Optical switching of azophenol derivatives in solution and in polymer thin films: The role of chemical substitution and environment

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Abstract: Design of polymer materials whose properties can be reversibly changed by illumination with light is a technology of particular scientific interest. Such materials contain molecular chromophors, which change their geometry and/or polarity upon absorption of light of a specific wavelength. The most prominent chromophores are azobenzene derivatives. Here, we present a systematic study on azobenzene derivatives in order to quantify the impact of chemical substitution and chemical environment on the dynamics of light-induced trans-cis isomerization (at 368 nm and 355 nm), thermal cis-trans relaxation, and light-induced cis-trans isomerization (at 434 nm). Systems under investigation were 4-hydroxyazobenzene (4-HAB) in acetonitrile (MeCN) solution and in a poly(methylmethacrylate) (PMMA) matrix. These two systems are compared to systems in which 4-HAB is esterified, namely 4-hydroxyazobenzene covalently bound (esterified) to PMMA matrix, and N-(tert-butoxycarbonyl)glycine-4- hydroxyazobenzene (Boc-Gly-4-HAB) in MeCN and in PMMA. Photoisomerization and thermal relaxation kinetics are monitored with UV-vis absorption spectroscopy and accompanied by quantum chemical calculations to shed light into the molecular origin of observed differences in switching properties. We find that the chemical environment (MeCN vs. PMMA) only has minor impacts (~10%) on trans to cis photoisomerization rates. Also, the impact of chemical environment on thermal cis to trans relaxation is small; with relaxation rates in PMMA beeing < 35% smaller compared to rates in MeCN solution. However, the thermal cis to trans relaxation rates of 4-HAB are clearly faster (factor > 400) than the rates of esterified systems. This difference is a clear result of the different substituents on the azobenzene moiety. Quantum chemical calculations suggest that the cis-configuration in the esterified systems is stabilized by an intramolecular H-bond between a carbonyl oxygen on the substituent and an H atom on the phenyl ring. In all systems, the cis to trans isomerization can be significantly accelerated by illumination with 434 nm light. For esterified systems, accelerations by factors of about 5700 – 15500 are observed. In the case of 4-hydroxyazobenzene covalently bound (esterified) to the PMMA matrix, complete light induced transfer from cis to trans is possible. In addition, it features a low thermal cis to trans isomerization rate and acceptable photoinduced trans to cis isomerization properties. With this, the material fulfills the basic requirements of a functional polymer material whose properties can be reversibly changed by illumination with light.

Keywords: Azobenzene Derivatives, Azophenol, Trans - Cis Isomerization, Photoisomerization, Thermal Relaxation, Chemical Environment, Chemical Substitution, Functional Polymer

1. Introduction

Using light for a variety of manufacturing, controlling, information processing and many other purposes is of particular interest in diverse fields. At the same time, the number of new applications involving light is increasing at an

exceptionally high rate, in particular in the field of high precision applications. In this regard, photoresponsive systems have received increasing attention over the last years, owing to their broad applicability in a number of key fields such as optical memories,[1-5] molecular machines,[6-11] molecular switches,[12-15] photocontrol of biomolecules[16-20] and polymers[21-23], and surface relief gratings[24,25] etc.

One promising technology of particular scientific interest involves polymer materials whose properties can be reversibly changed by illumination with light. Polymeric materials can be controlled by light if they contain molecular chromophors. Suitable chromophores are able to change their geometry and/or polarity upon absorption of light of a specific wavelength. And advantageously, the initial state can be restored with light of a different wavelength. If the chromophore is chemically bound to a polymer network, this principle can be used to reversibly change properties of the respective polymer material.

The ideal chromophore for such applications features two stable states (e.g. conformations). Selective and efficient light induced transfer between the states is possible and light induced cycling between the states can be performed an unlimited number of times.

Among the photoswitches available today, azobenzene and its derivatives are of particular interest in this regard.[1-3,7,12-26]

Figure 1. General scheme of the potential energy curves of the trans-cis isomerization process after excitation of the ππ* and nπ* transition for azobenzene in solution, adapted from the results of calculations reported in Ref. 27.

Azobenzene and its derivatives can be efficiently "switched" from their trans conformation to their cis conformation upon the absorption of light of a suitable wavelength (see Figure 1). In general, the trans conformation is the thermodynamical most stable conformation and the photoinduced switch to the cis conformation is characterized by high quantum yields. Furthermore, azobenzenes possess low photochemical fatigue and can be easily functionalized for a wide variety of photoactive materials. The photoinduced isomerization of azobenzene has been used to selectively change properties of azobenzene containing systems: absorption spectra, dielectric constants, refractive indices, oxidation/reduction potentials, phase transitions, and surface wettability.[28]

In general, the switching performance of azobenzene is influenced by chemical substituents and the chemical surrounding of the chromophore (e.g. solvents, polymer matrices, and temperature)[29-44] While a number of azobenzene-compounds with great switching properties is known from experiments in solution, it is not always clear how these properties change quantitatively when the azobenzene-molecules are incorporated into a polymer network. We have thus performed a systematic study in order to quantify the impact of a polymeric environment on the dynamics of light-induced trans-cis isomerization, thermal cis-trans relaxation, and light-induced cis-trans isomerization.

A particular focus of our study is on the thermal cis-trans relaxation, as the thermal stability of the cis-conformation (over days or even months) is a prerequisite for many applications e.g. in the field of optical storage devices.[45] In contrast, azobenzenes with a very fast thermal isomerization process (~ tens of milliseconds) are required for optical switching and real-time optical information processing.

In our systematic study, we investigated the switching properties of 5 systems (Figure 3):

(1) 4-HAB: 4-hydroxyazobenzene in acetonitrile (MeCN). In previous work, the thermal stability of cis-azobenzene was found to depend strongly on the chemical environment and the chemical substituents.[42,46,47] In particular, the thermal relaxation lifetime for cis-4-hydroxyazobenzene (4-HAB) at room temperature is very short (0.2 second) in protic ethanol solvent, whereas it is substantially longer in nonpolar toluene (31 min).[47] A limited number of studies has been devoted to the investigation of photochemical and thermal relaxation behaviors of 4-HAB and its derivatives in solution and in polymer matrices.[48]

(2) Boc-Gly-4-HAB: N-(tert-butoxycarbonyl)glycine-4-hydroxyazobenzene in MeCN. In this compound, the –OH group of 4-HAB is esterified. Compared to (1), differences in switching properties are thus a direct consequence of different chemical substituents.

(3) 4-HAB/PMMA: 4-hydroxyazobenzene embedded in poly(methyl methacrylate) (PMMA) matrix. The PMMA film contains individual 4-HAB molecules. The 4-HAB molecules are thus in a solid environment, whereas they are in liquid environment in (1).

(4) Boc-Gly-4-HAB/PMMA: N-(tert-butoxycarbonyl) glycine-4-hydroxyazobenzene embedded in PMMA matrix.
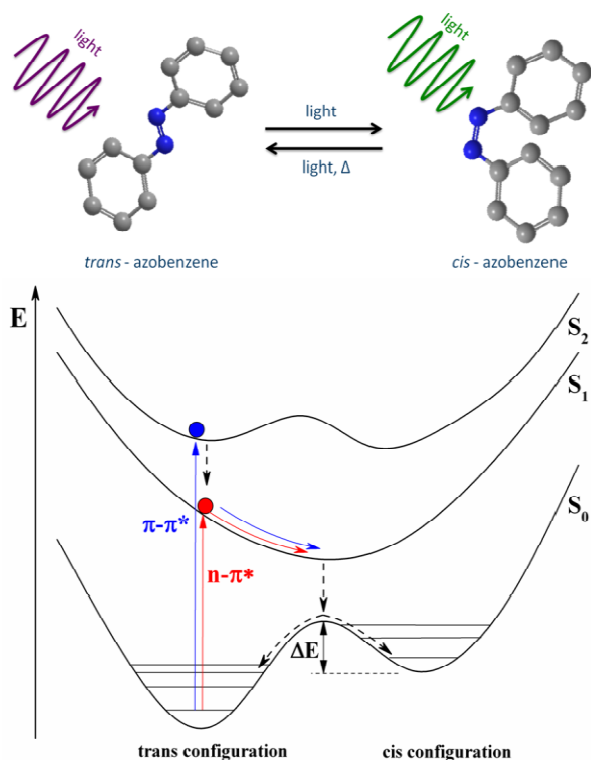
(5) 4-HAB-PMMA: 4-hydroxyazobenzene covalently bound to PMMA matrix. As in (3) and (4), the –OH group of 4-HAB is esterified.

With this systematic study we shed light onto the impact of chemical structure and chemical environment on the switching properties of azobenzene derivatives. The kinetics of photoinduced and thermal isomerization of systems (1)-(5) were monitored by UV-vis spectroscopy. Our experimental results were flanked by quantum chemical calculations to gain insights into the molecular origin of the observed differences in switching properties. The combination of experimental and theoretical investigations provides crucial information for the rational design of novel photoactive materials.

2. Experimental Section

Materials. All chemicals were purchased from Sigma-Aldrich and used as received. 4-Hydroxyazobenzene (4-HAB) was used after recrystallization from ethanol. Details on the syntheses and analytical data are given in the Appendix.

Synthesis of Boc-Gly-4-HAB (2). The coupling of N-(tert-butoxycarbonyl)glycine and 4-hydroxyazobenzene was performed using standard peptide coupling reagents like N,N,N',N'-tetramethyl-O-(benzotriazol-1-yl)uronium tetrafluoroborate and 1-hydroxybenzotriazole hydrate. The solvent was N,N-dimethylformamide and N-ethyldiisopropylamine was used as base. The reaction yielded 67% of an orange powder. Samples (1) and (2) were prepared by dissolving 4-HAB and Boc-Gly-4-HAB in MeCN, respectively. Concentrations were 20   mol dm-3.

Synthesis of 4-HAB/PMMA (3) and Boc-Gly-4-HAB/PMMA (4): The films were prepared by dissolving PMMA powder and 4-HAB or Boc-Gly-4-HAB in toluene. The solution was concentrated until most of the solvent was removed. Then, the solution was coated onto a stainless steel plate with a spatula. The films were removed after the solvent was completely evaporated. The obtained 4-HAB/PMMA and Boc-Gly-4-HAB/PMMA films were 0.3 mm and 0.5 mm thick, respectively, with 0.1 wt% azochromophores.

Synthesis of 4-HAB-PMMA (5): 4-(phenyldiazenyl)phenyl methacrylate was synthesized from 4-hydroxyazobenzene and methacryloyl chloride with triethylamine as base and diethylether as solvent according to literature procedure.[49] The reaction yielded 66% of an orange powder. 4-(phenyldiazenyl)phenyl methacrylate, methyl methacrylate, and AIBN (azobisisobutyronitrile) were mixed in a beaker and put in a domestic microwave oven. The reaction mixture was irradiated with a power of about 350 W in intervals of 90, 30 and 20 s, interrupted by 120 s breaks to avoid sputtering. The highly viscous mixture was poured in methanol and the precipitate was washed and dried at room temperature. For the film preparation, the polymer was solved in toluene and heated on a plate. The viscous mixture was coated of a stainless steel plate after most of the solvent was evaporated. The films were removed after evaporation of toluene. The

obtained film thickness was 0.5 mm with 0.03 wt% azochromophore (4-(phenyldiazenyl)phenyl methacrylate).

Physico-Chemical Characterization. The products were characterized by ^{1}H-NMR and ^{13}C-NMR using a BRUKER Advance Ultra Shield 600 MHz spectrometer with a 5 mm BBO probe head. The chemical shifts (δ) are given in parts per million (ppm) and referenced to the solvent signal. IR measurements were carried out on a FTS 6000 spectrometer from BIO-RAD using the ATR modus. The glass transition temperatures were measured with a DSC 8500 PERKIN ELMER (heating rate 10 K·min^{-1}, inert gas nitrogen). The determination of the molar mass was made via size exclusion chromatography (SEC) using dimethyl formamide as mobile phase with 0.33 ml·min^{-1} flow rate on a GRAM column (Company Polymer Standards Service, 4.6 mm diameter). The MS analysis was performed with a BRUKER „autoflex speed". The samples were crystallized on a pre-spotted AnchorChip (PAC) target with α-cyano-4-hydroxycinnamic acid (HCCA) matrix from a 1 μl acetonitrile/trifluoroacetic acid (TFA) (80:0.1) solution.

Photochromic experiments. The kinetics of photoinduced isomerization and thermal relaxation processes of the systems under investigation were followed by measuring UV-vis absorption spectra with a UV 2101 PC (Shimadzu) UV–vis spectrometer. Liquid samples (1) and (2) were measured in a 10 mm cuvette; solid films (3), (4), and (5) were inserted into a 1 mm cuvette. All experiments were performed at room temperature. A 450 W Xenon lamp (XBO 450, Osram) with a 5 cm water-filter and suitable interference filter (355 nm, 368 nm, 434 nm) was used for irradiation of the samples. We note that the bandwidth (FWHM) of the filters is 10 nm. The light intensity at the sample was 9 mW cm^{-2} for 355 nm, and 12 mW cm^{-2} for 368 nm and 434 nm.

Quantum Chemical Calculations. Quantum chemical calculations were done using the Density Functional Theory (DFT) B3LYP method[50,51] (Jaguar version 8.3 program)[52]. The structures of studied molecules were optimized at B3LYP/6-31(d,p) level both in gas phase and in solvent (acetonitrile). The interactions between the molecule and the solvent were evaluated at the same level of theory by Jaguar's Poisson-Boltzmann solver (PBF)[53] which fits the field produced by the solvent dielectric continuum to another set of point charges. The frequency analysis was made at the same level of theory to characterize the stationary points on the potential surface and to obtain thermodynamic parameters such as total enthalpy (H) and Gibbs free energy (G) at 298 K. The reaction enthalpies (ΔH) and Gibbs free energies of reaction (ΔG) were calculated as the difference of the calculated total enthalpies H and Gibbs free energies G between the reactants and products respectively. The electronic structure of studied molecules, namely molecular orbitals, Mulliken atomic charges, spin density distribution and energy of excited states were further analyzed using Gaussian 03 program.[54] The electronic transition spectra were calculated using time-dependent density functional theory (TDDFT)[55] both in the gas phase and with the PBF solvation model as implemented in Jaguar version 8.3 program package

with the full linear response approximation.[56]

3. Results and Discussion

3.1 UV-Vis Absorption Spectra of Samples (1) - (5) are Presented in Figure 2
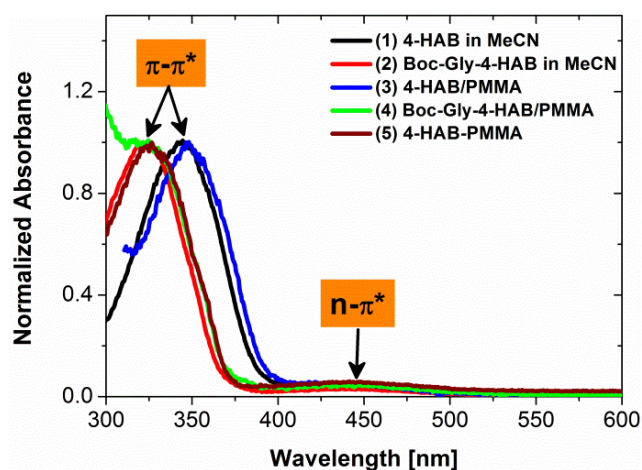

Figure 2. *UV-vis absorption spectra of samples (1) – (5)*

The spectra show the characteristic absorption bands of trans-azobenzene compounds, indicating that the azobenzene chromophores are in their thermodynamically most stable trans-configuration. The spectra exhibit a weak absorption band in the visible region, centered at about 440 nm, which corresponds to a symmetry-forbidden $n \rightarrow \pi^*$ transition. The strong absorption band centered at about 350 nm for samples (1) and (3), and at about 325 nm for (2), (4), and (5) corresponds to the symmetry allowed $\pi \rightarrow \pi^*$ transition. PMMA strongly absorbs below ~ 300 nm and prohibits evaluation of azobenzene-absorption bands below 300 nm for polymer samples (3)-(5). The spectral data of the investigated systems are given in Table 1. The spectral parameters of 4-HAB in MeCN agree well with the data in literature.[47] The $\pi \rightarrow \pi^*$ absorption band of 4-HAB in polar aprotic MeCN and the respective band in nonpolar PMMA matrix are similar. In the PMMA sample, a slight red shift of the band is detected, which we attribute to the different polarity of the environment.

In agreement with this finding, the spectra of Boc-Gly-4-HAB in MeCN and PMMA are similar.

Comparison of 4-HAB samples (1) and (3) with the esterified samples (2), (4), and (5) reveals the effect of different chemical substitution on the azobenzene moiety. The esterified samples exhibit a blue shift of the $\pi \rightarrow \pi^*$ band by about 20 nm. This shift is attributed to the electron-withdrawing character of the (–O–CO–) substituent.

3.2 Photoinduced Trans to cis Isomerization

In case the absorption spectrum of trans- and cis-configuration is significantly different, the kinetics of trans-cis isomerization can be monitored with UV-vis absorption spectroscopy. In the present experiments, we illuminated the samples with UV light at 368 nm and 355 nm (355 nm data shown in appendix). The experiments were performed as follows: A sample was irradiated for a certain amount of time and then inserted into the spectrometer to record a UV-vis absorption spectrum. Irradiation of the sample was afterwards continued and another spectrum was measured. The time needed for recording the spectrum, was kept to a minimum (approx. 45 s) to minimize inaccuracies from thermal cis-trans relaxation. The resulting series of spectra are shown in Figure 3. Irradiation of sample (1) 4-HAB in MeCN at 368 nm, results in a decrease of the absorption band at 350 nm and an increase of the absorption band at 440 nm. After a total irradiation time of 480 s, no further change in the UV-vis absorption spectrum upon further irradiation is observed (see Figure 3). This indicates that a photostationary state (PSS) is reached. The absorption spectrum in the PSS is distinctly different from the initial trans-spectrum indicating that photoinduced isomerization at 368 nm allows an almost complete transfer of trans- into cis isomer. We note that the irradiation wavelength of 368 nm was specifically selected to be on the red wing of the $\pi \rightarrow \pi^*$ transition, where absorption of the cis-isomer is small, allowing quantitative light-induced transition from trans to cis. Furthermore, the series of absorption spectra is characterized by the presence of two isosbestic points at 296 nm and 404 nm. This confirms the existence of only two absorbing species, i.e. the trans- and cis-isomers.
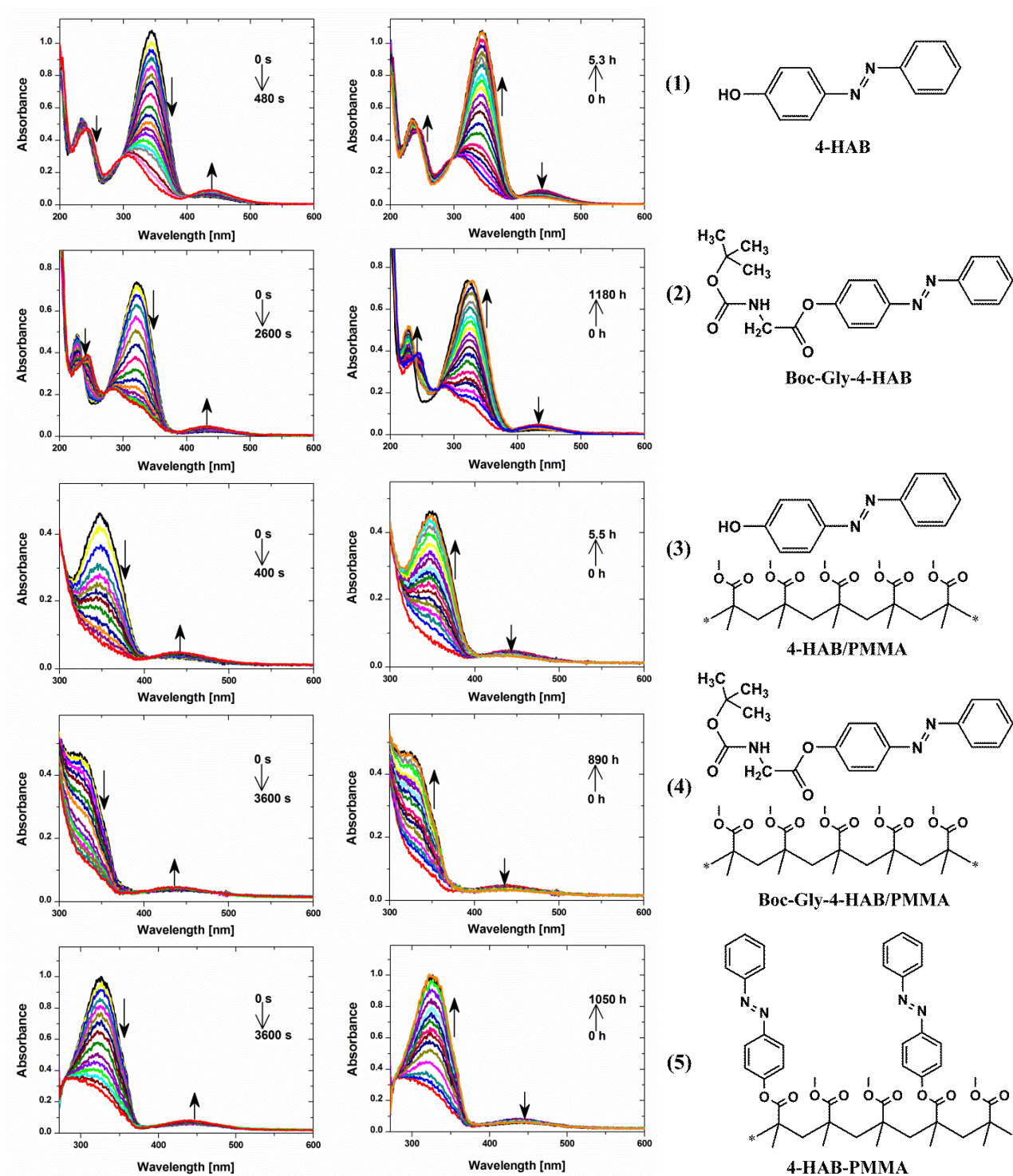
Table 1. *Spectral properties of samples (1) – (5). Values for Cis-isomers were extracted from the PSS-spectra of the photoinduced trans to cis isomerization experiments.*

		λ_{max} [nm] (ε [M^{-1} cm^{-1}])			
		Trans-		**Cis-**	
		$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$
1	4-HAB	346 (51000)	436 (2410)	308 (14900)	436 (4200)
2	Boc-Gly-4-HAB	325 (32000)	440 (950)	285 (10820)	438 (1850)
3	4-HAB/PMMA	348	436	-----	436
4	Boc-Gly-4-HAB/PMMA	325	438	-----	438
5	4-HAB-PMMA	327	440	-----	440

Figure 3. *Chemical structure of samples (1) – (5), and the variation of UV-vis spectra of sample (1) – (5) after illumination with 368 nm (left column) and thermally recovered (right column) at room temperature.*

Table 2. *Rate constants for photoinduced trans to cis isomerization (k_{tc}) at 368 nm and 355 nm, thermal cis to trans isomerization (k_b) and photoinduced cis to trans isomerization (k_{ct}) at 434 nm.*

		$k_{tc}^{368\,nm}$ a $[s^{-1}]$	$k_{tc}^{355\,nm}$ a $[s^{-1}]$	$k_{ct}^{434\,nm}$ a $[s^{-1}]$	$k_b\,[s^{-1}]$
1	4-HAB	$1.4×10^{-2}$		$2.1×10^{-2}$	$8.9×10^{-4}$
2	Boc-Gly-4-HAB	$2.3×10^{-3}$	$1.4×10^{-3}$	$1.4×10^{-2}$	$0.9×10^{-6}$
3	4-HAB/PMMA	$1.6×10^{-2}$	$1.3×10^{-2}$	$1.8×10^{-2}$	$5.8×10^{-4}$
4	Boc-Gly-4-HAB/PMMA	$2.3×10^{-3}$	$1.6×10^{-3}$	$8.5×10^{-3}$	$1.1×10^{-6}$
5	4-HAB-PMMA	$2.1×10^{-3}$	$1.5×10^{-3}$	$7.4×10^{-3}$	$1.3×10^{-6}$

a The error is ± 10%

The series of spectra obtained for sample (2) Boc-Gly-4-HAB in MeCN shows a similar behavior (Figure 3). Isosbestic points are found at 270 nm and 385 nm. The PSS is reached after a total illumination time of 2600 s. This indicates a slower kinetic of light-induced trans to cis isomerization compared to sample (1) 4-HAB for irradiation at 368 nm.

For the polymer film samples (3)-(5), the PSS is reached after a total illumination time of 400 s for sample (3) 4-HAB/PMMA, and after 3600 s for sample (4) Boc-Gly-4-HAB/PMMA, and sample (5) 4-HAB-PMMA.

In order to quantify these differences, photoisomerization kinetics of samples (1) - (5) were evaluated. According to equation (1), rate constants k_{tc} are obtained via the change in absorption at the wavelength at which the initial maximum of the $\pi \rightarrow \pi^*$ transition band is centered. These wavelengths are listed in Table 1 (values for the trans isomer).

$$\ln[(A_0 - A_{pss})/(A_t - A_{pss})] = k_{tc}\, t \qquad (1)$$

A_0, A_t and A_{pss} are the absorbances at this wavelength at times 0, t, and infinite (=PSS), respectively.[57] The plots of $\ln[(A_0 - A_{pss})/(A_t - A_{pss})]$ vs. illumination time (t) are shown in Figure 4.
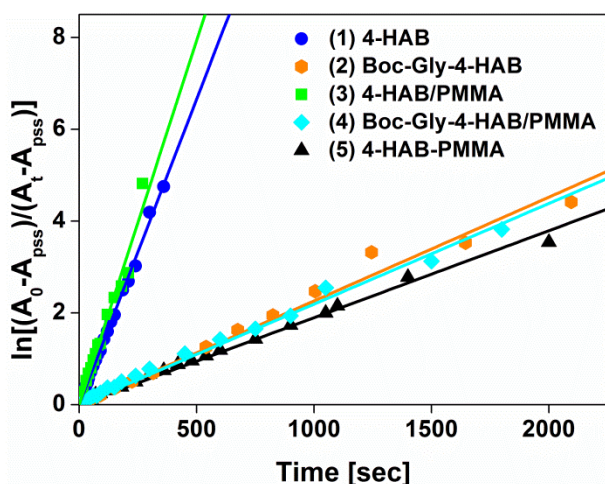

Figure 4. *Kinetics of photoinduced trans to cis isomerization of systems (1) – (5) with 368 nm. Linear functions (solid lines) are fitted to the data, and rate constants (k_{tc}) are obtained from the slopes of the linear functions.*

For all samples, the data in these plots is well represented by a linear function, indicating first-order kinetics. Rate constants (k_{tc}) are obtained from the slope of the linear function and summarized in Table 2.

We note that these rate constants are specific to the irradiation wavelength of 368 nm. According to equation (2) the rate constants (k_{tc}) for different systems depend on several parameters: [57]

$$k_{tc} = 2.303\ I\lambda\ (\varepsilon_t \Phi_{tc} + \varepsilon_c \Phi_{ct}) + k_b \qquad (2)$$

where Φ_{tc} and Φ_{ct} represent the quantum yields of the trans-cis and cis-trans photochemical reactions, ε_t and ε_c represent the molar extinction coefficients of the trans and cis isomers at the

illumination wavelength, I_λ is the intensity of the irradiation wavelength, and k_b is the rate constant for the thermal cis to trans isomerization. According to equation (2), the observed differences in rate constants in our experiments originate from two points:

(a) Differences in the molar extinction ε at the irradiation wavelength of 368 nm.
(b) Differences in quantum yields Φ related to the different chemical substituents on the azobenzene moiety and the chemical environment.

As k_b is small in all investigated systems at room temperature, its influence on the observed k_{tc} is small (see thermal relaxation section 2.2 and results in Table 2).

Table 2 demonstrates that rate constants for systems (1) 4-HAB in MeCN and (3) 4-HAB/PMMA are identical within experimental accuracy. Also identical are the rate constants for system (2) Boc-Gly-4-HAB in MeCN and (4) Boc-Gly-4-HAB/PMMA. As the molar extinction ε is not expected to change significantly with chemical environment (MeCN vs. PMMA), these results suggest that the quantum yields (Φ) are not influenced by the chemical environment.

A similar trend was observed by Paik et al.[30] and Sin et. al.[35] in experiments on polymers containing azobenzene side chains. The azobenzene moiety exhibited approximately similar photoisomerization kinetics in dilute solutions and in polymer films above and below the polymers glass transition temperature, respectively.

Another interesting finding is that the rate constants obtained for systems (5) 4-HAB-PMMA, (2), and (4) are identical within the accuracy of the experiment. Assuming that the molar extinction ε at the excitation wavelength is similar for these systems, this indicates that the far structure of the substituent, beyond the ester function directly attached to the azobenzene system, does not influence the photoisomerization kinetics.

We further find that rate constants of systems (2), (4), and (5) are one order of magnitude smaller than those of systems (1) and (3). This finding might be the result of different molar extinction coefficients at the excitation wavelength of 368 nm. We note that for systems (2), (4), and (5) this excitation wavelength is on the red edge of the $\pi \rightarrow \pi^*$ absorption band. However, additional experiments at 355 nm (see appendix and Table 2) indicate that also the quantum yields Φ are different for the two types of chemical substituents on the azobenzene moiety: -OH (in (1) and (3)) and ester (in (2), (4), and (5)).

3.3 Thermal Cis to Trans Isomerization

The kinetics of thermal cis to trans isomerization were monitored as follows: The samples were irradiated at 368 nm, according to the experiments described above, until the photostationary state was reached. Samples were then kept in the dark (at room temperature) and the thermal cis to trans relaxation was followed by recording UV-vis spectra. The resulting series of spectra for systems (1) - (5) are shown in Figure 3 (right column). Comparison to the start spectra of photoinduced trans to cis isomerization experiments (Figure 3,

middle column) demonstrates that complete recovery of the initial signal occurs. Only the final spectrum of (2) Boc-Gly-4-HAB in MeCN solution slightly deviates from the initial trans spectrum. We attribute this to inaccuracies in data recording, originating from the long time over which the sample has been measured during relaxation experiments.

Figure 3 reveals significant differences in the timescales of relaxation. While relaxation in systems (1) and (3) is completed within a few hours, complete relaxation in systems (2), (4), and (5) takes over one month.

We quantify the thermal cis to trans isomerization kinetics by evaluating the series of spectra obtained for systems (1) to (5) according to equation (3). Similar to the case of photoinduced trans to cis isomerization, rate constants are obtained via the change in absorption at the wavelengths at which the maximum of the $\pi \rightarrow \pi^*$ transition band (of the trans isomer) is centered. For all systems, these wavelengths are listed in Table 1 (values for trans isomer).

$$\ln[(A_\infty - A_0)/(A_\infty - A_t)] = k_b\, t \quad (3)$$

A_0 and A_t are the absorbances at this wavelength at times 0 and t, respectively (here $A_0 = A_{pss}$). A_∞ is the absorbance at infinite times, meaning at times for which no further change in the spectrum is observed. k_b is the rate constant of thermal cis to trans isomerization. The plots of $\ln[(A_\infty - A_0)/(A_\infty - A_t)]$ vs. illumination time (t) are shown in Figure 5. For all samples, the data in these plots are well represented by a linear function, indicating first-order kinetics. Rate constants (k_b) are obtained from the slope of the linear function and summarized in Table 2.

In our experiment, we find that the cis isomer of system (1) 4-HAB in MeCN has a thermal relaxation lifetime of 19 min. This lifetime is significantly longer than the lifetime (< 1 min) reported by Kojima et al.[47] for 4-HAB in MeCN. In constrast to Kojima et al. we have performed our experiments in MeCN, which contains < 0.01 wt% of water contamination. We find that the presence of water significantly decreases the thermal relaxation lifetime of 4-HAB. Indeed, in MeCN with a water content > 0.01 wt% we were unable to detect any change in the UV-vis spectrum upon irradiation of the sample at 368 nm and 355 nm, respectively. This indicates that the thermal relaxation lifetime is significantly below 1 minute, and thus not detectable with our experimental setup. The same result was observed for 4-HAB in methanol, indicating that the presence of polar protic molecules enables fast thermal cis to trans isomerization, possibly via the formation of hydrogen bound complexes of 4-HAB with protic solvents. Kojima et al.'s explanation of the fast relaxation by intermolecular hydrogen bonding between 4-HAB and MeCN seems less likely in the light of our experimental findings.

Comparison of thermal cis to trans relaxation lifetimes of systems (1) - (5) leads to the following findings:
System (1) 4-HAB in MeCN has a lifetime of 19 min which is slightly shorter than the lifetime of system (3) 4-HAB in PMMA with a lifetime of 29 min. Besides, system (2) Boc-Gly-4-HAB in MeCN exhibits a lifetime of about 250 hours, slightly shorter than (4) Boc-Gly-4-HAB in PMMA

with ~310 hours. This finding suggests that the thermal relaxation rate is only slightly influenced by the chemical environment. This is consistent with findings by Sin et. al.[35]. They investigated azobenzene-containing polymers in solution and in polymer matrix at room temperature and find that isomerization kinetics are similar in both cases. Our observation that relaxation rates in PMMA matrix are slightly smaller compared to MeCN may thus rather be the result of their different polarities than their different viscosities.
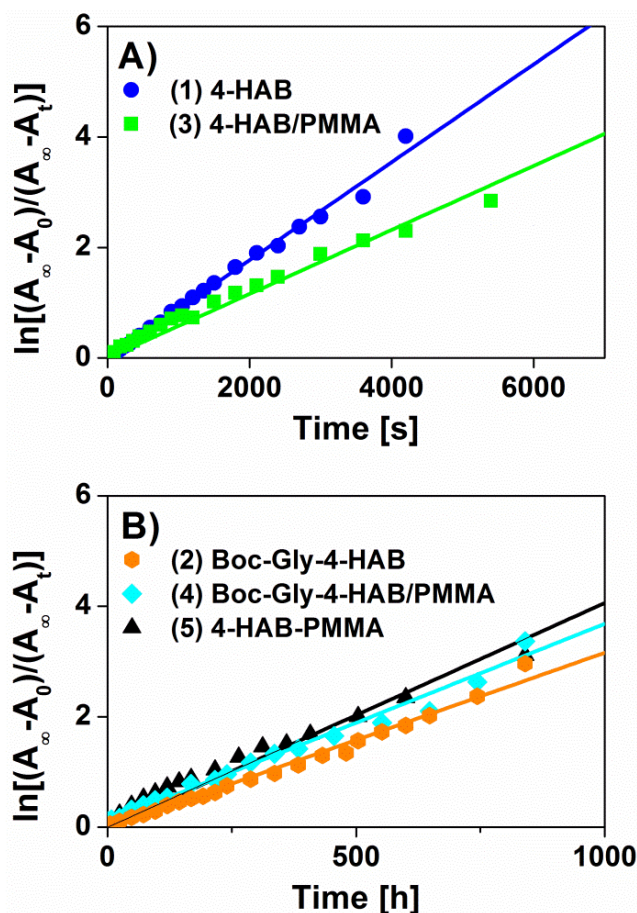

Figure 5. Kinetics of thermal cis to trans isomerization of (A): systems (1) + (3), and (B): systems (2) + (4) + (5). Linear functions (solid lines) are fitted to the data, and rate constants (k_b) are obtained from the slopes of the linear functions.

The thermal cis to trans relaxation lifetime of system (5) 4-HAB-PMMA is found to be about 210 hours, and thus comparable to the lifetimes of systems (2) and (4). These lifetimes are > 400 times longer than lifetimes for systems (1) and (3). This difference is a clear result of the different substituents on the azobenzene moiety. We have performed quantum chemical calculations (section 2.5) in order to understand how these substituents influence the stability of the cis-isomer.

3.4 Photoinduced Cis to Trans Isomerization

The thermal stability of cis isomers of systems (1) - (5) is high enough to allow experiments on the light induced cis to trans isomerization. In these experiments, the samples were irradiated with visible light at 434 nm in order to induce

cis-trans isomerization. Figure 6 shows the obtained spectral series for systems (1) - (5). For system (5) 4-HAB-PMMA we observe a complete transfer of cis to trans, as the final spectrum is identical with the initial trans spectrum of the sample. For systems (1)-(4), illumination with 434 nm results in a photostationary state. In the case of systems (1), (2) and (3) the PSS still contains significant amounts of cis isomer. Rate constants k_{ct} were obtained with the procedure described in section 2.2 (see Figure 7) and listed in Table 2. In all systems, the cis to trans isomerization can be significantly accelerated by illumination with 434 nm light. In the case of system (5), where complete light induced transfer from cis to trans is observed, the rate constant k_{ct} is more than a factor of 5500 higher compared to the thermal cis to trans relaxation rate k_b.

2.5 Quantum Chemical Calculations

The structures of studied systems (1)+(3) 4-HAB, (2)+(4) Boc-Gly-4-HAB and (5) 4-HAB-PMMA were optimized both in trans and cis forms. We use a structure containing three PMMA units to model 4-HAB-PMMA. In agreement with results of calculations with different methods on the trans-azobenzene structure[58], the optimized trans structures of studied molecules have both phenyl rings slightly distorted from planarity. Accordingly, the phenyl rings in trans-4-HAB are rotated by 1.1° relative to the N=N-C plane. The distortion from planarity is slightly larger for trans-4-HAB-PMMA (1.0° and 2.5° for both sites of N=N bond) and for trans-Boc-Gly-4-HAB (1.2° and 3.7°).
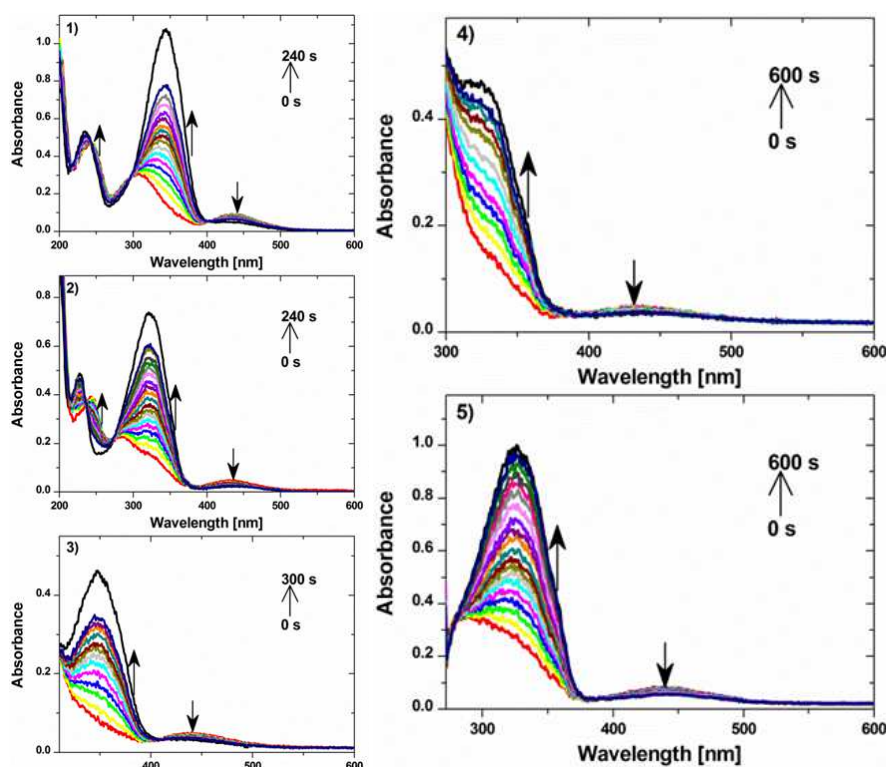

Figure 6. *Variation of UV-vis. spectra of sample (1) – (5) after illumination with 434 nm light.*
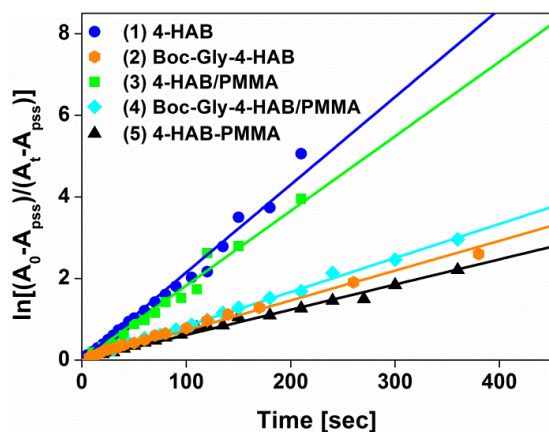

Figure 7. *Kinetics of photoinduced cis to trans isomerization of systems (1) – (5) with 434 nm light. Linear functions (solid lines) are fitted to the data, and rate constants (k_{ct}) are obtained fom the slopes of the linear functions.*

In all optimized cis-structures phenyl rings are strongly distorted from planarity. In the case of Boc-Gly-4-HAB and 4-HAB-PMMA, we find additional, energetically favored structures (denoted as cis*).

These structures feature a strong intramolecular hydrogen-bond between a carbonyl oxygen from the substituents and a H-atom on the phenyl ring. The optimized stable structures of 4-HAB-PMMA and Boc-Gly-4-HAB are shown in Figure 8

According to reported studies[48,59,60] the ground-state thermal isomerization of azobenzenes proceeds via rehybridization of one of the azo nitrogens rather than by rotation about the -N=N- bond. In this work calculations of activation energy for thermal cis-trans isomerization were performed for the systems 4-HAB and Boc-Gly-4-HAB, as well as for unsubstituted azobenzene (u-AB) for comparison.

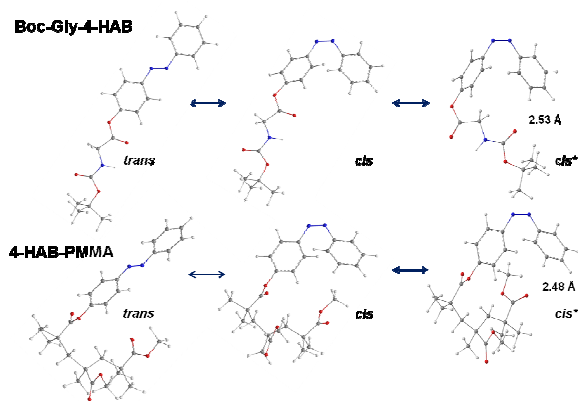Results of calculations are shown in Figure 9.

Figure 8. *Optimized structures (trans and cis forms) of Boc-Gly-4-HAB and structure of 4-HAB-PMMA bonded to model polymer PMMA (3 units). Here cis*structure forms intramolecular H-bond between carbonyl oxygen and H atom from phenyl ring.*
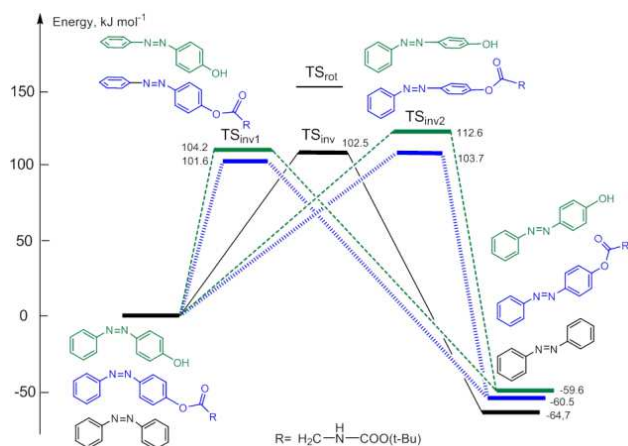

Figure 9. *Energy scheme for the ground-state thermal cis-trans isomerization calculated starting from optimized cis-isomer. Here TS$_{inv1}$ – transition state for the inversion on the site of free phenyl and TS$_{inv2}$ – on the site connected to substituent. TS$_{rot}$ – transition state for rotation about the -N=N- bond is energetically unfavorable and is not discussed here.*

The cis-trans isomerization barrier through inversion on -N=N- calculated by us for u-AB was 102.1 kJ mol^{-1}, which is in good agreement with the literature data.[48,68] In the case of 4-HAB and Boc-Gly-4-HAB molecules the activation barrier depends on the site of the -N=N- bond. As can be seen, the activation barrier is slightly higher for the inversion on the site connected to substituent. Thus, it is expected, that the thermal cis-trans isomerization through inversion should rather proceed on the site of the unsubstituted phenyl.

To get any idea on the large difference on the rate of the thermal cis-trans isomerization between free 4-HAB and both large molecules namely Boc-Gly-4-HAB and 4-HAB-PMMA bonded to model polymer PMMA, electronic structures, charge distributions and excitation energies were compared. For 4-HAB and Boc-Gly-4-HAB electron distributions of the two highest occupied molecular orbitals (HOMO and HOMO-1) and the lowest unoccupied molecular orbital

(LUMO), which are mostly involved into formation of S$_1$ and S$_2$ excited states are shown in Figure 10.

As can be seen, the large substituent in Boc-Gly-4-HAB does not have any essential effect on the electronic structure.
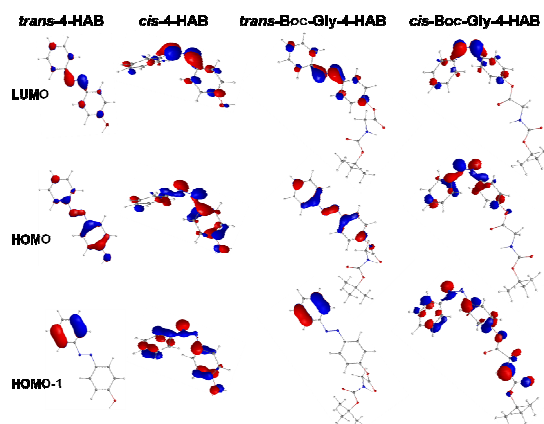

Figure 10. *Electron distributions from molecular orbitals mostly involved into formation of S$_1$ and S$_2$ excited states.*

The calculated excitations energies for all studied molecules are given in Table 3. The energies of excited states are in reasonable agreement with experimental spectra. The experimentally observed huge difference in the rate of the thermal cis-trans isomerization between systems (1)+(3) and (2)+(4)+(5) can thus not readily be explained by changes in electronic parameters caused by the different substituents. However, these differences may be explained by the possibility of intramolecular H-bond formation between a carbonyl oxygen on the substituent and an H atom on the phenyl ring, which is only possible in the cis conformation of systems (2), (4), and (5). The respective structures are denoted cis* and shown in Figure 8. The calculated Gibbs free energies ΔG of such intramolecular hydrogen-bond in the case of Boc-Gly-OAB and 4-HAB-PMMA molecules were 13.4 and 9.2 kJ mol^{-1} respectively. These values agree well with the typical strength of a O⋯H hydrogen bond (between 8.4 and 22 kJ mol^{-1}).[61] Apparently, such an H-bond hinders cis-trans isomerization via the inversion mechanism and may be the reason for the observed large thermal stability of the cis-form of systems (2), (4), and (5).

Table 3. *Excitation energies and oscillator strength (in parenthesis) of the investigated systems as calculated with time-dependent density functional theory (TDDFT) at B3LYP/6-31G(d,p) level.*

			λ[nm]	
			trans	*cis*
1	4-HAB (in MeCN)	S$_1$ (nπ*)	468 (0.0001)	469 (0.065)
		S$_2$ (ππ*)	345 (0.801)	325 (0.151)
		S$_3$ (ππ*)	235 (0.090)	299 (0.055)
		S$_4$ (ππ*)		262 (0.082)
2	Boc-Gly-4-HAB (in MeCN)	S$_1$ (nπ*)	479 (0.0003)	471 (0.062)
		S$_2$ (ππ*)	346 (0.969)	320 (0.072)
		S$_3$ (ππ*)	224 (0.057)	307 (0.129)
		S$_4$ (ππ*)		246 (0.099)
5	4-HAB-PMMA	S$_1$ (nπ*)	484 (0.0001)	480 (0.040)
		S$_2$ (ππ*)	342 (0.988)	305 (0.082)

3. Conclusions

We presented a systematic study on azobenzene derivatives in order to quantify the impact of chemical substitution and chemical environment on the dynamics of light-induced trans-cis isomerization, thermal cis-trans relaxation, and light-induced cis-trans isomerization. Systems under investigation were 4-hydroxyazobenzene (4-HAB) in acetonitrile (MeCN) solution and in poly(methylmethacrylate) (PMMA) matrix. These two systems are compared to systems in which 4-HAB is esterified, namely 4-hydroxyazobenzene covalently bound (esterified) to PMMA matrix, and N-(tert-butoxycarbonyl)glycine-4- hydroxyazobenzene in MeCN and in PMMA.

We find that different chemical environments (MeCN vs. PMMA) do not significantly influence the UV-vis absorption spectrum of azobenzene derivatives. However, the absorption spectra of 4-HAB are clearly different from the spectra of esterified systems.

The same trend is found for photoinduced trans to cis isomerization at 368 nm: chemical environment only has a minor impact on photoisomerization kinetics. Our results further indicate that the far structure of the substituent – in our case beyond the ester function directly attached to the azobenzene system – does not influence trans to cis photoisomerization kinetics.

In line with these findings, also the influence of chemical environment on the thermal cis to trans relaxation rate is found to be small. However, the relaxation rates of 4-HAB are clearly faster (factor > 400) than the rates of esterified systems. This difference is a clear result of the different substituents on the azobenzene moiety. Quantum chemical calculations indicate that the cis-configuration in the esterified systems is stabilized by an intramolecular H-bond between the carbonyl oxygen of the substituent and an H atom of the phenyl ring. Further experiments will be required to unambiguously prove this hypothesis, and to evaluate whether it can be used as a design principle for azobenzene-based materials with a low thermal cis to trans isomerization rate.

We further found indications that the presence of polar protic molecules (water or methanol) greatly enhances the thermal cis to trans isomerization rate of 4-HAB. Possibly via the formation of hydrogen bound complexes of 4-HAB with water and methanol, respectively.

In all systems, the cis to trans isomerization can be significantly accelerated by illumination with 434 nm light. In the case of system (5) 4-HAB covalently bound (esterified) to PMMA matrix, complete light induced transfer from cis to trans is observed. The rate constant k_{ct} is a factor of about 5700 higher compared to the thermal cis to trans relaxation rate k_b. In addition, it features a low thermal cis to trans isomerization rate and acceptable photoinduced trans to cis- isomerization properties. In summary, this renders it a promising starting point for the rational design of functional polymer materials whose properties can be reversibly changed by illumination with light.

4. Appendix

Synthesis of 4-(phenyldiazenyl)phenyl methacrylate

5.0 g (25.2 mmol) azobenzene was dissolved in 50 ml diethylether and 6.5 ml triethylamine was added. 3.5 ml (38.2 mmol) methyl methacryloyl chloride was added during 30 minutes with a dropping funnel under vigorous stirring at room temperature. The reaction mixture was kept at room temperature with a water bath. After 5.5 hours stirring 50 ml chloroform was added and additionally 30 minutes stirred. Then, 50 ml water was added and stirred till the clouding disappeared. The two phases were separated and the aqueous phase was extracted two times with 20 ml chloroform. The combined organic phases were washed with hydrochloric acid, water, NaHCO$_3$-solution and finally water and dried with sodium sulfate. The solvent was removed under reduced pressure. The crude product was recrystallized from ethanol/n-pentane (1/1, v/v) to yield 4.4 g (66%) orange powder. ^{1}H-NMR (600 MHz, acetone-d$_6$)δ (ppm): 2.06 (dd, 3 H), 5.88 (m, 1 H), 6.35 (m, 1 H), 7.41 (d, 2H), 7.61 -7.54 (m, 3 H), 7.94 (d, 2 H), 8.01 (d, 2 H); ^{13}C-NMR (125 MHz, acetone-d$_6$) δ (ppm): 18.9; 124.1; 125.2; 128.5; 130.7; 132.7; 137.2; 151.5; 153.8; 154.7; 166.4; IR (FT-ATR, cm^{-1}): 3105, 3058, 2975, 2954, 2922 (w), 1729 (s), 1193 (m), 1120 (s).

Synthesis of Boc-Gly-4-HAB

876 mg (5 mmol) N-(tert-Butoxycarbonyl)glycine, 892 mg (4.5 mmol) 4-Hydroxyazobenzene, 1.605 g (5 mmol) N,N,N',N'-Tetramethyl-O-(benzotriazol-1-yl)uronium tetrafluoroborate, and 675 mg (5 mmol) 1-Hydroxybenzotriazole hydrate were dissolved in 10 ml N,N-Dimethylformamide. 1.742 ml (10 mmol) N-Ethyldiisopropylamine was added and the reaction mixture was stirred overnight at room temperature followed by the addition of water and ethyl acetate. The two phases were separated and the organic phase was washed 4 times with water and dried with sodium sulfate. After evaporation of the solvent the crude product was re-crystallized from ethyl acetate/n-hexane to yield 1.06 g (3 mmol, 67 %) of an orange powder. MALDI-TOF-MS, m/z: 377.9 [M+Na]$^+$, ^{1}H-NMR (600 MHz, DMSO-d$_6$)δ (ppm): 1.44 (s, 9 H), 4.02 (d, 2 H), 6.94-7.97 (10 H); ^{13}C-NMR (150 MHz, DMSO-d6) δ (ppm): 28,0; 42,2; 78,4; 122,4; 122,5; 123,7; 129,3; 131,4; 149,6; 151,8; 152,4; 155,8; 169,0.

Polymerization of MMA with 4-(phenyldiazenyl)phenyl methacrylate: In a typical synthesis: 250 mg (0.95 mmol) 4-(phenyldiazenyl)phenyl methacrylate, 50 mg AIBN were dissolved in 10 ml (94 mmol) methyl methacrylate in a 100 ml beaker. The beaker was placed in a domestic microwave oven (PRIVILEG 8020) and the following time program at 350 W microwave power was performed: 90 – 30 – 20 s with 120 s breaks. The resulting viscous mixture was poured into 200 ml methanol. The precipitate was washed with methanol and dried at room temperature. The obtained polymer was the starting material for the film preparation. The best films for the UV/VIS experiments were obtained by dilution the abovementioned polymer with pure PMMA getting a final

azobenzene concentration of about 0.03 wt%.

Table A1. *Glass transitions and molecular weights of the polymer samples*

	Properties	T_G / °C	M_N / Da	M_W / Da
3	4-HAB/PMMA	94	44720	105655
4	Boc-Gly-4-HAB/PMMA	80	43592	107437
5	4-HAB-PMMA	62	35021	127300

Figure A1. *ATR-IR spectrum of 4-(phenyldiazenyl)phenyl methacrylate.*
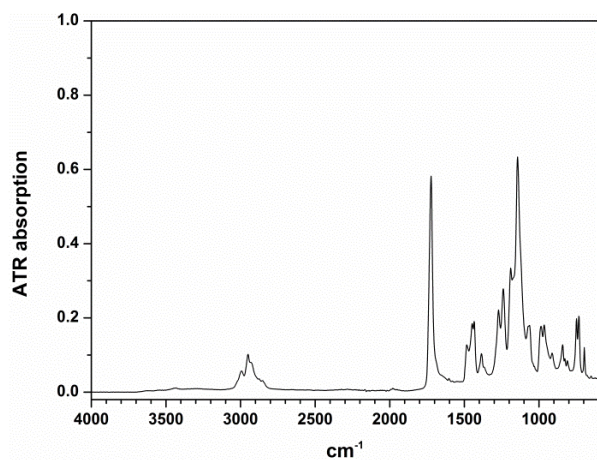

Figure A2. *ATR-IR spectrum of Boc-Gly-4-HAB.*

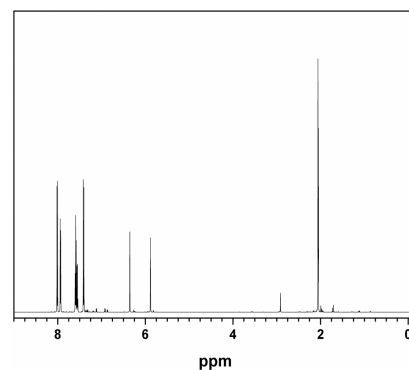**Figure A3.** *ATR-IR spectrum of 4-(phenyldiazenyl)phenyl methacrylate incorporated in PMMA.*

Figure A4. *^1H NMR spectrum of 4-(phenyldiazenyl)phenyl methacrylate, acetone-d_6.*
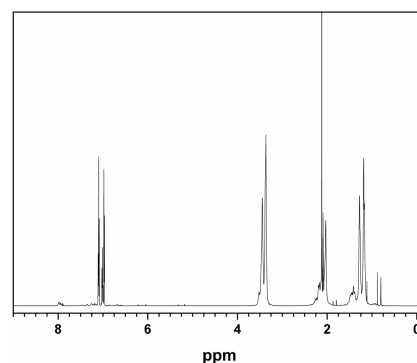

Figure A5. *^1H NMR spectrum of 4-(phenyldiazenyl)phenyl methacrylate covalently linked in PMMA, toluene-d_8.*
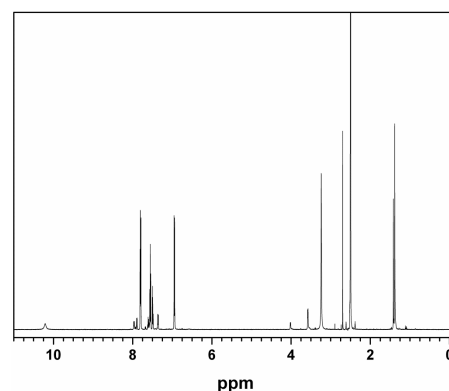

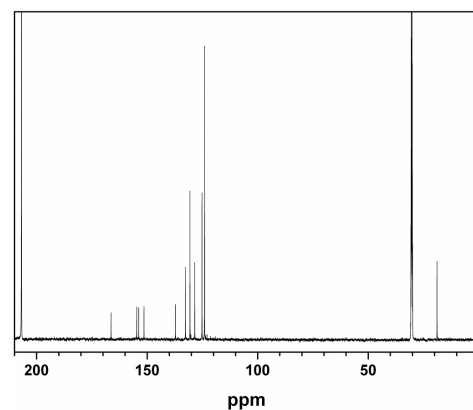**Figure A6.** *^1H NMR spectrum of Boc-Gly-4-HAB, DMSO-d_6.*

Figure A7. *^{13}C NMR spectrum of 4-(phenyldiazenyl)phenyl methacrylate, acetone-d_6.*

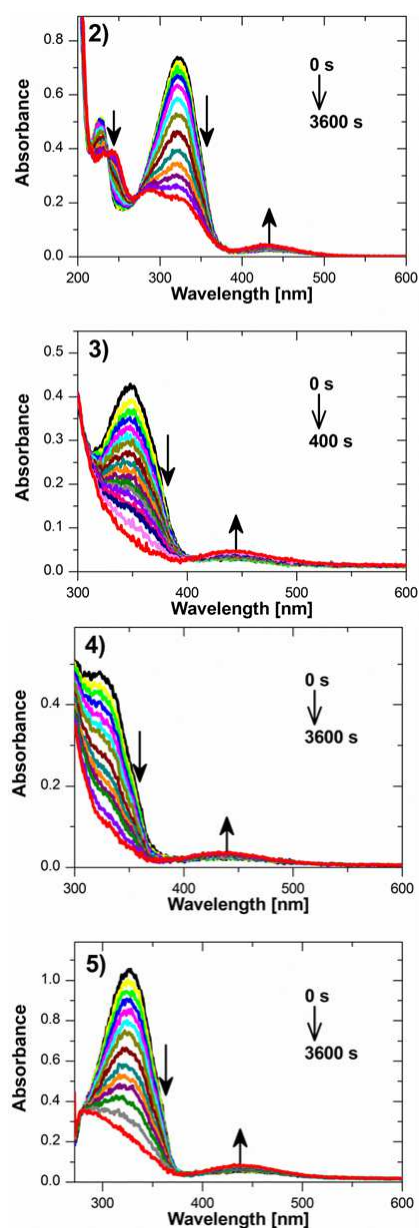**Figure A8.** *¹³C NMR spectrum of 4-(phenyldiazenyl)phenyl methacrylate covalently linked in PMMA, toluene-d₈.*
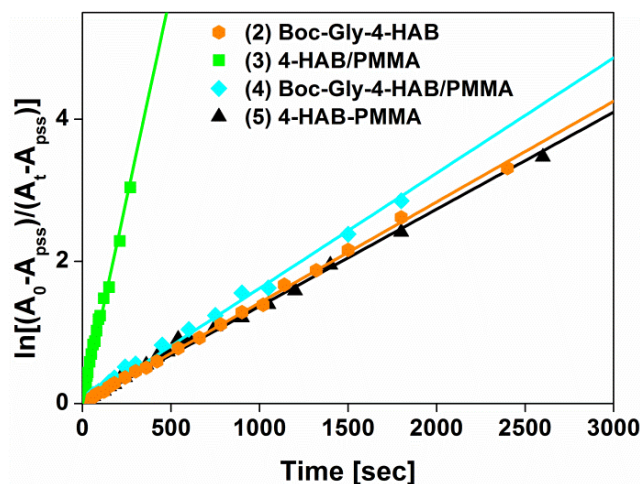

Figure A10. *Kinetics of photoinduced trans to cis isomerization of systems (2)-(5) with 355 nm light. Linear functions (solid lines) are fitted to the data and rate constants (k_{tc}) are obtained from the slopes of the linear functions.*

Figure A9. *Variation of UV-vis spectra of sample (2) – (5) after illumination with 355 nm light.*

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