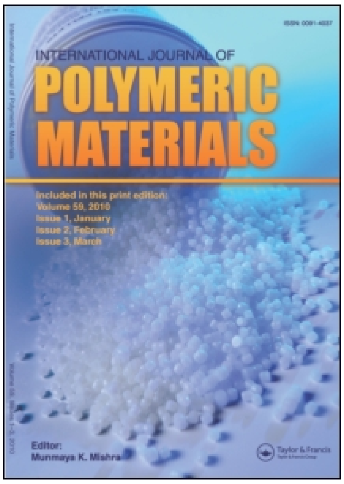

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Simulation of Direct Electronic Energy Transfer between Donors and Acceptors Embedded in a Rubbery Phase Network in Glassy Particles

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By direct electronic energy transfer fluorescence technique the temporal behavior of donors in the presence of acceptors when both types of molecules are embedded in a rubbery phase PIB forming an interconnected network within glassy PMMA spheres is studied. The experimental results are compared with simulations of the decay curves in (i) bag of marbles geometry where the PMMA particles are formed of glassy marbles, and the PIB fills the intervening spaces, (ii) the rubbery phase forms channels in the otherwise solid glassy PMMA sphere. For the latter case we analyzed both parallel and perpendicular PIB channels. The experimental and simulated data are compared by both the fractal analysis method and by obtaining the Klafter–Blumen dimension from the derivative of the $\ln(\ln I)$ with respect to $\ln t$. On the basis of our results we give preference to the rubbery PIB channels within solid glassy PMMA model over the bag of marbles model.

KEY WORDS Fluorescence decay, direct energy transfer, apparent dimension, model simulations.

1. INTRODUCTION

Nonradiative direct electronic energy transfer (DET) between donor and acceptor molecules, or groups in a condensed phase has been studied by many researchers over the last forty years. The conventional approach in these studies was to follow the quenching reaction of optically excited donors in the presence of ground-state acceptors. DET was first studied by Förster[1] in systems where the acceptors are randomly distributed in the three dimensional (3D) rigid medium. Theoretical formulation of the excitation transfer in two dimensions (2D) was proposed by Wolber and Hudson[2] and by Zumofen and Blumen.[3] Donor fluorescence decay functions were calculated by Hauser *et al.*[4] and Baumann and Foyer[5] in respective dimensionalities for excitation transfer processes. These ideas have been extended to DET on fractal structures with self-similarity and dilation symmetry by Klafter and Blumen.[6,7] Donor fluorescence decay in these systems was found to produce fractional dimensions.

When the donors and acceptors are confined to small spaces curious features appear in the donor fluorescence function,[8] which is due to the finite distribution of the molecules. The idea of DET consequence in a restricted geometry was first proposed by El-Sayeed[9,10] and developed theoretically by Klafter, Blumen and Zumofen. Some of these ideas were experimentally tested in porous silicas,[11] vycor glass,[10] cylindrical pore polymer membranes[12] and polymer colloids.[13,14] Fluorescent dyes and phosphorescent groups adsorbed on the surface in these spaces can undergo energy transfer within this restricted environment.

In the studies of polymer colloids, where the donors and acceptors are attached as labels to PIB which forms an interpenetrating rubbery network within glassy PMMA particles, various geometries have been suggested for the rubbery PIB phase.[14] The simplest model, where the PMMA forms a core and the PIB a shell around it, has been rejected. The bag of marbles model assumes that the PMMA particle is formed of small glassy spheres glued together with rubbery PIB. Such structure is roughly similar to concrete. Alternately the PMMA particles may be solid except for rubbery PIB channels penetrating them and forming a network.

As 95% of the medium is composed of the glassy material, we find it extremely unlikely that such a high filling factor is possible without mashing the constituent spheres. In this work the Monte-Carlo technique is used to determine the temporal behavior of the donor intensity $I(t)$ via direct dipolar energy transfer process in three geometries, namely long parallel cylinders, perpendicular cylinders and mashed spheres.

The parallel and perpendicular cylinders are representative of two PIB channels passing near each other. In an interpenetrating network there must be many instances of such channels being close to each other. The channels would pass by each other at random angles and various distances. We expect the Klafter–Blumen dimension $d_{\mathrm{KB}}(t)$ to lie somewhere between the two cases simulated here if this model is valid.

Mashed spheres with diameters greater than the distances between them are used to simulate the bag of marbles model. We feel that as 92 to 95% of the medium is composed of the glassy material, it is extremely unlikely that such high filling factors are possible without mashing the constituent spheres into each other.

The results are fitted to Klafter–Blumen equation and simulated data are analyzing to determine the dimension from the $\mathrm{dln}[-\ln I(t)]/\mathrm{dln}t$ versus $\ln t$ plot. The results were also tested by the fractal analysis (FA) technique.

The experimental results were analyzed by the FA technique[14] and the apparent dimensions d_{FA} were calculated as well as a degree of deviation χ^2. Here they were also tested by deconvolving them with their respective lamp functions and then obtaining the $d_{\mathrm{KB}}(t)$ as a function of $\ln t$.

2. THEORY

Following Förster[1] we note that the life-time of an isolated donor is determined by its natural decay rate. If there is an acceptor in the vicinity, the donor can also undergo induced decay via DET. For the donor-acceptor distance r, the combined decay of the donor is governed by

$$f(t,r) = \exp\left\{-\frac{t}{\tau_0}\left[1+\left(\frac{r_0}{r}\right)^6\right]\right\}. \qquad (1)$$

The neglect of the angular dependences corresponds to averaging over all angles. Here r_0 is the distance where the induced decay rate due to DET is equal to the natural radiative decay rate τ_0 of the donor.

If there is probability p that the acceptor site is full then the ensemble averaged probability that the donor has not decayed by the time t is

$$f(t,r) = \exp\left(-\frac{t}{\tau_0}\right)\left\{(1-p) + p\exp\left[-\frac{t}{\tau_0}\left(\frac{r_0}{r}\right)^6\right]\right\}. \quad (2)$$

In reality $p \ll 1$ as only a minute fraction of the many sites on a given lattice is filled. In this limit the binomial distribution can be replaced by the Poisson law distribution $g(j) = e^{-p}p^j/j!$. For many acceptors A_i occupying the sites $\boldsymbol{X}_i$, the life-time of a donor located at $\boldsymbol{Y}_j$ is governed by

$$f(t,Y_j) = \exp\left(-\frac{t}{\tau_0}\right)\exp\left\{-p\sum_i\left[1-\exp\left(-\frac{t}{\tau_0}\right)\left(\frac{r_0}{r_{ij}}\right)^6\right]\right\}, \quad (3)$$

where $r_{ij} = |\boldsymbol{X}_i - \boldsymbol{Y}_j|$.

For acceptors distributed uniformly the sum can be replaced with an integral. This has been generalized by Klafter and Blumen[6,7] to include all infinite and uniform media of euclidean or fractal dimension d, as

$$f(t,Y_j) = \exp\left(-\frac{t}{\tau_0}\right)\exp\left[-p\rho_0 V_d r_0^d \Gamma\left(1-\frac{d}{6}\right)t^{d/6}\right]. \quad (4)$$

Here Γ is the gamma function, ρ_0 is the density of acceptor sites and V_d is the volume of the unit sphere in d dimensions.

3. CALCULATION

We simulated the decay of the donors when they and the acceptors were placed in the following geometries: two long and parallel cylinders, and two long and perpendicular cylinders; in both cases the distance between the axes were set to be a few times the radii and much shorter than the length of the cylinders. We also placed the donors and acceptors in the spaces left outside the mashed balls. The balls were centered at the vertex points of a simple cubic lattice. We do not believe that the constituent balls form such a regular structure. But as we are interested in time-scales much less than the typical time when the donor "sees" the boundary of the unit cell the errors caused by this regularity are insignificant.

In each case the donor and acceptor sites were placed by assigning random coordinates within the object. For the cylindrical objects the z coordinate, azimuthal angle and the square of the radius were chosen randomly.[15] For the bag of marbles model random sites were chosen within the unit cell. The sites were then rejected, if they happened to occur within a constituent ball and accepted if they occurred in the rubbery phase. Only acceptors were placed in the surrounding cells.

The interaction between the donors and acceptors were treated according to Equation (4). Acceptor sites were assumed to have the Poisson distribution of average p-acceptors in them. The donor had equal probability of being in any of the randomly selected donor sites.

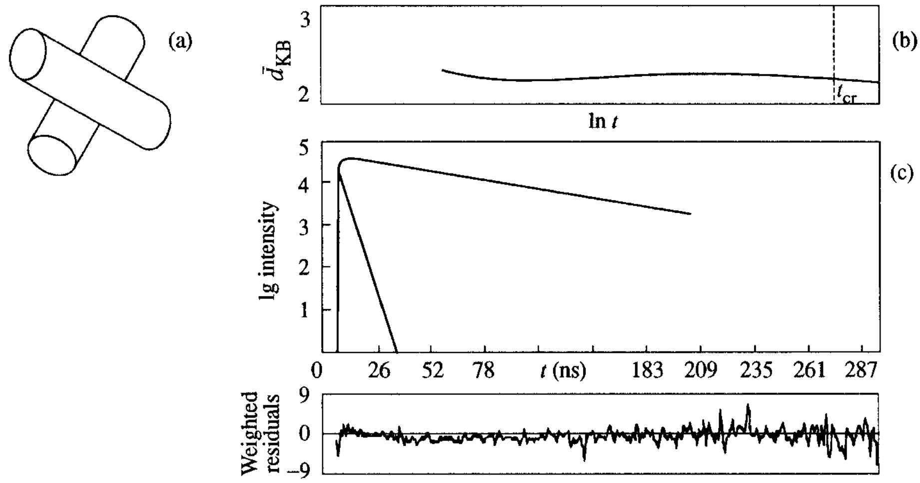

FIGURE 1 (a) Perpendicular cylinders. (b) Apparent dimension versus $\ln t$ for the perpendicular cylinders model. (c) Simulated lamp and donor decay functions for the perpendicular cylinders model. ($d_{FA} = 1.212$, $\chi^2 = 2.968$).

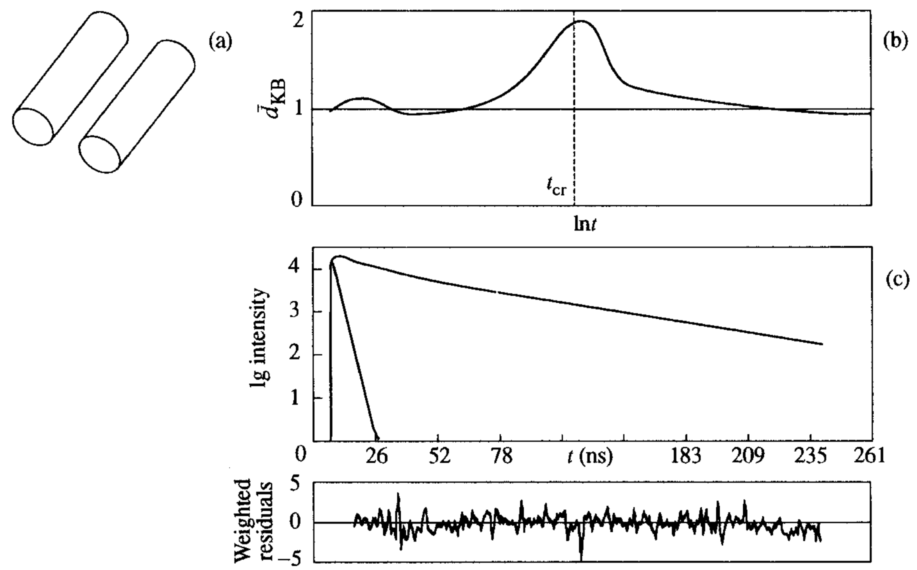

FIGURE 2 (a) Parallel cylinders. (b) Apparent dimension versus $\ln t$ for the parallel cylinders model. (c) Simulated lamp and donor decay functions for the parallel cylinders model. ($d_{FA} = 2.076$, $\chi^2 = 1.818$).

Factoring out the natural decay by defining $\Phi(t) = \exp(t/\tau_0)\sum f(t, Y_j)$ one obtains

$$\ln[-\ln\Phi(t)] = \ln[p\rho_0 V_d r_0^d \Gamma(1 - d/6)] + (d/6)\ln t. \tag{5}$$

For each object we plotted $d_{KB}(t) = 6\partial\ln[-\ln\Phi(t)]/\partial\ln t$ versus $\ln t$ (Figure 1–3). Equation (5) indicates that this is the dimension the donor sees at that time.

The experimental decay curves were deconvolved with the experimental lamp function data (Figure 4). They were then analyzed in the same way as the simulated data. Although

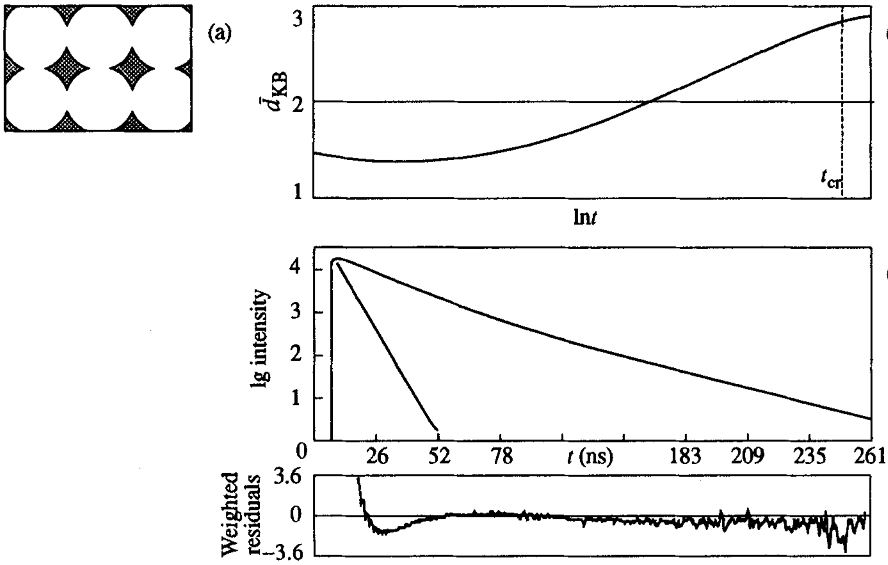

FIGURE 3 (a) Mashed spheres. (b) Apparent dimension versus $\ln t$ for the mashed spheres model. ($d_{FA} = 3.278$, $\chi^2 = 0.427$).

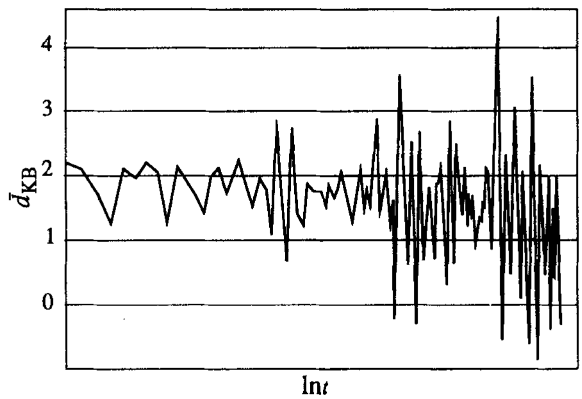

FIGURE 4 Apparent dimension versus $\ln t$ obtained by deconvolving the experimental donor decay curve with the relevant lamp function.

the reported results were recorded at the high noise level it can be seen from the Figure 4 that this analysis gives an apparent dimension of about 1.5.

The experimental data were fitted to Equation (5) giving an apparent dimension of 2. The simulated data were also fitted to this equation to obtain apparent dimensions for the studied models. For this analysis we convolved the simulated data with an assumed exponential lamp function. Then random noise was added to the data.

4. RESULTS AND DISCUSSION

The $d_{KB}(t)$ method gives d slightly above 1 for perpendicular rods (Figure 1a, b). For the parallel rods the dimension is about 2 at times comparable to the time-scale when the donors in one rod see the acceptors in the other one. At times much less and much greater than this time-scale, the apparent dimension is about one (Figure 2a, b). In actual case there will be tubes of rubbery PIB passing close to each other at various distances and angles. Then the apparent dimension according to this model is about 1.5.

The apparent dimension obtainable for the mashed balls model is somewhat above 2 for time-scales long compared to the time when the donors see the width of the filament they are in, and short compared to the time they see the edge of the unit cube. For times shorter and longer than this limit, the apparent dimension approaches 3 (Figure 3a, b). The long time limit is obviously stems from the regular structure assumed for the constituent balls. Since the actual structure is likely to be random, this long time limit is not applicable until the donors begin to see beyond the largest of the constituent balls. However, even in the interim region the apparent dimension is always above 1.5.

The apparent dimension obtainable for the experimental decay curves is between 1 and 2 (Figure 4). Thus penetrating rubbery PIB tubes model better explains the experimental data in $d_{\mathrm{KB}}(t)$ analysis even though the bag of marbles model can not be ruled out by this analysis alone.

The apparent dimension obtained by FA technique for the experimental data is 2.014. This method gives an apparent dimension of between 1 and 1.5 for the perpendicular cylinders with degree of deviation $\chi^2 = 2.97$ (Figure 1c) and between 2 and 2.2 with $\chi^2 = 1.8$ (Figure 2c) for the parallel ones at the time the donors see the other cylinder. The apparent dimension for the bag of marbles model is above 3 with deviation $\chi^2 = 0.43$ (Figure 3c). This analysis clearly favors the rubbery tubes model over the bag of marbles one.

Note that in all cases the FA method gave a larger value for the apparent dimension than the average value of $d_{\mathrm{KB}}(t)$. This difference may be due to noise. In simulations the dimension obtained from the FA method increased with increasing noise level when all other parameters were kept constant.

References

1. T. Förster, *Z. Naturforsch.*, **A**, 321 (1949).
2. P. K. Wolber and B. S. Hudson, *Biophys. J.*, **28**, 197 (1979).
3. G. Zumofen and A. Blumen, *J. Chem. Phys.*, **76**, 3713 (1982).
4. M. Hauser, U. K. Klein, and M. Z. Gösele, *Z. Phys. Chem.*, **101**, 255 (1976).
5. J. Baumann and M. D. Fayer, *J. Chem. Phys.*, **85**, 4087 (1986).
6. J. Klafter and A. Blumen, *J. Chem. Phys.*, **80**, 875 (1984).
7. J. Klafter and A. Blumen, *J. Lumin.*, **34**, 2632 (1985).
8. A. Blumen, J. Klafter, and G. Zumofen, *Optical Spectroscopy of Glasses*, Ed. I. Zschokke (Reidel, Dordrecht, Holland, 1986).
9. C. L. Yang, P. Evesque, and M. A. El-Sayeed, *J. Phys. Chem.*, **90**, 1284 (1986).
10. C. L. Yang, P. Evesque, and M. A. El-Sayeed, *J. Phys. Chem.*, **99**, 3442 (1989).
11. D. Rujans, *Phys. Rev. Lett.*, **56**, 2505 (1986).
12. W. D. Dozier, J. M. Drake, and J. Klafter, *Phys. Rev. Lett.*, **56**, 97 (1986).
13. Ö Pekcan, M. A. Winnik, and M. D. Croucher, *Phys. Rev. Lett.*, **61**, 641 (1988).
14. Ö Pekcan, L. S., M. A. Winnik, and M. D. Croucher, *Macromolecules*, **23**, 2210 (1990).
15. A. K. Akal, *Graduation Thesis*, İTÜ Phys. Dep. (1991).