Semiconductor Physics, Quantum Electronics & Optoelectronics, 2020. V. 23, No 3. P. 323-328.

Polarization holography in azobenzene polymeric films prepared using the new chemical method

N.A. Davidenko[1], **I.I. Davidenko**[1], **V.V. Kravchenko**[2], **V.A. Pavlov**[1], **V.V. Tarasenko**[1], **N.G. Chuprina**[1]

[1]*Taras Shevchenko Kyiv National University, 01601 Kyiv, Ukraine*
[2]*Institute of Physical Organic Chemistry and Coal Chemistry, 02160 Kyiv, Ukraine*
E-mail: IrynaDavydenko@gmail.com

Abstract The recording media for polarization holography based on azobenzene polymers are obtained by polymer-analogous transformations of polymethacrylic acid and its copolymers with alkyl methacrylates. Their informational properties were investigated when recording holograms of a plane wavefront. It has been found that the recording and relaxation times of holograms are approximately the same. They are defined mainly by the processes of trans-cis-isomerization of azobenzene groups without formation of surface relief of the polymeric film. The efficiency of the trans-cis-isomerization process decreases, if a heavy substituent is present in the azobenzene chromophore. These results are of practical interest in the choice of photosensitive materials for holographic recording media with optimal information characteristics.

Keywords: polarization holography, photophysical properties, isomerization, recording material, azobenzene.

https://doi.org/10.15407/spqeo23.03.323
PACS 42.40.Ht, 42.40.-i, 42.70.Ln, Lw

Manuscript received 13.05.20; revised version received 03.07.20; accepted for publication 10.09.20;

1. Introduction

Films of polymeric composites with monomers of azobenzene dyes or polymers containing azobenzene groups exhibit photoactive properties. They can be used for creation of electro-optical light modulators and recording media (RM) for polarization holography [1-5]. The principle of recording in these media is based on photoinduced optical anisotropy (PIA) that appears in these films under illumination with linearly polarized light from the absorption range of *trans*-isomers. It is attributed to the processes of *trans-cis*-isomerization of azobenzene groups. The photoisomerization reaction of azobenzene chromophores can cause conformational changes at the molecular level. In amorphous films, stable surface reliefs can be formed [5–16]. On the base of polymeric thin layers with azobenzene groups, one can develop many photonic elements, namely: diffraction gratings, arrays of microlenses, plasmon sensors, anti-reflection coatings, and nanostructured light polarization converters [1]. Holograms in these polymers are stable when stored below the softening temperature (T_s). The surface reliefs of RM can be erased by heating the samples above T_s. In this case, the polymeric film transfers into a viscous-fluid state and this relief is "healed". Up to date, there are a large number of azobenzene polymers and composites on their base, which find practical application in RM.

When creating materials for polarization-sensitive RM based on photoactive polymeric systems, the main methods for introducing the azobenzene fragments into the side chain of a macromolecule are radical (co)polymerization and polycondensation of the corresponding azobenzene monomers [7]. As an alternative to these methods, there are polymer-analogous transformations of polymers related to various classes of molecules containing free functional groups in the side chain. These transformations occurring with participation of reaction-capable azobenzene compounds are based on the use of many reactions. And among them, the Schotten–Baumann reaction (as one of the acylation variants); condensation, for example, between –OH, –COOH, $–NH_2$ groups of the azobenzene compound and the polymer; a combination of aryldiazonium salts with polymeric aromatic compounds (or a combination of polymeric aryldiazonium salts with aromatic compounds). In this approach, polymerization is not inhibited by functional groups located in the azobenzene chromophore. These concern the –N=N– and $–NO_2$ groups that are "traps" for free radicals during polymerization [17]. So, azobenzene-containing (co)polymers can be obtained by modifycation, in particular, with polyacryl chloride [18, 19], poly(meth)acrylic acid [17, 20], poly(2-(phenylethyl-amino)ethylacrylate) [21], poly(benzolisocyanate) [22], polyethyleneimine [23], epoxy polymers [24, 25], as well as “living” (co)polymers containing, for example, blocks of poly(2-hydroxyethylmethacrylate) [13, 26], isoprene [27, 28], butadiene [29, 30].

However, in the literature, the question of optimizing the methods for choosing photosensitive macromolecular structures suitable for creation of RM has not been sufficiently studied. This work is aimed at experimental studying the kinetics of recording and relaxation of holograms of a plane wavefront in RM based on various azobenzene polymers. They were obtained using the method of polymer-analogous transformations of polymeric matrices with recording beams of parallel and perpendicular polarizations.

2. Experimental

For investigations, copolymers **1**–**9** were synthesized. The structural formulas of these compounds have the general form shown in Fig. 1. Polymethacrylic acid (PMAA, samples **1**, **4**, **7**) were chosen as polymer matrices for photoactive azobenzene chromophores covalently bound with the side polymer chain and its 3:1 copolymers with methyl methacrylate (MAA-co-MMA, samples **2**, **5**, **8**) and butylmethacrylate (MAA-co-BMA, samples **3**, **6**, **9**) prepared using radical polymerization in the presence of AIBN.

Introduction of azobenzene fragments into the composition of polymer matrices led to condensation of the functional carboxyl groups of methacrylic acid that is part of all matrices with the corresponding 4-hydroxyazo compounds. N,N’-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino) pyridine (DMAP) in dry DMF were used as catalysts at room temperature.

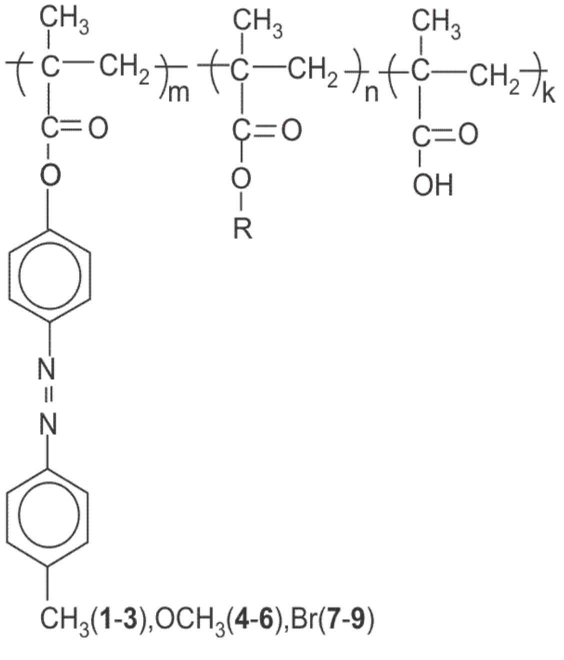

Fig. 1. Structural formulas of copolymers **1**–**3**, **4**–**6**, **7**–**9**.

The composition of copolymers is detailed in Table. The composition and structure of the synthesized compounds were identified by elemental analysis, ^{1}H NMR- and UV-spectroscopy. Elemental analysis of the obtained compounds was carried out on the CHNOS-elemental analyzer Elementar Gmbh “Vario Micro Cube”. ^{1}H NMR-spectra of the obtained compounds were recorded using the ^{1}H NMR-spectrometer Varian “Mercury 400” in DMSO-d$_6$ with the internal standard tetramethylsilane. A series of comonomers was chosen, since in their model range **1**–**3**, **4**–**6**, **7**–**9** the dipole moment of the azobenzene chromophore also increases. The softening temperature of polymeric films (PF) **1**–**9** is $T_s \geq 150$ °C. This temperature was measured using the known method [31].

For investigations, RM samples were prepared using a free surface glass substrate – PF. PF were prepared by watering with the solution of copolymer in methylene chloride deposited onto glass substrates and following drying for 24 hours in an oven at the temperature close to 80 °C. The thickness of PF was 2-3 μm. It was measured using the interference microscope. In the RM samples with a free PF surface, the spectra of optical density (D) and photoluminescence intensity (I_L) were measured. The same RM samples were also used to record holograms of a plane wavefront. A solid-state laser with diode pumping and frequency doubling with $\lambda = 532$ nm was used. The ratio of light intensities in the object (I_1) and reference (I_2) beams was 1:1, and the spatial frequency was 300 mm^{-1}. The light intensity $I_1 + I_2$ at the PM surface was $5 \cdot 10^3$ W/m^2. Holograms were recorded for parallel ($\boldsymbol{e}_1 \parallel \boldsymbol{e}_2$) and perpendicular ($\boldsymbol{e}_1 \perp \boldsymbol{e}_2$) orientations inherent to the electric vectors of the incident onto the object ($\boldsymbol{e}_1$) and reference ($\boldsymbol{e}_2$) light waves. The diffraction efficiency (η) of the hologram was determined according to the commonly accepted method [32] as the ratio of the light intensity in the –1st diffraction order to the intensity of the reference beam I_2 (it is also the recovery beam during reading) for parallel ($\boldsymbol{e}_1 \parallel \boldsymbol{e}_2$) and perpendicular ($\boldsymbol{e}_1 \perp \boldsymbol{e}_2$) orientations of the electric vectors of the recording light waves (designated as $\eta_{||}$ and $\eta_{\perp}$, respectively). The dependences $\eta_{||}(t)$ and $\eta_{\perp}(t)$ on time (t) were measured after the beginning and completion of exposing the hologram.

After reaching the maximum diffraction efficiency ($\eta_{||\max}$ and $\eta_{\perp\max}$, respectively), relaxation of the holographic image was monitored in two ways: 1) only the object beam was switched off ($I_1 = 0$) and the light intensity was continuously measured in the –1 diffraction order with the reading beam turned on; 2) both recording beams were switched off ($I_1 = 0$, $I_2 = 0$) and periodically (for a short time approximately 1 s) the reading beam was turned on to measure the light intensity in the –1 diffraction order. Each new measurement was carried out on a new RM area to exclude the influence of the previous experiment (memory of holographic recording). The measurement results were averaged over 3 samples of identical RM. All these measurements were carried out at room temperature close to 20 °C.

3. Results and discussion

Fig. 2 shows the normalized spectrum of the optical density of PF **1**–**9**. Within the visible region, the absorption of these PF was determined using the long-wave absorption edge of the azobenzene chromophores. Therefore, the spectra of PF groups **1**–**3**, **4**–**6**, **7**–**9** practically coincide. An insignificant bathochromic shift in this series of PF groups is related with the presence of substitutes with different electron donorship in the azobenzene fragment (Fig. 1). Photoluminescence of the same samples was not detected upon excitation by the laser with $\lambda = 32$ nm and $I_L = 0$.

Holograms of a plane wavefront were recorded in RM with PF **1**–**9** for the cases $\boldsymbol{e}_1 \parallel \boldsymbol{e}_2$ and $\boldsymbol{e}_1 \perp \boldsymbol{e}_2$. The main results of measuring $\eta_{\parallel\max}$ and $\eta_{\perp\max}$ as well as the kinetics of recording and relaxation of holograms of a plane wavefront are presented in Table and Fig. 3. It turned out that inside groups, these main results are similar but differ for different groups. For example, Fig. 3 shows the graphs of the dependences $\eta_{\parallel}(t)$ and $\eta_{\perp}(t)$ in the samples of RM with PF **1**, **4**, **7**.

From the presented results, it is seen that in the series of RM with PF **1**–**3**, **4**–**6**, **7**–**9** $\eta_{\perp\max} > \eta_{\parallel\max}$. This phenomenon was previously observed in RM based on other azobenzene-containing copolymers and metal complexes based on them [4, 5, 14-16]. The values of $\eta_{\perp\max}$ and $\eta_{\parallel\max}$ and the time of recording and relaxation of holograms decrease with transferring from groups **1**–**3**, **4**–**6** to the group PF **7**–**9**. This difference cannot be explained only by a change in the optical properties of azobenzene chromophores, because at the wavelength of used laser $\lambda = 532$ nm, the light absorption is the same and even slightly increases upon transition to the PF group **7**–**9** (Fig. 2).

Table. The composition of copolymers **1**–**9** and the measurement results of $\eta_{\parallel\max}$ and $\eta_{\perp\max}$ in RM with PF **1**–**9** immediately after exposure for 2 min.

Copolymer	Composition	$\eta_{\parallel\max}$, %	$\eta_{\perp\max}$, %
1	R = –H, n = k, m:k = 1:2	$9\cdot10^{-3}$	$2.6\cdot10^{-2}$
2	R = $-CH_3$, m:n:k = 1.08:1:1.92	$1\cdot10^{-2}$	$3.5\cdot10^{-2}$
3	R = $-C_4H_9$, m:n:k = 1.06:1:1.94	$6\cdot10^{-3}$	$2.4\cdot10^{-2}$
4	R = –H, n = k, m:k = 1:2	$2.2\cdot10^{-2}$	$3.2\cdot10^{-2}$
5	R = $-CH_3$, m:n:k = 1.46:1:1.54	$3\cdot10^{-2}$	$3.3\cdot10^{-2}$
6	R = $-C_4H_9$, m:n:k = 0.73:1:2.27	$1.1\cdot10^{-2}$	$1.2\cdot10^{-2}$
7	R = –H, n = k, m:k = 1:2	$2\cdot10^{-4}$	$7\cdot10^{-4}$
8	R = $-CH_3$, m:n:k = 0.53:1:2.47	$6\cdot10^{-4}$	$3\cdot10^{-3}$
9	R = $-C_4H_9$, m:n:k = 1.48:1:1.52	$7\cdot10^{-4}$	$3\cdot10^{-3}$

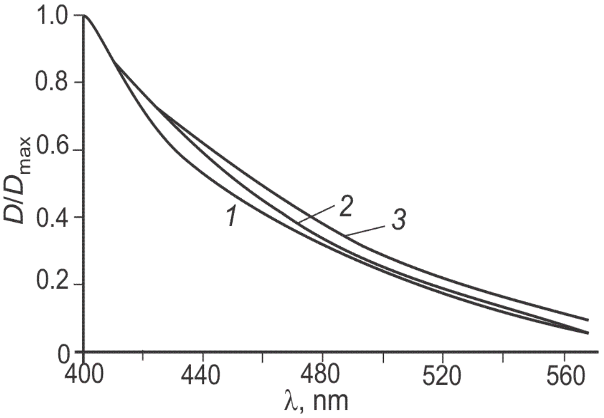

Fig. 2. Normalized spectra of the optical density of RM with PF **1**–**3** (*1*), **4**–**6** (*2*), **7**–**9** (*3*).

The peculiarity of the dependences $\eta_{\parallel}(t)$ and $\eta_{\perp}(t)$ is the presence of at least two kinetics sections: fast and slow. After the start of exposure of the hologram, the values $\eta_{\parallel}(t)$ and $\eta_{\perp}(t)$ rapidly increase, and then this increase slows down. The same regularity is observed after turning off one of the recording beams. However, the storage time of the hologram increases, if both recording beams are turned off after recording (curves *2* in Fig. 3). The latter indicates that one of the recording beams (used to restore the hologram after recording it) is an eraser of this record. This is confirmed by curves *3* in Fig. 3. Thus, $\eta_{\parallel}(t)$ and $\eta_{\perp}(t)$ decrease rapidly when the reading beam is turned on after recording and storing the hologram in the dark.

It is known [6–8, 14–16] that at T_s close to room temperature, the main mechanism for recording polarization holograms with a long relaxation (storage) time is the *trans*-*cis*-isomerization of azobenzene fragments. It occurs under action of linearly polarized light from the absorption range of the isomers of the azobenzene chromophore. In this case, the polymeric matrix is rearranged. It is this rearrangement of the polymeric matrix that is responsible for the long-term storage of holographic records.

For $\boldsymbol{e}_1 \parallel \boldsymbol{e}_2$ and $\boldsymbol{e}_1 \perp \boldsymbol{e}_2$, the azobenzene groups participating in photoisomerization are oriented in the corresponding directions. Additional deforming forces appear, effecting the main polymer chain. It results in formation of a geometric relief on the surface of PF as RM.

“Healing” the film surface relief occurs more slowly than relaxation of a latent holographic image in polarization-sensitive RM. Therefore, the presence of this relief generally increases the relaxation time of η. Similar structures on the PF surface are formed when recording relief amplitude holograms by using the photo-thermoplastic method on photoconductive polymeric films [33, 34]. The homogeneity of these structures ensures high information characteristics of RM and long-term storage of the holographic record.

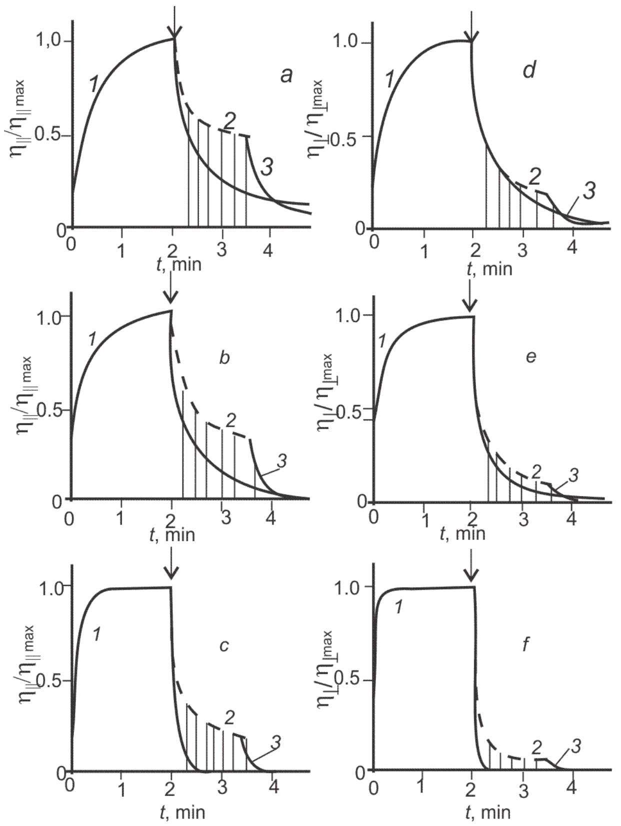

Fig. 3. Dependences $\eta_{||}$ (*a–c*) and $\eta_{\perp}$ (*d–f*) on t in RM samples with PF **1** (*a*, *d*), **4** (*b*, *e*), **7** (*c*, *f*): curves *1* (solid lines) after the start of recording the hologram ($t = 0$) and turning off the object beam at the time moment $t = 2$ min (when the object beam is switched off, it is marked by the vertical arrow pointing down); curves *2* (dashed lines) – after exposure of the hologram for a period of the time $t = 2$ min, turning off the recording beams at the time $t = 2$ min and subsequent short-term switching on the reading beam; curves *3* – after exposure of the hologram for the time $t = 2$ min, switching off the recording beams at the time $t = 2$ min and turning on the reading beam after 1.5 min.

In the case of RM with PF **1**–**9**, $T_s \geq 150$ °C. It may be the main reason for the short storage time of holograms (Fig. 3). In these PF, there is no radiative dissipation of the photoexcitation energy of azobenzene chromophores ($I_L = 0$). Therefore, during the exposure of the hologram, the absorbed light energy is spent on the *trans-cis*-isomerization of azobenzene fragments. The rest of absorbed energy is not sufficient for rearrangement of polymeric chains. Therefore, it is difficult to form a stable surface relief of PF. Besides, if after hologram registration instead of 2 recording beams, only one reference beam ($\boldsymbol{e}_2$) of the light wave (it is reading) remains, then photoinduced anisotropy (PIA) in PF can be leveled. This is caused by the equalization of the concentration of *cis*-isomers over the illuminated PF area. Then, in the case of preliminary recording with parallel ($\boldsymbol{e}_1 \parallel \boldsymbol{e}_2$) orientation of the electric vectors of light waves, “healing” of the PF relief is possible.

Previously formed periodic structures in PF disappear faster than this disappearance occurs naturally. This fact explains the delayed relaxation of holograms when all recording beams are turned off as compared with the case of using a single reading beam (curves *1* and *2* in Fig. 3). Thus, the fast and symmetric nature of the kinetics of recording and relaxation of holograms can be explained by the purely polarization nature of PIA creation. A small contribution is made by formation of the surface relief in PF due to mechanical rearrangement of molecular chains. The latter also explains the experimental result that for RM with PF **7**–**9** the values $\eta_{\perp\max}$ and $\eta_{||\max}$ as well as the recording and relaxation times of holograms are shorter than the same parameters for PF groups **1**–**3** and **4**–**6** (Table, Fig. 3).

Trans-cis-isomerization and rearrangement of polymer chains are caused by the mechanical movements of individual parts of the molecules. Therefore, the heavy substitute Br atom in the azobenzene chromophores of molecules **7**–**9** significantly complicates these processes.

But if we accept the same relaxation mechanism for the relief of PF to explain $\eta_{\perp}$ relaxation in the case of preliminary recording at the perpendicular ($\boldsymbol{e}_1 \perp \boldsymbol{e}_2$) orientation of the electric vectors of light waves, then we should expect the same speed, but not less (Fig. 3). To explain the observed kinetics of relaxation of the interference fields forming holograms with different polarization of the recording laser beams and the orientation distributions of the azobenzene groups created by these fields, one also cannot use the mechanisms accepted for RM based on polymethylmethacrylate films. They contain phenanthrenequinone molecules as a photosensitive additive [35–37]. The principle of recording in these RM is based on the ability of phenanthrenquinone to form a photoproduct attached to the macromolecules of the polymeric matrix.

Therefore, its mobility is extremely low. It is considered that due to the difference in the mobility of phenanthrenquinone and its photoproduct, post-exposure enhancement of holograms is realized. It is caused by the diffusion of phenanthrenquinone molecules. It provides time-efficient highly effective phase holograms. In this case, the phototransformations of phenanthrenquinone into PF lead to a change in the absorption spectrum of RM, and they become almost transparent within the visible range of the spectrum [37].

In our RM, the PIA formation mechanism has a completely different nature. Therefore, we are forced to admit that up to now one has no adequate explanation of the observed experimental facts concerning the difference in the relaxation mechanism for $\eta_{||}$ and $\eta_{\perp}$. Also, from a comparison of the values of $\eta_{\perp\max}$ and $\eta_{||\max}$ in Table, we see that the ratio of $\eta_{\perp\max}$ and $\eta_{||\max}$ is slightly affected by the composition of the components of PF providing the elastic properties of these PF.

4. Conclusion

The results of experimental investigations with new azobenzene-containing copolymers **1**–**9** confirm the previously observed regularity $\eta_{\perp} > \eta_{||}$ inherent to RM. This fact allows us to conclude that the ascertained feature is typical for a wide range of RM with films of azobenzene compounds. For the studied series of copolymers, the diffraction efficiency of holograms decreases in RM with PF **7**–**9** as compared with **1**–**3** and **4**–**6** due to the presence of a heavy substitute (Br atom) in the azobenzene chromophore. It complicates the *trans-cis*-isomerization of azobenzene fragments in the rigid polymer matrix of polymer-analogous copolymers. These results are of practical interest in the development and creation of new recording media for polarization holography and especially for dynamic polarization holography.

References

1. Barachevsky V.A. Current status of develoment of light-sensitive media for holography (a review). *Optics and Spectroscopy*. 2018. **124**. P. 373–407. https://doi.org/10.1134/S0030400X18030062.
2. Nikolova L., Ramanujam P.S. *Polarization Holography*. Cambridge, UK, Cambridge University Press, 2009.
3. Bian S., Williams J.M., Kim D.Yu. *et al.* Photoinduced surface deformations on azobenzene polymer films. *J. Appl. Phys*. 1999. **86**. P. 4498–4502. https://doi.org/10.1063/1.371393.
4. Davidenko N.A., Savchenko I.A., Davidenko I.I. *et al.* Hologram recording and electrooptic effect in azobenzene derivative polymers and azobenzene-cobalt polycomplexes. *Techn. Phys*. 2007. **52**. P. 451–455. https://doi.org/10.1134/S1063784207040093.
5. Davidenko N.A., Davidenko I.I., Pavlov V.A. *et al.* Adjustment of diffraction efficiency of polarization holograms in azobenzene polymer films using electric fields. *J. Appl. Phys*. 2017. **122**. P. 013101-1–6. https://doi.org/10.1063/1.4990995.
6. Priimagi A., Shevchenko A.J. Azopolymer-based micro- and nanopatterning for photonic applications. *Polymer Sci. Part B*: *Polymer Phys*. 2014. **52**. P. 163–182. https://doi.org/10.1002/polb.23390.
7. Natansohn A., Rochon P. Photoinduced motion in azo-containing polymers. *Chem. Rev*. 2002. **102**. P. 4139–4175. https://doi.org/10.1021/cr970155y.
8. Simonov A.N., Uraev D.V., Kostromin S.G. *et al.* Polarization-controlled optical recording in azocontaining amorphous polymer films. *Laser Physics*. 2002. **12**. P. 1294–1302.
9. Emoto A., Uchida E., Fukuda T. Optical and physical applications of photocotrollable materials: azobenzene-containing and liquid crystalline polymers. *Polymers*. 2012. **4**. P. 150–186. https://doi.org/10.3390/polym4010150.
10. Karageorgiev P., Neher D., Schulz B. *et al.* From anisotropic photo-fluidity towards nanomanipulation in the optical near-field. *Nature Materials*. 2005. **4**, No 9. P. 699–703. https://doi.org/10.1038/nmat1459.
11. Garrot D., Lassailly Y., Lahlil K. *et al.* Real-time near-field imaging of photoinduced material motion in thin solid films containing azobenzene derivatives. *Appl. Phys. Lett.* 2009. **94**. P. 033303-1–3. https://doi.org/10.1063/1.3073742.
12. Zhou J., Yang J., Ke Y., Shen J., Zhang Q., Wang K. Fabrication of polarization grating and surface relief grating in crosslinked and non-crosslinking azopolymer by polarization holography method. *Optical Materials*. 2008. **30.** P. 1787–1895. https://doi.org/10.1016/j.optmat.2007.08.011.
13. Häckel M., Kador L., Kropp D., Schmidt H.-W. Polymer blends in azobenzene-containing block copolymers in stable rewritable holographic media. *Adv. Mater*. 2007. **19**. P. 227–231. https://doi.org/10.1002/adma.200601458.
14. Davidenko N.A., Davidenko I.I., Pavlov V.A. *et al.* Recording media for polarization holography with diffraction efficiency adjusted using electric field. *Optik – Intern. Journal for Light and Electron Optics*. 2018. **158**. P. 1308–1312. https://doi.org/10.1016/j.ijleo.2018.01.018.
15. Davidenko N.A., Davidenko I.I., Pavlov V.A. *et al.* Recording medium based on the azobenzene copolymer with free surface and in sandwich-structure for polarization holography. *Optical Materials.* 2018. **76**. P. 169–173. https://doi.org/10.1016/j.optmat.2017.12.027.
16. Davidenko N.A., Davidenko I.I., Pavlov V.A., Tarasenko V.V. Experimental investigations of the relaxation of polarization holograms in films of azobenzene polymers with chromophores with different substitutes. *Optik*. 2018. **165**. P. 174–178. https://doi.org/10.1016/j.ijleo.2018.03.117.
17. Ushiwata T., Okamoto E., Kaino T. Development of thermally stable novel EO-polymers. *Mol. Cryst. Liquid Cryst.* 2002. **374**. P. 303–314. https://doi.org/10.1080/10587250210421.
18. Wu L., Tuo X., Cheng H., Chen Z., Wang X. Synthesis, photoresponsive behavior, and self-assembly of poly(acrylic acid)-based azo polyelectrolytes. *Macromolecules.* 2001. **34.** P. 8005–8013. https://doi.org/10.1021/ma002215z.
19. Kang E.-H., Liu X., Sun J., Shen J. Robust ion-permselective multilayer films prepared by photolysis of polyelectrolyte multilayers containing photo-cross-linkable and photolabile groups. *Langmuir*. 2006. **22**. P. 7894–7901. https://doi.org/10.1021/la0612320.
20. Viswanathan N.K., Balasubramanian S., Li L. *et al.* Surface-initiated mechanism for the formation of relief gratings on azo-polymer films. *J. Phys. Chem. Part B.* 1998. **102**. P. 6064–6070. https://doi.org/10.1021/jp981425z.

21. He Y., Wang H., Tuo X., Deng W., Wang X. Synthesis, self-assembly and photoinduced surface-relief gratings of a polyacrylate-based azo polyelectrolyte. *Opt. Mater*. 2004. **26**. P. 89–93. https://doi.org/10.1016/j.optmat.2004.01.014.
22. Goldenberg L.M., Kulikovsky L., Kulikovska O., Stumpe J. New materials with detachable azo-benzene: effective, colourless and extremely stable surface relief gratings. *J. Mater. Chem*. 2009. **19**. P. 8068–8071. https://doi.org/10.1039/B918130J.
23. Kamruzzaman M., Ogata T., Kuwahara Y., Ujiie S., Kurihara S. Thermal and photo alignment behavior of polymers in multiply-layered films composed of polyethylene imines having azobenzene side chain groups and polyvinyl alcohol. *Mol. Cryst. Liquid Cryst.* 2010. **529.** P. 32–41. https://doi.org/10.1080/15421406.2010.495688.
24. Wang X., Chen J.-I., Marturunkakul S., Li L., Kumar J., Tripathy S.K. Epoxy-based nonlinear optical polymers functionalized with tricyanovinyl chromophores. *Chem. Mater*. 1997. **9**. P. 45–50. https://doi.org/10.1021/cm950560a.
25. Wang X., Kumar J., Tripathy S.K. *et al.* Epoxy-based nonlinear optical polymers from post azo coupling reaction. *Macromolecules*. 1997. **30**. P. 219–225. https://doi.org/10.1021/ma961010g.
26. Breiner T., Kreger K., Hagen R. *et al.* Blends of poly(methacrylate) block copolymers with photo-addressable segments. *Macromolecules*. 2007. **40**. P. 2100–2108.https://doi.org/10.1021/ma0624907.
27. Mao G., Wang J., Clingman S.R. *et al.* Molecular design, synthesis, and characterization of liquid crystal-coil diblock copolymers with azobenzene side groups. *Macromolecules*. 1997. **30**. P. 2556–2567. https://doi.org/10.1021/ma9617835.
28. Hayakawa T., Horiuchi S., Shimizu H., Kawazoe T., Ohtsu M. Synthesis and characterization of polystyrene-b-poly(1,2-isoprene-ran-3,4-isoprene) block copolymers with azobenzene side groups. *J. Polym. Sci. Part A: Polym. Chem*. 2002. **40**. P. 2406–2414. https://doi.org/10.1002/pola.10330.
29. Frenz C., Fuchs A., Schmidt H.-W., Theissen U., Haarer D. Diblock copolymers with azobenzene side-groups and polystyrene matrix: synthesis, characterization and photoaddressing. *Macromol. Chem. Phys.* 2004. **205**. P. 1246–1258. https://doi.org/10.1002/macp.200400046.
30. Häckel M., Kador L., Kropp D., Frenz C., Schmidt H.-W. Holographic gratings in diblock copolymers with azobenzene and mesogenic side groups in the photoaddressable dispersed phase. *Adv. Fund. Mater.* 2005. **75**. P. 1722–1727. https://doi.org/10.1002/adfm.200500158.
31. Schwetlick K. *Organicum*. Wiley-VCH Verlag GmbH, 2001.
32. Collier R.J., Burckhart C.B., Lin L.H. *Optical Holography*. NY. -London: Academic Press, 1973.
33. Davidenko N.A., Davidenko I.I., Pavlov V.A. *et al.* Photo-thermoplastic recording media and its application in the holographic method of determination of refractive index of liquid objects. *Appl. Opt*. 2018. **57**. P. 1832–1837. https://doi.org/10.1364/AO.57.001832.
34. Davidenko N.A., Davidenko I.I., Ishchenko A.A. *et al.* Effect of azo dyes on the photoconductivity and diffraction efficiency of holographic recording media. *Theor. Exp. Chem*. 2018. **54**, No 5. P. 316–321. https://doi.org/10.1007/s11237-018-9576-4.
35. Mahilny U.V., Marmysh D.N., Tolstik A.L. *et al.* Phase hologram formation in highly concentrated phenanthrenequinone – PMMA media. *J. Opt. A: Pure Appl. Opt.* 2008. **10**. P. 085302. https://doi.org/10.1088/1464-4258/10/8/085302.
36. Mahilny U.V., Marmysh D.N., Stankevich A.I. *et al.* Holographic volume gratings in a glass-like polymer material. *Appl. Phys. B: Lasers and Optics*. 2006. **82**. P. 299–302. https://doi.org/10.1007/s00340-005-2006-z.
37. Marmysh D.N., Mahilny U.V. Polarization volume holograms in layers of polymethylmethacrylate with phenanthreneqinone. *Tech. Phys.* 2013. **58**. P. 1665–1670. https://doi.org/10.1134/S1063784213110182.

Поляризаційна голографія в полімерних плівках азобензолу, приготованих за новим хімічним методом

Н.А. Давиденко, І.І. Давиденко, В.В. Кравченко, В.А. Павлов, В.В. Тарасенко, Н.Г. Чуприна

Анотація. Реєструючі середовища для поляризаційної голографії на основі азобензольних полімерів отримують шляхом полімерно-аналогічних перетворень поліметакрилової кислоти та її сополімерів з алкилметакрилатами. Їх інформаційні властивості досліджувались під час запису голограм плоского хвильового фронту. Було встановлено, що час запису та релаксації голограм приблизно однаковий. Вони визначаються переважно процесами транс-цис-ізомеризації азобензольних груп без формування рельєфу поверхні полімерної плівки. Ефективність процесу транс-цис-ізомеризації знижується, якщо в хромофорі азобензолу присутній важкий замісник. Ці результати представляють практичний інтерес під час вибору світлочутливих матеріалів для голографічних реєструючих середовищ з оптимальними інформаційними характеристиками.

Ключові слова: поляризаційна голографія, фотофізичні властивості, ізомеризація, реєструючий матеріал, азобензол.