

# Energy transfer studies from polymer bound naphthalene to anthracene in solution: translational and segmental diffusion rates

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A graft copolymer of polyisobutylene with poly(methyl methacrylate) [PMMA] was prepared containing naphthalene [N] groups statistically distributed along the PMMA backbone. Fluorescence studies of dilute solutions of the polymer in ethyl acetate showed small amounts of N-excimer emission when the NMA/MMA ratio was 1:9, and undetectable excimer when the ratio was 2/98. Energy transfer experiments were carried out between polymer-bound naphthalene and anthracene [A] added to the solution. The rate constant for energy transfer,  $k_{ET}$ , for the process  $N^* + A \rightarrow N + A^*$  was found to be  $1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  at 22°, slightly smaller than that ( $1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) for energy transfer from naphthylmethyl pivalate to A. From the value of the rate constants, a value for the segmental diffusion coefficient of polymer bound naphthalene was calculated.

(Keywords: fluorescence; quenching; polymer dynamics; Stern–Volmer kinetics; poly(methyl methacrylate))

## INTRODUCTION

This paper presents the results of fluorescence energy transfer experiments between polymer-bound naphthalene [N] in dilute ethyl acetate solution and anthracene [A] molecules free in solution. The polymer itself has a somewhat unusual structure. It is a copolymer of methyl methacrylate [MMA] + 1-naphthylmethyl methacrylate [NMA] grafted onto polyisobutylene [PIB]. The PIB comprises somewhat less than 10-monomer-mol% of the polymer. This might be expected to perturb some of the properties of the polymer, such as its gel-permeation chromatography (g.p.c.) retention time, since PIB is insoluble in ethyl acetate. The fluorescence quenching and energy transfer results are quite normal. We focus our attention on certain interesting aspects of the data analysis and the interpretation of the data in terms of molecular diffusion of A and segmental diffusion of the N groups.

These materials were prepared originally as non-aqueous colloidal polymer dispersions in isooctane<sup>1,2</sup>. The PMMA or P(MMA-co-NMA) polymers formed the core of 2  $\mu\text{m}$  diameter particles and the PIB served as the steric barrier. These particles form transparent solutions (denatured colloids) in good solvents for PMMA. It was our intent to carry out these studies as a reference point for similar experiments in alkane solvents, where energy transfer would occur from naphthalene in the intact particle to anthracene in solution.

## PREPARATION AND CHARACTERIZATION OF THE POLYMER COLLOID

### *Synthesis of the colloids*

The PIB sterically stabilized PMMA colloids were prepared in a two-step procedure<sup>3</sup>. In the first step, short PMMA sequences were grafted onto a PIB sample of nominal molecular weight ( $10^4$ ). These PIB samples contain sites of unsaturation for reaction either with initiator radicals or growing PMMA chains. Polymerization is terminated before the PMMA sequences become sufficiently long, so as to render the polymer insoluble in the cyclohexane reaction mixture. This short graft copolymer, called the 'dispersant' is precipitated from the solution with methanol and purified.

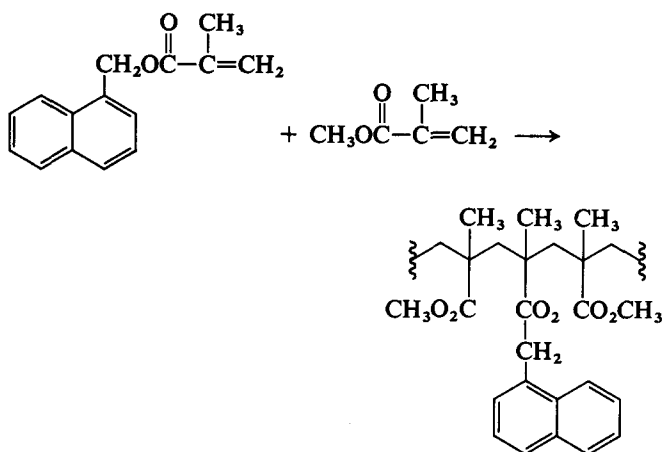
In the second step of the preparation, the dispersant, methyl methacrylate (MMA), an initiator and a methacrylate derivative of the desired chromophore are combined in cyclohexane solution and refluxed overnight. A cloudy dispersion forms. The reaction is stopped before all the monomer is incorporated into the dispersion. This procedure produces spherical particles of narrow distribution of sizes. Using 1-naphthylmethyl methacrylate (NMMA) as the comonomer yielded dispersions containing 1-alkylnaphthalene groups covalently bound in the core. Colloids were prepared containing 2 mole% naphthalene (N) and 10 mole% in the core. These are referred to as N-2 and N-10 respectively.

### *Characterization of the polymer colloids*

Scanning electron microscope studies indicated that N-2 and N-10 were spherical particles of essentially uniform

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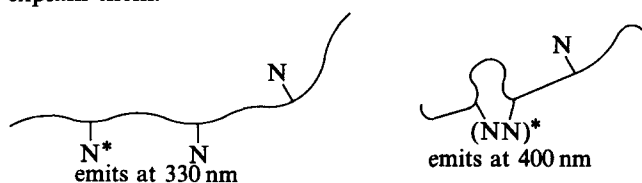
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size with a diameter of 2  $\mu\text{m}$ . The composition of these materials was determined by n.m.r. and u.v. absorption spectroscopy. The colloids could be solubilized into any solvent that would dissolve PMMA, including toluene, chloroform, ethylacetate, acetone and triethylamine. Clear homogeneous solutions were formed. These solutions, in  $\text{CDCl}_3$  gave sharp  $^1\text{H}$  n.m.r. spectra in which peaks could be assigned to PIB, to PMMA resonances, and to those of the naphthalene ring. Mole ratios of IB:MMA:N were determined to be 13:100:10 for N-10 and 13:100:2 for N-2, using a combination of n.m.r. and u.v. analysis.

#### Fluorescence studies

This paper focusses on the luminescence properties of N-2 and N-10 dissolved in ethyl acetate. These are homogeneous solutions and will serve as a benchmark for other studies of their colloidal dispersions. We report on two kinds of experiments we have carried out. First we describe steady state fluorescence and fluorescence decay measurements on solutions of N-2 and N-10 in ethyl acetate. These experiments have much in common with previous studies by fluorescence spectroscopy of poly(1-naphthylmethyl methacrylate) (PINMMA) and its copolymers with MMA. These experiments, by the research groups of Gueskens<sup>4</sup>, David<sup>4</sup>, Guillet<sup>5</sup>, Webber<sup>6</sup>, Soutar<sup>7</sup> and more recently Phillips<sup>8</sup> have had the objective of establishing the role of excitation energy migration ( $\text{N}^* + \text{N} \rightarrow \text{N} + \text{N}^*$ ) among naphthalene groups in the polymer. Some controversy surrounds the interpretation of these experiments because the data are more complex in detail than the predictions of the various models used to explain them.



Most of these experiments examine *excimer* formation between naphthalene groups along the polymer backbone. Excimers are excited dimers formed from an excited molecule plus its ground state counterpart. Since excimer pairs are bound only in the excited state and repel each other in the ground state, the excimer emission is substantially red-shifted with respect to fluorescence of the locally excited chromophore. N-2 and N-10 contain relatively few naphthalene groups. Consequently we anticipated that excimer formation would not be very

pronounced and that energy migration among naphthalene groups would have minimal importance in these solutions. Our experiments are the first to examine the fluorescence properties in solutions of ternary graft copolymers.

From our second set of experiments we discuss energy transfer between excited naphthalene groups on the polymer chains and anthracene molecules free in solution<sup>9</sup>. This energy transfer occurs by a dipole coupling (Förster) mechanism<sup>10</sup> and occurs over distances of 10 Å to 40 Å for this pair of chromophores. In other words, approach of an anthracene to within 20 Å of an excited naphthalene results in irreversible energy transfer to anthracene, which is observed as a decrease in the naphthalene emission intensity, a shortening of its fluorescence lifetime and a new emission due to anthracene fluorescence.

#### EXPERIMENTAL

$^1\text{H}$  n.m.r. spectra at 60 MHz were taken on a Varian T-60 n.m.r. Proton spectra at 80 MHz were run on a Bruker WP-80 instrument. U.v. absorption spectra were run on a Cary 210 instrument, with single-point measurements being carried out on a Cary 16 spectrometer. Fluorescence measurements were made using Hitachi-Perkin Elmer MPF44B and SLM 4400 fluorescence spectrometers. These spectra were not corrected.

#### Chromophore synthesis and purification

1-Naphthylmethacrylate was synthesized from 1-hydroxymethyl naphthalene (Aldrich) and freshly distilled methacryloyl chloride at 0°C in dry toluene in the presence of a slight excess of triethylamine. After an aqueous work-up, it was chromatographed on a silica gel column (50:50 benzene:cyclohexane) and stored in the presence of 1% hydroquinone. A sample was rapidly chromatographed to remove polymer and hydroquinone just prior to preparation of N-2 and N-10.

1-Naphthylmethyl pivalate was synthesized similarly using pivaloyl chloride (2,2-dimethylpropanoyl chloride, Aldrich). It was chromatographed on silica gel using 2% ethyl acetate in hexane. The ester was then distilled at 108°–110°C/0.2 mm and was shown to be 99.3% pure by gas chromatography (3% OV-101 on Chrom G, 6'  $\times$  1/8", 180°).

Anthracene (Eastman Organic) was chromatographed on silica gel using 2% ethyl acetate in hexane and then recrystallized three times from ethanol. Ethyl acetate was reagent grade, and was used as received. It showed no unexpected absorbances. It showed no detectable emission when irradiated in the 250–380 nm region.

#### Colloid synthesis

The preparation and characterization of N2 and N10 have previously been described<sup>1</sup>.

#### Fluorescence measurements

Quantum yields of fluorescence  $\phi_f$  were determined by comparing the area under the emission peak to that of a standard sample of known quantum yield.

$$\frac{\phi_{f1}}{\phi_{f2}} = \frac{\text{Area}_1 n_1^2 (1 - 10^{-A_1})}{\text{Area}_2 n_2^2 (1 - 10^{-A_2})} \quad (3)$$

where  $A$  is the absorbance of the sample at the excitation wavelength and  $n_1$  and  $n_2$  are the refractive indices of the pure solvents containing the sample (1) and the reference (2). Naphthalene in cyclohexane ( $\phi_f=0.23$ ) and anthracene in cyclohexane ( $\phi_f=0.36$ ) were chosen as standards. Solutions were prepared in matched square quartz cells, and degassed by argon bubbling. The absorbances were read directly on the Cary 16 spectrometer, and the emission spectra run immediately thereafter.

Fluorescence decays were measured by the time-correlated single photon counting technique. A Jarrell-Ash monochromator was used to determine the excitation wavelength. To isolate naphthalene emission, a combination of filters (Schott UG-11), Corning 3-37 and Corning 7-60) were used in series. These gave a window with maximum transmittance at 337 nm. Anthracene emission and naphthalene excimer emission were detected using Schott KV-370 plus KV-418 nm long pass filters. It was frequently necessary to use a Schott RG-25 band pass filter on the excitation side of the optics to prevent passage of the second harmonic of 280 nm excitation into the sample and detection system.

Sample decays and lamp profiles were recorded until the maximum counts in the early channels reached 20 000. All decays were measured at 0.798 ns/channel. Observed decay traces were fit by an iterative reconvolution 'match and compare' technique using a non-linear least squares algorithm<sup>1</sup>.

Fluorescence decay measurements and most steady state fluorescence measurements were made on samples in 13 mm o.d. quartz tubes. These were attached via graded seals and joints to a vacuum line. They were outgassed by four freeze-pump-thaw cycles and sealed at a pressure less than  $10^{-4}$  Torr.

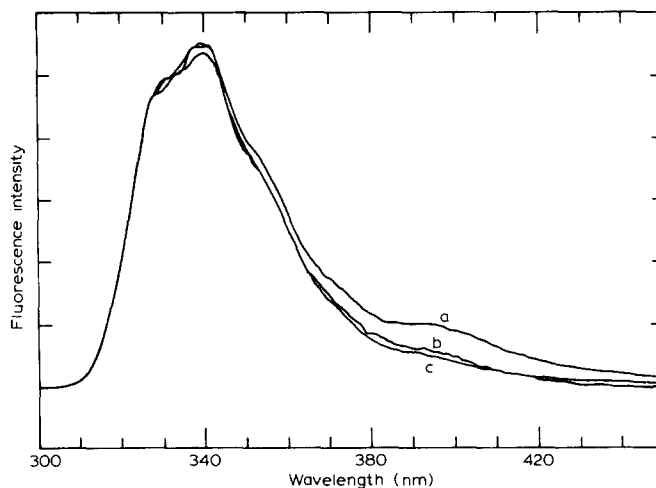
## RESULTS AND DISCUSSION

### Fluorescence studies of N-2 and N-10

Steady-state fluorescence spectra of N-2, N-10 and the model compound 1-naphthylmethyl pivalate (NMP) in deoxygenated ethyl acetate are shown in *Figure 1*. The spectra each contain  $\approx 2 \times 10^{-5}$  M naphthalene chromophores. These spectra are arbitrarily normalized at 320 nm. No excimer can be observed in the NMP spectrum at this wavelength. Weak excimer emission of increasing importance can be seen in N-2 and N-10. The relative intensity of the excimer to locally excited naphthalene emission ( $I_E/I_M$ ) remains unchanged when the polymer concentration is varied. Consequently we infer that the excimer seen in *Figure 1* is entirely intramolecular in origin.

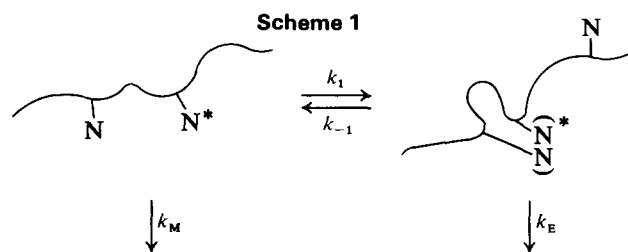
The fluorescence decay of the naphthalene group in N-10 solutions in ethyl acetate are double exponential with a long component of 37 ns and a short component of 11 ns. Naphthalene decay in N-2 can be fit to a single exponential with a lifetime of 37 ns, which indicates negligible excimer formation in this denatured colloid system. In these experiments, the fluorescence lifetime of NMP (34 ns) was found to be shorter than those of naphthalene in N-10 and N-2.

*Scheme 1* outlines the simplest model which accounts for excimer formation in naphthalene-containing polymers. Locally excited  $N^*$  decays at a rate determined by  $k_M$ , the sum of radiative and radiationless rate constants;  $k_M$  should have the same value as  $\lambda_{mod}$ , the exponential



**Figure 1** Luminescence spectra of (a) N-10, (b) N-2, (c) NMP in ethylacetate,  $\lambda_{ex}=280$  nm. Spectra were normalized at 340 nm. In all cases  $[N]=2 \times 10^{-5}$  M

decay rate of the model compound 1-naphthylmethyl pivalate (NMP). The rate constants  $k_1$  and  $k_{-1}$  describe the rates of excimer formation and excimer dissociation,



and  $k_E$  describes the sum of radiative and non-radiative rates of excimer decay to the groundstate. This mechanism predicts that the naphthalene emission decays as a sum of two exponential terms.

$$I_M(t) = a_1 \exp(-\lambda_1 t) + a_2 \exp(-\lambda_2 t) \quad (4)$$

where  $I_M(t)$  can appear to be exponential if  $a_2$  is small and  $\lambda_2$  is large. The excimer emission is predicted to rise and decay as the difference of two exponential terms.

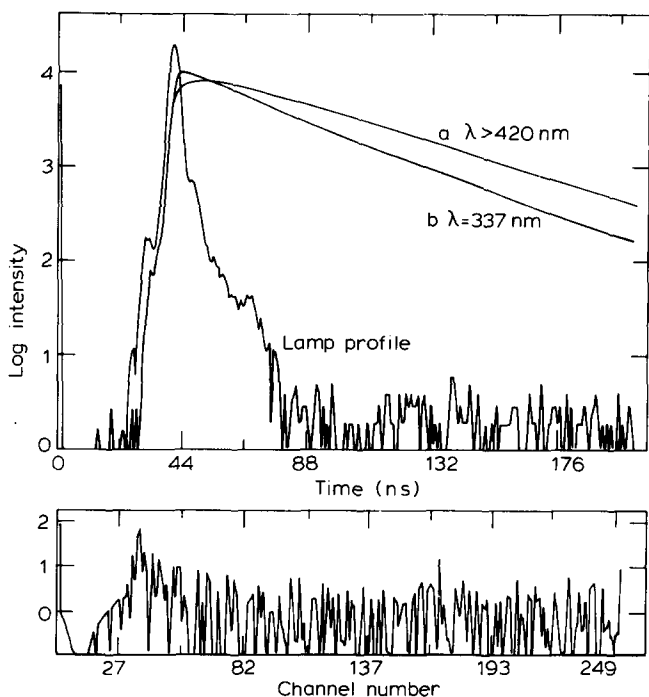
$$I_E(t) = a_3 \exp(-\lambda_3 t) - a_4 \exp(-\lambda_4 t) \quad (5)$$

Since there should be no excimer at time zero,  $a_3/a_4$  must equal 1.0. Furthermore *Scheme 1* predicts that  $\lambda_3$  must equal  $\lambda_1$  or  $\lambda_2$  and the other term must equal  $\lambda_4$ .

*Figure 2* shows the typical monomer and excimer fluorescence decay curves of N-10 in ethyl acetate solution. The slopes of the two decay curves at long time differ by an amount far greater than the experimental error in  $\lambda^{-1}$  (on the order of 2 ns). *Table 1* summarizes the results of the excimer and monomer life times of naphthalene groups in N-10.

While some aspects of these predictions fit the observed data, the fact that  $\lambda_1$  from  $I_M(t)$  corresponds neither to  $\lambda_3$  or  $\lambda_4$  in the excimer fluorescence decay measurements emphasizes that *Scheme 1* is an oversimplification of the excimer forming process. This result is expected in a polymer containing chromophores with a distribution of separations along the chain contour.

Phillips and coworkers<sup>8</sup> have studied some copolymers containing varying concentrations of aromatic chrom-



**Figure 2** Fluorescence decay traces of N-10 in ethylacetate  $\lambda_{\text{ex}}=280$  nm. (a) Excimer fluorescence  $\lambda_{\text{em}}>420$  nm, (b) Monomer fluorescence  $\lambda_{\text{em}}=337$  nm

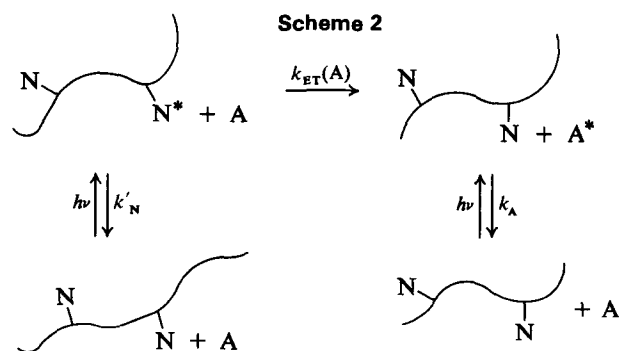
**Table 1**

N-10 in Ethyl acetate	Long component (ns)	Short component (ns)	$a_2/a_1$ or $-a_4/a_3$
Monomer	37	11	+ 0.297
Excimer	44	13	- 0.324

ophors and have shown that the conventional kinetic scheme of Birks<sup>10</sup> is not applicable. Some doubts concerning the applicability of Birks scheme in polymer systems have also been expressed by other authors<sup>11</sup>. Porter<sup>12</sup> has suggested that self-quenching occurs in naphthalene polymers leading to low apparent fluorescence quantum yields and to a decrease in the monomer lifetimes.

#### Energy transfer to anthracene

When small quantities of anthracene are added to solutions containing N-2 or N-10, excitation of the solution at 280 nm (the maximum in the naphthalene absorption) results in emission from both naphthalene and anthracene groups, *Figure 3*. Some of the anthracene emission results from its direct absorption of light ( $\epsilon_{280}=630 \text{ M}^{-1} \text{ cm}^{-1}$ ) and some from energy transfer from excited naphthalene groups. These processes are summarized in *Scheme 2*.



When the incident light intensity is  $I_0$ , then the time dependent rate equations of excited naphthalene and anthracene can be written as,

$$\frac{d[\text{N}^*]}{dt} = I_0 A_N - (k_{fN} + k_{nN})[\text{N}^*] - k_{\text{ET}}[\text{A}][\text{N}^*] \quad (6a)$$

$$\frac{d[\text{A}^*]}{dt} = I_0 A_A - (k_{fA} + k_{nA})[\text{A}^*] + k_{\text{ET}}[\text{A}][\text{N}^*] \quad (6b)$$

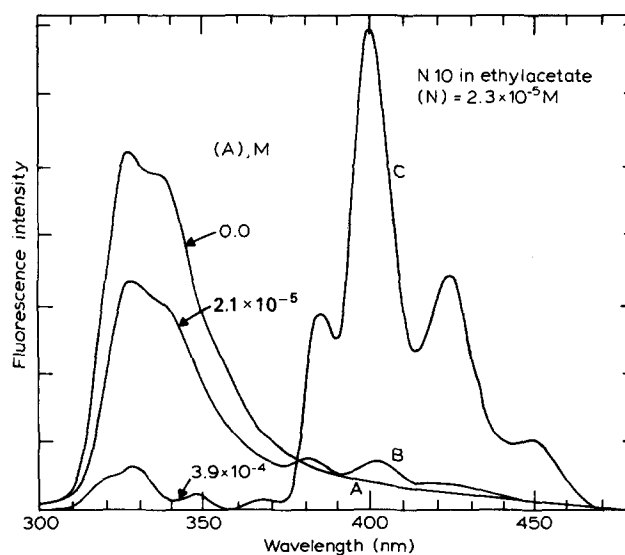
where  $k_{fN}$  and  $k_{fA}$  are the radiative rate constants respectively for naphthalene and anthracene fluorescence, and  $k_{nN}$  and  $k_{nA}$  are the rate constants describing the corresponding nonradiative decays.  $A_N$  and  $A_A$  are the Beer's Law absorbances, respectively, of naphthalene and anthracene. The equations make explicit the fact that anthracene fluorescence has two source terms; direct excitation from the incident light and energy transfer from naphthalene.

#### Steady-state fluorescence studies

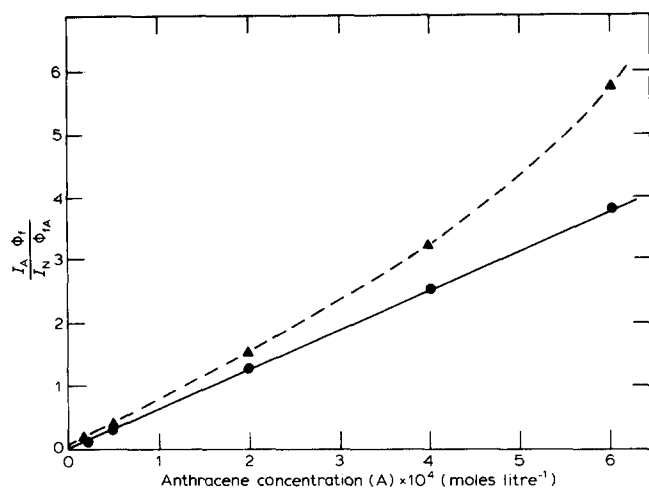
Equations (6a) and (6b) can be solved for the case of steady-state fluorescence measurements which provide the intensities of naphthalene ( $I_N$ ) and anthracene ( $I_A$ ) emission (cf. Appendix). These intensities are normalized by the intrinsic fluorescence quantum efficiencies of anthracene ( $\phi_{fA}$ ) and an appropriate naphthalene derivative ( $\phi_{fN}$ ) in the absence of external quenching (i.e. dilute solution). In equation (7) the product of  $I_A \phi_{fN} / I_N \phi_{fA}$  is related to the ratio of absorbances  $A_A$  and  $A_N$ , as well as to the ratio of  $k_{\text{ET}}[\text{A}]$  to  $k_N$ . For the purposes of analysis we chose the value of  $k_N$  to be the long-time component of the  $\text{N}^*$  decay in N-10 solutions when  $[\text{A}]=0$ .

$$\frac{I_A \phi_{fN}}{I_N \phi_{fA}} = \frac{A_A}{A_N} + \frac{k_{\text{ET}}[\text{A}]}{k_N} \left( 1 + \frac{A_A}{A_N} \right) \quad (7)$$

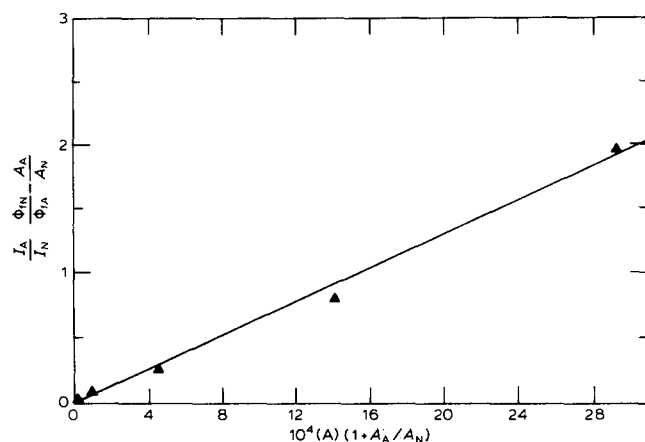
*Figure 4* shows a direct plot of  $I_A \phi_{fN} / I_N \phi_{fA}$  (corrected for trivial reabsorption of fluorescence of naphthalene by anthracene) for N-10 versus the concentration of anthracene  $[\text{A}]$ . Here the measured values of



**Figure 3** Luminescence spectra of (N-10 + A) in deoxygenated ethylacetate at three different  $[\text{A}]$  concentrations.  $\lambda_{\text{ex}}=280$  nm. (a)  $[\text{A}]=0$ , (b)  $[\text{A}]=2.13 \times 10^{-5} \text{ M}$ , (c)  $[\text{A}]=3.88 \times 10^{-4} \text{ M}$  in all cases  $[\text{N}]=2.2 \times 10^{-5} \text{ M}$ . Spectra were normalized at 378 nm



**Figure 4** Steady-state intensity ratios of (N-10+A) in ethylacetate, for different anthracene concentrations. Solid line indicates calculated absorbance ratios  $A_A/A_N$ .  $\phi_{FN}$  and  $\phi_{FA}$  are measured fluorescence quantum yield efficiencies of N-10 and anthracene in ethyl-acetate, respectively



**Figure 5** Plot of equation (7) Slope of the curves gives  $k_{ET}/\lambda_1 = 6.8 \times 10^2 \text{ M}^{-1}$ .  $k_{ET}$  is the energy transfer rate constant in (N-10+A) system in ethylacetate

$\phi_{fN}/\phi_{fA} = 0.12/0.27$  were used in the plot. The curvature arises from a superposition of direct anthracene fluorescence and that due to energy transfer from naphthalene.

The corresponding plot according to equation (7) is shown in Figure 5. From the slope of this plot ( $0.68 \times 10^{-3} \text{ M}^{-1}$ ) and the measured value of  $\lambda_1 = 2.71 \times 10^7 \text{ s}^{-1}$  we can calculate a value of  $1.83 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  for  $k_{ET}$ .

#### Fluorescence decay studies

Scheme 2 predicts that after excitation of a sample of N-2 or N-10 in the presence of anthracene by a  $\delta$ -pulse of light, the naphthalene ( $I_N(t)$ ) and anthracene ( $I_A(t)$ ) emission decays will follow the equations<sup>10</sup>,

$$I_N(t) = a'_1 \exp(-\lambda_1 t) \quad (8a)$$

$$a'_1 = k_{fN}(N^*)_0 \quad (8b)$$

$$\lambda_1 = k_N + k_{ET}[A] \quad (8c)$$

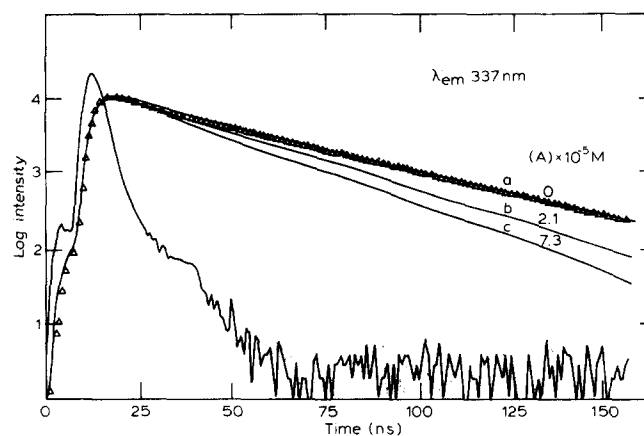
$$I_A(t) = a_5 \exp(-\lambda_5 t) + a_6 \{ \exp(-\lambda_6 t) - \exp(-\lambda_5 t) \} \quad (9a)$$

$$a_5 = k_{fA}[A^*]_0, \quad \lambda_5 = k_A \quad (9b)$$

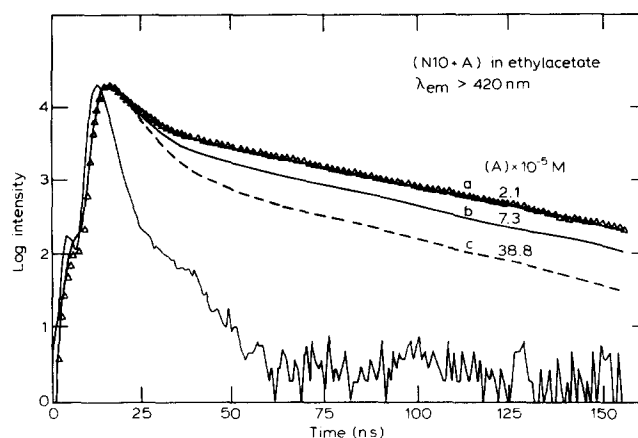
$$a_6 = \frac{k_{ET}k_{fA}[A][N^*]_0}{k_A - k_N}, \quad \lambda_6 = \lambda_1 \quad (9c)$$

Equation (8) describes an exponential naphthalene decay, which is observed for N-2; but, since Scheme 2 ignores excimer formation, equation (8) ignores the weak excimer emission.

Decay curves of naphthalene at 337 nm and anthracene at 420 nm are shown in Figures 6 and 7, respectively for the N-10+anthracene system. For 337 nm emission, decay curves are essentially exponential at long times for all anthracene concentrations. In N-10 there is also a weak second short component which we ignore in this analysis. The 420 nm emission decays are double exponential. They obey equation (9a), with the fast rising component of  $I_A(t)$  due to energy transfer from naphthalene obscured by the much more intense prompt fluorescence due to direct absorption by anthracene. Decay parameters were obtained from the curves of Figures 6 and 7 using an iterative reconvolution technique. The short lived components for 420 nm emissions are typical of anthracene decays with lifetimes of  $5.0 \pm 0.1 \text{ ns}$ . Lifetimes of the long-lived component of anthracene emission at 420 nm ( $\tau_{\text{long}}^{420}$ ) and of naphthalene emission at 337 nm ( $\tau_{\text{long}}^{337}$ ) were found to be concentration dependent.



**Figure 6** Fluorescence decay traces of naphthalene using a 337 nm interference filter for (N-10+A) system in deoxygenated ethylacetate.  $\lambda_{\text{ex}} = 280 \text{ nm}$ . (a)  $[A] = 0$ , (b)  $[A] = 2.13 \times 10^{-5} \text{ M}$ , (c)  $[A] = 7.30 \times 10^{-5} \text{ M}$ . In all cases  $[N] = 2.2 \times 10^{-5} \text{ M}$



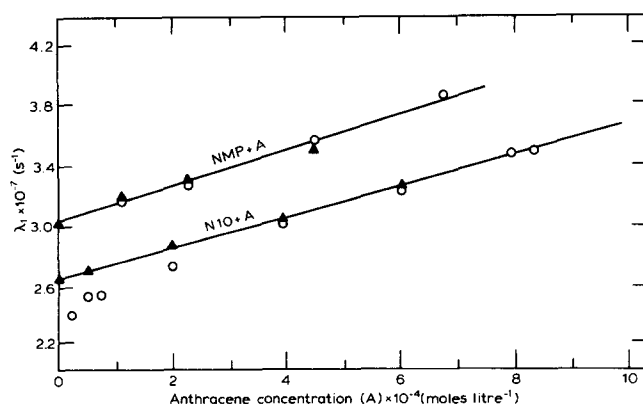
**Figure 7** Fluorescence decay traces of anthracene at  $\lambda_{\text{em}} > 420 \text{ nm}$ , for (N-10+A) system in deoxygenated ethylacetate,  $\lambda_{\text{ex}} = 280 \text{ nm}$ . (a)  $[A] = 2.13 \times 10^{-5} \text{ M}$ , (b)  $[A] = 7.30 \times 10^{-5} \text{ M}$ , (c)  $[A] = 3.88 \times 10^{-4} \text{ M}$

As the anthracene concentration increases, the lifetimes  $\tau_{\text{long}}^{420}$  and  $\tau_{\text{long}}^{337}$  decrease, indicating the energy transfer from  $N^*$  to A. The data follow the Stern–Volmer equation [ $\lambda_1 = k_N + k_{\text{ET}}[A]$ ]. Results are plotted in Figure 8 for N-10+anthracene in ethylacetate solution. In the N-10+anthracene system at low anthracene concentrations,  $\tau_{\text{long}}^{420}$  lifetimes were found to be longer than  $\tau_{\text{long}}^{337}$  lifetimes. These deviations might be due to the superposition of excimer emission and anthracene emission at 420 nm. Since the excimer lifetime (44 ns) is much longer than  $\tau_{\text{long}}^{420}$  this superposition makes the apparent lifetime of the long-lived component of anthracene seem longer. As the anthracene concentration increases, excimer intensity becomes negligible and  $\tau_{\text{long}}^{420}$  approaches  $\tau_{\text{long}}^{337}$ . The Stern–Volmer plot of N-2+anthracene system does not show any deviations between the long-lived lifetimes at 337 nm and 420 nm, consistent with the negligible amount of excimer in N-2 solutions.

Fluorescence decay curves of the NMP model compound ( $2.5 \times 10^{-5}$  M) at 337 nm were found to be single exponential for all anthracene concentrations. The long-lived component lifetimes of anthracene at 420 nm were found equivalent to  $\tau_{\text{long}}^{337}$  for the NMP+anthracene system, which proves that  $A^*$  are produced by energy transfer from  $N^*$ . Stern–Volmer results of NMP+anthracene system are compared with N-10 and N-2 systems in Figure 8.

Energy transfer rate constants ( $k_{\text{ET}}$ ), found from the equation  $\lambda_1 = k_N + k_{\text{ET}}[A]$ , are listed in Table 2 for N-10, N-2 and the NMP solutions in ethylacetate. Values of  $k_{\text{ET}}$  obtained by the single-photon counting technique were found to be similar to the value of  $k_{\text{ET}}$  found from steady-state fluorescence. The latter technique is less precise.

Energy transfer between unlike chromophores is usually described using the long-range dipole–dipole interaction of Förster<sup>10</sup>. It is customary to define a distance  $R_0$  called the Förster radius, at which the rate constants of the donor ( $k_N$ ) and the energy transfer to the acceptor are equal.  $R_0$  can be calculated from the spectroscopic properties of the participating donor naphthalene and acceptor anthracene molecules. For example, for 1-methyl-naphthalene transferring energy to anthracene,  $R_0$  (static) = 23 Å<sup>13</sup>. If donor and acceptor particles are mobile, then the effective  $R_0$  ( $R_0$ )<sub>eff</sub> can increase because diffusion during the donor lifetime allows the



**Figure 8** Stern–Volmer plots of (N-10+A) and (NMP+A) systems. Empty circles represent  $\lambda_{\text{em}} > 420$  nm, triangles are  $\lambda_{\text{em}} = 337$  nm. Here  $\lambda_{\text{ex}} = 280$  nm.  $k_{\text{ET}}$  parameters were found from the slope of the curves.  $\lambda_{\text{em}}$ : (▲) 337 nm (○)  $> 420$  nm

**Table 2** Rate constants for energy transfer and for naphthalene decay determined by fluorescence decay measurements

Rate constants in ethyl acetate	(N-10+A)	(N-2+A)	(NMP+A)
$k_{\text{ET}}(10^{10}\text{M}^{-1}\text{s}^{-1})$	1.07	1.1	1.22
$k_N(10^7\text{s}^{-1})$	2.62	2.61	3.05

**Table 3**

Förster Parameters	(N-10+A)	(N-2+A)	(NMP+A)
$c_0(10^{-3}\text{M})$	7.73	7.54	7.92
$(R_0)_{\text{eff}}(\text{Å})$	38.7	39.1	38.4

intermolecular separation to vary. A critical concentration can be defined for 76% efficiency energy transfer.

$$c_0 = \frac{3000}{2\pi^{3/2}NR_0^3} \quad (10)$$

When mass diffusion occurs ( $R_0$ )<sub>eff</sub> replaces  $R_0$  and as a result  $c_0$  decreases. Our experimental results were compared in Table 3 to N-10, N-2 solutions and NMP in ethylacetate.

( $R_0$ )<sub>eff</sub> values were found to be similar for polymeric and small molecular systems within the experimental error. ( $R_0$ )<sub>eff</sub> values are also nearly twice as large as  $R_0$ (static). From this observation plus the fact that our data follow Stern–Volmer kinetics we presume that diffusional processes are rate limiting in the energy transfer from  $N^*$  to anthracene.

The magnitude of  $k_{\text{ET}}$  is related to the diffusion parameters.

$$k_{\text{ET}} = \frac{4\pi N_0 D R_f}{1000} \quad (11)$$

where  $D$  is the appropriate diffusion coefficient and  $N_0$  is Avogadro's number. For NMP+anthracene system  $D$  can be written as  $D_{\text{AN}} = D_A + D_{\text{NMP}}$ ,  $D_A$  and  $D_{\text{NMP}}$  are the diffusion coefficients of anthracene and NMP, respectively. For N-2 and N-10 in solution, there are three contributors to the total diffusion coefficient  $D_{\text{A,pol}}$ :

$$D_{\text{A,pol}} = D_{\text{As}} + D_{\text{seg}} + D_{\text{Tr}} \quad (12)$$

$D_{\text{As}}$  describes the diffusion of A in the presence of polymer;  $D_{\text{Tr}}$ , the translational diffusion of the polymer itself, and  $D_{\text{seg}}$ , the motion of the N-containing segments of the chain.

According to Gösele<sup>14</sup>,  $R_f$  in equation (11) can be taken as,

$$R_f \approx 0.676 (\alpha/D)^{1/4}$$

where  $\alpha = R_0^6/\tau^0$ . Here  $\tau^0$  is the fluorescence lifetime of the excited donor in the absence of acceptor. Using this approach we calculated the  $R_f$  and  $D$  values of our systems. They are listed in Table 4.

Diffusion coefficients of the polymeric system in ethyl acetate are slightly smaller than the diffusion coefficient of the (NMP+A) system. If one can assume that the diffusion coefficients of NMP and anthracene in the solution are approximately equal, then  $D_A \approx D_{\text{NMP}} =$

**Table 4** Calculated values of  $R_f$  and  $D$  for energy transfer experiments in ethyl acetate

	(N-10+A)	(N-2+A)	(NMP+A)
$R_f$ (A)	8.11	8.21	7.94
$D$ ( $10^{-5} \text{cm}^2 \text{s}^{-1}$ )	1.90	1.88	2.13

$1.06 \times 10^{-5} \text{cm}^2 \text{s}^{-1}$  can be written. If one further assumes that  $D_A \approx D_{A_s}$ , i.e. that anthracene diffuses at the same rate in the presence or absence of polymer, a value for  $D_{\text{seg}}$  can be calculated. This is probably a poor assumption since the presence of polymer should cause a small decrease in the rate of anthracene diffusion. Nonetheless, from equation (12) one calculates  $D_{\text{seg}} + D_{\text{Tr}} = 0.84 \times 10^{-5} \text{cm}^2 \text{s}^{-1}$ . Since  $D_{\text{Tr}}$  has a much smaller value, it is not unreasonable to assign this value to the segmental diffusion coefficients of the N groups along the polymer chains. This motion makes an important contribution to the fluorescence energy transfer process.

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## APPENDIX

Equation (7) is derived from equations (A1) and (A2) using the steady-state hypothesis  $d[\text{N}^*]/dt = d[\text{A}^*]/dt = 0$ .

$$\frac{d[\text{N}^*]}{dt} = I_0 A_N - (k_{fN} + k_{nN})[\text{N}^*] - k_{ET}[\text{A}][\text{N}^*] \quad (\text{A1})$$

$$\frac{d[\text{A}^*]}{dt} = I_0 A_A - (k_{fA} + k_{nA})[\text{A}^*] + k_{ET}[\text{A}][\text{N}^*] \quad (\text{A2})$$

Here  $I_0$  is the intensity of the incident light, and  $A_N$  and  $A_A$  are the Beer's Law absorbances of naphthalene and anthracene respectively. The rate constants  $k_{fN}$  and  $k_{fA}$  describe the respective radiative rates, and  $k_{nN}$  and  $k_{nA}$ , the non-radiative rates, of decay from  $\text{N}^*$  and  $\text{A}^*$ . For convenience, we define  $k_N = k_{fN} + k_{nN}$  and  $k_A = k_{fA} + k_{nA}$ .

By definition, the quantum yields of fluorescence from  $\text{N}^*$  and  $\text{A}^*$  are  $\phi_{fN} = k_{fN}[\text{N}^*]/I_0 A_N$  and  $\phi_{fA} = k_{fA}[\text{A}^*]/I_0 A_A$ . In the absence of anthracene, the known value of the naphthalene quantum yield  $\phi_{fN}^\circ$  is equal to

$$\phi_{fN}^\circ = \frac{k_{fN}}{k_N} \quad (\text{A3})$$

and similarly for  $\text{A}^*$  in the absence of naphthalene

$$\phi_{fA}^\circ = \frac{k_{fA}}{k_N} \quad (\text{A4})$$

The ratio of fluorescence intensities  $I_A/I_N$  is equal to the ratio of quantum yields  $\phi_{fA}/\phi_{fN}$ , which in turn yields

$$\frac{\phi_{fA}}{\phi_{fN}} = \frac{k_{fA}[\text{A}^*]}{k_{fN}[\text{N}^*]} \quad (\text{A5})$$

Hence

$$\frac{I_A}{I_N} = \frac{\phi_{fA}^\circ k_A [\text{A}^*]}{\phi_{fN}^\circ k_N [\text{N}^*]} \quad (\text{A6})$$

Upon substitution of the steady-state values for  $[\text{A}^*]$  and  $[\text{N}^*]$  one obtains

$$\frac{I_A \phi_{fN}^\circ}{I_N \phi_{fA}^\circ} = \frac{A_A k_N + k_{ET}[\text{A}]}{A_N k_N} + \frac{k_{ET}[\text{A}]}{k_N} \quad (\text{A7})$$

Rearrangement of the terms in (A7) yields equation (7).