Cis−Trans Thermal Isomerization Rates of Bound and Doped Azobenzenes in a Series of Polymers

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A series of high-T_g side-chain azo aromatic polymers and small molecular weight azobenzenes dissolved in polymers were cast as thin films and subjected to a pump/relax procedure to analyze the thermal cis−trans isomerization behavior of the azo groups. All samples exhibit a fast isomerization process due to strained cis isomers trapped below the glass transition temperature of the film, followed by a slower isomerization process which can be analyzed by a monoexponential decay. Thermal isomerization rate constants are found to depend on the spectral type of the chromophore and type of attachment to the polymer backbone and, less importantly, on the glass transition temperature and the crystalline order of the polymer.

Introduction

Azobenzene-containing polymers see extensive use as polymeric dyes, molecular probes, electrooptic liquid crystals, and materials for nonlinear optics and optical storage. The most interesting recent studies, however, make use of the readily induced and reversible isomerization about the azo bond, and the resultant changes in both visible spectrum and geometry, to control macroscopic properties of thin films. Kippelen et al.[1] have reported formation of photorefractive gratings in azo polymer films, Ichimura et al.[2,3] use isomerization of thin films of azo polymers to change the orientation of adjacent layers of liquid-crystalline compounds, and many research groups are reporting azo polymer films as suitable materials for reversible optical storage.[4−6] Key to all of these applications are the trans−cis photoisomerization, cis−trans photoisomerization, and cis−trans thermal isomerization of the azobenzene chromophores. This thermal reconversion from the cis form to the trans is much slower than the photochemical reconversion and is the only isomerization mechanism under no irradiation, so it is often the rate-determining step for processes which involve repeated trans−cis−trans isomerization cycles. As the research in our group centers around rational design of azobenzene polymers for reversible optical storage, there is much interest in the extent to which polymer properties such as glass transition temperature, crystalline order, chromophore spectral type, and method of attachment to the polymer backbone affect the rate of thermal cis−trans isomerization.

The wide variety of azobenzene chromophores in use today displays a wide range of properties and can be most effectively subdivided into classes of spectral type. Rau characterizes azobenzenes into three types based on the energetic ordering of their (n,π^*) and (π,π^*) states as azobenzene type, aminoazobenzene type, and pseudo stilbene type.[7] Azobenzene type molecules display a low intensity $n \rightarrow \pi^*$ band in the visible region and a high intensity $\pi \rightarrow \pi^*$ band in the UV. Ortho or para substitution with an amino group leads to the aminoazobenzene type where the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands are very close or overlapped in the violet or near-visible UV, due to an increase in the π orbital energy, and a decrease in the energy of the π^* orbital. This effect is enhanced with the 4 and 4′ position substitution of electron-donor electron-acceptor (push/pull) substituents in the pseudo-stilbene class, increasing the charge-transfer character of the $\pi \rightarrow \pi^*$ transition and shifting the corresponding band far to the red, past that of the $n \rightarrow \pi^*$ to assume a reverse order. Cis−trans thermal isomerization can range from the order of hours and days for azobenzenes to seconds and milliseconds for pseudo-stilbenes. Debate over the mechanism of thermal isomerization of pseudo-stilbenes arose with their early study around 1970, and little has been clear since, with some research suggesting inversion, some research suggesting rotation, and some research suggesting a competition between both.[7]

Early studies of isomerization rates of substituted azobenzenes attached as polymeric side chains were carried out by Morawetz and Paik,[8] who in 1972 reported first-order thermal cis−trans isomerization in polymers in solution and in bulk above T_g but an anomalous fast relaxation component in the glassy state. Azobenzenes had long been characterized by their reversible isomerizations following first-order

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Table 1. Formulas of Materials Studied

abbreviation	polymer
(a) PDR1A	poly[4′-[((2-(acryloyloxy)ethyl)ethyl)amino]-4-nitroazobenzene]
(b) PDR1M	poly[4′-[((2-(methacryloyloxy)ethyl)ethyl)amino]-4-nitroazobenzene]
(c) PDR13A	poly[4′-[((2-(acryloyloxy)ethyl)ethyl)amino]-3-chloro-4-nitroazobenzene]
(d) PDR13M	poly[4′-[((2-(methacryloyloxy)ethyl)ethyl)amino]-3-chloro-4-nitroazobenzene]
(e) PMEA	poly[4-[2-(methacryloyloxy)ethyl]azobenzene]
(f) PDO3A	poly[4′-nitroazobenzene-4-acrylamide]
(g) PDO3M	poly[4′-nitroazobenzene-4-methacrylamide]
(h) PDR19t	poly[(4′-(4-nitroazobenzene)(hydroxyethyl)ethoxyamine-1′-carbonyl-2′-(4″-(1‴,2‴-enoic acid)phenyl)ene]
(i) PDR19b	poly[4′-(4-nitroazobenzene)(hydroxyethyl)ethoxyamine)-1′-carbonyl-4″-biphenoic acid]
(j) DR1	4′-[((2-hydroxyethyl)ethyl)amino]-4-nitroazobenzene
in PASH	poly[1-(4′-(1″-oxy-4‴-hydroxybisphenol A)benzoyl)-2-benzoyl-3,4,5,6-tetraphenylbenzene]
and PMMA	poly[methyl methacrylate]

kinetics (monoexponential thermal relaxation). This is well-known both in solution and in bulk,[9] with the notable exception of azobenzenes dissolved in glassy polymers. In these systems a fast component of thermal cis–trans relaxation ascribed to relaxation of azo groups trapped in strained conformations in the glassy state is observed[10-20] as described previously.[21] Relaxation curves in these systems were fit with either a biphasic decay[8,14] or a Williams–Watts function[15] which models a continuous distribution of relaxation rates reflecting the inhomogeneity of free volume at the strained sites. It has also been shown that the thermal cis–trans isomerization rates of azobenzene copolymers can follow a decay as a composite of three possible sequence triads and is hence triexponential.[21] In pseudo-stilbene homopolymers, however, only the strained and monoexponential components are observed, and whether or not this strained component is biphastic or continuous, there is agreement that these anomalous rate constants are 10–60 times higher than those of the monoexponential component,[8,10] and effects are then minimal a few seconds after pumping. Thermal cis–trans relaxation for a variety of azobenzene polymers was observed to be monoexponential from this point and exhibited a wide range of rate constants.

Experimental Section

The materials studied consist of azobenzene dyes covalently attached as side chains to acrylate, methacrylate, and acrylamide polymers, and a small molecular weight azobenzene chromophore dispersed in both poly(methyl methacrylate) (PMMA) and PASH at 10 wt %. Synthesis of the monomers and the polymers have been described previously.[6,22-24] Structures of materials are detailed in Figure 1a and formulas listed in Table 1.

Polymer films were prepared by spin-casting from tetrahydrofuran (THF) onto a glass substrate to yield films with an optical density near unity at the irradiation wavelength of 488 nm. With the exception of PMEA, all polymers displayed either maximum or strong $\pi \rightarrow \pi^*$ absorption at this wavelength. PMEA, with virtually no absorption at this wavelength, was irradiated at 350 nm. Trans–cis photochemical isomerization was induced by irradiation with a circularly polarized unfocussed beam from an argon laser (λ = 488 or 350 nm) for 1 s. A reading beam of the same wavelength but attenuated (2.5×10^{-4}) was passed through the sample coincident with the pump beam and into a photodiode, to monitor and digitally record the thermal cis–trans relaxation subsequent to pump irradiation similar to the procedure described by Dumont et al.[20] The very slow thermal relaxation of PMEA required construction of a composite relaxation curve where the amount of signal induced upon pump irradiation

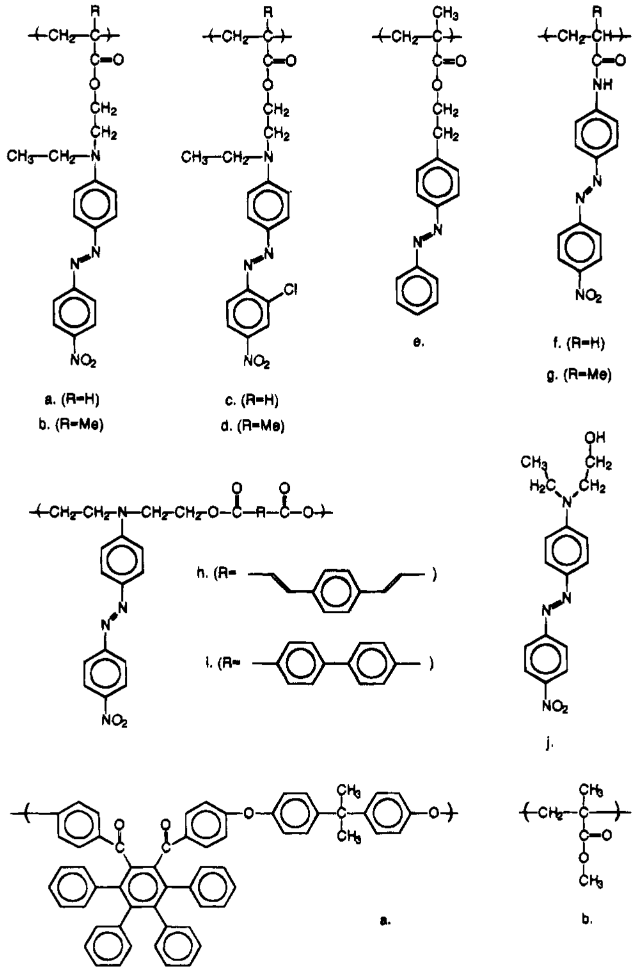

Figure 1. (a) Azobenzene polymers from DR1 (a), (b), (j); DR13 (c), (d); MEA (e); DO3 (f), (g); DR19 (h), (i). (b) Polymer hosts for DR1 dopant: (a) PASH; (b) PMMA.

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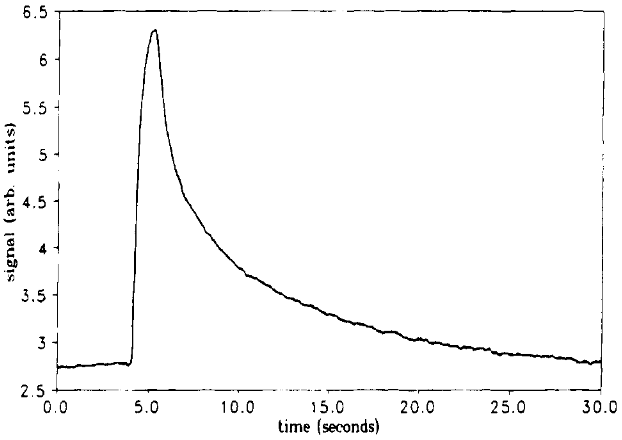

Figure 2. Pump/relax curve of PDO3M.

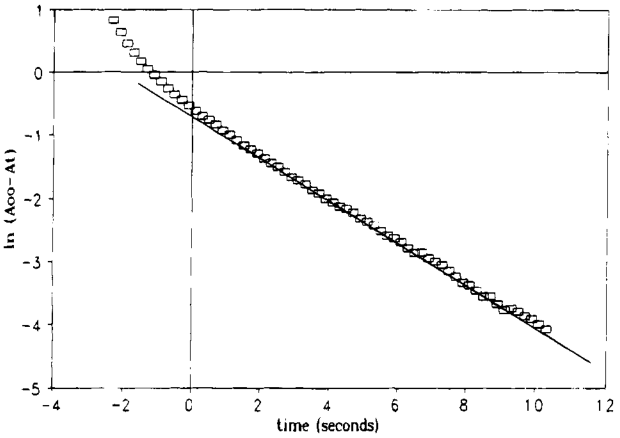

Figure 3. Plot of $\ln(A_\infty - A_t)$ vs t for PDR1M.

was measured for a series of pump/relax trials with various times between pumping (10 min to 8 h).

Results and Discussion

The azo polymers detailed in Figure 1 were cast as thin films and irradiated for 1 s near the $\lambda_{\max}$ to induce trans–cis isomerization (pumping). A probe beam of the same wavelength and low intensity was passed through the sample coincident with the pump beam and into a photodiode to record the absorbance changes at the trans absorbance over time (relaxation). A typical pump/relax curve for the pseudo-stilbene-type homopolymers is shown in Figure 2. The pump beam is switched on at $t \approx 4.5$ s and left on for 1 s. The induced trans–cis isomerization results in a sharp decrease in the absorbance at 488 nm and hence an increase in the intensity of light passing through the film and into the photodiode. As $[\text{trans}]_\infty = [\text{cis}]_t + [\text{trans}]_t$, this curve can be regarded as an indirect measure of [cis]. For a first-order reversible relaxation process where $[\text{trans}] \propto A$, a plot of $\ln(A_\infty - A_t)$ vs t should be linear with slope k, the rate constant for thermal cis–trans isomerization. A typical plot of $\ln(A_\infty - A_t)$ vs time is presented in Figure 3. As expected for isomerizations in the bulk glassy state, the decay is not strictly monoexponential but exhibits an anomalous fast component for the first few seconds. As discussed previously, this component has been observed and studied in glassy polymers below T_g.[8,10,11,13-20,25] While there still exists some debate as to whether this fast component is biexponential or a continuous distribution of rates, there is agreement that it is attributed to relaxations of azo groups trapped in strained conformations in the rigid glassy matrix, and effects are minimal a few seconds into relaxation. It has been estimated that up to 14% of these azo groups are strained and relax anomalously quickly.[8] Modeling decay of this fast component on estimates of a rate in excess of an order of magnitude higher than the monoexponential rates[8,10] shows that the fast decay is more than 99.5% complete after 3 s, and analysis of all curves begins at this point, relabeled as $t = 0$ in Figure 3. It can be seen that this rate plot (and the rate plots for all polymers) is linear after this point, and the rate constant k can be determined from the negative slope. The rate plot remains linear until A_t becomes very close to A_∞ and is lost in noise. The fast component was observed for all pseudo-stilbene-type samples and appeared to be a continuous distribution of rates in excess of an order of magnitude faster than the first order rates studied. The data analysis delay of 3 s proved to be sufficient for all samples, showing that effects of this fast component were not large enough to deviate observed relaxation from monoexponential behavior after this time. All polymer samples exhibited similar fast components, as the decay was also not observed to be monoexponential before this point for any irradiated films, suggesting similar free-volume requirements for the series of chromophores studied. This fast component was not studied further than to insure no interference with the monoexponential rates analyzed.

Table 2. Thermal Cis–Trans Rate Constants

polymer	k in s^{-1}
PDO3A	0.10 ± 0.006
PDO3M	0.12 ± 0.01
PDR19b	0.18 ± 0.02
PDR19t	0.20 ± 0.02
PDR1M	0.22 ± 0.01
PDR1A	0.24 ± 0.01
PDR13A	0.27 ± 0.01
PDR13M	0.29 ± 0.02
DR1 in PASH	0.31 ± 0.008
DR1 in PMMA	0.36 ± 0.006

The isomerization was found to be completely reversible, as subsequent pump/relax cycles on the same spot produced indistinguishable relaxation behavior both in the amount of signal that could be generated (A_0) and in the decay rate constant (k). Pump/relax cycles were performed on all pseudo-stilbene polymer films in this manner, decay was found to be monoexponential 3 s after irradiation, and the corresponding rate constants are shown in Table 2.

PMEA, the only polymer film of the azobenzene spectral class, required an irradiation wavelength near its 330 nm maximum in the UV. Subsequent thermal relaxation was very slow and required construction of a composite relaxation curve of many pump irradiations. The amount of signal induced upon pump irradiation (inversely proportional to the amount of cis isomer at that time) was recorded with various times between pumping from 10 min to 8 h. Irradiation after up to 10 min produced virtually no signal ([cis] saturation) and after 8 h the sample had relaxed (no [cis]) so that the signal that could be induced was maximum. The difference between the maximum signal and the signal

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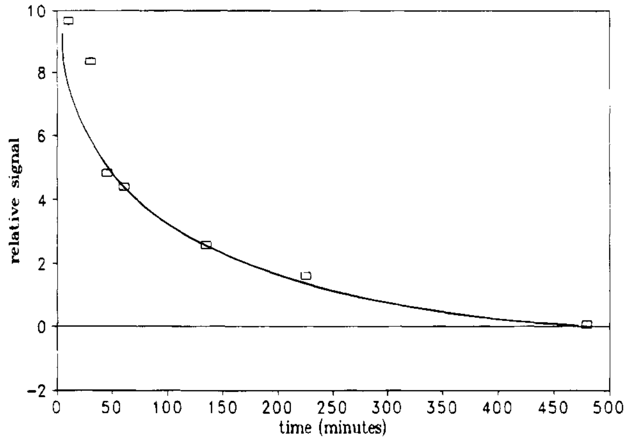

Figure 4. Composite thermal relaxation curve of PMEA.

Table 3. Absorbance Maxima and T_g Values for Azo Polymers

polymer	λ_{max}	T_g (°C)
PMEA	330	70
PDO3A	370	>180 (dec)
PDO3M	370	>180 (dec)
PDR19b	508	148
PDR19t	508	118
PDR1M	483	129
PDR1A	483	91
PDR13A	486	87
PDR13M	486	90
DR1 in PASH	464	171
DR1 in PMMA	464	60

that could be induced for intermediate times was plotted against time to produce the composite thermal relaxation curve shown in Figure 4. The data obtained in this manner were not suitable for curve fitting or observation of a fast component, and the rate constant reported is determined under the assumption of monoexponential behavior. For a first-order decay, the relative signal (S) decays as $S = e^{-kt}$ or $\ln S = -kt$. $k = 1/t$ when $S = 1/e$; therefore, k can be estimated at the point in time when S has decayed to the fraction 0.37 (1/e) of its initial value. This can be estimated graphically to occur at $t = 5400 \pm 850$ s and hence the thermal rate constant k for PMEA is estimated to be $1.9 \times 10^{-4} \pm 3 \times 10^{-5}$ s^{-1}, 3 orders of magnitude lower than the rest of the homopolymers.

This series of azobenzene polymers is comprised of materials which possess a relatively wide range of glass transition temperatures and λ_{max} and are either amorphous or semicrystalline, and the azo groups are attached to the backbone with spacers of various lengths. Some properties of the polymers studied are listed in Table 3. Through these rate constants, these polymers then allow an estimation of how thermal isomerization is influenced by polymer properties such as spectral type, glass transition temperature, crystalline order, and attachment to the backbone.

While the glass transition temperature and side-chain mobility may have appreciable influence on these decay rates, the most dominant effect appears to be the spectral type of the chromophore. As described previously, azo polymers can be broadly classified with the energetic ordering of their (n,π^*) and (π,π^*) states as azobenzene type, aminoazobenzene type, and pseudostilbene type.[9] The λ_{max} for all polymers are listed in Table 3. PMEA, the only example of the azobenzene spectral class with no electron donor–electron acceptor substituents, relaxes 3 orders of magnitude more slowly than the rest of the polymers, which do have some degree of electron donor–electron acceptor character. While the rest of the chromophores can all be classified broadly as pseudo-stilbenes, there still remains a range of donor/acceptor character, as evidenced by the large difference of λ_{max} values for the $\pi \rightarrow \pi^*$ band. DO3 polymers with λ_{max} at 370 nm, and the smallest influence of charge-transfer substituents relax thermally at only one-third the rate of the DR1 and DR13 polymers with λ_{max} near 480 nm. The rest of the polymers have similar electron donor–electron acceptor substituents and relax with similar rates.

While it is well-known that the glass transition temperature influences the thermal cis–trans isomerization rates of azobenzenes in polymers, effects are largest when the T_g of the material is close to the experimental temperature (T). Orientation studies of rigid groups in polymer matrices have shown that there is much free movement near T_g, decreasing as T_g increases, but leveling off when the difference between T and T_g is ~50 °C. Beyond this limit the influence of T_g is minimal with all matrices being regarded as "frozen".[12,26,27] T_g's of the homopolymers are listed in Table 3. DO3 polymers thermally decompose at 180 °C, before reaching this transition. In all samples the distance between experimental temperature and T_g is large, with most T_g values over 100 °C, and consequently the variation of T_g probably does not have a large effect on relaxation rates. Varying the main chain of identical chromophores to investigate T_g differences between acrylate backbones (generally lower T_g) and methacrylate backbones (generally higher T_g) also seemed to have little effect on relaxation rates. Both acrylate and methacrylate main chains were prepared for the samples of DR13, DR1, and DO3, and in all cases the thermal cis–trans isomerization rate constant for the acrylate polymers was, within experimental uncertainty, the same as that for the methacrylate. DR1 was also dissolved into both PMMA with T_g of the system = 60 °C and PASH with T_g of the system = 171 °C. The higher T_g material displayed a slightly slower thermal cis–trans isomerization, suggesting that there is some influence from the rigidity of the matrix, though not to a large extent, as the difference in T_g's of the matrices was 111 °C, but the relaxation rates differed by only 0.05 s^{-1}, under 15%.

Crystallinity of the sample likewise does not appear to play a major role, as evidenced by the relaxation rates of PDR19b and PDR19t. Both of these polymers are semicrystalline, determined for PDR19t as 16% crystallinity by X-ray diffraction.[28] The rates observed for PDR19b and PDR19t agree, however, with the rates of DR1 polymers with a similar chromophore yet completely amorphous matrix, showing that there are not appreciable differences in thermal isomerization rates between these amorphous and crystalline polymers. Large differences in orientation rates and extent for optical storage studies, however, have been reported

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between semicrystalline PDR19t and amorphous PDR1A,[28] attributed to the crystalline order. Furthermore, if a crystalline matrix afforded a significantly dissimilar relaxation environment to an azobenzene side chain, the crystalline and amorphous regions in PDR19t would relax with two independent and characteristic rates. Systems of this type, where two different components combine to a net relaxation, lead to a biexponential decay of signal, which can be resolved in the rate plot and the individual rate constants determined.[8,10,14,18,29] The monoexponential decay of PDR19t confirms that decay is governed by a single rate constant in both crystalline and amorphous regions.

The relaxation rates are also dependent on the mobility of the chromophore in the polymer matrix. This can be varied by lengthening the spacer that attaches the chromophore to the backbone from virtually none in the case of DO3 to a flexible ethylene spacer in the case of DR1 and, at an extreme, no attachment and full mobility in the case of DR1 dissolved in PMMA. The less-mobile DO3 azo groups relax much more slowly than DR1 polymers, though with a large difference between them in T_g and λ_{max} this relaxation difference cannot be attributed solely to spacer length. The rate of relaxation of dissolved DR1 in PMMA is much higher than that of the DR1 moiety covalently attached in PDR1A and PDR1M. This can be attributed to the increased mobility of the DR1 unit, free at either end to allow the large geometrical change involved with isomerization. Many studies of isomerization of azobenzene have been carried out in bound vs doped vs solvent systems[8,13,19,25,30-33] with the general agreement that azobenzene-doped polymers relax thermally much more quickly (near the rates observed in solution) than bound systems.

Conclusions

Irradiation of amorphous azo polymer films with light of an absorbing wavelength induces trans–cis isomerization, and the azobenzene groups then isomerize back thermally in the dark. All pseudo-stilbene polymer samples show at least two rate behaviors. A fast component, displaying a distribution of rates and attributed to cis isomers trapped in strained conformations in the rigid polymer matrix, dominates the decay for the first few seconds. The remainder of the relaxation can be described with a first order monoexponential rate. These thermal cis–trans isomerization rate constants are found to depend most strongly on the spectral type of the chromophore and type of attachment of the chromophore to the polymer backbone and less strongly on the glass transition temperature or degree of crystallinity.

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