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Formation mechanism and dynamics in polymer surface gratings

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We present the results of time-dependent x-ray and visible light (VIS) scattering measurements during formation of surface relief grating (SRG). These gratings are formed on polymer films containing azobenzene side groups during pulselike exposure with a holographic pattern of circularly polarized light at 488 nm. The SRG formation is accompanied by a density grating just below the film surface. Assuming viscoelastic flow, a change in polymer's elastic properties upon light exposure can explain the massive material transport. Finite element calculations reveal a dynamic model of grating formation characterized by different relaxation times. The simultaneous formation of a surface relief grating and of a density grating explains quantitatively the findings of the VIS experiment, but only qualitatively the findings of the x-ray measurements.

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It is well known that a surface relief pattern can be inscribed on polymer films containing azobenzene moieties [1–5]. This is done by exposing the sample to a periodic polarization pattern obtained when two contracircularly polarized light beams interfere. The absorption of this light induces material flow even at temperatures as low as 100 K below the glass transition temperature T_g of the polymers. The resultant surface relief has an approximately sinusoidal cross section. Depending on the power of illumination and on the state of light polarization, the grating depths may approach several hundreds of nanometers. A number of mechanisms had been proposed to explain the massive material displacement [6–8] but they do not describe the dynamics of surface relief grating (SRG) formation. Bian *et al.* and Kumar *et al.* [9,10] developed an optical gradient field force model for low-laser powers to describe the surface deformations during SRG formation. Unfortunately, this model is not able to describe the changes in the very initial stages of SRG development as well as all findings from x-ray investigations [11,12]. Thus, it is of particular interest to learn more about the nature of this light-induced material transport in polymers. In a previous experiment, we have shown that simultaneous probe by x-ray and visible light (VIS) can give additional information because these methods probe the sample at different length scales [11]. Both methods are now applied to study the time development of the grating formation process.

The sample investigated is a side-chain azobenzene polymer, poly{(4-nitrophenyl)[4-{[2-(methacryloyl-oxy)-ethyl]ethylamino}phenyl]diazene} (pDR1M), which has a glass transition temperature of $T_g = 129\,°\mathrm{C}$ [3,11]. A 400 nm thick film was deposited on a glass substrate by spin coating. Surface relief gratings with a period of $D \approx 1000$ nm were inscribed onto the polymer films using the interference pattern of two plane waves produced by counter-circularly polarized beams obtained from an argon-ion laser with a power density of 50 mW/cm^2. The x-ray experiments were performed at CHESS (Cornell University Ithaca, N.Y; $\lambda = 0.1238$ nm) using an incidence angle $\alpha_i = 0.5°$ with respect to the average surface and a charge-coupled device (CCD) camera (ADSC Quantum CCD, 1152×1152 pixels) as a two-dimensional detector. In addition, normal incidence laser scattering ($\lambda = 633$ nm) was performed at RMC Kingston using the same setup. *Ex situ* AFM inspection of several sample surfaces after short-time exposure has been performed using a Nanoscope IIIa (Digital Instruments) in tapping mode [12].

Figure 1 shows the time development of the first-order x-ray grating peak during the pulse-like exposure with blue light. It was detected simultaneously with the specular reflection and higher-order grating peaks (see inset) after exposure to a series of 5, 10, 15, and 60 s pulses. Each pulse was

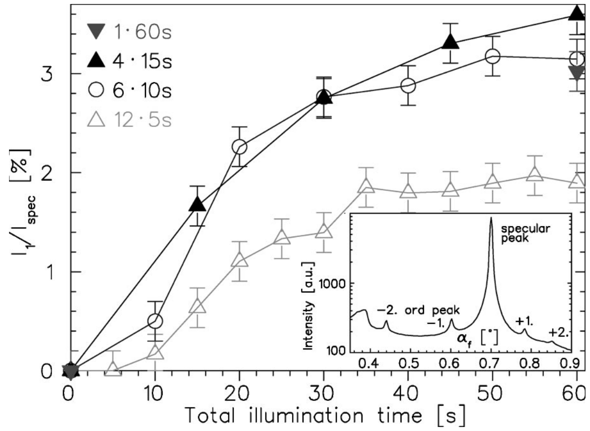

FIG. 1. Development of first-order x-ray grating peak intensity after exposure during 5, 10, 15, and 60 s with a holographic light pattern at 488 nm. The inset shows a line scan through the CCD frame.

followed by a 60 s delay in the dark and then the CCD was exposed to the x-ray signal for 30 s, the readout took 10 s. The peak intensity initially increases after each laser pulse and finally saturates. As clearly seen in Fig. 1, the maximum intensity, I_{x-max}, depends on the pulse length. For the same total exposure time, the series of 10, 15, and 60 s pulses approach almost equal $I_{x-max}\approx 3\%$, whereas the 5 s pulses gave much lower efficiency (2%) of the grating formation. Obviously, the 5 s is below a critical time of the formation process at the chosen illumination power. Unfortunately, we could not determine the critical time more precisely, as the time resolution of the x-ray experiment was limited.

Therefore, further experiments were performed outside the x-ray beamline using the VIS scattering only. The time resolution in this case was of the order of 1s. The samples were exposed to the blue light every 60 s with pulses of 5, 10, 15, and 60 s and held in the dark in between. Unlike in the x-ray experiment, the intensity of the first-order grating peak was detected continuously. A multistep development mechanism was observed and consisted of at least three different processes. (1) A very fast increase of the grating intensity in the beginning ($t<1$s); (2) A further increase at a rate that is up to 20 times smaller than the first one (Fig. 2); (3) An exponential decay of the intensity in the absence of illumination, indicating partial relaxation of the polymer. The remnant grating intensity also depends on the pulse duration. The first steep slope is the same for all pulse lengths and can be associated with an elastic process. Pulses shorter than about 1 s do not produce a grating [12]. Only the second inelastic process produces a permanent grating and its diffraction efficiency depends on the duration of the process. This qualitatively explains the findings of the x-ray measurements during the relaxation process.

Let us introduce a model that, we believe, describes the findings of coherent light scattering as well as the x-ray reflectivity data. We consider a two-dimensional problem with the x axis chosen to be parallel and the z axis perpendicular to the polymer surface, $z=0$ corresponds to the "polymer-substrate" interface. We assume that the holographic light pattern initiates trans-cis and cis-trans isomerizations of the azobenzene moieties and that this produces a periodic lateral force parallel to the sample surface. The model utilizes a sinusoidal force f_x varying in the x direction [5,9,14]. In keeping with the Lambert-Beer law, the force f_x decays exponentially with the distance from the film surface z

$$f=A\exp\left[\frac{z-[h(x)+h_0]}{\mu}\sin\left(\frac{2\pi x}{D}\right)\right], \tag{1}$$

where A is the force density, $h(x)$ is the surface relief grating, h_0 is the initial film thickness, μ is the light penetration depth, and D is the grating period. We apply the force in a self-consistent manner starting from $h(x)=0$.

In the present paper, we describe the polymer as an isotropic viscoelastic (VE) material. A simple linear VE approach with time-dependent shear modulus G was found to be sufficient to mimic the multiple inscriptions of gratings

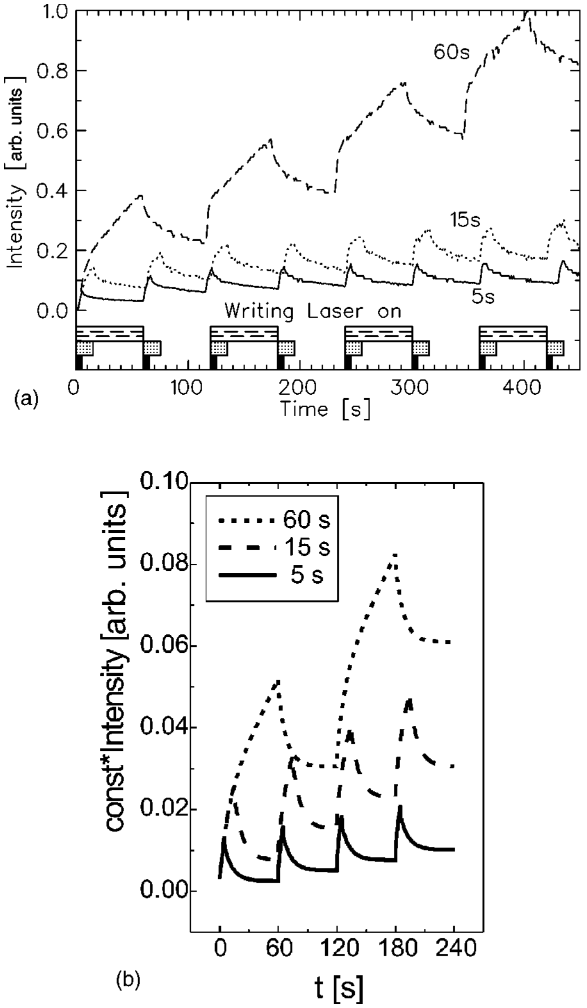

FIG. 2. Time development of the first-order VIS grating peak intensity during short pulse exposure: measurement (a), simulation (b).

$$G(t)=\sum_{k=1}^{N} G_k\exp\left(\frac{-t}{\tau_k}\right) \quad \text{and} \quad G_0=G(0)=\frac{E}{2(1+\nu)} \tag{2}$$

where E is Young's modulus, ν is the Poisson's ratio, and τ_k are particular relaxation times of the system. As the key point of our paper, we assume that due to the photoinduced cis-trans isomerization of azobenzene chromophores, the polymer film undergoes considerable plasticization, which reduces its original Young's modulus by at least three orders of magnitude. Thus, the value of Young's modulus falls into the range for a polymer around its glass transition temperature.

A finite element modeling (FEM) can reproduce the development of the surface profile, density distribution, and the ensuing scattering signal. A cleavage plane (x,z plane, $h_0=D=1$ μm) was calculated using the commercial software Mentat 3.2.0. The area was divided into 2500 square finite elements. Periodic boundary conditions were applied along the x direction. As a constraint, no displacement of sample was allowed at the polymer substrate interface.

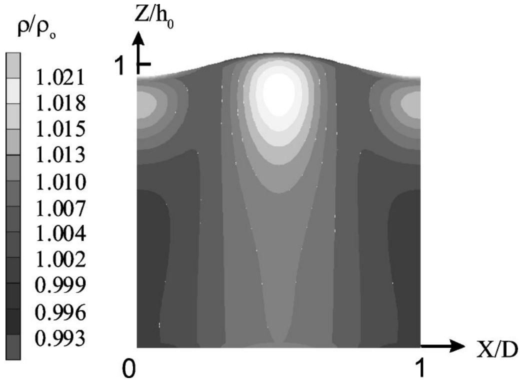

FIG. 3. FEM of the grating formation after continuous exposure of 90 s.

Figure 3 shows the results of the FEM for a constant load of $A = 100\ \mathrm{N/cm^3}$ and using the following material parameters: initial density $\rho_0 = 10^3\ \mathrm{kg/m^3}$, $E = 1$ MPa, $\nu = 0.40$, $G_1 = 0.9G_0$, $G_2 = 0.1G_0$, $\tau_1 = 2$ s, $\tau_2 = 50$ s. Already the use of two different shear moduli and time constants produces not only a sinusoidal relief at the surface, but a periodic density difference below the surface as well.

The application of a constant load produces an instantaneous elastic deformation followed by a continuous deformation with time (delayed elastic and viscous effects). In contrast to [7], the observed SRG formation appears to be not only a "surface initiated" process. The surface relief grating, as well as the lateral density variation below the surface, appears from the very beginning of the force application (instantaneous effect). During the first seconds of illumination, both profiles can be described by sinusoidal functions of equal period D (see Fig. 4). The polymer material is slightly compressed at the region of surface relief peaks and slightly expanded in between. As time increases this compressed region extends toward the substrate. At the same time the polymer material in the region of relief troughs (see Fig. 3) becomes compressed but this compressed region remains concentrated close to the surface. These results were obtained for $\mu = h_0 = 1.0\ \mu$m, which means that the light penetrates down to the substrate. When the penetration depth is decreased, the amplitude of the surface relief also decreases. For sufficiently small μ ($\mu = 0.1\ \mu$m) the relief height reaches about 20 nm after 2 min of illumination and is accompanied with a plastification of 2 and 1% at the ridge and valley regions, respectively. The height is similar to the value measured by AFM.

To simulate a transient behavior we applied a cyclic external force in the same manner as was done in the VIS experiment. Generally, VIS probes the grating formation via phase contrast, described by Bessel functions

$$I_{\mathrm{VIS}} = I_0 \left| \sum_i J_m[\phi_i(t)] \right|^2, \qquad \phi_i(t) = \frac{2\pi}{\lambda_{VIS}} (\Delta n \Delta d), \quad (3)$$

and depends on total index of refraction which includes density-induced difference Δn and on the relief height Δd index m is the grating order. Since Δd does not exceed 2% [see Fig. 3(b)] the scattered light intensity is a measure of the relief amplitude. The FE simulation does match the right functional behavior as found by the VIS experiment [Fig. 2(a)].

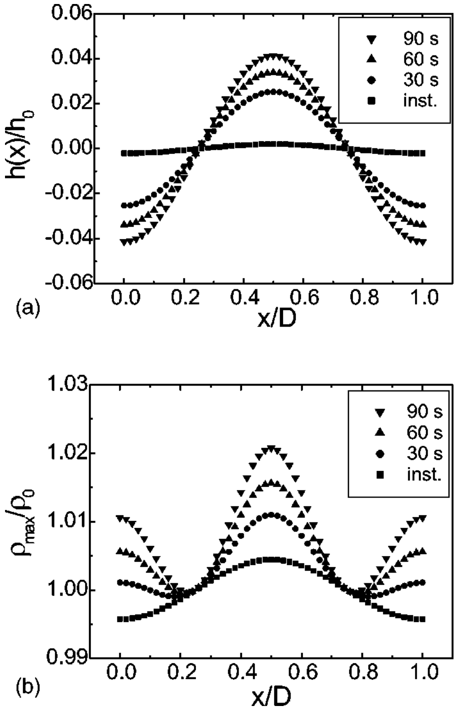

FIG. 4. Time development of the surface relief grating, $h(x)$, (a) and the density modulation, $r(x)$, (b) obtained by FEM just in the beginning and after 30, 60, and 90 s of light exposure.

In principle, the FE program cannot describe processes if one of the relaxation times is considerably smaller than an optimal time step chosen to cover the time scale of the experiment. Therefore, we developed an analytical solution for the one-dimensional transient problem with three relaxation times. As shown in Fig. 2(b), the elastic and inelastic response of the material is well described. The first cycle of exposure could be mostly fitted with the following material parameters: $G_0 = 1$ GPa, $G_1 = 0.999G_0$, $G_2 = 0.0008G_0$, $G_3 = 0.0002G_0$, $\tau_1 = 0.002$ s, $\tau_2 = 2$ s, and $\tau_3 = 50$ s. It means that after switching on the laser light the shear modulus falls from 1 GPa to 1 MPa within 0.002 s. Then, G_0 gradually decreases from cycle to cycle until reaching a saturation at about 0.5 GPa.

This result shows that further plastification takes place during the following light pulses, in spite of the transient nature of the applied force. Also, we found that τ_2 and τ_3 increase from cycle to cycle, reaching 5 and 400 s, correspondingly. This may be an indication of gradual unfreezing of cooperative motions of polymer molecules in the film, i.e., the addressing of an increased number of azobenzene side groups by the light.

The latter hypothesis is supported by *ex situ* AFM inspections performed after single short pulse inscription [12]. Up to an exposure time of 2 s there is no surface relief formation at all. The material response is entirely elastic. After 5 s of illumination, a speckled surface modification starts rising with an average height of 13 nm. Longer exposure time will saturate the relief height at about 22 nm, and the surface relief becomes rather uniform. This may be explained by the larger number of cis-trans photoisomerizations taking place at the material modification. Here again, some sort of "critical time constant" plays an important part in the process, but these times should strongly depend on the extent of isomerization, i.e., the illumination power.

Our simulation results also explain the x-ray results shown in Fig. 1. Assuming sinusoidal modulation, the time dependence of the intensity of the mth-order scattering grating peak is proportional to the square of the induced density difference $\Delta\delta$ parallel and perpendicular to the average sample surface [13]

$$I^{m}_{x\text{-}ray}(q_x,q_z,t)\approx I_0\left|\int\int \Delta\delta(x,z,t)\sin\left(\frac{2\pi m}{\lambda}x\right)\times\exp\{-i(q_x x+q_z z)\}dx\,dz\right|^2. \tag{4}$$

I^m x-ray is expressed in terms of the reciprocal space coordinates $q_z=2\pi/\lambda(\alpha_i+\alpha_f)$ and $q_x=\pi/\lambda(\alpha_i^2-\alpha_f^2)$. The x-ray experiment probes the density differences between surface relief and air as well as the light-induced density differences below the sample surface. Considering the time regime used for measurement, the x-ray grating intensity always represents the accumulated plasticization induced by each light pulse. Using Figs. 3 and 2(b) we can qualitatively understand why 5 s exposure gives much lower intensity compared with those given by longer pulses. If the elastic regime takes the first 2–4 s, the induced plasticization is small at 5 s but larger for longer pulses. Unfortunately, our model does not reproduce the saturation of intensity observed in Fig. 1. The Fourier transform of FEM pictures calculated for subsequent time steps always shows increasing intensity. Taking the surface tension into account the saturation of intensity might be expected due to the saturation of the surface profile growth.

In summary, the time-resolved x-ray and VIS scattering experiments can be explained by the simultaneous formation of a density grating below the film surface and a surface relief grating on top of the film. This obviously proves that the SRG formation is not solely a surface controlled process. Using the viscoelastic flow model we can understand that the response of the polymer material to the light-induced lateral force is entirely elastic during the first 2–4 s but plasticization takes place later on. The key assumption of our model is the light-induced reduction of the shear modulus during exposure down to values typical for polymers close to their glass transition temperatures.

Our experiments have been performed at low-laser power and on one azobenzene polymer material. To understand how high-laser powers, as well as changes in the material structure affect the formation of gratings, further experiments have to be performed and the modeling has to be improved as well. Several more experiments are under way to clarify the origin of the lateral force causing the material transport, which is still an unsolved question.

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