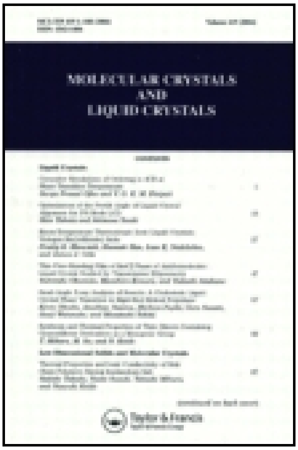


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Temperature Dependent Analysis of Grating Formation on Azobenzene Polymer Films

Padmanabh U. Veer [a], Ullrich Pietsch [a], Paul L. Rochon [b] & Marina Saphiannikova [c]

[a] Department of Solid State Physics, University of Siegen, Siegen, Germany

[b] Department of Physics, Royal Military College, Kingston, Ontario, Canada

[c] Leibniz Institute of Polymer Research, Dresden, Germany

Version of record first published: 22 Sep 2010

To cite this article: Padmanabh U. Veer, Ullrich Pietsch, Paul L. Rochon & Marina Saphiannikova (2008): Temperature Dependent Analysis of Grating Formation on Azobenzene Polymer Films, Molecular Crystals and Liquid Crystals, 486:1, 66/[1108]-78/[1120]

To link to this article: http://dx.doi.org/10.1080/15421400801917775

Mol. Cryst. Liq. Cryst., Vol. 486, pp. 66/[1108]–78/[1120], 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400801917775

Temperature Dependent Analysis of Grating Formation on Azobenzene Polymer Films

Padmanabh U. Veer[1], Ullrich Pietsch[1], Paul L. Rochon[2], and Marina Saphiannikova[3]
[1]Department of Solid State Physics, University of Siegen,
Siegen, Germany
[2]Department of Physics, Royal Military College, Kingston,
Ontario, Canada
[3]Leibniz Institute of Polymer Research, Dresden, Germany

The temperature dependence of surface relief grating formation was studied using continuous and pulse like exposure. Surface relief gratings were inscribed on amorphous azobenzene polymer thin films using a holographic pattern of circularly polarized light at wavelength equal to 514 nm in a vacuum chamber to avoid the hot air turbulence. The efficiency of the surface relief grating formation was probed using a He-Ne laser of wavelength 633 nm by monitoring the first order diffraction peak (I_1) as well as the specularly reflected intensity (I_s). Under continuous exposure permanent grating formation was observed up to a temperature of about 100°C only. The same was found under pulse like exposure but grating still exists as long as the actinic light is on. Above 100°C it relaxes entirely after switching the light off. This elastic component disappears at about 115°C, i.e., close to the glass transition temperature. Our findings can be interpreted by the competition between light-induced ordering of azobenzene side chains and temperature induced disorder. Because the accumulated stress within the polymer decreases with temperature, permanent grating formation can only be observed when the light-induced stress is above the yield stress.

Keywords: azobenzene polymer; surface relief grating; viscoplasticity

The authors are thankful to Dr. B. Schulz and B. Dietzel (IDM Teltow) for providing the polymer and preparing the samples. Dr. V. Toshchevikov (Institute of Macromolecular Compounds, Russian Academy of Science, St. Petersburg) is gratefully acknowledged for fruitful discussions.

Address correspondence to Padmanabh U. Veer, Department of Solid State Physics, University of Siegen, ENC, Siegen 57068, Germany. E-mail: veer@physik.uni-siegen.de

INTRODUCTION

It is well known that surface relief gratings (SRGs) can be inscribed on polymer films containing azobenzene chromophores using a periodic holographic light pattern of wavelength around 500 nm [1,2]. This wavelength is close to the absorption maxima of the *cis*- and *trans*-conformations of azobenzene. Illumination of the polymer at this wavelength initiates the *cis-trans* and *trans-cis* photoisomerisation which results in a light-induced material transport far below glass transition temperature, T_G. Under continuous holographic exposure of thin polymer films Rochon *et al.* [1] and Kim *et al.* [2] observed the formation of surface relief gratings of nearly sinusoidal shape. Later it has been shown that the SRGs can be also inscribed using pulse like illumination, whereby the scattering signal exhibited first an instantaneous jump followed by a smaller slope of increase. If the actinic light is switched off the intensity decays exponentially to a level larger than that before the pulse. Depending on pulse duration and laser intensity the plastic deformation can be accumulated and the scattering intensity increases as function of the number of pulses [3].

In order to reproduce these time-dependent scattering data, we modeled the process of grating formation under the assumption that the polymer is an isotropic viscoleastic material with finite compressibility [4]. The particular choice of this model deserves some explanation. It is well-known that above T_G a polymer response to an external deformation is not purely viscous but rather viscoelastic. This is true even in the melt state, where the elastic modulus can be as small as few tens of kPa. Such reduction of the modulus accompanied by the corresponding decrease of the viscosity is found after heating the sample by some tens of degrees above T_G. Slightly above T_G, the viscoelastic behavior is much more pronounced than in the melt state: here the elastic modulus is in the order of 1 MPa that is three orders of magnitude smaller than at the glassy state. The problem, however, is that, contrary to a well-spread belief, only a minute softening of the polymer layers was found under homogeneous visible illumination, using a number of experimental techniques [5,6]. Thus, one inevitably arrives to the conclusion that an inscribing force should be above a certain yield point of the illuminated azobenzene polymers. Therefore, the time-dependent visual scattering data should be modeled in terms of the viscoplastic material model, in which the light induced deformation has two components: the elastic and plastic ones [7].

A number of theories have been proposed to explain the origin of the inscribing force [8–13] but none of them could explain the complete process of grating formation depending on the polarization conditions and other parameters. Presently, the mechanism based on the light-induced reorientation of azobenzene moieties looks the most promising explanation [12,13]. This reorientation arises statistically, after a number of isomerization cycles, when the long axis of chromophores is mainly found to be perpendicular to the polarization direction [14,15]. It has been shown recently that the light induced stress arising due to reorientation of the chromophores is orders of magnitude higher than that given by the previous theories, being only slightly below a value of the yield stress expected for conventional polymers [13].

Temperature resolved measurements can help to clarify the process of elastic and plastic deformation caused by the light-induced ordering and thermally induced relaxation during grating formation. In this article we show such experiments under continuous exposure as well as under pulse like exposure.

EXPERIMENT

Thin films were prepared from polymer (poly-{4′[2-(methacryloxy) ethyl]-ethyl}) pDR1M having the glass transition temperature of about $T_G = 120^{\circ}\mathrm{C}$ [16]. SRGs were inscribed using a semiconductor disc laser from ELS GmbH operating at a green wavelength of 514 nm. This wavelength is close to the absorption maximum of azobenzene chromophores. The formation of SRGs was probed *in-situ* using a p-polarized He-Ne laser operating at a red wavelength of 633 nm and having an output intensity less than $5\,\mathrm{mW/cm^2}$. The wavelength of the probe laser was outside the absorption maxima of azobenzene chromophores and thus has no influence on the process of grating formation. To study the temperature dependence of the grating formation, the sample was heated steadily using a Peltier plate. At a certain temperature above the room temperature it was found that the wave front close to the sample surface was disturbed by the turbulence of hot air which led to attenuation of the grating formation process [17]. To avoid the air turbulence, the experiment was performed inside a closed chamber at pressure of about 1000 Pa created by a vacuum pump (Vacuubrand GmbH).

The experiment setup is shown in Figure 1. It consists of the inscribing laser followed by a lens system to expand the beam and a quarter wave plate ($\lambda/4$) to create the circular polarization of the light. The vacuum chamber hosts a mirror and the sample equipped on a Peltier plate. The mirror and the sample are arranged perpendicular to each other. For the used angles of reflection at mirror the polarization state of the reflected wave is still circular [18]. Thus, the

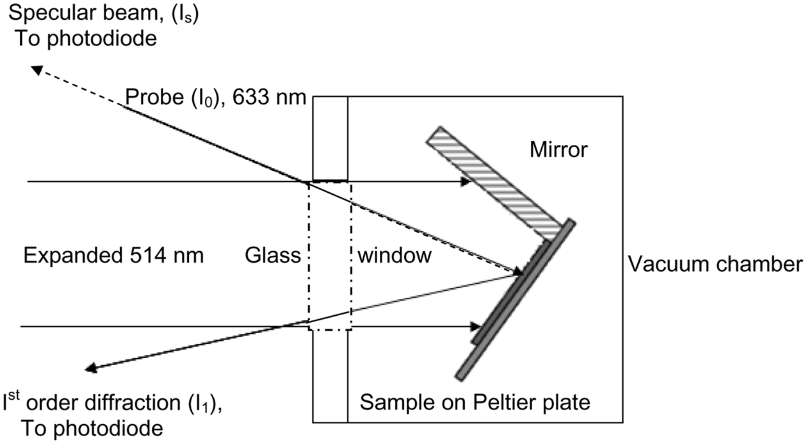


FIGURE 1 Optical setup for inscription of diffraction gratings.

interference of two contra circularly polarized beams results in a periodic rotation of electric field vector while the intensity remains nearly constant, which produces the gratings of the highest diffraction efficiency and surface modulations [9,19,20]. Already at room temperature the initially flat polymer film forms a sinusoidally shaped surface relief grating after few minutes of exposure as shown in Figure 2a. The scattered first order diffraction and the specular signal were detected in reflection geometry using a pair of photodiodes.

The chromophore orientation and relaxation is strongly affected by the presence of light. To study this behavior, pulse exposure technique has been exploited. In this technique the polymer sample was subjected to a cyclic inscribing force. This is achieved by designing a mechanical shutter that was allowing light to fall on a sample for a particular time period. The inscription process was initiated by a short light pulse of 2 s followed by much longer relaxation time of 20 s in dark. SRG formation was studied under continuous and pulse like illumination at sample temperatures varying between room temperature and T_G. The sample temperature was measured by means of a thermistor with accuracy of one degree.

RESULTS

Figure 3a shows diffraction curves measured at different temperatures under continuous exposure with laser intensity $I_p = 1\,\mathrm{W/cm^2}$. It is clearly seen that the scattering intensity of the first order peak varies significantly with temperature. At $T = 25°\mathrm{C}$ one observes

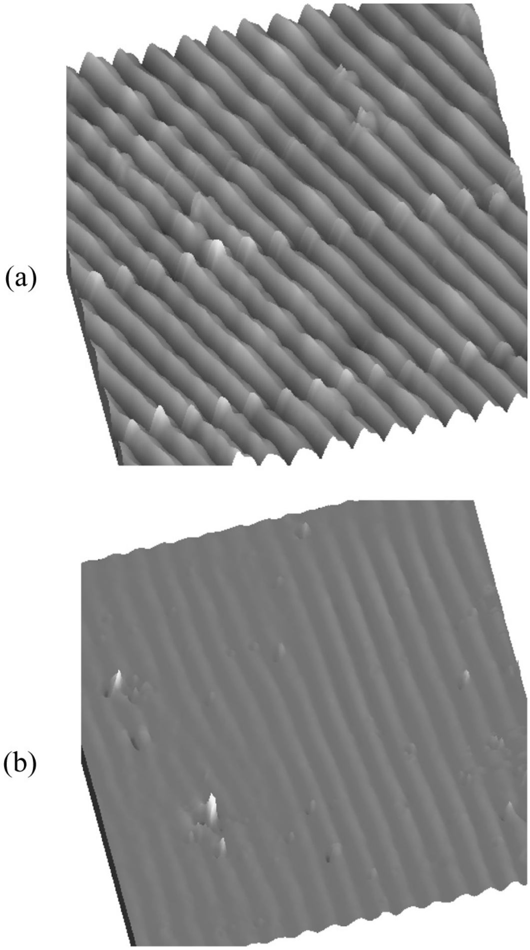
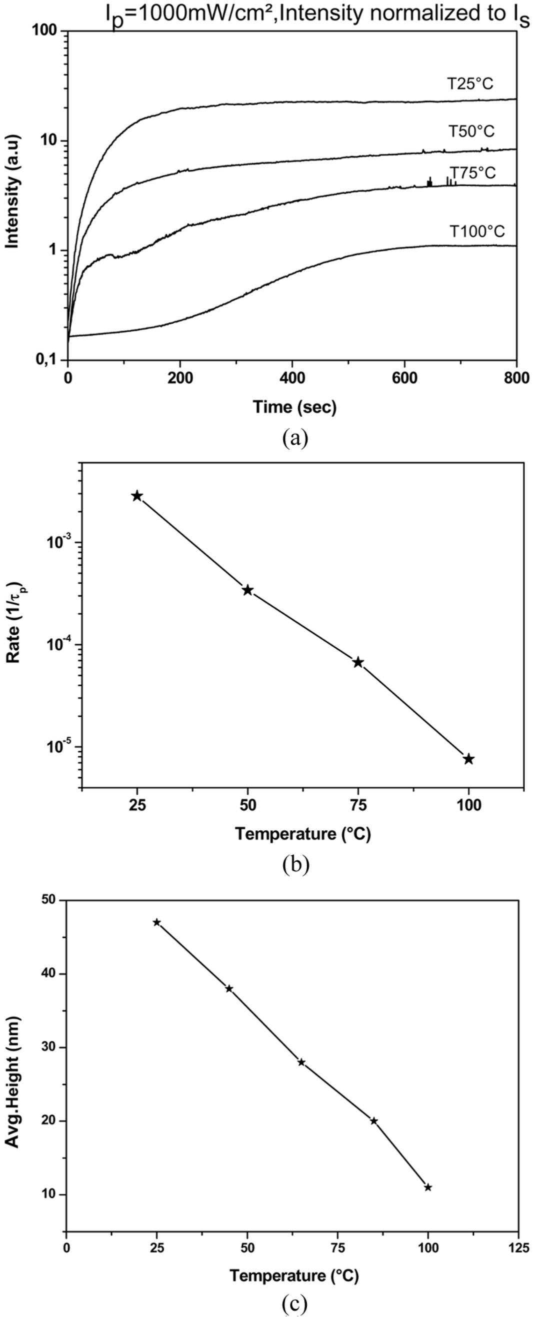


FIGURE 2 AFM images of the surface relief grating formed on the azobenzene polymer sample at room temperature, the grating height is 50 nm (a), and at 100°C, the grating height is 10 nm (b). The grating period is 700 nm.

a typical behavior known from the grating formation at room temperature [1,2]. The intensity increases exponentially at the beginning and reaches saturation later. The intensity at saturation reflects the achieved formation of a nearly sinusoidal SRG which is shown in Figure 2a. The measured intensity $I_1(t)$ is proportional to the square of the deformation $|\varepsilon|^2$ and can be described by

$$I_1(t) = I_{sat}(T)(1 - e^{-t/\tau_p(T)}) \tag{1}$$


Ip=1000mW/cm²,Intensity normalized to Is
Intensity (a.u)
100
10
1
0,1
T25°C
T50°C
T75°C
T100°C
0
200
400
600
800
Time (sec)
Rate (1/τp)
10-3
10-4
10-5
25
50
75
100
Temperature (°C)
Avg.Height (nm)
50
40
30
20
10
0
25
50
75
100
125
Temperature (°C)

(a)

(b)

(c)

where I_{sat} is the intensity after saturation and $1/\tau_p$ is the rate of grating formation. The rate of grating formation $1/\tau_p$ can be extracted from the initial steepness of the diffraction efficiency curve seen in Figure 3a. In contrast to room temperature, the efficiency of SRG formation is strongly reduced at higher temperatures. This is seen in the considerably reduced value of I_{sat} and in the lower slope of diffraction curves at the beginning of illumination. At $T = 100°\mathrm{C}$ practically no gain is achieved.

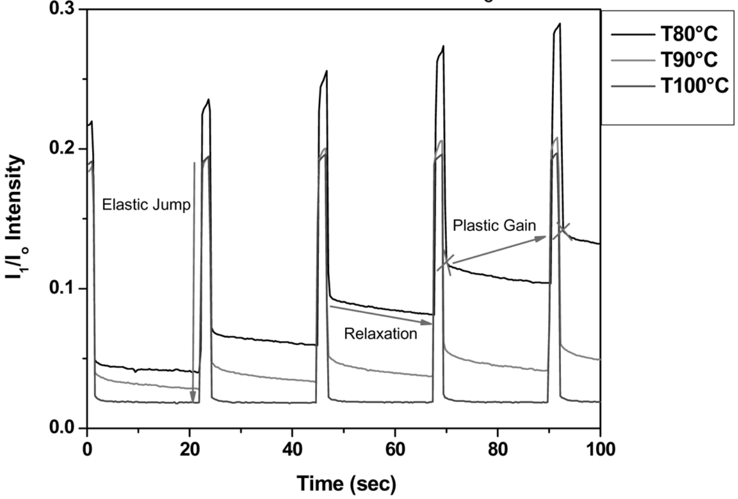
Figure 3b shows the rate of grating formation, taken from the initial slope of the diffraction curve between $0 < t < 25\,\mathrm{s}$, as a function of temperature. It is found to decrease exponentially with the increase of temperature. The time constant of this exponential decay varies with the intensity of the inscribing laser (not shown). At about 100°C the slope is almost flat. However, AFM inspection shows that the grating height decreases linear with increasing temperature (Fig. 3c). At 100°C the grating height is still in the order of 10 nm, as can be seen in Figure 2b.

The development of SRG under pulse like exposure was investigated using a cyclic inscribing force by monitoring the 1st order as well as the specular intensity signals. Both were normalized to the intensity of the incident light (I_0). Because the sum of the 1st order diffraction and the specular intensity was almost unity, the shape of the SRG is proved to be sinusoidal. As in case of continuous exposure, the diffraction intensity varies with the temperature. This variation becomes very significant at higher temperatures. Here we show the results taken at $T = 80°\mathrm{C}$ up to T_G for the laser intensity $I_p = 1\,\mathrm{W/cm^2}$. Between the exposures the temperature was increased in steps of 5°C (see Fig. 4a). When the light is switched on, the diffraction intensity jumps to a certain value, then increases further under illumination, and decays when the light is switched off. The difference in intensity between two subsequent pulses reflects the plastic gain in SRG formation. Subsequent pulses become accumulated which results in a stepwise increase of the grating height. The relaxation in dark shows exponential behavior as long as the temperature stays below 100°C. At this temperature no plastic gain is found and also no relaxation is found. SRG grating is pure elastic and appears under green light only.

◄

FIGURE 3 (a) Temperature dependent intensity of the first order diffraction peak of the forming SRG grating measured using $\lambda_{probe} = 633\,\mathrm{nm}$; (b) Temperature dependent rate of the grating formation measured under continuous exposure; (c) Temperature dependent grating height after continuous exposure, as measured using atomic force microscope.

(a) Intensity normalised to I_0



(b) Gain versus number of Pulses

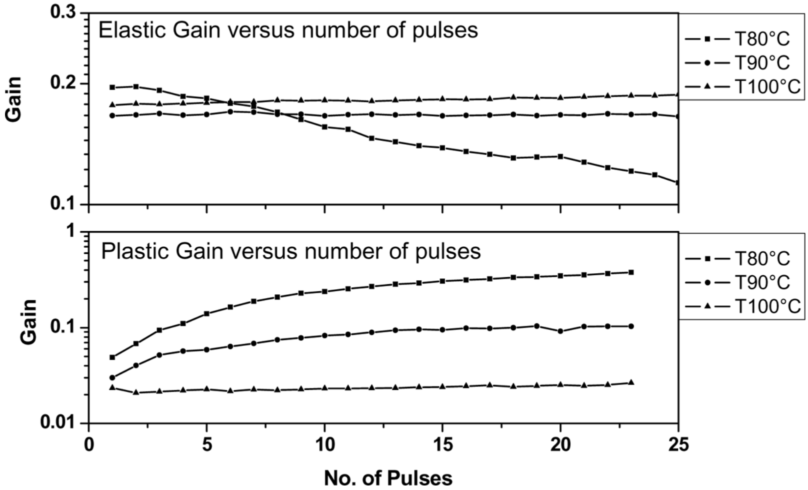


FIGURE 4 (a) Pulsed exposure intensity of the first order diffraction peak, measured using $\lambda_{probe} = 633\,\text{nm}$. Intensity of the inscribing laser is $1\,\text{W/cm}^2$; (b) Rise in the diffraction intensity per pulse: elastic jump (top) and plastic gain (bottom); (c) Temperature dependent rate of grating relaxation; (d) Temperature dependent elastic jump.

The temperature dependence of plastic gain is shown in the bottom part of Figure 4b. One can observe a qualitatively similar behavior to that found at the continuous exposure which can be described by

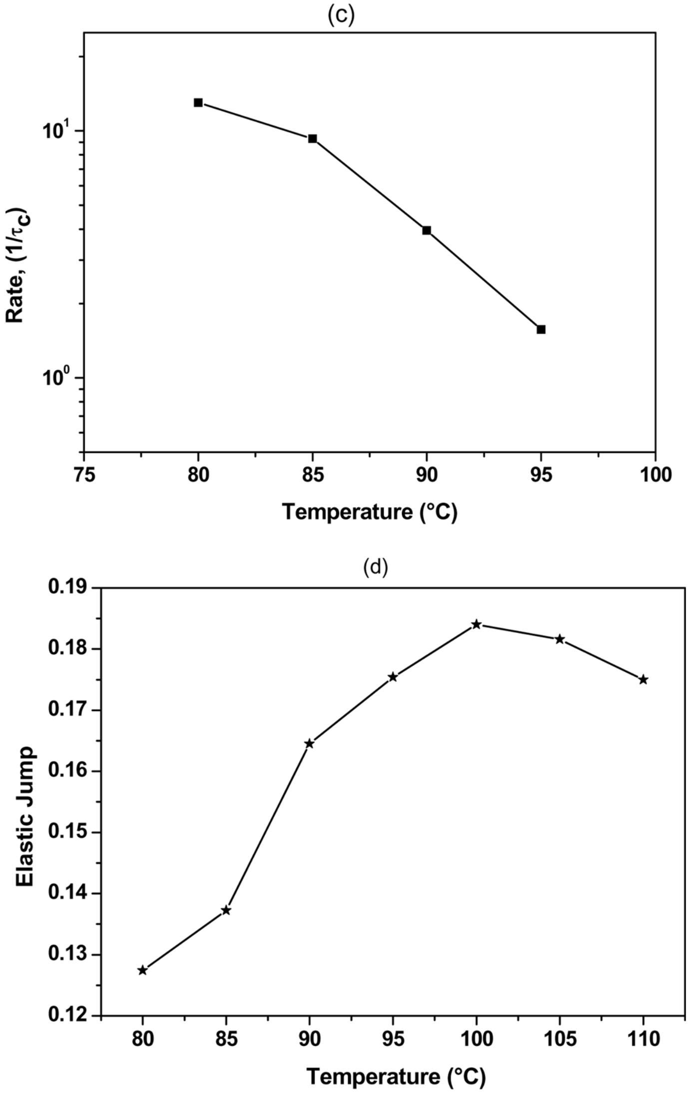


FIGURE 4 Continued.

equation similar to Eq. (1). The gain is accumulated from subsequent pulses. However, no plastic gain is found for temperatures of $T = 95$°C and higher. For lower temperatures the initial slope extracted from the gain of the first few pulses is already much smaller then that found at the continuous exposure. The time dependence of scattered intensity during relaxation process can be approximated as follows

$$I_2(t) = I_1(t)e^{-t/\tau_c(T)} \tag{2}$$

The rate of relaxation $1/\tau_c$ decreases with temperature and is no more measurable at $T = 100$°C (Fig. 4c). The rate of relaxation $1/\tau_c$ is given by the slope of the relaxation curve in Figure 4a. The slope of the relaxation curve is plotted in Figure 4c against temperature showing that the rate decreases with temperature as suggested by Eq. (2).

Figure 4d shows the height of the elastic jump as function of temperature. It increases up to 100°C and decreases after, i.e., the elastic response of the polymer to an actinic light is maximum at the temperature at which the plastic gain vanishes. At 100°C the elastic response amounts to 18%. After this temperature also the elastic gain decreases and vanishes completely above 110°C, at temperature close to the T_G. Finally the time dependence of the elastic jump is shown in the top part of Figure 4b. It decreases at low temperatures but becomes constant upon approaching 100°C.

DISCUSSION

The proper material description of the polymer deformation below the glass transition temperature is given by a viscoplastic model (= rate-dependent model with the yield stress) [7]:

$$\begin{cases} \sigma = E\varepsilon & \sigma \geq \sigma_Y \\ \sigma = \sigma_Y + \sigma_p & \sigma > \sigma_Y \end{cases} \tag{3}$$

For stresses below σ_Y, the polymer response is pure elastic, whereby the maximal elastic deformation, $\varepsilon_Y \equiv \sigma_Y/E$, does not exceed 2% for PMMA ($\sigma_Y = 50\,\text{MPa}, E = 3-4\,\text{GPa}$). Above the yield stress, the external stress can be considered as a sum of yield stress, σ_Y, and the plastic stress, σ_P. In case of continuous exposure, the plastic strain ε_P accumulated after sufficiently long time considerably exceeds the yield strain ε_Y, while in case of short pulse illumination these two contributions are comparable in magnitude.

As it was mentioned in Introduction, the origin of light-induced stress is statistical reorientation of azobenzene chromophores. This reorientation can be described in the terms of effective orientation potential [21]:

$$U_{eff}(\theta_{\mathbf{E}}) = U_0 \cos^2 \theta_{\mathbf{E}} \tag{4}$$

where $\theta_{\mathbf{E}}$ is the angle between the long axis of chromophore and the polarization direction $\mathbf{E}$. U_0 is the strength of potential given by [22]

$$U_0 = \frac{1}{2}\alpha v \tau(T) I_p \tag{5}$$

where α is the absorption coefficient, v is the volume of azobenzene, τ is the effective transition time between two isomer states which depends on temperature T and I_p is the laser intensity. From UV/VIS spectra, the absorption coefficient α was found to be $1.22 \pm 0.03 \cdot 10^5\,\mathrm{cm}^{-1}$ at $\lambda = 514\,\mathrm{nm}$ [23]. The volume of azobenzene v is about $10^{-21}\,\mathrm{cm}^3$ and the transition time τ is estimated to be $10^{-3}\,\mathrm{s}$ at room temperature [22]. Thus, for the laser intensity of $1\,\mathrm{W/cm}^2$ we receive U_0 of about $10^{-19}\,\mathrm{J}$.

The magnitude of light induced stress can be estimated from the derivative of the free energy over deformation assuming that the medium is purely elastic [13]. It can be shown that at the very beginning of deformation

$$\sigma \sim nU_0 = \frac{1}{2} n\alpha v \tau(T) I_p \tag{6}$$

where $n = 1.5 \cdot 10^{21}\,\mathrm{cm}^{-3}$ is the number density of azobenzenes [17]. Using this value, we receive the light induced stress of about 100 MPa which is high enough to cause yielding of the glassy polymer film at room temperature. At higher temperatures, the light induced stress should become smaller following decrease of the effective transition time τ due to gradual unfreezing of molecular motions. The temperature dependence of τ can be described by the Arrhenius equation

$$\tau(T) = \tau_0 \exp(E_a/RT) \tag{7}$$

where E_a is the activation energy, $R = 8.31\,\mathrm{JK}^{-1}\,\mathrm{mol}^{-1}$ is the gas constant and τ_0 is the limiting value of τ at $1/T \to 0$.

The temperature dependence of light induced stress can be clearly seen from the diffraction curves taken under continuous exposure. Figure 3 shows that the efficiency of grating formation decreases with temperature, so that no permanent grating can be inscribed at about 100°C. This is caused by the absence of plastic gain at 100°C as can be seen in the diffraction curved taken under pulse like exposure (Fig. 4a). According to Eqs. (6) and (7), the total stress induced by the light rapidly decreases with temperature. The activation energy E_a in Eq. (7) is found to be $0.33 \pm 0.05\,\mathrm{eV}$ ($32 \pm 5\,\mathrm{kJ\,mol}^{-1}$). At a certain temperature the light induced stress becomes smaller than the yield stress, which should be overcome in order to create a plastic deformation within the material. Therefore, the polymer response is pure elastic at 100°C and higher temperatures. With increase of temperature, the plastic gain diminishes which leads to considerable decrease of the height of the surface relief grating. Only 10 nm high SRG is measured at 100°C (Fig. 2b) after a long pulse like illumination.

At lower temperatures the polymer exhibits the viscoplastic behaviour which one can see as the continuous increase of intensity after the elastic jump. The plastic gain vanishes at about 15°C to 20°C prior to the glass transition temperature, whereas the height of the elastic jump increases between room temperature and 100°C, after which it decreases and vanishes completely at about 115°C. The temperature of disappearance of an elastic response is close to the glass transition temperature (see Fig. 4d). Also, the elastic jump decreases for subsequent pulses at low temperatures (Fig. 4b) which might be a manifestation of decrease of the elastic module due to viscoelastic flow as found in our previous studies [3]. On the other hand, no change in the elastic jump for subsequent pulses is found at higher temperatures. Surprisingly, the maximum of elastic jump is found at temperatures where the plastic gain vanishes.

SUMMARY AND CONCLUSION

The explained behaviour is related to the orientation of azobenzene chromophores. Under influence of actinic light the chromophores undergo a redistribution of orientation in direction perpendicular to the electric field vector. As seen in Figure 4a the orientation effect is faster than the time resolution of our experiment. The chromophores follow the light instantaneously (faster than 1 s). The force to orient the chromophores is in competition with that of thermal disorder. After switching the light off, the achieved ordering of chromophores relaxes due to thermal relaxation. After a certain temperature the effect of thermal disorder is always larger than the effect of orientation. This defines the yield stress beyond which no permanent grating can be created. At this condition (high temperatures) the surface deformation is purely elastic and exists only in the presence of illumination.

REFERENCES

[1] Rochon, P., Batalla, E., & Natansohn, A. (1995). *Appl. Phys. Lett.*, *66*, 136.

[2] Kim, D. Y., Tripathy, S. K., Li, L., & Kumar, J. (1995). *Appl. Phys. Lett.*, *66*, 166.

[3] Geue, T., Saphiannikova, M., Henneberg, O., Pietsch, U., Rochon, P. L., & Natansohn, A. L. (2002). *Phys. Rev. E*, *65*, 052801(1)–052801(4).

[4] Saphiannikova, M., Geue, T. M., Henneberg, O., Morawetz, K., & Pietsch, U. (2004). *J. Chem. Phys.*, *120*, 4039.

[5] Mechau, N., Saphiannikova, M., & Neher, D. (2005). *Macromolecules*, *38*, 3894.

[6] Mechau, N., Saphiannikova, M., & Neher, D. (2006). *Appl. Phys. Lett.*, *89*, 251902(1)–251902(3).
[7] Göldner, H. H. (1992). *Höhere Festigkeitslehre*, *Band 2*, 3rd ed., Leipzig Fachbuchverlag, 356.
[8] Barrett, C. J., Natansohn, A. L., & Rochon, P. L. (1996). *J. Phys. Chem.*, *100*, 8836.
[9] Jiang, X. L., Li, L., Kumar, J., Kim, D. Y., Shivshankar, V., & Tripathy, S. K. (1996). *Appl. Phys. Lett.*, *68*, 2618.
[10] Lefin, P., Fiorini, C., & Nunzi, J. M. (1998). *Pure Appl. Opt.*, *7*, 71.
[11] Bublitz, D., Fleck, B., & Wenke, L. (2001). *Appl. Phys. B*, *72*, 931.
[12] Pedersen, T. G., Johnsen, P. M., Holme, N. C. R., Ramanujam, P. S., & Hvilsted, S. (1998). *Phys. Rev. Lett.*, *80*, 89.
[13] Saphiannikova, M. & Neher, D. (2005). *J. Phys. Chem. B*, *109*, 19428–19436.
[14] Sekkat, Z. & Dumont, M. (1993). *Synth. Met.*, *54*, 373.
[15] Dumont, M. & Osman, A. E. (1999). *Chem. Phys.*, *245*, 437.
[16] Stiller, B., Geue, T., Morawetz, K., & Saphiannikova, M. (2005). *J. Microscopy*, *219*, 109.
[17] Henneberg, O. (2004). *In-situ* Untersuchungen zur Entstehung von Oberflächengittern in Polymeren. PhD-Thesis Universität Potsdam.
[18] Lagugne, F., Buffeteau, T., & Sourisseau, C. (2002). *Appl. Phys. B*, *74*, 129.
[19] Henneberg, O., Panzner, T., Pietsch, U., Geue, T., Saphiannikova, M., Rochon, P., & Finkelstein, K. (2004). *Z. Kristallogr.*, *219*, 218.
[20] Viswanathan, N. K., Kim, D. Y., Bian, S., Williams, J., Liu, W., Li, L., Samuelson, L., Kumar, J., & Tripathy, S. K. (1999). *J. Mater. Chem.*, *9*, 1941.
[21] Ilnytskyi, J., Saphiannikova, M., & Neher, D. (2006). *Condensed Matter Physics*, *9*, 87.
[22] Chigrinov, V., Pikin, S., Verevochnikov, A., Kozenkov, V., Khazimullin, M., Ho, J., Huang, D. D., & Kwok, H.-S. (2004). *Phys. Rev. E*, *69*, 061713(1)–061713(10).
[23] Pietsch, U. & Rochon, P. (2003). *J. Appl. Phys.*, *94*, 963.