Macromolecules **1980**, *13*, 145–152

reason may be understood to be the reduction of homogeneity of polymer deformation after the formation of submicrocracks in a stressed sample, that is some regions in the polymer are highly stretched and some regions are only weakly stretched. In the present case, too, such a heterogeneous stretching might occur detectably after approaching completion of the $\alpha \rightleftharpoons \beta$ phase transition.

Fibers such as PBT, keratin,[19] and rubber,[20] in which the reversible phase transition is induced by the reciprocation motion of successive extension and relaxation of the samples, can become a material with excellent mechanical properties such as high fatigue resistance because the strain energy added to the sample is consumed by the phase transition and a kind of cushion thus generated can keep the sample against the direct mechanical rupture. It may be important to develop such polymer materials.

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Energy Migration and Transfer in Molecularly Doped Polymers

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ABSTRACT: The migration and transfer of singlet excitation in polystyrene films doped with *N*-isopropylcarbazole as an energy donor has been investigated. Fluorescence decay measurements on these molecularly doped polymer films in the presence of two types of energy acceptor, dimethylterephthalate and perylene, are used to determine the mechanism for singlet migration among the donor subsystem of like chromophores. The donor concentration dependence of the fluorescence quenching process is found to be consistent with a mechanism in which the singlet excitation migrates by a series of random walk steps with each step involving a Förster dipole–dipole resonance transfer. Excitation diffusion lengths as a function of the donor concentration have been determined and shown to extrapolate in the limit of high concentration to a value close to that for poly(*N*-vinylcarbazole).

The migration of electronic excitation in organic molecular crystals is a photophysical process which has been extensively investigated over a period of many years.[2a] Perhaps the most dramatic evidence for this process is revealed in spectroscopic studies where it is generally observed that the fluorescence spectrum of the host crystal is dominated by fluorescence from unwanted impurities or by fluorescence from small concentrations of purposely added guest molecules.[3] More recently a variety of experiments have been carried out which lead to a greatly increased understanding of the dynamic aspects of the exciton migration process and of the nature of the various excited state interactions which can occur in these systems.[4] Emission spectroscopic techniques, both steady state and time resolved, have also been utilized to investigate the wealth of photophysical processes which occur in organic polymers.[5] The stimuli for the ever increasing body of literature concerning the photophysics of polymers can perhaps be considered to cover a somewhat broader spectrum than those which led to the vast literature on molecular crystals. While surely there is great interest in the photophysics of polymer systems from a purely scientific point of view, polymers are certainly of more technological importance than molecular crystals. For example, the ability to render stability to synthetic polymers by the addition of dopants is in many cases the result

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of excitation migration or transfer processes, and thus detailed understanding of these processes is of both fundamental and technological importance.[6]

In addition to the large number of investigations concerning energy migration in organic molecular crystals and polymers, another quite different type of system has also received considerable attention. These are dilute solid solutions containing energy donors and acceptors randomly dispersed in an inert matrix. In these systems, where the intermolecular separation between donor chromophores is so large that the probability for multistep excitation migration becomes vanishingly small, the transfer of electronic excitation from an initially excited donor to the acceptor occurs in a single step via Coulombic multipole–multipole interactions between the transition moments of the donor–acceptor pair. The case of dipole–dipole transfer between randomly dispersed donor–acceptor pairs was formulated nearly three decades ago by Förster.[7] Subsequently many elegant experiments have been carried out which are in quantitative agreement with the predictions of Förster's theory.[8-10]

The two types of molecular systems noted above provide the prototypes for investigations concerning two distinct regimes. Neat molecular crystals or polymer films are examples in which energy transfer is usually dominated by a process involving multistep migration of the excitation among molecules of the host followed by transfer to a guest impurity whereas in dilute rigid solutions energy transfer is a single step process where the rate constant for transfer is time dependent due to the random nature of the excited donor–acceptor separation. Molecular systems which can perhaps be considered intermediate to the two types noted above are those consisting of rather high concentrations of fluorescing chromophores dissolved in viscous solvents or in polymer matrices. Ample evidence for the homotransfer of excitation among a system of like chromophores exists as a result of measurements of self-quenching of fluorescence and particularly measurements which determine the degree of polarization of fluorescence as a function of concentration.[11] Doped polymer films constitute a particularly attractive medium for detailed investigations concerning the migration or transfer of excitation among a system of like chromophores. Surprisingly high concentrations of "small" molecules can be added to a variety of polymers while still maintaining the ability to cast thin films with excellent optical quality. The ability to alter at will the concentration of added fluorescent chromophores and hence their intermolecular separation enables one to design a variety of experiments in which the functional dependence of the intermolecular separation on different processes can be determined. This dependence yields important information regarding the mechanistic aspects of the physical process being monitored. This approach has recently been utilized with considerable success in determining the mechanism of charge carrier transport[12,13] and triplet energy migration in molecularly doped polymers.[14] In the present work, the results of a series of experiments designed to probe the distance dependence for singlet energy migration in molecularly doped polymers are reported. The conclusions reached regarding singlet energy migration in these systems should be applicable to the mechanism of this photophysical process in neat films of homo- and copolymers containing very weakly interacting chromophores and to the migration of electronic excitation along single polymer chains in dilute solutions.[15,16]

Experimental Section

Materials. 1. Solutes. *N*-Isopropylcarbazole (NIPC) (Eastman Kodak, white label) was purified by multiple recrystallization from isopropyl alcohol. Perylene, Aldrich Chemical Co. (puriss. grade), was used as received. Polystyrene, Pressure Chemical Co., was used as received. Dimethylterephthalate (DMT) (Eastman Kodak, white label) was purified by multiple recrystallization from isopropyl alcohol. 1,3-Bis(*N*-carbazolyl)propane (1,3-BCP) was in-house synthesized and purified as described elsewhere.[17]

2. Solvents. Benzene, Burdick and Jackson, was used as received. Toluene, Burdick and Jackson, was used as received. 2-Methyltetrahydrofuran (2-MeTHF), Eastman Kodak, was purified as described in ref 17. EPA (5:5:2 mixture of diethyl ether, isopentane, and ethyl alcohol), American Instrument Company, was used as received.

Film Preparation. Preparation of the thin molecularly doped polymer films proceeded in the following manner: typically 50–200 mg of polystyrene were weighed out on a microbalance and placed in a small glass vial followed by the appropriate quantity of energy donor. The concentration of the energy acceptor (DMT or perylene) in each film was too low to make it possible to weigh this material for each individual film and consequently a stock solution of the acceptor in the solvent (benzene or toluene) from which the films were cast was prepared. The variation in acceptor concentration was made by dilution of the stock solution and the concentration in each film calculated from the volume of solution added to the polystyrene–energy donor solid mixture. Films were then cast from the energy donor–acceptor polystyrene solution by placing a small amount of the solution onto carefully cleaned $^1/_8$ in. × 1.25 in. fused quartz disks. The solvent was evaporated by placing the disk on top of a small platform which in turn was on top of a hot plate. The disk–platform combination was enclosed by a larger beaker which allowed for loss of solvent vapor and provided a fairly uniform temperature environment. The resulting films appeared visually to be quite uniform in thickness and were optically clear. No effort was made to determine film thickness or to keep thickness constant. It was shown that this parameter had no effect on the experimental results. Films in which the number of moles of polystyrene, energy donor, and energy acceptor were the same but which were purposely made thick or thin by varying the volume of solvent used to dissolve the solid components yielded identical results. This along with the consistency of the experimental data in the various energy donor–acceptor series attests to the lack of a thickness dependence on these results.

Steady State Fluorescence Measurements. Exciting light was provided by a 250 W Hg-Xe source dispersed through a Jarrell-Ash 0.25 m monochromator. The emission, viewed at 90° to the exciting light, was focused onto the entrance slit of a 0.33 m McPherson monochromator and detected by an RCA IP-28 photomultiplier. Readout of the current output of the photomultiplier was made using a Keithley 610B electrometer and the emission spectra were recorded on a Mosely Model 7000AM XY recorder.

Polarized Luminescence Measurements. The experimental apparatus, the techniques, and the basis for photoselection measurements have been described in detail elsewhere.[18]

Fluorescence Decay Time Measurements. Fluorescence decay times were measured, using the method of time-correlated single photon counting.[19] The electronics required for assembly of the nanosecond fluorescence decay time system were all purchased from Ortec, Inc. Details concerning this system can be found in a previously published paper.[20]

Results and Discussion

Although the results to be presented below are concerned principally with the dynamic aspects of excitation delocalization in molecularly doped polymers as determined by fluorescence decay measurements, it might be useful to begin with the results of a photoselection investigation in which the polarization of the emission excitation spectrum of *N*-isopropylcarbazole (NIPC) is compared with that of 1,3-bis(*N*-carbazolyl)propane (1,3-BCP). Typical results are shown in Figure 1 where the polarization of the emission excitation spectrum of NIPC is compared with that of 1,3-BCP. Both spectra were measured under identical conditions with the concentration of 1,3-

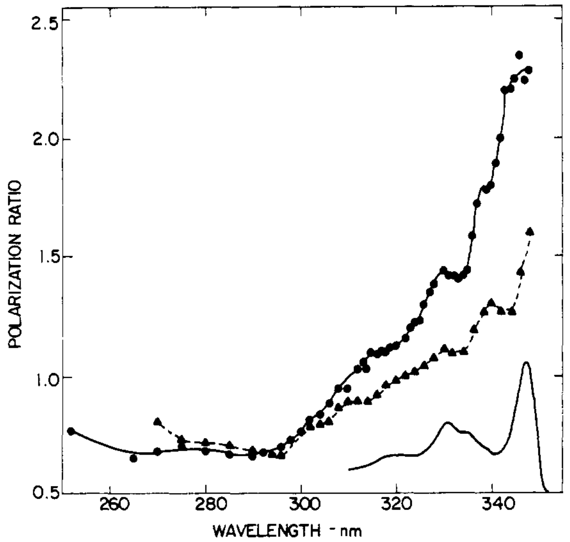

Figure 1. Polarization of the emission excitation spectrum for ~2 × 10^{-4} M *N*-isopropylcarbazole (●) and ~10^{-4} M 1,3-bis(*N*-carbazolyl)propane (▲) in 2-methyltetrahydrofuran at 77 K. The lower curve is the $^1L_b \leftarrow {}^1A$ absorption band of NIPC in 2-methyltetrahydrofuran at 77 K.

BCP being approximately one-half that of NIPC. Thus the concentration of carbazole chromophores is approximately the same in both cases; the essential difference between the two systems is of course that the propane chain 1,3-BCP fixes two carbazole units in close proximity to one another at a distance determined by the preferred ground state conformation of the propane chain that was achieved at temperatures somewhat above that at which the solvent becomes glassy. The fluorescence was monitored at a wavelength close to the (0,0) band with excitation at various wavelengths throughout the two lowest energy $^1L_b \leftarrow {}^1A$ and $^1L_a \leftarrow {}^1A$ absorption bands. The lower polarization ratios obtained throughout the $^1L_b \leftarrow {}^1A$ band system for 1,3-BCP indicate that the excitation initially localized on one of the carbazole groups can be transferred to the other, the result being a degree of randomization between absorbing and emitting transition moments. In all other aspects the rigid glass spectroscopies of NIPC and 1,3-BCP are virtually identical as are their respective fluorescence decay times. A similar photoselection experiment on dilute solution containing poly(*N*-vinylcarbazole) in 2-methyltetrahydrofuran gave completely unpolarized emission corresponding to complete randomization of absorbing and emitting transition moments implying a greater degree of excitation delocalization among pendant groups along the polymer chain.[21] While these results provide evidence for the existence of energy migration among the system of carbazole chromophores, conclusions of a quantitative nature regarding the extent of migration or the mechanism are virtually impossible to extract from this type of experiment.

The first system to be investigated utilizing fluorescence decay time measurements consisted of NIPC doped polystyrene films containing varying quantities of dimethylterephthalate (DMT) as the fluorescence quencher. DMT was choosen as the acceptor because its lowest lying single state lies considerably higher in energy than that of NIPC, and thus it cannot quench NIPC fluorescence through a single step long range energy transfer by the Förster dipole–dipole inductive resonance mechanism. It was determined, however, that in fluid solution DMT quenches NIPC fluorescence at a rate corresponding to the diffusion limit with the mechanism involving a charge transfer interaction between the electronically excited NIPC and ground state DMT. In a solid film of a host polymer such as polystyrene where translational diffusion of added guest molecules is vanishingly small, the following picture is intuitively expected. In the absence of excitation migration within the NIPC donor subsystem, the addition of increasing amounts of DMT would result in decreasing fluorescence intensity from excited NIPC; however, the fluorescence lifetime of NIPC would remain constant since only those excited NIPC molecules which have a DMT molecule within some critical interaction radius would be quenched while those without would fluorescence with their unperturbed lifetime. On the other hand, if the electronic excitation initially localized on a particular NIPC site can migrate throughout the donor subsystem, the excitation has a certain probability of arriving at a donor site containing a DMT molecule within its quenching spheres. In this case the fluorescence quenching is of a dynamic nature as opposed to the static case described above, and the fluorescence lifetime as well as the intensity is effected.[22] Thus at a particular NIPC concentration one would expect the fluorescence lifetime to decrease with increasing DMT concentration since more quenching sites are available, but more interesting is the expectation that the fluorescence lifetime should decrease with increasing NIPC concentration at a constant DMT concentration due to a greater diffusion length of the excitation. Both of these expectations are experimentally verified.

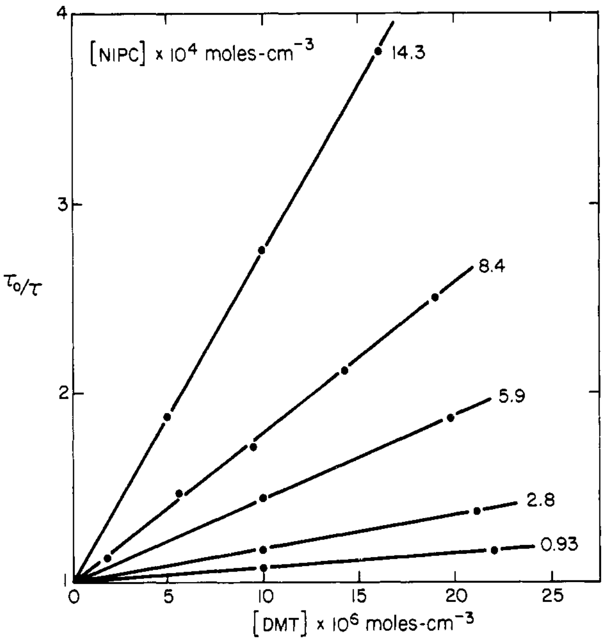

Figure 2. Fluorescence decay times for NIPC-doped polystyrene films as a function of DMT acceptor concentration.

Figure 2 presents the results of a series of fluoresence lifetime measurements on NIPC doped polystyrene films containing DMT where the concentration of DMT is varied at a constant NIPC concentration. The ratio of the lifetime of NIPC in the absence of DMT, τ_0, to that measured in the presence of DMT, τ, is plotted vs. the concentration of DMT. It is important to note that in the absence of DMT the NIPC fluorescence decay is essentially constant at all levels of NIPC doping with a lifetime just slightly shorter than the 16.6 ns observed in very dilute low-temperature glasses. Thus, there is no self-quenching of NIPC fluorescence due to the formation of species such as dimers, appropriately oriented to yield excimer fluorescence, which could serve as traps or quenching sites for the singlet excitation.[23] This is consistent with the absence of intermolecular excimer fluorescence in con-

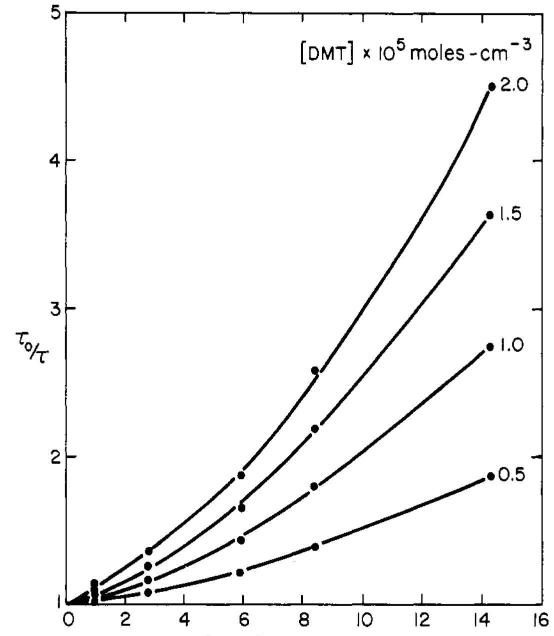

Figure 3. Fluorescence decay times for NIPC-doped polystyrene films as a function of NIPC donor concentration.

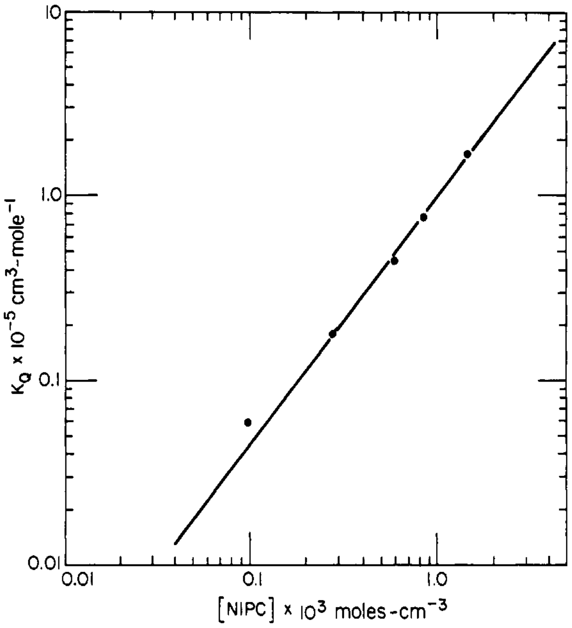

Figure 4. Donor concentration dependence of the fluorescence quenching constant for the NIPC–DMT–polystyrene system.

centrated solutions of carbazole or alkyl carbazoles.[17] The quenching of NIPC fluorescence by DMT follows the familiar Stern–Volmer equation (eq 1), where the quenching

$$\tau_0/\tau = 1 + K_q[\mathrm{DMT}] \qquad (1)$$

constant, K_q, is dependent on the concentration of the fluorescent solute, NIPC. Figure 3 shows a plot of τ_0/τ at particular levels of DMT doping as the concentration of NIPC is varied. These results clearly show that the singlet excitation, initially localized on a particular NIPC site, migrates in the donor subsystem until it arrives at a site containing a DMT molecule within some critical interaction radius where immediate quenching occurs. The distance traveled by the excitation is obviously dependent on the NIPC concentration and it is this concentration dependence which leads to important conclusions regarding the nature of the intermolecular interactions responsible for the migration among the system of like chromophores. The dependence of the diffusion length on the donor concentration is contained in the quenching constant, K_q.

Values of K_q at different NIPC concentrations are obtained from the results shown in Figures 2 or 3. K_q is simply the reciprocal of the DMT concentration where $\tau_0/\tau = 2$. When $\tau_0/\tau = 2$, the rate constant for fluorescence quenching by DMT is equal to the sum of rate constants for all other modes of deactivation of the NIPC excited singlet state. The values of K_q as a function of NIPC concentrations are shown in Figure 4. From this it is determined that K_q is proportional to the $^4/_3$ power of the NIPC concentration.

The implications and significance of this power dependence of the quenching constant on the donor concentration are discussed on the basis of the following equations. The time rate of charge of excited donor concentration following a light pulse is given by

$$-\mathrm{d}C_D^*/\mathrm{d}t = (k_F + k_I + k_M)C_D^* \qquad (2)$$

where C_D^* is the concentration of excited donor singlet states, k_F is the rate constant for fluorescence decay, k_I is the sum of rate constants for intramolecular radiationless decay, and k_M is the rate constant for quenching of the singlet excitation by acceptors. From this it follows that

$$\tau_0/\tau = 1 + k_M\tau_0 \qquad (3)$$

where the rate constant, k_M, within the exciton diffusion model is given by

$$k_M = 4\pi DRN_A[1 + R(\pi Dt)^{-1/2}] \qquad (4)$$

where D is the diffusion coefficient, R is the critical interaction radius for quenching, and N_A is the concentration of energy acceptors in molecules/cm^3.[24] The second term in brackets is neglected, as is generally the case, and it is valid to neglect it here based on the exponential nature of the fluorescence decays observed. Thus,

$$k_M = 4\pi DRNC_A \qquad (5)$$

where N is Avogadro's number, and C_A is the concentration of quenchers in mol/cm^3. Equation 3 can then be written as

$$\tau_0/\tau = 1 + 4\pi DRN\tau_0 C_A \qquad (6)$$

where now $4\pi DRN\tau_0$ can be identified with the Stern–Volmer quenching constant, K_q, of eq 1. The donor concentration dependence of K_q is thus contained in the diffusion coefficient D. Thus, experimentally $D \propto C_D^{4/3}$, and since the concentration of donors is proportional to the inverse third power of the donor–donor separation, r_d, i.e., $C_D \propto r_d^{-3}$, the diffusion coefficient is proportional to the inverse fourth power of the donor–donor separation, i.e., $D \propto r_d^{-4}$. Since the diffusion coefficient is given by

$$D = r_d^2 \cdot \beta \qquad (7)$$

where r_d is the average separation between donor molecules, and β is the rate for energy transfer from site-to-site, the transfer rate is proportional to r_d^{-6}. From this it can be concluded that in this system the mechanism for energy migration is a series of random walk steps with each step occurring with a probability or rate given by the Förster expression and involving dipole–dipole resonance transfer in the very weak coupling limit.[7]

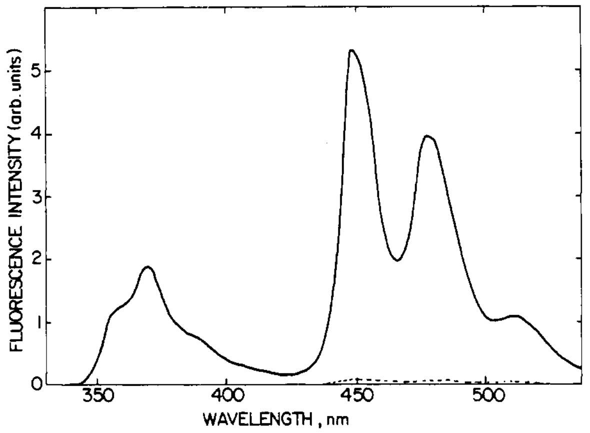

Figure 5. Fluorescence spectrum of a NIPC-doped polystyrene film containing perylene as acceptor. The lower dashed curve is the fluorescence spectrum of the equivalent film containing no NIPC.

From this one should, in principle at least, be able to determine excitation diffusion lengths from the expression

$$l = (2D\tau_0)^{1/2} \tag{8}$$

which when combined with

$$K_q = 4\pi DRN\tau_0 \tag{9}$$

yields

$$l = (K_q/2\pi RN)^{1/2} \tag{10}$$

In order to utilize the experimentally determined values for K_q to determine the excitation diffusion length, l (a parameter which is proportional to the $^2/_3$ power of the donor concentration), it is necessary to know the value for the critical interaction radius R for the NIPC–DMT pair. Based on the fact that DMT quenches NIPC fluorescence through a charge-transfer interaction, a reasonable choice for this interaction radius would perhaps be a value in the neighborhood of the sum of the two van der Waal's radii or the value of 9 Å shown by Nishijima and co-workers[25] to be the upper limit for the quenching distance in the carbazole–$(CH_2)_n$–terephthalic acid methyl ester bichromophore system. Rather than proceeding in this fashion, another NIPC energy donor–energy acceptor system was investigated for which a critical interaction radius could be determined, and from this excitation diffusion lengths could be calculated. The excitation diffusion lengths so determined can then be used to calculate the critical interaction radius for the NIPC–DMT system.

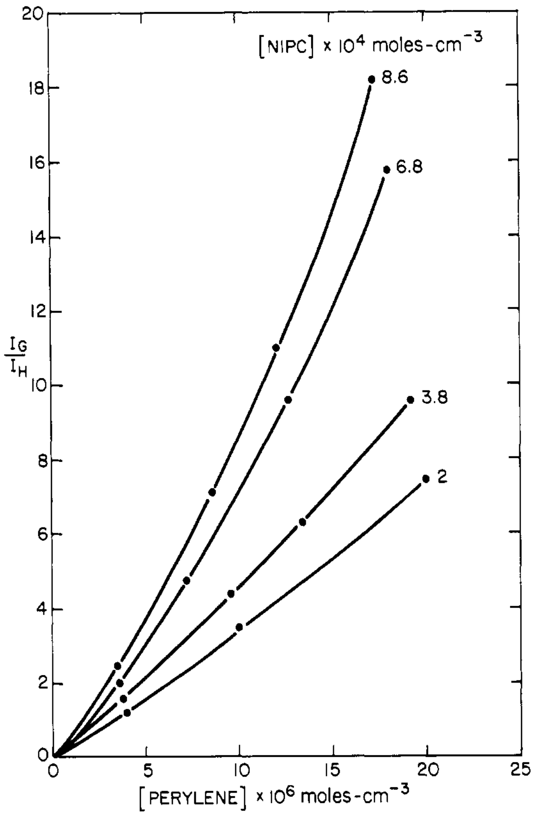

Figure 6. The ratio of perylene to NIPC fluorescence intensities for NIPC-doped polystyrene films containing perylene as the energy acceptor as a function of perylene concentration.

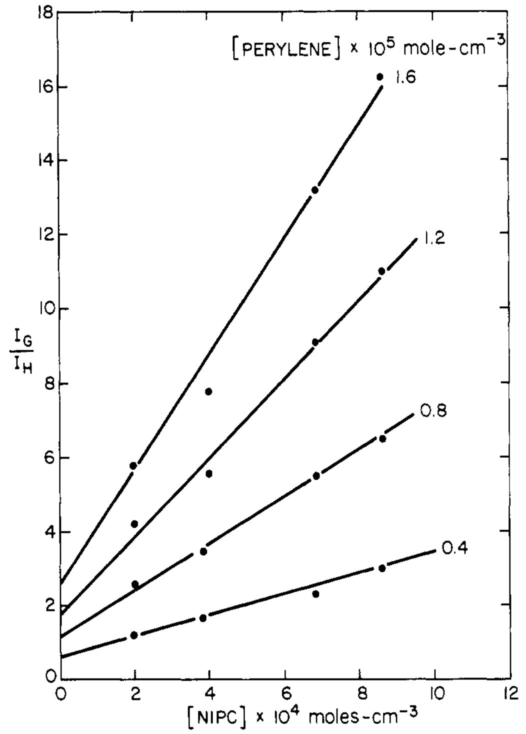

Figure 7. The ratio of perylene to NIPC fluorescence intensities for NIPC-doped polystyrene films containing perylene as the energy acceptor as a function of NIPC concentration.

The second molecularly doped polymer system investigated contained, as before, NIPC as the energy donor with perylene as an energy acceptor. This donor–acceptor pair satisfies the conditions for Förster resonance transfer contrary to the case of NIPC–DMT. Figure 5 shows a typical fluorescence spectrum of a polystyrene film containing 6.8×10^{-4} mol/cm^3 of NIPC and 3.6×10^{-6} mol/cm^3 of perylene. For comparison, the emission spectrum from a polystyrene film containing the same quantity of perylene with no NIPC is also shown. Both samples were excited at 313 nm, a wavelength where NIPC absorbs and perylene has a window. It is clear that the perylene fluoresence measured in the NIPC containing film results almost totally from transfer of electronic excitation from excited NIPC. The results of measurements of the ratio of the guest (perylene) fluorescence, I_G, to that of the NIPC (which is designated the host), I_H, are shown in Figures 6 and 7. The total intensity of the perylene fluorescence is taken to be proportional to the intensity measured at 478 nm, while that of NIPC is taken to be proportional to the intensity at 370 nm. These particular lines are selected instead of the two (0,0) bands, since at these wavelengths there is no distortion of the fluorescence spectra due to reabsorption of emission. While this is not a problem with perylene, since this is always at low con-

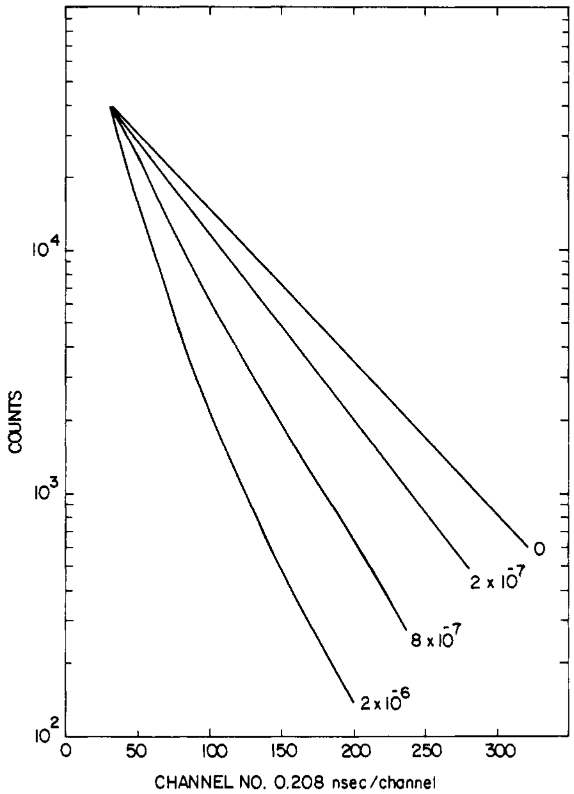

Figure 8. Typical fluorescence decay curves for dilute NIPC doped polystyrene films containing perylene as the energy acceptor. The values for each curve correspond to the total moles of perylene contained in approximately 0.097 cm^3 of solid film.

centration, reabsorption becomes increasingly severe in the case of the NIPC as its concentration proceeds to higher values. This is already evident in the example shown in Figure 5, where the NIPC (0,0) fluorescence band appears lower in intensity than the band at 370 nm. At very low NIPC concentration, where reabsorption of fluorescence is absent, the (0,0) band is in fact more intense than lower energy vibronic bands.[18] The behavior of the I_G/I_H ratios as the concentration of NIPC increases is also consistent with a qualitative picture in which electronic excitation migrates within the system of energy donors prior to being transferred to the acceptor. Although these results were not used in any quantitative fashion, it is interesting to note the different behavior in the limit as the concentration of perylene approaches zero at different NIPC concentrations as opposed to the case where the concentration of NIPC approaches zero at different perylene concentrations. Obviously as the acceptor concentration approaches zero the fluorescence intensity of the acceptor, I_G, approaches zero and $I_G/I_H = 0$. On the other hand, at perylene concentrations sufficiently high to yield detectable fluorescence, the ratio I_G/I_H approaches a finite value as the concentration of NIPC approaches zero. This is a consequence of the existence of single-step long-range energy transfer from excited NIPC to perylene.

As noted above, the principal reason for selection of the NIPC–perylene–polystyrene system for study was for purposes of determining a critical interaction radius, an important parameter which could not be experimentally determined in the NIPC–DMT system. Measurement of fluorescence decay curves for dilute rigid solutions of energy donors in the presence of energy acceptors is a particularly powerful means of determining this distance.[8] Figure 8 displays a fluorescence decay curve for an NIPC doped polystyrene film containing different levels of perylene as well as the fluorescence decay of NIPC in the absence of perylene. These particular films are made dilute in NIPC concentration to avoid, or at least to minimize, excitation migration among the energy donor system. In the absence of perylene the fluorescence decay of NIPC is first order with a lifetime of 14.6 ns. In the presence of perylene, the decay is more rapid and exhibits increasing departure from exponential decay with increasing perylene concentration. The fluorescence decay of NIPC in the presence of the perylene acceptor is described analytically by eq 11, when the energy transfer is

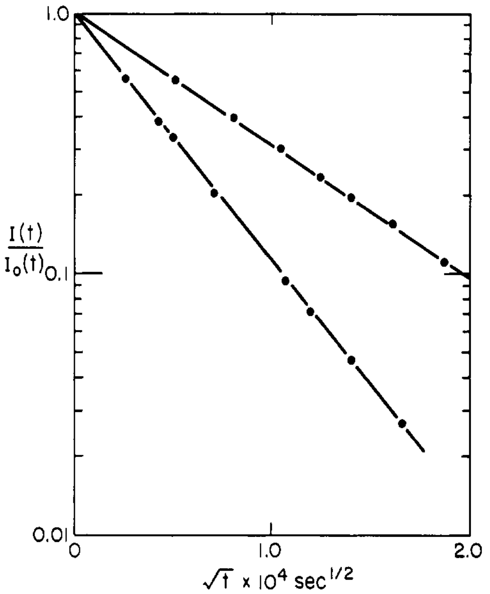

Figure 9. Fluorescence decay time results for dilute NIPC doped polystyrene films containing perylene as the energy acceptor plotted according to eq 14. The concentration of perylene is 8.25 × 10^{-6} mol/cm^{-3} for the upper curve and 2.06 × 10^{-5} mol/cm^{-3} for the lower curve.

$$I(t) = I(0) \exp[-t/\tau_0 - 2(C_A/C^0_A)(t/\tau_0)^{1/2}] \quad (11)$$

by the Förster dipole–dipole mechanism.[7] τ_0 is the donor fluorescence lifetime in the absence of acceptor, C_A is the concentration of added acceptor, and C^0_A is a critical concentration which is defined as that acceptor concentration where the rate constant for energy transfer from the excited donor to acceptor is equal to the sum of the rate constants for all other modes of deactivation of the excited donor. The fluorescence decay in the absence of acceptor is given by

$$I_0(t) = I_0(0) \exp(-t/\tau_0) \quad (12)$$

and thus

$$I(t)/I_0(t) = \exp[-2(C_A/C^0_A)(t/\tau_0)^{1/2}] \quad (13)$$

and

$$\ln I(t)/I_0(t) = -2(C_A/C^0_A)(t/\tau_0)^{1/2} \quad (14)$$

The critical acceptor concentration can then be determined from a plot of ln $I(t)/I_0(t)$ vs. $t^{1/2}$, and knowing the value of C^0_A one can calculate the critical interaction radius R from

$$R = (3/4\pi C^0_A)^{1/3} \quad (15)$$

where C^0_A is the concentration in molecules/cm^3. Plots of log $I(t)/I_0(t)$ vs. $t^{1/2}$ as obtained from the data of Figure 8 are shown in Figure 9. From the slopes of these curves a value for the critical interaction radius for energy transfer to perylene from NIPC is calculated to be 31 ± 2 Å. This then is the intermolecular distance between a ground state

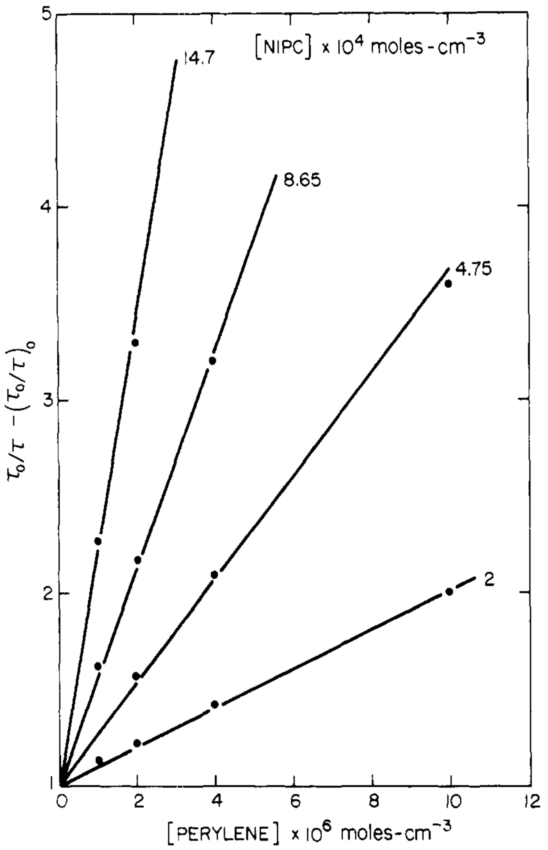

Figure 10. Fluorescence decay time results for NIPC-doped polystyrene films containing perylene as the energy acceptor as a function of the perylene concentration.

perylene molecule and an excited NIPC molecule where the probability for transfer is equal to deactivation by radiative and all other nonradiative processes.

Fluorescence decay curves were then determined for a series of NIPC doped polystyrene films as a function of perylene concentration. The results of these measurements are presented in Figure 10 where values of $\tau_0/\tau - (\tau_0/\tau)_0$ are plotted vs. the concentration of perylene. As before, τ_0 is the fluorescence decay time in the absence of acceptor, τ is the fluorescence decay time in the presence of acceptor, and $(\tau_0/\tau)_0$ is the ratio in the limit that the concentration of NIPC donor goes to zero. This later term becomes increasingly important at the higher levels of perylene concentration, irrespective of the NIPC concentration, and in essence constitutes a correction for the change in NIPC fluorescence decay time resulting from single step energy transfer to perylene, a process which occurs at any NIPC concentration. Because of the nonexponential decay of the NIPC fluorescence, the lifetimes utilized to determine the ratios plotted in Figure 10 are those required for the fluorescence intensity to decay to e^{-1} of its initial value. However, it is important to note that at the donor concentrations used in this series of experiments the departure from first order decay is small. This of course is a consequence of energy migration within the donor subsystem. As the rate of statistical mixing of the initial excitation exceeds the rate of transfer to perylene, the time dependence of the rate constant for transfer is absent since the variation in separation between excited donor and ground state acceptor is removed.

Proceeding in a fashion similar to what was done for the NIPC-DMT system, a quenching constant, K_q, is obtained from the data of Figure 10 and corresponds to the reciprocal of the perylene concentration at which the value of $\tau_0/\tau - (\tau_0/\tau)_0 = 2$. The dependence of this quenching constant on the NIPC donor concentration is shown in Figure 11. The slope of the log K_q vs. log [NIPC] plot yields a value of 1.35, indicating as was found earlier that $K_q \propto C_D^{4/3}$. The importance of the NIPC–perylene results is that now eq 10 can be used to calculate excitation diffusion lengths as a function of donor concentration since the value for the critical interaction radius R is known. The results of these calculations are shown in Figure 12. The value of the excitation diffusion length, l, obtained by extrapolation of the plot to 5×10^{-3} mol/cm^{-3}, a value corresponding to the approximate molar concentration of NIPC groups in a neat NIPC crystal or poly(*N*-vinylcarbazole), yields a diffusion length of about 250 Å. This value is just slightly greater than the value of approximately 200 Å obtained by Klöpffer for PVK.[26] It is interesting that a value close to the excitation diffusion length in PVK is obtained rather than the much larger

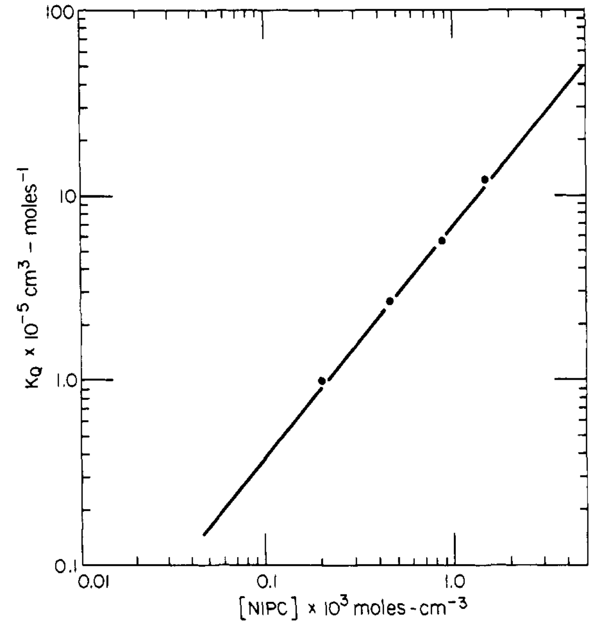

Figure 11. Donor concentration dependence of the fluorescence quenching constant for the NIPC–perylene–polystyrene system.

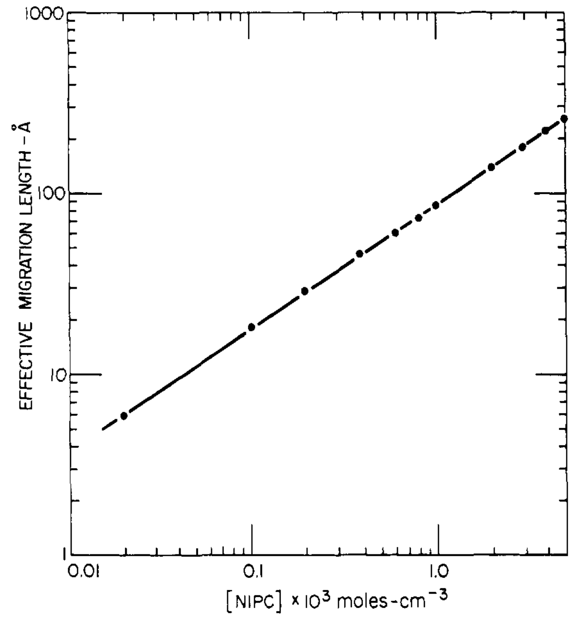

Figure 12. Donor concentration dependence of the excitation diffusion length for NIPC-doped polystyrene.

value of ~1300 Å obtained by Klöpffer for crystalline NIPC.[27] The migration of electronic excitation in a system consisting of molecularly dispersed NIPC in a polystyrene matrix would certainly be expected to follow its behavior in the amorphous neat polymer more closely than in the crystalline state.

The excitation diffusion lengths determined from the NIPC–perylene results can now be used along with the values of K_q determined for the NIPC–DMT system (see eq 10) to calculate a value for R, the critical interaction radius for quenching of the NIPC excited state by DMT. This calculation yields 3.4 Å for this interaction distance, a value which, although perhaps a little too short to be physically sound, is consistent with the charge transfer mechanism for quenching by DMT. In this regard it might be useful to recall that the quenching constant was defined as being the inverse of the DMT concentration where $\tau_0/\tau = 2$. However, the quenching sites in the NIPC–DMT system are not simply isolated DMT molecules, but in reality they consist of NIPC–DMT donor–acceptor pairs. Apparently the concentration of these species is somewhat less than the concentration of DMT in spite of the excess in NIPC concentration. This conclusion is consistent with the rather weak charge transfer interaction between ground state donor and ground state acceptor.[28]

Synopsis

In summary, the mechanism for singlet excitation migration among a system of like chromophores has been determined. For the case of NIPC-doped polystyrene films, the results are consistent with a mechanism in which the migration occurs by a series of random walk steps with each step involving dipole–dipole resonance transfer in the very weak coupling limit (Förster mechanism). These results should be applicable to an understanding of singlet energy migration in films of homo- and copolymers as well as along isolated chains in dilute solution in those cases where the pendant chromophores are weakly interacting. For this process to be important, however, it is necessary of course that there be considerable overlap between the absorption and fluorescence bands of the donor species. In the case of NIPC in the nonpolar polystyrene matrix, this condition is fulfilled. This mechanism cannot be important in systems in which the fluorescence band exhibits a considerable red shift or where the transition moment linking the donor ground and lowest excited singlet state is very weak. Experiments on pyrene-doped polystyrene films have in fact corroborated these expectations.[29] These results will be reported in detail elsewhere.

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