

## Fluorescence Depolarization of Chromophores in Polymeric Solids

K. A. Peterson, M. B. Zimmt,<sup>†</sup> and M. D. Fayer\**Department of Chemistry, Stanford University, Stanford, California 94305*

Y. H. Jeng and C. W. Frank

*Department of Chemical Engineering, Stanford University, Stanford, California 94305.**Received February 24, 1988; Revised Manuscript Received June 21, 1988*

**ABSTRACT:** Time-resolved fluorescence depolarization experiments are reported for systems of 1-pentylpyrene in polystyrene solid solutions. Two sources of fluorescence depolarization are examined: hindered rotational depolarization and electronic excitation transport induced depolarization. At low concentrations of 1-pentylpyrene, rotational depolarization is examined for free 1-pentylpyrene and for 1-butylpyrene end-tagged on polystyrene chains ranging in molecular weight from 3000 to 32 000. At high concentrations of free 1-pentylpyrene, electronic excitation transport increases the rate of depolarization with increasing concentration. In these room temperature samples, although the inhomogeneous optical line width is comparable to the available thermal energy,  $kT$ , dispersive transport is not in evidence for experiments conducted at a single wavelength. The dynamics of excitation transport can be accurately modeled by theories developed for chromophores distributed randomly in homogeneous liquid solution.

## I. Introduction

Time-resolved fluorescence depolarization and other depolarization techniques such as transient grating experiments have been used to examine rotational diffusion<sup>1-5</sup> and electronic excitation transport<sup>6,7</sup> in liquid solutions. In recent years, electronic excitation transport among chromophores both attached to and dispersed in polymers has been used increasingly as a quantitative probe of the structure of solid polymeric materials.<sup>8-10</sup> To utilize electronic excitation transport, we must be able to relate the transport to structure through experimental observables. The observables, such as fluorescence depolarization, are frequently influenced by chromophore rotational motions as well as excitation transport. In this paper we examine experimentally these phenomena for chromophores in a solid polymeric solution. The system consists of the chromophore 1-pentylpyrene in solid solutions of polystyrene (PS).

At low concentrations of 1-pentylpyrene in polystyrene, the chromophores are effectively isolated from each other, and electronic excitation transport does not take place. The chromophores have a random distribution of transition dipole directions. Following optical excitation with a polarized picosecond pulse of light, the ensemble of excited chromophores gives rise to polarized fluorescence. Since the glass transition temperature of polystyrene is about 100 °C, the polystyrene matrix will be glassy at room temperature. Thus there should be no large-scale cooperative motion, but hindered rotational diffusion can occur. The rotational diffusion followed by subsequent emission of light leads to a time-dependent depolarization of the fluorescence. Because of restrictions of the motion of the chromophore arising from the local packing of polymer backbones about the probe, the fluorescence is only partially depolarized in the polymeric glass.

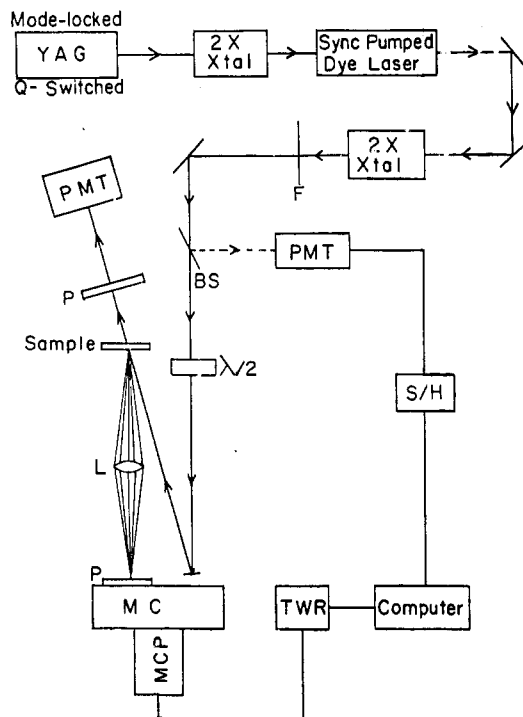
In this study, we compare the hindered rotational fluorescence depolarization of free 1-pentylpyrene and pyrene attached to the ends of polystyrene coils by a butyl chain. The molecular weights of the polystyrene coils that are end-tagged with the 1-butylpyrene range from 3000 to 32 000. When the butyl chain is attached to the polystyrene chain, the alkyl chain end is effectively fixed on the time scale of the fluorescence experiment. We find that the rotationally induced fluorescence depolarization

of the pyrene chromophore is identical for free 1-pentylpyrene and pyrene end-tagged on polystyrene via a butyl linkage. Thus, in systems in which chromophores are attached to a polymer chain with a flexible linkage, and in which knowledge of rotational dynamics is necessary as part of the interpretation of excitation transport experiments,<sup>9</sup> it is possible to use model chromophores which are not actually attached to the polymer backbone.

As the 1-pentylpyrene concentration is increased in the polystyrene solid solutions, an additional source of fluorescence depolarization becomes prominent. This concentration-dependent depolarization is due to electronic excited-state transport. The initially excited ensemble of chromophores is polarized along the direction of the excitation electric field. Excitations are transferred by electronic interactions (transition dipole-transition dipole interactions) to chromophores in their ground states.<sup>11,12</sup> The ensemble of molecules populated by excitation transfer has an effectively random distribution of transition dipole directions and therefore gives rise to depolarized fluorescence. Thus, the rate of excitation transport can be directly related to the time dependence of fluorescence depolarization in the absence of rotational depolarization. If there is also rotational depolarization, it is necessary to remove the rotational contribution from the data before analyzing the data for the rate of excitation transport.

The time and concentration dependence of excitation transport among molecules distributed randomly in liquid solutions have been examined in great detail. The theoretical treatment of Gochanour, Andersen, and Fayer<sup>13</sup> (GAF) has been shown to be a highly accurate description of transport for all experimentally accessible time scales.<sup>6,14</sup> However, this statistical mechanics theory is based on the Förster transfer mechanism, which assumes that the absorption spectrum of the chromophore is homogeneously broadened. At liquid helium temperatures, chromophores in polymeric solids display very broad, inhomogeneously broadened absorption spectra.<sup>15,16</sup> Chromophores in different physical environments have distinct transition energies. This leads to dispersive excitation transport. Chromophores with low transition energies in the inhomogeneously broadened line act as traps (irreversible acceptors) for excited chromophores with higher transition energies. The result is time-dependent excitation transport that is very different from that observed in room temperature liquid solutions. Dispersive transport has been observed experimentally in both small molecule<sup>17</sup> and polymeric<sup>18</sup> glasses at low temperature.

<sup>†</sup>Permanent address: Department of Chemistry, Brown University, Providence, RI 02912.



**Figure 1.** Experimental setup. The output of a mode-locked and Q-switched Nd:YAG laser is frequency doubled and synchronously pumps a dye laser. The dye laser output is doubled to 343 nm for excitation. The polarization of the excitation beam is controlled by a half-wave plate. The fluorescence from the sample is collected by a lens, passed through a polarizer and a monochromator, and detected by a multichannel plate coupled to a transient waveform recorder. See text for further details. BS = beam splitter, PMT = photomultiplier tube,  $\lambda/2$  = half-wave plate, S/H = sample and hold circuit, P = polarizer, L = lens, MC = monochromator, MCP = multichannel plate detector, TWR = transient waveform recorder, F = UV transmitting filter, and  $2 \times \text{Xtal}$  = second harmonic generating crystal.

In the experiments presented here, the room temperature solid polymeric solutions are physically inhomogeneous. There are many local environments for the chromophores. Measurements of the inhomogeneous optical line width at low temperatures show that it is comparable to the expected magnitude of homogeneous broadening ( $kT$ ) at room temperature. In this situation, the question is open as to the nature of the excitation transport. Can statistical mechanics theories based on the Förster mechanism be used, or is it necessary to treat the problem with the greatly increased complexity of dispersive transport? This is an important question since the theories which are being employed to interpret experiments on polymeric solids use the Förster mechanism.<sup>8,10</sup> Furthermore, recent experiments have produced evidence of dispersive transport in a room temperature polymeric solid.<sup>19</sup> These experiments showed a small but clear change in the rate of excitation transport with the wavelength of excitation. Nonetheless, as demonstrated by the experiments presented below, the time dependence of the excitation transport can be accurately described by using the Förster mechanism and the GAF theory so long as all measurements to be compared are made with the same excitation wavelength.

## II. Experimental Section

Figure 1 shows the experimental apparatus. The frequency-doubled (532 nm) output of an acoustooptically mode-locked, Q-switched Nd:YAG laser was used to synchronously pump a dye laser. The dye laser was cavity dumped with a Pockels cell to produce a single pulse at 686 nm that was then frequency doubled to give the  $\sim 25$ -ps excitation pulse at 343 nm. A small fraction

of each UV excitation pulse was measured with a phototube and sample-and-hold circuit and recorded by computer, so the fluorescence intensity could be normalized to the laser intensity. This eliminates effects due to laser intensity drift. The spot size of the excitation pulse at the sample was of the order of 1-mm diameter, and the pulse energies were typically  $0.5\text{--}1 \mu\text{J}$ . Careful examination of samples of various concentration demonstrated that no significant reabsorption of fluorescence occurred. The dependence of the recorded fluorescence intensity on the excitation intensity was linear, assuring that the microchannel plate was not saturated and that the sample was not being bleached.

Fluorescence from the sample was focused into a monochromator having an interference filter and polarizer on the entrance slit. A microchannel plate (Hamamatsu R1645U-01) coupled to a transient digitizer (Tektronix Model R7912) detected the fluorescence at 377 nm. A computer was used to store the fluorescence decays and average many decays (500–1000 per data set) to improve signal-to-noise. The time resolution of the detection system was 1.0 ns.

The intensities for fluorescence polarized parallel to the excitation polarization,  $I_{\parallel}(t)$ , and fluorescence polarized perpendicular to the excitation polarization,  $I_{\perp}(t)$ , were measured by rotating the polarization of the excitation pulse with half-wave plates and keeping the detector polarizer unchanged at vertical polarization. Since the detection efficiency of the monochromator and microchannel plate can vary with the polarization of the light, this method ensures that the absolute ratio of  $I_{\parallel}(t)$  to  $I_{\perp}(t)$  is preserved. Front face excitation and detection were used. A computer-controlled mechanical shuttle moved after each shot to alternate half-wave plates in the excitation beam. This resulted in an alternation of the excitation polarization between parallel and perpendicular. Two data sets,  $I_{\parallel}(t)$  and  $I_{\perp}(t)$ , were stored and averaged by the computer. The fluorescence anisotropy  $r(t)$  (see next section) is then calculated from this set of  $I_{\parallel}(t)$  and  $I_{\perp}(t)$  decays. The entire sequence was repeated for the same spot and different spots on the same sample. No substantial or systematic differences were observed. The  $r(t)$  curves calculated from these separate data sets were then averaged together. Switching back and forth between collecting fluorescence at the two polarizations minimizes any possible artifacts.

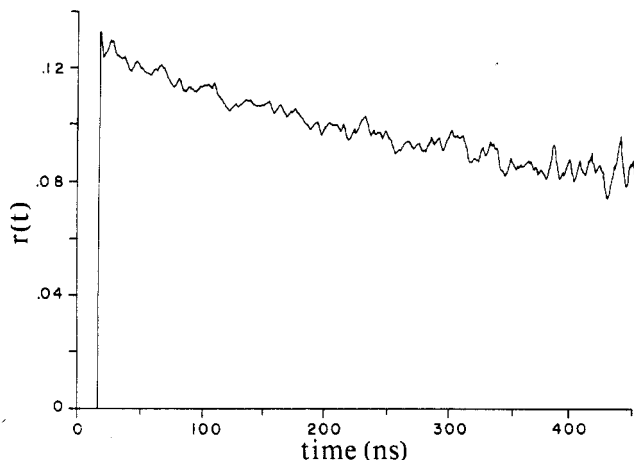
In addition to checking the birefringence of the samples in a polarizing microscope, we checked the birefringence of the spot actually excited by the laser beam by placing a polarizer and phototube in the excitation beam after it passed through the sample and measuring the ratio of the transmitted light parallel and perpendicular to the incident polarization. This ratio was 200/1 or higher for all samples and is large enough to ensure that there is no distortion in the data due to birefringence in the samples. Fluorescence data were also collected on samples of pure polystyrene host material. The fluorescence from these samples was negligible compared to the fluorescence from the pyrene containing samples.

Low-temperature absorption spectra were taken with the sample in a closed cycle helium refrigerator. The polymer sample was in thermal contact with the cold finger. A resistance thermometer was in direct contact with the polymer sample to provide an accurate measurement of the sample temperature. The spectra were taken with an arc lamp, 3/4-m scanning monochromator, phototube, and lock-in amplifier and recorded on a computer.

All samples were solid blends of the desired guest and the host polystyrene (Polysciences, 90 000 weight-average molecular weight) prepared by molding in a stainless steel piston above the glass transition temperature. The procedure is the same as that described previously.<sup>20</sup> The samples were optically clear with no significant birefringence along the direction in which the pressure was applied. This was checked by viewing the samples through a polarizing microscope. The density of the polystyrene samples was measured to be  $1.04 \text{ g/cm}^3$ . The synthesis of the 1-butylpyrene end-capped polystyrenes by anionic polymerization is reported elsewhere.<sup>21</sup>

## III. Results and Discussion

**A. Rotational Depolarization.** If a sample of randomly oriented chromophores is excited by a short pulse of plane-polarized light, the decay of the fluorescence in-



**Figure 2.** Fluorescence anisotropy,  $r(t)$ , calculated from experimental  $I_{\parallel}(t)$  and  $I_{\perp}(t)$ , for a low concentration of 1-pentylpyrene in solid polystyrene. There is no excitation transport; the fluorescence depolarization is due solely to hindered rotational motion. Note that  $r(t)$  is nonexponential.

tensities polarized parallel ( $I_{\parallel}(t)$ ) and perpendicular ( $I_{\perp}(t)$ ) to the exciting light can be written as

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

$\tau$  is the fluorescence lifetime, and  $r(t)$  is the fluorescence anisotropy.  $r(t)$  contains information about all sources of depolarization.  $r(t)$  can be obtained from the individual parallel and perpendicular components of the fluorescence intensity. From eq 1

$$r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)} \quad (2)$$

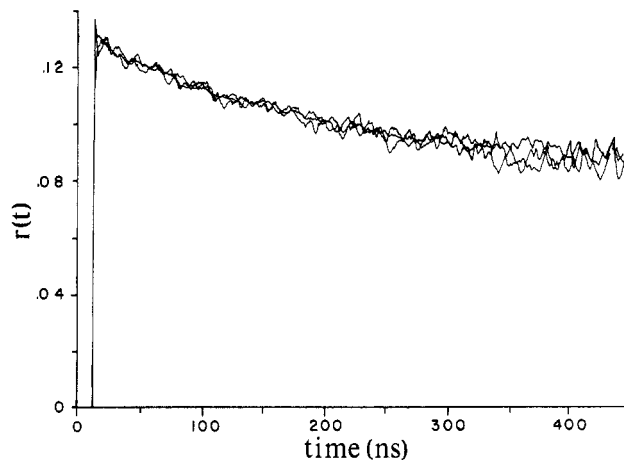
If the 1-pentylpyrene chromophores are in sufficiently low concentration, electronic excitation transport will not occur. The only source of time-dependent fluorescence depolarization is the hindered rotational diffusion of the chromophores. In this case

$$r(t) = C\Phi(t) \quad (3)$$

where  $\Phi(t)$  is the rotational correlation function and  $C$  is a time-independent constant that describes the degree of polarization of the excitation and emission transitions involved.

Figure 2 displays data for 1-pentylpyrene in polystyrene.  $r(t)$  was calculated from parallel and perpendicular fluorescence decays by using eq 2.  $r(t)$  is nonexponential. A chromophore in a liquid solution will exhibit an exponential decay of the polarization anisotropy.<sup>2-5</sup> There is essentially a single rate for the decay of the transition dipole directional correlation function. In a polymer glass, the chromophore is in a "pocket". There is some degree of freedom for reorientational motion. However, to completely lose directional correlation requires motions of the polymer chains forming the pocket that surrounds the chromophore.<sup>22</sup> Backbone motions in the glassy state occur on time scales much longer than the fluorescence lifetime. The result is only partial, nonexponential depolarization of the fluorescence.

Kawski et al.<sup>23</sup> have measured the steady-state fluorescence anisotropy ( $r$ ) of pyrene in cellulose acetate film at various temperatures. They observed a low value and a temperature dependence for  $r$  which could not be explained in terms of the macroscopic viscosity and attributed this to limited rotation of the chromophores



**Figure 3.** Time-resolved fluorescence anisotropies for three different pyrene-containing guests in solid polystyrene: free 1-pentylpyrene, 1-butylpyrene attached to ends of a 3190  $M_w$  polystyrene chain, and 1-butylpyrene attached to ends of a 32000  $M_w$  polystyrene chain. Rotational motion is the only source of depolarization in these samples. The three curves are identical, showing that the rotational dynamics are equivalent in the three samples.

sitting in "special free places". The data presented here are consistent with this interpretation. The partial nonexponential decay suggests a combination of hindered orientational motions. Experiments which measure  $r(t)$  with picosecond time resolution could provide more detailed information on the types of motions present and the size and time-dependent structure of the pocket.

Figure 3 displays  $r(t)$  values for three different samples. In each case the concentration of chromophore is low enough to prevent electronic excitation transport. Only rotational depolarization takes place. Three samples were prepared: free 1-pentylpyrene, 1-butylpyrene attached to both ends of a  $M_w$  3190 polystyrene chain, and 1-butylpyrene attached to both ends of a  $M_w$  32000 polystyrene chain. Each sample was randomly dispersed in solid polystyrene. Within experimental error, the three curves are identical. Thus the hindered rotational dynamics of the pyrene chromophores are identical in the three situations.

Attaching the chromophore (the pyrene) to a large mass through a chain of four methylenes does not affect the decay of the directional correlation function on the time scale of the fluorescence lifetime. These results demonstrate that out to times of hundreds of nanoseconds the motions of the pyrene are independent of the end of the methylene chain. On much longer time scales, which can be investigated with dynamic light scattering,<sup>22</sup> attaching the methylene chain to the polystyrene coil could have a significant effect. However, on a fast time scale, on which there is little or no backbone motion, chromophore motions are not modified by attachment to a polymer coil if the link is a flexible chain.

In addition to showing that side-chain attachment does not influence the chromophore motion at short times, it also suggests that a chromophore with a flexible side chain can be used as a model for a chromophore attached to a polymer with a flexible side chain. As discussed in the next section, interpretation of excitation transport experiments requires a knowledge of the chromophore rotational dynamics.

**B. Electronic Excitation Transport.** In systems involving donor-donor excited-state transport, the fundamental quantity of theoretical and experimental interest is  $G^s(t)$ ,<sup>6,9-10,13</sup> the ensemble-averaged probability that an

originally excited chromophore is excited at time  $t$ .  $G^s(t)$  contains contributions from excitations that never leave the originally excited chromophore and from excitations that return to the initially excited chromophores after one or more transfer events.  $G^s(t)$  does not contain loss of excitation due to lifetime (fluorescence) events.  $G^s(t)$  can be obtained experimentally from time-resolved fluorescence depolarization data.<sup>6</sup> It is also calculated in the GAF theory as part of the Green function solution to the transport master equation. The GAF theory provides a very accurate infinite-order approximation to the Green function. It has been demonstrated that it can reproduce excitation transport data in liquid solution systems without recourse to adjustable parameters when the necessary physical parameters which go into the theory are measured independently.<sup>6</sup> Since the theory has been shown to be accurate, it can be used as a test of the nature of transport in the solid polymeric solutions.

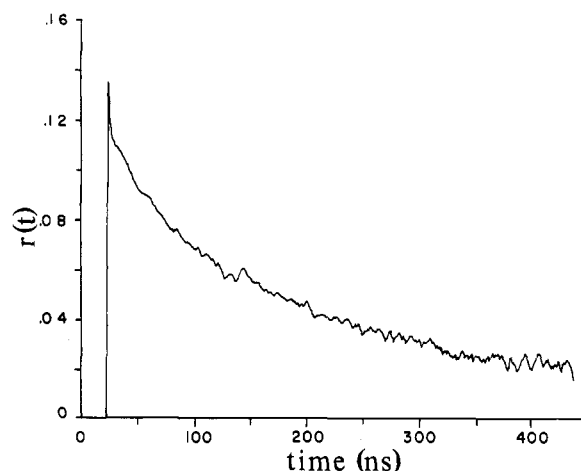
If the transition dipoles of the chromophores in a solid polymer matrix are randomly oriented and static, the source of depolarization in an experiment will be excitation transport. The initially excited ensemble is polarized along the direction of the excitation  $\vec{E}$  field and gives rise to polarized fluorescence. Transport occurs into an ensemble of chromophores with randomly distributed dipole directions, and the fluorescence becomes unpolarized. The random distribution is assured by the relatively low concentration of the chromophores. However, to some extent, on the time scale of interest, depolarization also occurs as a result of chromophore motion. In this case the fluorescence anisotropy is given by<sup>9</sup>

$$r(t) = C\Phi(t) G^s(t) \quad (4)$$

where  $\Phi(t)$  is the rotational correlation function that contains the effects due to motion of the chromophores.  $C$  is a time-independent constant that describes the degree of polarization of the excitation and emission transitions involved.

There are two approximations in eq 4. The first is that the rotational and energy transport contributions to depolarization are independent. This is true only when rotation is very slow relative to the time for energy transport so that the donor and acceptor dipoles can be considered fixed during the transfer of the excitation. Fredrickson has recently treated the case where energy transport and rotation occur on comparable time scales,<sup>24</sup> i.e., where rotation occurs during the transport event. The two sources of depolarization are then coupled, and the simple factorization in eq 4 is not valid. However, for the slow and small extent of rotational depolarization in polymer glasses, this is a good approximation. The second approximation is that  $G^s(t)$  decays to zero, resulting in complete depolarization; i.e., the irreversible transfer of excitation from the initially excited donor into the ensemble of unexcited donors results in total loss of polarization. For systems with a low concentration of randomly placed chromophores this is approximately true. The residual polarization is 4%, which results in an insignificant error.<sup>25,26</sup>

In order to obtain  $G^s(t)$  for a given sample, experiments on two different samples, referred to as A and B, must be performed. These samples differ only in the concentration of the guest chromophores. A is the sample of interest and has an appreciable number of chromophores, such that excitation transport will occur. Its fluorescence anisotropy,  $r_A(t)$ , is given by eq 4. Sample B has such a small number of chromophores that excitation transport is negligible ( $G^s(t) = 1$ ), and only chromophore motion contributes to its anisotropy,  $r_B(t)$ , which is given by eq 3.  $G^s(t)$  arising



**Figure 4.** Time-resolved fluorescence anisotropy for 1-pentylpyrene in polystyrene at a concentration of  $6.2 \times 10^{-2}$  mol/L. The increase in the rate of depolarization compared to the very dilute sample (Figure 2) shows that there is a significant amount of excitation energy transport.

from the excitation transport in sample A can be calculated from the two experimental anisotropies

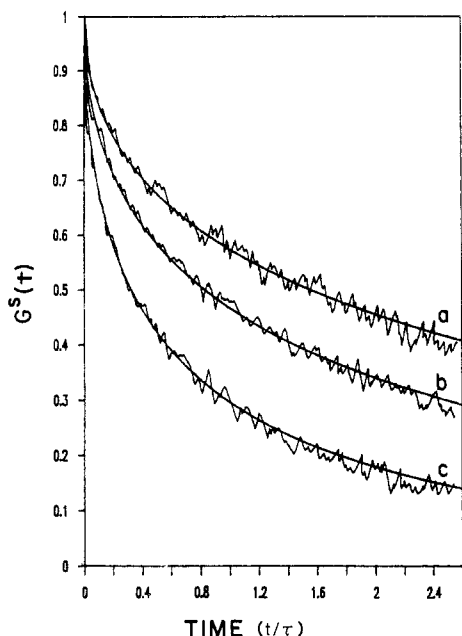
$$G^s(t) = r_A(t)/r_B(t) \quad (5)$$

This method of determining  $G^s(t)$  has the advantage that detailed knowledge of the parameters  $C$  and  $\Phi(t)$  is unnecessary.  $r(t)$  for any sample can be obtained from eq 2.

Figure 4 displays  $r(t)$  for 1-pentylpyrene in polystyrene at a relatively high concentration ( $C = 2.0$  mg/120.8 mg =  $6.2 \times 10^{-2}$  mol/L). If these data are compared to the data in Figure 2 we see that  $r(t)$  decays substantially faster. This is due to the additional depolarization caused by electronic excitation transport. To remove the contribution to  $r(t)$  from rotational depolarization, eq 5 is used. The low concentration rotation only  $r(t)$ , from Figure 2, is used as  $r_B(t)$  in eq 5. The  $r(t)$  values obtained from higher concentration samples, which include an excitation transport contribution, are the  $r_A(t)$  values in eq 5. The division yields  $G^s(t)$ , the quantity of interest for an excitation transport experiment.

Figure 5 displays three experimentally determined  $G^s(t)$  curves from polystyrene samples containing three different moderately high concentrations of 1-pentylpyrene. The GAF theory relies on the Förster transport mechanism, i.e., homogeneously broadened absorption lines. In liquid solutions at room temperature, molecular spectra are generally taken to be homogeneously broadened. Recent experiments by Shank and co-workers<sup>27</sup> have shown that inhomogeneous broadening of a chromophore in a room temperature liquid vanishes on a time scale longer than 100 fs. Since excitation transport, at moderate concentrations, occurs on time scales of subnanoseconds to tens of nanoseconds, the chromophores can be considered as having homogeneously broadened spectra on the time scale of excitation transport.

Chromophores in polymeric solids are distinct from chromophores in liquid solutions. The solid is typically well below its glass transition, and evolution of local structures does not occur on the very fast time scales found in liquids. The inhomogeneous width associated with the 1-pentylpyrene in polystyrene was measured by lowering the sample temperature. At room temperature the full width at half-maximum (fwhm) of the absorption origin is  $300 \text{ cm}^{-1}$ . As the temperature is lowered, the line width decreases as the thermal homogeneous broadening is re-



**Figure 5.**  $G^s(t)$ , the probability that an excitation is on the originally excited molecule at time  $t$ , provides a direct measure of the rate of energy transport. The three experimental curves are from three different concentrations of 1-pentylpyrene in polystyrene. The calculated curves are the best fits to the data from eq 6. All lie within  $R_0 = 16.7 \pm 0.5 \text{ \AA}$ : (a)  $c = 4.6 \times 10^{-2} \text{ M}$ , (b)  $c = 6.2 \times 10^{-2} \text{ M}$ , and (c)  $c = 9.3 \times 10^{-2} \text{ M}$ .

duced. At 110 K, the fwhm was reduced to  $190 \text{ cm}^{-1}$ . Measurements at lower temperatures, down to 80 K, showed no further reduction in the line width. Therefore,  $190 \text{ cm}^{-1}$  is the inhomogeneous width.

At room temperature ( $298 \text{ K}$ ),  $kT = 207 \text{ cm}^{-1}$ . This is comparable to the inhomogeneous broadening. In this situation the possibility that there is some degree of dispersive transport exists. In fact, it will be shown elsewhere<sup>19</sup> that careful wavelength-dependent studies reveal some degree of dispersive transport in a room temperature PMMA sample. Analysis of transport data including consideration of dispersive transport would greatly increase the complexity and reduce the utility of excitation transport experiments as probes of polymeric solids. The question addressed here is whether transport can be modeled with the Förster mechanism and an appropriate statistical mechanical theory in spite of inhomogeneous broadening, which is comparable to  $kT$ .

To determine if the dynamics of excitation transport in a room temperature solid polymeric solution can be modeled by using the Förster transport mechanism, we compare the data to theoretical treatments developed and applied previously to liquid solutions. As discussed above, the GAF theory is an accurate description of donor-donor excitation transport (no trapping) among molecules randomly distributed in a homogeneous solution. Because of the mathematical complexity of the GAF theory, it is preferable to use a formula derived by Huber<sup>28,29</sup> in the actual data analysis. The Huber treatment is in near perfect agreement with the GAF theory for short and moderate time scales. For the time scale in these experiments, the Huber treatment can be taken to be identical with the GAF theory. Therefore, if excitation transport behaves as if the solid polymeric solution is a randomly distributed homogeneous solution, the data should be described by

$$\ln G^s(t) = -\frac{2(2^{1/2})\pi c}{3} \left(\frac{t}{\tau}\right)^{1/2} \gamma_3 R_0^3 \Gamma\left(\frac{1}{2}\right) \quad (6)$$

where  $c$  is the number of chromophores per unit volume,  $\tau$  is the excited-state lifetime,  $R_0$  is the orientation-averaged critical transfer radius for donor-donor (Förster-type) excitation transport,<sup>11,12</sup>  $\Gamma$  is the  $\Gamma$  function, and  $\gamma_3 = 0.8452$  is a scaling factor necessary to account for the orientation dependence of the transfer rate in an orientationally static system.<sup>6,30</sup>

Pyrene is known to exhibit excimer fluorescence in liquid solutions and polymer glasses at concentrations similar to those used here. In order to ensure that the energy transport observed was due solely to donor-donor ("self") energy transfer without trapping effects from excimers, steady-state fluorescence spectra were measured (Spex Fluorolog 2, 340-nm excitation). The highest concentration sample used in these energy-transfer measurements was  $9.3 \times 10^{-2} \text{ M}$  in 1-pentylpyrene. No excimer fluorescence was observed at this concentration, whereas a sample with  $c = 1.9 \times 10^{-1} \text{ M}$  showed excimer fluorescence which was approximately 15% of the total fluorescence. Although Avis and Porter<sup>31</sup> observed excimer fluorescence from pyrene in poly(methyl methacrylate) films at concentrations above  $10^{-2} \text{ M}$ , with approximately 50% of the total fluorescence due to excimers at  $10^{-1} \text{ M}$ , Johnson<sup>32</sup> has reported fluorescence spectra and excimer/monomer intensity ratios which show a higher concentration is needed for excimer formation in polystyrene films. The lack of excimer fluorescence in the 1-pentylpyrene/PS samples assures that excimers are not acting as traps and that the time dependence reported here (Figure 5) is due to donor-donor energy transport.

In applying eq 6 to the data,  $c$  is known from the sample preparation, and  $\tau$  is obtained by measuring the fluorescence decay at the magic angle polarization (which eliminates time-dependent depolarization effects from the decay). The  $c$  values are given in the caption to Figure 5, and  $\tau = 128 \pm 3 \text{ ns}$ . The only unknown parameter is  $R_0$ . If eq 6 is a proper model of the excitation transport, then the functional form of the experimental and calculated curves should match, and a single value of  $R_0$  should be able to reproduce all of the experimental curves. The solid lines through the data in Figure 5 are the best fits calculated with eq 6 and one adjustable parameter,  $R_0$ . Several measurements on the three samples of Figure 5 and on three additional samples with different concentrations gave an average value of  $R_0 = 16.7 \pm 0.5 \text{ \AA}$ . In all cases the functional form of the experimental  $G^s(t)$  curve was accurately reproduced by eq 6.

These results demonstrate that at room temperature the Förster transfer mechanism with an appropriate statistical mechanical theory of the transport dynamics can accurately describe the experimental results. The important point is that a single value of  $R_0$  describes the transport at a variety of concentrations. Thus  $R_0$  can be used as a distance scale to probe the structure of polymer chains tagged with chromophores.<sup>8-10</sup> It will be demonstrated theoretically and experimentally in a future publication<sup>19</sup> that polymeric solids do display a small degree of dispersive transport at room temperature. Nonetheless, if  $R_0$  is determined by excitation transport experiments with excitation at a wavelength  $\lambda$ , and if the transport measurements for chromophores tagged on a polymer are made at the same  $\lambda$ , procedures which have previously been used to extract information about solid polymer systems provide accurate descriptions of the microscopic nature of polymeric solids.

**Acknowledgment.** This work was supported by the Department of Energy (Grant DE-FG03-84ER13251). Additional support was provided by the NSF-MRL pro-

gram through the Stanford Center for Materials Research. We would like to thank Dr. W. T. Tang and Dr. Georges Hadziioannou (IBM Almaden Research Center) for providing the end-tagged polystyrene.

**Registry No.** PS, 9003-53-6; 1-pentylpyrene, 80655-41-0.

### References and Notes

- (1) Eienthal, K. B.; Drexhage, K. H. *J. Chem. Phys.* **1969**, *51*, 5720.
- (2) Chuang, T. J.; Eienthal, K. B. *Chem. Phys. Lett.* **1971**, *11*, 368.
- (3) Fleming, G. R.; Morris, J. M.; Robinson, G. W. *Chem. Phys.* **1976**, *17*, 91.
- (4) von Jena, A.; Lessing, H. E. *Chem. Phys.* **1979**, *40*, 245.
- (5) Moog, R. S.; Ediger, M. D.; Boxer, S. G.; Fayer, M. D. *J. Chem. Phys.* **1982**, *86*, 4694.
- (6) Gochanour, C. R.; Fayer, M. D. *J. Chem. Phys.* **1981**, *85*, 1989.
- (7) Miller, R. J. D.; Pierre, M.; Fayer, M. D. *J. Chem. Phys.* **1983**, *78*, 5138.
- (8) Peterson, K. A.; Fayer, M. D. *J. Chem. Phys.* **1986**, *85*, 4702.
- (9) Peterson, K. A.; Zimmt, M. B.; Linse, S.; Domingue, R. P.; Fayer, M. D. *Macromolecules* **1987**, *20*, 168.
- (10) Fredrickson, G. H.; Andersen, H. C.; Frank, C. W. *Macromolecules* **1984**, *17*, 54.
- (11) Förster, Th. *Ann. Phys.* **1948**, *2*, 55.
- (12) Förster, Th. *Z. Naturforsch., A: Astrophys., Phys. Phys. Chem.* **1949**, *4*, 321.
- (13) Gochanour, C. R.; Andersen, H. C.; Fayer, M. D. *J. Chem. Phys.* **1979**, *70*, 4254.
- (14) Knoester, J.; van Himbergen, J. E. *J. Chem. Phys.* **1984**, *81*, 4380.
- (15) Carter, T. P.; Fearey, B. L.; Hayes, J. M.; Small, G. J. *Chem. Phys. Lett.* **1983**, *102*, 272.
- (16) Thijssen, H. P. H.; Van Den Berg, R.; Völker, S. *Chem. Phys. Lett.* **1983**, *97*, 295.
- (17) Jankowiak, R.; Bässler, H. *Chem. Phys.* **1983**, *79*, 57.
- (18) Peter, G.; Bässler, H.; Schrof, W.; Port, H. *Chem. Phys.* **1985**, *94*, 445.
- (19) Peterson, K. A.; Stein, A. D.; Fayer, M. D., to be published.
- (20) Ediger, M. D.; Domingue, R. P.; Peterson, K. A.; Fayer, M. D. *Macromolecules* **1985**, *18*, 1182.
- (21) Tang, W. T.; Hadziioannou, G.; Smith, B. A.; Frank, C. W. *Polymer* **1988**, *29*, 1718.
- (22) Oliver, N. H.; Pecora, R.; Ouano, A. C. *Macromolecules* **1985**, *18*, 2208.
- (23) Kawski, A.; Weyna, I.; Kojro, Z.; Kubicki, A. *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.* **1983**, *38A*, 1103.
- (24) Fredrickson, G. H. *J. Chem. Phys.*, in press.
- (25) Galinin, M. D. *Tr. Fiz. Inst. im. P. N. Lebedeva, Akad. Nauk. SSSR* **1950**, *5*, 341.
- (26) Craver, F. W.; Knox, R. S. *Mol. Phys.* **1971**, *22*, 385.
- (27) Brito Cruz, C. H.; Fork, R. L.; Knox, W. H.; Shank, C. V. *Chem. Phys. Lett.* **1986**, *132*, 341.
- (28) Huber, D. L. *Phys. Rev. B: Condens. Matter* **1979**, *20*, 2307.
- (29) Huber, D. L. *Phys. Rev. B: Condens. Matter* **1979**, *20*, 5333.
- (30) Fredrickson, G. H.; Frank, C. W. *Macromolecules* **1983**, *16*, 1198.
- (31) Avis, P.; Porter, G. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1057.
- (32) Johnson, G. E. *Macromolecules* **1980**, *13*, 839.