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Singlet Electronic Energy Transfer in Polymers Containing Naphthalene and Anthracene Chromophores

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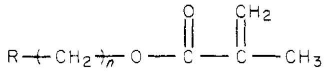
ABSTRACT: The efficiency χ of singlet electronic energy transfer from poly(1-naphthylmethyl methacrylate) and poly[2-(1-naphthyl)ethyl methacrylate] to anthracene end groups or copolymerized 9-anthrylmethyl methacrylate was measured as a function of trap density and solvent. Values of χ as high as 43% were obtained, even when anthracene constitutes only 0.5 mol % of the polymer. Fluorescence decay measurements and time-resolved spectroscopy show that energy transfer occurs over tens of nanoseconds and that the transfer time decreases with increasing naphthalene and anthracene concentrations. The proposed mechanism of energy migration involves a moderate number of Förster transfers between naphthalene chromophores, followed by Förster transfer to anthracene once the excitation energy has diffused to within about 2 nm of the anthracene chromophore. The results suggest that polymer chains can be efficient antennas for the collection and transport of photoexcitation energy.

Electronic energy transfer between chromophores attached to a polymer chain has been invoked to explain several phenomena in polymer photophysics, including excimer formation,[1-5] unusually efficient quenching by small molecules,[6-11] and energy transfer to chemically bound traps.[12-15] Besides being a challenging problem in chemical physics, energy transfer has practical consequences in the photodegradation and photostabilization of commercial polymers.[16-18] The role played in plant photosynthesis by energy migration between chlorophyll molecules has created further interest in this phenomenon.

Interpretation of excimer and small-molecule quenching experiments requires considerable caution, because the density of trap sites is difficult to measure. It is unknown, for example, what fraction of excimer sites exists in polymers prior to excitation and what proportion forms after excitation by a sequence of bond rotations. Similarly, in the quenching of polymers by small molecules, the concentration of quencher within the macromolecular coil may not correspond to the bulk concentration. Such a situation may lead to anomalous Stern–Volmer quenching constants. On the other hand, these problems do not exist when the quenching chromophore is chemically bound to the polymer, so that this third class of quenching phenomena may be easier to study.

In previous publications, electronic energy transfer was shown to occur from the naphthalene chromophores of poly(1-naphthyl methacrylate) (PNMA) to terminal 9-vinylanthracene traps.[13-15] The authors proposed that energy transfer occurred between naphthalene chromophores and finally to anthracene in order to explain the large proportion of anthracene emission in the steady-state fluorescence spectrum of the polymer.

The work of Aspler, Hoyle, and Guillet[14] is now extended to an investigation of the effects of polymer structure on energy transfer. Polymers of 1-naphthylmethyl methacrylate (NMMA) and 2-(1-naphthyl)ethyl methacrylate (NEMA) containing terminal anthracene traps or copolymerized 9-anthrylmethyl methacrylate (AMMA) have been synthesized:



$$R\!-\!(CH_2)_n\!-\!O\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!\overset{\overset{\displaystyle CH_2}{\|}}{C}\!-\!CH_3$$

NMMA, R = α-naphthyl; $n = 1$
NEMA, R = α-naphthyl; $n = 2$
AMMA, R = 9-anthryl; $n = 1$

Together with PNMA, this constitutes a series of polymers in which the naphthalene chromophore is progressively further from the main chain. The effects of solvent and polymer composition on the efficiency of energy transfer have been evaluated quantitatively. In addition, transient fluorescence measurements have been used to explore the mechanism and the time scale of the energy transfer process.

Experimental Section

Methacryloyl chloride and pivaloyl chloride, prepared from the corresponding acids and $SOCl_2$,[19] were fractionally distilled at reduced pressure.

1-Naphthylmethyl Methacrylate. To a solution of 24.4 g of 1-naphthalene methanol (Aldrich), 25 mL of dry Et_3N, and 125 mL of dry THF cooled to 0 °C, 20 mL of methacryloyl chloride was added over 1 h with stirring. After the solution was stirred an additional 1.5 h at 0 °C, H_2O (100 mL) was added to dissolve the amine salt. The product was extracted with ether; the combined extracts were washed with aqueous HCl, $NaHCO_3$, H_2O, and saturated NaCl and dried over Na_2SO_4. After removal of the solvent, the product was chromatographed on alumina, eluting with 1:1 benzene–cyclohexane. The product (18 g, colorless oil) is the first band off the column and was stored at −20 °C over a small amount of inhibitor: IR (neat) 1710 cm^{-1}; NMR ($CDCl_3$) δ 1.9 (s, 3 H, CH_3), 5.4 (s, 1 H, $=$CH), 5.5 (s, 2 H, $ArCH_2O$), 6.0 (s, 1 H, $=$CH), 7.15–8.1 (m, 7 H, aromatic ring H).

2-(1-Naphthyl)ethyl Methacrylate. 2-(1-Naphthyl)ethanol was prepared by $LiAlH_4$ reduction of 1-naphthaleneacetic acid in refluxing THF.[20] The methacrylate ester was prepared following the procedure for NMMA. Because of its high reactivity, it was rechromatographed on alumina immediately before use, eluting with cyclohexane, which precipitates any polymer formed on standing. The ester is a colorless liquid: IR (neat) 1730 cm^{-1}; NMR ($CDCl_3$) δ 1.9 (s, 3 H), 3.4 (t, 2 H), 4.5 (t, 2 H), 5.5 (s, 1 H), 6.08 (s, 1 H), 7.2–8.2 (m, 7 H).

9-Anthrylmethyl Methacrylate. This monomer was prepared by Dr. C. E. Hoyle from 9-anthracenemethanol (Aldrich) and methacryloyl chloride in a manner similar to that used for NMMA, except that the reaction mixture was refluxed briefly following addition of the acid chloride. The ester, purified by repeated crystallization from cyclohexane, was obtained as yellow crystals: mp 83–84 °C (uncorrected); IR (Nujol) 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.85 (s, 3 H), 5.42 (s, 1 H), 5.95 (s, 1 H), 6.13 (s, 2 H), 7.2–8.5 (m, 9 H).

9-(Bromomethyl)anthracene. 9-(Bromomethyl)anthracene was prepared from 9-anthracenemethanol and PBr_3.[21] The crude product was fractionally sublimed and stored in the dark at −20 °C.

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Table I
Properties of the Anthracene-Containing Polymer Samples

sample no.	monomer 1	monomer 2	structure[a]	mol % of anthracene: monomer mixture	mol % of anthracene: copolymer	M_n($\times 10^{-5}$)[b]
1	NMA	9-vinylanthracene	E	6	0.06	2[c]
2	NMMA	9-(bromomethyl)anthracene	E	5	0.50	0.41
3	NMMA	AMMA	R	0.093	0.074	1.03
4	NMMA	AMMA	R	0.26	0.174	1.09
5	NMMA	AMMA	R	0.50	0.348	1.10
6	NMMA	AMMA	R	0.89	0.665	1.11
7	NEMA	AMMA	R	0.32	0.196	5.5

[a] E = anthracene end group; R = random copolymer. [b] By membrane osmometry in toluene. [c] Reference 14.

9-Anthrylmethyl Pivalate. 9-Anthrylmethyl pivalate, prepared from 9-anthracenemethanol and pivaloyl chloride following the procedure for AMMA, was obtained as light yellow crystals (MeOH): mp 111-112 °C; IR (Nujol) 1720 cm^{-1}; NMR (CDCl$_3$) δ 1.17 (s, 9 H), 6.07 (s, 2 H), 7.2-8.5 (m, 9 H); UV (THF, Cary-14) 385 nm (8725 M^{-1} cm^{-1}), 365 (9400), 347 (6200), 330 (3050). The extinction coefficient at 280 nm is 660 M^{-1} cm^{-1}.

Polymers were prepared by azoisobutyronitrile-initiated radical polymerization in degassed benzene at 58 °C. They were purified by three precipitations from benzene into ethanol, washed thoroughly with ethanol and with spectroscopic grade *n*-pentane, and dried in vacuo over P_2O_5. No change in the polymer UV spectra was observed following several further reprecipitations. The synthesis of 9-vinylanthracene-terminated PNMA has been described previously.[14] The mole fraction of anthracene in the copolymers was determined by UV spectroscopy, using the measured extinction coefficients of 9-anthrylmethyl pivalate and 9-methylanthracene (MA) to approximate that of the polymer-bound anthracene. The compositions and molecular weights of the copolymers are listed in Table I.

For fluorescence spectroscopy, toluene was twice fractionated from P_2O_5. Tetrahydrofuran was refluxed over LiAlH$_4$ for 16 h and fractionally distilled under nitrogen. Polystyrene, prepared by emulsion polymerization from freshly purified styrene,[22] and poly(methyl methacrylate) (PMMA) (Eastman) were each precipitated twice from benzene into methanol. Polymer films containing 1% anthracene-terminated PNMMA were obtained by slow evaporation of a dilute solution of the two polymers in benzene on a distilled water surface. The films were dried in vacuo over P_2O_5.

Steady-state emission spectra of samples under nitrogen were recorded on a Hitachi Perkin-Elmer MPF-2A spectrofluorimeter and were corrected for the wavelength dependence of the detector response by comparison of spectra of quinine sulfate in ethanol and 1 M H_2SO_4 with corrected literature spectra.[23] Fluorescence quantum yields were measured as described previously.[14] The quantum yield standard 1-naphthol (Fisher) was fractionally sublimed three times under high vacuum. 9-Methylanthracene (Pfaltz and Bauer) was recrystallized twice and fractionally sublimed. Fluorescence lifetimes of both compounds agreed with literature values.[23] Energy transfer efficiencies were determined by resolving polymer emission spectra into their components. Fluorescence spectra of homopolymers and of small molecule anthracene model compounds were compared with those of the anthracene-containing copolymers. Since the anthracene emission is negligible in the 350-370-nm region, all emission in the copolymers in this region arises from naphthalene monomer and excimer. It was therefore possible to reconstruct the excimer band which lies under the anthracene emission of the copolymer, using the partially resolved excimer emission between 350 and 370 nm and the homopolymer spectrum as guides. In this way, the relative contributions of naphthalene and anthracene emission to the total spectrum were determined without direct subtraction of the anthracene model compound spectrum from that of the copolymer in which the anthracene bands are at a slightly different wavelength.

Fluorescence decays and time-resolved spectra were measured by single photon counting as described elsewhere.[13,14,24] Excitation of the naphthalene chromophore was at 280 nm through an interference filter, except for time-resolved spectra in toluene, where weak absorption by the solvent made it necessary to excite at 292 nm through a Jarrell-Ash monochromator. The anthracene chromophore was excited through a 366-nm interference filter. Since direct measurement of fluorescence quantum yields in polymer films was not practical, the approximation was made that quantum yields ϕ and decay times τ were related as in eq 1.

$$\phi_{\mathrm{THF}}/\phi_{\mathrm{film}} = \tau_{\mathrm{THF}}/\tau_{\mathrm{film}} \qquad (1)$$

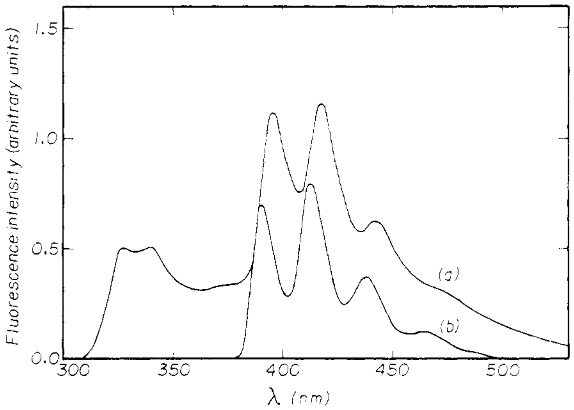


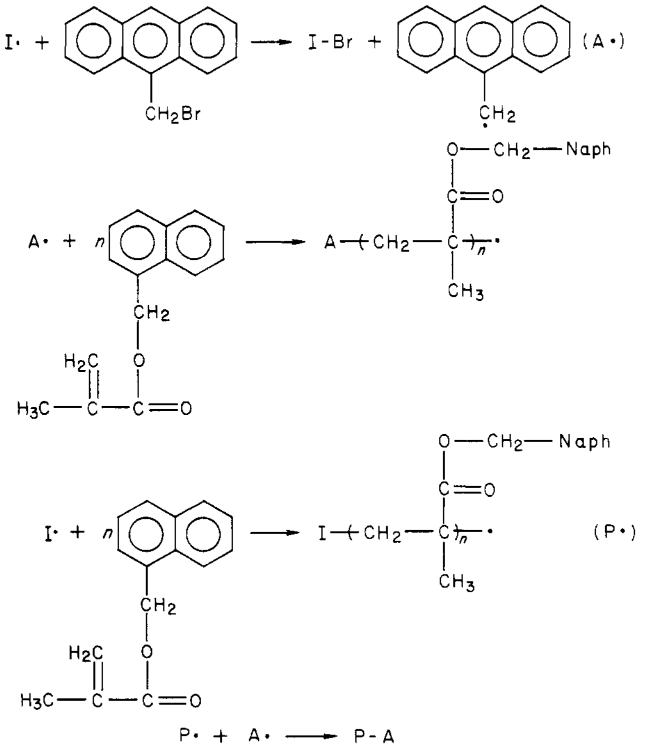
Figure 1. Steady-state fluorescence spectra in deoxygenated THF at 25.0 °C: (a) anthracene-terminated PNMMA, λ_{ex} = 280 nm, (b) 5 × 10^{-5} M 9-methylanthracene, λ_{ex} = 340 nm.

Results and Discussion

Steady-State Fluorescence Studies. The polymerization of NMMA in the presence of 5 mol % 9-(bromomethyl)anthracene gave a polymer with an average of 0.90 bound anthracene chromophores per chain. Figure 1 shows the steady-state emission spectrum of anthracene-terminated PNMMA in deoxygenated THF on excitation of the naphthalene chromophore at 280 nm. The spectrum of MA is shown for comparison. Although the low anthracene content of the polymer means that less than 0.1% of the exciting light is absorbed directly by the anthracene chromophore, structured anthracene emission at 380-440 nm dominates the polymer fluorescence spectrum. The positions of the anthracene absorption and emission bands are virtually identical with those of MA, indicating that anthracene is attached to the polymer through a 9-methylene linkage by the mechanism shown in Scheme I, where I· denotes an initiator fragment.

In Figure 2 the fluorescence spectrum of P(NMMA-AMMA) on excitation of the naphthalene chromophore is compared with that of 9-anthrylmethyl pivalate in the same solvent. Figures 1 and 2 both indicate that energy transfer occurs from naphthalene to anthracene. The highly structured nature of the anthracene emission and the close correspondence of the band shapes with those of model compounds permit resolution of the contributions from naphthalene monomer, naphthalene excimer, and anthracene emission to the total fluorescence spectrum.

Scheme I



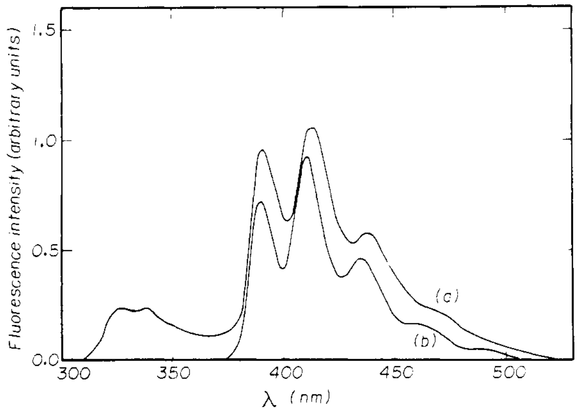


Figure 2. Steady-state fluorescence spectra in deoxygenated THF at 25.0 °C: (a) poly(NMMA-*co*-0.67% AMMA), λ_{ex} = 280 nm, (b) 5 × 10^{-5} M 9-anthrylmethyl pivalate, λ_{ex} = 340 nm.

This in turn allows determination of the quantum efficiency χ of energy transfer, defined in eq 2.

$$\chi = \frac{\text{no. of einsteins transferred to anthracene}}{\text{no. of einsteins absorbed by naphthalene}} \qquad (2)$$

Treating the total naphthalene emission as a homogeneously quenched band, the total quantum yield of fluorescence ϕ_f is given by

$$\phi_f = \chi\phi_A + (1 - \chi)\phi_N \qquad (3)$$

In eq 3, ϕ_A and ϕ_N are the fluorescence quantum yields of polymer-bound anthracene on direct excitation and of the corresponding homopolymer. Values of χ obtained using this relation are not very accurate if ϕ_A and ϕ_N are of similar magnitude or if χ is small. When measurable amounts of both naphthalene and anthracene emission are present, as in Figures 1 and 2, χ can be determined more precisely by comparing the relative areas I_A and I_N of the anthracene and naphthalene fluorescence bands. The dependence of the ratio I_A/I_N on χ is shown in eq 4.

Table II
Quantum Efficiencies χ of Energy Transfer to Anthracene in Polymers Based on the Naphthalene Chromophore

sample no.	solvent	mol % of anthracene	ϕ_A[a]	ϕ_N[a]	χ, %
1	$CHCl_3$	0.06	0.8	0.011[b]	0.6
1	EtOAc	0.06	0.8	0.020[b]	1.9
2	THF	0.50	0.88	0.092	10
2	toluene	0.50	0.85	0.142	13
2	polystyrene	0.50	0.66	0.092	29
2	PMMA	0.50	0.80	0.092	43
3	THF	0.074	0.58	0.092	3.7
4	THF	0.174	0.58	0.092	9.9
5	THF	0.348	0.58	0.092	18
6	THF	0.665	0.58	0.092	30
7	THF	0.196	0.58	0.116	8.7

[a] ϕ_A, ϕ_N = fluorescence quantum yields of trap and of corresponding homopolymer. [b] Reference 14.

$$\phi_N I_A/\phi_A I_N = \chi/(1 - \chi) \qquad (4)$$

Using eq 4, energy transfer efficiencies were calculated for the samples listed in Table I. The results are summarized in Table II, together with fluorescence quantum yields of the corresponding homopolymers and of the bound anthracene traps.

Energy transfer in 9-vinylanthracene-terminated PNMA is inefficient, once the large differences in fluorescence quantum yield between polymer and trap are taken into consideration. PNMA and similar naphthol ester polymers were found to undergo a photoFries reaction,[25] as suspected by Pasch and Webber,[26] similar to that of 1- and 2-naphthyl acetates.[27,28] The total quantum yield of ketonaphthol formation in PNMA is 0.08 in THF, several times that of fluorescence. Furthermore, excimer formation in PNMA is rapid.[29] The combination of photoreactivity and facile excimer formation gives the free naphthyl chromophore in PNMA a decay time of less than 2 ns. It is likely that the time available is too short to allow efficient energy transfer to anthracene.

In the anthracene-terminated PNMMA sample, where the objectives of photostability and reduced rate of excimer formation were achieved, χ is an order of magnitude higher. By dispersing the polymer in polystyrene or PMMA, χ approaches 50%. The slight haziness of some of these mixed films shows that they probably do not constitute true solutions. On the other hand, the films do not represent full separation into two homopolymer phases either, since in neat films of the anthracene-containing polymers χ is 100%. Moreover, high values of χ were still obtained when the weight fraction of anthracene copolymer in the matrix was reduced to 0.1%. Energy transfer in the mixed film is efficient because the matrix contracts individual PNMMA coils and raises the local concentration of naphthalene. Under optimum conditions, the amount of light transferred to anthracene is five times as high as the amount which normally would fluoresce from the naphthalene chromophore. In effect, anthracene intercepts energy which would otherwise decay nonradiatively on the naphthalene chromophore.

That efficient energy transfer occurs in a polymer glass is highly significant. In fluid solutions, mass diffusion and diffusion of excitation by energy transfer occur simultaneously and cannot be separated. However, in a polymer matrix, where mass diffusion is suppressed, the anthracene fluorescence would be suppressed if diffusion were the sole mechanism by which photoexcited naphthalene entered the Förster radius of the trap. Efficient migration in the

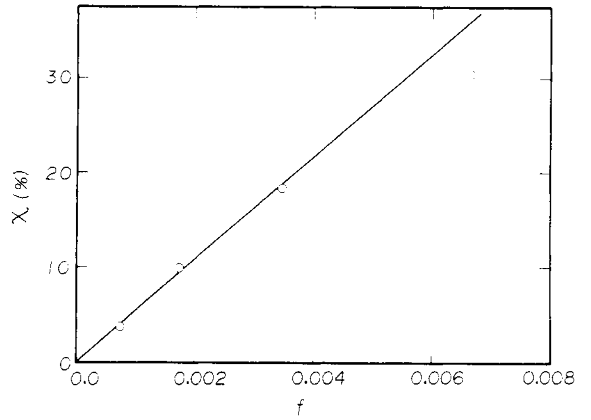


Figure 3. Variation of energy transfer efficiency χ with the mole fraction f of anthracene in copolymers of NMMA with AMMA.

solid phase is firm evidence that it is the excitation energy which migrates between chromophores on the polymer and that mass diffusion is unimportant in this process.

Because the synthesis of polymers quantitatively terminated with anthracene is a delicate problem, copolymerization affords an easier route to higher trap concentrations. In Table II the extent of energy transfer is shown to increase with increasing anthracene content in copolymers of NMMA with 9-anthryl methacrylate. The variation of χ with the mole fraction of anthracene f is plotted in Figure 3. Above an average of about two anthracene traps per chain, χ no longer increases linearly with increasing f. Possibly at increased trap density the probability of overlap of the domains quenched by individual anthracene chromophores also increases. The final entry in Table II shows that energy transfer is almost as efficient in a copolymer of NEMA with AMMA as in the NMMA–AMMA copolymer of similar composition.

The term "exciton", carried over from crystal theory, has been applied to energy migration in polymers.[1,3,7,30,31] This movement of an excitation wave down a polymer chain implies a highly ordered state with translational and orientational equivalence of each dipole and a sufficiently small interchromophore distance that there is a weak interaction between an excited chromophore and its ground-state neighbors. Philpott has represented a polymer by such an ideal "one-dimensional crystal" model and shown that exciton states could exist.[32] To what extent does the highly ordered state required by this theory exist in a randomly coiled polymer in solution? When a large chromophore is attached directly to the main chain, as in poly(*N*-vinylcarbazole) (PVCz), a certain degree of order may exist, leading to unique photophysics.[24,31] If electronic energy is transferred in polymers because of their ordered nature, then χ should decrease dramatically in the series PVCz, PNMA, PNMMA, and PNEMA. As Table II shows, no such behavior is observed. Energy migration occurs even in PNEMA where chromophores are 11 atoms apart, so that their orientations are virtually uncorrelated. The extreme sensitivity of exciton mobility to defects in three-dimensional crystals[33-35] suggests that PNMMA, having in effect a defect at every lattice point, transfers energy by a fundamentally different mechanism. Clearly energy transfer in the naphthalene-containing polymers synthesized here arises not from the order imposed by interactions along the polymer chain, but instead occurs as a result of the high local concentration of chromophores surrounding the polymer backbone. This conclusion agrees with that suggested by the work of Johnson,[36] who showed that polymer films doped with *N*-isopropylcarbazole transferred energy to acceptors as effectively as PVCz, allowing for differences in chromophore concentration.

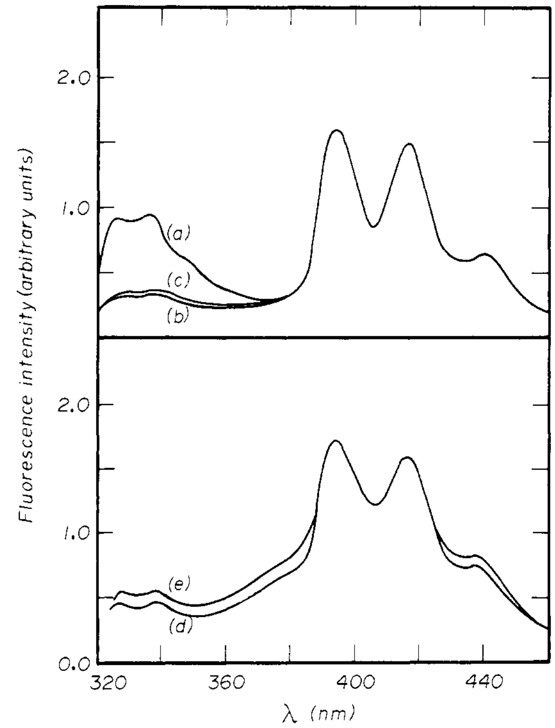


Figure 4. Time-resolved fluorescence spectra of anthracene-terminated PNMMA in toluene at 25.0 °C on excitation at 292 nm. Lower and upper time limits in ns from the maximum of the exciting pulse are (a) 0.0–2.2, (b) 11.5–13.8, (C) 21.0–24.0, (d) 44.3–48.6, and (e) 179.2–228.5. The curves are normalized to the same intensity at 390 nm.

Homopolymers of PNMMA and PNEMA show excimer emission, so that the question arises whether both monomer and excimer states are quenched by energy transfer to anthracene. If only one species were quenched, then a pronounced change in the ratio I_M/I_D of monomer to excimer emission with χ would be expected. No such effect was observed. Direct long-range transfer from the excimer to anthracene is unlikely because of poor spectral overlap. Second, the repopulation of quenched photoexcited monomer by excimer dissociation appears to be insignificant in these polymers. A more probable explanation for the attenuation of both monomer and excimer by similar amounts is that the anthracene chromophore competes with excimer sites for singlet excited naphthalene, so that it indirectly quenches both species. Because I_M/I_D does not vary significantly with the amount of anthracene in the polymer, the error in χ accompanying the assumption that the naphthalene emission is quenched homogeneously is small. The error is certainly far less than that which would have arisen if the contribution from naphthalene excimer emission had been included in the anthracene emission band.

Transient Fluorescence Measurements. Figure 4 illustrates the time-resolved spectrum of anthracene-terminated PNMMA in toluene on excitation of the naphthalene chromophore. Structured anthracene emission is prominent at all times. The ratio of anthracene to naphthalene monomer emission increases up to 20 ns from the maximum of the exciting pulse then decreases gradually over the next 200 ns.

Care must be taken in interpreting the evolution of the total emission spectrum following pulse excitation to allow for the different decay rates of the various emitting species.

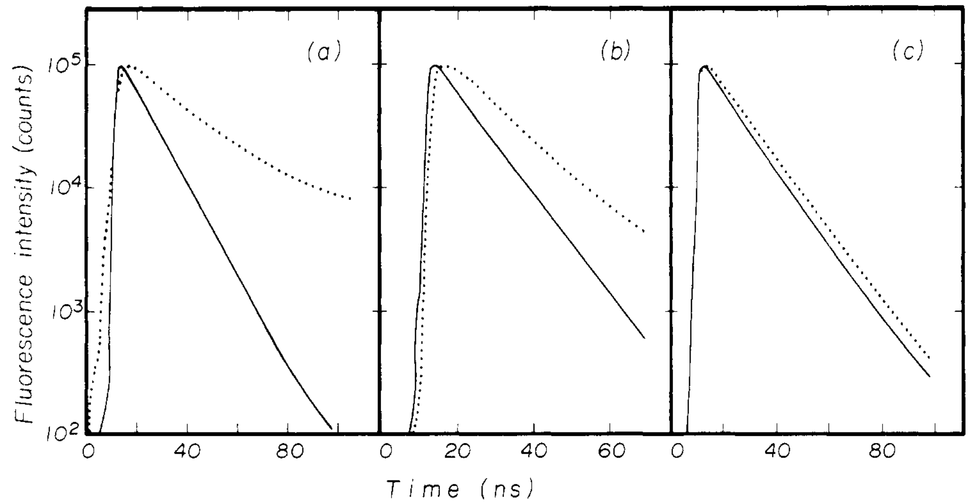


Figure 5. Decay of total emission at 400 nm on excitation at (—) 366 nm and (···) 280 nm: (a) anthracene-terminated PNMMA in toluene, (b) anthracene-terminated PNMMA 0.7% in PMMA film, (c) 1% MA in PNMMA film. All samples were under N_2 at 25.0 °C.

Let I_i be the relative intensity of species i in the time-resolved spectrum recorded between time intervals t_1 and t_2. I_i is then a function of the convolution of a decay law $I_i(t)$ with an exciting pulse $G(t)$, as shown in eq 5.

$$I_i = c_i \int_{t_1}^{t_2} [G{*}I_i](t)\,dt \qquad (5)$$

Equation 5 can be used to test the possibility of one-step Förster transfer from naphthalene to anthracene as a possible energy transfer mechanism. A one-step mechanism is obviously indicated in the copolymers synthesized by Tazuke and Banba,[37] for example, which were of very low molecular weight. This energy transfer process is very rapid within a characteristic radius surrounding the quenching chromophore. If one assumes that energy transfer is complete after 2 ns, then the earliest-time spectrum in Figure 4 can be used to evaluate the various c_i in eq 5. Later ratios of intensity of the emitting species are calculated using eq 5 and the decay laws of anthracene on direct excitation, together with those of the homopolymer monomer and excimer. Table III gives decay functions measured for a homopolymer of NMMA. The spectra synthesized by this method do not correspond at all to the experimental spectra. The computer simulation predicts that the contribution of anthracene emission to the total spectrum should die away rapidly from its initial high value and be nonexistent by 200 ns. It is evident that a rapid one-step Förster transfer mechanism is inadequate to describe the energy-transfer process.

Direct measurement of fluorescence decays of the anthracene trap provides further insight into the time scale of energy transfer. In Figure 5, the decay of the 400-nm emission is shown for three samples on direct excitation of anthracene at 366 nm and on excitation of the naphthalene chromophore at 280 nm. Figures 5a and 5b show similar features: the fluorescence decay produced by energy transfer to anthracene is shifted slightly to later time and rounded at the maximum. The apparent decay time of the anthracene chromophore is increased by several nanoseconds as a result of gradual energy transfer. Finally, at very long times, the anthracene emission dies away into the residual emission from the naphthalene excimer, which has a 55 ns decay time. Decay curves similar to those in Figure 5b are obtained for the copolymers with AMMA. Only when the anthracene concentration becomes high and when the naphthalene-containing polymer is made into a neat film do the curves produced by 280 and 366 nm excitation begin to coincide, as shown in Figure 5c.

Table III
Decay Parameters of PNMMA Monomer and Excimer in Toluene at 25.0 °C[a]

species	τ_1, ns	τ_2, ns	A_1/A_2
monomer	7	40	1.2
excimer	3	63	−1.0

[a] λ_{ex} = 280 nm; fitting function, $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$.

The presence of excimer emission in the decay curves on excitation at 280 nm complicates numerical analysis to the point where only qualitative conclusions can be made. Nevertheless, Figures 5a and 5b show that energy transfer to anthracene in PNMMA occurs over tens of nanoseconds. It is significant that there is a measurable delay in the rise of fluorescence from anthracene on 280 nm excitation. This observation is further evidence for a contribution from a slower energy transfer to anthracene from chromophores outside the Förster radius.

It is proposed that energy transfer between naphthalene chromophores occurs rapidly for sequences where all groups are within the small Förster radius (less than 1 nm) for energy transfer between like chromophores. Then a delay will occur at occasional sites along the polymer chain where the Förster radius is exceeded. Energy hopping across such a gap would occur more slowly or might require rotation of the naphthalene group or lateral motion of one of the side chains. One feature of PNMMA and PNEMA which would lead to energy transfer over a longer interval than that in PNMA[14] is the longer fluorescence lifetime of the transmitting species in the former two polymers. Most of the naphthalene chromophores in PNMMA have a 40 ns decay time, whereas in PNMA most of the transferring species decay with a 2 ns lifetime.

The decay function of the 400 nm emission is complex, as is evident from the curves shown in Figure 5. When decays are recorded on a somewhat larger time scale, it is possible to fit them with a trial function of the form $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where τ_2 is the decay time of the naphthalene excimer, and τ_1 is an apparent decay time of the anthracene trap. The difference $\Delta\tau$ between τ_1 and the true fluorescence lifetime of the bound anthracene, measured by direct excitation, is a qualitative

Table IV
Variation of Anthracene Decay Time on Direct Excitation at 366 nm and on Excitation of the Naphthalene Chromophore at 280 nm

system	solvent	τ,[a] ns	τ_1,[b] ns	$\Delta\tau$, ns
anthracene-terminated PNMMA	toluene	10.8	18	7
anthracene-terminated PNMMA	poly(methyl methacrylate)	10.1	13.6	3.5
1% 9-methylanthracene in PNMMA film		13.7	14.8	1

[a] λ_{ex} = 366 nm. [b] λ_{ex} = 280 nm.

estimate of the average energy transfer time. Table IV lists values of $\Delta\tau$ obtained from the three curves of Figure 5. The average energy transfer time appears to decrease in going from toluene to the chain-contracting solvent PMMA. In the PNMMA film doped with 1% 9-methylanthracene, all of the naphthalene emission is quenched, and the anthracene decay time approaches its true value. Increasing both the naphthalene local concentration and the anthracene density decreases the energy transfer time, an observation which probably reflects a corresponding decrease in the average energy transfer distance.

It must be stressed that where energy transfer times are of the order of nanoseconds, a Stern–Volmer kinetic analysis such as that proposed earlier by Aspler et al.[14] is no longer appropriate. Birks[38] has discussed the range of applicability of the Stern–Volmer and Förster[39] quenching models. The former applies to systems where the distance diffused by the naphthalene chromophore within the excited state lifetime is large relative to the Förster radius R_0 for one-step transfer from naphthalene to anthracene. The latter describes energy transfer under the other limiting case, where diffusion is negligible. North and Treadaway[6] suggested that energy transfer in polymeric systems falls in the intermediate region described by eq 6, where D is the matter diffusion constant, Λ is an excitation migration coefficient, and τ is the lifetime of the transferring species.

$$R_0 \simeq [6(D + \Lambda)\tau]^{1/2} \qquad (6)$$

The authors used an approximate treatment developed by Yokota and Tanimoto[40] to describe steady state quenching in the regime described by eq 6. In the present work, energy transfer efficiencies and acceptor decay curves are similar in solution and in a polymer matrix where D is negligible. These results are evidence that energy transfer between naphthalene chromophores does indeed play the role of a diffusion constant in the rigid matrix and that Λ in the matrix is at least as large as D in fluid solution.

Conclusions

In summary, it has been shown that energy transfer from naphthalene to anthracene on a polymer chain can be enhanced by nearly two orders of magnitude. To achieve this it was necessary to increase the naphthalene fluorescence lifetime by minimizing energy-wasting processes such as photoreaction and excimer formation. It was also necessary to increase the trap concentration and reduce the energy transfer distance by contracting the macromolecular coil in a poor solvent. Knowledge of the parameters which affect energy transfer efficiency should prove useful in the design of macromolecules capable of producing photochemical transformations and for solar collection devices.

Dynamic fluorescence studies of energy transfer show that singlet energy is indeed capable of transfer between like chromophores on a polymer chain. Because energy transfer is efficient in the solid phase, a mechanism involving diffusion of naphthalene groups into the Förster radius of the trap must be rejected. Furthermore, since energy transfer occurs for tens of nanoseconds after excitation in the polymer solid phase, static quenching cannot be the sole mechanism of energy transfer from naphthalene to anthracene.

Finally, energy transfer has been shown to be efficient even when the naphthalene chromophores are attached to the polymer by flexible three- and four-atom chains. Clearly electronic energy migrates in these polymers not because steric effects impose some semicrystalline type of order, but simply because a high chromophore concentration exists in a cylinder surrounding the polymer backbone. Such energy transfer is more appropriately described by an energy hopping mechanism involving a series of Förster transfers rather than an exciton migration model.

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Interpretation of the Fluorescence Decay Curves of Some Naphthalene-Containing Polymers

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ABSTRACT: Fluorescence decay curves of both the free chromophore and the excimer have been recorded for a number of polymers whose repeating units contain the naphthalene chromophore. Monomer decays in poly(1-naphthylmethyl methacrylate) and poly[2-(1-naphthyl)ethyl methacrylate] were nonsingle exponential in fluid solution at 25 °C, with the long lifetimes τ_2 corresponding closely to the decay times of model compounds in the same solvent. Excimer decay times were not equal to monomer τ_2 values. Similar decay curves were recorded when naphthalene polymers were dispersed in polystyrene or poly(methyl methacrylate) matrices. It is proposed that the long-lived monomer emission in these polymers is not produced by thermal dissociation of the polymeric excimer but results from singlet naphthalene unable to form an excimer within the excited state lifetime.

The study of excimer formation in polymers bearing aromatic chromophores is presently an area of considerable activity.[1] Particularly interesting is the fact that under certain conditions of polymer mobility the dominant excimer-forming process is by electronic energy transfer between chromophores on the polymer to a suitable trap site.[1,2] Such polymers can function as chromophore aggregates intermediate in order between molecular crystals and dilute solutions of small molecules and in this way bear more than superficial resemblance to the chlorophyll aggregates which play an energy-gathering role in plant photosynthesis.[3]

Early studies of excimer fluorescence in polymers concentrated on the effects of solvent, temperature, and polymer structure on the steady-state fluorescence spectra. With the development of improved methods of measurement of nanosecond fluorescence lifetimes,[4,5] transient measurements have been applied to analysis of the kinetics of excimer formation.[6-15]

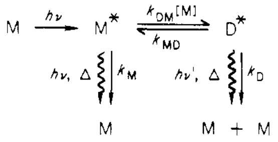
In all studies of homopolymers of naphthalene-containing monomers, the fluorescence decay function of the monomeric chromophore was not a single exponential[8,11,14,15] but could be represented adequately by a sum of two exponential decays. Because it generates decay laws of this functional form, the starting point for the interpretation of excimer kinetics in polymeric systems usually is a mechanism incorporating formation and subsequent dissociation of an excimer, as shown in Scheme I.[16]

In Scheme I, M* and D* represent the photoexcited free chromophore, or monomer, and the excimer, respectively. The fluorescence response functions of monomer and excimer have the forms shown in eq 1 and 2.[17]

$$I_{FM}(t) = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t) \qquad (1)$$

$$I_{FD}(t) = A_3[-\exp(-\lambda_1 t) + \exp(-\lambda_2 t)] \qquad (2)$$

Scheme I



The relation between λ_1 and λ_2 and the individual rate constants of Scheme I is complex:

$$\lambda_{1,2} = \tfrac{1}{2}\{X + Y \pm [(X - Y)^2 + 4k_{DM}k_{MD}[M]]^{1/2}\} \qquad (3)$$

where

$$X = k_M + k_{DM}[M] \qquad (4)$$

$$Y = k_D + k_{MD} \qquad (5)$$

The mechanism presented in Scheme I applies rigorously only to small molecules such as pyrene[17] or 1-ethylnaphthalene in fluid solution, where excimers are formed by mutual diffusion of two chromophores. In bichromophoric compounds and polymers, excimer sites are created by a sequence of bond rotations, so that excimer formation is the result of several processes. Kinetics in a polymer system are further complicated by energy transfer. Nevertheless, decays of the type shown in eq 1 and 2 are observed for 1,3-dicarbazolylpropane,[18] poly(*N*-vinylcarbazole)[6] (PVCz), poly(1-vinylnaphthalene)[11] (P1VN), and poly(1-naphthyl methacrylate)[14] (PNMA), so that it is generally assumed that excimer dissociation takes place in polymers at room temperature.

Fluorescence decay measurements on poly(1-naphthylmethyl methacrylate) (PNMMA) and poly[2-(1-naphthyl)ethyl methacrylate] (PNEMA) and their model

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