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Examination of refractive indices and propagation losses in PSLC mixtures with various monomer concentration

ANGELA PACHACZ[1], KATARZYNA RUTKOWSKA[2]

[1]RESEARCH AND DEVELOPMENT CENTRE OF RESEARCH AND DIDACTIC EQUIPMENT COBRABID Sp. z o.o.

[2]FACULTY OF PHYSICS, WARSAW UNIVERSITY OF TECHNOLOGY

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ABSTRACT:

In this research study on liquid crystalline materials mixed with other compounds, specifically with monomers, is presented. Research covers measurements of the refractive indices and the attenuation constant of the polymer stabilized liquid crystals (PSLCs). The latter are specific type of mixture, containing liquid crystal together with less than 10% weight concentration of the monomer and UV-sensitive activator. In this sense, the variety of available liquid crystals and monomers, gives a huge number of different mixtures that can be potentially obtained [1]. Each combination of particular compounds and their weight ratios, results in different physical properties of the mixture, so knowledge about, how each of these factors influences the final product, is fundamental. PSLCs, thanks to their tunable properties, provide wide range of potential applications in integrated optics as e.g. varifocal lenses, sensors, waveguiding layers, etc., but first their optical parameters have to be examined in detail [2, 3].

Badanie współczynników załamania i strat propagacyjnych w stabilizowanych polimerowo ciekłych kryształach (ang. PSLCs) o różnej koncentracji monomeru

Słowa kluczowe: optoelektronika, optyka zintegrowana, ciekłe kryształy

STRESZCZENIE:
W niniejszym artykule przedstawiono badania nad ciekłymi kryształami połączonymi z innymi materiałami, w szczególności z monomerami. Badania obejmują pomiary współczynników załamania oraz współczynnika tłumienia w ciekłych kryształach stabilizowanych polimerem (ang. PSLC). PSLC to rodzaj mieszaniny, w której skład, oprócz ciekłego kryształu, wchodzi mniej niż 10% wagowego stężenia monomeru oraz śladowe ilości aktywatora optycznego. Biorąc pod uwagę różnorodność związków ciekłokrystalicznych i monomerów, można uzyskać ogromną liczbę mieszanin o różnych właściwościach fizycznych [1]. Znajomość tychże właściwości jest kluczowa w kontekście praktycznego zastosowania mieszanin PSLC. Mieszaniny tego typu, dzięki możliwości uzyskania związku o konkretnych właściwościach fizycznych i chemicznych, można zastosować w optyce zintegrowanej, np. do zmiennoogniskowych soczewek, czujników, jako warstwy falowodowe itp., jednak zanim to nastąpi, należy szczegółowo zbadać i wyznaczyć ich parametry optyczne [2, 3].

1. INTRODUCTION

Liquid crystals (LCs) are object of scientific research from about hundred years and in this period of time they have revolutionized many branches of technology and industry. The main reason of their renown is unique combination of their properties like e.g. fluidity combined with molecular arrangement, optical birefringence, sensitivity to external fields or factors, and others [4]. Typical nematic liquid crystals (NLCs) consist of rod-like molecules with their geometrical parameters characterized by the long and short axis. It is worth noting that each molecule is randomly distributed in the volume of NLC, but in the macro scale, they tend to orient with long axis, along each other. It allows to define average molecular orientation direction that is referred to as director, described by the unit vector $\vec{n}$. It is known that long molecular axis determines direction of the optical axis in uniaxial NLCs, what directly influences the light propagation within. Specifically, for linearly polarized light, when its electric field vector oscillates parallel or perpendicular to the NLC director, only one, namely ordinary (n_o) or extraordinary (n_e) refractive index occurs, respectively. For linearly polarized light with its electric field vector oscillating at some angle to the director (excluding 0° and 90°) light beam splits into two components, each refracted at different angle, compatible with ordinary n_o and extraordinary n_e refractive index, as consequential to the Snell's law [5].

Liquid crystalline phases occur only in specific range of temperatures, strictly defined for given compound. For NLCs, belonging to thermotropic LCs, this specific phase occurs above the melting temperature of solid crystal and below the temperature of phase transition to isotropic state. The latter is obtained when the molecular order is lost and material is characterized by only one refractive index, n_{iso}, that slightly decreases while still heating.

Another parameter, crucial for LCs practical application, is attenuation constant, which is the measure of propagation losses in the material. According to the Beer-Lambert law, the light intensity of the beam, propagating in the medium, decreases exponentially and can be described as:

$$I = I_0 e^{-\beta z} \tag{1}$$

where I_0 is an input intensity, z is propagation distance and β [1/cm] is the attenuation coefficient, determined for the specific material. Attenuation of the light occurring in materials, specifically in NLCs, results mainly from two phenomena, which are scattering and absorption of the light [6]. Both of them can be described by attenuation rate β_{scat} and β_{abs}, respectively, and their sum gives total attenuation rate β of the material. Its value depends mainly on the molecular structure, chemical bonds, heterogeneity of the material and wavelength of propagating light. It is worth noting that the absorption in NLCs is the weakest in the visible region, so the main influence on the propagation losses in this spectral range comes from the light scattering [7].

NLCs likely mix with other compounds, especially nanoparticles and monomers. Thanks to variety of available substances, one can achieve mixtures with wide range of the chemical and physical properties. Characteristics of the resultant mixture depends, not only on kind of components being combined and their proportions, but also on temperature and wavelength of beam propagated in it. Polymer Stabilized Liquid Crystal (PSLC) is a kind of mixture of liquid crystal and monomer containing less than 10% weight concentration of the latter and small (<1 wt %) addition of photo-activator to initiate process of photopolymerization. In current work connecting single mers of monomer into long polymer chains has been carried under the light from specific spectra range (here UV) [8].

As it was mentioned before, knowledge of PSLCs properties and their dependence on internal and external conditions, is extremely important for potential application of PSLCs mixtures. Taking this as a main motivation of this research, their refractive indices have been measured as a function of temperature and monomer concentration, as well as the attenuation rate and its dependency on monomer concentration. Additionally, propagation losses (attenuation rate), has been studied for different molecular orientation in NLCs in reference to the direction of the linear light polarization.

2. CONTEXT

The main goal of the scientific project, that the presented research was the part of, was to create PSLCs waveguiding structures to guide light beams that could be potentially used as waveguiding channels or optical switches in integrated optics circuits. Prototype waveguides were created in typical LC cells filled with PSLC mixture, where selective irradiation through periodic amplitude mask (with strips of different widths) resulted in periodically located polymerized and unpolymerized areas. In such design, polymerized areas, where LC molecules were blocked in the certain position by the polymer network, acted as a cladding for unpolymerized area between them. Unpolymerized area, that was still responsive to adequate external electric field, acted like a waveguide core with adjustable refractive index [9, 10]. Due to the fact, that in the final setup of optical switches, light is supposed to propagate in the unpolymerized region, knowledge of this state of the PSLC mixture properties is fundamental [11].

3. EXPERIMENT

3.1 Materials and samples preparation

Materials used in the experimental work was nematic liquid crystal 6CHBT [12], monomer RM257 [13] and acetyl benzoyl [14] employed as the photo-activator. In most measurements, LC cells, made of transparent glass plates, covered with transparent ITO electrodes, have been applied. In particular, three types of cells have been used, namely with layers forcing planar (parallel to the glass surface) or homeotropic (perpendicular to the glass surface) LC molecular orientation and LC cells without orienting layers, where molecules have been freely orienting by themselves. The single LC cell glass plate size was around 2.00 ± 0.05 cm × 2.00 ± 0.05 cm with the thickness of tens of micrometres.

Considerable care has been taken during PSLC mixtures preparation. Procedure for the mixtures preparation was the same for all experiments and included precise weight of ingredients, with 1 mg accuracy, then heating up the liquid crystalline material to isotropic state and mixing it in ultrasound mixer to get rid of small clods of monomer and photo-activator. PSLC mixture was ready, when, right after mixing, in all phial there was only transparent liquid [1].

3.2 Refractive indices measurement method

Refractive indices measurement system was based on the wedge-geometry cell [15], filled with PSLC mixture. It enabled simultaneous data collection for both ordinary n_o and extraordinary n_e refractive indices for wide range of temperatures and wavelengths. This setup is suitable also for substances with high values of refractive index and significant optical birefringence.

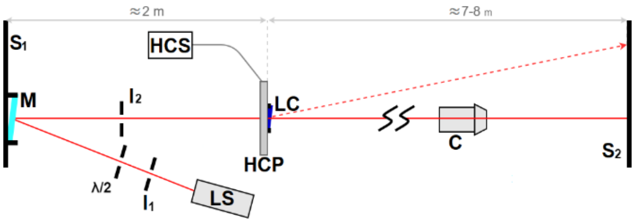

Figure 1 Scheme of refractive indices measuring system. Description of all components is given in the text

In order to obtain the wedge shape of the cell with an inclination angle of around single degrees, thick plastic spacer was placed on one edge, between glass plates. Then LC cell was placed on stabilizing heating-cooling platform (HCP) that allowed also to stabilize thermal conditions and to get information about current temperature of LC material. Constantly, the heating-cooling stage (HCS) is based on programmable controller, that allowed temperature regulation and reading. Regulator proceeded entered value to microscopic heating-cooling table connected to the fluid circulator that heated up or cooled down the distilled water in its tank. Then, the fluid at the proper temperature reached heating-cooling platform through the hose. The second hose drained water back to the circulator to adjust back its temperature. Measuring setup scheme is presented in Figure 1.

When designing the measuring system, monochromator can be used as a light source (LS), because of ease of wavelength tuning, or single monochromatic light source, e.g. laser diode. In the presented research the latter option has been applied. Importantly, the light beam has to be properly collimated all the way in the system, but it does not need to be coherent or linearly polarized in specific direction. The only condition is that the beam cannot be polarized linearly parallel or perpendicular to the LC molecules orientation, because as a result, only one light spot appears on the screen S_2, corresponding to ordinary O or extraordinary E ray, respectively. Laser beam propagates through iris I_1 and half-wave plate λ/2 to reach regulated mirror M. Position of that mirror is adjusted to guide the light beam through iris I_2 and further through LC cell in which the light beam is split into two beams, ordinary and extraordinary, finally reaching the screen S_2. To observe light spots on the screen S_2 and to record them for further analysis, the CCD camera C was placed straight in line with the heating-cooling platform (HCP) and iris I_2, as shown in Figure 1. Screen S_2 was covered with the diagram paper, that allowed to recalculate the distance on the photo (in graphic file) given in pixels into millimetres.

As it is shown in Figure 2, the first step of the measurement procedure is to construct empty wedge-shaped cell and to place it on the heating-cooling platform in such way that its front glass-plate is perpendicular to the direction of the light beam propagation, so that light, reflected from it, goes back through the same path to the mirror M. Light beam, reflected at the angle of 2α from the back plate, is registered as a light spot on the screen S_1. Once the angle of the wedge cell is measured in such way, the PSLC mixture is introduced carefully into cell with use of the syringe. After few seconds, light spots, observed on the screen S_2, are splitted up in two: ordinary and extraordinary one, refracted at the angle of ψ_o, ψ_e, respectively. The temperature step, when experimentally studying the temperature dependence of refractive indices, was 0.5°C or 1.0°C, depending on the current value and observed changes in the light spots positions. Sample was heated up until it reached its individual temperature characteristic for the phase transition into the isotropic phase and 2-3 Celsius degrees above.

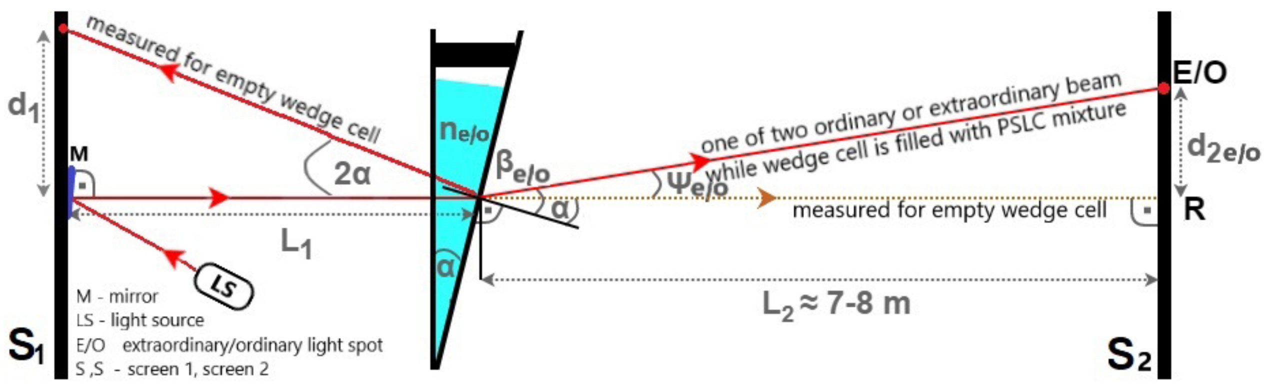

Figure 2 Scheme of experimental setup with indicated light beam propagation in the empty and filled with PSLC mixture wedge cell

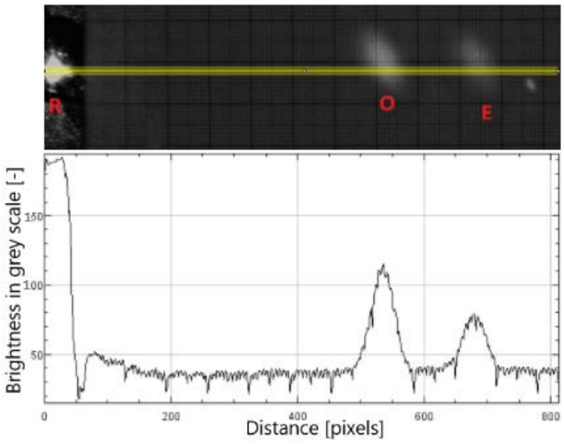

Figure 3 Top: Stitched photos of the screen S_2 while there is empty wedge cell and PSLC mixture filled in it. Yellow line indicates the analysed area.
Bottom: Plot of the pixel brightness along the analysed area got from the ImageJ software

Each photo of the screen S_2 (stitched photos of empty cell and cell filled with the PSLC mixture) was analysed with use of the ImageJ software that, allowed to obtain spatial profile of the light spots, expressed in pixels, in the area marked with a line of the adjusted width, as it is exemplarily shown in Figure 3. The line must include area with the reference R, ordinary O, and extraordinary E light spots with recognisable maxima, that allow the calculation of the distance between reference R and extraordinary/ordinary (E/O) light spots, marked as $d_{2e/o}$ in Figure 1, respectively. Measuring this value, together with the distance d_1 between spots in the empty wedge cell and distances L_1, L_2 between wedge cell and both screens, the refractive indices of the PSLC mixture can be calculated with use of the following formula:

$$n_{\frac{e}{o}} = \cos\psi_{\frac{e}{o}}\left(1+\frac{\tan\psi_{\frac{e}{o}}}{\tan\alpha}\right) = \frac{1}{\sqrt{(L_2{}^2+d_{2e/o}{}^2)}}\left(L_2+\frac{d_{2,e/o}\left(L_1+\sqrt{(L_1{}^2+d_1{}^2)}\right)}{d_1}\right) \quad (2)$$

Key factor of the proper measurement, is to guarantee long enough distance between LC cell and screen S_2 that allows for separation of the light spots coming from the ordinary and extraordinary light beams. To translate distances expressed in pixels to centimetres, one centimetre pattern has to be created. That was made thanks to the photo taken to the sheet of the graph paper placed on the screen S_2, that was also analysed with use of the *PlotProfile* function in the *ImageJ* software, where local minima of signal in brightness scale correspond to the grids of the sheet [1].

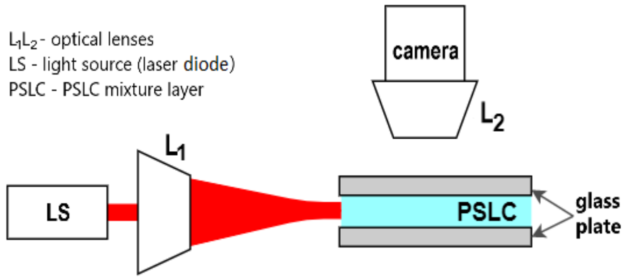

Figure 4 Scheme of the attenuation rate measurement system

3.3 Propagation losses measurement method

Attenuation coefficient measurement system, the scheme of which is shown in Figure 4, is applying the planar geometry of the LC cell filled with PSLC mixture. Light beam was launched into PSLC layer in such a way that the linearly polarized light was propagating with its propagation direction parallel to the glass plates surfaces. Layer of PSLC is thick enough to guarantee approximately homogeneous orientation of the LC molecules and a bit wider than the transverse dimensions of the light beam. Homogeneous orientation, specifically planar and homeotropic, of LC molecules was provided by mechanical rubbing and special chemical layer on the glass plates, respectively. The laser diode with a wavelength of λ = 680 nm was applied as a light source. Further, light beam was launched into LC cell with use of the microscopic focusing lens L_1 and with the waist of the beam reaching the PSLC layer at the input facet of the cell. Cell was placed on the stabilizing holder and adjustable in three directions with micrometer screws.

CCD camera placed over the cell was used to register an exponential light fading in the PSLC layer along the way of propagation. Each recorded photo was again analysed in the *ImageJ* software, which allowed to obtain characteristics of the light intensity (taken from the brightness of the pixels) from the propagation distance along the area adjusted by user. As shown on photo of light propagation and plot in Figure 5, intensity of the light beam propagating through the PSLC layer decreases exponentially, what is consistent with the Beer-Lambert law, described in the Section 1. So knowing I_0 as a maximum brightness and pixel brightness values I along with the position value z, attenuation coefficient β can be calculated, as

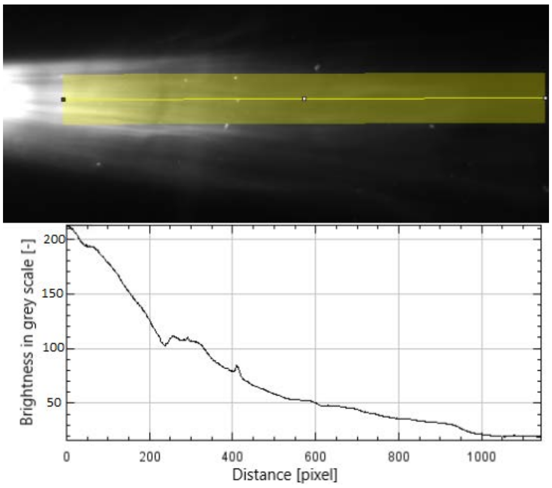

Figure 5 Top: Photo of the light propagation in the PSLC layer placed between two glass plates. Area marked with yellow line was analysed in the ImageJ software. Bottom: Plot of the photo brightness along the yellow line

a slope of a straight line obtained from the relationship given in equation (1) as:

$$\beta z = -\ln\frac{I}{I_0}\ \cdot \qquad (3)$$

While both sides of above equation are linear, so plotting right side of the Eq. (3) with use of data taken in experiment, allows to approximate the attenuation coefficient from the straight line with its slope β [18].

4. RESEARCH RESULTS AND DISCUSSION

Main purpose of the study was to measure influence of the percentage weight of the monomer in PSLC mixture on its selected physical properties. This section presents results of the performed research.

4.1 Refractive indices measurement results

Collected results allowed to plot temperature dependence of the refractive indices of the PSLC mixtures. Exemplary results obtained for the PSLC mixture with the monomer concentration of 2.28 wt % and 5.06 wt % are shown in Figure 6 and Figure 7, respectively.

As one can see in the charts shown in Figure 6 and Figure 7, temperature of the phase transition to isotropic state increases from the value of Tiso = 41° Tiso = 44° when concentration of monomer in PSLC mixture increases. However assuming the results for the phase transition temperatures obtained for all tested mixtures, no specific relationship has been found.

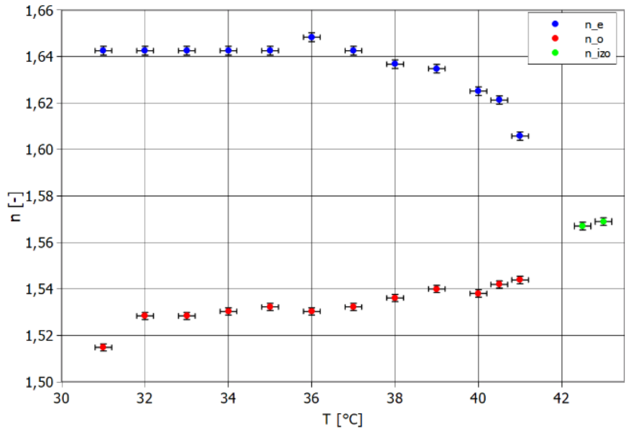

Figure 6 Temperature dependence of the refractive indices of the PSLC mixture for the monomer concentration of 2.28 wt % and the wavelength of λ = 680 nm

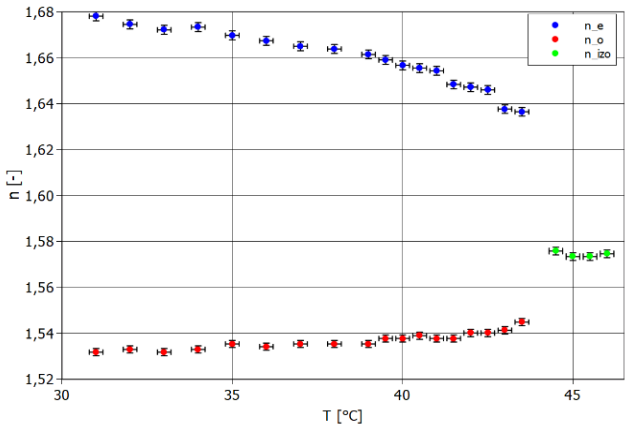

Figure 7 Temperature dependence of the refractive indices of the PSLC mixture with the monomer concentration of 5.06 wt % and for the wavelength of λ = 680 nm

Based on the collected results, dependence of the refractive indices on the percentage weight of monomer has been determined and plotted, what is shown in Figure 8. As one can conclude, increasing weight percentage of the monomer in the PSLC mixture causes growth of both ordinary and extraordinary refractive indices values. A sharp increase is observed for changes in the percentage concentration in the range of 2-3 wt %.

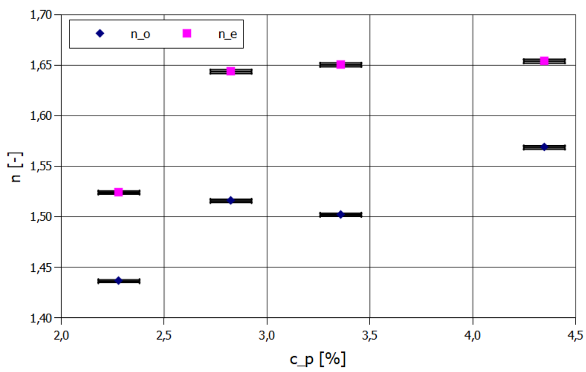

Figure 8 Refractive indices dependence on the monomer weight percentage in the PSLC mixture for the wavelength of λ = 680 nm

4.2 Attenuation rate measurement results

This part of the research includes attenuation rate measurements for the PSLC mixture in the measuring system with the cell with planar geometry and with various types of the orienting layers applied on the glass plates causing planar, homeotropic or no specific orientation of the liquid crystal molecules between the glass plates. As a light source, the laser diode with wavelength of λ = 680 nm and with the linear polarization, perpendicular to the cell glass plates was used. Below exemplary results for the PSLC mixture with the monomer weight percentage concentration of 2.28 wt % are presented. Specifically, the photos of the light beam propagation in the cell with planar (Fig. 9Ia), homeotropic (Fig. 9IIa)

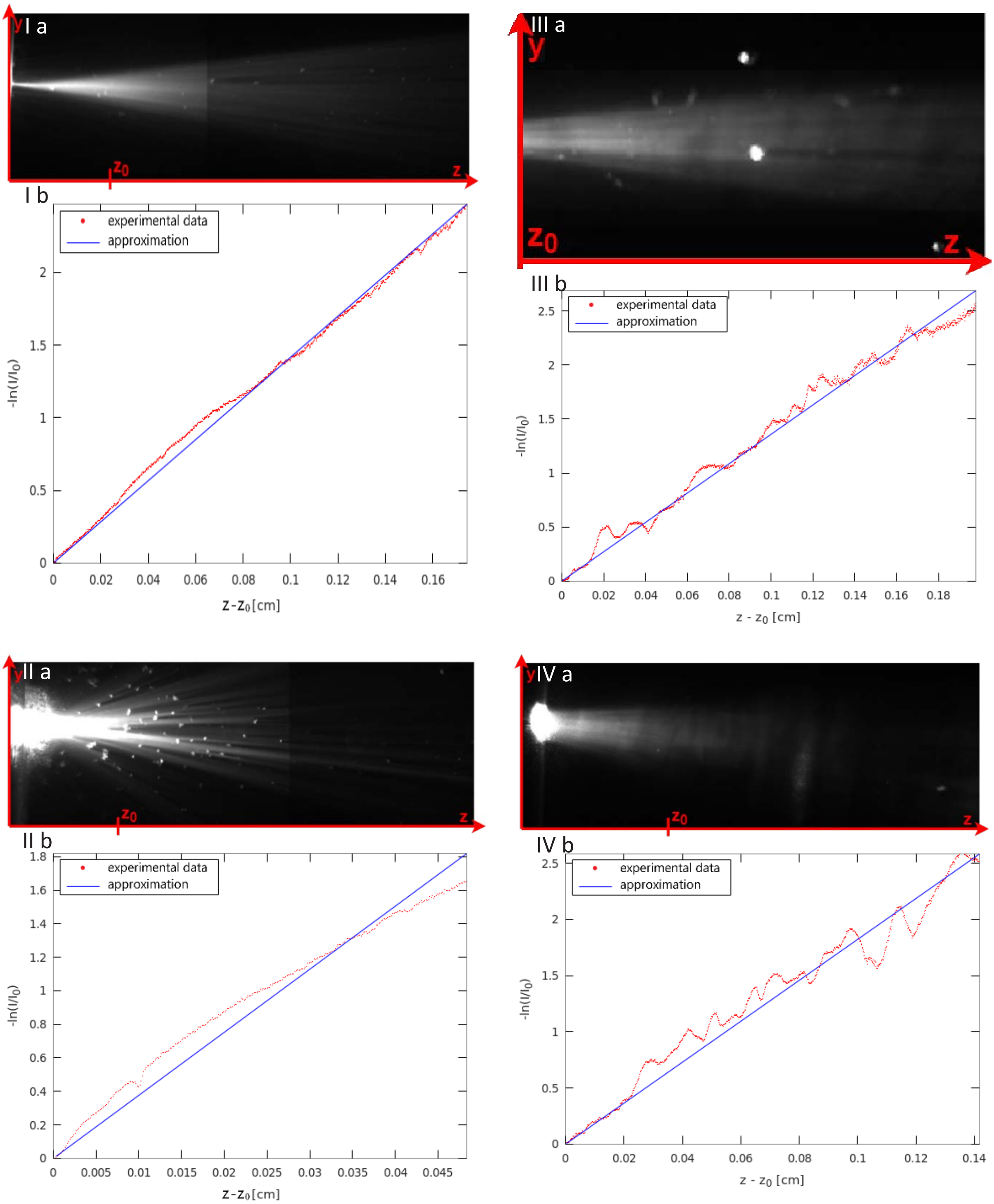

Figure 9 Case of the planar (I), homeotropic (II), and no specific (III) – before photopolymerization and no specific – after photopolymerization (IV) LC molecular orientation in the LC cell: a) the photo of the light propagation in the cell, b) plot of the logarithmized normalized light intensity from the photo for the PSLC mixture with the monomer concentration of 2.28 wt % and for the wavelength of λ = 680 nm

and with no specific (Fig. 9IIIa) LC molecular orientation with corresponding to them plots of the logarithmized normalized light intensity (represented by the pixels brightness) and the straight line fitted to the experimental data straight line (Fig. 9Ib, Fig. 9IIb, Fig. 9IIIb, respectively) are shown. For the comparison, PSLC mixture with the same concentration has been introduced into the cell with no specific orientation layer and then illuminated with the UV light of the intensity of 250 mW/cm^2 for 60 seconds. The latter initiated photopolymerization process in the PSLC mixture. Light propagation in such polymerized PSLC material and plot of the logarithmized normalized light intensity are presented in Fig. 9IVa and Fig. 9IVb, respectively.
The values of the attenuation rate for different concentrations of monomer in PSLC mixture were compared for two cell types, with planar and no specific liquid crystal molecular orientation, as shown in Figure 10 and Figure 11, respectively. As one can see with rising amount of monomer, attenuation rate of PSLC mixture grows in both planar and no specific orientation of LC molecules. In cell with planar orientation there is a larger spread of results, what may be consequence of forcing certain LC molecules orientation and efficiency of the process.
One of the key factors influencing the results was a distance of the light propagation, what was taken into account during calculations and for the line estimation. Choice of such distance was based mostly on the discrepancy factor that was given as a difference between pixel brightness value from the linear approximation and from the experimental data, so the smaller it was, the better experimental data was described by the linear approximation. That value had to be as small as possible, but simultaneously could not cause that the accounted distance to be shortened to more than 0.45 mm.

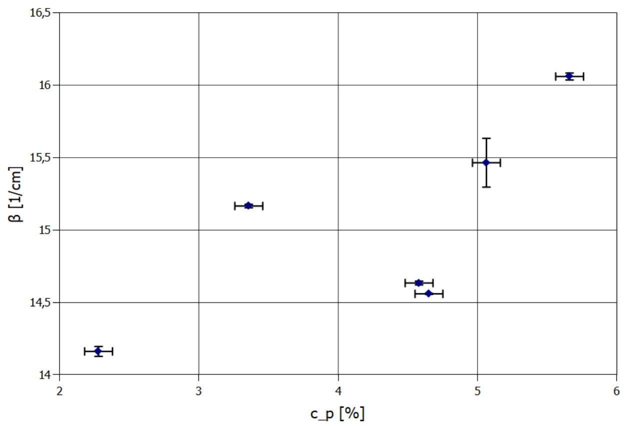

Figure 10 Attenuation rate dependence from the monomer concentration in the PSLC mixture in the LC cell with the planar molecular orientation and for the wavelength of λ = 680 nm

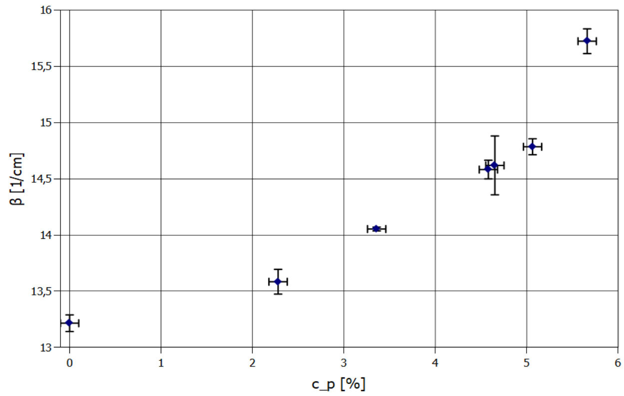

Figure 11 Attenuation rate dependence from the monomer concentration in the PSLC mixture, in the cell with no specific LC molecular orientation for the wavelength of λ = 680 nm

5. CONCLUSIONS

Refractive indices measuring system, based on the wedge-geometry cell, enables examination of the PSLC mixture in regards to temperature and the monomer concentration. It is also possible to measure these parameters as a function of the wavelength if one uses tunable light source, like e.g. monochromator. Also, while using monochromatic light source, there is no requirement to coherence and specific state of polarization. Refractive indices of the PSLC mixtures as a function of temperature, show similar tendencies as in pure liquid crystals. While heating PSLC compound, its extraordinary refractive index n_e slightly decreases and ordinary refractive index n_o increases or decreases with temperature. As was observed in the experimental procedure, the temperature of the phase transition to the isotropic state of the mixture has been different for each monomer concentration, but no specific relation describing these changes has been determined. Comparison of the refractive indices of the PSLC mixtures with various monomer concentration and in specific temperature, led to conclusion that with growing amount of the monomer in the PSLC mixture, values of both ordinary and extraordinary refractive indices increase.
Obtained experimental results lead to the conclusion that quantity of PSLCs attenuation coefficient for the wavelength of λ = 680 nm is similar

for cell with planar and no specific orientation layer. However, it is worth noting that its value was slightly lower for the second type of the LC cell, probably because of the forced liquid crystal molecular planar orientation and not satisfying effectiveness of this process. For the cell with homeotropic liquid crystal molecules orientation, attenuation rate value was significantly different, even tens of percent higher than for two other types of the cells, what results mostly from the liquid crystal molecular orientation approximately parallel to the linear polarization of the light beam, from the efficiency of linear polarization and efficiency of forcing LC molecules to orient perpendicularly to the glass plates. Also an increase in the attenuation rate was observed with the increasing weight percentage of the monomer in the PSLC mixture within one cell type. That was caused by increase in the light scattering on the polymer structure together with difficulties in liquid crystal molecules reorientation and ordering in polymer network. Comparing PSLC mixture attenuation rate in the cell with no orientation layer, before and after photopolymerization process, one can notice that the value of this parameter was tens of percent higher in the mixture after photopolymerization (in shown example it is 34%).

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