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Review Paper

Vectoral response under photo-excitation in amorphous chalcogenides and azobenzene polymer films: a comparison

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The combination of different features of light-sensitive materials, such as amorphous chalcogenides and azobenzene polymers has been considered. A considerable amount of experimental data describing different aspects of photostimulated transformations reflected in the changes of optical and mechanical properties of the given materials has been analyzed. The main attention has been paid to polarization-dependent (vectoral) effects. Stimulated orientational changes and opto-mechanical effects of different kind have been discussed. The possibilities of application of the effects and phenomena under analysis, in particular all-optical patternings have been speculated.

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1. Introduction

In the present work we give a brief review of results obtained for fundamental studies of non-crystalline chalcogenides and azo-dye containing polymers, paying a special emphasis on revealed astonishing congeniality and, separately, on indicated differences in the changes of properties of photo-responsive media under the actinic light illumination. Our main goal is not only to estimate a considerable volume of experimental and interpretation achievements got but proceeding from them to try to catch important details of the internal mechanism of transformations through which the sensitivity of these amorphous materials to the polarization state of light waves is revealed. It is usually accustomed to position the corresponding effects as being marked by the domination of vectoral (spatially anisotropic) response of the solid medium under its resonance interactions with the field of optical radiation. In our image about the nature of photostimulated transformations we tried to take into account the known interconnection and interdependence of accompanied changes, which was usually accepted to interpret separately the phenomena of photo-structural and photomechanical responses. Moreover, every time we concentrated our attention on the revealed correlations that according to our imagination dictate the integrated direction and temporary dynamics of substantial changes in structural, mechanical, optical and morphological properties.

The detailed information necessary for an independent, more profound and comprehensive comparative analysis of the behaviour of photosensitive amorphous chalcogenides and azobenbenzene copolymers can be found in the series of review articles [1-5] and [6-8], respectively. Thus, even the first smattering consideration of collected experimental achievements and developed interpretation on their basis during the last decade by two actually independent research communities exhibited the presence of a number of direct "cross-resonance" responses. Moreover, it is expedient to assume that structurally conditioned inherent prerequisites exist, which preset the mutual likeness of the photo-responsive behaviour of disordered media of amorphous chalcogenides (ACh) and azobenzene functional materials. By understanding this we began to search of uniting driving reasons of transformations through which is possible to declare agreement of dynamics of stimulated changes with the transformations themselves. The main attention has been paid to the results of studying the properties of ACh and azobenzene-containing polymers with the domination of effects of photo-stimulated linear reversible birefringence [9-11], [12-15], and dichroism [16], [17], polarization-sensitive light-induced material transport [18-21], [22]. We consider that usually interpreted as the scalar photoexpansion effect, it closely attaches to the above vectoral phenomena in whose dynamical changes the reversible and non-reversible components were definitely distinguished [23], [24].

We'll admit that both types of photosensitive media taken into consideration have a real perspective of practical applications. There are, firstly, active components for reversible and nonreversible optical storage and processing, submicron lithography, in which the realization of advantages of nanofabrication procedure becomes important, and secondly, all-optical switches, non-linear optical devices, diffractive optical elements and inscription of channel waveguides.

Trying to preserve the maximal correctness in the comparative analysis, further on we deliberately restricted the circle of consideration by well-known "classic" objects of study, as amorphous films of As-S(Se) systems and non-crystalline polymers of pDR1M type. For the latter azoaromatic Disperse Red (DR1) chromophores were chemically linked (covalently grafted) to a polymethylmetacrylate (PMMA) matrix.

2. Orientational memory and reversible optical anisotropy

Among well-known vectoral effects with which the behaviour of ACh and dye-functionalized polymers with polarized light illumination is altered one should recollect the phenomenon of optical anisotropy in the form of a linear birefringence and photodichroism.

For non-crystalline materials under consideration a synopsis of optical anisotropic effects was initiated in 1977 by the demonstration of reversible birefringence in amorphous a-As_2S_3. As it was reported for the first time by Zhdanov et al. [9], the parameter of negative birefringence $\Delta n = n_{||} - n_{\perp} < 0$ is of the magnitude $\sim -2\times10^{-3}$. Here $n_{||}$ and $n_{\perp}$ are the refractive indices, determined by polarization directions, parallel and perpendicular to the electric field vector of the initiating polarized light, respectively. The reversible (rewriting) birefringence had the same level of magnitude ($|\Delta n| < 3\times10^{-3}$) (Fig. 1, a) while studying a wide range of compositions of a-As-S(Se) films. It was also shown that the negative optical anisotropy (birefringence and photodichroism) in the medium of ACh could be induced with bandgap and sub-bandgap illumination of linearly or circularly polarized light. In both cases the parameter of normalized linear dichroism did not go outside the limit of ~ -0.02 [16].

On the other side, it was firstly reported by Todorov et al. [12] about the creation of negative birefringence in amorphous azobenzene polymer material under resonant linearly polarized visible light. Later the linear birefringence and accompanying photodichroism effect, stimulated under resonant condition, one by one was found in different photofunctional materials, containing azobenzene chromophores [17]. Among them there were distinguished as especially photosensitive azobenzene-attached amorphous polymers and liquid-crystalline (LC) media. The reversible photoinduced birefringence in amorphous azobenzene polymers was limited by -0.1 (Fig. 1, b). It is still known, that for semi-crystalline azobenzene-containing polymers the parameter $|\Delta n|$ went out the threshold of values for -0.3 [17,22].

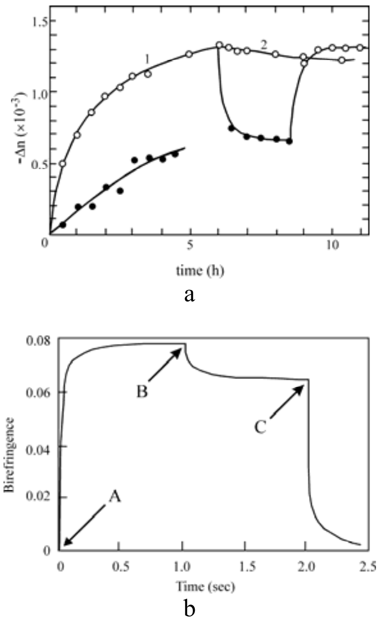


Fig. 1. The birefringence $\Delta n = n_{||} - n_{\perp}$ *evolution for* a-As_2S_3 *and* pDR1M *films: a,* As_2S_3 *film illuminated with linearly polarized (open circles) and circularly polarized (solid circles) light (λ=633 nm). The lines 1 and 2 with open circles reflect a writing process and relaxation in the dark, respectively [10]. b, Typical write/erase curve on the* polyDR1A *film. At point* A*, a linearly polarized light (λ=514 nm) is turned on; at point* B *it is turned off; at point* C *the same laser light, but circularly polarized, is turned on for erasure [14].*

It is important that in both ACh and non-crystalline azobenzene polymer films the reversible component of birefringence and dichroism (in the film surface) can be completely erased by thermal heating or overwriting the test spot with resonant circularly polarized illumination.

Trying to understand a possible nature of anisotropic photo-response in amorphous photochromic polymers and chalcogenides, which are, besides, able to reveal the effects of photoinduced girotropy [25,26], it is worthy to pay attention to distinct elements of the local structure designated by the features of polarity and chirality [3,27]. In any case the important role will be played by the creation of dipole moment under photoexcitation. The dipoles are able to acquire selective orientation reacting to the direction of the electric vector of the light wave.

Moreover, through polarization influence of dipoles upon their closest neighbouring one can expect the additional dipole-dipole interaction. Via the appearance of statistical correlation from dynamic interaction of dipoles with surrounding neighbours in the amorphous matrix the conformational character of transformations of a local structure is realized. The above factors, though differently, can be seen in the behaviour of amorphous azobenzene polymers and ACh.

In analyzed ACh getting the anisotropic photo-response is facilitated by several factors:

(i) the presence of hyperpolarized nonbonding long-pair electrons, which form weak (non-covalent) bonds;

(ii) the steric freedom of low coordinated atoms, which can alter their positions;

(iii) the resulting high level of the structural freedom of the non-crystalline state under photo-saturation condition when spatially defined (anisotropic) configuration structural changes may be initiated.

Azobenzene molecules used as parent molecules in azobenzene-polymers are characterized by the presence of rigid azo linkage (–N=N–) which bridges two phenyl rings. The outstanding peculiarity of these molecules is their property to suffer efficient photochemical isomerization that can occur near the azo linkage when the chromophore absorbs a photon. Each elementary isomerization event involves the rotation or inversion about the azo bond, by which the change of the inter-bond angles takes place. This is combined with the concerted twisting of the phenyl rings relative to the C–N=N–C plane. Repetitive *trans* ⇔ *cis* isomerization cycling presetting the continuity of mutual transitions of azo molecules between low-energy (thermally stable) planar *trans* configuration and high-energy (meta-stable) bent and twisted *cis* form give rise to a series of molecular motions (Fig. 2). In such a way the dynamically changeable nature of the photostationary state is disclosed.

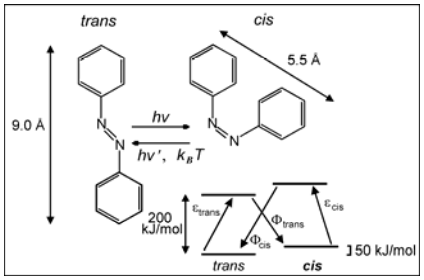


Fig. 2. The photoisomerisation cycle for azobenzene. The extinction coefficient is denoted as ε, whereas the quantum yields for the photoisomerization are labelled Φ.

Photoinduced molecular motions reduce the intra- and intermolecular interactions such as van der Waals force and hydrogen bonding by changing their interaction distances. Thus, the conformational changes in the polymer chains, which in turn lead to macroscopic variations in the chemical and physical properties of nearest surroundings and amorphous media become possible on the whole.

The interaction of an azobenzene-containing polymer with linearly polarized light results in a preferential alignment of the dipole axis of the azo groups perpendicular to the polarization axis of the irradiated light, leading to reversible birefringence and dichroism. One elementary isomerization event consumes 2 eV (within some picoseconds) and this energy can be gradually converted into considerable molecular rearrangements. The energy barrier to the photo-excited state is approximately 200 kJ/mol [28]. Note that the versatile *cis* molecules of chromophore are able to show more or less freely rotation. Even in the restrained surrounding of the polymeric backbone they can relax easier because they suffer from weaker constraints than *trans* isomers. The *cis* isomer population is the most sensitive to the nature of polarization of the irradiating light. After each elementary isomerization event the chromophore moieties may adopt any orientation, move and reorient slightly their optical transition moment axis. Molecular rearrangements are finally directed at the farthest removal of such an axis from the polarization direction of the initial light waves. The reorientation of the dipole's alignment vector under absorption leads to a statistical increase in the populations of chromophores with the dipole axis being perpendicular to the polarization direction and a decrease in the population aligned with the polarization. These transformations result in the birefringence and dichroism in the polymer film-plane.

In the obtained spatial orientation the side chains of the azobenzene polymer cannot be further addressed by the polarized field of the incident light. But it would be excessively simple to reduce the analyzed process (designated as the effect of photo-orientational depletion) as the one, which is defined by the dipole interactions and a singly present driving force aimed at the minimization of light absorption of azo groups. It is necessary to be taken into account both polar and steric factors because only by their combination the most efficient cooperative molecule's motions are preset. As a result long-living angular correlations are due to excitation statistics. Cooperative motions are consequences of frequent (extended) isomerization events. They come from anisotropic interactions between side chain groups and collective modes of polymeric environment.

As one can be sure [9-17], under the actinic polarized light illumination in the approximation to the dynamic light-saturation state a-As-S(Se) films and azobenzene-containing polymers show an astonishingly close behaviour while writing (erasing) of reversible optical anisotropy, checked by birefringence or dichroism parameters. It is possible to explain this phenomenon when at the center of our argument the concept of *dynamic heterogeneities* (DH) was put [29]. The latter especially actively discloses their presence under photoexcitation of amorphous media. We associated DH with elementary molecular rearrangement events, presumably localized within the "soft" structural regions [30,31]. However, through the activation of DH large-scale elastic perturbations arise, that results in macroscopic properties of amorphous materials. Spatially heterogeneous dynamics defines these changes, therefore they are reduced from successive local plastic rearrangements and corresponding delocalized non-affine displacement fields. In such a way the spatial-temporal heterogeneity of the microscopic structure reveals itself. Non-affine deformation fields are strongly correlated over the length scales. Introducing the additional microscopic degree of freedom (structural and mechanical subsystems) in the transformation makes it possible the significant displacements of groups of atoms (molecules). Even more, it is worthy to assume that the analyzed nanoinhomogeneous media at the short length scales acquire the properties, characteristic for weakly connected systems upon the influence of light illumination [31].

The "spatial fixation" of DH does not clearly coincide with definitely outlined sites of "soft" structural configurations. The reason for this lies in created dynamical correlation, by which divergence of non-affine elastic displacement fields outside limits of localized sites of soft atomic configurations is preset. The latter in the photoexcitation states actively interact with conventionally rigid nearest surrounding (stiff backbone).

We conducted the former consideration of stimulated irreversible transformations in ACh films on the basis of a phenomenological model of two-component states (TCS) [30,31]. This model besides spatial division of singled out states (i.e. of localization of soft and rigid atomic configurations) takes into account multi-level (hierarchical) character of interactions of structural and mechanical subsystems at stimulated irreversible transformations. Within the frames of TCS model the structural and mechanical changes were given in the comparison approaching them. They were estimated as mutually complementary features of photo-response. Thus, a photosensitive behaviour of amorphous media was derived from competing effects of interactions for separated local rigid and soft atomic configurations [31].

The TCS model should be adapted for consideration of the microscopic mechanism of reversible optical anisotropy in ACh [11,31]. We have to take into account the statistically anisotropic character of locally activated polymerization-depolymerization processes. For arsenic-rich a-As-S(Se) films the reversible optical anisotropy is close to optimal values. The explanation of this is as follows: an essential role is given to involvement of partly fragmented molecular formations of $As_4S(Se)_4$- and $As_4S(Se)_3$- type into the processes of anisotropic photo-responses [31-33]. However, for chalcogen-rich films (first of all it concerns a-Se) the main role in the photostimulation of optical anisotropy is given to shortened "soft" $S(Se)_n$ ($n \leq 3$) chains.

At the illumination of amorphous media by linearly polarized light some As-As bonds in fragmented molecular clusters preferentially break which were approximately parallel to the electric field vector of the initiating light (an alternative variant must take into account the statistically anisotropic reorientation of S(Se)-S(Se) bonds). Meantime, some homopolar As-As bonds perpendicular to the polarization of the light waves are restored with the participation of $As_4S(Se)_4$ or $As_4S(Se)_3$ molecules [31-33].

Let us look at comparative observations, which relate the optimization of reversible optical anisotropy in ACh and azobenzene-containing polymers. In both cases the maximum amplitude values of parameters of optical anisotropy directly depended on the concentration of "optically active" moieties. Thus, for azobenzene polymers the optimal parameters of reversible birefringence will be achievable in a sample, where the largest concentration of azo groups is present [13]. Still for a-As-S(Se) films the similar value have local sites of "soft" atomic configurations [30,31]. So, everything is defined by a remained concentration of non-connected ("isolated") molecular fragments of $As_4S(Se)_4$- type or by the presence of shortened $S(Se)_n$ chains. Note that for the films of different compositions the simulated amplitude values of optical anisotropy do not almost depend on the intensity of pumping illumination. The latter has an influence only upon the rate constant of birefringence growth. However, the temperature rise of the thermal bath in the amorphous matrix depresses the reversible optical anisotropy (the photo-writing effect is almost completely absent approaching temperature of glass transition T_g).

However, for polymers the azobenzene bulkiness strongly influences the efficiency of photostimulated orientation memory. For example, "simple" azobenzene polymer films (pDR1M type), bearing the strong NO_2 group as the electron-withdrawing substituent are characterized by higher level, rate and stability of reversible optical anisotropy in comparison with the ones, which include SO_2 group (pseudo-stilbenes) [6,34]. The rigidity of the linkage between azo-chromophores and the polymer backbone influences the formation of the optically anisotropic state. The steric hindrance imposed on the chromophores by a short spacer connecting the azobenzene to the copolymer environment should be taken to the account, too. The intramolecular interactions that include the bond stretch, bond bending and torsional terms are of great importance. The integrated rigidity of polymeric matrix greatly affects the photoisomerization efficiency and the reorientation motions. In total this restricts the rotational degree of freedom in polymer media.

Both polymers and ACh films with inherently larger parameter T_g intend to reveal maximally possible reversible optical anisotropy. We admit that key factors are not only the structurally-mechanical compliance got as a result of photoexcitation but also the restrictions laid on microscopic degrees of freedom in the vicinity of DH. A high level of anisotropic interactions with conditionally rigid (elastic) surroundings characterizes them. Trying to optimize the reversible optical anisotropy it is necessary to preserve the balance (trade-off) between the rigidity of backbone (which prevents the relaxing loss in an orientation) and the acquired local flexibility of "soft" areas or "weak spots".

The model TCS, within the frames of which we earlier analyzed the photostimulated transformations in ACh [31], discloses its own advantages while considering vectoral effects in mutually inhomogeneous networks. The mechanical photo-response in the inhomogeneous amorphous medium accompanies local structural transformations which we consider it possible to associate them with *shear transformation zones* (STZs) [35], viz. the so-called areas of positive shear modulus and areas of negative shear modulus [36], respectively. The latter are commensurate to the sites of molecular groups, which are most susceptible than their neighbours to a shear transformation in the same direction. The changes result from the activation of soft molecular groups being in the areas of a negative shear modulus. This means overcoming small energy barriers undergo the irreversible local shear-like transformations. Dynamic local transformations in the concept of potentional energy landscape are accompanied by the acts of creation and annihilation of inherent structures [37]. At the light-saturated state non-frequent well-localized yielding events must create a partial loss of rigidity amorphous medium, though it is not possible to be revealed in the changes of statistically average macro characteristics.

Under the influence of coherent polarized illumination the initiated elastoplastic transformations result in a rewriting orientational memory. The orientational memory is one of the universal features of local amorphous plasticity [35]. The possibility of appearance of the orientational memory and its main characterizations will completely depend on the inscription geometry of actinic polarized light illumination. In the light-saturated state for soft atomic/molecular configurations after prior extended shear transformation events further shear transformation will resist in the original direction. By altering the polarized light illumination the orientational memory can be repeatedly reoriented.

One connects the photostimulated processes of plural acts of local structural realignments with cascade rearrangements for specific groups of molecules [39]. For a nanoinhomogeneous amorphous medium under the polarized light illumination an unsteady balance of interactions is defined by the transitions between *locally jammed* (marginally stable) and *locally yielding states*. By characterizing the rewriting orientational memory, we have made use of a jamming paradigm, used in models of static forces in granular packs [38]. Jamming configurations are distinguished by a varying degree of positional and orientational orders. Locally jammed states, similarly as locally yielding states, are associated with localized sites of soft atomic configurations. For the former it is peculiar that some particles cannot move without catching the nearest particles in the same direction.

By altering the polarization inscription of incident light considerable restored transformations within the limits and in the vicinity of prior activated STZs (areas with a negative shear modulus). Then a strong requirement that reverse transition must bring the molecules back to exactly their original positions is avoided. The exchange of stability between locally jammed states where molecules are not moving and locally yielding states, for which a motion of molecules results in the annihilation and creation of STZs, will be shown in active interactions of amorphous material. Thus, the levels of viscoelastic and viscoplastic states will be embraced. The system retains the orientational memory due to local fluctuations, through which asymmetric structural irregularities in amorphous medium are fixed. However, the orientational memory may easily be erased (or rewritten). With altering the driving force (by changing the light wave polarization) the reinforcement of mutual transitions between locally jammed states and locally yielding ones will appear again. The respective character of transformations can give the possibility for the big groups of particles to move collectively.

With constant coming of the energy from outside and its dissipation under the conditions promoting self-conformed reinforcement of local fluctuations capable of embracing the levels of mesoscopic order, separated STZ-like events begin to activate. Yielding events initiate much more spatially dispersed atomic displacements and corresponding fluctuations spread out for a longer distance [39]. Through a successive “link” of transformations strong non-affine elastic fields are generated. As a result this leads to an anisotropic redistribution of the local stresses. Non-affine distorsions spatially extended to neighbouring areas with rigid molecular fragments (clusters). In the vicinity of the reorganized STZ the possibility of further stimulated or spontaneous transformations (a creation of new areas of yielding states) does not disappear. Resonant elastic interactions between isolated STZs are quite expected.

The TCS model in its main details correlates with the mechanism of transformations known as an angular selective hole burning (photo-selection). It was first proposed by Dumont and Osman [8] for consideration of spontaneous and photoinduced orientational mobility of dye molecules in polymers. The angular hole burning in an azobenzene polymer arises statistically followed by the angular reorientation after a number of isomerization cycles. The presence of a long-living angular correlation (as necessary attribute of the process of creating the stable optical anisotropy) is reduced from anisotropic interactions between side chain groups and collective modes of polymeric environment.

Actually, each of these two models is able to explain the light-induced vectoral (orientally defined) changes because both highly heterogeneous plastic and strong anisotropic elastic atomic displacements are easily introduced [39]. The macro-anisotropic elastic reaction of the amorphous medium reduced from local structural transformations shows itself in opto-mechanical effects most definitely.

3. Opto-mechanical effects

Azobenzene functional materials have revealed different opto-mechanical effects and macroscopic motions stimulated by light illumination for a long time. Already in 1966 Merian [40] reported that the products doped with azo-dyes contracted under light illumination. Almost at the same time Eisenbach [41] demonstrated an opto-mechanical effect in azobenzene chromophores. The contractions (0.25%) of pre-stretched, isotropic polymer networks were observed in the presence of the actinic light.

There are two distinct processes distinguished in photomechanical properties of azo liquid-crystalline (LC) networks: the reorientation normal to the light polarization and decrease in the LC ordering followed by the phase transition in the polymer network [42].

A low power laser beam is used to induce large and fast variations in the shape of freestanding azo LC polymer films due to contraction of the surface subject to the laser beam [43,44]. The direction of the photo-induced bending or twisting can be controlled by the polarization of the incident light. An extraordinary strong and fast mechanical response to the influence of the polarized laser beam can be achieved for LC polymer films [44]. Contrary to previously developed polymer material systems, this polymer is functional at room temperature, and a low power single laser beam can be controls its shape. The material is differentiated by the opportunity it provides for controlling not only the magnitude but also the sign of photoinduced deformation as well through the polarization state of the laser beam. Furthermore, the opto-mechanical effect might be heavily optimized: it was possible to vary the film orientation within ±70° [44]. In other experiments whose objects of study were thin films floating on the water, the contraction in the direction of light polarization was seen for azo LC polymers, whereas the expansion was observed for azobenzene-containing amorphous materials [45]. The photo-induced bending of a microcantilever coated with an azobenzene monolayer has expanded upon light irradiation [46].

Below the main attention will be paid to the revealed correlation peculiarities of the behaviour of azobenzene polymers of pDR1M-type and a-As-Se films in recently discovered vectoral phenomena, which we will conditionally denote as *initial opto-mechanical effects* (IOME) [45-47], [48] and *lateral opto-mechanical effects* (LOME) [49], [50], respectively.

As usual IOME demonstrates the fast reversible mechanical contraction and/or dilatation of the mirocantilever with amorphous media under initial orthogonal polarized illumination. For the materials under consideration the proximity of kinetics of IOME formation and immediate reversible optical anisotropy is the key feature of this phenomenon [47,48]. The revealed dependencies usually correspond to a stretched exponential Kohlrausch-Williams-Watt law. A considerable coincidence of stretched-exponential fits with opto-mechanical and photodichroism measurements were observed for a-As-Se films under coherent polarized light of moderate intensity illumination [48]. The revervible bending of a bilayer sample ($As_{50}Se_{50}$ film/Si_3N_4 microcantilever) can be controlled by changing relative directions of the electric field of linearly polarized light to a microcantilever axis. It is defined [48] that for ACh under the action of polarized light of non-high intensity in the film-plane the constricting mechanical stresses along the polarization direction of incident light waves and quasi-stretching (slight constricting) mechanical stresses in the orthogonal direction are initiated.

Under similar conditions of light exposure (an actinic flow of moderate intensity) the behaviour of amorphous azobenzene polymers [45] becomes exactly inverted, i.e. expansion in the direction of the electric field of linearly polarized light is revealed. Comparing characteristics of both types of materials we come to a conclusion: for amorphous films of azobenzene polymers and ACh the tendency to disclose contradicting behaviors (opposite effects) in IOME dominates. Note that such a peculiarity is completely restored in LOME studies, too.

It is strange but while studying IOME under similar experimental conditions the prevailing number of azo LC polymers [6] and ACh [48] are of the same behaviour demonstrating the considerable coincidence in experimental findings. It would be imprudent to make some conclusions as to the nature of this peculiarity.

The experiments of Bian et al. [47] elucidate this situation when an opto-mechanical effect in amorphous dye-polymers was studied in detail. Here as an optically activated cantilever (actuator) a short fiber of azobenzene-doped pDR1M was used. The important peculiarity of the experiment was the fact that a polymer matrix (PMMA) was uniformly doped by a minor quantity (1% by weight) DR1 dye. A laser beam of actinic linearly polarized light (λ=633 nm) is launched off-axis into the polymer fiber, and as a result fiber's bending was obtained. Relative changes in the fiber actuator length were controlled with high precision. The most important results of Ref. [47] obtained while studying IOME in pDR1M polymer materials are as follows:

(i) Under low-intensity linearly polarized light of reversible deformations of polymer matrix caused by temporary stretching mechanical stresses along the polarization direction of incident light waves are formed. At once quasi-constricting (slight stretching) mechanical stresses in the orthogonal direction are revealed. This peculiarity of IOME well agrees with the results given by Bublitz et al. [45]. Under such experimental conditions it is disputable to correspond a low-intensity IOME with a cooperative motion of structural units (dipolar interactions may become more important).

(ii) Under the action of higher-intensity linearly polarized light considerably stronger opposite reversible deformations of polymer matrix were achieved (constricting mechanical stresses along the polarization direction of initiating light was observed). The authors of Ref. [47] were quite right when connected this peculiarity of the effect with the elastic in nature collective alignment process. Dynamic rearrangements of internal elastic forces and sufficient conformational changes were their result.

One can assume that in the experiment under analysis the coupling between dynamic process of the chromophore reorientation and non-local elastic interactions in amorphous medium was definitely revealed.

Taking into the results of Refs. [18-21] it is necessary to expect that in ACh (a-As_2S_3 films) one could demonstrate the threshold inversion in experimental findings of IOME with sharp changes in the light intensity. This would mean that the replacement of constricting mechanical stresses along the polarization direction of an actinic light flux (low intensity of the bandgap illumination) by stretching ones (high intensity of the sub-bandgap illumination) had taken place.

There were much more previous demonstrations of LOME in the form of uncommon and unexampled large-scale photo-physical motions, discovered in pDR1M films [6,7,22]. It was then shown that a free surface of the thin film would be inhomogeneously deformed upon the influence of a coherent incident light with varying the intensity and/or polarization in the film-plane. Diversities in the configuration of relief patterns essentially complicated the interpretation of the nature of this effect. Similar by character inhomogeneously anisotropic micron-scale surface deformations were soon detected in a-As_2S_3 films [18-21]. Further information on inhomogeneous optical patterns in azobenzene polymers and ACh films will be given in the below section.

However, the results of LOME study in azo-polymers and ACh exhibited under homogeneous optical fields appeared to be the most demonstrative and convenient for interpretation. For the first time Karageorgiev et al. [49] and Trunov [50] was studied LOME for the amorphous azobenzene polymer and As-Se films in the above-mentioned format of the light action, respectively. The researchers noticed the presence of extraordinary anisotropic mechanical behaviours of pDR1M and a-$As_{20}Se_{80}$ films under the coherent polarized light illumination (Figs. 3 and 4). These experiments unambiguously witnessed to the fact that a long-term with homogeneous linearly polarized light initiates the large-scale mass transport (lateral molecular movement at the distance of some microns) in amorphous films. Kinetics of photostimulated molecular motion (a long-term exposure with duration of tens hours) does not absolutely remind a fast transition to the light-saturation state while forming the reversible optical anisotropy.

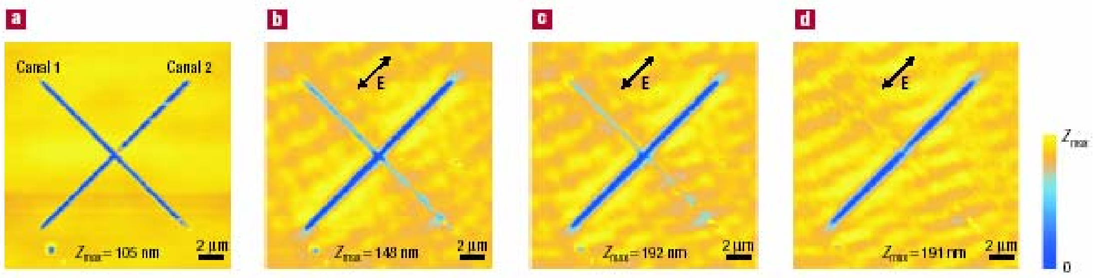


Fig. 3. Polarization-dependent photo-stimulated mass transport in pDR1M *film: a, In the initial state two perpendicular canals produced by* SEM *lithography are presented on the non-irradiated film surface. b-d, Images of the surface after 30 min (b), 150 min (c) and 195 min (d) illumination by linearly polarized light with* λ *= 532 nm and P=60 mW·cm*$^{-2}$*. The orientation of the E-vector of the light field and the* Z_{max} *are indicated on the image (b-d) [49].*

Experiments showed that for LOME the presence of laterally non-vanishing elastic force might be defining. In Ref. [49] this vectoral effect is fixed in pDR1M as a lateral molecular transport when the molecule's position was set by the irradiation duration of a low-power coherent linearly polarized light (λ=532 nm). The anisotropy of photoinduced motion of molecular units showed itself through the experimental connection of the long-range "expansion mass transport" in the direction parallel to the light polarization and the "conceivable constriction mass transport" in the orthogonal in-plane direction (see Fig. 3).

For a-$As_{20}Se_{80}$ under similar conditions (the polarized low-power bandgap illumination, λ=633 nm), as it could be possible to expect, an opposite effect in vectoral material transport was observed [50].

It is interesting to note that under the influence of linearly polarized light in pDR1M film the surface relief parallel to the E-vector of the light field is created, and this is accompanied by the canal expansion in the orthogonal direction (Fig. 3, b-d). At the same time the surface relief appearing in a-$As_{20}Se_{80}$ film is perpendicular to the E-vector of the light field, and we have a simultaneous of the corresponding canal narrowing (Fig. 4, b-d).

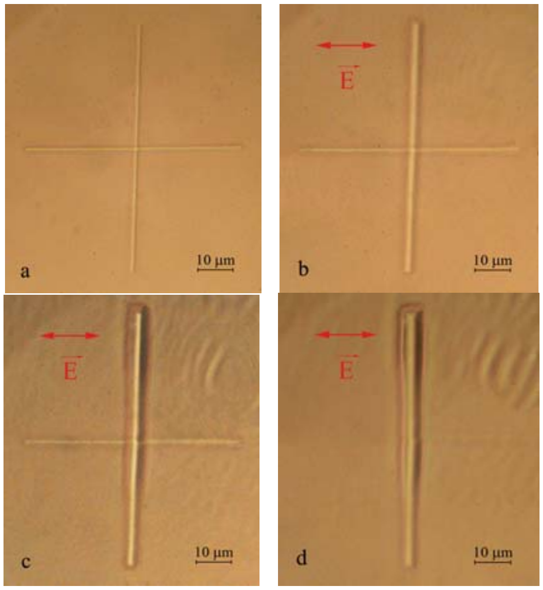


Fig. 4. Polarization-dependent photo-stimulated mass transport in as-evaporated a-$As_{20}Se_{80}$ *film (thickness ~ 2 µm): a, In the initial state two perpendicular canals are presented on the non-irradiated film surface. b-d, Images of the surface after 5 hours (b), 12 hours (c) and 16 hours (d) illumination by unfocused (d ~ 2 mm) linearly polarized laser with* λ*=633 nm and P=60 mW·cm*$^{-2}$*. The orientation of the E-vector of the light field is indicated on the image (b-d) [50].*

Comparing peculiar properties of both types of the materials we have come to the conclusion that the peculiarities revealed in them witness to the presence of asymmetry (of prevailing spatial directivity) in the integrated elastic response of the amorphous matrix. This is an indirect reaction of the matrix to local structural transformation events initiated by the light action. The resonant coherent (cooperative) interactions were capable of revealing in the processes of local transformations both during IOME initiation with entering the photo-saturation state and in further long-term transformations reflected in LOME. The successive local changes and related non-local reactions of structurally heterogeneous amorphous medium caused the self-consistence of dynamics in changes of microscopic and macroscopic system's parameters. The ordering at the mesoscopic level appeared to be an important link in the formation of anisotropy of macroproperties. This can explain the existence of common organizing motive in IOME and LOME realization.

A number of theories have been proposed to explain the vectoral material transport on the molecular level in the azo-polymers under the light illumination:

1) The asymmetric diffusion model [51], which reduces the reason in the process of photoisomerization of chromophores by which the asymmetric motion of dye molecules along their molecular axis is simulated. The mass transport is controlled by the polarization-dependent orientation of molecules and their statistically random walk. The inherent defect of the model is impossibility to properly estimate the hindering which lays the stiff polymer environment on the molecular diffusion.

2) Mass transport models are associated with photodegradation and thermal ablation [52]. These models do not absolutely foresee the appearance of vectoral effects.

3) The isomerization pressure mechanism [53] in which a light-induced gradient in pressure in the polymer is taken to account. The local pressure formation is developed from the increase in the *cis*-population within the illuminated region, due to an additional free volume requirement through the appearance of these configurations. Within the declared mechanism the influence of the initiating light polarization is not possible to take into account. It is also hard to foresee those changes in mass transport demonstrated by the experiment.

4) The models, which consider the interaction between the electric field of light waves and polarization-sensitive gratings formed in the photosensitive material [54-57]. Though these models, on the whole, correctly describe polarization-defined peculiarities of molecular transport, however for exact estimates and predictions they are fit badly.

5) The mean-field forces mechanism [58], which reduces the orientation and aggregation of chromophores from their attractive interactions. The photostimulated creation of micro-crystalline formations is foreseen, therefore this mechanism is more suitable for LC systems. It includes the peculiar properties of azobebzene polymers only to explain the photo-stimulated ordering of dipolar chromophores.

6) The inherent fluid dynamics mechanism [59-62], which accounts for the viscoelastic behaviour of azobenzene polymers under illumination. Both the surface tension force and the force that acts on the dipole that is induced in the polymer by the electromagnetic field were considered to be the driving forces for photoinduced mass transport. Although these models describe the polarization-sensitive behaviour of azobenzene polymers quite well but the estimates show that the expected forces are too small (at least for two orders) [63]. Especially this concerns the analysis of optical pattering formed with pulse-like polarized beams. The peculiarities revealed can't be explained in the frame of an incompressible fluid model. By the way, a specific kind of fluid dynamics mechanisms was proposed by Tanaka [21] to explain photostimulated expansion and macroscopic anisotropic deformation effects. The latter are well disclosed in ACh. Tanaka indicates to the basic driving motive for stimulated transformations in release and rearrangement of van der Waals force between the aligned segmental layers.

None of the above models well describe the light-induced molecular motions at the local levels. It is more important that they didn't give sufficient agreement with the experiments.

A particular attention will be paid to a recent entropic theory [64] for which the basic assumption is the fact that under homogeneous illumination an initially isotropic sample stretches itself along the polarization direction to compensate the entropy decrease produced by the photoinduced reorientation of azobenzene chromophores. Following the assignment by Lagugné-Labarthet et al. [65], in which both confocal Raman microscopy and second harmonic generation near-field scanning optical microscopy are used to determine the molecular orientations in different regions of an optical diffraction grating, in Ref. [64] the direction of the polymer chain transport was predicted. Having all advantages and drawbacks of the general approach the entropic theory still gives predictions agreed with experimental findings. In the entropic theory [64] it is reflected that a close coupling between chromophore orientation and the elastic deformation of the amorphous polymer films exists. Similarly, basing on the peculiarities of elastoplastic local transformations and symmetry considerations, it is possible to explain the photomechanical response in ACh. Unfortunately, till enough complete experimental data taken from structural investigations of the anisotropic memory in ACh are not found, in order to make use of advantages of this entropic theory for prognosis of vectoral effects details.

The approach used in Ref. [64] does not give a direct answer about the nature of a nonvanishing driving force. However, thoroughly considering the essence of the paper [64] it is expected the possibility for a driving expansion force reduced from a positive free volume requirement in amorphous polymers coming to the photo-stationary state. The same situation occurs through prevalence of the populations with dominating spatial assignment for orientation holes. It is known that the conversion from *trans* to *cis* forms demands local changes in the free volume when for each elementary isomerization event approximately 0.12 nm^3 is added to the act of inversion of the azo bond [66] and 0.28 nm^3 for a rotation about the azo bond [67]. An anisotropic constriction along some direction will be obtained when the photoactive moieties in a considerable quantity turn into a more compact form under the coherent polarized light irradiation. The succession of these changes is described by a simple scheme: the multiple photoisomerization cycles create a free volume, which manifests itself as the softening of the polymer material under resonant optical illumination with non-high light intensity.

Note that considerable divergences of opinion about the phenomenon of photosoftening in non-crystalline solids (other variants of terms – photofluidity, photoplasticization, photomelting, etc.) take place. Still to understand the nature of this phenomenon is necessary to elucidate the mechanisms of vectoral effects in dye-polymers and ACh. We emphasize that they are best revealed at the temperatures much lower than T_g. The concordance was achieved only in the fact that photosoftening is not thermal in origin but it has the photo-electronic nature [3,33,49,53,63,68,69,71-75].

The quantitative estimate of *local* viscosity parameter for a-As-S(Se) films [76,77] and azobenzene polymers of pDR1M type [49] was obtained under study of nanoindentation, kinetics with the circularly polarized actinic light illumination. In the initial stage of light irradiation the decrease in this parameter values to those at least comparable with that the value at the temperature of glass transition T_g was found. Moreover, as a result of changes the local viscoelastic properties of pDR1M film under loading fixed the peculiarity [49] interpreted as in such a way that the material behaves like a viscous fluid (this phenomenon was not found in ACh films in similar experiments [76]).

At the same time using both the quartz crystal microbalance [72] and the electromechanical spectroscopy [73,75] methods under similar conditions the photoinduced changes in the mechanical properties of azobenzene polymer layers have been investigated. There have been found much weaker photosoftening effect. At the room temperature, less than 10 % the increase in the plate compliance upon homogeneous circularly polarized illumination with an actinic light of the visible spectral range (Vis-light) was observed. At once they observed small changes in an elastic modulus (from 3.4 GPa to 0.9 GPa) under Vis-light illumination in pDR1M film [49].

It has also been observed that for pDR1M under ultraviolet illumination (UV-light) the plate compliance parameter first slightly increases but then gradually decreases [75]. A strong correlation between the time-dependent behaviour of the given parameter and dielectric constants under both Vis-light and UV-light irradiations has been revealed. The photosoftening of the polymer film manifests itself in the increase of the dielectric constants, whereas the photohardening is accompanied by the decrease in the dielectric constants.

The a-As-Se films of some compositions under bandgap circularly polarized light with non-high intensity have demonstrated an especially extraordinary behaviour [76-78]: Young's modulus increased (by a factor of two) on the local (nanoscale) level, while nanohardness decreased drastically.

To explain an unusual character of elastoplastic properties changes in azobenzene polymers and ACh films under actinic light illumination for the inhomogeneous system the mechanical models according to which stiff regions coexist with more "softer" areas (sites of "weak spots") have been independently proposed in Refs. [75] and [76]

For azobenzene polymer layers the manifestation of photohardening effect turned to be unexpected enough. However, and such peculiar behaviour found a simple explanation when it was reduced from a sharp increase in the concentration of the *cis* fraction under UV-light illumination [75]. It is known that a *cis* form is much less sensitive to UV-light than a *trans* configuration. Besides, *cis* isomers themselves with increasing their concentration are capable of entering strong collective interactions with the copolymer environment. The latter is absolutely not characteristic for *trans* isomers [75].

Having analyzed the peculiarities revealed all-in-all in the experiment we convinced that opto-mechanical effects in azobenzene polymer and ACh films are preferentially preset by anisotropic changes in the local structure (and this can't occur without substantial DH activation). Upon the influence of linearly polarized light the amorphous medium is able to reveal ambivalent properties defined by "anisotropically heterogeneous" decrease in the local viscosity of the medium, however, it becomes possible with weakly changeable stiffness of the basic matrix. It is possible to connect the anisotropy of photo-response, as it was above-mentioned, with strong non-affine displacement fields in elementary yielding events. In the state of unstable dynamic equilibrium after a series of transitions between locally jammed (non-deforming) and locally yielding states the situation is favorable for a special elastoplastic feedback effect to occur.

It is known that ACh films in the photo-saturation state considerably release the relaxational component of dissipative energy losses [70]. A direct connection exists between the process of the energy dissipation and corresponding acts of STZs annihilation and creation. As relaxational energy losses become much less than it was till the completion of the strongest irreversible photostructural transformations, the long-range elastic perturbations in the form of "back stress elastic fields" could occur. Stationary heterogeneous deformation fields probably relate to the second-order response in anisotropic local stresses. With integrated decrease in the stored elastic energy, which is an indirect consequence of irreversible relaxation transformations the anisotropic elastic reaction of the amorphous matrix to initiated local perturbations demonstrates itself in full. In such a case the above-mentioned directly concerns the nature of a nonvanishing driving force revealed in opto-mechanical effects.

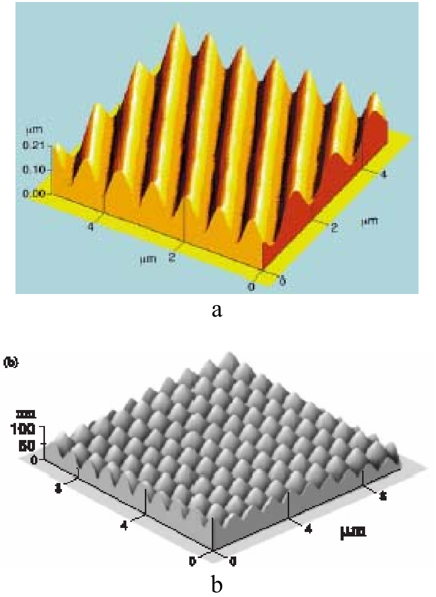
4. All-optical patterning

In the response to an incident polarized light the ACh films and azobenzene-containing polymers demonstrate vectoral surface mass patterning phenomena [6,7,18-22]. In a single-step process the amorphous films give rise to the direct surface modulation (surface deformation) when illuminated with inhomogeneous (by various intensity or polarization) light in their absorption band. Reversible topographic relief structures are formed upon exposure by the polarized light in different following optical patterns:

(i) the periodic surface topography that is the holographic reproduction of the incident polarized beam light-field [7,18-20,22,53,55,56];

(ii) localized downward "trenches" or extended "dents" in the surface induced in the single beam experiments that have used a focused Gaussian laser spot [7,18-22,56,61];

(iii) the nanostructures which are smaller than the optical wavelength produced by using near-field techniques [49,79-81].



a

b

Fig. 5. The typical 3-D view of the SRGs fabricated on amorphous azo-dye polymers: a, AFM surface profile of an optically inscribing linear grating on the pDR1M film [7]. b, AFM topography of an optically inscribing cross grating on the pDR1M film produced by two-step illumination. The second step of inscribing was performed after rotation the film by 60° about its normal [81].

It is expedient to assume that the formation mechanism of submicron-scale surface relief gratings (SRGs) (Fig. 5, a) has the same nature and is regulated by relationships connected with already considered LOME. The anisotropic light-driven reversible mass transport results in the rise of a sinusoidal SRG that agrees well with peculiarities mentioned above in the previous section.

Multiple gratings (topographic holograms) can be induced with their topographies added on top of one another (Fig. 5, b). The formation of complex surface structures includes the process of multiple exposures or scanning a laser spot.

The nature of SRGs recorded at low and higher intensities of a coherent light is very different [6,7]. Upon exposing an amorphous azobenzene polymer film by a periodic pattern of polarized light with low (moderate) intensities the polymer chains move out of the maximum light intensity regions in the direction of the polarization. In higher-intensity illumination regime the inverse changes with the transition from out-of-phase to in-phase grating are observed. This characteristic peculiarity of LOME is elegantly reflected in the experiment of Bian et al. (Fig. 6) [56] when the appearance of the transition zone of two kinds of SRG in the exposed spot was demonstrated. The 180° phase shift between the two kinds of SRG (higher and lower-intensity effects) might be expected in a-As_2S_3 films to which the results clearly indicate [18-20]. Again note that the ACh in the comparison with azobenzene polymers reveal an opposite effect: a lateral molecular movement into the illuminated regions when irradiated with low-powered band-gap light and mass transport into dark areas with illumination by the high-power subband-gap light. This will mean, for example, that for a-As_2S_3 film at the interference of low power beams the light intensity maxima lead to hills in the surface relief, with material depressing in the dark regions.

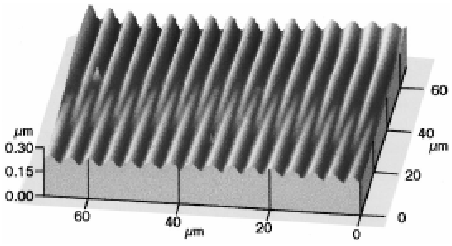


Fig. 6. A typical 3-D AFM *view of the transition zone of two gratings on the* PD03 *polymer films (λ=488 nm) [56].*

It should be remembered that with the formation of SRG in azobenzene polymers the superimposed periodic structures are synchronously created by the overlap of two polarized beams [65]:

(i) the isomerization absorbing grating;

(ii) the refractive index grating;

(iii) the birefringence grating through the photo-reorientation mechanism.

The same situation with superimposing gratings is true for a-As_2S_3 films [19].

The annealing of photoinduced gratings above T_g smoothes out them completely, however, weak density gratings in the polymer film remain behind [82].

Besides SRGs, which can be easily removed by the thermal or light procedure the non-rewriting relief gratings produced by the high-intensity mechanism were formed [56,84]. Their appearance, as it is considered, the photothermal effects or photochemical reactions such as degradation and bleaching of the chromophores are defined [52].

Analyzing known results of LOME study under exposure of amorphous films by homogeneous incident light flux it would be naturally anticipated that in the regime of inhomogeneous illumination the variation of polarization inscriptions leads to different extents of mass transport. The information got by using the homogeneous light flux can appear to be the basis for wishful "road map" with the help of which it would be possible to foresee a number of experimental findings while forming SRGs for main inscription geometries. In particular, here it is possible to make use of a simple scheme taken from a thermodynamic approach proposed in Ref. [64]. The respective predictions as to energetically favourable directions of molecular migration for ACh are most convenient to implement another approach developed by Bublitz et al. [60]. There the authors have managed to correctly explain the inscription of SRGs in LC azobenzene polymers.

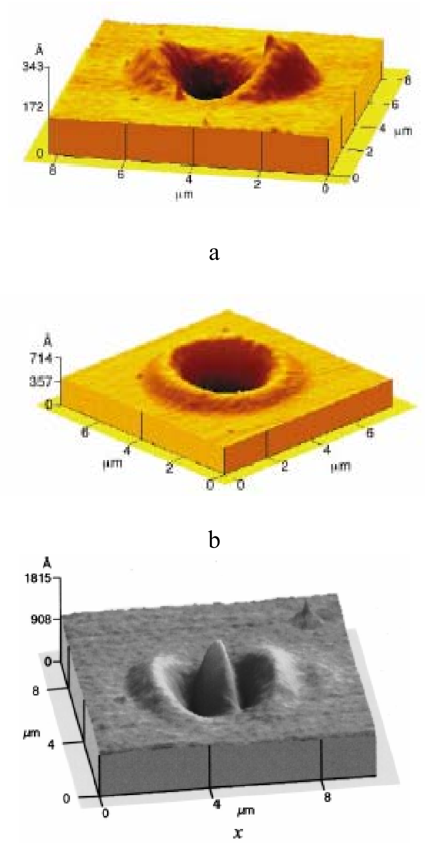
More often the creation of surface relief patterns is produced with different combinations of light polarization, namely the interference of *s* and (or) *p* polarization [6,7,55,56,65]. For example, the photo-responsive film medium can be irradiated by two interfering orthogonal (±45°) or parallel linearly polarized coherent light beams (horizontally polarized *p+p* or vertically polarized *s+s* configurations).

The SRGs with pure polarization gratings are formed in ACh and azobenzene polymer films when the polarized light intensity is uniform over the film surface [19,55,83]. The highest quality gratings in azobezene polymers are obtained by interfering of two circular counter-polarized light beams (*circ+circ* geometry) [7,55,65]. In azobenzene polymers the illumination of circular polarized light generates an expanding force in all directions of the film-plane. The interference of right- and left-handed circularly polarized beams creates alternating regions of high (elliptical) and low (linear) isomerization; while the interference of two linearly polarized beams creates alternating regions of low (linear) and no (completely destructive interference) izomerization [65]. With low intensities of interfering laser beams the polymer chains move into the nonilluminated regions in the case of the *s+s* and *p+p* inscription geometries. It is also interesting that for *circ+circ* geometry the same direction of chain transport as for the effective *p+p* geometry (from the regions where the electric field vector runs paralelly to the grating vector) is achieved [64,65].

The optical erasing of SRGs inscribed on pDR1M thin films was analyzed for various polarizations of the erasing single beam [84]. From a comparison of the most significant results obtained in Ref. [84] one may underline that, whatever the polarization configuration used in grating inscription, the erasure rate constants vary always for the used polymer in the order "*s*" < "*RCP*" < "*p*". Here "*p*", "*s*" and "*RCP*" respect to the horizontal and vertical direction of the linearly polarized and the right circularly polarized incident illumination, respectively.

Alongside with SRGs a sinusoidal density variation with the same period as that of the topography grating appears [63]. The regions of higher density should coincide with the ridges [65]. The polymer material (pDR1M) is stiffer at the SRG hills and more adhesive at the valleys. A higher stiffness at the hills could be explained in the terms of a higher density [65].

But, when the PD03 film was irradiated with the high power laser beam focused by a lens, quite an opposite tendency was observed: the polymer chains moved to the beam focus (Fig. 7, c) [55,56].



a

b

c

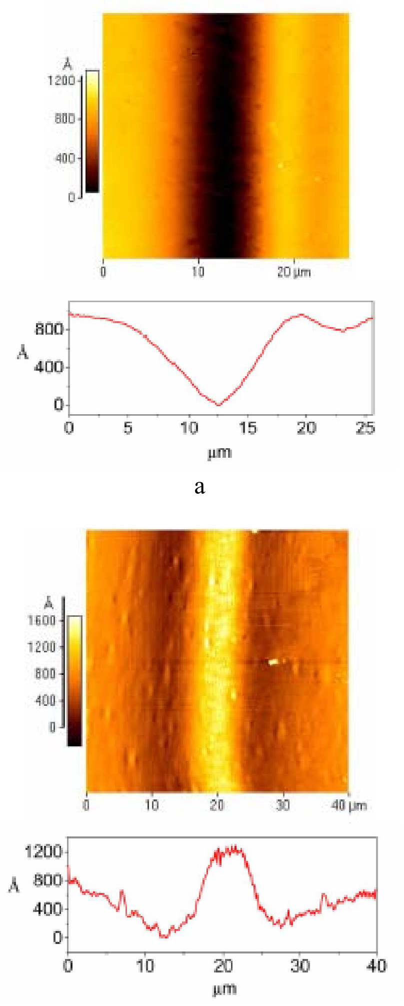
Fig. 7. AFM *of surface deformation induced in the* PD03 *polymer films by: a, Linearly polarized Gaussian beam with low intensity* (λ=488 nm, P=328 mW·cm^{-2}) *[55]. b, Circularly polarized Gaussian beam with low intensity [55]. c, Linearly polarized Gaussian beam (along the x axis) with high intensity* (λ = 544 nm, P=541 W·cm^{-2}) *[56].*

It is understandable which behaviour could be expected for a-As_2S_3 films under similar conditions (λ=633 nm, linearly polarized light with intensity in some hundreds W/cm^2) [21]: an anisotropic M-shaped deformation consisting of a central hollow and two peripheral hillocks. The detailed measurements of polarization-dependent Raman-scattering spectra in ACh films [21] showed that the Boson peak is the highest at un-illuminated region – intermediate at the hollow, and lowest at the hillock. In the hillock area the material is assumed to be highly compressed [21]. In the latter case it can be estimated as the so-called structural buckling effect.

The electrical poling method for enhancing SRGs in azo-containing polymer films turned to be effective when the induced additional polar ordering of molecules in a grating was achieved [85]. AFM studies of these films have shown that the polar ordering and mass density are the highest at the ridges and become lower away from the peak. These results are indirectly correlate with the results where the electric biasing effects on photodarkening have been examined in a-As_2Se_3 films [86].

Thus, we see that the key role in the effects under consideration is played by the presence of an optical field vector component in the direction of coherent light modulation. It should necessarily be connected with the photosoftening effect strongly revealed on local structural levels. Besides, the peculiarity at which only a little mass transport could be observed for azo-polymer films at interfering of two *s*-polarized beams of low (moderate) intensity is well-known [7,55,65]. But, for spin-coated films of azocellulose E21 it has been recently shown that in the given geometry the significant grating modulation can be achieved if an incoherent assisting light beam with orthogonal polarization is used [61] (Fig. 8).

We consider that this experiment is a demonstrative illustration of coherent behaviour on overmolecular level inherent for dissipative structures [11,31]. Such behaviour was revealed in ACh and azo-polymer films under coherent polarized light illumination, when favourable conditions are created for cooperative interactions. Without them it is hard to achieve the effective anisotropic long-time molecular transport. Distinct SRGs may be formed in a-As_2S_3 films, too. Though till now under standard conditions (two interfering non-higher power linearly polarized beams) the highest quality pattern is produced only with a specific mixture of light polarization, namely the interference of *s* and *p* polarization [19,20]. The alternative of search for the efficient inscription geometry and appropriate optimization of the recording regime of SRGs for ACh films could be successfully found if use the analogous procedure with an alternate incoherent assisting light beam, which strongly reduces the cohesive force of the amorphous material.



a

b

Fig. 8. AFM of surface deformation and its line profile on the E21 polymer films induced by laser beam (λ=488 nm) focused by a cylindrical lens without assisting beam (a) and with a uniform assisting beam (b). The writing beam polarization is parallel to the focal line (similar to s+s polarization) [61].

Hubert et al. [87] demonstrated the evidence for a interaction between a uniform laser beam and the azo-dye polymer films, where induced hexagonal structures on the surface of the polymer. The self-patterning process was observed to depend on several parameters such as the polarization of incident beam, the angle of incidence and the wavelength.

Till now it is insufficiently elucidated the nature of inverse change in spatial direction of the photoinduced molecular migration in azo-polymers and ACh at the transition from a low-power (moderate intensity) to a high-power light illumination. The considerable progress is achieved in experiment [88] when the effect of tightly focused, higher-order laser beams upon the surface deformations in pDR1M films is investigated. It is shown that the sensitivity of azo-dye molecules to the polarization direction gives rise to unusual surface deformations proportional to the longitudinal electric-field component, i. e., electric fields are polarized along the optical axis of the focused beam. These results are especially important from the point of view of probable applications of ACh and azobenzene polymer films in nano-optics. Recently the data while studying azo-polymers [80,81] have actualized this perspective. It was shown that the molecular transport could be easily generated at the subwavelength level using a scanning near-field optical microscope set-up (SNOM). The SNOM cantilever (fiber-tip) was used as an optical pen for inscription of both regular and non-regular nanostructures [81]. In such experiments it is necessary to have in mind that fiber-tips play the role of polarization filters. They almost do not cut off the longitudinal optical field component E_L. Therefore it is generally understandable, why the concentration of matter is mainly located in the maxima of longitudinal intensity $|E_L|^2$ [79-81,88].

Especially interesting is the manifestation of the self-organization phenomena while forming the SRGs in non-crystalline azo-polymer films [89]. Well-organized surface relief patterns were induced by the combination of a low-power coherent linearly polarized light illumination with incoherent laser beam of high (moderate) intensity.

The SRGs have been expended from the tiny localized area to the whole region exposed to the incoherent beam. The information brought by the coherent signal beam has come into the unique self-induced cooperative organization, although the assistant incoherent illumination, as it is considered, is able to independently initiate random molecular migrations only.

An unusual behaviour of photochromic polymer films in the cognitive ability experiments [89] was caused by the cooperative interactions, which embrace the overmolecular (mesoscopic) level. Here the coherence and self-consistent enhancement of local fluctuations within the boundaries and close vicinity of areas of "soft" states play the main role. The organized molecules under a direct influence of an actinic coherent light communicated non-local information about structural organization. However, in the formation of self-induced diffraction patterns a feedback effect can show itself. As a result, non-affine elastic deformation fields can have a direct relation to all this.

5. Summary

In this paper we have reviewed the most striking experimental results obtained while studying the vectoral effects in non-crystalline azobenzene polymer and ACh films preset by the peculiarities of photostructural and photomechanical responses initiated by the coherent light illumination.

We have considered the analyzed materials as hierarchical, multilevel dynamic systems whose behaviour is dictated by local interactions of component structural sybsystems (here it is important to take into account the revealed divergence of the sites of "soft" and "rigid" atomic states at the length scale). For nanoinhomogeneous viscoelastic media the cooperative and self-consistent character of these interactions is favourable for appearing a special "ladder" of mutually connected photostimulated vectoral effects: from a comparably quickly formed orientation memory (the reversible optical anisotropy) to the coherent behaviour on the overmolecular level, by which to a great extent the long-term anisotropic lateral mass transport is preset. The latter opens wide possibilities for all-optical patterning in amorphous film media.

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