Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Laser-induced “craters” and “hills” formation in the azobenzene-containing polymethacrylates films

Alexey Bobrovsky[a]*, Konstantin Mochalov[b], Daria Solovyeva[b], Valery Shibaev[a], Martin Cigl[c], Věra Hamplová[c], Alexej Bubnov[c]

Functional organic polymer materials with an ability to change their surface topography in response to external contactless stimuli, like light irradiation, attract considerable attention. This work is devoted to the study of contactless control of the surface topography and formation of the surface features in the amorphousized and liquid crystalline films of two azobenzene-containing polymers. The investigated polymers are side-chain polymethacrylates containing the azobenzene chromophores with two lateral methyl substituents in *ortho*-positions and differing in the length of flexible spacer with six and ten methylene units. Two lateral methyl substituents at azobenzene chromophore assure high photoresponse of these polymeric samples in whole visible spectral range. Irradiation of the polymethacrylate films by focused polarized light of green (532 nm) and red (633 nm) lasers induces a specific photodeformation of the films surface. In the case of the green light formation of the circular “craters” having anisotropic borders was found, whereas for the red light highly asymmetric “hills” were observed. The possible mechanisms of the surface topography formation and their features are discussed.

Introduction

Functional organic materials exhibiting contactless mass transport phenomena and contactless tuning of their mechanical properties attract noticeable attention from both the fundamental and practical point of view.[1-3] Creation of the different surface topographies and structures, as well as their further reconfiguration and relief tuning, is an one of the topics of the modern soft matter and material sciences. The point is that these films and coatings having variable topography of the surface provide great opportunities for the modification of the adhesion, wetting and other important physical properties of these smart systems.[1] Among the variety of the approaches for such control and tuning of the surface structure, light is the most useful and convenient tool, especially for contactless imprinting of the different reliefs on top of the films surfaces and coatings.[4, 5] In order to achieve such light sensitivity, the desired materials should contain photosensitive (photochromic) fragments capable of photoreaction, such as photoisomerization, photocyclization, photodegradation, etc.

Azobenzene moieties are the one of the most popular photochromic groups due to the fast and reversible *E/Z* isomerization[6] and photoorientation processes under polarized light action.[7-11] The *E/Z* isomerization leads to significant decrease in azobenzene group anisometry, and in the case of liquid crystalline (LC) systems often results in disruption of LC order[12-16] or changing of the different parameters and properties of the mesophases.[16-21] Irradiation with polarized light induces rotational diffusion of chromophores in the direction perpendicular to the polarization plane of the incident light.[7-11] This phenomenon is successfully used for the generation of photoinduced order, linear dichroism and birefringence. Moreover, irradiation by light with spatially modulated intensity or/and polarization is demonstrated to be powerful tool for the creation of different periodic structures.[5, 22-34] The most studied surface phenomenon in azobenzene-containing polymers is the formation of the so-called surface relief gratings (SRG) under irradiation with interfering coherent laser beams.[22-34] These periodic structures have period in the range of several micrometers and depth of hundred nanometers. Since the discovery of this effect in the middle of nineties a large number of papers devoted to the SRG formation has been published. SRG formation demonstrates a great potential for the creation of responsive materials with modified surface properties and as periodic media for the lasing generation.[22-34]

Another possibility of the creation of surface patterns is irradiation with collimated laser beam. Thus, in several papers [35-39] the interesting phenomenon of spontaneous periodic surface relief formation under single beam irradiation was investigated and possibility of surface patterns periodicity an amplitude control was demonstrated.

On the other hand, the effect of a single focused laser beam is much less studied phenomenon.[40-47] For amorphous polymer systems with the azobenzene chromophores laser beam action induces the formation of so called “holes” or “craters” with preferred mass-transfer along the polarization direction.[40, 41] For the LC polymers more complex behaviour is found.[44-46] For example, as is shown in [44] direction of the mass-transfer or preferred deformation for the nematic polymer studied does not depend on polarization direction and the initial alignment of the chromophores is responsible for this effect. It is noteworthy, that despite the huge amount of experimental data concerning mass-transfer phenomena, photodeformation and SRG inscription and also some theoretical works,[48] the exact mechanism of these processes is still unknown.

The *main objective of this work* is to study the formation of surface features and their tuning under single beam laser irradiation of the films of the two highly photosensitive LC polymethacrylates samples with the azobenzene containing side groups, denoted here as **PMDA 6/10** and **PMDA 10/6** (see details in further section). The utilized photochromic azobenzene moieties are modified by lateral methyl *ortho*-substituents providing extreme thermostability of the photoinduced *Z*-isomer and high photosensitivity. As it has been shown,[49] irradiation even with the red polarized light induces effective process of the photoorientation of the side photochromic groups in direction perpendicular to the polarization of the incident light. This effect makes these polymers different from the majority of azobenzene-containing systems without lateral methyl substituents.[50-52]

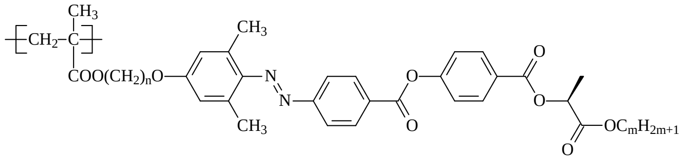
Taking into account a quite unique behaviour (as described above) of the laterally substituted polymethacrylates, the investigation of the surface phenomena in these polymers under focused laser beams action is a subject of much current and promising interest. A special attention is paid to the comparison of the effect of light irradiation of two different wavelengths, namely 532 nm and 633 nm, on the surface deformation of the polymethacrylate films.

This paper is organized as follows. The first part presents the investigation of the influence of different factors, such as wavelength of the excitation light, polymers chemical structure and phase state of the films on the peculiarities of the photoinduced surface deformation and mass-transfer. The second part is devoted to the analysis of the obtained results and discussion of some hypothesis explaining possible mechanisms of the observed processes of surface features formation and, hence will considerably contribute to better understanding of the contactless control of the surface topography, which is a very highlighted topic of the soft matter chemistry and physics.

Experimental

Materials

Polymethacrylates under study with flexible spacer (6 and 10 methylene units) and the same azobenzene chromophores with two lateral methyl substituents in *ortho*-positions were designed and synthesized by a radical polymerization of corresponding methacrylic monomers according to recently published procedure.[49] The mesomorphic behaviour of the respective monomers and resulted polymethacrylates together with some photo-optical properties were described.[49] The chemical structures of two laterally substituted polymethacrylate samples used are presented below.



n=6, m=10, **PMDA6/10**
n=10, m=6, **PMDA10/6**

It was shown that both methacrylates form the chiral nematic (cholesteric) and the orthogonal smectic A* (SmA*) mesophases depending on the spacer length (Table 1). The respective polymethacrylates are characterized by low values of the molecular mass and can be considered as oligomers. Both resulting polymethacrylates exhibit a very similar glass transition temperatures and molecular masses, but considerably differ in the mesomorphic behaviour and the phase transition temperatures. Broad chiral nematic phase (N*) has been detected for the **PMDA 6/10** polymethacrylate, while the orthogonal smectic A* (SmA_1*) phase was detected for the **PMDA 10/6** polymethacrylate.

Table 1. Mesomorphic behaviour (polarizing optical microscopy), glass transitions (DSC) and molecular mass characteristics of the designed polymethacrylates.

Polymer	Glass transition / °C	Phase transitions / °C	M_w	M_w/M_n
PMDA 6/10	~20	**N* 65–70 I**	11000	1.34
PMDA 10/6	~20	**SmA_1* 90–96 I**	10800	1.27

Samples preparation

The polymethacrylate films having free surfaces were prepared as follows. Small amount of the polymer sample was placed between two glass plates, heated up to 100°C. After 30 min of keeping at the same temperature two glass substrates were separated by shearing. As a result, two glass plates covered by polymeric film were obtained. After keeping in isotropic state (at 80°C for **PMDA 6/10** and at 100°C for **PMDA 10/6**), two different types of the films with thickness ca. 2-5 µm were obtained: (i) *Quenched films* were obtained by fast cooling from isotropic melt to room temperature. According to observation in polarizing optical microscope, these films are fully isotropic, i.e. in crossed polarizers they are completely dark (see Fig. S1a, c, e). (ii) *Annealed LC films* were obtained by annealing at 60°C during 3 days followed by slow cooling down (cooling rate1 °/min). These films are characterized by the birefringent textures (Fig. S1b, d, f).

Experimental setup for simultaneous AFM and POM investigations

For the photo-optical and surface investigations, the special experimental setup was designed as a part of the unique setup "System for probe-optical 3D correlative microscopy" (http://ckp-rf.ru/usu/486825/) [45] (see Scheme S1 in Supporting information). It is a combination of the Atomic Force Microscopy (AFM) scanning system, upright optical microscope, optical table for inverted optical microscopy and cross-polarized illumination system. The samples (**1**) prepared as described above were placed directly on the top of scanning the XY- piezostage (**2**) of the SPM NTEGRA BASE (NT-MDT) integrated with the home-built optical microscope. The AFM-head (**3**, SMENA, NT-MDT) was mounted onto the SPM NTEGRA BASE and a tip of AFM-probe was placed in few micrometers vicinity to the optical axis. The spot of the green (**4**, 532 nm, LCM-S-111, LASER-EXPORT Co. Ltd) or red (25LHP928-230, Melles-Griot) lasers used for sample irradiation was aligned to the same spatial area through the special adjusting mirror system as it is shown on the Scheme S1.

Light intensity for both wavelengths is 80 µW, as it has been checked by LaserMate-Q (Coherent) intensity meter; beam is focused into spot with diameter ca. 30 µm.

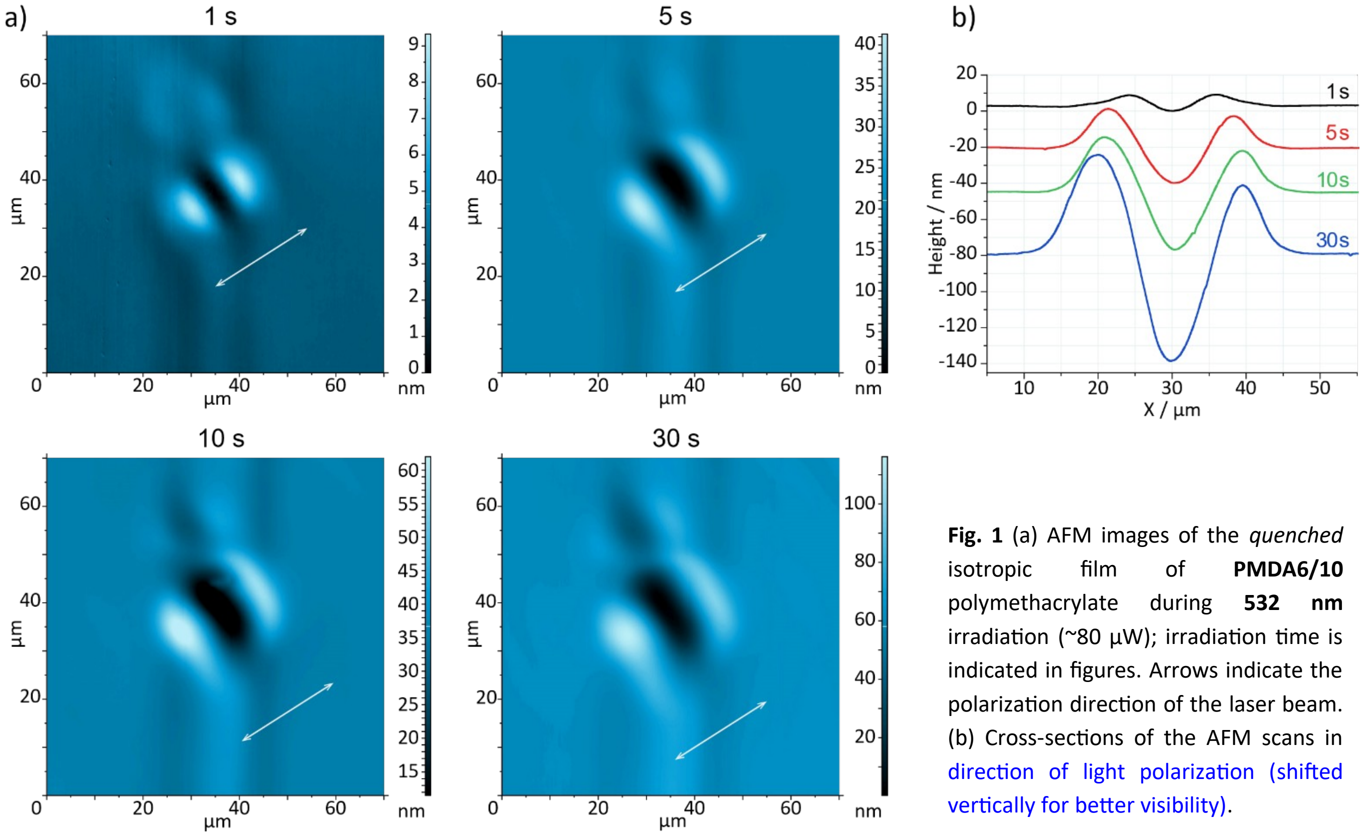


Fig. 1 (a) AFM images of the *quenched* isotropic film of **PMDA6/10** polymethacrylate during **532 nm** irradiation (~80 µW); irradiation time is indicated in figures. Arrows indicate the polarization direction of the laser beam. (b) Cross-sections of the AFM scans in direction of light polarization (shifted vertically for better visibility).

All optical images were obtained with Optem Zoom 125C upright microscope (**5**) adjusted to the overall optical axis passed through the same point as the AFM-probe tip.

The cross-polarized illumination system consists of the ACE® Light Source (**6**), the homemade condenser lens system (**7**), polymer linear polarizing film (as a polarizer) (**8**) placed directly on condenser at arbitrary and fixed angle and similar film as analyzer (**9**) placed into rotatable CCD/microscope coupler (**10**). Angle of the analyzer film was adjusted with rotation of CCD/microscope coupler up to achieving of darkest field as microscopic image.

Results and discussion

Surface features of the films irradiated by the green laser (532 nm)

Let us consider the effect of focused polarized green light (532 nm) on the surface of the quenched films of the investigated polymethacrylates. As it can be observed on Figs. 1-2, the irradiation with green laser light results in formation of the “craters”. It is noteworthy, that for nematogenic **PMDA 6/10** polymer “annular uplifts” or borders formed under irradiation, possess a strong anisometry (Fig. 1a) being much higher in the direction along the polarization plane of the incident beam. The depth of the crater after 30 seconds of the irradiation is ca. 60 nm, whereas the height of the crater borders is comparable and equal to ca. 45 nm.

Topography of the obserbed surface features does not depend on light intensity; irradiation with light of low intensity (~0.8 µW) induces the similar craters formation (Fig. S2a).

For the smectogenic **PMDA 10/6** polymer, the anisotropy of the craters is almost negligible (Fig. 2a). Moreover, for this polymer irradiation for more than 10 s induces the formation of the “hill” in the centre of the crater (Fig. 2a, b). This hill is more clearly visible on 3D images presented in Fig. 2. The depth of the craters and height of the “annular uplifts” for this polymer is lower than that obtained for **PMDA 6/10** polymethacrylate. Remarkably, in this case the height of the borders is even bigger than the depth of craters (Fig. 2b). These results are in very good accordance with previously obtained data on photoorientation process in films of these polymers.[48] The rate of the photoinduced dichroism growth and its maximal values are considerably smaller for the **PMDA 10/6** polymer with longer spacer than that for the **PMDA 6/10** polymethacrylate with shorter spacer.

Mass-transfer phenomenon and formation of craters was accompanied with clearly visible changes in the birefringence of the polymer films that appeared as bright or dark spots in the polarizing optical microscopy (POM) microphotographs (Fig. S1). For the quenched isotropic films in initially dark films in crossed polarizers bright circular spots have been appeared together with broad bright “wings” oriented along the polarization axis of the incident light (Fig. S1a, c, e). It can be assumed that appearance of such “wings” is probably associated with excitation light scattering on anisotropic crater “borders” (for green laser) or “hills” (for red laser). Scattered light causes photoorientation process in areas of films that are outside the main laser spot. For the annealed films photoinduced local changes in birefringence are less distinct (Fig. S1b, d, f) due to impeding of the photoorientation process in the LC state.[43]

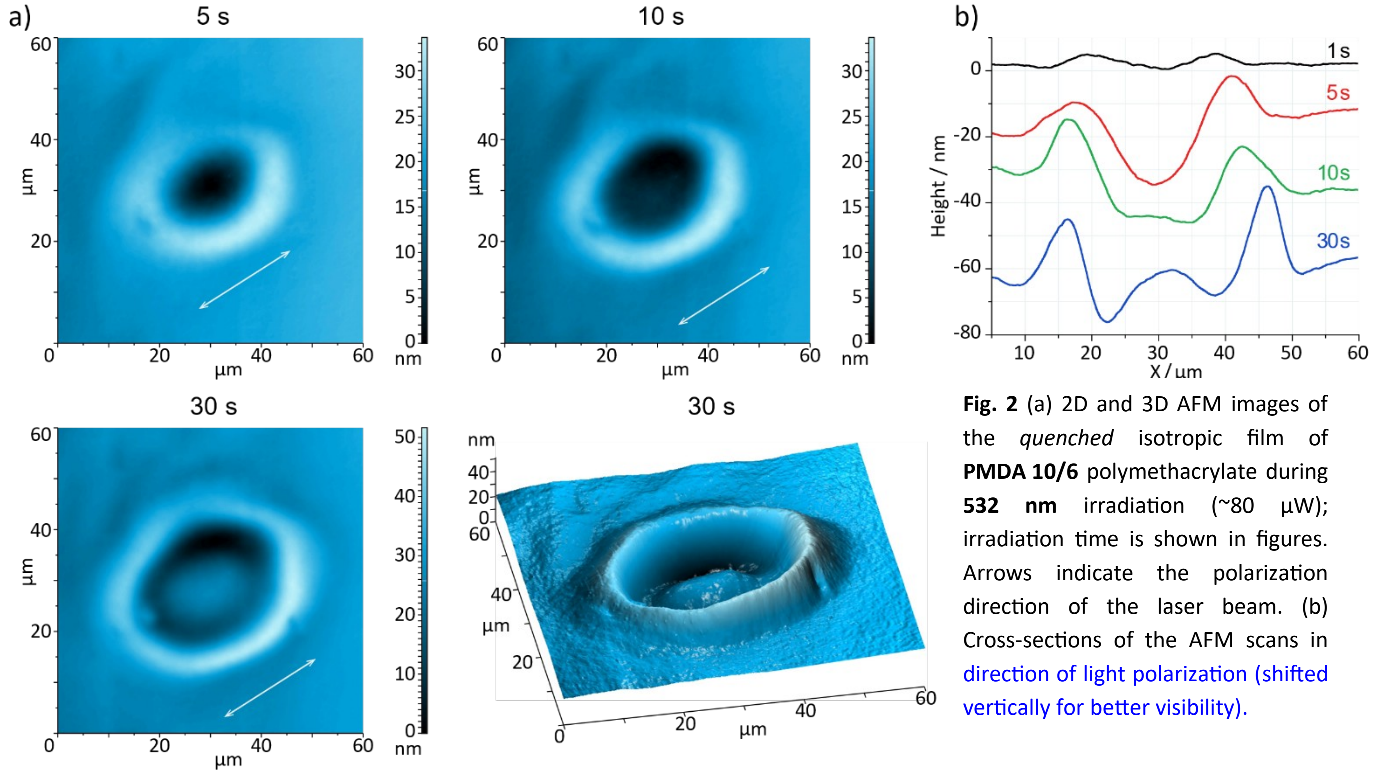


Fig. 2 (a) 2D and 3D AFM images of the *quenched* isotropic film of **PMDA 10/6** polymethacrylate during **532 nm** irradiation (~80 µW); irradiation time is shown in figures. Arrows indicate the polarization direction of the laser beam. (b) Cross-sections of the AFM scans in direction of light polarization (shifted vertically for better visibility).

For the annealed LC films of both polymethacrylates the same features in photoinduced surface deformation were found (Fig. 3, S2b; data for annealed **PMDA 10/6** film are not shown). Excitingly, the rate of the growth of the crater depth is considerably higher for the annealed films (Fig. 3b). Thus, formation of the LC order does not suppress (as it can be expected), but even accelerates the craters formation process.

Surface features of the films irradiated by the red laser (633 nm)

In contrast with the results obtained under green laser irradiation, the irradiation of the samples with focused beam of the red He-Ne laser (633 nm) induces formation of anisotropic “hills” in films for both polymethacrylates (Fig. 4). First minute of the irradiation results in the formation of symmetric annular groove, whereas further irradiation transforms this groove to the highly anisometric “hill”. These effects are the same for both polymethacrylates, but are found to be less distinct for the annealed LC films (Fig. S3, S4).

The speed of the surface features formation under the red light irradiation is about two orders of magnitude lower (in comparison to that obtained under green light) that adequately correlates with a very low absorbance of the film at 633 nm. Absorbance of the studied polymer films at 532 nm is ca. 80 times higher than that obtained at 633 nm (Fig. S5).

Thus, changes in wavelength value of the light used for the irradiation results in drastic changes in shape of the photoinduced surface anisotropic structures. The possible origin of the observed phenomena is discussed below.

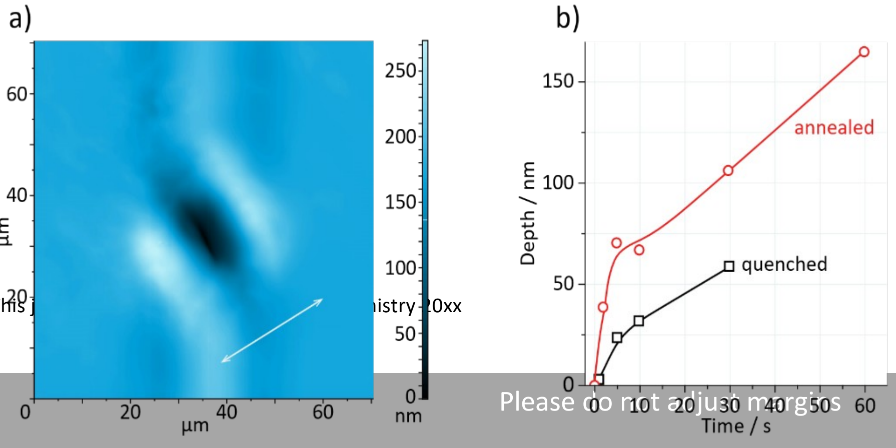


Fig. 3 (a) AFM image of the *annealed* **PMDA 6/10** polymethacrylate film during **532 nm** irradiation (~80 µW); irradiation time is 1 min. Arrow indicates the polarization direction of the laser beam. (b) Dependence of the crater depth on the irradiation time for quenched and annealed films.

Possible mechanisms for the “craters” and “hills” formation

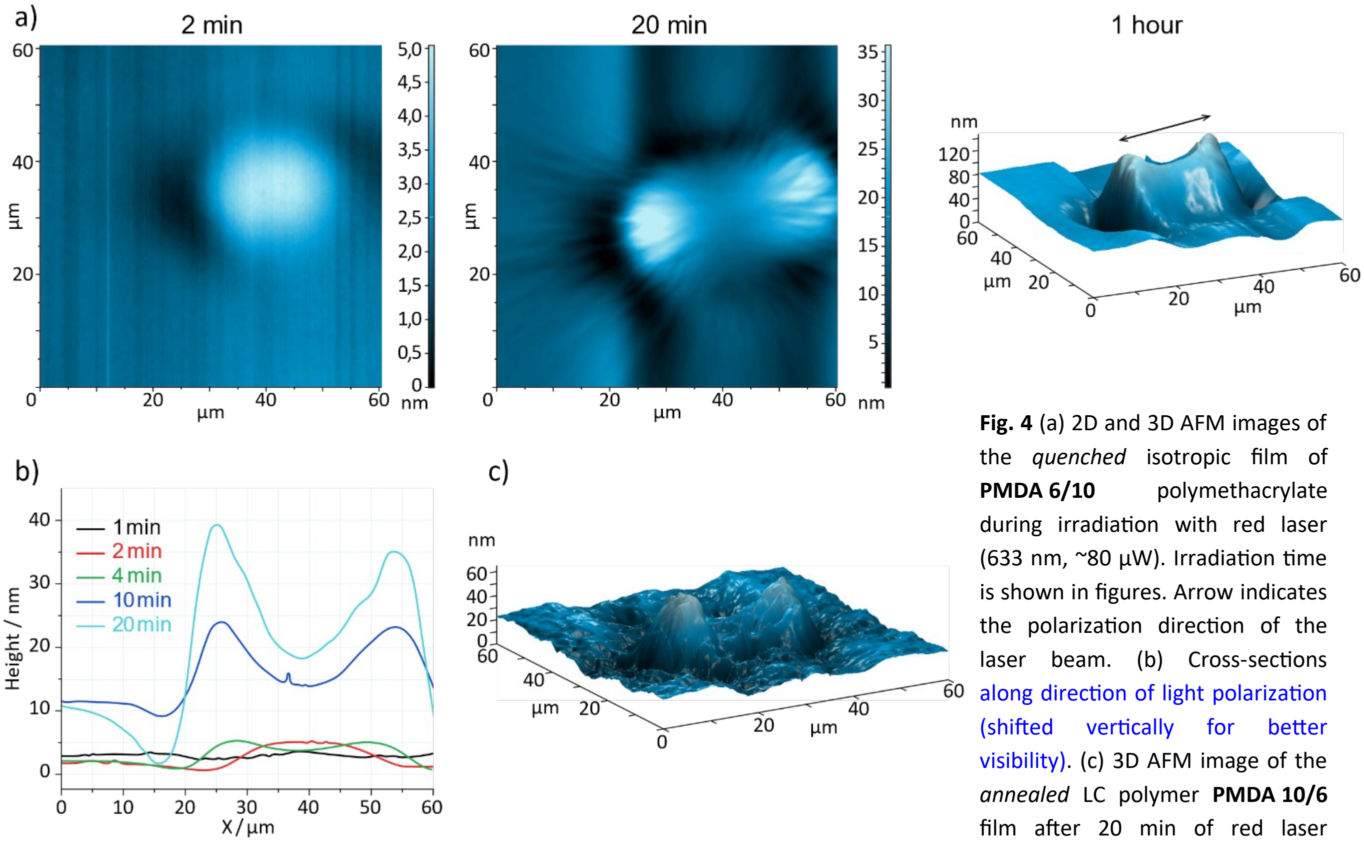


Fig. 4 (a) 2D and 3D AFM images of the *quenched* isotropic film of **PMDA 6/10** polymethacrylate during irradiation with red laser (633 nm, ~80 µW). Irradiation time is shown in figures. Arrow indicates the polarization direction of the laser beam. (b) Cross-sections along direction of light polarization (shifted vertically for better visibility). (c) 3D AFM image of the *annealed* LC polymer **PMDA 10/6** film after 20 min of red laser

Let us consider possible mechanisms of the “craters” and “hills” formation in films of the studied azobenzene-containing polymethacrylates. Herein we will discuss several possible hypothetical routes for the formation of the surface features.

The most plausible mechanism of the photomechanical deformation in azobenzene-containing films is related to the generation of internal opto-mechanical stress under polarized light action. Polarized light induces rotational diffusion or gradual rotation of the chromophores in direction perpendicular to the polarization plane during cycles of E-Z-E photoisomerization. This chromophores’ alignment can also cause reorientation of the methacrylate backbones, as the chromophores and polymer chains are covalently linked together. As result, macroscopic deformation in polymer films might take place due to the strong mechanical coupling between the two “subphases”, each containing chromophores and polymer backbones.[48, 54-58] This assumption lies in the base of the recently developed theory predicting mechanical stress generated under polarized light action in the range from 100 MPa up to ~2 GPa.[57-59] Specifically, this mechanism has been described in detail recently.[58] Apparently, the same explanation can be utilized in our case for the green polarized light.

The origin of the “hills” formation for the red laser beam is more challenging and probably explained by thermal expansion of the film under red light irradiation. It is well-known, [60, 61] that irradiation of dye-containing films rises their temperature. As already mentioned above, absorbance of the studied polymer films at 633 nm is ca. two order of magnitude less than at 532 nm (Fig. S5). Strong absorbance at 532 nm (about 2.5) results in small penetration length of the light of this wavelength, whereas red light freely penetrates the film. Long irradiation time and high penetration length of red beam induces local heating of the irradiated spot resulting in thermal expansion and “hill” appearance. However, green laser also can induce some thermal expansion. As seen from Fig. 2a 30 s of green light action also leads to slight “bloating” in the center of the crater.

Despite significant role of the heating on photoinduced processes, it is noteworthy, that thermal expansion cannot be the only one reason of the observed phenomena, because it cannot induce anisometry of the surface features. In other words, above-mentioned opto-mechanical stress under polarized light action eventually leads to deformation of the “hills”.

Another possible mechanism of “hills” appearance is the Marangoni effect.[62-64] This effect describes directional flow of the fluid near an interface due to a surface tension gradient. *E/Z* photoisomerization and photoinduced heating can alter the surface tension of our polymer films. As it’s been shown recently,[55] high local concentration of Z-isomer that arise under UV-irradiation, induces material flow from non-irradiated zones to the irradiated ones and results in surface relief formation. However, in case of a simple one-photon process the difference in *E/Z* isomer ratio of the azobenzene chromophores could not be considered as the possible reason for such difference because for both wavelengths, namely for 532 nm and 633 nm, the concentration of *Z*-isomers is negligibly small.

Most probably, Marangoni effect for the red laser beam can be associated with possible biphotonic processes. There are several recent works[65, 66] on two-photon-induced *E/Z* isomerization process of the azobenzene chromophores under the action of red or near-infrared (NIR) light. In most cases this process requires a very high power pulsed laser source, but there are definite specific exceptions especially for the laterally substituted azobenzene containing materials,[66] in which the *E/Z* isomerization is induced even by low-power NIR LED irradiation.

In our case, two-photon isomerization also cannot be excluded and its effect is similar to UV irradiation with 316.5 nm light wavelength. Ultimately, this process can lead to the formation of a high concentration of *Z*-isomer and, consequently, can result in surface tension and consequent formation of the hills.

Indirect confirmation of this hypothesis is spectral changes under light action of three wavelengths, 313 nm (which is close to 316.5 nm), 532 nm and low-intensity 633 nm (Fig. S6). Green and red light leads to relatively small decrease in absorbance corresponding to π-π^* electronic transition of the azobenzene chromophores (Fig. S6b, c), whereas UV light strongly decreases absorbance (Fig. S6a) indicating almost complete E-Z isomerization conversion.

Unfortunately, direct spectral observation of the biphotonic E-Z isomerization in our case is experimentally difficult because it requires absorbance spectra measurement in the small irradiated spot or using of HeNe laser of extremely high intensity. Thus, in order to confirm the principal possibility of the Marangoni effect in our studied systems, another additional experiment has been performed. Films of **PMDA6/10** polymethacrylate were irradiated by UV-light through the mask followed by annealing at temperature slightly higher than temperature of the glass transition (40°C). This specific temperature has been selected for two definite reasons: (i) in order to increase molecular mobility in the polymer films; (ii) to diminish back thermal *Z/E* isomerization keeping high concentration of photoinduced *Z*-isomer. The relief height of the irradiated zone is ca. 70 nm higher than that for the non-irradiated one (Fig. S7), that clearly confirms the occurrence of the Marangoni flow due to the difference in surface tension provided by different concentration of *Z*-isomer in studied polymethacrylate film.

Thus, two-photon-induced *E/Z* isomerization process followed by Marangoni-type flow is the most probable explanation of the “hills” formation under red light laser irradiation of the studied polymethacrylate films.

Conclusions

In conclusion, for the first time for the azobenzene-containing polymers with lateral substituents in the azobenzene chromophores the formation of the anisotropic surface features is studied. It has been found that the focused green and red laser beams evidently induce formation of anisotropic “craters” or “hills” on polymer films surface. An extreme difference in shape of the photoinduced surface features depending on the wavelength of the incident light has been observed for the first time. The peculiarities of the studied processes make them very promising for the future applications based on the contactless creation of complex surface morphologies in photochromic polymer films and also for emerging liquid crystal technologies.[1, 67, 68]

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was supported by the Russian Foundation for Basic Research (RFBR) (19-03-00337, 19-53-26007 (RFBR and Czech Science Foundation); synthesis and study of phase behaviour of polymethacrylates), by the Russian Science Foundation (19-13-00029; investigations of surface relief features), by the Czech Science Foundation (19-03564S; design and mesomorphic behaviour of the polymethacrylates) and by the MEYS of the Czech Republic (LTC19051; support of collaboration). Authors thank Mr. I. Vaskan for AFM scanning of the UV irradiated film and Dr. M. Bugakov for molecular mass measurements. The authors (M.C., V.H., A.B.) would like to acknowledge the contribution of the COST Action CA17139.

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