

Photon-Harvesting Polymers

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I. Introduction

It has been recognized for many years that if one member of a group of identical chromophores absorbs a photon, in general the resultant excited state cannot be considered as localized. In the simplest case of a rigid lattice the excitation is distributed over the entire volume as a wave-like linear combination of local excitations and is referred to as a tight-binding exciton.¹ While the detailed description becomes more complex as the "local" excitation is considered to disturb the lattice or to extend beyond a simple lattice point, the physical picture is straightforward: since an excitation localized on any site is degenerate with localization at any other site, it is possible for the energy to migrate among the lattice sites. If there is significant coupling to lattice vibrations the wave function is not expected to retain any specific phase and motion of the excitation can be regarded as a "random walk". While the early work in this area focused on molecular (i.e. van der Waals) crystals (especially of aromatic molecules), it was recognized that these processes were relevant to photosynthetic systems.² In this latter case there are approximately 400 "photon-harvesting" chromophores for every reaction center. While the detailed mechanism(s) that occur in the photosynthetic reaction center have not yet been completely elucidated, the role of the photon harvesting pigments is clear: light absorbed anywhere in this ensemble will be transferred to the reaction center where conversion to useful chemical potential occurs.

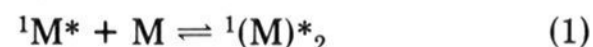
Polymer photophysics was discussed in a relatively small number of papers during the period when molecular crystals were most heavily studied. It was recognized in these earliest papers that energy migration along a polymer chain could occur and this mechanism was invoked to explain the ease of excited state



Stephen E. Webber received his B.A. degree in chemistry from Washington University (St. Louis) in 1962 and held Woodrow Wilson and National Science Foundation Fellowships at the University of Chicago before receiving his Ph.D. degree in 1965, working under the supervision of Stuart A. Rice. He held a National Science Foundation Postdoctoral Fellowship at University College (London) before taking up his present position in the Department of Chemistry at the University of Texas at Austin. His scientific interests have centered on experimental studies of excited-state phenomena including optical studies of rare gas solids (following theoretical work in this area for the Ph.D. degree), triplet-state studies, including the effects of magnetic fields on triplet-triplet annihilation in molecular crystals, and beginning in the late 1970s, the photophysics of polymers.

quenching in these polymers.³ Shortly thereafter there were a number of seminal papers by Fox et al.,⁴ David et al.,^{5,6} and Longworth et al.⁷ that clearly demonstrated triplet energy migration in some polymers containing aromatic chromophores, primarily by the observation of triplet-triplet annihilation or enhanced phosphorescence quenching. An interesting collection of papers having to do with polymer luminescence was published from the 1981 Eighth Katzir Conference.⁸ One of the pioneers in this area, J. E. Guillet has recently written a book that covers many aspects of polymer photophysics and photochemistry.⁹

The fluorescence spectroscopy of polymers with aromatic chromophores was observed to be dominated by excimer emission, which was not surprising considering the high local concentration of chromophores and their separation by a three-carbon chain (an example of the Hirayama rule¹⁰). However the detailed kinetics of excimer formation in polymers¹¹ could not be fit to the Birks scheme, which was originally derived for encounters between ground- and excited-state species:¹²



Given the complexity of intrapolymer motion it is hardly surprising that a nonclassical kinetic scheme is required to fit the observations. One contributing factor

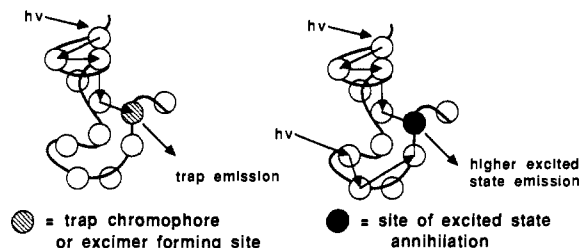


Figure 1. Schematic representation of intrapolymer energy trapping (left) and excited-state annihilation (right).

to this behavior is the possibility that some excimer states may be populated by energy migration along the polymer chain until a pair of chromophores is encountered that are in the appropriate mutual orientation and separation to form an excimer (the so-called "excimer-forming site"). Quite a lot of excellent detailed work on this process has been carried out, primarily by Frank and co-workers.^{13,14}

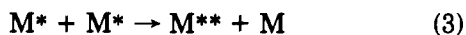
To our knowledge Fox and co-workers⁴ and Guillet and co-workers¹⁵ were the first to covalently attach a trap species to a polymer and study the efficiency of sensitizing the trap via excitation of the main polymer component. This phenomenon defines what is meant by a "photon-harvesting polymer" (this effect was referred to as the "antenna effect" by Guillet et al.¹⁶). A representation of this process is presented in Figure 1. We note that energy transfer to excimer-forming sites is also an example of photon harvesting by a polymer, but the density of traps is difficult to predict because of the complex relationships between this quantity and polymer structure, solvent, temperature, molecular weight, and tacticity. In the context of energy transfer to a chemically distinct species, excimer formation is detrimental because it provides intermediate trapping sites. Excimers may not be irreversible traps if they can thermally dissociate. It is possible in some cases that the excimer can also sensitize the chemically distinct trap via a single step Förster transfer.

In the preceding paragraph it was mentioned that evidence for down-chain energy migration was obtained from the observation of enhanced excited-state quenching or excited-state annihilation. The second-order quenching rate constant may be written as¹⁷

$$k_q = 4\pi N_0(D_Q + \Lambda_E)PR/1000 \quad (2)$$

in which D_Q is the normal diffusion constant of the quencher and Λ_E is the energy migration diffusion rate along the polymer (ordinary diffusional motion of the polymer is considered to be too slow to contribute to k_q). Equation 2 is crude but has been used by us and others⁵ to estimate Λ_E on the basis of simple fluorescence quenching experiments. While it is evident that eq 2 can rationalize efficient quenching of polymer excited states, it is possible for the energy migration process to be so rapid that migration away from a point of quencher contact with the coil diminishes the quenching efficiency.¹⁸ While this idea has not been worked out quantitatively, it does rationalize some anomalous results in the literature.

The annihilation process can be very important at higher excitation fluxes:



(annihilation can occur for any multiplicity of excited

TABLE I. Some Typical R_0 (in Å) Values for Aromatic Chromophores^a

	Naph	2-MeNaph	Phen	pyrene	Anth	DPA
Naph	7.35	11.02	13.16	29.32	23.16	23.27
2-MeNaph	6.76	11.75	13.82	30.74	24.63	24.75
Phen			8.77	14.43	21.72	25.08
pyrene				10.03	21.30	28.94
Anth					21.81	28.92
DPA					6.12	27.15

^a All values from ref 25. Abbreviations are as follows: Naph = naphthalene; 2-MeNaph = 2-methylnaphthalene; Phen = phenanthrene; Anth = anthracene; DPA = 9,10-diphenylanthracene.

state). In favorable cases M^{**} may emit in a characteristically different region than M^* , or perhaps undergo some useful chemical reaction (e.g. ionization). Excited-state annihilation is well-known in molecular crystals,¹² concentrated solution,¹⁹ and from intracoil electronic energy transfer^{20,21} (Figure 1). While annihilation processes represent a potentially useful application for polymeric photoreagents, we will not discuss this subject here. Recent reviews of singlet-singlet annihilation in polymers have appeared,²¹ and a few years ago the present author reviewed triplet-triplet annihilation in polymers.²²

There are two mechanisms that are normally considered in discussions of electronic energy transfer:



(1) long-range: Förster (dipole-dipole)²³

$$k_{DA}(R) = k_D^0(R_0^{DA}/R)^6 \quad (5)$$

(2) short-range: Dexter (exchange)²⁴

$$k_{DA}(R) = k_{DA}^0 \exp(-\alpha R) \quad (6)$$

In both eqs 5 and 6 R is the separation of the donor and acceptor and $k_{DA}(R)$ is the energy-transfer rate for this separation (there may be an orientational effect on $k_{DA}(R)$ ²³ but an average is used in most discussions). In eq 5 k_{DA}^0 is the unimolecular decay rate of the donor molecule and R_0^{DA} may be calculated by knowledge of the spectral overlap of the emission of D with the absorption of A,²⁵

$$(R_0^{DA})^6 = \frac{[(9000 \ln 10)\kappa^2\Phi_{D^*}/(128\pi^6n^4)] \int \epsilon_A(\nu)I_{D^*}(\nu)\nu^{-4}d\nu}{\epsilon_A(\nu)} \quad (7)$$

with the following definitions: $\epsilon_A(\nu)$ = extinction coefficient of the acceptor A and ν corresponds to the energy in wavenumbers, $I_{D^*}(\nu)$ = corrected emission spectrum of D^* (normalized to unity when integrated over all ν), Φ_{D^*} = fluorescence quantum yield of D^* , n = refractive index of the medium (usually regarded as constant over the integration), and κ^2 = average orientation factor, usually taken to be $2/3$ for rapidly randomizing transition dipoles. Many R_0^{DA} values have been tabulated by Berlmann²⁵ and some typical values are presented in Table I. Note that the values are also given for self-transfer, which is the relevant process for down-chain electronic energy transfer. It is also important to note that if the excimer-forming site has an absorption spectrum that is essentially identical with the isolated monomer, then energy transfer to the excimer-forming site will occur with the same rate as down-chain energy migration. This is the usual situation.

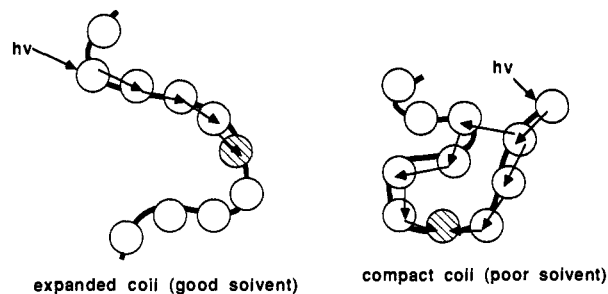


Figure 2. Schematic representation of effect of solvent on intracoll electronic energy transport (EET).

The parameters in eq 6 are not known with the same precision as those of eq 5, but certainly the energy transfer rate is a more rapidly decreasing function of R than for the dipole-dipole mechanism. Since the exchange mechanism involves the overlap of molecular orbitals of the D and A species it is probably best to think of R as the edge-to-edge separation and α would be typical of an atomic orbital exponent. Equation 6 is usually used to describe triplet energy or singlet energy transfer if the transition dipole of the emitting state is very weak (the triplet state is a special case of the latter). It is generally assumed that the maximum range for this transfer mechanism is ca. 10–15 Å.²⁶ Very recently Closs et al.²⁷ have examined triplet energy between donor-acceptor species attached to rigid spacer molecules and found a very consistent exponential decrease in triplet-energy-transfer rate with the number of sigma bonds separating the chromophores. The same workers also demonstrated that there exists a proportionality between triplet energy transfer and electron transfer.

A particular "polymer effect" in the above processes is that the density of chromophores covalently bound to a polymer depends on the thermodynamics of the polymer-solvent interaction. In general a good solvent causes the coil to be expanded, which may decrease the density of excimer-forming sites, but may also decrease cross-chain electronic energy transfer (if present). A more extreme example of this may occur with polyelectrolytes or polyacids in which electrostatic repulsion between repeating groups depends strongly on ionic strength, dielectric constant, or pH. These ideas are illustrated in Figure 2. It is very difficult to treat these effects analytically because there may exist correlations between pendent chromophores that greatly modify the rate of electronic energy transport (EET). These correlations may not be a simple function of coil density.

In general it is easy to demonstrate the existence or absence of photon harvesting in polymers and the efficiency of this process may be quite high in favorable cases. However it is difficult to distinguish the details of the phenomenon. For example, it is not known unambiguously if cross-chain EET is important. Likewise the relative importance of single-step Förster transfer and down-chain EET to the trap is not well-characterized. However the general concepts that underlie a rational design of photon-harvesting polymers are clear and one may hope that these "design principles" will be exploited to provide many interesting polymeric photoreagents in the future.

In the following sections we will describe some of the more detailed considerations of the photon-harvesting phenomena and provide some illustrative examples.

Most examples involve the singlet state since triplet-state trapping is more difficult to demonstrate except in low-temperature glasses or solid films.

II. Characterization of Sensitization. Steady-State Methods

Regardless of the detailed mechanism of sensitization, the most basic definition of the quantum efficiency (χ) of a process like eq 4 is²⁸

$$\chi = \frac{\text{no. of sensitized excited acceptor states}}{\text{no. of directly excited donor states}} \quad (8)$$

Another way of considering the sensitization phenomenon is the OD enhancement factor. The "apparent" OD of the acceptor at excitation wavelength λ is²⁹

$$\text{OD}(\lambda)_{\text{sens}} = \text{OD}(\lambda)_{\text{donor}}\chi + \text{OD}(\lambda)_{\text{acceptor}} \quad (9)$$

where $\text{OD}(\lambda)_{\text{acceptor}}$ and $\text{OD}(\lambda)_{\text{donor}}$ are the ODs of the individual donor and acceptor molecules. Thus the OD enhancement factor is

$$E_{\text{sens}} = (\text{OD}(\lambda)_{\text{donor}}\chi / \text{OD}(\lambda)_{\text{acceptor}}) + 1 \quad (10)$$

E_{sens} represents a kind of figure of merit since it is possible that χ decreases with donor concentration but the enhancement factor may continue to increase. From the point of view of depositing as many photons into the acceptor as possible it is this enhancement factor that is important. Of course E_{sens} diverges for wavelengths such that $\text{OD}(\lambda)_{\text{acceptor}} = 0$ so for some considerations one may prefer to use $\text{OD}(\lambda)_{\text{sens}}$ (eq 9). In either case the point is the same: for optimal photon harvesting it is the product $\text{OD}(\lambda)_{\text{donor}}\chi$ that must be maximized.

There have been several methods used to estimate χ . The first was originally proposed by Holden and Guillet:²⁸

$$(I_A/I_D)(\phi_D/\phi_A) = \chi_{\text{SS}}/(1 - \chi_{\text{SS}}) \quad (11)$$

In eq 11 I represents the fluorescence intensity (i.e. the integral of the corrected fluorescence spectrum) and ϕ the fluorescence yield. The subscript SS recalls that steady state spectroscopy is used to obtain the χ value. As it stands eq 11 does not correct for any direct excitation of the acceptor but I_A can be corrected for this effect. In practice one attempts to find an excitation wavelength for which direct excitation is minimized.

We have estimated χ_{SS} by comparing the absorption and excitation spectrum of the photon-harvesting system with the absorption spectrum of the acceptor alone.²⁹ It is assumed that there exists emission wavelengths that are unique to the acceptor. In such a case the excitation spectrum will be identical with the absorption spectrum of the donor-acceptor system if χ_{SS} is unity and will be identical with the acceptor alone if χ_{SS} is zero. The detailed expression is

$$\chi_{\text{SS}} = [(I_A(\lambda)/I_A(\lambda_A))f_A(\lambda_A) - f_A(\lambda)]/f_D(\lambda) \quad (12)$$

where $I_A(\lambda)$ = fluorescence intensity of the acceptor excited at wavelength λ which is absorbed by both donor and acceptor, $I_A(\lambda_A)$ as above except λ_A is absorbed only by the acceptor, and $f_D(\lambda)$, $f_A(\lambda)$, and $f_A(\lambda_A)$ = fraction of light absorbed by D or A at the indicated wavelength. Equation 12 is actually easy to use and does not require a separate determination of the

quantum yields of fluorescence for the donor and acceptor. In practice eq 12 may not be accurate if the OD of the acceptor is much lower than the donor. Equations 11 and 12 both assume that the quantum yield of fluorescence of the acceptor is the same for direct and sensitized excitation and that the fluorescence yield of the donor is decreased only by energy transfer. This latter assumption also suggests the relation

$$\chi_{SS} = 1 - (I_D/I_D^0) \quad (13)$$

in which I_D^0 is the fluorescence intensity for the donor in the absence of acceptor and I_D is the same quantity in the presence of acceptor. Since it is known that the quantum yield of fluorescence may be a function of molecular weight or chromophore loading, it is best if one can compare a given donor polymer with and without acceptors.

All methods that determine χ_{SS} assume that the fluorescence quantum yield and extinction coefficient of the donor is unchanged by covalent attachment of an acceptor. While this assumption seems reasonable there are several considerations:

(1) For copolymers the point of acceptor attachment may occur preferentially in regions that are rich or lean in donor. Hence the donor quantum yield of chromophores near the acceptor may not be typical of the full ensemble.

(2) The acceptor may alter the density of excimer-forming sites because of steric effects, which in turn could change the monomer fluorescence yield.

(3) Copolymerization of an acceptor species may alter the molecular weight of the tagged polymer. Alternately the efficiency of attachment of an acceptor to a polymer may be molecular-weight dependent (this situation is similar to 1, above).

Unfortunately there is no general method to check if these complications exist for a given system. In principle one can verify that the steady-state results are consistent with the time-dependent data.

III. Characterization of Sensitization. Time-Dependent Properties

In all cases energy transfer from a donor to an acceptor should shorten the lifetime of the donor excited state. We may write the time-dependent donor emission as

$$F(t)_D = e^{-t/\tau_D} G_D(t) \quad (14)$$

in which τ_D is the usual unimolecular lifetime of D^* and $G_D(t)$ is the modification of the decay that is induced by the polymer environment and/or energy transfer to the acceptor. Even in the absence of an acceptor $G_D(t)$ may differ from unity because of the heterogeneous environment that exists in polymers. We denote $G_D^0(t)$ as the decay function without any acceptors present and $G_D^x(t)$ the decay with x mole fraction of covalently attached acceptor. The steady-state intensity is proportional to the integral of $F(t)_D$:

$$\Phi_D^x \propto \int e^{-t/\tau_D} G_D^x(t) dt \quad (15)$$

An important point about eq 15 is that the functional form of $G_D^x(t)$ is not important. Thus one can use any convenient function to fit experimental data (e.g. multiple exponential decay) without assigning any

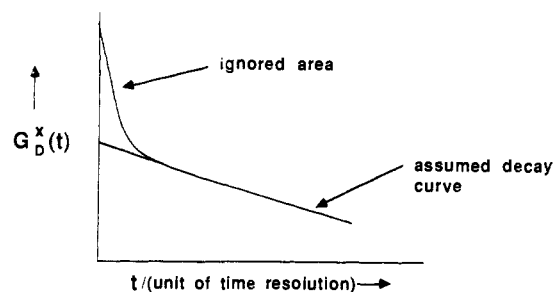


Figure 3. Illustration of the effect of a rapidly decaying component in G_D^x on F_D^x (refer to eq 15).

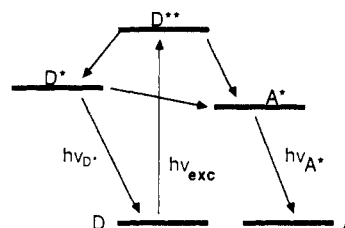


Figure 4. Representation of sensitization of A by nonemitting precursor state D^{**} .

particular physical significance to the parameters of the fitting function. However there is a great deal of information in the $G_D^x(t)$ function beyond eq 15. We will come back to this point later. The point of the present discussion is that from eq 15 one may compute

$$\chi_t = 1 - (\Phi_D^x/\Phi_D^0) \quad (16)$$

which may be compared to χ_{SS} obtained by eqs 11–13 from steady-state spectra. Disagreement would imply that the assumptions inherent in eqs 11–13 (e.g. chromophore fluorescence yield independent of acceptor attachment) or eqs 14 and 15 are not correct.

While eqs 14 and 15 are straightforward we have found $\chi_t < \chi_{SS}$ in some cases.^{29,30} This result can originate from experimental limitations. A rapidly decaying component of $G_D^x(t)$ may not be detected and consequently the extrapolated $G_D^x(t)$ obtained from a fit to the data will always underestimate I_D^x (see Figure 3). This situation is analogous to "static quenching" that is often encountered in photophysics. The only way to test for this is to improve the experimental time resolution. There is another situation that can lead to $\chi_t < \chi_{SS}$. Equations 15 and 16 assume that it is the donor-emitting state that is the sole precursor to A^* . However it is possible for the initially excited state to sensitize A before relaxing to the emitting state. This is represented schematically in Figure 4.

If D^* is the sole precursor of A^* then Fredrickson and Frank³¹ have pointed out that the time dependence of A^* is a convolution with $F(t)_D$:

$$F(t)_A = e^{-t/\tau_A} \int_0^t d\tau e^{-(1/\tau_D - 1/\tau_A)\tau} [-dG_D(\tau)/d\tau] \quad (17)$$

In eq 17 it is assumed that the A^* state decay can be represented by a single exponential. This is frequently the case. The validity of this equation could be very useful in establishing the details of the polymer photophysics. However the decay data must be of very high quality and corrected for typical experimental artifacts (e.g. wavelength effects on the time response of detectors which can distort the time response of D^* emission relative to that of A^*). Further complications arise

when one considers depopulation of the trap, as is often the case with excimers.^{32,33}

All detailed theories of EET focus on the time dependence of the D* population. In the polymer literature there have been a variety of approaches to this problem. Much of the earliest work used a multiexponential function

$$F(t)_D = \sum_{i=1}^N a_i e^{-t/\tau_i} \quad (18)$$

in which $N = 3$.¹¹ While such a function is often adequate to fit experimental data, the individual a_i and τ_i values may not be of direct physical significance. Quite often detailed kinetics schemes have been generated to rationalize the a_i and τ_i parameters, although it has not been possible to establish any unique scheme in general.

The problem of simultaneous energy migration and trapping has been studied theoretically by a number of workers for many physical systems, including polymers, and will be reviewed in the next section. A form like eq 18 can result but N corresponds to the size of the ensemble of chromophores (i.e. the degree of polymerization in the case of polymers). While some results have been reported in which a distribution of lifetimes is used to analyze the data,³⁴ this methodology has not yet been routinely applied in the polymer literature. It is our belief that this approach is the most generally useful if stable fits can be obtained, and it is understood that the individual components of a distribution do not necessarily have direct physical significance (see later).

IV. Theory of Photon Harvesting in Polymers

The theory of energy-transfer processes has been considered by a large number of workers. There are several limiting cases that permit analytical solutions: (1) low density of donors such that photon harvesting occurs via a single-step transfer, (2) a high density of donors (such that donor-donor multistep transfer can occur) at either short times or (3) in one dimension. The solution to energy migration and trapping within an arbitrary geometry at all times requires an explicit solution to the time-dependent equations. We have recently applied the Lanczos algorithm to this latter problem with encouraging results.³⁵ We now consider these various cases.

A. Low-Density Case: Direct Energy Transfer

Loring, Andersen, and Fayer³⁶ have defined the following dimensionless concentrations:

$$c_D = (4\pi/3)(R_0^{DD})^3 \rho_D \quad (19a)$$

$$c_T = (4\pi/3)(R_0^{DT})^3 \rho_T \quad (19b)$$

in which R_0^{DD} and R_0^{DT} are the Förster radii for donor-donor and donor-trap transfer and ρ_D and ρ_T are the average number densities of donor and trap. The appropriate limit for the results considered in this subsection is $c_D \ll c_T$. This limit is referred to as the direct energy transfer (DET) limit. The decay induced by the energy transfer (see eq 14) can be written^{37,38}

$$G_D(t) = \exp\left\{-\rho_T \int g(r)[1 - \exp(-w(r)t)]4\pi r^2 dr\right\} \quad (20)$$

In eq 20 $g(r)$ is the pair correlation function that de-

TABLE II. Factors F^a and g^b from Eq 21

	1-D	2-D	3-D
F	2	p	$4p/3$
	random	acceptor donor	acceptor \perp donor
g	1	1.2	0.90
(κ^2)	($2/3$)	($4/5$)	($3/5$)

^aFrom refs 38a and 39. ^bFrom ref 71. g represents the ratio between the κ^2 for the case of randomly randomizing dipoles ($2/3$) and constrained dipoles. The κ^2 values are given for comparison. The R_0 values usually quoted assuming that $\kappa^2 = 2/3$.

scribes donors and acceptors and $w(r)$ is the energy transfer rate as a function of distance, which is usually assumed to obey the Förster law (eq 5). The integral in eq 20 is over all available space and can be limited to a finite range. In practice an infinite volume is usually assumed. Equation 20 in one form or another has been known for a long time. For an infinite range in the integral it has been shown that³⁹

$$G_D(t) = \exp[-pF(R_0^{DT}/a)^d \Gamma(1-d/s)g(t/\tau_D)^{d/s}] \quad (21)$$

In eq 21 d is the dimensionality of the system and s is the power in the transfer law

$$w(R) = (g/\tau_D)(R_0^{DT}/R)^s \quad (22)$$

in which $s = 6$ is the usual case (cf. eq 5) and g is a factor that arises from the average over the orientation of the donors and acceptors. Usually $g = 1$ is appropriate but other values are possible under physically realistic conditions. F is a constant appropriate to the dimensionality. Both quantities are tabulated in Table II. The constant a is the lower limit of donor-acceptor separation, $\Gamma(1-d/s)$ is the Euler Gamma function and p is the fraction of the sites of the embedded geometry occupied by traps. For the experimental point of view the important result is that $G_D(t)$ may decay like

$$G_D(t) = \exp(-A(t/\tau_D)^n) \quad (23)$$

with $n = 1/6$, $1/3$, or $1/2$ for 1, 2, and 3 dimensions respectively. One would not expect a polymer to behave like a truly 1-D object if R_0^{DT} is on the order of the coil size or the average separation of nonbonded segments. We have argued²⁹ that for an infinite polymer described by a coil density⁴⁰

$$\rho \approx M/R_g^3 \propto R_g^{(1-3\alpha)/\alpha} \quad (24)$$

that the appropriate value of d is

$$d \approx 1/\alpha \quad (25)$$

For a θ -solvent $\alpha = 0.5$ and $n = 1/3$ in eq 23 is expected. This is a particular application of relations proposed by Klafter and Blumen³⁸ for nonclassical (fractal) geometries, for which eq 21 is valid (with the fractal dimension δ replacing the classical dimension d) and F is a shape factor that depends on the geometric model.

The main point of this discussion is that for classical and nonclassical geometries single-step energy transfer leads to nonexponential decays which in the limit $R_g \gg R_0^{DT}$ may be expected to be in the form of eq 23 (i.e. exponential decay with a fractional power of time). Because of the generality of eq 21 it has been proposed to use fluorescence decay to test structural models for pores³⁹ or interfaces.⁴¹ Related approaches have been used for biological molecules for years.⁴² Fayer and co-workers have used this type of approach to obtain

very precise R_g values for tagged polymers in solid solution.⁴³

B. Short-Time Expansions

There have been a number of important papers that have come out of the Stanford group (Frank, Fayer, Andersen, and co-workers) that have considered the problem of simultaneous donor-donor transfer and trapping for arbitrary geometry, concentration, and intermolecular distribution functions. A variety of mathematical approaches have been used to obtain the Laplace transform of $G_D(t)$ ($\equiv G_D''(\epsilon)$). From the standpoint of testing distribution functions for polymers some of the most useful results are in the low-density limit discussed in the previous subsection. An expansion of $G_D''(\epsilon)$ for the case of simultaneous donor-donor and donor-trap energy transfer was obtained by using a three-particle Padé approximation for infinite Gaussian chains:⁴⁴

$$G_D''(\epsilon) = \epsilon^{-1} \{ 1 + 2.309s_T(\epsilon\tau_D)^{-1/3} + 1.571c_T(\epsilon\tau_D)^{-1/2} + [1.397s_T^2 + \alpha_4(x)s_Ts_D](\epsilon\tau_D)^{-2/3} + [1.375s_Tc_T + \alpha_6(x)s_Tc_D](\epsilon\tau_D)^{-5/6} + [0.8966c_T^2 + \alpha_5(x)c_Tc_D](\epsilon\tau_D)^{-1} + \dots \} \quad (26)$$

In eq 26, $\alpha_n(x) = \text{constants}$ that are a function of $x = R_0^{DT}/R_0^{DD}$, $\tau_D = \text{normal lifetime of the donor in the absence of trapping, and}$

$$s_D = \pi q_D(R_0^{DD}/a)^2, \quad s_T = \pi q_T(R_0^{DT}/a)^2 \quad (27)$$

where q_D and q_T are the average number of donors or traps per statistical segment and a is the length of the statistical segment. c_D and c_T are the same as in eq 19. Equation 26 explicitly distinguishes bulk concentrations (c_D, c_T) from purely intracoil EET, which depends on s_D and s_T . The inverse transform of $G_D''(\epsilon)$ to obtain the highly nonexponential $G_D(t)$ can be carried out numerically for finite times. While the $G_D(t)$ curves depend systematically on the donor or trap concentrations and the segment length (chain stiffness), there is no simple property of the donor decay curve that can be uniquely related to the model parameters. This is likely to be a general difficulty in the application of multistep EET theories to polymer systems.

Trapping on disordered lattices has been considered by Klafter et al.³⁸ One expects that the number of unique lattice sites that have been visited by the excitation after m steps is approximated by

$$S_m \approx m^{d_s/2} \quad (28)$$

where d_s is the "spectral dimension". This dimension is related to the connectivity of the lattice with respect to EET (or any other transport process) and has the value of 1 and 2 for perfect 1-D and 3-D lattices, respectively. The decay function of the excitation is given by

$$G_D(t) \approx \exp(-pm^{d_s/2}) = \exp[-p(t/\tau_h)^{d_s/2}] \quad (29)$$

where in the second form the excitation hopping time, τ_h , has been introduced. The quantity p represents the mole fraction of traps (cf. eq 23). It is implicit in the above that energy transfer occurs only between adjacent lattice sites, like the model considered in the next

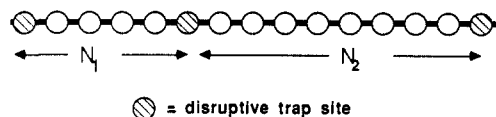


Figure 5. Representation of disruptively quenched 1-D chain.

subsection. Thus to the extent that a polymer may be treated as a disordered but nearly 1-D lattice with nearest neighbor transfer we expect

$$G_D(t) \approx \exp(-Apt^n) \quad (30)$$

with $n \geq 1/2$ (cf. eq 23).

C. Explicit Solutions

1. One-Dimensional Lattices

Pearlstein et al.⁴⁵ have considered EET on one-dimensional linear or circular lattices that contain traps within the chain ("disruptive") or in proximity to the chain ("nondisruptive"). The linear disruptive case is of most interest to us if we assume that irreversible trapping of the energy occurs. For a long chain with several traps the chain may be thought of as a group of segments each with a disruptive trap at the end. These ideas are illustrated in Figure 5. Fredrickson and Frank⁴⁶ have derived an expression for the probability of a segment of length N to occur in a chain of total length L to be

$$P(N) = (N/L)(L - N - 3)p^2(1 - p)^{N+1} \quad (31)$$

in which p is the mole fraction of traps. For each segment of length N with a disruptive quencher at each end the time dependent decay is given by Pearlstein et al.⁴⁵ as

$$G_D^N(t) = [2/(N + 1)N] \sum_{k=1}^n \cot(\alpha_k/2) \exp\{-4Wt \sin(\alpha_k/2)\} \quad (32)$$

where, $n' = N/2$ for N even; $n' = (N - 1)/2$ for N odd; $\alpha_k = (2k - 1)\pi/(N + 1)$. If N is large the lowest decay rate will asymptotically approach

$$\lim_{t \rightarrow \infty} G_D^N(t) = [(8/\pi^2)(N + 1)/N] \exp[-W\pi^2t/(N + 1)^2] \quad (33)$$

In eq 33 W corresponds to the rate of energy hopping between adjacent chromophores. The preexponential factor has a large value (ca. 0.8). Thus at long times one expects an exponential decay for any given segment length. Fredrickson and Frank⁴⁶ have averaged eq 32 using $P(N)$ in eq 31 to obtain

$$\lim_{p \ll 1, Wt \rightarrow \infty} \sum P(N) G_D^N(t) = (1 - p)^2 \exp(4p^2Wt) \operatorname{erfc}[2p(Wt)^{1/2}] \quad (34)$$

(erfc = complementary error function). Obviously eq 34 is a highly nonexponential function, and it has the advantage of being a reasonably easily manipulated analytical form (i.e. compare to eq 26). The limits in eq 34 are of physical interest because W^{-1} is likely to be on the order of 10–200 ps while the fluorescence lifetime of a typical chromophore is on the order of 5–25 ns. It is less clear how small p must be for eq 34 to be valid and what one might expect for typical polymer systems. Frank et al.¹⁴ have analyzed decay curves and

the integrated form (see eq 16) to estimate p for poly-(2-vinylnaphthalene) and polystyrene films to be 0.072 and 0.33, respectively.

The most significant concern with the results of this subsection is the limitation to one-dimensional and nearest neighbor energy transport. In the next subsection we describe an explicit and general numerical method to circumvent these limitations.

2. Use of the Lanczos Algorithm³⁵

A very general approach to the problem of EET is in terms of a probability vector \mathbf{p} and a rate matrix \mathbf{W} :

$$d\mathbf{p}/dt = \mathbf{W}\mathbf{p} \quad (35a)$$

$$\mathbf{p}(t) = e^{\mathbf{W}t}\mathbf{p}(0) \quad (35b)$$

Each element of $\mathbf{p}(t)$ represents the probability that the i th chromophore is excited and $\mathbf{p}(0)$ is the initial excitation distribution. Normally any of the N equivalent chromophores may be excited such that

$$p(0)_i = 1/N \quad (36)$$

(this is the same initial condition used by Pearlstein et al.⁴⁵ to derive eq (32)). Some additional sites may be traps, assumed to be irreversible in most studies to date, in which case the rate constant for energy transfer away from the site is zero. The solution to eq 35 may be written

$$\mathbf{p}(t) = \sum \langle \lambda_i | \mathbf{p}(0) \rangle e^{-\lambda_i t} | \lambda_i \rangle \quad (37)$$

in which λ_i and $|\lambda_i\rangle$ are, respectively, the i th eigenvalue and eigenvector of \mathbf{W} and $\langle \lambda_i | \mathbf{p}(0) \rangle$ is a scalar product. The experimental observable is not the individual elements of $\mathbf{p}(t)$ but the total probability that any of the chromophores remain excited,

$$S(t) = \sum p(t)_i \quad (38)$$

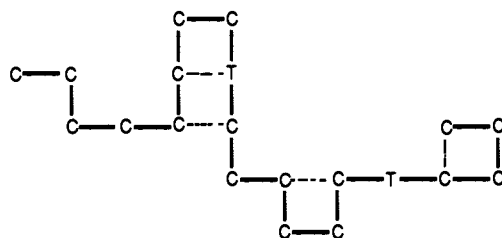
While these relations are well-known, obtaining the eigenvalues and eigenvectors of \mathbf{W} can be quite time consuming for large N . Furthermore in the present context the eqs 35–38 must be averaged over many different polymer conformations, each of which has a different rate matrix \mathbf{W} .

The Lanczos algorithm is ideally suited to this problem because the matrix \mathbf{W} is primarily tridiagonal with a small number of other elements (i.e. a “sparse matrix”). This is illustrated in Figure 6 for a simple cubic-lattice polymer model.³⁵ With this method the important eigenvalues and the appropriate projections required in eqs 37 and 38 are obtained very efficiently. Thus one can explicitly construct the ensemble average (a_i represents the i th element of the scalar product in eq 37):

$$\langle S(t) \rangle = \langle \sum a_i e^{-\lambda_i t} \rangle \equiv G_D(t) \quad (39)$$

Note that the fundamental form of the solution is a sum of closely spaced exponentials. Thus one may compute $G_D(t)$ for finite size polymers and any conformational model desired. Furthermore one is not limited to nearest-neighbor hops. Non-nearest neighbor energy hops can occur either because of intrachain non-nearest neighbor contacts (see Figure 6) or because of long range EET (e.g. the Förster model with $R_0^{DD} >$ average chromophore spacing).

While eq 39 is general, it is not expressed as any simple function of parameters (cf. eq 34). We have



$$\mathbf{W} = \begin{matrix} -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & -2 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & -2 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & -2 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & -3 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & -3 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & -2 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & -2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & -3 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -2 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -3 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -2 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -2 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & -3 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -3 & 1 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -2 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -2 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -2 \end{matrix}$$

Figure 6. Representation of a polymer coil with a small number of non-nearest neighbor contacts and the corresponding sparse \mathbf{W} matrix. Diagonal elements in bold type correspond to chromophores with more than bonding nearest neighbors. Underlined diagonal elements correspond to chromophores placed next to a trap.

found that the properties of $\langle S(t) \rangle$ vary smoothly as a function of a simple polymer coil model.^{35,47} There are many ways to characterize the extremely nonexponential decay of $\langle S(t) \rangle$. A form that we have found to vary systematically as a function of model parameters is $\alpha(t)$ defined by the following (cf. eqs 23 or 29):

$$\langle S(t) \rangle = \exp\{-A(t)t^{\alpha(t)}\} \quad (40)$$

$\alpha(t)$ may be interpreted as the effective spectral dimension and is expected to lie between ca. $1/3$ and 1. The former corresponds to single-step transfer on an ideal Gaussian chain (i.e. θ -solvent), which would be expected to be valid for short times. The latter arises from the domination of $\langle S(t) \rangle$ by the smallest eigenvalues at long time (see eq 39). Both $A(t)$ and $\alpha(t)$ vary systematically with time and model parameters but we have found $\alpha(t)$ to be more useful. Typical plots of $\alpha(t)$ are presented in Figure 7. We should emphasize that the exponential form in eq 40 can be applied to any nonexponential decay data, even a traditional three-exponential fitting function (however this latter function is not a good mimic of the very short time behavior). These approaches are in the early stages of development and will be the subject of future research publications.⁴⁷ The general subject of EET on disordered lattices has been the focus of considerable theoretical and experimental effort in recent years and is discussed in two recent books.^{48,49}

After this review was completed Van Rensburg et al.⁵⁰ published an explicit calculation of intrapolymer EET using a model essentially identical with that described above. One of the primary motivations of their work was to examine scaling and limiting behavior of exciton dynamics.

TABLE III. Photophysics of Naphthalene-Containing Polymers

abbreviation ^a	ref(s)	comments
1. P1VN	72-74, 76	excimer can thermally dissociate to form monomer excited state
2. P1VN-co-MMA	75, 76	temperature dependence of I_M/I_E
3. P2VN	74, 52	multiple exponential decay, temperature dependence of I_M/I_E demonstrates complex photophysical scheme
4. R = CH ₃ ; P(2VN- <i>alt</i> -MMA) R = H; P(2VN- <i>alt</i> -MA)	29	excimer fluorescence repressed in alternating copolymer except in aqueous solution; in H ₂ O I_M/I_E is pH dependent
5. P2VN- <i>alt</i> -MAA	63	strong excimer fluorescence in aqueous solution; I_M/I_E a function of pH and nonalternation
6. P2IPN	53	excimer fluorescence persists in 77K glasses, strong excimer fluorescence seems to be tacticity effect
7. P2IPN- <i>alt</i> -MAA	77	excimer fluorescence function of pH and nonalternation
8. PtBu2VN	78, 79	bulky <i>tert</i> -butyl group decreases excimer formation but L_S similar to P2VN; high energy excimer observed
10. R = H; P2NMMA R = CH ₃ ; P1(2N)EMA	81, 82	strong effect of R on I_M/I_E and L_S
11. P2NA, P1NA, R = H P2NMR, P1NMR R = CH ₃	83, 74, 84 58	solvent effect on I_M/I_E ; R = CH ₃ tends to increase I_M/I_E ; isotactic sequences decrease I_M/I_E
12. $n = 1$; P2NMMA; P1NMMA $n = 2$; P2NEMA; P1NEMA $n = 3$; P2NPMA; P1NPMA	85, 86	I_M/I_E dependent on n
13. PAcN	5, 87, 58, 60, 61	reduced excimer fluorescence
14. PAcN- <i>alt</i> -MMA	75	I_M/I_E as function of composition; fluorescence depolarization implies energy migration
15. PAcN- <i>alt</i> -MAN	87	interesting comparison with PAcN
16. PAcN-co-AN PAcN-co-MAN PAcN-co-2VN	60	significant energy migration implies by fluorescence quenching, unusual variation with polymer composition report

^aFor structures see Chart I.

TABLE IV. Photophysics of Polymers with Chromophores Other than Naphthalene

chromophore	ref	comments
1. biphenyl	88	compare photophysics of random and alternating copolymers with methyl methacrylate; moderate values of L_S deduced from quenching
	89	singlet-singlet annihilation studied
2. phenanthrene	90, 91	9-methyl ester; look at EET and sens of anthracene; time-dependence and χ values characterized
	64	block copolymers of 9-vinylphenanthrene with methacrylic acid; excimer formation as a function of solvent, MW
	92	compare photophysics of 9-vinylphenanthrene in random and alternating copolymers with methacrylic acid, MMA
3. carbazole	93, 94, 95	effect of different points of vinyl substituent on polymer photophysics; discussion of different excimer structures; effect of MW of polymer on photophysics in film of polystyrene or PMMA
	96	analysis of fluorescence decay in terms of monomer/excimer species and the use of model compounds
	30	significant EET deduced from quenching studies
4. pyrene	97	fluorescence totally dominated by excimer, even at low temperature
5. anthracene	98	different substituted anthracenes; EET studied by comparative quenching
	99, 100	copolymers of phenyl anthracene and styrene; EET characterized by quenching
	101	study of singlet-singlet annihilation in poly(vinylidiphenylanthracene)

V. Polymer Architecture for Photon Harvesting

Polymer architecture can be varied by the following: (1) choice of chromophore, (2) method of attachment to polymer, (3) tacticity, and (4) copolymerization.

Obviously the choice of chromophore is the most critical variable in designing photon harvesting polymers, since the polymer environment usually does not significantly modify fundamental photophysical properties (except for encouraging excimer formation). All things being equal, the largest R_0^{DD} (self-transfer) is desired (see Table I). If the average chromophore separation is a then the average energy hopping rate will be given approximately by

$$k_h = 1/\tau_h = (1/\tau_D)(R_0^{DD}/a)^6 \quad (41)$$

The 1-D energy migration constant is given by

$$\Delta_E = (1/2)(a^2/\tau_h) \quad (42)$$

and the mean energy diffusion length is given by

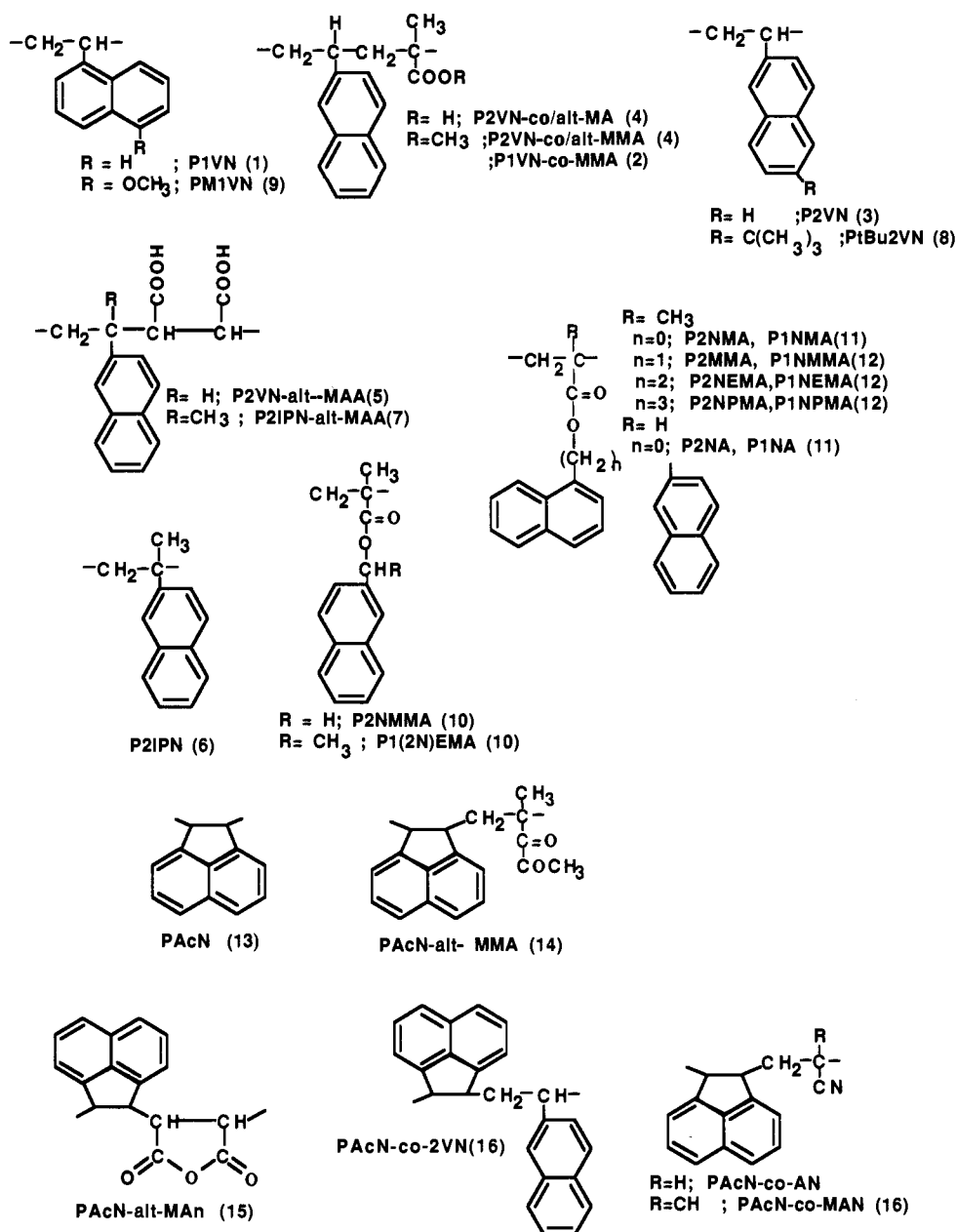
$$L_E = (2\Delta_E\tau_D)^{1/2} = (R_0^{DD})^{3/2}/a \quad (43)$$

Thus at this level of approximation the lifetime of the excited state does not matter. In general one expects long lifetimes to be advantageous because mechanisms other than Förster dipole-dipole may be operative. Triplet energy transfer is the classical example of this.

The above discussion ignores the complexity of excimer formation. The importance of excimer formation depends on the properties of the chromophore itself and its mode of attachment to the polymer. For example, naphthalene and carbazole form very stable excimers but phenanthrene and diphenylanthracene do not,⁵¹ 2-vinylnaphthalene^{30,52} and isopropenylnaphthalene⁵³ polymers have very strong excimer fluorescence, acenaphthylene polymers less,⁵ and there is virtually no excimer fluorescence for 2-*tert*-butyl-6-vinylnaphthalene⁵⁴ (see Chart I for structures). Some of the photophysical properties of some typical and heavily studied polymer-bound chromophores are presented in Table III (naphthalenic systems) and Table IV (chromophores other than naphthalene).

In principle polymer tacticity can greatly modify the ability to form excimers and also the average chromo-

CHART I



phore-chromophore separation. DeSchryver et al. have demonstrated the important differences in excimer-forming rates for model compounds that represent different polymer diads.⁵⁵ While the specific rate differences obtained in this model compound work cannot be taken directly over to the polymer systems (the conformational energies and rates of conversion will be very different), this work demonstrates clearly that tacticity must play an important role. Unfortunately the tacticity of polymers used in most photophysical studies is neither pure nor has it been characterized. So far as we know this has been studied only for polystyrene by David et al.⁵⁶ and Ishii et al.,⁵⁷ and for 1- and 2-naphthyl methacrylate by Boudevska and Brutchkov.⁵⁸

Copolymerization of a spectroscopically inert group with the chromophore imparts different solubility properties to the polymer and also serves to increase the average chromophore separation. Lowering the mole fraction of the chromophore decreases the importance of excimer formation, but likewise may slow

the average rate of energy migration. There also exists the possibility that energy migration cannot occur across a single spacer molecule, or "runs" of the spacer. In some of the earliest polymer photophysics Soutar et al.⁵⁹ examined EET as a function of sequence distribution. While these studies presented a consistent picture, there is some doubt if the fundamental premise that EET cannot occur past spacer groups is correct (see following). Cabaness et al.⁶⁰ have examined copolymers of acenaphthylene (AcN) and found little variation in the apparent exciton mean free path (eq 43) with AcN loading. However these workers did not independently determine the excited-state lifetime as a function of loading, such that the quenching constants are suspect.

We and others have examined alternating copolymers in which the reaction ratios are such that the monomers tend to alternate along the backbone. Some examples that have been examined are presented in Tables III and IV. In most cases the alternating copolymer has much less excimer formation than the parent homopolymer, although polyacenaphthylene provides an

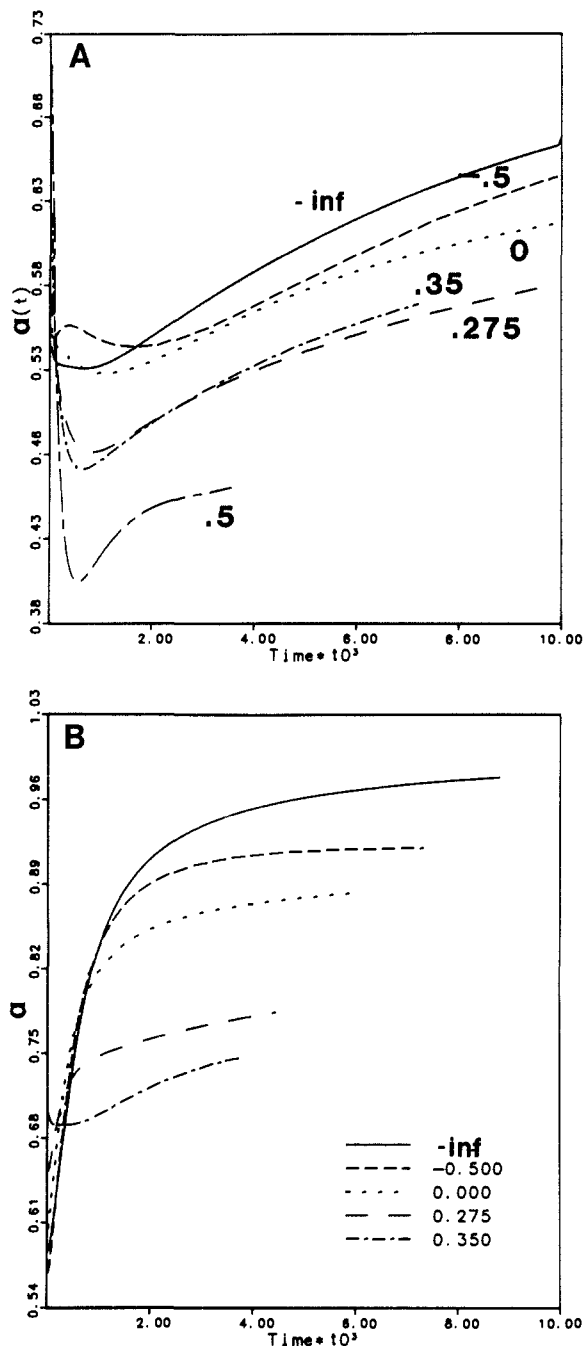


Figure 7. Computed $\alpha(t)$ plots for a polymer chain of length 100, 2 traps per chain randomly placed (A) or placed at polymer ends (B), for thermodynamic parameter (ϕ) indicated ($\phi = 0.275$ is equivalent to θ -point, $\phi < 0.275$ represents a thermodynamically good solvent (see ref 35).

exception.^{61,62} It has been proposed by Morishima et al.⁶³ that in some cases a small amount of head-to-head chromophore juxtaposition occurs, perhaps as a result of a termination reaction. EET to these sites can yield predominantly excimer fluorescence if EET is facile.

Finally, it is possible to prepare block copolymers, usually by anionic polymerization. There have been two reports of the photophysics of such polymers we are aware of: (1) A-B-A type with A = methacrylic acid and B = 9-phenanthryl,⁶⁴ and (2) A-B type with A = naphthalene and B = 9,10-diphenylanthracene.⁶⁵ For the first case only the phenanthryl group is photoactive and the methacrylic acid groups permit dissolution in water. There is evidence for EET in this system on the basis of quenching studies but photon harvesting per

se was not studied. Presumably energy donors or traps could be covalently bound to the acid groups via an ester or amide linkage. The second copolymer was designed to demonstrate "unidirectional" energy migration, from one end of the polymer to the other. This directionality has utility if one end of the polymer could be fixed to a substrate. This arrangement is feasible via appropriate termination of an anionic living polymer but was not explored in the initial report. While it is possible to consider a variety of interesting morphologies with block polymers, the requirements for block anionic polymerization are demanding and not suitable for many polymerizable chromophores. Thus it would be of interest to develop other synthetic strategies to produce polymers of this type.

VI. Experimental Results. Naphthalene Polymers with Anthracene Traps

While the concept of a photon-harvesting polymer is very general, the number of chemically distinct polymer systems that have been studied from this point of view is not large. Many photophysical studies have been carried out on naphthalene-containing polymers. These polymers exhibit strong excimer fluorescence, in part because of EET to excimer-forming sites. From the point of view of elucidating energy trapping, the excimer-forming site presents difficulties because the density of these sites is not known. Excimer formation represents an example of short-range trapping. Because the excimer state does not have a distinct absorption spectrum the Förster radius for transfer into an excimer-forming site is identical with self-transfer between chromophores. It would be interesting to covalently bind traps that have a similar R_0 value in order to test theories of intrapolymer EET (an example might be an exciplex-forming species) but so far as we know this has never been done. It would also be interesting to look at triplet-state transfer to traps. However most triplet-state work has been reported on triplet-triplet annihilation.^{22a}

By far the most popular combination of chromophores has been naphthalene as a donor and anthracene as an acceptor. This pair of chromophores has certain experimental advantages: (1) there is a range of wavelengths (ca. 290–320 nm) in which naphthalene can be excited with minimal direct excitation of the anthracene; (2) there is a large amount of background work on the naphthalene polymers; (3) there are several ways to covalently bind anthracene moieties to naphthalene polymers; (4) the anthracene fluorescence is quite distinct from that of the naphthalene monomer (but there is considerable overlap with the naphthalene excimer), and (5) R_0 for naphthalene-anthracene is ca. 25 Å while for naphthalene self-transfer $R_0 \cong 11$ Å (see Table I). Thus energy trapping by the anthracene is often quite efficient. On the other hand this large R_0 makes it relatively difficult to distinguish down-chain EET from single-step Förster transfer (the DET limit discussed earlier).

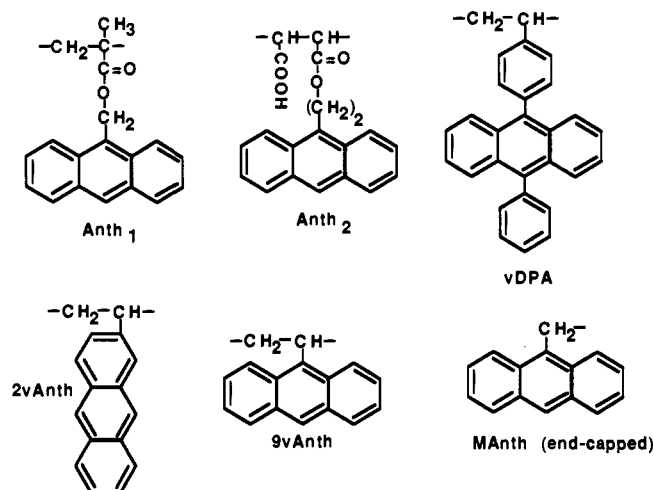
Because naphthalene-based polymers have been studied so extensively we have collected example studies in Table III with some qualitative comments. We have only included cases in which the naphthalene content was at least 50 mol %, such that effective down chain EET might be expected. This listing is representative

TABLE V. Naphthalene-Anthracene Copolymers

polymer type ^a	ref	x_{anth}	χ	comments
1. P2VN-MA-Anth ₁	68	0.003–0.013	high	no time dependence reported
	29	0.005–0.012	0.24–0.60	aqueous solutions studied; time dependence reported
		(alt)	0.007–0.04	
		(random)		
2. P2VN- <i>alt</i> -Anth ₂	77	0.009	0.57–0.79	effect of pH in aqueous solution reported; time dependence measured
3. P2VN- <i>blk</i> -vDPA	65	0.04–0.10	0.6–1.0	block polymer; time dependence studied
4. P2VN-2vAnth	66	0.002–0.02	0.25–0.63	time dependence not measured
5. PtBu2VN-2vAnth	66	0.004–0.036	0.17–0.72	time dependence not measured
6. P1NMA-9vAnth	15	0.0006	–	interesting solvent dependence reported
7. P1NMA-MAnth	28	0.008	0.30	strong effect of solvent extensive time dependence study
P1NEMA-MAnth	102			
P1NPMA-MAnth (end-capped)				
8. P1NMA- <i>co</i> -acrylic acid-MAnth (end-capped)	67	0.003	0.12	dioxane
			0.70	aq NaOH; extensive time dependence study

^a For structure of naphthalene portion of polymer see Chart I; for structure of anthracene portion of polymer see Chart II.

CHART II



and not comprehensive. In Table V we have collected all the cases known to us of naphthalene-anthracene polymers. When available, the χ values are included. It is also indicated if time-dependent studies were carried out. It is usually the case that the time-dependent fluorescence was fit to two or three exponentials with inadequate time resolution to properly test some of the details predicted by theories discussed earlier.

There are some general comments that can be made from the data presented in Table III. The work of Nakahira et al.⁶⁶ compared 2-vinylnaphthalenes with and without steric hindrance. The *tert*-butyl-substituted polymer exhibited much less excimer fluorescence but the χ_{SS} values for sensitization of copolymerized 2-vinylanthracene (see Chart II for structures) were similar for both polymers and for comparable mole fractions of trap, the unhindered naphthalene was superior. It seems likely that the average naphthalene-naphthalene separations (and/or mutual orientation) were perturbed by the *tert*-butyl groups in such a way that down-chain EET was diminished. It would be interesting to have high-quality time-dependent data on this system to provide some further insights. However this system demonstrates that diminishing the density of excimer-forming sites does not necessarily enhance χ .

Aspler, Hoyle and Guillet¹⁵ copolymerized 9-vinylanthracene with 1-naphthyl methacrylate and demon-

strated a very clear solvent (CHCl_3 , CH_2Cl_2 , ethyl acetate) and temperature effect on the fraction of sensitized anthracene present in the steady-state fluorescence. The χ values were not calculated (although relative quantum yields were). The time dependent fluorescence of anthracene demonstrated that the anthracene moiety was sensitized on a time scale of less than 1 ns. The time dependence of the naphthalene fluorescence was not reported. 9-Vinylanthracene is a difficult trap to work with because it is capable of copolymerizing or acting as a chain-transfer agent. Perhaps the clearest conclusion from this work is that a thermodynamically poor solvent can enhance trap sensitization because the coil dimensions decrease.

Holden and Guillet²⁸ studied some naphthyl methacrylates in which bromomethylanthracene was deliberately added as a chain transfer agent. In this case the anthracene trap will reside exclusively at the chain ends. Intuitively one expects the sensitization efficiency to be diminished because the average number of steps required to reach the ends is larger than for randomly placed traps. While Holden and Guillet do not present directly comparable data for random traps, the χ_{SS} value is a little lower than some other polymer systems with comparable anthryl loading in Table V. Guillet and Randall have also studied 1-naphthylmethyl methacrylate-acrylic acid copolymers with anthracene termination. These polymers obtain χ_{SS} values as high as ca. 0.70 in basic aqueous solutions but decrease to ca. 0.15 in dioxane. This strong solvent dependence is ascribed to "hypercoiling" of the hydrophobic naphthalene and anthracene units.⁶⁷

Ng, Yoshiki, and Guillet⁶⁸ examined copolymers of 2-vinylnaphthalene and 9-anthrylmethanol methacrylate. While it is obvious from the spectra presented that sensitization has occurred, χ values were not measured. Bai, Chang, and Webber²⁹ prepared random and alternating copolymers of methacrylic acid and 2-vinylnaphthalene. The acid group was esterified by reaction with diazomethane for some studies in organic solvents. The most remarkable feature of alternating polymers is that excimer formation is essentially eliminated, presumably because there are no nearest neighbor naphthyl groups. Unlike the sterically hindered polymers of Nakahira et al.,⁶⁶ χ_{SS} was substantially higher for the alternating polymer than the random polymer, for equivalent loading of anthracene traps. In this case the naphthalene monomer decay curves were measured

with reasonably good precision, and it was found that the lifetime shortening was less than one would expect based on the χ_{SS} value. This was especially noticeable in the 77K glass. It was proposed that the initially excited naphthalene (Franck-Condon state) can sensitize nearby anthracenes before relaxing to the emitting naphthalene monomer state. If this is the case then $\chi_t < \chi_{SS}$ can be rationalized (see the discussion following eq 16 and Figure 4).

Bai et al.²⁹ also observed that the long lifetime component of the naphthalene fluorescence decay was slightly shorter in the presence of the anthracene trap. Ng and Guillet⁶⁹ have discussed this phenomenon for phenanthrene polymers and have concluded that it can be rationalized as a long-lived exciton state (i.e. continued down-chain mobility of the singlet excitation) that continues to sensitize the trap at long times. Conversely, if the long-lived component of the naphthalene is identical with the undoped polymer then one may conclude either (1) the naphthalene excitation self-traps, or (2) the naphthalene is on a polymer that contains no anthracenes. This latter condition is quite easily achieved for low molecular weight polymers with low loading.

In our work on P2VN-*alt*-MA-co-Anth we have been able to fit the donor decay to a fractional time expression like eq 23 or 30.²⁹ While the uniqueness of this type of fit is not established, the results were suggestive, since the fractional powers were approximately to what one expects for 1-D lattices for the lowest anthryl loading ($n \approx 1/2$) (see eq 30) or to that expected for single-step transfer (see eqs 21-25) ($n \approx 1/3$) for the highest loading. It remains to be seen if similar fits will be possible for related polymers. The sensitized anthracene fluorescence decay was also measured for these polymers. In all cases there was a rapid growth (ca. 0.2-1.5 ns) followed by decay at a much slower rate than directly excited anthracene. This is what is expected when there is a long-lived precursor state (i.e. the donor naphthalene singlet).

A unique block copolymer of 2-vinylnaphthalene and vDPA prepared by a stepwise anionic polymerization was reported by Sowash and Webber.⁶⁵ As expected χ_{SS} is reasonably high and once again it is found that $\chi_t < \chi_{SS}$. Except for one sample, χ_{SS} increases as the ratio of anthracene to naphthalene increases. When one considers the large mole fraction of anthracene in these polymers the value of χ_{SS} is not so large. We believe this illustrates the relatively low efficiency of traps at polymer ends.

Finally we come to P2VN-*alt*-MA-co-Anth in aqueous solution (for pH \geq 6).⁷⁰ This kind of study can only be carried out only for the alternating polymer because the corresponding random copolymer cannot be dissolved in water. One expects a structure in which naphthyl groups are in contact because of the hydrophobic interaction, and indeed a small amount of excimer fluorescence is observed for the anthracene-free polymer. For a polymer containing ca. 1 mol % anthracene the sensitized anthracene fluorescence is very strong and χ_{SS} is estimated to be greater than 0.9. The naphthalene fluorescence decay is much shorter in this environment, presumably because of rapid EET to excimer-forming sites and the anthracene. Consequently the estimates of χ_t are not accurate. These aqueous

solutions are not easy to study because of aggregation effects that lower the experimental reproducibility. Nevertheless they illustrate the profound effect that coil collapse can have on EET processes.

The available experimental results for naphthalene-containing polymers with anthracene traps demonstrate many of the possibilities and difficulties in designing photon harvesting polymers. The following general conclusions may be drawn:

(1) Ordinarily excimer formation may be regarded as a competing pathway and should be avoided. However steric or structural features that diminish excimer trapping may also diminish down-chain EET. Consequently one would prefer as large an R_0 for self-transfer and as long an excited-state lifetime as possible. However these quantities are chromophore specific, and the choice of chromophore may be dictated by other considerations.

(2) For equivalent trap loading, traps located at polymer ends will not be as efficient as randomly placed traps.

(3) Time-dependent studies can be quite revealing. The lifetime shortening can be compared with steady-state spectra and if $\chi_t < \chi_{SS}$ (within experimental error) one may conclude that there exists a very rapid sensitization step. At long times the fluorescence decay of the donor should be shortened by EET. If this is not the case either the donor excitation has self-trapped or the excitation is located on a segment that cannot communicate with a trap-doped segment (in the extreme case there may be polymers that do not contain traps). In principle time-dependent studies may be analyzed in terms of detailed structural models although this is in an early stage of exploitation in the case of extensive down-chain EET.

(4) Any effect on coil density can dramatically change the efficiency of energy trapping. Usually this is accomplished by the choice of solvent or temperature. While increasing the coil density can increase the density of excimer forming sites and/or induce self-quenching, in the cases in which this has been studied coil collapse has tended to enhance χ . It is expected that as a polymer becomes less one-dimensional that energy trapping will become more efficient.

VII. Summary

In this review we have examined the phenomenon of electronic energy transport within polymer coils. This phenomenon can be easily demonstrated to exist for many polymer systems and clearly has the potential to be exploited to collect light energy at trapping sites along the polymer chain. The efficiency of this process may approach 100% in favorable cases although the efficiency is more commonly found to be in the 30-60% range (see Table V). While the underlying physical model of intracoil EET is understood, it is difficult to quantify these ideas because of the intrinsic complexity introduced by the ensemble of polymer conformations and the possibility of intracoil excimer formation and/or self-quenching. On the other hand, it is possible that the complex kinetics of down-chain EET and trapping can be exploited to test conformational models of polymers in a unique fashion that is sensitive to pendant group contacts and correlations.

Given our general understanding of polymer and

chromophore properties and how these are related to their photon-harvesting properties, it now remains for the polymer synthetic chemist and the photochemist to design systems that provide even a fraction of the useful applications of nature's model, the antenna pigments in photosynthesis.

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