Refractive-index determination of solids from first- and second-order critical diffraction angles of periodic surface patterns

Christoph Meichner', Andreas E. Schedl, Christian Neuber, Klaus Kreger, Hans-Werner Schmidt', and Lothar Kador'

Citation: AIP Advances **5**, 087135 (2015); doi: 10.1063/1.4928654
View online: http://dx.doi.org/10.1063/1.4928654
View Table of Contents: http://aip.scitation.org/toc/adv/5/8
Published by the American Institute of Physics

Refractive-index determination of solids from first- and second-order critical diffraction angles of periodic surface patterns

Christoph Meichner,[1,a] Andreas E. Schedl,[2] Christian Neuber,[2] Klaus Kreger,[2] Hans-Werner Schmidt,[2,b] and Lothar Kador[1,c]
[1]*University of Bayreuth, Institute of Physics and Bayreuth Institute of Macromolecular Research, Universitätsstrasse 30, 95447 Bayreuth (Germany)*
[2]*University of Bayreuth, Macromolecular Chemistry I, Bayreuth Institute of Macromolecular Research and Bayreuth Center for Colloids and Interfaces, Universitätsstrasse 30, 95447 Bayreuth (Germany)*

(Received 16 June 2015; accepted 3 August 2015; published online 11 August 2015)

We present two approaches for measuring the refractive index of transparent solids in the visible spectral range based on diffraction gratings. Both require a small spot with a periodic pattern on the surface of the solid, collimated monochromatic light, and a rotation stage. We demonstrate the methods on a polydimethylsiloxane film (*Sylgard*® 184) and compare our data to those obtained with a standard Abbe refractometer at several wavelengths between 489 and 688 nm. The results of our approaches show good agreement with the refractometer data. Possible error sources are analyzed and discussed in detail; they include mainly the linewidth of the laser and/or the angular resolution of the rotation stage. With narrow-band light sources, an angular accuracy of ±0.025° results in an error of the refractive index of typically $\pm 5 \cdot 10^{-4}$. Information on the sample thickness is not required. [http://dx.doi.org/10.1063/1.4928654]

I. INTRODUCTION

The precise knowledge of the refractive-index dispersion of solid materials is required for numerous applications such as thin-film coatings, fiber optics, optical elements, and many more.[1,2] Hence, new methods for its determination are still being devised today,[3] many of which are optimized for a particular type of application. In liquids, the refractive index can be measured precisely with common techniques[4] which, however, become demanding when applied to solids. The Abbe refractometer, for example, often requires index-matching fluids of high refractive index to optically couple the solid sample to the prism. Immersion liquids tend to be chemically or physically aggressive and can dissolve the sample or even the surface of the prism. The dispersion of the prism must be known to high accuracy, and tedious calculations are necessary to correct the refractometer scale for different wavelengths. Spectral ellipsometry is an alternative method for investigating thin solid films. However, this technique is more elaborate and the accuracy of the results depends strongly on the model used to evaluate the experimental data. Exact information about the refractive index of the substrate and the thicknesses of all layers on the sample is necessary. Similar arguments apply to refractive indices derived from reflectance or transmittance spectra. Even though the method is simple and effective, the thickness of the sample must be known to the desired accuracy and needs to be constant across the entire illuminated area. Otherwise numerical modeling is required or the spectroscopic technique becomes more complicated (e.g., involving angle-dependent measurements).[5]

[a]Electronic mail: christoph.meichner@uni-bayreuth.de
[b]Electronic mail: hans-werner.schmidt@uni-bayreuth.de
[c]Electronic mail: lothar.kador@uni-bayreuth.de

Here we present two versions of a novel method which can be applied to transparent solids or solid films with a periodic pattern on a spot at or near their surface. In contrast to other methods, they allow the direct measurement of the index of refraction from the grating constant and/or the diffraction angles. Other, independently measured, quantities, e.g., the film thickness, are not required.

Periodic surface patterns can, for example, be embossed or imprinted with lithographic techniques, or generated holographically. In the latter case, all parameters can directly be obtained within the experimental setup. Holographic exposure of many azobenzene derivatives gives rise to photo-induced mass transport over macroscopic distances, which results in the formation of surface relief gratings (SRGs).[6,7] However, the applicability of our method is not limited to photo-active systems because it only requires the periodic pattern. We demonstrate this for a transparent colorless polydimethylsiloxane (PDMS) working stamp. The surface pattern was generated by imprinting a SRG, which was holographically fabricated on an azobenzene glass.

II. THEORY

Let us consider a transparent film with refractive index n_{mat} on a substrate and with an interface to air on its upper side. A periodic pattern with periodicity Λ shall be present on a small spot at the surface as sketched in Fig. 1. The cross-sectional shape of the structure is not important; it can vary over a wide range (sinusoidal, rectangular, etc.). A monochromatic plane light wave with wavelength λ (in air) incident at angle $\varphi_{l,\mathrm{in}}$ is then diffracted into different orders l inside the material under angles $\varphi_{l,\mathrm{out}}$. The angles are given by the grating equation

$$n_{\mathrm{mat}} \sin \varphi_{l,\mathrm{out}} = n_{\mathrm{air}} \sin \varphi_{l,\mathrm{in}} + l \frac{\lambda}{\Lambda} \tag{1}$$

which can be derived from simple geometrical considerations. A less heuristic approach presented by Petit[8] shows that this equation is valid for any periodic structure (strictly speaking, of infinite lateral extension). In the limit of the Bragg regime,[9–11] valid for thick gratings, the diffraction shows angular selectivity, i.e., the intensity of orders other than $l = 0$ and $l = 1$ is zero. To avoid this situation, the grating amplitude must be sufficiently small, which is usually the case for periodic

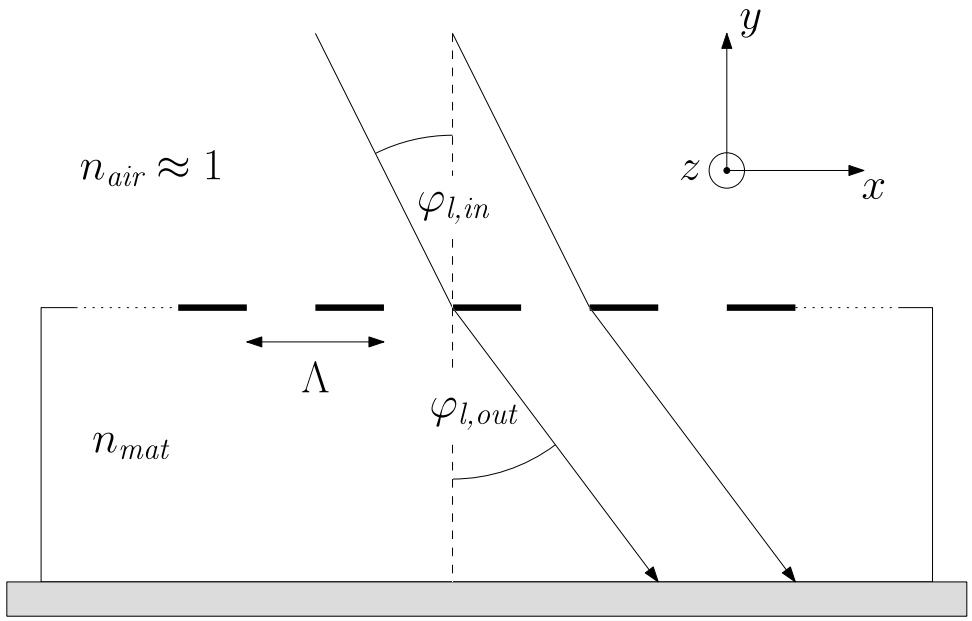

FIG. 1. Sketch of a light beam incident onto a film carrying a periodic surface pattern. Only one diffraction order l is shown for clarity.

surface structures. The 0th order simply follows Snellius' law of refraction, so its angle $\varphi_{0,\mathrm{out}}$ inside the material is smaller than the angle $\varphi_{0,\mathrm{in}}$ in air. Higher orders, on the other hand, can propagate in the material at angles $\varphi_{l,\mathrm{out}} > \varphi_{l,\mathrm{in}}$ for suitable values of the ratio λ/Λ. In this case we can orient the sample in such a way that, e. g., the first order, which is usually most intense, has an angle of $\varphi_{1,\mathrm{out}} = \pi/2$. Eq. (1) then becomes

$$n_{\mathrm{mat}} = \sin \varphi_{1,\mathrm{in}}^{90^\circ} + \frac{\lambda}{\Lambda} \tag{2}$$

with n_{air} set to 1. This simple expression allows us to determine the refractive index n_{mat} of the material without knowledge of its thickness or of parameters of the substrate. Only the quantities λ, Λ, and $\varphi_{1,\mathrm{in}}^{90^\circ}$ must be known to the desired accuracy.

An alternative access to n_{mat} is obtained by writing down an expression analogous to Eq. (2) for the second diffraction order and subtracting it from Eq. (2),

$$\frac{\lambda}{\Lambda} = \sin \varphi_{1,\mathrm{in}}^{90^\circ} - \sin \varphi_{2,\mathrm{in}}^{90^\circ}. \tag{3}$$

Inserting Eq. (3) into Eq. (2) finally yields

$$n_{\mathrm{mat}} = 2 \sin \varphi_{1,\mathrm{in}}^{90^\circ} - \sin \varphi_{2,\mathrm{in}}^{90^\circ}. \tag{4}$$

The refractive index n_{mat} can be calculated either from Eq. (2) or (4), depending on which experimental parameters are known to higher accuracy. Eq. (2) requires the knowledge of the periodicity Λ, which can be obtained, e. g., from AFM or SEM investigations, and of the wavelength λ of the probing laser according to Eq. (3). If the grating is inscribed holographically, its period can easily be calculated by $\Lambda = \lambda_w [2 \sin(\phi/2)]^{-1}$.[12] In the case of Eq. (4), the error margin depends solely on the accuracy of angle measurements.

The refractive index in Eq. (2) is calculated from two terms, the sine term and the ratio λ/Λ. If λ/Λ is chosen too small (i.e., Λ too big), large values of n_{mat} cannot be measured, since the first term contributes a maximum value of 1. However, this constitutes no limitation to our approach. In a more general form, one can write the condition which an arbitrary diffraction order l has to fulfill in the form $l\,\lambda/\Lambda < n_{\mathrm{mat}} < 1 + l\,\lambda/\Lambda$. If we assume, for example, that the refractive index is to be determined near a typical wavelength of 500 nm and Λ is chosen as 1000 nm, one can measure refractive indices within the range $n_{\mathrm{mat}} < 1.5$ with an angular measurement of the first propagating order ($l = 1$). The second order ($l = 2$) allows determination of refractive indices between 1 and 2, and the third order ($l = 3$) between 1.5 and 2.5. Hence, there is always the possibility to measure any refractive index with an appropriate choice of the diffraction order. Similar arguments apply to the determination of the refractive index with Eq. (4).

III. EXPERIMENTAL

We demonstrate our method on a cast film of PDMS. The periodic surface grating was prepared in a way similar to the procedure described in Ref. 13. First a thin film of a photo-addressable molecular glass, a spirobischroman-based 6,6',7,7' tetraester, containing four azobenzene moieties per molecule[14] was prepared by spin-casting from a 7 wt.% THF solution on a glass substrate. The substrate was spun at 700 rpm for 60 s, resulting in a film thickness of approximately 1 μm as determined by a step profiler. The film was annealed at 80 °C for 1 h under nitrogen atmosphere to remove residual solvent. Subsequently, it was exposed to holographic illumination with two coherent p-polarized laser beams (λ_w = 489 nm, diameter ca. 2 mm) of equal intensity (1 W/cm^2 per beam). The angle between the beams was adjusted to $\phi = 28.3^\circ$, resulting in a grating period Λ of 1000.6 ± 1.7 nm. During 100 s of exposure, a SRG with a height of approximately 400 nm (minimum to maximum) is developed. SRGs were inscribed at different spots across the film surface to verify reproducibility.

In a second step 1 g of *Sylgard*® 184 cast resin (siloxane/curing agent = 10:1 (w/w)) was placed on top of the azobenzene film with the inscribed grating and pressed to a film with a second glass slide from above. Its thickness was adjusted with two spacers of Scotch tape on both sides of

the substrate. In this way, the negative pattern of the SRG was imprinted on the PDMS film. Curing of the PDMS was performed at room temperature overnight, followed by a thermal curing step at 80 °C for 2 h. After curing, the two films on their substrates could easily be separated from each other. The resulting sample for the refractive-index measurements was a glass slide carrying a flat transparent PDMS coating of about 100 μm thickness with several negative type SRGs at different spots.

The PDMS sample was placed on a rotation stage and illuminated with collimated laser beams of 9 different wavelengths. A multi-color He-Ne laser provided lines at 593.932, 604.613, 611.802, and 632.816 nm, while different diode and diode-pumped solid-state lasers were used for the wavelengths 489.20, 532.06, 660.3, 671.8, and 688.4 nm. All lasers were s-polarized. The sample was rotated about the z axis as indicated in Fig. 1 to measure the angles $\varphi_{l,\mathrm{in}}^{90^\circ}$ to an accuracy of 0.025°. The diffracted orders passed PDMS film and glass substrate and were totally reflected at the back side of the substrate. The angle of incidence, for which a given diffraction order just does not reach the boundary between PDMS film and substrate, is the angle $\varphi_{l,\mathrm{in}}^{90^\circ}$. These angles could be determined for the first two diffraction orders (l = 1 and 2); for higher orders, Eq. (1) had no solution.

The results of the refractive index are compared with data measured with a Abbe refractometer (Zeiss Abbe-Refraktometer Modell A). A PDMS strip of size 4×1 cm^2 and thickness 2.5 mm was prepared to perfectly fit its prism size. Owing to the softness of the material and its adhesion to the prism, no immersion fluid was needed. For dispersion measurements, the internal scale of the refractometer had to be re-calculated for each wavelength at the neutral position of the compensator as described by the manufacturer. All experiments were conducted at room temperature.

IV. DISCUSSION

Figure 2 shows the wavelength-dependent refractive-index data of the PDMS elastomer as obtained by the different measurement procedures. The data of the Abbe refractometer are represented by open squares; their error bars result from the precision of its internal scale. With increasing wavelength, the refractive index decreases from 1.421 to 1.412, as is expected for a transparent, colorless material (normal dispersion). The refractive-index values measured with our approach are shown as open circles (calculated with Eq. (2)) and open triangles (Eq. (4)). All data points were

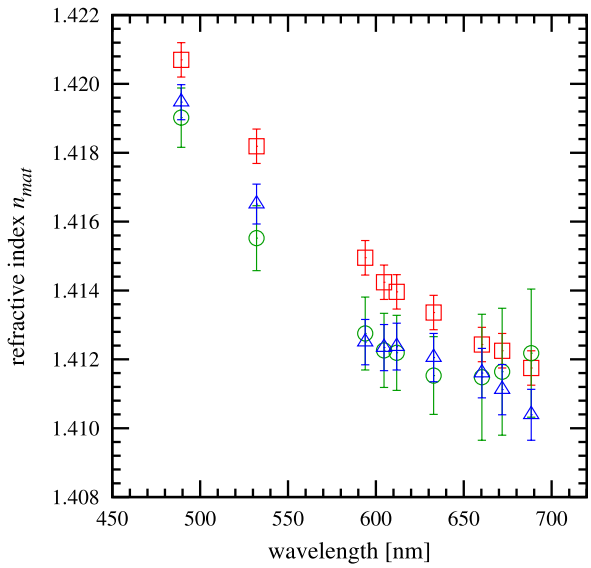

FIG. 2. Wavelength-dependent refractive index of the *Sylgard*® 184 PDMS elastomer as obtained by different techniques. Open squares: Abbe refractometer data; open circles: As calculated from Eq. (2); open triangles: As calculated from Eq. (4).

obtained with light diffracted off the same imprinted surface pattern. They show a similar behavior, yet, with subtle deviations from the refractometer results. Most of them have systematically lower values. Whereas the deviation is roughly constant (ca. −0.002) when determined with Eq. (4), the refractive index increases in the case of Eq. (2) for wavelengths larger than 650 nm to a value slightly above the last refractometer point. No anomalous dispersion is observed here, because the sample is a transparent, colorless solid. This finding is confirmed by the dispersion data obtained with the Abbe refractometer.

The data calculated with Eq. (2) and Eq. (4) are affected by different experimental error sources. Eq. (4) is sensitive only, but to a larger extent, to inaccurate determination of the angles of incidence, whereas Eq. (2) suffers also from errors of the light wavelength λ and the grating periodicity Λ (as indicated by the larger error bars). Specifically, if Λ is not known exactly, an offset is caused in the whole data set. Hence, an inaccurate grating constant Λ cannot introduce errors only at longer wavelengths. Similarly, errors in the angle determination cannot be responsible for the increase of the refractive index, since the data calculated with Eq. (4) would be affected as well. This indicates that the inserted wavelengths λ of the laser sources are responsible for the effect.

If three decimal digits of the refractive index are to be determined, the wavelength of the probing light must be known to an accuracy of about 1 nm. Also its spectral width is important, since the angle $\varphi_{1,\mathrm{in}}^{90^\circ}$ is determined by the experimental criterion that the first diffraction order does not propagate into the substrate. If the light source has a non-zero spectral width, Eq. (1) implies that the shortest wavelength of its spectrum becomes evanescent for the largest angle $\varphi_{1,\mathrm{in}}^{90^\circ}$. Hence, inserting the peak wavelength into Eq. (2) gives rise to a systematic error if the spectral width is comparable to, or larger than, the error margin of 1 nm mentioned above. In our experiment, this is the case for the diode lasers providing the long wavelengths 660.3, 671.8, and 688.4 nm. Their spectral width (FWHM; full width at half-maximum) was measured as 2.8 nm in a spectrometer, whereas all other laser sources have spectral widths below 0.1 nm.

A possibility to correct for this systematic error consists in replacing the peak wavelength λ of the laser in Eq. (2) by a wavelength λ′ close to the blue edge of its spectrum. Since the spectral profile of the diode lasers is Gaussian, it is reasonable to choose λ′ as the wavelength at which the intensity has decreased to $1/e^2$ of its peak value. This leads to wavelengths λ′ of 658.8, 669.9, and 686.9 nm, respectively, for the three diode lasers. Inserting them into Eq. (2) (with all other data unchanged) yields the refractive indices shown in Fig. 3. Now their values decrease monotonously

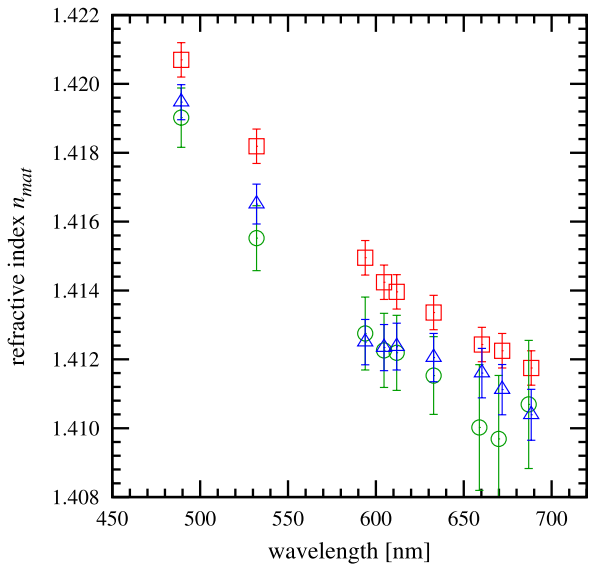

FIG. 3. Same as Fig. 2, but with the corrected wavelengths 658.8, 669.9 and 686.9 nm inserted into Eq. (2) instead of the peak wavelengths 660.3, 671.8, and 688.4 nm, respectively.

as expected and are in good agreement with the data calculated with Eq. (4). The error bars are quite large for the wavelengths above 650 nm, however.

The refractive indices calculated with both Eq. (2) and (4) are systematically smaller than those of the Abbe refractometer. The data obtained from Eq. (2) become slightly larger when the grating period Λ determined from the parameters of the holographic inscription is replaced by $\bar{\Lambda} = 999.7 \pm 1.0$ nm, the average of the Λ values calculated from Eq. (3). This gives only rise to a minor change and affects only Eq. (2), so the data are not shown.

To further investigate possible error sources, the influence of the laser polarization was checked. No difference of the refractive indices was found in measurements performed with s- and p-polarized light, so no anisotropy or birefringence was present in the PDMS sample. Furthermore, the measurements were repeated with gratings of different spots. All these experiments yielded identical data. Rotating the sample in the opposite direction and measuring $\varphi^{90^\circ}_{-1,\mathrm{in}}$ and $\varphi^{90^\circ}_{-2,\mathrm{in}}$ for the negative diffraction orders also resulted in the same refractive-index values. This demonstrates the robustness of our method with respect to slight variations of the surface quality of the sample.

We were not able to determine a clear origin of the offset between the refractometer data and those obtained with our method. Taking the error bars into account, the offset is almost negligible. The only quantity which enters in both Eq. (2) and Eq. (4) is the angle $\varphi^{90^\circ}_{1,\mathrm{in}}$ of the first diffraction order. Hence, one possibility is that the offset of the data is due to a small systematic error in determining this angle. There is always some degree of ambiguity in the decision, at which position the intensity of a diffracted beam can be considered exactly zero, so the angles might be slightly larger than measured. In our experiments, the angles were determined by the criterion that the respective diffracted orders were just invisible to the human eye. If each angle $\varphi^{90^\circ}_{1,\mathrm{in}}$ is increased by as little as 0.05°, our refractive indices coincide with the refractometer data within the error margins.

V. CONCLUSION

We have presented a method for measuring the refractive indices of solids, which is precise to about three decimal digits. Two different approaches of data evaluation were discussed which are sensitive to different experimental error sources. Our method is based on the diffraction of monochromatic laser light off a periodic surface pattern which must be present on a spot of the material. The profile of the grating (sinusoidal, rectangular, etc.) is not important, nor is the thickness of the material. Only the wavelengths and/or angles of incidence of the light must be known or measured precisely. Because periodic patterns can be obtained with various techniques (e.g., holographic inscription, embossing, imprinting, or others) the method offers a broad scope of applications.

ACKNOWLEDGMENTS

This publication was funded by the University of Bayreuth in the funding program Open Access Publishing. The research leading to these results has received funding from the European Union's Seventh Framework Programme FP7/2007-2013 under Grant Agreement No. 318804 (SNM: Single Nanometer Manufacturing for beyond CMOS devices). We wish to thank W. Köhler for the loan of the Abbe refractometer and helpful instructions for its use.

[1] H. A. Macleod, *Thin Film Optical Filters*, third edition ed. (Institute of Physics Publishing, 2001).
[2] F. M. Mitschke, *Fiber Optics Physics and Technology* (Springer, 2009).
[3] R. J. Nussbaumer, M. Halter, T. Tervoot, W. R. Caseri, and P. Smith, "A Simple Method for the Determination of Refractive Indices of (Rough) Transparent Solids," J. Mater. Sci. **40**, 575–582 (2005).
[4] S. Singh, "Refractive Index Measurement and Its Applications," Phys. Scripta **65**, 167–180 (2002).
[5] B. Šantić, "Measurement of the Refractive Index and Thickness of a Transparent Film From the Shift of the Interference Pattern Due to the Sample Rotation," Thin Solid Films **518**, 3619–3624 (2010).
[6] H. Audorff, R. Walker, L. Kador, and H.-W. Schmidt, "Polarization Dependence of the Formation of Surface Relief Gratings in Azobenzene-Containing Molecular Glasses," J. Phys. Chem. B **113**, 3379–3384 (2009).
[7] H. Audorff, K. Kreger, R. Walker, D. Haarer, L. Kador, and H.-W. Schmidt, "Holographic Gratings and Data Storage in Azobenzene-Containing Block Copolymers and Molecular Glasses," Adv. Polym. Sci. **228**, 59–121 (2010).
[8] R. Petit, *Electromagnetic Theory of Gratings* (Springer, 1980).
[9] M. G. Moharam, T. K. Gaylord, and R. Magnusson, "Criteria for Bragg Regime Diffraction by Phase Gratings," Opt. Commun. **32**, 14–18 (1980).

[10] H. Kogelnik, "Coupled Wave Theory for Thick Hologram Gratings," Bell Syst. Tech. J. **48**, 2909–2947 (1969).
[11] R. Magnusson and T. Gaylord, "Analysis of Multiwave Diffraction of Thick Gratings," J. Opt. Soc. Am. **67**, 1165–1170 (1977).
[12] R. Magnusson and T. Gaylord, "Diffraction Efficiencies of Thin Phase Gratings with Arbitrary Grating Shape," J. Opt. Soc. Am. **68**, 806–809 (1978).
[13] R. Walker, H. Audorff, L. Kador, and H.-W. Schmidt, "Synthesis and Structure-Property Relations of a Series of Photochromic Molecular Glasses for Controlled and Efficient Formation of Surface Relief Nanostructures," Adv. Funct. Mater. **19**, 2630–2638 (2009).
[14] H. Audorff, R. Walker, L. Kador, and H.-W. Schmidt, "Holographic Investigations of Azobenzene-Containing Low-Molecular-Weight Compounds in Pure Materials and Binary Blends with Polystyrene," Chem. Eur. J. **17**, 12722–12728 (2011).