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Molecular Weight Effects on Triplet Sensitization of Poly(2-vinylnaphthalene) in Benzene[†]

James F. Pratte and Stephen E. Webber*

Department of Chemistry and Center for Polymer Research, The University of Texas at Austin, Austin, Texas 78712. *Received September 30, 1981*

ABSTRACT: The triplet state of poly(2-vinylnaphthalene) (P2VN) can be sensitized by a large number of molecules excited at 337.1 nm (N_2 laser), where P2VN has negligible absorption. It has been found that in benzene solution the sensitization rate (k_q) varies with the degree of polymerization according to the proportionalities $k_q \propto P^{-0.41}$ for exothermic sensitizers ($\Delta E_T > 3$ kcal mol^{-1}, where ΔE_T is the sensitizer-naphthalene energy gap) and $k_q \propto P^{-1}$ for $\Delta E_T < 3$ kcal mol^{-1}. The former dependency has been rationalized on the basis of the coil dimensions (radius of gyration) and the latter on the basis of residual unsaturation at the chain ends created by the chain termination during the polymerization reaction.

Introduction

We reported earlier that the quenching of the triplet state of poly(2-vinylnaphthalene) (P2VN) by piperylene displayed a pronounced molecular weight effect.[1] Likewise, there have been other reports of molecular weight and coil effects on small-molecule-polymer reactions in room-temperature solutions such as macroradical-scavenger reactions,[2] triplet-state sensitization, and quenching of polymers.[3-5] We have previously argued[1] that the bimolecular rate constant for a very efficient reaction of a small molecule with a side group of a homologous polymer should depend on the coil density according to the porportionality

$$k \propto [\eta]^{(a-2)/3a} \qquad (1)$$

where the variable a is the exponent in the Mark-Houwink relationship $[\eta] = KM^a$. However, the above proportionality is expected to hold only for very efficient reactions. As Winnik and Maharaj[6] have argued, if the reaction rate becomes slow, then all molecular weight effects should vanish. Our original aim in this study is to systematically examine the molecular weight effect on the bimolecular rate constant for P2VN when the small-molecule-polymer reaction becomes less efficient. Our experimental method is to study the triplet sensitization of P2VN with sensitizers that vary with respect to the energy of the lowest triplet state. The sensitization of P2VN was studied in preference to the quenching of the P2VN triplet because of the ambiguity that may result from the effect of triplet energy migration along the polymer of the bimolecular quenching rate constant.[1] As discussed in the Discussion, the triplet sensitization of P2VN with efficient sensitizers followed a proportionality like that of eq 1 but deviated from this relationship as the sensitization reaction became less efficient. The deviation is discussed in terms of a "two-state" model.

Experimental Section

Poly(2-vinylnaphthalene) was radically polymerized by outgassing a benzene solution (~20 wt %) of 2-vinylnaphthalene (twice vacuum sublimed) with a weight percent of azobis(isobutyronitrile) initiator from 0.04 to 0.64 for samples 1-3. The

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[†] This work was reported at the 28th Congress of the International Union of Pure and Applied Chemistry, Aug 16-22, 1981, Vancouver, B.C., Canada.

Table I
Polymers Used in This Study

sample	$M_w{}^a$	$M_w/M_n{}^a$
1	1.3×10^4	1.39
2	2.7×10^4	1.44
3	6.89×10^4	1.77
4	21.89×10^4	1.70

[a] Determined by GPC elution curves and calibration curve based on polystyrene standards (Pressure Chemical Co.). Previous experience has shown that the M_w of P2VN is approximately twice that derived from the polystyrene elution volume. The values in this table reflect that correction.

solution was subjected to several freeze–pump–thaw cycles before sealing. The sealed tube was then heated at 60–70 °C for 1 day, and for the last hour the temperature was raised to 80–90 °C to destroy any remaining radicals. The high molecular weight polymer sample 4 was bulk polymerized in a outgassed reactor tube following the same heating cycle as that used for polymer samples 1–3. The reactor tube was then opened and the polymer solution precipitated in spectrograde methanol. Three more reprecipitations of dichloromethane solutions into methanol were done to all polymer samples to remove any remaining unreacted monomer. The weight-average molecular weight and the polydispersity were determined by using a Waters Model 600A GPC and comparing the elution curves to those of monodisperse polystyrene standards (Pressure Chemical Co.). The molecular weight properties of these polymers are given in Table I.

The sensitizers were purified by various methods. Chrysene (Aldrich, 95%), fluoranthene (Columbia Organic), phenanthrene, and pyrene were treated with maleic anhydride by a method similar to that used by Marvel and Anderson.[7] Chrysene, prior to maleic anhydride treatment, was chromatographed on activated alumina, with toluene as the eluent. Chyrsene, fluoranthene, and phenanthrene were then recrystallized several times from methanol, while pyrene was recrystallized several times from ethanol and then sublimed before being used. Benzophenone and fluorenone were purified by several recrystallizations from ethanol. Benzil was purified by sublimation before and after several recrystallizations from ethanol. 3-Acetylphenanthrene (Aldrich, 90%, technical grade) was recrystallized from methanol 3 times and then sublimed. Anthracene (Aldrich Gold Label, 99+%) was used without further purification. Benzene (MCB, spectrograde) was washed with sulfuric acid and then aqueous sodium carbonate. The washed benzene was then dried over $CaCl_2$ and distilled. The purity of the sensitizers was checked by comparing their triplet lifetimes in benzene to those reported in the literature. When available in the literature, TT absorption spectra of the sensitizers were also checked. When sufficient information was available (ϵ_{TT}, ϕ_{isc}, etc.), the concentration of the sensitizer was adjusted to produce similar concentrations of sensitizer triplets by the laser excitation. However, the concentration of sensitizer triplets was always adjusted to minimize TT annihilation (see below), which in turn depends on the triplet lifetime.

The laser flash photolysis experiments were carried out at the Center for Fast Kinetics Research, University of Texas at Austin. A nitrogen laser (337.1 nm, 3 mJ, 15-ns pulse width) was used as the excitation source, which was 90° to a 150-W xenon arc lamp that was used as the interrogation source. The transient decay curves were captured on a Biomation 8100 transient recorder and transferred to a PDP11/34 computer, where data collection, storage, and processing were accomplished. Solutions were outgassed in situ by bubbling nitrogen in the cell throughout the experiment. Data were collected after 10 min of bubbling nitrogen. Time-resolved triplet–triplet absorption spectra were assembled by combining decay curves taken at 5-nm intervals. Sensitization rates were determined by measuring the rate of decay to the sensitizer triplet as a function of naphthalene concentration. It is necessary to attenuate the excitation intensity in order to minimize the effect of sensitizer triplet–triplet annihilation on the decay curve. To accomplish this it was necessary to use neutral-density filters (typical OD ~1.5) and a cylindrical lens to focus the laser beam into the observed volume. The amount of attenuation of the excitation intensity was adjusted to the point that an almost single-exponential decay curve was obtained for the unquenched sensitizer solution. Because of this attenuation and the concomitant loss of signal to noise, we signal averaged our decay curves (typically 3–5 curves were combined for fitting). When possible, the observation wavelength was picked to eliminate TT absorption overlap of sensitizer and naphthalene triplets ($^3S^*$ and $^3N^*$). Only in the cases of efficient energy transfer from the $^3S^*$ to $^3N^*$ (e.g., for benzophenone and phenanthrene) was biexponential decay unequivocally observed because of the absorption overlap (i.e., there were enough naphthalene triplets produced to be optically detected in the sensitizer absorption). For less efficient sensitizers such as pyrene there were not enough naphthalene triplets produced to be optically detected in the sensitizer TT absorption. All absorption and fluorescence spectra were taken with a Cary 14 and SPEX Fluorolog spectrometer, respectively, using air-saturated solutions.

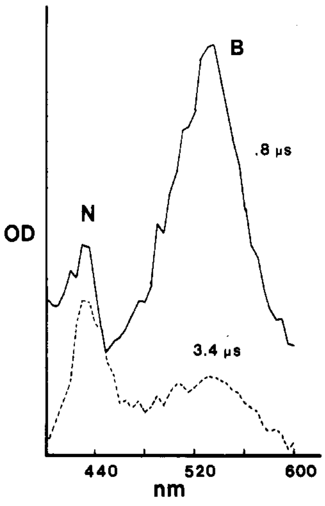

Figure 1. Time-resolved absorption spectrum of 10^{-2} M benzophenone + 2×10^{-3} M (in naphthalene units) P2VN at 0.8 and 3.4 µs after the N_2 laser pulse. The benzophenone and naphthalene regions of the spectra are labeled B and N, respectively.

Results

As mentioned in the Experimental Section, all the decay curves with the exception of those of benzophenone and phenanthrene show exponential behavior. A time-resolved triplet–triplet absorption spectrum of 10^{-2} M benzophenone + 2×10^{-3} M in naphthalene groups (P2VN-2) is given in Figure 1. At early times (0.8 µs after the laser flash) the spectrum shows predominantly benzophenone absorption with some naphthalene absorption. At later times (3.4 µs after the laser flash) the benzophenone absorption has decayed to a relatively small value, with the naphthalene triplet still present. The naphthalene TT absorption for P2VN in benzene is broad and somewhat unresolved, with a significant tail extending to the red of λ_{max} = 430 nm.[8] This long-wavelength feature has been ascribed to triplet excimer absorption by Lim et al.[9] from their study of β,β-dinaphthylakanes. The lifetime of this feature decays at essentially the same rate as that of the naphthalene absorption at 430 nm. It is not known whether this absorption is due to triplet "excimer" or is from the broadening of the naphthalene absorption in the polymer environment. As the sensitization reaction becomes less efficient for monomeric naphthalene, one no longer observes a significant buildup of 430-nm absorption nor biexponential decay at this observation wavelength. Sensitizers of this type are chrysene and fluorenone. 3-Acetylphenanthrene is nearly isoenergetic with the P2VN monomeric triplet state and exhibits behavior intermediate between the two previous cases. Figure 2 shows time-resolved spectra for 5×10^{-4} M 3-acetylphenanthrene in benzene and 5×10^{-4} M 3-acetylphenanthrene + 1.15 ×

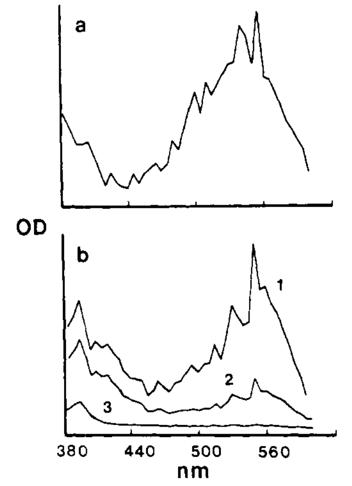

Figure 2. (a) Transient absorption spectrum of 5×10^{-4} M 3-acetylphenanthrene in benzene (~1 μs after the N_2 laser pulse). The "fine structure" is the noise that results from combining decay curves at different wavelengths to form the final spectrum. (b) Transient absorption spectra of 5×10^{-4} M 3-acetylphenanthrene in benzene with 1.15×10^{-2} M (in naphthalene groups) P2VN-1: spectrum 1, 0.8 μs; spectrum 2, 3.4 μs; spectrum 3, 14.9 μs (times refer to time delay from the N_2 laser pulse).

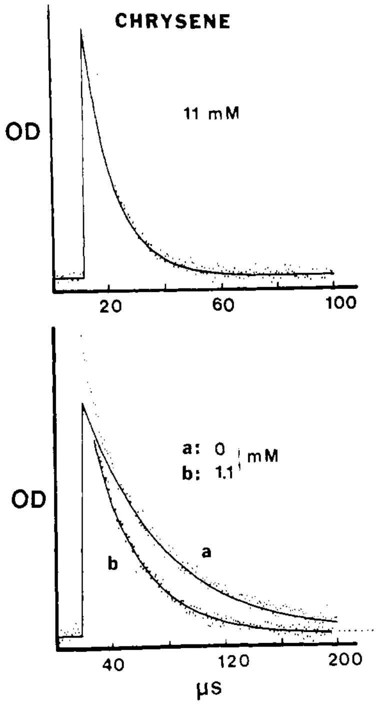

Figure 3. Typical decay curves of ^{3}(chrysene)* transient absorption with different concentrations of polymer (concentrations given are in terms of naphthalene groups). Note change of time scale for upper curve.

10^{-2} M in naphthalene groups (P2VN-1) in benzene. From Figure 2a, λ_{max} for 3-acetylphenanthrene is somewhere between 540 and 550 nm.[10] Figure 2b shows three different absorptions. At $\lambda \cong 540$ nm is the sensitizer absorption maximum, which decays off rapidly. The shoulder at 430 nm is probably due to the small amount of naphthalene triplet being sensitized. The third peak occurs at $\lambda \cong 385$ nm with a lifetime of ~500 μs. This latter absorption species is tentatively assigned as being due to a species to be discussed in more detail below.

Figure 3 shows typical decay curves for a sensitizer (chrysene) solution containing different concentrations of P2VN (given in millimolar concentration of naphthalene chromophores). The exponentiality of the decay curves indicates that back-transfer (i.e., $^3N^* + S \rightarrow N + ^3S^*$) is not significant. The unimolecular decay constant as a function of naphthalene concentration is given by $k = k_T^0 + k_q[N]$, where k is the observed unimolecular decay constant, k_T^0, the unimolecular decay constant of the unquenched sensitizer, k_q, the sensitization rate constant, and [N], the naphthalene concentration. The sensitization rate was obtained from the slope of the plot of k as a function of naphthalene concentration. Figure 4 shows a plot of k against concentration of naphthalene, [N], for the four different molecular weights of P2VN with chrysene as the sensitizer. The fit to a linear regression is satisfactory. As can be seen, the slopes decrease as the molecular weight of P2VN increases. This trend of the molecular weight effect of P2VN was seen for all the sensitizers in which a molecular weight study was done (i.e., benzophenone, phenanthrene, fluorenone, and 3-acetylphenanthrene). We return to this point shortly.

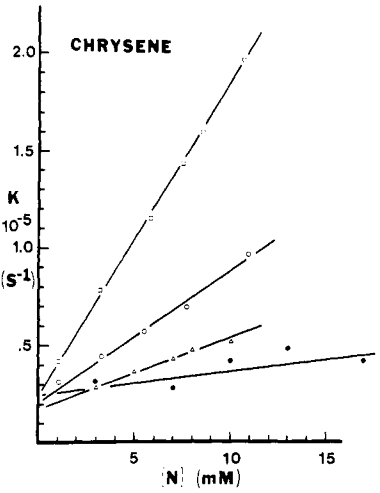

Figure 4. Stern-Volmer plot of k vs. naphthalene concentration for chrysene + P2VN: (□) P2VN-1; (○) P2VN-2; (△) P2VN-3; (●) P2VN-4.

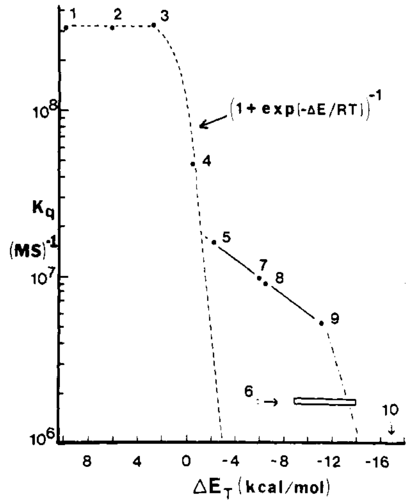

Figure 5. Semilogarithmic plot of k_q vs. ΔE_T (for P2VN-1). The dashed line given by $(1 + \exp[-\Delta E/RT])^{-1}$ is the expected behavior for a single triplet acceptor state. The numbers correspond to the numbering in Table II. Sensitizer 6 is benzil; see note *e* of Table II.

In Figure 5 we have plotted k_q vs. ΔE_T (sensitizer triplet energy–P2VN monomer triplet energy gap). In comparison with the results of Bäckström and Sandros[11] on triplet energy sensitization by biacetyl, the first plateau and falloff region for positive ΔE_T follows the expected behavior for sensitization of the monomeric naphthalene on the poly-

Table II
Triplet Energies of Sensitizers and P2VN Used in This Study

no.	sensitizer	$k_q{}^a \times 10^{-8}$, L mol^{-1} s^{-1}	E_T,^{b} kcal mol^{-1}
1	benzophenone	3.2×10^8	68.9
2	biphenyl	$3.4 \times 10^{8\,c}$	65.4^d
3	phenanthrene	3.2×10^8	62.0
4	3-acetylphenanthrene	4.7×10^7	59.0
5	chrysene	1.6×10^7	57.0
6	benzil	1.8×10^6	53.4 (donor state estimated to to be lower by 3–6 kcal mol^{-1})^e
7	fluorenone	1.0×10^7	53.3
8	fluoranthene	9.2×10^6	52.9
9	pyrene	5.4×10^6	48.2
10	anthracene	$<1 \times 10^6$	42.3
	P2VN (0–0 band of phosphorescence at 77 K)		59.3^f

[a] For P2VN-1. [b] Average of determinations quoted in: Engle, P.; Monroe, B. *Adv. Photochem.* **1971**, *8*, 245 (usually based on low-temperature phosphorescence). [c] Value determined by Bensasson et al.[4] for a P2VN sample of comparable molecular weight. [d] One determination of E_T that was significantly higher than the others (69.5 kcal mol^{-1}) was eliminated from the average. [e] See: Sandros, K. *Acta Chem. Scand.* **1973**, *27*, 3021. [f] Determined in this work. This is to be compared with the naphthalene value of 60.9 kcal mol^{-1}.

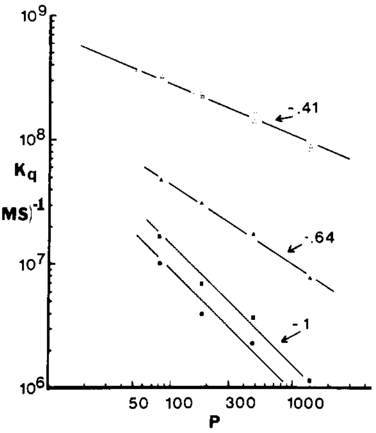

Figure 6. log–log plot of k_q for P2VN-1 as a function of P (degree of polymerization). Exothermic group (slope −0.41): (▲) benzophenone; (○) biphenyl; (□) phenanthrene. Endothermic group: (■) chrysene (slope −1); (●) fluorenone (slope −1); (▲) 3-acetylphenanthrene (slope −0.64).

mer chain (e.g., dependent on $(1 + \exp[-\Delta E/RT])^{-1}$. However, our plot also displays a second "plateau" and falloff region for negative ΔE_T values.[12] A natural explanation for this behavior is that there exists a second triplet-state site in the polymer that is of lower triplet energy than the monomeric naphthalene triplet. Table II lists the values for k_q and the triplet energy levels for the various sensitizers for P2VN-1. One may estimate that the value of this second triplet energy level is somewhere between 48 and 42 kcal/mol since the falloff region occurs in this area and anthracene was not detected to be quenched by P2VN. This energy correlates well with the lifetime of the third species at 385 nm seen in Figure 2b (estimated as ~500 μs) since most aromatic hydrocarbons with triplet-state energies in this range also have very long lifetimes in benzene (e.g., anthracene and pyrene).

Another interesting difference exists between quencher in which ΔE_T is positive and those in which ΔE_T is negative, illustrated in Figure 6. As noted above, there is a clear molecular weight effect on the rate of sensitization, and as shown in Figure 6, the molecular weight dependence is a function of the exothermicity of the sensitization reaction. For those sensitizers with positive ΔE_T (benzophenone, biphenyl,[13] and phenanthrene) the slope of log k_q vs. P is −0.41 (least-squares fit to all the data taken as a group).[14] For fluorenone and chrysene, which clearly have a negative ΔE_T, a line with slope −1 fits the k_q dependence (a least-squares fit was not performed in this case), while for 3-acetylphenanthrene an intermediate slope of −0.64 is obtained. We will try to rationalize the first two molecular weight dependencies in the Discussion.

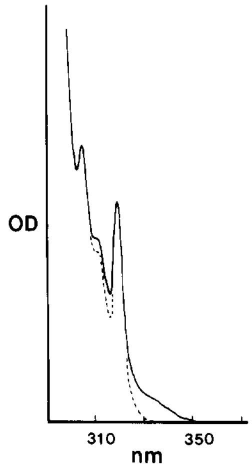

Figure 7. Absorption spectra of P2VN-1 (solid line) and P2VN-4 (dashed line) matched to equal OD at 320 nm in benzene.

Table III
Ratio of OD at 340 and 320 nm for P2VN Samples

sample	$(OD)_{340}/(OD)_{320}$
1	0.0587
2	0.0388
3	0.0225
4	0.0113
1-H	0.0441

We now turn our attention to the possible origin of the second triplet state in the polymer chain. Figure 7 shows absorption spectra of P2VN-1 and P2VN-4 with approximately the same optical density at 320 nm. As can be seen from the spectra, the absorption for the lowest molecular weight polymer (P2VN-1) is broadened to the red of 320 nm to a greater extent than the highest molecular weight polymer (P2VN-4). Table III gives the ratio of the optical density at 340 nm to that at 320 nm for the polymer set studied. This ratio decreases with the molecular weight increases according to the proportionality $(OD)_{340}/(OD)_{320} \propto P^{-0.48}$. Irie et al.[15] have observed a similar broadening in the excitation spectrum of low molecular weight P1VN and P2VN samples. They ascribe the broadening to ground-state dimer absorption. We see the same behavior in methylene chloride and benzene solvents for all our polymer samples as they did for mixed solvents of cyclohexane and THF. Since our lowest molecular weight sample is 4 times the molecular weight of that of Irie et al.,[15] we were not able to dissolve any of our samples in cyclohexane at 20 °C in order to compare our polymer set to theirs. Close scrutiny of their excitation spectra and emission spectra of P1VN and P2VN indicates that they saw a species in the polymer chain with vinylnaphthalene optical characteristics (we return to this point in more detail at the end of this section). The peaks in the absorption spectrum in cyclohexane from ref 15 are similar to that reported for 2-vinylnaphthalene in ethanol.[17] A vinylnaphthalene moiety can be formed in the polymer chain by a chain termination step of disproportionation. Since it was possible that the second triplet in the polymer could be from such a group, a hydrogenation similar to that attempted by Irie et al.[15] was performed on the lowest molecular weight sample, P2VN-1. The polymer was dissolved in THF and a 5% palladium on activated carbon catalyst was added.[18] Instead of stirring the solution over 1 atm of hydrogen as Irie et al.,[15] we used a slightly more vigorous set of conditions (stirring the solution in a bomb with 3.5 atm of hydrogen for 20 h). The catalyst was then filtered off and the polymer reprecipitated by addition of methanol. Three more precipitations of methylene chloride solutions of the polymer into methanol were performed. The absorption spectrum of the hydrogenated P2VN-1 showed a decrease in the $(\mathrm{OD})_{340}/(\mathrm{OD})_{320}$ ratio. This value is listed in Table III as sample 1H and approaches the value of the next lowest weight, P2VN-2. The sensitization experiment using 3-acetylphenanthrene was repeated and a k_q value of 3.2×10^7 L mol^{-1} s^{-1} was obtained. This value is slightly greater than that for P2VN-2. Thus it seems that the second triplet in the polymer originates in a reducible species. We presume that the reduction under the above conditions must not have completely reduced all the reducible species in the polymer chain.

If a vinylnaphthalene species is the source of the second triplet, then it must quench sensitizers with negative ΔE_T fairly efficiently. A sensitization experiment with fluoranthene as the sensitizer and 2-vinylnaphthalene as the quencher showed little quenching of fluoranthene triplet. Thus, the triplet state of the reducible species must not be identical with that of 2-vinylnaphthalene. It may be possible that a vinylnaphthalene moiety could interact with a nearby naphthalene group to form a low-energy triplet acceptor state.

We also compared the excitation and fluorescence spectra for P2VN-1 and 2-vinylnaphthalene. For the polymer we find that excitation at longer wavelengths (337.5 nm) leads to a spectrum that is blue shifted relative to that excited at 295 nm (Figure 8A). Except for the lack of structure in the former case this observation is similar to that of Irie et al.[15] However, this spectrum is not structured like that of 2-vinylnaphthalene (Figure 8B), nor is the excitation spectrum like that of 2-vinylnaphthalene.[19] Thus while it seems reasonable that the second triplet arises from some moiety with vinylnaphthalene conjugation, it does not seem to correspond to the most obvious monomer model compound that occurred to us.[20]

Discussion

As was stated in the Introduction, the initial goal of this work was to determine the molecular weight effect on the reaction rate constant for a small molecule and polymer-bound species when the rate constant is diminished. When the magnitude of the triplet energy difference between the sensitizer and the polymer is less than 3 kcal/mol, back-transfer (rate constant $k_{\bar{q}}$) becomes important in the kinetic scheme given by the following reactions:

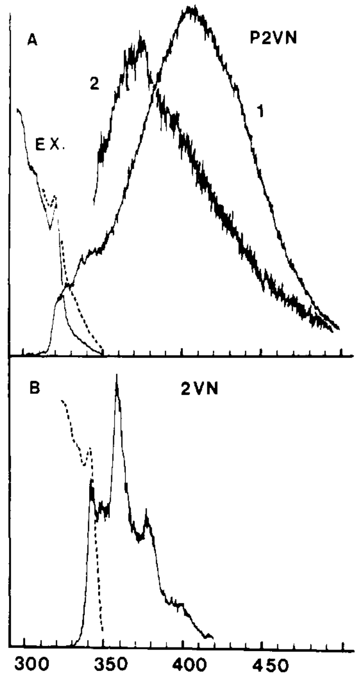

Figure 8. Excitation and fluorescence spectra for P2VN-1 and 2-vinylnaphthalene. (A) P2VN-1: spectrum 1, fluorescence excited at 295 nm; spectrum 2, fluorescence excited at 337.5 nm. Spectra marked EX are excitation spectra: solid line, $\lambda_{\mathrm{obs}} = 405$ nm; dashed line, $\lambda_{\mathrm{obs}} = 360$ nm. (B) 2-Vinylnaphthalene: solid line, fluorescence spectrum; dashed line, excitation spectra.

$$^3\mathrm{S}^* \xrightarrow[k_T{}^0]{} \mathrm{S} \tag{2a}$$

$$^3\mathrm{S}^* + \mathrm{N} \underset{k_{\bar{q}}}{\overset{k_q}{\rightleftharpoons}} {}^3\mathrm{N}^* + \mathrm{S} \tag{2b}$$

$$^3\mathrm{N}^* \xrightarrow[k_P]{} \mathrm{N} \tag{2c}$$

where S and N represent the ground state of the sensitizer and polymer-bound naphthalene, respectively, and $^3\mathrm{S}^*$ and $^3\mathrm{N}^*$ represent the excited triplet states. The solution to kinetic equations 2a–c is straightforward.[1,16,21] The general form is

$$[\mathbf{E}(t)] = \sum_{j=1}^{2} \sum_{i=1}^{2} a_{\mathrm{E},i} \hat{\mathbf{c}}_{i,j} e^{\Lambda_i t} \tag{3}$$

in which $[\mathbf{E}(t)]$ is a vector of the concentrations of $^3\mathrm{S}^*$ and $^3\mathrm{N}^*$, $a_{\mathrm{E},i}$ is a coefficient dependent on the $t = 0$ boundary conditions of the problem, and $\hat{\mathbf{c}}_i$ and Λ_i are the eigenvectors and eigenvalues of the matrix of the rate constant

$$\mathbf{R} = \begin{bmatrix} -K_1 & k_q[\mathrm{N}] \\ k_{\bar{q}}[\mathrm{S}] & -K_2 \end{bmatrix} \tag{4}$$

where $K_1 = k_T{}^0 + k_q[\mathrm{N}]$ and $K_2 = k_P + k_{\bar{q}}[\mathrm{S}]$. The eigenvalues are given by

$$\Lambda_i = -(1/2)(K_1 + K_2) \pm (1/2)[(K_1 - K_2)^2 + (4k_q k_{\bar{q}}[\mathrm{S}][\mathrm{N}])]^{1/2} \tag{5}$$

Thus for any sensitizer in which $k_{\bar{q}}$ is significant, one should see biexponential behavior of the sensitizer decay curve. As was stated earlier, none of the sensitizers showed significant biexponential behavior unless there was spectral overlap in the TT absorption. There are two possible explanations for this behavior. The first possibility is that as the reaction between the sensitizer triplet and the monomeric naphthalene sites on the polymer becomes less efficient (such that back-transfer would be expected to be important), the second triplet state on the polymer chain is the primary quenching species. Thus there would be a lower population of triplet naphthalenes bound to the polymer that could back-react with the sensitizer molecule. It is also important to note that the concentration of sensitizer tends to be fairly low, which would also reduce the back-transfer rate. The second possibility is that the difference between the exponents Λ_+ and Λ_- was not sufficient to distinguish a biexponential curve. In our experience, a clear biexponential curve will be observed only if the rate constants differ by a factor of 3–5.[22] It has been pointed out by one of the referees that for a biexponential curve given in eq 3, it is the ratios of the coefficient $a_{E1}\hat{c}_{11}/a_{E2}\hat{c}_{21}$ that determine whether one can observe deviations from exponential decay. The precision of our data in Figure 3 implies that the second exponential would have to make a substantial contribution (ca. 20%) to the decay curve in order to be observed.

For the exothermic sensitization reactions the molecular weight dependence we have observed in the present work is similar to that observed previously by us for P2VN triplet quenching. We repeat briefly our earlier discussion, based on an idea of Behzadi et al.[2b] The classical expression for the collision-limited reaction rate between a sensitizer and the polymer coil is given by

$$\sum = 4\pi(r_S + r_P)(D_S + D_P)(N_0/10^3) \tag{6}$$

where $r_{S,P}$ and $D_{S,P}$ are the radii and diffusion constants for the sensitizer and polymer, respectively, and N_0 is Avogadro's number. If we take the appropriate radius for the polymer to be the radius of gyration (R_g), which is much larger than r_S, and furthermore assume $D_S \gg D_P$, then we expect

$$\sum \propto R_g \tag{7}$$

Using the two proportionalities[23]

$$[\eta] \propto R_g^3/P \tag{8a}$$

$$[\eta] \propto P^a \tag{8b}$$

we find

$$\sum \propto P^{(a+1)/3} \tag{9}$$

The concentration of polymer coils is given by the naphthalene concentration divided by P, so the relation between the calculated quenching rate and the degree of polymerization is

$$k_q^{\text{calcd}} = \sum/P \propto P^{(a-2)/3} \tag{10}$$

The Mark–Houwink a parameter for P2VN in benzene is approximately 0.72,[24] which yields a predicted proportionality $k_q^{\text{calcd}} \propto P^{-0.43}$, remarkably close to the observed $P^{-0.41}$ dependence.

It was our original expectation that as the sensitization reaction becomes less efficient (i.e., for $\Delta E_T < -3$ kcal mol^{-1}), the molecular weight effect would decrease. This expectation is based on the idea that the $^3S^*$ molecule could diffuse in and out of the polymer coil many times during its triplet lifetime such that it would experience an equal number of collisions with the polymer regardless of the size of the coil. This idea was put forward by Winnik and Maharaj,[6] who also presented experimental evidence of this limit for the case of hydrogen abstraction from n-alkanes by the long-lived benzophenone triplet. The abstraction rate was shown to be independent of the chain length for n from 6 to 36. Also, Horie and Mita[25] have seen no molecular weight effect for the quenching of benzil phosphorescence by polystyrene. These two experimental results obviously had bimolecular rate constants much lower than the diffusion-limited value. However, our results for inefficient sensitizers of the polymer-bound naphthalene group showed an *increased* molecular weight effect (e.g., chrysene and fluorenone). We believe the following argument is a plausible explanation for this effect. We presume that the species responsible for the quenching in these cases is the "second triplet" that is related to the reducible species. As stated previously, one reasonable source for such a species would be vinyl moieties at the chain ends created by chain termination via disproportionation. If the species responsible for the second triplet is an end group, it is reasonable to take the concentration of end groups to be proportional to P^{-1}. Other work in this laboratory has implied that the rate of reaction of a small molecule with a P2VN end group (pyrene) does not depend on P,[26] so a simple P^{-1} dependence is predicted, in agreement with experiment. The chemical identity of this end group is unknown at present, but we believe that it is not a simple vinylnaphthalene moiety (see Results). We note that 3-acetylphenanthrene is nearly isoenergetic with $^3N^*$ such that sensitization of both $^3N^*$ and the "second triplet" is likely to be of significance. We presume that it is for this reason that the quenching rate constant is proportional to $P^{-0.64}$ (i.e., intermediate between −0.41 and −1.0).

In the preceding we have tried to rationalize the molecular weight dependence of the sensitizer–polymer reactions, but the absolute values of k_q have not been considered. In Table II we observe that the bimolecular rate constants for exothermic sensitizers are 20–30 times smaller than diffusion-limited rate constants for reactions of small molecules. If we take the ratio of the expression for a collision-limited rate constant (k_0) to our expression in eq 6, we obtain

$$(k_0/k_q^{\text{calcd}}) = (r_A + r_S)(D_A + D_S)P/R_gD_S \tag{11}$$

where $D_{A,S}$ are the diffusion constants of the small-molecule acceptor and sensitizer, respectively, $r_{A,S}$ are the corresponding molecular radii, and P relates the concentration of coils to the naphthalene concentration. If we assume that $D_A \simeq D_S$ and $r_A \simeq r_S$, we obtain

$$k_q^{\text{calcd}} = (R_g/4r_SP)k_0 \tag{12}$$

We estimate an R_g value of 42 Å for a polymer of similar molecular weight to P2VN-2 by using viscosity data on some earlier P2VN samples[1,27] and the equation $[\eta] = (6.308 \times 10^{24}E^3R_g^3)/M$.[23] Assuming $r_S = 3$ Å and $P = 160$, we find $k_q^{\text{calcd}} \cong 0.024k_0$. Our experimentally determined value for benzophenone sensitizing 2-ethylnaphthalene was 6.4×10^9 L mol^{-1} s^{-1}. If we take this value as k_0, we obtain a value of 1.5×10^8 L mol^{-1} s^{-1} for benzophenone sensitizing P2VN-2. The calculated value for P2VN-2 is 2.1×10^8 L mol^{-1} s^{-1}, which is within a factor of 2 of the experimental value. We also note that the rate constant obtained from Figure 6 by extrapolating back to $P = 1$ is approximately half the observed rate for 2-ethylnaphthalene and benzophenone. This is an appropriate result because the model for k_q^{calcd} (eq 12) presumes no diffusion by the naphthalene moiety. Thus it is possible that the relationships used to derive eq 10 and 12 have a quantitative validity beyond the rationalization of the observed molecular weight dependences. It is our plan to extend these studies to other polymer systems to see if our observations for P2VN are general.

Summary

Radically polymerized poly(2-vinylnaphthalene) (P2VN) and AIBN as the initiator contains two triplet state sites in the polymer chain. The higher triplet state site is due to the polymer-bound naphthalene monomer state in which E_T is $\approx$1.5 kcal/mol lower than 2-ethylnaphthalene (as derived from the 0–0 band of the low-temperature phosphorescence spectrum of P2VN). This value correlates well with the dependency of k_q on ΔE_T (energy gap between sensitizer and polymer triplet state). The lower triplet state site in the polymer chain is believed to be that of a reducible species possibly created by the chain termination step in the polymerization. The value of the triplet state level determined by sensitization lies somewhere between 48 and 42 kcal/mol. Kinetic models encompassing the molecular weight effect on k_q, the sensitization rate, were presented for the cases of efficient and inefficient sensitizers.

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