Micropatterning of light-sensitive liquid-crystal elastomers

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We demonstrate that photoisomerizable liquid-crystal elastomer soft films can be used as tunable holographic gratings. Optomechanical mechanism of imprinting one-dimensional grating structure into the soft matrix by two-beam uv laser interference can be clearly resolved from the time dependence of the reading beam diffraction patterns. We analyze the observed response in terms of *cis-trans* isomerization-controlled modulation of the grating profile. The grating period can be tuned reversibly by stretching or contraction of the specimen, either thermomechanically or by applying external stress. Temperature-induced modifications of the grating parameters in the vicinity of the nematic-paranematic phase transition are also examined.

Optical diffraction gratings with tunable grating period have many potential applications in spectroscopy, laser systems, optical communications, display devices, and optical sensors. As the tuning range of solid-state gratings is rather limited, several research activities have focused on grating structures made of soft materials, such as polymers and elastomers [1,2]. It was shown that large reversible straining of an elastomeric film can provide grating period modifications up to 400% [3,4]. Electrical control of the period of elastomeric gratings was demonstrated by the use of piezoelectric [5], comb-drive [6], and electroactive polymer actuators [7]. As optical patterning of the conventional light-sensitive elastomers is very ineffective [2], in all these grating structures the main role of the elastomer was to provide for tuning, while the grating itself was imprinted in one or more subsequent layers deposited on top of the elastomeric substrate. The drawback of this principle is that the fabrication of such multilayer structures usually requires quite complicated assembling procedures. An additional drawback is that the additional layers also have to be deformable like the elastomers on which they are deposited.

A profoundly more effective direct patterning of the elastomeric material can be achieved by the use of light-sensitive liquid-crystal elastomers (LCEs). In light-sensitive LCEs, liquid-crystalline orientational order of the mesogenic molecular units is coupled with the conformation of the photosensitive molecular units, for instance, photoisomerizable azobenzene derivatives. Due to this coupling, even relatively minor perturbations in the concentration of *trans-* and *cis-*isomers cause strong modifications of the orientational order and consequently of the refractive index of the medium. This provides for a possibility to record efficient volume holograms of the phase grating type. In monodomain LCEs, the orientational order of the mesogenic units is coupled also to the macroscopic dimensions of the sample [8–13], which means that holographic patterning can be used for fine structuring of the sample shape.

Practically all experiments with light-sensitive LCEs reported until now used homogeneous illumination to stimulate the optomechanical response. However, patterned illumination opens up a broad range of novel structures and possible applications. Sungur *et al.* recently showed that a grating structure fabricated in the LCE film by "direct writing" with a tightly focused laser beam exhibited a large modification of the grating period by the modification of the temperature [14]. In this work, we report an investigation of optical diffraction gratings fabricated in light-sensitive LCEs by means of holographic patterning. We reveal the kinetics of the grating recording and erasing processes, demonstrate reversible modification of the grating period by subsequent stretching and retraction of the film, and explain huge temperature-induced modifications of the grating properties in the vicinity of the nematic-paranematic phase transition.

Macroscopically aligned (monodomain) side-chain LCE films with the thickness of 150 μm were prepared according the two-step "Finkelmann cross-linking procedure" [15]. The polymer backbone is based on a commercial hydroxymethyl polysiloxane, which is cross linked by 1,4-bis(undec-10-en-1-yloxy) benzene used as the cross-linker unit. The side-chain moieties are composed of usual rodlike mesogens [4-methoxyphenyl 4-(but-3-en-1-yloxy) benzoate] and light-sensitive azomesogens [1-(4-(hex-5-enyloxy)phenyl)-2-(4-methoxyphenyl) diazene] in the ratio of 9:1 (Fig. 1). The synthesis, basic characterization of the constituents, and the
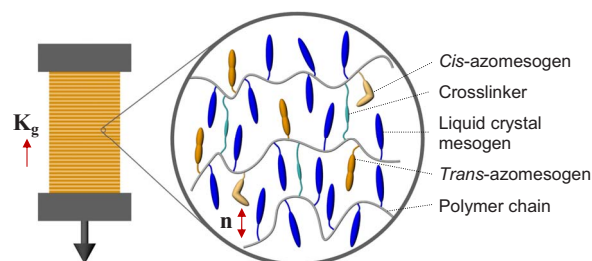

FIG. 1. (Color online) Schematic drawings of the grating structure and molecular composition of the light-sensitive LCE system.

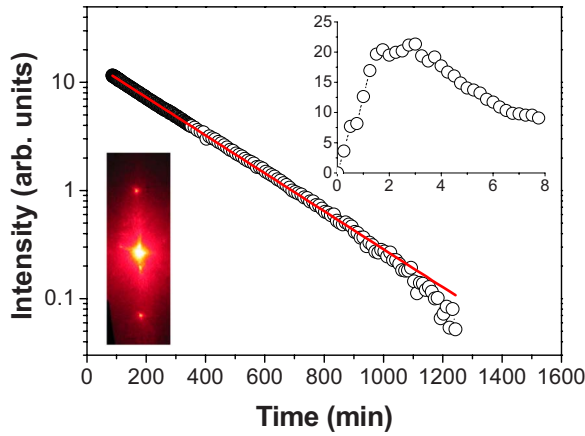*Corresponding author. irena.drevensek@ijs.si

FIG. 2. (Color online) Diffraction intensity of the first-order diffraction peaks as a function of time after termination of the recording and during the recording (inset in top right corner). Solid line is a fit to the exponential decay. The inset in the bottom left corner shows a far-field optical diffraction pattern of the He-Ne beam.
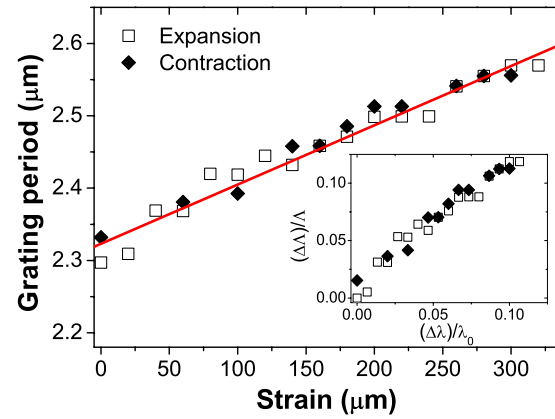

FIG. 3. (Color online) Grating period as a function of the elongation during expansion (open symbols) and retraction (solid symbols) of the sample in the direction of the nematic director. The measurements were performed at $T=25$ °C. Solid line is a fit to the linear dependence. The inset shows fractional grating spacing change $(\Delta\Lambda)/\Lambda$ as a function of the fractional length change $(\Delta\lambda)/\lambda_0$.

main steps of the LCE film preparation will be described elsewhere. Optical transmission gratings were recorded by placing the film with the size of 5×5 mm^2 in the interference field of two expanded beams from an argon ion laser operating at a wavelength of $\lambda_r=351$ nm, which stimulates *trans-* to *cis*-isomerization of the azomesogens. The transmittivity of the films at λ_r was around 10^{-3}. The writing beams of equal intensity ($I_r=10$ mW/cm^2) entered the film symmetrically with respect to the sample normal, so that a transmission grating with the grating spacing $\Lambda=2\pi/K_g$ $=2.3$ μm was recorded. The beams were linearly polarized along the direction of the nematic director **n**. The grating vector $\mathbf{K}_g$ was parallel to **n** (Fig. 1). Optical diffraction of the gratings was probed by a He-Ne laser beam at $\lambda_p=633$ nm that entered the film at a normal incidence and was also linearly polarized along **n**. Far field diffraction pattern was recorded by a charge-coupled device camera and the images were analyzed with the MATLAB image analysis software. The transmittivity of the films at λ_p was 40%.

The lower left inset of Fig. 2 shows a far-field diffraction pattern as observed on a white screen placed behind the sample. At room temperature the ±1st-order diffraction peaks have a diffraction efficiency $\eta=I_{\pm1}/I_p$ of around 1% ($I_{\pm1}$ and I_p denote the intensities of the diffracted and the incident probe beams, respectively). If the grating is recorded at temperatures above the nematic-paranematic phase transition, the diffraction efficiency is more than two orders of magnitude lower, which indicates that the liquid crystallinity of the elastomer film is vital for the efficient patterning. This is so since optical diffraction is primarily caused by the refractive index modulation, which originates from the uv illumination-induced perturbation of the scalar nematic order parameter Q [$Q=\langle(3\cos^2\theta-1)/2\rangle$, where θ is the angle between the long axis of the mesogenic molecules and **n**] through changes in the local concentration of *cis*-isomers $N_c(\mathbf{r})$. Taking into account the sinusoidal interference pattern of the uv light, $N_c(\mathbf{r})$ is given as [9,10]

Figure 2 shows the time dependence of the first-order diffraction intensity during the recording process (inset in the top right corner) and after the termination of the uv exposure. A nonmonotonous behavior observed during the recording is associated with the saturation of N_c in the bright regions of the interference pattern, which originates from the spatial variation of τ_{ef}. Due to the saturation, the profile of $N_c(\mathbf{r})$ and consequently the profile of refractive index variation become less and less sinusoidal, resulting in a decrease in the diffraction efficiency. The optimal recording time at our recording conditions is 3 min. After the termination of the uv exposure, the value of A is zero and $N_c(\mathbf{r})$ exponentially decays with time. The corresponding erasing time of the grating τ is 247.5 ± 0.4 min.

To probe the effects of straining, the upper sample edge was fixed to the sample holder, while the lower edge was attached to the translation stage (Fig. 1). Figure 3 shows the dependence of grating period Λ during the 10% expansion of the film and subsequent contraction. The value of Λ linearly and reversibly follows the elongation. During the experiment, the diffraction intensity exponentially decays with time, as evident from Fig. 2. The inset of Fig. 3 shows the fractional grating spacing change $(\Delta\Lambda)/\Lambda$ as a function of

$$N_c(\mathbf{r}) = \frac{A\tau N_0(1+\cos\mathbf{K_g r})}{1+A\tau(1+\cos\mathbf{K_g r})}[1-e^{-t/\tau_{ef}}], \qquad (1)$$

where t is the recording time, $(1/\tau_{ef})=[A(1+\cos\mathbf{K_g r})+1/\tau]$, A is a rate constant of the light-induced *trans-* to *cis*-isomerization, τ is the relaxation time of the thermally induced *cis-* to *trans*-isomerization, and N_o is the concentration of azomesogens. Due to the strong absorption of the uv light, the value of A decreases with increasing sample depth and consequently the recording process is less and less effective. Measurements of the angular dependence of the diffraction efficiency revealed that the grating structure is recorded in the surface layer with the effective thickness of around 20 μm.
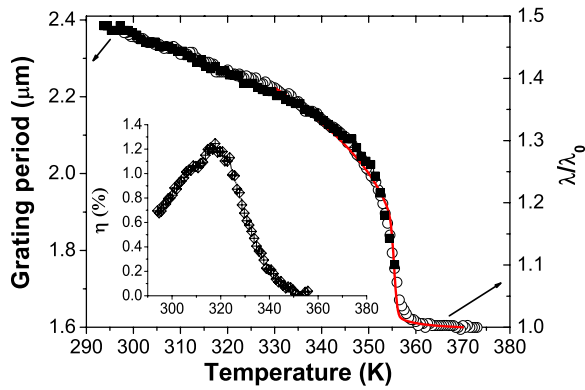
FIG. 4. (Color online) Grating period (solid squares), relative elongation of the sample (open circles), and diffraction efficiency η (inset) as functions of temperature during heating of the grating from the nematic to the paranematic phase. Solid line is a fit to distributed internal field model [16].

the fractional length change $(\Delta\lambda)/\lambda_0$. The proportionality constant is slightly larger than 1 due to clamping effects.

To probe the temperature-induced effects, the lower edge of the sample was suspended freely in air, loaded with the weight of 1 g. The strain induced by the load was negligible. The grating was recorded at room temperature. Then the uv beams were blocked and the grating temperature was raised at a constant rate of 3 K/min. The dependence of Λ on temperature is shown in Fig. 4. Heating from room temperature to the nominal nematic-paranematic transition temperature T_{NI} causes about 40% modification of Λ. As anticipated, $\Lambda(T)$ matches the temperature dependence of the thermal elongation of the sample $\lambda(T)$, i.e., $\Lambda(T) \propto \lambda(T)$. Contrary to $\Lambda(T)$, which cannot be measured at temperatures above T_{NI} due to a low diffraction efficiency, $\lambda(T)$ is easily measurable in that region. Modeling of $\lambda(T)$ by conventional Landau–de Gennes free-energy functional with the inclusion of "distributed internal fields" shows that our LCE network behaves supercritically in the thermodynamical sense [16].

Very interesting is the dependence of $\eta(T)$. Despite the fact that after the termination of the recording process $N_c(\mathbf{r})$ monotonously decays with time due to *cis-* to *trans-*isomerization, the value of η in the beginning increases with temperature and yet at $T \sim 50$ °C starts to decrease. This effect is associated with the nonlinear relation between N_c and Q and consequently the refractive index modulation. In

the simplest scenario [10], the creation of *cis*-isomers gives rise to a downward shift of the nominal transition temperature, i.e., $T_{NI}(N_c) = T_{NI}(0) - \beta N_c$. Consequently, at higher temperatures the same spatial variation of N_c causes larger relative spatial variation of Q and in turn also larger modulation of the refractive index. This effect competes with the decrease in the refractive index modulation due to the transient decay of N_c. As a consequence of this competition a position of the maximum of $\eta(T)$ is dependent on the heating rate.

The observed decay of the grating structure in time is certainly a drawback for many applications and an appropriate procedure for permanent grating imprinting has to be developed to pave the way toward practical devices. One of the possibilities is to perform the holographic patterning *in situ* during the material fabrication process. The uv-visible absorption spectra of our samples signify that *cis*-isomers are present in a relatively large proportion already before the uv illumination. This suggests that *cis-trans* back-isomerization may be hindered by the surrounding polymer network, a fact which can be employed in recording permanent tunable grating structures. Let us also note that, in our samples, azomesogens are chemically attached to the polymer backbone. In a system, doped with free azomesogens, the grating profile should decay more rapidly in time due to translational diffusion of azomesogen molecules. This fact could potentially be employed to determine the diffusion coefficient of photoisomerizable dopants. The holographic writing in light-sensitive LCEs can also be exploited to create various surface relief patterns [17], which might lead to light-controlled microtransporting devices.

In summary, we have shown that holographic micropatterning of light-sensitive LCEs is much more efficient than holographic patterning of usual (nonliquid crystalline) light-sensitive elastomers. We also demonstrated that the lattice distance of such holographic structures can be easily tuned either by temperature modification or by straining. The main goal of our work was to prove the principle; therefore, the experiments were limited to simple transmission gratings fabricated from the standard material composition. The next step is to fabricate materials optimized for holographic recording and to record complex two- and three-dimensional tunable diffractive optical structures, which can be used in imaging elements with a tunable focus, photonic band-gap structures with tunable stop bands, and many other optical elements.

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