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Photoresponsive Behavior of Azobenzene-Based (Meth)acrylic (Co)polymers in Thin Films

Henk J. Haitjema, Gijs L. von Morgen, Y. Yong Tan, and Ger Challa*

Laboratory of Polymer Chemistry, University of Groningen, Nijenborgh 4,
9747 AG Groningen, The Netherlands

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ABSTRACT: The reversible photoisomerization and the thermal isomerization of azobenzene-based (Az.b.) groups covalently bound to (meth)acrylic (co)polymers were investigated in thin films. For the amorphous polymers it was found that a broad range of the thermal *cis* → *trans* isomerization rates could be obtained by varying the substituent, spacer, and copolymer composition. The liquid crystalline (LC) polymers showed an interesting behavior of the orientation of the stable *trans* state when exposed to visible light, during which the orientation of the Az.b. groups changed from more or less random to more perpendicular (photoselection process). This change of orientation of the Az.b. groups may be suitable for optical data storage. In principle, the orientation change is permanent, but it can be easily erased by heating the LC polymer above its isotropization temperature, on which the original random orientation is largely restored.

1. Introduction

Optical data storage materials are mainly based on organic molecules. To be suited for use as an optical data storage material, molecules have to be photochromic; i.e., they must be capable of being reversibly switched between two spectroscopically distinct forms by use of light.[1] The photochrome that we have chosen is a substituted azobenzene, which shows a *cis–trans* isomerization as illustrated in Figure 1.

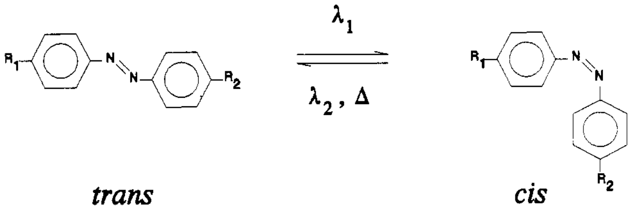

Figure 1. *Cis–trans* isomerization of Az.b. compounds (for azobenzene $R_1 = R_2 = H$).

By irradiation with light of wavelength λ_1 or λ_2 the geometric configuration of the azo bond in azobenzene-based compounds can be reversibly switched from *trans* to *cis*. The two states have distinct absorption spectra. This feature would allow reversible storage of data on the basis of *cis* and *trans* states with the aid of λ_1 and λ_2. However, the *cis* state is thermodynamically unstable with respect to the *trans* state; therefore a thermal relaxation process occurs in the dark (at room temperature) denoted in Figure 1 as Δ. This thermal back-reaction strongly limits the lifetime of the *cis* state, and it is influenced by the substituents R_1 and R_2, catalysts, temperature, and the environment (solvent polarity, type of polymer matrix) (e.g., refs 2–7).

An important factor which strongly affects the rates of both the thermal isomerization and the photoisomerization of Az.b. compounds is incorporation in a polymer matrix, either as a low molecular dispersion or incorporated in the main chain or the side chain of a polymer. The effect is dependent on the free volume distribution in the polymer matrix.[6,7] If the volume in which the Az.b. group is located is smaller than the volume that is necessary for the *trans* → *cis photo*isomerization to occur, its rate decreases because of a lower quantum yield and leads to a lower content of *cis* in the *photo*equilibrium. On the contrary, the *thermal* isomerization was accelerated and multiexponential decay kinetics was found. The explanation for the deviating kinetics in the thermal isomerization is that it is probably caused by the individual characteristics of an Az.b. group/free volume combination. If sufficient free volume is available, normal first-order decay is found; if not, a *series* of first-order decays is found.[7]

Two methods using the *trans* ↔ *cis* isomerization have been developed for use in optical data recording. The first system is based on a *photoselection* process, introduced by Wendorff et al.[8] and also used by other investigators (e.g., refs 9 and 10). It involves a change of the orientation of the *trans* azobenzene side groups with the aid of linearly (for *orientation*) polarized light. *Trans* molecules oriented parallel to a substrate but perpendicular to the plane of incoming polarized light are almost inert for *photo*isomerization and will therefore not be converted to *cis*. If a *trans* molecule is converted to *cis*, its original direction of orientation is lost. The direction of orientation of the *trans* after thermal back-reaction from *cis* is random; however, *trans* molecules perpendicular to the plane of polarization of the incoming light again are not available for *photo*isomerization. So after some irradiation time mainly perpendicular oriented (with respect to the plane of polarization of the writing beam) *trans* azo groups remain. Rapid thermal isomerization is essential for this system, since a large number of isomerization steps are necessary for the reorientation.

In the second system the *trans* ↔ *cis* isomerization of the azo compounds is used to influence a LC phase (e.g., refs 11 and 12). Now the *photo*isomerization of *trans* to *cis* destroys or changes a surrounding LC phase which is heated close to the isotropization temperature (T_i), due to the destabilization caused by the large geometrical difference between the bent configuration of the *cis* state (*cis* does not "fit") and the rodlike configuration of the *trans* state. This change in ordering after irradiation can be retained by cooling below T_g. The written data (irradiated areas) can be read with light if the sample is placed between crossed polarizers, and it can be erased by heating the LC polymer above T_i and quenching below T_g (if desired, in the presence of a magnetic or an electric field).

In this study the influence of the (co)polymer composition, substituent, spacer, and the addition of complemen-

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* Author to whom correspondence should be addressed.

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Table 1. Survey of the Structure and the Results for the Investigated Polymers

polymer code	substituent		spacer		copolymer		additions	$\lambda_{max}(t)$ (nm)	$t_{1/2}$[b] (min)
	X	Y	n	m	p	q			
I	H	$N(CH_3)_2$	0	0	0	1	—	405	120
II	H	$N(CH_3)_2$	0	0	0.5	0.5	—	405	110
III	H	$N(CH_3)_2$	6	1	0.8	0.2	—	405	60
IV	H	CO_2Et	0	0	0	1	—	325	2700
V	H	$N(CH_3)_2$	6	1	0	1	—	405	*a*
VI	CH_3	CO_2H	6	1	0	1	—	360	550
VII	CH_3	CO_2Et	6	1	0	1	—	360	*a*

[a] These LC polymers show a peculiar photoresponsive behavior and are discussed in section 4.2. [b] $t_{1/2}$ denotes the half-life time of *cis*.

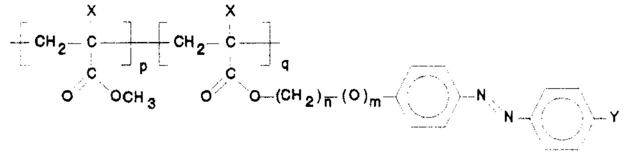


Figure 2. General structure of the (co)polymers.

tary polymers on the *thermal isomerization* will be discussed, because it has a large influence on the time needed for the writing process. The polymer systems that were studied (see Table 1) possess the general structure presented in Figure 2.

An azobenzene group with substituent Y (CO_2H, $N(CH_3)_2$, or CO_2Et) is bound to a (meth)acrylate (co)polymer, with methyl acrylate as comonomer for the acrylates and methyl methacrylate for the methacrylates, through a $-(CH_2)_n-$ spacer with n = 0, 6, or 11. The *amorphous* polymers **I** ($Y = N(CH_3)_2$; X = H; $n = 0$, $m = 0$; $p/q = 0/1$), **II** ($Y = N(CH_3)_2$; X = H; $n = 0$, $m = 0$; $p/q = 0.5/0.5$), **III** ($Y = N(CH_3)_2$; X = H; $n = 6$, $m = 1$; $p/q = 0.8/0.2$), **IV** ($Y = CO_2Et$; X = H; $n = 0$, $m = 0$; $p/q = 0/1$), and **VI** ($Y = CO_2H$; $X = CH_3$; $n = 6$, $m = 1$; $p/q = 0/1$) were investigated to establish the dependence of the rate constant of the thermal *cis* → *trans* back-reaction $k(T_{isom})$ on substituent, spacer length, and copolymer composition. After this the LC polymer **V** ($Y = N(CH_3)_2$; X = H; $n = 6$, $m = 1$; $p/q = 0/1$) was investigated in detail.

2. Experimental Section

Materials. The synthesis and the characterization of the Az.b. monomers and (co)polymers are described elsewhere.[14] The solvents used, 1,2-dichloroethane (Merck, Germany), *p*-dioxane (Janssen Chimica, Belgium), and EtOH (Merck, Germany), were of p.a. quality and used without purification. DMF (Janssen Chimica, Belgium) was distilled before use and stored over 4 Å molecular sieves. Polymers **I**, **II**, **III**, **IV**, **V**, and **VII** were dissolved in 1,2-dichloroethane, and polymer **VI** was dissolved in DMF.

Spin-Coating. Thin polymer films were prepared by spin-coating polymer solutions with a concentration of 1 wt % polymer. The layer thickness was tuned to such a level that the absorbance in the UV–vis region did not exceed the value of 1 in order to obey the law of Lambert and Beer, which is necessary to justify further kinetic analysis. The layer thickness was estimated by dissolving a spin-coated polymer film in a known amount of solvent. The concentration of the azo groups could be found by comparing the absorbance at $\lambda_{max}(t)$ of the solution with polymer solutions of known concentration. After estimation of the polymer density (≈1.5 g·cm^{-3}) in the film and measurement of the dimensions of the substrate, an estimation of the layer thickness could be obtained. The estimated thicknesses of the polymer films were on the order of 150 (±20) nm. Several substrates (glass, quartz, gold, or silicon) were used depending on the type of measurement. The UV spectra of all spin-coated films were blue-shifted compared to the UV spectra of the same polymer in solution. The shift can be ascribed to an increased interaction between the Az.b. groups within the polymer matrix.

Irradiation Apparatus. The film irradiation with UV was performed with a 1000 W xenon lamp combined with a monochromator and a shutter. The intensity was measured at 450 nm using a Spectroline DRC-100X radiometer. Films were irradiated at an intensity of 800 μW·cm^{-2} at $\lambda_{max}(t)$. The irradiated polymer films were transported in the dark to a separate Pye-Unicam SP8-200 UV–vis spectrophotometer. The films were exposed to visible light to increase the rate of *cis* → *trans* isomerization for "switching" experiments using a 15 W light bulb placed at a distance of 3 cm from the film. Its light intensity was 200 μW·cm^{-2} at 450 nm and 30 μW·cm^{-2} at 360 nm.

UV Measurements. A Pye-Unicam SP8-200 UV–vis spectrophotometer connected to a microcomputer was used to record the UV spectra as a function of time. The substrates for the films were glass slides (9 × 30 × 1 mm) for polymers **I**, **II**, **III**, and **V** and quartz (same dimensions) for polymers **IV**, **VI**, and **VII**.

IR Measurements. Infrared measurements were performed with a Bruker IFS88 FT-IR spectrophotometer equipped with an MCT-A detector. A germanium Brewster angle IR polarizer was used for both the grazing incidence reflection (GIR) and transmission experiments. GIR spectra were recorded in an 80° specular setup with light polarized perpendicular to the surface. Films were spin-coated onto a gold layer; a clean gold layer was used as a reference. Transmission spectra were recorded from films spin-coated onto a silicium substrate using 10 cycles of 1000 scans according to the method of Arndt.[13] The spectra were baseline corrected. Both GIR and transmission FT-IR have been used to determine the orientation of the Az.b. side groups in the LC polymers before and after UV and/or visible light exposure.

Polarization Microscopy. The morphology of the spin-coated films was studied with a Zeiss Axiophot polarization microscope with a camera mount and a Mettler FP-82 hot stage. The films were studied with crossed polarizers to reveal LC phases. In this case the films were spin-coated from a 10 wt % solution to obtain layers thick enough to be visible.

Degradation Experiments. The degradation experiments were performed with a Karl Zeiss MA 56 apparatus at 365 nm with an intensity of 7.1 mW·cm^{-2}.

3. Kinetic Analysis

All measurements were performed at room temperature. The thermal isomerization rate constant $k(T_{isom})$ was determined by performing UV measurements as a function of time. The amount of *trans* Az.b. group is assumed to be linearly related with its absorbance at $\lambda_{max}(t)$ since during the whole process the absorbance was less than 1. Furthermore, the *thermal cis* → *trans* back-isomerization is an irreversible process. By applying eq 1 $k(T_{isom})t$ can be computed. Plotting $k(T_{isom})t$ versus time t gives a curve with slope $k(T_{isom})$.

$$k(T_{isom})t = \ln\left(\frac{A_{trans} - A_{cis}}{A_{trans} - A_t}\right) \tag{1}$$

A_{trans} is the absorbance reached at infinite time, which is (normally) also the starting situation after storage in the dark before irradiation with UV light. A_{cis} is the absorbance measured directly after irradiation, A_t is the absorbance at time t after irradiation. Values for the absorbance were taken at $\lambda_{max}(t)$. The half-life times $t_{1/2}$ of the *cis* state were derived from

$$\text{absorption at } t_{1/2} = A_{cis} + (A_{trans} - A_{cis})/2 \tag{2}$$

$$t_{1/2} = \ln 2/k(T_{isom}) \tag{3}$$

Since eq 3 assumes a first-order process and $k(T_{isom})$ was not found to be constant during the process of thermal back-isomerization, $t_{1/2}$ was determined from eq 2.

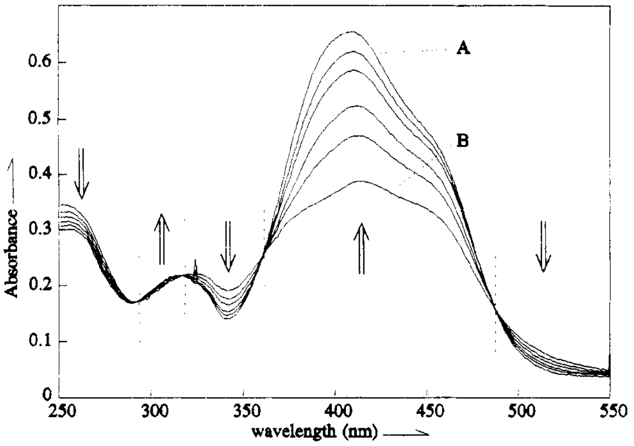
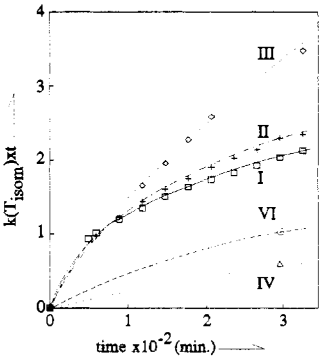


Figure 3. *Cis* → *trans* thermal back-isomerization of polymer **II**. Curve A is *trans* before UV exposure; curve B is *cis* and *trans* in equilibrium directly after UV exposure. The arrows denote the direction of the thermal back-isomerization, and the dashed lines denote the isosbetic points.



		X	Y	n	q
□	I	H	$N(CH_3)_2$	0	1
+	II	H	$N(CH_3)_2$	0	0.5
◇	III	H	$N(CH_3)_2$	6	0.2
△	IV	H	CO_2Et	0	1
○	VI	CH_3	CO_2H	0	1

Figure 4. Plots of $k(T_{isom})t$ vs time t for the amorphous polymers.

4. Results and Discussion

4.1. Amorphous Polymers. Amorphous polymers **I**, **II**, **III**, **IV**, and **VI** were irradiated by the UV xenon lamp at $\lambda_{max}(t)$ (see Table 1) during 25 min at an intensity of 800 μW/cm^2. The thermal back-isomerization process from *cis* to *trans* for polymer **II** ($Y = N(CH_3)_2$; X = H; $n,m = 0$; $p/q = 0.5/0.5$) is shown in Figure 3. The isosbestic points (denoted by dashed lines) at 485 and 360 nm are characteristic for the existence of two distinct absorbing species in equilibrium with each other. The results for the kinetic analysis ($t_{1/2}$, see Experimental Section) are gathered in Table 1 and Figure 4.

As indicated in Figure 4, the $k(T_{isom})t$ versus t relation is not linear, as would be expected for first-order kinetics. This nonlinearity is thought to be caused by the difference in the environment of the azobenzene groups.[7] The rate of the thermal isomerization is enhanced by steric factors such as limited free volume in the polymer matrix or (movements of) neighboring chain segments. The slope of $k(T_{isom})$ versus t can be regarded as a summation of individual k values, in which in the beginning fast azo groups enhance the overall rate and only slow groups remain after a period of time. This makes it impossible to give one absolute value for $k(T_{isom})$.

The various (co)polymers can be compared better by using the half-life times of the *cis* state ($t_{1/2}$), as presented in Table 1. It can be seen that a broad range of stability of the *cis* can be reached ($t_{1/2}$ ranges from 60 to 2700 min) by varying the Y substituent, spacer length, and copolymer composition.

Copolymerization with acrylate, i.e., "dilution" of the azobenzene group, has only a slight effect on the rate of the thermal isomerization (polymers **I** and **II**, Table 1). The introduction of a spacer (polymer **III**, Table 1) results in a decrease of $t_{1/2}$ by a factor of 2 due to the increased floppiness of the azobenzene group.

The variation of the substituent has the largest effect on the rate of the thermal back-isomerization. Changing from a $N(CH_3)_2$ substituent (polymer **I**) to CO_2Et (polymer **IV**) causes an increase of $t_{1/2}$ by a factor of 22, which is caused by an increase of the activation energy for the thermal isomerization due to a smaller overlap between the π–π^* and the n–π^* states. This difference in overlap can be attributed to the electronegativity difference between the substituents of the Az.b. side group.[1] The $N(CH_3)_2$ group is a strong electron donor and induces an asymmetric electron distribution within the azobenzene group resulting in a push–pull type of azobenzene (large overlap), whereas in the case of the ester group a more symmetric electron distribution is found (small overlap).

The *photo*isomerization and the thermal back-isomerization in the dark can be repeated many times, demonstrating its reversibility. Figure 5 illustrates the A_t of polymer **II** as a function of time in three UV/dark cycles. Each time the same starting absorption and a similar thermal back-isomerization process (curves A, B, and C) could be found. This process was repeated over 15 cycles without any signs of fatigue.

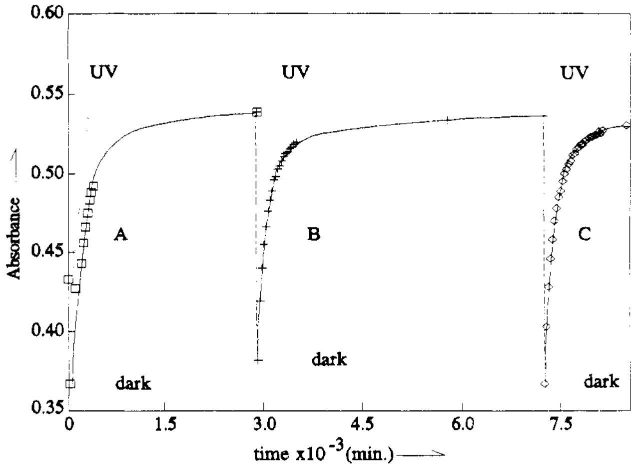


Figure 5. Repeated UV/dark cycles with polymer **II**. Curves A, B, and C show the thermal back-isomerization directly after UV exposure.

The relation between the reached *cis* concentration in the *photo*isomerization and the duration of the exposure time for polymer **II** ($Y = N(CH_3)_2$; X = H; $n,m = 0$; $p/q = 0.5/0.5$; Figure 6) indicates that exposure times of about 1 min are sufficient to reach a photostationary state with the light intensities used. This could be shortened by applying a higher light intensity. Compared to similar experiments for the same polymer **II** in solution,[14] only half of the total *trans* azobenzene groups could be converted into *cis* in a thin solid polymer film. Apparently not all Az.b. side groups in the polymer matrix are available for *photo*isomerization, which is probably mainly due to steric hindrance.

None of the polymers showed any signs of degradation during the repeated UV/dark cycles at the intensities used (800 μW·cm^{-2}), which was established with several spectroscopic techniques. To test the stability, degradation experiments were performed with 365 nm UV light with a very high intensity of 7.1 mW·cm^{-2}. These showed no change in the UV absorption spectra within 30 s. After about 5 min of irradiation the absorption in the whole UV spectrum had decreased by a few percent, but still no

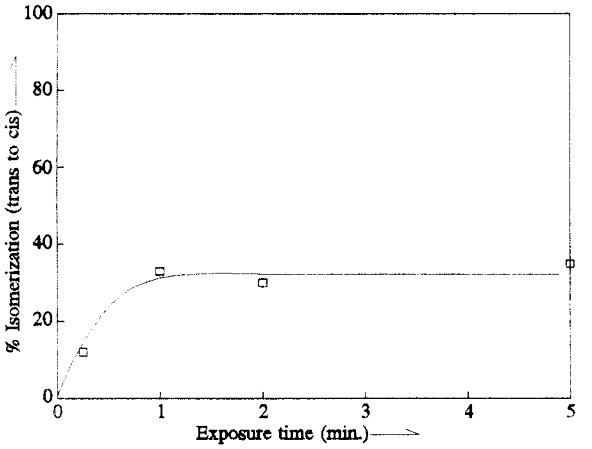


Figure 6. Conversion to *cis* as a function of UV irradiation time at $\lambda_{max}(t)$ for polymer **II**.

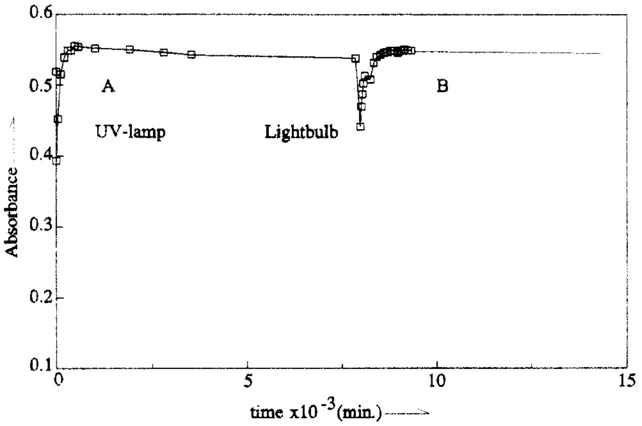


Figure 7. Absorbance at 405 nm of amorphous polymer **III** on a hydrophilic glass substrate after UV irradiation (A) and light bulb irradiation (B).

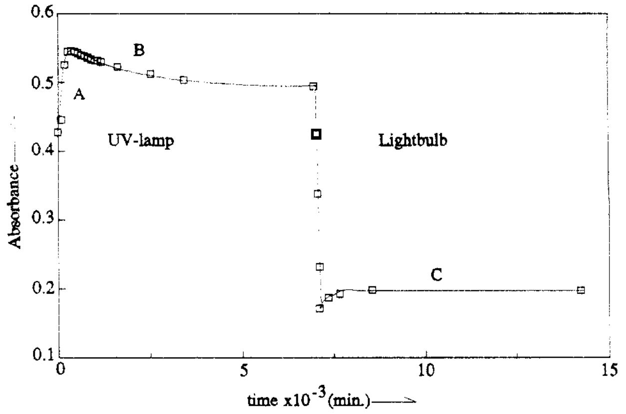


Figure 8. Absorbance at 405 nm of LC polymer **V** on a hydrophilic glass substrate after UV irradiation (A, B) and after light bulb irradiation (C).

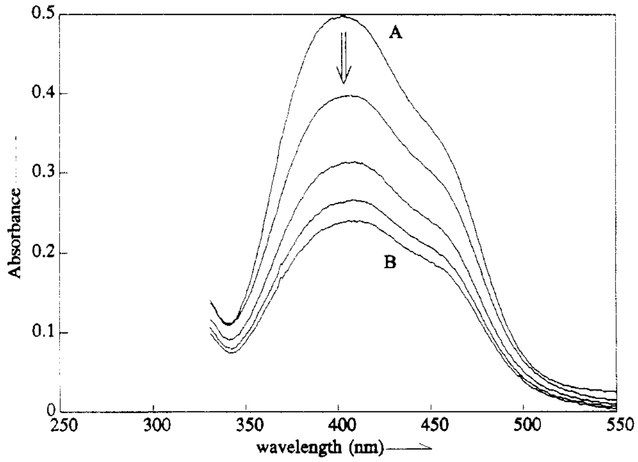


Figure 9. UV spectra of polymer **V** before (A), during (denoted by the arrow), and after (B) light bulb irradiation.

degradation products could be detected. However, the concentrations of *cis* that could be reached were about 25% lower, so obviously some degradation must have taken place.

4.2. LC Polymers. The LC polymers **V** and **VII** showed a peculiar photoresponsive behavior which strongly deviated from that of the amorphous polymers, as will be illustrated for polymer **V** ($Y = N(CH_3)_2$; $X = H$; $n = 6$, $m = 1$; $p/q = 0/1$). The absorbance at $\lambda_{max}(t)$ as a function of time (A_t) after UV and visible light exposure is depicted in Figure 8 and is compared with the amorphous analogue polymer **III** ($Y = N(CH_3)_2$; $X = H$; $n = 6$, $m = 1$; $p/q = 0.8/0.2$) in Figure 7.

First, the behavior of the polymer film *after UV irradiation* at $\lambda_{max}(t)$ (405 nm) was studied. The amorphous polymer **III** shows an increase of A_t (Figure 7, curve A) until a maximum is reached, which can be attributed to the thermal back-isomerization. The LC polymer **V** behaves differently. At first an increase of A_t (Figure 8, curve A) and then a slight decrease (Figure 8, curve B) can be noticed. This first increase can again be assigned to thermal back-isomerization because the corresponding UV spectra show isosbestic points at 485 and 360 nm as would be expected for an isomerization process in which only two distinct species are present. However, when A_t decreases again (Figure 8, curve B), these isosbestic points are not observed. Obviously, in this case no isomerization but a small change in orientation occurs (see later).

Secondly, the behavior *after visible light exposure* (by a 15 W light bulb) to promote reversible *cis* ↔ *trans* isomerization was investigated. For the amorphous polymer **III** (Figure 7) A_t decreases during exposure and increases in the dark (curve B). This could be fully ascribed to *photo*isomerization and thermal back-isomerization, respectively, according to the isosbestic points in the UV spectra. Obviously, the light bulb promotes the *photo*-isomerization rather than the *thermal* isomerization. The LC polymer **V** again shows a different behavior (Figure 8). A_t decreases sharply during the visible light irradiation and increases only slightly to a stable level in the dark after the irradiation (curve C). During irradiation no isosbestic points are found in the corresponding UV spectra (Figure 9), and the sharp decrease of A_t during visible light exposure occurs also when the glass surface was made hydrophobic. The sharp decrease will be attributed to a change in the orientation of the *trans* Az.b. side groups, and the very small increase in the dark after irradiation is caused by thermal back-isomerization. This means that the remaining low absorption is not caused by the *cis*, which was confirmed by the corresponding UV spectra showing a typical *trans* spectrum.

Reorientation of *Trans* Azobenzene Groups. The behavior of the LC polymer during visible light irradiation will be ascribed to a change in the orientation of the Az.b. side groups. This can be deduced from FT-GIR and transmission measurements. The IR spectra of the polymer film before and after exposure to visible light and the resulting difference spectra are presented in Figures 10 and 11.

The transmission spectra (Figure 10) show a *decrease* of the absorptions in the region 1800–1000 cm^{-1} (from the Az.b. side groups; see Table 2) induced by the visible light

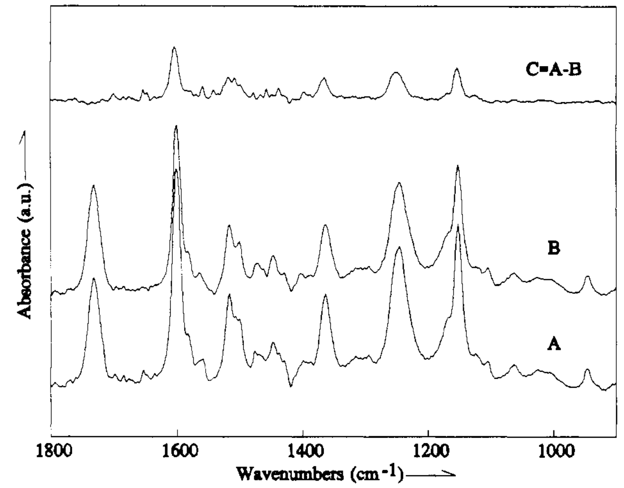


Figure 10. IR transmission spectra of polymer V before (A) and after (B) light bulb irradiation. C is the difference spectrum A–B.

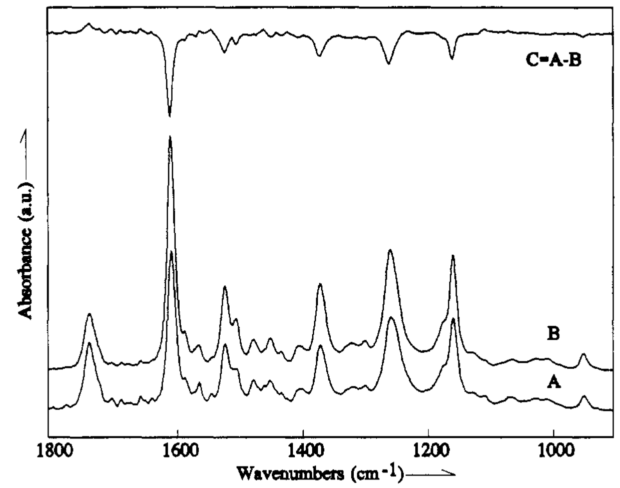


Figure 11. IR-GIR spectra of polymer V before (A) and after (B) light bulb irradiation. C is the difference spectrum A–B.

Table 2. Absorbing Groups in the IR Spectrum of Polymer V

wavenumber (cm^{-1})	absorbing group
1731	C=O stretch
1601	C=C aromatic stretch
1517	C=C aromatic stretch
1363	C—N Ar-amine
1246	coupled motion C—O—C
1152	C—O ether

irradiation. The same absorptions *increase* in the GIR spectra (Figure 11). This indicates clearly that during the visible light irradiation the Az.b. side groups reoriented from a more or less random orientation (with larger absorptions in the transmission spectrum) to a more *perpendicular* orientation (with larger absorptions in the GIR spectra) relative to the substrate surface.

Process of Reorientation. To distinguish between the effects of local heating caused by the light bulb used on the one hand and the *photo*isomerization of the azo groups on the other hand, the samples were kept in the dark at elevated temperatures above T_g and below T_i. A hydrophilic substrate was used to prevent the polymer from creeping up, as it did with a hydrophobic substrate in a similar experiment. It was found that the azo group did not reorient from random to perpendicular as in the case of light bulb irradiation. Thus the heating of the LC phase alone is not enough for the reorientation process to take place.

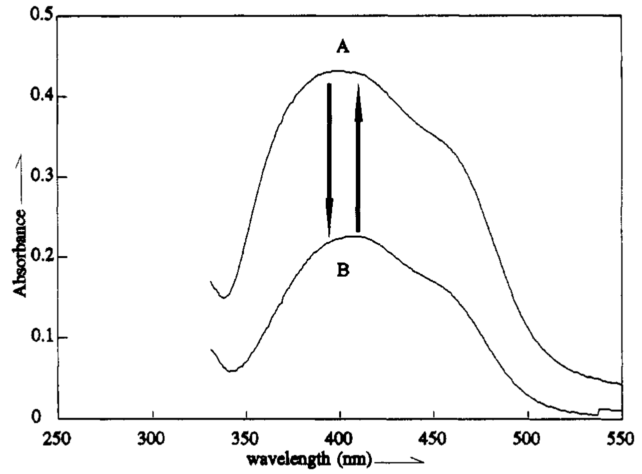


Figure 12. Reversible change of the orientation of the Az.b. side groups in polymer V. B is reached after light bulb exposure, and A is reached after heating above T_i and quenching to $T < T_g$.

Four types of light irradiation were used in the experiments: UV light consisting of a narrow ($\lambda_{max}(t) \pm$ 5 nm) or a broad ($\lambda_{max}(t) \pm 50$ nm) wavelength area with high intensity, or a light bulb with light consisting of a very broad wavelength area (360–800 nm) with low or high intensity. The reorientation process *only* occurred if light consisting of a broad wavelength area was used, and it was accelerated by an increase of the intensity of irradiation. Irradiation with a broad wavelength area instead of a narrow one resulted in a photostationary state in which less *cis* is present, due to an enhanced *photo-back*-isomerization from *cis* to *trans*, compared to irradiation with a wavelength at $\lambda_{max}(t)$ which results in a *cis*-rich photostationary state.

Apparently, the original LC (nematic) ordering will be broken up by the isomerization processes in such a way that the LC groups are relatively free to alter their orientation without losing the LC ordering completely. Increasing the intensity of the irradiation results in a larger number of excitation events and also in an increase of the chain movements, both of which enhance the speed of the reorientation. The most favorable orientation seems to be perpendicular to the substrate surface, which is most probably due to the *photoselection effect* described in the Introduction. As the Az.b. side groups in the LC polymers interact with each other, it is conceivable that the reorientation of a few Az.b. side groups in a LC domain reorient the whole domain, which makes the reorientation process much more effective than in the case of the amorphous polymers.

Read–Write Cycles. The lower absorbance corresponding with the enhanced (perpendicular) orientation introduced by light bulb irradiation (Figure 12, B) can be erased when polymer V is heated above T_i and cooled quickly below T_g. In this way a more or less random orientation (with respect to the substrate) is formed again and as a result the overall absorptions increase again (Figure 12, A).

Read–write cycles, as shown in Figure 13, can be achieved by irradiation (C) with visible light containing both λ_1-(*trans*) and λ_2(*cis*) (see Figure 1), which results in a strong decrease of the overall absorption in the UV–vis spectra (from level A to B), and subsequent heating above T_i and quenching of the sample (D), which results in a restoration of the absorption level (from B to A).

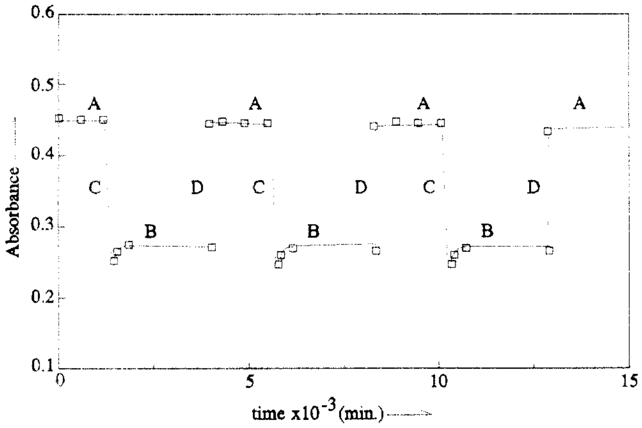


Figure 13. Polymer V read and write cycles: writing with light bulb exposure (C) from absorbance level A to B which can be read and erasing by heating above T_i and quenching (D) to restore absorbance level A.

The information that is stored as a change in the orientation of the Az.b. side groups can be read with low-intensity light bulb radiation (a few μW.cm^{-2}) in the absorption band of the Az.b. side groups, but this might still lead to some loss of contrast in the stored information because also the previously nonirradiated areas are irradiated now. Because the orientation in the irradiated and the nonirradiated areas is different, and hence the indices of refraction, the optical readout probably can also be done with light *outside* the absorption band of the Az.b. side groups. In that case the readout might be completely nondestructive.

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