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RAMAN MICROSCOPY AND MAPPING OF SURFACE-RELIEF GRATINGS RECORDED ON AZOCELLULOSE FILMS

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Dedicated to the memory of Professor Sukant K. Tripathy.

ABSTRACT

Raman spectra and mapping of surface-relief grating (SRG) recorded on a solution cast azocellulose film are reported. The Raman spectra clearly show that the chromophores adopt the *trans* conformation. Within the detection limit of the measuring system the chromophores appear to be randomly oriented on the crest and in the valley of each groove in the grating, as a result of relaxation following the inscription procedure of the SRG. The presence of the SRG was detected as a variation of the peak intensity, which is in agreement with the surface modulation of the grating morphology.

INTRODUCTION

Since the discovery of the direct photoinscribing process of surface relief gratings (SRGs) on azobenzene-containing polymers [1, 2], considerable effort

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has been directed to identify the mass transport mechanisms that can take place over micrometer distances. These gratings are formed by interference of coherent laser beams with appropriate polarization. It is now well established that for laser intensities from a few mW cm^{-2} up to a few hundred mW cm^{-2}, the mass transport for grating inscription is primarily driven by light [3]. Polymers amenable to SRG inscription must necessarily contain an azochromophore, as the trans-cis-trans photoisomerization cycles are essential to allow photoinduced mass transport. SRGs can be written at room temperature, i.e., much below the glass transition temperature of the polymer, and can be erased optically in most cases by irradiating with a single laser beam of appropriate polarization and wavelength, or thermally by heating the sample over the glass transition temperature. The depth of the SRG depends on the writing laser polarization and the writing time duration, and its peaks correspond to the weakly illuminated regions of the interference pattern. Such features can be accounted for by a model [4] based on a force associated with the field gradient, according to which significant grating formation is only achieved when there are variations in both light intensity and resultant electric field on the azopolymer films. In addition to those resulting from light-driven mass transport, SRGs have also been inscribed with high laser powers [5] or even laser pulses [6,7], where thermal effects play an important role.

For SRGs resulting from light-driven mass transport, one important question is whether there is any difference in orientation, and state of isomerization, of the chromophores between the peaks and valleys of SRGs. Earlier microRaman results by Labarthet *et al*. [8, 9] on SRGs recorded with contracircularly polarized light were interpreted using the Jones matrix approach. It was inferred that the polymer in the valleys shows higher orientation (perpendicular to the writing laser light polarization) than the material accumulated at the crest. This was attributed to competing forces and/or to more or less efficient cooperative (or dye-intermolecular) orientation effects during the SRG formation. In the present work an attempt is made to investigate the state of chromophores, also using Raman mapping, in an SRG recorded via light-driven mass transport on an azocellulose film. We succeeded in establishing the conformation of the chromophores, and did not observe differences between the crests and valleys of the SRG, which may be due to the limited spatial resolution of the measurements.

EXPERIMENTAL

Azobenzene modified cellulose polymer (azocellulose) was synthesized by linking 4-cyanophenylazophenol to natural cellulose via Mitsunobu reaction as described elsewhere [10, 11]. The azocellulose polymer was obtained with a degree of substitution (DS) varying form 0.13 to 0.99 by changing the molar ratio of the reactants. The sample used in this study had a DS of 0.2. The azocellulose was dissolved in a mixture of hexafluroisopropanol and trifluroacetic acid (80:20 by volume), and films were cast from solution on glass substrates in an oven, with vacuum being immediately applied for twenty minutes. The films were dried at 90°C in vacuum for 12 hours. SRGs were fabricated using a two beam interferometric set-up [12] at 488 nm from an Ar^+ laser with an intensity of 200 mW/cm^2. The polarization angle of the Ar^+ laser beam was set at ±45° with respect to the s-polarization. The grating spacing was set at 2 μm, by using an angle of 14° between the interfering beams. A low power He-Ne laser at 633 nm was used to monitor the first order diffraction efficiency during SRG formation. The recording process was stopped when the first order diffraction efficiency reached a steady state value.

The Raman scattering (Stokes) and Raman line mapping spectra were obtained with a Renishaw Research Raman Microscope System RM2000 equipped with a computer controlled 3-axis encoded (xyz) motorized stage with a minimum step of 0.1 μm. The RM2000 uses a Leica microscope (DMLM series) and a 50x-microscope objective to focus the laser beam onto a spot of ca. 1.0 μm^2. A polarizer and a half-plate were used to collect the scattered light in two directions on the substrate plane: perpendicular and parallel to SRG grooves. The spectrum is recorded using a Peltier cooled (-70°C) CCD array. The spectrograph is equipped with a 1200 g/mm grating and the Raman spectra were recorded at room temperature with ca. 4 cm^{-1} resolution. The high throughput of the instrument permits the use of very low power lasers at the sample. Various powers were employed for the 633 nm laser line, viz. 900 μW, 450μW, 40μW and 3 μW - while for the 780 nm laser line the power of 2 μW was used.

The Raman point-to-point mapping between 1700-1000 cm^{-1}, is obtained collecting spectra along a line with a well-defined spatial step. The line maps using 450μW of the 633 nm laser line were recorded along 100 μm with steps of 1 and 0.5 μm, 1 accumulation, 1 s collection time and high gain. Line mapping using 2 μW of the 780 nm laser line was recorded along 60 μm with steps of 1 μm and 0.5 μm, 1 accumulation, 1 s collection time and high gain. Data acquisition and analysis were carried out using the WIRE software for Windows and Galactic Industries GRAMS/32™ C software including the 3D package.

RESULTS AND DISCUSSION

The chemical structure of the azocellulose and the UV-vis. spectrum of the azocellulose solution cast film are shown in Figure 1. It can be seen that the 633 nm laser line is in pre-resonance with the electronic absorption, while the 780 nm laser line is not (not shown). This is an important property since the probe laser light exciting the Raman spectra could in principle affect the sample. In fact, even though the laser power used is very low, the beam is focused on a very small spot (1 μm^2) giving a high light intensity at the sample. Control experiments performed with various laser powers for the 633 nm line showed that the laser beam was not damaging the film.

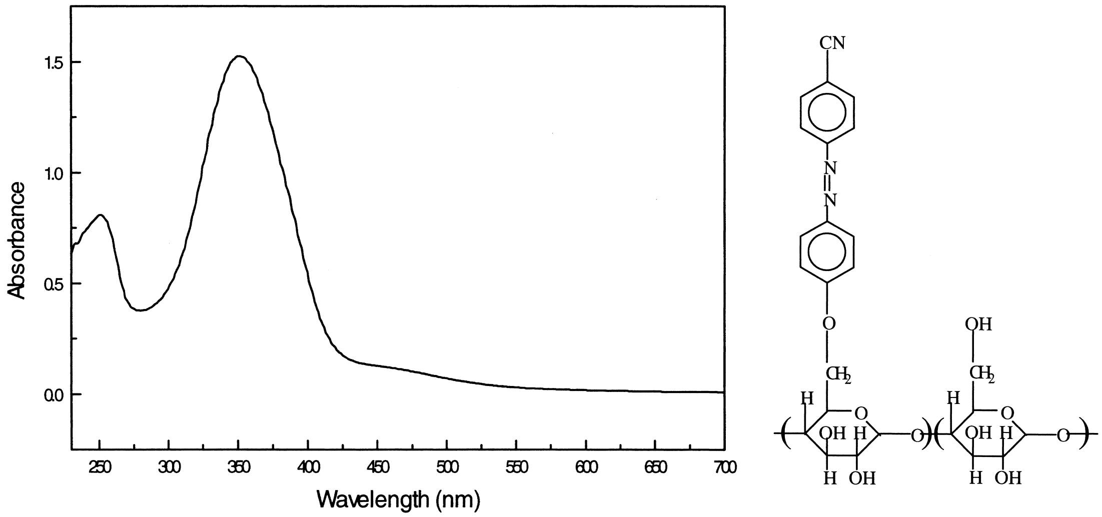

Figure 1. Uv-vis spectrum and chemical structure of azocellulose.

Raman spectra obtained in three distinct regions of an azocellulose film are illustrated in Figure 2: outside the SRG region, on an SRG crest and in the SRG valley. It is important to note that the measurements were taken several months after the SRG was inscribed. Notably, the spectrum taken outside the SRG has the highest fluorescence background. The baseline corrected results are shown in Figure 3 for the 780 nm laser line. Similar results were observed for the 633 nm laser line (not shown). Table 1 summarizes the vibrational assignment for the observed Raman bands. In each case, data were collected for two polarizations of the scattered light, either at 0 or 90 degrees with respect to the grating line direction. According to the assignments in Table 1, the chromophores are present in the *trans* conformation. Hence, the process of writing may be considered as a photodynamic process, where photoisomerization only takes place during writing. These processes are short-lived, and are not detectable in SRGs that have been inscribed for one or more days. The spectra on a given spot for distinct polarizations show that the Raman peaks occur at identical shifts and their intensities varied with the polarization in much the same way for all peaks. The latter holds for the three distinct spots measured using both 633 and 780 nm laser lines. Therefore, within the detection limit of the point-to-point mapping (for a beam spot of 1 μm^2) the azocellulose molecules may be assumed to be distributed randomly, with no preferential orientation, both in the flat portions of the film (no SRG), as well as in the regions where an SRG was inscribed. In summary, as shown in Figure 3, the Raman spectra are essentially identical for the distinct parts of the SRG, and indeed even outside the SRG. The SRG on the azocellulose film was produced with an interference pattern of ±45° polarized beams, which provides light contrast that should lead to different degrees of chromophore orientation as one scans across the SRG groove. It is known from optical storage measurements that chromophore orientation induced by uniform irradiation of the

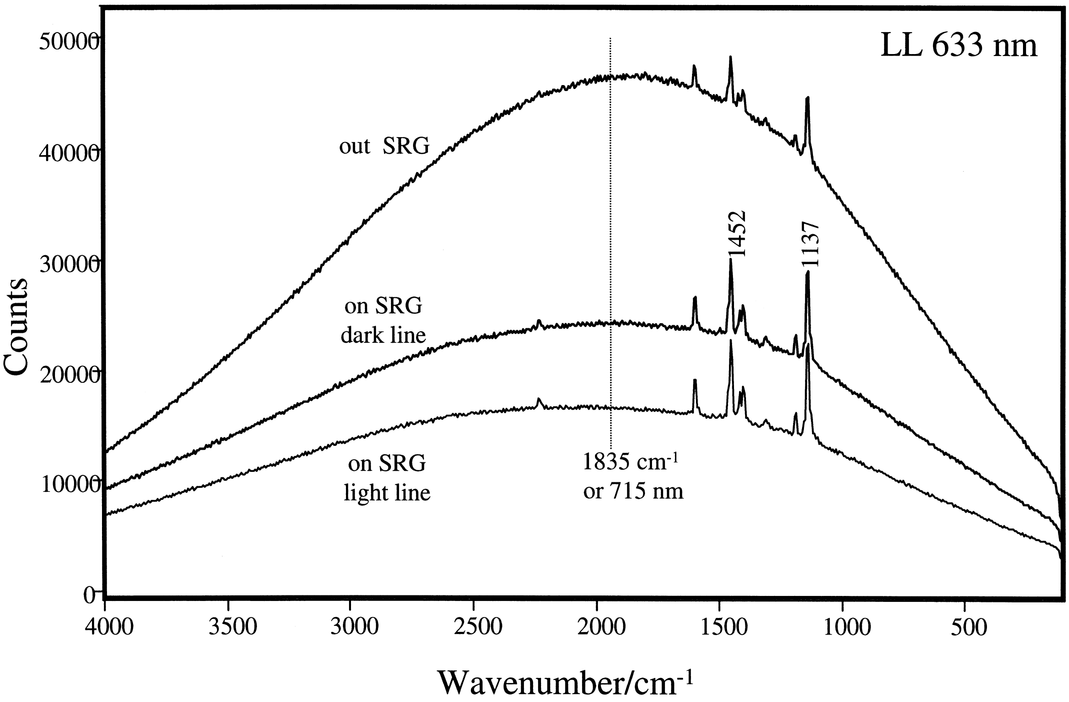

Figure 2. Raman spectra with no baseline correction using the 633 nm laser line.

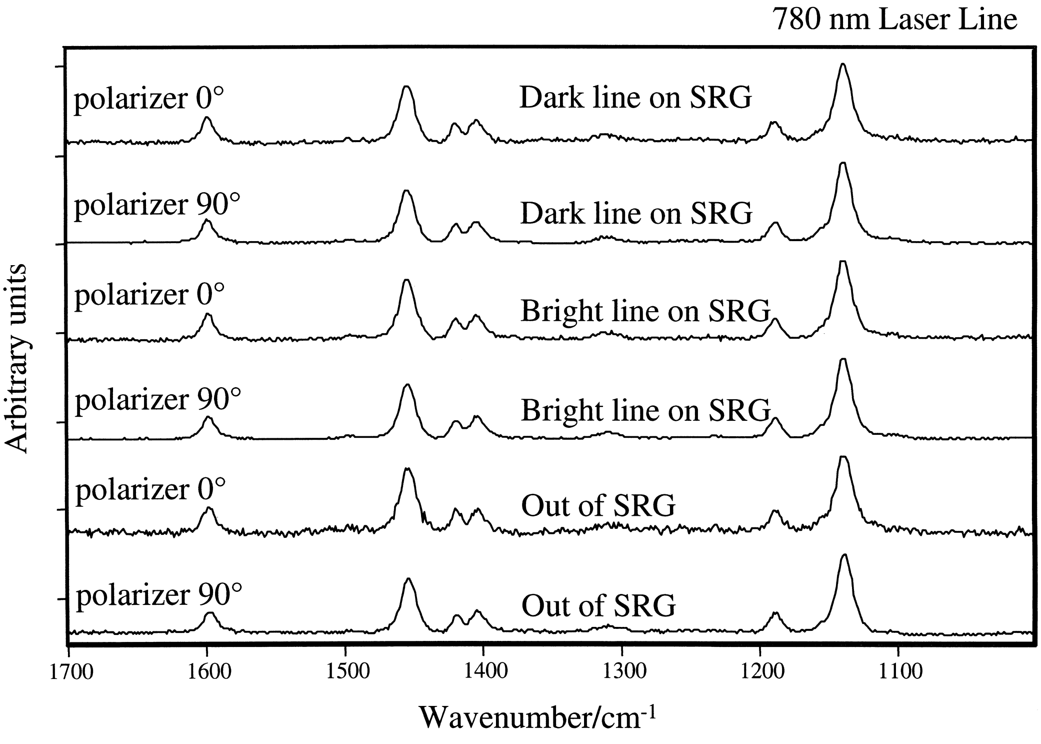

Figure 3. Raman spectra with baseline correction collected using the 780 nm laser line from 3 distinct regions of the azocellulose film: no SRG was inscribed; crest of the SRG and valley of the SRG. In all cases, identical spectra were obtained for two polarizations of the scattered light.

Table 1. Center (C), Full Width at Half Maximum (FWHM) in cm^{-1}, and Relative Intensities (RI) of the Observed Raman Bands for Both 633 and 780 nm Laser Lines

Out of SRG, 633 nm, 0°	Out of SRG, 780 nm,0°	Assignments
C/FWHM/RI	C/FWHM/RI	
2230 (19) *10*	2228 (19) *4*	CN stretching
1598 (13) *34*	1598 (12) *30*	Phenyl ring stretching
1454 (14) *76*	1454 (16) *75*	-N=N- stretching (trans)
1420 (10) *27*	1419 (9) *25*	C-H bending
1404 (15) *31*	1403 (13) *26*	C-H bending
1308 (17) *9*	1305 (39) *7*	C-H bending
1189 (13) 24	1188 (11) *22*	C-O stretching
1139 (16) *100*	1139 (14) *100*	Phenyl-N stretching

sample with a linearly polarized light lasts for many months. Therefore, some preferred orientation leading to a birefringence grating should be observed in the most illuminated region, at least for the bulk of the azopolymer. The identical spectra obtained for all regions thus indicate that the resolution of the point-to-point mapping may not have been sufficient to detect differences in orientation since the light contrast was not high for the ±45° writing polarization. In addition, relaxation due to the large-scale mass transport might have played an important role in randomizing the expected alignment of chromophores during the photoisomerization cycles, which would be consistent with the results obtained for SRGs on LB films [13]. In the latter, surface enhanced measurements allowed the chromophores at the surface (on the SRG) to be probed.

The presence of the SRG is detectable using micro Raman, when a line mapping set of spectra are recorded. Mapping along a line, selecting the 1452 cm^{-1} Raman band, using both 780 and 633 nm laser lines are shown in Figure 4. The Raman scattering intensity varies according to the surface profile of the SRG. The resolution of the mapping is poor, and hence the precise features of the SRG modulation cannot be reproduced, but the periodicity of ca. 2 μm in average was nevertheless found to be consistent with that measured with optical microscopy (see Figure 5) or atomic force microscopy. It should be pointed out that in control experiments, scanning over a film region where no SRG was inscribed shows no variation in intensity.

Notably, the conclusion that the azochromophores have the same organization in the crests and valleys does not hold for SRGs produced through mechanisms involving photodegradation. MicroRaman studies for SRGs recorded on electrostatically assembled layer-by-layer films of Congo Red alternated with poly (diallyldimethylammonium chloride) (PDAC) revealed that there are more degraded chromophores in the valleys than in the crests of the SRG [14]. The latter was expected considering that the valleys correspond to the illuminated regions of the interference pattern. Considerable differences in the Raman spectra were also detected after scanning birefringence gratings (not SRGs) recorded on

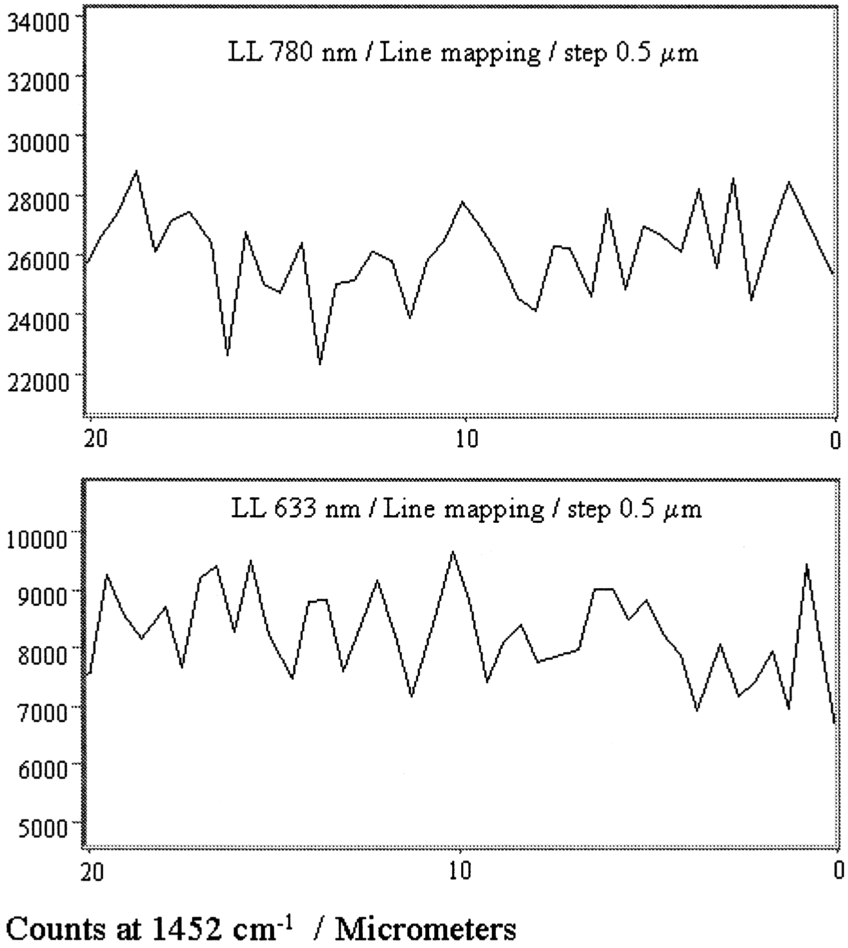

Figure 4. Variations of the integrated area for the Raman peak at 1452 cm^{-1} attributed to -N=N- (stretching) (trans) along 20 μm scanning of the 633 nm and 780 nm laser lines of the SRG inscribed on the azocellulose film. Both SRG line mappings were recorded with a 0.5 μm step. A complex pattern can be observed due to differences in the surface of the film with the intensity of the Raman band being shifted up and down. This pattern follows the modulation of the SRG, whose period of ca. 2 μm found in average agrees with the 2 μm obtained from an optical image.

Disperse Red 1-doped organically modified sol-gel films [15], where photo bleaching of the chromophore was detected.

CONCLUSION

Raman spectra with identical relative intensities were obtained for all regions of an SRG recorded on an azocellulose film, as well as for the region out-

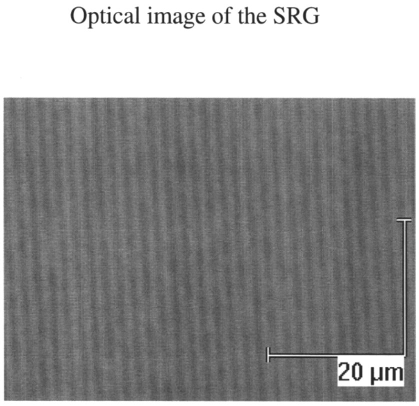

Figure 5. Optical image from the film region where the SRG was inscribed. The dark stripes correspond to the tops of the SRG.

side the SRG. From the spectral data it can be extracted that the azochromophores were randomly oriented, at least within the detection limit of the point-to-point mapping. It was concluded that any preferential orientation imposed upon recording of the SRG with a linearly polarized laser light has been lost through mechanical relaxation following the inscription procedure. The spectra also showed that after the SRG has been recorded all chromophores have relaxed to the *trans* conformation. These conclusions can probably be extended to SRGs resulting from light-driven mass transport for which similar mechanical relaxation may take place. The morphology of the SRG is also detected in the chemical imaging generated with micro-Raman mapping.

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