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On the Proper Use of Concentration Profiles for Determining Polymer Diffusion Coefficients via Fluorescence Nonradiative Energy Transfer

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Much effort has been devoted to measuring diffusion coefficients (D) of polymers and small molecules in a polymer matrix using fluorescence nonradiative energy transfer (NRET),[1−21] which is also called direct energy transfer. This method takes advantage of an increase in NRET when "donor" and "acceptor" chromophores come into close proximity and has been used to study interdiffusion of latex particles[2−14] and probe diffusion in rubbery and glassy polymers.[18−20] While this represents a significant experimental advance, there are concerns related to the analysis for calculating D values, namely the use of improper concentration profiles which is occurring in NRET studies and leading sometimes to unphysical interpretations. This note, limited to interdiffusion of identical distributions of species, discusses such cases in order to reduce confusion in the analysis of NRET data used for quantitatively measuring diffusion.

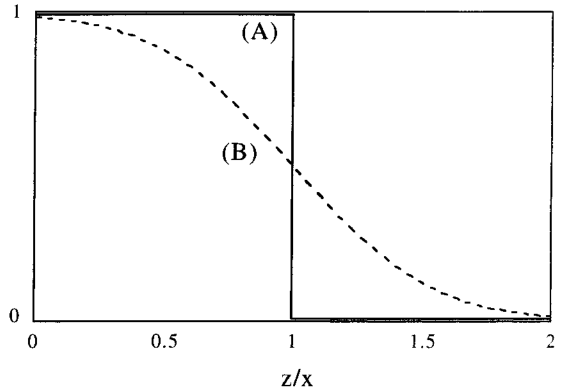

Figure 1. Normalized concentration profile for donor-labeled polymers interdiffusing into acceptor-labeled polymers of identical chemical species and molecular weight (A) before annealing and (B) at annealing times long enough to be described by Fickian diffusion. Note that at very short annealing times, before some or all of the chains have diffused distances on the order of their radius of gyration, the profile is not expected to be Fickian,[22] as effects of reptation and/or segmental motion rather than center-of-mass diffusion tend to dominate the profile at such short times.

Figure 1 shows a model NRET system for measuring polymer diffusion. The system consists of two sandwiched films, one having chains labeled with donor, the other with acceptor. Upon interdiffusion, NRET increases, allowing calculation of D given proper data analysis. This requires use of appropriate concentration profiles of donor- and acceptor-labeled chains, a troublesome issue in the NRET literature. At very short diffusion times, before chains have diffused a few radii of gyration, the concentration profile is not Fickian and may be very complex, as with long chains annealed for times less than the reptation time.[22] After chains have interdiffused more than a few radii of gyration, diffusion is Fickian, provided the chains are monodisperse and chemically identical. Under these conditions, the normalized concentration profiles of donor- and acceptor-labeled chains are[23]

$$C_{DN}(z,t) = \frac{C_D}{C_{DO}} = q\left\{1 + 2\sum_{n=1}^{\infty} \frac{\exp[-(\pi nq)^2\beta]\,\sin(\pi nq)\,\cos\left(\frac{\pi nqz}{x}\right)}{\pi nq}\right\} \tag{1a}$$

$$C_{AN}(z,t) = \frac{C_A}{C_{AO}} = 1 - C_{DN}(z,t) \tag{1b}$$

where C_D and C_A are donor and acceptor concentrations, C_{D0} and C_{A0} are initial donor and acceptor concentrations prior to annealing, t is diffusion time, x is donor film thickness, y is acceptor film thickness, z is the spatial coordinate through the film, $q = x/(x + y)$, and $\beta = Dt/x^2$. An alternate expression for the donor concentration profile, valid for $t < x^2/(16D)$, is[24]

$$C_{DN}(z,t) = \frac{1}{2}\left[1 - \mathrm{erf}\left(\frac{z - x}{2\sqrt{Dt}}\right)\right] \tag{2}$$

Equation 2 is derived assuming that diffusing molecules at the front of the profile never reach a physical boundary; i.e., a boundary condition at infinity is used. Problems in the literature are a result of improper application of such equations.

The most common employment of improper concentration profiles in NRET studies is the use[2−10,14,17] of eq 2 (or an equivalent form with another coordinate system) rather than eq 1a for times when eq 2 is not valid. At long times, $t > x^2/(16D)$ in the case of Figure 1,[24] the full solution (eq 1) must be used. Inspection of the literature[2−10,14,17] reveals that NRET data taken at long times (when eq 2 is invalid[25]) have been fit with eq 2 (or an equivalent error function form[26]) to calculate D values. The effect on determined D values is shown in figure 2 for a hypothetical polystyrene system[16] ($D = 1 \times 10^{-14}$ cm^2/s, $x = 1$ μm, molecular weight $M = 20\,000$, and a Förster radius of 2.2 nm). D values obtained from eq 2 relative to those from eq 1a ($D = 1 \times 10^{-14}$ cm^2/s) were calculated as a function of time. Figure 2 shows that D values from eq 2 are identical to those from eq 1a at short times, but diverge at later times, because eq 2 is invalid when $t > x^2/(16D)$. (The Figure 2 inset shows the invalidity of the error function profile at long times.) Thus, there is a dramatic effect when incorrect concentration profiles are used in analyzing NRET data, yielding an apparent trend in D that is not representative of the nature of diffusion.

A second example of improper analysis is the use of a Fickian profile for extremely short diffusion times. It has been noted[1] that conventional modeling[16] of the case in Figure 1 may be suspect if profiles are extremely steep, i.e., when there are large gradients in concentration over distances for which NRET occurs (~2−4 nm). A correction factor was introduced to account for this, and calculations[1] indicated that this problem is significant at extremely short times (when diffusion distance $(Dt)^{1/2}$ is comparable to the polymer radius of gyration).

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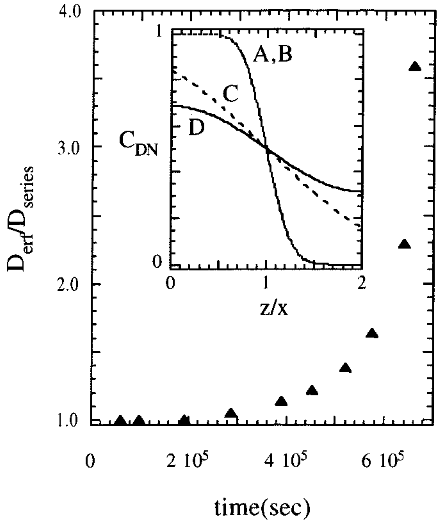

Figure 2. Polymer diffusion coefficients as a function of time calculated from eq 2 (D_{erf}) relative to those calculated from eq 1 (D_{series} − the actual value), for NRET simulations on a polystyrene system of the geometry in Figure 1 with molecular weight M = 20 000, having a diffusion coefficient $D = 1 \times 10^{-14}$ cm^2/s, with a donor-labeled film of thickness $x = 1\ \mu$m, and an acceptor-labeled film thickness $y \geq x$, using a Förster radius of 2.2 nm. Inset: concentration profiles for donor-labeled chains for this system, calculated from both eqs 1 and 2, at two different times, $t = 2 \times 10^4$ s and $t = 5 \times 10^5$ s. (A) Key: eq 1 at $t = 2 \times 10^4$ s; (B) eq 2 at $t = 2 \times 10^4$ s; (C) eq 2 at $t = 5 \times 10^5$ s; (*D*) eq 1 at $t = 5 \times 10^5$ s).

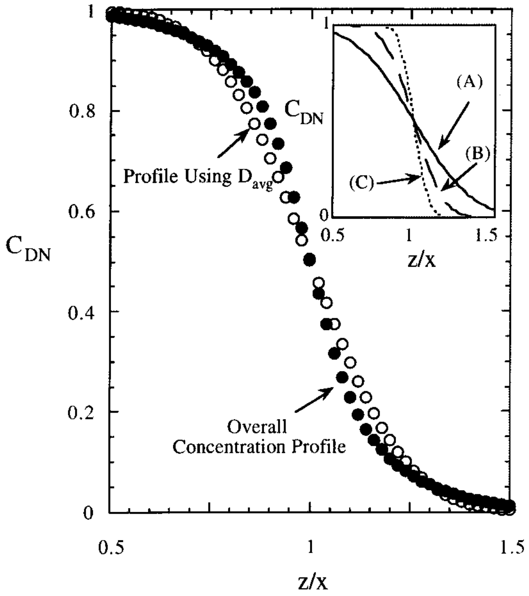

Figure 3. Overall concentration profile for a system with 1/3 by number of each of three chain lengths, *n*: $n = 1000$, 2000, and 4000 at $(D_{1000}t)^{1/2}/x = 0.2$, calculated two separate ways: (●) adding up the three profiles and dividing by 3 and (○) using the average diffusion coefficient D_{av} in eq 1. Inset: Fickian concentration profiles for each of these three chain lengths, assuming an M^{-2} scaling dependence for *D*. Key: (A) $n = 1000$; (B) $n = 2000$; (C) $n = 4000$).

However, these calculations[1] were done assuming a Fickian profile. Since diffusion is not Fickian[5,22] at such short times, the validity of the correction is in doubt.

A final problem is the use of eqs 1 and 2 in NRET analysis of polydisperse systems.[2−14] Rigorously, the overall concentration profile of a polydisperse system is a weighted sum of contributions from each molecular weight. While the profile is Fickian for an individual molecular weight, the sum is not. Figure 3, which considers a system with equal numbers of chains of length $n = 1000$, 2000, and 4000, shows that fitting a polydisperse system with a Fickian profile is invalid. Assuming reptation ($D \sim M^{-2}$), the overall concentration profile of donor-labeled chains (calculated via eq 1) is plotted at a time corresponding to $(Dt)^{1/2}/x = 0.2$ (*D* for $n = 1000$) and compared to the profile generated by assuming that energy transfer efficiencies can be analyzed by inserting the appropriate D_{av} into eq 1. Clearly, the profiles do not overlap; inserting D_{av} into eq 1 does not describe the system.[27] Thus, if the overall profile is fit to eq 1 for an apparent diffusion coefficient, it may not be strictly meaningful from a diffusion standpoint.

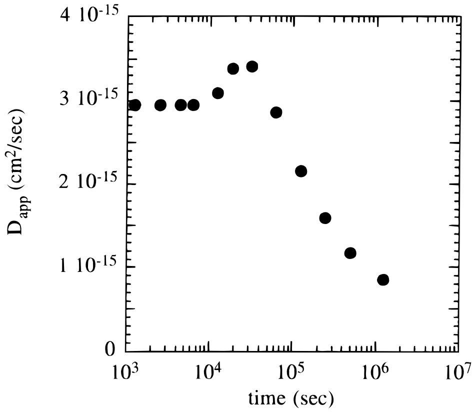

Figure 4. Apparent diffusion coefficient D_{app} that would be calculated for the system in Figure 3 as a function of time if the overall concentration profile were fit to eq 1 for one diffusion coefficient. (A value of $D_{1000}/x^2 = 1.6 \times 10^{-5}$ s is used for all calculations.) Since the system is polydisperse, one apparent diffusion coefficient does not describe the system, leading inherently to a D_{app} that changes with time.[32]

A commonly reported trend[2−10] of *D* values decreasing with increasing time in latex interdiffusion is partially related to this practice. The explanation for the apparent decrease has been that in polydisperse systems short chains diffuse faster than long chains, so diffusion at early times is more sensitive to short chains. However, as long as the matrix into which the chains diffuse does not change with time, the case for identical polydisperse latex particles, the *D* value of any single chain will be time invariant (chains must be experiencing Rouse diffusion or annealing times in excess of the reptation time).[28] Thus, the average diffusion coefficient, D_{av}, is time invariant, and the reported *D* values are not related to D_{av}.[29] The fact that *D apparently* drops with diffusion time is a consequence of the analysis. This is shown in Figure 4, which illustrates the *apparent* drop in *D* that occurs[30,31] when the polydisperse system in figure 3 is analyzed as if it were monodisperse; i.e., the overall concentration profile is fit to eq 1 to calculate one diffusion coefficient D_{app}. This is another example of an apparent diffusion trend having nothing to do with the physics of the system but which is the result of inappropriate analysis.

In summary, NRET is a powerful, inexpensive tool for measuring diffusion in polymers and, in certain cases, as for latex interdiffusion and small molecule diffusion in polymers, offers significant advantages over other methods. Many researchers,[1−14,16−20] especially Winnik, have contributed toward making NRET measurement of diffusion in polymers nearly routine. However, before the use of improper concentration profiles becomes standard in this area, it is essential to provide our best understanding of the correct analysis method. Most importantly, the use of the error function form of the Fickian profile must be limited to sufficiently short diffusion times for which it is valid.[31] Additionally, a Fickian profile is invalid at diffusion times so short that center of mass displacement has not exceeded several polymer radii of gyration,[28] and a single Fickian profile is not strictly correct for polydisperse systems. For polydisperse systems it is suggested that NRET data be analyzed via a diffusion distribution postulated from the known molecular weight distribution (connected to it via Rouse and/or reptational laws) and fitting the resulting weighted sum over eq 1 to the data. Such an approach is practiced in pulsed-field-gradient NMR analysis of diffusion. It is also suggested that data at the shortest annealing times not be used in determination of D, because precision dictates that the concentration profile should be developed before D can be extracted with confidence and because of the complexity and uncertainty in describing the concentration profile for long chains which have not undergone an annealing time in excess of the reptation time. Failure to apply these rules may result in unphysical, apparent trends in diffusion which relate only to the analysis method. While these points may require reconsideration of interpretations reached in some studies, they in no way diminish the power of NRET or the advances made in developing the technique for measuring diffusion in polymers. In fact, with use of appropriate concentration profiles in NRET analysis, highly reliable, quantitative interpretations of diffusion in polymeric media are possible.

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References and Notes

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(25) The error function profile also proves invalid in interdiffusion of latex particles analyzed via spherical coordinates, as in refs 2−5, 13, and 14, when the use of an infinite boundary condition is no longer valid. This occurs when diffusion from a donor-labeled particle into an acceptor-labeled particle occurs over sufficiently long times that the donor concentration profile begins to overlap with that from a second donor-labeled particle also interdiffusing into the acceptor-labeled particle, i.e., when a boundary condition at infinity is invalid.
(26) Similar effects would be observed for latex particles when an error function concentration profile is used with spherical coordinates; the invalidity of employing the error function profile at long times is not due to the coordinate system used in the analysis.
(27) This theoretical sample has a polydispersity of 1.29, well below that for a sample made by free radical polymerization. As a result, given that the differences between "overall" and assumed Fickian diffusion profiles are evident in Figure 3 for this sample, even larger differences would be expected for samples used in typical experiments. Finally, a rigorously correct, overall diffusion profile can be calculated for a continuous molecular weight distribution sample such as that resulting from free radical polymerization (and characterized by gel permeation chromatography).
(28) Farinha et al.[5] noted the questionable nature of using an error function Fickian concentration profile for polydisperse systems when the longer chains have not had sufficient annealing time to exceed their reptation time (equivalent to diffusing several radii of gyration or more). This is because such longer chains do not experience Fickian diffusion at such short times.[5,22] (In another manuscript, Farinha et al.[1] missed this point and analyzed diffusion with a Fickian concentration profile for time frames too short for their chains to diffuse several radii of gyration.)
(29) Winnik and co-workers[6] considered effects of polydispersity by simulating a fluorescence donor intensity decay curve assuming a distribution of diffusion coefficients and then determining the appropriateness of fitting such a profile with an apparent diffusion coefficient using a single Fickian concentration profile. The appropriateness of such an approach to describe diffusion of a polydisperse system was determined by obtaining a small enough χ^2 value for the fit of the simulated data. While this is a necessary condition for determining appropriateness, it is not sufficient as one must also consider whether unphysical interpretations (diffusion slowing with annealing time) result from the fits. In systems with interdiffusion of identical distributions of species, at times in excess of the reptation time all species maintain time invariant diffusion coefficients; therefore, both instantaneous and average (time-averaged and averaged over species) diffusion coefficients should be time invariant as well.
(30) We note that the slight increase in "apparent" diffusion coefficient observed at intermediate times in Figure 4 is not normally reported in Winnik's studies but is not entirely at odds with his experience. In ref 6, a small increase in D was reported at intermediate times prior to a decrease at longer times when analysis was done for a simulated, relatively narrow polydispersity sample. However, we caution that one should not associate a specific physical cause with this increase as we it find to be associated with the vagaries of the minimization of error in the fitting routine.
(31) Another caution concerning the fitting of diffusion data from polydisperse samples is that eq 1, modified to account for a summation of mobilities in accord with the molecular weight distribution, should be used at all times sufficiently long for the assumption of a boundary condition at infinity to be invalid for the shortest chains in the system, i.e., when the error function concentration profile is invalid for the shortest chains. For a system of high polydispersity, as with the presence of oligomers in latex particles, this may require that the summation form of the Fickian concentration profile be used at nearly all diffusion times.
(32) D_{app} would be expected to deviate from its initial value at earlier times for systems of latex spheres, due to the overlap in concentration profiles caused by multiple spheres interdiffusing with one another; see ref 25.

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