We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support of this work. G.L. thanks the University of Toronto for a Connaught Scholarship and for a University of Toronto Open Fellowship. J.E.G. is grateful to the Canada Council for support in the form of a Killam Research Fellowship.

References and Notes

(1) Liu, G. J.; Guillet, J. E.; Al-Takrity, E. T. B.; Jenkins, A. D.; Walton, D. R. M. *Macromolecules* **1990**, *23*, 1393.

(2) See, for example: Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1969.

(3) Katchalski-Katzir, E.; Haas, E.; Steinberg, I. Z. *Ann. N.Y. Acad. Sci.* **1981**, *366*, 44.

(4) Smoluchowski, M. *Z. Phys. Chem.* **1918**, *92*, 129. Chandrasekhar, S. *Rev. Mod. Phys.* **1943**, *15*, 1.

(5) Feller, W. *An Introduction to Probability Theory and Its Applications*, 3rd ed.; Wiley: New York, 1968; Vol. 1, p 358.

(6) Bueche, F. *Physical Properties of Polymers*; Interscience: New York, 1962.

(7) Liu, G. J.; Guillet, J. E. *Macromolecules*, in press.

(8) Crank, J. *The Mathematics of Diffusion*; Oxford University Press: London, 1956.

Application of the "Spectroscopic Ruler" to Studies of the Dimensions of Flexible Macromolecules. 4. Theoretical Discussion of the Effect of End-Group Diffusion

Guojun Liu and J. E. Guillet*

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

Received July 24, 1989; Revised Manuscript Received November 14, 1989

ABSTRACT: The relative diffusion between polymer chain ends during donor excitation lifetimes has been shown to increase the energy-transfer efficiencies experimentally observed between energy donor and acceptor groups attached at the ends of polymer chains. The relative diffusion of the end groups has also been shown to alter both donor and acceptor fluorescence decay curves. The feasibility of using these techniques for experimental measurement of relative diffusion coefficients of polymer chain ends is discussed.

I. Introduction

In previous papers in this series[1] it was shown that the root-mean-square end-to-end distances for end-labeled PMMA samples measured by the "spectroscopic ruler" technique in nonviscous solvents are shorter than those measured by other techniques, e.g., viscometry. The diffusion of the end groups during the donor fluorescence lifetime is thought to be responsible for these discrepancies. In this paper a model is developed that takes the diffusion of the end groups into account and allows one to formulate the energy-transfer efficiency between donor and acceptor groups measured in nonviscous media. Under favorable experimental conditions, this model will enable one to evaluate the coefficient of relative diffusion between the end groups.

Extensive experimental results concerning energy transfer between small molecules have shown that diffusion of donor and acceptor groups during donor fluorescence lifetimes enhances energy-transfer efficiency.[2,3] Birks and Leite,[4] for example, studied energy transfer between naphthalene and 9,10-diphenylanthracene in fluid solution. When Förster's theory was used, the critical transfer distance was calculated to be 24 Å. Due to diffusional motion, the experimentally observed effective critical energy-transfer distance was found to be 65 Å, almost 3 times as large.

Knowledge of the diffusion coefficients of polymer chain ends is of both theoretical and experimental importance. Theoretically, the diffusion coefficient of a segment is related to the diffusion coefficient of the center of mass of the polymer chain.[5,6] The diffusion coefficient of the center of mass can be measured by techniques such as photon correlation spectroscopy,[7] sedimentation,[8] and NMR pulse-gradient spin–echo experiments.[9] In contrast to extensive documentation of diffusion coefficients of polymer samples, experimental results on diffusion coefficients of polymer segments are rare. This makes the verification of theoretical computations difficult.

Measurement of the diffusion coefficients of polymer chain ends should help provide a better understanding of the kinetics of intramolecular cyclization reactions[10] and also the kinetics of termination processes in free-radical polymerization reactions.[6] For diffusion-controlled intramolecular cyclization reactions, knowledge of the coefficients of relative diffusion between polymer end groups enables the immediate estimation of the rate constant of cyclization using the Smoluchowski equation[11] and therefore the quantum yield of the cyclization product. In free-radical polymerization reactions, two end radicals react and terminate the polymerization. This mechanism of termination requires two cooperative diffusional processes: (a) the translational diffusion of the center of mass of polymer molecules and (b) the relative translational and rotational diffusion of those segments bearing active chain ends. It was experimentally inferred that the segmental diffusion process of the chain end is the rate-determining process in the case of alkyl methacrylates.[12,13] Knowledge of the coefficients of the relative diffusion between chain ends will therefore also contribute to the better understanding of polymer radical termination kinetics.

There have been two reported cases of studies of the diffusion coefficients of chain ends. Katchalski-Katzir et al.[2] monitored the effect of diffusion on fluorescence decays of donor end groups attached to one end of oligopeptide chains. In cases of significant diffusion, the fluorescence of the donor end group decayed much faster. From fitting the decay curves, they estimated the coefficients of relative diffusion between fluorescence donor and acceptor end groups. Xu and Winnik[14] studied the kinetics of exciplex formation between pyrene and *N,N*-dimethylaniline using pyrene monomer and excimer fluorescence decay measurements. The time dependence of the diffusion-controlled rate constants skews the decay curves. By taking this so-called transient effect into account, they also developed a method for the measurement of end-group diffusion coefficients. This technique can, however, be obscured by inappropriate data treatment, as is discussed elsewhere.[15]

II. Theory

In our theoretical treatment, it was assume that the energy-transfer studies are carried out in Θ solvents for the polymer chains and that the introduction of the energy donor and acceptor groups onto the ends of polymer chains does not perturb the conformations of the chains. The diffusive behavior of Gaussian chain ends has been discussed in detail in a previous paper,[16] where it was shown that in the absence of sink terms the probability, $S(r, t)$, of finding a chain possessing an end-to-end distance r at time t obeys the differential equation

$$\frac{\partial S(r,t)}{\partial t} = D\left\{\frac{\partial^2 S(r,t)}{\partial r^2} + \left(\frac{3r}{R_n^{\,2}} - \frac{2}{r}\right)\frac{\partial S(r,t)}{\partial r} + \left(\frac{2}{r^2} + \frac{3}{R_n^{\,2}}\right)S(r,t)\right\} \tag{1}$$

where D is the coefficient of relative diffusion between the end groups and R_n is the root-mean-square end-to-end distance of the connecting chair. It was also shown from the numerical solutions of $S(r, t)$ for chains started from different end-to-end distances R that in the absence of any sink terms, such as energy transfer or fluorescence decay

$$\sum_{i=1}^{n} S(r_i, t) = 1 \tag{2}$$

i.e., the probability of finding the other end somewhere in the space is always equal to 1. That is, the particles diffuse in space but the quantities are conserved and not consumed.

This paper describes a different phenomenon. Suppose that N Gaussian chains are attached at both ends with energy donors and acceptors. At time $t = 0$, the donor groups are excited and the end-to-end distances of these chains are specified by a Gaussian probability function. At subsequent times, the excitation energy of the donor group is dissipated by either transfer of energy from the donor ends to the acceptor ends or by intrinsic dissipation mechanisms such as fluorescence decay, intersystem crossing, etc. It is assumed that the dissipation of the excitation energy of a donor end group changes the feature of the chain and in subsequent times the probability of finding this chain goes to zero. $S(r, t)$ denotes the probability of finding a donor end that is still in the excited state at time t and separated from the other end by a distance of r. $S(r, t)$ satisfies eq 1 with two more sink terms

$$\frac{\partial S(r,t)}{\partial t} = D\left\{\frac{\partial^2 S(r,t)}{\partial r^2} + \left(\frac{3r}{R_n^{\,2}} - \frac{2}{r}\right)\frac{\partial S(r,t)}{\partial r} + \left(\frac{2}{r^2} + \frac{3}{R_n^{\,2}}\right)S(r,t)\right\} - \frac{S(r,t)}{\tau} - \frac{1}{\tau}\left(\frac{R_0}{r}\right)^6 S(r,t) \tag{3}$$

where τ is the fluorescence lifetime of the donor end group in the absence of energy transfer and the term $-S(r, t)/\tau$ describes the sink rate of $S(r, t)$ due to intrinsic decay of excitation energy of the donor group; the second sink term comes from energy transfer.

Equation 3 can also be derived from the difference equation method used previously.[16] When one end of the polymer chain is pictured making jumps of distance δ_r at a frequency of ψ, the probability of finding the donor end group that is still excited and separated by an end-to-end distance of r at time $(t + 1)/\psi$ is given by

$$S(r, (t+1)/\psi) = \rho(r+\delta_r \rightarrow r)S(r+\delta_r, t)\left[1 - \frac{1}{\psi\tau} - \frac{1}{\psi\tau}\left(\frac{R_0}{r+\delta_r}\right)^6\right] + \rho(r-\delta_r \rightarrow r)S(r-\delta_r, t)\left[1 - \frac{1}{\psi\tau} - \frac{1}{\psi\tau}\left(\frac{R_0}{r-\delta_r}\right)^6\right] + [1 - \rho(r \rightarrow r-\delta_r) - \rho(r \rightarrow r+\delta_r)] \times S(r,t)\left[1 - \frac{1}{\psi\tau} - \frac{1}{\psi\tau}\left(\frac{R_0}{r}\right)^6\right] \tag{4}$$

where τ is the fluorescence lifetime of the donor group in the absence of energy transfer. Equation 4 leads to eq 3 after some simple mathematical manipulations.

The necessary boundary conditions for the solution of the differential equation shown in eq 3 are

$$S(r,0) = 4\pi r^2\left(\frac{3}{2\pi R_n^{\,2}}\right)^{3/2} \exp\left[-\frac{3}{2}\left(\frac{r}{R_n}\right)^2\right] \tag{5}$$

and

$$S(r > m_x, t) = 0 \tag{6}$$

The boundary condition given by eq 5 states that the end-to-end distance of the chain initially obeys the Gaussian distribution function and that boundary condition given by eq 6 specifies that the two ends are tied together by a Gaussian chain of contour length m_x.

A more realistic model should recognize the fact that any approach of the donor and acceptor groups within an effective reaction radius, R_a (of the order of contact distances between the donor and acceptors), should result in instantaneous energy transfer. This results in the boundary condition given by eq 7.

$$S(r < R_a, t) = 0 \tag{7}$$

This boundary condition is easy to understand. When naphthalene and anthracene are used as the energy donor and acceptor groups, the direct contact distance is ca. 7 Å. The critical transfer distance is ca. 17 Å. At such short separation, the rate constant for energy transfer through the dipole–dipole mechanism is given by

$$K_{ET} = (17/7)^6(1/\tau) = 2.05 \times 10^2(1/\tau) \tag{8}$$

Since τ is $\sim 10^{-8}$ s, the value of K_{ET} is $\sim 2.05 \times 10^{10}$ s. Assuming that only dipole–dipole energy transfer and self-dissipation are responsible for donor fluorescence decay, the probability for the donor excitation to survive 0.5 ns after the δ-pulse excitation at $t = 0$ is given by

$$\rho\ (0.5\ \text{ns}) = \exp\left\{-\frac{5 \times 10^{-10}}{\tau}\left[1 + \left(\frac{17}{7}\right)^6\right]\right\} = 3.3 \times 10^{-5} \tag{9}$$

which is close to zero. Since the coefficient of relative diffusion between the chain ends is of the order of 10^{-6} cm^2/s, the root-mean-square distance change between the end groups in 0.5 ns is given by

$$\langle L^2 \rangle^{1/2} = (2Dt)^{1/2} \tag{10}$$

and is ~3 Å. Before the end-to-end distance can change significantly, it is certain that the donor excitation has already been transferred. Under actual experimental conditions, energy transfer can also occur by the electron-exchange mechanism when the donor and acceptor groups are so close in space. Our assumption is thus further validified for chains with even higher relative end-to-end diffusion coefficients. As will be noted in later discussions, the boundary condition given by eq 7 is not necessary for chains with relative diffusion coefficients lower than 1.0×10^{-5} cm^2/s, because in this range of diffusion coefficients the sink term from energy transfer is strong enough to cause the instantaneous deactivation of donor excitation before any significant diffusion occurs. Since polymer chain ends have diffusion coefficients lower than 1.0×10^{-5} cm^2/s, this technique is free of the problem of estimating an effective reaction radius as was the case in the studies of exciplex formation between groups attached at polymer chain ends.[14]

Solution of $S(r, t)$ from eq 3 allows the calculation of the survival probability of donor excitation at time t

$$\Omega(t) = \int_{R_a}^{m_x} S(r, t)\ \mathrm{d}r \tag{11}$$

$\Omega(t)$ is proportional to the fluorescence intensity at time t. Plotting $\Omega(t)$ versus time t yields the theoretical fluorescence decay curves as has been shown by Katchalski-Katzir et al.[1]

The expression for transient energy-transfer efficiencies at time t can be derived as follows. Consider an infinitely short time interval between time t and $t + \delta t$. At time t, the probability for the survival of the donor excitation is given by $\Omega(t)$. At time $t + \delta t$, if the donor excitation decays both through the energy-transfer mechanism and through intrinsic decay mechanisms characterized by decay rate constant $1/\tau$, the probability that the excitation still survives is $\Omega(t + \delta t)$. During this time interval, one can also imagine a process in which the donor excitation decays only through intrinsic decay mechanisms. If this occurs, the probability that the donor excitation survives at time $t + \delta t$ is denoted as $\Omega^0(t + \eta t)$. The probability for energy transfer during the infinitely short time interval is then given by

$$E(t) = \frac{\Omega(t + \delta t) - \Omega^0(t + \delta t)}{\Omega(t + \delta t) - \Omega(t)} = 1 - \frac{\Omega^0(t + \delta t) - \Omega(t)}{\Omega(t + \delta t) - \Omega(t)} \tag{12}$$

The energy-transfer efficiency averaged over time is given by

$$E = \sum_t E(t)\ [\Omega(t + \delta t) - \Omega(t)] \Big/ \sum_t [\Omega(t + \delta t) - \Omega(t)] \tag{13}$$

r as $\delta t \to 0$

$$E = \int_0^\infty E(t)\ \mathrm{d}\Omega(t) \Big/ \int_0^\infty \mathrm{d}\Omega(t) \tag{14}$$

Integration gives

$$\int_0^\infty \mathrm{d}\Omega(t) = \Omega(\infty) - \Omega(0) = 0 - 1 = -1 \tag{15}$$

and insertion into eq 14 yields

$$E = -\int_0^\infty E(t)\ \mathrm{d}\Omega(t) \tag{16}$$

Fluorescence decay curves of the acceptor groups are of significant interest. Suppose that the kinetic scheme of fluorescence decay of the acceptor group is described by eqs 17 and 18

$$\mathrm{D}^*{\sim}\mathrm{A} \xrightarrow{k(t)} \mathrm{D}{\sim}\mathrm{A}^* \tag{17}$$

$$\mathrm{D}{\sim}\mathrm{A}^* \xrightarrow{1/\tau_\mathrm{A}} \mathrm{D}{\sim}\mathrm{A} \tag{18}$$

where $k(t)$ is the time-dependent rate constant for energy transfer and τ_A is the fluorescence lifetime of the acceptor group. The kinetic equation for the probability (abbreviated as $A(t)$) for D~A* chains to exist at time t is given by

$$\frac{\mathrm{d}A(t)}{\mathrm{d}t} = k(t)\ \Omega(t) - 1/\tau_\mathrm{A} A(t) \tag{19}$$

The solution of the first-order differential equation yields a convolution equation

$$A(t) = \int_0^t k(s)\ \Omega(s)\ \exp[-(1/\tau_\mathrm{A})(t - s)]\ \mathrm{d}s \tag{20}$$

The time-dependent rate constant for energy transfer at time t is

$$k(t) = \lim_{\delta t \to 0}\left[-\frac{\delta\Omega'(t)}{\delta t}\right] \tag{21}$$

where $-\delta'\Omega(t)$ is the probability that the donor excitation has been transferred to the acceptor via energy transfer in the time interval δt. In terms of $\Omega(t + \delta t)$ and $\Omega^0(t + \delta t)$, $\delta\Omega'(t)$ is given by

$$\delta\Omega'(t) = \Omega(t + \delta t) - \Omega^0(t + \delta t) \tag{22}$$

Comparing with eq 12, one can further have

$$\delta\Omega'(t) = E(t)\ \delta\Omega(t) \tag{23}$$

Inserting eqs 21 and 23 into eq 20, one obtains

$$A(t) = -\int_0^t E(s)\ \Omega(s)\ \exp[-(1/\tau_\mathrm{A})(t - s)]\ \mathrm{d}\Omega(s) \tag{24}$$

Numerical solution can be easily carried out for the above equation.

III. Results and Discussion

Numerical solutions of relevant equations were performed on an Apollo computer. Solution of eq 3 was achieved by reducing the variables t and r to nondimensional variables T and h. The variables T and h are defined as

$$T = Dt/R_n^{\ 2} \tag{25}$$

and

$$h = r/R_n \tag{26}$$

In terms of the new variables, eq 3 is rewritten as

$$\frac{\partial S(h, T)}{\partial T} = \frac{\partial^2 S(h, T)}{\partial h^2} + \left(3h - \frac{2}{h}\right)\frac{\partial S(h,T)}{\partial h} + \left(\frac{2}{h^2} + 3\right)S(h, T) - \frac{S(h,T)}{D\tau}R_n^{\ 2} - \frac{R_n^{\ 2}}{D\tau}\left(\frac{R_0}{R_n h}\right)^6 S(h, T) \tag{27}$$

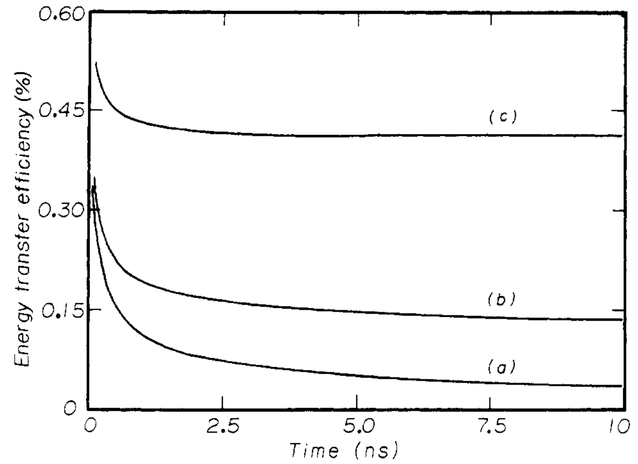

Figure 1. Transient energy-transfer efficiencies, $E(t)$, computed from eq 12. Results are obtained by assuming that any approach of the end groups by a distance R_a lower than 7 Å results in instantaneous energy transfer: (a) $D = 1.0 \times 10^{-8}$ cm^{-2} s; (b) $D = 4.0 \times 10^{-6}$ cm^{-2} s; (c) $D = 3.0 \times 10^{-5}$ cm^{-2} s.

Table I
Energy-Transfer Efficiencies Calculated Using Different Diffusion Coefficients, D[a]

D, ×10^{-7} cm^{-2} s	E, %	E (R_a = 7 Å), %	D, ×10^{-7} cm^{-2} s	E, %	E (R_a = 7 Å), %
0	6.51	6.51	80	21.5	22.1
0.1	6.64	6.64	100	23.8	24.7
1.0	7.04	7.04	150	28.7	30.3
4.0	8.04	8.04	200	32.7	35.0
10.0	9.77	9.78	300	38.7	42.6
40	15.7	16.0			

[a] R_0 = 17 Å, β = 4 Å, τ = 10 ns, n = 80.

Figure 1 illustrates transient energy-transfer efficiencies from naphthalene to anthracene groups attached to the ends of a hypothetical Gaussian chain with 80 repeat units and a statistical bond length β = 4.0 Å. The critical energy-transfer distance for the end groups is assumed to be 17 Å, and a value of 10 ns is used for the fluorescence lifetime of the donor group in the absence of energy transfer. Last, it is assumed that any approach of the donor and acceptor groups within the distance of 7 Å results in instantaneous reaction. When these values were input, transient efficiencies were computed for the chain assuming three different diffusion coefficients.

Transient energy-transfer efficiency curves change sensitively as a function of chain-end diffusion coefficients. For curve a, the diffusion coefficient of 1.0×10^{-8} cm^2/s was used. Transient energy-transfer efficiency does not reach a steady value in the time duration studied (10 ns). At time t = 10.1 ns, the transient energy-transfer efficiency decreases to 3.38% and experiences a further decrease. For curve b, the relative diffusion coefficient between the ends was assumed to be 4.0×10^{-6} cm^2/s. Transient energy-transfer efficiency does not reach a steady value during the time period studied. At time t = 10.1 ns, the transient energy-transfer efficiency decreases to 13.27% and experiences a further decrease, but the decreasing rate is much slower than that for curve a. For curve c, the diffusion coefficient of 3.0×10^{-5} cm^2/s was used. Transient energy-transfer efficiency reaches its steady value of 41.0% about 6.0 ns after its excitation.

Time-averaged energy-transfer efficiencies for the above hypothetical chains were computed using eq 13. The results are shown in Table I and Figure 2. As the diffusivity of the chain ends increases, the energy-transfer efficiency increases. Using the D value of 1.0×10^{-8} cm^2/s, the statistically averaged energy-transfer efficiency, E, given by eq 13 is calculated to be 6.64%, while the energy-transfer efficiency calculated from the equation used in previous papers,[2] assuming D = 0, is 6.51%. It is expected that by decreasing the D values, the limit of energy-transfer efficiency calculated from eq 14 should approach the E value of 6.51%.

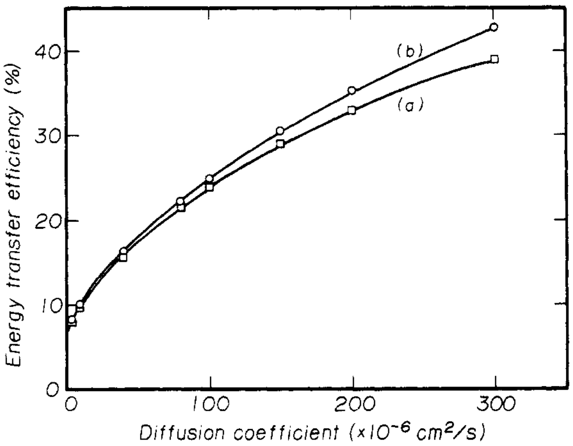

Figure 2. Time-averaged energy-transfer efficiency, E, computed from eq 13 for chains possessing different end-group diffusion coefficients: (a) R_a value assumed to be 0; (b) R_a value assumed to be 7 Å.

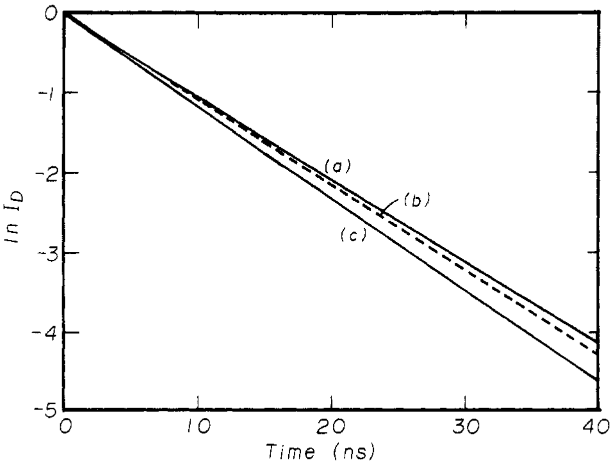

Figure 3. Donor fluorescence decay curves computed from eq 11: (a) $D = 1.0 \times 10^{-8}$ cm^{-2} s; (b) $D = 1.0 \times 10^{-6}$ cm^{-2} s; (c) $D = 4.0 \times 10^{-6}$ cm^{-2} s.

In Table I and Figure 2, two sets of energy-transfer efficiency values are given, one assuming that any approach of the two reactive species within a reactive radius of 7 Å results in instantaneous reaction and the other calculated without making the former assumption. No significant difference is observed between the two sets of values if $D < 1.0 \times 10^{-5}$ cm^2/s. Since the diffusion coefficients of the polymer chain ends are expected to have values around 1.0×10^{-6} cm^2/s, it can be concluded that this technique will not be obscured by the uncertainty in the estimation of the effective reactive radius between the chain ends.

Features of the fluorescence decay curves for end-labeled oligopeptides have been discussed by Katchalski-Katzir et al.[1] They showed that fluorescence decay curves were sensitive functions of the diffusion coefficients of chain ends. When eq 11 is used and no effective reaction radius is assumed, the computed fluorescence decay curves for the hypothetical polymer discussed above are shown in Figure 3. As the diffusion coefficient increases, donor fluorescence intensity decays faster.

In Figure 4, acceptor fluorescence decay curves for the

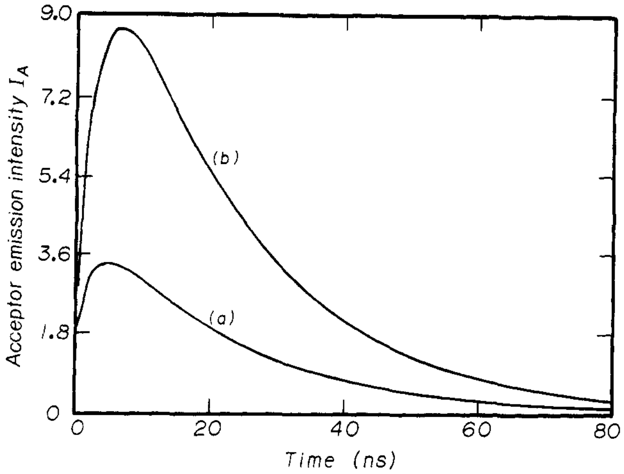

Figure 4. Acceptor fluorescence profile computed from eq 24 for chains with different end mobility: (a) $D = 1.0 \times 10^{-8}$ cm^{-2} s; (b) $D = 1.0 \times 10^{-5}$ cm^{-2} s.

polymer chains considered are shown. In the computation using eq 24, a critical energy-transfer distance of 17 Å is used, no effective reactive radius is assumed, and the fluorescence lifetime of the acceptor group is assumed to be 20 ns. Compared to the donor fluorescence decay curves shown in Figure 3, the acceptor fluorescence decay curves vary markedly when different mobilities are assumed for the polymer chain ends. The fluorescence decay curves of the acceptor group in Figure 4 were obtained assuming identical experimental conditions but different diffusivity. Under these conditions, the relative areas of the fluorescence decay curves experimentally obtained should be equal to the ratio between the areas of the two decay curves shown in Figure 4. That is, as diffusivity increases, the signal intensity increases. Identical experimental conditions are difficult to achieve; however, one is usually interested only in the shape of the fluorescence decay curves. On expanding curve a, so that the maxima of the two curves have the same value, we obtain Figure 5. The maximum positions for the two curves are different. Assuming the diffusion coefficient of 1×10^{-8} cm^2/s, the maxima of fluorescence decay occur at 2.26 ns. Assuming the diffusion coefficient of 1×10^{-5} cm^2/s, the maxima shift to 3.56 ns.

IV. Conclusions

From these studies we conclude that the relative diffusion between polymer chain ends enhances the energy-transfer efficiencies measured from steady-state techniques. Furthermore, the fluorescence decay features of the donor and acceptor groups obtained from transient measurement are also altered. These features allow one to study the diffusivity of polymer chain ends by either steady-state energy-transfer efficiency measurement or transient fluoresence techniques.

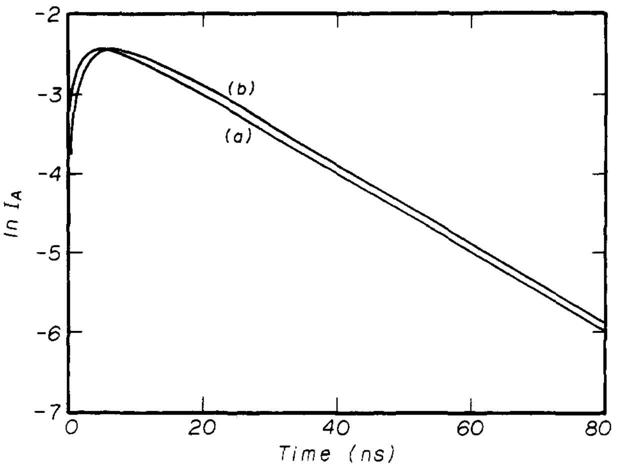

Figure 5. Acceptor fluorescence profile comparison.

Acknowledgment. We thank Prof. S. Whittington of the University of Toronto for helpful suggestions and discussions with regard to the development of the model. We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support of this work. G.L. thanks the University of Toronto for a Connaught Scholarship and for a University of Toronto Open Fellowship. J.E.G. is grateful to the Canada Council for support in the form of a Killam Research Fellowship.

References and Notes

(1) (a) Liu, G. J.; Guillet, J. E. *Macromolecules* **1990**, *23*, 1388. (b) Liu, G. J.; Guillet, J. E.; Al-Takrity, E. T. B.; Jenkins, A. D.; Walton, D. R. M. *Macromolecules* **1990**, *23*, 1393.
(2) (a) Katchalski-Katzir, E.; Haas, E.; Steinberg, I. Z. *Ann. N.Y. Acad. Sci.* **1981**, *366*, 44. (b) Hass, E.; Wilchek, M.; Katchalski-Katzir, E.; Steinberg, I. Z. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 1807.
(3) For example, see: Berlman, I. B. *Energy Transfer Parameters in Aromatic Compounds*; Academic Press: New York, 1973; pp 39–44.
(4) Birks, J. B.; Leite, M. S. C. P. *J. Phys.* **1970**, *B3*, 513.
(5) (a) Kirkwood, J. G.; Riseman, J. *J. Am. Chem. Soc.* **1948**, *16*, 565; *J. Chem. Phys.* **1954**, *22*, 626. (b) Mandelkern, L.; Flory, P. J. *J. Chem. Phys.* **1952**, *20*, 211.
(6) Mahabadi, H. K.; O'Driscoll, K. F. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 283.
(7) See, for example: Selser, J. C. *Macromolecules* **1981**, *14*, 346.
(8) See, for example: Schachman, H. K. *Ultracentrifugation in Biochemistry*; Academic Press: New York, 1959. Williams, J. W. *Ultracentrifugation of Macromolecules*; Academic Press: New York, 1972.
(9) See, for example: Meerwall, E. V.; Grigsby, J.; Tomich, D.; Antwerp, R. V. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1037.
(10) Semylen, J. A., Ed. *Cyclic Polymers*; Elsevier Applied Science: London, 1985.
(11) Smoluchowski, M. *Z. Phys. Chem.* **1918**, *92*, 129.
(12) North, A. M.; Reed, G. A. *Trans. Faraday Soc.* **1961**, *57*, 859.
(13) North, M.; Reed, G. A. *J. Polym. Sci., Part A* **1963**, *1*, 1311.
(14) For example, see: Xu, H. M.S. Dissertation, University of Toronto, 1988.
(15) Liu, G. J.; Guillet, J. E. *Macromolecules*, in press.
(16) Liu, G. J.; Guillet, J. E. *Macromolecules*, preceding paper in this issue.

Registry No. Naphthalene, 91-20-3; anthracene, 120-12-7.