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Studies of the Antenna Effect in Polymer Molecules. 3. Role of Singlet Electronic Energy Migration in Naphthalene Polymer Photophysics

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ABSTRACT: Excimer kinetics were investigated in copolymers containing isolated bis(1-naphthylmethyl) fumarate units. These copolymers show excimer emission in THF in the absence of singlet energy migration, even though none is observed in a number of dimeric small-molecule model compounds. Fluorescence polarization measurements on naphthalene-containing model compounds and polymers confirm that depolarization of the fluorescence from the polymers arises from singlet energy migration between naphthalene chromophores. The absence of depolarization in certain small-molecule dimers showed that the distance over which singlet excitation could transfer between the naphthalene groups was relatively small, on the order of 1 nm.

Introduction

A number of studies of polymer photophysics have implied that electronic excitation can pass between identical chromophores attached to a polymer chain.[1,2] The term "energy migration" has been adopted for such isoenergetic transfer processes, with "energy transfer" being reserved for transfer of excitation to low-energy traps.[3] Both singlet and triplet excitation can migrate from one chromophore to another. Such processes are being investigated because they may affect the photostability of commercial polymers and because they suggest the possibility of creating synthetic macromolecules which gather electronic excitation in the same way as the antenna pigments of plant chloroplasts.[4-8]

Triplet energy migration is relatively easy to detect through the phenomenon of delayed fluorescence.[1,2] In this process, two triplet states annihilate, with the creation of one singlet excited and one ground-state chromophore. The excited chromophore emits at fluorescence wavelengths, but with a decay time approaching half the phosphorescence lifetime. Unfortunately, no such emission at a new wavelength conveniently indicates the presence of singlet energy migration, which has proven more difficult to identify and study.

One phenomenon that has proven useful in the study of energy migration is fluorescence depolarization. The relative orientations of the absorption and emission dipoles of a chromophore in a rigid matrix are fixed, so that if the chromophore absorbs polarized radiation, its emission will retain memory of the excitation polarization. Fluorescence polarization is described by a quantity P, defined by

$$P = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp}) \qquad (1)$$

where $I_{\parallel}$ and $I_{\perp}$ are the relative emission intensities with parallel and perpendicular orientation, respectively, of the polarizing filters. For randomly oriented chromophores P varies from $-{}^{1}/_{3}$ to $+{}^{1}/_{2}$. Singlet energy migration from one chromophore to another of different orientation results in depolarization: a value of P closer to zero than is observed for an isolated chromophore.[10,11]

Several authors have observed that the fluorescence from polymers in low-temperature glasses and films is completely depolarized, although small-molecule model compounds and copolymers containing low mole fractions of the fluorescent monomer show nonzero P values.[12-19] In random copolymers of a fluorescence monomer M_1 with a nonfluorescent monomer, the degree of depolarization increases with the mole fraction of M_1.[14,16,17-20] Reid and Soutar found that P^{-1} varied linearly with $\bar{l}_{M_1}$, the mean sequence length of M_1 species. Johnson observed that the polarization of the dimer 1,3-bis(9-carbazolyl)propane was only half that of 9-isopropylcarbazole, a result attributed to singlet energy migration in the dimer.[21] On the other hand, MacCallum and Rudkin found that the value of P for the excimer fluorescence in a polystyrene film at room temperature was 0.77,[22] a result incompatible with excimer formation by singlet energy migration to an excimer site.

There are enough sources of error in polarization experiments to justify cautious interpretation of the results. Scattering by condensed ice and birefringence caused by sample inhomogeneity or uneven cooling can lead to anomalously low values of P. For chromophores such as naphthalene, whose $S_1 \rightarrow S_0$ transitions are symmetry forbidden, symmetry breaking arises by vibronic coupling and the value of P depends on the nature of the vibrational modes in the molecule.[23,24] For this reason, meaningful comparisons between the P values of a polymer and its model compound can only be made if the two molecules have very similar structures. Delayed fluorescence is known in several of the polymers on which polarization measurements have been made.[1,2,25-27] The delayed emission is depolarized because it involves triplet energy migration, and if it represents a significant part of the total fluorescence, low P values could occur without the existence of singlet energy migration.[28]

This article describes the results of an investigation of the photophysics of a number of polymeric and small-molecule esters of 1-naphthylmethanol and 2-(1-naphthyl)ethanol. Studies of excimer fluorescence in copolymers I containing minor amounts of bis(1-naphthylmethyl) fumarate (NMF) show the limited extent to which singlet energy migration contributes to excimer formation in these polymers and reveal a significant difference be-

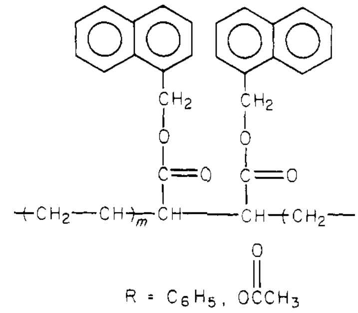

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Table I
Properties of the Polymer Samples

sample	mol % naphthalene monomer	$10^{-3} \times \bar{M}_n$[a]
poly(1-naphthylmethyl methacrylate)	100	410
poly(1-naphthylmethyl acrylate)	100	150
poly(2-(1-naphthyl)ethyl methacrylate)	100	340
poly(styrene-NMF)	1.1	69
poly(vinyl acetate-NMF)	0.8	120
poly(vinyl acetate-NMF)	2.9	85
poly(styrene-NMMA)	0.4	53

[a] Determined by membrane osmometry.

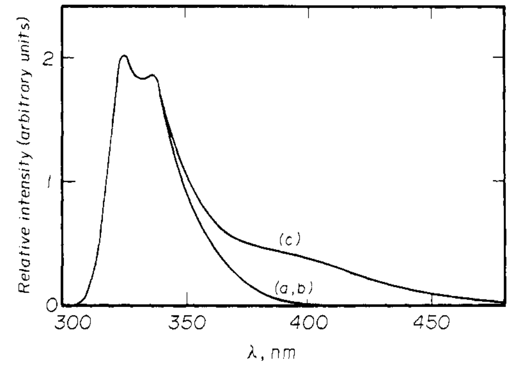


Figure 1. Fluorescence spectra of (a) 1-naphthylmethyl pivalate, (b) bis(1-naphthylmethyl) butanedioate and, (c) poly(vinyl acetate-*co*-0.8 mol % NMF) in deoxygenated THF at 25 °C; λ_{ex} = 280 nm. The chromophore concentrations are 10^{-4} M.

tween the polymers and analogous small-molecule dimers.[29] The effects of structure on fluorescence polarization were investigated in solid films and in glassy solutions at 77 K. Since all the compounds have identical structures up to the fourth atom away from the chromophore, meaningful comparisons between the *P* values of different compounds could be made. In addition, polarization measurements were performed at low excitation intensity so that interference from delayed fluorescence was eliminated.

Experimental Section

The synthesis and purification of 1-naphthylmethyl methacrylate (NMMA) and 2-(1-naphthyl)ethyl methacrylate were described in a previous publication.[5] 1-Naphthylmethyl acrylate was prepared and purified following the method for NMMA. Styrene and vinyl acetate were washed with aqueous NaOH to remove inhibitor, dried, and distilled at reduced pressure immediately before use.

Bis(1-naphthylmethyl) Fumarate. To a solution of 6 g of 1-naphthylmethanol and 5.5 mL of dry Et_3N in 50 mL of dry THF, 2.05 mL of distilled fumaroyl dichloride[30] was added dropwise with stirring. After 1 h of reflux, water was added and the organic products were extracted into CH_2Cl_2. The combined extracts were washed with 1 M aqueous HCl, 5% $NaHCO_3$, and saturated NaCl solution. Slow evaporation of the solvent gave leaflets, which were separated, washed with benzene, and recrystallized twice from hot benzene: mp 130–131 °C; NMR ($CDCl_3$) δ 5.6 (s, 4 H, $2CH_2$), 6.8 (s, 2 H, CH=CH), 7.1–8.0 (m, 14 H, aromatic ring H); UV (THF) 316.5 nm (463 M^{-1} cm^{-1}), 312.5 (815), 291 (9320), 281 (13 800), 270.5 (11 800).

Polymers were prepared by azobis(isobutyronitrile)-initiated radical polymerization in degassed benzene at 58 °C and were purified by multiple precipitation from benzene into ethanol. The exception was the vinyl acetate–NMF copolymer, which was precipitated from benzene into cyclohexane, from chloroform into dry ether, and finally from benzene into ACS hexanes. The mole fractions of naphthalene in the copolymers was determined by UV spectroscopy using the extinction coefficients of the repeating unit of poly(NMMA): UV (THF) 317 nm (208 M^{-1} cm^{-1}), 313.5 (384), 292 (5150), 281.5 (7530), 272 (6400). The differences in copolymer composition calculated using the extinction coefficients for 1-naphthylmethyl pivalate amounted to about 15%. Molecular weights were determined by membrane osmometry, using toluene or dioxane as solvent. Table I lists the properties of the polymers used in the present study.

Model compounds were obtained by the condensation of 1-naphthylmethanol with the appropriate acid chloride. 1-Naphthylmethyl pivalate (2,2-dimethylpropanoate) and 2-(1-naphthyl)ethyl pivalate were available from a previous study.[31]

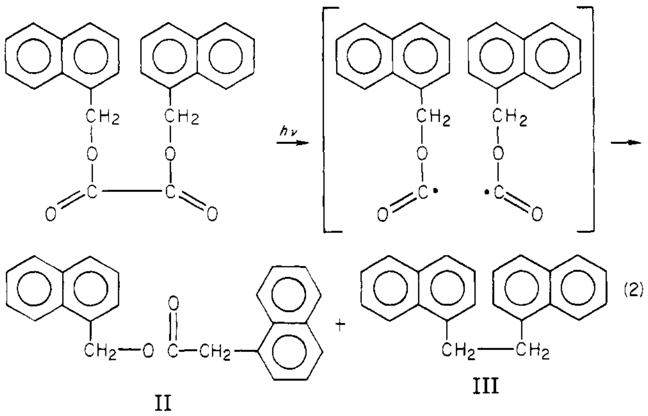
***meso*-Bis(1-naphthylmethyl) 2,3-Dimethylbutanedioate.** (meso-NDB) was prepared from the dichloride of *meso*-2,3-dimethylsuccinic acid[32] (Aldrich) and 1-naphthylmethanol following the procedure for NMF, except that pyridine was used as the base. Unreacted starting alcohol was sublimed from the crude product at 70 °C and 0.1 mmHg pressure, and the product was chromatographed on alumina, eluting with benzene. The product, which is the first major band off the column, crystallized with difficulty after evaporation of the solvent and storage under high vacuum. It was recrystallized twice from ACS hexanes to give colorless crystals: mp 78.5–79 °C; IR (Nujol) 1725 cm^{-1}; NMR ($CDCl_3$) δ 1.13 (d, 6 H), 2.80 (m, 2 H), 5.43 (s, 4 H), 7.1–8.0 (m, 14 H). In a similar manner bis(1-naphthylmethyl) pentanedioate, bis(1-naphthylmethyl) butanedioate (mp 121.5–122 °C), and bis(1-naphthylmethyl) ethanedioate (NE) (mp 104.5–105.5 °C) were synthesized, with satisfactory IR, NMR, and UV spectra.

Fluorescence spectra were recorded on a Hitachi Perkin-Elmer MPF-2A instrument (150-W Xe arc excitation source) and are shown corrected for the wavelength dependence of the photomultiplier response. Low-temperature and polarization measurements were performed with accessories provided with the instrument. Polarizations were corrected for anisotropy produced by the diffraction gratings of the monochromator.[33] A quartz tube having a 1.5-mm inside diameter served as the cell for low-temperature measurements. Samples were slowly cooled in the vapor above the liquid nitrogen coolant before being fully immersed, in order to minimize strain. During measurements the sample compartment was purged with dry nitrogen. The excitation and emission spectral bandwidths were 5 and 8 nm, respectively, for polarization measurements. Under these excitation conditions, delayed fluorescence was not observed for model compounds and dimers and made up less than 2% of the total fluorescence in the homopolymers. Solid poly(NMMA) films were obtained by casting dilute solutions in benzene on a water surface and were removed and dried in vacuo. Emission was viewed from the front face of the film positioned at an angle of 30° to the excitation beam.

Fluorescence decays were measured by single photon counting as described elsewhere[4,34] and were analyzed by iterative reconvolution.[34,35] Samples were excited at 280 nm through an interference filter. Emission at 325 or 440 nm was observed at right angles to the excitation pulse through a Jarrell-Ash 0.25-m monochromator, together with suitable cutoff filters to remove scattered light. The solvents tetrahydrofuran and 2-methyltetrahydrofuran (Matheson Coleman and Bell) were purified by distillation from $LiAlH_4$ under nitrogen and were stored under N_2 at 0 °C.[36]

Results and Discussion

Excimer Kinetics in Fluid Solution. Figure 1 compares the fluorescence spectra of 1-naphthylmethyl pivalate, bis(1-naphthylmethyl) butanedioate, and a vinyl acetate–NMF copolymer in THF solution. Only in the copolymers is substantial excimer emission observed; none of the dimers exhibited excimer fluorescence. Bis(1-naphthylmethyl) ethanedioate is almost nonluminescent in fluid solution, an observation in marked contrast to that of Samulski and Chapin[37], who claimed that this compound also showed excimer emission. Prolonged 290-nm irradiation of NE in THF gave a photoproduct whose emission spectrum resembled that of 1-naphthylmethyl pivalate. The absence of fluorescence by NE arises from its photoreactivity:



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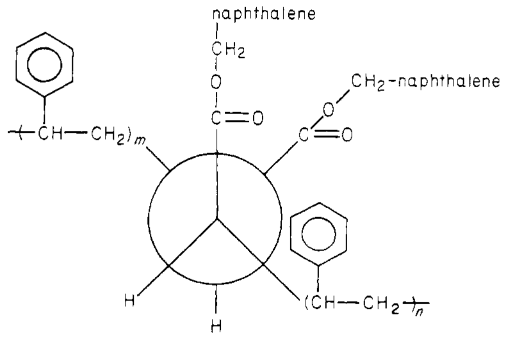
Both thermal scission and photochemical scission of the central C–C bond of oxalate diesters are known.[38-41] The spectrum reported by Samulski and Chapin may arise from the products II and III.

During the synthesis of the NMF copolymers the degree of conversion was kept small, so that only a fraction of the NMF was incorporated. It is unlikely that these copolymers consist of mixtures of NMF-rich copolymer with styrene or vinyl acetate homopolymer. The ratio I_E/I_M of excimer to monomer emission intensity remains almost unchanged when the mole fraction of NMF in the vinyl acetate copolymer is tripled to 3%. In addition, this ratio is only slightly increased by dilution of a THF solution of the copolymer with the poor solvent cyclohexane to the point where the polymer precipitates. For these reasons it is likely that excimer formation in these copolymers occurs almost exclusively between the naphthalene chromophores of isolated NMF units.

Because of the low naphthalene content of the NMF copolymers, singlet energy migration between long NMF sequences is not available as a mechanism for populating excimer sites. (Electronic energy migration between the two chromophores of a single NMF unit does not enhance excimer formation because the same excimer is formed from a NN* or a *NN pair.) Nevertheless excimers do form in these copolymers even though the chromophores are eight atoms apart and even though no excimer emission is observed in the meso small-molecule dimer. Thus the polymer chain must play a role in bringing the naphthalene groups closer together than they are in an unsubstituted or a methyl-substituted dimer. One possibility is that the greater size of the long-chain substituents in the copolymer causes them to prefer a trans configuration, which forces the naphthalene groups of isotactic sequences closer together than in the meso dimer. The resulting conformation is illustrated for the copolymer in the Newman projection IV:



IV

Differences in the contribution of excimer fluorescence to the total emission have been observed both in polymers of different tacticity[42-44] and in diastereomeric small-molecule dimers.[45-47] These have also been attributed to differences between the most stable ground-state conformation and the excimer configuration on the rotational energy surface.

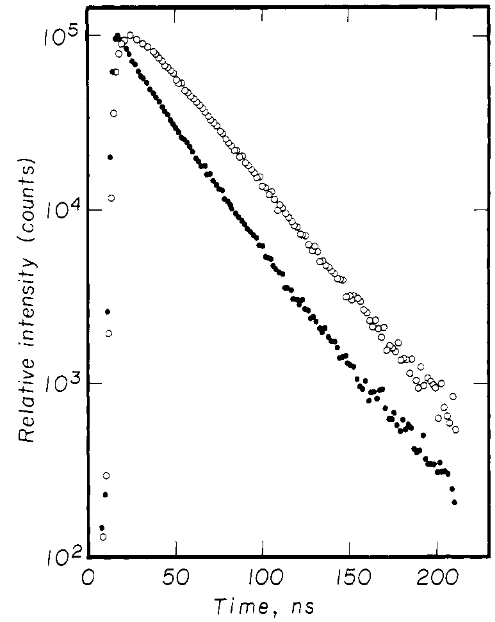


Figure 2. Fluorescence decays of poly(vinyl acetate-*co*-0.8 mol % NMF) in deoxygenated THF at 25 °C, λ_{ex} = 280 nm: (●) monomer, 325 nm; (○) excimer, 440 nm.

Table II
Fluorescence Decay Parameters of Naphthalene Monomer and Excimer in Poly(styrene-NMF) and Poly(vinyl acetate-*co*-0.8 mol % NMF)[a]

	poly(styrene-NMF)	poly(vinyl acetate-NMF)
	Monomer[b]	
τ_1, ns	9.2	7.2
τ_2, ns	44.1	31.0
A_1/A_2	0.15	0.42
χ^2_R	1.43	1.37
	Excimer[b]	
τ_1, ns	7.0	5.9
τ_2, ns	45.9	34.5
A_1/A_2	−0.65	−0.74
χ^2_R	1.16	1.06

[a] In deoxygenated THF at 25 °C; λ_{ex} = 280 nm. [b] Fitting function: $I_F(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$.

Figure 2 illustrates the fluorescence decays of the monomer and excimer emission of poly(vinyl acetate-*co*-0.82 mol % NMF) in THF. Unlike the small-molecule dimers the copolymer decays are nonexponential but could be fitted with a biexponential decay of the form

$$I_F(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \qquad (3)$$

Values of the best-fit decay parameters τ_1, τ_2, and A_1/A_2 are listed for the styrene and vinyl acetate copolymers in Table II. The naphthalene monomer decays show a minor contribution from a rapidly decaying component whose τ_1 value is close to that of the excimer. The slowly decaying component of the monomer emission corresponds to emission from naphthalene chromophores which are unquenched by excimer formation.[31] If the assumption is made instead that the long-lived monomer emission arises from excimer dissociation, as in the Birks scheme for small-molecule excimer kinetics,[3,48] then unrealistically high excimer dissociation rates are obtained for the copolymers.

Table III
Polarization P of the Excimer Emission from a Poly(1-naphthylmethyl methacrylate) Film

temp, K	λ_{ex}, nm	λ_{em}, nm	P^a
298	300	400	-0.002
77	280	390	-0.002
77	315	390	-0.003
77	300	420	0.002

[a] Error ±0.005.

According to the Birks scheme, the excimer decay is represented by a function consisting of a difference of two exponentially decaying terms having the same preexponential factor, as in

$$I(t) = A[-\exp(-t/\tau_1) + \exp(-t/\tau_2)] \quad (4)$$

When the experimental decays were analyzed with eq 4 as a trial function, poor fits were obtained, with values of χ^2_R, the reduced sum-of-squares of the residuals, from 6 to 10. When the ratio of the preexponential terms was allowed to vary, values of χ^2_R close to 1.0 were obtained an no systematic deviations between experimental and reconvoluted decay curves were observed. Since other excimer systems give $A_1 = -A_2$ using our lifetime measurement apparatus,[49] it appears that the effect shown in Table II is genuine.

Contamination of the excimer decays by monomer emission is unlikely since the fluorescence spectrum of 1-naphthylmethyl pivalate does not extend out to the wavelength at which the excimer decays were collected. An estimate of the contribution of the excimer fluorescence to the total intensity at 325 nm was obtained from the time-resolved spectrum of solid poly(NMMA) film at long times after the excitation pulse. Since this spectrum contains essentially only excimer emission, the relative intensities of the excimer fluorescence at 325 nm and at the peak maximum could be obtained. It was concluded that overlapping excimer fluorescence contributed less than 0.5% to the total emission at 325 nm in the case of the NMF copolymers.

The deviation of the excimer decay function from that predicted by Birks' scheme likely arises because the formation of excimers in polymers is not described by a single time-dependent rate constant, a consequence of the large number of available ground-state conformations. Thus a certain fraction of the excimer in the NMF copolymer may be formed virtually instantaneously, so the excimer decay function is actually

$$I(t) = A_1[-\exp(-t/\tau_3) + \exp(-t/\tau_4)] + A_2(-t/\tau_4) \quad (5)$$

Such "static quenching", arising from absorption by naphthalene chromophores in ground-state conformations close to the excimer configuration, was invoked by De Schryver to explain the extremely short risetime of the excimer fluorescence of poly(2-vinylnaphthalene).[50]

Fluorescence Polarization Measurements. The fluorescence spectrum of a poly(1-naphthylmethyl methacrylate) film both at room temperature and at 77 K consists primarily of excimer emission. Values of the polarization of the excimer fluorescence of the film are listed in Table III. In every case depolarization of the emission is complete. The film is transparent and shows no strain-induced birefringence under crossed polarizers. MacCallum reports that the excimer emission from poly(vinylnaphthalene) is partially polarized,[28] so the poly(NMMA) result does not arise because the intrinsic polarization of the naphthalene excimer is close to zero. The absence of a strong temperature effect on the extent of excimer formation indicates that chromophore motion is not the mechanism of excimer formation. Excimers are created by migration of the singlet electronic excitation to suitable sites.

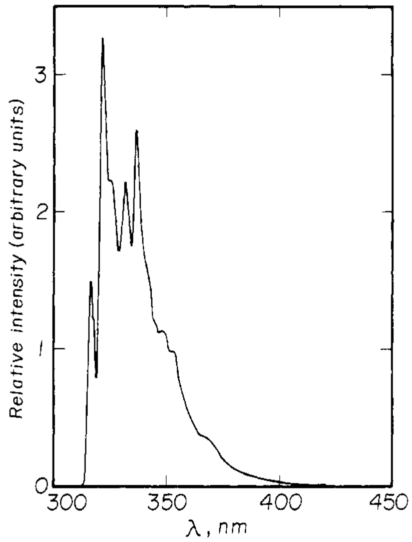


Figure 3. Fluorescence spectrum of 10^{-4} M *meso*-NDB in 2-methyltetrahydrofuran at 77 K on excitation at 290 nm. The emission spectral bandwidth is 2 nm.

Table IV
Polarization P and Fluorescence Lifetimes τ of Naphthalene-Containing Model Compounds and Polymers[a]

	compound	P^b	τ, ns
1.	poly(styrene-*co*-0.4 mol % NMMA)	0.194	
2.	1-naphthylmethyl pivalate	0.190	90
3.	2-(1-naphthyl)ethyl pivalate	0.186	
4.	bis(1-naphthylmethyl) pentanedioate	0.172	
5.	bis(1-naphthylmethyl) butanedioate	0.151	
6.	bis(1-naphthylmethyl) ethanedioate	0.159	88
7.	poly(styrene-*co*-1.1 mol % NMF)	0.118	
8.	poly(vinyl acetate-*co*-0.8 mol % NMF)	0.089	90
9.	*meso*-NDB	0.081	99
10.	poly(NMMA)	0.036	87
11.	poly(2-(1-naphthyl)ethyl methacrylate)	0.015	
12.	poly(1-naphthylmethyl acrylate)	0.010	

[a] In 2-methyltetrahydrofuran at 77 K; chromophore concentrations 2 × 10^{-4} M. [b] λ_{ex} = 300 nm; λ_{em} = 321 nm.

The depolarization of the excimer emission in solid poly(NMMA) is in contrast with the absence of depolarization in polystyrene film.[22] The naphthalene-containing polymer may differ from polystyrene in having a lower density of excimer sites and thus a greater contribution from energy migration.

Depolarization of the excimer fluorescence of solid poly(NMMA) film indicates the presence of singlet energy migration in the solid polymer, but not necessarily within a single macromolecule, where the chromophore density is much lower. Polarization measurements were carried out on dilute glassy solutions of naphthalene-containing polymers and model compounds in order to test this possibility. Figure 3 shows the fluorescence spectrum of the meso dimer in 2-methyltetrahydrofuran at 77 K. The other compounds gave spectra superimposable with that of the meso dimer; in no system was excimer fluorescence observed. The fluorescence decays of the compounds were exponential, with lifetimes of 87–99 ns, as shown in Table IV. Thus the differences in photochemical reactivity and extent of excimer formation displayed by these systems in room-temperature fluid solution are erased in low-temperature glasses.

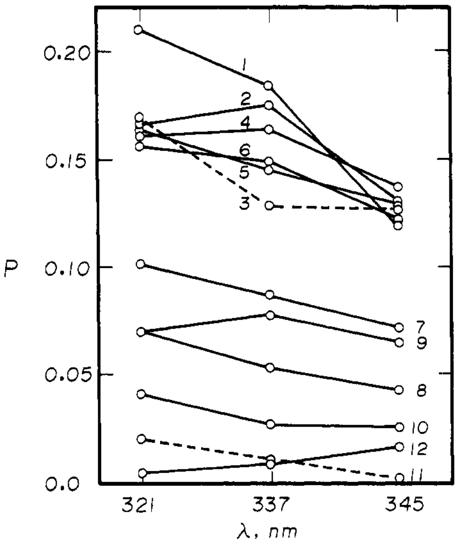


Figure 4. Histogram showing the fluorescence polarization P at three wavelengths of the naphthalene compounds listed in Table IV. Solutions in 2-methyltetrahydrofuran at 77 K, λ_{ex} = 290 nm.

Representative values of the fluorescence polarization are listed in Table IV and are plotted schematically in Figure 4. While the value of P depends on excitation and emission wavelengths, the polarization data show the same trends at every wavelength. Model compounds containing a single chromophore, dimers in which the chromophores are far apart, and copolymers containing isolated chromophores show high values of P. Copolymers containing chromophores in adjacent pairs and a meso dimer whose ground-state conformation places the chromophores close together show lower P values. Homopolymers in which each chromophore has two neighbor chromophores show almost complete depolarization.

The ten naphthylmethyl esters listed in Table IV have virtually identical absorption spectra, emission spectra, and fluorescence lifetimes, and yet their fluorescence polarizations vary by an order of magnitude. Depolarization of the absorbed light by certain dimers, copolymers, and homopolymers is therefore attributed to singlet electronic energy migration between chromophores. The interchromophore distance over which excitation can pass in 100 ns must be small (on the order of 1 nm) because in sufficiently extended dimers such as bis(1-naphthylmethyl) pentanedioate, no significant depolarization occurs.

In going from an isolated chromophore to the NMF copolymer, the decrease in P is only about 50%, not as great as expected for energy transfer between randomly oriented chromophores. A similar effect was observed by Johnson in the carbazole system.[21] In copolymers and homopolymers there may be considerable correlation between the orientations of two adjacent chromophores, so that the randomization is incomplete.[14] In addition, the possibility of back-transfer exists in isoenergetic energy transfer.

Unlike other naphthalene-containing polymers,[14,15,17,18] the depolarization of the emission from poly(NMMA) and similar polymers is incomplete. This difference could arise from the greater average distance between naphthalene chromophores in poly(NMMA) than in poly(vinylnaphthalene), for example, so that the rate of singlet energy hopping relative to the deactivation rate is smaller in poly(NMMA).

Several mechanisms may contribute to singlet energy hopping between naphthalene groups. Singlet energy transfer between identical chromophores is allowed by a Förster dipole–dipole interaction.[51] In this process energy transfer occurs efficiently within a characteristic radius R_0, which is related to the energy overlap between donor and acceptor states and the oscillator strengths of the transitions between these states, and drops off sharply for separations greater than R_0. In the case of naphthalene chromophores, the low oscillator strength of the $S_0 \rightarrow S_1$ transition and the fairly large Stokes shift between absorption and emission causes the overlap integral for naphthalene–naphthalene transfer to be small. This is reflected in comparatively small Förster radii, about 1 nm for the literature calculations compiled in Table V. The question arises whether electron-exchange or other short-range interactions[54] might enhance the energy transfer radius beyond the value expected for Förster transfer. Table VI lists approximate interchromophore distances in the three naphthalene dimers whose fluorescence showed no depolarization. These distances were calculated assuming fully extended chains, and there is a further approximation introduced by neglecting the angular dependence of the energy transfer rate.[56] More sophisticated calculations are planned, however. Nevertheless the interchromophore separations in these dimers are equal to or slightly larger than the spectroscopic falloff radii listed in Table V. Thus the distance beyond which naphthalene–naphthalene energy transfer is inefficient is consistent with distances calculated assuming that one-step Förster transfer is the dominant transfer mechanism. It should be noted that these mechanisms are "compartmentalizations" introduced by the theoretical chemist through treating the various interaction terms one at a time. It may be unrealistic to say that the total coupling between two naphthalene chromophores arises solely from one effect or the other.

Table V
Calculated Förster Interaction Radii R_0 for Naphthalene-Naphthalene Singlet Energy Transfer

compound	R_0, Å	ref
naphthalene	7.4	52
1-methylnaphthalene	8.3	52
2-methylnaphthalene	11.8	52
poly(1-vinylnaphthalene)	12.5	53

Table VI
Estimated Interchromophore Distances r for Some Bis(1-naphthylmethyl) Esters[a]

compound	r, Å
bis(1-naphthylmethyl) ethanedioate	8.7
bis(1-naphthylmethyl) butanedioate	11.3
bis(1-naphthylmethyl) pentanedioate	12.5

[a] Calculated for fully extended chains using bond radii taken from ref 55.

Conclusions

Studies of the photophysics of several naphthalene-containing polymers and model compounds have clarified the relationship between excimer formation and singlet energy migration in these systems. Excimer fluorescence between adjacent chromophores in a polymer was observed in the absence of energy migration, even when none was found in the meso small-molecule dimer. Steric restrictions imposed by other substituents on the main chain of a polymer apparently bring adjacent chromophores into conformations different from those in dimers, conformations closer to the excimer geometry.

Low-temperature fluorescence depolarization measurements show that singlet energy migration occurs in naphthalene-containing polymers. Partial depolarization in these new copolymers containing isolated dimer chromophores confirms that singlet energy migration can occur between adjacent naphthalene groups. The absence of depolarization in certain dimers was attributed to the relatively short distance over which naphthalene–naphthalene energy transfer can occur. Antenna polymers in which singlet energy migration occurs over long distances will require chromophores whose interactions extend over larger distances than in the case of the naphthalene chromophore.

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