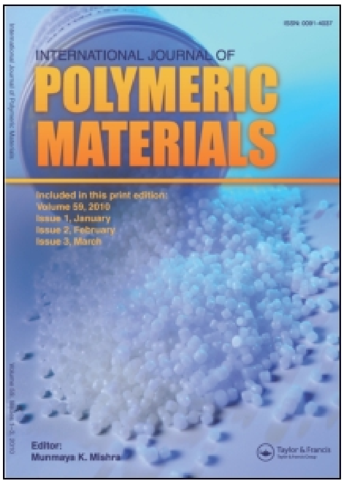

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Highly Swelled Networks in Polymer Particles; an Application of Exponential Series Method

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Highly Swelled Networks in Polymer Particles; an Application of Exponential Series Method

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The direct energy transfer method was used to trace swelling phenomena in rubbery network of glassy polymer particles. Fluorescence measurements were carried out in poly(vinyl acetate) particles which were prepared by dispersion polymerization in isooctane using a copolymer of 2-ethylhexyl methacrylate as a steric stabilizer. These reactive particles were treated with 2-(1-naphthyl)ethanol to produce particles specifically labelled in the stabilizer phase. Energy transfer experiments were carried out on the N-labelled particles doped with a hydrocarbon soluble anthracene derivative which dissolved exclusively in the rubbery poly(2-ethylhexyl methacrylate) (PEHMA) phase. Donor fluorescence decay profiles were measured, and the data were fitted to the Klafter–Blumen (KB) model for energy transfer on fractal. The exponential series method was used to obtain the lifetime distributions and the inverted KB equation was applied to interpret the results. The finding that the effective dimensionality $d = 2$ for this energy transfer process was interpreted in terms of a crossover in a restricted geometry if PEHMA was present in the form of interconnected long viggle threads. This idea was supported by our data that swelling agents for PEHMA, such as hexadecane, are also taken up by the particle from the pentane solution. Experiments on these particles yield d values that increase with increasing hexadecane until d becomes equal to 3.0. Further swelling measurements were performed with the cyclohexane as a swelling agent. We found that energy transfer kinetics obeyed the Stern–Volmer type of relation in the highly swollen, nonrestricted PEHMA phase.

KEY WORDS Direct energy transfer method, fluorescence, graft copolymer.

INTRODUCTION

The direct energy transfer (DET) method and fluorescence decay measurements are routinely applied to many heterogeneous systems. The distribution of probe molecules embedded in fractal lattice[1] or in restricted geometries[2] has been described using fluorescence spectroscopy with DET. Special attention has been given to porous glass,[3] silica[4] and polymer membranes.[5]

Recently we reported that a local structure of interpenetrating network-like morphology can be characterized by the DET technique in polymer membranes[6] as well as in latex particles.[7]

In such systems one might expect the distribution of donor life times. The exponential series method (ESM)[8–10] has been used to establish fluorescence lifetime distributions from both simulated and experimental decay data.[11–16] This method is based on obtaining the coefficients of an exponential series with the fixed lifetime. In fact, obtaining of fluorescence distribution lifetimes from the fluorescence decay data is closely related to inversion of the Laplace transforms. In other words, the fluorescence law can be described by the Laplace transform of a known distribution function. The inverse Laplace transform of the well-known Förster decay law[3,4] in high viscous systems has been used to interpret some simulated and experimental decay data.[1,2]

A more general form of the Förster decay law is known as the Klafter–Blumen (KB) equation.[5,6] The KB equation was derived to explain the donor decay in a fractal object in the presence of acceptors, however it was used to study effective dimensionality in restricted geometries.[2,7,17]

In this paper we used the Laplace transform of the KB equation. The obtained distribution function was compared with the experimentally determined lifetime distributions which were derived from polymer particles. ESM was used to find an underlying distribution of lifetimes from experimentally obtained donor decays.

In this work we report the results of swelling experiments on submicron poly(vinyl acetate) (PVA_c) particles which contain 4 monomer mol % of poly(2-ethylhexyl methacrylate) (PEHMA) in the form of the PVA_c-PEHMA graft copolymer.[18] These particles are prepared by the dispersion polymerization technique.[19] We have previously shown that much of the PEHMA is trapped in the interior of these particles,[18] and suggested an interpenetrating network (IPN) model for the global morphology of the particles.[20] Here we consider the usage of fluorescence spectroscopy and ESM measurements to characterize the local structure of such systems with a global IPN morphology.

We have applied the ESM method to examine how a PEHMA phase with an effective dimensionality $d = 2$ can be changed to $d = 3$ within the submicron particles. Using a highly swollen agent, we have shown that in these PVA_c particles the PEHMA phase can be swollen to diffusion controlled media.

THEORETICAL CONSIDERATIONS

A number of fitting methods has been proposed in order to analyze non-exponential fluorescence patterns and obtain information on the underlying systems. A very useful relation was derived by Klafter and Blumen[15] to analyze the fluorescence decay profiles of an excited donor surrounded by acceptors in a fractal object. They made use of the classical DET method to find the following functional form

$$\phi(t) = \exp(-at - bt^{\beta}), \tag{1}$$

where

$$a = \tau_0^{-1}, \qquad b = P\tau^{-\beta}, \qquad P = A\Gamma(1 - d/6)$$
$$\text{and} \quad \beta = d/6. \tag{2}$$

Here τ_0 is the excited donor lifetime, A is the time independent constant proportional to the number of acceptors within the critical DET radius R_0, $\Gamma(x)$ is the gamma function and d represents the fractal dimension $(1 < d < 3)$. It is noteworthy that without other characterization techniques, fitting non-exponential decay curves to Equation (1) may not confirm or even imply that the underlying structure is really a fractal. Similar non-exponential patterns, which are described by Equation (1) with a fractional dimension, can also be obtained in restricted geometries of known shapes.[17–22] When DET experiments are performed on conventional geometric systems of sizes small enough to influence molecular reactions, nonintegral values of d can result from the crossover phenomena between classical dimensions.[5,7,23] For geometric systems such as cylinders and spheres characterized by their radius R, it is the relation between R_0 and R that determines the decay behavior of $\phi(t)$ during the DET experiments.

In this study a relation is derived for distinguishing the system of conventional geometries from the self-similar structures. Here a self-similar structure means that there is no typical length to characterize it, R_0 remaining the only length during the DET processes. Equation (1) was inverted by using the following relation

$$\phi(t) = \int_0^\infty F(k)\exp(-kt)\mathrm{d}k, \tag{3}$$

where $k = \tau^{-1}$.

Applying the straightforward Laplace transform techniques, the inverted form of the KB equation is obtained as:

$$F(k) = R(\beta)^{-1/2}\exp\left(-\frac{(k-a)^\beta}{\beta b}\right)^{(\beta-1)^{-1}}, \tag{4}$$

where

$$R(\beta) = 2\pi(\beta-1)\beta b\left(-\frac{(k-a)}{\beta b}\right)^{(\beta-2)/(\beta-1)} \tag{5}$$

$F(k)$ represents the distribution of inverse lifetimes ($\tau = k^{-1}$) with the dimensionality ($\beta = d/6$) and contains more information than Equation (1). (See below).

The distribution function $F(k)$ becomes meaningful, when the experimentally observed fluorescence decay curve $I(t)$ is fitted to Equation (3) by using

$$I(t) = \int_0^t L(t)\phi(t-s)\mathrm{d}s. \tag{6}$$

Here $L(t)$ is the instrument response function. This is a well known fitting procedure called the exponential series method.[8–11]

EXPERIMENTAL

The molecules 1-naphthylmethyl pivalete (NMP) and 9-anthrylmethyl pivalete (AMP) were purified by chromatography over silica and twice recrystallized from pentane, thereafter they were used as model compounds. The polymer materials were prepared by dispersion polymerization (isooctane) of vinyl acetate in the presence of PEHMA containing 5 mol % reactive-NCO groups. Small amounts of naphthalene groups were attached to the PEHMA component by reaction with 2-(1-naphthyl)ethanol, with the remaining NCO groups reacting with n-octanol thereafter.[21]

These materials were analyzed for composition, purity, and chromophore content by ^{1}H-NMR ($CDCl_3$ solutions), UV-spectroscopy (ethyl acetate solutions), and gel permeation chromatography (also ethyl acetate). The N-labelled particles contained

4.1 monomer mol % (8.3 wt %) PEHMA and 4.4×10^{-6} M g^{-1} N groups (0.69 mol % N in the PEHMA phase) and are referred to as No. 7.

Samples of No. 7 were placed into a centrifuge tube to be then dispersed in n-pentane. Then certain amounts of AMP were added. After 3 h, the samples were centrifuged, decanted and dried under vacuum (10^{-1} Torr, 24 h). The powder obtained was placed in a 0.2 cm quartz UV cell for fluorescence decay analysis (front surface geometry). Subsequently, all the samples were dissolved in a certain amount of ethyl acetate, and the AMP concentration was determined by UV spectroscopy. A film of this solution was then prepared on the inner surface of a 12 mm outer diameter quartz tube using a rotary evaporator, with fluorescence decay measurements made on this transformed sample.

Alternatively, known amounts of the No. 7 particles, AMP and hexadecane were mixed with pentane in a small round-bottom flask. After 3 h, much of the pentane had evaporated, and the remainder was removed under vacuum on a rotary evaporator. The particles were dried overnight under vacuum (10^{-1} Torr) and then transferred as was described above to a 0.2 cm quartz UV cell. Some experiments were carried out on dispersions of the No. 7 particles in hexadecane and on NMP-AMP mixtures in hexadecane. Here certain amounts of material were weighed and mixed and then placed in 0.2 cm quartz UV cells for the fluorescence decay measurements. Some experiments in cyclohexane were carried out by using 4-mm inner diameter quartz tubes. Each sample here was outgassed by bubbling oxygen-free N_2 through the sample for 2 min. Cyclohexane was chosen as a highly swollen agent for No. 7 particles. NMP-AMP mixtures in cyclohexane were used for comparison and out-gassed by bubbling N_2 as described above.

Fluorescence decay profiles were obtained using a home-built apparatus for time correlated single photon counting measurements. Decay curves were analyzed using an iterative non-linear least-squares analysis program. The samples were excited (front face geometry) at 284 nm, which corresponds to the absorption band of naphthalene, with the decay profiles measured at 337 nm. In order to eliminate the color shift effect of the photomultiplier tube, the delta pulse convolution method[21] was used, with a response curve from a dilute solution of 1.4-bis (5-phenyl-1, 3-oxazol-2-yl) benzene in cyclohexane ($\tau = 1.1$ ns). Light scattering from the samples was minimized by optical alignment as well as by using proper filters.

In the ESM analysis, $F(k)$ amplitudes were constrained to be positive in order to prevent the results from oscillating.[8] The ratio between the largest and smallest amplitudes was chosen 1–3% to obtain lifetimes from the distribution curve. The χ^2 cut off was chosen as 0.001 and $\lambda^2 < 1.20$ was obtained from both ESM and Fractal analysis. To prevent misunderstanding the amplitudes in the least square analysis were chosen to be equal.

RESULTS AND DISCUSSION

In order to interpret the results described below, it is essential that the donor group itself decays exponentially. Here we discovered unexpectedly that the No. 7 sample, in a powder form or cast as a film from a solvent, yields fluorescence decay profiles that were purely exponential over 3 decades of the decay with $\tau_0 = 66$ ns.

Energy transfer experiments were carried out on No. 7 particles doped with AMP. These particle samples were prepared by incubating a pentane dispersion of the No. 7 particles with AMP for 3 h, with the subsequent centrifuging, decanting, and drying under vacuum.

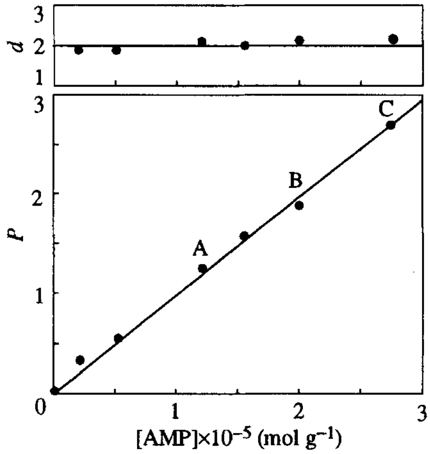

FIGURE 1 Plots of d and P versus the AMP concentration for No. 7 particles doped by the AMP. The parameters were obtained by fitting fluorescence data to Equation (1). (Samples indicated by A, B, and C were analyzed by the ESM).

The same samples were also examined after the destruction of the particle morphology. The particles dissolved to form true solutions in ethyl acetate or chloroform. UV measurements in these solutions were used to establish the AMP content of the particles. Transparent films were formed when the solutions had been placed in quartz tubes and spun-dry on a rotary evaporator.

Our assumption, which we believe to be correct, was that the initial process allows the AMP to enter only the PEHMA phase of the particles whereas, when a film is cast from the solution, the AMP is divided into both phases. The second part of the assumption can be confirmed by energy transfer measurements performed on the films. When fluorescence decays were fitted to Equation (1), we obtained $d = 3.00 \pm 0.05$ consistent with simple energy transfer in three dimensions.

When a fluorescence decay curve from a powder sample of No. 7 doped with AMP is fitted to Equation (1), we find that $d = 2$. Samples were prepared at various concentrations of AMP. In each case $d = 2$ and P values were proportional to the AMP content of the particles. These data are summarized in Figure 1.

We note that Equation (2) is fulfilled, and the line is plotted on the data points passing through the origin. After the particles had been dissolved and the components cast into a film, remeasurement of the decay profiles showed $d = 3$ in all cases.

As we stated above $d = 2.0$ does not necessarily imply that the underlying structure is a fractal. In order to explain the dimensionality of $d = 2.0$, ESM analysis was applied to experimental fluorescence decay curves, from No. 7 samples indicated by A, B, and C in Figure 1. Distribution of lifetimes recovered from ESM analysis is shown in Figure 2 for the corresponding samples with increasing AMP concentrations. Single broad distributions were observed from AMP doped No. 7 samples. A single spike at 3 ns channel was omitted from the distribution curve. Such spikes may be an artifact which commonly arises when analyzing broad distributions.[10] As concentration of AMP increased, the $F(k)$ distribution shifted to the left side of the graph.

The behavior of experimental $F(k)$ distributions may be understood by making use

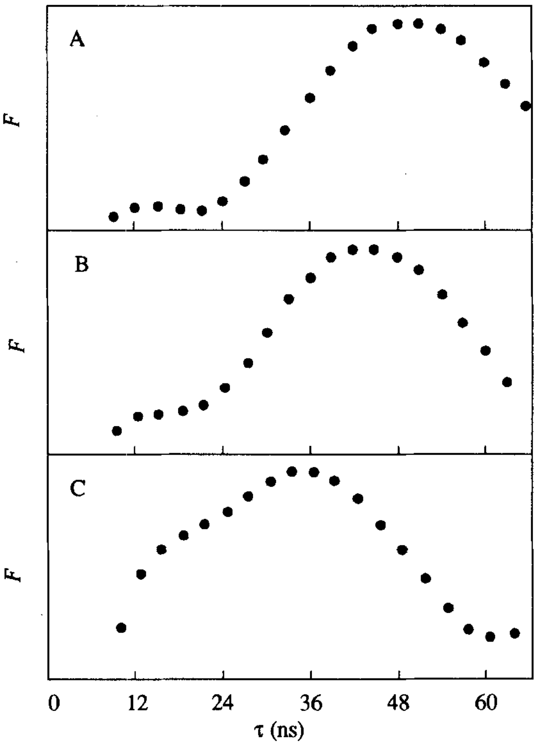

FIGURE 2 Distribution of lifetimes recovered by ESM analysis of fluorescence data for samples indicated by A, B, and C in Figure 1.

of theoretical distributions of Equation (4). In Figure 3a, b distributions obtained from Equation (4) for $d = 3$ and $d = 1.26$ are shown respectively. In both cases we took $a = 0.015\ \text{ns}^{-1}$ ($\tau_0 = 66$ ns). Superposition of these distributions is presented in Figure 4c.

In order to keep $F(k)$ amplitudes within the same scale, $b = 0.3$ and $b = 4.5$ were chosen for $d = 3$ and $d = 1.26$, respectively. Theoretical distributions from Equation (4) were generated for different combinations of $\beta(d/6)$ and b parameters for $a = 0.015\ \text{ns}^{-1}$. Superposition of these combination pairs was plotted in Figure 4a, b. When the theoretical $F(k)$ distributions in Figure 4 are compared with the ESM results in Figure 2, it is seen that the agreement is quite satisfactory. $F(k)$ distributions are found to depend strongly on the b values. As b values increase, the $F(k)$ distribution is shifted to the left, in agreement with the experimental ESM distributions in Figure 2.

From this we conclude that the ESM analysis revealed that the dimensionality $d = 2.0$ obtained from Equation (1) can be divided into to two distinct dimensions of $d = 3$ and $d = 1.26$. Here it will be meaningful to refer to the dimension in Equation (1) as an "apparent dimension" (d_{app}) which can be calculated using the theoretical $F(k)$ distribution as follows:

$$d_{\text{app}} = \frac{3\int_0^{\tau_0} F_3(k)\mathrm{d}k + 1.26\int_0^{\tau_0} F_1(k)\mathrm{d}k}{\int_0^{\tau_0} F(k)\mathrm{d}k}. \tag{7}$$

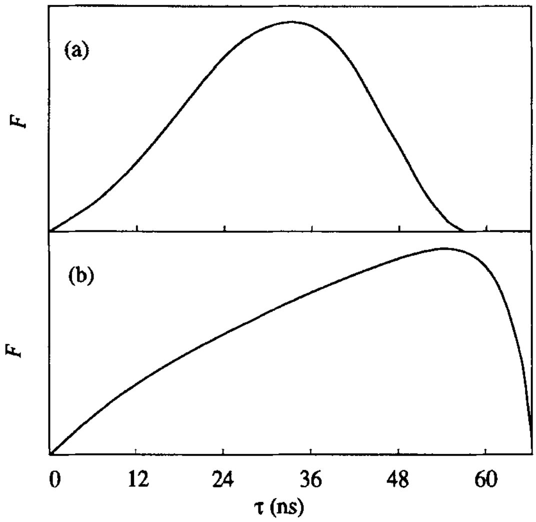

FIGURE 3 Theoretical lifetime distributions obtained from Equation (4): (a) for $d = 3$ and $b = 0.3$; (b) for $d = 1.26$ and $b = 4.5$. In both cases $a = 0.0151$ ns^{-1} was used.

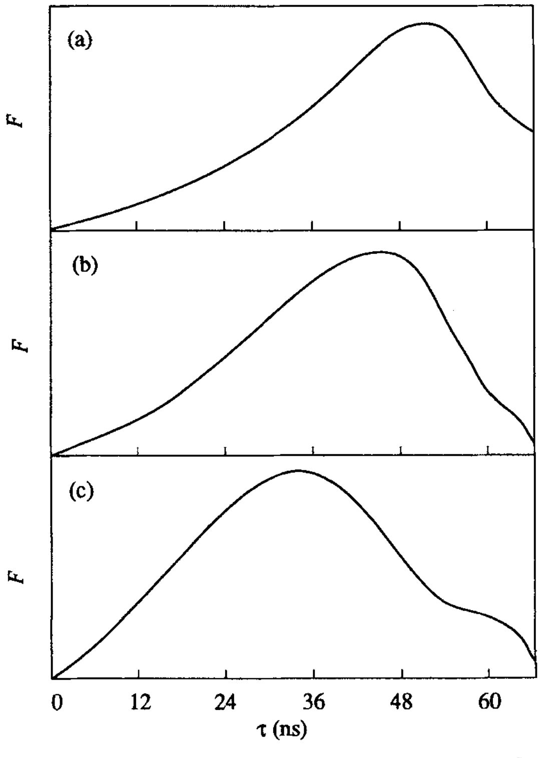

FIGURE 4 Superposition of theoretical lifetime distributions obtained from Equation (4): (a) for $d = 3$, $b = 0.17$ and $d = 1.26$, $b = 3.0$; (b) for $d = 3$, $b = 0.21$ and $d = 1.26$, $b = 4.0$; (c) for $d = 3$, $b = 0.3$ and $d = 1.26$, $b = 4.5$. In all cases $a = 0.0151$ ns^{-1} was used.

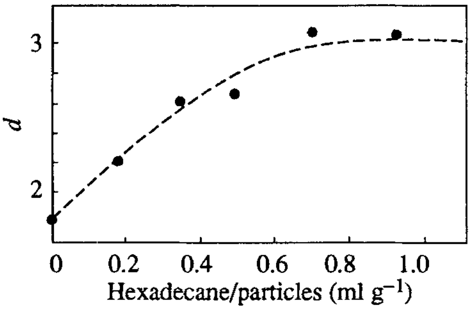

FIGURE 5 Evaluation of the effective dimensionality of d of the PEHMA phase as a function of added hexadecane.

Using the above equation the apparent dimensions of systems in Figure 4a, b, c were calculated and found to be $d_{\mathrm{app}} = 2.26, 2.37$, and 2.38, respectively. The corresponding apparent dimensions for No. 7 samples A, B, and C in Figure 1 were found to be $d_{\mathrm{app}} = 2.34$, 2.28, and 2.34.

Agreement between theoretical and experimental results is here highly provocative. ESM results may be explained by the concept of restricted geometries.[2,17,22] For instance, if the donor and acceptor molecules are randomly distributed in the IPN of highly wiggled PEHMA thread of radius R, the decay occurs in an effectively $d = 3$ region where only the immediate neighborhood inside the thread is probed in the limiting case of short times $t \ll (R/R_0)^6\tau_0$. However, for long time periods, $t \gg (R/R_0)^6\tau_0$ where the long range distribution of the acceptors is probed, the decay corresponds to DET in fractal region of $d = 1.26$, implying a Koch curve-like structure for the "threads".

Hexadecane is a good solvent and a swelling agent for PEHMA. When particle dispersions of No. 7 in pentane are mixed with hexadecane and AMP and then evaporated to dryness, both solutes mix with the PEHMA phase. We cannot establish which fraction of the hexadecane enters the particles and which remains on the surface. The results shown in Figure 5 demonstrate that increasing amounts of hexadecane added in this way cause d to increase. The PEHMA threads grow thicker until $d = 3$.

The PVA$_c$ particles form stable colloidal dispersions in both hexadecane and cyclohexane. We wished to find out what would happen to the shape of the decay profiles for the No. 7 particles when they were dispersed in hexadecane and cyclohexane containing AMP. The fluorescence decays for the hexadecane dispersions give reasonable fits to Equation (1) and yield the data plotted in Figure 6. The effective dimensionality was found to be $d = 2.93$ (indistinguishable from $d = 3$).

$F(k)$ distributions of ESM results and their theoretical counterparts are presented in Figure 7 for the hexadecane dispersion indicated by D, E, and F in Figure 6. These $F(k)$ distributions are much narrower than those of powder No. 7 samples. The ESM results of powder samples are compared with the hexadecane samples in Figure 8. The resolution between the dimensions of $d = 2.3$ and $d = 3.0$ is quite satisfactory, which suggests that the inverted KB equation together with the ESM analysis is a powerful tool to analyze the dimensionality in such complicated systems.

Dispersions of No. 7 in cyclohexane containing AMP yield simple exponential fluorescence decays, and the obtained lifetimes fit the Stern–Volmer equation. We write this

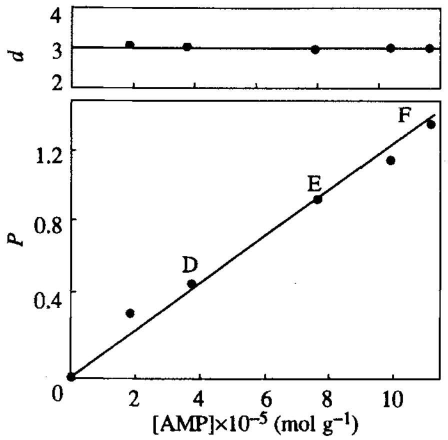

FIGURE 6 Plot of d and P for samples of No. 7 dispersed in hexadecane containing various concentrations of the AMP (samples D, E, and F).

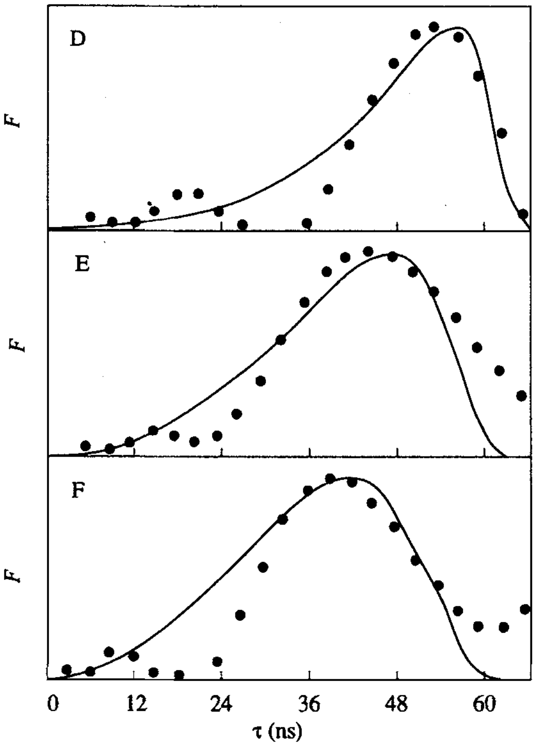

FIGURE 7 Comparison of theoretical $F(k)$ distributions (solid curves) with distributions of lifetimes recovered by the ESM analysis of fluorescence data for samples indicated by D, E, and F in Figure 6. Theoretical distributions are obtained from Equation (4). In all cases $d = 3$ and $a = 0.0151$ ns^{-1} were used.

expression as

$$I_D(t) = I_0\exp(-t/\tau_N) \tag{8}$$

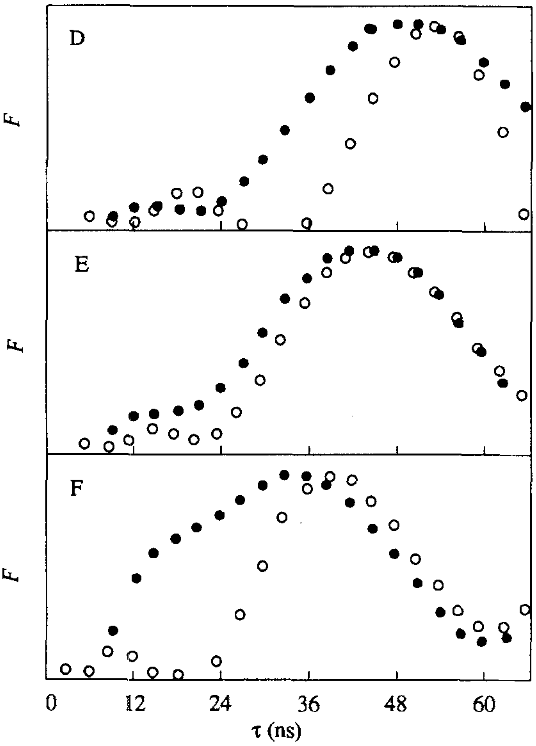

FIGURE 8 Comparison of ESM distributions of powder No. 7 particles with hexadecane swollen particles for samples indicated by D, E, and F in Figure 6 at different values d. ●, $d = 2$; ○, $d = 3$.

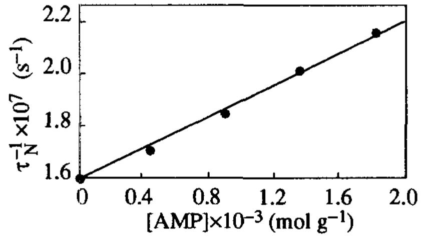

FIGURE 9 Plot of the Stern–Volmer relation in Equation (7) for dispersion of No. 7 particles in cyclohexane for various AMP concentrations.

to emphasize the exponential form obtained for the fluorescence decays, where

$$\tau_N^{-1} = \tau_0^{-1} + ak_q[\text{AMP}]. \tag{9}$$

We plotted τ_N^{-1} versus [AMP] concentration in Figure 9. The slope of this plot was ak_q, where a was the partition coefficient for AMP in the system. If $a = 1$, we obtained $k_q = 3.3 \times 10^9$ M^{-1} s^{-1}, which was 3.7 times smaller than the values obtained for NMP plus AMP in cyclohexane.[24] In the latter experiment, both species could diffuse whereas in the labelled particle only AMP diffusion contributed to the energy transfer. As a consequence, the assumption that $a = 1$ suggests that diffusion of AMP in the cyclohexane-swollen PEHMA phase is only about 1.8 times slower than in cyclohexane. We refer to this region as a diffusion-controlled medium.

Fluorescence decay from particles dispersed in hexadecane and cyclohexane shows very different behaviors. The first set obeys Equation (1), which suggests the absence of a diffusion contribution to energy transfer, whereas the second set obeys Equation (8), where the presence of hydrocarbon liquid promotes a diffusion controlled energy transfer.

In this work we have shown that the inverted KB equation (Equation (4)), together with the ESM analysis can be used to obtain morphological information about the disordered condensed matter system.

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