Index and Relief Gratings in Polymer Films for Organic Distributed Feedback Lasers

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A styrene copolymer of 4-vinylbenzyl thiocyanate (PST-*co*-VBT) was employed as recording material for optical interference patterns with periods $\Lambda < 1\ \mu$m. Using lower intensity laser irradiation (4 mJ cm^{-2}, $\lambda = 266$ nm), refractive index gratings were produced in PST-*co*-VBT by an UV-induced photoisomerization SCN $\rightarrow$ NCS. Subsequent modification of the patterns with gaseous amines yielded surface relief gratings via the formation of derivatives of thiourea. Laser irradiation with higher pulse energies (7 mJ cm^{-2}, $\lambda = 266$ nm) directly produced surface relief gratings via laser ablation (modulation depth 30 nm). Also these gratings were reactive toward amine reagents and allowed a selective functionalization of the grooves of the relief ("reactive gratings"). Under selected conditions, a doubling of the grating frequency was achieved by postexposure modification with gaseous amines. Optically inscribed gratings in PST-*co*-VBT were employed as optical resonators for distributed feedback (DFB) lasing. With a laser dye (DCM) dissolved in PST-*co*-VBT, optically pumped DFB laser action was observed after inscribing index and relief gratings. The pumping threshold for lasing I_{th} was 250 nJ cm^{-2} at $\lambda = 532$ nm.

Introduction

Distributed feedback (DFB) lasers based upon inorganic laser materials are well-developed. Since the pioneering work of Kogelnik and Shank[1] DFB lasers based upon organic compounds as gain materials have been realized as a further step to applications of organic materials in the field of optoelectronics. Low molecular weight laser dyes in polymer matrixes and conjugated polymers [e.g. derivatives of poly-*p*-phenylenevinylene (PPV)[2,3] and ladder-type poly-*p*-phenylene (m-LPPP)[4,5]]

have been used as active materials. In most cases the active layer is spin-cast as a thin film on a substrate (e.g. SiO$_2$ or PET). For DFB lasing, a periodic change of the effective refractive index (n_{eff}) and/or the gain in the waveguide is required.

In one convenient approach for organic DFB lasers, a relief grating is produced on top of the substrate. Relief patterning can be done by common photoresist technology and involves several process steps: (1) spin-casting of the photoresist, (2) patterned irradiation of the resist, (3) development of the resist, (4) etching of the sub-

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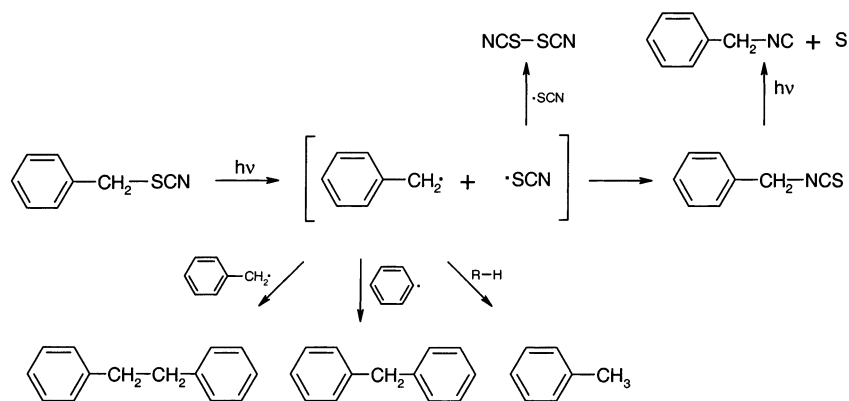(1) Kogelnik, H.; Shank, C. V. *Appl. Phys. Lett.* **1971**, *18*, 152.
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Scheme 1. Photolysis of Benzyl Thiocyanate

strate, and (5) removal of the resist film. Such techniques are also employed to produce masters for embossing techniques. To reduce the number of process steps required, there is an interest in alternative techniques that render direct imprinting possible.

In a different approach, a periodic variation of the refractive index of the active layer can be achieved. Although Kogelnik and Shank[1] showed in 1971 that index gratings in films of gelatine can be used to set up DFB lasers, only a few systems have been subsequently reported where the organic light-emitting layer is patterned instead of the substrate. For DFB laser applications, the use of a photoreactive material that changes its refractive index under UV irradiation is advantageous. In this case, the patterning process can comprise only one step (the irradiation) and—if necessary—a subsequent development step. All wet chemical steps such as etching and removal of resists can be avoided. In a similar fashion, photoreactive polymers that produce relief gratings upon UV irradiation are useful for DFB applications. Examples of photoinduced relief formation in organic polymers are UV polymerizable formulations containing acrylates,[6] photopatterning of polymers bearing pendant azobenzene units,[7] and the formation of DFB gratings in dye-doped poly(methyl methacrylate) and polycarbonate by interference illumination.[8]

The formation of relief and index patterns in polymer films is a common practice in the field of holography. For DFB laser structures based upon index gratings, it is important that the range of irradiation wavelengths used in the patterning step are different from the wavelengths of laser action. Otherwise, the inscribed index patterns would be wiped out during operation of the device. For laser operation in the visible, the recording material should thus only change its refractive index under UV irradiation. With the aim of writing short grating periods, deep UV irradiation with $\lambda < 300$ nm is advantageous.

The photoreaction of organic thiocyanates was found to be useful for the recording of optical patterns. Under deep UV irradiation (e.g., with $\lambda = 254$ nm) benzyl thiocyanate undergoes an irreversible isomerization to benzyl isothiocyanate.[9] This photoreaction proceeds via free radical intermediates as shown in Scheme 1.[10] In recent contributions we reported on the synthesis and photoreactivity of polymers of 4-vinylbenzyl thiocyanate (VBT).[11–13] The photoisomerization of the SCN substituents also proceeds in these polymers and yields up to 30% of the corresponding isothiocyanate. A schematic representation of this transformation is given in Figure 1. The photoreaction in the polymers is accompanied by free radical cross-linking, and consequently, polymers of VBT are classified as negative photoresist materials. We have focused our investigations on a copolymer of VBT with styrene (PST-*co*-VBT) containing 67 mol % of VBT. Upon UV irradiation ($\lambda = 254$ nm) of PST-*co*-VBT, an increase of the refractive index n_{633} by up to 0.02 was observed, which is a direct result of the SCN → NCS photoisomerization.[12] Using the homopolymer, even larger changes of n_{633} can be obtained after prolonged UV irradiation (Δn_{633} up to 0.03). Moreover, it was demonstrated that positive and negative relief images can be produced by UV irradiation ($\lambda = 193$ and 248 nm) through a mask followed by development with a gaseous amine compound.[13] For negative images, the gas phase reaction with amines transforms the photochemically generated NCS groups in the polymer film into derivatives of thiourea (−NH−(C=S)−NH−), which gives rise to additional changes of n and the formation of a surface relief.[12,13] This process is sketched in Figure 1. From these results, the polymer PST-*co*-VBT appeared to be a promising matrix polymer for the setup of organic DFB laser devices.

The present paper is concerned with the formation of index and relief gratings in PST-*co*-VBT produced by interference illumination with $\lambda = 266$ nm and subsequent modification of the gratings with gaseous amines. Patterned films of PST-*co*-VBT containing a laser dye (DCM) were optically characterized and investigated with regard to DFB laser activity.

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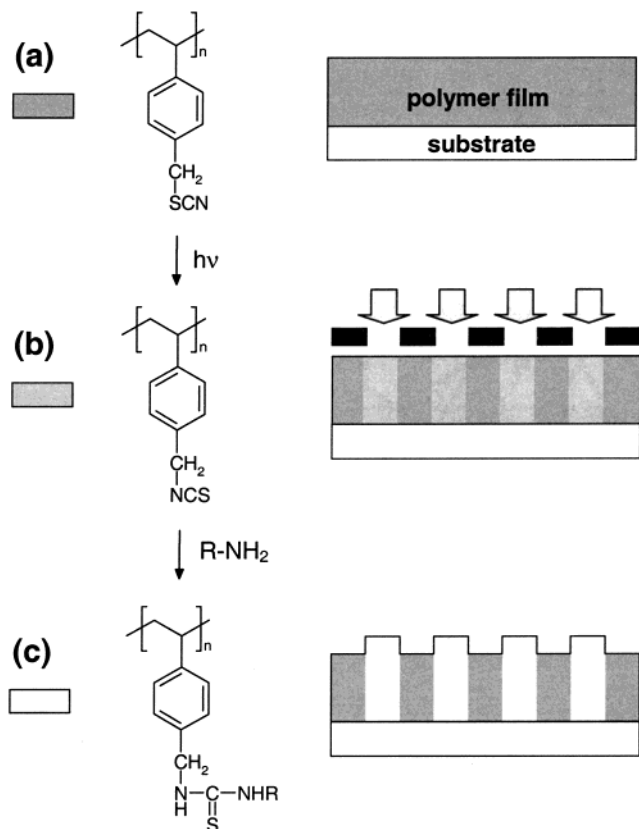
Figure 1. Formation of index and relief gratings: (a) film of PST-*co*-VBT on a CaF$_2$ substrate, (b) patterned illumination of PST-*co*-VBT (schematic) to give an index grating, and (c) formation of a relief grating after postexposure treatment with gaseous amines.

Experimental Section

Polymers. 4-Vinylbenzyl thiocyanate (VBT) was synthesized according to a procedure reported earlier.[11] Poly(styrene-*co*-4-vinylbenzyl thiocyanate) (PST-*co*-VBT) was obtained via free radical copolymerization of VBT and styrene (molar ratio feed 2:1). The polymerization was carried out in tetrahydrofuran at 60 °C reaction temperature under nitrogen atmosphere with azo-bis-isobutyronitrile as initiator. The copolymer contained 67 mol % of VBT and 33 mol % of styrene units as derived from elemental analysis (C, 75.8 wt %; H, 6.12 wt %; N, 5.47 wt %; S, 12.0 wt %). The weight-average molecular weight M_W of PST-*co*-VBT was 110 000 g mol^{-1} (polydispersity index ∼ 2), as determined by size exclusion chromatography (Viscotek Model 200 differential refractometer/viscosimeter as detector; universal calibration).

Films of PST-*co*-VBT were spin-cast from filtered CHCl$_3$ solutions (0.2 μm filter) onto CaF$_2$ disks using a Suss RC5 spin-coater. The film thickness was about 400 nm. For ASE and DFB experiments, PST-*co*-VBT films containing 2 wt % of 4-dicyanmethylene-2-methyl-6-4*H*-pyran (DCM, from Radiant Dyes) were prepared from CHCl$_3$ solutions by spin-coating. Film thicknesses were controlled by spectroscopic ellipsometry.

UV Irradiation. For flood illumination, the 254 nm line of a high-pressure mercury lamp (Heraeus, 1300 W) was used. The 254 nm line was separated with an interference filter (Melles Griot). Hg lamp irradiation was carried out under nitrogen atmosphere. The light intensity was varied between 30 and 50 mJ cm^{-2} min^{-1} (ferrioxalate actinometer).

For interference illumination, the fourth harmonic of a Nd:YAG laser (Spectra Physik/Quanta Ray-GCR 170-10) at λ = 266 nm was used. The laser beam was split into two beams with a beam splitter (Laser Components BS266/45 S50). The two laser beams (7 mm diameter each) were crossed on the sample plane at an angle θ to give a periodic fringing pattern. By changing the incident angle θ of the laser beams interfering
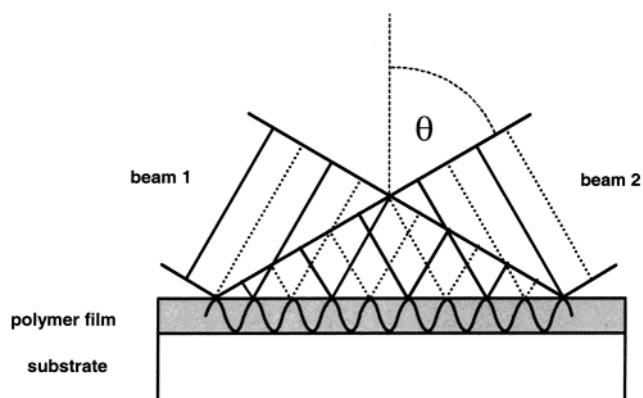

Figure 2. Principle of interference illumination. The interference of the wave fronts of two coherent laser sources produces a periodic fringing pattern in the polymer film.

at the sample surface (see Figure 2), the grating period Λ was adjusted according to the following equation

$$\Lambda = 0.5\lambda(\sin\theta)^{-1} \qquad (1)$$

In this equation, λ is the wavelength of irradiation and θ is the angle of the incident writing beam. The smallest grating period, Λ_{min}, that can theoretically be produced amounts to $\lambda/2$. The energy density of the two beams was varied between 4.0 and 7.0 mJ cm^{-2} per pulse. Pulse energies were determined with a pyroelectric joulemeter (Gentec ED-200). UV irradiations were carried out with 30 or 50 pulses at a frequency of 10 Hz. All interference illuminations were carried out under air.

Postexposure Modification of Illuminated Films of PST-*co*-VBT. For conversion of the photogenerated NCS groups to thiourea units, the polymer samples were placed over solutions of propylamine and ethylenediamine (propylamine, 2.5 wt % in toluene; ethylenediamine, 1.0 wt % in toluene). The modification reactions were carried out at 20 °C for 120 s. For reaction with ammonia, the illuminated polymer films were placed in an IR cell (Graseby-Specac) thermostated at 50 °C, which was filled with gaseous ammonia (reaction time 60 min). Hydrazine hydrate (from Aldrich) was dehydrated with solid KOH following a literature method[14] and placed in a thermostatically controlled vessel (70 °C). Vapors of hydrazine carried in a stream of dry nitrogen were passed through a reaction chamber containing the polymer sample at 20 °C (reaction time 30 s). After the postexposure modification, the samples were stored in vacuo to remove excess reagents. All operations with hydrazine were carried out under appropriate safety precautions in a well-ventilated hood.

Atomic Force Microscopy. Atomic force micrographs were taken with instruments from Digital Instruments (Nano Scope IIIa and Dimension 3100). All measurements were carried out in the tapping mode.

Absorption Spectra. Absorption spectra were taken with a Varian Cary 300 spectrometer. The absorption spectra of films of PST-*co*-VBT were calculated from the transmission interference fringes (TIF) data using the following expression[15]

$$T = \frac{16 n_0 n_f^2 n_s A}{C_1^2 + C_2^2 A + 2 C_1 C_2 A \cos(4\pi n_f d_f/\lambda)} \qquad (2)$$

where $C_1 = (n_f + n_0)(n_s + n_f)$, $C_2 = (n_f - n_0)(n_s - n_f)$, and $A = \exp(-\alpha d_f)$. In these equations T is the transmittance, A is the absorbance, n_0 is the refractive index of air, n_s is the refractive

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index of the substrate, n_f is the refractive index of the polymer film, d_f is the thickness of the film, and α is the film absorption coefficient.

Equation 2 gives the absorbance A of a weakly absorbing film on a much thicker transparent substrate. The data for n_f were taken from the refractive index measurements of undoped PST-*co*-VBT (see ref 12) assuming that doping with DCM has only a minor effect on the overall refractive index of the polymer film. The film thickness was used as a fitting parameter to give a flat absorption profile through the emission range of DCM. The resulting absorption spectra (as calculated from the values of A) represent a single pass of light through the film.

Photoluminescence, Amplified Spontaneous Emission (ASE), and DFB Lasing. Photoluminescence measurements were carried out with a JY Horiba Fluoromax 2 spectrometer. For measurements of the absolute photoluminescence quantum yield (PLQY), the polymer films were placed in an integrating sphere in accordance with the method of Greenham et al.[16] For excitation, a Kimmon HeCd laser ($\lambda = 442$ nm; 0.3 mW) was used. The emitted light was detected with a fiber-coupled CCD spectrometer.

For ASE measurements, a nitrogen laser pumped dye laser (Photon Technology Int.) operating at 470 nm was employed for excitation (500 ps pulses at 10 Hz). The beam was focused onto the sample using a cylindrical lens onto the sample to give an illuminated stripe with an area of 4 mm $\times$ 0.2 mm. The incident light intensity was controlled with calibrated neutral gray filters. The emitted light was detected from the end of the stripe using a fiber-coupled CCD spectrograph.

For the detection of DFB lasing in the patterned films, the second harmonic of a Nd:YAG laser ($\lambda = 532$ nm) was employed as pumping source (pulse duration 5 ns, repetition rate 10 Hz). A CCD spectrometer (Oriel) was used as detector. The propagation of TE and TM modes in the polymer film was calculated according to the dispersion formula of an asymmetric planar waveguide.[17]

$$2\pi\lambda^{-1}d_f\sqrt{(n_f^2 - n_{eff}^2)} = m\pi + \phi_0 + \phi_1 \qquad (3)$$

n_{eff} denotes the effective refractive index of a propagating mode and m is an integer. ϕ_0 and ϕ_1 are the phase shifts at the film/air and the film/substrate interfaces with

$$\phi_0 = \arctan\sqrt{(n_f n_0^{-1})^{2\rho}(n_{eff}^2 - n_0^2)(n_f^2 - n_{eff}^2)^{-1}} \qquad (4)$$

and

$$\phi_1 = \arctan\sqrt{(n_f n_s^{-1})^{2\rho}(n_{eff}^2 - n_s^2)(n_f^2 - n_{eff}^2)^{-1}} \qquad (5)$$

In these equations $\rho = 0$ for TE modes and $\rho = 1$ for TM modes.

Results and Discussion

Index Patterns in PST-co-VBT and Formation of Relief Gratings via Gas-Phase Derivatization. In previous work[11–13,18] we described the photoreactions of poly(4-vinylbenzyl thiocyanate) (PVBT) and poly-(styrene-*co*-4-vinylbenzyl thiocyanate) (PST-*co*-VBT). At wavelengths $\lambda > 300$ nm, these polymers are fully transparent and insensitive toward UV irradiation. Irradiation with wavelengths $\lambda < 300$ nm causes the homolytic cleavage of the benzyl−SCN unit. Free radical recombination then leads to the formation of the cor-

responding isothiocyanate, which is thermodynamically more stable by 32 kJ mol^{-1}.[19] As reported earlier, the refractive index of films of PVBT at 589 nm ($n_{589} = 1.629$) increases by up to 0.03 upon deep UV irradiation. For PST-*co*-VBT, n_{589} is 1.616, and prolonged UV illumination increases this value by 0.02.[12] These data refer to films with a thickness (d_f) between 600 and 700 nm after irradiation with the 254 nm light of a Hg lamp (energy density $E \sim 8$ J cm^{-2}). With $E = 1$ J cm^{-2}, Δn amounted to $\sim$0.015 for both polymers (the error limit for ellipsometric data on n_{589} was $\pm$ 0.0025.)[12] In the present investigations only PST-*co*-VBT was investigated, because this copolymer has better film-forming properties than the homopolymer PVBT. From solutions of the copolymer in chloroform or methylethyl ketone, films of excellent optical quality were obtained by spin-coating onto CaF$_2$ substrates.

For the production of DFB gratings, interference illumination was employed. With this lithographic technique, it is possible to produce gratings in resist materials in a convenient way. We employed a pulsed Nd:YAG laser at $\lambda = 266$ nm (fourth harmonic) as writing laser. Films of PST-*co*-VBT were prepared on CaF$_2$ plates and exposed to interference illumination as depicted in Figure 2. In one series of experiments low laser intensities were employed (beam intensity: 4.0 mJ cm^{-2} per pulse). After irradiation with 30 pulses, no changes of the surface roughness were detectable by AFM (see Figure 3). In the (overall) FTIR spectrum of the patternwise irradiated sample, the evolution of broad signals at 2085 and 2170 cm^{-1} indicated the presence of NCS units in the illuminated zones, while unreacted SCN units (mainly present in the dark areas) displayed their characteristic sharp band at 2151 cm^{-1}. Generally, the photoisomerization SCN $\rightarrow$ NCS can be followed easily by infrared spectroscopy; see the FTIR spectra of PST-*co*-VBT in Figure 4. After the reaction of NCS units with amines, the FTIR signals at 2085 and 2170 cm^{-1} disappear almost quantitatively.

Upon exposure of the illuminated film to gaseous propylamine (20 °C for 2 min), a relief image was produced. Figure 3 displays the results of the AFM investigation (section analysis). The grating period Λ amounted to 430 nm, the modulation depth of the grating was ca. 2 nm. It is obvious that the development of the relief is a result of the reaction of propylamine with the NCS units present in the illuminated areas. This view is backed by the concomitant decrease of the NCS signals in the FTIR spectrum of the polymer film. Under the conditions employed during the gas-phase derivatization, no reaction was observed between propylamine and the unirradiated zones of PST-*co*-VBT. The overall process is sketched in Figure 1, which also depicts the chemical transformations of PST-*co*-VBT during the process steps.

It is thus demonstrated that interference irradiation of PST-*co*-VBT with $\lambda = 266$ nm produces index gratings with the higher refractive index in the illuminated zones (generation of NCS units). Upon reaction with gaseous amines, a relief structure is imposed on this pattern by formation of derivatives of thiourea.

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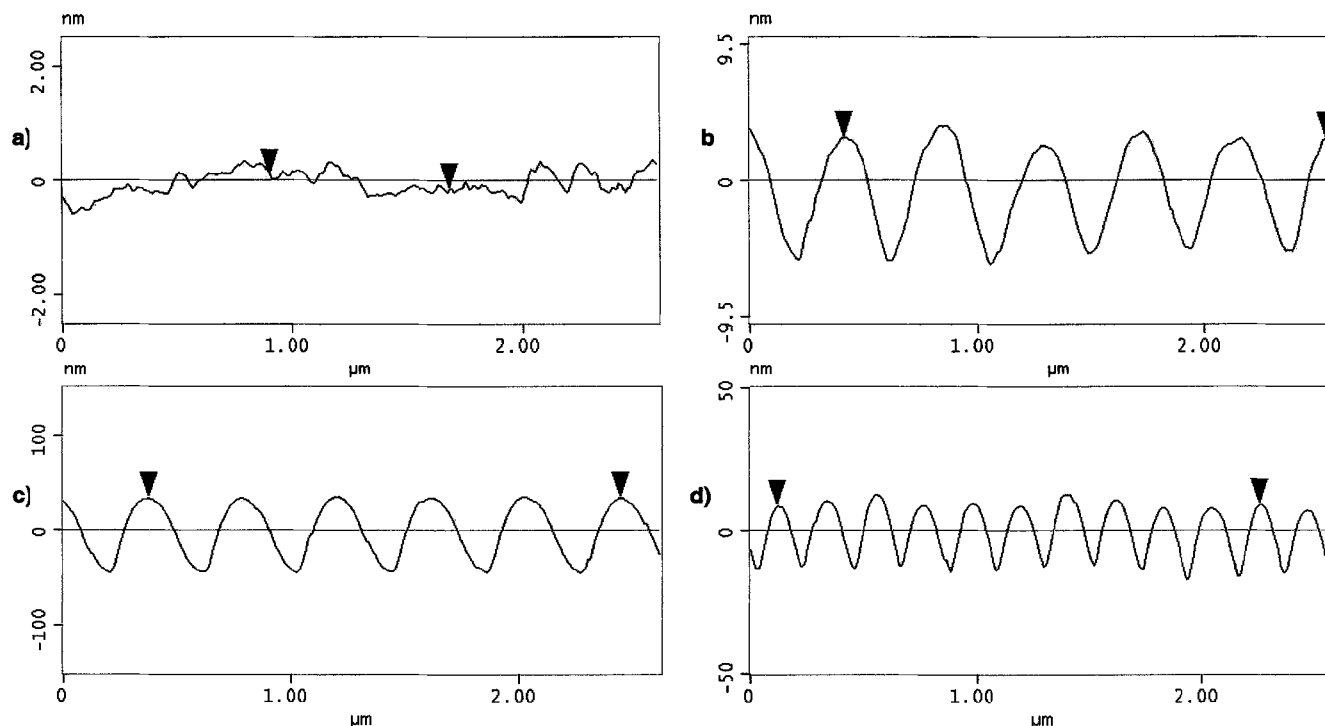
Figure 3. AFM section analysis of surfaces of PST-*co*-VBT after interference patterning: (a) Surface after interference illumination at lower intensity of the laser beam (4.0 mJ cm^{-2} per pulse, 30 pulses) and (b) this surface after subsequent postexposure modification with propylamine. (c) Surface of PST-*co*-VBT after interference illumination at higher intensity of the laser beam (7.0 mJ cm^{-2} per pulse, 50 pulses) and (d) this surface after subsequent postexposure modification with ethylenediamine. Note the different scaling of the ordinates in the diagrams a–d.
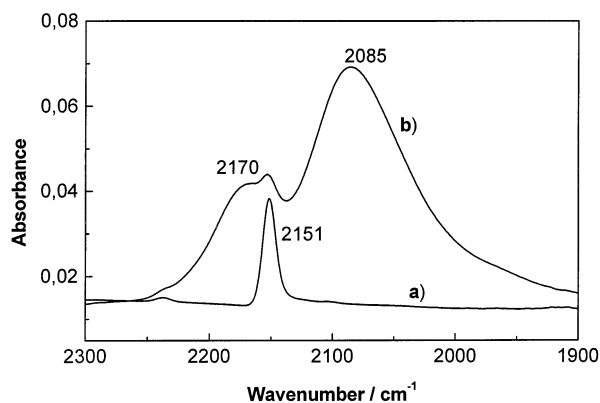

Figure 4. FTIR spectra of PST-*co*-VBT (a) prior to and (b) after UV irradiation. The SCN units (signal at 2151 cm^{-1}) are transformed into NCS units (2085 and 2170 cm^{-1}). The NCS signals disappear upon treatment with gaseous amines.

Direct Inscription of Relief Gratings in PST-co-VBT. In another series of experiments, the intensity of the 266 nm laser beam was increased to 7.0 mJ cm^{-2} per pulse. After irradiation of a film of neat PST-*co*-VBT with 50 laser pulses, the generation of a surface relief was observed *without* exposing the irradiated sample to gaseous amines. In this case, the pattern was apparently generated by laser ablation. The AFM image of this surface is shown in Figure 5. A very regular grating with a period of 430 nm was produced, as evidenced by the AFM section analysis; see Figure 3. The structures have an almost sinusoidal shape with a modulation depth of ~70 nm. The AFM micrograph does not show any deposits of debris at the surface of the patterned film. Similar reliefs were obtained with samples of PST-*co*-VBT that contained 2 wt % of the laser dye DCM.
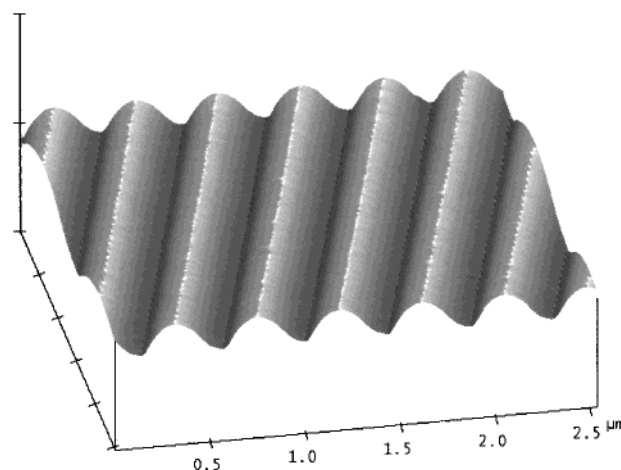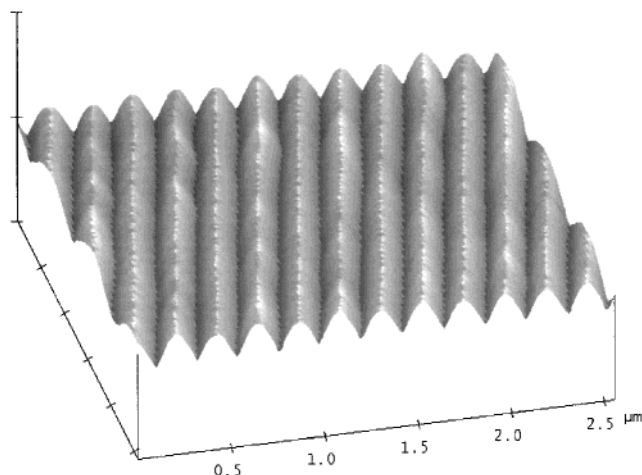

Figure 5. AFM micrograph of an interference pattern at the surface of PST-*co*-VBT films. The surface relief grating was obtained directly by laser ablation ($\lambda = 266$ nm, pulse energy 7.0 mJ cm^{-2}).

When the laser-patterned samples of PST-*co*-VBT were exposed to an atmosphere containing gaseous amines, additional changes of the surface structure were observed. Figure 6 displays the AFM image that was recorded after irradiation of PST-*co*-VBT with 50 pulses (7.0 mJ cm^{-2} per pulse) and subsequent development with ethylenediamine (2 min at 20 °C). The corresponding section analysis is shown in Figure 3. A second pattern was produced as a result of the gas-phase derivatization. Section analysis indicates that additional elevations were formed in the grooves of the primary relief pattern that had been obtained by the laser ablation process. In the grooves, NCS groups are present

Table 1. Summary of the Optical Properties of DCM-Doped PST-*co*-VBT Films before and after UV Irradiation and Subsequent Chemical Modification

PST-*co*-VBT process steps	DCM λ_{abs} (nm)	DCM λ_{em} (nm)	DCM PLQY[a] (%)	DCM λ_{ASE} (nm)	DCM λ_{laser} (nm)
nonirradiated	478	607	29	618	
UV-irradiated	474	604	20	618	630.8
UV-irradiated, propylamine	480	615	23	629	633.0
UV-irradiated, ethylenediamine	482	624	20	650	635.5
UV-irradiated, hydrazine	480	620	14	637	633.3
UV-irradiated, ammonia	480	615	18	631	634.5

[a] Quantum yield of photoluminescence.

Figure 6. AFM micrograph of the surface relief grating shown in Figure 5 after subsequent treatment with gaseous propylamine. The grating frequency is doubled.

as a result of the photoisomerization during laser irradiation with $\lambda = 266$ nm. These NCS groups react with ethylenediamine and elevations are produced in a similar fashion as lined out in Figure 1.

From the AFM micrograph in Figure 6 and the corresponding section analysis, it is evident that the generation of additional elevations leads to a doubling of the frequency of the grating. However, the grooves of the primary relief grating are shallowed and the modulation depth is reduced to ~25 nm as a result of the modification process.

Summing up, in the photoresponsive polymer PST-*co*-VBT, surface relief gratings are produced by laser ablation. "Reactive gratings" are then obtained whose grooves can be *selectively* modified by a postexposure treatment with amine compounds. Under selected conditions, gratings of double frequency can be produced by this treatment.

Absorption and Emission Spectra of DCM in Films of PST-co-VBT. PST-*co*-VBT was designed as a matrix polymer for the setup of an optically pumped DFB laser, where the enscribed index and relief gratings provide the optical feedback required for laser action. In the present investigation, DCM was used as laser dye. Films of PST-*co*-VBT containing 2 wt % of DCM were prepared on CaF_2 substrates (film thickness ca. 400 nm) and characterized with respect to optical absorption and photoluminescence quantum yield (PLQY).

The transmission spectra of these films showed interference fringes that arise from resonance effects in reflection from the surfaces of the thin films. The absorption spectra were calculated from the transmission interference fringes (TIF) data using eq 2; see the Experimental Section.

The resulting absorption spectra (as calculated from the values of *A*) closely resembled the absorption of DCM in ethanol solution. The absorption peak wavelength λ_{abs} of DCM in PST-*co*-VBT was at 478 nm in the unirradiated sample. After flood illumination with 254 nm UV light, λ_{abs} shifted to 474 nm. The postexposure modification with gaseous amines (ammonia, propylamine, ethylenediamine, and hydrazine) caused a shift of λ_{abs} to longer wavelengths (λ_{abs} between 480 and 482 nm; see Table 1).

The photoluminescence spectra of DCM in PST-*co*-VBT matrix also underwent a small spectral shift as a result of UV irradiation and subsequent modification with amines (see Table 1). The peak wavelength of emission λ_{em} for the unirradiated sample was at 607 nm; after 254 nm UV irradiation, λ_{em} was shifted to 604 nm. Subsequent modification of the irradiated sample with amines caused additional shifts (ammonia, $\lambda_{em} = 615$ nm; propylamine, $\lambda_{em} = 615$ nm; hydrazine, $\lambda_{em} = 620$ nm; ethylenediamine, $\lambda_{em} = 624$ nm). The variations of λ_{abs} and λ_{em} reflect the different chemical environment of the laser dye DCM in the matrix polymer PST-*co*-VBT at different stages of processing.

The intensity of the emitted light was much stronger for the unirradiated samples than for all other samples. Therefore, the absolute values of the photoluminescence quantum yield (PLQY) of DCM in PST-*co*-VBT matrix were determined. A HeCd laser ($\lambda = 442$ nm) was used as excitation source, and the emitted light was measured in an integrating sphere using a CCD spectrometer. The measured values of PLQY are shown in Table 1. The values are estimated to be accurate to 10% of the value.

The PLQY of DCM in an unirradiated film of PST-*co*-VBT was 29%. We found that irradiation of the samples with 254 nm UV light tended to reduce the PLQY to 20%. The subsequent treatment of PST-*co*-VBT with amines had little further effect on the PLQY of DCM. After reaction with different amines, the values of PLQY ranged between 14% (hydrazine) and 23% (propylamine). Summing up, PLQY of DCM in PST-*co*-VBT remains respectably high even after UV irradiation and postexposure treatments, although noticeable bleaching occurs during the UV illumination step.

Amplified Spontaneous Emission of DCM in PST-co-VBT Matrix. For ASE measurements, a dye laser with $\lambda = 470$ nm was employed as excitation source. ASE measurements were performed with samples of PST-*co*-VBT containing 2 wt % of DCM. Both nonirradiated and UV irradiated films ($\lambda = 254$ nm) were investigated, as well as films that had been subsequently modified with gaseous amines. Spectral line narrowing due to ASE was observed at elevated pump energies in all of the hosts. Figure 7 displays ASE
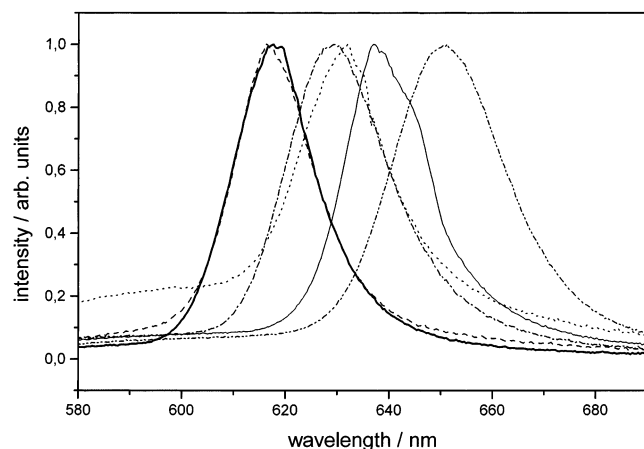
Figure 7. ASE spectra of DCM (2 wt %) in PST-*co*-VBT: unirradiated film (—); UV-irradiated film (- - -); UV-irradiated films after postexposure modification with ammonia (···), propylamine (-··-··-), ethylenediamine (-···-···-), and hydrazine (—).
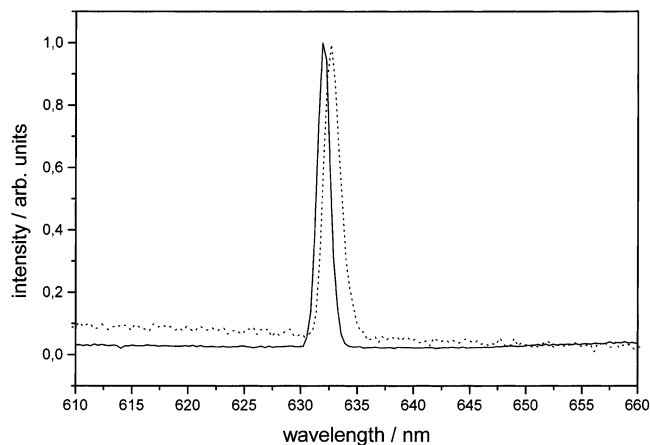

Figure 8. Laser action of DCM (2 wt %) in PST-*co*-VBT: (—) index grating in PST-*co*-VBT obtained by interference illumination; (···) relief grating in PST-*co*-VBT after modification of the patterned film with propylamine.

spectra for the different samples. In all cases, the full width at half-maximum (fwhm) of the DCM emission was narrowed to 18 and 25 nm. The peak wavelength λ_{ASE} of the spectral line narrowing in both the nonirradiated and the UV-irradiated samples was 618 nm. The postexposure modification of the illuminated films with amines caused a strong shift of the ASE maximum (ethylenediamine, $\lambda_{ASE} = 650$ nm; hydrazine, $\lambda_{ASE} = 637$ nm; ammonia, $\lambda_{ASE} = 631$ nm; propylamine, $\lambda_{ASE} = 629$ nm). These shifts qualitatively match the observed peak shifts in the absorption and emission spectra of DCM, although the shifts are much larger in the case of ASE. It is well-known that ASE occurs preferentially at the wavelength that experiences the maximum net gain (i.e., at which stimulated emission overcomes the absorption and scattering losses by the greatest margin). The large spectral shifts in the line-narrowed spectra therefore imply that the postexposure modifications to the films cause increased losses at wavelengths in the tail of the DCM absorption spectrum, pushing the optimum gain to longer wavelengths.

The threshold for the spectral line narrowing was in the range between 120 and 310 nJ cm^{-2} per pulse with the lowest threshold observed for the nonirradiated sample. The increase in threshold for the processed samples can be explained by their corresponding drop in PLQY. For example, the sample modified with propylamine shows the second highest PLQY and also the second lowest ASE threshold. When the pump energy was further increased beyond the threshold for ASE, all samples emitted a collection of sharp peaks that are indicative of random lasing in the film. The feedback is probably provided by random scattering points in the film.

DFB Lasing in Photopatterned Films of PST-co-VBT. Generally, in DFB lasers the observed wavelength (λ_{laser}) of emission is determined by a phase matching condition between forward and backward modes as

$$\lambda_{laser} = 2\Lambda n_{eff} m^{-1} \qquad (6)$$

where Λ is the grating period, n_{eff} is the effective refractive index of the structure, and m is the order of

feedback. The reactivity of PST-*co*-VBT under 266 nm laser radiation was utilized to generate a periodical modulation of n_{eff} along the laser cavity. Films of PST-*co*-VBT containing 2 wt % of DCM were prepared on CaF$_2$ plates. The films had a thickness $d_f \sim 400$ nm. In a series of experiments, refractive index gratings were inscribed by interference illumination using the fourth harmonic of a Nd:YAG laser ($\lambda = 266$ nm) at a pulse energy of 4.0 mJ cm^{-2} (no laser ablation effects, as verified by AFM; cf. Figure 3). The angle θ of the incident writing beam was adjusted to give a grating period $\Lambda \sim 440$ nm. Upon pumping with a Nd:YAG laser ($\lambda_{pump} = 532$ nm), these samples displayed DFB lasing with $\lambda_{laser} = 632$ nm.

By exposure of the index gratings to gaseous propylamine, a regular relief pattern developed, as described in the previous section. AFM analysis evidenced a grating period $\Lambda = 440$ nm. The DFB laser emission wavelength remained at $\lambda_{laser} = 632$ nm after the postexposure treatment. In both cases the fwhm of laser emission was ca. 1 nm. The DFB laser lines recorded are displayed in Figure 8.

In another series of experiments, interference illumination with pulse energies of 7.0 mJ cm^{-2} was used to inscribe surface relief gratings in PST-*co*-VBT containing 2 wt % of DCM. Under these irradiation conditions, the relief grating was produced by laser ablation. The initial film thickness d_f was 380 nm, and the grating period Λ of the inscribed reliefs was 410 nm, as determined by AFM. One sample was investigated directly after interference patterning, the other samples were patterned and subsequently modified with gaseous amines. All specimens exhibited laser emission upon excitation with $\lambda_{pump} = 532$ nm. The fwhm of the emission was about 1 nm, which is the resolution of the CCD spectrometer used.

The laser emission wavelength λ_{laser} of the TE modes shifted slightly, depending on the amine compound used in the postexposure treatment of the samples. Prior to modification with amines, the emission line was found at $\lambda_{laser} = 630.8$ nm. Modification with gaseous amines caused a shift to longer wavelengths (λ_{laser} between 633.0 and 635.5 nm; see Table 1). The shift of the laser lines indicates a slight increase of the overall value of n_{eff} during the gas-phase reaction of the polymer film
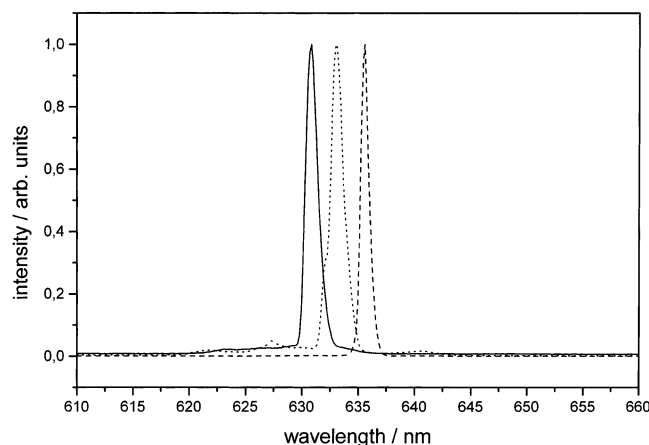
Figure 9. Laser action of DCM (2 wt %) in PST-*co*-VBT: relief grating in PST-*co*-VBT obtained by laser ablation during interference illumination (—); modified relief gratings in PST-*co*-VBT obtained by postexposure reaction with propylamine (···) and hydrazine (- - -).

with the amines. Exemplary laser lines obtained with these DFB structures are shown in Figure 9.

In all cases the order m of feedback was 2 and the laser light was coupled out perpendicular to the surface of the samples by first-order diffraction. With the polarization of the pump beam parallel to the grating, also the laser emission was fully polarized (ratio TE: TM > 250:1). The pumping threshold I_{th} for lasing was found at a pulse energy of $\sim$ 250 nJ cm^{-2}. With the experimental data on λ_{laser} and Λ for these DFB gratings, a value of $n_{eff} \sim 1.54$ was calculated for a propagating TE mode. This value of n_{eff} closely matched the theoretical prediction given by eq 3.

Due to the reduction of PLQY of DCM in PST-*co*-VBT matrix during UV processing, gain modulation will also play a role in the DFB lasing observed. Nevertheless, we assume that optical feedback is mainly provided by the formation of index and relief gratings in PST-*co*-VBT. The laser mode outputs for various polarization and pump conditions will be discussed in more detail in a forthcoming contribution.[20]

Conclusions

It has been shown that both index and relief gratings with periods Λ < 1 μm can be produced in (co)polymers

of 4-vinylbenzyl thiocyanate using interference illumination with λ = 266 nm. At lower energies of the writing beam, pure refractive index gratings are generated via a photoisomerization SCN $\rightarrow$ NCS.

These index gratings can be transformed into surface relief gratings by a postexposure modification with gaseous amines (generation of derivatives of thiourea). At higher energies of the writing beam, relief gratings are directly inscribed by laser ablation (30 nm modulation depth). Also these gratings retain their reactivity toward gaseous amines and the illuminated zones can be modified selectively. Consequently, photochemically inscribed patterns in PST-*co*-VBT may be regarded as "reactive gratings".

Furthermore, it has been demonstrated that PST-*co*-VBT can be used as a matrix polymer to set up organic DFB lasers. Using DCM as a laser dye, DFB laser emission was observed from patterned PST-*co*-VBT. Both with index and relief gratings DFB laser emission was recorded. Generally, the postexposure modification of the gratings with amines caused a shift of both ASE and DFB laser emission wavelengths.

In contrast to other materials capable of recording an optical grating, PST-*co*-VBT allows a selective functionalization of the illuminated zones via coupling reactions to the NCS moieties generated. Such "reactive gratings" may be useful for the coupling of dyes, conjugated oligomers, biomolecules, and other molecules. Under selected conditions, a doubling of the frequency of the grating can be achieved by a postexposure treatment with gaseous amines. In addition, the shift of the emission wavelength upon treatment with amines may be exploited for sensor elements. Besides DFB laser applications, materials such as PST-*co*-VBT may find use in the field of integrated optics. Work on the laser activity of conjugated polymers in PST-*co*-VBT matrix as well as on conjugated polymers functionalized with UV-sensitive CH$_2$SCN units is in progress.

(20) Kranzelbinder, G.; Toussaere, E.; Zyss, J.; Kavc, T.; Langer, G.; Kern, W. *Appl. Phys. Lett.* In press.