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LINE NARROWING EFFECTS IN KINETICS OF DISPERSIVE FIRST-ORDER REACTIONS

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Abstract The onset of thermally induced configurational fluctuations in a polymer near the glass transition can be monitored by the ensemble averaged isomerization reaction of probe molecules subject to a significant sterical hindrance. The decay patterns can be rationalized in terms of a distribution of activation barriers together with a temperature dependent correlation time for the matrix cages. Experimental support is given by data of a spiropyran/PBMA system investigated in the temperature range near T_g.

INTRODUCTION

Upon lowering the temperature of a polymer beyond the melting point generally no phase transition is observed due to its inability to crystallize. Instead, a gradual increase of the viscosity accompanies the cooling process until solidification at $\approx 10^{13}$ Poise sets in at the glass transition temperature T_g. In this state the dynamical disorder of the liquid phase is preserved on a quasistatic time scale. Even in this solid state thermally induced motional modes are still active as observable via Brillouin or photon correlation spectroscopy as well as NMR techniques.[1] Especially in the vicinity of T_g the extent of motional freedom of the glass constituents depends critically on temperature.

Consider a probe molecule embedded in a polymer glass which undergoes a reaction whose activation barrier is governed by the specific polymer cage constraining the sterical freedom of the probe. In the case of static

disorder the variety of differing conformations will lead to a dispersive, i.e. non-exponential, overall decay scheme whereas fast fluctuations of the impeding structures give rise to single exponential kinetics due to effective averaging of site specific contributions as observed in liquids. The kinetics in the intermediate regime where the correlation time of the polymer cage and the mean reaction time of the probe become comparable should, therefore, carry information on the fluctuations of the glass as detected by the cage sensitive reaction. In the following a model is presented which accounts for the gradual loss of the dispersive character of a reaction by regarding temperature dependent correlation times for the site specific activation energies. The applicability is demonstrated for the photochromic isomerization reaction spiropyran-merocyanine as a probe within a PBMA film.

MODEL

The situation considered is an ensemble of reactants subject to individual energy barriers, the reactions independently following first-order behaviour. The manifold of activation barriers is reflected by a normalized density of barriers $d(\epsilon)$. The observable kinetic pattern is simply given by the expression

$$M(t) = \int d(\epsilon)\cdot\exp[-r_o t\cdot e^{-\epsilon/kT}]\, d\epsilon = \int n(\epsilon,t)\, d\epsilon \qquad (1)$$

for an Arrhenius-type activated transition with a preexponential frequency r_o. In general the resulting decay of the sum of all educt states will be non-exponential because reactants subject to low barriers only will react first subsequently followed by transitions involving higher barriers and thus slower rates. This feature is paralleled by the temporal evolution of the density of barriers $n(\epsilon,t)$ of those reactants who are still in the educt state at time t. In the short time regime $n(\epsilon,t)$ is depleted at low

values of ϵ only, the long time decay being governed by the residual high ϵ wing of this distribution. The temporal evolution of $n(\epsilon,t)$ is illustrated in fig.1 indicating that the mean barrier of residual educt states shifts with increasing time towards higher barriers. Up to this point

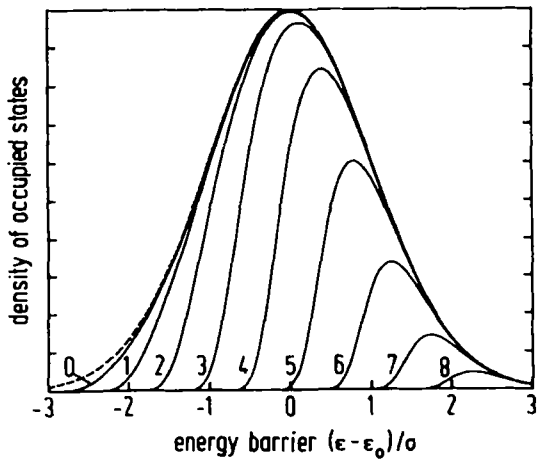

FIGURE 1. Energy density $n(\epsilon,t)$ of educt states at times $\log(t) = 0...8$ for a Gaussian $n(\epsilon,0)$ (broken).

it has been assumed that the reactants retain the initially defined barriers throughout the course of the reaction. Allowing for temporal fluctuations of the individual barriers is to a first approximation accomplished by introducing a single rate K at which a given barrier ϵ is altered, K being independent of ϵ. The effect is that on average after a time 1/K a barrier is redefined yielding a new value which is a random selection from the given density of ϵ, i.e. old and new values of ϵ are not correlated. Because reactants at low barriers will react at first a random redefinition at barrier heights must eliminate longer waiting times and consequently reduce the degree of dispersion of the overall decay. Guided by the experimental results shown below a Gaussian density of barriers $d(\epsilon)=n(\epsilon,0)$ with width σ and centered at ϵ_0 is assumed for the following although any other density is

compatible with the present approach. The resulting ensemble averaged, normalized decay M(t) thus depends on σ, r_o and K and is given by [2]

$$dn(\epsilon,t)/dt = -r_o\, e^{-\epsilon'}\, n(\epsilon,t) - K\, n(\epsilon,t) + K\, n(\epsilon,0)\, M(t)$$

$$n(\epsilon,0) = 1/\sqrt{2\pi\sigma'}\, \exp[-(\epsilon-\epsilon_o)^2/2\sigma^2],\ \sigma'=\sigma/kT,\ \epsilon'=\epsilon/kT$$

$$M(t) = \int n(\epsilon,t)\, d\epsilon \qquad (2)$$

where the temperature dependence of the decay pattern is cast into the parameter K=K(T). $n(\epsilon,t)$ is defined through its time derivative consisting of three terms, namely depletion via the actual reaction, removal from its ϵ position at rate K and arrival at ϵ from anywhere else on

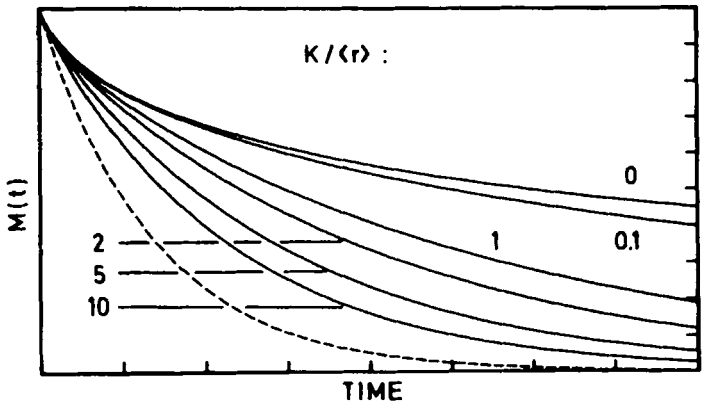

FIGURE 2. M(t) profiles after eqn.(2) for various ratios K/<r>. The K=∞ limit is the broken exponential curve.

the ϵ scale, with respect to the above order. In the K≈0 limit a dispersive decay is obtained, the degree of dispersion being gradually lowered upon increasing K(T) which ultimately leads to a pure exponential decay in the K≈∞ limit, i.e. for high temperatures, as depicted in fig.2. It should be noted that the dispersion depends on K/<r> rather than on the absolute K, <r> being the mean reaction rate.

The varying degree of kinetic dispersion of a set of data curves as in fig.2 will appear as a set of barrier distributions where the approach to the exponential decay translates into a falling tendency of the resulting 'apparent' breadth σ^{app} of the Gaussian $d(\epsilon)$ if $d(\epsilon)$ is obtained via eqn.(1), i.e. if motional effects are disregarded. The apparent contradiction that σ^{app} is thermally decreased although the system disorder should increase with T is then easily overcome by recognizing that motional effects as introduced by K(T) can rationalize the course of σ^{app}. The most significant effect of the motional averaging to the decay will thus be the narrowing of the observable line width of the density of active barriers. Because of the analogy to the motional averaging of inhomogeneously broadened resonance lines observed in NMR experiments we adopt the term 'motional line narrowing' for the present feature.

EXPERIMENT

The applicability of the above model has been tested for an isomerization reaction which converts the ring opened coloured merocyanine (MC) molecule to its ring closed form spiropyran (SP) embedded at low concentration in a PBMA film[2]. After driving the MC concentration to an equilibrium value by UV irradiation the [MC] kinetics have been monitored via the extinction of MC in the range near T_g, in which a transition from a dispersive to exponential decay character is well known.[3] From a numerical analysis of the decay traces at various temperatures a set of barrier spectra is obtained which match the decay results within the range of the signal noise of $\approx 10^{-3}$. Fig.3 illustrates the thermal narrowing of the spectral lines characterized by σ^{app} for both results achieved with no bias input concerning the density of barriers as well as for the Gaussian density approximation which appears appropriate within the present resolution (for details see ref.4).

Eqn.(2) allows for disentangling $\sigma^{app}(T)$ into σ and K(T) with the static line width σ of the barrier distribution taken from the low temperature data (K≈0). The observerd line narrowing shown in fig.4 in the range from σ^{app}=1.3kT at 14K below T_g to practically zero at ≥30K above T_g is perfectly paralleled by eqn.(2) on the basis of a

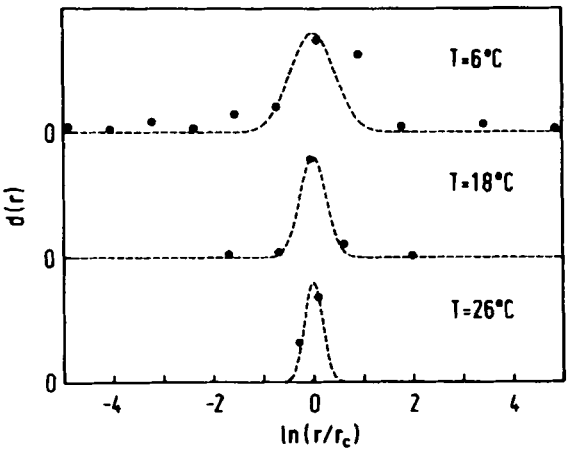

FIGURE 3. Observed line narrowing of the spectrum of energy barriers for the SP/PBMA sample.

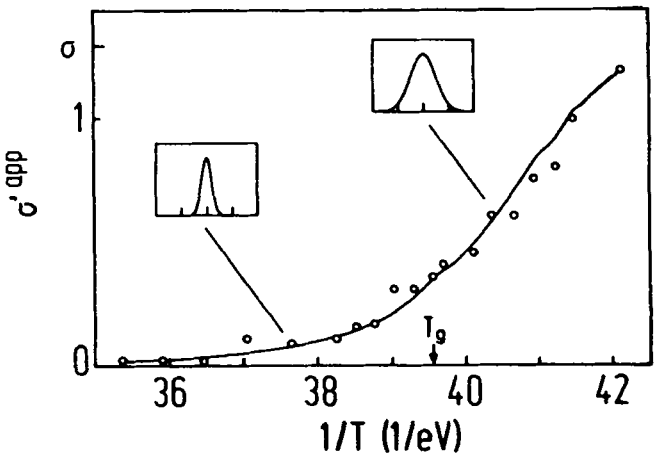

FIGURE 4. Experimental result for σ^{app} versus temperature for the SP/PBMA sample. Insets indicate the corresponding barrier spectra schematically.

temperature independent σ and K(T) which is approximated by an Arrhenius expression for the experimental temperature regime. $\sigma^{app}(T)$ thus translates into K(T) represented by an activation energy of 200kJ/mol. For the PBMA polymer the resulting cage correlation time at T_g=20°C is ≈300s. This indicates that the steric hindrance probed by the isomerization is governed by chain segments rather than side groups which show rotational freedom at T_g in PBMA[5].

The above model implies a stringent test method for its applicability to the experiment on the basis of the follwing notions. Both directions of the reaction considered, the UV driven SP->MC and the thermal SP<-MC transitions, are subject to the same distribution of activation barriers within a static matrix, i.e. at temperatures well below T_g. If the UV irradiation which builds up the [MC] prior to its backreaction is turned off well

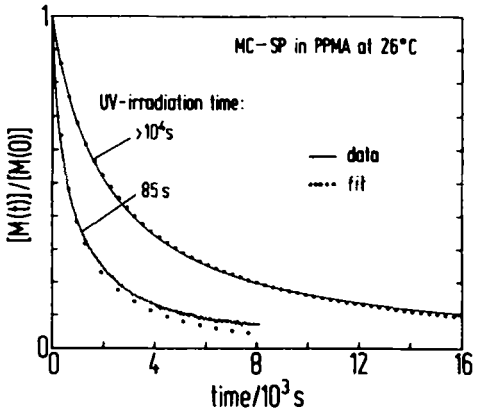

FIGURE 5. Observed decay curves for long and short UV-illumination times and the predicted fits after eqn.(2). The discrepancy of the curves indicate that the probe molecules retain their cage configuration in course of the reaction.

before equilibrium conditions are attained only a selected subset of MC states are formed which are subject to lower barriers relative to the stationary distribution (see fig.1 at reversed time scale). Consequently, this subset of MC

molecules will exhibit a faster MC->SP backreaction but with similar dispersion as does the normal case. The kinetics for different UV illumination times can be calculated on the basis of eqn.(2) and coincides perfectly with the experimental findings as shown in fig.5. At temperatures above T_g where the kinetics are pure exponential no sensitivity to the UV illumination time is found. It can be concluded that these findings for both temperature limits correspond to the cases of 'infinite' and vanishing correlation times for the matrix cage configuration modelled by K=0 and K=∞, respectively.

CONCLUSIONS

It has been shown that motional effects in disordered matrices affect configuration sensitive chemical reactions in a qualitative fashion. The dispersive nature of the decay gradually vanishes if the mean lifetime of site specific matrix cages falls below the mean reaction time. Intro-duction of an activation barrier correlation time to the inhomogeneously dispersed kinetics accounts for the observed effects quantitavely. The thermal course of the correlation time can be calculated from experimental decay data. Therefore, the above approach serves as tool for detecting the temporal stability of molecular arrangements, e.g. in polymers, on the spatial scale of the probe molecule.

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