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Dynamic Bragg Angle Shift in the Course of Volume Hologram Formation

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Real-time investigation of Bragg angle shift during volume hologram formation is presented in an organic cationic ring-opening polymerization material. Positive as well as negative values of optical shrinkage are found, assumedly related to mechanical deformations of the volume and a change of the average refractive index, respectively. Ruled by the interplay of polymerization and diffusion, the originate grating formation mechanisms prove to represent competing effects regarding the contribution to the optical shrinkage. The influence of sample preparation and holographic exposure procedure on the effects observed is investigated and the usability for minimization of total Bragg resonance detuning is considered.

Keywords: Photosensitive Polymer, Volume Hologram Formation, Phase Gratings, Bragg Selectivity, Optical Shrinkage

Introduction The act of volume hologram formation in photopolymers is of high interest for practical applications [1–5] and under extensive studies both in theoretical and practical terms.[6,7] A research challenge of considerable importance concerns the optical shrinkage in the course of hologram formation.[8,9] The photocuring is always linked to shrinkage of the volume, as a result of the shortened particle distance in the covalent bond, compared with the individual van der Waals radii prior to the curing.[9] Shrinkage during or post illumination represents a significant drawback with respect to the requirements of holographic recording,[10] which, not only in case of high capacity data storage,[11] imposes near-perfect fidelity of the reconstructed image. In particular volumetric deformations may cause a Bragg angle detuning by means of altered grating constants with the result of a disturbed selectivity and optical functionality.[12] As a consequence, many efforts are made to reduce shrinkage as an undesired side effect in terms of advanced material compositions,[9,13,14] special material processing [15] or by means of incorporation of inorganic substances.[16,17]

Cationic ring-opening polymerization (CROP) systems show some advantages compared with the free-radically polymerizing materials. While the free-radical polymerization involves a significant shrink of the volume, the CROP is accompanied by moderate volume

changes.[9] This originates from the expansion of the volume in the course of the ring-opening process, actively opposed to the effect of shrinkage within covalent bonding. An extended particle distance in the open ring results in an overall reduction of the shrink in course of the curing process. Furthermore, CROP systems allow for the shrinkage control technique by means of pre-imaging, incoherent-light exposure; however, with the disadvantage of consuming significant amounts of the materials total dynamic range.[11]

Here, we report about an epoxy-based CROP material with a convincing performance and a free surface that shows great promise for advanced integrated systems.[4, 5] Mechanical stability gains particular importance in view of the high-resolution nanostructures achievable with material based on SU-8 photoresist [18] and with regard to further reduction of feature sizes.[8] Epoxides are used as cationically polymerizable monomer to obtain high performance in terms of inducible refractive index contrast,[4] energetic sensitivity [19] as well as mechanical stability.[20] With the aim of optimization, we consider possibilities to further reduce undesired volumetric deformations. To achieve this, a deeper understanding of the basic principles involved in volume changes is required.[21] With this purpose, we apply time-resolved investigations of the Bragg angle. Observing the time course of optical shrinkage poses special

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requirements in terms of the experimental realization. At the same time, it provides a unique opportunity to study the underlying processes and mechanisms related to the particular material transformations.

This article is structured as follows. First, methods used for the investigations and analysis are described. Among those are special techniques, enabling time-resolved investigations in the first place. Basics and resulting expectations with regard to the material transformations are also addressed. Subsequently, experimental results on the optical shrinkage during and post exposure are presented. This includes classification of the different behaviours found, as well as investigations on the influence of the exposure duration and of the materials viscosity.

We interpret the findings on the basis of the Δn -transition theory.[5] Dealing with the time course of grating growth, this theory proceeds from the idea of an initial, light-induced, positive change of the refractive index, being gradually converted to a negative one and triggered by diffusion of low index species. On the dimensionless time scale the transition is taking place at $\tau = 1$, accompanied by a depletion of the diffraction efficiency with the result of the characteristic two-step growth curves.[5]

Methods All investigations are based on the recording and analysis of one-dimensional, plane-wave volume holograms. The holographic exposure is performed by two freely propagating recording beams. For details on sample preparation and hologram recording, see [3]. Additionally an *in situ* part for the real-time observation of the grating formation process was implemented. The *in situ* observation is accomplished by a first-order Bragg-matched 633 nm HeNe laser and a position-sensitive device (PSD). Details on the hologram formation process have already been reported.[5]

In general, the optical shrinkage consists of mechanical deformations of the volume on the one hand and a change of the average refractive index on the other hand.[22] Consequently, the subject matter of investigations is the product of grating period Λ and refractive index n , namely in the case of transmission-type gratings:

$$\Lambda \cdot n = \frac{\lambda}{2 \sin \theta}, \quad (1)$$

with the invariant probe wavelength λ and the Bragg angle θ . According to Equation (1), a Bragg resonance detuning by means of optical shrinkage can be observed in terms of a spectral shift of the Bragg wavelength or in terms of a Bragg angle shift, respectively.

Special techniques are required to access the time course of optical shrinkage $\partial(\Lambda \cdot n)/\partial t$. The application of a PSD in combination with a slightly focused probe

beam enables to observe the Bragg angle shift in real-time, parallel to the grating formation process. By means of the abandoned probe beam collimation, a fractional part is diffracted throughout the entire hologram formation time, regardless of possible modifications of the Bragg condition, resulting from volumetric deformations or index modifications. The position-sensitive detection of the first diffraction order involves information on the Bragg angle and thereby on the desired product of grating period and refractive index by means of Equation (1).

A time-resolved PSD measurement enables tracking of $\partial(\Lambda \cdot n)/\partial t$ and consequently provides information on the change of the volume in the direction of the grating vector. Herein $\partial(\Lambda \cdot n)/\partial t < 0$ represents negative optical shrinkage, i.e. mechanical shrinkage of the volume or a decrease in the average refractive index, respectively. Whereas positive optical shrinkage $\partial(\Lambda \cdot n)/\partial t > 0$ is linked to mechanical expansion or an increasing refractive index, respectively.

With respect to the originate grating formation mechanisms, it is expected to find mechanical shrinkage of the volume and an increase in the average refractive index throughout the polymerization process.[5,23] While the former represents a negative contribution, the latter results in positive values with regard to the optical shrinkage. Usually the negative contribution is predominant.[22] But in principle, the two effects are capable to cancel each other out with the aspired result of invariant Bragg resonance. However, in the case of $\partial(\Lambda \cdot n)/\partial t \neq 0$ the sign of the optical shrinkage provides information on the preponderance of mechanical shrinkage of the volume ($\partial(\Lambda \cdot n)/\partial t < 0$) or refractive index increase ($\partial(\Lambda \cdot n)/\partial t > 0$), respectively.

With the objective of standardization, we additionally examine the relation to the extend of grating formation $\eta(t)$. The ratio of optical shrinkage to diffraction efficiency serves as scaling factor, i.e. a measure of the relative optical shrinkage. Thus defining

$$\zeta(t) = \frac{\partial(\Lambda \cdot n)(t)/\partial t}{\eta(t)} \quad (2)$$

enables to compare the individual behaviours of optical shrinkage, independent of the grating strength.

Results Since volumetric deformations as well as refractive index modifications are a result of the material transformations involved in the formation of the hologram, the optical shrinkage naturally proceeds synchronous to the grating formation. However, this does not apply to the relative optical shrinkage ζ . As will be shown, the scaling strongly depends on the materials viscosity and on the exposure duration, as well as in general on the stage of grating formation, i.e. on time.

Low Viscosity: Invariant Time Response. A special case is obtained with low viscosity and short exposure duration. Under this circumstance, ζ appears to be time invariant. This case is illustrated in Figure 1, showing grating growth and the time-resolved relative optical shrinkage on a dimensionless time scale for preponderance of negative and positive optical shrinkage, respectively.

In case of low viscosity and short exposure, the relative optical shrinkage is constant over time regardless of whether mechanical shrinkage or refractive index increase is predominant. The corresponding transition times for the grating growth curves in Figure 1 are 90 and 20 s, respectively. Exposure duration was 4 s in each case. Low viscosity was accomplished by means of short prebake duration (80°C for 30 min).

High Viscosity: Characteristic Time Response. For higher viscosity or longer exposure duration, this time

invariance is infringed and a special characteristic is progressively arising, depending on the sign of the optical shrinkage, i.e. whether mechanical shrinkage or the refractive index increase is predominant. Time courses $\zeta(t)$ for both cases, each in comparison with the corresponding growth curves, are presented in Figure 2 on a logarithmic dimensionless time scale.

Figure 2 clearly reveals the decisive role of the transition time ($\tau = 1$) for the dynamics of optical shrinkage. Thus, a reasonable distinction appears between the first ($\tau < 1$) and the second ($\tau > 1$) growth step. This justifies to interpret the findings on the basis of the Δn -transition theory, after which an initial, light-induced, positive change of the refractive index, resulting in the first growth step, is gradually converted to a negative one, triggered by diffusion of low index species during the second growth stadium.[5] The corresponding transition times for the grating growth curves in Figure 2 are 580 and 16 s, respectively. Exposure durations were 15 and 10 s, respectively.

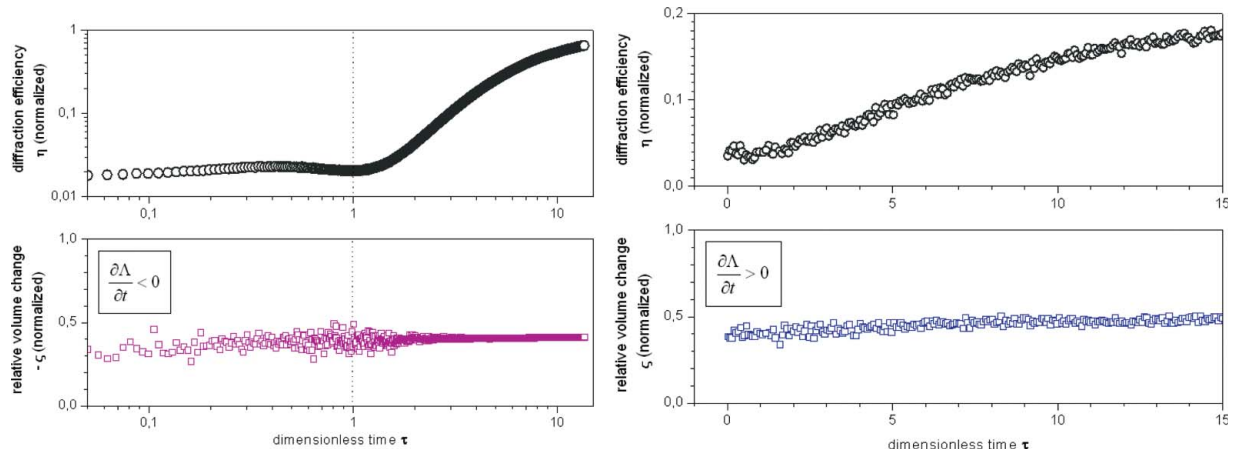


Figure 1. Invariant time response: growth curve (top) and corresponding progression of the relative optical shrinkage (bottom) for low viscosity and short exposure duration. Both in case of negative (left) and positive total optical shrinkage (right), the scaling ζ is constant in time.

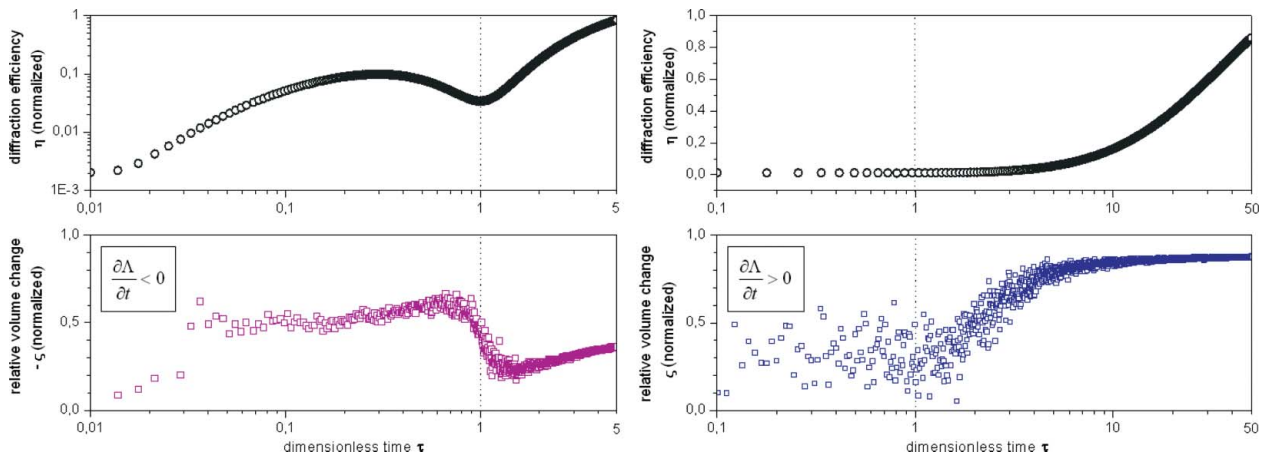


Figure 2. Characteristic time response: growth curves (top) and the corresponding progression of relative optical shrinkage (bottom) for long exposure duration in the case of mechanical shrinkage (left) and refractive index increase (right) preponderance.

With the help of Figure 2, we compiled the results as follows. Mechanical shrinkage domination is accompanied by a decrease of $\zeta(t)$ (Figure 2, left). Thus, the first growth step is more dominated by shrinkage than the second step. In the case of refractive index increase preponderance (Figure 2, right), the situation is vice versa: $\zeta(t)$ is increasing—the second stadium is more dominated by the increasing refractive index.

Interpretive Consequences: Transitional Time Response.

Comparison of the effects arises in a consistent performance, namely an increase of $\partial(\Lambda \cdot n)/\partial t$ in the course of the grating formation time, resulting in a decrease in mechanical shrinkage and increase in the refractive index rise, respectively. With respect to the Δn -transition theory this indicates that the crosslinking by means of polymerization is linked to mechanical shrinkage of the volume, while component diffusion and subsequent curing contribute to the increasing average refractive index.

These results suggest that there might be a transition between negative and positive optical shrinkage, formally expressed as follows:

$$\frac{\partial(\Lambda \cdot n)}{\partial t} < 0 \rightarrow \frac{\partial(\Lambda \cdot n)}{\partial t} > 0 \quad (3)$$

to be observed within the time course of one single grating formation. In fact such an effect was observed and is shown in Figure 3. The corresponding transition time for the grating growth curve in Figure 3 is 4,000 s, exposure duration was 15 s.

In this case, the relative optical shrinkage shows negative values in terms of mechanical shrinkage for the first growth step and positive values by means of increasing refractive index for the second stadium of growth. It can be observed that the transition from negative to positive ζ is slightly shifted towards later times, compared with the Δn -transition at $\tau = 1$. This indicates overweight of the mechanical shrinkage effect over the rising refractive index part, i.e. a certain amount of monomer diffusion is needed for predominance of the positive ζ . Even at the end of the grating formation, mechanical shrinkage is slightly predominated. Again interpretation succeeds on the basis of the grating formation theory: monomer diffusion comes to a standstill by the end of the grating formation and only the polymerization is completed, which is, as outlined above, linked to mechanical shrinkage. Once again the time course of the relative optical shrinkage is in line with the previous results, i.e. the increase of $\partial(\Lambda \cdot n)/\partial t$ in the course of the Δn -transition is confirmed.

Impact of Exposure Duration. To complete the picture, the influence of the exposure duration on the relative optical shrinkage is required. The dependence of the Δn -transition process, particularly of the transition time on the exposure and on the prebake procedure was reported earlier.[5] Figure 4 shows corresponding results with respect to ζ . In the case of negative optical shrinkage it is $-\zeta(t = 300 \text{ s})$ and it is $\zeta(t = 180 \text{ s})$ for positive values of ζ .

Figure 4 illustrates that mechanical shrinkage declines with increasing exposure duration, while the preponderance of refractive index increase becomes more

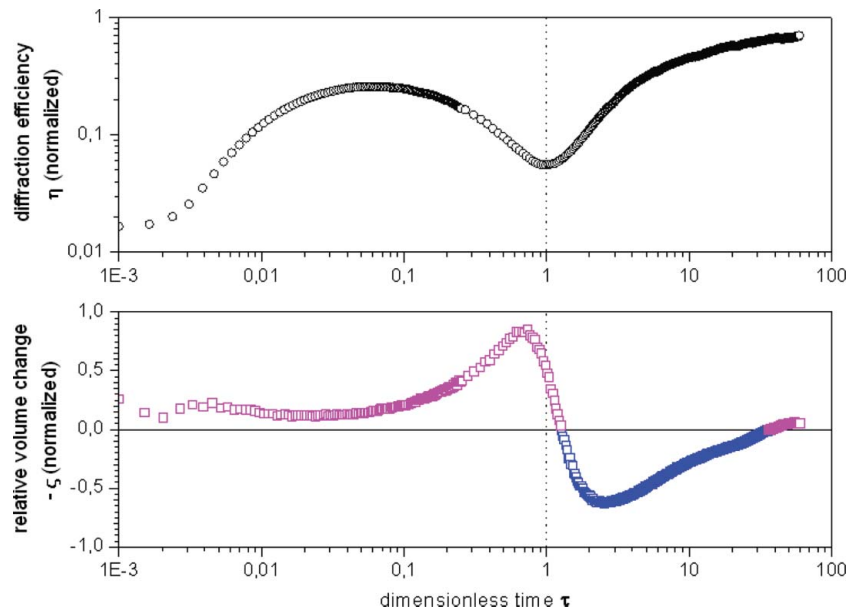


Figure 3. Transitional time response: growth curve (top) and the corresponding progression of the relative optical shrinkage (bottom) with transition from negative ($\zeta < 0$, magenta) to positive values ($\zeta > 0$, blue).

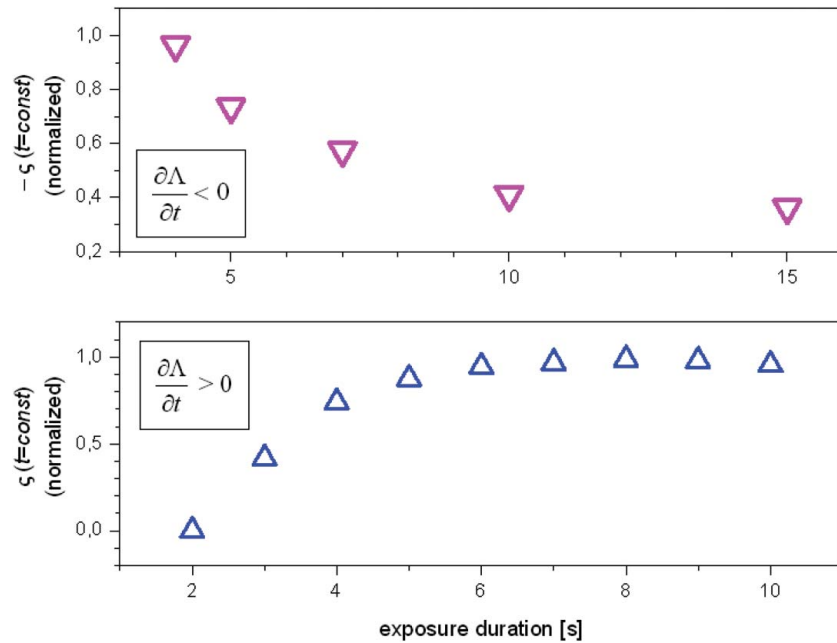


Figure 4. Influence of the exposure duration on the relative volume deformation ζ in the case of mechanical shrinkage (top) and refractive index increase (bottom) preponderance, respectively.

and more pronounced up to saturation. This leads to the hypothesis of a transition by means of Equation (3), triggered by a progressively limited flexibility of the system in the form of higher viscosity and/or in terms of curing as a result of longer exposure duration, respectively. Experimental validation of this effect remains outstanding. However, preliminary results indicate that internally as well as externally accessible parameter, i.e. the materials viscosity and the exposure duration, respectively, could provide a tool for control and adjustment of the optical shrinkage. Applying such an inherent shrinkage control seems to be most promising beyond pre-imaging exposure with the associated disadvantages in terms of consumption of the materials dynamic range [11] and might represent an auspicious approach to assure high fidelity.

Conclusion Focused on a promising new organic photosensitive material,[4] we revealed correlations between holographic grating growth and subsequent optical shrinkage. Our findings may lead to a possibility to reduce undesired instability of the angular response, based on the knowledge of competing contributions to the optical shrinkage in terms of mechanical shrinkage of the volume on the one hand and increasing refractive index on the other hand, possibly capable to cancel each other out. For this purpose, we have shown the time-resolved shift of the Bragg angle during hologram formation. The issue of whether negative or positive values of optical shrinkage are predominated seems to be ruled by the materials viscosity and by the exposure duration. All

results arise in one unified principle: an increase in the optical shrinkage in the course of the Δn -transition, taking shape whether in the form of decreasing mechanical shrinkage or increasing refractive index rise, respectively. With respect to the Δn -transition theory,[5] we can summarize that the photo-induced crosslinking seems to be linked to mechanical shrinkage, while component diffusion and subsequent curing assumedly contributes to the increasing refractive index. A transition from one to the other was demonstrated in the course of the Δn -transition and hypothesized with respect to a limited flexibility of the system in terms of higher viscosity or longer exposure duration. Further investigations will have to demonstrate to what extent the control and adjustment of the optical shrinkage can be accomplished.

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