

# Diffusion of Probe Molecules in Polymer Gels as Observed by Fluorescence Quenching Techniques

A. V. Barzykin and M. Tachiya\*

National Institute of Advanced Industrial Science and Technology (AIST), Higashi 1-1-1, Tsukuba, Ibaraki 305-8565, Japan

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Material transport and diffusion-controlled reaction kinetics in polymer gels are discussed on the basis of a phenomenological model. The model assumes that molecules diffuse freely within pores, while their long-range transport is described as pore hopping or diffusion in an effective medium with a low diffusion coefficient. Recent experiments by Masuda et al. (*J. Am. Chem. Soc.* **2001**, *123*, 11468–11471) on fluorescence quenching in aqueous solutions of hyaluronan are analyzed on the basis of the present theory. It follows that the conventional mesh size of the polymer network may only poorly characterize obstruction to diffusion. New experiments are suggested to clarify this point.

## Introduction

Material transport characteristics of inhomogeneous fluids, such as polymer gels, should generally depend on the experimental observation time, i.e., on the average distance of diffusion. This has recently been demonstrated most clearly by Masuda et al.<sup>1</sup> in their study of diffusion in aqueous solutions of hyaluronan (HA) by applying two different techniques, pulsed-field-gradient NMR (PFG-NMR) and photochemical quenching, using the same set of probe molecules, Ru(bpy)<sub>3</sub><sup>2+</sup> and cytochrome *c* (Cyt<sub>c</sub>).

HA is a high molecular weight linear biopolysaccharide which occurs in many living substrates.<sup>2</sup> Its hydrodynamic behavior is quite unique. Even at fairly low concentrations, aqueous solutions of HA show extremely high macroscopic viscosity as a result of a transient network formation by HA chains. The mesh size  $\xi$  of the network, defined as the average distance between the entanglement points in the “blob” model of de Gennes,<sup>3</sup> is about 15 nm. Many experiments by different techniques agree on this value.<sup>4–7</sup> The mobility of small molecules, such as urea, sugars, and proteins, with their size being less than  $\xi$ , is still relatively fast in HA solutions. This is the key element for the biological functionality of HA.

In PFG-NMR experiments by Masuda et al., the observation time scale is in the ms range and thus the diffusion distance is several tens of  $\mu\text{m}$  ( $\gg \xi$ ). Almost no effect of HA was found on the diffusion of water molecules of 0.3 nm diameter, and Ru(bpy)<sub>3</sub><sup>2+</sup> with a diameter of 1.0 nm was only slightly retarded. On the other hand, the diffusion coefficient  $D$  of Cyt<sub>c</sub> with a diameter  $d$  of 3.4 nm was found to decrease rapidly with increasing HA concentration,  $c$ , according to the empirical law:  $-\ln D/D_0 \sim d c^{0.5}$ , where  $D_0$  is the diffusion coefficient in the absence of HA. This finding is consistent with the results obtained by other techniques, such as sedimentation<sup>8</sup> and fluorescence recovery after photobleaching.<sup>5</sup> Theory explains this peculiar change of  $D$  with polymer concentration as a hydrodynamic screening effect,<sup>9,10</sup> although many different models exist.<sup>3,11</sup>

Diffusion-controlled fluorescence quenching of Ru(bpy)<sub>3</sub><sup>2+</sup> by Cyt<sub>c</sub> can be monitored on the time scale of about 300 ns,

the lifetime of the excited Ru(bpy)<sub>3</sub><sup>2+</sup>. This method allows one to probe diffusion on the distance scale of about 15–30 nm.<sup>1,7</sup> Since this is comparable to (and even somewhat larger than) the estimated average mesh size  $\xi$ , one would expect to see certain effect of obstruction on the quenching kinetics. However, the observed fluorescence decay curves were single exponential with an ordinary Stern–Volmer dependence on quencher concentration, as in homogeneous solutions.<sup>1</sup> The quenching rate constant, and thus the mutual diffusion coefficient of Ru(bpy)<sub>3</sub><sup>2+</sup> and Cyt<sub>c</sub>, was found to be independent of the HA concentration and quite consistent with the diffusion-controlled rate constant estimated for an aqueous solution without HA. There is no apparent interference of diffusing molecules with the mesh on the scale of  $\xi$ . Then, what is the relevant length scale? In this paper, we consider this point on the basis of a phenomenological approach. We discuss two models for diffusion-controlled reactions in nonhomogeneous systems: continuous time random walk (CTRW) and effective medium approximation (EMA). Although neglecting structural peculiarities, these models take into account the most important effect of distance-dependent mobility of reactants. This approach could be a useful starting point in analyzing fluorescence quenching experiments in any nonhomogeneous environments. But since our original interest in this problem was motivated by the work on HA solutions, we will limit our presentation to that context.

## Phenomenological Models

**A. Continuous Time Random Walk.** The movement of a probe through the network can be viewed as a process which involves an activation energy. One can think of different contributions to the energy barrier. Penetration through a narrow hole/channel in a rigid network involves an entropic barrier. On the other hand, the activation energy may be determined by the elastic free energy that is coupled with the expansion of the mesh when the probe passes through it.<sup>3</sup> The overall motion can thus be described as pore hopping. We define the hopping rate constant,  $k_e$ , in such a way that

$$D_e = \frac{1}{6} k_e L^2 \quad (1)$$

where  $L^2$  is the mean-squared displacement and  $D_e$  is the long-time diffusion coefficient, which is supposed to be measured by the PFG-NMR method. We also define an effective pore radius,  $R$ , in such a way that the pore volume,  $V = (4/3)\pi R^3$ , equals  $L^3$ . Note that  $R$  is not necessarily equal to  $\xi$ .

Kinetics of bimolecular quenching reaction in a confined system is approximately described by a single exponential with a rate constant given by (see eq 11.53 in ref 12)

$$k_0 \approx 3D_0 a/R^3 \quad (2)$$

where  $a$  is the sum of the radii of the reactants and  $D_0$  is the diffusion coefficient in a pore. Rigorously speaking, both reactants are moving but instead we will assume that the excited probe is immobile (the so-called target problem). It is well-known that this assumption does not introduce a serious error,<sup>13</sup> particularly at low quencher concentrations,  $c_q$ . We only need to consider  $D_e$  and  $D_0$  as the corresponding mutual diffusion coefficients (the sum of individual diffusion coefficients). Finally, we neglect self-deactivation of the excited state (it can always be factored back in) and we also neglect any other interactions for simplicity.

The CTRW approach gives solution to the above problem<sup>14</sup> for the excited-state survival probability,  $P(t)$ ,

$$\ln P(t) = -\bar{n} \int_0^t d\tau k(\tau), \quad (3)$$

where  $\bar{n} = c_q V$  is the average number of quenchers per pore,  $k(t)$  is the time-dependent rate coefficient, and its Laplace transform is given by

$$\hat{k}(s) = \frac{1}{s} \left[ \frac{1}{k_0} + \frac{1}{s + k_e} G\left(0, \frac{k_e}{s + k_e}\right) \right]^{-1} \quad (4)$$

Here  $G(0, x)$  is the generating function for the occupancy of the starting site. Methods for calculating this function are known.<sup>15</sup> We can see that at short times the kinetics is exponential with the rate constant  $k_0$ , while at long times it is again exponential but with

$$k_\infty = \frac{k_e k_0}{k_e + k_0 G(0, 1)} \quad (5)$$

$G(0, 1)$  is a lattice-specific constant close to unity, e.g., 1.516 for a simple cubic lattice, 1.3932 for a body-centered cubic (bcc) lattice, etc.

**B. Effective Medium Approximation.** *1. The Model.* It is hard to imagine that a polymer gel would form a regular network. To circumvent the complexity of dealing with an irregular structure, we use an effective medium approximation. We place an excited probe at the center of a sphere of radius  $R$  and allow the quenchers to diffuse with different diffusion coefficients inside,  $D_0$ , and outside,  $D_e$ , the sphere. The external diffusion coefficient is related to the permeability of the interface. Reaction occurs irreversibly at encounter,  $r = a$ . Formally, the number density  $\rho_i(r, t)$  of quenchers inside ( $i = 0$ ) and outside ( $i = e$ ) the sphere obeys the diffusion equation,<sup>16</sup>

$$\frac{\partial}{\partial t} \rho_i = D_i \nabla^2 \rho_i, \quad (6)$$

with the initial condition

$$\rho_i(r, 0) = 1 \quad (7)$$

and the boundary conditions,

$$\rho_0(a, t) = 0, \quad (8)$$

$$\rho_e(\infty, t) = 1 \quad (9)$$

$$-D_0 \frac{\partial}{\partial r} \rho_0(r, t)|_{r=R} = -D_e \frac{\partial}{\partial r} \rho_e(r, t)|_{r=R} = \kappa (\rho_0 - \rho_e) \quad (10)$$

where  $\kappa$  is the permeability of the interface.

The permeability can generally be identified with a certain potential barrier. In the limit of small barrier width,  $\delta$ , one can define permeability as

$$\kappa = \frac{D}{\delta} \exp(-u^*) \quad (11)$$

where  $u^*$  is the barrier height in units of  $k_B T$ . The nature of the barrier, potential or entropic, is of no significant consequence. What is important is that it offers transport resistance, quantified in terms of  $\kappa$ .

Before we relate  $D_e$  and  $\kappa$  let us analyze the solution of the above posed problem. Our goal is to calculate the time-dependent second-order rate coefficient defined by

$$K(t) = 4\pi a^2 D_0 \frac{\partial}{\partial r} \rho_0|_{r=a} \quad (12)$$

We obtain

$$\frac{K(t)}{K_0} = 1 + \mathcal{L}^{-1}[a(sD_0)^{-1/2} f(s)] \quad (13)$$

where  $K_0 = 4\pi D_0 a$  is the Smoluchowski rate constant,  $\mathcal{L}^{-1}$  denotes the inverse Laplace transform, and  $f(s)$  is given by

$$f(s) = \frac{\alpha_1 q \sinh[q(1 - a/R)] - \alpha_2 \cosh[q(1 - a/R)]}{\alpha_1 q \cosh[q(1 - a/R)] - \alpha_2 \sinh[q(1 - a/R)]} \quad (14)$$

with  $q = (s R^2/D_0)^{1/2}$ ,  $\alpha_1 = 1 + \gamma q + \gamma^2 \tilde{\kappa}$ ,  $\alpha_2 = \alpha_1 - \tilde{\kappa}(1 + \gamma q)$ ,  $\tilde{\kappa} = \kappa R/D_0$ , and  $\gamma = (D_0/D_e)^{1/2}$ . At short times ( $s \rightarrow \infty$ ), one can see that  $f(s) \rightarrow 1$  and the usual Smoluchowski kinetics is recovered,

$$\frac{K(t)}{K_0} = 1 + (\pi D t/a^2)^{-1/2} \quad (15)$$

As expected, there is no effect of the interface. In the limit of  $t \rightarrow \infty$  ( $s \rightarrow 0$ ),  $K(t)$  tends to a constant,  $K_\infty$ , given by

$$\frac{K_0}{K_\infty} = 1 + \frac{a}{R} \frac{1 + \tilde{\kappa}(\gamma^2 - 1)}{\tilde{\kappa}} \quad (16)$$

The survival probability  $P(t)$  is obtained as

$$\ln P(t) = -c_q \int_0^t d\tau K(\tau) \quad (17)$$

By comparing eqs 3 and 17 and noting the relation  $\bar{n} = c_q V$  one can see that the first-order rate constant  $k(t)$  is related to the second-order rate constant  $K(t)$  through

$$k(t) = K(t)/V \quad (18)$$

*2. Relationship between  $D_e$  and  $\kappa$ .* To relate the effective diffusion coefficient and the interface permeability, we consider the following auxiliary problem. Let a point particle diffuse

along  $x$ . Diffusion is free, except that permeability barriers are put at  $x_n = L(n - 1/2)$ . Between the barriers ( $x_n \leq x \leq x_{n+1}$ ), the probability density,  $\rho_n(x)$ , obeys the diffusion equation

$$\frac{\partial}{\partial t} \rho_n(x, t) = D_0 \frac{\partial^2}{\partial x^2} \rho_n(x, t) \quad (19)$$

while at the barriers we have the boundary conditions

$$-D_0 \frac{\partial}{\partial x} \rho_n(x, t)|_{x=x_n+1} = -D_0 \frac{\partial}{\partial x} \rho_{n+1}(x, t)|_{x=x_n+1} = \kappa (\rho_n - \rho_{n+1}) \quad (20)$$

Our goal is to calculate the bulk effective diffusion coefficient,  $D_e$ , which can be defined in terms of the characteristic function (Fourier transform,  $C(q, t)$ ) of the diffusion propagator,<sup>17</sup>

$$D_e = - \lim_{t \rightarrow \infty} \frac{\ln C(q, t)}{q^2 t} \quad (21)$$

where  $q$  is the wavevector.

In a standard way using the Bloch–Floquet theorem, we search the solution in the form

$$\rho(x, t) = u(q, x) e^{iqx - \lambda t} \quad (22)$$

where  $u(q, x)$  is a periodic function in  $x$ ,  $u(q, x + L) = u(q, x)$ . Since we require the solution to be bounded for  $x \rightarrow \pm\infty$ ,  $q$  must be real. The  $q$  values can be restricted to the first Brillouin zone,  $-\pi/L \leq q \leq \pi/L$ . The diffusion equation and the boundary conditions are satisfied by the following eigenfunctions,

$$u(q, x) = A \left( \sin \left[ (q + p) \frac{L}{2} \right] e^{-i(q-p)x} + \sin \left[ (q - p) \frac{L}{2} \right] e^{-i(q+p)x} \right) \quad (23)$$

where  $p^2 = \lambda/D_0$  and the equation for the eigenvalues reads

$$\cos qL = \cos pL - \frac{pD_0}{2\kappa} \sin pL \quad (24)$$

At long times, we are interested only in the  $q \rightarrow 0$  limit of the above equation, i.e.,

$$\lambda = \frac{D_0 \kappa L}{D_0 + \kappa L} q^2 \quad (25)$$

Therefore, the effective long-time diffusion coefficient is given by

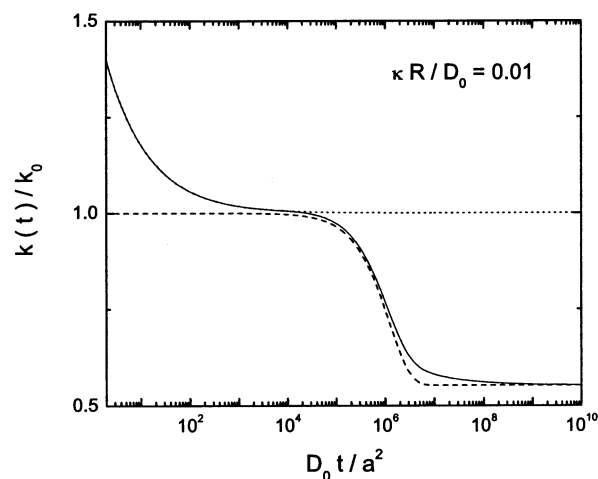
$$\frac{1}{D_e} = \frac{1}{D_0} + \frac{1}{\kappa L} \quad (26)$$

This result is physically quite reasonable.

In principle, one can determine the full spectrum of the problem and define the time-dependent diffusion coefficient. However, this leads to a rather cumbersome expression even in the simplest case just considered. Instead, we combine the obtained relationship between  $D_e$  and  $\kappa$  with the EMA. If we substitute  $\gamma^2 = 1 + D_0/(\kappa L)$  into eq 16 we obtain

$$\frac{1}{K_\infty} = \frac{1}{K_0} + \frac{1 + R/L}{4\pi R^2 \kappa} \quad (27)$$

Here  $4\pi R^2 \kappa$  gives the flux of quenchers through the interface. Recall that the effective sphere radius was defined in such a



**Figure 1.** Normalized time-dependent rate coefficient of the pseudo-first-order excited-state quenching within the EMA model for  $a/R = 0.005$  and  $\kappa R/D_0 = 0.01$ . Solid line corresponds to eq 13, dashed line is described by eq 30, and dotted line shows the usual Smoluchowski kinetics (without any obstruction). The excitation self-decay is not included.

way that  $V = (4/3)\pi R^3 = L^3$ , i.e.,  $R \approx L$ . When the interface permeability is sufficiently low, one can define the first-order rate constant for exit,  $k_e$ , to characterize the initial stage described by the single-exponential decay in the population of quenchers inside the sphere, in the absence of reaction,<sup>16</sup>

$$k_e = \frac{4\pi D_0 R}{V} \left( \frac{1}{5} + \gamma^2 + \frac{D_0}{\kappa R} \right)^{-1} \approx \frac{4\pi R^2 \kappa}{V} (1 + R/L)^{-1} \quad (28)$$

Therefore, we can rewrite eq 27 as follows:

$$\frac{1}{k_\infty} = \frac{1}{k_0} + \frac{1}{k_e} \quad (29)$$

where we have used the relation between the first-order and the second-order rate constants,  $k_0 = K_0/V$  and  $k_\infty = K_\infty/V$ . Basically, this is equivalent to eq 5 with  $G(0, 1) = 1$ , implying that the EMA corresponds to a lattice with an infinite coordination number. In the CTRW model,  $G(0, 1)$  reflects the memory of the lattice structure. In the EMA, there is no memory as there is no structure.

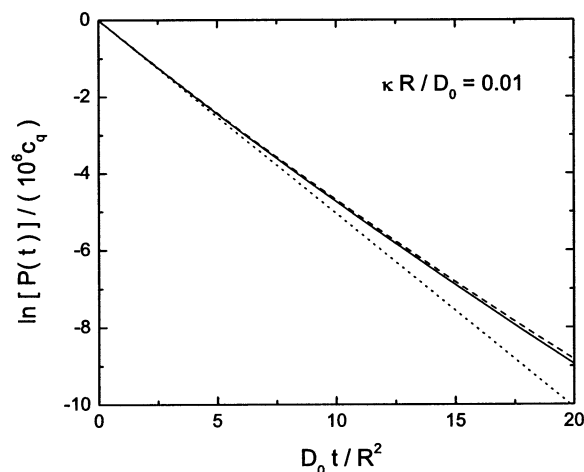
**3. Simplified Micelle-like Model.** It has been shown<sup>16</sup> that for sufficiently low permeability, the EMA is basically equivalent to the well-known stochastic model for luminescence quenching in micelles accompanied by the interphase exchange of quenchers.<sup>12,18,19</sup> Within this model, the survival probability is again given by eq 3 but with the rate coefficient

$$k(t) = \frac{k_e k_0}{k_e + k_0} \left( 1 + \frac{k_0}{k_e} \exp[-(k_e + k_0)t] \right) \quad (30)$$

This approach may be more appealing because it is much simpler while the basic physics is retained. The initial stage of the kinetics is described by  $k_0$ , while at long times we are led to  $k_\infty = k_e k_0/(k_e + k_0)$ , i.e., eq 29.

## Numerical Results and Discussion

First of all, let us compare eqs 13 and 30. Figure 1 demonstrates that they are in reasonable agreement, except at short times where nonstationary stage of the Smoluchowski kinetics is pronounced. One should note, however, that it is not the time-dependent rate coefficient but the survival probability



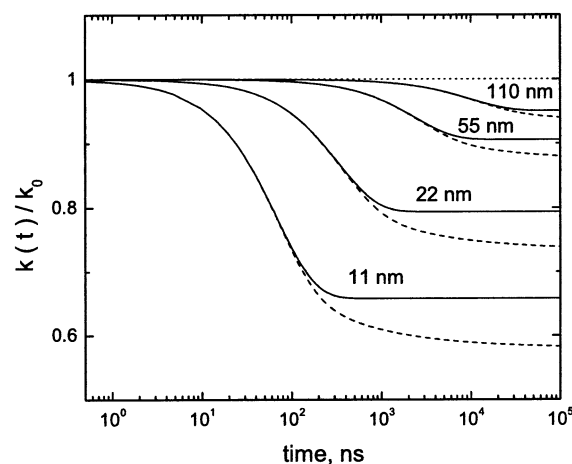
**Figure 2.** Decay of the excited-state survival probability in the presence of quenchers within the EMA model. Parameters and line types are the same as in Figure 1.

that is measured experimentally. A much better agreement is seen in Figure 2 where  $P(t)$  is depicted. Moreover, the Smoluchowski boundary condition for reaction at contact is rather artificial and placing the excited probe at the center of the sphere is rather idealistic. By modifying any of these conditions the initial stage of the kinetics is considerably changed. In other words, it is sufficient, at the level of the EMA model, to describe the quenching kinetics inside the sphere by the time-independent rate constant  $k_0$  and the whole kinetics by  $k(t)$  given by eq 30.

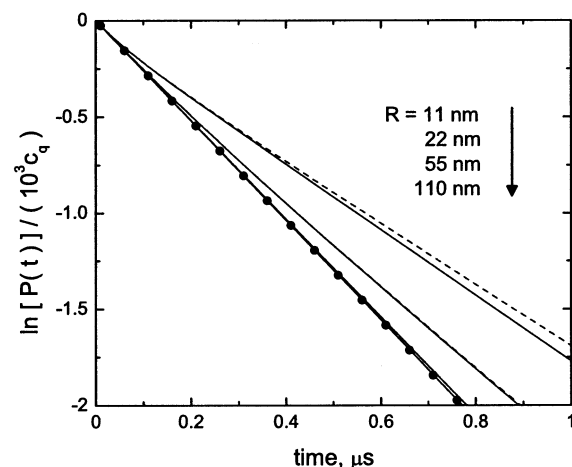
Let us now compare EMA versus CTRW for a set of parameter values corresponding to a real HA solution.<sup>1</sup> Our goal is also to estimate the effective pore radius for which single-exponential diffusion-controlled kinetics determined by  $D_0$  (in other words,  $k_0$ ) is observed within the time window of the fluorescence quenching experiment. Thus we take  $a = 2.2$  nm,  $D_0 = 2D_e = 10^{-9}$  m<sup>2</sup> s<sup>-1</sup>, and vary  $R$ . The results are shown in Figures 3 and 4, both for the time-dependent rate coefficient and for the decay kinetics. For CTRW the bcc lattice is assumed, since it gives the simplest generating function in 3D,<sup>15</sup>

$$G(0, x) = \frac{4}{\pi^2} K^2\left(\frac{1}{2} - \frac{1}{2}\sqrt{1-x^2}\right) \quad (31)$$

where  $K(z)$  denotes the elliptic integral. Numerical Laplace inversion was performed by using the Stehfest algorithm. It is possible that only the initial exponential stage of the kinetics is observed in the time window described above, but only provided that  $R$  is considerably larger than  $\xi$ . Otherwise, a crossover is observed from the short- to the long-time behavior. In the case of CTRW, this conclusion holds for any type of lattice, as it was checked for all periodic 3D lattices where  $G(0, x)$  is available analytically (results not shown). As shown in Figure 3, crossover to the long-time behavior is faster in the EMA model because effectively it corresponds to a lattice with an infinite coordination number. For the same reason, the EMA predicts a larger value for the long-time rate constant,  $k_\infty$ . The maximum difference between the two models is in the factor of  $G(0, 1)$  for  $k_\infty$ , as can be verified by comparing eqs 5 and 29 in the limit of  $k_0 \gg k_e$ .  $G(0, 1)$  plays a role of a structure factor. For a diamond lattice with the coordination number of 4, the lowest in 3D,  $G_d(0, 1) \approx 1.79$ , while for a highly interconnected face-centered cubic lattice with the coordination number of 12,  $G_{fcc}(0, 1) \approx 1.34$ . One may safely expect that an apparent structure factor corresponding to a real irregular system would



**Figure 3.** Normalized time-dependent rate coefficient of the pseudo-first-order excited-state quenching in a polymer gel in the pore hopping model for different effective pore radii:  $R = 11, 22, 55$ , and  $110$  nm. The sum of diffusion coefficients of probe and quencher without a polymer gel is  $D_0 = 10^{-9}$  m<sup>2</sup> s<sup>-1</sup>, the contact distance is  $a = 2.2$  nm. The sum of the long-time diffusion coefficients in a polymer solution is  $D_e = 0.5D_0$ . Dashed lines correspond to the CTRW calculation for a bcc lattice (i.e., eqs 4 and 31). Solid lines were calculated using the effective medium model (i.e., eq 30). Dotted line shows the rate constant in the absence of a polymer,  $k_0$ . The excitation self-decay is not included.



**Figure 4.** Decay of the excited-state survival probability in the presence of quenchers in a pore-hopping model for different effective pore radii:  $R = 11, 22, 55$ , and  $110$  nm. Parameters are the same as in Figure 3. Dashed lines correspond to the CTRW calculation for a bcc lattice (i.e., eqs 3, 4, and 31). Solid lines were calculated using the effective medium model (i.e., eqs 17 and 30). They are indistinguishable for  $R = 55$  and  $110$  nm. Circles show the decay in the absence of a polymer,  $\ln P(t) = -c_q K_0 t$ . The excitation self-decay is not included.

be somewhere between these two values. On the other hand, the EMA model assumes  $G(0, 1) = 1$ . Figure 4 shows that this kind of difference between the EMA and the CTRW is hardly detectable experimentally.

One may speculate that the polymer network is more of sponge-like structure with a high connectivity between the pores (at least on the length scale probed by the fluorescence quenching experiment). Then, even if there is obstruction, it plays no significant role because the diffusion-controlled reaction kinetics is not sensitive to effective dimensionality of the diffusion space when this effective dimensionality is higher than 2.<sup>20</sup> Experimental example from a somewhat different field is triplet-state diffusional deactivation in bicontinuous phases of nonionic and ionic water-oil-amphiphile systems.<sup>21</sup> The observed quenching decays showed no detectable deviation from



the usual Smoluchowski kinetics, although there should be considerable obstruction to diffusion in such structures. One may alternatively speculate that the network structure is not rigid. Dynamical fluctuations of the structure may allow small molecules to diffuse almost freely within a certain range of distance, larger than the mesh size. Before any definite conclusion could be drawn on the mechanism of this interesting phenomenon, it would be very important to observe experimentally a crossover of the type illustrated in Figure 4 by using long-lived excited states, such as triplets. We suggest that the models described in this work could be useful in analyzing the results of such experiments. Should the crossover be observed, it would be possible to estimate the effective pore radius, i.e., the average distance the molecules diffuse freely within a polymer network before encountering a potential barrier.

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