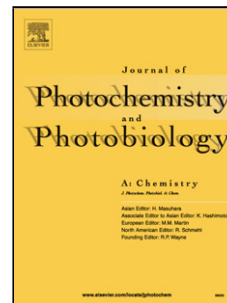# Accepted Manuscript

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Induction of the vector polyphotochromism in side-chain azopolymers

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Graphical Abstract
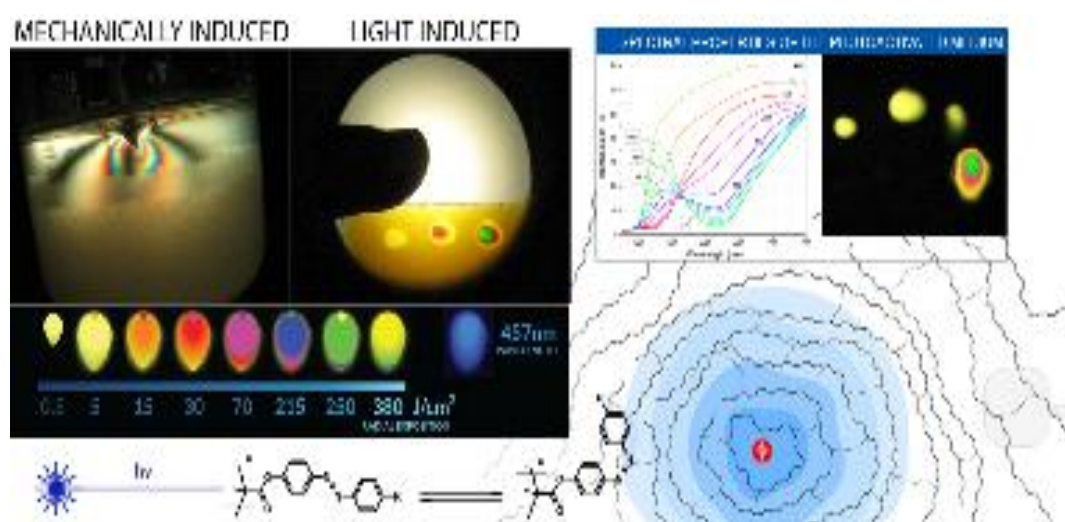
Highlights

- We found the effect of photoinduced changes in the spectral properties of the material within the entire visible range.
- The further investigation of this vector polyphotochromic effect is presented.
- Phenomenon is related to the photoelastic interference quenching of probing beams.
- We prove the relationship between the chemical composition and material optical properties.

ABSTRACT

The phenomenon of vector photochromism was observed in some high-efficient polarization-sensitive materials depending on the radiant exposure of the inducing linearly polarized actinic light. When radiant exposure exceed certain value specific to each material, a sharp change in the transmission spectrum of the probing linearly polarized nonactinic beam is observed after analyzer. While probing with unpolarized light the transmission spectrum is practically unchanged and does not depend on the magnitude of the radiant exposure. The mechanism of this phenomenon is discussed. The effect is an interference nature and depends on the path difference between the ordinary and extraordinary rays in material with photo-induced anisotropy. It is shown that the kinetics of this effect depends on the photosensitive layer thickness and the concentration of the chromophore.The beams with a wavelength away from the

absorption band of the material were used as a probing. It is shown that in this case birefringence has made the main contribution in photoanisotropy. The experiments were carried out for polarization-sensitive materials with varying degrees of components integration, in particular, two synthesized side-chain azopolymers obtained by immobilization of polar azo dyes on polymethylmethacrylate backbone. It is shown that the maximum value of the birefringence Δn = 0.162 achieved in azopolymers with covalently bonded components. In this case a third order of interference of the probing beam is observed.

1. INTRODUCTION

As is well known scalar photochromism is a reversible phototransformation of a chemical structure between two forms having different absorption spectra. It is observed under the action of actinic light regardless of its polarization state. This property is widely used in science and engineering. This phenomenon is well studied and a large number of papers are devoted both to the study of this phenomenon and to its applications [1], [2] and [3]. It is known that in conventional polarization-sensitive materials photoanisotropy is induced under the action of actinic polarized light. It reaches its maximum and then remains unchanged even after long exposure, remaining at a level of saturation, during which there is the maximum transmission of the probe beam (Figure 1, curve 1) [4-10].

Unlike this in some high-efficient polarization-sensitive materials obtained by us, we have observed the anomalous kinetics of photoanisotropy induction after reaching its maximum value when material is exposed by actinic linearly polarized radiation and simultaneously is probed by monochromatic nonactinic linearly polarized light beam [11], [12] and [13] the intensity of the transmitted probing beam starts decreasing with radiant exposure of inducing light increasing and almost reaches zero for the given wavelength of the probing beam (Figure 1, curve 2). The intensity of the probing beam passing through the exposed material essentially depends on radiant exposure of the inducing light, on a wavelength of the probing beam and on the thickness of the material film.

It was shown [11], [12] and [13] that this phenomenon has purely vector nature because the transmission of the material is practically unchanged at different radiant exposures during probing by nonpolarized light. However, an essential change in transmission was observed under probing the sample by linearly polarized nonactinic light. This phenomenon can be observed between crossed polarizers. It has been shown [11] that this phenomenon has an interference nature and it is related to the increase in path difference of the ordinary and extraordinary rays when the probing beam passes through the sample.

In this paper the results of the further investigation of this phenomenon in side-chain azopolymers are presented and the kinetic curves of transmission are shown, which were obtained for two wavelengths of probing beam (532 nm and 635 nm) and for different exposure with linearly polarized light, actinic for material under investigation (445 nm). It is also shown that the kinetics of the effect depends on the degree of the molecular integration of the material components by the cohesion of both ways the electrostatic forces (by use mineral electrolytes and polyelectrolytes) and the covalent bonds (azopolymers based on different chromophores), as well as on the photosensitive layer thickness and the concentration of the chromophoric component. The mechanism of the phenomenon is discussed.

2. PHOTOMETRIC MEASUREMENTS

For quantitative description of anisotropy induced by polarized light the method of description photoinduced anisotropy is based on the characteristic which can be obtained by one measurement. This parameter was introduced and investigated in [14] and was called the effective anisotropy of the medium.

Let the anisotropic medium is described by the Jones matrix [15]

$$M = \begin{pmatrix} \exp\left(-i\kappa d \hat{n}_1\right) & 0 \\ 0 & \exp\left(-i\kappa d \hat{n}_2\right) \end{pmatrix} \qquad (1)$$

.

Here $\hat{n}_1$ and $\hat{n}_2$ are complex refractive indexes of the medium, d is the thickness of the medium, $\kappa = \frac{2\pi}{\lambda}$,

λ is a wavelenghth of the inducing light.

The module of the anisotropic invariant of the matrix (1), which was called effective photoanisotropy of the medium, is presented as [14]

$$A_{eff} = \frac{1}{4}\left|\exp\left(-i\kappa d\hat{n}_1\right) - \exp\left(-i\kappa d\hat{n}_2\right)\right|^2 = \frac{1}{2}\exp\left[-2\kappa d\left(\overline{n\tau}\right)\right]\left[ch\kappa d\Delta\left(n\tau\right) - \cos\kappa d\Delta n\right], \quad (2)$$

where $\left(\overline{n\tau}\right) = \frac{1}{2}\left[(n\tau)_1 + (n\tau)_2\right]$ is the average absorption coefficient, $\Delta(n\tau)$ and Δn characterize the anisotropy of absorption and birefringence respectively.

We can see from (2) that the value of effective anisotropy is defined by joint contribution of anisotropic characteristics of the material (birefringence and anisotropy of absorption) and its transmission. The analysis of the expression (2) shows that with the growth of Δn and $\Delta(n\tau)$ a multiplier in brackets taking into account the summary contribution of birefringence and anisotropic absorption. This parameter allows different light-sensitive materials to be described and to be compared by a simple way.

If probing is carried out by the light beam with a wavelength outside the absorption band then we obtain from (2)

$$A_{eff} == \frac{1}{2}\left[1 - \cos\kappa d\Delta n\right] \qquad (3)$$

It follows from (3) that

$$,\Delta n = \frac{1}{\kappa d}\arccos\left(1 - 2A_{eff}\right) + m\pi \qquad (4)$$

where $m = 0, 1, 2, \ldots$ in the maximum and minimum points of the kinetic curve (however, we have fractional values of m at intermediate points of the kinetic curves corresponding to the values of A_{eff} for this radiant exposure).

For the experimental measurement of effective anisotropy in [14] it was shown that A_{eff} is equal to the transmission of anisotropic medium placed between crossed polarizers at an angle between the axis of anisotropy and the axis of one of the polarizers equal to 45^0 and it is measured in units of intensity. But it is convenient to measure this value in the experiment in % relative to the transmission of the unradiated sample placed between parallel polarizers.

To study the properties of the polarization-sensitive materials and kinetic of photoanisotropy induction in them under the action of polarized actinic light, we used the laboratory photometric set-up, the optical scheme of which is shown in Figure 2.

.

In the experimental scheme we used DPSS laser emitting the light with a wavelength of 445 nm which is actinic for all the used materials as they have a reasonable spectral absorption on that wavelength to induce the essential phototransformation of the azodye chromophore component molecules. As a probing beam we used laser at a wavelength of 532 nm and 635 nm.

A linearly polarized actinic laser beam induced the photoanisotropy in the investigated samples and then was blocked behind the sample by an appropriate filter. Simultaneously the probing beam passed the sample through the photoactivated area. This beam is linearly polarized at an angle of 45 degrees to the polarization of the inducing beam. The analyzer is oriented orthogonally to the polarization of the probing beam. In case of the absence of photoanisotropy (if the sample is isotropic) the probing beam did not pass through the

analyzer. In case of optical anisotropy induction, the axis of which corresponds to the direction of the polarization vector of the inducing beam (that is, makes 45 degrees with the polarization vector of the probing beam) some portion of the intensity of the probing beam passes through the analyzer and this intensity unambiguously depends on the value of inducing photoanisotropy. Note that both the wavelengths of probing (532 and 635 nm) are far away from the absorption band of the polarization-sensitivity material. In this case linear birefringence has a major role and dichroism can be neglected.

For some samples of high-efficiency polarization-sensitive material the anomalous behavior of kinetic curve for A_{eff} (Figure 1, curve 2) have obtained. The value of A_{eff} reached nearly zero at high exposures.

3. VECTOR POLYPHOTOCHROMISM

We have observed the unusual course of the kinetic curve of the probing beam transmission (Figure 1, curve 2) in some high-efficient polarization-sensitive materials during their by linearly polarized actinic radiation and simultaneous probing by monochromatic nonactinic linearly polarized light beams. The result of an interaction of light with the observed materials depends on the probing light wavelength and on the actinic light exposure rate. The preliminary results of the investigation of this phenomenon were presented [11], [12] and [13].

In [12] and [13] we used the high-efficient polarization-sensitive material in the form of a solid solution based on the ammonium salt of the polyhydric acid azodye Mordant Pure Yellow (MPY-NH$_4$) doped into the matrix of photogelatin. We used the samples with the thickness of about 20 μm. The absorbance spectra were obtained in polarized light for different exposures from 0 to 250 J/cm^2 and a series of experimental spectral curves was obtained and converted to the transmission curves subsequently (Figure 4). At the same time, the transmission spectra in unpolarized light differ insignificantly for the various radiant exposures (Figure 3).

We have assumed that this phenomenon is related to the interference quenching of probing beam, which occurs as a result of the path difference between the ordinary and extraordinary rays when the probing beam passes through the photoactivated medium. The value of the path difference depends on the photoelastic coefficient and thickness of the material film. As a result of the selective absorption of a quantum of inducing linearly polarized light the chromophore molecule undergoes trans-cis isomerization, which in turn leads to the appearance of ordered microstrains in polymer matrix of the material. And since the polymer matrix possesses photoelasticity, then the ordered microstrains result in macroscopically observed anisotropy. When reach a certain level of photoanisotropy for which the birefringence coefficient Δn reaches such magnitude that the path difference of the ordinary and extraordinary rays of the probing light equals to the half of its wavelength, in this case the transmission of the probing beam for given wavelength will be maximum. A further increase in exposure leads to increase in Δn and, accordingly, to increase in the path difference, which in turn results in interference quenching and in case the path difference equals to wavelength the probing beam is totally quenched [11].

It must be emphasized that in this case the value of photoanisotropy actually increases even though the intensity of the probing beam is reduced periodically. In order to confirm this assumption, the kinetics of the probe beam transmission has been investigated in case of gradual increase in the components interaction at the molecular level. In particular, by increasing an interaction between the components (molecules chromophores and polymeric matrix), gradually increasing their electrostatic interaction by introducing different electrolytes with various concentration, as well as immobilization via strongest (covalent) bond between the molecule of the chromophore and the polymer matrix, by synthesis azopolymers of a side-chain type.

We have used hydrophilic polymer as a matrix for the investigated materials. This circumstance leads to a condition of using only water-soluble dye as chromophore components. According to our assumption the level of attainable photoanisotropy in water-soluble media should be raised all the more. This is expected due to formation of dipole-dipole bonds between the polymer macromolecules (Figure 5a) and even more durable, ion-dipole bounds (Figure 5b) that are already formed between the polar dye and polymer molecules. That is really confirmed experimentally in the results of the further investigation of materials obtained entirely in the water-soluble basis.

We have obtained several series of the samples of the high-efficient polarization-sensitive materials with electrolytes introduced in them with increasing concentrations. Molecules of these electrolytes have a high dipole moment. The latter play a role of ion cross-agents for gelatin matrix having polyampholytic nature and connect their macromolecules with additional, stronger cross-interacting forces (Figure 5 (b)).

Three types of high-polar electrolytes with different dipole moments of their molecules were selected for investigations: sodium and ammonium chloride and potassium bromide [16]. Samples were obtained with addition of these electrolytes with different concentrations. Each sample was irradiated with linearly polarized laser beam with a wavelength of 445 nm and probed with polarized light beam at 635 nm. The kinetic curves of transmission were obtained.

The results of the investigation concerning incorporation of electrolytes into the material have confirmed that this polyphotochromatic effect is revealed the brighter, the more polar electrolytes are added into material. For the purpose of adequate comparison, an investigation was carried out in case of conservation of physical parameters for all test samples and also of the same content of the same amount of polymer and chromophore components in it. The necessary difference was regulated by addition of electrolytes of different nature and variation of their amount in the total composition.

As the base material the solid solution of gelatin was used containing chromophore Mordant pure yellow, in which the role of a weak electrolyte plays water molecules Figure 5 (a). Then, NaCl (sodium chloride), NH$_4$Cl (ammonium chloride) and KBr (potassium bromide) were individually doped to the compositions of the materials and samples were created with various amounts of these electrolytes. The character of the phenomenon was investigated on example of the probing light at 635 nm. The results are shown in Figure 6.

It is seen from these curves that the material with ammonium chloride is most effective and although the polarity of its molecule is slightly worse than the polarity of potassium bromide molecule, it is more soluble in water and this leads to the possibility of increasing its concentration. Thus the addition of efficient electrolyte leads to greater integration of the components of the material, results in faster growth of photoanisotropy and in more pronounced effect of vector photochromism.

In addition, the thickness of the samples has a significant impact to the effect based on interference with the path shifting between the ordinary and extraordinary rays and as a result on the brighter appearance of vector polyphotochromatic effect. The results of the investigation of dependence on the thickness are shown in Figure 7.

in the material samples based on MPY-NH4 with thickness: (a) 5 - 27 microns; (b) 33-80 microns.

These curves clearly show that the increase in the thickness causes the increase of this effect.

We identified several conditions enhance the described light-induced effect, one of the most influential which turned out to be obvious is the degree of a mutual integration of the material component molecules [12]. To the end, we have synthesized a side-chain type azopolymers [17] and [18] which are immobilized

azodyes 4-[4-(trifluoromethyl)phenyl]phenol and 4-[(4-hydroxyphenyl)diazenyl]benzonitrile on polymethylmethacrylate (Figure 8, Formula B). In these azopolymers the chromophores are linked to the polymer by a covalent bond.

We have investigated the kinetics of the probing beam transmission through the exposed area of the synthesized materials (Figure 9):

Optical density and thickness in samples of all materials were the same. For comparison, in the bottom of Figure 6 there are the kinetic curves of the transmission for solid solutions in methylmethacrylate (without covalent bonds) with the same optical density of actinic light as in side-chain azopolymers. It is seen from Figure 6 that the covalent bond obviously increases the level and speed of achievement high values of photoanisotropy which results in appearing the vector polyphotochromism effect. In addition, the thickness of the samples has a significant impact on the path difference between the ordinary and extraordinary rays and as a result on the appearance of this effect. The dependence on the thickness is shown in Figure 7.

The curves of changes in the probing beam intensity when it passes through the sample are found to have a different shape in case of probing beams with different wavelengths. Figure 10 shows the kinetic curves of transmission obtained by means of photometric set-up (Figure 2) and the corresponding values of birefringence Δn induced in the samples of MY-26/GEL and Material-2 obtained by probing beam with wavelengths of 635 nm and 532 nm. The inducing radiation with a wavelength of 445 nm and an irradiance of about 750 mW/cm^2 have been used.

As can be seen from the curves on Figure 10, the value of induced photoanisotropy and rate of its rise increases significantly with increasing mutual integration of the polarization-sensitive material's components. For materials with the strongest integration, in the side-chain azopolymers with covalent bonds between the chromophore and polymer matrix molecules the third order of interference of the probing beam is observed in the kinetic of transmission. In this case the maximum value of the induced birefringence reaches 0.162 for the Material-2.

4. CONCLUSIONS

We have carried out the further investigation of the phenomenon of vector polyphotochromism. It was shown that the kinetics of the effect depends on the degree of integration of the component of the polarization-sensitive material and the value of induced photoanisotropy and rate of its rise increases significantly with increasing the mutual integration of the polarization-sensitive material's components.

Vector photochromism observed in materials in which at least a second order of interference of the ordinary and extraordinary rays is achieved (the path difference is more than λ/2), and respectively Δn is more than 0.04. In materials with the strongest integration, in the side-chain azopolymers with covalent bonds between the molecules of the chromophore and the polymer matrix the third order of interference of the probing beam is observed in the transmission kinetics and thus the maximum value of the induced birefringence reaches 0.162.

Vector polyphotochromic effect may be used for creating the spectrally selective dynamic polarization holographic gratings recorded in two beams of equal intensity with varying energy exposures; as a result, the beam diffracted on the grating will have different wavelengths. Such dynamic gratings in turn can be used in wavelength-division multiplexing (WDM) technology for all-optical switches, as well as for creating light-controlled spectral valves. Similarly, this effect can be used for indicators and displays and also for creating spatial light modulators and dynamic polarization spectral filters controlled by light.

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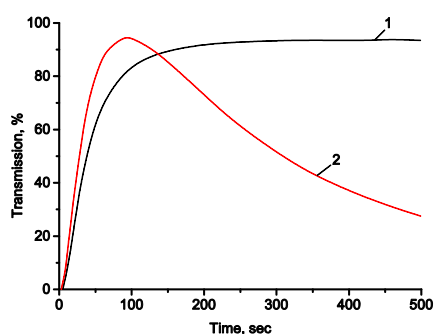

Figure 1. Kinetic curves of photoanisotropy induction:
1 – usual course; 2 – unusual course
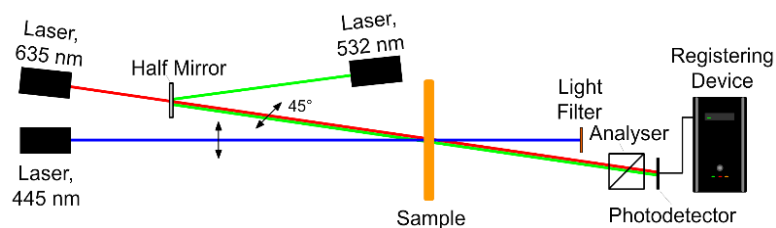
Figure 2. Experimental setup for investigation of the photoanisotropy kinetics.

EXPOSITION	H0	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
J/cm^2	0	30	60	80	86	94	106	130	170	215	250
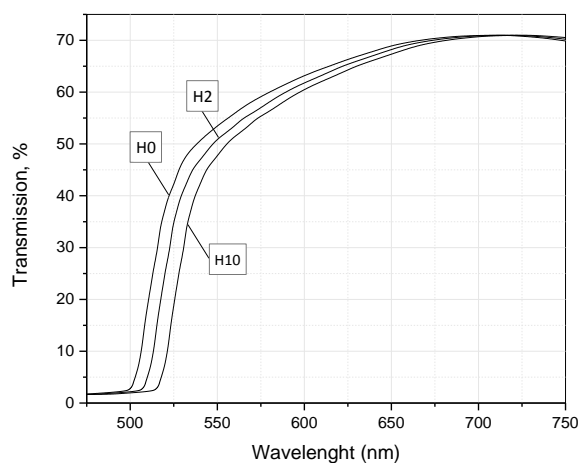
Figure 3. Transmission spectra of the sample material

in case of **unpolarized** probing beams for the different

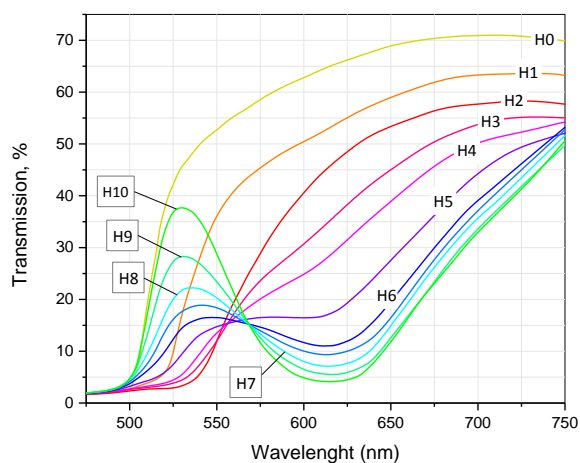actinic light exposures from 0 up to 250 J/cm²

Figure 4. Transmission spectra of the sample material

in case of linearly **polarized** probing beams for the

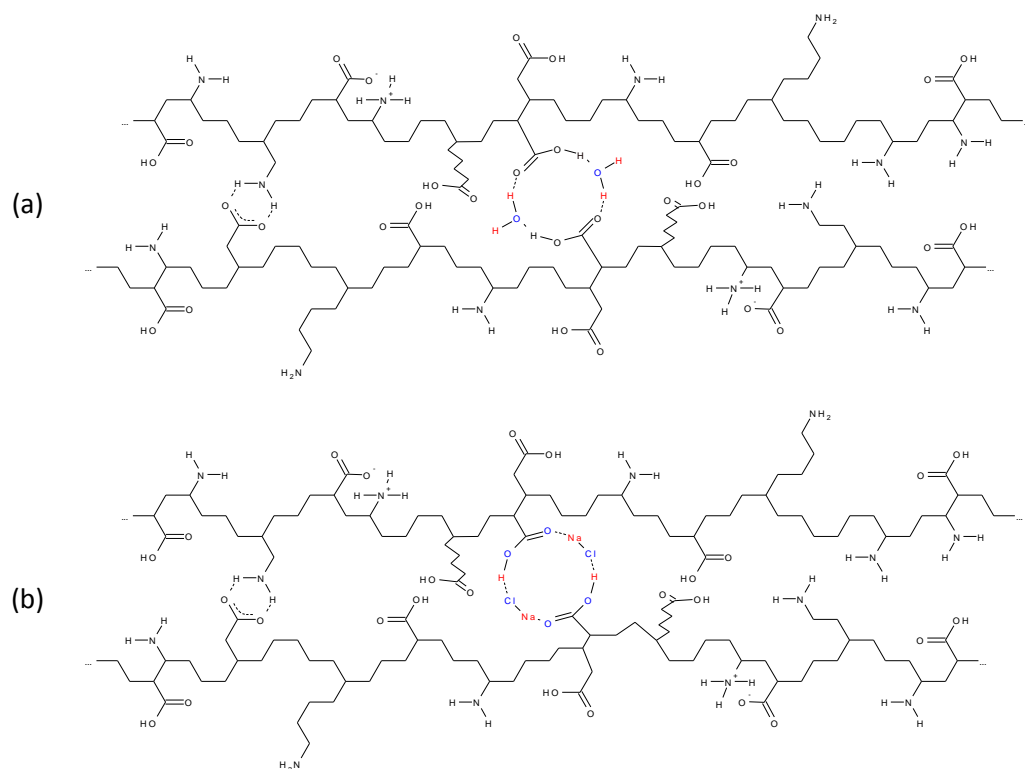different actinic light exposures from 0 up to 250 J/cm²

Figure 5. Scheme of the formation of dipole-dipole (hydrogen bonds) (a) and ion-dipole (b) intermolecular bonds

(via electrolytes) in polar water-soluble compositions. Example is given for the gelatin based materials.
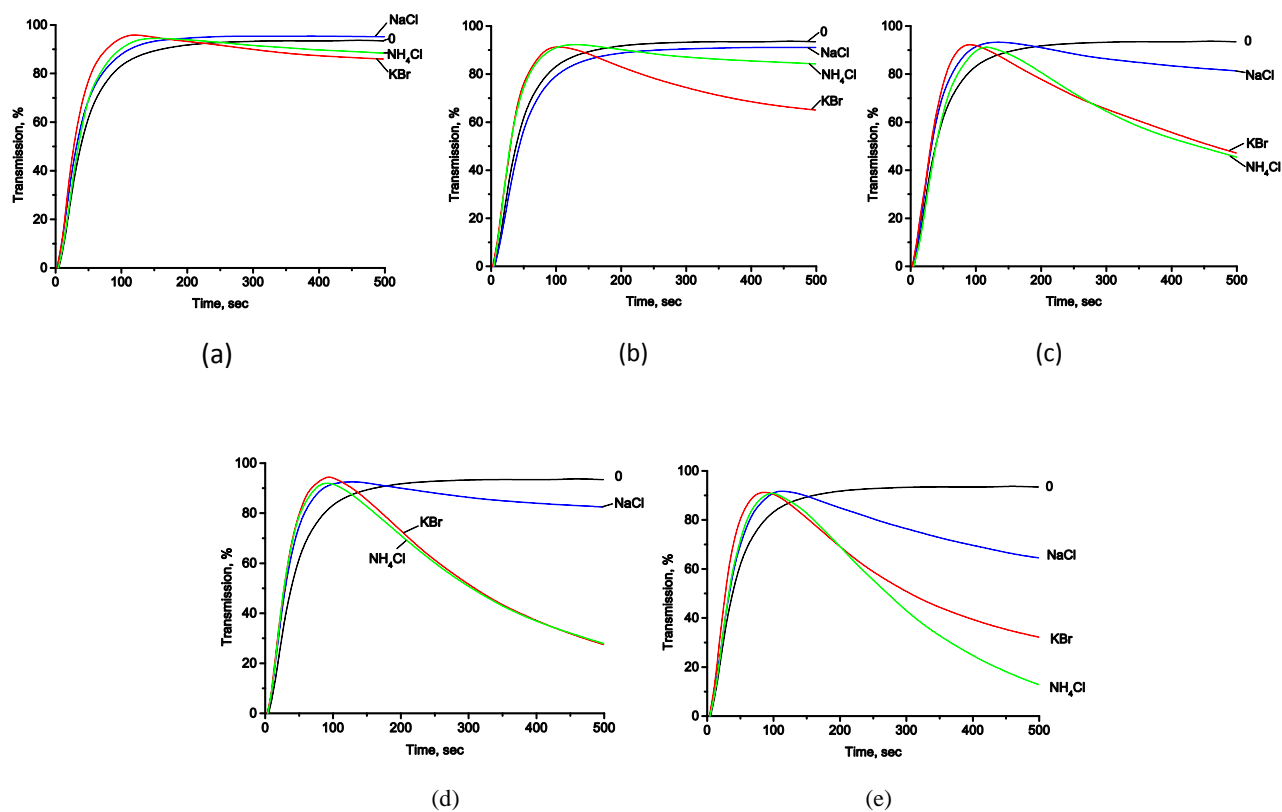
Figure 6. The curves of the kinetics of photoanisotropy induction in polarization- sensitive materials with various electrolytes quantity: (a) 50 micromoles; (b) 100 micromoles; (c) 200 micromoles; (d) 400 micromoles; (e) 800 micromoles. Probing beam wavelength is of 635 nm.
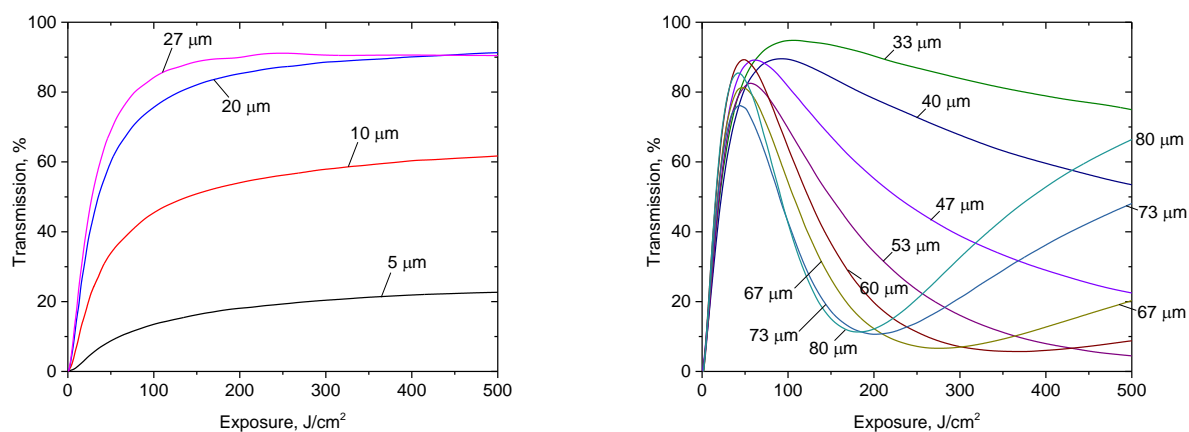
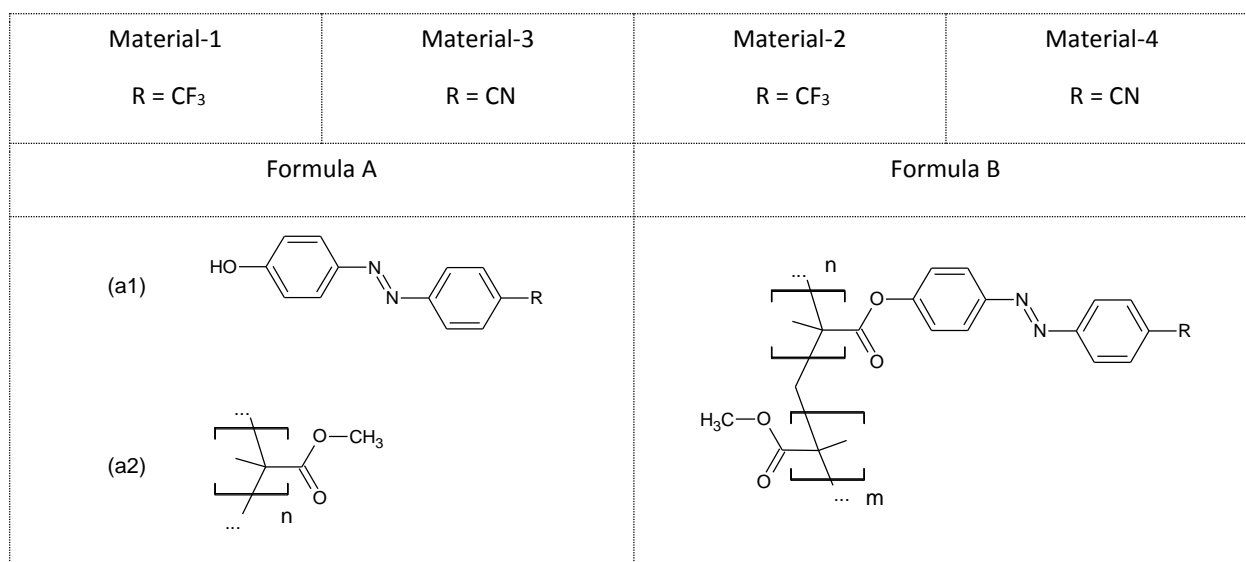Figure 7. Dependence of the kinetics of the probing beam transmission on the thickness obtained

Material-1	Material-3	Material-2	Material-4
R = CF₃	R = CN	R = CF₃	R = CN

Where R = CF$_3$, R = CN, R = CF$_3$, R = CN

Formula A		Formula B	
(a1)	[chromophore structure]		[integrated polymer structure with n and m]
(a2)	[polymeric structure with n]		

Figure 8. **Formula A** - components of photosensitive material: chromophore (a1) and polymeric (a2);

Formula B – integrated material: polymethylmethacrylate azopolymer containing azodye R-phenylazophenol

in side chain in molar proportion of n = 1; m = 7. Where in **Material-1** and **Material-2** radical R = CF₃ and

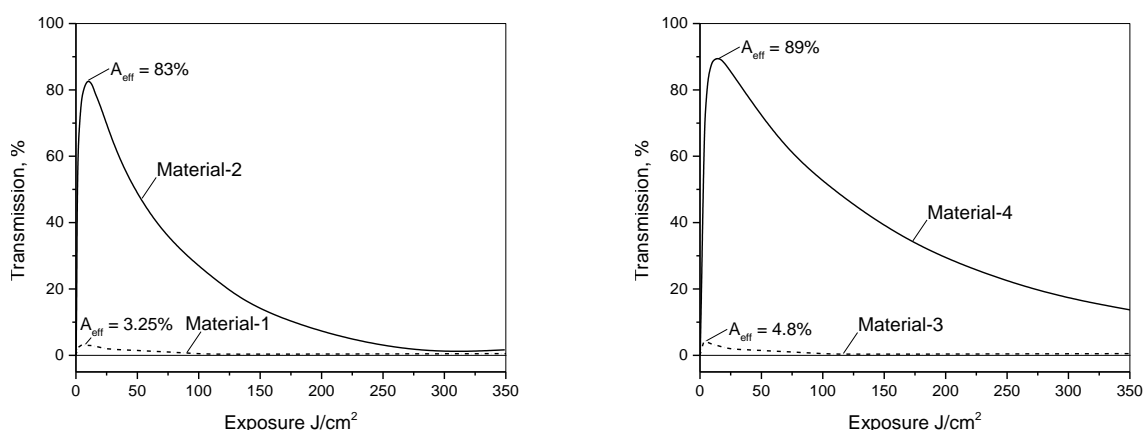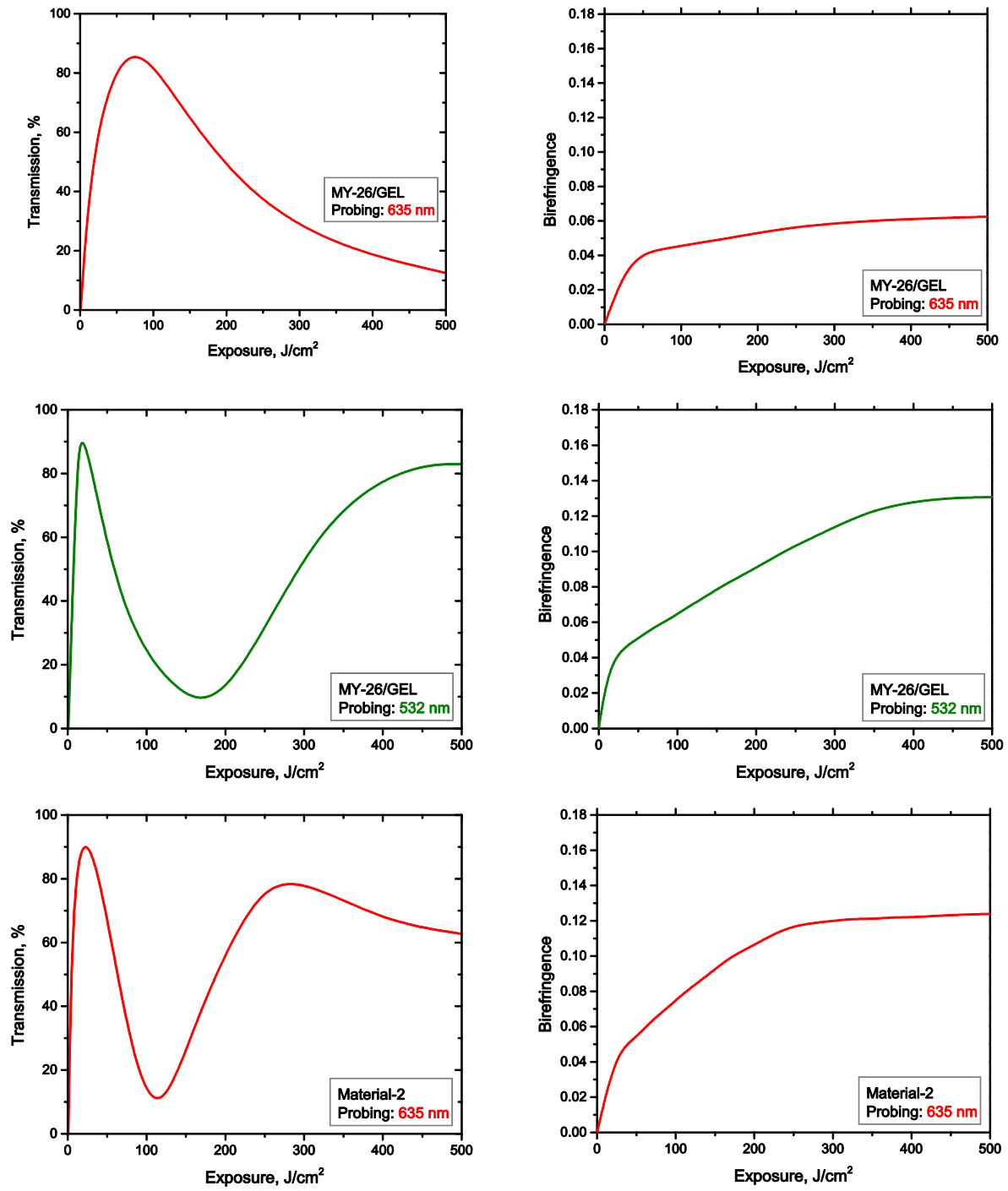in **Material-3** and **Material-4** radical R = CN.

Figure 9. Kinetics of the probe beam transmission by the researched materials (see Figure 5 for structures):
curves **Material-1** and **Material-3** are the solid solutions of components without covalent binding; curves

Material-2 and **Material-4** are azopolymers with components connected by covalent bonds (for 635 nm
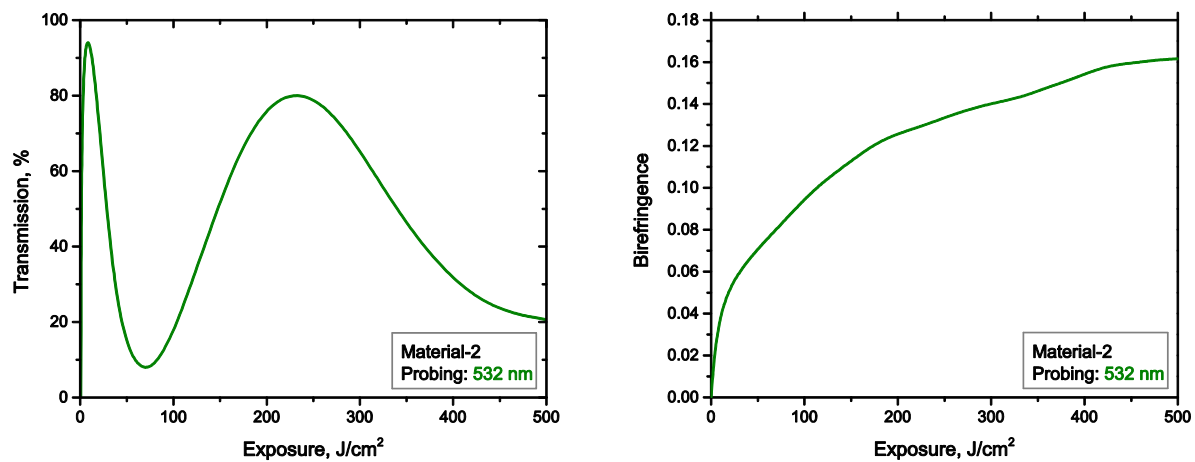
probing beam).

Figure 10. Kinetics of transmission of the probing beam intensity and kinetics of birefringence Δn to be induced in a sample of the material based on MY-26/GEL and Material-2 for two wavelengths of the probing beam 635 nm and 532 nm. Irradiance of the inducing beam (445 nm) was about 750 mW∕cm².