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Novel Kinetic Model in Amorphous Polymers. Spiropyran–Merocyanine System Revisited

Marcia Levitus,[†] Marcio Talhavini,[‡] R. Martín Negri,[†] Teresa Dib Zambon Atvars,^{*,‡} and Pedro F. Aramendía^{*,†}

INQUIMAE, Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellón 2, Ciudad Universitaria, 1428 Buenos Aires, Argentina, and Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, CEP 13083-970, Campinas, SP, Brazil

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A kinetic model for the description of non-monoexponential decay of unimolecular reactions in amorphous polymers is developed. The thermal decay of the merocyanine (MC) form of 1,3',3'-trimethyl-6-nitrospiro-[2H-1-benzopyran-2,2'-indoline] (spiropyran, SP) in poly(alkyl methacrylates) is taken as an example. The model assumes that the time dependent first-order rate constant describing the decay relaxes from an initial value k_0 to a completely relaxed value k_∞ with a relaxation time τ_m that depends on the matrix. A rate equation similar to the one provided by this model is found in fluorescence quenching either in micelles or in the picosecond range in solution. The fit of the temperature dependent decays of MC to SP with this model is as good as or better than the one obtained by other models such as the sum of exponential terms or the stretched exponential equation. The simple relaxation picture is unable to account for the decay at temperatures far below the glass transition temperature of the polymer. In this range, the average values of rates, represented by k_0 , k_∞ , and τ_m , poorly describe the real distribution of them. The values of k_0 , k_∞ , and τ_m for MC decay show an Arrhenius behavior in the polymers studied.

Introduction

Unimolecular reactions in amorphous polymers very often follow non-monoexponential decay kinetics.^{1–7} The origins of this behavior are the non-homogeneous microenvironment around each reacting molecule and the fact that the rigid polymer matrix relaxes from the nonequilibrium situation or changes configuration in comparable or longer time scales than the decay kinetics.^{1,2} The same phenomenon in solution is the origin of the inhomogeneous broadening or of time dependent fluorescence spectra that are sometimes observed in viscous solvents.⁸ The rigid polymer environment shifts the time scale in which these effects can be observed. The fact that some unimolecular processes which behave non-monoexponentially in amorphous polymers obey first-order kinetics above the polymer glass transition temperature (T_g), when the polymer becomes fluid,¹ supports the previous arguments.

Many kinetic models have been introduced to qualitatively and quantitatively describe the decay of probes in polymers. (i) The simplest model introduces a sum of two or more exponential terms to fit the decay kinetics.⁹

$$P(t) = \sum_{i=1}^n A_i \exp(-k_i t); \quad n \geq 2 \quad (1)$$

where $P(t)$ represents the time dependent probe concentration, and A and k are amplitude factors and first-order rate constants associated with each exponential term. This behavior describes

the existence of two or more different populations of probe. Two typical different locations in this model are the amorphous environment and the boundary between the amorphous and the pseudocrystalline domains.¹⁰ (ii) A dispersive first-order chemical reaction scheme postulates that the probe is located in different environments having a distribution of activation energies that is Gaussian with a dispersion that decreases with increasing temperature.^{4,6,11}

$$P(t) = \frac{P_0}{\sqrt{2\pi}\sigma} \int_{-\infty}^{\infty} \exp\left[-\frac{(\epsilon - \epsilon_0)^2}{2\sigma^2}\right] \exp(-k(\epsilon)t) d\epsilon \quad (2)$$

where P_0 represents the initial excited probe concentration, σ is the width of the activation energy distribution (ϵ), $k(\epsilon) = \nu \exp(-(\epsilon_m - \epsilon)/kT)$ is the energy (site) dependent first-order rate constant, ν is an energy independent frequency factor, and ϵ_0 and ϵ_m are the energies of the center of the distribution and the maximum of the energy barrier, respectively. (iii) A stretched exponential behavior is of the form

$$P(t) = P_0 \exp[-(t/\tau)^\alpha] = P_0 \exp[-(kt)^\alpha] \quad (3)$$

where P_0 represents the initial excited probe concentration, and $0 < \alpha \leq 1$. Equation 3 proved to accurately describe the kinetics in many cases.^{1,3,5} A rate equation of this type can be deduced in different ways,¹² taking into account that many polymer relaxation modes with different characteristic times contribute to prepare the matrix for probe decay,¹³ or that the decay is produced when a defect reaches the probe position and that diffusion of defects is rate limiting.¹⁴

Model i has two adjustable parameters, an amplitude A , and a first-order rate constant k , per exponential term (see eq 1).

* To whom correspondence should be addressed. E-mail: tatvars@iqm.unicamp.br; pfa@q1.fcen.uba.ar.

[†] Universidad de Buenos Aires.

[‡] Universidade Estadual de Campinas.

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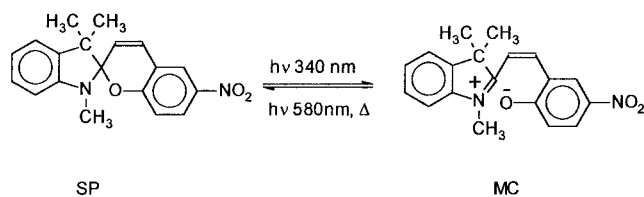


Figure 1. Molecular structure of spiropyran (SP) and merocyanine (MC). For MC only the zwitterionic structure is shown.

This gives a minimum of four adjustable parameters for a non-monoexponential decay. Model ii has a total of three adjustable parameters: the amplitude factor P_0 , the rate constant $k(0)$, and the dispersion of the Gaussian distribution, σ (see eq 2). Model iii, as described by eq 3, also has three adjustable parameters: the total amplitude P_0 , the rate constant k , and α .

Consider a ground-state molecule that is excited by light yielding a product, which can be either an electronically excited state or a metastable ground state, and consider that this product decays to the original state. Three limiting cases can be distinguished by comparing the rate of medium relaxation, measured by an average relaxation time τ_m , and the rate of probe decay, measured by an average time τ_p . If $\tau_m \gg \tau_p$, the molecule decays in a frozen environment, which corresponds to the environment equilibrated previous to light excitation. In this case a great departure from first-order kinetics is expected and the kinetics should be described by^{4,13}

$$P(t) = \int g(w) \exp(-k(w)t) dw \quad (4)$$

where w is some parameter characterizing the distribution function of molecules in the different environments, $g(w)$, which decay with site dependent rate constant $k(w)$. Equation 4 represents a statistical distribution of exponential decays and may greatly resemble a sum of exponential terms, like eq 1.

When τ_m and τ_p are comparable, the probe and polymer relax simultaneously. In this case $g(w,t)$ also depends on time, and a dynamic model is required to describe the kinetics. This is the most complicated situation.

Finally, the limit of a simple first-order decay is reached normally at temperatures above the T_g of the polymer. In this case, $\tau_m \ll \tau_p$ and the medium rapidly equilibrates during the probe decay. The situation is very similar to common fluid solvents: every molecule experiences the same temporal average environment during its lifetime.

The three models have monoexponential behavior as a limit if in model (i) the two or more time constants of the exponential terms tend to a common limit upon temperature increase; in model (ii) the dispersion of the Gaussian distribution tends to zero;⁴ or in model (iii) the exponent α tends to 1 in eq 3.³

Upon UV irradiation spiropyran (SP) isomerizes by ring aperture to a highly polar merocyanine (MC) form, as schematized in Figure 1.¹⁵ MC is a ground-state isomer which thermally decays back to the stable SP form. The great molecular shape and dipole moment changes accompanying isomerization greatly perturb the polymer matrix, which controls the thermal decay kinetics of MC.^{5,9,11,16} The system is adequate to monitor the coupling between polymer matrix relaxation and probe decay, and it was used in this respect previously.⁶

In this paper we introduce a kinetic model which takes into account the simultaneous relaxation of the matrix and the probe in an explicit equation, the assumption being that the matrix relaxation modifies the average first-order rate constant of the probe decay from an initial value k_0 immediately after excitation to a relaxed value k_∞ . The rate of change of the rate constant from k_0 to k_∞ is governed by a matrix mean relaxation time τ_m .

The model is adequate to quantitatively describe the decay kinetics of MC in a series of poly(alkyl methacrylates), both below and above T_g . The advantages and limitations of the model are discussed, and it is compared to other models described in the literature.

Experimental Section

Chemicals. Spiropyran (1,3',3'-trimethyl-6-nitrospiro-[2H-1-benzopyran-2,2'-indoline]) and poly(alkyl methacrylates) (polymethyl (PMMA), polyethyl (PEMA), and polyisobutyl (PIBMA) methacrylate, secondary standard polymers with certificate) were purchased from Aldrich and were used as received. Molecular weight (M_w) and polydispersity (M_w/M_n) were, respectively, 102 600 and 2.1 for PMMA; 340 000 and 2.7 for PEMA, and 340 000 and 2.1 for PIBMA. Chloroform was analytical grade, freshly distilled.

Thermal Analysis. T_g values of the different polymer samples were determined by DSC in a DuPont calorimeter, Model v2.2 A990. The values were 103 °C for PMMA, 61 °C for PEMA, and 51 °C for PIBMA.

Preparation of Polymer Films Containing Spiropyran. Weighted amounts of polymer and spiropyran were dissolved in chloroform. The solution was extended on a glass cuvette window, and the solvent was allowed to evaporate. The sample was further dried overnight in an oven at 60 °C. Samples containing 1/200 to 1/2000 dye to monomer molar ratio were prepared in this way and used for the spectroscopic and kinetic measurements.

Irradiation and Spectroscopic Measurements. All kinetic experiments at fixed monitoring wavelength were carried out on a HP-8452 diode array spectrophotometer provided with Peltier accessory HP-89090A for temperature control. The samples were irradiated using a high-pressure 80 W Hg lamp. The light was filtered by a 2 mm thick UG1 Schott optical filter and collimated into a quartz optic fiber, which was used to irradiate the sample in the spectrophotometer cell holder. More details of this setup are given in ref 17.

Spectra at different times after irradiation were measured on a Shimadzu 3101-PC spectrophotometer at room temperature. In these experiments, polymer films were irradiated in a photolysis apparatus by using a 450 W Xe arc lamp provided with a water filter and a monochromator tuned at 340 nm (20 nm bandwidth). The photon flux at 340 nm, measured using the potassium ferrioxalate actinometer,^{18,19} was 5.6×10^{14} photons $s^{-1} cm^{-2}$.

By using the Xe arc lamp a conversion versus incident dose curve was measured by varying the exposure time from 1 to 300 s. All kinetic experiments were performed at conversions within the linear part of this curve.

Samples were measured either supported on the glass plate where they were extended or detached from it. No difference in spectra or kinetics was observed.

Results and Discussion

Samples irradiated at low doses (see Experimental Section) are completely thermal and photochemically reversible, spectra are at any time proportional to each other in the visible region, and isosbestic points appear in the UV. This means that only one species is formed upon irradiation. On the other hand, when the dose and conversion is increased, spectral deconvolution in the visible region (performed by bilinear regression²⁰) shows the existence of two species which decay with different kinetics. One of these species has a spectrum similar to the species formed at low conversions. Under these conditions, samples are not completely photoreversible; this behavior is shown in

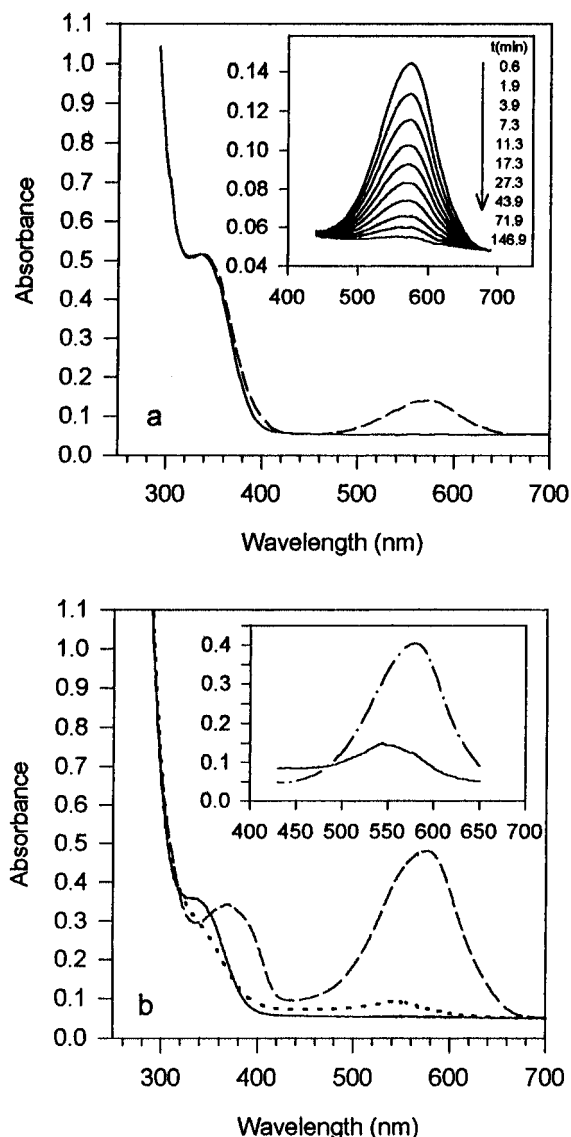


Figure 2. Spectra after irradiation of a SP in PEMA film at 340 nm with a Xe arc lamp: (a) Low conversion: spectra before (solid line) and immediately after (dashed line) 5 s irradiation. The inset shows spectra in the visible at different times, indicated in minutes. Spectra before irradiation and after complete decay coincide. (b) High conversion: spectrum before irradiation (solid line), 30 s after 20 min irradiation (dashed line), and after 18 h decay (dotted line) shown together with the spectra, extrapolated to time zero, of the two components obtained by spectral deconvolution (in the inset). All spectra were taken with air in the reference beam; for this reason the baseline absorbance in the visible is not zero.

Figure 2. The kinetic analysis that follows was performed with data obtained under conditions where only one species is formed upon irradiation, i.e. at low conversions. As spectra are always proportional under these conditions, the absorbance at a fixed wavelength was monitored as a function of time to obtain the kinetic data. Normally the maximum of absorption of MC in the visible was chosen. Experiments were carried out at temperatures between 20 and 80 °C. Decay curves at a constant temperature for the three polymer matrixes are shown in Figure 3.

Kinetic Model. The unimolecular decay of MC, which does not obey first-order kinetics, can be formally described by a rate law:

$$\frac{d[\text{MC}]}{dt} = -k(t)[\text{MC}] \quad (5)$$

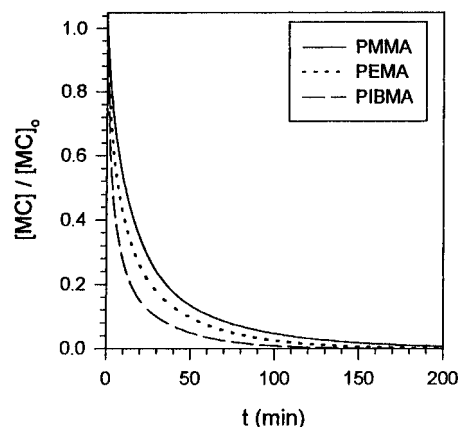


Figure 3. Decay of the absorption at the MC maximum in the visible as a function of time in PMMA, PEMA, and PIBMA at room temperature. Samples were irradiated 10 s at 366 nm with a high-pressure Hg lamp and 2 mm UG1 Schott filter through a quartz fiber optic.

where the first-order decay constant, $k(t)$, is time dependent and is calculated as the derivative of the logarithm of the concentration with respect to time. A decay law of the type of eq 5 leads to the stretched exponential of eq 3 if³

$$k(t) = \alpha k^\alpha t^{(\alpha-1)} \quad (6)$$

When MC is built up, the polymer matrix is initially at the equilibrated conformation of the SP form; afterwards the medium starts to relax to the suitable conformation for MC. If the relaxation takes place with an average time τ_m , we may postulate that the first-order decay rate constant, $k(t)$, changes from its initial value k_0 to its final value k_∞ in the form

$$k(t) = k_\infty + (k_0 - k_\infty) \exp(-t/\tau_m) \quad (7)$$

$k(t)$ monotonously decreases with time as matrix relaxation makes MC more stable; thus $k_0 > k_\infty$ always.

If we replace eq 7 in eq 5 and integrate, taking into account that MC initial concentration is $[\text{MC}]_0$, we obtain for the time dependent $[\text{MC}]$

$$[\text{MC}] = [\text{MC}]_0 \exp\{-k_\infty t - [k_0 - k_\infty]\tau_m[1 - \exp(-t/\tau_m)]\} \quad (8)$$

Equation 8 indicates that after the medium relaxes the second term in the exponential vanishes and the system decays with a rate constant k_∞ . In this model the departure of the matrix from its equilibrium configuration is responsible for the non-monoexponential behavior. Rate equations of the type of eq 8 are also obtained under similar conditions when the decay is not single exponential because of medium departure from equilibrium, as is the case for fluorescent probe quenching in micelles out of quencher diffusion equilibrium²¹ or of fast quenching in solution sometimes considered "static quenching" or for non steady state of quencher diffusion.²²

In eq 8 the three rate parameters, k_0 , k_∞ , and τ_m , must be regarded as average values. It is not a realistic picture to consider that only one matrix movement can be responsible for complete relaxation of the matrix. In this respect, the stretched exponential model, which considers the participation of many relaxation modes with different time constants, is more suitable, but eq 3 fails to assign a value for a relaxation time. Neither does the model represented by eq 1.

A modification of the Gaussian model (ii), represented by eq 2, introduces a constant $K(T)$ to account for the change of

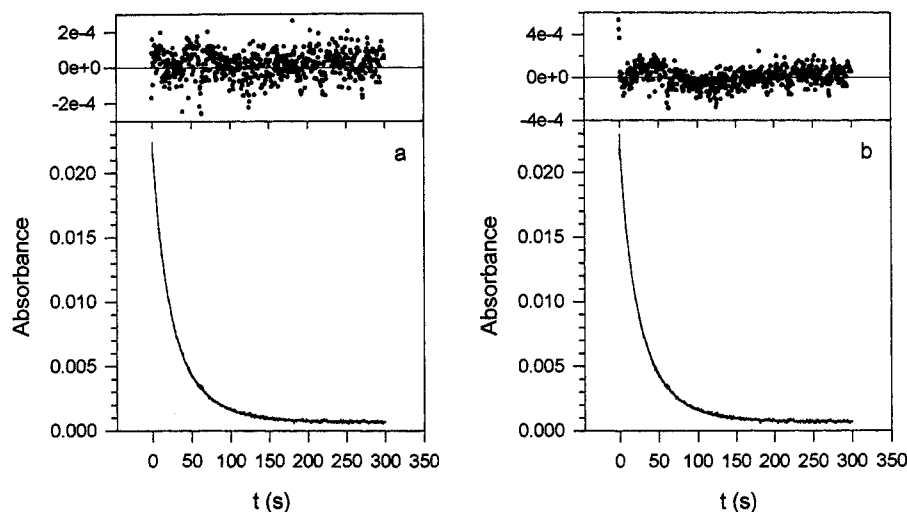


Figure 4. MC decay in PEMA at 64 °C. The actual data, the fitted curve, and the residuals are plotted for (a) the relaxation model of eq 8 and (b) the stretched exponential of eq 3.

the polymer site where the probe is located.⁶ In this way, the model incorporates the dynamics of the matrix during probe decay. The evaluation of $K(T)$ is not straightforward, as it cannot be introduced into an explicit equation and must be computed numerically. Another difference between the model we propose and the Gaussian distribution model is that in the latter the activation energy distribution of the first-order rate constant is invariant in time; the effect that $K(T)$ introduces is an exchange between sites. In our model the activation energy distribution changes from the value of k_0 to that corresponding to k_∞ .

Equation 8 was derived under the conditions that we called dynamic range in the Introduction, i.e. when τ_m and τ_p are comparable. We shall now analyze the ability of the model to describe the probe decay in the other two regimes.

When the medium relaxes very rapidly compared to the decay, k_0 in eq 8 loses its significance and the decay proceeds in a monoexponential way with rate constant k_∞ . It can also be considered that k_0 and k_∞ coincide, as only one first-order rate constant characterizes the decay.

The model fails to account for the non-monoexponential decay when matrix relaxation is much slower than probe decay. This follows from the assumptions made to derive eq 8; as in the case of a frozen environment, the decay should be described by eq 4, which contains a distribution of decaying sites. In the model of eq 8 the distribution is replaced by a single mean value of the time dependent decay rate constant (eq 6), and in this approximation lays the inability of eq 8 to explain the decay in the frozen medium limit. To successfully achieve this, a distribution for k_0 , k_∞ , and τ_m should be considered, but this greatly complicates eq 8, which loses its simplicity (see below). The complex decay will be accurately described by eq 8 as long as the real distributions of decay times of the probe and relaxations times of the matrix can be replaced by a single mean value.

Finally, single relaxation time equations have been used satisfactorily to account for the time dependent fluorescence spectra observed in very viscous solvents.⁸ In this case, the dielectric relaxation of the solvent was considered responsible for the effect, in close relation to our model.

Analysis of Kinetic Data. Data as those in Figure 3 for the three polymer matrixes between 20 and 80 °C were analyzed by fitting them to a sum of exponential terms, to a stretched exponential, and to the relaxation model of eq 8. Under these conditions PMMA is under its T_g , and the range covers temperatures below and above T_g of PEMA and PIBMA.

The sum of exponential terms (eq 1) did not provide good fits in most situations. At temperatures much lower than T_g , the sum of three terms is needed,⁹ and many times even these fail to provide good agreement with experiment. Three terms in eq 1 mean six adjustable parameters to fit the decay; this is too much, and for this reason the model was discarded as a realistic one.

The stretched exponential provided good fits in almost all cases, with the exponent approaching 1 above T_g , where a first-order decay was obtained.

The relaxation model fits the data as good as and generally better than the stretched exponential, as judged by the distribution of residues (χ^2 is very similar for both fits to the same decay). For comparison, an example is shown in Figure 4. The fitted parameters according to both models are summarized in Table 1. The agreement between k_0 of the relaxation model and the rate constant k of the stretched exponential is remarkable. If we take into account the validity of the stretched exponential to adequately describe the decay in many situations, k must be a representative mean value of a decay parameter and so must k_0 . The agreement is not a consequence of the mathematical properties of eqs 3 and 7.

The results of Table 1 show that upon increasing the temperature, τ_m approaches zero and k_0 and k_∞ tend to a common limit, as the decay approaches the first-order behavior.

Arrhenius plots for k_0 , k_∞ , τ_m , and k are presented in Figures 5–7. The corresponding Arrhenius parameters are listed in Table 2. Arrhenius behavior for decay rate constants of the MC form of other spiropyrans was previously reported when the probe was dissolved in the polymer matrix.^{6,9} The values of the Arrhenius activation energy, E_a , for k_∞ are always larger than for k_0 . This is consistent with the fact that MC is more stabilized when the polymer relaxes. When a sum of three exponentials was used to describe the kinetics of a similar MC in PMMA and in PIBMA, E_a values between 90 and 135 kJ/mol were obtained for the two biggest first-order decay constants,^{9a} in agreement with our results. For MC decay in poly(butyl methacrylate), using model ii with a reorganization rate constant $K(T)$, E_a values of 100 kJ/mol were obtained for the frequency factor and 200 kJ/mol for $K(T)$.⁶ As $K(T)$ can be compared to τ_m of the present model, the activation energies are also in agreement.

TABLE 1: Fitting Parameters for the Decay of MC in PMMA, PEMA, and PIBMA at Different Temperatures

PMMA					
<i>T</i> (°C)	relaxation model			stretched exponential	
	<i>k</i> ₀ (s ⁻¹)	<i>k</i> _∞ (s ⁻¹)	τ _m (s)	<i>k</i> (s ⁻¹)	α
40	0.0062	0.0016	168	0.0044	0.59
50	0.0116	0.0022	159	0.0108	0.60
60	0.0309	0.0051	77	0.0294	0.66
70	0.0771	0.032	24	0.0676	0.78
80	0.165	0.070	16	0.149	0.86

PEMA					
<i>T</i> (°C)	relaxation model			stretched exponential	
	<i>k</i> ₀ (s ⁻¹)	<i>k</i> _∞ (s ⁻¹)	τ _m (s)	<i>k</i> (s ⁻¹)	α
40	<i>a</i>			0.00469	0.56
50	<i>a</i>			0.0112	0.72
60	0.0309	0.0066	135	0.0287	0.84
64	0.0456	0.0243	35	0.0404	0.84
65	0.0465	0.0186	57	0.0430	0.84
68	0.0669	0.0405	25	0.0607	0.87
70	0.0905	0.0705	15	0.0847	0.93
70	0.0816	0.0550	34	0.0777	0.93
80	0.223	0.191	2	0.203	0.96

PIBMA					
<i>T</i> (°C)	relaxation model			stretched exponential	
	<i>k</i> ₀ (s ⁻¹)	<i>k</i> _∞ (s ⁻¹)	τ _m (s)	<i>k</i> (s ⁻¹)	α
50	0.0268	0.0074	52	0.0219	0.65
53	0.0321	0.0075	58	0.0288	0.66
55	0.0394	0.0118	43	0.0345	0.69
57	0.0425	0.0124	48	0.0378	0.73
60	0.0588	0.0274	40	0.0539	0.84
70	0.166	0.101	21	0.158	0.92
70	0.171	0.102	17	0.161	0.91
80	0.452	0.386	2	0.424	0.96

^a The fit was not adequate.

The values of *k*₀, *k*_∞, τ_m, and *k* in PIBMA were fitted to a free volume equation of the type²³

$$\log(a(T)/a(T_0)) = \frac{-C_1(T - T_0)}{C_2 + (T - T_0)} \quad (9)$$

In eq 9 *a*(*T*) represents any of the rate constants or relaxation times, and *C*₁, *C*₂, and *T*₀ are adjustable parameters, dependent on the polymer. The fitted values of *C*₁ and *C*₂ were far from the expected values in this polymer;^{23,24} particularly for *C*₂ a negative value was obtained. No attempt was made either for the data in PMMA, as they are all under *T*_g, or for the data in PEMA, as very few data are available under *T*_g (see Table 1).

The weakest point of eq 8 is that it does not take explicitly into account the heterogeneity in the distribution of reaction sites, which is characteristic of polymeric systems.^{1,4} We will consider the incorporation of relaxation into the Gaussian model. This implies at least the addition of two new parameters to the model, which are a relaxation time and an amplitude of variation of the magnitude that relaxes with time. As a consequence, the static Gaussian model of eq 2⁴ would have five adjustable parameters and the Gaussian model with fluctuations⁶ would have six. For this reason, we decided to extend the model of eq 2. The Appendix includes the assumptions made and the derivation of the resulting eq 10, which is identical to eq A5:

$$\frac{[MC]}{[MC]_0} = \frac{1}{\sqrt{2\pi s}} \int_{-\infty}^{\infty} \exp\left(-\frac{x^2}{2s^2}\right) \times \exp\left[-k_0 e^x \int_0^{\infty} \exp\left[-\frac{\Delta\epsilon}{kT}(1 - e^{-t/\tau_m})\right] dt\right] dx \quad (10)$$

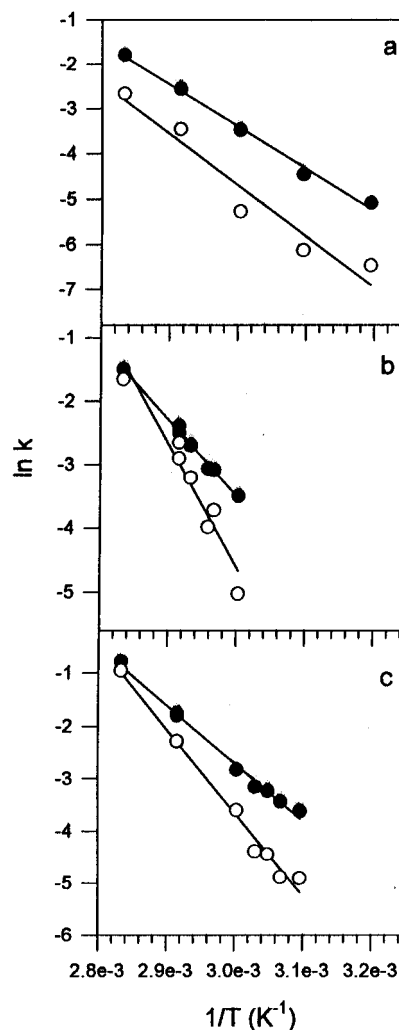


Figure 5. Arrhenius plot for *k*₀ (filled circles) and *k*_∞ (hollow circles) as fitted according to eq 8 of the text in (a) PMMA, (b) PEMA, and (c) PIBMA.

There are five fitting parameters in eq 10, namely, [MC]₀, *s*, *k*₀ (the three usual parameters of the static Gaussian model of Richert⁴), Δε, and τ_m (the two parameters associated with the variation of the site energy with time). There are too many fitting parameters in this model for most of our data, and for this reason the fits do not give meaningful parameters. For the lowest temperatures, where all other models fail, eq 10 gives the best results. In PIBMA at 30 °C the fit to eq 10 has practically the same nonrandom residual distribution as the fit to eq 2 but with half the mean deviation. In PEMA at 40 °C the fit to eq 10 has a random distribution of residuals and half the deviation as the fit to eq 2. The improvement of the fit obtained through the use of eq 10 does not compensate its greater complexity as compared to eqs 2 or 8. Measurements at lower temperatures are not feasible because the spectrophotometer cannot assure the long-term stability required by the data to test the equations.

Finally in Figure 8 we compare the time derivative of the ln([MC]/[MC]₀) obtained by the fit of a representative decay curve by eq 8 and eq 2. The fact that both coincide during most of the decay (>90%) confirms the ability of eq 8 to adequately describe the mean value of the first-order decay constant at all times.

Conclusions

The model developed in this work quantitatively describes the decay of MC in amorphous polymers. It is based on

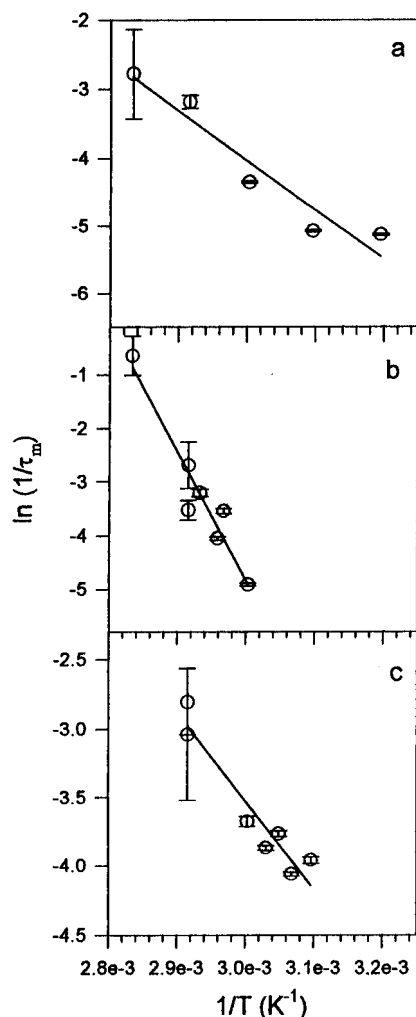


Figure 6. Arrhenius plot of τ_m , as fitted according to eq 8 of the text for (a) PMMA, (b) PEMA, and (c) PIBMA.

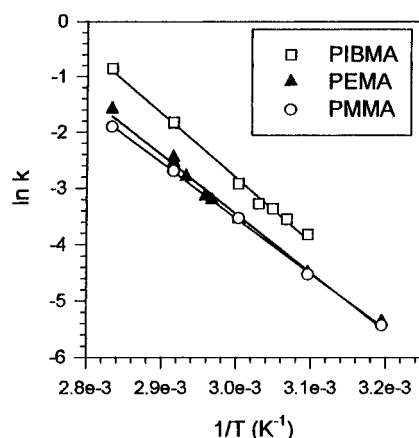


Figure 7. Arrhenius plot of k as fitted according to eq 3.

considering that a time dependent average first-order rate constant characterizes the decay kinetics. The rate of change of the first-order decay constant is governed by a relaxation of the polymer, represented also by an average relaxation time. Compared to established decay laws the fit to experimental data is as good or better. The assumptions of the model render it inadequate to describe the kinetics in frozen environments as average values of rate constants poorly describe the real distribution of this parameter in this case. Unlike the other models in the literature, the one developed here provides a value for the relevant relaxation time of the matrix. Equation 8 has an additional advantage because the time dependent first-

TABLE 2: Arrhenius Parameters for the Rate Constants for k_0 , k_∞ , $1/\tau_m$, and k Derived from Figures 5–7

	k_0	k_∞	$1/\tau_m$	k
PMMA				
E_a (kJ/mol)	78 ± 4	94 ± 14	60 ± 10	82 ± 1
\log (A s)	10.69 ± 0.56	12.7 ± 2.2	7.7 ± 1.6	11.29 ± 0.17
PEMA				
E_a (kJ/mol)	99 ± 3	160 ± 18	197 ± 26	87 ± 3
\log (A s)	14.02 ± 0.52	23.2 ± 2.8	28.8 ± 4.0	11.98 ± 0.43
PIBMA				
E_a (kJ/mol)	92 ± 3	133 ± 6	54 ± 8	95 ± 3
\log (A s)	13.17 ± 0.48	19.2 ± 0.9	6.88 ± 1.2	13.72 ± 0.39

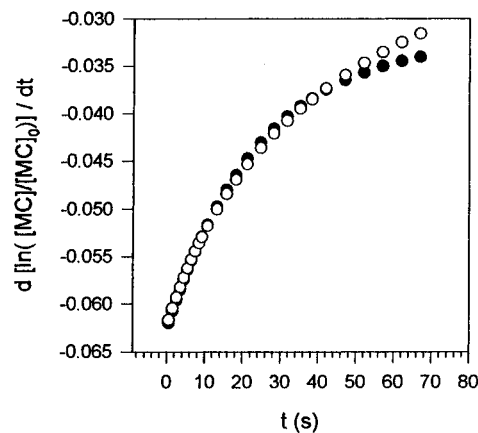


Figure 8. Plot of the average first-order decay rate constant (as measured by the derivative $d \ln([MC]/[MC]_0)/dt$) as a function of time for the decay of MC in PIBMA at 60 °C obtained from the fit to eq 8 (filled circles, see fitting parameters in Table 1) and to the Gaussian distribution model of eq 2 (hollow circles, fitting parameters: $k(\epsilon_0) = 0.0538 \text{ s}^{-1}$; $\sigma/kT = 0.54$). The interval plotted includes 95% of the decay.

order rate constant of the relaxation model does not diverge at time zero (see eq 7), as eq 6 predicts for the relaxation model of eq 3.

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Appendix

Following Richert in ref 4, we assume an initially Gaussian distribution of energies, and we assume further that the energy of a site, $\epsilon(t)$, depends on time as

$$\epsilon(t) = \epsilon_i - \Delta\epsilon[1 - \exp(-t/\tau_m)] \quad (\text{A1})$$

where ϵ_i is the values of the site energy at time zero, $\Delta\epsilon = \epsilon_i - \epsilon_f$ is the energy difference of each site between time zero and infinite, and τ_m is the relaxation time. We assume that $\Delta\epsilon$ and τ_m are the same for all sites.

Accordingly, the rate constant depends on energy and time as

$$k[\epsilon(t)] = \nu \exp[-(\epsilon_m - \epsilon(t))/kT] \\ = \nu \exp[-(\epsilon_m - \epsilon_i)/kT] \exp\left[\frac{\Delta\epsilon}{kT}(1 - e^{-t/\tau_m})\right] \quad (\text{A2})$$

where ϵ_m is the energy of the top of the barrier and ν is a frequency factor independent of ϵ .

The fraction of molecules, with ϵ_i , that are left at time t , $p(\epsilon_i, t)$ is

$$p(\epsilon_i, t) = \exp\left[-\int_0^t k[\epsilon(t)] dt\right] \\ = \exp\left[-\nu \exp\left(-\frac{\epsilon_m - \epsilon_i}{kT}\right) \int_0^t \exp\left[-\frac{\Delta\epsilon}{kT}(1 - e^{-t/\tau_m})\right] dt\right] \quad (\text{A3})$$

where the last expression is obtained taking into account eq A2. The total probability of survival is obtained summing over the initial energy distribution.

$$n(\epsilon, 0) = \frac{1}{\sqrt{2\pi}\sigma} \exp[-(\epsilon_0 - \epsilon)^2/2\sigma^2] \quad (\text{A4})$$

This gives for [MC] the result

$$\frac{[\text{MC}]}{[\text{MC}]_0} = \frac{1}{\sqrt{2\pi}s} \int_{-\infty}^{\infty} \exp\left(-\frac{x^2}{2s^2}\right) \times \\ \exp\left[-k_0 e^x \int_0^t \exp\left[-\frac{\Delta\epsilon}{kT}(1 - e^{-t/\tau_m})\right] dt\right] dx \quad (\text{A5})$$

where

$$x = -\frac{(\epsilon_0 - \epsilon_i)}{kT} \quad s = \sigma/kT \quad (\text{A6})$$

$$k_0 = \nu \exp\left(-\frac{\epsilon_m - \epsilon_0}{kT}\right) \quad (\text{A7})$$

and ϵ_0 is the center of the initial Gaussian distribution.

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