

Optical Storage in Pentaalkynylbenzene Derivatives. Strong Gain Effect by Recrystallization Processes

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Optical storage experiments were performed on pentaalkynylbenzene derivatives carrying functional azobenzene groups as well as on equimolar mixtures with the acceptor TNF. These materials are partially crystalline yet can be prepared in an amorphous state. The light-induced optical responses, i.e., the diffraction efficiency of an induced grating, was rather weak for amorphous films as prepared by spin-coating. Strong amplification effects occurred, however, on a subsequent annealing step performed with the writing light switched off. The diffraction efficiency was found to increase by more than a factor of 500. This strong gain effect is controlled by the selective growth of crystals in the nonirradiated areas.

I. Introduction

Side-chain liquid crystalline polymers containing azobenzene derivatives as mesogenic groups have been used with considerable success as materials for digital and holographic storage as well as for the manufacturing of holographic optical components. The storage effect is based on modifications of the local refractive index via polarized light.^{1–10} This effect arises from reorientational motions of the azobenzene group induced by the light.

The role of the liquid crystalline environment has turned out to be two-fold:^{11–15} it provides a stabilization of the induced orientational order even at temperatures

above the glass-transition temperature, and it results in a strong amplification of the optical response. This has become obvious from the observation of a gain effect for materials which could be frozen-in into an amorphous state and became liquid crystalline only on annealing at elevated temperatures.^{16–20} The storage performed in the amorphous state gave rise to weak optical effects. These became strongly enhanced on annealing even in the absence of the writing light.

This effect is of potential interest because optical storage requires transparent films, and these can be achieved for liquid crystalline materials only if one is able to induce a monodomain throughout the whole storage medium. This meets with increasing problems as the film area becomes large. On the other hand, the preparation of large areas of transparent storage films is an easy task if one uses amorphous materials. Quenching liquid crystalline materials into the amorphous state and annealing them after exposure to light thus constitutes a very efficient approach.

We have previously shown that this approach can be exploited not only for nematic side-chain polymers but also for low-molar-mass smectic materials and columnar discotic materials.^{18–20} We furthermore demonstrated that the gain effect manifests itself in many instances, not only in the bulk material. Surface relief gratings, which tend to accompany isomerization processes and the reorientational motions induced by light, are also subjected to gain effects. We found that the amplitude of the surface relief gratings becomes greatly enhanced on annealing.^{18–20}

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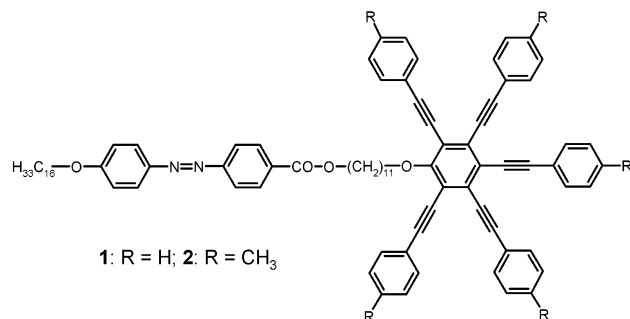
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Scheme 1. Chemical Structure of the Investigated Materials

This paper explores a further aspect of the optical gain effect in materials containing azobenzene derivatives. It seemed to us that materials which can be frozen-in into an amorphous state, yet which can crystallize on annealing, might also give rise to amplification effects. The assumption is that both the presence of a higher concentration of cis-molecules, as well as the orientational order induced by polarized light, may affect the growth of crystals on annealing at elevated temperatures.

The choice of the material was guided by the consideration that the tendency of the material to crystallize should be weak. Otherwise, we would induce the growth of large crystals thereby reducing the spatial resolution. In addition, we wanted the materials to display crystallization properties which are already sensitive to small disturbances of the order within the amorphous state. A polymer would, in general, be a good choice in this respect, but polymer synthesis is a much more complex task than preparation of low-molar-mass materials. With polymers one might also easily encounter the problem that the crystallization is totally suppressed.

The concept was thus to start from materials having a tendency to display a liquid crystalline phase rather than a crystalline one and to make small changes to push the system slightly toward crystallization. On the basis of our previous investigations on discotic pentaalkynylbenzene derivatives, we used these materials as the starting point. A liquid crystalline columnar state was observed for a combination of the disclike donor connected, via the rodlike azobenzene group, to an acceptor.²¹ In the approach reported in this paper, we just combined the rodlike azobenzene group and the pentaalkynylbenzene group, thus omitting the acceptor group which tends to induce a columnar packing (Scheme 1).

Different peripheral substituents were attached to the pentayne subunit in order to influence the crystallization tendency and the transition temperatures, whereas all further molecular parameters were kept constant. We investigated the two pentaalkyne derivatives **1** and **2** in their pure state, as well as equimolar mixtures of the two systems with the acceptor 2,4,7-trinitrofluorene-9-one TNF.

II. Experimental Section

II.1 Materials. To prepare the azobenzene-modified pentakis(phenylethynyl)benzene compounds **1** and **2**, 4-(4-hexa-

decyloxyphenylazo) benzoic acid was converted into the corresponding acid chloride by reaction with oxalyl chloride followed by esterification with the respective hydroxy-substituted radial pentaalkynes.

The hydroxy-terminated pentakis(phenylethynyl)benzene derivatives have been described previously.^{22,23} The 4-(4-hexadecyloxyphenylazo) benzoic acid used as starting material was obtained by etherification of 4-(4-hydroxyphenylazo) benzoic acid²⁴ with *n*-hexadecyl bromide using ethanol as solvent and potassium hydroxide as the base.

Pentakis(phenylethynyl)benzene Derivatives 1 and 2. General Procedure. A mixture of 600 mg (1.30 mmol) of 4-(4-hexadecyloxyphenylazo) benzoic acid and 4.5 mL of oxalyl chloride was heated under reflux with stirring for 3 h. After the mixture was cooled to room temperature, the excess of oxalyl chloride was removed under reduced pressure. Under a nitrogen atmosphere a solution consisting of 1.30 mmol of the appropriate hydroxy-substituted pentaalkyne, 0.4 mL of dry pyridine, 40 mg of 4-*N,N*-dimethylaminopyridine, and 10 mL of dry dichloromethane was added to the crude acid chloride. The reaction mixture was maintained under reflux with stirring for 18 h. The solution was concentrated to dryness in vacuum and the residual crude product was purified by flash chromatography using Kieselgel 60, 230–400 mesh (E. Merck, Darmstadt) using light petroleum/ethyl acetate 10:3 as eluent.

11-[Pentakis(phenylethynyl)phenoxy]-undecyl 4-(4-hexadecyloxyphenylazo) Benzoate, 1. Yield: 54%, C₈₆H₈₈N₂O₄ (Mw 1213.7). IR (KBr): $\nu = 2207, 1715, 1600, 1467, 1252 \text{ cm}^{-1}$. ¹H NMR (CDCl₃): δ (ppm) = 8.15 (d, 2H, azobenzene, *J* = 8.2 Hz), 7.91 (dd, 4H, azobenzene, *J* = 8.9 Hz), 7.61 (m, 10 H, phenyl), 7.37 (m, 15H, phenyl), 6.99 (d, 2H, azobenzene, *J* = 8.6 Hz), 4.39 (t, 2H, CH₂-O-CO, *J* = 6.1 Hz), 4.33 (t, 2H, CH₂-O-phenyl, *J* = 6.6 Hz), 4.03 (t, 2H, CH₂-O-phenyl, *J* = 6.2 Hz), 2.04–1.26 (m, 46H, CH₂), 0.88 (t, 3H, CH₃, *J* = 6.8 Hz).

11-[Pentakis(4-methylphenylethynyl)phenoxy]-undecyl 4-(4-hexadecyloxyphenylazo) Benzoate, 2. Yield: 36%, C₉₁H₉₈N₂O₄ (Mw 1283.8). IR (KBr): $\nu = 2202, 1715, 1600, 1467, 1250 \text{ cm}^{-1}$. ¹H NMR (CDCl₃): δ (ppm) = 8.15 (d, 2H, azobenzene, *J* = 8.5 Hz), 7.91 (dd, 4H, azobenzene, *J* = 9.0 Hz), 7.50 (m, 10 H, phenyl), 7.16 (m, 10H, phenyl), 6.99 (d, 2H, azobenzene, *J* = 8.9 Hz), 4.36 (t, 2H, CH₂-O-CO, *J* = 6.5 Hz), 4.33 (t, 2H, CH₂-O-phenyl, *J* = 6.9 Hz), 4.03 (t, 2H, CH₂-O-phenyl, *J* = 6.5 Hz), 2.39 (s, 15H, CH₃), 2.04–1.26 (m, 46H, CH₂), 0.90 (t, 3H, CH₃, *J* = 7.0 Hz).

II.2 Characterization Methods. The crystallization and melting behavior was studied calorimetrically with a temperature-modulated differential scanning calorimetry (Mettler Toledo ADSC 821^e). For the X-ray analysis we employed a Siemens D 5000 goniometer equipped with a heating cell. The grating experiments were performed with a setup described in detail previously.^{10,15} Intensity gratings with a grating constant of $\lambda = 5.1 \mu\text{m}$ were obtained by interference of two coherent, s-polarized laser beams in the plane of the sample. We used a cw argon ion laser operating at 488 nm and laser intensities in the range of 30–1600 mW/cm² for writing gratings. In this range we found no dependence of the holographic growth characteristics on the intensity.

The resulting refractive index modulation

$$n(x) = n_0 + n_1 \cdot \cos\left(\frac{2\pi x}{\Lambda}\right) \quad (1)$$

was read out via the diffraction of a HeNe laser beam at 633 nm. The experimentally obtained diffraction efficiency is proportional to the square sine of the induced refractive index change n_1 , which in turn is related to the induced orientational order of the optical axes of the azo dyes.

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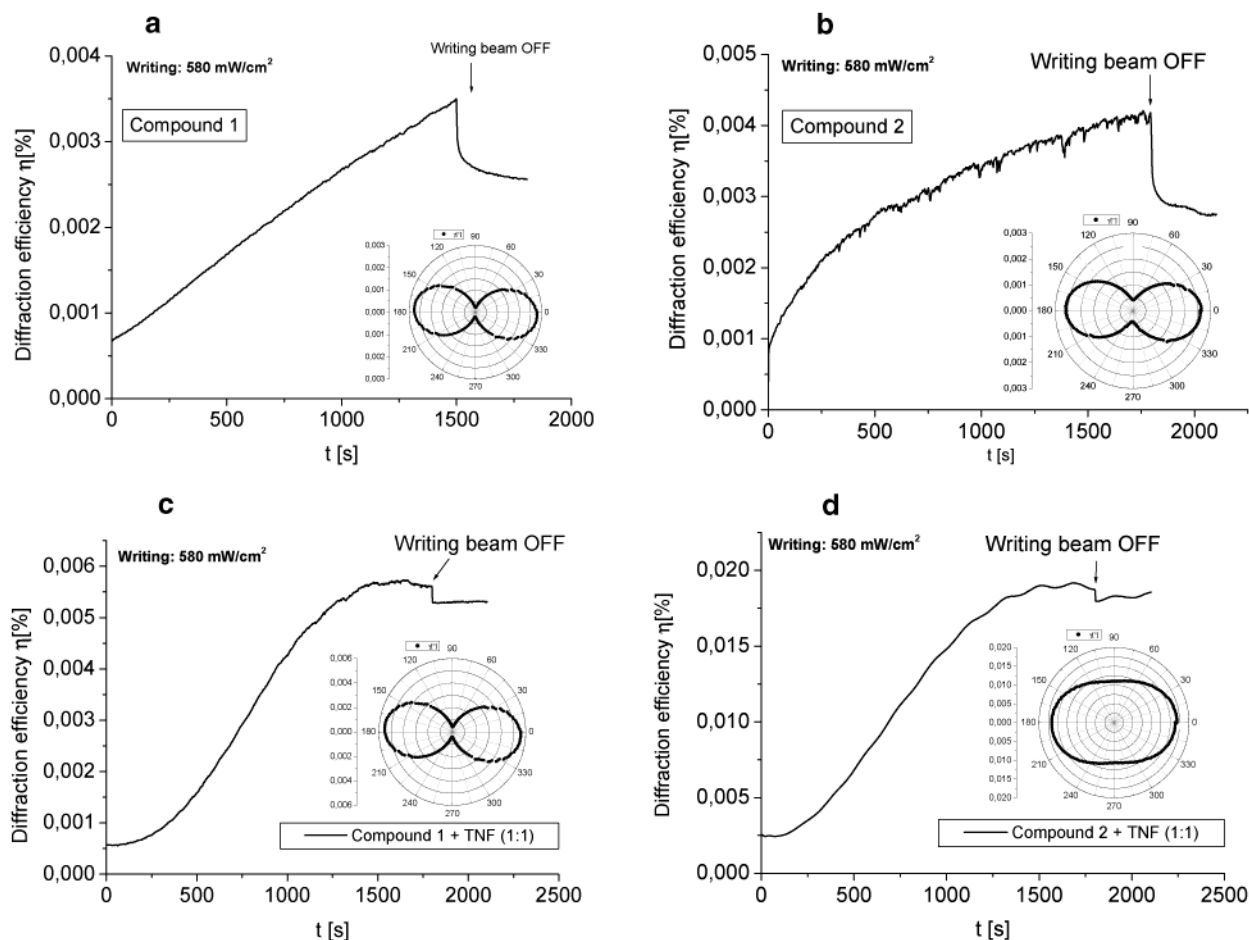


Figure 1. (a and b) Holographic growth curve of compounds **1** and **2** (the nonzero diffraction efficiency at $t = 0$ results from the background noise originating from the optical setup). (c and d) Holographic growth curve of the doped compounds with TNF.

III. Results and Discussion

III.1 Grating Experiments. The grating experiments were performed on thin films spin-coated from solutions. The high-quality films had a thickness on the order of 500–600 nm. They turned out to be transparent and homogeneous in thickness. Figure 1a and b display the diffraction efficiency as a function of the irradiation time for the two undoped samples. The growth curve is nearly linear for compound **1** and slightly curved for compound **2**. The linear increase is usually attributed to changes in the optical properties due to the isomerization and the curved part to the regime where the reorientation takes over. The switching off of the writing beam gives rise to a significant relaxation of the diffraction efficiency originating from thermal *cis*–*trans*-back relaxations. The polar diagram of the diffraction efficiency is displayed as an insert. It has a shape which corresponds roughly to the one reported by us for other liquid crystalline materials.^{14,15,18}

The experimental results obtained for the doped systems (Figure 1c and d) deviate strongly from the ones reported above for the undoped substances. One difference is that the diffraction efficiency growth curves are no longer linear at the beginning but rather sigmoidal. A second difference is that the backrelaxation after the switching off of the writing light is much lower than that reported above for the undoped materials. A third difference is the larger magnitude of the diffraction efficiencies of the doped samples as compared to the

undoped ones at constant writing energy. This is particularly evident for the sample compound **2**. Finally, the polar diagram of the diffraction efficiency of the samples of compound **2** is quite different from the ones observed for all other cases. The diffraction efficiency is close to being isotropic for this particular case.

We are currently unable to account for the strong modification of the diffraction efficiency growth curves due to doping. Doping seems to affect the molecular processes, giving rise to the optical storage i.e., the isomerization and the light-induced reorientation, greatly. One factor certainly is an enhanced thermal back-relaxation taking place during writing. Yet, this paper will focus in the following on the gain effect.

The gain effect is documented for the undoped and doped system of compound **1** in Figure 2 a,b. Plotted is the diffraction efficiency as a function of the temperature to which the samples are heated after the writing process and the switching off of the light source. Observed in all cases is a very strong increase of the diffraction efficiency within a very narrow temperature interval, i.e., a strong gain effect takes place. The decrease of the diffraction efficiency at still higher temperatures is also quite steep.

The gain effect is much stronger than that usually observed for liquid crystalline materials. It amounts to up to more than 2 orders of magnitude as compared to 1 order of magnitude typically encountered in liquid crystalline systems. It thus seems that materials which

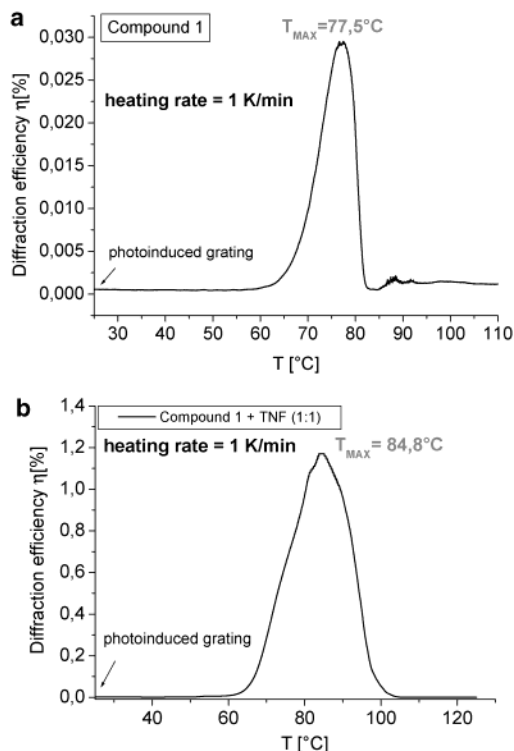


Figure 2. (a and b) Thermal development for the undoped and doped, respectively, photoinduced grating of compound **1**.

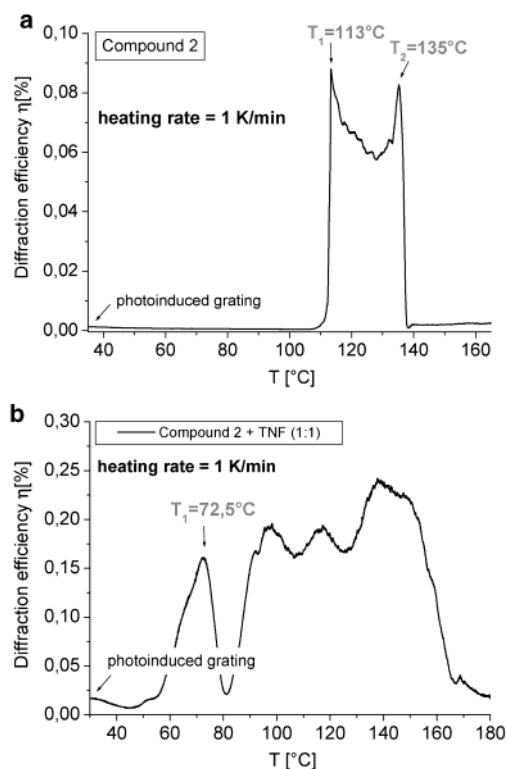


Figure 3. (a and b) Thermal development for the undoped and doped, respectively, photoinduced grating of compound **2**.

have a tendency to crystallize are a good choice for enhancing gain effects. We will discuss the particular temperature range in which the gain effect takes place in more detail below.

Next we will discuss the undoped and doped systems of compound **2** as shown in Figure 3 a,b. Again strong gain effects take place, yet the temperature dependence

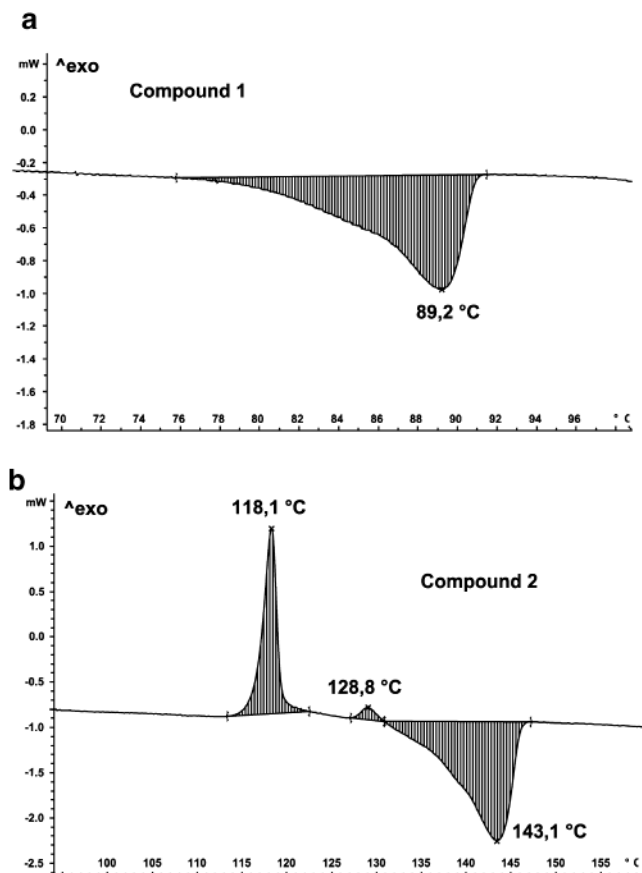


Figure 4. (a and b) Conventional DSC results for the two compounds **1** and **2**, respectively.

of the diffraction efficiency is much more complex than the one found for compound **1**. Several peaks are observed as a function of the temperature, indicative of competing processes. The gain effect amounts again to up to 2 orders of magnitude as in the case of the compound **1**.

Growth of the diffraction efficiency has to be correlated with the onset of some kind of structure-formation processes within the materials, whereas the decay probably arises from a destruction of the ordered regions, i.e., from a melting process. Optical microscopy, X-ray scattering, and calorimetric studies were performed to learn more about the processes controlling the gain effect.

III.2 Calorimetric Investigations. To determine correlations between the gain behavior and structural transitions happening within the storage material, we performed calorimetric studies on samples quenched from the molten state. These studies revealed that quenched samples display recrystallization processes on heating and subsequently a melting process, as apparent from Figure 4.

The heating curve obtained for the compound **1**, as cooled from the melt, shows a broad endothermic peak at about 92 °C. Compound **2** displays on heating an distinctive exothermic peak at about 118 °C and a weak one at about 129 °C. The melting range sets in at about 131 °C with a very broad melting peak at about 143 °C. These results indicate that the gain effect takes place within the temperature range where DSC reveals structural changes. In fact, the complex gain effect curves of compound **2** are to a certain extent reflected

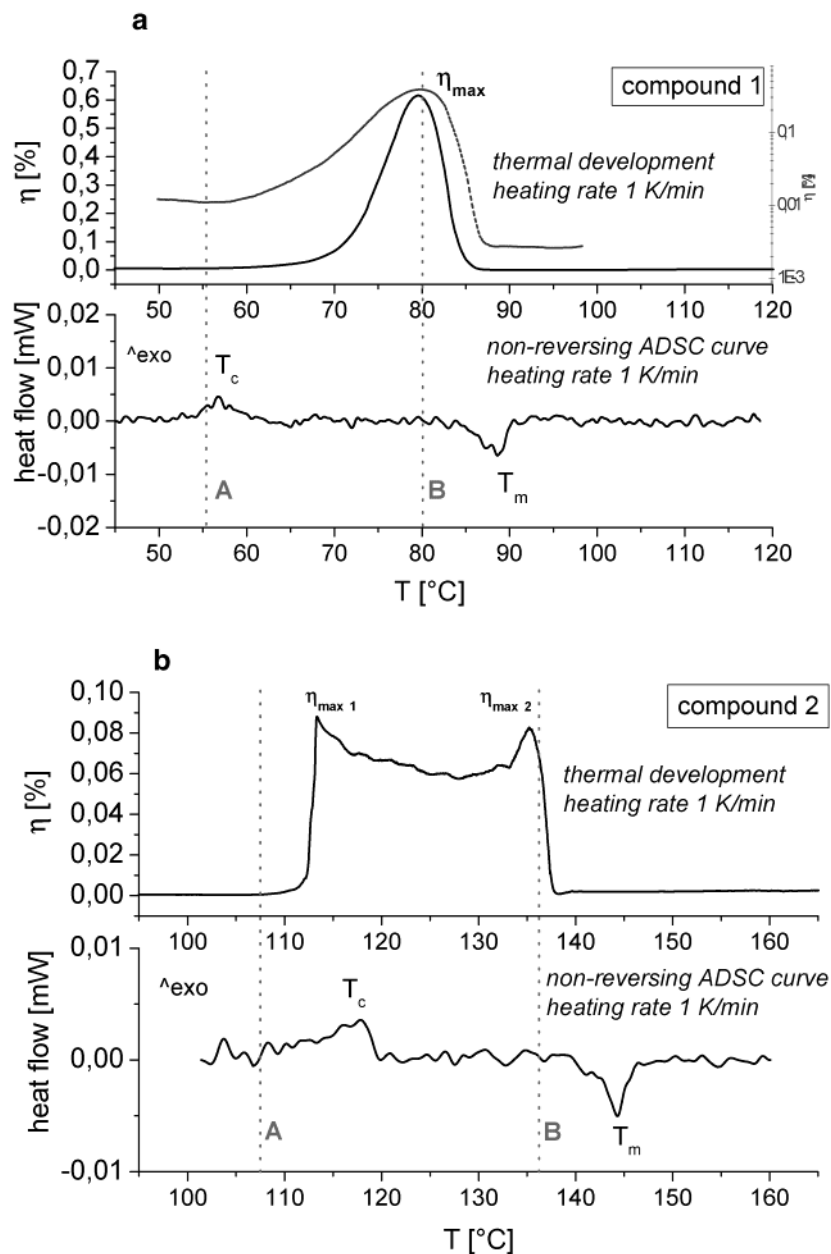


Figure 5. (a and b) Gain process in comparison with the thermal behavior (dashed line: semilogarithmic scale).

in more complex DSC-curves. A second rather weak exothermic peak is found at about 126 °C.

The problem is, however, that thin films on substrates as used for the storage experiments may possess different thermal histories and may also display structure formation kinetics which differ from those of bulk samples. Conventional DSC techniques are not able to resolve thermal processes in thin films on solid substrates where the weight of the film amounts to about 0.1 mg or even less.

We therefore applied the temperature-modulated differential scanning calorimetry (TMDSC) which allows a thermal characterization for such small amounts of material as thin spin-coated films (0.05–0.15 mg) located on glass substrates. TMDSC differs from conventional differential scanning calorimetry by the fact that the linear heating is superimposed with a periodic temperature oscillation.^{25–28}

The analysis involves separation of the total heat flow into the reversing and nonreversing components. The quenched samples were investigated with a heating rate of about 1 K/min, an amplitude of 2 K/min, and a period of 1 min.

Figure 5 displays the results of these calorimetric investigations simultaneously with the results obtained from gain effect studies.

It is obvious that a very good correlation between the beginning of the crystallization process exists on one hand and the increase of the diffraction efficiency on the other. The nonreversing heat flow of compound 1 shows the beginning of the exothermic crystallization process at a temperature of 55 °C (107 °C for compound 2) and the endothermic melting process starting at a

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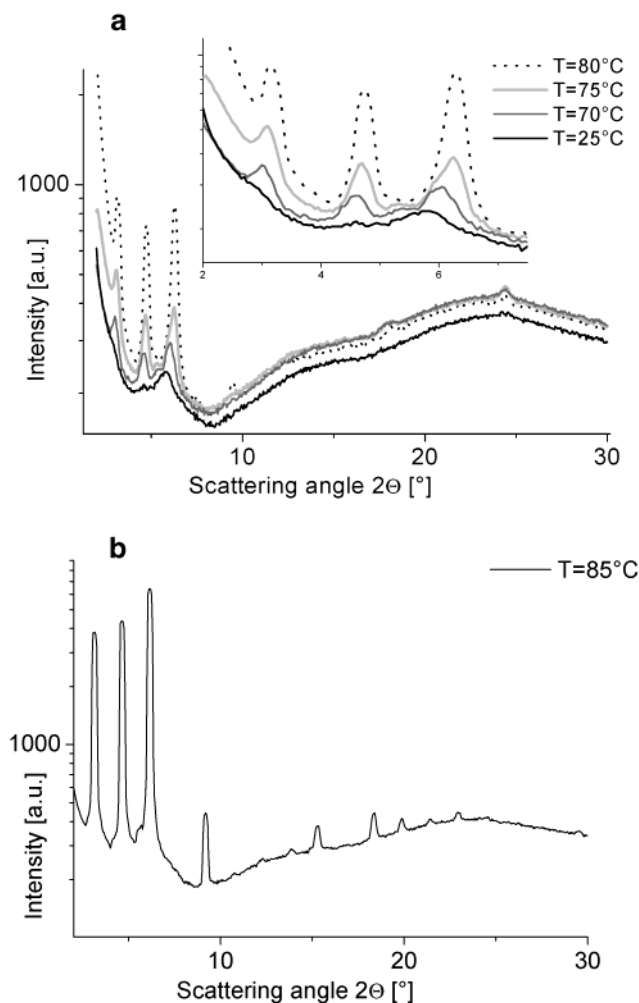


Figure 6. (a and b) Wide-angle X-ray diffractogram obtained for different temperatures of compound **1**.

temperature of 82 °C (136 °C for compound **2**). We performed X-ray studies to analyze in more detail the character of the structure formation processes taking place.

III. 3 Results of X-ray Studies. The X-ray diagram of the spin-coated films is characterized by a broad halo in the wide-angle range and a small broad reflection in the small-angle regime as apparent from Figure 6a for compound **1**. To correlate gain effect and structure formation we subjected the films to the same thermal history that we used to analyze the gain effect.

The observation is that no significant changes take place as long as the temperature was kept below about 65 °C. A further increase of the temperatures results in the occurrence of several sharp reflections in the small angle range as displayed in Figure 6a. The height of the peaks increases with rising temperature as long as the temperature is limited to temperatures below about 80 °C. Note that the intensity is plotted on a logarithmic scale in the diagrams.

The corresponding variation of the X-ray diagram in the wide-angle range is surprisingly small. Only a few, but weak, reflections are observed even for well-annealed samples. Films that were annealed for several hours at a temperature in the vicinity of the melting range of about 85 °C show a scattering diagram with such weak additional reflections as displayed in Figure 6b.

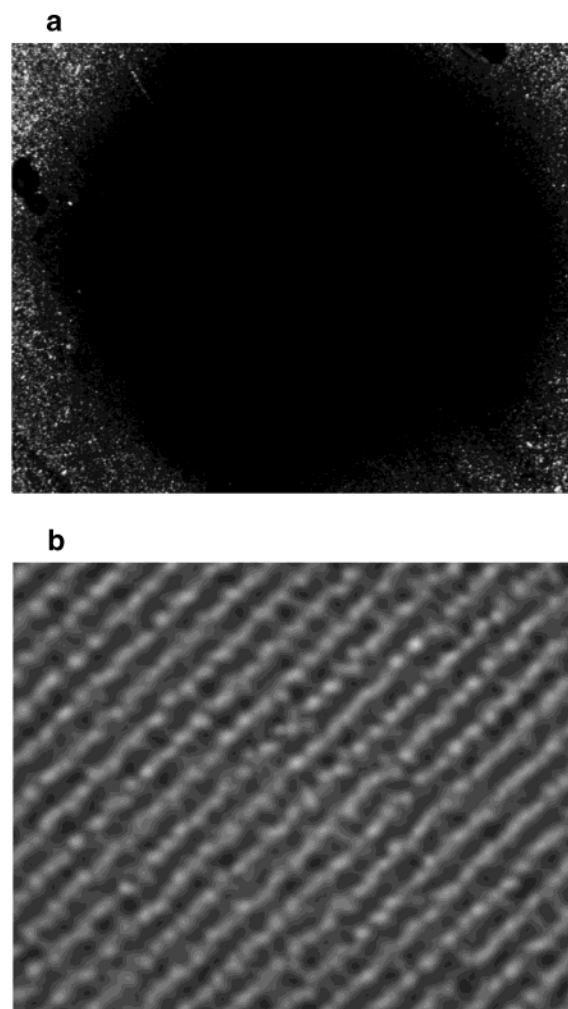


Figure 7. (a) Irradiated and annealed film of compound **2** considered with crossed polarizers. (b) Selective growth of crystals along the grating normal in the unirradiated regions.

The general conclusion is that a temperature increase and prolonged annealing leads to crystallization effects. The reflections observed in the small-angle regime are strong, yet the X-ray diagram displays a low number of weak reflections in the wide-angle range. This makes a structural assignment close to impossible.

Very similar results were obtained for the doped systems. It is for this reason that we will not discuss these results in detail. In any case, the X-ray results did not give any indication why the gain processes exhibit significant differences for doped and undoped samples.

These results and those obtained via calorimetric studies show that crystals grow if the films are subjected to thermal treatments identical to the ones used to study the gain effect. In the following section we will consider the results of microscopical studies, which should allow us to understand in more detail the role of crystals with respect to the optical diffraction.

III.4 Optical Microscopy. Two types of experiments were performed. One consisted of illuminating a large area of the film with constant intensity for a given time. The films were subsequently heated-up to higher temperatures using the same heating rate as was used for the investigation of the gain effect. Optical microscopy revealed that crystals were nucleated and grew in those

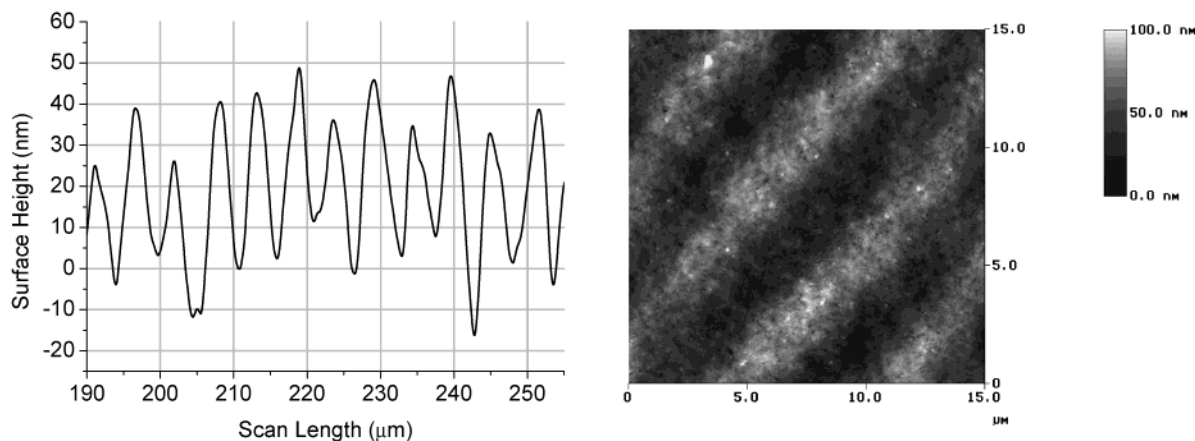


Figure 8. (a and b) Profile scan and AFM image, respectively, of the thermal-developed photoinduced grating of compound 1.

areas that were not subjected to irradiation. The final state is characterized by a dense population of crystals with diameters in the range of a few micrometers. On the other hand, no crystals were formed in the illuminated areas (Figure 7). It is thus apparent that the crystallization process is strongly suppressed in areas where isomerization processes have taken place.

To quantify this effect we have illuminated the films with a given intensity for different amounts of time. The finding is that the films have to be subjected to a threshold energy in order to suppress the crystallization. The films were irradiated well above the threshold energy with an irradiation on the order of 2250 mW/cm² for 10 min.

The second kind of experiments consisted of performing grating experiments and analyzing the morphology by optical microscopy. The microscopical analysis revealed a periodic variation of the number of small crystals varying from zero in the illuminated areas to high concentrations in the nonilluminated areas, as apparent from Figure 7b. The wavelength of this variation corresponds to the one detected in the grating studies. Therefore, it is obvious that the gain effect originates from crystallization processes.

III.5 Surface Topology. The crystallization gives rise to modulations of the surface. This is apparent for both the large area illumination experiments as well as from the grating experiments. Figure 8 a and b displays the surface grating as measured by a surface profiler and AFM. It seems that each individual crystal gives rise to a peak on the surface of the films, whereas a valley is observed for the immediate surrounding. Transport of material to the growing crystal obviously is the reason for the surface modulation.

IV. Conclusions

Illumination of the amorphous films with linearly polarized light leads to the onset of isomerization processes and consequently to reorientational processes. This is obvious from the polar diagram of the diffraction efficiency which agrees with previous reports on light-induced reorientational motions. In addition, polarizing

microscopical studies prove the induction of an orientational order — i.e., birefringence — via polarized light. These results are not unexpected.

The unexpected finding is that crystallization processes are suppressed due to the irradiation with light. It is well-known that an increased concentration of cis-isomers may induce a phase transition at constant temperature from an ordered to an amorphous state as shown for instance for liquid crystalline phases. Yet in those cases the destruction of order was shortlived; the order returned again due to the thermal back relaxation of the cis to the trans state. It seems that this does not happen for the thermal conditions characteristic of the gain effect. We thus have to assume that the cis-isomers are stable for a prolonged time even at elevated temperatures. Unfortunately, we are not able to monitor the cis concentration spectroscopically because the corresponding absorption band is superimposed by the absorption band from the group. We know in any case that the irradiation does not lead to irreversible changes of the material. After heating to temperatures well above 100 °C and after subsequent cooling to room temperature we observe crystallization processes in the once-illuminated areas. The previous history can thus be completely erased.

The storage properties and the optical properties of the gratings are rather complex. First, reorientational processes take place during storage with polarized light, as apparent from the polar diagram of diffraction efficiencies. Second, the crystals that cause the gain effect will give rise to scattering effects. The orientational order is not erased during this process, as apparent from the polar diagram. Finally, the growth of crystals gives rise to a specific surface pattern to periodic variations of the film thickness.

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