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Thermal Cis-Trans Isomerization Rates of Azobenzenes Bound in the Side Chain of Some Copolymers and Blends

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ABSTRACT: Copolymers of 4′-[[2-(acryloyloxy)ethyl]ethylamino]-4-nitroazobenzene (DR1A) with methyl methacrylate (MMA) and of the respective methacrylate monomer (DR1M) with MMA were cast as films and subjected to a pump/relax procedure to analyze the thermal cis-trans isomerization behavior of the azo groups. Blends of polyDR1A with polyMMA were also used in a similar manner. All samples show a fast isomerization process due to strained cis isomers, trapped below the glass transition temperature of the film, followed by a slower isomerization process. The homopolymers, all blends, and the copolymers with very low azo concentrations can be analyzed by a monoexponential decay for the slow process. The isomerization of all other copolymers is analyzed as a sum of three monoexponential processes, in which each process is the isomerization of an azo-centered triad. The rate constants found for the individual processes indicate that isomerization is faster when more azo groups are neighboring the central azo group in the triad. This is proof for the neighboring effect on motion of the azo groups, even in these completely amorphous samples.

Introduction

Azobenzene-containing polymers have a variety of potential practical applications and have received a lot of attention in the last few years.[1] We proposed the use of amorphous high-T_g azobenzene-containing polymers in reversible optical storage,[2] taking advantage of the reversibility of the photoinduced trans-cis isomerization in donor-acceptor-substituted azobenzenes.[3] Changing the orientation direction in liquid crystalline polymer films had been previously explored.[4]

Early studies of cis-trans thermal isomerization rates of substituted azobenzenes attached as side chains in various polymers were carried out by Morawetz and Paik[5] who, in 1972, reported first-order behavior when the polymers were in solution or above their glass transition temperature. The relaxation had an anomalously fast component for polymers in the glassy state. It has been known for a long time that the cis-trans thermal isomerization of azobenzenes can be characterized by first-order kinetics both in solution and in bulk.[3] Azobenzenes dissolved in glassy polymers however, present an anomalously fast component of the thermal cis-trans isomerization which has been attributed to a nonuniform distribution of free volume in the glassy state.[6-8] This fast component has been observed and studied in main-chain azoaromatic polymers,[9-11] side-chain azoaromatic polymers,[5,12-14] azobenzenes covalently attached to a silica gel matrix,[15], and polymers doped with various azobenzenes.[16-20] The general agreement is that the photochemically induced trans-cis isomerization process occurs on picosecond time scale[21] and that the thermal cis-trans isomerization is much slower and can be described by a first-order kinetics when the polymers are in solution, in monolayer films, in bulk above T_g, or even below T_g if they are irradiated above T_g. When the solid polymers are in the glassy state, there are at least two processes: one anomalously fast which is assigned to the relaxation of azo groups trapped in strained conformations; and another one which can usually be described by a first-order process. The decays of the cis concentration were fit either with a biexponential[4,12] or a Williams-Watts function,[13] which models a continuous distribution of decay rates, reflecting the inhomogeneity of free volume at the strained sites. The biexponential models show that the strained rate constants are 10-60 times greater than the "normal" rate constants.[5,6] Paik and Morawetz[5] estimated that about 14% of the azobenzene groups are strained and relax anomalously fast. It is very important to note that all these studies were performed on copolymers containing a single low azo group concentration.

The only report on a series of copolymers containing various amounts of azobenzene groups concentrated on liquid crystalline copolymers.[13] No monoexponential behavior was noted for this series and a biexponential decay was also not a good enough fit. Either a triexponential decay or a Williams-Watts function could be used to fit the experimental data. As there was no physical interpretation for a triexponential, a continuous distribution of decay constants was chosen as the solution and the constants were reported.

This paper presents the measurements of the thermal cis-trans isomerization rate on two series of copolymers and one series of blends based on disperse red 1 monomers. Our results show that, after the anomalously fast decay, the isomerization can be described by a triexponential model in which each of the three possible azo-centered triads has a characteristic monoexponential decay.

Experimental Section

4′-[[2-(acryloyloxy)ethyl]ethylamino]-4-nitroazobenzene (DR1A) and 4′-[[2-(methacryloyloxy)ethyl]ethylamino]-4-nitroazobenzene (DR1M) were synthesized as previously reported.[2] Copolymers of DR1A with methyl methacrylate (MMA) [poly(DR1A-*co*-MMA)] and of DR1M with MMA [poly(DR1M-*co*-MMA)] were synthesized by free radical polymerization at 60 °C under nitrogen in toluene solutions.[22] Their triad sequence distribution was calculated using first-order Markov statistics at high conversion and experimentally determined by solution ^{13}C-NMR spectroscopy.[22] Blends of polyDR1A with polyMMA were prepared by coprecipitation in methanol from tetrahydrofuran (THF) solutions. The two polymers showed miscibility at the molecular level in any proportion.[23] All polymers are amorphous and show no mesomorphic behavior. The glass transition temperatures of all samples analyzed in this paper are listed in

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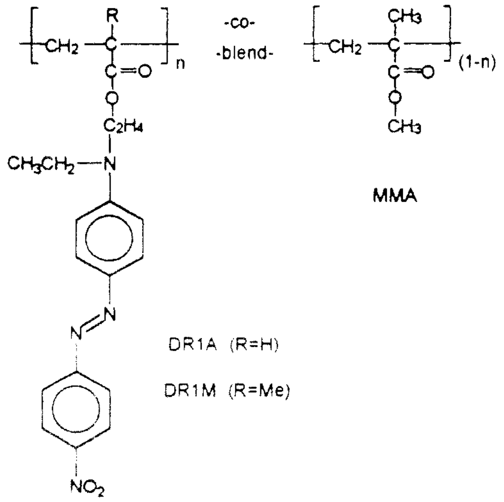
Table 1. Composition and Glass Transition Temperatures for All Samples

series	mole fraction azo	T_g (°C)
poly(DR1A-*co*-MMA)	0.02	92
	0.08	91
	0.12	92
	0.23	91
	0.42	91
	0.57	94
	0.69	95
	0.81	102
	1.00	91
poly(DR1M-*co*-MMA)	0.05	114
	0.12	112
	0.17	110
	0.28	116
	0.36	120
	0.46	120
	0.65	119
	0.82	122
	1.00	129
polyDR1A-*blend*-polyMMA	0.04	92
	0.07	90
	0.24	91
	0.34	91
	0.64	92
	0.79	91
	0.86	91
	0.92	90

Scheme 1



poly(DR1A-co-MMA) : n = 0.02, 0.08, 0.12, 0.23, 0.42, 0.57, 0.69, 0.81, 1

poly(DR1M-co-MMA) : n = 0.05, 0.12, 0.17, 0.28, 0.36, 0.46, 0.65, 0.82, 1

PDR1A - blend - PMMA : n = 0.04, 0.07, 0.24, 0.34, 0.64, 0.79, 0.86, 0.92

Table 1. A summary of the samples analyzed in this work is presented in Scheme 1.

Films of homopolymers, copolymers and blends were prepared by spin casting from THF onto glass substrates. They were preheated briefly to eliminate residual THF. The film thickness was fairly low; it varied between 100 and 500 nm in order to avoid complete absorption of the light beam.[24] Trans–cis photochemical isomerization was induced by irradiation with a circularly polarized unfocused 10-mW beam from an argon laser (488 nm) for about 1 s. The procedure is similar to that reported in the literature.[19] Circularly polarized light was used to avoid reorientation of the azobenzene groups and uneven distribution of absorbance in different directions. The beam was unfocused in order to avoid heating the sample at the point of contact. Under these conditions the assumption is that the rate is measured approximately at room temperature.

A probe beam of the same wavelength but going through an attenuator (2.5×10^{-4}) to provide very low intensity was passed through the sample coincident with the pump beam and into a photodiode. The intensity of light transmitted through the polymer film was monitored and digitally recorded over time to observe the thermal cis–trans relaxation. A typical curve read at the photodiode is shown in Figure 1. The pump laser is switched on at 3 s and off at 4 s. There is an initial fast decay of the photodiode signal, which reflects the strained cis isomers, followed by a slower decay. The data points were analyzed starting at 2.8 s after the pump beam was turned off. This point was estimated by assuming that the anomalously fast decay is at its lower limit (10 times the "normal" decay), modeling it, and taking as the starting point the time at which 99% of this fast decay is finished.

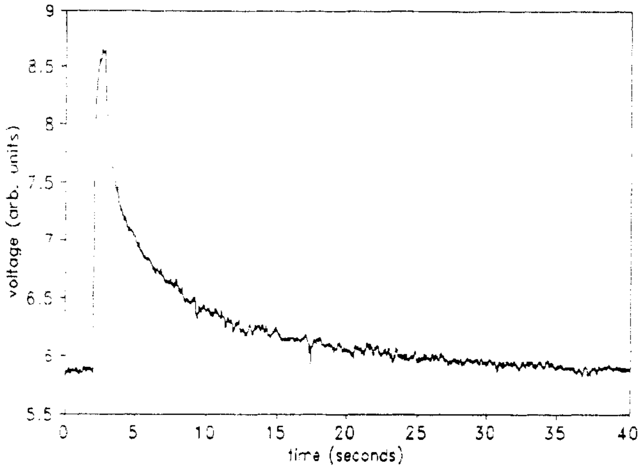


Figure 1. Pump/relax curve for poly(DR1A-*co*-MMA) with 23 mol % DR1A structural units.

The experiments could be repeated immediately or after a long time, on the same or on a different spot of the same film with very good reproducibility of the results. The DSC curves show no supercooling effect in the films.

Results and Discussion

Pump/relax experiments were performed repeatedly on the same spot of the polymer film and generated reproducible results, indicating complete reversibility of the isomerization. For a first order cis–trans thermal isomerization:

$$-\mathrm{d[cis]}/\mathrm{d}t = \mathrm{d[trans]}/\mathrm{d}t = k[\mathrm{cis}] \qquad (1)$$

where k is the rate constant. Since the isomerization is reversible

$$[\mathrm{trans}]_\infty = [\mathrm{cis}]_t + [\mathrm{trans}]_t \qquad (2)$$

i.e., the sum of the concentrations of cis and trans isomers at any time equals the concentration of the trans isomer at an "infinitely" long time after the experiment has started. The absorbance of the thin film is then given by

$$A_t = A_{\mathrm{cis}} + A_{\mathrm{trans}} \qquad (3)$$

where the absorbances from the cis and trans isomers are given by:

$$A_{\mathrm{cis}} = \alpha_c[\mathrm{cis}]_0 e^{-kt} \qquad (4)$$

and

$$A_{\mathrm{trans}} = \alpha_t[[\mathrm{trans}]_\infty - [\mathrm{cis}]_0 e^{-kt}] \qquad (5)$$

with α_c and α_t being respectively the absorbances of the cis and trans isomers at the probe wavelength. Then the absorbance is given by

$$A_t = A_\infty - (\alpha_t - \alpha_c)[\mathrm{cis}]_0 e^{-kt} \qquad (6)$$

and a plot of $\ln(A_\infty - A_t)$ should be linear with a slope of $-k$.

The A_∞ values are taken as A_t after a suitably long time. The pumped cis fraction in the homopolymer samples returns to 10^{-5} of the initial value after 45 s. To measure A_∞, times of 60 s and longer were used. Although A_∞ is approached asymptotically, the difference between A_∞ and A_t after 45 s is so small that it lies well inside the experimental noise. An upper and a lower A_∞ estimate were made to give the upper and lower experimental limits on k.

As expected for isomerization in bulk glassy state, an anomalous fast decay was observed for all samples, its effects being important up to 2.8 s after turning the light off. Analysis of the decay after 2.8 s for the azo homopolymers, the copolymers with the lowest azo concentration and all blends show a fairly good monoexponential behavior, as illustrated in Figure 2.

The rate constants calculated from this monoexponential behavior are 0.24 s^{-1} for polyDR1A, 0.22 s^{-1} for polyDR1M, 0.08 s^{-1} for poly(DR1A-*co*-MMA) (2 mol % DR1A), 0.07 s^{-1} for poly(DR1M-*co*-MMA) (4 mol % DR1M), and about 0.15 s^{-1} for all blends of polyDR1A with polyMMA, independent of composition. It is interesting to note that the rate constant for the homopolymers is about three times higher than the rate constants for the respective copolymers containing very few azo structural units. This result suggests that if an azo group is adjacent to other azo groups, its cis–trans isomerization rate is faster. In other words, a neighboring azo group would accelerate the thermal cis–trans isomerization of its neighbor. This is not very surprising, as confirmed by many reports in the literature of cooperative motion. For example, liquid crystals can be oriented by an oriented wall,[25] increased birefringence is obtained at high azo contents in semicrystalline copolymers,[26] "inert" mesogens are reoriented by neighboring azo groups movement,[27] and Langmuir–Blodgett films can act as "command surfaces" for liquid crystal layers.[28] The findings presented here suggest that the neighboring group effect is important in amorphous polymers as well. We will also report separately an increase in laser-induced birefringence for the copolymers presented here at higher azo contents.[29]

For all other copolymer samples, the data do not fit a monoexponential decay. Biexponential decays also do not fit any of the data. An approximation for a straight line (monoexponential behavior) generates an apparent rate constant. All real and apparent rate constants are plotted in Figure 3. The most interesting finding in Figure 3 is that the apparent rate constants do not depend only on the sample composition. At the same composition, the two copolymers show quite a different thermal cis–trans isomerization rate, especially when the azo component is between 40 and 80 mol %. The real isomerization rate for blends is constant over the whole composition range.

If the composition is not the only determining factor for the thermal cis–trans isomerization rate in copolymers, the next logical parameter to be investigated is the distribution of the azo groups within the copolymer chain. Indeed, a sequence distribution analysis and calculation[22] suggested that the two copolymer series have a quite different triad distribution. DR1A- and DR1M-centered triads are important for this analysis. MMA units are noted as M, and the azo units are noted as D. The three significant triads are then MDM, MDD, and DDD. Figure 4 shows the normalized triad distribution as a function of composition for the two series of copolymers. The distribution was calculated for the actual conversion using probabilities and reactivity ratios determined previously, and it was verified for the poly(DR1A-*co*-MMA) series by ^{13}C-NMR spectra.[22]

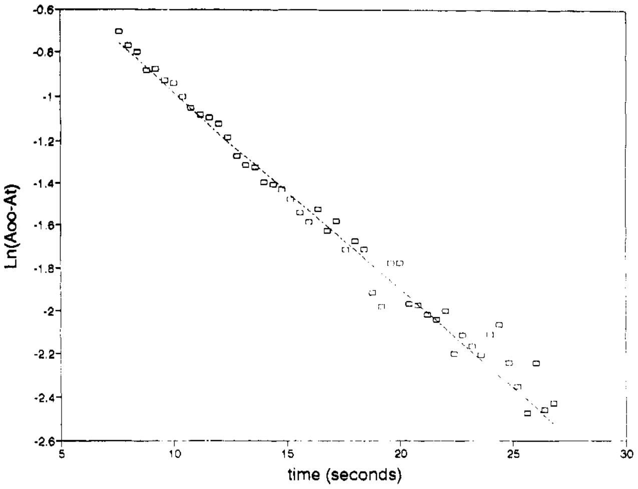


Figure 2. Plot of $\ln(A_\infty - A_t)$ as a function of time for a copolymer sample containing 2 mol % DR1A units. From the slope, a rate constant of 0.08 s^{-1} can be calculated.

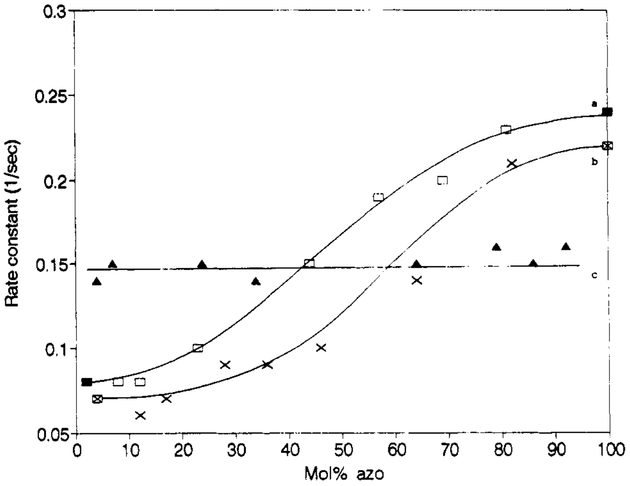


Figure 3. Real and apparent rate constants for (a) poly(DR1A-*co*-MMA) (real closed box; apparent open box), (b) poly(DR1M-*co*-MMA) (real crossed box; apparent cross), and (c) polyDR1A–polyMMA blends (closed triangle). The lines are drawn to help the eye.

It is clear in Figure 4 that at very low azo concentrations most azo groups are in MDM triads, i.e. have only MMA neighbors. As explained above, these copolymers show a monoexponential thermal cis–trans isomerization behavior. At very high azo concentrations, most azo groups are in DDD triads, i.e. have mainly other azo groups as neighbors. The homopolymers are the best approximation for this situation, and their thermal cis–trans isomerization can be also described by a monoexponential decay. Copolymers containing between about 20 and 80 mol % azo groups contain a mix of triads, and they do not obey either a monoexponential or a biexponential behavior. Thus, the thermal cis–trans isomerization of these samples was analyzed in terms of triads. We suppose that each type of triad behaves as a separate entity and that the remaining cis concentration at a certain time is the result of three independent processes, as in the following equation:

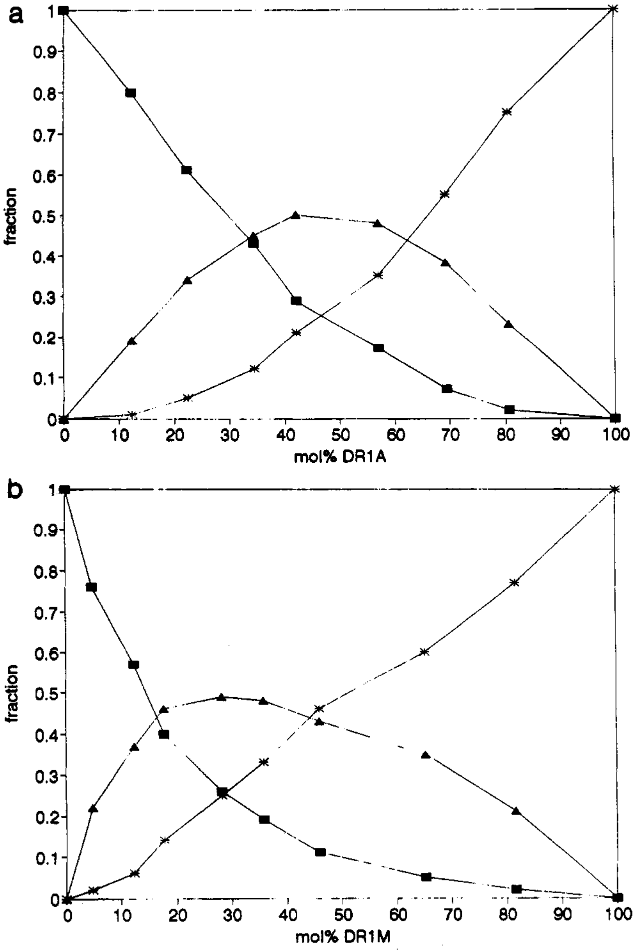


Figure 4. Normalized triad distribution in (a) poly(DR1A-*co*-MMA) and (b) poly(DR1M-*co*-MMA). M = MMA; D = DR1A-(M). Symbols are as follows: (*) f_{DDD}; (▲) f_{DDM}; (■) f_{MDM}.

$$[\text{cis}]_t/[\text{cis}]_0 = f_{DDD}\exp(-k_{DDD}t) + f_{DDM}\exp(-k_{DDM}t) + f_{MDM}\exp(-k_{MDM}t) \quad (7)$$

where f_{ijk} are the normalized fractions of the respective triads and k_{ijk} are the rate constants for the individual triad cis–trans thermal isomerization. For each copolymer series, k_{DDD} can be approximated with the constant for the respective homopolymer cis–trans isomerization, i.e. $k_{DDD} = 0.24$ s^{-1} (for polyDR1A) and $k_{DDD} = 0.22$ s^{-1} (for polyDR1M); while k_{MDM} can be taken as the rate constant for the monoexponential isomerization of the samples with the lowest azo content (2 mol % in the DR1A copolymers, 4 mol % in the DR1M copolymers). Then the constants are, respectively $k_{MDM} = 0.08$ s^{-1} for poly(DR1A-*co*-MMA) and $k_{MDM} = 0.07$ s^{-1} for poly(DR1M-*co*-MMA). The triexponential behavior for each sample can then be fitted for a single parameter: k_{DDM}. An example of a fit is illustrated in Figure 5. The average values for k_{DDM} are found to be 0.16 ± 0.02 s^{-1} for poly(DR1A-*co*-MMA) and 0.14 ± 0.01 s^{-1} for poly(DR1M-*co*-MMA). Also included in Figure 5 are two theoretical curves for the two copolymers having the closest composition to the sample analyzed. These two curves illustrate that the model proposed here is very sensitive to minor changes in composition and/or sequence distribution. The two theoretical curves clearly show quite a different decay behavior from the poly(DR1A-*co*-MMA) sample containing 69 mol % DR1A units.

One could then assume that the copolymers previously reported in the literature[13] behave in a similar way and their thermal cis–trans isomerization could be approximated by a triexponential fit considering the appropriate triad fractions. The data presented in that paper are not enough to attempt such a calculation.

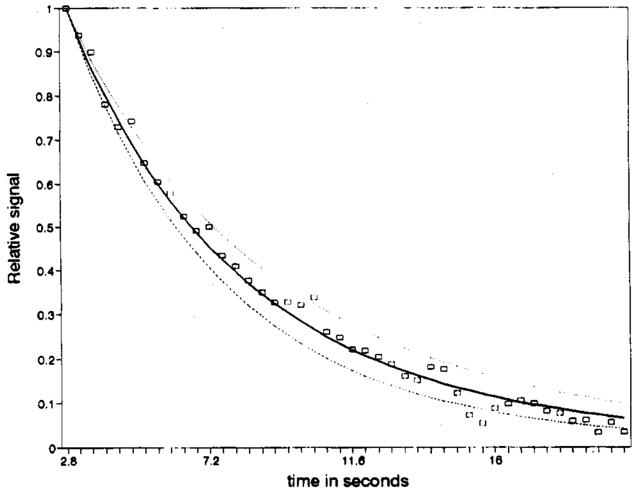


Figure 5. Experimental points (□) obtained for the thermal cis–trans isomerization of poly(DR1A-*co*-MMA) with 69 mol % DR1A units and theoretical fit (—) with a triexponential decay ($k_{DDM} = 0.16$ s^{-1}). Also presented are the theoretical curves calculated for poly(DR1A-*co*-MMA) with 81 mol % DR1A units (- - -) and for poly(DR1M-*co*-MMA) with 57 mol % DR1M units (···).

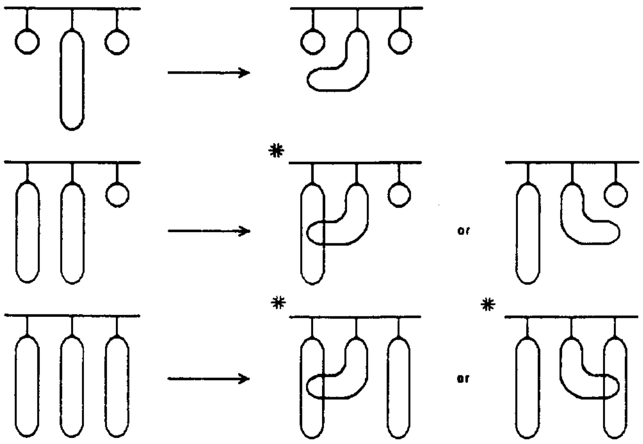
Table 2. Monoexponential Rate Constants for Individual D-Centered Triads

copolymer	k_{MDM}	k_{DDM}	k_{DDD}
poly(DR1A-*co*-MMA)	0.08	0.16	0.24
poly(DR1M-*co*-MMA)	0.07	0.14	0.22

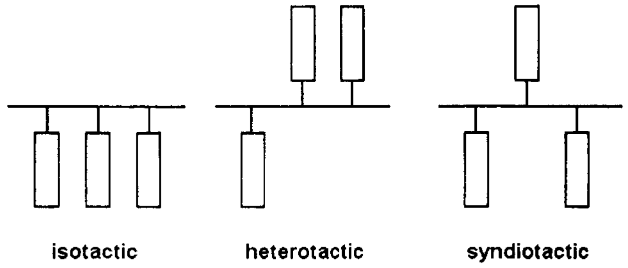
A summary for the individual rate constant values is given in Table 2.

The data in Table 2 indicates again that there is an autoacceleration process in the thermal cis–trans isomerization of an azo group if that group has azo neighbors. For the same concentration of azo groups in the cis configuration, the rate of thermal isomerization doubles if these groups have one other neighbor and becomes three times higher if they have two azo neighbors. This suggests the existence of a neighboring effect in the cis–trans isomerization. Two factors may be affecting the isomerization rate: a steric effect dictated by the available free volume which is different in different sequences and a dipolar interaction between neighboring azo groups. First let us consider the steric effect. The trans–cis isomerization requires free volume, since the cis isomer is bulkier than the trans isomer. There is more free volume available if the neighbor is a M unit than if the neighbor is another D unit. Scheme 2 shows the differences in the trans–cis isomerization for the central unit in the three D-centered triad. When looking at the central D structural units, one must remember that the probability for its next neighbor D unit to be in the trans configuration is close to unity. This was experimentally proven recently by Blanchard and Mitchell.[30] Under irradiation at room temperature for a polyMMA film containing about 7 wt % *dissolved* disperse red 1, they estimated that the photostationary state consists of 4% cis isomers. During the thermal relaxation process, the concentration of cis units decreases rapidly, hence all next neighbors of a cis D unit may be assumed to have a trans configuration. Scheme 2 suggests that for the structures noted with an asterisk, the cis isomer would be extremely strained and hence would tend to revert to trans faster than for the other two structures. This agrees with the increased rate constants for DDM and

Scheme 2



Scheme 3



DDD triads. One could say that the presence of a trans azo neighbor increases the probability for the central group to isomerize to the same trans state, some kind of alignment by "sympathy". The super-linear increase in the level of birefringence for copolymers with higher azo contents also suggests that alignment in concert with the neighboring groups is an important mechanism of reorientation.[29]

The decrease of the cis lifetime due to the presence of nearby azo groups also points to important dipole–dipole interactions. In the case of azo groups with donor–acceptor ends the dipole electric field at the nearest neighbor could be strong enough to not only favor alignment of the trans molecules, but also decrease the effective energy required for the thermal cis to trans isomerization. Dipolar interactions of this type have been reported in the literature as acting effectively to maintain orientation.[31]

It is fairly interesting to note that the tacticity of the polymer chain does not seem to have any measurable effect on isomerization. All the discussion above assumes that two azo groups neighboring each other are spatially close to each other. This is only true for isotactic triads (Scheme 3). In syndiotactic triads, the three azo groups may be far apart from each other. The tacticity of poly(DR1M-*co*-MMA) has been analyzed by solution ^{13}C-NMR spectroscopy,[22] and the probability of a racemic occurrence (on opposite sides of the main chain, leading to syndiotactic triads) decreases steadily from 80% for polyMMA to 60% for polyDR1M as the amount of DR1M structural units increases. This means that the probability of two azo groups being on the same side of the main chain, i.e. in close spatial proximity, increases slightly as the concentration of azo groups in the copolymer increases, but the total amount of azo groups in close proximity to each other is always less than half of all azo groups. We have no information about the tacticity of poly(DR1A-*co*-MMA), but we could assume that the syndiotacticity of such a copolymer (a methacrylate–acrylate pair) is probably even less than that of poly(DR1M-*co*-MMA) (a methacrylate–methacrylate pair).[32] This may account for the rate constant difference between polyDR1A ($k_{\mathrm{DDD}} = 0.24\ \mathrm{s}^{-1}$) and polyDR1M ($k_{\mathrm{DDD}} = 0.22\ \mathrm{s}^{-1}$). PolyDR1A probably has more azo groups in isotactic triads than polyDR1M. One also has to take into account the fact that the azo groups are bound to the polymer chains through a medium-size spacer (two methylene groups) which may allow a variety of orientations of the azo group, thus making the tacticity less important.

Finally, it is very interesting to note that the rate constant found for all polymer blends does not depend on composition, which confirms the interpretation that the neighboring groups have a significant effect in isomerization. The isomerization is monoexponential for all blends, and indeed—independent of composition—the surrounding environment for any azo group is unchanged. The azo groups are part of the polyDR1A homopolymer used in blending. What is surprising, though, is the fact that the rate constant found for the blends is about two-thirds of the rate constant found for polyDR1A and about equal to the rate constant for a triad with only one azo neighbor. One possible explanation may be related to the fact that the above discussion only considers single chain entities, while in a real film there must be significant influences from the other surrounding polymer chains. The environment around a certain azo group is then quite different in a homopolymer film, where a chain is surrounded by other similar chains, and in a blend film, where a chain containing azo groups is surrounded by variable amounts of polyMMA chains.

Conclusions

The apparent continuous distribution of thermal cis–trans isomerization rates in copolymers below their glass transition temperatures can be fairly accurately modeled by three azo-centered triad monoexponential processes. The presence of a second and third azo group in the triad produces an incremental increase of the rate constant for the process. This increase is due to a neighboring effect of the azo groups and can be explained by a combination of steric and dipolar effects. To our knowledge, this is the first report of a neighboring effect on side-group motion in completely amorphous polymers.

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