Direct Nonradiative Energy Transfer in Polymer Interphases: Fluorescence Decay Functions from Concentration Profiles Generated by Fickian Diffusion

J. P. S. Farinha and J. M. G. Martinho*

Centro de Quimica–Fisca Molecular, Instituto Superior Tecnico,
1096 Lisboa Codex, Portugal

A. Yekta and M. A. Winnik*

Department of Chemistry and Erindale College, University of Toronto,
Toronto, Ontario M5S 1A1, Canada

Received March 20, 1995; Revised Manuscript Received June 8, 1995[⊗]

ABSTRACT: A model is presented describing direct nonradiative energy transfer (DET) occurring between energy donors and acceptors attached to polymer chains diffusing across a planar interface. The model considers the fact that each donor is surrounded by a nonuniform concentration of acceptors. Previous models of energy transfer in slowly diffusing systems have considered that both the donors and acceptors are distributed according to concentration profiles generated through diffusion but have simplified the problem by assuming that, in any thin slice through the profile, the acceptor concentration can be taken to be uniform. We show that this mean local concentration model provides a good description of the system when the concentration gradients are broad, but it fails when the concentration gradients are steep or when R_0, the critical Förster distance, is large. The proposed model is expected to be particularly important for the description of the early stages of the diffusion process where one may wish to distinguish reptation effects from Fickian diffusion.

Introduction

The diffusion of polymer chains across interfaces has been a subject of intense interest for more than 10 years.[1] From a polymer physics point of view, the main issue concerns the early time diffusion, which is strongly influenced by the configuration of the chains adjacent to the interface. A variety of methods have been applied to study such systems, perhaps the most powerful of which has been specular neutron reflectivity.[2] We are concerned with direct nonradiative energy transfer (DET) measurements to monitor interdiffusion between chains labeled with donor chromophores (D) and acceptor chromophores (A), respectively.[3,4] As in all such labeling experiments, the D-labeled polymer and A-labeled polymer are brought together to form a sharp interface at time zero, and then the sample is annealed for various periods of time, t_{an}. Interdiffusion leads to mixing of donor and acceptor groups, which is measured through an increase in energy transfer between them. While many such experiments have been reported, the analysis of such experiments to obtain reliable values of the diffusion coefficient is problematic. Figure 1 shows a drawing of the expected distribution functions of donors and acceptors before annealing and after annealing.

At issue is the proper analysis of the experimental data. This is a problem of energy transfer in restricted geometry, a topic itself of considerable interest over the past several years. Since the work of El-Sayed[5] and of Klafter and Blumen,[6] it is recognized that energy-transfer kinetics in infinite media, either in Euclidean dimensions or on fractal structures, depends upon the distribution of acceptors but not on the location of the donors. In restricted dimensions, one has to take account of the locus of the donors. Previous contributions in this area have considered systems where there is a unique locus for the donors: on the surface of a sphere, along the center, or on the surface of a cylinder.[7]
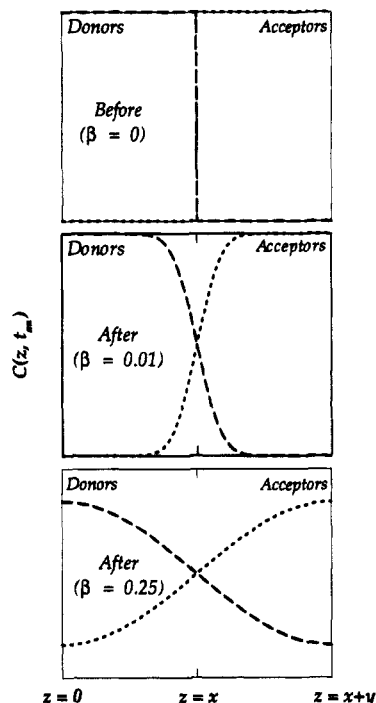
Figure 1. Representation of the diffusion geometry considered here. The system consists of a sandwich of two thin polymer films, one of thickness x labeled with donors and the other of thickness y labeled with acceptors. For convenience in the drawing we choose the case of $x = y$. We show the distribution functions before annealing (a) and after annealing for relatively short (b) and longer (c) times.

When both the donors and acceptors have a distribution of sites, as in the polymer interdiffusion experiment, one must integrate over both distributions. This is a difficult problem, and we know of no such case where an exact solution has been presented.

To analyze the experimental data obtained in experiments on polymer interdiffusion in latex films, Winnik and his group employed a simplified model of energy

transfer.[4,8] This model considers three distinct domains: homogeneously mixed donor/acceptor labeled chains separated from two unmixed domains containing donor- and acceptor-labeled chains, respectively. In this "step-function" model, diffusion leads to the growth in size of the mixed domains, accompanied by shrinking of the unmixed domains. The donor in the unmixed domain decays with an intrinsic lifetime τ_D, while in the mixed domain the decay is more complex owing to electronic energy transfer to the acceptors that surround them. It was assumed that the donor decay follows the Förster equation,[9] given by

$$I_D(t) = \frac{q_D}{\tau_D} n_D{}^*(0) \exp\left\{ -\frac{t}{\tau_D} - 2\gamma\left(\frac{t}{\tau_D}\right)^{1/2} \right\} \quad (1)$$

where t (typically in nanoseconds) is the time following pulsed excitation, $n_D{}^*(0)$ is the initial concentration of excited donor molecules, q_D is the intrinsic fluorescence quantum yield of the donor, τ_D is its unquenched lifetime, and $\gamma = C_A/C_{A0}$ where C_A (mol L^{-1}) is the concentration of acceptors. C_{A0} is the critical concentration given by

$$C_{A,0} = \frac{3000}{2\pi^{3/2} N_A R_0{}^3} \quad (2)$$

with N_A being Avogadro's number and R_0 (cm) the critical Förster distance for a dipole−dipole energy-transfer mechanism. In the step-function approach, the decay curve following interdiffusion across the interface is given by[4,8]

$$I_D(t,t_{an}) = B_1(t_{an}) \exp\left\{ -\frac{t}{\tau_D} - 2\gamma\left(\frac{t}{\tau_D}\right)^{1/2} \right\} +$$
$$B_2(t_{an}) \exp\left\{ -\frac{t}{\tau_D} \right\} \quad (3)$$

where the prefactors B_1 and B_2 are proportional to the number of excited donor molecules in the mixed or unmixed domains, respectively. This model is unrealistic in that it ignores the details of the concentration profiles in the system of donors $C_D(z,t_{an})$ and acceptors $C_A(z,t_{an})$ which evolve as a function of annealing time t_{an}.

Recently Dhinojwala[10] and Liu[11] independently proposed improvements for eq 3 which take into account the donor/acceptor concentration profiles generated by interdiffusion. In both approaches, one subdivides the concentration profile into slices and then assumes that within each slice the donors "see" a uniform local concentration of acceptors. This local concentration within the ith slice depends only upon the coordinate of the slice of donors considered. We can consider this to be a "mean-local-concentration" ($\langle C_{A,i}\rangle$) model. Summing for all the slices of donors, one obtains the following equation, expressed in the Dhinojwala and Torkelson[10] notation, for the donor decay curve (one dimensional diffusion)

$$I_D(t,t_{an}) =$$
$$\int_0^{x+y} dz\, C_D(z,t_{an}) \exp\left\{ -\frac{t}{\tau_D} - 2\gamma(z,t_{an})\left(\frac{t}{\tau_D}\right)^{1/2} \right\} \quad (4)$$

Here x and y are the initial film thicknesses pertaining to donor and acceptor domains, respectively (cf. Figure 1). $C_D(z,t_{an})$ is the concentration of donors, and $\gamma(z,t_{an})$ is defined as in eq 1. By mass conservation, when $x =$

y, $C_A(z,t_{an}) = C_A(0)\,[1 - C_{DN}(z,t_{an})]$, with $C_A(0)$ being the initial concentration of acceptors.

The mean-local-concentration model is an improvement over the step-function model because a different value of γ is considered for each slice of the sample, while in the step-function model an overall average value is taken. Even though an improvement, the mean-local-concentration model still has a fundamental limitation. In employing the Förster expression to derive eq 4, it is implicitly assumed that each donor is surrounded in a three-dimensional space by a *uniform* concentration of acceptors. This assumption is in contradiction with the presumption of an acceptor concentration gradient and brings us face to face with the essential difficulty of evaluating energy-transfer kinetics in a restricted geometry where both D and A are described by distribution functions.

We can see one consequence of this approximation by scrutinizing the behavior of eq 4 at zero annealing time. Equation 4 predicts that, at $t_{an} = 0$, no energy transfer occurs, since $C_A(z,0) = 0$ for all the donor-containing slices. In reality, donors close to the interface "see" acceptors across the interface (cf. Figure 1). We infer that, for sharp profiles or for slices whose thickness is on the order of R_0, excited D can transfer energy to A species in neighboring slices. The mean local concentration approximation will be less accurate for donor/acceptor pairs with large R_0 values, especially at small annealing times when the distribution functions have very sharp gradients. For long annealing times, the distribution functions become flatter, and then both the step-function and the mean-local-concentration models become more accurate.

It is the aim of this work to develop a model of energy transfer in such systems by considering the distributions of donor and acceptor groups. We will also derive the conditions under which the mean-local-concentration model provides an excellent description of the energy-transfer process across the interface, using both analytical and numerical results. Throughout our analysis, we assume that there is no feature of the diffusion that might cause the D and A groups to select a preferential orientation of their transition dipoles.

The Model

We consider direct nonradiative energy transfer accompanying one-dimensional interdiffusion. Diffusion occurs along the z-axis, and the initial interface lies in a plane perpendicular to that axis at $z = x$. The profile is divided into slices which can be arbitrarily thin. The donor concentration is assumed sufficiently low that no donor−donor energy transfer (energy transport) can occur. The donors in each slice can transfer energy to the acceptors that surround them. We place no constraint on which A can accept energy from D; thus, DET can occur to A groups distributed nonuniformly in a three-dimensional space.

The donors in each slice are surrounded by different acceptor distributions, and, consequently, their fluorescence decay behavior is different. Thus, the donor decay must be evaluated as a sum over all slices

$$I_D(t,t_{an}) \propto$$
$$\exp\left\{ -\frac{t}{\tau_D} \right\} \int_0^{x+y} dz\, C_D(z,t_{an}) \exp\{ -g(t,z,t_{an}) \} \quad (5)$$

The exponential term inside the integral expresses the survival probability of the donors in the slice positioned at coordinate z due to all energy-transfer-related paths

of decay. The function $g(t,z,t_{an})$ can be derived from the general formalism developed by Blumen and Klafter,[6] taking into account the nonuniform distribution of acceptors surrounding each donor.

$$g(t,z,t_{an}) = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} d\theta \, d\varphi \, dr \, r^2 \sin\varphi \, C_A(d,t_{an}) \times$$
$$[1 - \exp\{-\alpha t/r^6\}] \quad (6)$$

where $\alpha = R_0^6/\tau_D$ and d is the distance of the acceptor from the plane perpendicular to z at $z = 0$. Unlike the mean-concentration model, eq 6 considers a nonuniform distribution of acceptors surrounding each donor, and the concentration of the acceptor is allowed to vary with the donor–acceptor distance. Here, however, the integral has to be evaluated numerically because of the complicated dependence of the acceptor concentration on r.

Two features of eq 6 simplify the evaluation of $g(t,z,t_{an})$. First, the term $r^2[1 - \exp\{-\alpha t/r^6\}]$ is a sharply peaked function of r/R_0. This term goes to zero for r values much larger than $2R_0$, so that the range over which one has to carry out the integration is limited. Second, eq 6 can be rewritten in a more satisfactory way if we realize that, for the planar geometry under consideration, the distribution function of acceptors is uniform in any thin vertical slice of a spherical shell centered on the donor coordinate (Figure 2).

In order to perform the integration, it is first necessary to evaluate the elementary volume of a ring defined by the intersection of the spherical shell of radius r and width dr, with the vertical slice having a width dz. The volume of the ring is $dv_{ring} = 2\pi \, r dr \, dz$, from which we rewrite eq 6 in the form

$$g(t,z,t_{an}) =$$
$$2\pi \int_0^{\infty} dr \, r[1 - \exp\{-\alpha t/r^6\}] \int_{z-r}^{z+r} dz' \, C_A(z',t_{an}) \quad (7)$$

As energy transfer is only significant for small donor/acceptor distances ($r \sim R_0$), we can develop a series expansion of the parametric integral around z

$$\int_{z-r}^{z+r} dz' \, C_A(z',t_{an}) =$$
$$2rC_A(z,t_{an}) + \frac{r^3}{3}\frac{\partial^2}{\partial z^2} C_A(z,t_{an}) + \dots \quad (8)$$

Substituting the value of the integral by its approximation in eq 7, after performing the integration over r, we recover

$$g(t,z,t_{an}) = 2\gamma(z,t_{an})\left(\frac{t}{\tau_D}\right)^{1/2} \times$$
$$\left\{1 + \frac{\Gamma(1/6)}{\Gamma(1/2)}\frac{1}{30}(t/\tau_D)^{1/3}\frac{R_0^2}{C_A(z,t_{an})}\frac{\partial^2}{\partial z^2} C_A(z,t_{an}) + \dots\right\} \quad (9)$$

Introducing this into eq 5, we obtain, as the first term, the expression for the mean-local-concentration model (eq 4). The other terms correct for the effect of a nonuniform acceptor distribution. The correction term is rather complex. Nevertheless, it is possible to show that the correction is significant only for large values of R_0 and small root mean-square diffusion lengths ($\langle z^2 \rangle^{1/2}$).

In order to have a better appreciation of the correction term, in Figure 3 we plot several donor decay curves calculated from the mean-local-concentration model (eq 4) and the proposed model (eqs 5 and 7), without
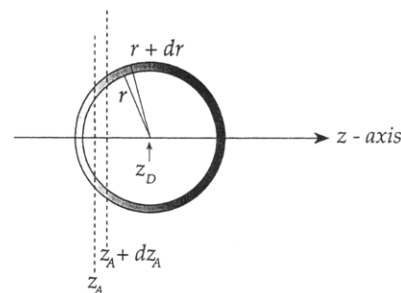

Figure 2. Drawing depicting the distribution of acceptors around a donor located at a distance z from the initial sharp interface (at $z = 0$) prior to the onset of diffusion. The change in gray scale in the circle surrounding the donor implies a gradient in the concentration of acceptors.
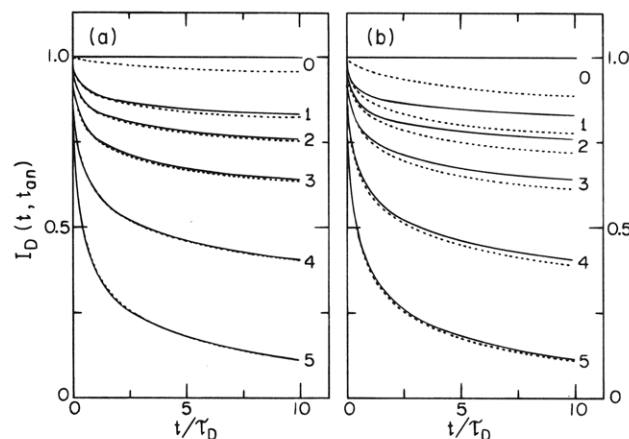

Figure 3. Comparison of donor fluorescence decay curves obtained from the proposed model (eq. 5) and for the mean-local-concentration model (eq 4), for $\tau_D = 44$ ns, $x = y = 65$ nm, $C_A(0) = 0.1$ M ($C_A(0)/C_{A,0} = 2.12$), $D = 10^{-15}$ cm^2 s^{-1}, and (a) $R_0 = 22.3$ and (b) 60 Å. The dashed lines refer to data calculated with eq 5, and the solid lines, to data calculated with eq 4 for several annealing times (t_{an}): (0) 0, (1) 3.5, (2) 7, (3) 15.8, (4) 44, and (5) 113 min.

considering the intrinsic decay of the donor, before annealing, and for several annealing times, using a donor lifetime of 44 ns, $D = 10^{-15}$ cm^2 s^{-1}, and values of R_0 of 22.3 (a) and 60 Å (b), keeping the ratio of $C_A(0)/C_{A,0} = 2.12$, with $C_A(0) = 0.1$ M.

The normalized concentration profile resulting from a one-dimensional Fickian diffusion of polymer chains across the planar interface can be written as[12]

$$C_{DN}(z,t_{an}) = \frac{C_D(z,t_{an})}{C_D(0)} =$$
$$q\left\{1 + 2\sum_{n=1}^{\infty}\frac{\exp[-(\pi n q)^2\beta] \sin(\pi n q) \cos(\pi n q z/x)}{\pi n q}\right\} \quad (10)$$

where $C_D(0)$ is the initial donor concentration before diffusion starts, $q = x/(x + y)$ and $\beta = Dt_{an}/x^2$. The concentration profile is derived on the assumption that the polymer chains diffuse in a film of finite thickness ($x + y$). We note that, for $x = y$, we obtain the expected final concentration of donors at $t_{an} = \infty$ as half the initial concentration ($C_D(\infty) = {}^1\!/_2 C_D(0)$). The acceptor concentration is simply given by

$$C_A(z,t_{an}) = C_A(0) [1 - C_{DN}(z,t_{an})] \quad (11)$$

By examining Figure 3 we note that the differences between the model evaluation of eq 5 and the mean-

local-concentration approach are more significant for large values of R_0 and small annealing times, in agreement with the predictions of the correction term expressed in eq 9. The errors increase substantially if the initial acceptor concentration or R_0 is increased. This can be an impediment if one wishes to observe energy transfer at the early stages of interdiffusion. We conclude that the mean-local-concentration model describes reasonably well the picture of the energy transfer accompanying interdiffusion across an interface for long annealing times, but the general treatment developed in this work should be used if one is studying the early stages of interdiffusion. The early stages are particularly important from the point of view of polymer theory, because the rich features of reptation occur when the distance traveled by the polymers at the interface is smaller than their radius of gyration.

Determination of Diffusion Coefficients

To compare the present model with various simplified approaches applied in the past, we make use of simulated data. We simulate distributions of donors and acceptors with the concentration profiles $C_D(z,t_{an})$ and $C_A(z,t_{an})$, respectively. The diffusion coefficients can be evaluated from the fitting of the donor decay curve to the theoretical expression given by eqs 5 and 7.

We note first that noise-free fluorescence intensity decay curves generated from eqs 5 and 7 could not be fitted to eq 3. It may seem curious that an expression used successfully on numerous occasions to fit experimental data derived from donor–acceptor distributions similar to those simulated here fails to fit the simulated data. This is a common occurrence when one compares curve fitting to noise-free data and curve fitting to similar data to which the Poisson noise associated with single-photon timing experiments has been added. For example, Drake and co-workers[13] comment that the Klafter–Blumen equation,[7,14] commonly used to analyze decay profiles for restricted geometry DET experiments, fails to fit simulated but noise-free data but gives reasonable results when used to analyze simulated experimental data, i.e., data containing Poisson noise and convoluted with a lamp profile prior to analysis.

If we were interested in examining the magnitude of the error in analyzing experimental data with eq 3 followed by calculation of D values from the ratio $B_1/(B_1 + B_2)$, we should take the simulated data, add Poisson noise, and convolute the data with a realistic lamp profile to generate realistic decay profiles for a system whose D value is known. Fitting of this data followed by calculation of an apparent diffusion coefficient D_{app} would allow the extent of error in D_{app} to be determined. We defer this kind of analysis for a future paper. Here we are interested in the fundamental behavior of the present theory and the consequences of employing simplifying assumptions. Under these circumstances, it is more informative to examine noise-free data from the simulations, and we conclude that simplifications leading to eq 3 represent a poor description of the system.

Another procedure which we have used in the past to evaluate experimental data involves the normalized efficiency of energy transfer, f_m^{ET}, calculated from fluorescence quantum yields.

$$f_m^{ET} = \frac{A(t_{an}) - A(0)}{A(\infty) - A(0)} \qquad (12)$$

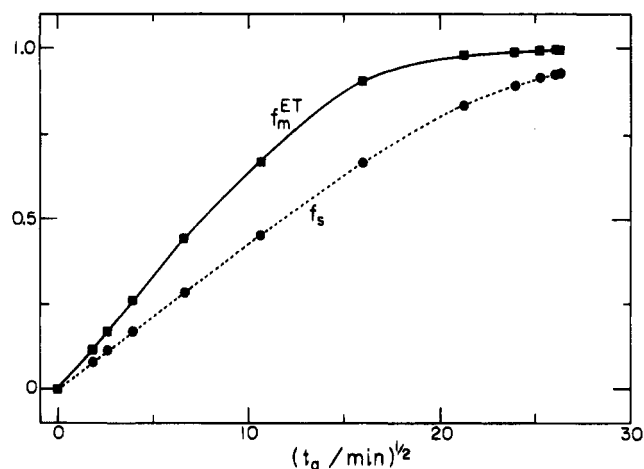where A represents the area under the donor decay curve at different annealing times. We have assumed

Figure 4. Normalized efficiency of energy transfer f_m^{ET} calculated from eq 12 (—) and mass fraction of mixing f_s calculated from eq 13 (···) versus annealing time, for $\tau_D = 44$ ns, $R_0 = 22.3$ Å, $x = y = 65$ nm, $C_A(0) = 0.1$ M ($C_A(0)/C_{A,0} = 2.12$), and $D = 1 \times 10^{-15}$ cm^2 s^{-1}.

that the normalized efficiency of energy transfer is equal to the true fraction of mixing calculated from the distribution function

$$f_s = 2\left(1 - \frac{1}{x}\int_0^x dz\, C_{DN}(z,t_{an})\right) \qquad (13)$$

This is a situation analyzed in detail by Dhinowajala and Torkelson,[10] who point out that f_s and f_m^{ET} (E_n in their notation) are not equal but are proportional during the early stages of the interdiffusion process. They evaluate the proportionality constant and show that it depends upon the concentration of acceptors in the acceptor-labeled phase.

Figure 4 shows a plot of f_m^{ET} and f_s versus annealing time for one-dimensional diffusion corresponding to typical conditions for film formation studies using the phenanthrene- and anthracene-labeled polymers ($\tau_D = 44$ ns, $R_0 = 22.3$ Å, $x = y = 65$ nm, and $C_A(0) = 0.1$ M ($C_A(0)/C_{A0} = 2.12$). Here we use $D = 10^{-15}$ cm^2 s^{-1} in the numerical simulation of the fluorescence decay profiles. One sees that the f_m^{ET} curve rises much faster than that for f_s, and we find that, for lower values of $C_A(0)/C_{A,0}$ it approaches that for f_s. We also note that the two curves are proportional for all values of $f_m^{ET} < 0.7$. These results correspond to those of Dhinojwala and Torkelson.

When D_{app} is calculated from f_m^{ET} by assuming that it is equal to f_s, one obtains D_{app} values that are too large. We plot the ratio of D_{app}/D in Figure 5 as a function of $t_{an}^{1/2}$. These differences between D and D_{app} are small at short annealing times but become very large at long annealing times. It appears that D_{app} can become $10-1000$ times too large. This aspect of the results is misleading. Under normal circumstances, experiments are run to the point where $f_m^{ET} \approx 0.7$, corresponding here to $t_{an}^{1/2} = 10$ min$^{1/2}$. With the values of $C_A(0)/C_{A,0}$ employed in the simulation, D_{app}/D values are too high by a factor of $2-3$, except at the very end of the experiment. These differences will be smaller at lower values of $C_A(0)/C_{A,0}$. This may in part explain why such good agreement in D values was obtained when film formation experiments examined by DET were compared with those obtained by small-angle neutron scattering for polymer samples of identical composition and very similar molecular weights and molecular weight distributions.[8a]
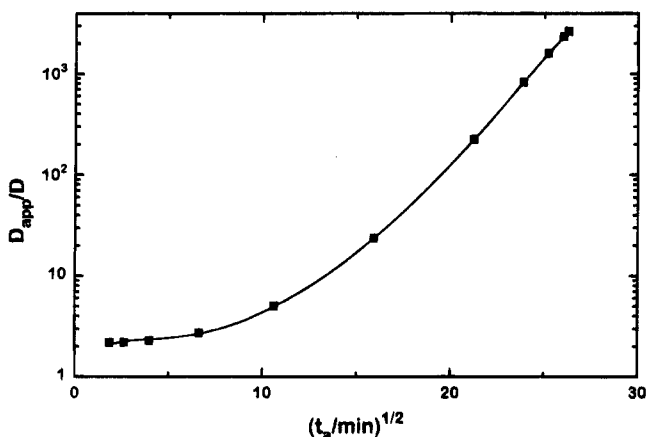
Figure 5. Ratio of the calculated diffusion coefficient (D_{app}) and the diffusion coefficient used in the simulation of the decay curves (D) versus annealing time, for the parameters given in Figure 4.

f_m^{ET} defined in eq 12 does not describe the true quantum efficiency of energy transfer corresponding to polymer interdiffusion. The correct expression for the efficiency of energy transfer[15] at a given annealing time t_{an} is given by

$$f^{ET}(t_{an}) = 1 - \frac{\int_0^\infty dt\, I_D(t,t_{an})}{\int_0^\infty dt\, I_D^0(t)} \qquad (14)$$

where $I_D(t,t_{an})$ describes the fluorescence decay profile in the presence of a given concentration of acceptors, and $I_D^0(t)$ is the profile in the absence of acceptors. We note that ideally $I_D^0(t)$ should be a single exponential decay with $\int_0^\infty dt\, I_D^0(t) = \tau_D$. In many polymer interdiffusion experiments, however, the fluorescence decay profile of the newly formed sample before any annealing (i.e., $I_D(t,0)$) decays faster than $I_D^0(t)$, and, as a result, $\int_0^\infty dt\, I_D(t,0) < \tau_D$. We understand this difference to arise from energy transfer across the boundary of the initial interface. In terms of the model developed here, we can calculate the extent of energy transfer expected for a sharp interface, and also, presumably, explain somewhat greater extents of energy transfer in terms of roughness of the interface or small extents of interdiffusion accompanying sample preparation.

Under circumstances where one does not apply this model, an acceptable methodology is to use the normalized efficiency of energy transfer expressed by eq 12 and assume that it is equal to the true efficiency of energy transfer as described by eq 14. This approach is particularly useful when one wishes to examine the effect of perturbations on the rate or extent of interdiffusion. Since the evolution of the concentration profile in a diffusion process is dependent upon the product of D and t_{an}, experimental modifications to the system such as increases in temperature or addition of small amounts of plasticizer affect both D and the time scale over which interdiffusion occurs. Equation 12 represents a viable and useful method for analyzing data to quantify *changes in D* induced by these perturbations to the system.

Conclusion

A model has been developed describing the nonradiative energy transfer occurring between donors and acceptors attached to polymer chains diffusing across a planar interface. This model allows for the analysis of DET in nanostructures with donor–acceptor distribution functions of planar symmetry.[16] It can be used to

study polymer diffusion across interfaces and to verify the occurrence of reptation dynamics from donor–acceptor concentration profiles. The predictions of the present model are compared with those obtained from previous models in which various simplifying assumptions have been made. The most important of these considers there to be a uniform concentration of acceptors surrounding a particular donor in a thin slice across the concentration profile. We show that this model has the limitation that slices cannot be taken so thin as to approach R_0 in magnitude. Nevertheless, the comparison shows that the approximation of a locally uniform distribution of acceptors is very good for long annealing times or other circumstances where the concentration profiles of donors and acceptors is relatively broad. It is poor for large values of R_0, at early stages of the interdiffusion process, and in other situations where the donor and acceptor concentration profiles have a very sharp gradient. Finally we show that fluorescence measurements provide a good method for extracting relevant information about polymer diffusion across an interface if the appropriate models of energy transfer are used.

References and Notes

(1) (a) Kausch, H. H.; Tirrel, M. *Annu. Rev. Mater. Sci.* **1989**, *19*, 341. (b) Wool, R. P.; Yuan, B.-L.; Mcgarel, O. J. *Polym. Eng. Sci.* **1989**, *29*, 1340.

(2) (a) Russell, T. P.; Karin, A.; Mansour, A.; Felcher, G. P. *Macromolecules* **1988**, *21*, 1890. (b) Russell, T. P.; Delvie, V. R.; Dozier, W. D.; Felcher, G. P.; Agrawal, G.; Wool, R. P.; Mays, J. M. *Nature* **1993**, *365*, 235.

(3) Tirrell, M.; Adolf, D.; Prager, F. *Springer Lecture Notes Appl. Math.* **1984**, *37*, 1063.

(4) (a) Wang, Y.; Zhao, C. L.: Winnik, M. A. *J. Chem. Phys.* **1991**, *95*, 2143. (b) Zhao, C. L.; Wang, Y.; Hruska, Z.; Winnik, M. A. *Macromolecules* **1990**, *23*, 4082.

(5) (a) Yang, C. L.; Evesque, P.; El-Sayed, M. A. *J. Phys. Chem.* **1985**, *89*, 3442. (b) Yang, C. L.; El-Sayed, M. A.; Suib, S. L., *J. Phys. Chem.* **1987**, *91*, 4440.

(6) (a) Klafter, J.; Blumen, A. *J. Chem. Phys.* **1984**, *80*, 875. (b) Blumen, A.; Klafter, J.; Zumofen, G. *J. Chem. Phys.* **1986**, *84*, 1397. (c) Ediger, M. D.; Domingue, R. P.; Fayer, M. D., *J. Chem. Phys.* **1988**, *89*, 5224. Baumann, J.; Fayer, M. D. *J. Chem. Phys.* **1986**, *85*, 4087.

(7) Levitz, P.; Drake, J. M.; Klafter, J. *J. Chem. Phys.* **1984**, *80*, 1246.

(8) (a) Wang, Y.; Zhao, C.-L.; Winnik, M. A. *J. Chem. Phys.* **1991**, *95*, 2143. (b) Wang, Y.; Winnik, M. A. *J. Phys. Chem.* **1993**, *97*, 2507. (c) Wang, Y.; Winnik, M. A.; Haley, F. *J. Coatings Technol.* **1992**, *64* (811), 51. (d) Kim, H.-B; Winnik, M. A. *Macromolecules* **1994**, *27*, 1007.

(9) (a) Förster, Th. *Z. Naturforsh.* **1949**, *4A*, 321. (b) Förster, Th. *Ann. Phys.* **1948**, *2*, 55. (c) Förster, Th. *Discuss. Faraday Soc.* **1959**, *7*, 27.

(10) Dhinojwala, A.; Torkelson, J. M. *Macromolecules* **1994**, *27*, 4817.

(11) Liu, Y. S.; Feng, J.; Winnik, M. A., *J. Chem. Phys.* **1994**, *101*, 9096.

(12) Vyprachticky, D.; Morawetz, H.; Fainzilberg, V. *Macromolecules* **1993**, *26*, 339.

(13) Levitz, P.; Drake, J. M.; Klafter, J. *Chem. Phys. Lett.* **1988**, *148*, 557.

(14) Ni, S.; Zhang, P.; Wang, Y.; Winnik, M. A. *Macromolecules* **1994**, *27*, 5742.

(15) The fluorescence quantum yield $q_D = k_f \int_0^\infty dt\, I_D(t)$, where k_f is the radiative rate constant and $I_D(t)$ is the normalized decay profile.

(16) Yekta, A.; Duhamel, J.; Winnik, M. A. *Chem. Phys. Lett.* **1995**, *235*, 119.