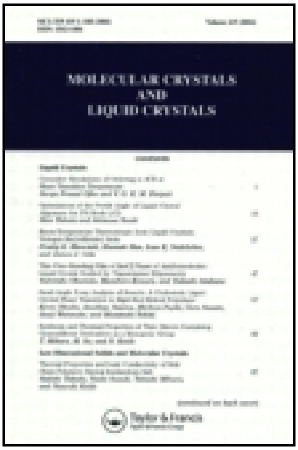

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 16 Jun 2008

To cite this article: A. Richter, M. Nowicki & B. Wolf (2008): A Nanoindentation Study of Photo-Induced Changes in Polymers Containing Azobenzene, Molecular Crystals and Liquid Crystals, 483:1, 49-61

To link to this article: http://dx.doi.org/10.1080/15421400801898108

Mol. Cryst. Liq. Cryst., Vol. 483, pp. 49–61, 2008
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400801898108

A Nanoindentation Study of Photo-Induced Changes in Polymers Containing Azobenzene

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Irradiation of materials by light of suitable photon energy can cause structural alterations of either permanent or temporary character that are reflected in their mechanical properties. Nanoindentation is particularly well suited to characterise small representative volume elements of materials with gradual or discrete changes of their mechanical properties. It is, therefore, an ideal technique for investigation of thin films, nanocomposites and other specimens with inhomogeneities in the nanometer to micrometer length scale that are either inherently existing in the material or externally stimulated. In this article, nanoindentation was applied to study the mechanical properties of pDR1m surface relief gratings containing azobenzene. Hardness and elastic modulus increase after and during irradiation of the pDR1m film correlated with an increase in the polymer density after light exposure. Permanent structural changes in the pDR1m film are related to crosslinking and photo-isomerisation. In-situ nanoindentation under controlled periodic light illumination exhibits a week photomechanical switching and results finally in a permanent stiffer polymer network.

Keywords: light exposure; mechanical properties; nanoindentation; polymers

INTRODUCTION

Though nanoindentation [1–4] became a wide spread tool of mechanical probing at small scales not only in basic research, but with extended use in engineering sciences and industry, its importance as

We gratefully acknowledge supply of pDR1m samples and surface relief gratings from the Institute of Physics, Potsdam University, and thank Burkhard Stiller, Knut Morawetz and Ronald Ries for their support, permanent interest in this work and many fruitful discussions.

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a technique for experimental studies of fundamental processes in physics and chemistry is still growing. During a typical depth sensing indentation experiment, force and displacement are recorded simultaneously as the indenter tip is pressed into the specimen using a well defined loading/unloading scheme. This technique is of particular advantage when samples of mechanical inhomogeneities in the nanometer to micrometer length scale are addressed, or when the interest is focussed onto the dynamics of deformation, showing distinct events like pop-in excursions in crystals or a dynamic response to intensity-modulated illumination [3].

Light irradiation can cause structural alterations of materials that have an impact onto their mechanical properties. Depending on light penetration depth, the outermost layer is very often affected by light absorption only, and surface sensitive methods are required to study possible resulting effects. In order to exclude thermal impacts, the light intensity should be sufficiently small, which also results in small volumes of material alteration and favors the application of the nanoindentation technique.

Polymers are known to be sensitive to UV radiation which can be either a benefit exploited in the resist technology in semiconductor processing, e.g., but very often leads to unwanted degradation resulting in increased brittleness, color changes and other modifications [5]. It is well known that polymers exposed to natural sunlight containing a certain fraction of ultraviolet (UV) radiation exhibit long-term changes of their properties which arise from light induced modifications in the chemical structure and are strongly related to radiation intensity and exposure time. The most significant reactions occurring in a polymer upon its exposure to UV irradiation, are main chain scission, oxidation, side groups abstraction, or destruction. Since the photodegradation of solid polymers starts in a very thin surface layer, it has been successfully studied by nanoindentation [6]. An increase of hardness and indentation modulus and a considerable loss of visco-elasticity were observed when samples were exposed to UV irradiation. The nanoindentation experiment was performed after the UV treatment of the samples.

Reversible hardness modifications by light are reported for semiconductors of sphalerite structure such as ZnSe [3,7,8]. In this class of materials dislocations can be electrically charged. Mobile charge carriers generated by the internal photoelectric effect can move to dislocations and may alter the dislocation charge. As a consequence electrostatic forces between two dislocations, between a dislocation and electrically active point defects, or between dislocations and the entire crystal lattice are changed giving rise to different dislocation mobility and consequently to a variation of the hardness. The hardness can increase under illumination (positive photo-plastic effect) or it can decrease during illumination (negative photo-plastic effect) [3,8]. An experimental setup for in-situ nanoindentation during illumination was developed [3] that allows direct laser light exposure using a glass fibre guide. The light can be turned on and off due to a definite time schedule and changes in the load-displacement curves can be recorded immediately. Thus the reversible impact of light on plasticity of matter known as the dynamic photo-plasticity effect can be studied in detail [3].

Surface relief gratings (SRG) [9–16] generated on azobenzene containing polymers have attracted much attention because of their unique potential of applications such as in diffractive device fabrication, optical storage or integrated optics. Grating periods range from a few μm resolution [16] down to 100 nm size [13,14]. The amplitude of the light induced surface modification can be as big as 700 nm [16] with a sinusoidal grating profile. The surface relief formation is not completely understood. All models consider neither swelling nor ablation of the material as a reason for surface deformation, but suggest a mass transport well below the glass transition temperature of the polymer. Photochemistry of azobenzene containing polymers is widely studied [10,17] and includes the reversible trans-cis-trans photo-isomerisation, reversible photo-orientation of chromophores, photorefractive effects, photo-induced switching in amorphous and liquid-crystalline polymer films and many more reactions. Likewise, the size of the molecule, its mobility, the flexibility of the polymer chain etc. play an important role in determining the course of the photo-chemical reaction. It is widely accepted that alterations in the polymer network and phase changes in the material are reflected in the mechanical properties [12,13,18–22]. A reversible photomechanical effect in an azobenzene containing polymer blend was explained by physical crosslinking and decrosslinking of the polymer chains [18]. The functional states of molecular imprinted polymer films with empty or filled molecular cavities could be distinguished by their nanomechanical properties [21,22]. Reversible photo-mechanical properties of azobenzene based polymer films were investigated by nanoindentation [19]. After UV irradiation the stiffness of the films increased by about 10–28% compared to the pristine polymer. The altered mechanical properties were attributed to conformational changes in the polymer chains via a trans-cis isomerisation of the chromophors.

The aim of the present article is to apply nanoindentation to study the mechanical properties of surface relief gratings in comparison to pristine azobenzene containing polymer pDR1m films. Top and bottom positions of an already manufactured grating, were subject to nanoindentation to establish differences in their mechanical properties, hardness and elastic modulus in particular. Different exposure times are applied to study the light induced structural changes in more detail. In a further experiment, virginal polymers were indented *in-situ* under controlled light illumination to study the light influence onto the dynamics of tip penetration.

EXPERIMENTAL

Nanoindentation [1–4] is a widely used technique for the determination of nanomechanical properties and especially well suited to probe small scale material volumes. It has been applied to polymers to study their mechanical properties in more detail and to get information on alterations in their structure and network reflected in hardness properties and their elastic and visco-elastic response [6,19–26]. Recently, nanoindentation has been proved to act as a finger print method to identify unknown polymers [25], to distinguish between polymers with different molecular weight in crosslinks of glassy polymers [20] or to differentiate between functional states in molecularly imprinted polymer films [21,22].

It is a very straightforward idea to exploit the potential of the scanning probe techniques for small scale nanoindentation. However, the simple use of very stiff cantilevers and application of comparatively high forces in the upper μN-range, by 3 to 5 orders of magnitude higher than in classical atomic force microscopy (AFM)-mapping, are complex, applicable only in special cases and not practical as a standard test method to obtain mechanical parameters. Additionally, lateral forces due to the cantilever bending, prevent the generation of a well defined indent. Thus common nanoindentation equipment is based on scanning probe microscopy, but force generation takes advantage of special tools, an electrostatic transducer in case of our experimentation. The transducer combines the functions of actuator (force generator) and depth sensor in one tool, and is laterally moved by the piecoelectric tube scanner of an AFM. All nanoindentation experiments were performed using the electrostatic transducer of the Hysitron triboscope [27] attached to a Nanoscope MultiMode IV scanning force microscope at room temperature.

A diamond tip mounted onto a hard, rigid stylus is pressed into the test body by electrostatic forces with high precision adjustment of vertical load. Force and penetration depth are simultaneously recorded during loading and unloading. From the load–displacement curve, mechanical properties, including the elastic modulus E and the hardness *H*, can be estimated based on data analysis via the standard Olivier–Pharr-approach [2]. Direct visualisation of the generated impressions and determination of their geometrical dimensions is not necessary, though it can be an advantage. Investigations are performed with a 90° diamond cube corner tip. Tip calibration took advantage of the standard technique using fused quartz as a reference material. From a series of impressions of different size the area function A_c (h_c) at the contact depth h_c was derived assuming a constant elastic modulus. In this work a comparatively blunt indenter (tip radius $r \approx 700\,nm$) was intentionally used to avoid cracking and to minimize visco-elastic contribution to material flow.

An illumination facility (see Fig. 1) is installed at the nanoindentation set up to study alterations of mechanical properties during or immediately after light exposure. Alternatively the sample can be illuminated directly by a fibre-lit white light source, an UV lamp or a laser. As visible in the schematic experimental setup in Figure 1, the transducer geometry limits the angle of incidence to $\alpha_{max} \approx 20°$. Furthermore illumination from top results in unwanted shadowing by the diamond tip. In the experiments presented in this article, a diode pumped solid state Nd-doped laser with frequency doubling is operated. The wave length for illumination is 532 nm (green) with 1 mW output power. The maximum power density used was lower than $10\,mW/cm^2$. The light was focussed into a small spot directly beneath the indenter tip. Depth sensing indentation was applied to several materials to determine their mechanical properties during and after irradiation with ultraviolet and visible light. Irradiation of the above intensity can change the network structure in polymers

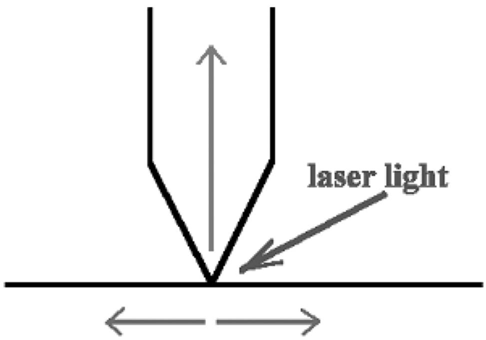


FIGURE 1 Schematic view of the experimental setup for indentation under illumination of the sample with indication of possible lateral and vertical heat propagation marked by arrows.

and alter their mechanical properties [6], but can also cause photoplasticity in II-VI semiconductors [3].

Light illumination is generally accompanied with heat generation in the light spot of the sample. Heat propagation may occur inside the film plane resulting in lateral expansion and perpendicular to the film surface as indicated in Figure 1 by the arrows. Particularly the height drift disturbs experiments in which the illumination state is changed during indenting. Generally, the heat generated in the light spot distributes quickly over the sample surface, so that the temperature increase is very small. Additionally, the total heat energy absorbed by the sample can be kept very small by cutting off the wavelength region which is not photoactive. That means that a white light source causes a larger heat input than a monochromatic laser beam. The heat generation is also decreased for a small illumination spot even at high luminescece. Thermal drift experiments were performed at different standard materials such as PMMA and Polystyrene (PS). The thermal drift was measured and an actual correction factor determined [26]. Mostly the drift rate decreases exponentially during a test. Typical drift rates range up to 0.2 nm/s without light illumination. In such cases, where the drift speed was larger, the indentation result was not used for further consideration. This drift rate did not change with light exposure, thus no additional thermal drift was observed, that means that no temperature increase happens during light illumination with our experimental parameter set.

For our experiments, the main source of information is the load-displacement curve and its change owing to illumination either during the tip penetration procedure itself, or when having performed light exposures a short time before the indentation measurement. The global shape of the load-displacement curve differs from one material to the next one, and these variations usually reflect different mechanical properties. Of more interest to the present article are local details in the load-displacement curve, which may signal the operation of discrete physical events beneath the indenter tip. Plastic and elastic deformation merge to form the loading curve whereas the unloading curve is assumed to originate from pure elastic deformation. This is valid for stiff materials, however, some visco-elastic flow is superimposed onto back-deformation in many polymers [6,20,21,26]. An effective elastic modulus can be derived from the unloading curve and differences between illuminated and non-illuminated state were found and quantified if the same time-scale is used in all experiments.

Single and multi-cycling load-time functions (Fig. 2) with specific loading/unloading and holding segments are applied. It was found that the penetration depth of the indent should not exceed 30% of

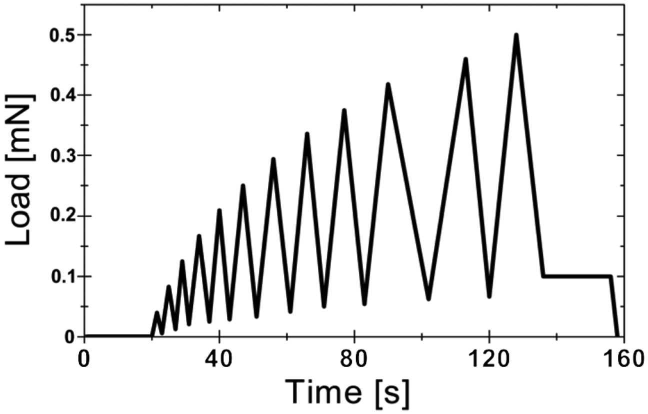
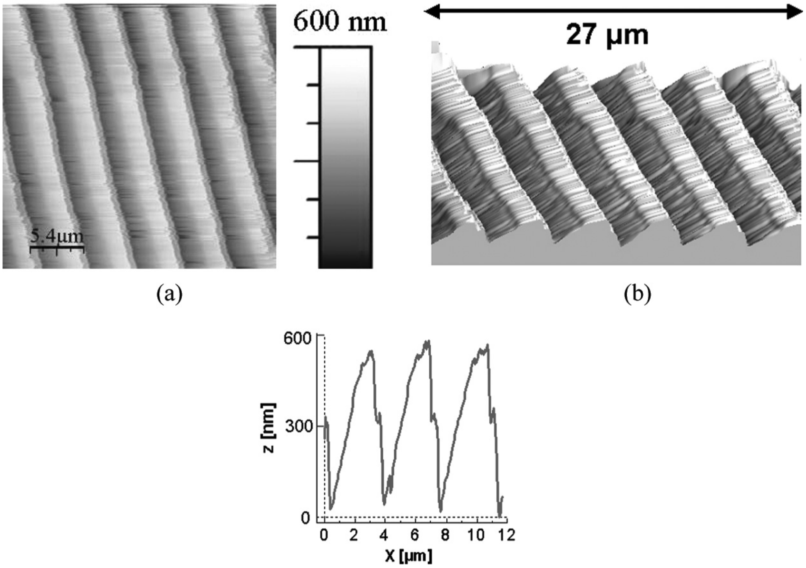


FIGURE 2 Multi-cycling load-time function for indentation with 500 μN maximum load and total time of 160 s.

the polymer film thickness to avoid substrate effects. Thus the maximum load is restricted to less than 500 μN, however most experiments have been performed with a lower value. Effects of external vibrations and thermal drift become more and more important the longer the indentation time lasts. Therefore, an optimum duration should be considered for the indent. The maximum time for an indent reported in this article was 160 s, but most experiments were performed at 85 s.

Depth dependent mechanical properties such as hardness and elastic modulus are easily achieved through indentation tests where repeated loading and unloading are performed at the same place on the sample surface [3,26] resulting in multi-cycling indents (Fig. 2). After loading, the load is decreased to a load minimum, then the sample is reloaded to a maximum load. If the unloading curve is not purely elastic, hysteresis loops appear and hint to inelastic contributions as back-deformation, most probably visco-elasticity in case of polymers [6,26].

For the present investigations, an amorphous azobenzene side-chain homopolymer (poly{(4-nitrophenyl)[4-[[2-(methacryloyloxy)-ethyl] ethylamino] phenyl] diazene} (pDR1 m) with a glass transition temperature of $T_g = 129°C$ was used [14]. The polymer is dissolved in tetrahydrofurane with 0.5 to 2.5 weight% and then spin coated on thin Corning glass plates at 1500 to 2500 rpm. The resulting films have a pinhole-free surface, are very flat with a roughness R_{ms} of 2 to 5 nm and have a thickness of 900 nm. Nanoindentation on the pristine pDR1 m film and directly after light illumination of different time with



(a) (b)

(c)

FIGURE 3 AFM image of a surface relief grating in pDR1 m with a period of 4 μm, a width of the plateau of 1.8 μm and a depth of 574 nm: 2-dimensional (a) and 3-dimensional topography (b) and line scan (c).

the laser of wavelength 532 nm were performed. *In-situ* experiments with periodic light modulation during single indentation are achieved that could provide information on the process of grating formation.

A ready pDR1 m line surface relief grating with a sinusoidal period of 4 μm and a height of 575 nm was investigated with nanoindentation on the relief top and relief bottom. In Figure 3 an AFM surface topography is presented. There is a flat plateau of 1.8 μm accompanied with a small step visible in the 3-dimensional topography and the line scan (Figs. 3b and c). The roughness R_{ms} along the plateau line is 48 nm.

RESULTS AND DISCUSSION

Multi-cycling nanoindentation was applied to the top and the bottom of the pDR1 m surface relief grating. Values for the hardness and the elastic modulus are given in Table 1 in comparison to values of a pristine non-illuminated pDR1 m film. For the light treated material of the grating a drastic increase of the hardness and the elastic modulus is observed. Since the polymer becomes stiffer under light

TABLE 1 Indentation Modulus E and Hardness H Measured on a Pristine pDR1 M Polymer Film and after Generation of a Surface Relief Grating on the Top and Bottom of the Structure

	Pristine pDR1 m	Grating top	Grating bottom
Indentation modulus E [GPa]	4.7	7.3	8.4
Hardness H [GPa]	0.25	0.45	0.55

irradiation, temperature effects can be excluded to be dominant and the alterations of the mechanical features can be attributed to structural changes such as photo-chemical reactions, crosslinking, photo-isomerization and others. These photo-chemical reactions are also reported in the literature. The effect of light hardening was observed also in UV irradiated standard polymers by means of nanoindentation [6]. The increase of the elastic modulus of a hybrid organosilicate glass surface relief formation due to photo-induced stress is reported in [12]. Here, the elastic modulus at the dark zones, that is on top of the gratings is much larger than in the bright zones correlated to the valleys. Thin films containing azobenzene chromophores exhibit an increase of the stiffness by about 10–28% after UV irradiation [19]. Photo-mechanical switching in a polymer blend composed of azobenzene results in a reversible modulus change arising from UV-controlled isomerization of the azobenzene moiety [18]. Stiller et al. [14] made investigation of the mechanical properties of the surface relief by measuring locally the force-distance curves in the AFM pulsed force mode and found that the grating hills are stiffer and not as adhesive as the valleys. A local variation of the mechanical properties is a clear indication that the polymer film density changes. The large observed increase in elastic modulus and hardness in the pDR1 m gratings (Table 1) cannot be caused only by photo-induced crosslinking. The light controlled isomerization of the azobenzene moiety forms relief structures by means of mass transport [13].

In Figure 4 results of depth dependent elastic modulus and hardness are presented. Almost no depth dependence is observed for multi-cycling indentation into the pristine pDR1 m film. Nano-indentation measurements after 10 min. light exposure are performed immediately and after 30 min. without illumination to allow material relaxation. Light exposure again causes an increase in the mechanical properties as observed for the ready gratings. There is a slight reduction of the mechanical properties when the material has some time for relaxation after illumination (here 30 min), but the generated changes in the polymer are permanent. Compared to the pristine

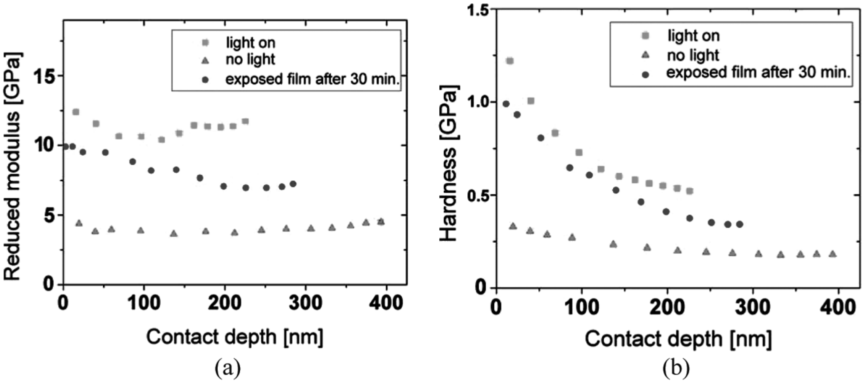


FIGURE 4 Depth dependent indentation modulus *E* (a) and hardness *H* (b) for nanoindentation in a pristine pDR1 m film of 900 nm thickness without light exposure (triangles), after 10 min of illumination: immediate measurements (squares) and re-measurements after 30 min without light exposure (dots).

pDR1 m film the hardness of the illuminated films shows a strong indentation size effect [3]. The indentation size effect can be taken as a measure for the defects generated during the penetration of the tip compared to defects inherent in the material. It seems that the pristine pDR1 m film contains more disorder and defects than the light exposed polymer film. The hardness is large for very small penetration and decreases drastically with increasing penetration depth. The increase of the mechanical properties can therefore be attributed to photo-izomerization in the azobenzene containing polymer film with a higher degree of molecular order and crystalinity.

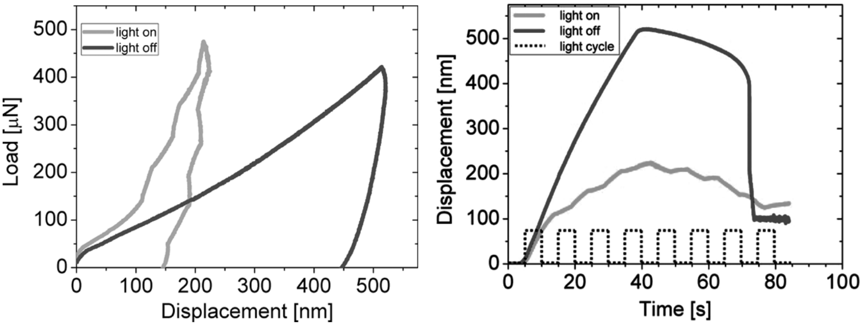
The increase of the elastic modulus and the hardness in dependence on the exposure time is demonstrated in Table 2. Nanoindentation is started immediately after the different illumination times. Already after 10 s light exposure an increase of 20% in the mechanical parameters is observed. With increasing exposure time up to 300 s the stiffness increases gradually. This seems to indicate that the photo-izomerisation is a continuous process and not correlated with a threshold light intensity.

Finally *in-situ* nanoindentation simultaneously with periodic light modulation was investigated (see Fig. 5). A single indent of 85 s total duration was performed in pristine pDR1 m and under periodic light exposure with the laser switched on for 5 s and switched off for 5 s. The load-displacement curve for this measurement is given in Figure 5a. After a smooth start of the loading curve the switching

TABLE 2 Indentation Modulus E and Hardness H Measured after Different Exposure Times

Exposure time [s]	E [GPa]	H [GPa]
0	*5.0*	*0.25*
10	6.0	0.30
20	6.3	0.31
30	6.3	0.31
40	6.1	0.29
50	6.4	0.30
60	6.3	0.30
120	6.7	0.35
300	6.7	0.34

cycle becomes visible in both the loading and unloading curve. Irrespective of the alterations in the load displacement curve, the illuminated polymer appears stiffer than the non-irradiated one proved by the lower total penetration depth. The variation of the displacement with increasing and decreasing load in dependence on time is shown in Figure 5b. With the second light cycle the penetration depth for the illuminated period is diminished, whereas the penetration depth relatively increases during the periods where the light is switched off. The switching cycle is not retarded. For the unloading displacement the cycle continuous, however, the elastic material relaxation



(a) (b)

FIGURE 5 Single indentation of 500 µN maximum load and 85 s duration for loading and unloading into a pDR1 m film: load-displacement (a) and displacement-time (b) curves for a pristine film and one with light modulation of 5 s light switched on and 5 s light switched off as indicated by the dot line.

is larger during light exposure. The penetration depth of the unloading curve changes only a little for the periods with the laser turned off.

These investigations cannot explain the physical origin of the optically induced mass transport to generate the surface relief gratings in azobenzene containing polymers. It is however evident, that the illumination results in a stiffer polymer during all different time stages, that means from the very beginning of the light exposure till the ready grating. Softening of the pDR1 m polymer under light illumination with properties of a visco-elastic fluid could not be detected.

CONCLUSION

Alterations of mechanical properties of azobenzene containing pDR1 m polymer films due to light illumination were studied by nanoindentation. Light exposure resulted in a harder and stiffer polymer film in comparison to the pristine pDR1 m films for all practiced time stages. This is reflected by the drastic increase of elastic modulus and nanohardness. Mechanical data were inferred from (i) indentation into a surface relief grating, (ii) indentation into a virginal polymer film after light illumination of different exposure times and *in-situ* measurements with a modulation of the light intensity during tip penetration (modulation period a few seconds). Switching on of the laser is prompted by changes in the load-displacement curve correlated with a hardening of the material, that gradually increases with exposure time. No threshold value for the light intensity to initiate the structural changes could be observed. Photo-isomerization and cross-linking are expected to be the processes that cause the permanent structural changes in the pDR1 m polymer. Periodic light modulation gives rise to moderate oscillations in load-displacement and displacement-time curves indicated by a weak switching cycle. Hardness and indentation modulus, derived from the completed impression, are again considerably increased.

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