

DISPERSIVE ELECTRONIC EXCITATION TRANSPORT IN POLYMERIC SOLIDS AT AND NEAR ROOM TEMPERATURE

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Time-resolved fluorescence depolarization is used to examine electronic excitation transport among naphthalene chromophores in a polymeric solid as a function of excitation wavelength between 300 and 50 K. The characteristics of the wavelength and temperature dependences reveal, for the first time, that dispersive transport occurs at and near room temperature. The rate of excitation transport depends on the wavelength of excitation. A theoretical treatment is able to reproduce the essential features of the wavelength and temperature dependences without recourse to adjustable parameters by avoiding the complexities of the relationship between the difference in energy of a pair of molecules and the pairwise transfer rate.

1. Introduction

During the past decade there have been tremendous advances in understanding electronic excitation transport and in utilizing the phenomenon as a probe of the spatial distribution of molecules in complex molecular systems. In studies of randomly distributed molecules in solution [1-3], molecules on surfaces [4], chromophores in micelles [5], and chromophores in polymeric systems [6-10], the emphasis has been on the relationship between the spatial distribution of the chromophores and an observable related to excitation transport. The development of accurate statistical mechanical transport theories [11,12] has turned excitation transport into a powerful probe of the structure of complex material.

In these room temperature studies, the basic quantum mechanical description of the distance dependent pairwise transfer rate is that given by Förster in his pioneering work forty years ago [13]. Förster's theory expresses the pairwise transfer rate in terms of the spectral overlap of the emission spectrum of the donor and the absorption spectrum of the acceptor. Consider donor to donor transfer; the accep-

tor is chemically identical to the donor. The Förster theory assumes that the donors' spectral lines are homogeneously broadened, i.e. thermal fluctuations in the solvent broaden the spectrum to an extent which is much greater than the inhomogeneous linewidth. Since all donors are assumed to have identical energies, it is unnecessary to consider explicitly how thermal energy will be taken up from or given off to the heat bath (solvent) to make up electronic excitation energy mismatches between donors.

At low temperature (≈ 4 K) it is well established that inhomogeneous linewidths in both glasses [14] and crystals [15] are much greater than the homogeneous widths. Experimental work by a number of investigators [16-20] has been concerned with donor-donor (DD) excitation transport in this situation. When kT is much less than the inhomogeneous linewidth, an excitation not only moves spatially, but it also cascades toward lower energy. The excitation can move toward the red edge of the absorption line by transferring to a lower energy donor and emitting a phonon (heat). Once the excitation has moved to lower energy, absorption of a phonon is required to transfer to a higher energy donor. At low temperature, the necessary phonons are not available. As the excitation moves to the red, the rate of excitation transport slows because the density of molecules available to accept the excitation is reduced. This type

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of excitation dynamics has been termed dispersive transport. In these experiments, as time evolves, fluorescence or phosphorescence is observed to broaden and shift towards lower energy [16-20].

Here, we report the first observation of dispersive energy transport at higher temperatures, up to room temperature. By monitoring the rate of fluorescence depolarization from chromophores in a polymer glass, we have measured different rates of energy transport as the excitation frequency is changed across the S_0 - S_1 electronic absorption of naphthyl chromophores attached to a polymer chain. The sensitivity of the fluorescence depolarization observable makes it possible to investigate dispersive transport at high temperatures where previous experimental methods, e.g. observation of spectral broadening and spectral diffusion, have not been successful.

Theoretically modeling dispersive transport is complex because it is necessary to treat the influence of the differences in chromophore transition energies on transport dynamics in addition to considering the spatial distribution of chromophores. At low temperatures, where the inhomogeneous linewidth is much greater than the homogeneous width, a narrow distribution of energies is initially excited and essentially all transfer events move the excitation to lower energy. Since the typical energy difference between the donor and the acceptor is large ($>kT$), back transfer to the original donor is not possible. Theories which consider phonon assisted hopping [21] or a trapping rate constant which depends on time [16,22] have been proposed for such conditions. Monte Carlo simulations [16,22,23] have been compared to the theories and in some cases used to model experimental results.

At room temperature the problem is more complex because the inhomogeneous and homogeneous linewidths are comparable. Many chromophores will reside within a spread of energies of width kT about the initial donor energy. Therefore, for many of the transfer events, back transfer to the initially excited chromophore is possible. Because the homogeneous linewidth is broad, initial excitation populates a wide distribution of energies across the inhomogeneous line. Therefore in calculating an observable, it is necessary to consider dispersive transport which begins at a large number of positions in the inhomogeneous line simultaneously. Furthermore, in describing the

dynamics of chromophores attached, in low concentration, to the backbone of a polymer chain, it is necessary to include the nonrandom spatial distribution of chromophores in a calculation.

We have developed a description of high temperature dispersive transport based on a cumulant expansion treatment of nondispersive transport developed by Huber et al. [24] for randomly distributed systems and extended by Peterson and Fayer [25] to handle finite size polymer systems. Although the method is approximate, it is able to come close to reproducing the wavelength and temperature dependences of the transport observable without recourse to adjustable parameters.

2. Experimental procedures

The experimental apparatus for measuring time-resolved fluorescence depolarization has been described previously [7,8]. A 25 ps UV pulse from a frequency doubled, Nd:YAG pumped dye laser excites naphthyl chromophores in the origin of the S_0 - S_1 electronic transition which is centered at 319.5 nm (31299 cm^{-1}). Fluorescence polarized parallel (I_{\parallel}) and perpendicular (I_{\perp}) to the polarization of the incident light is detected with a microchannel plate photomultiplier, digitized, and stored on a computer. Temperature measurements below room temperature are made in a He closed cycle refrigerator.

The polymer samples are solid blends of poly(2-vinylnaphthalene-co-methyl methacrylate) and poly(methyl methacrylate) made by heat molding above the glass transition temperature. The copolymers contain vinylnaphthyl monomers which were incorporated randomly into the chain by a free radical polymerization following the procedure of Fox et al. [26]. Two different copolymers were used in this study: (I) $M_w \approx 22700$, $M_w/M_n = 1.3$, with 9% vinylnaphthyl monomers, (II) $M_w \approx 50000$, with 1 or no vinylnaphthyl monomer per chain. The preparation of the copolymers and blends have been described previously [6-8]. The copolymers are present in the blend in such a low concentration (0.38% by weight for (I)) that no interchain electronic energy transport can occur. Thus, if energy transport occurs, it is three dimensional among naphthyl chromophores on a single polymer chain.

The fluorescence polarized parallel to the excitation light (I_{\parallel}) and the fluorescence polarized perpendicular to the excitation pulse (I_{\perp}) are related to the fluorescence anisotropy $r(t)$ of the naphthyl chromophores by

$$\begin{aligned} I_{\parallel}(t) &= \exp(-t/\tau) (1 + 2r(t)), \\ I_{\perp}(t) &= \exp(-t/\tau) (1 - r(t)), \end{aligned} \quad (1)$$

where τ is the fluorescence lifetime. $r(t)$ is obtained from the parallel and perpendicular data sets

$$r(t) = [I_{\parallel}(t) - I_{\perp}(t)] / [I_{\parallel}(t) + 2I_{\perp}(t)]. \quad (2)$$

$r(t)$ is independent of the fluorescence lifetime; the anisotropy decays in time as a result of chromophore motion and excitation transport.

In blends containing copolymer (I) excitation transport is the main source of time-dependent fluorescence depolarization. Excitation transport takes the initial excitation into the ensemble of other unexcited chromophores with random transition dipole directions. Subsequent emission results in fluorescence depolarization [27]. Rotation of the chromophores is also responsible for a small amount of time-dependent depolarization on the time scale of this experiment. There is also a time-independent source of depolarization, i.e. the naphthyl transition is not perfectly polarized.

The initial fluorescence polarization is lost by transport as $G^s(t)$, the probability of finding the excitation on the initially excited chromophore, decays [27]. $G^s(t)$ is a fundamental quantity which characterizes transport [27]. As described in previous work [6-8] $G^s(t)$ is obtained from $r(t)$ determined from two different samples. One sample is a blend of copolymer (I) in PMMA. The other blend is composed of copolymer (II) in PMMA, in which excitation transport does not take place ($G^s(t) = 1$), but rotational and time-independent fluorescence depolarization occurs. The time-resolved fluorescence anisotropy from all sources of depolarization is given by

$$r(t) = G^s(t) \Phi(t) C. \quad (3)$$

$\Phi(t)$ is the contribution to the time-dependent anisotropy from rotational motion, C is from the time-independent sources of depolarization. $G^s(t)$, the transport contribution to the time-dependent an-

isotropy, is obtained by dividing the anisotropies obtained from the two samples:

$$G^s(t) = r_I(t) / r_{II}(t). \quad (4)$$

3. Results and discussion

The inhomogeneous linewidth of the S_0 - S_1 transition was measured by absorption spectroscopy at low temperatures. Measurements at a number of low temperatures showed that the spectral linewidth was independent of temperature (see table 1). The inhomogeneous width is a substantial portion of the total linewidth at room temperature.

Fig. 1 shows the excitation wavelength dependence of excited state transport ($G^s(t)$) at 250 K. $G^s(t)$ is the probability that the originally excited chromophore is still excited at a later time t . It has two contributions, excitations which have not left the originally excited chromophore and excitations which transfer away but then return to the initially excited chromophore. The decay of $G^s(t)$ is determined by the transfer rates among chromophores and the spatial distribution of chromophores [25]. In fig. 1, it can be seen that $G^s(t)$ depends on the S_0 - S_1 transition energy of the initially excited chromophores. As the excitation wavelength is shifted to lower energy, the decay of $G^s(t)$ slows down. The 2 nm shift corresponds to 194 cm^{-1} , which is a significant fraction of the inhomogeneous width. Thus, excited state transport among the naphthyl subunits in these polymer blends is dispersive. A similar, but less pronounced, wavelength dependence was observed at room temperature [28].

To describe these results and the temperature-dependent data presented below, we will briefly outline a theoretical treatment which will be presented in detail elsewhere [28]. A theory has previously been developed to calculate $G^s(t)$ for a given distribution

Table 1
Absorption linewidth of naphthyl tagged PMMA

Temperature (K)	kT (cm^{-1})	Measured fwhm (cm^{-1})
297	206	410
100	70	300
50	35	300

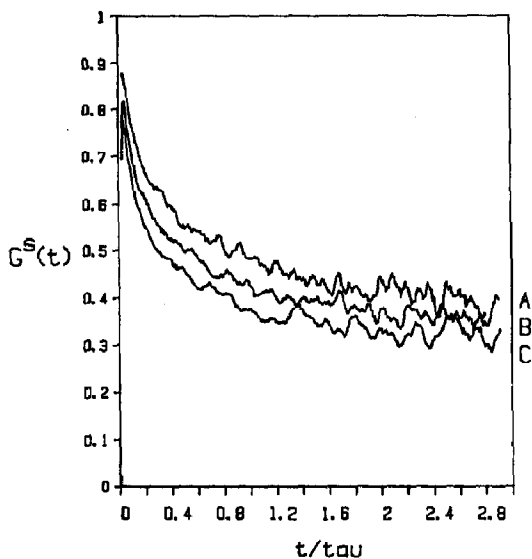


Fig. 1. $G^s(t)$ for 2-vinylnaphthyl donors excited at three different wavelengths in the absorption line: (A) 322 nm (31056 cm^{-1}), (B) 321 nm (31153 cm^{-1}), (C) 320 nm (31250 cm^{-1}). The decay of $G^s(t)$ reflects the rate of excitation transport. The rate of excitation transport depends on the excitation wavelength. This is the signature of dispersive excitation transport. The sample temperature is 250 K. The sample is a solid blend of 0.38% by weight poly(2-vinylnaphthalene-co-methyl methacrylate) in bulk PMMA. The copolymer ($M_w \approx 22700$) contains 9% 2-vinylnaphthalene monomers randomly distributed along the polymer chain.

of chromophores, random or nonrandom, in a finite volume [25]. The theory is an extension of a first order cumulant expansion developed by Huber et al. [24], for nondispersive donor-donor (DD) transport. It is also possible to extend the Förster treatment of donor-trap (DT) transfer, in which only forward transfer can take place, to nonrandom finite volume systems [29]. These expressions are unified by a scaling factor λ [29],

$$\ln G^s(t) = -(\rho/\lambda) \int \{1 - \exp[-\lambda\omega(\mathbf{r})t]\} u(\mathbf{r}) d\mathbf{r}, \quad (5)$$

where $\lambda=1$ for DT and $\lambda=2$ for DD transfer. $u(\mathbf{r})$ is the chromophore pair correlation function, ρ is the density of chromophores, and $\omega(\mathbf{r})$ is the rate of excitation transfer by a dipole-dipole mechanism and is given by

$$\omega(\mathbf{r}) = (1/\tau) (R_0/r)^6 \gamma^2. \quad (6)$$

τ is the excited state lifetime and R_0 is the critical Förster transfer radius [13]. $\gamma=0.8468$ is a factor which accounts for the static transition dipole orientations of the chromophores in the polymeric glass [27].

The dispersive excitation transport shown in fig. 1 can be modeled by assuming that some of the chromophores available for transfer undergo DD transfer with the excited chromophore and the others undergo DT transfer. There is also a fraction of chromophores that are spatially close enough for transfer but have too high a transition energy to receive the excitation from the excited molecule. Once it is determined how many donors and traps there are, the calculation of $G^s(t)$ proceeds as a nondispersive transport problem in a system of donors and traps on the polymer chain. The method maps the donor-only dispersive transport problem onto the nondispersive donors and traps transport problem. This allows the powerful methods developed to handle complex nondispersive systems to be brought to bear on the dispersive transport problem.

Briefly, the calculation proceeds in the following manner. At all temperatures, the inhomogeneous absorption line is taken to be Gaussian with a full width at half maximum equal to that of the low temperature line (table 1). We assume that each site is homogeneously broadened by thermal energy, and its homogeneous lineshape is a Lorentzian of full width at half maximum equal to kT . The overlap of these Lorentzians with the excitation wavelength determines the initial distribution of excitation energies. The fractions of chromophores available for DD or DT transfer, or unavailable for transfer, are determined by spectral overlap of an initially excited Lorentzian with all other Lorentzians across the inhomogeneous line. Each excitation wavelength has its own fractions of DD, DT, and unavailable chromophores. This calculation is repeated for all chromophores which can be initially excited; and a weighted average gives $G^s(t)$. Although it ignores the details of the excitation-phonon interactions, the spectral overlap is used to account for phonon assisted transfer.

Once the DD, DT and unavailable fractions are determined, it is necessary to have a method to describe nondispersive excitation transfer in a system of donors and traps which is mathematically

straightforward enough to be used in the extensive averaging over the initial excitation energies and complex spatial geometries. While more sophisticated methods are available for infinite randomly distributed systems [30,31], the cumulant treatment given in eq. (5) has the necessary simplicity.

To handle the donor and trap problem, λ in eq. (5) is scaled linearly between the limits of $\lambda=1$ (pure DT) and $\lambda=2$ (pure DD), and ρ is appropriately scaled. We have shown that a linear scaling of λ ,

$$\lambda = 1 + D/\rho, \quad (7)$$

$$\rho = D + T, \quad (8)$$

gives a reasonable approximation for a system of donors and traps. D is the number density of chromophores which can undergo DD transfer, and T is the number density of chromophores which can participate in DT transfer.

For chromophores randomly distributed in an infinite volume, eq. (5) has an analytical solution [24]. For a given concentration of donors and traps, λ is obtained from eq. (7). Fig. 2 compares the linear scaling approach to the results of an accurate infinite

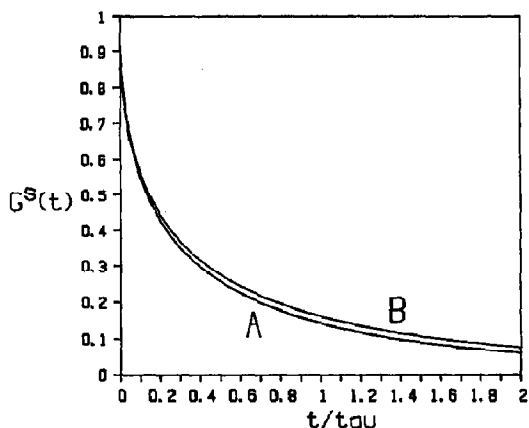


Fig. 2. Comparison of two theories for nondispersive excitation transport among randomly distributed donors and traps in an infinite volume. Curve (A) was calculated using the Loring, Andersen and Fayer theory [31], an accurate infinite order approximation. Curve (B) was calculated using the extension (described in the text) of the first order cumulant expansion method of Huber et al. [24], to a system of donors and traps. This demonstrates that a linear scaling of λ in eq. (5) permits an accurate approximation. The dimensionless, reduced concentrations used in the calculation are $C_D=0.34$ and $C_T=0.83$ ($C = \frac{4}{3} \pi R_0^3 \rho$).

order diagrammatic expansion of the Green function solution to the transport master equation [31] for the same concentrations of donors and traps. The agreement between the two theories is good, demonstrating that the linear scaling of λ provides a simple and accurate method of handling the nondispersive donor and trap problem.

Fig. 3 is a calculation of $G^S(t)$ for three different excitation wavelengths at 250 K, the temperature of the data in fig. 1. Comparing figs. 1 and 3 shows that the trend and the actual magnitudes of the curves are in near quantitative agreement. The parameters which enter into the calculation are the inhomogeneous linewidth measured at low temperature, the number of chromophores on the polymer chain (determined previously [7]), the chains' radius of gyration (determined previously [7]), R_0 (determined previously [6,8]), the excitation wavelength, and the temperature. All of these quantities are known. The reasonable agreement between figs. 1 and

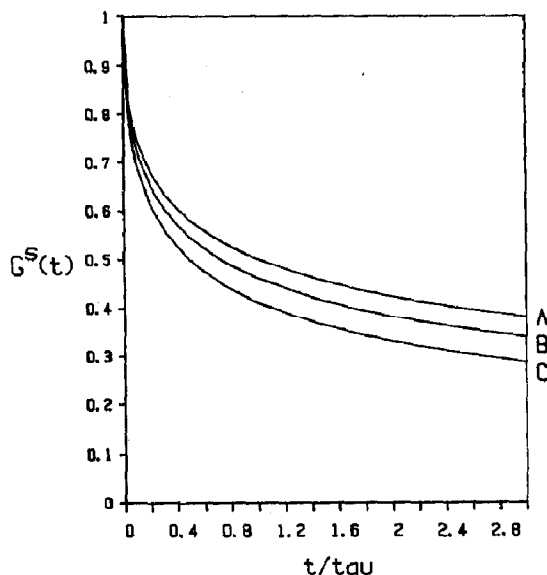


Fig. 3. Calculation of the extent of dispersive excitation transport, $G^S(t)$, for chromophores attached to a polymer chain as the excitation wavelength is varied. The temperature is 250 K, the inhomogeneous linewidth is 300 cm^{-1} , centered at 319.5 nm (31299 cm^{-1}). In curve (A) the excitation wavelength is 322 nm (31056 cm^{-1}), (B) 321 nm (31153 cm^{-1}), (C) 320 nm (31250 cm^{-1}). There are no adjustable parameters in the calculations. Comparing this figure with fig. 1 shows the near quantitative agreement between theory and experiment.

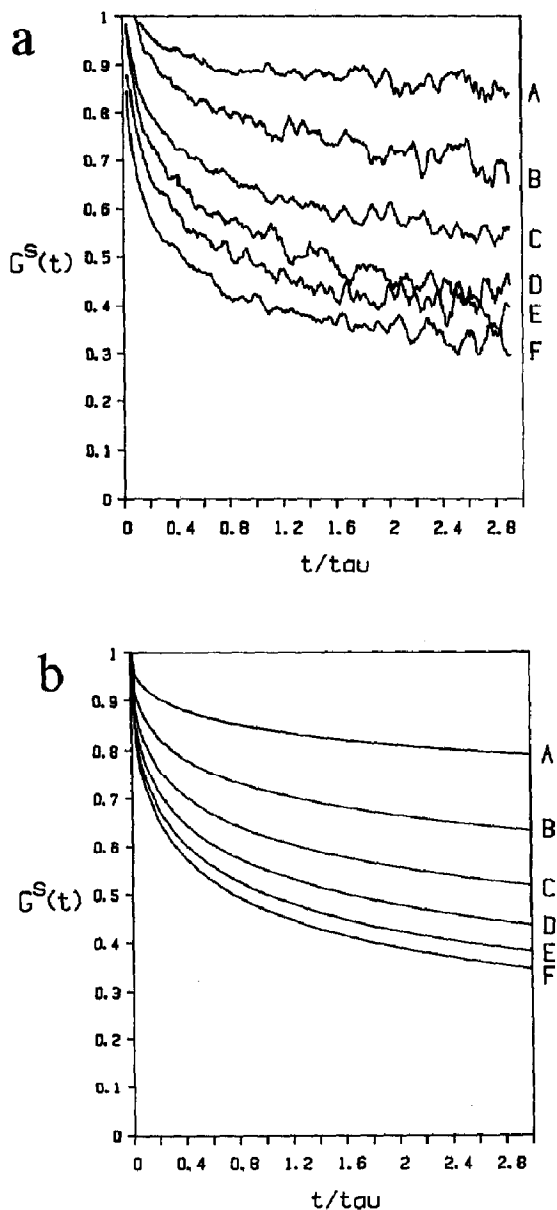


Fig. 4. (a) Temperature dependence of $G^S(t)$, which is directly related to the rate of excitation transport, for naphthyl chromophores attached to a polymer chain. The excitation wavelength is 322 nm (31056 cm^{-1}), on the red side of the naphthyl S_0-S_1 electronic transition. (A) $T=50 \text{ K}$, (B) 100 K , (C) 150 K , (D) 200 K , (E) 250 K , (F) 297 K . As the sample temperature is reduced, the rate of excitation transport is decreased. (b) Calculation of dispersive excitation transport, with no adjustable parameters, for the conditions of (a). See text for input parameters. (A) 50 K , (B) 100 K , (C) 150 K , (D) 200 K , (E) 250 K , (F) 297 K .

3 is achieved with *no adjustable parameters*.

Fig. 4a shows the variation of $G^S(t)$ with temperature for a single excitation wavelength, 322 nm. Fig. 4b displays the results of the calculations, again with no adjustable parameters. The agreement between the experiment and calculation is again reasonable. As the temperature is lowered, the width of the homogeneous line is reduced. This makes less spectral overlap at a given energy difference between two chromophores. Thus, the number of chromophores which can participate in donor-donor transfer is reduced. The relative number of chromophores participating in DT is increased, but the total number of chromophores accessible for any energy transfer is reduced, because there is less probability of transferring to chromophores higher in energy than the excitation frequency. The effect is more pronounced as the excitation wavelength is moved from the line center towards the red edge of the absorption line. It is clear from figs. 1, 3 and 4 that the basic approach used in the theoretical calculations provides a reasonable description of the wavelength and temperature dependence of dispersive transport at and near room temperature.

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