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Recording medium based on the films of azobenzene copolymer with free surface and in sandwich-structures for polarization holography

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ABSTRACT

Peculiarities of the polarization holographic recording in the samples with the films of copolymer poly[4-((2-nitrophenyl)diazenyl)phenylmethacrylate-*co*-octylmethacrylate] with free surface and in the sandwich-structures with solid covering layer are investigated. Time of the holographic recording and its storage is less in the sandwich-structures. It was concluded, that in the sandwich-structures, geometric relief of the film surface does not appear during the recording.

1. Introduction

The films of polymeric composites containing monomers of azobenzene dyes or azobenzene lateral groups chemically bonded to the main polymer chain demonstrate photoactive properties, and can be used in electrooptical light modulators and in recording media (RM) for polarization holography [1–9]. Photoinduced optical anisotropy (PIA) appears under influence of linearly polarized light caused by the processes of *trans-cis*-izomerization of the azobenzene groups. This process is determining for application of the considered materials as RM for polarization holography. Azobenzene polymers are unique material platforms where photoisomerization of the azobenzene molecules can result in significant material shifts on molecular, mesoscopic and even microscopic length scale. In particular, amorphous azobenzene polymeric films can form stable models of the surface relief under the influence of light [1,7]. Last time, there is progress in development of the azobenzene polymers with surface relief technique for photonic applications.

Azobenzene polymers are widely studied as optical materials. The mechanisms of PIA formation and related changes of characteristics of the optical constants are described, see for example [10–12]. The holograms recorded in these polymers are stable below the softening temperature (T_S). However, a lot of azobenzene functional polymers possess T_S within the range 70–250 °C. Thus, before the holographic recording, RM should be heated up [13,14] until the temperature close to T_S. The surface relief in RM can be erased optically even below T_S or by heating the samples above T_S. Azobenzene polymers with quite low T_S were synthesized recently [15] which allow using RM without special heating. However, in these RM, long exposure is required for the holographic recording due to peculiarities of the rheological properties of the azobenzene polymers. Possibility of the polarization holographic recording in RM with the azobenzene films where PIA is not accompanied by the appearance of the surface relief is not completely investigated yet. That is why the present work is aimed at the comparative study of the polarization holographic recording in the films of azobenzene polymers with the free surface and in sandwich-structures where the film is placed between solid coatings. In the sandwich-structures, the coatings prevent the formation of the surface geometric relief.

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2. Experimental

Copolymer poly[4-((2-nitrophenyl)diazenyl)phenylmethacrylate-*co*-octylmethacrylate] (CooAzo3) and copolymer styrene with octylmethacrylate (SOM) were synthesized for the investigations (Fig. 1).

The softening temperature T_S was measured using known methodology [16], it was 70 ± 1 °C for CooAzo3 and 39 ± 1 °C for SOM. The investigated samples were prepared as the structures with free surface of the polymeric film: (glass substrate) – (ITO) – (CooAzo3 film), and as the sandwich-structures: (glass substrate) – (ITO) – (CooAzo3 film) – (SOM film), (glass substrate) – (ITO) – (CooAzo3 film) – ITO – (glass substrate), (glass substrate) – ITO – (CooAzo3 film) – (SOM film) – ITO – (glass substrate), where ITO is the conducting layer SnO_2:In_2O_3. The thickness of the glass substrates was 2 mm. CooAzo3 films were placed onto the glass substrates with ITO layer by watering a copolymer solution in methylene chloride. After this, the samples were dried in the heat chamber at 80 °C during 24 h. SOM films were placed onto the CooAzo3 films from alcoholic solution. The films thickness was ~2 μm and was measured using an interference microscope.

Spectra of optical density (D) were registered in the samples with free surface of the films CooAzo3 and SOM within the range of light wavelength λ = 400–700 nm using spectrophotometer Varian Gary 50. The surface electric potential (V_P) after charging the films in the corona discharge was measured without illumination and under illumination with laser light λ = 532 nm. The corona discharge was formed for positive and negative potential of the corona electrode, respectively, to the ITO layer. After charging in the corona discharge, the value (V_{Pmax}) of the film surface potential, respectively, to the ITO layer was ± (180–200) V. A specially developed device was used for creation of the corona discharge. In the device, the corona discharge appears due to application of d.c. electric voltage ~10 kV between the ITO layer and metallic wire above the film surface. The same device is usually employed for the holographic recording by the photothermoplastic technique [17,18]. Dynamic probing (Kelvin technique [19]) was used for measurements V_{Pmax} and V_P. The probe sensor was Ag plate with diameter 4 mm. The frequency of the probe vibration was 80 Hz. Kinetics $V_P(t)$ was registered by the memory oscilloscope Textronix TDS1001B.

The holograms of plane wave front were registered in the samples with free surface of the polymer film and in the sandwich-structures. A semiconductor laser with λ = 532 nm was used for recording with the ratio between the light intensities in object (I_1) and reference (I_2) beams being 1: 1. The spatial frequency was 300 mm^{-1}. The power of laser irradiation was 50 mW. Diffraction efficiency (η) of the hologram of plane wave front was determined by the usual technique [20] 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 finish of the hologram exposure were measured. These dependencies were compared for parallel ($\boldsymbol{e}_1 \parallel \boldsymbol{e}_2$) and perpendicular ($\boldsymbol{e}_1 \perp \boldsymbol{e}_2$) orientations of electric vectors of object ($\boldsymbol{e}_1$) and reference ($\boldsymbol{e}_2$) light waves. Each new measurement was done at new RM area to avoid the influence of the previous experiment (memory of holographic recording). Dependency of dielectric loss tangent (tgδ) on the frequency (f) of sinusoidal alternating voltage with amplitude 5 V applied to the electric contacts was measured in the sandwich-structures. All measurements were fulfilled at a room temperature 20 °C.

3. Results and discussion

The spectrum of optical density of the samples with the films CooAzo3 and CooAzo3 – SOM are shown in Fig. 2. Absorption of the samples within the visible range is determined by long-wave edge of absorption of azobenzene chromophores of CooAzo3 and it does not depend on presence of SOM film.

Samples with the films CooAzo3 and CooAzo3 – SOM possess high electric conductivity, photoconductivity is practically absent. As result, quick decay of the surface potential after charging the films in the corona discharge is observed (Fig. 3). Characteristic time of $V_P(t)$ decay does not depend on the polarity of potential of the corona electrode. Thus, electric conductivity of the investigated films is determined by ionic and/or polarization conductivity. However, velocity of decay of the surface potential in the samples with CooAzo3 – SOM is lower than in the samples with CooAzo3 (Fig. 3). This is evidence of higher electric conductivity of the films CooAzo3 compared to the SOM films.

Experimental results shown in Fig. 4 also demonstrate the difference between electrooptical properties of the films CooAzo3 and CooAzo3 – SOM. Electric dipoles present in the films CooAzo3 possess higher sensitivity to changes of the direction of the force lines of the external electric field resulting in low value tgδ and its weak dependency on f (curve *1*, in Fig. 3). Presence of the additional layer SOM in the samples CooAzo3 – SOM creates difficulties for rotation of the dipole moments under change of the direction of the force lines. As result, the value tgδ increases and it depends on f more strongly (curve *2*, Fig. 4). Observed differences of the properties of the samples with CooAzo3 and CooAzo3 – SOM reveal

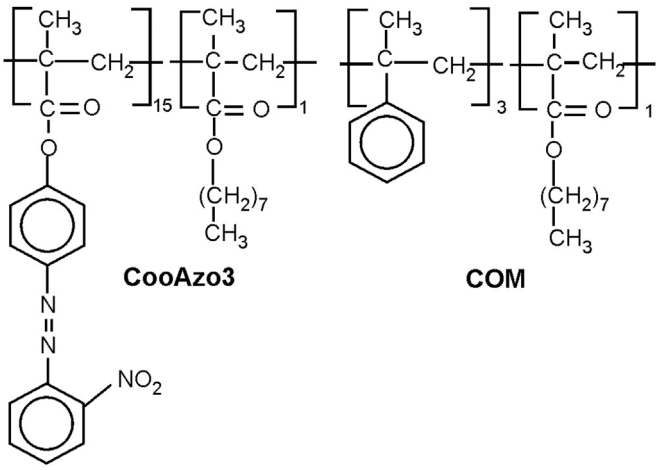

Fig. 1. Structural formulas CooAzo3 and SOM.

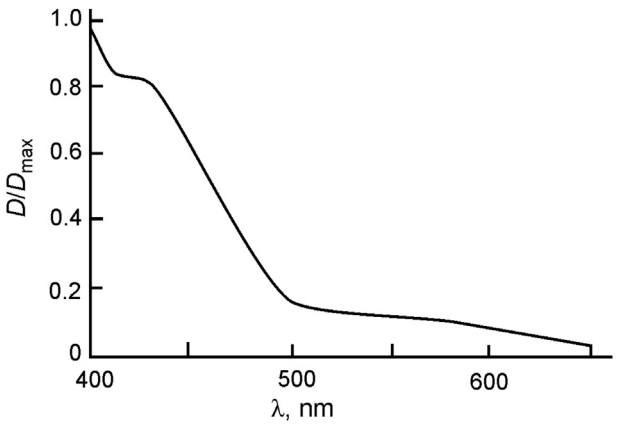

Fig. 2. Normalized spectrum of optical density of RM with the CooAzo3 film.