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Rate-Memory and Dynamic Heterogeneity of First-Order Reactions in a Polymer Matrix

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ABSTRACT: The kinetics of the photochromic first-order reaction merocyanine → spiropyran in PPMA (*Macromolecules* **1988**, *21*, 923) is reanalyzed. We apply a method which is conceptually analogous to a technique for discriminating between homogeneous or heterogeneous dynamics on the basis of generalized time correlation functions. The requirement for such an analysis is to selectively prepare a fast or slow subensemble of relaxation sites and to monitor their dynamics relative to those of the entire ensemble, which has been realized experimentally for an isomerization reaction probing the potential barriers imposed by the polymer matrix. For the case of heterogeneous dynamics expected here, a prediction can be made for the decay related to a subensemble of the fast relaxors which does not involve assumptions about the extent of the rate memory or, equivalently, of the temporal fluctuations of activation barriers.

Introduction

Relaxational processes in polymers or in other disordered materials are notorious to display nonexponential temporal patterns,[1−3] which are often well described by the stretched exponential or Kohlrausch−Williams−Watts[4,5] (KWW) function

$$\phi(t) = \phi_0 \exp[-(t/\tau_{\mathrm{KWW}})^{\beta_{\mathrm{KWW}}}] \qquad (1)$$

In this expression τ_{KWW} is a characteristic relaxation time and β_{KWW} within the range $0 < \beta_{\mathrm{KWW}} \leq 1$ quantifies the extent of deviation from a single exponential ($\beta_{\mathrm{KWW}} = 1$) decay. Similarly, the degree of the relaxation time dispersion can be expressed in terms of a probability density $G(\ln \tau)$ for finding a site related to the single time constant τ. The ensemble averaged decay in this case reads

$$\phi(t) = \phi_0 \int_{-\infty}^{+\infty} G(\ln \tau) e^{-t/\tau}\, d \ln \tau \quad \text{with} \quad \int_{-\infty}^{+\infty} G(\ln \tau)\, d \ln \tau = 1 \qquad (2)$$

Due to the fact that any monotonic decay $\phi(t)$ can be cast into the form of eq 2 with a non-negative $G(\ln \tau)$, such a fit to the ensemble averaged decay is not decisive regarding the nature of the underlying processes. With respect to the ensemble average, two extreme pictures are usually discussed:[6−10] the heterogeneous case, where each site contributes exponentially but with a distribution of site specific time constants τ, and the homogeneous case, where each site identically contributes nonexponentially. A simplified sketch of these limiting situations is shown in Figure 1, which no longer holds if the $\ln \tau$'s fluctuate in time. A discrimination between the two situations on the basis of $\phi(t)$ data alone remains impossible. Note that the above statements are meant to outline the ideas of dynamic heterogeneity and homogeneity, without actually defining these terms.

It is important to realize that the term heterogeneity in the present context refers to the dynamics of molecules or polymer segments being a spatially varying quantity. The presence of such dynamical heterogeneity does not necessarily imply a spatial distribution of physically distinct states. It is rather a signature of subtle changes in density or mutual orientations relative to the macroscopic average values in a material which is otherwise physically and chemically uniform in space.

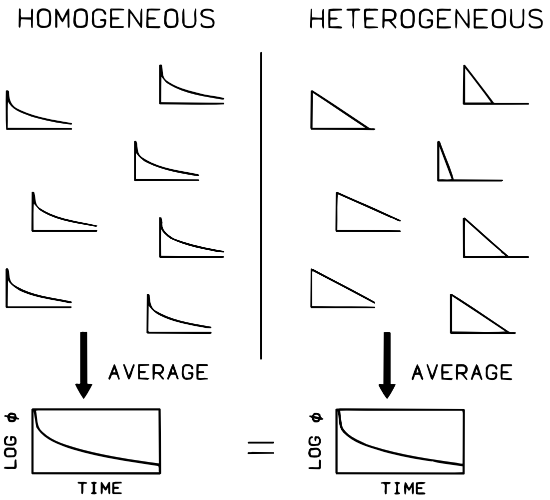

Figure 1. Sketch of a simplified discrimination between the homogeneous and heterogeneous character of a relaxation process. The small graphs are meant to display single-site decay patterns in terms of $\log[\Phi(t)]$ versus time. The ensemble averaged relaxations (lower frames) can be indistinguishable, even though the two scenarios are quite different in nature.

One approach to the details of a relaxation process is to selectively prepare the fast (slow) sites for a subsequent relaxation and to identify experimentally if these sites on average relax faster (slower) relative to the entire ensemble. The possibility of distinctly probing the fast or slow relaxors is exploited in recent reduced 4D-NMR experiments, which have unambiguously identified heterogeneity of relaxations in polymers near their glass transition temperature T_g.[10−12]

The purpose of the present work is to reexamine kinetic data obtained previously[13] for a photochromically doped polymer, in which the polymer matrix is believed to impose a distribution of site specific activation barriers on the first-order decoloration isomerization of merocyanine into the spyropyran form. Because the foregoing coloration process is UV driven, it was possible to prepare the equilibrium density and a fast subensemble as observable educt states by varying the irradiation time. In this manner the photochromic sites are employed for probing the nature of the local polymer environments. The previous experiment and data analy-

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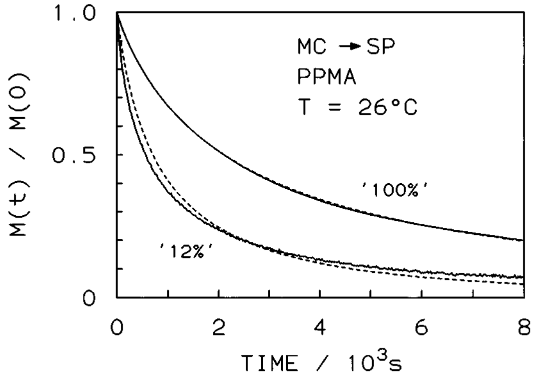

Figure 2. Experimental results for the MC → SP relaxation in PPMA at 26 °C shown as solid lines. The curve labeled '100%' refers to a stationary ($t_{UV} \geq 10^4$ s) MC concentration at $t = 0$; the case of selecting the fast sites ($t_{UV} = 85$ s) is labeled '12%'. The upper, $M_{100\%}(t)$, and lower, $M_{12\%}(t)$, dashed curves are fits according to eqs 3 and 4, respectively.

sis concerning the time scale in which a site memorizes its current rate constant are briefly reviewed. The main issue is to then analyze these results in the framework of a formalism similarly used to define dynamic homogeneity and heterogeneity based on higher order time correlation functions.[14] This latter method turns out to be a general and effective tool for characterizing the dynamical nature of a relaxation process. As a result, the first-order nature of the individual transitions is strongly confirmed, although the ensemble averaged decay is highly nonexponential and although the site specific rate constants may fluctuate.

Experiment and Results

The polymer poly(propyl methacrylate) (PPMA), having a calorimetric glass transition at $T_g \approx 35$ °C, has been doped on a percent level with the photochromic compound 1,3,3-trimethylindolino-6′-nitrospirobenzopyran (SP) and was solvent cast onto a glass slide in order to obtain a clear film of ~100 μm thickness, which is then carefully dried in order to suppress any solvent effects. Upon UV irradiation at 348 nm SP undergoes an isomerization reaction into its colored merocyanine (MC) form, so that the thermally driven decoloration kinetics MC → SP are easily monitored in terms of [MC](t) or M(t) by recording the optical density of the film at 577 nm. The sample has usually been UV-irradiated for a time t_{UV} until no further increase in the concentration [MC] occurs and the time $t = 0$ of the subsequent kinetics is defined by blocking the UV beam. Experimental details are stated elsewhere.[15] Here we show only two results obtained for a SP/PPMA sample at 26 °C, i.e. in the glassy state.The upper solid curve in Figure 2 shows the decay of $M(t)$ after UV irradiation until stationary conditions are achieved ($t_{UV} \geq 10^4$ s). Experiments using different UV intensities have indicated that the sample is not being heated by the 348 nm beam and that only a fraction of SP molecules is converted to MC. The lower solid curve refers to the same experiment but with $t_{UV} = 85$ s only. Both curves are plotted after normalization to $M(0) = 1$. However, it is important to note that the $t_{UV} = 85$ s case resulted in an initial concentration [MC](0) being 12% relative to the initial [MC] for the $t_{UV} \geq 10^4$ s case set to 100% (stationary condition). The striking feature of the curve labeled '12%' is the time scale of the decay being approximately a factor of 4 faster relative to the '100%' curve. At temperatures significantly above the glass transition, effective fluctuations of barrier heights ultimately lead to purely exponential decays for the ensemble average and t_{UV} no longer affects the $M(t)$ results for $T > T_g$.[13]

Discussion

The isomerization reaction SP ↔ MC in polymer matrices is well investigated and can be considered as a model system for an ensemble of parallel, i.e. uncoupled, first-order reactions but subject to the effect of the disordered matrix.[15] The effect of the matrix on the decay is to introduce a distribution of rate or time constants by virtue of statistically distributed potential barriers which have to be thermally overcome by the sterically demanding isomerization process. On the basis of the central limit theorem, it is natural to expect a Gaussian distribution of barrier heights, or equivalently of ln(τ).[15,16] The concomitant ensemble-averaged normalized decay $M(t)$ reads

$$M_{100\%}(t) = \frac{1}{\sqrt{2\pi\sigma^2}}\int_{-\infty}^{+\infty} \exp\left[\frac{-\ln^2(\tau/\tau_0)}{2\sigma^2}\right] e^{-t/\tau}\, \mathrm{d}\ln(\tau) \tag{3}$$

equivalent to eq 2 with $G(\ln\tau) = \tau \cdot g(\tau)$ being a Gaussian probability density for ln(τ) centered at ln(τ_0) and with Gaussian width σ. Equation 3, actually with $\tau_0 = \tau_0(T)$ and $\sigma = \sigma(T)$ being temperature dependent parameters, has been shown to describe a large number of decay data for photochromic reactions in polymer matrices.[13,15–17] In the present particular case of the '100%' curve, such a fit is included in Figure 2 as the upper dashed line using the parameters $\tau_0 = 3366$ s and $\sigma = 1.146$. This particular choice for $G(\ln\tau)$ is denoted $G_{100\%}(\ln\tau)$ in the following.

We now assume the simplest case of a dynamically heterogeneous limit, where each site is related to a purely exponential decay with site specific ln(τ)'s assumed not to change with time. An important consequence is that, at a certain site, ln(τ) or the activation barrier is identical for both the UV driven coloration and the thermal decoloration kinetics.[16] Therefore, the case with $t_{UV} = 85$ s, leading to 12% of the stationary MC concentration, should have selectively transformed a fast subensemble of the SP molecules. Their probability density $G_{12\%}(\ln\tau)$ is given by the expression $G_{12\%}(\ln\tau) = G_{100\%}(\ln\tau)[1 - \exp(-t_0/\tau)]$, where $t_0 = 257$ s has to be selected such that one obtains $\int G_{100\%}(\ln\tau)[1 - \exp(-t_0/\tau)]\ \mathrm{d}\ln\tau = 0.12$. These two densities, $G_{100\%}(\ln\tau)$ and $G_{12\%}(\ln\tau)$, are plotted in Figure 3. A prediction for the '12%' decay along the above lines is thus obtained by inserting $G_{12\%}(\ln\tau)$ in eq 2, which yields

$$M_{12\%}(t) = \frac{1}{\sqrt{2\pi\sigma^2}}\int_{-\infty}^{+\infty} \exp\left[\frac{-\ln^2(\tau/\tau_0)}{2\sigma^2}\right] e^{-t/\tau}[1 - e^{-t_0/\tau}]\, \mathrm{d}\ln(\tau) \tag{4}$$

The decay resulting from eq 4 with $\tau_0 = 3366$ s, s = 1.146, and $t_0 = 257$ s is plotted as the lower dashed line in Figure 2. It is easily seen that eqs 3 and 4 satisfy the relation

$$M_{12\%}(t) = M_{100\%}(t) - M_{100\%}(t + t_0) \tag{5}$$

Obviously, the significant difference between the two experimental curves is accounted for by the above calculation to a good degree of accuracy. This method has been identically applied in the original paper, but

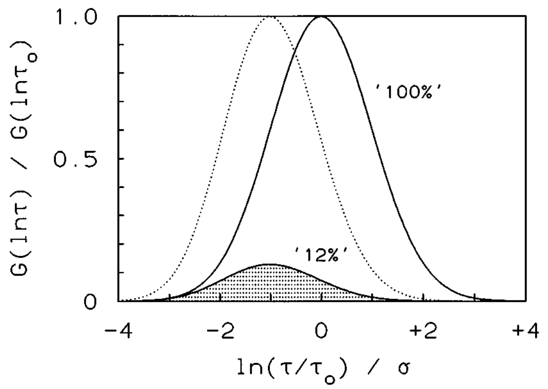

Figure 3. Probability densities for the two experimental situations. Solid lines: The peak-normalized curve '100%' refers to the stationary density $G_{100\%}(\ln\tau)$ obtained for a long UV irradiation time ($t_{UV} \geq 10^4$ s). The lower curve with the shaded area is presented on the same scale as $G_{100\%}(\ln\tau)$ and represents the calculated density $G_{12\%}(\ln\tau)$ obtained by a short irradiation time ($t_{UV} = 85$ s). The shaded area is 12% of the area under the upper solid curve. The dotted line shows again $G_{12\%}(\ln\tau)$ but normalized to its peak value.

with some numerical approximations so that the calculated curves shown here differ slightly from the previous[13] ones. On the basis of the agreement between eq 4 and the experimental result for the '12%' case, it has been concluded in the original paper[13] that temporal fluctuations of barrier heights ($\propto \ln\tau$) are absent or negligible at this temperature and on the time scale of the experiment.

It should be noted that no analogous characterization of the kinetic nature would have been possible without assuming a *static* distribution of time constants. For temperatures near or above T_g it has been demonstrated that it is precisely the temporal fluctuation of $\ln\tau$ which ultimately leads to exponential kinetics for the ensemble average in a matrix of lower viscosity.[17] In this case, the analogous experiment with differing irradiation times t_{UV} yields purely exponential decays which no longer depend on t_{UV} after normalization to $M(0) = 1$.[13] The simplest approach to a fluctuation of individual $\ln\tau$'s involves a single and τ-independent rate K, at which a specific site looses memory to its current $\ln\tau$ while the underlying $G(\ln\tau)$ remains unchanged. For this situation the kinetics can be stated by[17]

$$\frac{\partial m(\ln\tau,t)}{\partial t} = \frac{1}{\tau}m(\ln\tau,t) - K\cdot m(\ln\tau,t) + m(\ln\tau,0)\cdot K\cdot M(t) \quad (6)$$

with

$$m(\ln\tau,0) = G(\ln\tau) \quad \text{and} \quad M(t) = \int_{-\infty}^{+\infty} m(\ln\tau,t)\,\mathrm{d}\ln\tau$$

Even with the given severe and unrealistic restrictions regarding the fluctuation rate K, a prediction for $M_{12\%}(t)$ in the case that $M_{100\%}(t)$ takes the form of eq 6 does not seem possible analytically.

The alternative approach relative to the calculation outlined above is a special case of a recently proposed formalism[14] for defining and discriminating dynamic homogeneity and heterogeneity in terms of higher order time correlation functions. The appropriate quantities in this context are conditional probabilities of the general form $q_3(\sigma,t|\sigma_0,t_0)$, where σ and σ_0 are Boolean variables and t and t_0 are time intervals. The quantity expressed by q_3 is the probability that a reactant does not ($\sigma = 0$)/does ($\sigma = 1$) change its state during a time interval t, under the condition that it did not ($\sigma_0 = 0$)/did ($\sigma_0 = 1$) change its state during the previous time interval t_0. The analogous nonconditional probability is denoted $q_2(\sigma,t) \equiv q_3(\sigma,t|1,\infty)$ and measures the probability that a reactant does not ($\sigma = 0$)/does ($\sigma = 1$) change its state during the time interval t. A comparison of the definitions of q_2 and q_3 with the experimental situation leads to identifying

$$M_{100\%}(t) \equiv M_2(t) = q_2(0,t) \quad (7)$$

$$M_{12\%}(t) \equiv M_3(t_0,t) = q_3(0,t|1,t_0)\cdot q_2(1,t_0) \quad (8)$$

In eq 8 the term $M_3(t_0,t)$ expresses that the experimental result $M_{12\%}(t)$ did depend on the preparation condition t_{UV}, which is closely linked to t_0. In this terminology we can equate $M_{100\%}(t) \equiv M_2(t) \equiv M_3(\infty,t)$, noting that $M_{100\%}(t)$ has been obtained under the condition $t_{UV} \approx \infty$ and thus $t_0 \approx \infty$.

The conditional probabilities q_2 and q_3 defined above satisfy the following two rules

$$q_2(0,t_0)q_3(0,t|0,t_0) = q_2(0,t_0+t) \quad (9)$$

$$q_3(0,t|1,t_0)\ q_2(1,t_0) + q_3(0,t|0,t_0)\ q_2(0,t_0) = q_2(0,t) \quad (10)$$

We can now employ eqs 7−10 in order to establish a relation between $M_3(t_0,t)$ and $M_2(t)$ which involves *no* assumptions about the possible fluctuations of rate constants:

$$\begin{aligned} M_3(t_0,t) &= q_2(0,t) - q_2(0,t_0)\ q_3(0,t|0,t_0) \\ &= q_2(0,t) - q_2(0,t_0 + t) \\ &= M_2(t) - M_2(t_0 + t) \end{aligned} \quad (11)$$

which is precisely the relation between $M_{12\%}(t)$ and $M_{100\%}(t)$ stated in eq 5. Consequently, the fit (dashed line) to the '12%' curve in Figure 2 is equally predicted by eq 11, but now without the knowledge of $G(\ln\tau)$ and independent of the effect of fluctuations regarding the barrier heights in the course of the reaction. More specifically, the small but systematic deviations between the '12%' curve in Figure 2 and its fit cannot be attributed to finite fluctuations, as concluded previously. In light of this analysis the more probable cause for these deviations is the macroscopic mechanical responses to the progress of the photochromic reaction which can have a feedback on the density $G(\ln\tau)$.

The validity of eq 10 is the crucial step of our analysis. The left hand side can be interpreted as the probability that a reactant does not change its state during *t and* does not or does change its state during t_0. Since the reactant has to fulfill one of the two latter options, no information about the behaviour during t_0 is contained in this probability, hence justifying the validity of eq 10. This argument is no longer valid if the rate constants for the MC → SP reaction are uncorrelated to those of the SP → MC reaction. In such a case the basis of our formalism breaks down because then one also had to distinguish in which state the reactant is. As a consequence, eq 11 would no longer hold. However, the validity of eq 11 is not affected if the rates for the two reaction directions differ by a constant factor, equivalent to a transition in asymmetric double-well potentials with possibly fluctuating barrier heights but associated with a common asymmetry for all double-well potentials. This intramolecular asymmetry leading to $t_0/t_{UV} \approx 3$ originates from the ratio of the rate constant for the thermal back-reaction to that for the UV-driven coloration process, where the latter must depend on the UV intensity because this direction involves the optical cleavage of a C−O−pyran bond. Therefore, the observed asymmetry is not coupled to the statistics of barriers imposed by the polymer matrix. This is supported by the previous observation, that the distribution of activation barriers is identical for both reaction directions[16] and independent of the overall speed of the reaction, if varied by 2 orders of magnitude.[13] Our general analysis is not hampered by such an asymmetry, because we refrain from demanding identical values for t_{UV} and t_0.

From the definition of the conditional probabilities q_2 and q_3 it is clear that the reactant is attributed to two distinct states only, educt and product states. Furthermore, the transition MC → SP is not accompanied by a parallel back-reaction, because the experimental $M(t)$ eventually decays to zero MC concentration. In contrast to more general relaxation processes, e.g. NMR or dielectric relaxation, dispersive reactions are bound to display only a heterogeneous component in their dynamics if the elementary step can be considered a simple first-order reaction. The second important prerequisite for applying the formalism outlined in eqs 7−11 is a probability density $G(\ln \tau)$ which is time-invariant, although fluctuations of time constants within this density may occur.

With these above requirements for the applicability of the very general relation $M_3(t_0, t) = M_2(t) - M_2(t_0 + t)$ we can now compile the nontrivial conclusions which can be drawn from the experimental verification of eq 11: Although only the ensemble averaged dispersive decay is observable, the above analysis clearly indicates that the first-order character of the elementary reaction step is preserved in the glassy polymeric matrix. Secondly, the activation barriers ($\propto \ln \tau$) are identical for both directions of the MC ↔ SP transition, except for a constant factor in τ, indicating that the statistics of activation barriers is solely a consequence of the disordered state of the polymer imposing site-specific environments on the photochromic molecules. Thirdly, deviations from the prediction inherent in eq 11 are not decisive regarding the time scale in which a site memorizes its current activation barrier or τ, since no assumptions about the temporal fluctuations of barrier heights are implied in the formalism.

The possible statements regarding fluctuations of $\ln \tau$ on the basis of only the curves presented here reduce to the observation that the rate at which fluctuations can occur is not significantly faster than the average reaction rate, because otherwise the ensemble-averaged decay would be a single exponential function. Equivalently, such effective fluctuations leading to almost purely exponential decay profiles force the two patterns $M_3(t_0,t)$ and $M_2(t) - M_2(t_0 + t)$ to collapse onto a single curve; i.e., t_{UV} is no longer expected to affect the normalized $M(t)$ results, as observed for suffciently high temperatures $T > T_g$.[13]

Conclusions

The measurement of decoloration kinetics in a polymer matrix can be conducted such that higher order time correlation functions become accessible for a system where the elementary relaxation step in solution is well defined. The resulting relaxation patterns thus reflect an appropriate model system for investigating data analysis techniques related to characteristic properties of the dynamics like heterogeneity, rate memory, fluctuations, and character of the elementary step. As a result, reaction kinetics in a polymer matrix can preserve their first-order-type process on a molecular level and are inherently heterogeneous, even if only nonexponential patterns are observed. Analyzing the details of fluctuations calls for access to the next order conditional probability function q_4, which involves an evolution period inserted between preparation and relaxation processes and for which photochromic fulgide derivatives are ideal candidates. It should be emphasized that analogous conclusions based on measuring $q_2(\sigma,t)$ alone must remain speculative.

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