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Jaroslaw Mysliwiec,[1,a)] Maciej Czajkowski,[1] Stanislaw Bartkiewicz,[1] Krystian Zygadlo,[2] Zbigniew Galewski,[2] and Bouchta Sahraoui[3]

[1]*Wroclaw University of Technology, Wybrzeze Wyspianskiego 27, Wroclaw 50-370, Poland*
[2]*University of Wroclaw, Joliot-Curie 14, Wroclaw 50-383, Poland*
[3]*University of Angers, Moltech-Anjou UMR CNRS 6200, University of Angers, Angers 49-045, France*

We present results of dynamic and fast switching of birefringence in a photochromic liquid-crystalline system as a function of the sample temperature. The system consists of photochromic molecules of 4-heptyl-4′-methoxyazobenzene showing a liquid-crystalline nematic state close to room temperature. An experiment of dynamic birefringence switching was done in optical Kerr-effect set-up, where for the sample excitation, a picosecond-pulsed laser was used. Measurements were done for different temperatures of the sample in the liquid-crystalline nematic phase. We have proposed a mathematical model of dynamic, fast, and fully reversible birefringence changes. Theoretical estimations and experimental results have shown very good agreement. © *2011 American Institute of Physics*. [doi:10.1063/1.3665123]

I. INTRODUCTION

Azobenzene-based photochromic materials have proved many times their high potential in photonic applications. It has been shown that these particular systems, in which the phenomenon of photoinduced anisotropy (birefringence) is observed, can be used for retrieval of optical information, optical switching, lasing, or dynamic data storage.[1–11]

Liquid crystals (LC) are materials with unique properties mostly based on self-organization, long-range order, co-operative motion and interaction, and what can be used, e.g., in the field of real-time holography, or in visualization systems such as liquid-crystalline displays.[12–20]

Azobenzene liquid crystals have been developed as materials in which some of the above properties can be found and where azo-molecules play a role as mesogenes and photosensitive chromophores.[21–30]

The mechanism of photoinduced optical birefringence is based on the *trans-cis-trans* reversible photoisomerization of azochromophores, where the resonant polarized light is able to initiate the molecular reorientation because the transition dipole moment of azobenzenes is along the molecular axis of elongated *trans*-isomer. The *trans* form of azobenzene derivatives is rod-like, which stabilizes the LC phases, whereas the *cis* form is bent and destabilizes the LC phases when it is present.[10] It was shown that there is a strong influence of voltage and temperature on the dynamics of molecular switching and diffraction grating formation in liquid-crystalline azobenzene-based systems, where the times of grating formation depend on the temperature according to the Arrhenius relation, and the mechanism of the dynamic diffraction grating creation is related to the growth of the isotropic domains.[10,28,29]

In this paper, we report on the dynamic switching of the liquid-crystalline photochromic system optical birefringence induced by a pulsed laser in an optical Kerr-effect (OKE) experiment set up as a function of the sample temperature.

II. METHODS AND MATERIALS

OKE is the third-order nonlinear process resulting in photoinduced changes of a material's birefringence. Such behavior can be achieved via interaction between the electric field of linearly polarized pumping laser light and the molecules in the material, which are in an isotropic initial state. The pumping beam produces birefringence in the material via molecular reorientations, which introduces ellipticity to the initially linearly polarized probing beam incident at an angle of $45°$ to the pump. Change of linear polarization of the probe is caused by phase retardation between two perpendicular components of the polarization vector.

The studied compound, 4-heptyl-4′-methoxyazobenzene (7ABO1), has a rod-like shape and exhibits a nematic phase in the range from $T = 34 °C$ to $T = 63 °C$. More details about synthesis and liquid-crystalline properties of 4-heptyl-4′-alkyloxyazobenzene (7ABO1) were described in our earlier papers.[28–30] The 7ABO1 compound, as all azobenzene derivates, has photochromic properties and undergoes a reversible *trans-cis-trans* geometrical isomerization on –N=N– double bond, upon the light illumination (Fig. 1).

For measurements, we have used a specially designed photochromic liquid-crystalline panel (PcLCP), where pure material of liquid-crystalline photochromic molecules was inserted into sandwich-like cells consisting of two glasses. Thickness of the photoactive material layer was about 4 μm.

To investigate the influence of $\lambda = 532$ nm light on the liquid-crystalline samples, the picosecond-pulsed Nd:YAG laser was used as an excitation source with energy of around $E \approx 1$ mJ/cm^2. The excitation light counter-propagated through the sample film against a probe beam of wavelength $\lambda = 632.8$ nm. Detection of the birefringence induced in the sample located on a heating stage, where the temperature

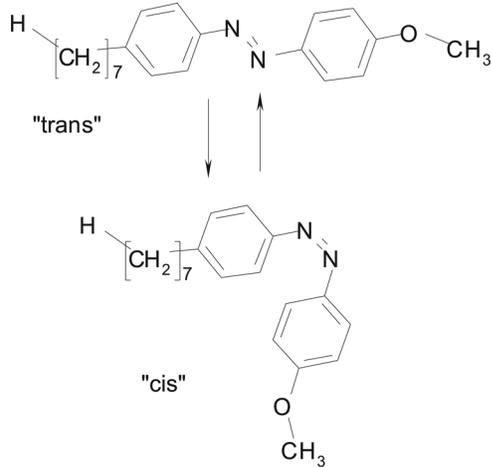a)Author to whom correspondence should be addressed. Electronic mail: jaroslaw.mysliwiec@pwr.wroc.pl.

FIG. 1. Chemical structure of photochromic 4-heptyl-4′-methoxyazobenzene.

was changed in the range of $T = 34\,°C$–$55\,°C$ (the nematic phase of the 7ABO1 azo-molecule), was via a crossed polarizer and analyzer system placed at $\lambda = 632.8$ nm of cw He–Ne laser beam. These transmission axes were perpendicular to each other and at 45° azimuthal angle to the electric field direction of the ps-pulsed laser excitation beam. A glass filter rejecting 532-nm-wavelength light was placed on the fast photodiode head to ensure that only light coming from the He–Ne laser is detected. The fast pin photodiode was connected to the oscilloscope (Tektronics, TDS 3034) enabling observation of light intensity changes after the ps-pulsed laser light excitation.

III. EXPERIMENTAL RESULTS AND DISCUSION

In Fig. 2, experimental results of temporal behavior of birefringence changes in the PcLCP sample for four different

temperatures $T = 34\,°C$, $T = 42\,°C$, $T = 52\,°C$, and $T = 54\,°C$, together with theoretical fit are presented. We can see that there is a strong correlation between the temperature of the sample and the total time of the OKE signal evidence, which is in the range of single milliseconds.

The mechanism of photoinduced changes of birefringence in photochromic nematic liquid-crystalline molecules can be divided into four consecutive states (A, B, C, and D), characterized by three different rate constants k_1, k_2, and k_3:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D. \tag{1}$$
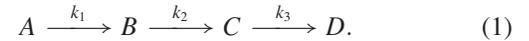
Dynamic changes of birefringence for each process can be expressed in the form of mathematical equations, where c_i is the concentration of LC molecules in the ith stage.

$$c_A = a \cdot e^{-k_1 t}, \tag{2}$$

$$c_B = b \cdot \frac{k_1}{k_2 - k_1} \cdot [\exp(-k_1 t) - \exp(-k_2 t)], \tag{3}$$

$$c_C = c \cdot \left[\frac{k_1 k_2}{(k_2 - k_1)(k_3 - k_1)} \cdot [\exp(-k_1 t) - \exp(-k_3 t)] \right.$$
$$\left. - \frac{k_1 k_2}{(k_2 - k_1)(k_3 - k_2)} \cdot [\exp(-k_2 t) - \exp(-k_3 t)] \right]. \tag{4}$$

The A is the initial state when the sample is in the nematic phase, according to the applied temperature, with partial randomly aligned molecules, and before the illumination by the picosecond-pulsed laser (cf. Fig. 3(a)). After the sample irradiation, the linearly polarized light beam selectively pumps molecules whose transition dipole moment axis is parallel to its polarization (probability $\propto \cos^2\alpha$, where α is the angle between the long axis of the *trans* molecule and the polarization of light), and we start to observe molecular reorientation
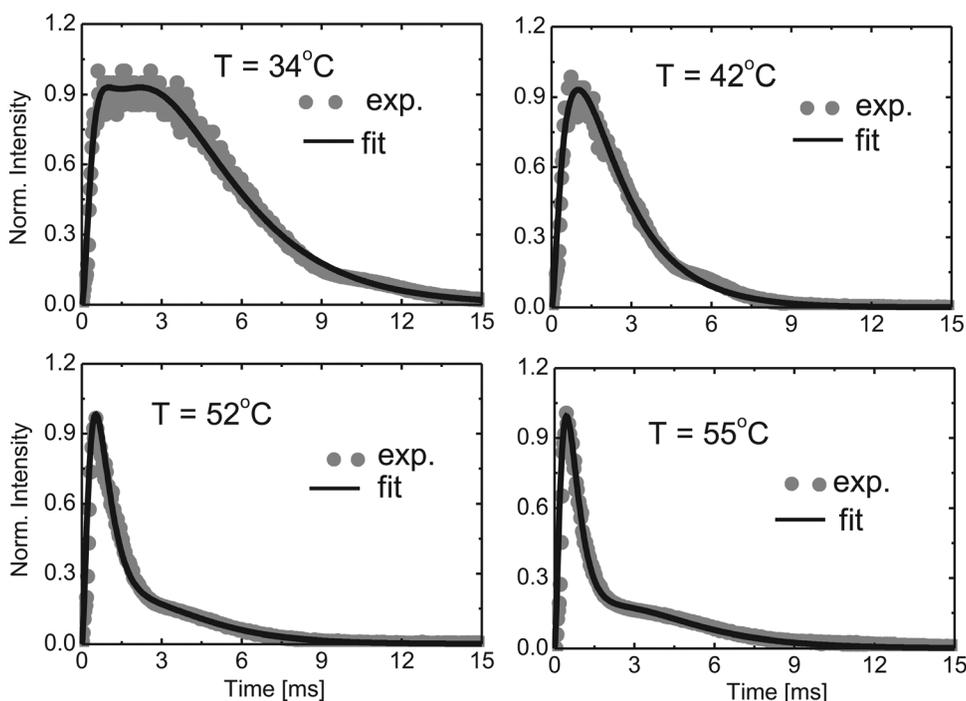

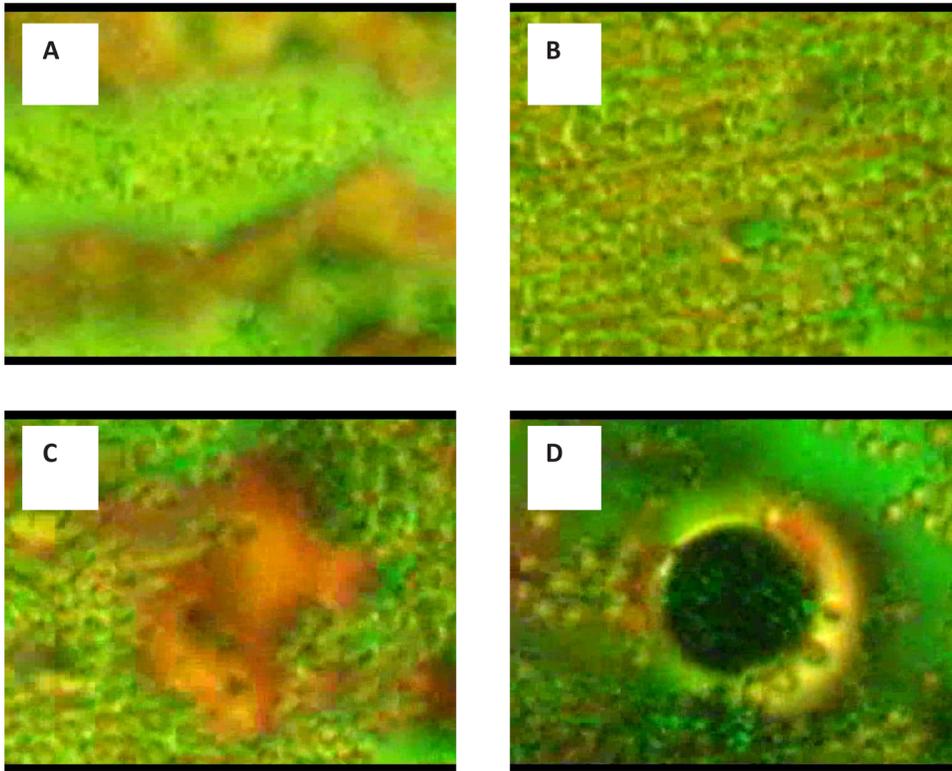FIG. 2. Pulsed-laser-induced OKE signal for different temperatures T.

FIG. 3. (Color online) Optical micrographs of PcLCP sample being in: (a) initial state, (b) state based on the molecular reorientation, (c) state based on common interaction between the molecules, and (d) isotropic final state.

with the amplitude a and rate constant k_1, which reaches the metastable B state (cf. Fig. 3(b)). The second consecutive process, characterized by the amplitude b and rate constant k_2, and which leads to the C state, is a consequence of common interaction between the molecules being in the same liquid-crystalline domain, and which forces the resultant position of the molecules (cf. Fig. 3(c)). Finally, we start to observe the relaxation from C to D state, with the rate constant k_3 and amplitude c (cf. Fig. 3(d)).

Example photos done by a polarizing microscope, which show the PcLCP sample in A, B, C, and D states, are presented in Fig. 3.

According to Malus's law, measured OKE signal intensity I is a function of two phenomena described above, which are related to the interaction between the electric field of electromagnetic wave and liquid-crystalline photochromic molecules (B) and common interaction between the liquid-crystalline photochromic molecules in the domains (C).

$$I = i_b \cdot \sin^2 c_B + i_c \cdot \sin^2 c_C. \tag{5}$$

Both states are characterized by the amplitudes i_b and i_c, respectively.

In Fig. 4, we present an example of the experimental curve of the pulsed laser-induced OKE signal I, for temperature $T = 52\,^{\circ}\mathrm{C}$, fitted by the theoretical curve, which is a sum of both B and C states according to Eq. (5).

The changes of the amplitudes b and c of both processes as a function of temperature are presented in Fig. 5. One can clearly observe that there is a strong linear dependence between the size of the amplitude and temperature of the PcLC sample. Increasing the temperature, we change the domination of the molecular reorientation process on the mechanism of the interaction between the molecules in the domains.

Determined values of the rate constants k_i and their temperature dependences in the studied PcLCP system are presented as Arrhenius plots (cf. Eq. (6)) in Fig. 6.

$$\ln k_i = -\frac{E_{ai}}{RT} + \ln f_i, \tag{6}$$

where E_{ai} is the activation energy, R is the gas constant, T is the absolute temperature, and f_i is a constant correlated with the frequency factor of the ith process.

Using Eq. (6), we have calculated the activation energies for each process, which are: $E_{a1} = 32$ kJ/mol, $E_{a2} = 84$ kJ/mol, and $E_{a3} = -39$ kJ/mol. The calculated time constants τ_i and amplitude values b and c obtained, fitting the experimental curves for different temperatures T, are collected in Table I.
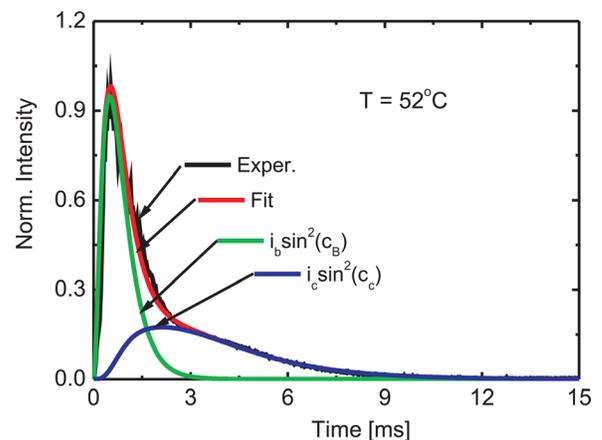

FIG. 4. (Color online) Experimental and theoretical curves of the pulsed-laser-induced OKE signal for temperature $T = 52\,^{\circ}\mathrm{C}$.
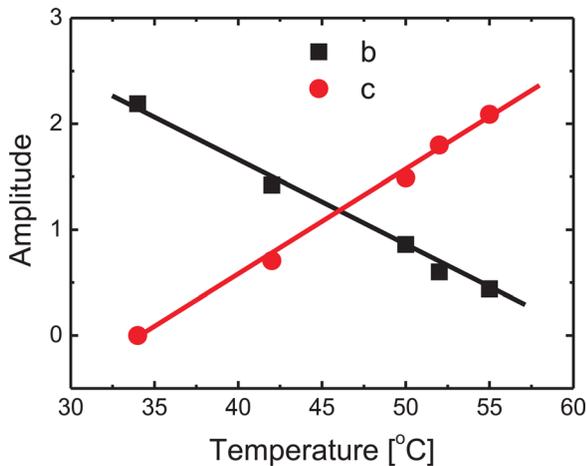
FIG. 5. (Color online) OKE amplitude changes as functions of temperature.

TABLE I. Estimated values of OKE time constants τ_i and amplitudes b and c for different temperatures T.

T (°C)	τ_1 (ms)	τ_2 (ms)	τ_3 (ms)	b	c
34	0.61	5.30	1.73	2.19	0.00
42	0.44	2.60	2.55	1.42	0.71
50	0.33	1.10	3.74	0.86	1.49
52	0.31	0.90	4.00	0.60	1.80
55	0.28	0.70	4.63	0.44	2.09

Obtained experimental data and calculated values show that there is a strong influence of temperature on time constants and amplitudes of each of the three processes. For the first process, which is responsible for the reorientation of the LC molecules (cf. Fig. 3(b)), the time constant τ_1 decreases from 610 μs down to 280 μs, and this process is characterized by the activation energy of $E_{a1} = 32$ kJ/mol. The second consecutive process, which is responsible for the reorientation of the LC molecules in the formatted domains (cf. Fig. 3(c)), because of the common interaction between the liquid-crystalline photochromic molecules, also strongly depends on the temperature of the system. The τ_2 decreases from 5.3 ms down to 0.7 ms for the temperature $T = 34$ °C up to 55 °C, respectively. We also observe that amplitude b of this process decreases as a function of temperature, which means that sizes of the domains containing molecules in the nematic phase decrease as well. This process is characterized by the activation energy of $E_{a1} = 84$ kJ/mol.

For the last process, we observe a completely different behavior. The time constant τ_3 increases from 1.73 ms up to 4.63 ms for the temperature $T = 34$ °C up to 55 °C, respectively, and it is important that this process is characterized by the negative activation energy of $E_{a1} = -39$ kJ/mol.
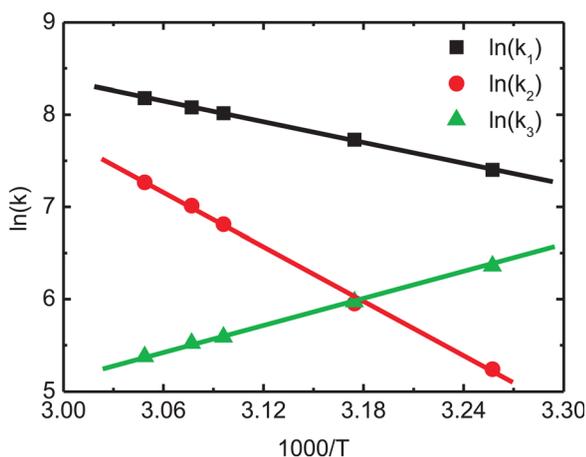
Unfortunately, we could not find an exact explanation of such behavior. In our opinion, these dependences can be understood as the sum of two phenomena, which lead to the isotropic domain formation (cf. Fig. 3(d)). The first is due to the dominance of molecules in the *cis* state, which destabilizes the LC phase, and the second is due to the temperature of the system, which destabilizes the LC phase as well.

Finally, when there is no liquid-crystalline state and molecules are in an isotropic state, we stop to observe the OKE signal, but it does not mean that there is no interaction between the pump light and molecules. In the isotropic phase, there are no common and collective interactions between the molecules and the effective signal, which could be observed in an extremely weak state. The opposite situation occurs when the sample is in the crystalline state. We also do not observe the modulation of incoming light, but, in this case, the molecules are highly packed, with not enough space for efficient reorientation.

IV. CONCLUSIONS

In summary, dynamic switching of optical birefringence in an optical Kerr-effect experimental set-up was measured for photochromic liquid-crystalline molecules in the nematic phase, as a function of temperature. Very short switching time (in the range of microseconds) was observed. The mechanism of OKE signal formation and dynamic optical switching is based on molecular reorientation and interaction between the molecules in the liquid-crystalline domains upon the pulsed laser light illumination and temperature changes. It was observed that there is a strong correlation between the amplitudes and rate constants of each process as a function of temperature. Very short times of OKE signal formation and full reversibility make this material a very promising candidate for, e.g., all optical switching or retrieval of optical information.

For a better understanding, as well as approval of, the switching times and activation energy in this kind of material, further studies, like microscopic measurements or the influence of changes of the length of side chain groups, are required.

FIG. 6. (Color online) Logarithmic plots of the rate constants k_i vs inversed temperatures.

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