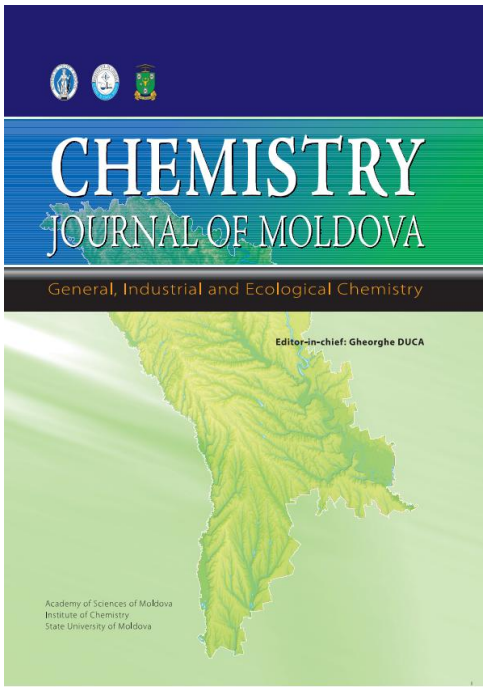

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INFLUENCE OF SOFTENING TEMPERATURE OF AZOBENZENE POLYMERS AND EXTERNAL ELECTRIC FIELD ON DIFFRACTION EFFICIENCY OF POLARIZATION HOLOGRAMS

Nicolay Davidenko[a], Irina Davidenko[a*], Nicolay Kuranda[a], Elena Mokrinskaya[a], Valeriy Pavlov[a], Viacheslav Solntsev[b], Sergey Studzinsky[a], Vladimir Syromyatnikov[a], Vitaliy Tarasenko[a], Nicolay Chuprina[a]

[a]*Kiev Taras Shevchenko National University, 64/13, Volodymyrs'ka Str., Kiev, 01601, Ukraine*
[b]*V. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, 41, pr. Nauki, Kyiv 03028, Ukraine*
**e-mail: IrynaDavydenko@gmail.com; phone: (+38) 044 239 33 90*

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[a]*Kiev Taras Shevchenko National University, 64/13, Volodymyrs'ka Str., Kiev, 01601, Ukraine*
[b]*V. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, 41, pr. Nauki, Kyiv 03028, Ukraine*
**e-mail: IrynaDavydenko@gmail.com; phone: (+38) 044 239 33 90*

Abstract. The growth of the diffraction efficiency and recording velocity were found in the films of the 4-[(2-nitrophenyl)diazenyl]phenyl methacrylate copolymers with octyl methacrylate at room temperature holographic recording with a plane wavefront from parallel and orthogonal orientation of polarization of light beams for copolymer with less softening temperature. The effect of strengthening the diffraction efficiency was observed when charging the surface of investigated copolymers films with the recorded hologram in corona discharge. This effect is explained by growth of amplitude of regular geometric relief of the film surface appearing during formation of the polarization hologram in the copolymer with azobenzene chromophore.

Keywords: azobenzene polymer, optical anisotropy, polarization holography, thermoplastic property, surface relief.

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Introduction

The films of polymeric composites with monomers of azobenzene dyes or containing azobenzene lateral groups chemically bonded to main polymer chain possess photoactive properties. These can be used for electrooptical light modulators and recording media (RM) for polarization holography [1-8]. Photoinduced optical anisotropy appearing in these films under the influence of linearly polarized light is caused by the *trans-cis*-isomerization processes of azobenzene groups. This effect is the determining factor for employing these materials as RM for polarization holography. Azobenzene polymers are unique material platforms, where photoisomerization of azobenzene molecules can involve significant material motion at molecular, mesoscopic and even microscopic length scale. In particular, amorphous azobenzene polymer films can form stable models of surface relief under light influence [1,7]. This feature allows creating periodic micro- and nanostructures of large square by very simple methods. Latterly, one can observe progress in development of azobenzene polymers based on technology of surface relief for photonics applications. Starting from thin layers of azobenzene polymers it is possible to create a lot of photonic elements such as diffraction gratings, plazmon sensors, antireflective coatings and nanostructured converters of solar energy. This phenomenon was investigated in different classes of azobenzene polymers and polymeric matrices such as epoxy, polyacrylate, polyesters and conjugate polymers. Possibilities of formation of the surface relief were studied in the azobenzene polymers both with lateral and main chain. The gratings with high level of surface modulation were obtained. Holograms in these polymers are stable at temperature below the glass transition temperature (T_g). However, in the most azobenzene functional polymers T_g is within 70 – 250 ^oC range. Therefore, RM medium usually is heated [9,10] until the temperature close to T_g before recording the polarization holograms. Surface relief grating (SRG) can be erased optically even below T_g or thermally by heating the samples above T_g.

Since preparation of the RM for holographic recording often includes additional stage of heating of the azobenzene polymer films, the present study is aimed at search for RM with T_g close to room temperature. Besides, we have first investigated the possibilities of SRG strengthening of the azobenzene polymer films

during polarization holograms registration. Similar effect is employed for the surface relief amplification of photoconducting films in photothermoplastic holographic recording technique [11-13].

Experimental

Following the main goal of the present study, copolymers poly[4-((2-nitrophenyl)-diazenyl)phenyl methacrylate-co-octyl methacrylate] CooAzo1 (Figure 1a) and CooAzo2 (Figure 1b) were synthesized. These copolymers were used for the investigation of the value and kinetics of diffraction efficiency of the holograms recorded in the films of azobenzene copolymers with octyl methacrylat and the influence of external electric field on the diffraction efficiency.

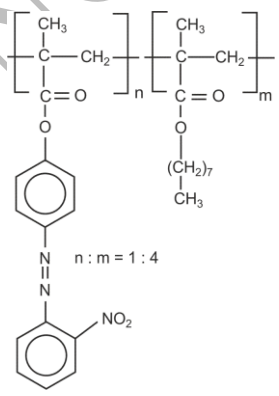
The investigated CooAzo1 and CooAzo2 copolymers were prepared by the radical copolymerization of 4-[(2-nitrophenyl)diazenyl]-phenyl methacrylate with octyl methacrylate in a 10 wt % dried dimethylformamide solution (the relative molar ratio of monomers 4-[(2-nitrophenyl)diazenyl]phenyl methacrylate : octyl methacrylate was 1 : 4 and 1 : 1, respectively), with α,α'-Azoisobutyronitrile (AIB) as a free radical initiator (5 wt % with respect to the comonomers mass) at 80 ^{o}C for more than 60 hours in a thermostat. The obtained copolymers were precipitated in ethanol and purified by reprecipitation from dimethylformamide into ethanol, and then dried at 60 ^{o}C to constant weight.

The softening temperature T_S was measured by known technique [14]: when the solid copolymer sample placed on heated surface starts to adhere to the surface, the temperature was determined. Glass plate with conducting layer SnO_2:In_2O_3 (ITO) was used for the heating. Electric current passing through the ITO layer produces Joule heat which is transferred to the investigated solid copolymer sample. The ITO layer temperature was controlled by the thermocouple. High precision of the temperature measurement is reached by current adjustment in the ITO layer. The T_S value can be determined quite precisely at the moment of the investigated copolymer sample adhesion to the ITO surface. T_S for CooAzo1 and CooAzo2 are 21 ± 1 ^{o}C and 29 ± 1 ^{o}C, respectively.

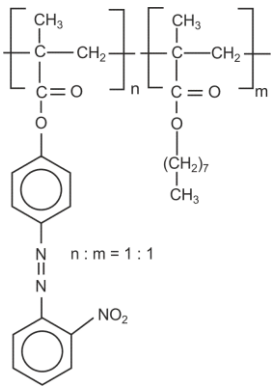
The samples were prepared as usually for similar investigations [12,13] as the structures: (glass substrate) – ITO – (CooAzo1 film) and (glass substrate) – ITO – (CooAzo2 film). The copolymer films were deposited onto the glass substrates with ITO layers by splashing the copolymer solution in methylene chloride. Next, the samples were dried in the heat chamber at +80 ^{o}C during 24 hours. The film thickness was 1.8 – 2.0 μm. It was measured using the interference microscope.

The optical density (D) spectra of prepared samples were registered using spectrophotometer Varian Cary 50 within the light wavelength range λ = 400 ÷ 700 nm. Electric potential (V_p) of the films surface also was measured after charging in corona discharge without illumination and under illumination with laser light λ = 532 nm. After charging in corona discharge value (V_{pmax}) of the potential of the film surface respectively to the ITO layer was +(180 ÷ 200) V which corresponds to the electric field strength inside the film $E_{max} = 1 \cdot 10^8$ V/m.

A specially developed device was used for creation the corona discharge. In the device the corona discharge appears due to application of constant electric voltage ~ 10 kV between the ITO layer and metallic wire above the film surface. The same device usually is employed for the holographic recording by photothermoplastic technique [11-13].



(a)



(b)

Figure 1. Structural formulas of CooAzo1 *(a)* and CooAzo2 *(b)*.

Dynamic probe (Kelvin technique [15]) was used for V_{pmax} and V_p measurements. Ag-plate with diameter 4 mm was the probe sensor. Frequency of the probe vibration was 80 kHz. Kinetics $V_p(t)$ was registered by memory oscilloscope Tektronix TDS1001B. Decay velocity of the film surface potential was estimated from the time interval ($t_{1/2}$) when V_{pmax} 2-fold decreases.

Semiconductor laser with λ = 532 nm was used for recording the holograms of plane wave front with 1 : 1 ratio between the light intensities in object (I_1) and reference (I_2) beams. The spatial frequency was 600 mm^{-1}. The intensity of laser irradiation was $1 \cdot 10^4$ W/m^2. Diffraction efficiency (η) of the hologram of plane wave front was determined usually [16] as the ratio between the light intensity in -1 diffraction order and the reference beam intensity I_2.

Dependencies η on time (t) after start and termination of the hologram exposure were measured. These dependencies were compared for parallel P:P ($\boldsymbol{e}_1 \| \boldsymbol{e}_2$) and perpendicular S:P ($\boldsymbol{e}_1 \perp \boldsymbol{e}_2$) orientations of the polarization vectors of the object ($\boldsymbol{e}_1$) and reference ($\boldsymbol{e}_2$) light waves. Besides, dependency $\eta(E)$ was measured after the hologram recording during the process of its relaxation. Electric field in the copolymer film was formed by corona discharge. Each new measurement was done at new RM area to avoid influence of the previous experiment (memory of holographic recording). All measurements were fulfilled at room temperature.

Results and discussion

Normalized optical density spectra of the samples with CooAzo1 and CooAzo2 films are shown in Figure 2. The spectra of the CooAzo1 and CooAzo2 films are identical within the visible spectral part. This fact testifies the absence of interaction between the chromophores of azobenzene groups when their concentration increases in the investigated oligomers. The investigated samples possess observable electrical conductivity and small photoconductivity. These features reveal themselves in quite quick decay of the surface potential of CooAzo1 and CooAzo2 films after their charging in corona discharge ($t_{1/2}$ = 30 ± 2 s) and in insignificantly small change $t_{1/2}$ during illumination with light.

The holograms for $\boldsymbol{e}_1 \| \boldsymbol{e}_2$ and $\boldsymbol{e}_1 \perp \boldsymbol{e}_2$ cases were registered in the investigated samples with CooAzo1 and CooAzo2 films. The influence of external electric field on η was observed. The dependencies $\eta(t)$ for the $\boldsymbol{e}_1 \perp \boldsymbol{e}_2$ case in the recording process, during η relaxation after the object beam was ceased, after switching on the corona discharge and after its ceasing are shown in Figure 3.

The velocity of the holographic recording of plane wave front and the value η are larger in RM with the CooAzo1 films as compared to CooAzo2 due to lower T_S value and better plastic properties of the CooAzo1 copolymer.

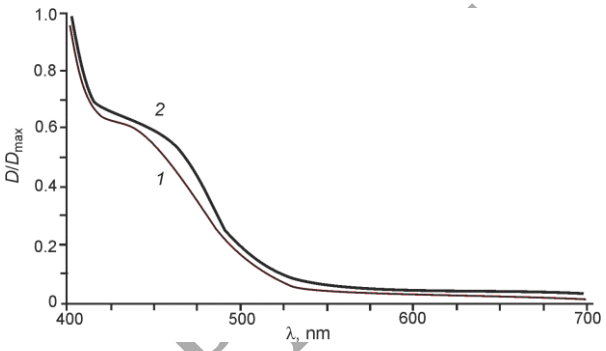


Figure 2. Normalized optical density spectra of RM with CooAzo1 (*1*) and CooAzo2 (*2*) films.

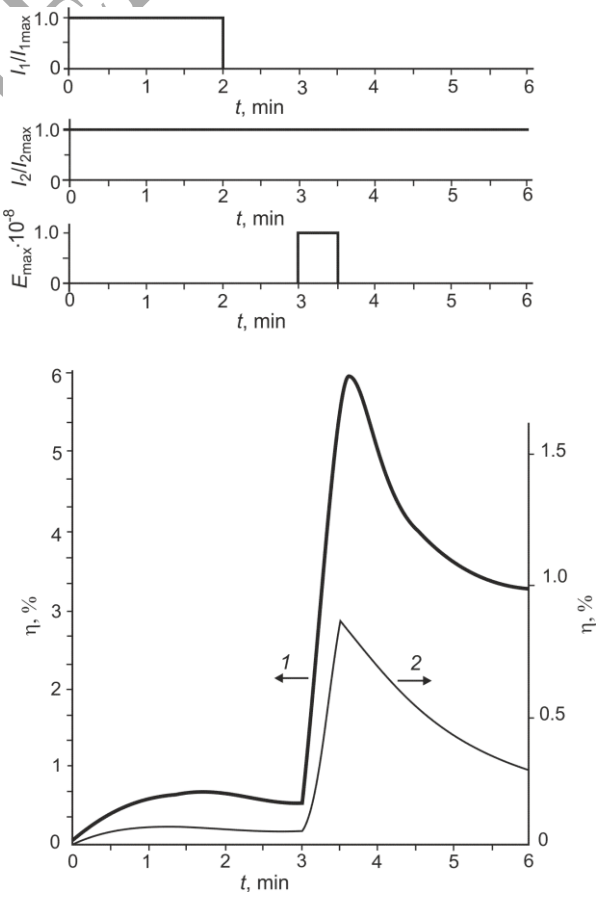


Figure 3. Diagrams of dependencies $I_1(t)$, $I_2(t)$, $E(t)$ and $\eta(t)$ in RM with CooAzo1 (*1*) and CooAzo2 (*2*) films for the $e_1 \perp e_2$ case of holographic recording of plane wave front.

The same peculiarity was observed in the holographic recording for the $\boldsymbol{e}_1 \| \boldsymbol{e}_2$ case, but the relaxation velocity of the hologram after ceasing the object beam slows down as compared to $\boldsymbol{e}_1 \perp \boldsymbol{e}_2$. This feature is attributed to formation of the latent holographic image by polarization modulation in the first case and by the modulation of intensity of interfering beams in the second case. The second case ($\boldsymbol{e}_1 \perp \boldsymbol{e}_2$) provides better conditions for the geometric relief of the RM surface formation.

Significant η growth (many times more) (Figure 3) appears in external electric field. The value and velocity of η growth in the samples with CooAzo1 exceed those in the samples with CooAzo2. The same peculiarity was observed in holographic recording for the $\boldsymbol{e}_1 \| \boldsymbol{e}_2$ case. During long influence of corona discharge η can reach 6%, it slowly relaxes after the corona discharge is ceased, but the reconstructed image becomes noisy.

Tendencies of η changes are illustrated by photos of the screen (Figure 4) where the images of the reconstructed holograms of plane wave front are projected: (a) – two-beams recording after exposure during 2 min without influence of the corona discharge; (b) – one-beam illumination after exposure during 2 min without influence of the corona discharge, following ceasing of the object beam and charging of the film surface in the corona discharge during 30 s; (c) – two-beams recording after exposure during 2 min without influence of the corona discharge, following ceasing of the object beam and charging of the film surface in the corona discharge during 10 min. RM with the CooAzo1 film was used. These photos show that as a result of corona discharge influence, brightness of diffraction orders increases. Extinction of the diffraction orders when polarization of reconstructing beam changes from the condition $\boldsymbol{e}_1 \perp \boldsymbol{e}_2$ to the condition $\boldsymbol{e}_1 \| \boldsymbol{e}_2$ indicates polarization nature of the recorded holograms.

One can conclude that photoconducting properties of CooAzo1 and CooAzo2 films do not have decisive influence on the latent hologram image formation because photoconductivity of the films is small. *Trans-cis*-isomerization of azobenzene fragments happens under influence of linearly polarized light with wavelength from the absorption range of azobenzene chromophores isomers. The difference between the relaxation times of the recorded holograms for the $\boldsymbol{e}_1 \| \boldsymbol{e}_2$ and $\boldsymbol{e}_1 \perp \boldsymbol{e}_2$ cases can be explained by different structural rearrangement of the polymeric matrix in the process of intensive *trans-cis*-isomerization of lateral azobenzene groups. It is considered [1-3,6,7] that namely rearrangement of the polymeric matrix is responsible for long-term conservation of the recorded holograms. In both cases $\boldsymbol{e}_1 \| \boldsymbol{e}_2$ and $\boldsymbol{e}_1 \perp \boldsymbol{e}_2$ the azobenzene groups involved into isomerization reorient toward the corresponding directions and additional deforming forces arrear. These forces act on the main polymeric chain resulting in formation of the geometric relief.

Photos presented in Figure 5 show the areas of the free surface of RM with the CooAzo1 film after recording the hologram of plane wave front for the $\boldsymbol{e}_1 \perp \boldsymbol{e}_2$ case during 2 min and following charging of the RM surface in corona discharge during 30 s (a, b) and 10 min (c) which corresponds to the photo in Figure 3c.

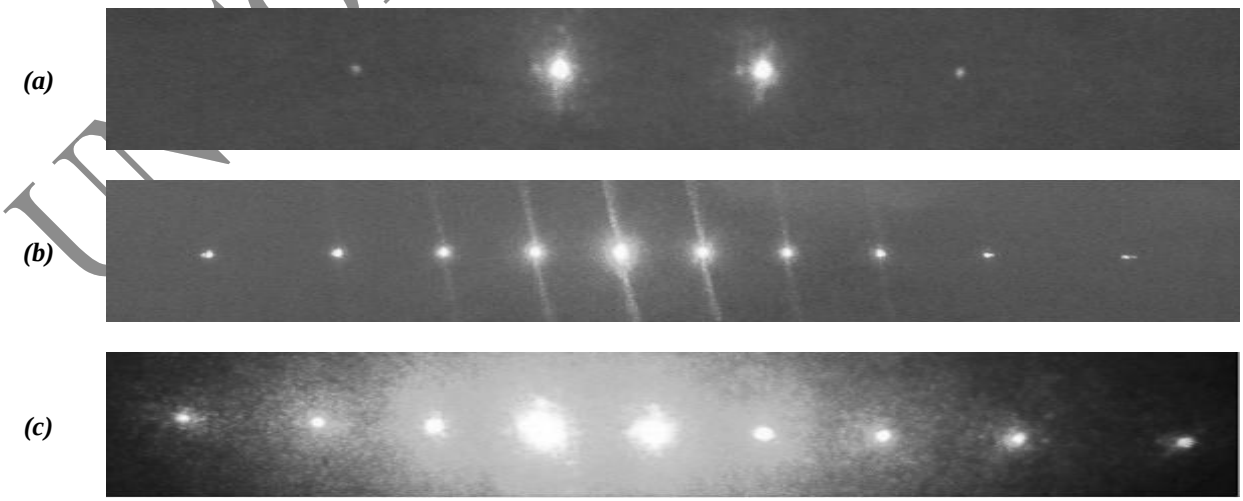


Figure 4. Photos of the screen with projected reconstructed image of the hologram of plane wave front recorded in RM with CooAzo1 for $\boldsymbol{e}_1 \perp \boldsymbol{e}_2$ after exposure during 2 min *(a)*, after ceasing the object beam and charging of the RM surface in corona discharge during 30 s *(b)* and 10 min *(c)*.

The photos were made in usual (a, c) and interference microscope modes. In these photos, modulation of the surface geometric relief is about 0.2 μm providing high diffraction efficiency of the RM after charging of its surface in corona discharge during 30 s. Vanishing of the surface relief occurs slower than relaxation of the latent holographic image in polarization sensitive RM. That is why existence of such relief causes increasing the relaxation time of the diffraction efficiency as a whole.

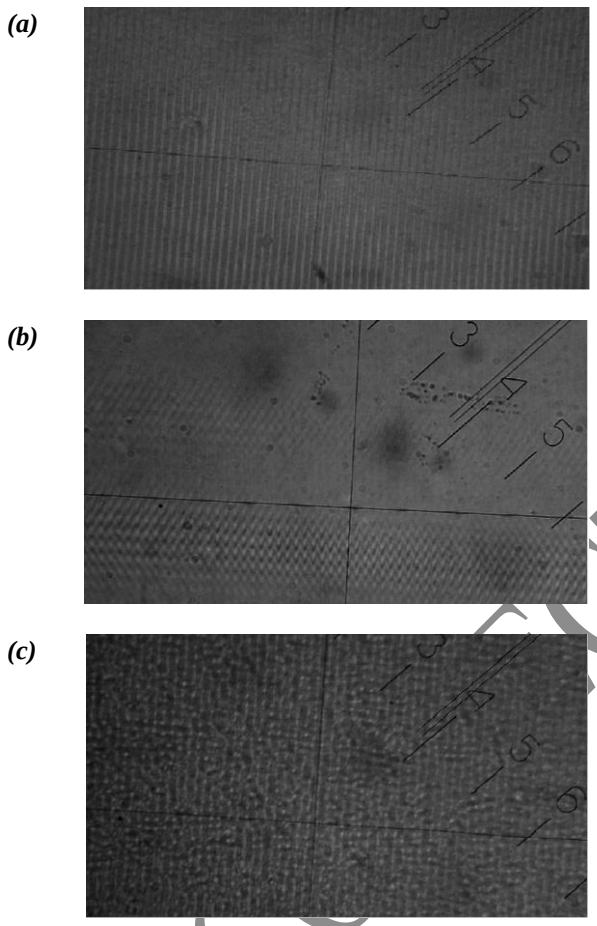


Figure 5. Photos of surface area of RM with the CooAzo1 film after recording the hologram of plane wave front for $e_1 \perp e_2$ during 2 min and following charge of RM surface in corona discharge during 30 s *(a, b)* and 10 min. The photos were done by interference microscope usual mode *(a, c)* and interference mode *(b)*.

The depth of the surface relief modulation can be increased by application of the corona discharge similarly to the holographic recording by photothermoplastic technique [11-13]. Ions deposited onto the film surface in the corona discharge form an electric field in the film volume with force lines directed from the free film surface to the ITO layer. The polymeric film thickness is different in maximums and minimums of the surface relief. That results in different values of the electric field strength in these film areas. The field strength is larger in minimums of the film thickness as compared to maximums. Aggregate state of the film is close to viscous fluid when the temperature is close to T_S. Thus, Coulomb forces of attraction between ions on the film surface and ITO layer enhance the difference of the film thickness at the areas with maximums and minimums of the surface relief. This mechanism is responsible for η growth in the investigated RM in corona discharge. The same mechanism is the reason of noise occurrence in the holographic image after long effect of the corona discharge (Figure 4c). The effect is attributed to appearance of chaotic "frosty" deformation of the film surface with low T_S which is charged in corona discharge [17]. In this case, the film surface is deformed not only by regular relief formed during recording the hologram of plane wave front but also by chaotic holes (Figure 5c).

Conclusions

Developed RM based on copolymers CooAzo1 and CooAzo2 can be used for polarization holography at room temperature due to quite low T_S value. Conditions for the surface relief formation are more favourable in RM with the CooAzo1 films because of the lower T_S value. But, in this case it increases the risk of reducing the time for long-term conservation of the holograms due to possibility of vanishing the surface relief under environmental temperature changes. Investigations of influence of the corona discharge on the diffraction efficiency in RM with CooAzo1 and CooAzo2 films result in detection of the effect of η growth caused by strengthening of the surface relief modulation.

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