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Studies of the Antenna Effect in Polymer Molecules. 7. Singlet and Triplet Energy Migration and Transfer in 2-Vinylnaphthalene–Phenyl Vinyl Ketone Copolymers

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ABSTRACT: The luminescence of copolymers of 2-vinylnaphthalene with phenyl vinyl ketone was studied in 2-methyltetrahydrofuran glasses at 77 K. The naphthalene singlet state is quenched by singlet energy migration and transfer to the aromatic ketone. Steady-state quenching efficiencies and the nonexponential fluorescence decays of the donor suggest that the singlet energy migrates over a maximum of 30 ± 5 naphthalene chromophores during the excited-state lifetime. The ketone triplet states are in turn quenched by triplet energy transfer to naphthalene, a process that leads to enhanced naphthalene phosphorescence intensity. An increase in the efficiency of creation of delayed fluorescent states with increasing ketone content is further evidence for sensitization of the naphthalene triplet state. This effect offsets the disruption of energy migration resulting from the breaking up of naphthalene monomer sequences by the ketone monomer.

Introduction

Photosynthesis uses absorbed light to drive a sequence of reactions leading to the separation of charge and ultimately results in the synthesis of high-energy chemical products.[1] In green plants the primary charge-separation process occurs in reaction sites that contain only a small fraction of the total pigment material. The bulk of the chlorophyll in the chloroplast is photochemically inert, functioning as "antenna pigment" by transferring light through nonradiative interactions to the reaction centers.[1] In this way the turnover rate per reactive site is increased, because the effect of this energy-transfer process is the same as if the extinction coefficient of the reactive center could be increased by a factor of over 10^2.

An analogous situation exists in a macromolecule bearing a chromophore at every repeating unit on the chain. Such polymers also display efficient electronic energy transfer to low-energy traps.[2-8] The function of the connecting macromolecular chain and the plant thylakoid membrane is similar, in that both serve as anchors, supporting high local concentrations of chromophores. Synthetic polymers can thus mimic the function of the light-harvesting pigment layers, without reproducing their exact structure.

There are a number of reasons for the current interest in "antenna polymers". Besides the challenge of pursuing this analogy between natural chloroplasts and synthetic polymer systems, there is relevance to the stabilization of synthetic polymers against photodegradation. It is also possible to use energy transfer to reactive groups to create polymers with enhanced degradation rates. It may be possible to develop polymeric photocatalysts that are effective at extremely small concentrations.

In previous publications the energy-transfer behavior of polymers containing fluorescent anthracene traps was described.[4,6-8] Fluorescence from these traps was analyzed to provide information on the mechanism and the time scale of singlet energy transfer from the donor chromophores. On the basis of the fluorescence decay curves of the acceptor following pulsed excitation of the donor, it was proposed that energy transfer involved two processes, illustrated schematically in Figure 1.[7,9] The first is one-step dipole–dipole transfer from the donor to anthracene.[10,11] This Förster transfer occurs when the photoexcited donor lies within a sphere of radius R_0, characteristic of the strength of the dipole–dipole interaction between the two chromophores.[11] This spherical picture is a simplification, in that there is an angular dependence of the rate of transfer in the Förster mechanism.[12] The second process involves singlet energy migration between donor chromophores,[13] followed by Förster transfer to the acceptor once the excitation resides on a chromophore a distance on the order of R_0 from the trap.[9] It has been proposed that this energy migration can be described by a random walk of discrete hops of the excitation[14-16] and that the chromophore separations over which donor–donor transfer occurs are consistent with those predicted by the Förster mechanism.[17,18]

One feature of the previous work on antenna polymers is that the Förster radius for one-step transfer from the donor to the trap was fairly large, about 2.5 nm.[19] The high efficiency of one-step transfer partially obscured the effects of singlet energy migration. In the present work energy migration and transfer were investigated in copolymers of 2-vinylnaphthalene (2VN) with phenyl vinyl ketone (PVK). Because the $S_0 \rightarrow S_1$ absorption of the aromatic ketone is symmetry-forbidden, the oscillator strength is low, so that the range R_0 of the dipole–dipole interaction between naphthalene and ketone chromophores is only 1.0 nm.[10] The contribution from singlet energy migration to quenching of the naphthalene singlet by the ketone group is more readily established in this system. By carrying out measurements on copolymers dissolved in rigid glasses at 77 K, we were also able to avoid the severe complication of the fluorescence decay kinetics that accompanies formation of the naphthalene excimer.[20-23]

Experimental Section

2-Vinylnaphthalene was purified by column chromatography on alumina, eluting with cyclohexane. The monomer was then sublimed three times under high vacuum. Phenyl vinyl ketone was prepared by the dehydrochlorination of β-chloropropiophenone[24] and was fractionally distilled under yellow light immediately before use. Copolymers were prepared by AIBN-initiated radical polymerization in degassed benzene at 60 °C. The polymers were precipitated from benzene to methanol several times and were stored in the dark at −20 °C. Copolymer compositions were determined by IR spectroscopy, using chloroform as solvent. The concentration of aromatic carbonyl groups was determined with the extinction coefficient of the 5.95-μm ketone band of a homopolymer of PVK.[25] Number-average molecular weights were determined by membrane osmometry in dioxane. Table I lists the properties of the polymer samples used in luminescence experiments.

Fluorescence and phosphorescence spectra were recorded on a Hitachi-Perkin Elmer MPF-2A instrument, using techniques

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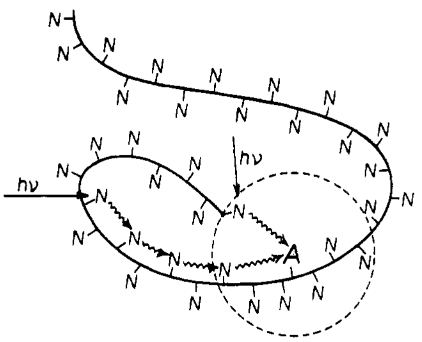

Figure 1. A conceptual illustration of singlet energy transfer to an acceptor A in an antenna polymer. Reprinted from ref 7 with permission.

Table I
Properties of the 2-Vinylnaphthalene–Phenyl Vinyl Ketone Copolymers

mol % ketone in copolymer	$M_n \times 10^{-3}$ [a]	mol % ketone in copolymer	$M_n \times 10^{-3}$ [a]
0.00	137	1.04	63
0.17	82	3.8	61
0.35	90	8.0	42
0.68	77	12.0	33
0.995	66		

[a] Number-average molecular weight, measured by membrane osmometry in dioxane.

described in previous publications.[17,26] Polymer solutions in 2-methyltetrahydrofuran were prepared having optical densities of 0.30 in a 0.1-cm cell at the exciting wavelength (280 nm). This optical density corresponds to a chromophore concentration of 2.5×10^{-4} M at room temperature and approximately 50% higher at 77 K because of the volume contraction of the solvent. The solvent was purified by fractional distillation from $LiAlH_4$ under nitrogen. The sample solutions were deoxygenated in a stream of nitrogen saturated with the solvent vapor. They were then cooled gradually in the vapor over the liquid nitrogen before being fully immersed, in order to avoid mechanical stresses that could have introduced errors in the measured values of the fluorescence polarization and to prevent formation of voids within the glass that would have changed the effective path length of the solution. In all cases, the glasses were perfectly clear, a result that indicates that these polymers remain dissolved in 2-methyltetrahydrofuran at 77 K. In order to minimize the effects of fluctuations in the intensity of the excitation source, each experiment on a copolymer sample was followed immediately by the same measurement on 2VN homopolymer. Fluorescence polarizations P were measured by using techniques described elsewhere.[17] P was calculated from eq 1, where $I_\parallel$ and $I_\perp$ are the fluorescence intensities recorded

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

with parallel and perpendicular orientations, respectively, of the excitation and emission polarizers, and G is a small correction factor (0.98–1.02) for grating-induced anisotropy.[27]

Fluorescence decays were recorded by single-photon counting, as described previously.[6,7] Samples were excited through a 280-nm interference filter, and emission was viewed at 337 nm through the combination of a Jarrell-Ash 0.25-m monochromator and a Corning 7-37 filter (330–370-nm band-pass). A cylindrical quartz lens at 50-mm focal length was positioned between the sample tube and the monochromator to increase the counting rate and to improve the rejection of scattered light.

Results and Discussion

Steady-State Fluorescence Quenching. Figure 2 illustrates the fluorescence and phosphorescence spectra of poly(2-vinylnaphthalene) (P2VN) in 2-methyltetrahydrofuran at 77 K. In copolymers containing increasing amounts of phenyl vinyl ketone the naphthalene fluorescence intensity decreases and the naphthalene phosphorescence intensity increases, but no new emission bands are observed. In 2VN–PVK copolymers the fluorescence of the naphthalene chromophore is quenched by singlet energy transfer to the ketone group. The quenching of naphthalene luminescence by ketones has been mentioned several times in the literature,[26,28-33] but the effect has not been studied quantitatively in a polymer system. Values of the efficiency χ of energy transfer from the donor to the acceptor were calculated from fluorescence intensities I_F at constant excitation intensity by means of eq 2:

$$\chi = 1 - [(I_F)_{\text{copolymer}}/(I_F)_{\text{homopolymer}}] \qquad (2)$$

Table II shows the variation of χ with ketone content for copolymer solutions in 2-methyltetrahydrofuran at 77 K. Under these conditions there is no excimer emission, so that the resolution of spectra into components is unnecessary. The data of Table II can be compared with values of χ for copolymers of 9-anthrylmethyl methacrylate with 1-naphthylmethyl methacrylate, obtained under identical conditions and listed in Table III.[7] The short-range ke-

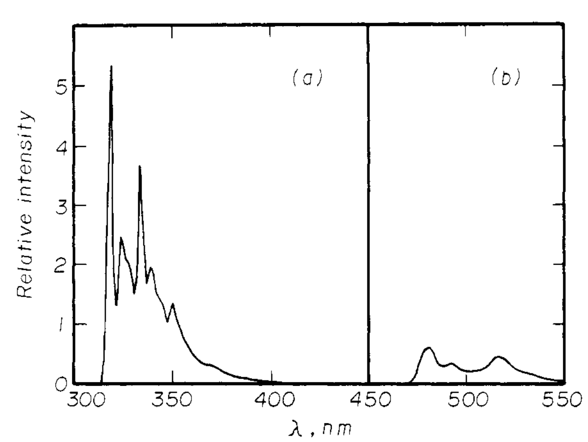

Figure 2. (a) Fluorescence spectrum of P2VN in 2-methyltetrahydrofuran at 77 K on 280-nm excitation. The excitation and emission bandwidths are 8 and 1 nm, respectively. (b) Phosphorescence spectrum of P2VN in 2-methyltetrahydrofuran at 77 K on 280-nm excitation. The excitation and emission bandwidths are 18 and 5 nm, respectively. The intensity scale is in arbitrary units.

Table II
Efficiency χ of Quenching of Naphthalene Fluorescence by Aromatic Ketone in 2-Vinylnaphthalene–Phenyl Vinyl Ketone Copolymers[a]

mol % ketone in copolymer	χ, %	no. of donors quenched by each acceptor
0.17	12	71
0.35	21	60
0.68	35	51
0.995	49	50
1.04	51	49
3.8	71	(18)[b]
8.0	92	(12)[b]
12.0	94	(8)[b]

[a] Solutions in 2-methyltetrahydrofuran at 77 K. [b] Overlap of quenching domains prevents analysis.

Table III
Efficiency χ of Quenching of Naphthalene Fluorescence by Anthracene in Copolymers of 1-Naphthylmethyl Methacrylate with 9-Anthrylmethyl Methacrylate[a]

mol % anthracene in copolymer	χ, %
0.174	8
0.348	15
0.665	22
1.42	61
2.06	70

[a] Solutions in 2-methyltetrahydrofuran at 77 K. Data from ref 7.

Table IV
Polarization P of the Fluorescence of Poly(2-vinylnaphthalene) in 2-Methyltetrahydrofuran at 77 K

λ, nm	λ_{em}, nm	P (± 0.005)
270	325	0.000
290	320	0.004
290	333	0.000
290	345	0.001
300	345	−0.003

Table V
Effect of Copolymer Composition on Relative Phosphorescence Intensity I_p and Efficiency q of Formation of Delayed Singlets in P2VN-PVK Samples[a]

mol % ketone in copolymer	I_p[b]	q[c]
0.0	1.0	1.0
0.17	1.03	1.2
0.35	1.3	1.1
0.68	1.3	1.4
0.995	1.1	1.8
1.04	1.7	1.8
3.8	2.0	1.9
8.0		3.0
12.0	3.6	2.3[d]

[a] Solutions in 2-methyltetrahydrofuran at 77 K. Excitation at 280 nm. [b] From total emission spectrum. [c] From delayed emission spectrum, corrected for quenching by copolymerized ketone. See eq 5 for definition of q. [d] Delayed fluorescence is too weak to measure accurately.

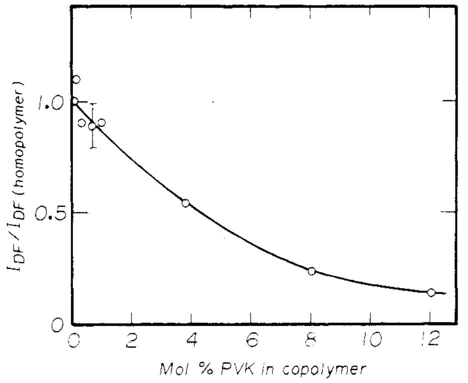

Figure 3. Variation of delayed fluorescence intensity I_{DF} with copolymer composition at constant excitation intensity for P2VN-PVK samples in 2-methyltetrahydrofuran at 77 K. The intensities are corrected to a constant moleculer weight of 6 × 10^4.

tone quencher and the anthracene trap, whose one-step quenching radius is much larger, quench the naphthalene emission with comparable efficiencies. It is possible that less effective one-step transfer in the ketone system is offset by more efficient singlet energy migration in P2VN. It is also possible, however, that P2VN forms more compact coils than poly(1-naphthylmethyl methacrylate) in 2-methyltetrahydrofuran, so that comparisons between the two polymer systems are not justified.

Analysis of the quenching data of Table II gives an upper limit for the range of singlet energy migration in P2VN. If an isolated PVK unit is capable of quenching n naphthalene chromophores, then

$$f_A n = \chi \tag{3}$$

where f_A is the mole fraction of PVK in the copolymer. Equation 3 is valid only at very low values of f_A, where the overlap of quenched sections of the polymer is negligible. The last column of Table II lists values of n for the P2VN-PVK copolymers. Below 1% PVK, n is fairly constant at 60 ± 10 chromophores.

When the P2VN chain is fully extended, the contribution to quenching of the naphthalene fluorescence made by singlet energy migration is greatest relative to the contribution from one-step Förster transfer to the ketone acceptor. In this hypothetical geometry the number of donor chromophores lying within the direct-quenching sphere of radius R_0 around the acceptor is lowest. Then, assuming that the excitation migrates in 2VN sequences on both sides of the acceptor, the above value of n corresponds in P2VN to a mean range of singlet energy migration within the excited-state lifetime of 30 ± 5 chromophores.

Of course P2VN is a random coil in 2-methyltetrahydrofuran solution and not a rigid rod. Thus a greater percentage of the donor emission may be quenched by one-step transfer to the acceptor than was assumed in the previous analysis, because the chain can fold back on itself. Nevertheless, the complete absence of excimer fluorescence from P2VN in 2-methyltetrahydrofuran glasses and the absence of a shortening of the monomer fluorescence lifetime (to be discussed in a later section) show that the P2VN coil is not highly contracted in this solvent. In mixed systems where P2VN is known to undergo phase separation,[34,35] excimer fluorescence is intense, even at 77 K.[36] One-step transfer to the ketone trap is thus unable to account for the high quenching efficiency.

Fluorescence Polarization of P2VN. Some uncertainty surrounds values of the polarization P of fluorescence from naphthalene-containing polymers in low-temperature glasses. Several groups reported values of P of zero or near-zero,[17,37-41] while a recent publication reports $P = 0.33$ for P2VN.[42] Table IV lists values of P at several excitation and emission wavelengths for the P2VN sample used in the present study. The P2VN fluorescence is completely depolarized within experimental error. Since P for a large number of monomeric naphthalene compounds lies between 0.1 and 0.21,[17] it is most unlikely that P for P2VN should be higher than that of the model compound. It therefore appears that the recent value of MacCallum[42] is in error. A communication by Gupta and co-workers[43] shows that preirradiation of polystyrene leads to gradually increasing values of the polarization of the excimer fluorescence, a consequence of the buildup of photodegradation products. Perhaps this observation is also relevant to the photophysics of the naphthalene-containing polymers.[42] It is proposed that the depolarization of the fluorescence of P2VN arises from singlet energy migration between naphthalene chromophores of different orientation[18,38,44] and that this process enhances the efficiency of transfer to the copolymerized ketone traps.

Studies of Delayed Luminescence. Table V lists the relative intensity of naphthalene phosphorescence from P2VN-PVK samples in 2-methyltetrahydrofuran at 77 K. The data are taken from total emission spectra under excitation at constant intensity. No ketone phosphorescence was observed in any copolymer, a result that indicates efficient triplet energy transfer from the carbonyl group to the naphthalene chromophore. The results in Table V show that as the fluorescence of naphthalene is quenched by increasing amounts of copolymerized PVK, a parallel rise in naphthalene phosphorescence is observed. The ketone group functions as a sensitizer of the naphthalene triplet.

Figure 3 shows the effect of copolymer composition on the relative intensity I_{DF} of delayed fluorescence in P2VN-PVK spectra recorded under constant excitation intensity. The value of I_{DF} is known to be a function of molecular weight M.[45,46] Data for the unfractionated samples listed in Table I were therefore normalized to a

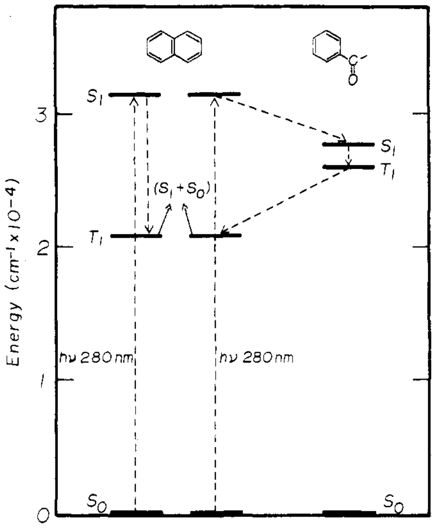

Figure 4. Energy level diagram for P2VN-PVK. The dashed line represents the path traced by the system during the sensitization of delayed fluorescence by the copolymerized ketone.

molecular weight of 6×10^4 using eq 4, valid for copolymers of the same composition but having different molecular weights:

$$(I_{DF})_1/(I_{DF})_2 \simeq M_1^{1/2}/M_2^{1/2} \qquad (4)$$

This correction for differences in molecular weight does not change the overall trend of the data in Figure 3. With increasing PVK content the intensity of delayed fluorescence decreases, both relative to the intensity of phosphorescence and in absolute terms. In order to determine the relative efficiency q of creation of delayed singlets, however, the values of I_{DF} must be corrected for the fact that the delayed singlet, once formed by triplet-triplet annihilation, is in turn quenched by energy transfer to the copolymerized ketone. Allowance for the quenching of delayed fluorescence is made by using eq 5:

$$q = \left(\frac{I_{DF}}{I_{DF}^0}\right)\left(\frac{\phi_f^0}{\phi_f}\right) = \left(\frac{I_{DF}}{I_{DF}^0}\right)\left(\frac{1}{1-\chi}\right) \qquad (5)$$

where ϕ_f denotes the naphthalene fluorescence quantum yield and the superscript 0 refers to the homopolymer of 2VN. The variation of q with copolymer composition is presented in Table V. These results show that the yield of delayed naphthalene singlets actually increases with increasing ketone content once the singlet quenching by the ketone is allowed for.

An explanation of the sensitization of delayed fluorescence is provided by the energy level diagram of Figure 4. The naphthalene singlet is quenched by energy migration and the transfer to the ketone singlet, which then undergoes intersystem crossing to the triplet with essentially unit quantum efficiency. The ketone triplet is quenched quantitatively by energy transfer to the lower energy naphthalene triplet. The result of the cyclic energy transfer in the ketone-containing copolymers is that a slightly higher proportion of naphthalene triplets is created at constant excitation intensity. The observation of sensitization of delayed fluorescence suggests that the inhibition of triplet energy migration produced by the breakup of 2VN sequences by the copolymerized ketone monomer is a secondary effect.

Fluorescence Decay Measurements. Figure 5 illustrates the fluorescence decays of the 2VN-PVK copolymers on pulsed excitation of the naphthalene chromophore. The decay of the emission from P2VN is exponential at 77 K in the absence of copolymerized ketone, with a decay time τ_0 of 80.5 ns. With increasing PVK mole fraction, the donor decay becomes increasingly nonexponential and the $1/e$ decay time shortens considerably.

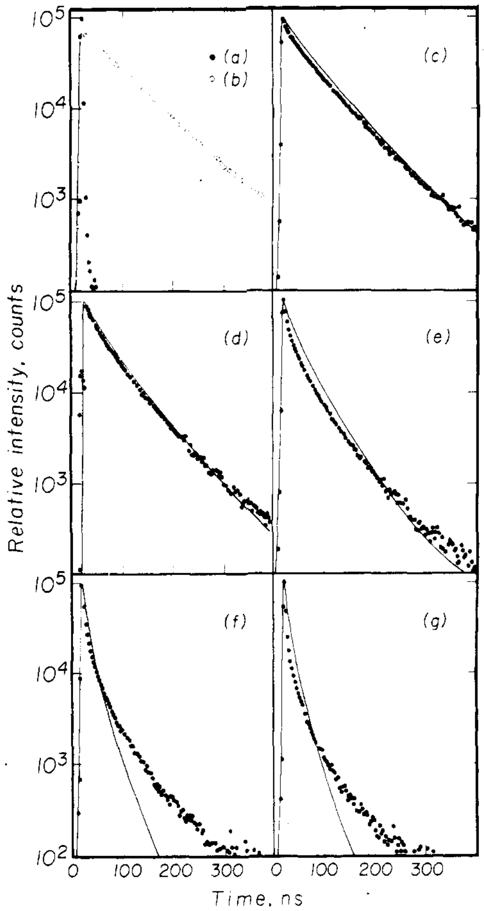

Figure 5. Fluorescence decays (points) on 280-nm excitation of polymers in 2-methyltetrahydrofuran glasses at 77 K. Observation wavelength 337 nm. (a) Lamp profile; (b) P2VN; (c) P2VN-0.68% PVK; (d) P2VN-1.04% PVK; (e) P2VN-3.8% PVK: (f) P2VN-8.0% PVK; (g) P2VN-12.0% PVK. Solid curves were calculated for one-step Förster transfer from randomly distributed donors to acceptors, in the absence of diffusion and energy migration. The curves are convoluted with the lamp profile (a). Values of the concentration parameter c, calculated from eq 8, are (c) 0.257, (d) 0.451, (e) 0.840, (f) 2.33, and (g) 2.50.

The absence of exponential decay for all PVK contents shows that singlet energy migration between the naphthalene groups, which depolarizes the naphthalene emission, cannot occur over sequences of hundreds of naphthalene chromophores, as occurs in triplet energy migration. If it did, the quenching kinetics would be exponential and the decay curves $I_F(t)$ would be described by Stern-Volmer kinetics:[47,48]

$$I_F(t) = \text{const} \times \exp\{-[k_Q' f_A + (1/\tau_0)]t\} \qquad (6)$$

where k_Q' is a rate parameter for quenching and f_A is the mole fraction of the acceptor PVK in the copolymer.

On the other hand, it also is not possible to fit the decay curves with a model based on one-step Förster transfer to the bound trap. With the crude approximation of a random three-dimensional distribution of donors around each acceptor, the donor decay curve is predicted to have the following form:[11,47,48]

$$I_F(t) = \text{const} \times \exp(-t/\tau_0) \exp[-2c(t/\tau_0)^{1/2}] \qquad (7)$$

where c is a parameter describing the dependence of the energy-transfer efficiency on the acceptor concentration. The choice of c for the copolymers presents a problem, because the local concentration of PVK is unknown. One can calculate c from the steady-state quenching data, using eq 8, derived by Förster:[11]

$$\chi = \pi^{1/2} c (\exp c^2)(1 - \operatorname{erf} c) \qquad (8)$$

Figure 5 shows curves calculated by using values of c corresponding to the steady-state quenching efficiencies listed in Table II. These calculated curves were convoluted with the experimental excitation pulse profile of Figure 5a. The predicted curves are visible nonexponential and their slopes do not approach values of $-\tau_0^{-1}$ within the 400-ns time window of the experiment. Nevertheless these curves show considerable differences from the experimental decay curves. The calculated curves decay too slowly in the initial part of the curve and do not show the same long-time behavior as the experimental curves. The agreement between experimental and calculated curves is much poorer than that observed for copolymers of phenyl isopropenyl ketone with 2-naphthyl methacrylate[26] or for copolymers of 9-anthrylmethyl methacrylate with 1-naphthylmethyl methacrylate.[7] It is possible that the smaller separation between naphthalene chromophores in P2VN than in the other naphthalene-containing polymers increases the effects of singlet energy migration, so that a model ignoring these effects shows poorer agreement with the experimental data. Other effects besides singlet energy migration may cause deviations between experimental and calculated decay curves. The donor distribution around each acceptor is not in fact random for polymer systems. If the chain is sufficiently extended in solution, the problem should actually be approached from the point of view of Förster transfer in a one-dimensional system.[49]

The P2VN–PVK system possesses the simplest energy-transfer kinetics of any antenna polymer yet devised. In a low-temperature glass the problems of diffusion and the complexities of excimer kinetics are removed entirely. This copolymer system was chosen deliberately because its Förster radius for one-step transfer was small. The radius of direct quenching by the ketone encompasses only a very few nearest neighbors and the effects of singlet energy migration predominate. It is possible that a more sophisticated model can be developed that can extract values of the rate of energy hopping from donor decay curves such as those shown in Figure 5.

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Registry No. (2VN)·(PVK) (copolymer), 30898-08-9.

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