European Polymer Journal, 1973, Vol. 9, pp. 609–622. Pergamon Press. Printed in England.

ENERGY MIGRATION AND TRANSFER IN POLYMER SYSTEMS

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(*Received* 11 *December* 1972)

Abstract—Theoretical treatments of singlet energy transfer are reviewed with the objective of determining the expressions most relevant for polymeric systems. Observations of singlet energy transfer from 1,3 diphenyl oxazole to 1,4 di[2-(4-methyl 5-phenyl oxazolyl)]-benzene, anthracene and benzophenone confirm that the Förster relationships are valid for dilute solutions of these small molecules.

For a polymer donor in which there exists spectral overlap in absorption and emission, there is the possibility of energy migration along the chain. Under these conditions, and where acceptor diffusion may be important, it is found that relationships due to Yokota and Tanimoto are the most useful in both fluid and polymeric environments. Coefficients for migration of singlet energy down chains of poly(*N*-vinyl carbazole), poly(2-vinyl) naphthalene) and copolymers of *N*-vinyl carbazole with methyl acrylate have been evaluated. They are consistent with a model in which energy is transferred by a random walk series of Förster interactions between spectroscopically active nearest neighbours.

INTRODUCTION

ENERGY transfer processes in polymer systems are of importance in a number of different situations. Perhaps most importantly, polymer photodegradation is often controlled by the photophysical processes that occur after a photon impinges on the polymer but before the various chemical steps constituting the actual molecular degradation. In addition the use of polymeric matrices for phosphors and scintillators, or in situations exposed to high energy radiation, necessitates an understanding of electronic energy transfer processes.

The transfer of electronic energy between molecules may be influenced both by the relative diffusive motion of donor and acceptor and by radiationless migration of the donor excitation energy. Theories(1–5) have been developed to deal with the efficiency of singlet energy migration; the validities differ according to the relative importance of the different transfer processes.

Since one of the treatments(5) which seems to us to be unsuitable (see below) is used in the interpretation of transfer phenomena in polymer systems, we first list useful theories noting conditions where their applicability may be suspect. In the second part of this paper, one such theory is used to interpret energy transfer and migration phenomena in the polymers poly(2-vinyl napthalene), poly(*N*-vinyl carbazole) and in copolymers of *N*-vinyl carbazole with methyl acrylate. In particular, interest is focussed upon the relative importance of molecular diffusion and energy migration in the overall radiationless transfer process.

We define a relative "molecular energy migration" distance $\mathbf{r}$ such that

$$\mathbf{r} = (2\,[D + \Lambda]\,\tau_0)^{1/2}, \qquad (1)$$

where D is the relative molecular diffusion coefficient of donor and acceptor. Λ is the donor excitation energy migration coefficient and τ_0 is the donor fluorescence lifetime in absence of acceptor. Let R_0 be a critical transfer distance defined by Förster(1) such that, at this separation of donor and acceptor, the probability of resonance transfer equals the probability of decay of donor excitation by all other processes.

Two extreme situations can be visualised:

(i) when $\mathbf{r} \ll R_0$, the molecules remain effectively stationary during excitation and transfer, and the relationships of Förster and Galanin are applicable:

(ii) when $\mathbf{r} \gg R_0$, the donor excitation energy is effectively completely mobile and the chemical kinetic techniques of Stern and Volmer may be applied.

However, in many systems of interest, an intermediate situation exists. There are two approaches to such a region derived either from the Förster–Galanin scheme or from theories of diffusion-controlled reactions.

REVIEW OF THEORY

A. Förster kinetics

If we define a transfer efficiency for non-radiative energy transfer from one state to another as

$$f_{NR} = 1 - \frac{I}{I_0}. \tag{2}$$

I_0 = the intensity of donor fluorescence in the absence of acceptor.
I = the intensity of donor fluorescence in the presence of acceptor.
then

$$f_{NR} = 1 - \frac{1}{\tau_0}\int_0^\infty \frac{i_D(t)}{i_D(0)}\,\mathrm{d}t. \tag{3}$$

$i(t)$ is the intensity of donor fluorescence (on an arbitrary scale) with respect to time. τ_0 is the donor excited state lifetime. This equation will be valid regardless of other mechanisms of populating or depopulating the states involved (as by conversion to or from excimer states).

$$\frac{i_D(t)}{i_D(0)} = \exp\left\{-\frac{t}{\tau_0} - 2\gamma\left(\frac{t}{\tau_0}\right)^{1/2}\right\}. \tag{4}$$

Letting $\gamma = c/c_0$ where c_0 is the critical acceptor concentration, defined as

$$c_0 = \frac{3000}{2\pi^{3/2}\, NR_0{}^3}. \tag{5}$$

R_0 is defined as before, and is a direct function of the spectral overlap.

$$R_0{}^6 = \frac{8{\cdot}8 \times 10^{-25}\,\kappa^2\,\phi_D}{n^4}\int_0^\infty f_D(\nu)\,\epsilon_A(\nu)\,\frac{\mathrm{d}\nu}{\nu^4} \tag{6}$$

where $f_D(\nu)$ is the donor fluorescence spectrum normalised to unity, $\epsilon_A(\nu)$ is the acceptor absorption spectrum, n is the solvent refractive index, ϕ_D is the fluorescence quantum yield and κ is an orientation factor⁽²⁾ depending on the relative orientation of the transition dipoles.

Thus

$$f_{NR} = \pi^{1/2}\,\gamma \exp(\gamma^2)\{1 - \operatorname{erf}\gamma\} \tag{7}$$

where
$$\operatorname{erf}\gamma = \frac{\pi^{1/2}}{2}\int_0^{\gamma} \exp(-x^2)\,\mathrm{d}x. \tag{8}$$

B. Stern–Volmer kinetics

Here
$$\frac{i_D(t)}{i_D(0)} = \exp\left(-\frac{t}{\tau}\right), \tag{9}$$

where τ is the donor fluorescence lifetime in the presence of acceptor.

This reduces to:

$$f_{NR} = \frac{2{\cdot}05\,c/c_0}{1 + 2{\cdot}05\,c/c_0}, \tag{10}$$

where the factor 2·05 is chosen to give the same "half value" concentration (the concentration of acceptor when the transfer efficiency is 0·5) as the Förster theory.

C. Intermediate kinetics

(i) *Theories developed from diffusion theory.* These theories involve solution of the diffusion equation:

$$\frac{\partial c}{\partial t} = D\nabla^2 c, \tag{11}$$

where c = concentration of diffusing species and D is the diffusion coefficient.

In the case of spherical symmetry:

$$\frac{\partial c}{\partial t} = D\left(\frac{\mathrm{d}^2 c}{\mathrm{d}r^2} + \frac{2}{r}\cdot\frac{\mathrm{d}c}{\mathrm{d}r}\right). \tag{12}$$

The differences between the theories arise from the various boundary conditions employed.

Many of the theories have been developed for the case of diffusion only and it must be noted that, in order to account for energy migration, we must use a cumulative diffusion parameter, D^*.

$D^* = D + \Lambda$
D = mutual diffusion coefficient
Λ = energy migration coefficient.

Noyes and Yguerabide, Dillon and Burton⁽³⁾ have developed fairly general expressions. These can be applied to the case of fluorescence quenching. However, as stated by Burton,⁽²⁾ these methods should not be applied for systems in which energy transfer occurs via the long-range Förster process. They are more applicable to cases involving collisional quenching e.g. by carbon tetrachloride.

Voltz *et al.*(5) have produced expressions for two cases:

(i) A process in which the rate of transfer is diffusion-controlled and has the conditions:

probability of reaction $= 0{\cdot}5$ for $r < R_0$.
probability of reaction $= 0$ for $r > R_0$.

(ii) A process which involves collisional transfer in addition to long-range transfer. From these postulates, they develop the following expressions:

$$i_D(t) = i_D(0) \exp\left\{-\frac{t}{\tau_0} - a[A]t - 2b[A]t^{1/2}\right\}. \tag{13}$$

In practice the integrated form of this equation is evaluated numerically.

in case (i)
$$a = 2N.10^{-3}\, DR_0 \tag{14}$$

$$b = 2N.10^{-3}.R_0^2(\pi D)^{1/2} \tag{15}$$

in case (ii)
$$a = 4\pi N.10^{-3}\, DR\left(1 + \frac{R_0^6}{12D\tau_0 R^4}\right) \tag{16}$$

$$b = 4N.10^{-3}\, R^2(\pi D)^{1/2}\left\{1 + \frac{R_0^6}{12D\gamma_0 R^4}\right\}. \tag{17}$$

R is the collisional interaction distance.

Birks(6) has compared the Voltz theories with experimental data and found a considerable discrepancy in both cases. This is due to the incorrect assumption of the boundary conditions:

$$p = 0{\cdot}5 \text{ for } r < R_0$$

$$p = 0 \quad \text{for } r > R_0$$

when in fact

$$p \propto \left(\frac{R_0}{r}\right)^6.$$

Of the numerous other theories in this class, most are similar to the above treatments and thus suffer from similar drawbacks.

Povinelli,(7) in a more exact treatment, derived the following expression for the rate of transfer:

$$\text{k(mole l.}^{-1}\text{ sec}^{-1}) = \frac{8NR_0^{3/2}\, D^{3/4}}{3000\, \tau_0^{1/4}}. \tag{18}$$

This result is virtually identical to that obtained by Yokota and Tanimoto(8) using the scattering length method.

(ii) *Theories developed from Förster theory.* These theories are essentially statistical in nature in that they consider a microscopic environment and use some mathematical approximation (or numerical evaluation) to apply this to a macroscopic system. A typical example is the work by Yokota and Tanimoto[8] who used the Padé approximant[9] to solve the problem:

$$i_D(t) = i_D(0)\exp\left\{-\frac{t}{\tau_0} - 2B\gamma\left(\frac{t}{\tau_0}\right)^{1/2}\right\}. \tag{19}$$

Where $\gamma = \dfrac{c}{c_0} \quad c_0 = \dfrac{3000}{2\pi^{3/2} N R_0{}^3}$

and $B = \left\{\dfrac{1 + 10{\cdot}87x + 15{\cdot}50x^2}{1 + 8{\cdot}743x}\right\}^{3/4}.$

In B, $x = D^* \alpha^{-1/3} t^{2/3}$

and $\alpha = \dfrac{R_0{}^6}{\tau_0}.$

Again in practice the integrated form of this equation is evaluated numerically.

Steinberg and Katchalski[10] have numerically solved the problem using Fick's Laws of diffusion and a $1/r^6$ potential. They solve the equation

$$\frac{\partial C_A(r,t)}{\partial t} = -\frac{1}{\tau_0}\left(\frac{R_0}{r}\right)^6 C_A(r,t) + \frac{D^*}{r^2}\cdot\frac{\partial}{\partial r}\cdot\left\{r^2\,\frac{\partial C_A(r,t)}{\partial t}\right\}. \tag{20}$$

Using the boundary conditions:

$$C_B(a,t) = 0$$

$$C_B(r,0) = \overline{C_B} \text{ for } r > a,$$

a is the distance at which the reaction probability can be taken as unity (usually 0·1–0·3 of R_0).

Birks[6] has compared the Yokota–Tanimoto theory with experimental values for the naphthalene–diphenyl-anthracene system and has found excellent agreement. The Steinberg–Katchalski method gives virtually identical values to the Yokota–Tanimoto theory confirming the validity of the Padé approximant.

The choice of correct boundary conditions is essential when experimental transfer efficiencies are being discussed in terms of migration characteristics. In this work, use is made of the Yokota–Tanimoto expressions which seem to offer the optimum combination of simplicity in use with rigour of the basic model. Data are reported for systems

(a) in which low molecular weight donor and acceptor molecules are studied in fluid solutions and polymer matrices in which there is little spectral overlap between the active molecules and the diluent.

(b) in which the initial photon absorber forms part of a polymer chain, and the energy acceptor is a small molecule: again mobile solvents and polymer matrices were used as diluent.

EXPERIMENTAL

1. *Materials*

1,4 Diphenyl oxazole (PPO), 1,4-di-(2-[4-methyl-5-Phenyloxazolyl])-benzene (DMPOPOP): Koch Light Laboratories, Scintillation Grade. Used as received.

Anthracene: BDH analytical grade, recrystallised three times from benzene.

Benzophenone: BDH analytical grade, recrystallised three times from diethyl ether.

Tetracene: Zone refined.

Crystalline monomers (2-vinyl naphthalene, *N*-vinyl carbazole): Purified by multiple recrystallisation.

Liquid monomers (styrene, methyl acrylate: were purified in the usual manner.

Solvents (toluene, tetrahydrofuran, N.N. dimethylformamide): were fractionally distilled.

Polymers were prepared by free-radical polymerisation with 0·5% azoisobutyronitrile at 40°. Polymerisations were carried out in the absence of air and light to conversions of 10 per cent or less. All polymers were purified by multiple reprecipitations.

2. *Techniques*

Copolymer compositions were determined by u.v. absorption spectroscopy and by microanalysis (for the *N*-vinylcarbazole copolymers). Compositions so determined agreed with those calculated using literature values for the monomer reactivity ratios.

Fluorescence intensities were measured on a Perkin–Elmer 203 spectrofluorimeter. Initial measurements were made using the sample configuration shown in Fig. 1(a). Later measurements on the small molecule systems and on all polymer systems (both fluid and solid) were made using the sample configuration shown in Fig. 1(b).

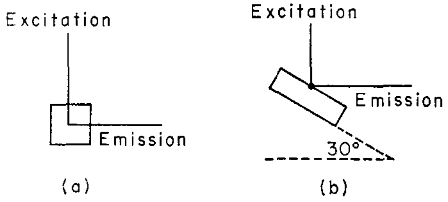

FIG. 1. Sample geometries.

By use of relatively high ($\sim 10^{-2}M$) donor concentrations in system (b), the effective emission path length can be made extremely small while still minimising donor–donor intermolecular transfer. This reduces the contribution by radiative donor–acceptor transfer and increases the accuracy of measurement of non-radiative transfer. In order to eliminate the effect of any transfer between donor molecules (or between polymer chains), several donor concentrations were used and measurements extrapolated to infinite dilution.

Measurements were made using exciting wavelengths of 285 and 275 nm and the transfer efficiencies were found to agree at both wavelengths. The emission spectrum consisted of a broad monomer fluorescence centred at 350 nm with a very small tail due to excimer fluorescence around 400 nm. The integrated intensity due to excimer emission (as far as could be estimated by giving the monomer fluorescence emission a spectral shape the same as for low molecular compounds such as *N*-methyl carbazole and then resolving the emission spectrum accordingly) contributed less than 5 per cent of the total emission. Since fluorescence emission was measured at 340, 350 and 360 nm and results at each wavelength were in agreement, and since excimer emission is negligible at this wavelength, it was concluded that the existence of excimer fluorescence exerted negligible effect on the measurement of monomer fluorescence intensities.

Polymer films were prepared by evaporation of a solution of donor, polymer diluent and quencher. The films were cast into Teflon®/Melinex dishes, facilitating removal of the deposited film. Film thicknesses were 0·1 mm. On each piece of film (two from each sample), eight intensity measurements were made (four from each side) giving a total of 16 measurements, all from different portions of the sample. Each measurement was made at four separate wavelengths, the final transfer efficiency being an average of these four values. Four separate donor concentrations were considered so as to eliminate the possibility of interchain energy transfer.

Although vinyl carbazole polymers are incompatible with polystyrene and poly(methyl methacrylate) when mixed in equivalent amounts, all physical observations (clarity, transparency, etc.) failed to give evidence of phase separation of the small amounts of *N*-vinyl carbazole-derived polymers used in these studies. Consequently it was assumed that the donor polymer molecules were dispersed as in a true solution. This conclusion was confirmed by the general agreement between studies in fluid solvents and polymer matrices.

Fluorescence lifetimes were determined using a method quoted by Berlman.(10) This method compares the intensities of oxygenated and de-oxygenated solutions of the fluorescent species. The ratio of intensities is compared with a calibration plot in order to determine the lifetime. The method is accurate for lifetimes above 10 nsec. Good agreement has been found using polymers measured by other techniques. Thus for poly(2-vinylnaphthalene), the experimental value is $3{\cdot}2 \times 10^{-8}$ sec compared with a literature(12) value of $3{\cdot}0 \times 10^{-8}$ sec, and for poly(*N*-vinylcarbazole) the experimental and literature values are $1{\cdot}4 \times 10^{-8}$ sec and $1{\cdot}35 \times 10^{-8}$ sec, respectively.

Although this simple procedure is strictly valid when there is only one component in the fluorescence decay, the fact that excimer emission is a negligible proportion of the total emission in this case means that errors so introduced are no larger than those from other sources. As confirmation, the agreement with values measured by conventional techniques is excellent.

RESULTS

1. *Small molecule donor–acceptor systems exhibiting Förster energy transfer: liquid and polymer diluents*

The simplest systems are those in which there is considerable spectral overlap between donor emission and acceptor absorption, and in which migration of donor excitation energy by diffusion or intermolecular transfer is unlikely. Such systems should exhibit Förster non-radiative energy transfer.

The most obvious examples include dilute solutions of small molecule donor species. The dilution effectively prevents energy migration between donor molecules and the rapid transfer to acceptor outweighs any effects due to relative diffusion of donor and acceptor.

A number of systems involving energy transfer from 1,3 diphenyl oxazole (PPO) have been studied to confirm the simple basic point that the Förster mechanism operates and is unchanged in fluid and solid matrices. The three acceptors selected {1,4-di-[2-(4-methyl-5-phenyloxazolyl)]-benzene (DMPOPOP), anthracene and benzophenone} exhibit respectively decreasing absorption overlap with PPO emission. The experimentally determined efficiencies of non-radiative transfer for various acceptor concentrations (donor concentrations 10^{-5}–10^{-2} M) are illustrated in Fig. 2, along with the lines giving the best fit of the Förster relationships to the experimental points. The values of the critical transfer distance calculated from the spectral overlap (Eq. 6) and from the transfer efficiencies (Eq. 7,8) are compared in Table 1. The error in R_0 in these systems is $\pm 0{\cdot}2$ nm.

It can be seen that, with the exception of PPO–DMPOPOP in cyclohexane, the energy transfer characteristics to this acceptor are as expected for Förster exchange. The systems PPO–DMPOPOP and PPO–anthracene have been further studied (donor concentration 10^{-4}–10^{-2} M) in polymer matrices, Fig. 3 and Table 1. The error in R_0 in these systems is $\pm 0{\cdot}4$ nm. Again the data are adequately represented by the Förster mechanism, and the critical transfer distances agree well with those observed in fluid media. The obvious corollary is that the transfer characteristics of such systems can be obtained from the easier measurements on fluid systems and applied with confidence to polymer systems.

The transfer efficiency PPO–benzophenone is low so that diffusion becomes important ($r \sim 2{\cdot}5$ nm) and better agreement is obtained using the Yokoto–Tanimoto theory.

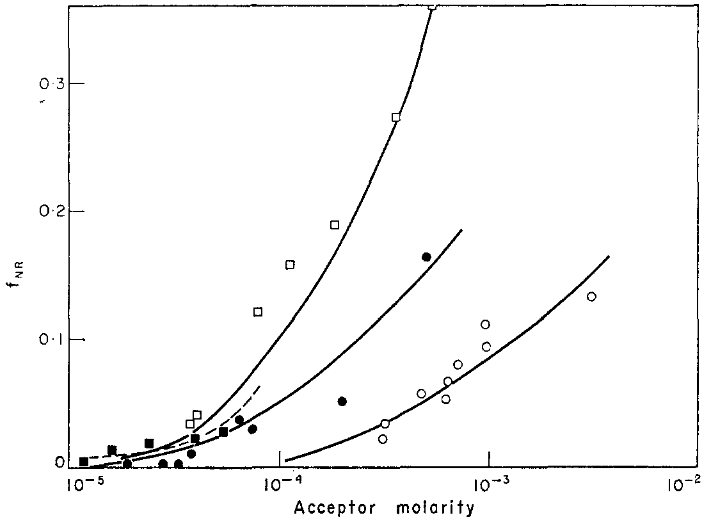

Fig. 2. Small molecule energy transfer efficiencies in fluid solvents. ● PPO to anthracene in cyclohexane; ○ PPO to benzophenone in cyclohexane; ☐ PPO to DMPOPOP in cyclohexane; ■ PPO to DMPOPOP in dimethylformamide.

2. *Homopolymer donor–small molecule acceptor systems: the best theory*

The first complexity introduced by the use of homopolymer donors is that, for monomer units exhibiting absorption and emission overlap, energy migration may occur along the chain of donor segments before transferring to acceptor. Of course relative diffusion of donor and acceptor may also occur. The net result is that energy 'migration' may be important as well as donor-acceptor 'transfer'. This is the situation often interpreted using the Voltz relationship (Eqns. 13–17).

Table 1. Critical transfer distances

System	Solvent	R_0 spectroscopic (nm)	R_0 transfer (nm)
PPO–DMPOPOP	Cyclohexane	5·0	6·3
PPO–DMPOPOP	Dimethyl formamide	4·8	5·0
PPO–anthracene	Cyclohexane	4·3	4·6
PPO–benzophenone	Cyclohexane	2·0 (F) 2·6 (Y.T.)	2·9
PPO–DMPOPOP	Polystyrene	4·4	5·2
PPO–DMPOPOP	Poly(methylmethacrylate)	4·9	5·4
PPO–anthracene	Poly (methylmethacrylate)	4·3	4·2

To investigate the suitability of the various equations, measurements have been made on dilute (10^{-2} weight %) solutions of poly(*N*-vinyl carbazole) in poly(methyl methacrylate) quenched by anthracene, see Fig. 4 which shows the experimental transfer efficiencies and the theoretical curves calculated from spectral data for normal

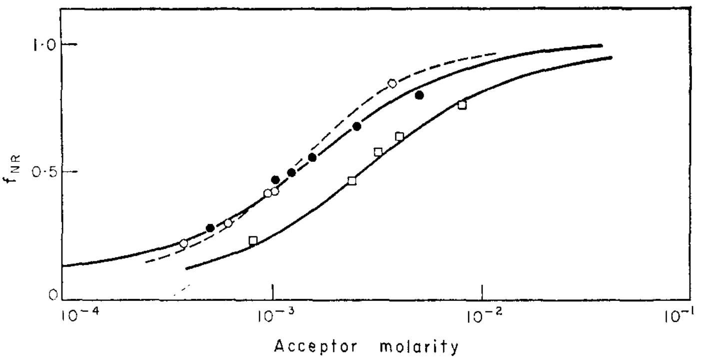

FIG. 3. Small molecule energy transfer efficiences in polymer matrices. ● PPO to DMPOPOP in polystyrene; □ PPO to anthracene in poly(methyl methacrylate); ○ PPO to DMPOPOP in poly(methyl methacrylate).

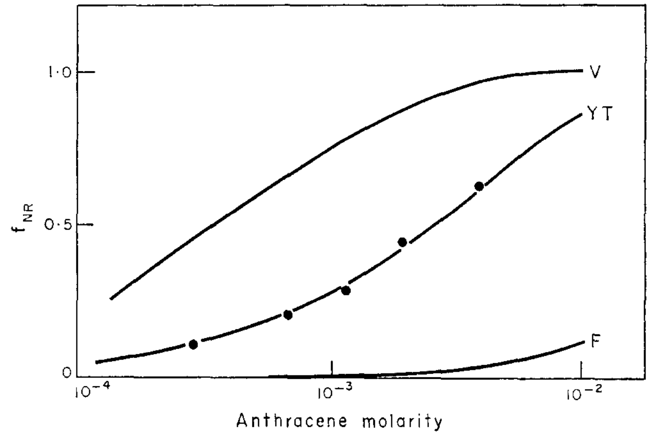

FIG. 4. Energy transfer from poly(*N*-vinyl carbazole) to anthracene in poly(methyl methacrylate). ● experimental points, V Voltz expression, YT Yokota–Tanimoto expression, F Förster expression.

fluorescence using the Voltz, (V), Yokota–Tanimoto (Y.T.) and Förster (F) relationships. The emission quantum yield, measured in the normal way with reference to quinine sulphate, was 0·05. The theoretical migration coefficients for insertion into the Voltz and Yokota–Tanimoto relationships were calculated from the spectral overlap in absorption and emission of chain segments assuming that the migration occurs by a random walk series of Förster interactions with nearest neighbours (see discussion). The greater relevance of the Yokota–Tanimoto theory is apparent. Similar studies on other systems confirm this observation.

Table 2 compares migration coefficients so calculated with those observed by fitting the Yokota–Tanimoto relationship to experimental transfer efficiencies.

In these calculations a diffusion coefficient of $1{\cdot}0 \times 10^{-5}$ cm^2 sec^{-1} has been used for the mobility of anthracene in toluene(14) and $0{\cdot}8 \times 10^{-5}$ cm^2 sec^{-1} for tetracene in tetrahydrofuran. The agreement between the spectroscopic calculated data and those obtained from the fluorescence quenching using the Yokota–Tanimoto theory is indeed remarkable.

TABLE 2. HOMOPOLYMER MIGRATION COEFFICIENTS

Polymer	Acceptor	Segment R_0 spectroscopic (nm)	Λ spectroscopic (cm^2 sec^{-1} × 10^5)	Λ transfer (cm^{2}sec^{-1} × 10^5)
Poly(vinyl naphthalene) in tetrahydrofuran	Tetracene	1·25	13·6	13·1
Poly(N-vinyl carbazole) in toluene	Anthracene	1·03	9·0	8·9
Poly(N-vinyl carbazole) in poly(methyl methacrylate)	Anthracene	1·06	7·2	7·3
Poly(N-vinyl carbazole) in polystyrene	Anthracene	1·06	7·2	7·8
Poly(N-vinyl carbazole) in toluene	Anthranilic acid	1·03	9·0	9·2

3. *Copolymer donor–small molecule acceptor systems: energy migration in copolymers with inactive comonomer units*

Energy transfer efficiencies for *N*-vinyl carbazole–methyl acrylate copolymer donors to anthracene acceptor for infinite dilution of donor and various acceptor

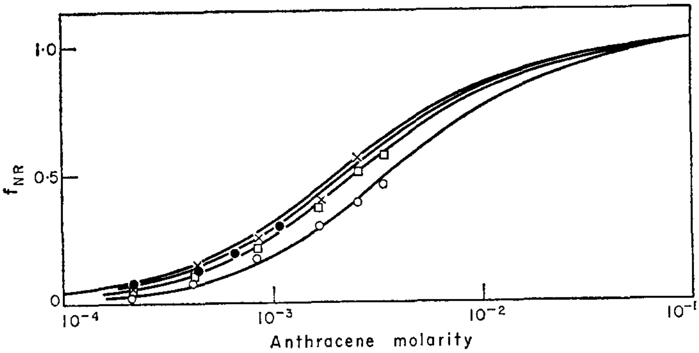

FIG. 5. Energy transfer efficiencies, copolymers of *N*-vinyl carbazole with methyl acrylate to anthracene into luene. Mole fractions of N-vinyl carbazole × 1·0; ● 0·84; □ 0·79; ○ 0·70.

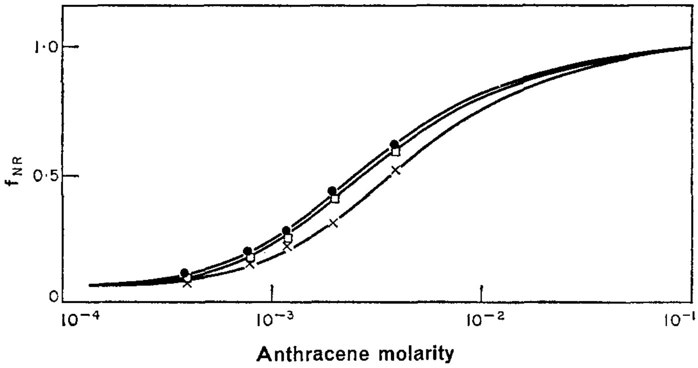

FIG. 6. Energy transfer efficiencies, copolymers of *N*-vinyl carbazole with methyl acrylate to anthracene in poly(methyl methacrylate). Mole fractions of *N*-vinyl carbazole ● 1·0; □ 0·84; × 0·70.

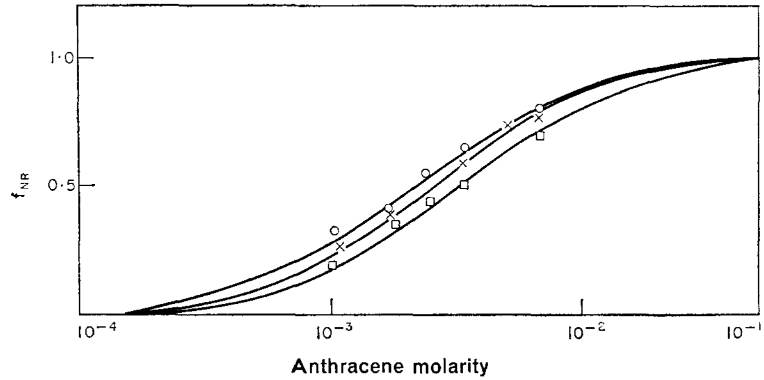

FIG. 7. Energy transfer efficiencies, copolymers of *N*-vinyl carbazole with methyl acrylate to anthracene in polystyrene. Mole fractions of *N*-vinyl carbazole ○ 1·0; × 0·79 ☐ 0·70.

concentrations in toluene are illustrated in Fig. 5, in poly(methyl methacrylate) in Fig. 6, and in polystyrene in Fig. 7. The corresponding coefficients for intrachain energy migration, calculated using the Yokota–Yanimoto relationship, are listed in Table 3.

TABLE 3. MIGRATION COEFFICIENTS IN N-VINYL CARBAZOLE–METHYL ACRYLATE COPOLYMERS: ANTHRACENE ACCEPTOR

Mole fraction donor units	Diluent	Λ (cm^2 sec^{-1} × 10^5)
1·0	Toluene	8·9
1·0	Poly(methyl methacrylate)	7·3
1·0	Poly(styrene)	7·8
0·84	Toluene	7·9
0·84	Poly(methyl methacrylate)	6·2
0·79	Toluene	7·0
0·79	Polystyrene	5·6
0·70	Toluene	4·4
0·70	Poly(methyl methacrylate)	3·9
0·70	Polystyrene	4·2

DISCUSSION

The observations on PPO confirm that the singlet energy transfer characteristics of dilute solutions of small molecules obey the Förster relationships similarly in fluid and polymeric environments. This is with the proviso, of course, that the diluent is spectroscopically inactive and that correct allowance is made for its refractive index. In simple terms, the observations on anthracene and benzophenone show that the Förster relationships hold even when R_0 is only twice **r** (4·3 and 2·5 nm, respectively) but are appreciably in error when R_0 and **r** are comparable.

The observations on PPO–DMPOPOP in cyclohexane are anomolous, the transfer being more efficient than predicted by the simple Förster relationship. The discrepancy is beyond the significance limit of ±0·2 nm in R_0, and as in all measurements in configuration (b) of Fig. 1 the standard deviation in the transfer efficiency is ± 5 per cent. It was noted that DMPOPOP was only very sparingly soluble in cyclohexane; it is possible that donor–acceptor and acceptor–acceptor aggregation occur in this solvent.

The observations on the homopolymers have been used to test the relevance of the Förster, Voltz and Yokota–Tanimoto expressions. It is necessary to add a word of caution here, since the calculation of theoretical transfer efficiencies requires the insertion of reasonable values for the molecular diffusion and energy migration coefficients. The values used for molecular diffusion coefficients are reliable since they are drawn from independent measurements, and in any case are effectively zero in polymer matrices. The strict interpretation of the results, as in Fig. 4, is that the predictions of the Voltz and Förster expressions are well outside the 5 per cent uncertainty in f_{NR}, and that the prediction based on the Yokota–Tanimoto expression is within this uncertainty, when theoretical migration coefficients are calculated in a particular way. In the method chosen, an average separation of spectroscopically active groups was computed from molecular models (0·25 nm for poly *N*-vinyl carbazole) and the assumption made that the singlet energy migrated down the chain by a series of random-walk steps each occurring with a probability defined by the Förster expression. Thus the probability of each step is defined by the spectral overlap in absorption and emission of the polymer units. The migration coefficient is then given by

$$\frac{2\Lambda}{r^2} = \frac{1}{\tau}\left(\frac{R_0}{r}\right)^6 \tag{21}$$

where r is the mean separation of chain neighbours. Because the migration coefficient varies as the inverse fourth power of the neighbour separation, further neighbours can be ignored.

It is necessary to comment on the possible significance of excimer formation on (a) the observed normal fluorescence intensities, (b) the calculated transfer efficiencies and (c) the energy migration coefficients.

As has been shown earlier, the excimer emission intensities are so low relative to the normal emission that measurements of normal fluorescence at 340–360 nm are not seriously in error. The fact that predicted transfer efficiencies are observed both with anthracene (in which excimer emission exhibits spectral overlap with acceptor absorption at 380 nm) and with anthranilic acid (in which there is no spectral overlap) points out that transfer to acceptor via the excimer state is relatively unimportant.

The observed migration coefficients, of course, do not define whether or not energy has been converted to "excimer" form and then reactivated to "monomer" form during progression down a polymer chain. They are derived simply from a migration distance. The significance of excimer formation during migration is tested by the applicability of the simple model of random walk Förster exchanges of normal "monomer" singlet excitation. Since the model does appear to be applicable, and since both excimer fluorescence and transfer are relatively unimportant, it is fair to conclude that excimer formation is not a major factor in energy migration in these systems.

The results illustrated in Table 2 show that the Yokota–Tanimoto expressions and this model for energy migration are self-consistent in the fluid and polymer environments, and with polar and non-polar acceptors, to such a remarkable extent that one must give considerable credence to both the theory and the model.

The results on the copolymers confirm that when the sequences of spectroscopically active units are interrupted by inactive comonomer units, the effective singlet migration coefficients are decreased. In these measurements, the different transfer efficiencies in fluid and polymeric matrices stem mainly from the different lifetimes, the differences being due to variations in oxygen quenching. Once again the overall variations in the observed intra-chain migration coefficients are greater than the estimated maximum uncertainty of ±8 per cent.

In conclusion, it can be stated that examination of the spectral characteristics of singlet energy donor–acceptor species allows preliminary judgement of whether Förster expressions are applicable. For polymeric donor species, it is better to use the Yokota–Tanimoto relationships because of the finite effect of energy migration along the chain. This migration in its turn can be treated as a random walk series of nearest-neighbour Förster transfer interactions.

Acknowledgement—The authors acknowledge with pleasure the award of a B.P. studentship to M.F.T.

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Résumé—On examine les études théoriques portant sur le transfert d'énergie singulet afin de déterminer l'expression la plus adaptée pour les systèmes polymériques. L'observation de transfert d'énergie singulet du diphényl 1-3 oxazole au di-1,4(méthyl-4-phényl-5 oxazolyl)2 benzène, anthracène et benzophénone confirme que les relations de Förster sont valables pour les solutions diluées de ces petites molécules.

Pour un polymère donneur, dans lequel il existe un recouvrement spectral dans l'absorption et l'émission, il y a une possibilité de migration d'énergie le long de la chaîne. On a trouvé que dans ces conditions, et quand la diffusion de l'accepteur peut être importante, les relations de Yokota et Tanimoto sont les plus adéquates dans les milieux fluides et polymériques. On a évalué les coefficients de la migration de l'énergie singulet le long des chaînes de poly(N-vinylcarbazole), de poly(vinyl-2-naphtalène) et de copolymères du N-vinylcarbazole avec l'acrylate de méthyle. Ils sont en accord à un modèle basé sur l'hypothèse d'un transfert d'énergie par une série de cheminement au hasard d'interactions de type de Förster.

Sommario—Si sono riviste le trattazioni teoriche riguardo il trasferimento di energia da singoletto, con l'obbiettivo di determinare le espressioni più rilevanti per i sistemi polimerici. Delle osservazioni sul trasferimento di energia da singoletto dall'1,3-difenil-ossazole all'1,4-di[2-(4-metil-5-fenil-ossazoil)]-benzene, antracene e benzofenone, confermano che le relazioni di Förster sono valide per soluzioni diluite di queste piccole molecole.

Per un donatore polimerico per il quale vi sia un ricoprimento spettrale nell'assorbimento ed emissione, vi è la possibilità di migrazione lungo la catena. Con queste condizioni, e qualora la diffusione dell'accoglitore possa essere importante, si trova che le relazioni di Yokota e Tanimoto sono le più utili sia in ambienti fluidi che polimerici. Si esprimono numericamente i coefficienti di migrazione dell'energia da singoletto lungo le catene di poli(N-vinil-carbazole), poli(2-vinil)naftalene) e copolimeri di N-vinil-carbazole con metil-acrilato. Essi sono coerenti con un modello in cui l'energia viene trasferita mediante serie casuali di interazioni di Förster, trai limitrofi spettroscopicamente attivi.

Zusammenfassung—Die theoretische Behandlung der Singlett-Energieübertragung wird überprüft mit dem Ziel, möglichst zutreffende Ausdrücke für Polymersysteme abzuleiten. Beobachtungen der Singlett-Energieübertragung von 1,3-Diphenyloxazol auf 1,4-Di-[2-(4-methyl-5-phenyloxazolyl)]-benzol, Anthracen und Benzophenon bestätigen, daß die Förster-Beziehung für verdünnte Lösungen dieser kleinen Moleküle gültig ist.

Für polymere Donatoren mit spektraler Uberlagerung von Absorption und Emission besteht die Möglichkeit der Energiewanderung entlang der Kette. Unter diesen Bedingungen, unter denen auch die Diffusion des Acceptors eine Rolle spielen kann, werden die Beziehungen nach Yokota und Tanimoto als die gefunden, die am besten sowohl in fluiden wie in der Umgebung Polymerer angewendet werden können. Koeffizienten für die Wanderung der Singlett-Energie entlang der Polymerkette von Poly-N-vinylcarbazol, Poly-2-vinylnaphthalin und von Copolymeren von N-Vinylcarbazol mit MMA wurden abgeleitet. Sie passen auf ein Modell, in dem die Energie durch statistische Förster-Wechselwirkungen zwischen spektroskopisch nächsten Nachbarn übertragen wird.