Spectroscopic Investigation of the Thermal Cis−Trans Isomerization of Disperse Red 1 in Hybrid Polymers

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ABSTRACT: The thermal cis−trans isomerization of disperse red 1 in hybrid polymers has been investigated. We employed transient absorption spectroscopy in order to measure the reaction kinetics of doped and functionalized systems of three matrices. The matrices show different rigidity. In most of the cases the thermal decay of the cis-isomers can be fitted by a sum of two first-order reactions, a slow and a fast one, which are interpreted on the basis of rotational and translational relaxation processes of chain segments. We found that the rate constants of the two reactions increase and the fraction of the fast reacting cis-isomers (x_b) decreases with increasing rigidity of the matrix. The apparent influence of the matrix rigidity on x_b—which is associated with the cooperative translational movement of chain segments—is greater in doped systems than in the functionalized ones due to a more rigid organic network. Chromophores which are freely distributed in a polymer can be more easily enclosed in the synthesis, thus being less disturbing in the buildup process of the organic polymer. The polymer around the chromophore is more regular, and a cooperative translational motion of adjacent chain segments is more likely.

Introduction

Azo-dye-doped and dye-functionalized polymers have attracted increasing attention over the last few years.[1,2] This is due to their mechanical as well as optical properties which make them candidates for a variety of essential practical applications. Special emphasis was put on the influence of the polymer on the chromophore, in the course of which many studies were performed on the photochemical and thermal cis−trans isomerization of the azo aromatic compound. Generally, photochemical reactions in a solid matrix differ considerably from their behavior in solution.[3−7] These differences are attributed to particular interactions between the chromophore and the surrounding matrix. Since cis−trans isomerization of the −N═N− bond is a reversible photochromic process, it is an ideal system for the demonstration and investigation of the matrix effect on photoreactions.

One of the first investigations of the photochemical as well as the thermal cis−trans isomerization of azo aromatic residues in the side chain of polymers was carried out by Paik and Morawetz[3] in 1972. The rate of the photoreaction was found to be essentially lower than in solution. For polymers in solution or above their glass transition temperature, the thermal cis−trans isomerization follows completely a first-order reaction scheme. However, in glassy specimen a portion of the azo aromatic groups reacts fast. The fast component has been observed and studied in main-chain azo aromatic polymers,[7−9] side-chain azo aromatic polymers,[3,4,10−12] and polymers doped with various azobenzenes.[13−16] This phenomenon was attributed to a restriction in the mobility of the photochrome itself by the surrounding matrix and to different chain segmental mobilities of the polymer. All the studies show that the kinetics of the thermal cis−trans isomerization of a chromophore incorporated in a polymer matrix are very sensitive to the structure, morphology, and viscoelastic properties of the surrounding polymer.

All the studies mentioned above are concerned with organic polymers as hosts for the chromophores. In this work we report first measurements of the thermal cis−trans isomerization of disperse red 1 (DR1) in hybride polymers. In this new material organic and inorganic networks are connected on a molecular scale. Because of their high optical damage threshold and mechanical stability as well as their great malleability, the organic modified ceramics have attracted much interest as materials for the emerging field of optoelectronics.[17−20] Designing new materials and elaborating the final device need a precise optical characterization of the material. In the course of our recently started work on azo dyes incorporated in sol−gel matrices, we present in this paper the investigation of the thermal cis−trans isomerization of DR1 in three different polymers for various temperatures. Investigations have been performed by means of transient absorption spectroscopy. The cis−trans isomerization of the azo dye DR1 is well-known,[14,15,21,22] which made DR1 the preferred chromophore in our investigations. While one of these polymers (MZ) possesses a three-dimensionally cross-linked and therefore rather stiff inorganic network, the other two materials (TM and BM) contain only Si−O−Si chains. In addition the spacer group of MZ is considerably shorter, so inorganic and organic polymer components are tightly connected together and give rise to very small pores.

TM and BM differ only in the number of methacrylate groups available for polymerization, which is higher for TM. In addition, the spacer group of TM is shorter than the one of BM. Therefore the matrix rigidy increases in the order MZ > TM > BM.

The photoactive dyes we employed were DR1 and methacrylated disperse red 1 (DR1MA). While DR1 is only physically incorporated in the pores of the matrix

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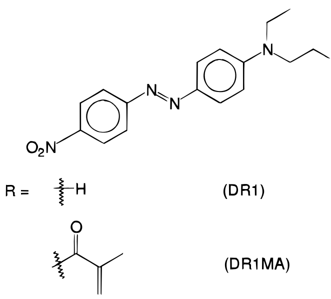

Figure 1. Employed azo dyes disperse red 1 (DR1) and disperse red 1 methacrylate (DR1MA).

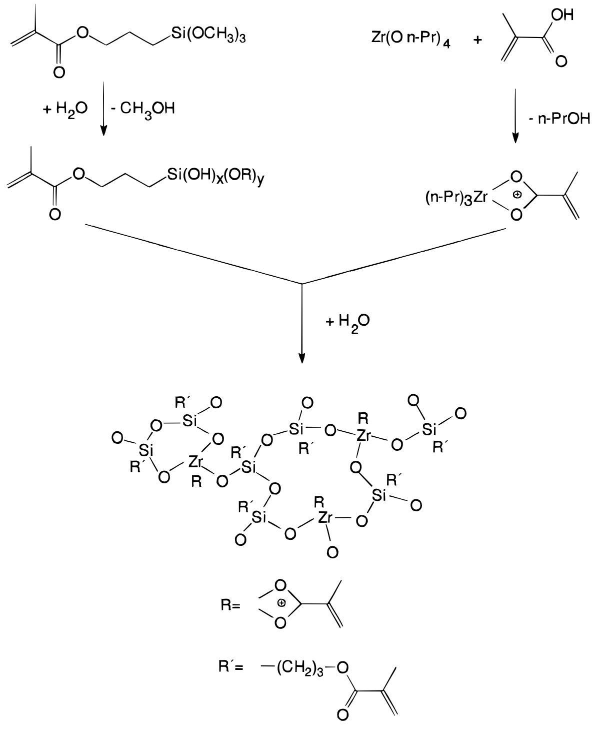

Figure 2. Synthesis of the MEMO/Zr sol. A three-dimensional inorganic network is present.

network, DR1MA is chemically linked to the organic network.

Experimental Section

Materials. All chemicals were used without further purification. DR1MA was prepared from DR1 as described in detail elsewhere,[23] using toluene instead of benzene as the solvent. Their structures are shown in Figure 1.

1. Preparation of the Sols: MEMO/Zr (MZ) Sol (See Figure 2). The synthesis of the MZ sol has been previously described in the literature;[24] 24.84 g (0.1 mol) of [(methacryloxy)propyl]trimethoxysilane (MEMO) and 2.7 g (0.15 mol) of water were mixed at 273 K and stirred overnight. The resulting hydrolysate was added dropwise to an ice-cooled propoxyzirconium methacrylate solution, which was prepared by dropping 1.78 g (0.02 mol) of methacrylic acid to 8.54 g (0.02 mol) of Zr(OPr)$_4$ at 273 K followed by 30 min of stirring at this temperature. After the MEMO/water addition and further stirring for 30 min, 0.54 g (0.03 mol) of H_2O was added, and stirring was continued for 1 h at room temperature to complete hydrolysis. The sol was used without further workup.

TMPTA/MPMDM (TM) and BPADA/MPMDM (BM) Resins (See Figure 3). The synthesis of the TM resin has been previously described in the literature;[25,26] 118.5 g (0.4 mol) of 1,1,1-trimethylolpropane triacrylate (TMPTA) and 61.3 g (0.34 mol) of (mercaptopropyl)methyldimethoxysilane (MPMDM) were dissolved in 450 mL of ethyl acetate and cooled in an ice bath. Applying N_2 atmosphere, a solution of 0.25 g (4.4 mmol) of KOH in 30 mL of EtOH was added dropwise under vigorous stirring. During this step, the temperature must not exceed 293 K. Immediately afterwards the solution was hydrolyzed with a mixture of 4.05 g of H_2O and 5.95 g of 1 N HCl and stirred for 2 h in the absence of light. The resulting mixture was washed three times with 70 mL of saturated NaCl solution, the organic phase was dried over Na_2SO_4, and the solvents were evaporated under reduced pressure.

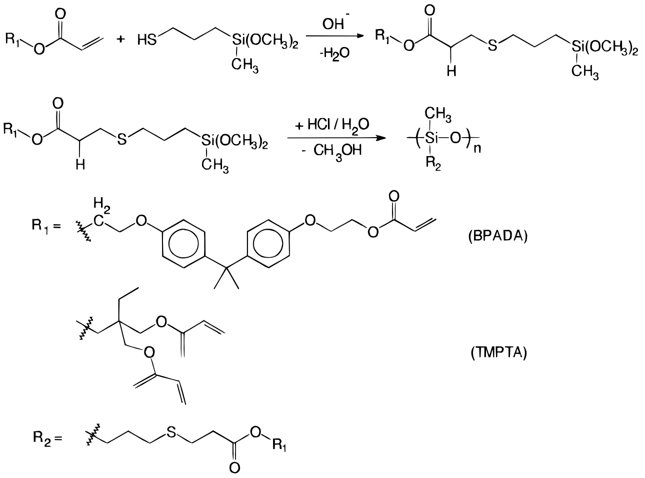

Figure 3. Synthesis of BPADA/MPMDM (BM) and TMPTA/MPMDM sols. Here a two-dimensional inorganic network is present.

The BM resin was prepared in the same way, using ethoxylated bisphenol−A diacrylate (BPADA) instead of TMPTA.

2. Sample Preparation. The percentage data given in the following section are related to the solids portion of the resins in charge.

Resin (10 g) was diluted with ethyl acetate to a solids content of 40%; 10% (w/w) dye and 5% photoinitiator IRGACURE 500 were dissolved in this solution. By means of this procedure, six mixtures were obtained where each of the three sols (MZ, TM, and BM) were colored once with DR1 and once with DR1MA. For the sample manufacture 10×10 cm^2 glass substrates were spin coated with the sols (20 s, 2000 rpm), dried for 1 h at 353 K, and UV cured for 60 s (1000 W) to build up the organic network by means of radical polymerization of the acrylic moieties. In this way, the dye was either dissolved in (DR1) or covalently attached (DR1MA) to each of the three matrices (MZ, TM, and BM).

The rigidity of the various materials was determined by Taber−Abrazer measurements (DIN 52347) as MZ > TM > BM.

Isomerization Studies. We employed a standard experimental setup for our transient absorption measurements. Trans−cis photochemical isomerization of DR1 was induced by irradiating the sample with a circularly polarized unfocused laser beam of a dye laser (Molectron DL300)—in the following called “pump beam”—that was pumped by the third harmonic of a pulsed Nd:YAG laser (Spectra Physics Quanta Ray GCR4). The pulse repetition rate was 15 Hz and the pulse duration about 7 ns. The wavelength of the pump beam was fixed at 490 nm which is the wavelength of maximum absorption for the trans-form of DR1. The pulse energy of the pump beam was determined to be 0.15 mJ. A probe beam coming from either another dye laser (Molectron DL200) with a wavelength of 492 nm or the Nd:YAG laser (third harmonic, 355 nm) was attenuated by different neutral density filters to provide intensities as small as 15 nJ/pulse. This experimental setup with tunable dye lasers allowed us to employ a probe beam wavelength different from that of the pump beam in order to avoid disturbing stray light from the pump beam. The probe beam was passed through the sample coincident with the pump beam and detected by a photomultiplier (RCA model C31024A). Additional stray light rejection was achieved using a double monochromator (Spex 1680) as filter. The sample was placed in a closed-cycle helium-cryostat (Cryophysics

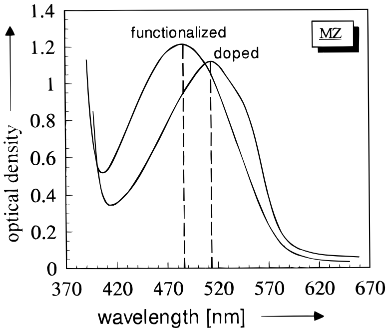

Figure 4. Absorption spectra of MZ-DR1MA (functionalized) and MZ-DR1 (doped).

model 22) which allowed us to perform measurements with temperatures ranging from 200 to 330 K. In order to avoid heating by the pump beam, we left it unfocused. We employed circularly polarized light for the pump beam to prevent an orientation of the chromophores which would result in dichroism.

The thermal cis−trans relaxation was followed by recording the intensity of the light transmitted by the polymer film over time. We found that the trans−cis isomerization process is completely reversible in the investigated materials, and we did not observe any bleaching of the samples.

Results and Discussion

It is well-known that the azo aromatic group can undergo reversible trans-to-cis isomerization around the azo linkage when exposed to light near its absorption maximum. Generally, the trans-form is more stable than the cis-form. In the case of azobenzene, the energy difference between the ground state of the trans- and cis-isomers is about 50 kJ/mol.[27] The cis-to-trans interconversion can occur thermally and/or photochemically. We have investigated the thermal cis−trans isomerization of DR1 in organically modified ceramics at different temperatures. The absorption spectra of the trans- and cis-forms of DR1 were published recently by Sekkat and Dumont.[28] The absorption spectrum of the trans-form was measured, and that of the cis-form was determined following the method described by Rau *et al.*[29] based on Fischer's method.[30] Since the absorption spectrum of the trans-form in our samples is the same as given in that paper—except the one of MZ-DR1 which will be discussed later—we assume that the cis-spectrum will also be about the same. This approximation is supported by measured transients irradiated at 490 nm and probed at 492 and 355 nm. The transient for 355 nm shows an inverted shape compared to that for 492 nm. This only can be explained by assuming absorption spectra similar to those shown in ref 28. There the isobestic point (cis-absorption = trans-absorption) is at 405 nm, and therefore, 492 and 355 nm probe right and left of this crossing, respectively. The absorption spectrum of MZ-DR1 (doped) differs from that of the rest of the samples which can be seen in Figure 4. Compared to the absorption spectrum of MZ-DR1MA (functionalized), the absorption spectrum of MZ-DR1 (doped) is shifted toward higher wavelengths. We can conclude that in this sample the chromophore and its photochemical behavior are strongly influenced by the surrounding polymer.

With the pump laser light on, the system reaches a photostationary state. After turning the light off, the thermal cis−trans isomerization follows first-order kinetics in solution as well as above the transition temperature in glassy polymers. In glassy matrices below the glass transition, the thermodynamically unstable cis-form isomerizes thermally to the more stable trans-form, deviating from first-order kinetics.[3,6−8]

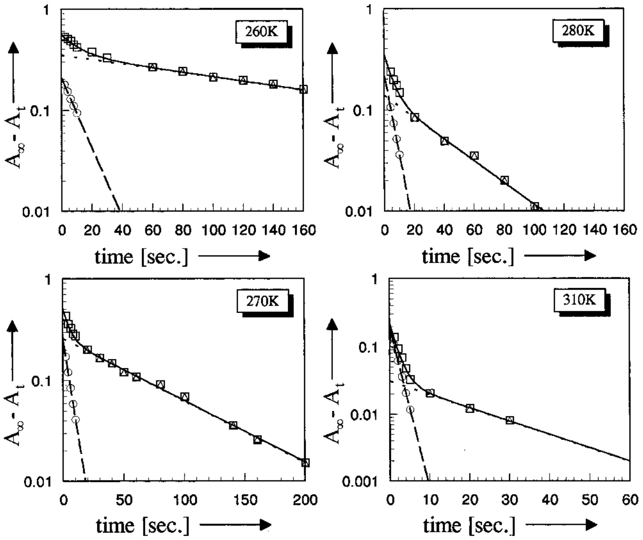

Figure 5. Thermal cis−trans isomerization of BM-DR1MA (□) for different temperatures as indicated. The experimental data were fitted by a sum of two first-order reactions (solid line); a portion of DR1 reacts much faster (○, dashed line), whereas the remainder isomerizes slower (△, dotted line) than in solution.

Accordingly, first-order plots (FOP's) of the thermal cis−trans isomerization of DR1 in the matrices used in this work show a nonlinear behavior. Applying a biexponential kinetics,

$$\log[A_\infty - A_t] = \log[a_0 \exp(-k_1 t) + b_0 \exp(-k_2 t)] \qquad (1)$$

the decay of the cis-isomer can be described for our experimental data. A_∞ and A_t are the absorbances at infinite time and at time t after the pump beam is switched off, respectively. Since the absorbance at infinite time can be related to be absorbance of the pure trans-isomer, the difference ($A_\infty - A_t$) depends on the relative absorbance of the cis-isomer. The experimental transient shows that the kinetics consist of at least two parts, a fast and a slow one. k_1 and k_2 are the rate constants of these two reactions, respectively. a_0 and b_0 represent the corresponding concentrations of the cis-isomer. First, the steep part of the transient is fitted assuming a monoexponential kinetics. From this the kinetic parameters k_1 and a_0 can be extracted. Taking these values, the experimental curve is fitted using eq 1 varying the parameters k_2 and b_0 only. This procedure is repeated iteratively. The results are illustrated in Figure 5 for BM-DR1MA for different temperatures. From this we learn while parts of the chromophores react with a decay rate comparable to that in solution, another part of the cis-isomers reacts much faster. Although many researchers found the same behavior, only Paik and Morawetz[3] and Eisenbach[4−7] have made attempts to explain the occurrence of two first-order reactions. Paik and Morawetz observed that about 14% of the azo groups isomerize much faster than the remainder. This portion was independent of the reaction temperature as long as the irradiation took place below the glass transition temperature, T_g. This behavior was interpreted as being caused by cis-isomers which are trapped in a strained conformation. Under the same experimental circumstances, Eisenbach found that the fast isomerizing fraction, $x_b = b_0/(a_0 + b_0)$, of the total cis-isomer concentration increased with increasing reaction temperature. He explained this in terms of two different relaxation mechanisms which are shown in ref 5. Here the basic principle is that the isomerization process of the dye is considered to be linked directly to the local segmental mobility around the chromophore. These segments may relax in either a rotational or translational motion. The fast isomerization is attributed to a translational relaxation mechanism, for which Eisenbach found a smaller activation energy, whereas the slower isomerization is associated with a rotational relaxation having a higher activation energy. The latter is only possible if sufficient free volume is present in the direct neighborhood of the chromophore. This means that at time zero (moment of switching the pump beam off) only a certain part of the dye relaxes by means of the rotational mechanism and the relaxation of the remainder is associated with a translational movement of chain segments, providing the space for isomerization. With increasing temperature, larger segments can be moved in a cooperative process. This explains the increasing portion of fast reacting cis-isomers with temperature. Additionally, Eisenbach states that the polymer has a kind of catalytic effect on the thermal cis−trans isomerization, since the activation energies are less compared to solution. Since we also observed an increasing portion of the fast reaction with temperature and small activation energies for the processes, in the following we tend to interpret our results according to Eisenbach's model.

First of all we considered the kinetics of the doped (DR1) and functionalized (DR1MA) systems (Figures 6−8) comparing the reaction rates as well as the fraction of the fast reacting cis-isomers. The reaction rates were determined using Arrhenius plots. We note that in general we did not observe any curvature of the Arrhenius plots, indicating an overall apparent activation energy which is independent of temperature for both reactions. Since it is not possible to determine an exact glass transition temperature of hybride polymers,[31] we cannot interpret our measurements in terms of William−Landel−Ferry (WLF)[32] and Doolittle[33] equations, as is often done in literature. Figure 6A shows the reaction rates k_1 (boxes) and k_2 (circles) and Figure 6B the fraction of the anomalously fast reaction for BM-DR1 (filled symbols) and BM-DR1MA (empty symbols). Obviously, the rate constants of the doped systems are somewhat higher compared to the functionalized system. Moreover for the doped system the fraction of the fast reacting cis-isomers is higher than that found for the functionalized system, in particular at lower temperatures. Nearly the same is observed for TMPTA.

Figure 7A shows the reaction rates, k_1 (boxes) and k_2 (circles), and Figure 7B the fraction of the anomalously fast reaction for TM-DR1 (filled symbols) and TM-DR1MA (empty symbols). Here, the reaction rates are nearly the same for both systems, while the fraction of the fast reacting cis-isomers is likewise higher at lower temperatures compared to the functionalized system. This behavior can be explained by applying the model mentioned above. The rotational relaxation process (k_1, x_a) can only proceed when a certain amount of free volume is accumulated immediately around the chromophore. Referring to our experimental results, this amount is higher for systems in which the chromophore is chemically linked to the organic polymer network. This is reasonable, since for these systems due to its linkage the chromophore cannot be pushed into a position suitable for the network buildup. Therefore, it can immediately provide more space around itself while the organic network is cross-linked. This also means that the polymer network of the functionalized systems is not that rigid and regularly connected. A cooperative motion of adjacent chain segments which is required for the translational relaxation mechanism (k_2, x_b) may be hampered. In contrast to this, chromophores freely distributed in a polymer can be more easily enclosed during the synthesis, thus being less disturbing in the buildup process of the polymer. The polymer around the chromophore is more regular, and a cooperative motion of adjacent chain segments is more likely. Consequently, the difference between doped and functionalized systems gains in significance at lower temperatures.

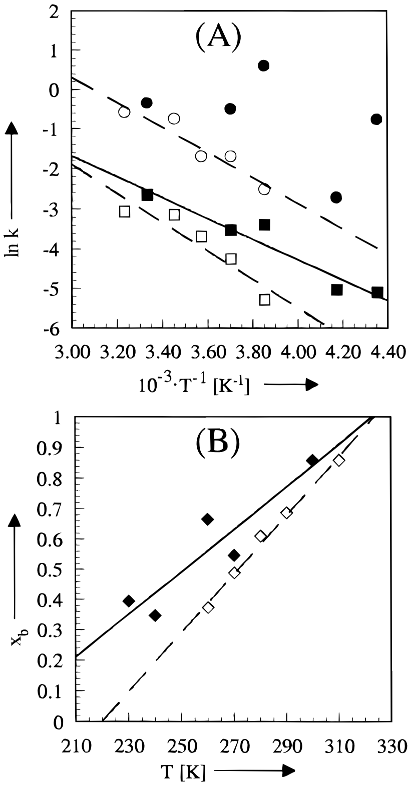

Figure 6. Arrhenius plot (A) and temperature dependence of the fraction x_b of the cis-isomers showing a fast isomerization reaction (B). Filled symbols show results for BM-DR1 and empty symbols those for BM-DR1MA. Boxes and solid lines show experimental data and line fits for the slow reaction, respectively. Circles and dashed lines are used for fast reaction data.

Regarding Figure 8, the above explanation becomes more evident. It shows the reaction rates k_1 (boxes) and k_2 (circles) for MZ-DR1MA and just one reaction rate for MZ-DR1 (filled triangles). The fact that we observe only one reaction rate for the doped MZ-system supports the basic principle stated above. Since in MZ a very rigid three-dimensional inorganic and organic network is present, a cooperative motion of chain segments is no longer possible in the case that a network is fully built up. This is obviously the case when the chromophore is embedded in MZ. Therefore, the chromophore only isomerizes when there is enough space in its surroundings. In the absorption spectrum we already observed a much greater influence of the polymer matrix on the chromophore in MZ-DR1 (see Figure 5). In the functionalized system the polymer matrix is not as rigid as in the doped system, so here again we observe two first-order reactions.

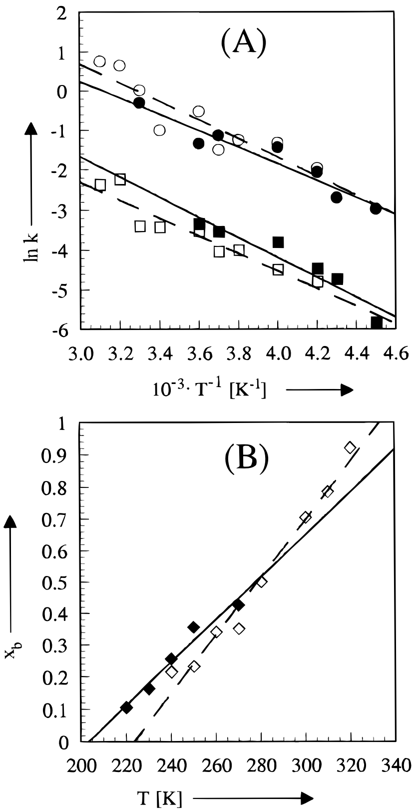

Figure 7. Arrhenius plot (A) and temperature dependence of the fraction x_b of the cis-isomers showing a fast isomerization reaction (B). Filled symbols show results for TM-DR1 and empty symbols those for TM-DR1MA. Boxes and solid lines show experimental data and line fits for the slow reaction, respectively. Circles and dashed lines are used for fast reaction data.

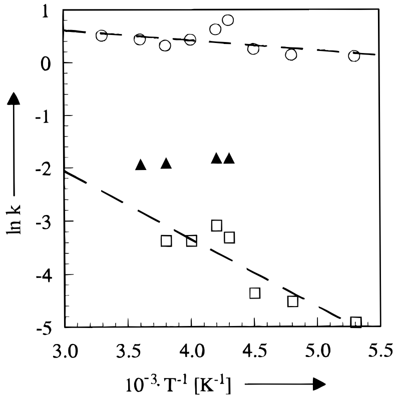

Figure 8. Arrhenius plot for MZ-DR1 (▲) compared to MZ-DR1MA (○, □). The data obtained for MZ-DR1MA were fitted using a linear regression (dashed lines). Boxes represent the reaction rates of the slower reaction, whereas circles show the reaction rate of the fast reaction. We note that for MZ-DR1 only one reaction is observed.

As BM and TM are comparable polymers, just differing in the rigidity of their organic network, a comparison of x_b will provide more information about the dye−polymer interactions. In Figure 9a comparison between BM (filled boxes) and TM (filled triangles) for the doped and functionalized systems is shown. We note that the fraction of the fast reaction is higher for BM in both cases and that the difference is larger in the doped compared to the functionalized system. As BM is the softer matrix, a cooperative translational movement of chain segments is more likely, so these results reflect exactly what we expected. It is reasonable that the

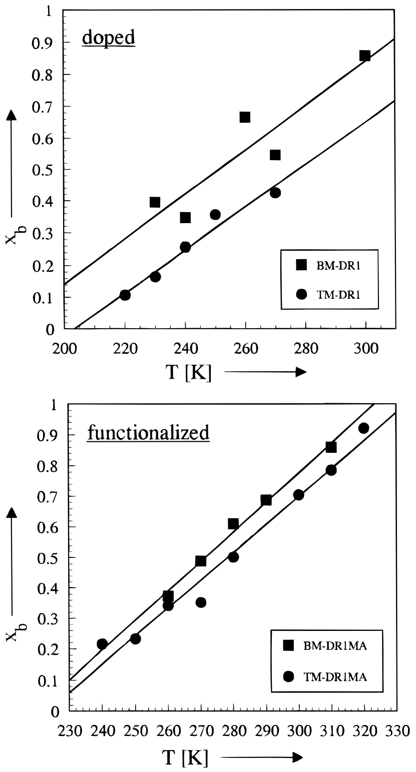

Figure 9. Temperature dependence of the fraction x_b of the cis-isomers showing a fast isomerization reaction with doped and functionalized systems of BM and TM.

Table 1. Activation Energies Determined for the Slow Reaction ($E_a(1)$) and the Fast Reaction ($E_a(2)$) Seen for the Different Investigated ORMOCER's

polymer	$E_a(1)$ (J/mol)	$E_a(2)$ (J/mol)
BM-DR1	312	166
BM-DR1MA	425	381
TM-DR1	302	252
TM-DR1MA	266	285
MZ-DR1MA	161	23

difference is larger in the doped regime since the properties of the specific matrix become more evident when built up without being disturbed.

Comparing the Arrhenius plots of all three functionalized polymer systems, we observed a kind of catalytic effect of the polymer on the thermal cis−trans isomerization as already described by other authors.[3,4,7] Especially at lower temperatures, the rate constants for the processes are higher for the more rigid matrices. A comparison of the activation energies (E_a) (see Table 1) also shows that E_a decreases with increasing rigidity of the matrix. This may be caused by an increasing strain being present in these matrices.

Conclusions

In the present work the thermal cis−trans isomerization of disperse red 1 in hybrid polymers has been investigated. In order to obtain information on the influence of this new polymer material on the isomerization process, we measured the isomerization kinetics by means of transient absorption spectroscopy. We chose doped and functionalized systems for three kinds of matrices. These matrices show different rigidity. The experiments were performed at temperatures in the range of 50−200 K. In most of the cases the thermal decay of the cis-isomers could be fitted by a sum of two first-order reactions, a slow and a fast one, which were interpreted on the basis of rotational and translational relaxation processes of chain segments. We found that the rate constants of the two reactions increased and the fraction of the fast reacting cis−isomers (x_b) decreased with increasing rigidity of the matrix. The apparent influence of the matrix rigidity on x_b, which is associated with the cooperative translational movement of chain segments, is greater in doped systems than in the functionalized ones. This is due to a more rigid organic network, whose buildup is less "disturbed" for doped systems. The effect becomes particularly evident for an extremely rigid matrix (MZ). Here, in the doped case, the matrix is too rigid to allow a cooperative chain segmental motion.

When exposed to linearly polarized light due to the absorption maximum of the incorporated azo dye, our samples also show dichroism and birefringence. Results on further investigations considering these effects will be published in due course.[34]

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