

Photo-orientation of azobenzene side chain polymers parallel or perpendicular to the polarization of red HeNe light

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2003 J. Phys.: Condens. Matter 15 S813

(<http://iopscience.iop.org/0953-8984/15/11/306>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.119

The article was downloaded on 19/05/2010 at 08:18

Please note that [terms and conditions apply](#).

Photo-orientation of azobenzene side chain polymers parallel or perpendicular to the polarization of red HeNe light

Christian Kempe, Michael Rutloh and Joachim Stumpe¹

Fraunhofer Institute for Applied Polymer Research, Geiselbergstrasse 69, 14476 Golm, Germany

Received 5 December 2002

Published 10 March 2003

Online at stacks.iop.org/JPhysCM/15/S813

Abstract

The mechanism of the light-induced orientation process of azobenzene-containing polymers caused by irradiation with linearly polarized red light is investigated. This process is surprising because there is almost no absorption at 633 nm. Depending on the photochemical pre-treatment and the exposure time, the azobenzene moieties can undergo two different orientation processes resulting in either a parallel or a perpendicular orientation with respect to the electric field vector of the incident light. The fast orientation of the photochromic groups with their long axis in the direction of the light polarization requires a photochemical pre-treatment in which non-polarized UV light generates Z-isomers. Due to this procedure the film becomes 'photochemically activated' for the subsequent polarized irradiation with red light. But on continued exposure a second, much slower reorientation process occurs which establishes an orientation of the azobenzene groups perpendicular to the electric field vector. The fast mechanism is probably caused by an angle-selective photo-isomerization of the Z-isomers to the E-isomers, while the subsequent slow reorientation process is caused by the well-known conventional photo-orientation taking place via the accumulation of a number of photoselection steps and the rotational diffusion minimizing the absorbance of the E-isomer. This process occurs in the steady state but at this wavelength with a very small concentration of Z-isomers. The competing mechanisms take place in the same polymer film under almost identical irradiation conditions, differing only in the actual concentration of the Z-isomers.

1. Introduction

Polymeric glasses containing photochromic groups are important for many applications, such as in optical data storage, the alignment of liquid crystals, optical elements and optical shutters.

¹ Author to whom any correspondence should be addressed.

In the last two decades it was found that in addition to the well-known molecular photoreactions, some of these reactions can trigger physical processes such as light-induced orientation and photo-induced diffusion. Both processes take place in polymer films below the glass transition temperature. In this way, significant changes of the morphology, the anisotropy and the surface profile can be generated. The photo-induced orientation and mass transport processes in glassy states of polymers are of special interest; their extents are very surprising. Thus, the photo-orientation of azobenzene side groups causes the cooperative orientation of non-photochromic groups and holographic exposure generates surface relief gratings via lateral mass transport of the photochromic macromolecules over micrometre distances. So far it is not well understood how the molecular photoreactions couple to the dynamics of the polymers or, in other words, how the order and dynamics of the polymers are modified by the photochemical processes in the glassy state.

Different mechanisms of light-induced orientation processes of polymers have been found in the last few years [1–4]. The conventional photo-orientation of azobenzene-containing polymers, which has been well known for years, results in comparatively high values of the optical anisotropy due to the irradiation with linearly polarized light of low power density. The process is based on the angle-selective E–Z photo-isomerization of azobenzene upon irradiation with linearly polarized light and rotational diffusion in the steady state of the photoreaction. The probability of excitation of the photochromic groups depends on the angle between the direction of the transition moment and the polarization of the incident light. Thus, E-isomers which are oriented in the polarization direction of the light are preferentially excited and those perpendicular to it can not be excited any longer. This complex process results in the preferred orientation of the E-azobenzene moiety perpendicular to the electric field vector. The driving force of the process is the minimization of the light absorption of the azobenzene groups. The photostationary equilibrium is a necessary condition for the process, allowing repeated angle-selective photoselection. The process is generated by all wavelengths of the absorption spectrum, such as UV, blue and green light. The induction of this process in the case of strong donor–acceptor-substituted azobenzenes using polarized red light has also been shown in some recent papers [5]. This photo-orientation process enables a lot of applications, such as in optical data storage and producing anisotropic optical elements.

A new process of orientation of azobenzene-containing polymers, based on the subsequent irradiation with two frequencies has been described recently, where a parallel orientation of the azobenzenes with respect to the polarization direction of red light is generated [6–9]. So far this mechanism remains unexplained. This process is probably responsible for some orientational effects found in holographic experiments by different groups, but unfortunately in these studies there is no information about the orientation direction, so one cannot decide which mechanism is responsible for the effect [10–12]. It was shown that this orientation is induced by a two-step irradiation process (unfortunately this procedure, characterized by two steady states, was called ‘biphotonic’ by some authors).

As a first step, the polymer films were irradiated with non-polarized UV light causing a sensitization to the subsequent irradiation with the linearly polarized red light of a HeNe laser at 633 nm. In contrast to the conventional photo-orientation process described above, the red light orientation process leads to an orientation of the photochromic side chains parallel to the direction of the light polarization.

In this study it will be shown that two completely different processes take place in the same polymer film, resulting in dichroisms with opposite signs modified only by the photochemical pre-treatment. The conditions for both processes will be discussed, allowing us to formulate the mechanism of the two-steady-state parallel orientation process.

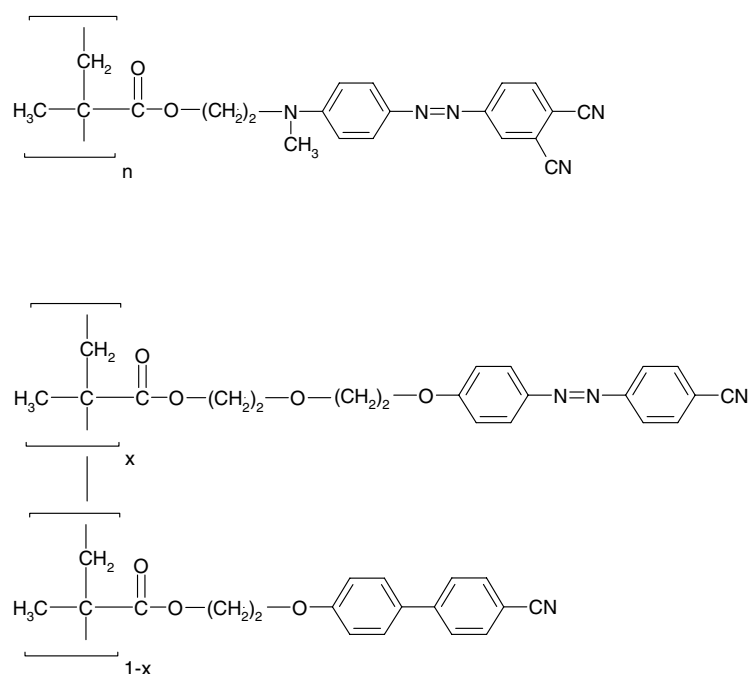


Figure 1. The chemical structures of homopolymer P1, copolymer P2 ($x = 0.6$) and homopolymer P3 ($x = 1.0$).

Table 1.

Polymer	Name	Thermal properties	Literature
P1	HP3645	G (143 °C) I	[13]
P2	ZPK60	G (77 °C) I	[14]
P3	Kost340	G (58 °C) S _A (116 °C) I	[14]

2. Experimental section

2.1. Polymers investigated

Different azobenzene-containing side chain polymers which differ mainly in the substitution of the azobenzene group were investigated. The synthesis and properties of the polymers were described in previous papers [13, 14]. The homopolymer P1 and the copolymer P2 (figure 1) are amorphous, with glass transition temperatures T_g of 143 and 77 °C respectively. In contrast, the homopolymer P3 (figure 1), which contains the same photochromic group as P2, is liquid crystalline with a broad smectic phase and a glass transition temperature of 58 °C (table 1).

All polymers investigated have good solubility in tetrahydrofuran (THF). THF was used as the solvent for the investigation of the polymers in solution and the preparation of the films. Polymer films were prepared by spin-coating on glass or silica substrates using a solution with a concentration of 20 mg ml⁻¹. Films with a layer thickness between 0.1 and 0.5 μm were prepared by variation of the spin-coating parameters.

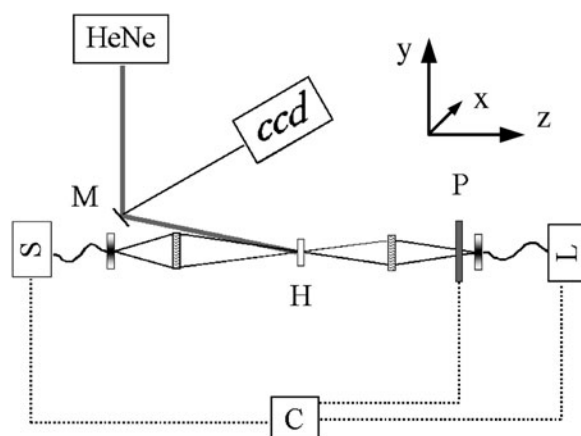


Figure 2. Optical set-up; HeNe: helium–neon laser; M: mirror; S: spectrometer; C: computer; H: sample holder; P: polarizer; L: measurement light source; ccd: CCD camera.

2.2. Optical experiments

The optical set-up shown in figure 2 was used for the irradiation and the measuring of the polarized absorption spectra. It permits irradiation of thin films with linearly polarized red light (633 nm) of a HeNe laser (HNA 188-S, Carl Zeiss Jena) with a power density of $(600 \pm 50) \text{ mW cm}^{-2}$, whereas the electric field vector points in the direction of the x -axis. Simultaneously, the change of the UV/visible spectra and the anisotropy of the films are measured using a diode array spectrometer (Polytec X-dap-04). Both the irradiating and the measuring beam lie in the film normal direction (z -axis), so the anisotropy in the x - y plane is measured by a spectroscopic method. The UV/visible measurement is carried out within the area of the laser spot by focusing of the measuring light. For the polarization-dependent measurements, a computer-controlled linear polarizer is positioned before the sample. The irradiation with non-polarized UV light was carried out in an adjacent set-up using an XBO lamp with a power density of $8 \pm 2 \text{ mW cm}^{-2}$ at $\lambda = 365 \text{ nm}$. The conventional photo-orientation was also investigated in the blue range using an Ar^+ laser at 488 nm with a power density of $100 \pm 3 \text{ mW cm}^{-2}$. To derive the power density of the HeNe laser, the profile of its beam was measured by a CCD camera (Cohu 4700, Coherent).

The optical anisotropies of the systems investigated can be estimated by calculation of the dichroic ratio or the dichroism from the measured UV/visible spectra for different polarization directions of the measuring light. If A_i denotes the absorbance at the maximum of the π - π^* transition, where i denotes the polarization direction (either parallel or perpendicular to the preferred direction), these quantities can be derived as follows [9]:

$$R = \frac{A_{\parallel}}{A_{\perp}} \quad (1)$$

$$D = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + A_{\perp}}. \quad (2)$$

The definition of the dichroism is used for oriented systems with a preferred direction. To distinguish between different orientation directions in the same system, e.g. whether the director is pointed in the x -direction or in the y -direction, an additional sign for the dichroism is defined (j denotes the direction of the orientation director in the laboratory coordinates). This is only done to allow comparison of the two mechanisms, because we are sure that no other orientation

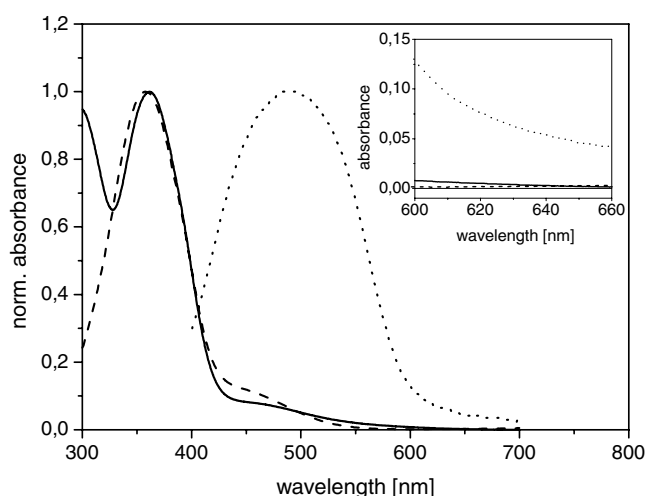


Figure 3. Spectra of spin-coated films of the polymers P1 (dotted curve), P2 (full curve) and P3 (dashed curve).

direction is generated:

$$D_j = \begin{cases} +D & \text{for } j = x \\ -D & \text{for } j = y. \end{cases} \quad (3)$$

3. Results and discussion

The polymers investigated were selected on the basis of the substitution of the azobenzene moieties, in order to facilitate comparison of amorphous and liquid crystalline polymers. The spectra of the polymers are shown in figure 3. While the maximum of the π - π^* absorption of 4-cyano-4'-alkoxy-azobenzene is located at 360 nm and the n - π^* transition at 450 nm, the 3,4-dicyano-4'-*N*-methylamino-azobenzene has a bathochromically shifted π - π^* transition at 470 nm. In addition to the spectral change, the push-pull substitution causes a strong decrease of the lifetime of the thermodynamically unstable *Z*-isomer. While the 4-cyano-4'-alkoxy-azobenzene has a rate constant of the thermal *Z*-*E* isomerization of $k_{P2} = 2.45 \times 10^{-3} \text{ s}^{-1}$, the corresponding value for the push-pull-substituted azobenzene amounts to $k_{P1} = 30.8 \text{ s}^{-1}$.

3.1. Conventional photo-orientation with red light

Spin-coated films of the amorphous polymers P1 and P2 were irradiated with linearly polarized red light. In spite of the fact that for polymer P2 there is almost no or only a very low absorbance at 633 nm, the irradiation with the HeNe laser leads to an observable orientation perpendicular to the electric field vector. The orientation rates for the two polymers are different by orders of magnitude (figure 4). In particular, the dynamics of the polymer P2 is so slow that the saturation value could not be established during 40 h of exposure. In the case of polymer P1, the orientational dynamics could be described by a bi-exponential function (4) and two rate constants, of $k_1 = 3.2 \times 10^{-3} \text{ s}^{-1}$ and $k_2 = 4.7 \times 10^{-4} \text{ s}^{-1}$, were obtained [16]:

$$D = A_1(1 - e^{-k_1 t}) + A_2(1 - e^{-k_2 t}). \quad (4)$$

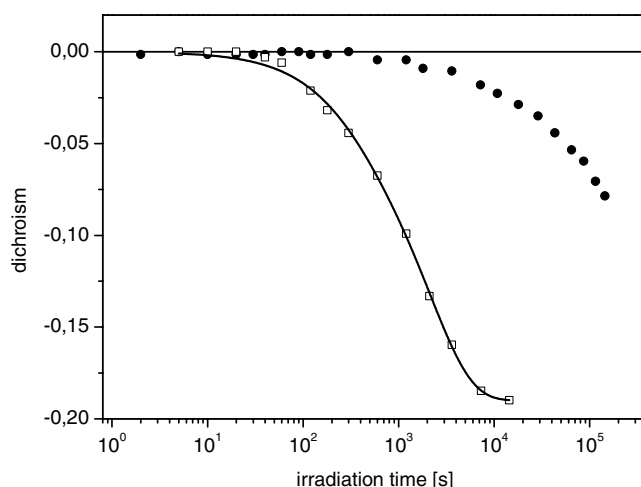


Figure 4. Conventional photo-orientation of P1 (open squares) and P2 (filled circles) by irradiation with linearly polarized red light. The line shows the bi-exponential approximation using formula (4).

In contrast to the usual case of photo-orientation using the Ar⁺ laser lines at 488 or 514 nm, which correspond to the excitation of the $\pi-\pi^*$ transition of the push-pull-substituted P1 and the $n-\pi^*$ transition in the case of P2, the red line of a HeNe laser at 633 nm is far away from any transition band visible in the spectra. For the prepared films of the polymer P2, we could not detect any absorbance higher than the noise at this wavelength; however, the experiments demonstrate that there must be a photoreaction. This is in agreement with other publications, where the authors speculated about a transition at this wavelength [17]. The investigation of a highly concentrated solution of P2 in THF shows an observable increase of the measured absorbance at 633 nm during the irradiation with unpolarized light at 365 nm. This illumination should be caused by an E-Z isomerization of the azobenzene units. Thus the observed absorbance must be related to the outermost flank of the $n-\pi^*$ transition of the Z-isomers. The corresponding absorbance in the $n-\pi^*$ transition of the E-isomers is considerably smaller, since this transition is symmetry forbidden.

Thus, it was shown that, even in the films of P2 investigated, both isomers absorb with a small probability. As a consequence, the rate of the conventional photo-orientation process induced by the red light is very low due to the very small absorption.

There are two ways to increase the orientation rate. On one hand, in the case of donor-acceptor-substituted azobenzenes, the band of the $\pi-\pi^*$ transition is for both isomers bathochromically shifted, so it can be assumed that the absorbance at 633 nm increases, resulting in the faster induction process of this polymer (figures 3 and 4). On the other hand, in the case of azobenzenes with very low absorbance at 633 nm, the orientation rate can be increased by increasing the irradiation time or the power density of the light.

Because of the higher extinction coefficient, irradiation with the blue line of an Ar⁺ laser results in a considerably faster establishing of the orientation, whereas the saturation value of the dichroism lies in the same range (table 2).

3.2. Competition between the two photo-orientation mechanisms

The polymer P2 was used to investigate the two-step orientation process taking place via the subsequent irradiation with two different wavelengths. So, a freshly prepared film of P2

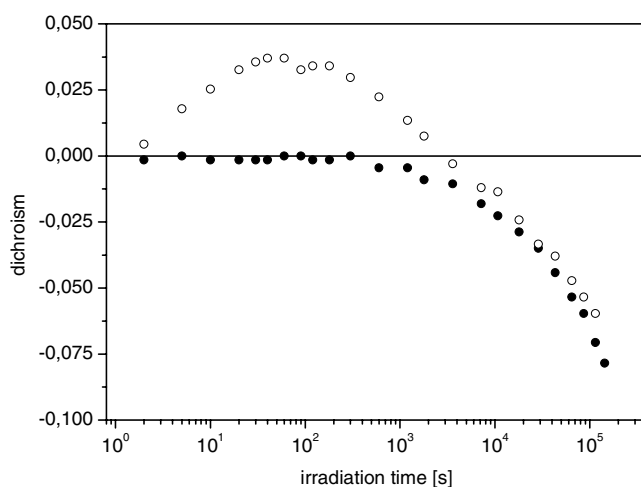


Figure 5. Comparison of the orientation behaviours of polymer P2 irradiated with linearly polarized light at 633 nm with (open circles) and without (filled circles) UV pre-treatment. Red light illumination starts at the time $t = 0$.

Table 2.

Polymer	P1	P2	P3
Lifetime of Z-isomer ^a	32.5 ms	405 s	405 s
Dichroism (D) induced by irradiation at 488 nm	-0.21	-0.22	-0.33
Dichroism (D) induced by long-time irradiation at 633 nm	-0.17	-0.07	-0.14
Amplification of the dichroism (D) by annealing at 70 °C	0	0	-0.60
Dichroism (D) induced by non-polarized irradiation at 365 nm followed by polarized irradiation at 633 nm for several seconds	0	0.04	0.028
Amplification of the dichroism (D) by annealing at 70 °C	0	0	0.62

^a The half-lives of Z-isomers of 1, 3-di-cyano-4'-aminomethyl-azobenzene and 4-[4-(6-bromohexyloxy)phenylazo]-benzotrile in THF at room temperature were measured.

was initially irradiated with non-polarized UV light at 365 nm, establishing a photostationary equilibrium which contains a significant content of Z-isomers. Immediately after switching off the UV light, the pre-treated film was irradiated with linearly polarized red light at 633 nm. The lifetime of the Z-isomer of 4-cyano-4'-alkoxy-azobenzene is comparatively long (table 2), so we can neglect the influence of the short time gap of a few seconds between the two illumination procedures. Figure 5 shows the orientational behaviour caused by this illumination procedure.

One can appreciate that a fast orientation of molecules into the x -direction takes place (positive dichroism); however, the order generated, $D = 0.04$, is quite small. But on continued exposure, the induced dichroism goes through a maximum, then passes zero and finally a preferred orientation perpendicular to the electric field vector is slowly generated (negative dichroism). This results in a quite similar orientational order to that observed upon red light

exposure without UV pre-treatment (figure 5). This change of the orientational direction of the light-induced anisotropy was observed for the first time. It indicates the competition of two different photo-orientation processes. It can be supposed that the special conditions leading to the transient parallel orientation were generated by the pre-treatment with UV light and, moreover, that these conditions disappear with the continuation of the red light exposure. In other words, it can be concluded that the photogeneration of Z-isomers is a necessary condition for parallel photo-orientation.

This conclusion can be confirmed by the behaviour of the polymer P1 with a strong donor-acceptor-substituted azobenzene group. It does not show any orientation into the x -direction, in contrast to that of the polymer P2 under the same conditions even after an intermediate UV irradiation. The reason for this can be seen in the fact that in this case the lifetime of the Z-isomer is so short that it is already transformed to the E-isomeric form before the red light irradiation process starts. So, the process establishing the parallel order cannot take place.

As discussed in the previous section, the $n-\pi^*$ transition should be responsible for the red light absorption of polymer P2, whereas that of the E-isomers is considerably smaller than that of the Z-isomers. The isotropically distributed Z-isomers therefore should be able to isomerize after absorption, but the probability for absorption also depends on the angle between the light polarization direction and the transition moment, which is for Z-isomers directed parallel to the nitrogen double bond. The question is now how it can be explained that most of the Z-isomers are incorporated in this angle-dependent photoreaction.

The orientational distribution of the azobenzene groups is constantly changed by rotational diffusion. This occurs even in the glassy state and is dependent not only on the matrix rigidity and the existence of free volume, but also on the molecular mobility and geometry of the azobenzene units and their intermolecular interactions with the polymer matrix [18]. Thus, the rotational motion of the globular Z-isomer with its much lower length-to-width ratio should be much faster compared to that of the rod-like E-isomer. The different mobilities of Z- and E-isomers on the one hand and the angle-selective Z-E isomerization on the other hand lead on average to a small enrichment of the E-isomers with their longitudinal axis in the x -direction. Thus the ensemble of all E-isomers in the film are no longer isotropic and therefore a small anisotropy parallel to the light polarization (positive dichroism) direction can be observed.

The orientation process would end after converting all Z-isomers, if the E-isomers were not able to absorb red photons. But the results with polymer P2 show that the initially induced anisotropy is erased after some minutes (figure 5). This is a consequence of the beginning of re-orientation. The possibility of any thermal influences may be excluded because of the polarization dependence of the effect. A non-zero absorbance of the E-isomers at 633 nm is assumed, which gives the molecules the ability to photo-isomerize and to establish a steady state with a small content of Z-isomers. As a result of angle-selective photo-isomerization cycles, an orientational order perpendicular to the electric field vector is established, which is typical for the conventional photo-orientation.

The order generated due to angle-selective Z-E photo-isomerization is destroyed by angle-selective photo-isomerization cycles minimizing the absorption in the polarization direction. Because only a small number of Z-isomers can be angle-selectively transformed by linearly polarized red light, the conventional photo-orientation with its multi-step accumulation will dominate as long as no other process changes the E/Z ratio, as in the case of the initial UV light irradiation.

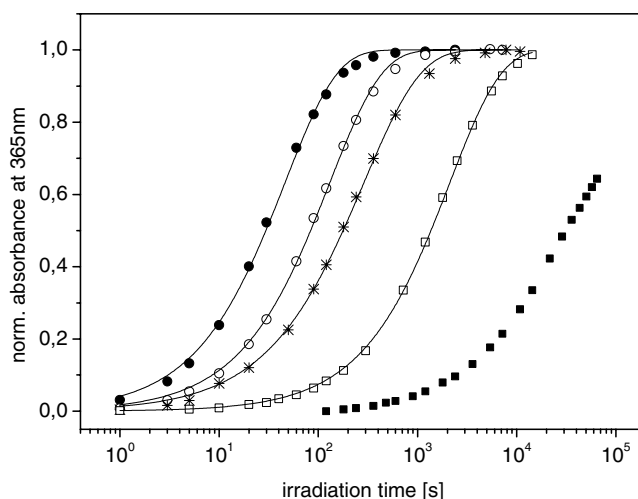


Figure 6. Comparison of photo-induced Z–E isomerizations in films of polymer P2 caused by irradiation at 633 nm with power densities of 600 mW cm^{-2} (filled circles), 300 mW cm^{-2} (open circles), 130 mW cm^{-2} (stars), 50 mW cm^{-2} (open squares) and the thermal Z–E isomerization (filled squares). The curves describe the time-dependent absorption at the maximum of the π – π^* transition of the E-isomer after UV light irradiation, which indicates the content of E-isomers. The lines indicate the approximation obtained by using the KWW function.

3.3. Red-light-induced Z–E isomerization

To confirm the postulated assumption that irradiation with red light results in an efficient Z–E photo-isomerization, the kinetic behaviour of the isomerization in thin films of polymer P2 was investigated as regards the dependence on the irradiation with red light of different power densities.

To induce a high content of Z-isomers, a number of P2 films were irradiated initially with unpolarized UV light (365 nm). After establishing the photostationary equilibrium, the absorption of the π – π^* transition of the E-isomer is measured in the individual films during the irradiation with red light at 633 nm with varied power densities ($600, 300, 130, 50, 0 \text{ mW cm}^{-2}$). The change of absorbance at 365 nm indicates the E-isomers being rebuilt by the thermal Z–E isomerization and photo-isomerization. Figure 6 demonstrates that the steady state is established in shorter times with increasing power density of the illumination. This demonstrates that Z–E photo-isomerization takes place.

Generally the Z–E isomerization behaviour in the glassy state cannot be described by a mono-exponential function, because this process is influenced by the polymer matrix. For this case the so-called Kohlrausch–Williams–Watts (KWW) (5) approximation was developed, which describes the process as a distribution of relaxations [16]. The average rate constants k_{KWW} for the photo-induced isomerization process could be derived with a β -value of 0.82 (5). The influence of the thermal Z–E isomerization could be neglected in the case of polymer P2 (figure 6). A linear dependence of the time constant of the photo-isomerization on the power density for the range up to 600 mW cm^{-2} was found, which corresponds to the Lambert–Beer law (figure 7). In other words, in this range of power densities, the photo-isomerization process does not depend on the light dose

$$A = C(1 - e^{-(k_{KWW}t)^\beta}). \quad (5)$$

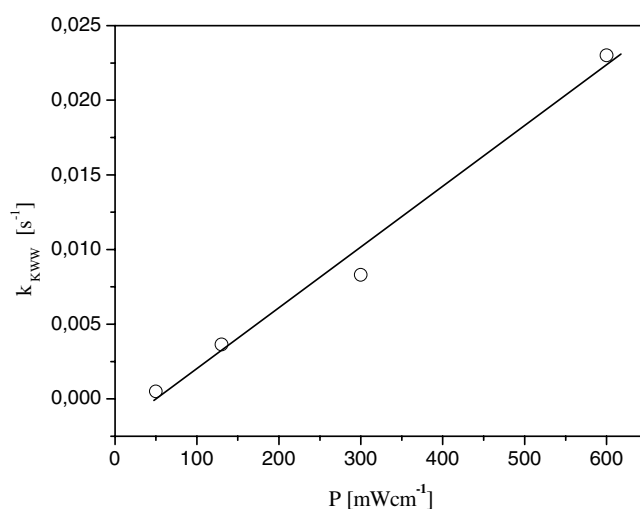


Figure 7. The dependence of the average rate constants calculated by means of the KWW approximation on the power density of irradiated light, fitted by a linear function.

3.4. Amplification of the photo-induced order

In the case of the amorphous polymers the photo-induced anisotropy generated in the glassy state is erased by annealing the films above T_g . Using the liquid crystalline homopolymer P3, the influence of the thermotropic self-organization on the photo-induced order was investigated. The thermal properties of the polymers are summarized in table 1.

The photo-induced order is for both photo-orientation processes amplified due to annealing at 70 °C, which is 12 K above T_g and therefore within the smectic mesophase of the polymer. A comparison of the dichroisms induced by the different photo-orientation processes and their amplification by annealing in the liquid crystalline phase (if possible) is given in table 2.

It can be seen that in the case of P1, irradiations with blue light at 488 nm and red light at 633 nm result in quite similar orders. In the case of P2 and P3, a comparison is not possible, because the maximum dichroism could not be established by red light illumination. After annealing, a dichroism of about 0.6 was generated in polymer P3 via both photo-orientation processes connected with the thermotropic amplification in the smectic phase. In the case of the parallel photo-orientation process, this corresponds to an amplification factor of about 22 comparing the photo-induced and the final order.

4. Conclusions

This study demonstrates that the irradiation with linearly polarized red light (633 nm) results alternatively in orientation of the azobenzene side groups parallel or perpendicular to the electric field vector of the incident light of a HeNe laser. Both orientation processes take place, although the absorbance of both azobenzene isomers is very small at 633 nm.

Without any pre-treatment, the photochromic azobenzene moieties become oriented perpendicular to the electric field vector due to the conventional photo-orientation process caused by irradiation with linearly polarized light at 633 nm.

In contrast, an orientation parallel to the light polarization was induced in all cases in which a temporary concentration of Z-isomers was generated. The process does not occur

without such photochemical pre-treatment. Moreover, it does not take place in the case of strongly push–pull-substituted azobenzene moieties because of the very short lifetime of the Z-isomers. In the last case, the conventional photo-orientation process takes place even after an initial UV irradiation.

The driving force of the conventional photo-orientation is the angle-dependent minimization of the absorbance of the incident laser light via lots of isomerization cycles. In contrast to this, the new process is based on a totally different mechanism: the angle-selective formation of a rod-like photoproduct parallel to the electric field vector.

The differences in absorbance of the two isomers at 633 nm and the related steady states are a necessary condition for this process. In contrast to the cases for all other wavelengths, most Z-isomers are transformed to thermodynamically stable E-isomers due to exposure to red light. So, the photochemical switching of a Z-rich to a Z-poor steady state by means of linearly polarized red light causes the parallel orientation.

In the case of 4-cyano-4'-alkoxy-azobenzene studied here, this order disappears on subsequent exposure and a perpendicular orientation is generated which is characteristic for the conventional photo-orientation process. This indicates that there exists a steady state of the two isomers.

The photo-induced order parallel to the electric field vector is quite small compared to that of the conventional mechanism of photo-orientation. However, the photo-induced order can be amplified by thermotropic self-organization in the case of liquid crystalline polymers. This amplification works to comparable extents for the two mechanisms, establishing either a parallel or a perpendicular orientation.

Acknowledgments

We would like to thank R Ruhman (ACA Berlin) and S Kostromin (Bayer AG, Leverkusen) for the polymers.

References

- [1] Durbin S D *et al* 1981 *Phys. Rev. Lett.* **47** 1411–14
- [2] Janossy I 1994 *Phys. Rev. E* **49** 2957–63
- [3] Stumpe J *et al* 1996 *Thin Solid Films* **284/285** 252–6
- [4] Stumpe J *et al* 1999 *Liquid Crystals III; Proc. SPIE* vol 3800, ed I Ch Khoo (Bellingham, WA: SPIE Optical Engineering Press) pp 150–63
- [5] Wu Y *et al* 2000 *Liq. Cryst.* **27** 749–53
- [6] Rutloh M *et al* 1998 *Polym. Preprints* **39** 324–5
- [7] Rutloh M *et al* 2000 *J. Inf. Rec.* **25** 39–46
- [8] Rutloh M *et al* 2000 *J. Inf. Rec.* **25** 481–6
- [9] Kulinna Ch *et al* 1994 *Macromol. Symp.* **83** 169–81
- [10] Bach H 1996 *J. Phys.: Condens. Matter* **100** 4135–40
- [11] Wu P *et al* 1998 *Phys. Rev. B* **57** 3874–80
- [12] Sanchez C *et al* 2001 *J. Appl. Phys.* **89** 5299–306
- [13] Rodekirch U *et al* 1998 *Macromol. Chem. Phys.* **199** 1943–9
- [14] Kostromin S *et al* 1996 *Polym. Sci. A* **38** 1030ff
- [15] Kulinna Ch *et al* 1998 *Macromolecules* **31** 2141–51
- [16] McArdle C B 1989 *Side Chain Liquid Crystal Polymers* (Glasgow: Blackie)
- [17] Wu P 1998 *Phys. Rev. B* **57** 3847
- [18] Eisenbach C D 1978 *Makromol. Chem.* **179** 2489–506