secondary and tertiary sites is about equal. This should not, however, affect the main thesis of this work, since β scission of secondary radicals is unlikely to occur. According to our mechanism the scission will occur primarily from attack at tertiary carbon atoms.
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Polymeric Photosensitizers: Effects of Intramolecular Energy Migration on Sensitization Efficiencies

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Received March 4, 1983

ABSTRACT: The occurrence of intramolecular energy migration was found to have no significant effect on the efficiency of ketyl radical formation via hydrogen abstraction from cumene by benzophenone (BP) or poly(vinylbenzophenone) (PVBP). Rate constants were found to be 1.1×10^6 and 0.81×10^6 M^{-1} s^{-1} for the small molecule and the polymer, respectively. The large difference in rate consants, 9.6×10^6 and 22.2×10^6 M^{-1} s^{-1} for BP and PVBP, respectively, when tetrahydrofuran was used as a quencher is probably attributable to preferential solvation. Conversely, intramolecular energy migration was found to significantly enhance the overall efficiency of triplet energy transfer to 1-methylnaphthalene (MeN). Rate constants for formation of ^{3}MeN were found to be 0.94×10^9 and 1.85×10^9 M^{-1} s^{-1} for BP and PVBP, respectively. An energy migration coefficient, Λ, of 3.28×10^{-5} cm^2 s^{-1} and a frequency of energy migration, ω, of 7.88×10^{10} s^{-1} were calculated for PVBP. For a series of copolymers of methyl methacrylate with vinylbenzophenone, values of Λ and ω were strongly dependent on the ketone content of the polymer and decreased sharply at 40 mol % VBP or less.

Introduction

While it is found that generally, the photoprocesses typical of a chromophore covalently linked to a polymer chain do not deviate remarkably from those in their small-molecule analogues, significant differences can and do occur quite regularly. These differences are usually a reflection of the somewhat unusual environment that the polymeric chromophores find themselves in. Their attachment at regular intervals to a long carbon–carbon chain leads to very high effective local concentrations and hence interactions that may be significantly larger than those seen in solutions of equimolar but isotropically distributed small molecules. A particularly striking example of this is the observation that for solutions of polystyrene and ethylbenzene, both 10^{-3} M in phenyl rings, the total emission spectrum for the former is dominated by excimer emission while the latter displays only normal fluorescence.[1,2]

Equally of interest, but more difficult to quantify, is the occurrence of intramolecular energy migration along the polymer chain. The first good evidence for this process was reported by Fox and Cozzens[3] through the observation of P-type delayed fluorescence resulting from triplet–triplet annihilation in dilute (10^{-3} M) solutions of poly(vinylnaphthalene). Since then, numerous systems have been investigated[4,5] and intramolecular energy migration seems to be the rule rather than the exception in polymers containing chromophores that absorb in the near UV.

If intramolecular energy migration is sufficiently facile, its migration distance may begin to approximate the polymer chain length. Since the entire macromolecule (rather than a single chromophore attached to it) can now be considered as the reactive species, the net result is an increase in the effective collisional radius for reactions with small-molecule substrates. In principle, this could lead to increased efficiencies in photosensitized reactions through the use of polymeric rather than small-molecule photosensitizers.

Attempts to demonstrate the feasibility of this approach have centered about the photosensitized isomerization of *cis*- and *trans*-stilbene. Moser and Cassidy[6] and Irie et al.[7] have shown that poly(phenyl vinyl ketone) is no more efficient as a sensitizer than are small-molecule triplet-energy donors such as acetophenone. Similar results were obtained by Serle et al.[8] and Hammond et al.[9] However, Irie et al.[7] have reported enhanced sensitization of stilbene isomerization when copolymers of phenyl vinyl ketone with a small amount of 2-vinyl naphthalene were used. Also of great interest, Kamachi et al.[10] have reported that the rate constant for hydrogen abstraction from tetrahydrofuran was roughly twice as large for poly(4-vinylbenzophenone) as for benzophenone itself. Both groups have proposed that intramolecular energy migration in the polymer chain plays an important role in the enhancement of photosensitization efficiencies.

In the course of parallel investigations, we have had cause to partially reexamine some of these interpretations. We report here results that strongly suggest the absence of any polymer effect when the sensitization step proceeds at rates that are considerably below the diffusion-controlled limit. Conversely, in donor–quencher interactions that begin to approach the diffusion-controlled limit, intramolecular energy migration does lead to an enhancement of photosensitization efficiencies.

Experimental Section

Benzene (Fisher Spectranalyzed Grade) was further purified by refluxing over P_2O_5 for several hours followed by distillation.

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Table I
Polymerization Conditions

polymer	mol % VBP in feed	mol % VBP in polymer	polym time,[a] h	% conversion
PMMA-VBP-1	5	7.3	12	60
PMMA-VBP-2	10	24.1	4	18
PMMA-VBP-3	20	39.3	5.5	23
PVBP	100	100.0	12	33

[a] In degassed benzene solutions, 60 °C, 0.5 mol % AIBN initiator.

Tetrahydrofuran (THF) was refluxed over sodium metal for 3 h and then distilled. Cumene was washed with concentrated H_2SO_4 until the acid no longer discolored. This was followed by water washings, drying over anhydrous magnesium sulfate, and then distillation.

Benzophenone (BP) (Aldrich) was purified by multiple recrystallizations from warm ethanol solutions followed by vacuum drying.

Methyl methacrylate monomer (MMA) was distilled under reduced pressure immediately prior to use. 4′-Vinylbenzophenone monomer (VBP) was synthesized by the method of Sanchez and Knoesel.[11]

The polymers were prepared via free-radical polymerization of the monomers in benzene solutions, using 0.5 mol % of 2,2′-azobisisobutyronitrile (AIBN) as initiator. The solutions, contained in Pyrex tubes, were thoroughly degassed by repeated freeze–thaw cycles at 10^{-5} torr prior to being sealed off and heated to 60 °C. Monomer feed ratios, polymerization times, and percent conversions are listed in Table I. The polymers were purified by repeated reprecipitations from benzene solutions into a large excess of methanol.

The UV spectra of the polymers in THF solutions were measured with a Cary 219 spectrometer. The extinction coefficient for the poly(vinylbenzophenone) homopolymer (PVBP) was found to be 180 M^{-1} cm^{-1} at 342 nm. This value was used to calculate the mol % of VBP monomer in the poly(methyl methacrylate-co-vinylbenzophenone) copolymers (PMMA–VBP). These values are also listed in Table I.

Triplet lifetimes and transient absorbance spectra were measured by using the pulsed output of a Molectron UV-400 nitrogen laser (337.1 nm, 8 ns, 3 mJ) as the excitation source. Details of this apparatus have been previously described.[12] Solutions for these studies were contained in 3-mm path length, rectangular Suprasil quartz cells and were thoroughly purged with oxygen-free argon immediately prior to use.

Results and Discussion

The transient absorbance spectrum of BP in deaerated benzene solution is shown in Figure 1. The spectrum displays a maximum at about 537 nm and can be attributed[13] primarily to triplet benzophenone, ^{3}BP. Spectra measured at longer times after the laser flash changed only in absolute intensity from that in Figure 1. When 0.7 M THF is added, the spectrum undergoes a red shift. The peak maximum now occurs at 547 nm and the absorbance at 600 nm has almost completely disappeared. This spectrum is typical[13] of the benzophenone ketyl radical, BP·. The transient absorbance spectra of PVBP and the three copolymers PMMA–VBP-1, -2, and -3, in the absence and presence of THF, were identical with those of BP under the corresponding conditions.

The quenching of ^{3}BP by a quencher, Q, in dilute fluid solution can be described by the following scheme:

$$\mathrm{BP} + h\nu \rightarrow {}^1\mathrm{BP} \rightarrow {}^3\mathrm{BP} \qquad (1)$$

$$ {}^3\mathrm{BP} \rightarrow \mathrm{BP} \qquad k_2 \qquad (2)$$

$$ {}^3\mathrm{BP} + \mathrm{Q} \rightarrow \mathrm{BP}\cdot + \mathrm{Q}\cdot \qquad k_3 \qquad (3)$$

$$ {}^3\mathrm{BP} + \mathrm{Q} \rightarrow \mathrm{BP} + {}^3\mathrm{Q} \qquad k_4 \qquad (4)$$

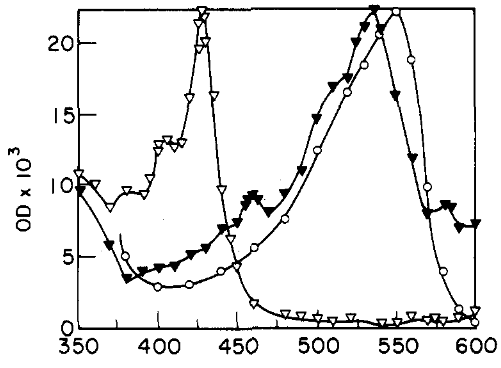

Figure 1. Transient absorbance spectra in deaerated benzene solutions: (▼) BP (5 × 10^{-3} M), immediately after the laser flash; (○) BP (5 × 10^{-3} M) and THF (0.7 M), 1 μs after the laser flash; (▽) BP (5 × 10^{-3} M) and MeN (10^{-2} M), 40 ns after the laser flash.

Equation 1 represents excitation into the first excited singlet state of BP followed by rapid intersystem crossing to the lowest triplet state. Equation 2 is a composite of all reaction pathways depleting ^{3}BP in the absence of Q and is given by the sum of k_p (phosphorescence), k_{isc} (intersystem crossing back to BP), $k_q[O_2]$ (quenching by residual oxygen), and k_s[S] (hydrogen abstraction from the solvent, S). Equations 3 and 4 represent quenching of triplet benzophenone by hydrogen abstraction from and by energy transfer to the quencher, Q, respectively.

With THF as quencher, eq 4 can be neglected. Since the ketyl radical is very long-lived (14 × 10^{-6} s or more) in comparison to ^{3}BP, its absorbance does not decay on the time scale of the experiment. In this case it is simple to show from the above scheme that the rate of decay of ^{3}BP, k_{exp}, can be determined according to

$$\ln\,[(\mathrm{OD}_t - \mathrm{OD}_\infty)/(\mathrm{OD}_0 - \mathrm{OD}_\infty)] = -k_{exp}t \qquad (5)$$

where OD_0, OD_∞, and OD_t refer to the optical densities of the solutions immediately after, at times long in comparison to the experimental time scale, and at some time t following the laser pulse, respectively.

Measurements of k_{exp} as a function of [Q], the quencher concentration, then result in the determination of the rate constant, k_3, for the quenching of the triplet ketone according to

$$k_{exp} = k_2 + k_3[\mathrm{Q}] \qquad (6)$$

where k_2 is the rate constant for the decay of the triplet in the absence of Q. Since k_{exp} and k_2 are equal to the inverse of the quenched and unquenched triplet lifetimes, τ and τ_0, respectively, eq 6 can be rewritten as

$$\tau_0/\tau = 1 + k_3\tau_0[\mathrm{Q}] \qquad (7)$$

The quenching of BP and PVBP, plotted according to eq 7, is shown in Figure 2. Values of the unquenched triplet lifetimes, τ_0, and of k_3, the rate constant for hydrogen abstraction from THF, are listed in Table II.

It can be seen that values of τ_0 in the polymers decrease significantly as mol % VBP increases. There is no evidence in the decay curves for an increasing amount of long-lived ketyl radical absorbance as the carbonyl content of the copolymers increases. Intramolecular hydrogen abstraction can therefore be ruled out as the cause of the trend in the τ_0 values. In all probability, the decrease in lifetimes from PMMA-VBP-1 to PVBP is a result of increased self-quenching as the ketone content increases.[14]

It can also be seen from Table II that k_3 for BP is not significantly different from those for the three PMMA–VBP copolymers. There is also no correlation between mol

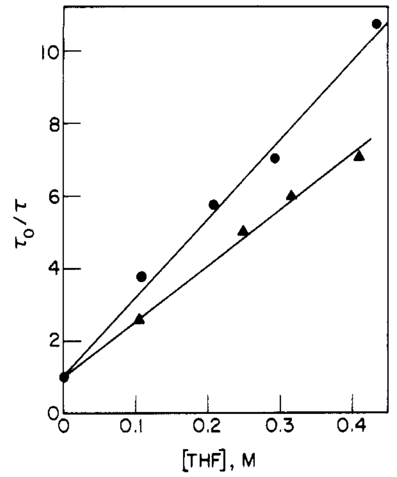

Figure 2. Quenching of triplet carbonyl lifetimes by THF in deaerated benzene solutions: (●) BP; (▲) PVBP.

Table II
Lifetimes and Quenching of Carbonyl Triplet States

sample	τ_0,[a,b] s × 10^6	k_3,[c,d] M^{-1} s^{-1} × 10^{-6}	k_3',[d,e] M^{-1} s^{-1} × 10^{-6}	k_4,[f] M^{-1} s^{-1} × 10^{-9}
BP	2.93	9.6	1.10	0.94
PMMA-VBP-1	4.09	8.0	0.76	0.31
PMMA-VBP-2	2.00	10.0	0.83	0.51
PMMA-VBP-3	1.00	9.3	0.70	1.40
PVBP	0.78	22.2	0.81	1.85

[a] All samples 5 × 10^{-3} M in BP unit; deaerated benzene solutions. [b] Triplet lifetime in absence of quencher. [c] Triplet carbonyl quenching by THF, ±1.0. [d] Evaluated by using eq 7. [e] Triplet carbonyl quenching by cumene, ±0.1. [f] Rates of sensitization of ^{3}MeN, ±0.1.

% VBP in the copolymers and their rate of hydrogen abstraction from THF. However, the value of k_3 for PVBP, at 22.2 × 10^6 M^{-1} s^{-1}, is roughly twice that for BP, reflecting behavior identical with that reported by Kamachi et al.[10] These authors have attributed this increased efficiency of PVBP to the occurrence of intramolecular energy migration in the homopolymer.

Alternative rationales are possible. Of these, preferential solvation seems the most likely. A freely diffusing small-molecule quencher may well have a different concentration inside the polymer coil than outside due to differences in polymer–quencher and quencher–solvent interactions.[15] From a consideration of their dielectric constants, 2.28 and 7.58 for benzene and THF,[16,17] respectively, it seems very probable that THF molecules should prefer the more polar environment of the PVBP coil. The effective concentration of THF within the coil would thus be higher than that calculated assuming an isotropic distribution of quencher molecules throughout the solution. The net result would be lower slopes for plots such as in Figure 2 when [THF] is adjusted upward. Lower values of k_3 for PVBP would then be obtained, reducing the difference from that for BP.

In order to ascertain the extent to which preferential solvation might account for the differences in k_3 between BP and PVBP, a less polar quencher, cumene, was also used. With a dielectric constant[16] of 2.38 as compared to 2.28 for benzene, it was expected that the ratio of quencher molecules to solvent molecules should remain the same both inside and outside the polymer coil.

The values for the rate constants for quenching of the carbonyl triplet states via hydrogen abstraction from cumene, k_3', are also listed in Table II. The prime is used to differentiate them from those measured with THF quencher. It can be seen that now, no difference is found for the efficiency of hydrogen abstraction by PVBP as compared to BP. This is strongly suggestive that the large increase in k_3 for PVBP when THF is the quencher is due to preferential solvation.

It should be noted that Kamachi et al.[10] have considered this rationale for their results. It was eliminated on the basis of nearly identical values for the intrinsic viscosity of their PVBP polymer in benzene and THF solutions. However, a significant change in intrinsic viscosity would require a change in the coil dimension and configuration. The solubility characteristics of the PVBP sample used in the current study imply that its molecular weight is very low, probably due to steric effects during chain growth. Its intrinsic viscosity in benzene solution at 22 °C was roughly measured to be only 0.3 ± 0.05, slightly lower than that for the polymer used by Kamachi et al.[10] From this it can be inferred that, due to steric interactions between neighboring polymeric benzophenone groups, the short PVBP chain probably exists in a relatively extended form in both benzene and THF solutions. Thus, significant configurational changes are not necessarily expected on going from one solvent to the other and intrinsic viscosities may not be the most reliable indicator of the differences in PVBP–THF and PVBP–benzene interactions.

Both THF and cumene quench the carbonyl triplet states with rate constants 2–3 orders of magnitude below that expected for a diffusion-controlled reaction. Takemura et al.[18] have shown that exothermic triplet energy transfer between aromatic carbonyls and naphthalene occurs at nearly diffusion-controlled rates. Accordingly, rates of sensitization of the triplet state of 1-methylnaphthalene (MeN) were measured in order to ascertain if a "polymer effect" existed.

With MeN, the primary means of triplet ketone quenching becomes eq 4 rather than eq 3 in the above scheme. MeN is not directly excited by the 337.1-nm laser light. Its triplet state is very much longer-lived than are the carbonyl triplets and exhibits a strong absorbance at 425 nm. Its triplet–triplet absorbance spectrum, normalized to that of ^{3}BP for display convenience, is shown in Figure 1.

From eq 1, 2, and 4 and neglecting the decay of ^{3}MeN due to its long lifetime, it is easily shown that the concentration of ^{3}MeN at any time t following the laser pulse is given by

$$[^3\mathrm{MeN}]_t = -(k_4[\mathrm{MeN}]/(k_2 + k_4[\mathrm{MeN}])) \times (\exp(-(k_2 + k_4[\mathrm{MeN}])t) - 1) \quad (8)$$

The maximum concentration of triplet naphthalene, $[^3\mathrm{MeN}]_\infty$, is identified by letting $t \rightarrow \infty$ as the preexponential ratio of rate constants in eq 8 and rearranging slightly:

$$[^3\mathrm{MeN}]_\infty^{-1} = 1 + (k_4\tau_0[\mathrm{MeN}])^{-1} \quad (9)$$

where τ_0 is the unquenched triplet ketone lifetime. Since the optical density, OD, due to ^{3}MeN is directly proportional to its concentration, eq 9 becomes

$$\mathrm{OD}_\infty^{-1} = a + a(k_4\tau_0[\mathrm{MeN}])^{-1} \quad (10)$$

where a is a constant. The magnitude of a does not need to be explicitly determined, as $k_4\tau$ is obtained from the intercept to slope ratio of plots of the inverse of the maximum ^{3}MeN absorbance vs. $[\mathrm{MeN}]^{-1}$.

Plots of ^{3}MeN sensitization by some of the ketones used in this study are shown in Figure 3. The resultant values of k_4 are listed in Table II. It can be seen that for the copolymers, k_4 increases as the mol % VBP does. For

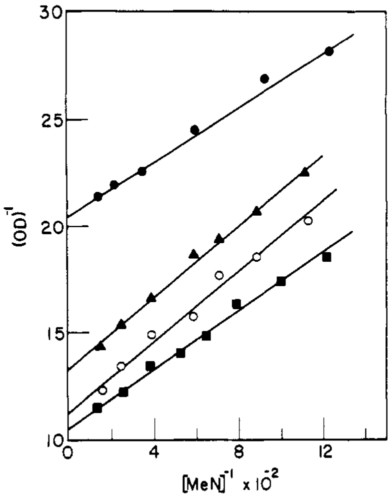

Figure 3. Sensitization of ^{3}MeN in deaerated benzene solutions: (●) BP; (○) PMMA–VBP-1; (▲) PMMA–VBP-2; (■) PVBP.

PMMA–VBP-3 (39.3 mol % VBP), k_4 is only slightly less than that for the PVBP homopolymer, which, in turn, is roughly twice that for the small molecule BP.

The behavior of the copolymers is similar to results reported by David et al.[19] for a series of poly(styrene-*co*-vinylbenzophenone) copolymers in 77 K glasses. These authors found a sharp increase in the extent of phosphorescence depolarization when the VBP content reached 50 mol %, indicative of a large increase in the extent of intramolecular energy migration. A comparison of the k_4 values of PMMA–VBP-3 and PVBP then implies that relatively efficient intramolecular energy migration in fluid solutions of the polymers begins to occur when the VBP content is at 40 mol % or more.

The diffusion-controlled rate of quenching of ^{3}BP by MeN, k_{diff}, can be calculated from the Smoluchowski[20] equation:

$$k_{diff} = 4\pi rDN/1000 \qquad (11)$$

where r and D are the sums of donor and acceptor collisional radii and diffusion coefficients, respectively, and N is Avogadro's number. The transient term introduced by Ware and Novros[21] and by Yguerabidi et al.[22] is negligible due to the long carbonyl triplet lifetimes.

Gorrel and Dubois[23] have calculated a collisional radius of 3.1×10^{-8} cm for naphthalene. Since the value for MeN should not be significantly different, the diffusion coefficient, D_A, for the energy acceptor MeN in benzene at 22 °C can be calculated from the Stokes–Einstein equation:

$$D_A = RT/6\pi\eta r_A \qquad (12)$$

where η, the viscosity of benzene[16] at 22 °C, is 0.635 cP, and R and T are the gas constant and temperature, respectively. A value of 1.1×10^{-5} cm^2 s^{-1} is obtained for D_A. The equivalent values of r_D and D_D for the donor ^{3}BP are not available but should not differ significantly from r_A and D_A since the molecules are of similar size.

A value of 1.03×10^{10} M^{-1} s^{-1} for k_{diff} for ^{3}BP quenched by MeN in benzene solution at 22 °C can be calculated from eq 11. If an efficiency of quenching, α, is defined as the ratio k_4/k_{diff}, a value of 0.09 is obtained. This is roughly a third of the efficiency Wagner and Kochevar[24] reported for the quenching of valerophenone by dienes in benzene solutions at 25.5 °C, a reflection of the increased steric hindrance about the carbonyl in BP as compared to phenyl alkyl ketones.

Voltz et al.[25] have modified the Smoluchowski equation to include the possibility of an energy migrational term assuming some importance. The result is a rate constant, k'_{diff}, which now reflects a collisional rate arising from both diffusion and energy migration:

$$k'_{diff} = 4\pi rN(D + \Lambda)/1000 \qquad (13)$$

where Λ is the energy migration coefficient and the transient term has again been neglected.

Table III
Intramolecular Energy Migration Parameters[a]

polymer	mol % VBP	k'_{diff}, M^{-1} s^{-1} × 10^{-10}	Λ, cm^2 s^{-1} × 10^5	ω, s^{-1} × 10^{-10}
PVBP	100.0	2.06	3.28	7.88
PMMA-VBP-3	39.3	1.56	2.22	5.33
PMMA-VBP-2	24.1	0.57	0.11	0.27

[a] From sensitization of ^{3}MeN in deaerated benzene solutions at 22 °C.

In the application of eq 13 to polymeric–small-molecule acceptor interactions, it is commonly assumed that the collisional radii are identical in acceptor and donor, i.e., that $r_A = r_D$. This implies that the quencher can be considered as interacting only with a single carbonyl group and not the entire macromolecule. Furthermore, Heskins and Guillet[26] have shown that the diffusion of the center of mass of the polymer in solution is negligible in comparison to that of the small-molecule quencher. Therefore, in eq 13, D equals the diffusion coefficient of MeN alone and $r = 2r_A$.

The energy migration coefficient can be calculated if the magnitude of k'_{diff} is known. The value of k'_{diff} is determined[27] as k_4/α, where α represents the quenching efficiency, taken to be 0.09 as found for the BP–MeN interaction (see above). Equal quenching efficiencies are assumed for PVBP–MeN and BP–MeN because the low molecular weight of the polymer should result in minimal coil penetration effects. This would not necessarily be valid in the case of high polymer–small molecule interactions as steric hindrances due to the coiled polymer chain would likely result in lowered quenching efficiencies from that determined for the BP–MeN interaction.

The frequency of energy migration, ω, can be calculated from

$$\omega = 6\Lambda/r^2 \qquad (14)$$

where r is the separation between the carbonyl chromophores on the polymer chain. For vinyl polymers, the average distance between neighboring pendant groups is generally[27] taken to be 5×10^{-8} cm.

The resultant values of k'_{diff}, Λ, and ω are listed in Table III for PVBP, PMMA–VBP-3, and PMMA–VBP-2. Similar calculations could not be done for PMMA–VBP-1 as the magnitude of k'_{diff} for this polymer was equal, within experimental error, to the rate constant for quenching of polymeric chromophores assuming only material diffusion of MeN to be significant.

The value of Λ for PVBP is slightly higher than that for poly(acrylophenone) in benzene solutions, reported to be 1.8×10^{-5} cm^2 s^{-1} by Kilp and Guillet.[28] Similarly, the frequency of energy migration at 7.88×10^{10} s^{-1} is slightly higher than values of 4.3×10^{10}, 5×10^{10}, and 3×10^{10} s^{-1} for poly(acrylophenone) as determined by Kilp and Guillet,[28] Faure et al.,[27] and Bays et al.[29]

From Table III, it can be seen that the energy migration coefficients and frequencies of energy migration are very dependent upon the mol % VBP in the polymer. PMMA–VBP-3, at 39.3 mol % VBP, has parameters only slightly less than those for PVBP homopolymer, indicative of quite efficient energy migration and mirroring the re-

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sults of David et al.[19] When mol % VBP decreases to 24.1% as PMMA-VBP-2, both Λ and ω drop by at least a full order of magnitude. What little energy migration may be present in this copolymer probably occurs via nonnearest-neighbor interactions.

Conclusions

Intramolecular energy migration in polymers does not lead to an enhancement of their efficiencies as photosensitizers when the rate-determining sensitization step occurs at several orders of magnitude below the diffusion-controlled limit. Any apparent polymer effect in this case is in all probability due to preferential solvation. For sensitization reactions approaching the diffusion-controlled limit, a polymer effect is seen when the mole fraction of sensitizer monomer in the polymer becomes sufficiently high to permit facile intramolecular energy migration.

Acknowledgment. This work was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2448 from the Notre Dame Radiation Laboratory.

Registry No. Benzophenone, 119-61-9; poly(4′-vinylbenzophenone) (homopolymer), 25668-24-0; 1-methylnaphthalene, 90-12-0; cumene, 98-82-8; tetrahydrofuran, 109-99-9; methyl methacrylate–4′-vinylbenzophenone copolymer, 30421-95-5.

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Electronic Excited-State Transport and Trapping on Polymer Chains

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ABSTRACT: A theoretical analysis of incoherent transport and trapping of electronic excitations among chromophores on polymer chains is presented. The theory is applicable to macromolecules in viscous solution, to polymers dispersed in amorphous solid materials, and to bulk polymers. The chains are assumed to contain a small concentration of randomly placed donor and trap chromophores. A density expansion for the transport Green function is the basis of the theory. The approach is general, but calculations are performed for the special case of Förster transfer and ideal chains. Padé approximants for the Green function that include two- and three-particle correlations are constructed for this case. Various limits of these approximate solutions are discussed. Connections are made between the Green function and the observables in time-dependent and photostationary fluorescence depolarization experiments and also to the observables in transient and steady-state trap fluorescence experiments.

I. Introduction

The application of fluorescence techniques to the study of polymer structure and dynamics is an important branch of polymer physics.[1,2] Techniques that utilize electronic excitation transfer (EET), such as concentration fluorescence depolarization[3] and trapping by excimers,[4] are extremely sensitive probes of local segment density and motion. Until recently, however, the theoretical foundation for the many-body aspects of EET problems in noncrystalline materials had not been established.

The problem of incoherent excitation transfer in a homogeneous material containing stationary randomly distributed donor chromophores was formulated in the language of statistical mechanics by Haan and Zwanzig[5,6] and solved approximately by various methods,[5-9] including the graphical analysis of Gochanour, Andersen, and Fayer (GAF).[7] The GAF method was extended to the case of a two-component homogeneous mixture of randomly distributed donor and trap chromophores by Loring, Andersen, and Fayer (LAF).[10] In a recent paper[11] (hereafter referred to as paper I), we applied the GAF analysis to the case of transport among chromophores randomly distributed on a polymer chain. In this problem, unlike the problems mentioned above, there are correlations among the positions of the chromophores because they are attached to the backbone of the same polymer chain. Ediger and Fayer[12] have also addressed the EET problem in polymeric systems, using a different model for the chromophore statistics.

In paper I, we performed calculations for the special case of Förster transfer among chromophores distributed randomly on an isolated ideal Gaussian chain. We investi-

0024-9297/84/2217-0054$01.50/0