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The Effect of Dye-Polymer Interactions on the Kinetics of the Isomerization of 4-Dimethyl-Aminoazobenzene and Mercury Dithizonate

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Neste trabalho as isomerizações térmica e fotoquímica do 4-dimetilaminoazobenzeno e do ditizonato de mercúrio foram estudadas tanto em solventes quanto em matrizes poliméricas. A cinética destas reações foi estudada usando-se funções exponenciais para o cálculo das constantes aparentes de velocidade. Observou-se que o comportamento cinético em soluções pode ser descrito por uma função mono-exponencial, enquanto que em sistemas poliméricos têm-se que empregar funções bi-exponenciais. As constantes de velocidades são fortemente influenciadas pelas interações soluto/solvente (ou polímero) além de, também, serem influenciadas pelos processos de tratamento térmico dos filmes poliméricos. Observou-se que, em geral, as reações são mais rápidas em meios mais polares (solventes e polímeros) devido a estabilização de diferentes tautômeros.

Thermal and photo-isomerization reactions of mercury dithizonate and 4-dimethylaminoazobenzene were studied in solutions and in polymer matrices. We used exponential functions to calculate the rate constants for both processes. The kinetic behavior was well described by mono-exponential functions for these dyes dissolved in solvents, although bi-exponential functions are required when these dyes are dissolved in polymers. The rate constants are strongly influenced by dye/solvent and dye/polymer interactions, as well as by the aging processes of the polymer matrix. In general, the reaction is faster in more polar mediums, solvents or polymer matrices, since stabilization of different tautomers takes place. We also showed that larger molecules isomerize slowly and slower isomerization has also been observed for annealed samples. Both results are attributed to the importance of free-volumes in polymeric matrices.

Keywords: 4-dimethylaminoazobenzene, mercury dithizonate, polystyrene, poly(methyl methacrylate), thermoisomerization

Introduction

Azo-dyes are one of the most important and versatile classes of synthetic organic compounds, with an enormous variety of applications.[1-4] Technological applications of these dyes result from the combination of the properties of the azo-group and several types of aromatic-substituted ligands that confer to them intense color over the whole visible range, thermal and photochemical stability, non-complex synthetic methodologies and low costs of production. More recently, some of these dyes have been studied as materials for non-linear optical applications when they contain substituents on the aromatic rings with push-pull electron ability.[1,2,5,6] This confers to the dye a very large permanent electrical dipole moment improving the non-linear optical properties.[7]

Non-linear optical properties of several types of azo-dyes make them very useful for photonic devices, surface gratings,[8-12] photo-alignment in liquid crystalline polymers,[13] storage information among other applications.[14] One requirement for second order non-linear susceptibility is to produce materials without centrosymmetry order of the dye arrangement.[7] Thus, to avoid the presence of a centrosymmetry and to enhance the non-linear optical properties, several types of polymeric materials containing azo-dyes have been prepared.[1,2,5-13]

There are two general methodologies to incorporate dyes into polymeric materials: one produces a solid-state solution where the dye is a guest in a polymer host.[15,16] Usually, for technological purposes this is a less employed methodology since very low concentrations of the dye can be incorporated into the material.[1] The second methodology uses chemical attachment of the dye in the polymer chain either by chemical modification of the pre-

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formed polymer or by polymerization reactions using a monomer labeled with the azo-dye.[1,9,10,13-16] For both types of materials films can be prepared by casting, spin coating, self-assembly or Langmuir-Blodgett monolayer deposition.[1,9,10,12,13] Moreover, the alignment of the azo-dyes in polymer matrices should be induced by several types of methodologies including poling,[17] deposition by self-assembling[1,6] or by Langmuir-Blodgett,[1,6,13] by macroscopic stretching[18,19] or by photoinduction.[1,5,7, 9-13]

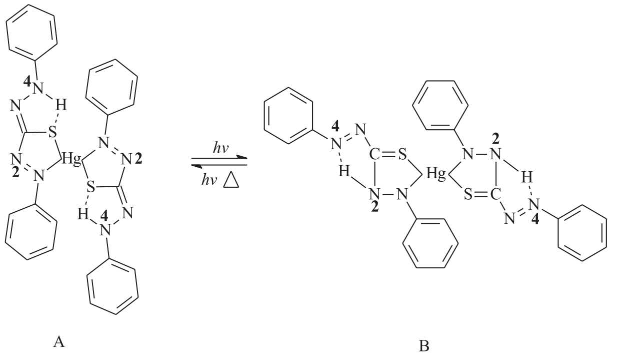
Azo-dyes as guests in hosts or attached to the polymer chains can undergo photo and thermal isomerization reactions from the most stable anti-form to the syn. In general, these reactions produce remarkable changes of the dipole moments of these molecules leading to photoinduced optical birefringency.[1,7,13] The sequential reversible isomerization anti-syn-anti leads to the possibility of optical storage,[1,5,6,9,13] photoinduced switching,[9] formation of surface gratings,[1,6,9,10,13] photoinduced electrical polarization[6,9] and command surface for liquid crystal alignment.[13] All of these properties are based on the reversibility of the isomerization reactions where both isomers exhibit distinguishable values of the electrical dipole moments, the polarizabilities and the geometries.

The photonic applications of these materials require a good control of constant rates of the reversible isomerization reactions. There are some parameters controlling the rate constants of the isomerization reactions:[1,2,5,6,9,13] (*i*). the structure of the azo-dyes, usually classified as azo-benzene, aminoazobenzenes and pseudo-stilbenes;[2] (*ii*). the size and the shape of the molecules; (*iii*). the type of microenvironment where the group is located (solvent, polymer matrix, liquid crystals); (*iv*). the relative orientation of the dye in the matrix; (v). the relative orientation of the dye ensemble into the matrix; (*vi*). the polarization of the light inducing the photoisomerization, among others. Here we make an attempt to discuss two effects over the rate constants for the isomerization: the size of the azo-dye and the dye-polymer interactions.

Unlike dyes in solvents, kinetics of the isomerization in polymers are complex and usually they can not be described by a single rate constant. Among the several models already described,[20,21] the kinetics can be represented by a biexponential function for polymers below the glass transition temperature. Assuming that the polymer matrix is a biphasic system, two rate constants are required to fit the experimental data below the glass transition temperature: a slower process which occurs with molecules located in cavities with smaller free-volumes and a faster process which occurs with molecules located in the polymer matrix with larger free-volumes.[1] Probably, for a more precise description, we should employ a bimodal distribution for the rate constants where each distribution would result in average values for rate constants. In addition, these rate constants also depend on the temperature, on the molecular volume and on the physical aging of the polymer matrix.[22,23]

The present work studies the isomerization reactions of two categories of dyes (mercury dithizonate ($Hg(DTZ)_2$) and 4-dimethylaminoazobenzene (DAB)) dissolved in some polymer matrices (polystyrene, poly(methyl methacrylate), poly(vinyl acetate) and poly(vinyl alcohol) as an attempt to analyze the influence of the size of the dye and the dye-polymer interaction on the kinetics of the reaction. Although these two molecules have different sizes and shapes and they are located in cavities whose geometry is compatible with them, these cavities are not static pre-formed free-volumes since polymer film is produced by casting from a solution containing dye molecules. In consequence, there is a synergic effect involving size and shape of the probe that interfere with the size and shape of the cavity during the solvent evaporation. Nevertheless, once formed, the isomerization reaction takes place without significant diffusion for different free-volumes.

The isomerization reactions of several dithizonate complexes with metallic ions have already been studied in solutions and some polymers.[24-28] The photochemical reaction proceeds through a rotational movement of the dithizone, involves the cleavage of the hydrogen-nitrogen-4 bond followed by a rotation around the N=C bond accompanied by the formation of a new bond between hydrogen and nitrogen-2 (Scheme 1).[24-27] Since both ligands of the mercury dithizonate ($Hg(HDZ)_2$) participate in the isomerization reactions (Scheme 1), this reaction involves a very large change of molecular volume and demands a large free-volume to be available in the polymer matrix.[24-28] Further, absorption spectra of mercury dithizonate contain a strong absorption band centered at

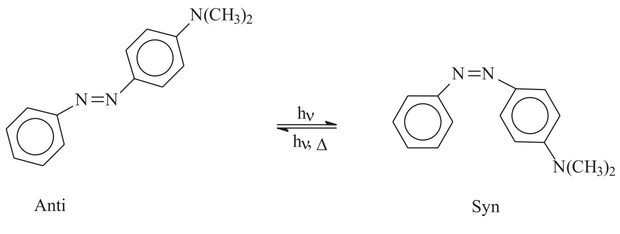


Scheme 1. Isomerization reaction of $Hg(HDZ)_2$. Absorption band of form A (orange form) is centered at 409 nm in PS and of form B (blue form) absorbs at 605 nm.

490 nm assigned to the transition involving the ligand group[25] and after irradiation a new absorption centered at 610 nm appears, which can be reverted in the dark. An isosbestic point at 535-545 nm is also observed.

The second dye is an amino-type azo, whose isomerization is illustrated in Scheme 2.[29-32] Again the anti-syn-anti reactions involve changes of the molecular volume.[33] In general, the $\pi_N \rightarrow \pi_N^*$ and $n \rightarrow \pi_N^*$ transitions of amino-azo groups and the spectral positions of the correspondent bands are influenced by the solvent properties.[2,29-32,34,35] Moreover, for amino-azo dyes and, in particular, for DAB the absorption bands of the two isomers are well separated and thus photoisomerization of the anti isomer can be performed without interferences of the syn back-reaction. In addition, the influence of solvents on the DAB properties is produced by the dye/solvent interactions with the two basic centers in the molecule: the b-nitrogen of the azo-group and the nitrogen of the amino-group and a tautomeric equilibrium takes place (Scheme 3). The stabilization of one or other tautomers depends on the dye/polymer interaction. For instance, protonation of the azo-group leads, preferentially, to the species A[32] and, the absorption spectrum shifs to the blue.[2,32,34]

Here we report the influence of the dye-polymer interaction on thermal (syn to anti) and photoisomerization (anti to syn) reactions employing three types of polymers: polystyrene (non-polar and non-protic material); poly(methyl methacrylate) and poly(vinyl acetate) (polar non-protic materials) and (poly(vinyl alcohol) (polar protic material). The kinetics are also studied in some similar solvents for comparison. Moreover, since the isomerization modifies the molecular volume of every molecule, it depends on the available free-volume in the polymer host. Thus, we submitted the polymer films to annealing and quenching processes to evaluate the effect of the free-volume on the rate constants.



Scheme 2. Isomerization reactions of DAB. Absorption band of the syn form is centered at 325 nm in PS while the anti form absorbs at 412 nm.

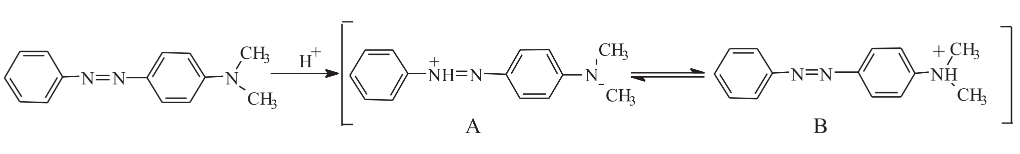
Experimental

4-Dimethylaminoazobenzene (DAB) was supplied by Paragon Testing Laboratories and was precipited from ethanol by the addition of cold water. Mercury dithizonate was synthesized using dithizone (Aldrich Chemical Co.) according to a method described elsewhere.[36] This dye was precipited from a chloroform solution using ethanol. Both dyes were characterized by infrared and electronic absorption spectroscopies.

Pellets of atactic polystyrene (PS) (M_w = 230 kg mol^{-1} and 2.3) were supplied by Poliestireno do Sul (Brazil) type EDN 89. Poly(vinyl acetate) (PVAC) (M_w /M_n = 234 kg mol^{-1} and M_w /M_n = 2.9) was supplied by Aldrich Chemical Co. Poly(vinyl alcohol) (PVA), 100% hydrolyzed, M_w = 115 kg mol^{-1} (data from the supplier), was also supplied by Aldrich Chemical Co. Poly(methyl methacrylate) (PMMA) (M_w = 75 kg mol^{-1} and M_w /M_n = 2.6) was from Polyscience Inc. All polymers were free of additives and stabilizers and were employed without further purification.

The molecular weight and the polydispersity of the polymers were determined by gel permeation cromatography (GPC) (Waters cromatograph model 410, IR detector) using THF as mobile phase with flow rate of 1 mL min^{-1} and polystyrene standards. A system of three columns Ultrastyragel, with particle size of 7 μm, dimension 7.8x300 mm, for size separation range it 2000 to 4x10^6 g mol^{-1} was employed with column temperature of 40 °C.

Films of PS, PVAC and PMMA with both dyes were prepared by casting a dichloromethane solution containing both the polymer and the dye in Petri dishes. The surface of these dishes was silanized with the dimethyl-di-chloro silane to avoid adhesion of the material. The solvent was evaporated at room temperature for 30 h and the film was further dried in an oven at 70 °C for 24 h. Film thickness was 100 μm. The concentrations for both dyes in the polymer films were ca. 1x10^{-5} mol L^{-1} (< 0.02% by mass) to avoid aggregation. Films of PVA containing DAB were



Scheme 3. Tautomeric equilibrium of DAB in acid media.

prepared by casting a 1/1 by volume solution of ethanol/water at 70 °C to which a solution of the dye in ethanol was added. The solvent was evaporated at room temperature for four days, dried in an oven at 60 °C for two days and then at 80 °C for 1 hour. The solvent evaporation was evaluated by thermogravimetric analysis in a DuPont V2-2a-990 thermoanalyzer, using a heating rate of 10 °C min^{-1} in an argon atmosphere. Films of PVA using $Hg(HDZ)_2$ were not prepared due to the reduced solubility of the dye in this polymer. After preparation, all films containing the dyes were maintained in the dark.

PS and PMMA films were also submitted to an annealing process with the samples heated at 85 °C, between two glass slices under a N_2 atmosphere, for 120 h. Then the samples were slowly cooled to room temperature while being maintained under a N_2 atmosphere until the experiment. They were also submitted to quenching, after being heated to 120 °C ($\cong T_g + 10$ °C) for 15 min, by immersing in liquid nitrogen, where they were stored until the measurements. Kinetic studies using annealed and unannelead samples were compared.

The thermal transitions of the films were determined by differential scanning calorimetry (DSC) (DuPont, model v2.2A 90), calibrated with indium as standard, with a heating rate of 10 °C min^{-1}. Two runs were scanned: the first from –150 °C to 150 °C, then the sample was cooled down to –150 °C at a rate of 20 °C min^{-1} and again heated at the same rate to 150 °C. The glass transition temperatures were determined using the data from the second heating cycle, using films with and without dye. No differences were noted.

Slices of the polymer films of 4.5 cm x 1.2 cm x 100 μm were employed for both the UV-Vis spectral recording (Intralab DMS 100 UV-Vis spectrophotometer) and for the kinetic studies.

Samples were irradiated with a high pressure 80 W Hg lamp from which the external glass cover was removed to enhance the total emission of the lamp. The lamp is mounted in a housing with a frontal quartz window. The light beam is filtered with a water cell sealed with quartz (Oriel Co.) windows having a 7 cm optical path and 5 cm diameter to remove infrared radiation. An electro-mechanical shutter (Ealing 22-8411) was employed to alternatively irradiate the sample and record the spectra. The optical glass filter selects the spectral range to excite each specific dye. Under our conditions, each samples is irradiated with $\lambda > 400$ nm to minimize the photochemical back-reaction. The light beam is focused onto an optical fiber bunch that direct the beam to the sample located in the spectrophotometer chamber. Absorption spectra were periodically recorded in the range of 40 nm around the center of the absorption band of each dye and absorbance versus time was plotted for kinetic analysis.

Results and Discussion

Thermal-isomerization reactions

The spectra for the anti-isomer in solvents and in polymer matrices (PS, PMMA, PVAC and PVA) are depicted in Figure 1. This figure shows that the DAB absorption spectra are strongly influenced by the solvent-dye (Figure 1a) and polymer-dye (Figure 1b) interactions, following the same trend as observed for other solvents and azo-dyes.[29-34] The higher intensity band attributed to the $\pi_N \rightarrow \pi_N^*$ band localized in the azo-group is red-shifted when the polarity of the medium increases: 409 nm, 412 nm, 412 nm and 419 nm for PS, PMMA, PVAC and PVA, respectively. While the spectrum for PS is very similar to that obtained for toluene, the spectrum obtained for PVA is very similar to those obtained for this dye in water or alcohols.[34,35] This effect is explained by the interaction of the polar or protic group of the polymer with the β-nitrogen of the azo-group which shifts the tautomeric equilibrium stabilizing the species A (Scheme 3). In addition to the red shift, there is a remarkable decrease of the intensity compared to the $\pi_\phi \rightarrow \pi_\phi^*$ of the phenyl group, centered at 217 nm. This confirms that the dye-polymer interaction due to hydrogen bonds with the azo-groups disturbs both the energy transition and the transition moment.

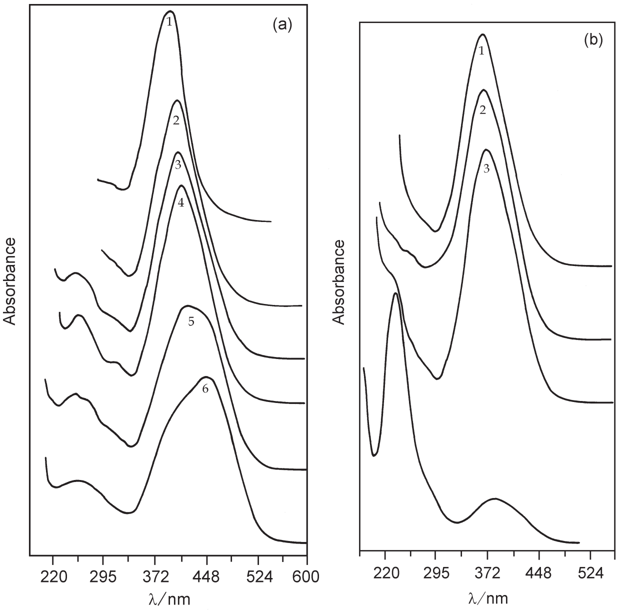


Figure 1. Electronic absorption spectra of DAB in solvents (a): 1. n-heptane, 2. toluene, 3. ethanol, 4. dichloromethane, 5. ethanol/water, 50/50 by volume, 6. water (concentration 2 10^{-5} mol L^{-1}); and in polymers (b): 1. PS, 2. PMMA, 3. PVAC and 4. PVA (concentration of DAB 0.02% by mass). Numbers from the top to the bottom.

When $Hg(DTz)_2$ is dissolved in solvents or in PS and PMMA, the spectra in the visible region is composed of an absorption band centered at 490 nm (isomer A) that was shifted under irradiation to 610 nm (isomer B) (Scheme 1). Nevertheless, we observed that this dye was completely bleached when incorporated in acidic media.[34]

The thermal-isomerization reactions of both dyes in toluene were followed spectrophotometrically (Figure 2). A continuous decrease of the band of the anti-isomer and the continuous increase of the intensity of the band of the syn-isomer takes place. An isosbestic point demonstrates the interconversion between only two species. The kinetic analysis was performed monitoring the absorbance at the peak and the experimental data were analysed according to the equation 1:

$$\ln \frac{[syn]_t}{[syn]_0} = \ln \frac{(A_\infty - A_t)}{(A_\infty - A_0)} = k\,t \qquad (1)$$

where A_0, A_t and A_∞ are the absorbances of the more stable isomer undergoing the iomerization at the starting, at time t and after the complete conversion of the more stable isomer. In the case of DAB this isomer is the anti isomer and, in case of $Hg(HDZ)_2$, it is the form A. Plots of $\ln \frac{(A_\infty - A_t)}{(A_\infty - A_0)}$ versus time were employed for the determination of the constant rate, and a linear plot is expected only if one constant rate is required for a good description of the experimental data.

Although the kinetic curves obtained for DAB in toluene are linear (Figure 3a) those obtained for DAB in polymers are not linear (Figure 3b), implicating that, although the reaction is unimolecular, the kinetics can only be well represented if two rate constants are employed. Therefore, a model considering the polymer matrix below its glass transition as a biphasic system was utilized to analyze these data.[37] Under this assumption, and

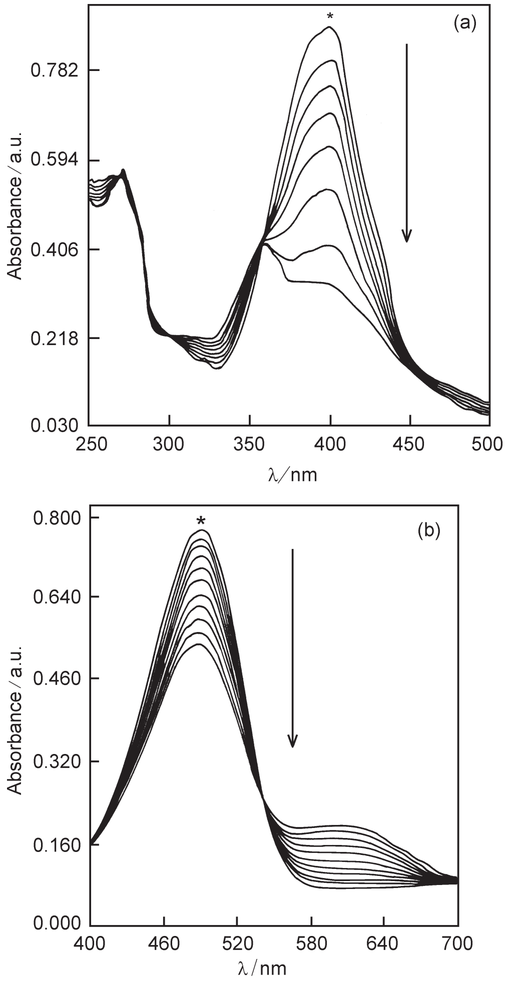


Figure 2. Spectral changes of the absorption spectra during the thermal-isomerization of DAB (a) and $Hg(HDZ)_2$ (b) in toluene. Concentration is 2 10^{-5} mol L^{-1}. The arrows indicate the sequence of the measurements. Measurements at 30 °C.

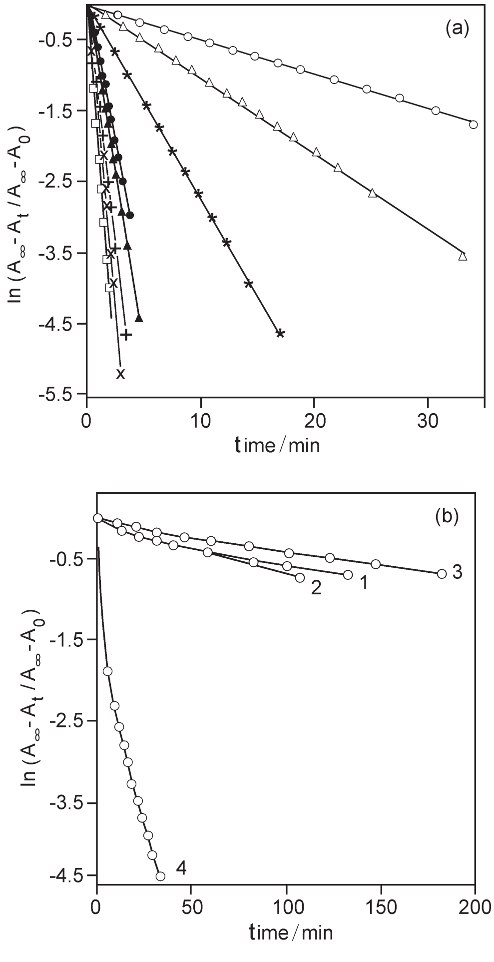


Figure 3. Kinetic curves for the thermal-isomerization of the DAB in (a) solvents (○ - mineral oil, △ - dioxane, ★ - n-butanol, ● - toluene, ▲ - n-heptane, × - n-hexane, ✚ - n-pentane, ☐ - ethyl acetate) and (b) polymer matrices: 1. PS, 2. PMMA, 3. PVAC and 4. PVA. Measurements at 30 °C.

monitoring the absorbance of one species, the rate constant can be determined by (equation 2):

$$\frac{A_t}{A_0} = \alpha\, e^{-k_1 t} + (1-\alpha)\, e^{-k_2 t} \qquad (2)$$

where: k_1 and k_2 are the rate constants for the fast and slow processes, a is the fraction of each phase in the matrix.[20-23] Usually, the faster component is similar to the rate constant for the reaction in a solvent with similar viscosity.[19-23] Thus, the experimental curve was fitted to this bi-exponential function. According to this model, and considering that the isomerization process requires a certain minimum volume, it has been suggested that the a parameter is proportional to the fraction of molecules localized in a free volume larger than the critical radius necessary for the isomerization, which depends on the size of the molecule undergoing isomerization. This model has been successfully applied for several types of dyes and is also able to explain linear behavior at temperatures higher than the glass transition, above which the medium behaves as a viscous homogeneous solvent.[19-23,33] The rate constants calculated using this model for the thermal-isomerization reactions of DAB $2\text{x}10^{-5}$ mol L^{-1}, at 30 °C, in several solvents are: 1.96 for ethyl acetate, 1.74 for n-pentane, 1.35 for n- hexane, 1.35 for n-heptane, 0.972 for toluene, 0.273 for n-butanol, 0.104 for dioxane and 0.047 for nujol. Similar values for polymer matrices are showed in Table 1.

Table 1. Apparent rate constants for the thermal-isomerization reactions of DAB in PS, PMMA, PVAC and PVA, at 30 °C. T_g are the glass transition temperatures for these polymers determined by dsc

Polymer	T_g / °C	k_1 / min^{-1}	k_2 / min^{-1}
PS	104	1.5 10^{-2}	3.2 10^{-3}
PMMA	95	1.1 10^{-2}	5.2 10^{-3}
PVAC	32	1.0 10^{-2}	2.9 10^{-3}
PVA	80*	1.9 10^{-2}	8.3 10^{-3}

* PVA is a semicrystalline polymer with a melting temperature, T_m = 150 °C.

As we can see, the rate constants for DAB thermal-isomerization obtained for polymer matrices (Table 1) are at least 100 times slower than in solvents of similar polarity: 1.96 for ethyl acetate, 0.812 in toluene and 0.273 in n-butanol.[35] Moreover, these values also show that both rate constants are faster for PVA than for the other non-protic polymers. This effect is similar to that observed for solvents and is explained by the stabilization of the electronic excited state by hydrogen bonds involving the nitrogen of the azo-group of the anti-isomer due to polymer-dye interaction. In conclusion, although the rate constants were always slower for polymer matrices compared to the solvents, the dye-polymer interaction influences both the spectral characteristics and the rate constants of the thermal-isomerization reactions.

Photochemical isomerizations

Irradiation of the samples of both dyes in PS and PMMA, which were initially maintained in dark, induces a photo-isomerization reaction. Under our experimental conditions, only the more stable forms were excited and back-photoreactions were minimized. Again, for both dyes the kinetics of the photo-isomerization in polymer matrices were not linear and two rate constants are required to fit the experimental data. Furthermore the time scales for the photochemical reactions of these dyes were at least one order of magnitude slower for $Hg(HDZ)_2$ than for DAB (Figure 4, Table 2), showing once more that the rate constants for the smaller molecules are faster. Thus, in agreement with other reported data, larger molecules require larger free-volumes in the matrix.[1,9,10,13,20,37]

Table 2. Apparent rate constants for the photoisomerization reactions of DAB and $Hg(HDZ)_2$ in PS and PMMA, at 30 °C under different thermal conditions

	PS		PMMA	
k_1 x (10^3 min^{-1})	DAB	$Hg(HDZ)_2$	DAB	$Hg(HDZ)_2$
Initial	3.8	0.53	4.0	0.37
annealed	9.3	0.86	4.2	0.43
quenched	13.3	0.95	9.4	0.58
	PS		PMMA	
k_2 x (10^3 min^{-1})	DAB	$Hg(HDZ)_2$	DAB	$Hg(HDZ)_2$
Initial	3.1	0.038	2.0	0.019
annealed	3.4	0.039	2.0	0.024
quenched	4.7	0.046	1.5	0.020

It is also note worthing that the faster photo-isomerization rates are of the same order of magnitude as the thermal-isomerization reactions, while the slower component is, approximately, one order faster for the photo than for the thermal-isomerization. Considering that the mesurements were performed under similar conditions (the same concetration of dyes and using the same light source at the same intensity), the other remarkable observation is that both thermal and photo-isomerization reactions are faster for DAB in PMMA (a polar polymer matrix) than in PS (a non-polar matrix), revealing again that, similar to solvents, the polymer-dye interactions strongly affect the rate constants.

The necessity of larger free-volumes for the reactions was also demonstrated in studies of the photoisomerization reaction in a polymer matrix submitted to quenching or

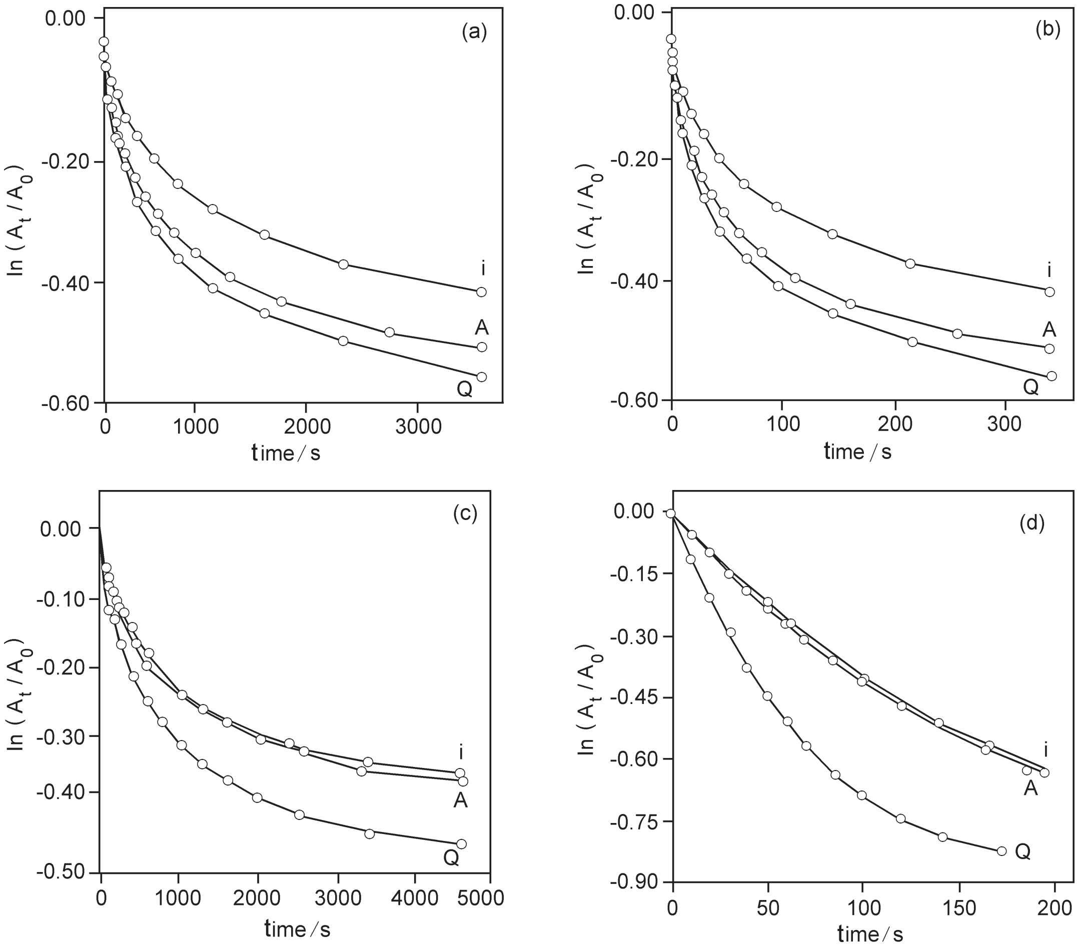


Figure 4. Kinetic curves for the photoisomerization of DAB and Hg(HDZ)$_2$ in PS (a,b) and PMMA (c,d) submitted to physical aging: initial (i), annealed (A), and quenched (Q) samples.

annealing processes (Figure 4). These physical aging processes influence both the amount and the distribution of the free-volume sizes. It has been known for a long time that annealing is a physical aging process that decreases the relative amount of the larger free-volumes, compared with smaller local free-volumes and sharpens the total distribution of free-volumes.[34-37] In contrast, quenching increases the relative amount of the larger free-volumes and, for semicrystalline materials it also reduces the degree of the crystallinity.[37,38]

Data obtained for both dyes in PS show that the rate constants for the initially prepared sample were slower than the annealed and the quenched samples (Figure 4a,b and Table 2). Moreover, the rate constants for the faster processes (those occurring with the dyes located in larger cavities of the polymer matrix) for both dyes were more influenced by the thermal aging than were the slower component. Since all films were initially prepared by casting the solution and further exhaustively dried (the solvent was evaporated at room temperature for 30 hours, then the film was further dried in an oven at 70 °C for 24 h) we assume that, under these experimental conditions, the systems are thermally equilibrated. Consequently, the rates in the smaller free-volumes are, on average, lower and the rate constants reflect these reaction rates. In addition, since the faster rate constants were more influenced by the physical aging than the slower ones, we also assume, in agreement with other reports,[37] that the larger free-volume undergoes greater reduction, compared to smaller, and a sharper distribution of free-volume is also achieved.

We also observed that the rate constants of DAB (smaller molecular volume) are more influenced by quenching than those of Hg(HDZ)$_2$ (larger molecular volume). This is explained considering that the DAB molecules are distributed in the cavities with smaller sizes compared to Hg(HDZ)$_2$. Therefore, quenching greatly increases the size of the initially smaller cavities, where the DAB molecules are preferentially located.

In the case of PMMA, a polymer with a larger polar lateral group, the rate constants for both the initial and the annealed samples are almost equivalent for both dyes, demonstrating that, again, the optimal conditions in terms of thermal equilibrium of the samples were achieved during the preparation of the samples. Further annealing does not change the size and the distribution of sizes of the cavities in the polymer matrix. Nevertheless, the rate constants for the quenched samples are always faster than the untreated initial or the annealed samples, as expected since this process enlarges the cavities of the matrix and broadens the distribution of the free-volumes. Thus, faster photo-isomerization is observed, as expected.

It was determined using molecular probes of different sizes that the average local free-volume in unannealed PS was around 260-280 Å^3, with over 90% larger than 100-120 Å^3 and practically none larger than 400 Å^3.[37] It has also been demonstrated that PMMA possesses a broader overall local free-volume distribution than PS.[37] Assuming that this volume distribution is valid for our experimental conditions, we may consider that there is a very small amount of molecules located in cavities with volumes larger than the molecular volumes of DAB or Hg(HDZ)$_2$, whose volumes were calculated[39] as $V_{M(DAB\text{-}syn)}$ = 262 Å^3, $V_{M(DAB\text{-}anti)}$ = 236 Å^3, $V_{M(Hg(HDZ)2\text{-}A)}$ = 544 Å^3 and $V_{M(Hg(HDZ)2\text{-}B)}$ = 419 Å^3, and which undergo reactions involving rotations or inversions of large groups. Therefore, the photo-isomerization or thermal-isomerization of these probes should be slower processes.

In addition to the kinetic data, the dsc curves (Figure 5) show that quenched samples exhibit a peak of stress during the glass transition that can be removed by annealing for both the PS and the PMMA samples. Thus, in addition to the modifications of the free-volume size and distribution of sizes, the quenching process also produces a stressed solidified amorphous material that relaxes under heating.

Conclusions

We showed that the isomerization rates of azo-dyes in some polymer matrices as well as in some solvents, depend on dye-polymer (dye-solvent) interactions. Specifically, we observed that, for both DAB and Hg(HDZ)$_2$, the isomerization reactions are faster for more polar solvents/polymers. We also observe that the isomerization reactions in polymer matrices depend on the molecular size and, thus, the polymer matrix imposes strong steric hindrance to the molecular motions of the dyes undergoing isomerization. For solvents, these reactions are well represented by mono-exponential functions while for polymers good fits require, at least, bi-exponential functions. Above the glass transition temperature good fits can be obtained using single exponentials. In general, it is assumed that the amount, size and shape of the free-volume control the rate constants and that the proportion of the faster and slower components can be modified by prior thermal treatments of the sample, such as annealing or quenching.

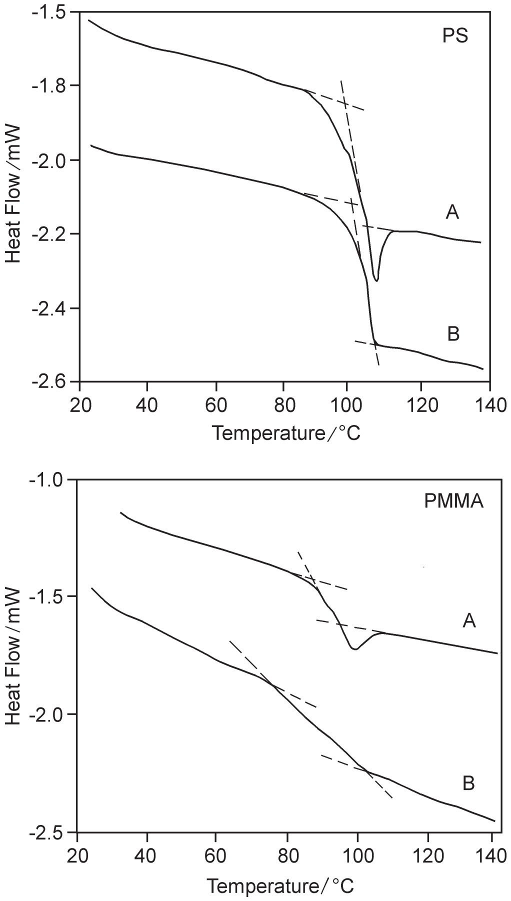


Figure 5. DSC traces for the PS and PMMA samples submitted to annealing (A) and quenching (Q) processes.

Good control of the rate constants is very important for different applications of azo-dyes. For instance, the best dyes for photoinduced orientation are pseudo-stilbenes whose π-π^* and n-π^* bands strongly overlap and photoinduced anti-syn reaction takes place simultaneously with the back-reaction (syn-anti). Thus, intrinsic polarity of the dye controls the velocity of the reactions in both directions. Here we employed a different approach to control the reaction rates, i.e., by controlling the properties of the medium. More polar polymer induces greater reaction rates, and the reason is attributed to the changes of the tautomeric equilibrium of the dye.

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