Macromolecules **1996,** *29,* 6351−6352

Direct Energy Transfer in Solutions of Diffusing Tagged Polymers

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Received May 8, 1996

Introduction

The measurement of direct incoherent energy transfer has been recognized as a powerful technique to explore the structure of various heterogeneous systems, polymers in particular.[1,2] Recently, it has also been applied to study polymer diffusion.[3,4] The basic idea of the method is to label two kinds of polymers with donor and acceptor dyes, respectively, create a concentration gradient of the labeled species in the sample, and then monitor their interdiffusion with time toward the equilibrium by measuring donor fluorescence intensity, which is sensitive to the local concentration of acceptors in the vicinity of an excited donor. In analyzing energy transfer kinetics in the presence of polymer diffusion, the authors[3,4] employed a classical Förster expression[5] for the ensemble-averaged donor decay in three-dimensional systems with *random* spatial arrangements of acceptor molecules and with isotropic dipole−dipole donor−acceptor interactions. They accounted for the existing spatial nonhomogeneity by simply replacing the constant acceptor concentration in the Förster decay function by the concentration profile obtained from the diffusion equation. This approximation needs certain scrutiny. Since the Förster equation is a result of spatial averaging over essentially a homogeneous acceptor distribution, it is not obvious whether such a replacement makes it applicable for nonhomogeneous systems with a concentration gradient. For instance, energy transfer dynamics in systems of lower dimensionality are quite different from the kinetics in three dimensions.[6] However, if the characteristic diffusion length is much larger than the critical transfer distance and the concentration gradient is significantly gentle, one can expect that the Förster law with variable acceptor concentration may still hold. The purpose of this Note is to perform the spatial averaging properly over a nonhomogeneous acceptor distribution and derive the criteria for the applicability of the above approximation. We treat the direct energy transfer problem in its classical formulation[5,7] with a focus on spatial averaging, neglecting any complications such as dipole rotational anisotropy. We assume that diffusion and energy transfer are not coupled and reactant concentration profiles at any instant may be regarded as frozen in calculating the excitation decay. Finally, we neglect reptation effects[8] and consider, for simplicity, suitably short polymer chains which are believed to follow the Fickian model of diffusion.

General Formalism

Consider an excited donor at a position $\mathbf{r}_0$ surrounded by n acceptors at $\mathbf{r}_1, ..., \mathbf{r}_n$. The energy can be transferred irreversibly from the donor to any acceptor. Acceptors are assumed to act independently and thus contribute multiplicatively to the excitation decay. The survival probability of the donor $\Phi_n(\mathbf{r}_0,t)$ averaged over possible spatial configurations of the acceptors is given by

$$\Phi_n(\mathbf{r}_0,t) = \left\{\frac{1}{V}\int_V \exp[-tw(r_{01})]f(\mathbf{r}_1)\,\mathrm{d}^3\mathbf{r}_1\right\}^n \qquad (1)$$

where $r_{01} = |\mathbf{r}_0 - \mathbf{r}_1|$, $w(r)$ is the energy transfer rate constant, V is the total volume of the system, and $f(\mathbf{r}_1)$ is the spatial distribution function of an acceptor. The self-decay term is factored out. We thus focus on pure energy transfer dynamics. The spatial distribution function is normalized, $\int_V f(\mathbf{r}_1)\,\mathrm{d}^3\mathbf{r}_1 = V$, so that $\Phi_n(\mathbf{r}_0,0) = 1$. In a standard fashion, we take the thermodynamic limit and obtain[9]

$$\Phi(\mathbf{r}_0,t) = \exp\{-c\int_V (1 - \exp[-tw(r_{01})])f(\mathbf{r}_1)\,\mathrm{d}^3\mathbf{r}_1\} \qquad (2)$$

where $c = \lim_{n\to\infty, V\to\infty} (n/V)$ is the acceptor number density. Experimentally observable is the average of $\Phi(\mathbf{r}_0,t)$ over the donor spatial distribution.

Restricting further discussion to dipole−dipole coupling, which is responsible for the singlet−singlet energy transfer in many organic chromophores, and considering the dipoles to be in fast isotropic rotation, we have $w(r) = (1/\tau)(R_F/r),^6$ where R_F is the Förster radius and τ is the radiative fluorescence lifetime. If the acceptors are distributed homogeneously in three dimensions, $f(\mathbf{r}_1) = 1$, the survival probability is independent of the position of the donor and is given by

$$\Phi(t) = \exp(-cV_F\sqrt{\pi t/\tau}) \qquad (3)$$

where $V_F = {}^4/_3\pi R_F{}^3$. This is a classical result.[5] Strictly speaking, eq 3 holds only for low acceptor concentrations.[6]

Model of Dhinojwala and Torkelson.[3] Consider a "sandwich" of two thin polymer films layered on top of each other, one labeled with donors and the other with acceptors. When the sample is heated to a temperature above T_g, the polymers diffuse across the interface. Therefore, the spatial distribution of both donors and acceptors in this direction is nonhomogeneous until the sample is completely mixed. A cylindrical coordinate system is most appropriate in this case with the axis passing through the excited donor molecule and perpendicular to the interface. Let x_0 denote the position of the donor relative to the interface. The position of an acceptor is defined by the projection on the axis, x, and the radial distance from the axis, y. In analogy to eq 2, we can write

$$\begin{aligned}\Phi(x_0,t,\tilde{t}) &= \exp\{-c\int_{-L}^{L} f(x,\tilde{t})\,\mathrm{d}x \times \\ &\qquad \int_0^\infty (1 - \exp[-tw(r)])2\pi y\,\mathrm{d}y\} \\ &= \exp[-cJ(x_0,t,\tilde{t})] \end{aligned} \qquad (4)$$

where L is the layer thickness, $f(x,\tilde{t})$ is the normalized acceptor concentration profile at time $\tilde{t}$ after the diffusion started, and $r^2 = (x - x_0)^2 + y^2$. Here c stands for the concentration in the whole sample. Performing integration over y we obtain

$$\begin{aligned}J(x_0,t,\tilde{t}) = \int_{-L-x_0}^{L-x_0} f(x + x_0,\tilde{t})[\xi^{1/3}\gamma({}^2/_3,\xi) - \\ 1 + \exp(-\xi)]\pi x^2\,\mathrm{d}x \end{aligned} \qquad (5)$$

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S0024-9297(96)00675-4 CCC: $12.00

where $\xi = tw(x)$ and $\gamma(p,\xi) = \int_0^{\xi} z^{p-1}e^{-z}\,dz$ is the incomplete gamma function. The observable decay function is obtained by further averaging eq 4 over the donor concentration profile

$$\Phi(t,\tilde{t}) = \frac{1}{2L}\int_{-L}^{L} f_0(x_0,\tilde{t})\exp[-cJ(x_0,t,\tilde{t})]\,\mathrm{d}x_0 \qquad (6)$$

The initial distribution of acceptors in the sample is $f(x,0) = 2\theta(x)$, where $\theta(x)$ is the Heaviside step function. For donors, $f_0(x,0) = 2\theta(-x)$. The concentration profile is changed with time due to diffusion toward the equilibrium. For $\tilde{t} < L^2/4D$, with D being the polymer diffusion coefficient, and end effects can be neglected and

$$f(x,\tilde{t}) = 1 + \mathrm{erf}\left(\frac{x}{\sqrt{4D\tilde{t}}}\right) \qquad (7)$$

where $\mathrm{erf}(x) = (2/\sqrt{\pi})\int_0^x \exp(-z^2)\,dz$ is the error function. For donors, $f_0(x,\tilde{t}) = 2 - f(x,\tilde{t})$.

The Förster radius is typically of the order of several nanometers, that is much smaller than the polymer film thickness. Therefore, at short times $\tilde{t}$ the energy transfer takes place only in a close vicinity of the interface, and the limits of integration in eqs 4 and 6 can be effectively extended to infinity. At $\tilde{t} = 0$ we have

$$J(x_0,t,0) = \frac{2\pi}{3}\,{x_0}^3\left[1 - \exp(-\xi_0) + 3{\xi_0}^{1/3}\gamma\left(\frac{2}{3},\xi_0\right) + 4\sqrt{\pi}{\xi_0}^{1/2}\gamma\left(\frac{1}{2},\xi_0\right)\right] \qquad (8)$$

where $\xi_0 = tw(x_0)$. Note that $J(0,t,0) = V_\mathrm{F}\sqrt{\pi t/\tau}$, being equal to $J(t)$ in a homogeneous solution. $\Phi(t,0)$ is obtained from

$$\Phi(t,0) = \frac{1}{L}\int_{-L}^{0}\exp[-cJ(x_0,t,0)]\,\mathrm{d}x_0 \qquad (9)$$

Equation 4 can be approximated to a very good accuracy by a simpler expression at sufficiently long times $\tilde{t}$. Since the energy transfer is effective only for very short distances and the concentration profile is a slowly varying function for $\tilde{t} > 0$, we can safely expand $f(x+x_0,\tilde{t})$ in a power series around x_0, truncating terms higher than the second order. Neglecting the end effects we obtain

$$J(x_0,t,\tilde{t}) = f(x_0,\tilde{t})V_\mathrm{F}\sqrt{\pi t/\tau} + f''(x_0,\tilde{t})V_\mathrm{F}\,\frac{\Gamma\left(\frac{1}{6}\right)}{10}\left(\frac{t}{\tau}\right)^{5/6}{R_\mathrm{F}}^2 \qquad (10)$$

Substituting eq 7 into eq 10, one can see that the second term contains parameter $R_\mathrm{F}^2/D\tilde{t}$, which becomes very small soon after the diffusive mixing starts. Therefore, except at very short times $\tilde{t}$, $J(x_0,t,\tilde{t})$ is well approximated by the first term and the survival probability is given by

$$\Phi(t,\tilde{t}) = \frac{1}{L}\int_{-L}^{L}\left[1 - \frac{1}{2}f(x_0,\tilde{t})\right]\exp[-cf(x_0,\tilde{t})\,V_\mathrm{F}\,\sqrt{\pi t/\tau}]\,\mathrm{d}x_0 \qquad (11)$$

This equation is essentially the same as that used by Dhinojwala and Torkelson. It is a very good approximation for thick samples: $L \gg R_\mathrm{F}$. One can further integrate the survival probability over time t to obtain the steady-state energy transfer efficiency.

Model of Liu, Feng, and Winnik.[4] Now let us consider a radial problem modeling interdiffusion of polymer molecules at the interface between a latex sphere and its surrounding. Let r_0 and r_1 be the distance of a donor and an acceptor, respectively, from the center of the sphere, and φ denote the angle between $\mathbf{r}_0$ and $\mathbf{r}_1$. In analogy to eq 4 we can write

$$\begin{aligned}\Phi(r_0,t,\tilde{t}) &= \exp\{-c\int_0^{\infty} f(r_1,\tilde{t})2\pi{r_1}^2\,\mathrm{d}r_1 \times \int_0^{\pi}(1 - \exp[-tw(r)])\sin\varphi\,\mathrm{d}\varphi\}\\ &= \exp[-cJ(r_0,t,\tilde{t})]\end{aligned} \qquad (12)$$

where $r^2 = {r_0}^2 + {r_1}^2 - 2r_0r_1\cos\varphi$. For the dipole–dipole mechanism

$$J(r_0,t,\tilde{t}) = \frac{\pi{R_\mathrm{F}}^2}{r_0r_1}\left(\frac{t}{\tau}\right)^{1/3}\int_0^{\infty} f(r_1,\tilde{t})[G(\xi_-) - G(\xi_+)]{r_1}^2\,\mathrm{d}r_1 \qquad (13)$$

where $G(\xi) = \gamma(^2/_3,\xi) - \xi^{-1/3}[1 - \exp(-\xi)]$ and $\xi_\pm = tw(r_0 \pm r_1)$. To obtain the overall survival probability, we should further average eq 12 over the donor spatial distribution, $4\pi{r_0}^2f_0(r_0,\tilde{t})$. The initial conditions are $f_0(r_0,0) = \theta(R - r_0)$ and $f(r_1,0) = \theta(r_1 - R)$, where R is the radius of the sphere. The evolution of the concentration profiles with time $\tilde{t}$ is described by

$$f_0(r,\tilde{t}) = \frac{1}{2}\left\{\mathrm{erf}\left[\frac{R + r}{\sqrt{4D\tilde{t}}}\right] + \mathrm{erf}\left[\frac{R - r}{\sqrt{4D\tilde{t}}}\right]\right\} - \frac{1}{r}\left(\frac{D\tilde{t}}{\pi}\right)^{1/2}\left\{\exp\left[-\frac{R - r}{\sqrt{4D\tilde{t}}}\right] - \exp\left[-\frac{R + r}{\sqrt{4D\tilde{t}}}\right]\right\} \qquad (14)$$

and $f(r,\tilde{t}) = 1 - f_0(r,\tilde{t})$.

Like in the layered system, after a short initial stage of mixing, $J(r_0,t,\tilde{t})$ is very well approximated by the bulk expression and the survival probability is given by

$$\Phi(t,\tilde{t}) = \frac{3}{R^3}\int_0^{\infty} f_0(r_0,\tilde{t})\exp[-cf(r_0,\tilde{t})V_\mathrm{F}\sqrt{\pi t/\tau}]{r_0}^2\,\mathrm{d}r_0 \qquad (15)$$

This approximation is valid only if $R \gg R_\mathrm{F}$.

In conclusion, we have addressed a problem of direct incoherent electronic energy transfer in a system with nonhomogeneous spatial distribution of donors and acceptors. The criteria for the applicability of the classical Förster decay function with variable acceptor concentration in analyzing energy transfer kinetics in the presence of polymer diffusion have been established.

Note Added in Proof. When this manuscript was already in press, we became aware of the recent paper by Farinha et al.[10] where the problem of energy transfer between tagged polymers diffusing in planar geometry has been considered.

References and Notes

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MA960675F