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Optically Induced Dichroism and Birefringence of Disperse Red 1 in Hybrid Polymers

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ABSTRACT: We report results of dichroism and birefringence measurements on Disperse Red 1 (DR1) in hybrid polymers. To investigate the influence of the matrix−chromophore interaction, we employ doped and functionalized systems using three kinds of matrices with different rigidity. Writing, erasing, and rewriting processes are performed on the polymer films at temperatures ranging from 50 to 300 K. Two processes are recognized, the photochemical cis−trans isomerization of the dye molecules and a thermal motion of the photoactive chromophore inside the surrounding matrix. By comparing results obtained from the different network systems, we find that the main parameter correlated with the extent of induced anisotropy is the degree of mobility of the chromophore within the surrounding matrix.

Introduction

Materials exhibiting photoinduced anisotropy are promising candidates for optical storage devices. Recently, the optical anisotropy of azo dyes induced by photochemical trans−cis isomerization has been extensively studied. Todorov et al.[1] were the first to report on reversible photoinduced birefringence of azo dyes embedded in a polymer matrix. Employing methyl orange dissolved in poly(vinyl alcohol) (PVA), they obtained birefringence values of $>10^{-3}$. Subsequently, many investigations focused on a controlled orientation of dye molecules in polymers in order to achieve macroscopic permanent or reversible anisotropy suitable for optical storage[2−6] or macroscopic transient anisotropy for polarization holography.[7−9] Studies were also carried out on polymer films containing azo dyes with respect to their applicability as optoelectronic devices and for second harmonic generation.[10−13]

The majority of the investigated systems consisted of organic polymers, mainly PVA or PMMA, as the host matrices for the photoactive chromophores. First investigations on photoinduced anisotropy in an organic−inorganic composite material in which the azo dye Disperse Red 1 (DR1) is covalently bound to the silica network were performed by Chaput et al.[14] in 1993. They demonstrated the capability of hybrid polymers containing DR1 to store optical information. In this paper we present the results of our investigations on dichroism and birefringence of DR1 embedded in hybrid polymers carried out at different temperatures ranging from room temperature down to 50 K. In this new class of materials organic and inorganic moieties are connected on a molecular scale. The preparation procedure essentially consists of a sol−gel process providing the inorganic network, followed by a polymerization reaction, in the course of which the organic network is built up. Because of their high optical damage threshold and mechanical stability as well as their good processibility, hybrid polymers have attracted much interest as materials for the emerging field of optoelectronics.[15−18]

To characterize these materials with regard to their light induced anisotropic properties we have investigated three kinds of polymers with various rigidities. While one of these polymers, MZ (MEMO/Zr sol, MEMO = methacryloxypropyltrimethoxysilane), possesses a three dimensionally cross-linked and therefore rather stiff inorganic network, the other two materials, TM (TMPTA/MPMDM resin, TMPTA = 1,1,1-trimethylolpropane triacrylate, MPMDM = mercaptopropylmethyldimethoxysilane) and BM (BPADA/MPMDM resin, BPADA = ethoxylated Bisphenol-A diacrylate) contain only Si−O−Si chains. In addition the spacer group of MZ is considerably shorter, so inorganic and organic polymer components are tightly connected together and give rise to very small pores.

TM and BM differ only in the number of methacrylate groups available for polymerization, which is higher for TM. In addition, the spacer group of TM is shorter than the one of BM. Therefore, the matrix rigidity increases in the order of MZ > TM > BM.

The photoactive dyes we employed were Disperse Red 1 (DR1) and methacrylated Disperse Red 1 (DR1MA). While DR1 is only physically incorporated in the pores of the matrix network, DR1MA is chemically linked to the organic network.

Experimental Section

Materials. All chemicals were commercial and used without further purification. Disperse Red 1 methacrylate (DR1MA) was prepared from Disperse Red 1 (DR1) as described in detail elsewhere,[19] using toluene instead of benzene as the solvent. Their structures are shown in Figure 1.

(1) Preparation of the Sols. MEMO/Zr (MZ) Sol (See Figure 2). The synthesis of the MZ sol has been previously described in the literature.[20] First, 24.84 g (0.1 mol) of methacryloxypropyltrimethoxysilane (MEMO) and 2.7 g (0.15 mol) of water were mixed at 273 K and stirred overnight. The resulting hydrolysate was added dropwise to an ice-cooled propoxyzirconium methacrylate solution, which was prepared by dropping 1.78 g (0.02 mol) of methacrylic acid into 8.54 g

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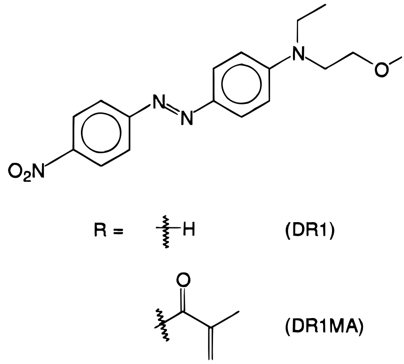

Figure 1. Investigated azo dyes Disperse Red 1 (DR1) and Disperse Red 1 methacrylate (DR1MA).

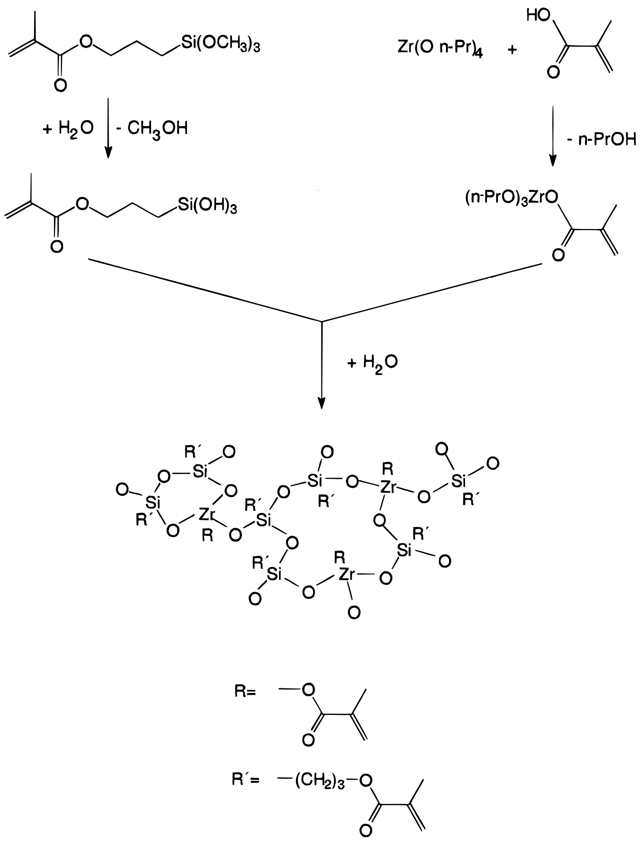

Figure 2. Synthesis of the MEMO/Zr resin.

(0.02 mol) of $Zr(OPr)_4$ at 273 K followed by 30 min of stirring at this temperature. After the MEMO/water addition and further stirring for 30 min, 0.54 g (0.03 mol) of H_2O was added and stirring was continued for 1 h at room temperature to complete hydrolysis. The sol was used without further work-up.

TMPTA/MPMDM (TM) and BPADA/MPMDM (BM) Resins (see Figure 3). The synthesis of the TM resin has been previously described in the literature.[21,22] First, 118.5 g (0.4 mol) of 1,1,1-trimethylolpropane triacrylate (TMPTA) and 61.3 g (0.34 mol) of mercaptopropylmethyldimethoxysilane (MPMDM) were dissolved in 450 mL of ethyl acetate and cooled in an ice bath. Under an N_2 atmosphere, a solution of 0.25 g (4.4 mmol) of KOH in 30 mL of EtOH was added dropwise under vigorous stirring. During this step, the temperature must not exceed 293 K. Immediately afterward the solution was hydrolyzed with a mixture of 4.05 g of H_2O and 5.95 g of 1 N HCl and stirred for 2 h in the absence of light. The resulting mixture was washed three times with 70 mL of saturated NaCl solution, the organic phase was dried over Na_2SO_4, and the solvents were evaporated under reduced pressure. The BM resin was prepared in the same way, using ethoxylated Bisphenol-A diacrylate (BPADA) instead of TMPTA.

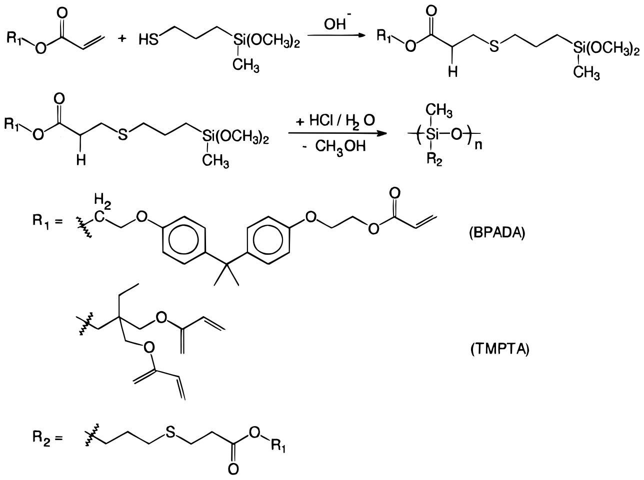

Figure 3. Synthesis of BPADA/MPMDM (BM) and TMPTA/MPMDM (TM) resins.

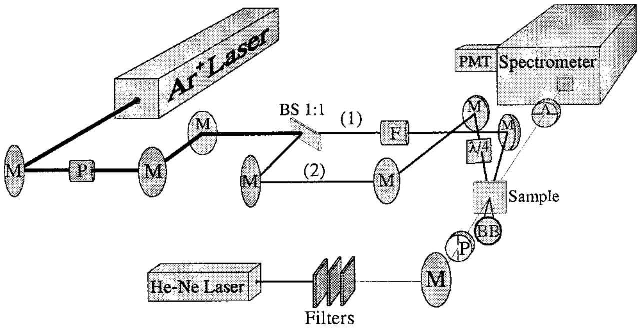

Figure 4. Experimental setup used for the birefringence measurements (M = mirror, P = polarizer, BS = beam splitter, F = double Fresnel-Rhombus, BB = beamblock, A = analyzer, and PMT = photomultiplier tube).

(2) Sample Preparation. The percentage data given in the following section are related to the solids portion of the resins in charge.

First, 10 g of the resin was diluted with ethyl acetate to a solids content of 40%. Then 10% (w/w) of the dye and 5% of the photoinitiator IRGACURE 500 were dissolved in this solution. By means of this procedure, six mixtures were obtained where each of the three sols (MZ, TM, BM) were colored once with DR1 and once with DR1MA. For the sample manufacture 10 × 10 cm^2 glass substrates were spin coated with the sols (20 s; 2000 rpm), dried for 1 h at 353 K, and UV cured for 60 s (1000 W) to build up the organic network by means of radical polymerization of the acrylic moieties. In this way, the dye either was dissolved (DR1) in or covalently attached (DR1MA) to each of the three matrices (MZ, TM, BM).

Birefringence Studies. The experimental setup used in our studies is schematically shown in Figure 4. Anisotropy was induced by illuminating the sample with a linearly polarized unfocused laser beam (1) and erased with a circularly polarized unfocused laser beam (2), both provided by an Ar+ laser (Spectra-Physics 2085 BeamLok). The laser beams had an intensity of 100 mW/cm^2. The wavelength was 488 nm which corresponds to the maximum absorption of the trans form of DR1. Beam 1 was passed through a double Fresnel-Rhombus which allows a variation of the polarization direction and is then deflected onto the sample. Beam 2 was circularly polarized by a K-Prism and was then passed through the sample on the same spot as beam 1. The angle between beams 1 and 2 was about 1°.

The induced birefringence in the sample was probed by an unfocused He–Ne laser beam using a wavelength of 633 nm which is far from the absorption bands of the trans and the cis isomeric forms of the dye. The probe beam was attenuated by different neutral density filters to provide intensities as small as 0.3 μW/cm^2. In this way an influence of the probe beam on the induced birefringence could be excluded. The polarization direction of the probe beam was adjusted by a Glan-Thompson prism. The polarized beam was then deflected onto the sample coinciding with beams 1 and 2, and analyzed by another polarizing prism. The signal behind the analyzer was detected by a photomultiplier (RCA, model 31034A-02). Additional stray light rejection was achieved using a double monochromator (Spex 1404) as filter. To ensure a complete overlap of the probe and the pump beam on the sample surface, we passed the probe beam through a pinhole to make it half of the diameter of the pump beams. The angle between the probe and the pump beam was approximately 1−3 degrees.

The sample was placed in a closed-cycle helium cryostat (Cryophysics model 22), which allowed us to perform measurements with temperatures ranging from 50 to 300 K.

Dichroism Studies. For our dichroism studies we used the same Ar+ laser (488 nm) and the same detection system as described above. The Ar+ laser beam was split by a 1:10 beam splitter into a probe and a pump beam. The polarization direction of the probe beam was left unchanged in our experiment in order to maintain constant detection conditions. The probe beam was attenuated by different neutral density filters to provide intensities of about 3 mW/cm^2. Thus, the influence of the probe beam on the induced dichroism was negligible. The pump beam was passed through a double Fresnel-Rhombus in order to change its polarization direction with respect to the probe beam.

The intensity of the probe beam transmitted by the sample was recorded as a function of the pump beam intensity. The polarization direction of the pump beam was chosen to be once parallel and once perpendicular to the probe beam.

Results and Discussion

The mechanism of inducing anisotropy in azo dye doped polymers involves reversible trans-to-cis isomerization of the azo aromatic group around the azo linkage. The absorption of light near the absorption maximum transfers the dye molecules into an electronically excited state followed by a nonradiative decay either into the trans or cis form of the electronic ground state. The cis form can undergo a photoinduced cis-to-trans interconversion or spontaneously relaxes back to the trans form with time constants depending on the nature of the surrounding matrix.[23] In the trans form the dye molecules can be considered to exist in a rodlike structure. Therefore, the probability of absorption of a photon is proportional to $I \cos^2 \theta$, where I is the pump laser intensity and θ is the angle between the molecular axis and the electric field vector of the exciting light. Assuming that the matrix around the chromophore allows an angular motion of the dye molecules, a series of trans−cis−trans isomerization cycles occurs until the orientation of the molecular axis is perpendicular to the pump laser polarization direction ($\cos^2 \theta = 0$) in order for the system to reach an energy minimum. This procedure is superimposed by a Brownian-like motion of the molecules caused by the thermal interaction with the host medium. Although the thermal motion does not affect the macroscopic average orientation of the molecules (perpendicular to the pump laser polarization), the induced optical anisotropy is reduced, especially at high temperatures.

Dichroism and birefringence measurements have been carried out (applying a pump−probe technique) in order to investigate the induced optical anisotropy and its dependence on the temperature and the matrix material.

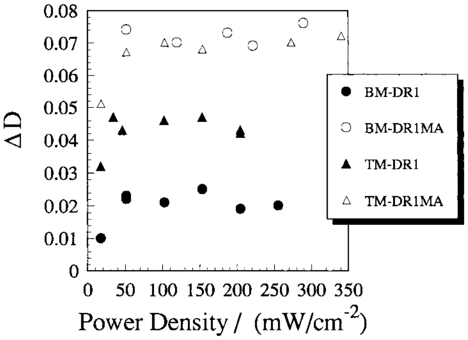

Figure 5. Photoinduced dichroism ΔD as a function of the pump laser intensity of the exciting laser beam.

Dichroism Measurements. The photoinduced dichroism is given by

$$\Delta D = \frac{D_\perp - D_\parallel}{D_\perp + D_\parallel} \quad (1)$$

where $D_\perp$ and $D_\parallel$ are the optical densities perpendicular and parallel to the pump laser polarization direction, respectively. The dependence of ΔD on the intensity of the exciting laser beam was determined for the different samples, as shown in Figure 5. It should be noted that the systems MZ-DR1 as well as MZ-DR1MA do not show any induced dichroism at all. An angular motion of the azo dye molecules by means of an isomerization cycle must be hindered in this matrix. This is reasonable since in the MZ matrix material a three-dimensional inorganic network is present which encircles the chromophore very tightly. This is in agreement with the results reported in a previous paper,[23] where we observed a great influence of this type of matrix on the cis-to-trans relaxation behavior of DR1.

As shown in Figure 5, ΔD saturates at an intensity of about 50 mW/cm^{-2} for all investigated systems. This is a relatively high threshold for optical induced anisotropy compared to other systems such as methyl orange in poly(vinyl alcohol)[8] where saturation already occurs at 5 mW/cm^{-2}. Another interesting observation is that the systems in which DR1 is chemically linked to the network backbone (TM-DR1MA and BM-DR1MA) exhibit a larger anisotropy compared to the doped systems.

Birefringence Measurements. Along with dichroism, light birefringence is induced under irradiation with polarized Ar+ light (488 nm). We have investigated birefringence at 633 nm, outside of any absorption band, so that the signal which is transmitted by the analyzer arises solely from the photoinduced birefringence. According to our dichroism studies, we could not measure any birefringence in the systems MZ-DR1 and MZ-DR1MA, owing to the high rigidity of this matrix type.

We have investigated the dependence of the signal intensity (probe beam) on the polarization direction of the pump beam, keeping the polarizer and the analyzer of the probe beam perpendicular to each other. A variation of the polarization direction of the pump laser simultaneously rotates the perpendicular oriented dye molecules. We observed a signal intensity which is proportional to $\sin^2(2\theta)$, where θ is the angle between the polarization directions of the pump and the probe beam. As an illustration, Figure 6 shows this dependence for the system TM-DR1MA. In the following

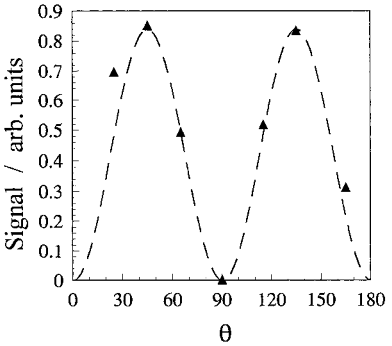

Figure 6. Signal intensity as a function of the angle θ between the orientation of the molecular axis and the polarization direction of the probe beam. The analyzer of the probe beam was adjusted perpendicular with respect to the polarizer.

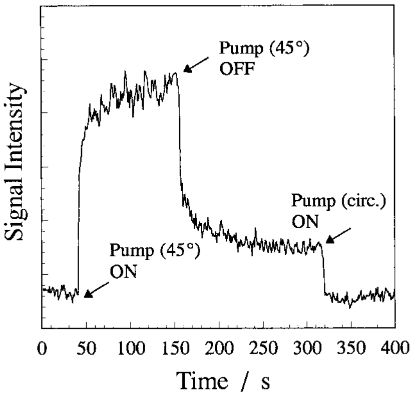

Figure 7. Typical writing−erasing sequence on a TM-DR1MA film at 298K. The times for switching on and off the linearly polarized writing beam [Pump (45°)] and the circularly polarized erasing beam [Pump (circ.)] are marked by arrows.

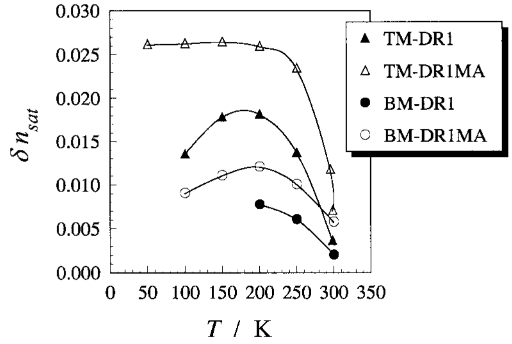

Figure 8. Temperature dependence of the saturated photoinduced birefringence δn_{sat}.

experiments the angle θ was fixed at 45° corresponding to the maximum signal intensity.

A typical writing−erasing sequence is presented in Figure 7. Initially the orientation of the molecules is isotropic. The rest light transmitted by crossed polarizers is caused by diffuse scattering of the probe beam at the sample surface. Birefringence is induced when the linearly polarized pump beam is switched on. The signal intensity consequently increases and finally saturates after a certain time, which depends on the surroundings of the active chromophore. Switching the pump beam off, the birefringence decreases to a certain value essentially depending on the sample temperature and the related motion of the chromophores. The measurement shown in Figure 7 was performed at 298 K. Although the induced optical anisotropy was not completely preserved after the writing process, a significant fraction of anisotropy remained. At a third stage, the sample is retransformed to an isotropic state by “overwriting” the test spot with circularly polarized light, thus again randomizing the orientation of the dye molecules.

Todorov et al.[1] in their work investigated the optical anisotropy which was induced in the azo dye methyl orange (MO), introduced in poly(vinyl alcohol) (PVA). This system showed a high value for the birefringence ($\delta n > 10^{-3}$). They found that the time needed for the destruction of the stereoregularity strongly depended on the matrix and in the darkness lasted several days for PVA. For methyl red (MR) in poly(methyl methacrylate) (PMMA), a smaller value for the birefringence was found[7] ($\delta n \approx 2 \times 10^{-4}$) pointing to the strong dependence on the dye−matrix interaction. In our own experiments, we also found this dependence, which seems reasonable as for such high values of birefringence one has to assume that also the matrix is changed during the recording.

Todorov et al.[8] also investigated the temperature dependence of photoinduced birefringence in rigid solutions of MR and MO azo dyes in polymer matrices (PVA and PMMA). They found that the value of birefringence reaches a maximum for a certain temperature (≈290 K). Furthermore, an investigation of the dependence of the birefringence on the pump laser intensity yielded a saturation for an intensity as small as 5 mW/cm^2. Above this value no change of temperature dependence and birefringence values could be seen.

In Figure 8 we present the temperature dependence of the birefringence after saturation (δn_{sat}) for all investigated samples. Photoinduced birefringence is determined by the intensity of the probe beam transmitted through the crossed polarizers

$$I_{\mathrm{A}} = I_0 \tan^2 \frac{\delta\varphi}{2} \qquad (2)$$

where I_0 is the probe beam intensity at parallel orientation for polarizer and analyzer and $\delta\varphi$ is the phase difference between ordinary and extraordinary wave and is given by

$$\delta\varphi = \frac{2\pi}{\lambda}\,\delta n\; d \qquad (3)$$

where d is the sample thickness and $\delta n = n_{\perp} - n_{\parallel}$ is the photoinduced birefringence. $n_{\parallel}$ and $n_{\perp}$ are the refractive indices of the sample for parallel and perpendicular polarization directions of the pump and the probe beam. Figure 8 shows that the photoinduced birefringence of all investigated systems reaches a maximum at about 150−200 K and considerably decreases when the temperature is increased. This temperature is considerably lower than that found in the experiments discussed above.[8] The maximum signal intensity can amount up to 350% of its value at room temperature. Obviously, there is a strongly temperature-dependent process involved, which increases in significance at higher temperatures. At the same time the extent of alignment of the chromophores decreases, so we assign this process to a thermal angular randomization of the dye molecules. The thermal motion of the dye molecules seems to play an important role for the photoinduced anisotropy and is reflected in our results for the different matrix systems: DR1 in the more rigid TM matrix exhibits higher values of photoinduced

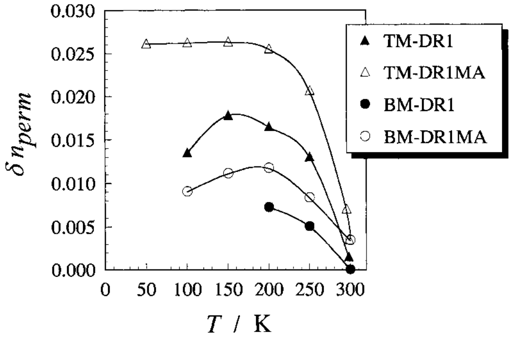

Figure 9. Temperature dependence of the permanent photoinduced birefringence δn_{perm} which remains after the linearly polarized pump beam is switched off.

anisotropy than the softer BM matrix. Additionally, the functionalized dye–matrix systems (TM-DR1MA and BM-DR1MA) exhibit higher birefringence values compared to the doped systems, which is in accordance with the results we obtained in our dichroism studies. Covalent attachment of the optically active molecules to the surrounding matrix leads to reduced relaxation—and this is exactly what one would expect.

Regarding the permanent photoinduced birefringence (δn_{perm}) after the linear polarized pump beam is switched off (see Figure 9), we observe the same temperature dependence as for δn_{sat} (see Figure 8). In particular, we point out that up to 150 K none of the systems shows any decrease of the induced birefringence after the pump beam is switched off, so there is no memory loss at all. At these temperatures the thermal motion of the dye molecules is "frozen" and a randomization of the orientation of the dye molecules is suppressed.

As already mentioned in the last subsection, we found a saturation of the light-induced anisotropy of the systems at about 500 mW/cm^{-2} which is 100 times the value found by Todorov et al.[8] for the systems MO and MR in DVA or DMMA. Otherwise, the same dependence on the laser intensity could be found. The birefringence experiments were performed at an pump laser intensity of about 100 mW/cm^2 where saturation effects due to the laser intensity do not play any role.

As mentioned above, photoinducing optical anisotropy in rigid solutions of azo dyes is based on reversible trans–cis isomerization of the dye molecules. The interaction of the pump laser light with the dye molecules results in transitions trans → cis as well as cis → trans. Additionally, the instable cis isomeric form thermally isomerizes back to the trans isomeric form. While the absorption of the rodlike trans isomeric form is strongly anisotropic, that of the cis isomeric form is isotropic. Therefore, the photoinduced change in the refractive index at 633 nm is attributed primarily to the trans molecules.[24]

On the basis of these considerations, recently simple models had been developed, simulating the write–erase process in different systems.[8,3] For example Natansohn et al.[3,6] investigated the optical anisotropy induced in films of pDR1A. They found writing and erasing curves which were qualitatively the same as those found in our experiments (compare with Figure 7). For a given temperature, these could be well reproduced by the rate equations describing the photochemical and thermal isomerization and ordering processes. Therefore, we did not repeat these model calculations.

However, to gain more information on the influence of the temperature on the writing procedure, we performed the writing for several temperatures. The writing curve cannot be described by a simple first-order kinetics. This is consistent with the findings of other scientists.[8,3,10] Without developing a new rate model, we just used a simple biexponential function which was able to simulate the experimental data quite well:

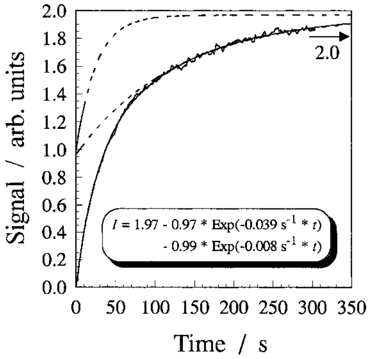

Figure 10. Biexponential fit of a writing sequence on a TM-DR1MA film at a temperature of 200 K. The solid line represents the biexponential fit given in the inset. Additionally, the two exponential functions are shown (dashed lines).

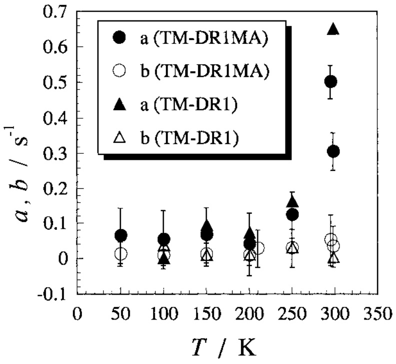

Figure 11. Temperature dependence of the rate constants *a* and *b*, obtained by a biexponential kinetical model applied to the writing procedures of the systems TM-DR1MA and TM-DR1. As examples error bars are shown for the rate constants of TM-DR1MA.

$$I = I_{\max} - A \exp(-at) - B \exp(-bt) \qquad (4)$$

Here, I is the signal intensity passing through the pair of crossed polarizers, $I_{\max}$ is the maximum signal intensity achieved at infinite time while the pump laser is on. A and B are the weighting factors for the two exponential functions and a and b are the rate constants for the two processes. In Figure 10 this is illustrated for a writing sequence on a TM-DR1MA film at a temperature of 200 K. The results of the fits were checked using the saturation value of δn which was determined after about 30 min of irradiation.

Comparing the rate constants a and b for different temperatures, we found for all investigated systems, that a is—in contrast to b—strongly temperature dependent. This is shown in Figure 11 for the systems TM-DR1 and TM-DR1MA. The rate constants b might have a slight tendency to rise with temperature. However, within the estimated error of the experiment as well as the fitting procedure, no conclusive statement can be made here. To give an estimate of the quality of the fitting process, as an example in Figure 11 error bars are shown for the rate constants a and b obtained for TM-DR1MA. As mentioned above, Todorov et al.[8] found a strong temperature dependence for the writing process. For an explanation, they assumed in their model that when the temperature increases, the state of the matrix leads to an increase of the probability for the optically activated transition cis → trans, compared to the trans → cis transition. They further assumed that the probability for an optically activated transition from cis into trans is much greater than the probability for a thermal transition from cis into trans, therefore neglecting the latter's contribution. However, Natansohn et al.[6] as well as Dumont and co-workers[25] found that the cis−trans thermal isomerization constant is on the order of 0.2 s^{-1} at room temperature. This value is comparable to the rate constants a found in our experiments for this temperature. This result could point to the fact that a describes the thermal isomerization process. As b does not change considerably with temperature, it might be related to a process which is determined by photochemical isomerization. However, one would expect higher rate constants for such a process. The contribution of the two exponential functions are weighted by the factors A and B. The ratio between these values changes from $A/B \approx 0.4$ at 50 K to $A/B \approx 4.8$ at 300 K. This again supports the assumption that a belongs to a thermally determined process.

To gain more information on the dependence of the writing process on temperature, further investigations have to be performed. In particular the considerable contribution of a process which only slightly depends or even does not depend on temperature has to be investigated more closely.

Conclusions

In the present work dichroism and birefringence of Disperse Red 1 (DR1) in hybrid polymers have been investigated. We chose doped and functionalized systems of three kinds of matrices showing different rigidity.

Dichroism and birefringence is caused by an alignment of the dipole moments of the dye molecules perpendicular to the polarization direction of the pump beam. We observed that the systems with the matrix exhibiting the highest rigidity (MZ) do not show any induced anisotropy at all. Since in this type of matrix a very rigid three-dimensional inorganic network is present, an angular motion of the azo dye molecules by means of an isomerization cycle induced by linearly polarized light is not possible.

To study the temperature dependence of the writing process in our birefringence measurements, we repeated the writing at different temperatures. The writing sequence could not be simulated using a first-order kinetical model. Applying a biexponential function, we found two rate constants. The rate constant of the faster process strongly depends on the temperature and is on the order of the constant found for the cis−trans thermal isomerization. Within the errors, the smaller rate constant shows no considerable dependence on temperature. Further investigations will be necessary in order to give a correct interpretation for these findings. At about 150−200 K the photoinduced birefringence was found to increase up to 350% of its value at room temperature. The maximum birefringence was $\delta n \approx 3 \times 10^{-2}$ for DR1 in a TM matrix.

The thermal motion of the dye molecules seems to play an important role for a correct interpretation of the photoinduced anisotropy. This is reflected in our results for the different copolymer systems: the more rigid TM matrix exhibits higher values of photoinduced anisotropy compared to the softer BM matrix, because the thermal motion of the dye molecules is reduced in the more rigid copolymer.

Additionally, we observed that the systems in which the azo dye is covalently linked to the organic network show larger values of photoinduced anisotropy compared to the doped systems. This is caused by a reduction of relaxation owing to one-sided anchoring of the optically active molecules. Moreover, it was demonstrated that the thermal motion of the dye molecules becomes less significant when the temperature is reduced.

Thus, the overall controlling parameter correlated with the extent of induced anisotropy is the degree of mobility of the chromophore in its surroundings, which strongly depends on the host system. Therefore, a future task will be the design of new polymer materials in order to optimize the ability of storing optical information. The hybrid polymers seem to be very well suited for this purpose owing to the great variety of available organic side groups.

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