

Photoinduced translational molecular mobility in solid nanostructured azo dye films

A.A. Ezhov, V.M. Kozenkov, S.A. Magnitskii, N.M. Nagorskii, V.I. Panov

Abstract. A new mechanism controlling the molecular motion in thin azo-containing films during a photoinduced change in the surface nanorelief is found. It is shown experimentally that exposure of a solid AD-1 azo dye, deposited on a glass substrate, to incoherent linearly polarised light leads to formation of nanostructures with a characteristic size of 200 nm, which are similar to droplets of melt of this dye on the same substrate. It is shown that photoinduced mass transport in a solid AD-1 azo dye film can be explained by the mobility of molecules related to their *trans*–*cis*-photoisomerisation, which leads to film softening with subsequent formation of spherical protrusions under surface tension forces.

Keywords: nanophotonics, azo dye, mass transport, nanorelief.

1. Introduction

One of peculiar effects that occur upon interaction of light with matter is the photoinduced molecular mobility in solid polymer and amorphous media [1]. It is especially pronounced in media based on azo dyes [2], as a result of which the latter attract much attention of the researchers. For example, it was demonstrated in [3] that a thin polymer film containing azo dye molecules, being exposed to polarised light, undergoes bending and unbending. Such effects can be used to design light-controlled mechanical nanomachines [4].

The interest in the materials based on azo dyes was aroused by their strong photoinduced anisotropy, which manifests itself in the form of absorption dichroism and birefringence [5], as well as their photoinduced orientational mobility [6] and ability of ordering surrounding molecules, for example, polymer chains and liquid crystal molecules [7].

Note that the physics of molecular reorientation in solid matrices has not been completely understood. In terms of the widest spread concept the rotation mechanisms are based on *cis*–*trans*-isomerisation of molecules during exposure to light [8]. However, molecules can be reoriented under illumination in the absence of photoisomerisation; hence, we considered some other mechanisms of molecular rotation [9, 10].

In this paper, we report the results of studying another promising property of azo dyes: translational photoinduced mobility of their molecules, which leads to photoinduced mass transport at distances as large as several micrometers. This molecular motion occurs under weak illumination, which does not heat the material. Another important feature of this manifestation of photoinduced activity of azo dye molecules is that the structural change is retained after the illumination. Generally, photoinduced molecular motion manifests itself in a change in the thin film relief under exposure to light with modulated intensity or polarisation [11, 12]. These effects were investigated most thoroughly in azopolymers [13]. Similar manifestations of molecular motion were detected in molecular azoglasses [1] and liquid crystals containing azo dye molecules [14].

Different mechanisms of changing the relief of azo-containing polymer films have been proposed to explain the nature of the forces arising. It was shown that thermal effects are not responsible for the relief formation in most cases [15]. A number of other mechanisms were proposed based on diffusion along the ordering direction [16], the interaction with the electric field of incident light [17], the occurrence of pressure gradient in the presence of intensity gradient in the light field [18], and the change in the mean field due to the orientational ordering of molecules [19].

In this paper we report the establishment of a new mechanism, which manifests itself in an AD-1 azo dye film under illumination. This mechanism leads to the growth of subwavelength droplet-like inhomogeneities on the surface of a film exposed to weak incoherent linearly polarised light. Generally, experiments on the photoinduced change in the relief of azo dye films are performed using two interfering laser beams, which modulate the light intensity or polarisation over the sample surface. Changes in the relief correspond generally to intensity modulation. However, the investigations revealed that nanostructured AD-1 films change their relief [20] under illumination uniform in both intensity and polarisation.

2. Samples

In [21–23] we proposed a new type of thin nanostructured films of pure AD-1 azo dye (Fig. 1). Their main difference from all currently used samples is that AD-1 has two azo groups, high stability to bleaching, and a very high level of induced optical anisotropy [7]. In addition, the films under study have no matrix; hence, they consist of only azo dye molecules (in contrast to amorphous and liquid-crystal azopolymers). AD-1 films cannot be assigned to molecular glasses, because they are nanostructured and consist of closely adjacent domains, which are apparently formed by groups of

A.A. Ezhov, V.M. Kozenkov, N.M. Nagorskii, V.I. Panov Department of Physics, M.V. Lomonosov Moscow State University, Vorob'evy Gory, 119991 Moscow, Russia;

S.A. Magnitskii International Laser Center, M.V. Lomonosov Moscow State University, Vorob'evy Gory, 119991 Moscow, Russia; e-mail: magn@mem3.phys.msu.ru, sergeymagnitskiy@gmail.com

Received 3 September 2011; revision received 21 October 2011
Kvantovaya Elektronika 41 (11) 1003–1009 (2011)
Translated by Yu.P. Sin'kov

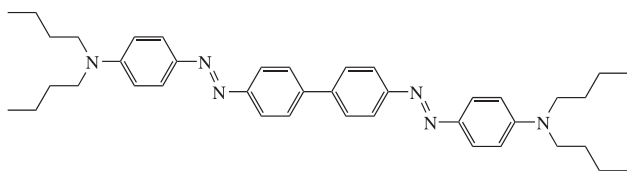


Figure 1. Structural formula of AD-1 azo dye molecule.

molecules acquiring identical orientation during film preparation.

As one would expect, azo dye films in this peculiar aggregate state have specific properties. For example, the effect of strong polarisation scattering anisotropy was found in [22], and orientational ordering of azo dye molecules upon two-photon excitation was obtained for the first time in [21, 23].

The samples of nanostructured AD-1 azo dye films used by us were prepared in the same way as in [21, 23].

3. Experimental setup and technique

The film was exposed to incoherent radiation of a high-brightness LED, equipped with a collimator to reduce the light beam divergence to 20° . The shape of the LED spectrum was similar to Gaussian, with a width of ~ 20 nm and a peak in the vicinity of 465 nm, i.e., in the absorption range of AD-1 molecules. The LED was installed at a distance of about 30 cm from the sample; in this geometry, the light intensity on the sample surface was ~ 1 mW cm $^{-2}$. The LED beam was incident normally to the sample surface. The light was linearly polarised using a film polariser. The illumination was performed from the side of the free film surface. The latter was scanned with a Solver PRO atomic-force microscope (AFM) (Russia), which operated in the intermittent-contact regime.

Standard silicon cantilevers were used in all measurements. The preliminary measurements showed that multiple scanning of the surface does not lead to any changes in its relief.

The AFM profile of the film surface, measured prior to illumination, is shown in Fig. 2a. The film thickness was about 320 nm. The film was illuminated in several stages, with the AFM cantilever removed from the surface to exclude distortion of the incident light field. To align reliably the AFM images obtained at different instants, the films were cut through to the glass substrate by two intersecting notches. The areas of pure glass in the AFM images were used to determine the sample slope and the film thickness.

In the first stage the sample was exposed to linearly polarised light for 30 min. The film surface profile after the illumination is shown in Fig. 2b. One can clearly see significant changes in the relief, which, however, do not cover the entire surface because of the anisotropic domain structure of the film. Light can be absorbed only in the domains with a director oriented along the polarisation direction of activating light. In the domains with director orientation perpendicular to the electric field vector of the light wave, light is not absorbed; therefore, the surface relief of these domains cannot change.

The chosen exposure time turned out to be sufficient to implement optical anisotropy in the film, close to maximum. In this case, mobile molecules are rotated perpendicularly to the polarisation direction of the light wave and cease to absorb light. If the orientational and translational mobilities of molecules are interrelated, the relief should stop changing when the anisotropy becomes maximum. Indeed, the additional illumination of the same film for 30 min did not lead to any significant variations in its relief (Fig. 2c).

When exposed to linearly polarised light, molecules are rotated in the plane oriented perpendicularly to the polarisation direction. Therefore, the rotation of the initiating-light

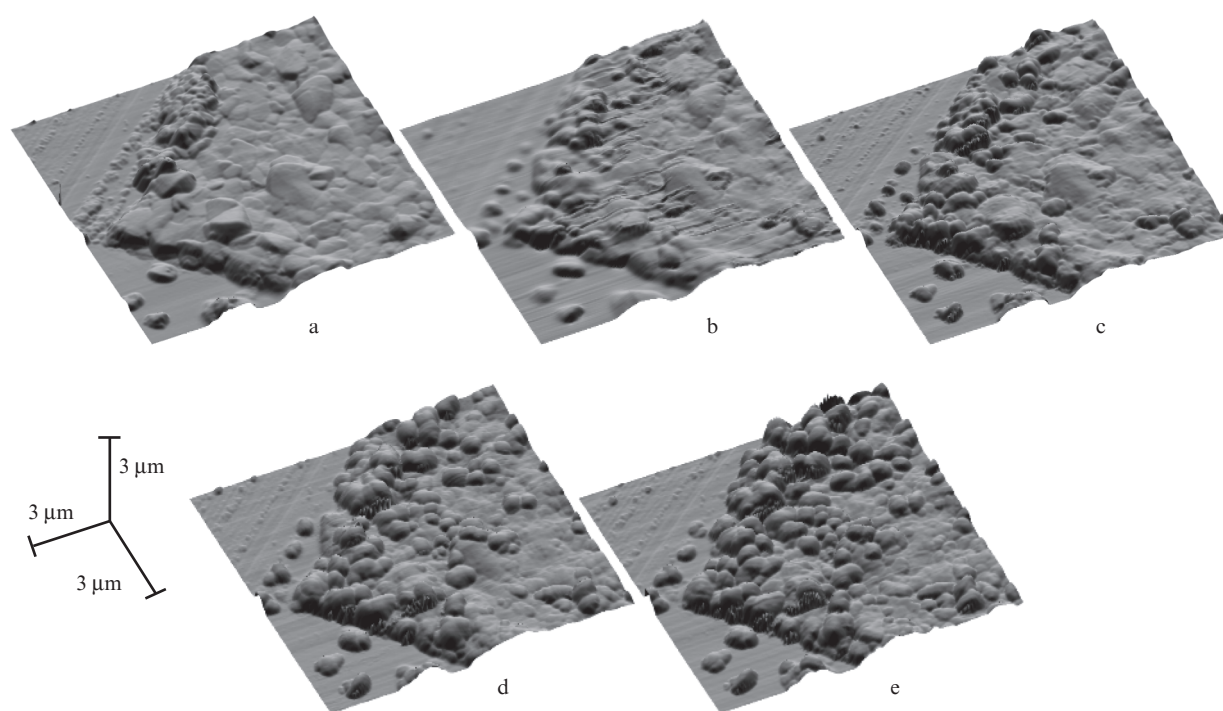


Figure 2. AFM images of the film surface (a) before the illumination and after the (b) first, (c) second, (d) third, and (e) fourth illumination stages.

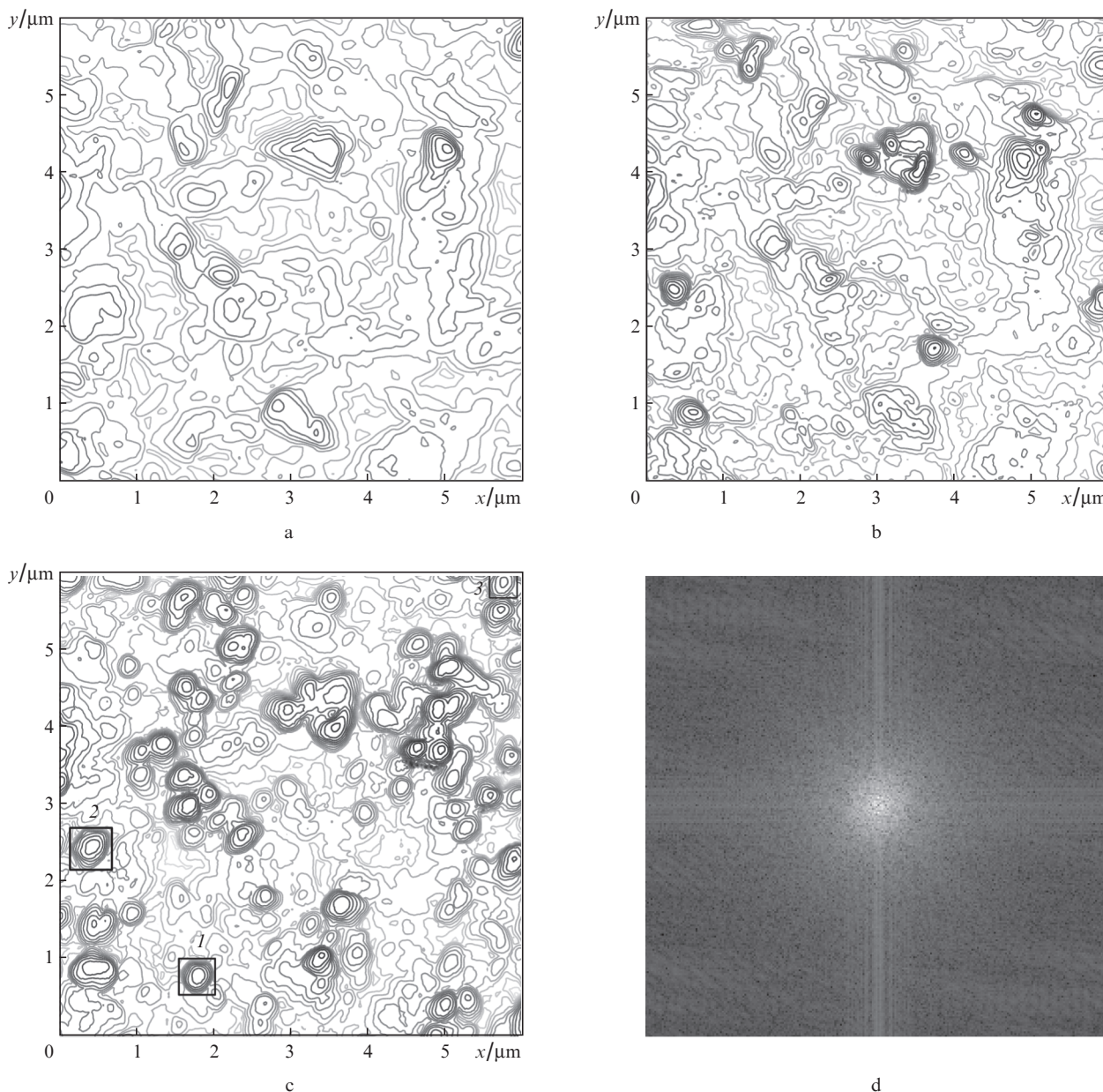


Figure 3. Formation of a random nanorelief on the film surface under illumination: (a–c) lines of constant height for a sample $6 \times 6 \mu\text{m}$ in size (a) before illumination, (b) after exposure to linearly polarised light, and (c) after additional exposure to light with orthogonal polarisation; (d) a Fourier transform of the final film profile on the logarithmic scale. The squares in Fig. 3c indicate the protrusions shown in Fig. 4. The isolines are drawn with a step of 20 nm.

polarisation by 90° involves even more mobile molecules in absorption than in the first stage. Indeed, the changes in the relief after the rotation of polarisation and additional 30-min illumination are much more pronounced than in the first stage and cover almost entirely the film surface. Further illumination also changes significantly the surface relief but not so dramatically as in the third stage (Fig. 2d).

The images in Fig. 2 were obtained by subtracting the constant slope and aligning the AFM scans via searching the maximum of cross-correlation function.

The structures formed do not exhibit periodicity, as is evidenced by the Fourier transform of the final film profile (Fig. 3g). However, these structures have a very important feature, which is most pronounced in the images of lines of

equal height (Fig. 3). It can be seen that illumination leads to the formation and growth of structures on the film surface, the shape of which is similar to hemispherical, with a characteristic radius of $\sim 200 \text{ nm}$ [20]. This is especially pronounced in Fig. 4, where several film areas around newly formed protrusions are shown on enlarged scale (these areas are framed in rectangles in Fig. 3c). Some deviation of the protrusion shape from spherical can be related to the specificity of AFM measurements (namely, the probe shape). Due to the finiteness of the tip angle and the asymmetric shape of the cantilever tip, the maximum slope of the surface that can be detected in AFM images is $\sim 70^\circ$ for a slope in the direction of the x axis, $\sim 80^\circ$ for the slope along the y axis, and $\sim 60^\circ$ for the slope in the opposite direction.

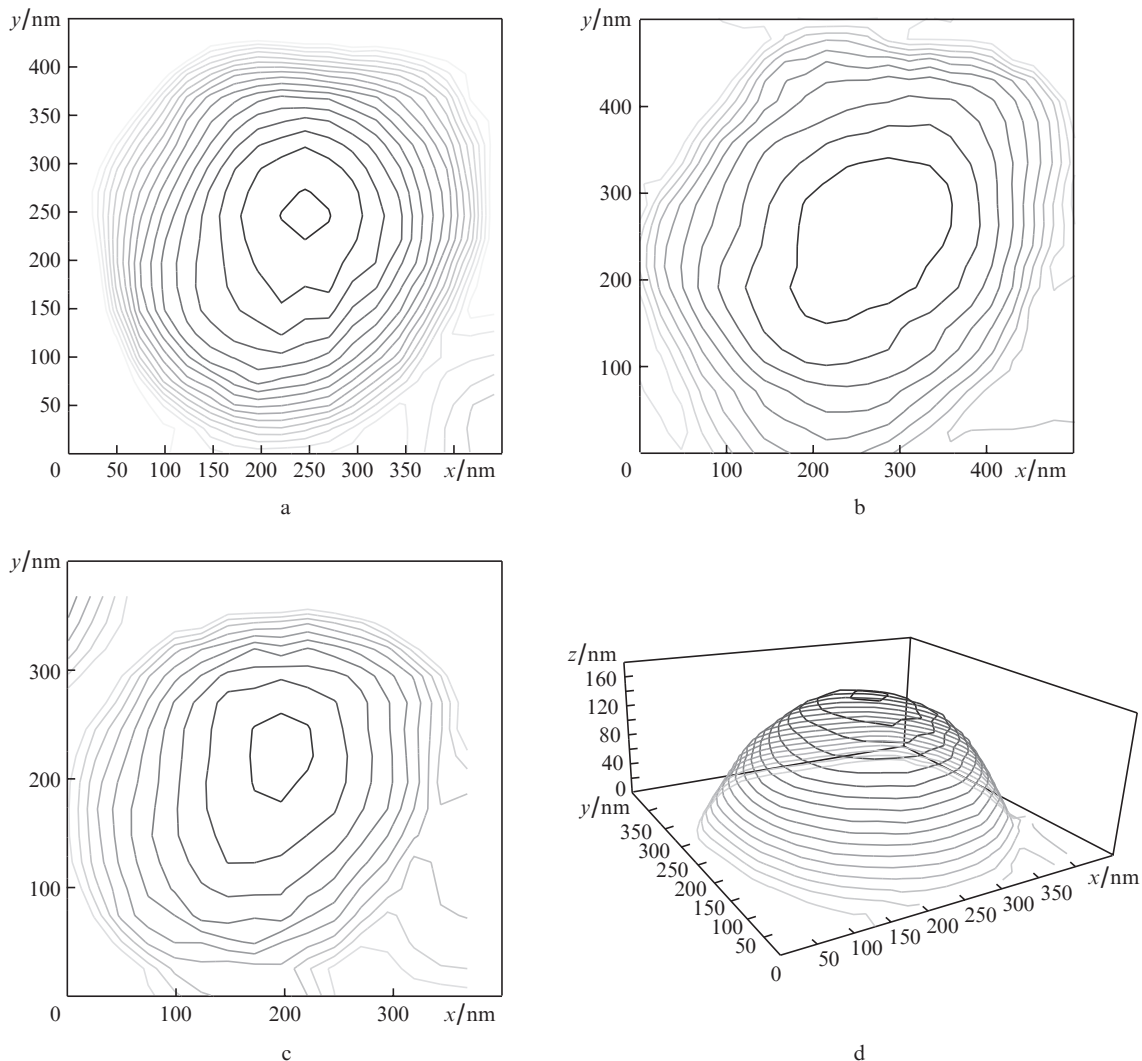


Figure 4. Enlarged contour image of the film surface profile in the regions where spherical protrusions are formed. The position of protrusions on the sample surface is shown by rectangles in Fig. 3c (numbers 1, 2, and 3 correspond to panels a, b, and c). Panel d shows a 3D image of the first protrusion. The intervals between isolines are (a, d) 10 and (b, c) 20 nm.

4. Results and discussion

The formation of spherically shaped structures, observed in the experiment, cannot be explained within any of proposed theoretical models. It is most likely that there is another mechanism controlling the photoinduced molecular motion. The fact that this phenomenon was not observed previously can be explained by the specific features of the nanostructured film under study: it consists of only azo dye molecules, without a forming matrix, and has a peculiar anisotropic nanostructure.

The experimentally observed process resembles the formation of a liquid droplet on a poorly wetted surface. This dynamics suggests that the photoinduced motion of azo dye molecules is mainly controlled by the surface tension forces. The presence of a fairly thick (on the nanoscale) film layer hinders interpretation of the surface tension effect. The point is that the film is not entirely involved in the formation of nanodroplets on its surface. The optical density of the dye film is about 0.5; therefore, approximately only third of the activating-light power reaches the bottom layers of the film. In addition, the mobility of the bottom molecular layers can be reduced due to the adhesion to the glass substrate.

Thus, the properties of the material on which a droplet is formed are unclear, because an unaffected azo dye layer with uncertain properties serves as a substrate in this case. The reason for this uncertainty is as follows: the degree of ordering of this layer (which arises during the film formation on a centrifuge) is unknown; therefore, one cannot estimate the surface tension coefficient for the boundary between a droplet formed and the bottom dye layer that is not involved in the photoinduced mass transport.

The physical pattern becomes more definite when the bottom dye layer is excluded from consideration. Figure 5 shows the AFM images of the film edge before and after illumination. In the forefront one can see two very thin (~ 20 nm) dye strips on the glass. As was mentioned above, a geometrically regular notch (it is clearly seen in the images) was intentionally cut to the glass for spatial alignment of different images. The brightest evidence of the concept of surface tension forces is the observation of the modified relief of these thin dye layers. One can clearly see that under illumination the dye is divided into droplets like a liquid on a nonwettable surface.

Note that there were indications in the literature to the participation of surface tension forces in the effects of photo-

induced change in the azo-containing film relief. In particular, Pedersen et al. [19] determined the film profile $h(x)$ by minimising the functional

$$F[h] = \int_{-\infty}^{\infty} [\sqrt{1 + (dh/dx)^2} - 1] dx - K \int_{-\infty}^{\infty} S_{\text{eff}}^2(x) h(x) dx + \alpha \int_{-\infty}^{\infty} [h(x) - d] dx. \quad (1)$$

The first term presents the contribution of the surface tension; the second term describes the volume energy interaction of molecules, expressed through the phenomenologically introduced order parameter S_{eff} (which is determined by the polarisation state of activating radiation); and the third term provides conservation of volume (α is the Lagrange factor and d is the initial film thickness).

On the assumption that the film is sufficiently uniform, the description of our experiment within the model [19] should

yield opposite results. Indeed, since the polarisation is not modulated in our case, the orientational state should be the same at all surface points; therefore, the second term in Eqn (1) becomes invalid. Then the minimum of the functional will obviously be attained for a flat film surface.

Undeniably, the AD-1 azo dye film under study cannot be considered as homogeneous on the submicron scale. Therefore, the order parameter can be spatially modulated. The energy of a molecule in the mean field of the neighboring ordered molecules can be described by the Maier–Saupe potential [24]:

$$W = -\frac{AS}{R^6} \left(\frac{3}{2} \cos^2 \beta - \frac{1}{2} \right), \quad (2)$$

where β is the angle between the director and the molecular axis; $S = \langle \frac{3}{2} \cos^2 \beta - \frac{1}{2} \rangle$ is the order parameter; and R is the average distance between molecules. The volume energy of intermolecular interaction is obtained by averaging poten-

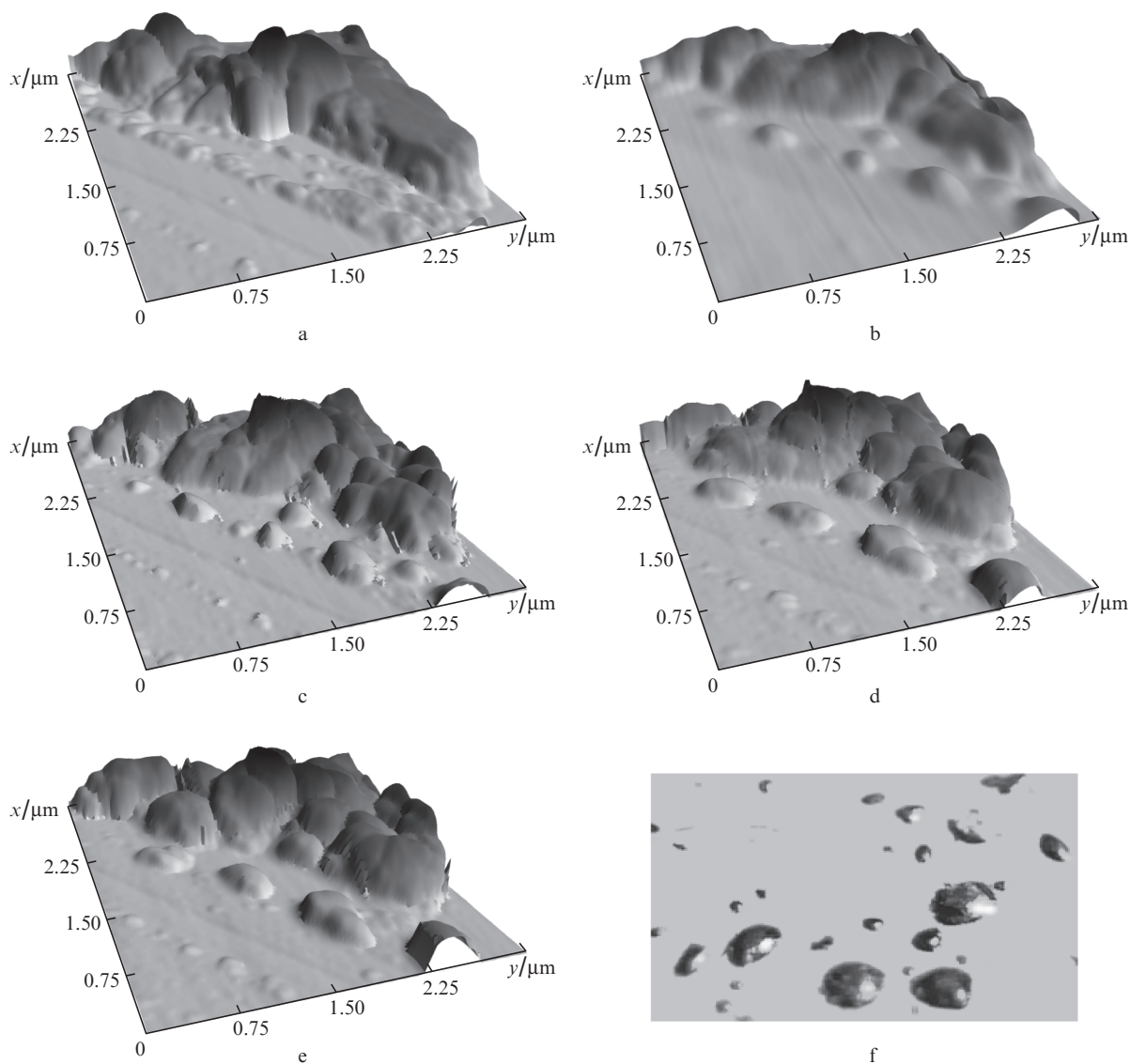


Figure 5. Formation of droplet-like protrusions on the glass substrate: (a) the initial film profile; (b–e) the profiles after the first, second, third, and fourth illumination stages, respectively; and (f) solidified droplets of AD-1 melt on a glass substrate. The height scale is equal to the scale in the lateral plane.

tial (2) over the angle β between the molecular axis and the director: $W = -AS^2/R^6$.

If the dye molecules are mobile, the film profile should change toward minimisation of the volume interaction energy. In the one-dimensional case this change corresponds to minimisation of the second term in formula (1). As a result, molecules should be displaced toward the region with a large order parameter. However, since the azo dye molecules have a highly elongated shape, the direction of intermolecular forces is significantly anisotropic, a fact that must be taken into account. As follows from the consideration of the Gay–Berne potential [25], the interaction between molecules occurs generally in the direction perpendicular to their orientation. Since light polarisation aligns molecules in the direction perpendicular to the electric vector, it should determine the dominant mass transport direction. Therefore, the surface relief, which changes under exposure to linearly polarised light, should have a pronounced elongated structure in the direction perpendicular to the polarisation direction; however, this situation is not observed experimentally.

As in [19], in all mechanisms of photoinduced change in the film relief that take into account the surface tension, the role of the latter is to hinder the relief formation and smooth the film surface [18, 26, 27].

In contrast to this approach, our experimental data on AD-1 azo dye films suggest that the illumination serves only to make molecules mobile, and their motion is controlled by surface tension forces. However, to explain the results presented in Fig. 5, it is necessary to take into account the contribution of the surface energy E_s not only at the dye–air interface but also at the dye–glass and glass–air interfaces:

$$E_s = \int_{S_1} \gamma_1 dS + \int_{S_2} \gamma_2 dS + \int_{S_3} \gamma_3 dS, \quad (3)$$

where S_1 , S_2 , S_3 are the surface areas of the dye–air, glass–dye, and glass–air interfaces, respectively, and γ_1 , γ_2 , and γ_3 are the surface-tension coefficients at the corresponding interfaces. The balance of the surface tension forces and, therefore, the shape of the structures formed during irradiation are mainly determined by the ratio of the γ_1 , γ_2 , and γ_3 coefficients. Naturally, these parameters are unknown, and, therefore, one cannot calculate the expected droplet shape. In this context, we chose another way. The film under study is actually a solid; hence, we can suggest that the melt of the same dye on the same substrate should behave similarly, because the coefficients γ_1 , γ_2 , and γ_3 in both cases must be fairly close. To study the behaviour of AD-1 azo dye melt, the sample was heated to melting temperature, and its state was monitored with an optical microscope. When passing through the melting point, the dye melted with subsequent fast formation of droplets (Fig. 5f), the shape of which was very close to that of the structures obtained on a glass surface at a photoinduced change in the relief. Thus the mechanism proposed was confirmed.

Based on the above considerations, one can explain the formation of droplet-like structures on the surface of thick films (Figs 2, 3). However, in this case, it is critically important to take into account the mutual orientation of molecules in a droplet and in the sublayer on which this droplet is formed. The experiments showed that, under exposure to linearly polarised light, the relief changes only on some part of the film surface. This result is in agreement with the suggestion that molecules in individual regions are oriented in a certain

way during film preparation, thus forming domains [22]. Indeed, illumination by linearly polarised light leads to activation of molecules in only those domains where the director is oriented along the polarisation direction. If we assume that the interface between domains is fairly sharp, the energy functional should also include the surface energy at the domain interface. With allowance for the strong dependence of the Gay–Berne potential on the mutual orientation of molecules, this energy can be close to the surface energy at the dye–air interface. In this case, a domain is isolated from the environment, and, if the molecules in this domain are mobile, the surface tension forces can transform it into a sphere. However, molecules are reoriented perpendicularly to polarisation of activating light, simultaneously with the mass transport; as a result, the mobile molecules cease to absorb light, and further motion stops.

Thus, the proposed mechanism of a photoinduced change in the dye film relief is based on the surface tension forces, which divide the dye into droplets similar to liquid droplets on a poorly wetted surface. In this case, the activating radiation provides molecular mobility, similar to that of molecules in a very viscous liquid. Based on the mechanism proposed, one can explain the effects of photoinduced change in the relief of azo-containing films under uniform (in intensity and polarisation) illumination. The revealed effect of photoinduced change in the relief of AD-1 films can be used in nanophotonics to form anisotropic structures on subwave spatial scale.

Acknowledgements. We are grateful to A.M. Dubrovkin for his help in the experiments. This study was supported in part by the Russian Foundation for Basic Research (Grant Nos 10-02-01089, 08-02-01460-a, and 09-02-01306-a).

References

1. Neckers D.C., von Büнау G., Jenks W.S. (Eds.) *Advances in Photochemistry* (Hoboken: Wiley, 2002) Vol. 27.
2. Chigrinov V., Prudnikova E., Kozenkov V., Kwok H., Akiyama H., Kawara T., Takada H., Takatsu H. *Liquid Crystals*, **29**, 1321 (2002).
3. Yu Y., Nakano M., Ikeda T. *Nature*, **425**, 145 (2003).
4. Yager K.G., Barrett C.J. *J. Photochem. Photobiol. A: Chem.*, **182**, 250 (2006).
5. Sekkat Z., Dumont M. *Appl. Phys. B: Lasers and Optics*, **53**, 121 (1991).
6. Yager K., Barrett C. *Current Opinion Sol. State Mater. Sci.*, **5**, 487 (2001).
7. Chigrinov V.G., Kozenkov V.M., Kwok H.S., in *Optical Applications of Liquid Crystals* (Bristol: IOP, 2003).
8. Dumont M., Froc G., Hosotte S. *Nonlinear Optics*, **9**, 327 (1995).
9. Kiselev A. *J. Phys.: Condensed Matter*, **14**, 13417 (2002).
10. Chigrinov V., Pikin S., Verevochnikov A., Kozenkov V., Khazimullin M., Ho J., Huang D.D., Kwok H.S. *Phys. Rev. E*, **69**, 061713 (2004).
11. Rochon P., Batalla E., Natansohn A. *Appl. Phys. Lett.*, **66**, 136 (1995).
12. Kim D.Y., Tripathy S.K., Li L., Kumar J. *Appl. Phys. Lett.*, **66**, 1166 (1995).
13. Natansohn A., Rochon P. *Chem. Rev.*, **102**, 4139 (2002).
14. Holme N.C.R., Nikolova L., Hvilsted S., Rasmussen P.H., Berg R.H., Ramanujam P.S. *Appl. Phys. Lett.*, **74**, 519 (1999).
15. Yager K.G., Barrett C.J. *J. Chem. Phys.*, **120**, 1089 (2004).
16. Lefin P., Fiorini C., Nunzi J.M. *Pure Appl. Opt.*, **7**, 71 (1998).
17. Kumar J., Li L., Jiang X.L., Kim D.Y., Lee T.S., Tripathy S. *Appl. Phys. Lett.*, **72**, 2096 (1998).
18. Sumaru K., Yamanaka T., Fukuda T., Matsuda H. *Appl. Phys. Lett.*, **75**, 1878 (1999).
19. Pedersen T., Johansen P., Holme N., Ramanujam P., Hvilsted S. *Phys. Rev. Lett.*, **80**, 89 (1998).

20. Dubrovkin A.M., Ezhov A.A., Kozenkov V.M., Magnitskii S.A., Nagorskii N.M., Panov V.I. *Kvantovaya Elektron.*, **40**, 286 (2010) [*Quantum Electron.*, **40**, 286 (2010)].
21. Dzhang Ya. C., Kozenkov V.M., Magnitskii S.A., Nagorskii N.M. *Kvantovaya Elektron.*, **36**, 1056 (2006) [*Quantum Electron.*, **36**, 1056 (2006)].
22. Dubrovkin A., Jung Y., Kozenkov V., Magnitskii S., Nagorskiy N. *Laser Phys. Lett.*, **4**, 275 (2007).
23. Magnitskiy S., Nagorskiy N., Kozenkov V. *Laser Phys.*, **18**, 1400 (2008).
24. Maier W., Saupe A. *Zeitschrift für Naturforschung A*, **14**, 882 (1959).
25. Gay J., Berne B. *J. Chem. Phys.*, **74**, 3316 (1981).
26. Barrett C.J., Natansohn A.L., Rochon P.L. *J. Phys. Chem.*, **100**, 8836 (1996).
27. Barrett C., Rochon P., Natansohn A. *J. Chem. Phys.*, **109**, 1505 (1998).