Effects of Solvent Viscosity and Polarity on the Isomerization of Azobenzene

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ABSTRACT: Isomerization of azobenzene has been studied for many years, but some aspects are still unclear or controversial. This work provides further insight and clarifies the role that environmental parameters play in determining the reaction kinetics of azobenzene derivatives in solution. Detailed spectroscopic measurements of the photoisomerization and thermal isomerization kinetics in mixtures of various solvents and polystyrene have been carried out. The results indicate a strong dependence of both photoisomerization and thermal isomerization rates on the polarity, but not on the viscosity of the solvent.

1. Introduction

Isomerization of azobenzene and its derivatives has been extensively studied for the past 50 years because this molecule presents many interesting features and its applications range from electronics to biomedicine. It has been used as a model molecule for all the biological processes that involve similar reactions,[1−3] like the isomerization of retinal in rhodopsin, or as a probe for measuring the free volume in polymers.[1,4] More recently, its characteristic response to the polarization of light made it a suitable molecule for surface patterning.[5,6] Finally, azobenzene-containing elastomers constitute an interesting area of inhomogeneous photomechanical effects and their applications as photoactuators and artificial muscles are under study.[7−10]

However, in spite of the large literature on the subject, many fundamental mechanisms and effects have not been clarified yet. It is known that the isomerization reaction is very sensitive to both electrical and mechanical characteristics of the environment which surrounds the molecules, but identifying and separating these effects is a difficult and often ambiguous task.

UV−vis spectroscopy constitutes an appropriate tool for the study of this system because during isomerization the rearrangement of the molecular orbital energy levels induces a change in the molecular absorption spectrum.[3] When the azobenzene molecule is in the ground-state *trans* configuration, the transition with the highest quantum yield is that between the bonding and antibonding ($\pi-\pi^*$) orbitals: the result is a big absorption peak around 320 nm. The absorption of this high-energy photon stimulates the molecular transition into the metastable *cis* configuration. In this state the highest quantum yield belongs to the nonbonding−antibonding ($n-\pi^*$) transition, which is identified by a peak around 440 nm.[1,3] This *cis*−*trans* transition can occur spontaneously, when thermal fluctuations carry the molecule over the energy barrier; it can also be stimulated by absorption of a low-energy 440 nm photon. During isomerization, the relative intensity of these two peaks changes, and in this way one can follow the course of the reaction.

Different chemical groups can be attached to the basic azobenzene molecule. These substitutions dramatically change the spectroscopic properties, affecting the relative position and intensity of the two absorption peaks, and the kinetics of isomerization. This allows fine-tuning of the optical response to many purposes; for this reason different azobenzene-based molecules have been used as probes in a wide range of wavelengths. In addition to molecular substitutions in the chromophore molecule, environmental parameters like solvent polarity and viscosity also play a role. Over 30 years ago, Whitten et al.[11] found an increase of several orders of magnitude in the thermal isomerization rate of an azobenzene derivative, with an aminic and a nitrate group as substituents, in solvents at increasing polarity. At the same time, only a little change was detected using a molecule with a simple aminic substitution.[11] An increase of the speed of the reaction in some azobenzene molecules was also reported by Gille[12] and Asano.[13] Bortolus reports an increase in quantum yield of *cis*−*trans* photoisomerization in nonpolar environment for azobenzene molecules.[14] Sanchez and De Rossi studied in detail the effect of polarity on thermal *cis*−*trans* transition, and they found that hydroxide ion plays an important role in speeding up the *cis*-to-*trans* isomerization for azobenzene compounds with aminic substitutions.[15]

The effect of solvent viscosity has been investigated too, but no universal conclusion has been reached. Gegiou et al. reported only a slight effect on the photostimulated *cis*−*trans* isomerization quantum yield, but they observed a viscosity-dependent quantum yield in the *trans*−*cis* isomerization.[16] Gille et al. reported a slowing of thermal relaxation (γ) in viscous environment,[12] while Eisenbach found no effect at all.[17] Many groups have therefore studied the effect of a very viscous matrix, i.e., a molten or glassy polymer instead of a solution, and the results agree that the kinetics is the same as in solution if the polymer is in rubbery state, but below the glass transition temperature its characteristics change.[17−20]

The models that were proposed for reaction kinetics are basically first-order, with the important exception of azobenzene in glassy polymers. In solution, the fraction of isomers in the *cis* state, c, varies in time as[21,22]

$$\frac{\mathrm{d}c}{\mathrm{d}t} = Ik_{\mathrm{TC}}(1-c) - Ik_{\mathrm{CT}}c - \gamma c \tag{1}$$

where I is the irradiation intensity, k_{CT} and k_{TC} are the *cis*−*trans* and *trans*−*cis* constants of photoisomerization, respectively, and γ is the rate of spontaneous thermal *cis*−*trans* isomerization. Accordingly, $(1-c)$ represents the fraction of molecules in the ground-state *trans* configuration. There is an assumption that the rate of spontaneous thermal *trans*−*cis* isomerization is negligible at room temperature, supported by the estimates of the energy barrier much exceeding $k_{\mathrm{B}}T$. The

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law of photoinduced kinetics is exponential and is characterized by a relaxation time τ_P, which depends on the three rate constants. Assuming all the molecules in the *trans* state before the irradiation and the derivative of c is zero at the photostationary state at $t \rightarrow \infty$, the resulting solution is

$$c(t) = \tau_P I k_{TC}\left(1 - \exp\left(-\frac{t}{\tau_P}\right)\right) \tag{2}$$

where

$$\tau_P = \frac{1}{\gamma + I(k_{TC} + k_{CT})} \tag{3}$$

This formula is especially important for absorption studies because the Lambert−Beer law guarantees the proportionality between the concentration of species (C) in molar units and the measured absorbance (Abs) at each wavelength:

$$\log\left(\frac{I_0}{I}\right) \equiv \mathrm{Abs} = \epsilon C d \tag{4}$$

where d is the sample thickness and ϵ the molar absorption coefficient. After a long period of photoisomerization, in the photostationary state the plateau value is given by

$$c_{MAX} = \tau_P I k_{TC} = \frac{I k_{TC}}{\gamma + I(k_{TC} + k_{CT})} \tag{5}$$

In glassy polymers the kinetics can no longer be modeled with a single exponential because the system shows a faster initial isomerization kinetics followed by a slower one. Eisenbach explained this by the occurrence of two characteristic times for translational and rotational motion in glass,[23] while others have modeled the function as a stretched exponential $c(t) = A \exp[-(t/\tau)^{\beta}]$, which has been physically explained as the consequence of the distribution of relaxation times in the polymer matrix.[19,20,24] Also in view of this consideration, it is important to distinguish the effects of the mechanical constraints from the electrical and chemical ones.

This paper addresses an important issue of how (or whether) the solvent viscosity and polarity affect the reaction of photoisomerization and thermal isomerization under low-intensity illumination and in low solute concentration conditions (the same as used in earlier literature), i.e., when the linear Lambert−Beer law is valid and phenomena of aggregation between molecules are negligible. As mentioned above, the role of these factors in the isomerization kinetics is not yet clear, and the debate has gone on for years. In order to detect a dependence on viscosity, it was important to test it over several orders of magnitude: for this reason working with a polymer solution at different concentrations in solvents seemed an appropriate choice. Polystyrene was chosen because it is soluble in relevant solvents and because it does not phase-separate from the azobenzene chromophore. We examine the change in isomerization rates of a ordinary low-molecular-weight azobenzene derivative in three solvents, differing in their polarity, and we find a strong effect of polarity on the transition rates. In spite of modifying the solvent viscosity by over 3 orders of magnitude, the careful analysis shows that viscosity has little effect, and all of the results can be scaled onto a universal master curve by accounting for the effective dipole moment per molecule of solvent.

2. Materials and Methods

The molecule 4′-hexyloxy-4-((acryloyloxyhexyloxy)azobenzene (abbreviated as AC_6AzoC_6) was synthesized in our lab by Dr. A. R. Tajbakhsh. This molecular structure is shown in Figure 1. The synthesis of this molecule starts from a 4-hydroxyaniline (HO−Ph−NH_2) protected by an acetic anhydride, which form an acetanilide. The alkylation with $BrC_6H_{12}OH$ gives a 1-hydroxyhexyloxyacetanilide, which is then hydrolyzed with HCl. Afterward, diazotization with concentrated HCl and sodium nitrite and coupling with phenol give HO−C_6H_{12}−O−Ph−N=N−Ph−OH. Adding $C_6H_{12}Br$ leads to the formation of the carbon tail, and the esterification with acryloyl chloride completes the synthesis of the monomer.

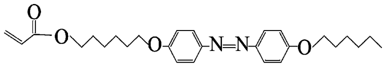

Figure 1. Monomer used AC_6AzoC_6 has an acrylate head group followed by a carbon chain where the azo group is attached.

Three different solvents were used, characterized by different molecular polarity: the least polar toluene, chloroform, and the highly polar *N*-methylpyrrolidone (NMP). For changing viscosity, Sigma-Aldrich high molecular weight polystyrene (PS, M_w = 280 000) was used without further purification to modify the viscosity of the dye solution. A very viscous stock solution of polystyrene in chloroform (c ca. 15 g of polystyrene in about 40 mL of solvent) was prepared, and different dilutions were used for measurements (100%, 75%, 50%, 25%, and 0% of stock solution). A solution of AC_6AzoC_6 0.3 mg/mL in chloroform was prepared, and subsequently 100 μL was injected in 10 mL of every dilution of chloroform and polystyrene; the solutions were mixed with a magnetic stirrer for at least 2 h and left to equilibrate afterward, all in the dark. In each case the absorbance was around 0.25 (i.e., within the range of validity of the Lambert−Beer law). The same procedure was followed substituting chloroform with other solvents: less polar toluene and more polar NMP. The stock solutions were prepared in the same way: 5 g of polystyrene was dissolved in 15 mL of toluene, which corresponds to a weight fraction of 0.39 polystyrene/toluene weight, and 3 g of polystyrene was dissolved in NMP. (The solubility of polystyrene is lower in this solvent than in chloroform and toluene, so the stock solution was less concentrated.) The stock solutions were then used to prepare working solutions with different viscosities, by adding different percentages of pure solvent (25, 50, and 75% in toluene and 30 and 60% in NMP). AC_6AzoC_6 was then added, mixed, and left to equilibrate in the dark.

Viscosity measurements were performed on a Perkin-Elmer “Rheometrics” dynamic stress rheometer (SR200); stress was measured at low strain (with limits of 0.5−5%) at a frequency of 1 Hz using 25 mm diameter parallel plates and a distance of about 0.5 mm between the plates. The linearity of the bulk viscous response has been verified. All measurements were performed at room temperature. The measured viscosity corresponds well to the expected values for different polystyrene concentrations.

For the measurements of light absorption a Thermo-Oriel MS260i spectrometer (focal length 260 mm) was used. The apparatus is composed by quartz probe lamp with an adjustable slit, a quartz cuvette with 1 cm optical path, an optical liquid light guide to conduct the light from the cuvette to the spectrometer, a 50 μm slit at the entrance of the spectrometer, and the Andor linear-array CCD camera connected to a computer. The wavelengths were split by two gratings in the spectrometer, and all the signal was detected by the CCD array at the same time: this configuration can measure spectra at all the wavelengths together, and for this reason it allows a good statistics and a response as fast as 0.021 s. Before every absorption spectrum, a background and a reference spectrum were collected: the background is the spectrum collected without the illumination from the probe lamp, and the reference was the spectrum collected with the probe lamp on from the cuvette filled with solvent (without the chromophore dye). The absorbance was then calculated from the counts of the detector as

$$\mathrm{Abs} = \log\left(\frac{\text{reference} - \text{background}}{\text{signal} - \text{background}}\right)$$

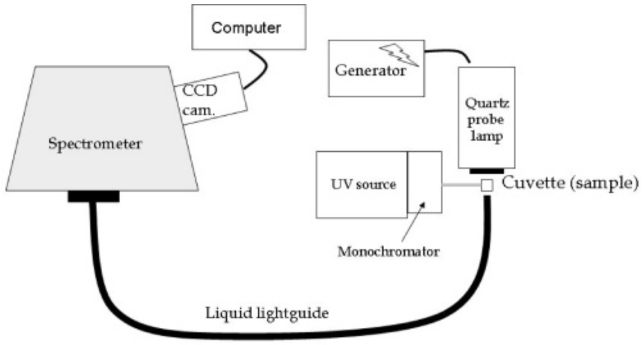

Figure 2. Instrument setup, with the probe lamp for the spectra measurements and the irradiating light which induces the isomerization.

All the spectra shown in the next section are a mean of 100 measurements, each with an exposure time of 0.021 s. All the experiments were performed at room temperature in the dark ambient conditions, with the exception of those reported in the Appendix.

The illumination to stimulate the isomerization of azobenzene was provided by a lamp Schott KL 1500 LCD (power 150 W, illumination flux 600 lm); the lamp was monochromated and placed at 90° with respect to the incident probe light and the optical fiber that collects the light from the sample. In this way the cuvette was irradiated with UV light while the absorption spectrum was recorded along the perpendicular beam path, so the absorption could be followed in real time without interference of the illumination light. A shutter was placed in front of the lamp so that the sample can be screened from the irradiating UV light rapidly. A scheme of the apparatus is sketched in Figure 2.

The intensity of the illuminating light after passing through the monochromator was measured with a low-energy thermal detector Ophir (3A-SH); the intensity of the monochromated light at 385 nm (used for many measurements) was $I = 30 \pm 3\ \mu\mathrm{W\ cm}^{-2}$ at a distance of 3.5 cm from the monochromator, which was the same distance between the monochromator and the cuvette during the actual experiments. The error was determined as the maximum fluctuation of the value over a period of 30 s.

The illuminating lamp was switched on some minutes before starting the kinetic measurements in order to reach the stable intensity. All isomerization reactions were followed for 90 min, which was a sufficient time for reaching the respective photostationary states. After this, the lamp was switched off and the absorbance was measured during thermal isomerization in the dark. Tests with different illumination intensities showed that our conditions and material constants span from the regime of low-intensity illumination, which is defined by $I \ll \gamma/(k_{\mathrm{TC}} + k_{\mathrm{CT}})$, to the high-intensity regime.

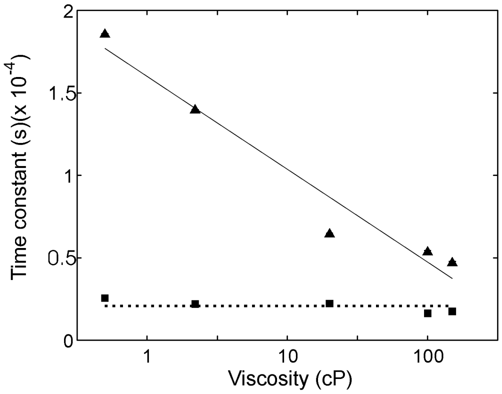

Figure 4. Photoisomerization time constants (τ_{P}, ■) and thermal relaxation time constants (γ^{-1}, ▲) for $\mathrm{AC_6AzoC_6}$ in mixtures of chloroform and polystyrene of different viscosities. The photoisomerization time constants are shifted upward by 600 s to allow both data on the same scale. The lines are a guide for the eye.

3. Results and Discussion

The photoisomerization and thermal isomerization kinetics of $\mathrm{AC_6AzoC_6}$ was followed and absorbance was measured every 10 s. Figure 3 shows a typical series of absorption spectra at successive times during the stimulated photoisomerization and the spontaneous thermal isomerization in the dark. For this molecule, the maximum which corresponds to the $\pi-\pi^*$ transition is at 360 nm, while the $\mathrm{n}-\pi^*$ transition has its maximum at 440 nm. The time dependence of the absorbance at these two wavelengths is well fitted with a single exponential corresponding to the first-order kinetics: eq 2 for the *trans*−*cis* reaction and $c \propto \exp[-\gamma t]$ for the thermal relaxation. From these fits we were able to extract the relevant parameters like the rate constants and the absorbance at the photostationary state. Since the peak at 360 nm is more intense, all the further analysis will refer to this peak. In all cases, by photoisomerization we refer to the stimulated *trans*−*cis* process, since all the relaxation measurements were carried out in the dark.

Figure 4 shows the time constants of photoisomerization and thermal isomerization as a function of viscosity: while the photoisomerization times do not change significantly, the thermal relaxation time constant clearly decreases with increasing solvent viscosity. This is unexpected, because it implies that the thermal equilibration is faster in more viscous environments. However, we shall see that there is an alternative explanation; that is, the trend actually reflects the change in effective solvent

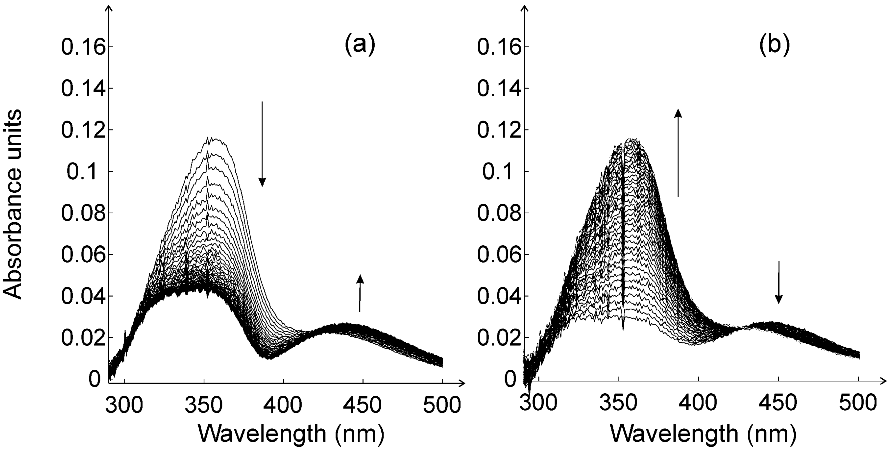

Figure 3. Photoisomerization (a) and thermal (b) isomerization curves of $\mathrm{AC_6AzoC_6}$ recorded as a time sequence. The arrows indicate the direction of the peak movement during the reaction. The isosbestic point is seen at 425 nm, where the absorbance is independent of the reaction state, and the reversible red shift of the peak at 440 nm during photoisomerization.

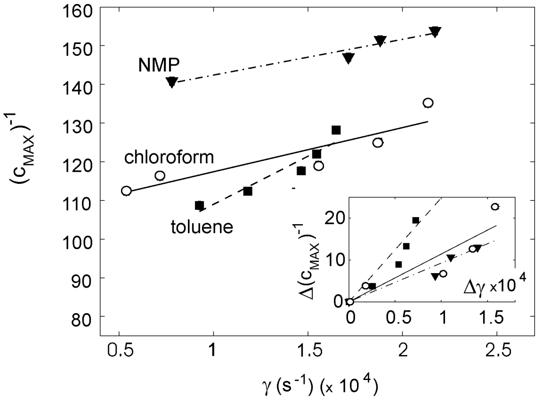

Figure 5. Inverse of fraction of *cis* molecules at the photostationary state $(c_{\mathrm{MAX}})^{-1} = A_0/(A_0 - A_{\mathrm{MIN}})$ as a function of the thermal isomerization rate γ in different solvents at various viscosities. Linear fits are for $c_{\mathrm{MAX}}{}^{-1} = a + b\gamma$. In the inset, the increments are plotted to highlight the variation in the slope for the three solvents.

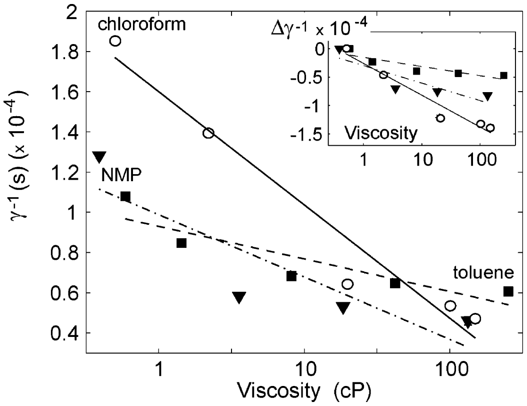

Figure 6. Thermal relaxation times γ^{-1} for isomerization in different solvents as a function of the solution viscosity. In the inset, the increments with respect to the value in pure solvent are plotted.

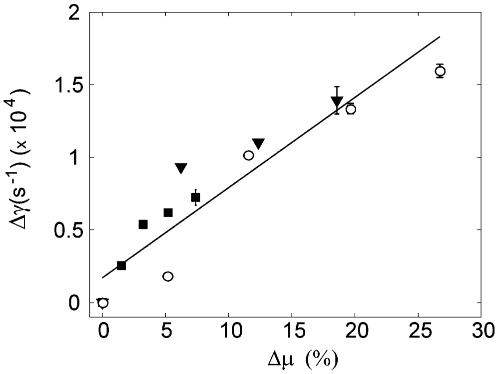

Figure 7. Shift of thermal isomerization rate in various solutions as a function of the percentage change of permanent dipole moment (symbols for NMP, chloroform, and toluene are the same as in Figures 5 and 6).

Table 1. Dipole Moments of the Substances[25,26]

substance	μ (D)
toluene	0.36
chloroform	1.01
NMP	4.09
polystyrene	0.29

polarity rather than viscosity. Polystyrene is a nonpolar polymer, while chloroform is a polar solvent; therefore, the effective polarity of mixtures changes according to the fraction of each component. In order to test the effect of the solvent polarity, the same experiment was performed substituting chloroform with other solvents: less polar (toluene) and more polar (NMP). In all three cases the thermal rate constants increased with increasing viscosity, but in toluene and NMP the effect was less pronounced.

It is also important to notice that the fraction of isomerized *cis* molecules, which can be calculated from the absorbance at the wavelength of the peak corresponding to the *trans* form at the photostationary state, changes. According to eq 5, a linear relation holds at the photostationary state between $c_{\mathrm{MAX}}{}^{-1}$ and γ, $c_{\mathrm{MAX}}{}^{-1} = \gamma/Ik_{\mathrm{TC}} + (1 + k_{\mathrm{CT}}/k_{\mathrm{TC}})$, as shown in Figure 5. The slope of the lines are $(Ik_{\mathrm{TC}})^{-1}$ and from the plot it is possible to see that k_{TC} is bigger in more polar solvents. Considering the curve for chloroform, and the value of intensity $I = 30$ μW cm^{-2}, the estimate for k_{TC} is $k_{\mathrm{TC}} \approx 7 \times 10^{-6}$ cm^2 s^{-1} μW^{-1}. It is important to point out that this value refers to the illumination wavelength of 385 nm, which is not exactly at the *trans*-peak maximum (365 nm).

As the constant of proportionality depends on illumination intensity, it is important to verify that polystyrene does not affect the transmittance at 385 nm (the wavelength of the illuminating lamp): this was actually the case, as polystyrene has a small absorption peak at 300 nm, but at 385 nm the decrease in transmittance was always smaller than 2%, i.e., not enough to justify the big difference in the photostationary state absorbance.

The thermal relaxation time constants γ^{-1} were then related to the logarithm of the solution viscosity, and the results are shown in Figure 6. The relation seems to be linear in all solvents, but with different slopes (in this case chloroform shows the biggest effect). The difference of behavior between the three solvents again suggests an effect of polarity rather than viscosity, since the change in this parameter depends on the difference between polystyrene and solvent polarity.

In order to verify this hypothesis, a value of the effective molecular dipole moment was estimated for all the solutions as an average between the dipole moment of pure solvent and that of polystyrene. Dipole moment μ of polystyrene was calculated according to Debye's equation

$$\left[\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right]\frac{M_{\mathrm{w}}}{\rho} = \frac{4}{9}\pi N_{\mathrm{A}}\frac{\mu^2}{kT} \approx 20.6\mu^2$$

with the values of dielectric constant $\epsilon = 2.6$, index of refraction $n = 1.57$, density $\rho = 1.05$ g cm^{-3}, and molecular weight $M_{\mathrm{w}} = 104$.[25] The dipole moment of the solution was estimated according to the mixing relation $\mu_{\mathrm{mixture}} = \mu_{\mathrm{solvent}}f_{\mathrm{solvent}} + \mu_{\mathrm{poly}}f_{\mathrm{poly}}$, where f indicates the weight fraction of solvent and polystyrene in each solution. The values used for the dipole moments are shown in Table 1.

In order to compare the different sets of data, the shifts in rate constants with respect to pure solvents were plotted as a function of the percentage shift of the dipole moment

$$\Delta\mu = \frac{\mu_{\mathrm{solvent}} - \mu_{\mathrm{mixture}}}{\mu_{\mathrm{solvent}}}$$

The results are shown in Figure 7: all the data scale to the same line, thus confirming that the dominant effect on the shift of thermal relaxation rate is the polarity and not the viscosity of the solvent (in spite of its change over 3 orders of magnitude).

It might seem more appropriate to use dielectric constant ϵ, instead of dipole moment, as a polarity indicator because the measurements were performed in liquids. However, dielectric constant depends not only on absolute dipole moment but also on polarizability; using dielectric constant instead of dipole moment, the data do not scale on the same line, and this is an indication that the permanent molecular dipole moment is the defining parameter.

4. Conclusions

In order to test the effect of polarity and viscosity, the kinetics of photoisomerization and thermal isomerization of the acrylate azobenzene-containing molecule AC_6AzoC_6 was characterized in various solutions of solvent with different polarity (toluene, chloroform, and NMP) mixed with different amounts of polystyrene, which increased the viscosity. The considered range includes over 3 orders of magnitude of viscosities. In low illumination conditions the photoisomerization cannot take place in full, and the thermal isomerization constant affects the extent of the conversion between *trans* and *cis*. The photoisomerization constant can be calculated from the relation between thermal isomerization constant and the amount of isomerized molecules; the data show a slight dependence of photoisomerization constant on solvent polarity. The thermal isomerization constant was correlated with solvent viscosity and polarity, and the second factor appears to be much stronger in affecting the kinetics: the observed shift in the time constant is explicable with the change in dipole moment due to polystyrene addition.

From these data it is possible to hypothesize only a second-order effect of viscosity, but further experiments would be needed to identify it clearly; on the other hand, it is important to consider that in the measurements the azobenzene dye was dispersed in the viscous polymer solution. In fact, there is strong experimental evidence that at the glass transition temperature the isomerization kinetics of azo-dyes incorporated in the polymer chain (in the main chain or as lateral group) changes[17,19,27] and that the amount of isomerized molecules scales with the free volume. One possible explanation is that the range of viscosity investigated is still far from the viscosity of a glassy matrix: in that range new effects can emerge and viscosity can determine the change of kinetics. It could be possible, though, that the determinant factor is the attachment of the dye to the polymer network: preliminary work by Eisenbach[18] suggests the effect is analogous in disperse dyes and in dyes attached as lateral groups, but this field requires more comparative studies.

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Appendix

The photoinduced *cis*−*trans* reaction can be stimulated by an ambient light, as it is likely to contain the blue region of the spectrum. Here we show the comparison of measurements, carried out in the dark and in an ambient light, to establish how significant is this effect.

Given the ambient intensity at ∼440 nm is J, the corresponding stimulated *cis*−*trans* transition rate is $k_{CT}J$. One can find its effect in the value of photostationary c_{MAX} during UV illumination and in the relaxation process. The kinetic equation that describes the *cis*−*trans* isomerization is

$$dc/dt = -(\gamma + k_{CT}J)c \equiv -(\gamma + \tilde{K})c \tag{6}$$

In the experiments which were performed in ambient light in chloroform, the thermal relaxation had a characteristic constant $\gamma + \tilde{K} = 4.5 \times 10^{-4}\ s^{-1}$ for azobenzene in pure chloroform and $\gamma + \tilde{K} = 5.4 \times 10^{-4}\ s^{-1}$ for azobenzene in chloroform/polystyrene mixture at the highest polystyrene concentration of 0.38 mg/mL. Substituting for γ the values previously obtained during the measurements in the dark (at low and high viscosity, respectively), the two values of $\tilde{K}$ are the same: $\tilde{K} \equiv k_{CT}J = 3.7 \times 10^{-4}\ s^{-1}$. It appears that the constant of *cis*−*trans* isomerization stimulated by ambient light is independent of viscosity.

We could provide a separate independent measurement of $\tilde{K}$ using the kinetic data from the UV-stimulated *trans*−*cis* isomerization experiment. Assuming that the ambient light J does not contain any radiation at 365 nm interfering with k_{TC}, the rate characterizing this process modified by the ambient light becomes

$$\tilde{\tau}^{-1} = I(k_{TC} + k_{CT}) + \tilde{K} + \gamma$$

(see eqs 1 and 3). From the experimental values of the rate τ_P^{-1} in chloroform solutions (using the parameters previously calculated in the dark), the new measurement of $\tilde{\tau}^{-1}$ results in $\tilde{K} = 3.2 \times 10^{-4}\ s^{-1}$, which is in reasonable agreement with the previous value. Moreover, a further confirmation of the reliability of this value can be obtained analyzing the photostationary state c_{MAX}: the difference between the two expressions for c_{MAX}, in the ambient light and in the dark, is

$$\Delta c_{MAX} = \frac{k_{TC} I \tilde{K}}{((k_{TC} + k_{CT})I + \gamma)((k_{TC} + k_{CT})I + \gamma + \tilde{K})}$$

Using the parameters found from measurements in pure chloroform, this formula gives $\Delta c_{MAX} = 0.33$. We previously measured the value in the dark, $c_{MAX} = 0.87$, which means that the photostationary value in ambient light should be $c_{MAX} = 0.53$. In fact, this is in very good agreement with the actual experimental measurement, giving 0.54.

In chloroform/polystyrene mixture at highest viscosity, the measurements give $c_{MAX} = 0.34$ in ambient light and $c_{MAX} = 0.69$ in the dark, making a difference $\Delta c_{MAX} = 0.35$. This is very close to Δc_{MAX} obtained in pure chloroform, which demonstrates that $\tilde{K}$ at different viscosities, or polarities, remains constant. In the same way, experiments in toluene and NMP in ambient light lead to values of $\tilde{K} \approx 3.9 \times 10^{-4}$ and $\tilde{K} = 4 \times 10^{-4}\ s^{-1}$, respectively. This indicates that the photo *cis*−*trans* isomerization constant is also essentially independent of the solvent.

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