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Dielectric and Photoorientation Studies in Semicrystalline Melamine Monomers and Amorphous Melamine Networks Containing Azobenzene Chromophores

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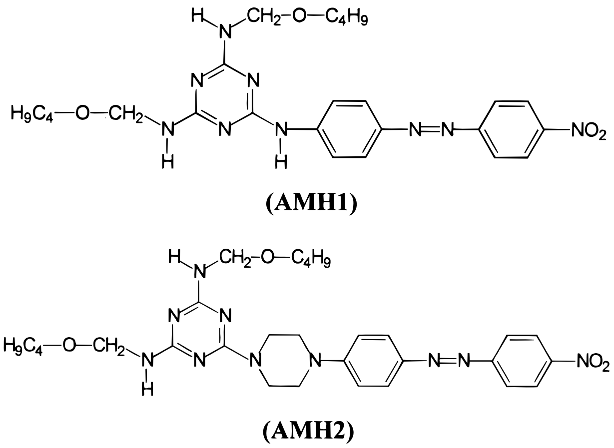
ABSTRACT: We demonstrate optical storage by means of trans−cis isomerization within melamine monomers as well as within the corresponding cross-linked melamine resins using holographic grating experiments. The melamine monomer is chemically linked with a photoaddressable azobenzene group. By thermal treatment the semicrystalline monomers can be converted into the amorphous cross-linked resin. Both the monomer material and the cross-linked resins display a photoinduced trans−cis isomerization of the azo groups, a stable photoorientation under irradiation with linear polarized light, and a stable storage of holographic gratings. The photokinetics in the different environments are found to be similiar but somewhat faster for the amorphous resins.

1. Introduction

Linearly polarized light is known to induce a reorientation of azobenzene groups in the glassy state of amorphous[1,2] and liquid-crystalline[3] polymers. After an optical irradiation for a sufficiently long time, the materials are characterized by a preferential chromophore orientation perpendicular to the polarization direction of the light (so-called orientational bleaching). Such polymers have been considered for applications in the area of digital and for holographic reversible optical storage.[4] Materials that are suitable for such applications are required to display a high thermal and mechanical stability as well as photostability. It is well-known that melamine resins are highly transparent and possess an unusually high thermal and mechanical stability.[5] However, the synthesis of melamine resins with groups carrying optical functions such as azobenzene chromophores poses a severe problem due to the strong intermolecular reactivity of the melamine−aldehyde precondensate. This leads to polycondensation before the chromophores can be linked to the system. Thus, there are only a few investigations on melamine resins as photoaddressable polymers.[6] The problem of combining the melamine with such chromophores can, however, be solved by attaching at first the chromophore to the triazine and by transferring the newly synthesized chromophore subsequently into a cross-linkable melamine−chromophore.[7,8] The azo dye containing melamine monomer can be processed easily into the polymeric resin by thermal treatment at temperatures above 120 °C.

The question as far as applications in the area of optical storage are concerned arises if a stable photoorientation can be induced in both the monomeric and the polymeric form of the material and if the cross-links have any influence on the photokinetics of the light-induced process. Dielectric relaxation spectroscopy turned out to be a useful method to get a detailed insight into the processes of molecular relaxation and chemical cross-linking and thus on the dependence of the molecular environment on the photoorientation process.

Scheme 1. Chemical Structures of the AMH1 and AMH2 Monomers



The molecular relaxation behavior of two azo dye containing melamine monomers and their corresponding resins is characterized in this contribution by means of dielectric relaxation spectroscopy. The photoorientation induced via irradiation with linearly polarized light is compared for the semicrystalline monomers and the amorphous resins by using holographic grating experiments and birefringence measurements.

2. Experimental Section

2.1. Sample Preparation. The chemical structure of the melamine monomers AMH1 and AMH2 with chemically attached side groups of Disperse Orange 3 and a modified Disperse Red 1 is shown in Scheme 1. Details of its chemical synthesis as well as details on the characterization of the corresponding resins are given in refs 7−10 and in the patent,[11] which describes a novel route for the synthesis of very stable chromophore resins for optical and optoelectronic applications.

For the optical investigations thin transparent films of the monomers with thicknesses in the range 0.2−0.7 μm were

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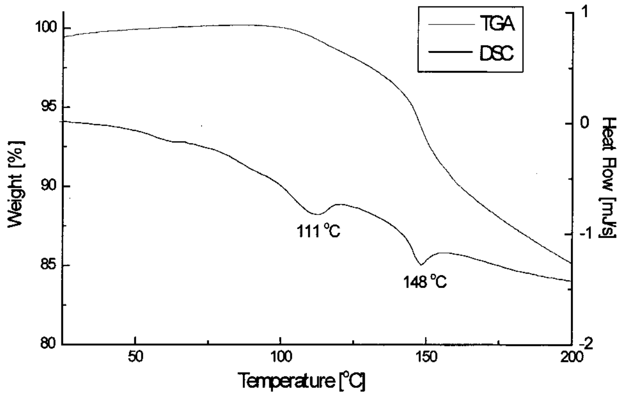
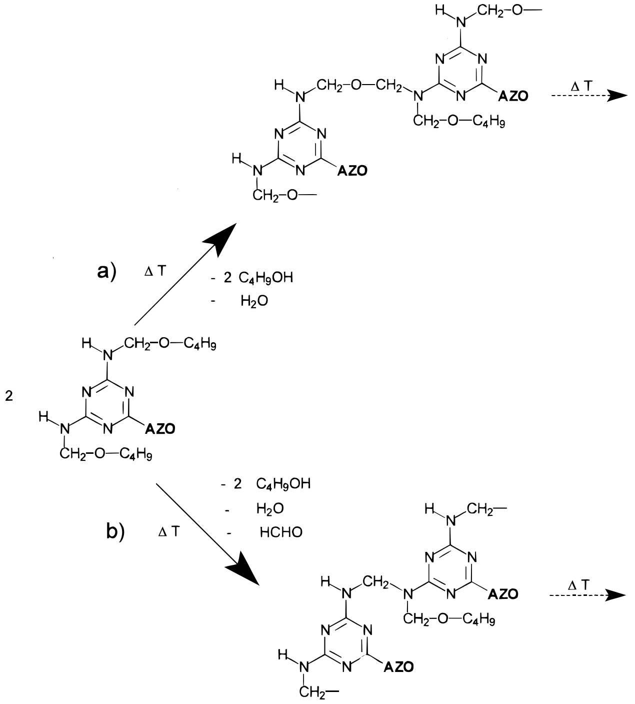


Figure 1. DSC and TGA diagram for the first heating of AMH1 (heating rate 6 K/min).

Scheme 2. Thermal Cross-Linking Reaction



prepared on glass substrates from a 10^{-3} M solution in ethanol by spin-coating. By heating the samples above 120 °C, the monomers can be cross-linked to yield transparent films of the corresponding melamine resins (Scheme 2).

Scheme 2 illustrates the two principal reaction paths of the cross-linkable melamine-chromophores: (a) the condensation of the triazines forming ether bridges ($-N-CH_2-O-CH_2-N-$); (b) the condensation of the triazines forming methylene bridges ($-N-CH_2-N-$). The two reaction types coexist; further thermal treatment leads to a rigid, insoluble, and infusible network, the resin.

X-ray investigations revealed that the monomers are organized in a semicrystalline structure with degrees of crystallinity of 29 and 44 wt % for AMH1 and AMH2, respectively, whereas the cross-linked samples are found to be completely amorphous.[7,12] By DSC a melting point is detected at 111 °C for the transition from the semicrystalline to the amorphous state, as shown in Figure 1 for the momomer AMH1. The additional endothermic peak at 148 °C results from the cross-linking process of the monomers. For AMH2 a melting point at 129 °C is detected.

2.2. Dielectric Relaxation Spectroscopy. For the dielectric investigations the thermally untreated solids (i.e., monomer) of AMH1 and AMH2 were placed between two stainless steel plates with a diameter of 10 mm and a thickness of 30−50 μm. We used a Hewlett-Packard impedance analyzer (HP 4284A), covering a frequency range from 100 Hz to 1 MHz, and a nitrogen gas heating system, with a precision of 0.1 K within a temperature range of 100−473 K. The experimental setup has been described in detail elsewhere.[13]

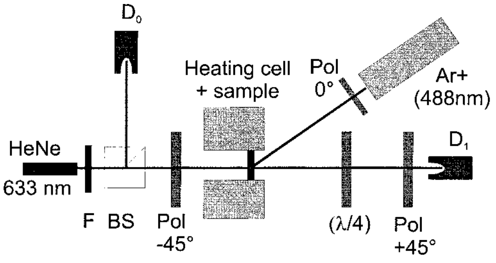


Figure 2. Setup for the measurement of photoinduced birefringence.

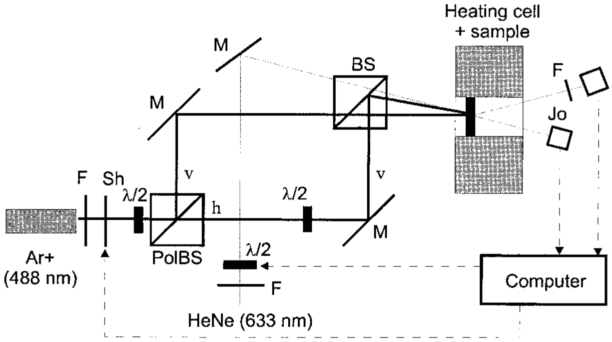


Figure 3. Setup of the holographic grating experiment. Pol = polarizer; F = filter; Sh = shutter; BS = beam splitter; PolBS = polarizing beam splitter; M = mirror; λ/2 = half wave plate; D_0, D_1 = detector; the letters v and h denote the vertical and horizontal polarization directions of the writing beam, respectively.

2.3. Measurement of the Photoinduced Birefringence. To study the kinetics of photoinduced reorientation of the azo groups, we determined the time dependence of photoinduced birefringence induced by irradiation with linearly polarized light of a CW argon ion laser operating at $\lambda = 488$ nm. The birefringence was measured by monitoring the intensity of a HeNe-probe beam ($\lambda = 633$ nm) which passes through crossed polarizers and the sample which is positioned in between polarizer and analyzer (Figure 2).

A photoinduced orientation of the rodlike chromophores in a preferred direction causes a phase shift to the probe beam and leads thus to a nonzero intensity of the probe beam after passing the crossed polarizers. The photoinduced birefringence Δn then can be calculated from the transmitted intensity of the HeNe beam according to the following expression:

$$\Delta n = \frac{\lambda_{\mathrm{HeNe}}}{\pi d}\left(\arcsin\sqrt{\frac{I}{K_{\mathrm{A}} I_0}}\right) \qquad (1)$$

2.4. Holographic Grating Experiments. Stable optical storage was demonstrated using a holographic grating experiment,[14] as schematically sketched in Figure 3. Intensity gratings with a grating constant of $\Lambda = 5.1$ μm were obtained by the interference of two coherent, linearly polarized laser beams in the plane of the sample. We used a CW argon ion laser operating at 488 nm. The resulting refractive index modulation

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

was read out via the diffraction of a HeNe laser beam at 633 nm. The experimentally obtained diffraction efficiency is

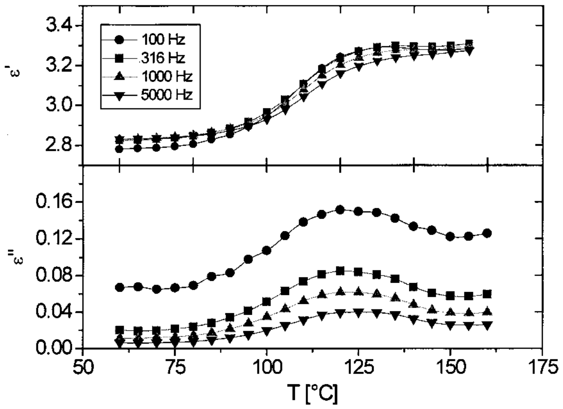


Figure 4. Dielectric loss as a function of temperature for the cross-linking process of AMH2.

directly related to the induced refractive-index modulation:

$$\eta = \frac{I}{I_0} \approx \sin^2\left(\frac{\pi n_1 d}{\lambda_{\mathrm{HeNe}} \cos \theta_{\mathrm{HeNe}}}\right) \tag{3}$$

which in turn is related to the induced orientational order of the optical axes of the azo dyes.

We employed a polarizing beam splitter and half-wave plates in order to achieve equal polarization directions for the writing and the reading beams, as well as two writing beams of equal intensity.

3. Results and Discussion

3.1. Dielectric Investigations. By measuring the complex dielectric constant $\epsilon^* = \epsilon' - \epsilon''$, the process of cross-linking of the melamine monomers was monitored during a first heating cycle. A strong relaxation curve that is only weakly frequency dependent is found for AMH1 as well as for AMH2 in the range 100−150 °C (Figure 4).

This relaxation is a consequence of the irreversible cross-linking process which takes place in this temperature range. It is absent if the thermally treated sample is heated for a second time. The thermally induced reaction results in the formation of butanol molecules (Scheme 2) which contribute to the dielectric relaxation process. Experiments concerning the solubility of the resins revealed that they are almost insoluble in butanol. It seems reasonable to conclude that the initially homogeneous material will thus change to a biphasic system during the cross-linking reaction, and we tentatively propose that a relaxation behavior similar to the one known to occur in heterogeneous systems (Maxwell−Sillars−Wagner relaxation[15]) takes place.

Of more relevance for the discussion of photoorientation is the question if there are additional local relaxations of molecular groups in the solid state of the sample and if these relaxation processes show any dependence on the presence of cross-links. Indeed, we observed two secondary relaxation processes at low temperatures which occur in the monomers as well as in the cross-linked resins nearly within the same temperature range. Figure 5 shows as an example the two relaxations for the monomer sample of AMH2.

The temperature dependence can be described by an Arrhenius law of the form

$$\ln(\nu_{\mathrm{max}}) = \ln(\nu_0) - \frac{E_{\mathrm{A}}}{RT} \tag{4}$$

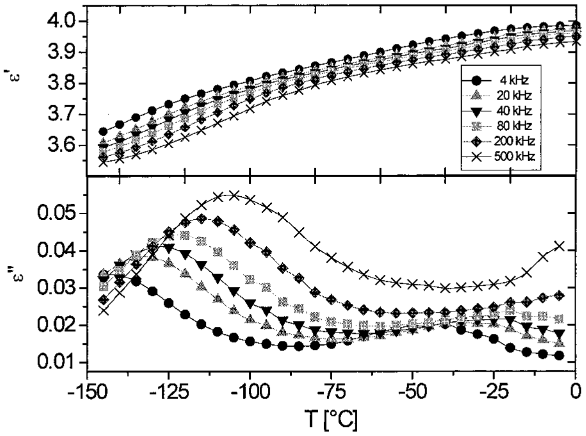


Figure 5. Secondary relaxation processes for the monomer sample of AMH2.

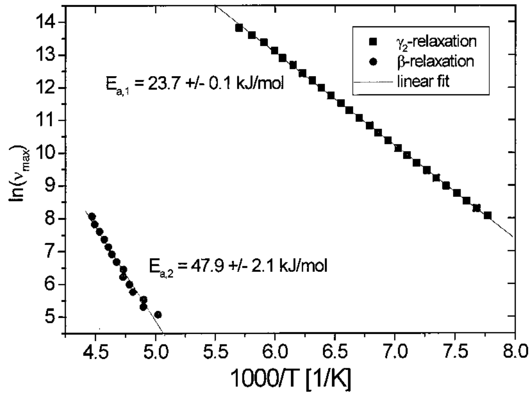


Figure 6. Arrhenius plots for the temperature dependence of the γ_2- and β-relaxation for the monomer of AMH2.

where ν_{max} is the frequency at the maximum of ϵ'' and E_{A} is the activation energy for the process. Figure 6 shows the temperature dependence of the two thermally activated secondary processes.

These activation energies are in the range 20−25 kJ/mol for the lower temperature process (−150 to −70 °C) and 45−50 kJ/mol for the higher temperature process (−60 to +20 °C) for both AMH1 and AMH2. The activation was found not to be influenced by the cross-linking of the monomers.

The process at higher temperatures can be attributed to a local movement of the azo group around its long molecular axis. For this process, which is known as β-relaxation, activation energies of 40−80 kJ/mol are typical,[15,16] and it is obvious that such a molecular motion of the azo group should not be very much affected by the cross-linking of the triazine rings.

The dielectric properties of the lower temperature process are typical for the so-called γ_2-relaxation of terminal alkoxy groups.[15,17] It can be attributed to a local motion of the terminal butoxy groups of the monomer samples. Thus, a complete cross-linking involving all relevant groups of the monomer should result in the disappearing of the γ_2-relaxation for the thermally produced resin, which is not observed for AMH1 and AMH2. However, by comparing the relaxation strength for the monomeric and cross-linked sample, a strong decrease of the signal is apparent for the cross-linked resin. We chose the amplitude of tan δ ($=\epsilon''/\epsilon'$) which is independent of the sample thickness for the comparison between the monomer and the cross-linked

Table 1. Results of the Birefringence Curve Fitting with a Biexponential Fit Function

	AMH1		AMH2	
fit parameter	monomer	resin	monomer	resin
τ_1 [s]	1.5 ± 0.09	0.8 ± 0.09	21.8 ± 0.4	14.2 ± 0.4
τ_2 [s]	8.8 ± 0.26	6.2 ± 0.2	126.6 ± 1.5	90.5 ± 1.7
A	$0.032 \pm 3\times 10^{-3}$	$0.033 \pm 3 \times 10^{-4}$	$0.10 \pm 4 \times 10^{-4}$	$0.10 \pm 7 \times 10^{-3}$

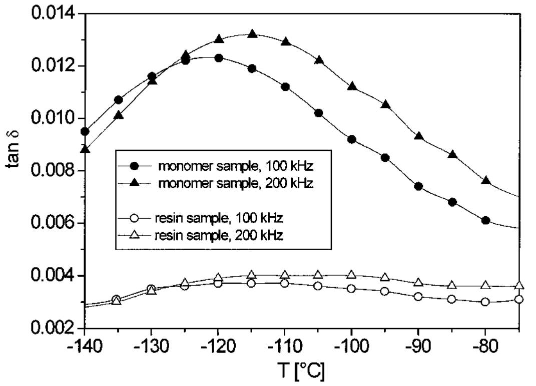


Figure 7. Comparison of the magnitude of the tan δ values for the monomer and cross-linked sample of AMH1.

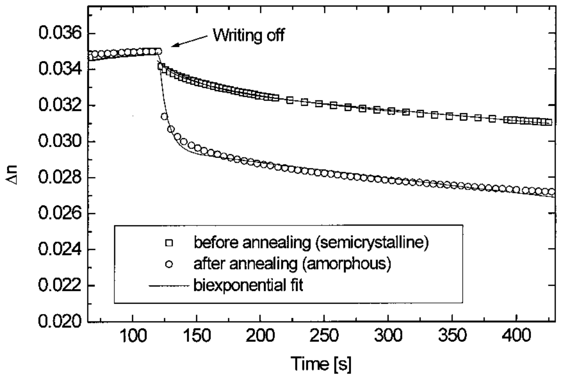


Figure 9. Relaxation of the photoinduced birefringence after writing for AMH1.

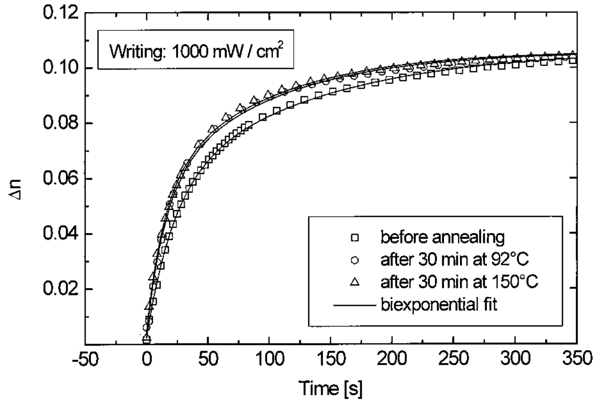


Figure 8. Time evolution of the photoinduced birefringence and biexponential fits for a sample of AMH2 after three different annealing conditions.

materials since the sample thickness can change slightly during the thermal treatment. Figure 7 shows the result for AMH1.

These experiments revealed that the relaxation strength of the γ_2-relaxation is reduced to about one-third after the first heating cycle. During the dielectric analysis the sample is heated from room temperature to 180 °C within 5 h under air, and thus the cross-linking process is almost completed. The results indicate that approximately $^2/_3$ of the linkage groups are converted through the thermal process.

3.2. Photoinduced Reorientation. The dielectric investigations showed that the β-motion of the rigid azo group is principally not affected by the cross-linking of the molecular environment. However, a reorientation of the azo chromophore around its short molecular axis induced by means of the photoinduced isomerization cycles may be expected to depend more strongly on the molecular arrangement of the environment. Figure 8 shows the time evolution of the photoinduced birefringence for differently annealed samples of AMH2.

We were able to use a biexponential fit function for achieving a quantitative representation for the photoorientation kinetics. It is tempting to speculate that the two processes result from the relatively fast isomerization and a somewhat slower rotational diffusion process of the chromophores.[18] However, a more detailed consideration shows that the observed rise of the birefringence signal is the result of a complex interaction of several isomerization processes and conformational changes and that the rise times τ_1 and τ_2 of the biexponential fit cannot simply be interpretated as the times needed for isomerization and reorientation. The biexponential behavior rather reflects the complex kinetics of the photoorientiation process on the whole.

$$\Delta n = A_0 + A\left(1 - \frac{1}{2}(e^{-t/\tau_1} + e^{-t/\tau_2})\right) \tag{5}$$

The results of the fitting procedure for the momomeric and cross-linked samples of AMH1 and AMH2 are summarized in Table 1.

The results depicted in Figure 8 and Table 1 demonstrate that the cross-links obviously do not cause a slowing down of the kinetics of photoorientation. On the contrary, a slight increase of the rate of the photokinetics is observed for the annealed samples. For an interpretation of this result we have to take into account the fact that the momomer samples show a semicrystalline morphology which is gradually changed to an amorphous structure on heating, already before the cross-linking reaction is completed. So we have to conclude that the photoorientation of the azo chromophores is not influenced by the cross-linking itself but that it depends rather on the crystalline arrangement of the molecules and thus on the aggregation and local free volume distribution around the chromophores. These kinetic results are in good agreement with those obtained from investigations on the photoinduced trans–cis isomerization of AMH1 by analyzing the changes in the surface potential using the Kelvin-probe technique.[7,9] There, it was shown that both the photoinduced trans–cis isomerization and the thermal back-relaxation from cis to trans are faster in the thermally treated sample than in the monomeric material. In fact, we also observed a faster relaxation of the photoinduced birefringence for the cross-linked sample as obvious from Figure 9:

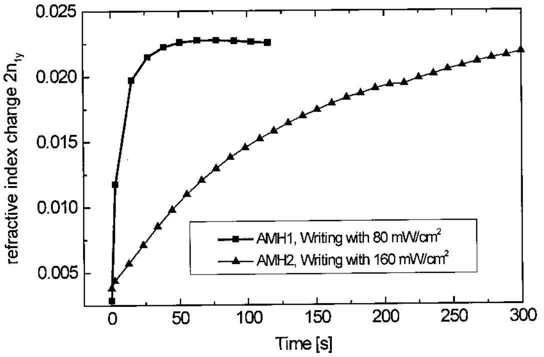
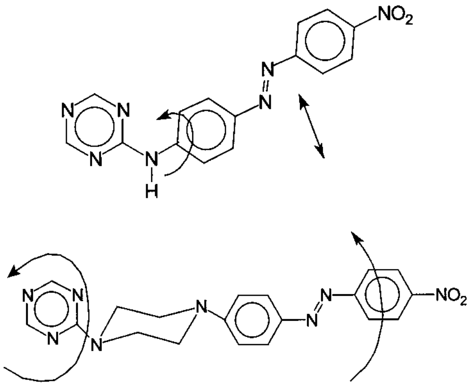


Figure 10. Holographic growth curves for the resins of AMH1 and AMH2.

Scheme 3. Influence of the Bridging Amino and Piperazino Group, Respectively, on the Reorientation of the Azo Chromophore



Nevertheless, despite this slight difference in the relaxation kinetics, the monomeric material as well as the resin seems to be capable to store information with remarkably high values for the photoinduced birefringence (0.1 for AMH2 and 0.034 for AMH1) and with a good long-term stability of the photoinduced refractive index changes. To obtain more detailed information, we performed a holographic writing process and we read out the resulting diffraction efficiency of a photoinduced holographic grating with a grating period of $\Lambda = 5.1\ \mu\text{m}$.

As can be seen from Figure 10, a stable photoinduced grating is recorded in the cross-linked AMH1 within a time scale of seconds by using a laser intensity of 80 mW/cm^2. In the same way a grating can be produced in AMH2, but here the process of formation is significantly slower, although the 2-fold irradiation intensity was used. This effect can be interpreted on the basis of the differences in the chemical structures of the two materials. The main difference consists in the nature of the linkage between chromophore and backbone: In AMH1 the azo chromophore is linked to the triazine system via a flexible amino group whereas AMH2 contains the relatively unflexible piperazino group as the linkage unit (Scheme 3).

In the case of the amino group the azo chromophore can reorient relatively independently of the backbone, whereas in the case of the unflexible piperazino bridge the reorientation of the chromophore will be accompanied by an alignment change of the chemical backbone as well. This is expected to slow the process of photoorientation. These results are in good agreement with previous investigations on the photokinetics of amino- and piperazino-bridged side group polymers.[19]

4. Conclusions

Azobenzene containing melamine resins are a class of photosensitive materials which are characterized by a very high thermal, optical, and mechanical stability. Transparent films of the insoluble melamine resin can be obtained by spin-coating of the soluble monomer material and an additional thermal treatment, yielding a very inert recording material as far as thermal decomposition is concerned. These properties together with the high values of photoinduced birefringence (up to 0.1 for AMH2) make these materials promising media for holographic information storage.

Moreover, it was demonstrated that the presence of cross-links has no significant influence on the photoinduced reorientation to the terminal azo groups. The slower photokinetics in the case of the monomer film can be explained by a reduced mobility of the chromophores due to the semicrystalline environment.

References and Notes

(1) Wang, C.; Xia, J. *J. Phys. Chem.* **1992**, *96*, 190.
(2) Ivanov, M.; Todrov, T.; Nikolova, L.; Tomova, N.; Dragostinova, V. *Appl. Phys. Lett.* **1995**, *66*, 2174.
(3) Eich, M.; Wendorff, J. H. *Macromol. Chem., Rapid Commun.* **1987**, *8*, 467.
(4) Zilker, S. J.; Bieringer, T.; Haarer, D.; Stein, R. S.; van Egmond, J. W.; Kostromine S. *Adv. Mater.* **1998**, *10*, 855.
(5) Updegraff, I. H. Amino resins. In *Encyclopedia of Polymer Science and Engineering;* Mark, H. F., Menges, G., Bikales, N. M., Overberger, C. G., Eds.; John Wiley & Sons: New York, 1985; Vol. 1, pp 752−789.
(6) Jeng, R. J.; Hsiue, G. H.; Chen, J. I.; Marturunkakul, S.; Li, L.; Jiang, X. L.; Moody, R. A.; Masse, C. E.; Kumar, J.; Tripathy, S. K. *J. Appl. Polym. Sci.* **1995**, *55*, 209.
(7) Mahler, J. Ph.D. Thesis, Berlin, 1998. Also available from the Internet: http://www.diss.fu-berlin.de/1998/20/index.html.
(8) Mahler, J.; Rafler, G. *Opt. Mater.* **1999**, *12*, 363.
(9) Mahler, J.; Rafler, G.; Stiller, B. *Mater. Sci. Eng. C* **1999**, *8/9*, 417.
(10) Mahler, J.; Rafler, G.; Stiller, B. *ECOF 7* (*E*uropean *C*onference Thin *O*rganised *F*ilms 7), Potsdam, Sept 1998, Proceedings, 347.
(11) Mahler, J.; Rafler, G. DE 197 37 815.
(12) Stracke, A. Ph.D. Thesis, Marburg 1999. Also available from the Internet: http://archiv.ub.uni-marburg.de/diss/z1999/0381.
(13) Kremer, F.; Boese, D.; Meier, G.; Fischer, E. W. *Prog. Colloid Polym. Sci.* **1989**, *80*, 129.
(14) Eichler, H. J.; Guenter, P.; Pohl, D. W. *Laser Induced Dynamic Gratings;* Springer-Verlag: Berlin, 1986.
(15) Runt, J. P.; Fitzgerald, J. J. (Hrsg.) *Dielectric Spectroscopy of Polymeric Materials*; American Chemical Society: Washington, DC, 1997.
(16) Pschorn, U.; Spiess, H. W.; Hisgen, B.; Ringsdorf, H. *Makromol. Chem.* **1986**, *187*, 2711.
(17) Zentel, R.; Strobl, G.; Ringsdorf, H. *Macromolecules* **1985**, *18*, 960.
(18) Brown, D.; Natansohn, A.; Rochon, P. *Macromolecules* **1995**, *28*, 6116.
(19) Meng, X.; Natansohn, A.; Rochon, P. *Supermol. Sci.* **1996**, *3*, 207.

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