Macromolecules **1988**, *21*, 923–929 **923**

tration, 3.0×10^{-5} mol dm^{-3}) or film (thickness, 0.01 mm) state. The solution optical path length was 1 cm.

Registry No. **1a**, 113008-87-0; **1a** (homopolymer), 113008-88-1; **1b**, 113008-89-2; **1b** (homopolymer), 113008-90-5; **1c**, 113008-91-6; **1c** (homopolymer), 113008-92-7; **1d**, 113008-93-8; **1d** (homopolymer), 113008-94-9; **1e**, 113008-95-0; **1e** (homopolymer), 113008-96-1; **1f**, 113008-97-2; **1f** (homopolymer), 113008-98-3; **1g**, 113008-99-4; **1g** (homopolymer), 113009-00-0; **1h**, 113009-01-1; **1h** (homopolymer), 113009-02-2; **1i**, 113009-03-3; **1i** (homopolymer), 113009-04-4; **1j**, 113009-05-5; **1j** (homopolymer), 113009-06-6; **2**, 72602-64-3; **3a**, 74-88-4; **3b**, 1520-21-4; 3-$H_2C{=}CHC_6H_4NH_2$, 15411-43-5; 4-$H_2C{=}CHC_6H_4CH_2Cl$, 1592-20-7; CH_3OH, 67-56-1; 4-$H_3CC_6H_4CH_2OH$, 589-18-4; 4-$H_3CC_6H_4NH_2$, 106-49-0; 3-$H_3CC_6H_4NH_2$, 108-44-1.

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Merocyanine–Spiropyran Photochemical Transformation in Polymers, Probing Effects of Random Matrices

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ABSTRACT: Isomerization kinetics of the merocyanine–spiropyran transformation in several poly(alkyl acrylates) are detected by time-resolved absorption spectroscopy. The decay of the colored merocyanine exhibits significant deviations from first-order patterns. The energy of activation can be separated into a stabilization energy for the isomer and an activation inherent to the amorphous matrix by observing the decoloration patterns for the corresponding photoisomerization. These observations can be explained by matrix effects in the isomerization modeled by statistics and fluctuations of matrix-site energies. Quantification of matrix effects is based on the concept of transport theories in random media applied to reflect the dynamics of potential energies. The gradual decrease of dispersion of reaction rates with rising temperature is correlated to the time a chromophore remembers its initial matrix cage, thereby extending the kinetic model to the range above the glass transition.

Introduction

The glassy state of matter gives rise to a wide variety of properties absent in counterpart states of higher regularity, e.g., crystalline systems. In most cases the characteristic phenomena of vitreous configurations can be explained on the basis of a statistical spread of microscopic contributions like site energies, intersite coupling, and relaxation times together with the notion that glasses are outside of thermodynamic equilibrium. The experimental elucidation of the glassy state covers practically all forms of spectroscopy as documented by Wong and Angell.[1] Apart from directly detecting the dynamics and structure of glasses, there are different methods of probing an amorphous matrix via guest sites as done, for instance, by hole-burning spectroscopy[2] and possibly with any observable guest property which is sensitive to its matrix cage. A well-known example for such indirect probing in a liquid matrix is the solvent shift of an absorbing dopant.

The effect of a rigid matrix on a (nondiffusive) reaction which is microscopically of first order is often the introduction of deviations from exponential kinetics observed for hole-burning,[3] proton-transfer reactions,[4] dielectric relaxation,[5] and photochromic isomerization.[6-10] Formally, any deviation from first-order kinetics can be modeled by an appropriate dispersion of rate constants to match experimental data.

Photochromic isomerization reactions as a probe for matrices combine the ease of detection via absorption spectroscopy with a high sensitivity of the kinetics to the configuration of its matrix cage. Transformation kinetics of azo compounds and spiropyrans in solution and polymer matrices are well investigated.[6-11] Following first order in solution,[8] they are notorious in exhibiting dispersive reaction patterns in rigid matrices[6-10] in the sense that the rate of isomerization decreases significantly during the course of the reaction. The extent of dispersion is found to decrease as the temperature is raised within a range far below the glass transition temperature T_g.[6] The sensitivity of decoloration kinetics to the extent of irradiation, driving the coloration reaction, has also been reported.[7] Practically all results concerning photochromic labels in polymer matrices argue for the kinetics reflecting the statistics of the matrix[8] and the amount of free volume,[10] also supported by azo labels shown to indicate physical aging of amorphous polymers.[12]

Extending previous work,[6] matrix effects on the decoloration kinetics of spiropyran are investigated in various poly(alkyl acrylates) thereby covering a temperature range from 75 K below to 95 K above T_g. The basis for rationalizing decay kinetics is the model of a Gaussian spread of energy barriers accounting for the statistics of individual reaction cages within the amorphous polymer. This interpretation reduces a decay pattern to its mean reaction rate and the dispersion of energy barriers which allows extracting an activation energy albeit observing nonexponential decoloration. To overcome the inconsistency of a simple Arrhenius law with thermal data, a model is advanced which describes the increase of motional freedom as the temperature is raised, predicting the matrix inherent energy barrier to follow a $1/T$ law.[13] Although such a temperature dependence cannot uniquely be established by experimental data covering a narrow temperature interval, the model allows disentangling the energy of activation into a part representing a stabilization energy of the merocyanine isomer (78 kJ/mol) and a part imposed by the steric hindrance of the matrix (16 kJ/mol), in analogy to the notions of Kryszewski et al.[8] This notion is strongly supported by a decrease of the activation energy

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appearing in the kinetics by approximately 80% upon additional visible irradiation during the decoloration process, arguing that the stabilization is only effective in the electronic ground state of merocyanine. The observation that the spread of energy barriers decreases with rising temperature in the vicinity of T_g is rationalized by an onset of motion of polymer subunits at T_g.

Experimental Section

The thin polymer films were prepared from a solution of the poly(alkyl acrylate) in toluene solvent doped with 1,3,3-trimethylindolino-6′-nitrospirobenzopyran (SP) as purchased from Kasei, Tokyo. Unless otherwise stated, these films of 50–500-μm thickness were dried for several days at 60 °C and ambient pressure after slow solvent evaporation. Seven different polymers served as matrices: poly(butyl acrylate), PBA; poly(ethyl acrylate), PEA; poly(methyl acrylate), PMA; poly(butyl methacrylate), PBMA; poly(propyl methacrylate), PPMA; poly(ethyl methacrylate), PEMA; and poly(methyl methacrylate), PMMA.

The course of the reversible merocyanine (MC) ↔ SP transformation was followed by detecting the transmission of a film at 577 ± 5 nm. The coloration reaction SP → MC was forced by continuous UV irradiation at 348 ± 8 nm, generally until no further change in optical density was observed. This condition is essential to the application of the analysis described below and should be regarded if data presented herein are compared with previous results since the irradiation time affects the decoloration.[7] The sample was enclosed in a frame of high thermal capacity and variable temperature within the range 5–110 °C with a typical stability of ±0.3 K. Two photomultipliers of identical type using a common voltage source are installed, one serving as transmission detector, the other monitoring the incident probing beam to adjust its intensity to a constant level ±0.5%. Sufficient attenuation of the probe beam assured that optical excitation of MC molecules, known to increase their decoloration rate,[9] was negligible. Preliminary measurements did not indicate the normalized MC → SP kinetics to be sensitive to the UV irradiation intensity, possibly due to sample warmup. In order to detect the MC → SP transformation at additional photon assistance of the reaction, the sample was exposed to the beam of a 5-mW He–Ne laser, defocused to cover the total sample area. The laser, having high output stability and random polarization, operated at 632.8 nm, where the optical density of the sample is ≲0.3, assuring that the photon flux at a particular chromophore is independent of its depth below the sample surface.

Since some of the SP molecules undergo an irreversible reaction upon UV excitation to a nonphotochromic product[14,24] also absorbing within the visible regime, all results have been corrected for the appropriate zero- and unity-transmission values. Prior to analysis all 4096 data points per scan were transformed to the time dependent concentration of MC, normalized to unity at the start of the MC → SP back-reaction, defined as the termination of the UV irradiation.

Results

The absorption spectrum of a SP–PPMA film at 20 °C is shown in Figure 1 for various times relative to the UV excitation, together with the spectral positions of the probe beam, He–Ne laser, and UV irradiation. The absorption spectrum within the visible regime shows no significant change in shape while decaying in intensity. Therefore, it can be concluded that the chromophores exhibit no correlation between absorbing wavelength and decay rate, assuming that the absorbance at an arbitrary wavelength is representative for the total MC absorption band. In addition, no indication of preferential reactivity of any isomers was found.

The thermally induced decay of the MC concentration has been acquired at two temperatures for six different matrics and at eight temperatures for PPMA, all in the range 25–60 °C. The effect of residual solvent is also documented for several matrices. In all cases, the course of the MC → SP transformation is nonexponential as depicted in Figure 2. The decay curves were analyzed by a fitting procedure on the basis of a total decay of absorbing sites exhibiting a Gaussian density profile of activation energies with width σ centered at E_a in conjunction with the preexponential frequency ν. This model is discussed elsewhere.[6,15] It predicts the merocyanine concentration to follow

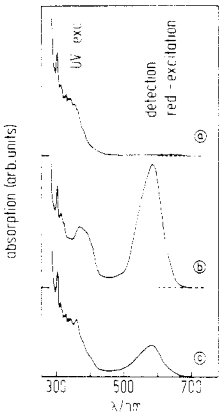


Figure 1. Absorption spectra of SP in PPMA at 20 °C: (a) before UV irradiation; (b) directly after irradiation; (c) ~30 min after UV exposure. The maximum of the MC absorption band (b) corresponds to an optical density ≃1. Spectral positions of the UV excitation, detector beam, and laser irradiation are included.

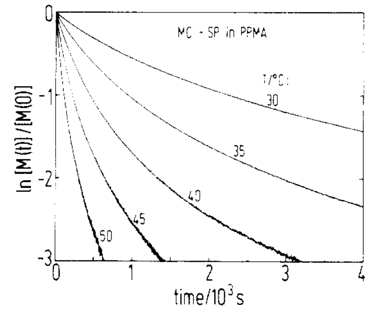


Figure 2. Progress of the merocyanine decoloration in PPMA at various temperatures, normalized to unity concentration at $t = 0$. The first-order plot illustrates the deviations from an exponential decay law.

$$M(t) = \frac{1}{\sigma(2\pi)^{1/2}} \int_{-\infty}^{\infty} \exp\left[-\frac{(E_a - \epsilon)^2}{2\sigma^2} - \nu t e^{-(\epsilon/kT)} \right] d\epsilon \quad (1)$$

Under the premise that this model reflects the deviation from first-order kinetics, a fit revealed the mean rate ν_0 corresponding to the center of initial activation energies E_a and the spread of rates represented by σ. A typical example of an experimental decay curve with its fit, shown in Figure 3, justifies characterizing the decay results by means of the two parameters ν_0 and σ. Figure 4 summarizes the complete set of kinetic results on a temperature scale normalized to the glass transition value T_g of each polymer matrix.

Within the accessed temperature range an Arrhenius plot of the decoloration rate in PPMA shows no systematic deviation from simple activated temperature behavior, which is also believed to hold for the other samples. Table I lists the activation energies and preexponential frequencies ν_a of the MC → SP back-reaction as a function of the polymer matrix.

A second set of kinetic results is obtained by detecting the temporal decrease of MC concentration while exposed continuously to a 632.8 nm photon flux of constant intensity and random polarization. The first qualitative observation is illustrated in Figure 5, indicating a marked

Table I
Activation Energies and Preexponential Frequencies for the Decoloration of Merocyanine in Various Matrices[a]

		Arrhenius		T^2 model		
matrix	T_g, K	E_A, kJ/mol	log (ν_a), s	E_S, kJ/mol	log (ν_s), s	E_m, kJ/mol
PBA	218	108	16.5	93	15.2	8.4
PEA	247	98	14.2	78	12.6	10.8
PMA	282	121	17.7	95	15.5	14.1
PBMA	293	(114)	(17.0)			
PPMA	308	116	16.8	85	14.2	16.8
PEMA	338	(111)	(16.4)			
PMMA	378	(124)	(18.4)			

[a] According to the Arrhenius law (E_A) and following the T^2 model splitting the apparent activation into the stabilization energy of the MC isomer (E_S) and matrix inherent barriers (E_m at 20 °C). Values in parentheses are obtained for samples of unknown residual solvent content.

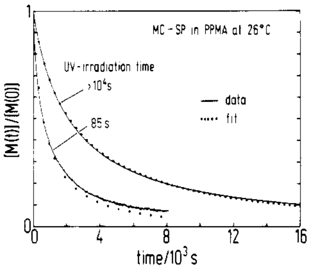


Figure 3. Normalized decay of MC concentration in PPMA at 26 °C after two different irradiation times. The fit to the upper curve represents eq 1. The lower fit is predicted on the basis of a Gaussian density of energy barriers assuming correlated barrier heights for both reaction directions and accounting for the short irradiation time. The initial concentration of the lower data set is actually 0.12 relative to the upper curve.

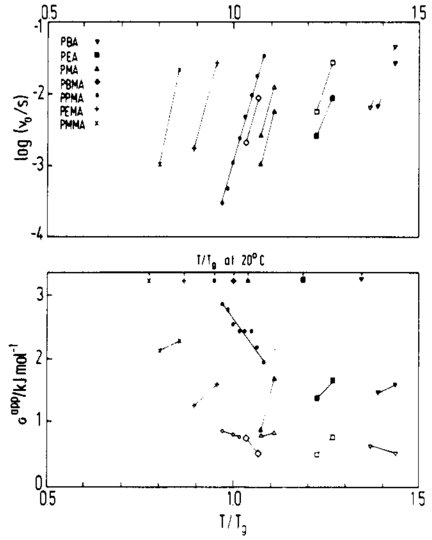


Figure 4. Mean decoloration rate ν_0 and Gaussian width of barrier height σ^{app} describing the experimental decay results of MC → SP within various matrices. Only solid symbols denote data taken for matrices of no or negligible solvent content. The temperature scale is normalized to the individual values of T_g, listed at T/T_g at 20 °C for the various matrices.

increase of the reaction rate upon additional irradiation, an effect which is common to all spiropyrans.[14] This effect is common to all matrices and is not restricted to certain wavelengths of the photon flux, while the increase of the decay rate depends on the irradiation intensity. The kinetics of the MC → SP isomerization, under conditions of optical stimulation, have been recorded with a SP–PPMA sample within the temperature range 5–20 °C, where the corresponding rates under pure thermal activation are negligible compared to the rates achieved with the laser. The thermal course of the increased rate yields an energy of activation of 23 ± 5 kJ/mol. The decay patterns obtained under this condition are subject to the same deviations from first-order kinetics as observed for the thermally induced case. Application of the above fitting procedure indicates that this data set also follows the model of Gaussian activation energies, σ being unaffected by the laser irradiation within experimental resolution. In this case the mean rate constant scales with the laser intensity.

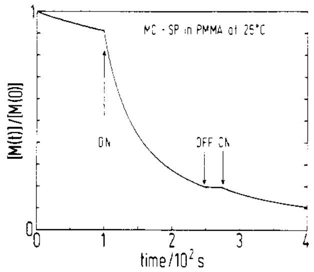


Figure 5. Decoloration of MC/PMMA at 25 °C with and without additional exposure of the sample to a 5-mW, 632.8-nm laser beam. The on/off sequence of the laser beam in the course of the decay is indicated by arrows.

As mentioned above, the UV-driven buildup of the MC concentration prior to every decay scan was carried out until equilibrium conditions are reached. Violating this condition resulted in an increased rate for the back reaction after terminating UV irradiation. The effect of different UV excitation times is depicted in Figure 3, the resulting decay rates differing by a factor of ~4, with the faster decay, corresponding to the incomplete UV excitation, not obeying the model of a Gaussian density of activation energies. The stationary MC concentration has been reached after ~10^4 s of UV irradiation, the case of incomplete UV exposure (85 s) converts 12% to MC with respect to the former case. A similar experiment was conducted for a SP–PBA sample with high residual solvent content. The decay of MC concentration was purely exponential for this case and the decay pattern showed no sensitivity to a variation of the UV irradiation time.

Computer Simulation

The results presented in the former section are summarized by two parameters per decay curve, relying on the model of a Gaussian density of activation energies, experimentally tested in previous work.[6] Extending the temperature range to values far beyond T_g raises the need to modify this kinetic model to account for the increasing rate of molecular or submolecular motion as T is raised. An inherent premise of the dispersive kinetic interpretation is that the energy barriers of a site be static prior to its reaction, restricting the validity of the model to the low-temperature regime ($T < T_g$). An extension of modeling the reaction kinetics within matrices of lower viscosity, i.e., $T \gtrsim T_g$, therefore must account for reorganization of barrier heights during the course of the reaction. In the high-temperature limit, representing the case of a fluid matrix, rearrangements of the matrix will occur fast compared to the time scale of an isomerization reaction leading to first-order kinetics whose rate is governed by a single mean energy barrier. The case of moderate viscosities is treated by computer simulation applying the following procedure.

The initial formation of reactands is represented by an array of 5000 sites, each site connected with an activation energy which is selected at random from within a Gaussian density. In conjunction with a common preexponential reaction frequency the actual reaction time is picked out of an exponential density to yield on average a first-order decay for the subset of sites accidentally having the same activation energy. The resulting total decay is then easily calculated by decreasing the initial amount of sites subsequently at the resulting reaction times. It should be noted that there is no correlation between site index and any random variable, ruling out an interaction between adjacent sites within this model calculation. Up to this point, the simulation results are identical with the kinetics calculated via eq 1. Introduction of the temporal rearrangement of matrix cages is achieved by rerandomizing the activation energy of a statistically selected site if it is still in the excited state at equidistant times. The parameter of the simulation reflecting the matrix temperature or viscosity is the mean time t_{mem} a site remembers its initial cage configuration. Intuitively it seems reasonable to express the velocity of matrix reorientation in terms of the memory time normalized to the initial lifetime of the reactand, i.e., $x_{\mathrm{mem}} = t_{\mathrm{mem}}\nu_{\mathrm{max}}$, where ν_{max} is the reaction rate at $t = 0$.

The qualitative result of introducing a finite t_{mem} into the dispersive kinetics is that a decrease of t_{mem} forces the decay to approach first-order behavior, resulting in a decay $\exp[-\nu_{\mathrm{max}}t]$ for $x_{\mathrm{mem}} = 0$, because matrix motions will, on average, maintain their initial configuration thereby concurring with the decay primarily of those sites with low-energy barriers. Although the results for moderate values $0 < x_{\mathrm{mem}} < \infty$ no longer strictly follow eq 1, the "static" model still reflects the more generalized calculation to a good approximation if both parameters ν_0 and $\hat{\sigma} = \sigma/kT$ are adjusted appropriately. The effect of σ on the decay pattern scales with kT, so that $\hat{\sigma}$ is a measure of the deviation from exponential kinetics, in contrast to σ itself. In this way, the decays of arbitrary x_{mem} are represented by the parameters of a fit on the basis of the "static" calculation (eq 1) which are apparent values $\nu_0^{\mathrm{app}},\hat{\sigma}^{\mathrm{app}}$ in contrast to $\nu_0,\hat{\sigma}$ representing the initial configuration. Figure 6 indicates the course of ν_0^{app} and $\hat{\sigma}^{\mathrm{app}}$ normalized to ν_0 and σ, respectively, as x_{mem} is varied.

Discussion

1. Arrhenius Analysis. Prior to focusing on the temperature dependence of the MC decolorization rate it should be noted that the assignment of a single rate to a given temperature is nontrivial in the case of dispersive, i.e., nonexponential, decay kinetics. All experimental results presented herein as well as previous work on the isomerization kinetics of spiropyran[6-12] exhibit more or less significant deviations from a first-order law. Modeling the kinetics by a Gaussian dispersion of activation energies has led to a satisfactory agreement between eq 1 and experimental data.

The results argue for the picture of a dispersion of barrier heights, where the fast removal of sterically weakly hindered molecules followed by the reaction of sites connected to higher energies of activation gives rise to the observed decrease of the momentary rate as the reaction proceeds. On the other hand, two particular rates can be defined: ν_0, the rate of sites at the center of the Gaussian density, and the maximum occurring rate, $\nu_{\mathrm{max}} = \nu_0 \exp[{}^1/_2(\sigma/kT)^2]$,[15] depending on the spread σ of energy barriers. Consequently, the following thermal results are based on the rate $\nu_0(T)$, reflecting the height of the average energy of activation.

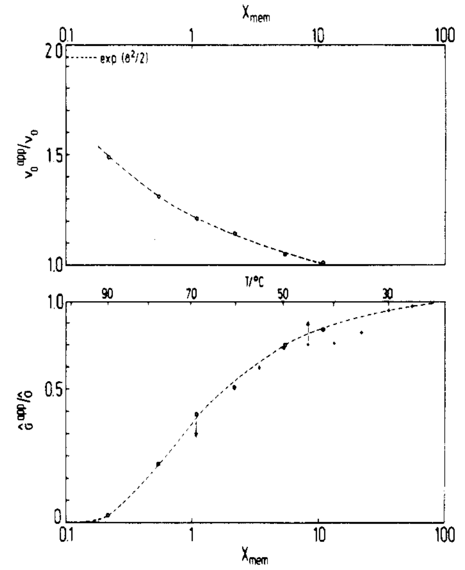


Figure 6. Simulation results (circles) of the apparent Gaussian spread $\hat{\sigma}^{\mathrm{app}}$ of activation energies and mean rate ν_0^{app} normalized to the $x_{\mathrm{mem}} = \infty$ limits $\hat{\sigma}$ and ν_0, respectively, which are chosen to reflect the experimentals for PPMA at 26 °C. exp ($\hat{\sigma}^2/2$) indicates the low x_{mem} limit for $\nu_0^{\mathrm{app}}/\nu_0$. Crosses denote data of the SP/PPMA sample on the temperature scale included, which has been fitted to x_{mem} (see text).

Thermal analysis of the decoloration rate in PPMA in the range 25 °C $\leq T \leq$ 60 °C reveals an Arrhenius type behavior in the case of no additional photostimulation with an energy of activation E_a = 116 kJ/mol and preexponential frequency $\nu_a = 6.3 \times 10^{16}$ s^{-1}. Similar values are obtained for other matrices. The high-temperature limit for the rate of reaction, ν_a, reveals values well above typical phonon frequencies of order $kT/h \simeq 10^{13}$ s^{-1}, pointing toward a significant entropy change $\Delta S^{\ddagger}$ for the isomerization within the matrix. Within the framework of the Arrhenius model ν_a and $\Delta S^{\ddagger}$ are related via $\nu_a = kT/h \exp(\Delta S^{\ddagger}/R)$, yielding $\Delta S^{\ddagger} \simeq 8.7R$. This exceeds the entropy change for the melting process of similar systems which certainly represents an upper limit for the SP ← MC conversion. This result leads one to question the assumption inherent in the Arrhenius interpretation of thermal behavior, that the activation barrier is independent of temperature.

The model of statistically varying activation energies implies that the energetics of the reaction molecules are at least partially governed by the configurations of the polymer matrix by imposing site-specific energy barriers to the isomerization process. As the sample temperature is raised, the polymer will lose viscosity which, in a simple picture, is believed to be the macroscopic manifestation of an increase of free volume. This in turn lowers the mean thermal energy needed to induce the steric reorientation of MC. The qualitative consequence would be a decrease of the average barrier height with increasing temperature, contrary to what the Arrhenius law predicts. A model accounting for this notion is described in the following subsection.

2. T^2 Model. The viscosity of supercooled liquids is generally described via the empirical Vogel–Fulcher (VF) law $\eta(T) = \eta_0 \exp[A/(T - T_0)]$, which only holds for a

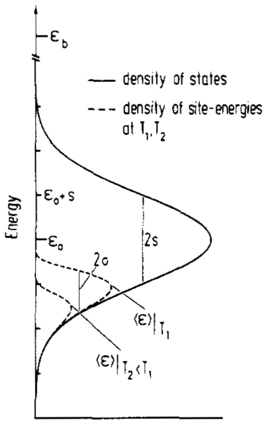


Figure 7. Schematic picture of energy levels for two arbitrary temperatures as proposed by the T^2 model. The dashed lines illustrate the dynamical equilibrium populations at given temperature; the solid line reflects the high-temperature limit population. ϵ_b denotes the barrier height controlling the MC–SP isomerization.

narrow temperature interval well above T_g. Bässler has recently proposed a novel interpretation of the thermal change in viscosity of glasses,[13] based on the idea that the molecular dynamics are governed by the potential energies of discrete sites subject to temporal fluctuations within a given density of accessible states. The model, in the following referred to as the T^2 model, takes advantage of the results known for random-walk transport of elementary excitations viewed as an analogy to the molecular dynamic of supercooled liquids. In the course of conformational fluctuations of site energies within the amorphous matrix, similar to transport phenomena of excitons or charge carriers in a disperse density of states (DOS), the mean potential energy of a molecule tends to settle into a dynamic equilibrium, predetermined by the DOS function, intersite coupling, and temperature. In this model, the temporal start of the energetic relaxation process is the beginning of cooling a liquid from far above T_g to a rigid glass. Consequently, experiments in supercooled liquids will in general probe a system which is at least close to dynamic equilibrium.

The basics of the T^2 model, fitting viscosity data superior to the VF law, are a Gaussian density in energy of occupiable states and the competition of thermally activated jumps to energetically higher states and unrestricted downward jumps into the low energy tail of the DOS. Approximate theoretical calculation and computer simulation of such stochastic dynamics[16] have shown the mean equilibrium energy $\langle\epsilon\rangle$ of the quasi-particles considered to follow $\langle\epsilon\rangle = \epsilon_0 - s^2/kT$ for a Gaussian DOS centered at ϵ_0 with standard deviation s as schematically indicated in Figure 7. The results relevant for analysis of the MC–SP kinetics in polymers are that the thermal activation of the matrix to a local liquid state demands an activation energy $\epsilon_0 - \langle\epsilon\rangle = s^2/kT$, where ϵ_0 reflects the mean energy of a glass in the high-temperature limit, i.e., in the liquid state. Furthermore, the Gaussian width s is termed to be proportional to T_g ($s = \alpha k T_g$), at least within a class of substances. For details see ref 13.

Based on this concept, it seems reasonable to divide the apparent activation energy of the reaction into a part inherent to the MC molecule ϵ_m and an activation of the matrix itself, namely, $\epsilon_0 - \langle\epsilon\rangle$. By definition, ϵ_m should be close to the energy of activation of the MC decoloration process in a liquid host. For the additional activation associated with the matrix we have

$$\epsilon_0 - \langle\epsilon\rangle = s^2/kT = (\alpha k T_g)^2/kT \qquad (2)$$

which now depends on T and thus rules out an Arrhenius law. An energy level diagram is schematically depicted in Figure 7. The temperature dependence of the decoloration rate, regarding eq 2, can be written as

$$\nu(T) = \nu_s \exp[-\epsilon_m/kT - (s^2/kT)/kT] \qquad (3)$$

or

$$\nu(T) = \nu_s \exp[-\epsilon_m/KT] \exp[-\alpha^2(T_g/T)^2]$$

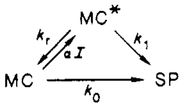
If T_g of the sample is known, the only new parameter introduced by means of eq 3 is $\alpha = s/kT_g$.

A second consequence of describing the molecular dynamics within a random-walk framework concerns the temporal response of a liquid to a jump in temperature, e.g., from its melting point to below T_g. As the relaxation of site energies into the low energy regime of the DOS proceeds, the number of accessible states will decrease rapidly thus slowing down the energetic relaxation. In the long time limit, further relaxation of a site is likely to proceed only after thermal activation of energy barriers, expanding the time scale of relaxation. This predicts macroscopic properties like viscosity to respond only slowly to a sudden change in temperature, a quality known as physical aging.[12]

3. Application of the T^2 Model. Interpretation of the thermal data in terms of eq 3 involves an estimation for α, which can be accomplished on the premise that α be independent of the matrix within the set of poly(alkyl acrylates). Since the ϵ_m, the activation energy of the MC → SP transformation not regarding the matrix, should exhibit no systematic dependence upon T_g, α is chosen to yield the least variation of $\epsilon_m(T_g)$. The results of this calculation for $\alpha = 2.5$ are listed in Table I including only samples with negligible residual solvent to assure validity of the T_g values. The preexponential frequencies are in accord with an entropy change of ~3*R*, believed to be more reasonable compared to the corresponding Arrhenius result of 8.7*R*. Importantly, eq 3 allows separating the energy of activation into the part inherent to the isomerization and an additional part imposed by the matrix. If the energy barrier ascribed to the chromophore itself does represent the stabilization of the MC isomer, the two components of the apparent activation energy should be verified experimentally by photostimulation of the isomerization process.

For the SP/PPMA sample the resultant energies of activation are 85 kJ/mol for the molecular part and the matrix effect ranging from 16.4 to 14.5 kJ/mol within the experimentally covered range 26 °C $\leq T \leq$ 60 °C. Quantitatively equivalent results have been obtained by Kryszewski et al.,[8] comparing the energies of activation of the MC → SP transformation within polymeric matrices with those observed in the corresponding monomeric solutions. By these results it cannot be expected that the change in energy of ~1% could have been resolved experimentally. A more stringent test of this interpretation is believed to be found with the observation that the decoloration rate is raised significantly upon additional visible irradiation.

The experimental findings in conjunction with the additional photon flux (638.2 nm) experiment argue for the following. Local heat dissipation at the absorber sites is believed to be excluded since the optical density of the sample and the light intensity are low, and this effect should not result in a drastic change in apparent activation energy. More likely, the MC form of SP may be electronically stabilized within the ground state of the absorbing electronic system. If this stabilization is effective in the ground state only, excitation via photon absorption of sufficient energy can greatly reduce the thermal activation needed for the isomerization to proceed within the lifetime of this electronically excited state. As the isomerization rates without additional photon assistance were negligible with respect to the case of current interest, it can be concluded that all of the MC–SP transformation is governed by the reaction path opened via photostimulation. Comparing the mean barrier height of ~23 kJ/mol found for the photoinduced case with the former results for PPMA, 85 + 16 kJ/mol, would mean that ~80 kJ/mol or practically all of the stabilization energy is overcome upon optical excitation. The results evidenced by the photon assisted kinetics suggest the following reaction scheme:



with [MC*] = $(\alpha I/k_r)$[MC] and d[MC]/dt = $-(k_0 + (\alpha I/k_r)k_1)$[MC].

MC* denotes the electronically excited state of MC, αI and k_r denote the absorption and relaxation rate, and k_0 and k_1 represent the isomerization paths. By analogy to the details of cis–trans photoisomerization,[21] the upper pathway via MC* probably involves population of the lowest MC triplet state which destabilizes the π-electron system prior to rotation.

Modeling the dispersive kinetics via a Gaussian spread of potential energies to be thermally overcome does not permit the assignment of the energetic dispersion to either the barrier heights of the ground-state energies, evident in eq 1. On the other hand, the observation that the dispersion of activation energies σ^{app} for the dark and photon-assisted reaction are identical strongly indicates that σ^{app} is governed by the statistics of the matrix configurations since the stabilization energy of MC is no longer involved in the case of visible irradiation during the reaction. Therefore, it seems reasonable to identify the density of activation energies extracted from the kinetic analysis with the energy profile of matrix sites which, at a given T, have settled into the low-energy tail of the density of accessible matrix states. This is supported by a crude estimate of the density of equilibrated matrix-site energies by the width $\simeq kT$, since the site energy is controlled by thermal activation from tail states of the DOS (see Figure 7), recalling that the observed spread of energy barriers is also of order kT in the low-temperature limit.

4. Effect of Matrix Dynamics. In the former section it was concluded that the fluctuation σ of activation energies reflects the configurational statistics of the matrix. Recalling that the MC decoloration follows first-order kinetics in fluid solution,[8] the identification of σ resembling the statistics of matrix cages must be restricted to the low-temperature regime where molecular configurations appear static on the time scale of the reaction. Experimentally covering temperatures above T_g invokes the need of accounting for the decrease in viscosity, i.e., a rise in orientational freedom of matrix molecules or submolecular segments.

The results of the computer simulation, Figure 6, show that matrix reorientations give rise to a lowering of the σ as apparent from kinetic studies. Due to the simplicity of the simulation model a temperature scale is initially not included in the parameter x_{mem}. The static Gaussian width $\hat{\sigma} = 1.51$ used in the calculation has been adapted to meet the experimental value of σ for the SP/PPMA sample at 26 °C, the lowest temperature of that data set. Comparing the observed and simulated σ-values to correlate x_{mem} to T involves proving that σ (26 °C, PPMA) is at least close to the case of infinite matrix cage memory time x_{mem}.

An order of magnitude estimate of the mean time for which a reactand remembers its initial matrix cage configuration is possible, taking advantage of the fact that also the UV-driven reaction SP → MC is kinetically governed by the bulk polymer as is the back-reaction. As both isomerization processes follow similar reaction patterns,[6] UV irradiation of the SP sample will subsequently build up the Gaussian density of energy states, with sites of higher steric freedom dominating the coloration kinetics in the short irradiation time regime, followed by reactands of increasing energy barriers imposed by the matrix. In the case of slow diffusional processes within the matrix, it can thus be expected that the decoloration kinetics depend on UV exposure time as shown for the SP/PPMA sample at 10 K below T_g. Knowledge of the fit parameters of the slower curve and of the time dependence of the mean energy of activation in the course of increasing the MC concentration,[15] symmetrical to the corresponding decrease of MC, allows one to predict the decay of the most easily formed 12% of MC sites pronounced at a UV exposure time of 85 s. The result of this calculation together with the experimental curve is included in Figure 3. Deviations between the observed and predicted decay are reasonable since the density of energies after only partial SP → MC conversion is not expected to exhibit a Gaussian profile, assumed for ease of calculation. The agreement in slope for the total reaction time indicates that the shift in mean energy barrier height due to incomplete irradiation, exceeding the width of variations σ, is remembered for the time scale of the reaction, which in terms of the computer simulation would be expressed as a high x_{mem} value. The sensitivity of the decoloration kinetics to the extent of coloration, no longer observed for $T \gg T_g$, shows that the energy barriers for both reaction directions must be highly correlated within a rigid matrix. Furthermore, these results are considered to represent an unambiguous consistency proof for the kinetic model advanced herein.

Having shown that the 26 °C data for PPMA approximately exhibit the low-temperature limit value of x_{mem}, it is reasonable to identify the experimentally apparent value of the spread of activation energies, σ^{app}, with the static spread σ. This allows normalization of the experimental results to the form $\sigma^{\mathrm{app}}/\sigma$, then comparable to the simulation results, which casts the simulation parameter x_{mem} on to a temperature scale as depicted in Figure 6. This scaling reveals the thermal course of $\nu_0^{\mathrm{app}}/\nu_0$, the relative change in reaction rate due to matrix reorganization with temperature. Formally, this increase of the rate is described by an activation energy of 7 kJ/mol within the experimental temperature range. This thermal behavior of the isomerization rate, not included in the above models, is a consequence of matrix dynamics and thus must be accounted for upon separating the apparent energy of activation into a molecular and a matrix portion. The former assignment of 16 kJ/mol to the matrix is then increased by 7 kJ/mol, leaving 78 kJ/mol for the stabilization energy of the MC isomer. The resulting energy of activation inherent to the matrix, 23 kJ/mol, is in perfect agreement with the activation of 23 ± 5 kJ/mol observed upon additional photostimulation, where the π-electron system of MC is destabilized due to the optically induced $\pi \rightarrow \pi^*$ transition.

Conclusions

The decoloration of MC in a glassy polymer follows dispersive kinetics, the dispersion of barrier heights arising from the statistics of matrix configurations. Although claimed to represent a Gaussian density, it is not believed that the conclusions drawn from kinetic analysis depend critically on the shape of this density. The temperature dependence of the decoloration rate is to a great extent governed by an activation energy connected to the MC molecule itself, thereby obscuring the temperature-dependent matrix effects on the rate. Two crucial parameters are introduced to adjust the kinetic models quantitatively to fit the experimental findings: the spread σ of activation energies invoking the dispersion of reaction rates and the width s of the Gaussian density of potential energies reflecting the statistics of matrix configuration. Assignment of the different activation energies of the reaction to the configurationally unique matrix cages closely connects both parameters. As depicted in Figure 7, the dispersion of activation energies indicate the potential site energies as they have equilibrated at a given temperature within the Gaussian DOS characterized by the width s.

Although experimental data do not indicate a deviation from an Arrhenius-type behavior, the T^2 model turns out to be more appropriate for understanding the thermal course of reaction rates, because the corresponding entropy change is more realistic and the estimate of the mean energy barrier imposed by the matrix is in good agreement with the experimental value. Furthermore, the resulting activation connected to the intramolecular reorganization of merocyanine is close to the value of 70 kJ/mol obtained in propyl methacrylate solution by Kryszewski et al.[8]

Within this experimental study it has been attempted to observe the effect called physical aging which describes the quality of supercooled liquids responding slowly to a temperature drop. Macroscopically this is documented for example by the enthalpy relaxing to its equilibrium value logarithmically in time after annealing above T_g.[17,18] A similar behavior is also reported for the volume of polymers[19] and the decoloration of azochromophores attached to polyurethane chains.[12,20] The fact that physical aging was not detectable at the time resolution of several minutes achieved here is understood when one recalls that molecularly dispersed SP probably probes the dynamics of polymer subunits, dominant on a time scale much shorter than that of motions related to viscous flow. Consequently, the Gaussian DOS of matrix potential energies governing the decoloration kinetics will not necessarily represent the configurations dominant for viscosity phenomena. Energies of activation observed for structural relaxation are on the order of several 100 kJ/mol,[1] exceeding the 16 kJ/mol barrier height inherent to the matrix as observed here. This latter energy of activation can only be viewed as the mean activation needed to create the free volume necessary for this specific isomerization reaction to proceed.

A brief comparison to literature data appears in order. The kinetics of SP or azo compound decoloration has been subject to detailed experiments, raising different activation energies for temperatures above and below T_g.[10,22,23] The experimental findings are quantified by the WLF equation, arguing for a correlation between free volume and photochromism (see, e.g., ref 10). Taking account for the deviations from first-order decay behavior, the authors separate the decay into a couple of distinct rates with different thermal activations, where the change in activation energy at T_g critically depends on the selected rate.[23] These notions are not in contradiction to the kinetics and temperature dependencies presented here, since the Arrhenius behavior is claimed only for the "mean" rate ν_0, the change in kinetic behavior at T_g being described by the course of σ, which accounts for the spread of rate parameters and is claimed to decrease significantly near T_g.

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