

[27] Anderson D.G., Wettermark G., *Photoinduced isomerizations in anils*, Journal of the American Chemical Society **87**(7), 1965, pp. 1433–1438.

[28] Wettermark G., Weinstein J., Sousa J., Dogliotti L., *Kinetics of cis–trans isomerization of para-substituted N-benzylideneanilines*, Journal of Physical Chemistry **69**(5), 1965, pp. 1584–1587.

[29] Haselbach E., Heilbronner E., *Elektronenstruktur und physikalisch-chemische Eigenschaften von Azo-Verbindungen. Teil XIV: Die Konformation des Benzalanilins*, Helvetica Chimica Acta **51**(1), 1968, pp. 16–34.

[30] Warren C.H., Wettermark G., Weiss K., *Cis–trans isomerization about the carbon–nitrogen double bond. Structures of the isomers of N-benzylideneaniline*, Journal of the American Chemical Society **93**(19), 1971, pp. 4658–4663.

[31] Maeda K., Fischer E., *Photoformation of (Z)-isomers in diarylazomethines. Part IV. Direct and sensitized photoisomerization of pyridyl analogues of benzylidene-aniline and absorption spectra of their (Z)-isomers*, Helvetica Chimica Acta **66**(7), 1983, pp. 1961–1965.

[32] King N.R., Whale E.A., Davis F.J., Gilbert A., Mitchell G.R., *Effect of media polarity on the photoisomerization of substituted stilbene, azobenzene and imine chromophores*, Journal of Materials Chemistry **7**(4), 1997, pp. 625–630.

[33] Gaenko A.V., Devarajan A., Gagliardi L., Lindh R., Orlandi G., *Ab initio DFT study of Z–E isomerization pathways of N-benzylideneaniline*, Theoretica Chimica Acta **118**(1), 2007, pp. 271–279.

[34] Ho M.S., Natansohn A., Rochon P., *Azo polymers for reversible optical storage. 7. The effect of the size of the photochromic groups*, Macromolecules **28**(18), 1995, pp. 6124–6127.