overestimate the magnitude of the decay rates of the internal motions. Experimentally the normalized data $(\Gamma_e/\bar{\Gamma}_1)_{c\to 0}$ may become very close to the theoretical Ω/D_0q^2 values, because our D_0 $(=(\bar{\Gamma}_1)_{c\to 0}/q^2)$ and $(\Gamma_e)_{c\to 0}$ indicate the same magnitude (15%) of deviations from theories.

In Figure 4 we plot the normalized experimental values of $(\Gamma_e/Dq^2)_{c\to 0}$ against $X^{1/2}$ for three samples with higher M_w. The solid curve represents the theoretical curve[4,10] calculated for the nondraining flexible coil with the preaveraged Oseen tensor at the Θ temperature. All the data points fall completely on the theoretical curve. It should be noted that the theoretical curve calculated without the preaveraged Oseen tensor results in a worse fit. As far as we see the normalized quantity Γ_e/D_0q^2, we thus confirm the validity of the nondraining chain model with the preaveraged hydrodynamic interaction.

A similar result has been obtained by Han and Akcasu.[30] They have studied the X dependence of the first cumulant Ω divided by q^3k_BT/η_0 on PS in cyclohexane at 35 °C and found that the data agree, with the same magnitude of deviation as ours, with the theoretical predictions with the preaveraged Oseen tensor. In the range $X^{1/2} > 2$, they have estimated Ω by shape function analysis. As mentioned before, Ω and Γ_e are identical in definition but are estimated by different analytical methods. In order to test this identity, we have analyzed our $A(\tau)$ data by using the asymptotic shape function in parallel with the histogram method. The results indicate that Ω gives a value only 3–6% larger than Γ_e within the limit of experimental error when $X^{1/2} > 2$. The difference does not alter the conclusion described above.[31]

In conclusion, we can affirm that the dynamic behavior of a polymer chain in dilute solution at the Θ temperature is apparently described by the nondraining chain model with preaveraged hydrodynamic interaction. A 15% difference between theories and experiments observed in D_0, in $(\Gamma_e)_{c\to 0}$, and also in the exponent of M_w dependence of k_D indicates that serious defects are involved in the present theories especially in the treatment of hydrodynamic interactions of polymer chains in dilute solution.

Registry No. Polystyrene, 9003-53-6.

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Molecular Weight Effects of Triplet Sensitization of Poly(4-vinylbiphenyl) in Benzene

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ABSTRACT: The rate of sensitization of the triplet state of poly(4-vinylbiphenyl) (P4VBP) is measured for a number of triplet-state donors. The dependence of the sensitization rate (k_Q) on the energy of the triplet-state donor implies at least two acceptor states are present in P4VBP, one at ca. 67 kcal/mol (shifted to slightly lower energy relative to 4-methylbiphenyl) and the other at ca. 56 kcal/mol, which is assigned to a polymer-bound species, probably an end group. It has been found that $k_Q \propto P^{-0.45}$, in good agreement with the exponential value predicted from earlier work. The fluorescence of the P4VBP has demonstrated the presence of at least two species in addition to normal biphenyl. One of these is correlated with the species with a low-energy triplet state, but the other abnormal species is not identified. Because of the molecular weight dependence of these two abnormal species it is likely that they are both end groups.

Introduction

In previous studies on the triplet-state quenching and sensitization of poly(2-vinylnaphthalene) (P2VN) in room-temperature benzene solutions, a molecular weight dependence of the bimolecular rate constant for the small molecule–polymer reaction has been observed.[1,2] As part of our ongoing study of the triplet-state properties of poly(vinyl aromatics), we have investigated the triplet sensitization of poly(4-vinylbiphenyl) (P4VBP). Once again, a molecular weight effect in the bimolecular rate

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Table I
Properties of P4VBP Samples

sample	mol wt	P	M_w/M_n[a]	$[\eta]$,[b] dL/g
P4VBP-1	27 100	149	1.44	0.119
P4VBP-2	45 400	249	1.72	0.163
P4VBP-3	79 500	437	1.55	0.231
P4VBP-4	225 000	1236	1.55	0.440

[a] GPC, CH_2Cl_2 mobile phase. [b] Benzene, 20 °C (see ref 4 for Mark-Houwink parameters).

constant has been observed. We[1,2] as well as others[3] have shown that the bimolecular rate constant k_Q for a "diffusion-limited" reaction of a small molecule with a side group of a homopolymer depends on the intrinsic viscosity of the polymer as

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

where the variable a is the exponent in the Mark–Houwink relationship $[\eta] = KM^a$.

In our previous work on P2VN a plot of k_Q vs. E_T (triplet energy of sensitizer) revealed at least two distinct acceptor triplet states.[2] One triplet state at higher energy was apparently a slightly shifted naphthalene state while a low-energy triplet acceptor was assigned to some chemical impurity in the polymer chain. We have speculated that this species arises from the polymerization termination reaction. The present investigation of P4VBP will examine the molecular weight and the E_T dependence of k_Q. The results are similar to those of P2VN, except that there are a larger number of "minority species" that are part of the P4VBP polymer (as revealed by fluorescence spectroscopy) than was the case for P2VN.

Experimental Section

Poly(4-vinylbiphenyl) was polymerized with the radical initiator azobis(isobutyronitrile) (AIBN) in an outgassed benzene solution (~15 wt %) of twice sublimed 4-vinylbiphenyl (Aldrich and Columbia Organic Chemicals). The weight percents of AIBN initiator used for the high (P4VBP-4) and low molecular weight (P4VBP-1) polymers were 0.07% and 0.5%, respectively. The solutions were subjected to several freeze–pump–thaw cycles before the reactor tubes were sealed. The sealed tubes were heated at 60 °C for 1 day, and for the last hour the temperature was raised to 75 °C to quench the remaining radicals. The reactor tubes were then opened, and the polymer solution was precipitated in spectrograde methanol. Several reprecipitations of dichloromethane solutions into methanol were performed for all polymer samples to remove any remaining unreacted monomer. The polydispersity was determined by using the Waters Model 600A GPC and comparing the elution curves to those of monodisperse polystyrene standards (Pressure Chemical Co.). Molecular weights were determined by viscometry, using the Mark–Houwink parameters of Utracki and Simha[4] for P4VBP in benzene at 20 °C ($K = 2.14 \times 10^{-4}$, $a = 0.619$). The values for the polydispersity, molecular weight, intrinsic viscosity, and degree of polymerization are listed in Table I.

All the sensitizers used in this experiment with the exception of triphenylene and *N*-ethylcarbazole were purified by methods previously described.[2] Triphenylene (Aldrich, 98%) was recrystallized from methanol several times. *N*-Ethylcarbazole (Aldrich, 98%) was dissolved in toluene and chromatographed on alumina. It was then recrystallized in methanol 3–4 times. The material was sublimed immediately before use. Benzene was purified by the same method as before.[2] Spectrograde methylene chloride (MCB) was used as received for the fluorescence measurements.

2,4,6-Triisopropylphenylsulfonyl hydrazide (TSPH) has been found to be a convenient source of diimide that reduces olefins (e.g., *trans*-stilbene) to alkanes.[5] In order to reduce the possible olefinic groups present in the polymer chain caused by a disproportionation termination step, we treated our lowest molecular weight sample, P4VBP-1 (P = 149), by the following procedure: 300 mg of TSPH, synthesized by the method of Cusack et al.,[6] was dissolved in 15 mL of tetrahydrofuran (THF) and stored in the refrigerator until needed. P4VBP-1 was dissolved in THF (185 mg/10 mL) and then refluxed at 65 °C. Four equal aliquots of the TSPH solution were added at 0.5-h intervals to the refluxing polymer solution. After the last aliquot was added, the solution was allowed to reflux for an additional 2 h. The polymer solution was then reprecipitated in methanol. Several more reprecipitations from methylene chloride and THF into methanol were carried out in order to free the polymer from decomposition products. This hydrogenated sample is denoted P4VBP-1H. A Spex Fluorolog fluorimeter (Model 1902) was used to take the emission and excitation spectra of the hydrogenated and nonhydrogenated polymer samples.

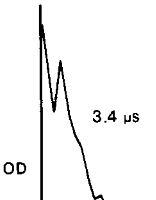

Figure 1. Time-resolved absorption spectrum at 0.8 μs (---), benzophenone only, and 3.4 μs (—), biphenyl only, for a solution 10^{-2} M in benzophenone and 10^{-2} M biphenyl base units (excitation at 337.1 nm, OD in arbitrary units).

The laser flash photolysis unit was the same as that used previously[2] at the Center for Fast Kinetics Research, The University of Texas at Austin, except that a Quantel Nd:YAG laser (355 nm, 100 mJ, 15-ns pulse width) was used as the excitation source in addition to a N_2 laser. Sensitizer concentrations were the same as in the P2VN experiment.[2] As was the case in the P2VN experiments,[2] sensitizer concentrations and excitation intensity must be chosen carefully in order to minimize sensitizer triplet–triplet (T–T) annihilation. Care must be exercised in using triphenylene as a sensitizer since Porter and Wilkinson[7] have found that the decay kinetics and T–T absorption spectrum are concentration dependent. Consequently, the concentration of triphenylene was kept at 10^{-3} M or lower. The bimolecular rate constants, k_Q, were obtained from the slope of the plot of the sensitizer decay rate as a function of biphenyl base molar concentration. The error in k_Q was larger for sensitizers in which the observation wavelength overlapped significantly with the biphenyl triplet–triplet absorption (e.g., *N*-ethylcarbazole and triphenylene) or for those sensitizers with k_Q values less than 10^6 M^{-1} s^{-1}. Data collection, analysis, and assembling of the T–T absorption spectrum have been described elsewhere.[1,2]

Results

The T–T absorption spectrum of 10^{-2} M benzophenone and 10^{-2} M P4VBP-1 in benzene is shown in Figure 1. At early times, the benzophenone absorption with λ_{max} = 530 nm dominates the spectrum. At later times, only the absorption due to the biphenyl moiety on the polymer with λ_{max} = 380 nm is present. The lifetime of the biphenyl triplet is approximately 40–50 μs (i.e., 4–5 times longer than that of P2VN[2]). In some cases the energy gap between the sensitizer and the P4VBP triplet states is small, such that one must consider the possibility of back-transfer of energy. In such a case, one expects to observe (1) a persistent T–T absorption feature of the sensitizer and (2) a biexponential decay of T–T absorption in those regions free of sensitizer–acceptor spectral overlap. In those cases where these criteria could be tested, there was no evidence that back-transfer was important (i.e., in Figure 1 the

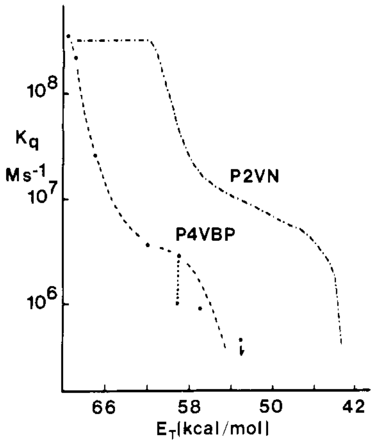

Figure 2. Quenching rate constant of P4VBP-1 as a function of E_T, the triplet energy of sensitizer (see Table II). The previous results for P2VN[2] are plotted for comparison. The point indicated by the solid square is the change upon hydrogenation (P4VBP-1H; see text).

Table II
Dependence of k_Q on Triplet Energy of Sensitizer

sensitizer	E_T,[a] kcal/mol	K_Q, M^{-1} s^{-1}
N-ethylcarbazole	70.1[b]	$3.5 \times 10^8 \pm 0.9$
benzophenone	68.9	$2.2 \times 10^8 \pm 0.03$
triphenylene	67.0	$2.5 \times 10^7 \pm 0.9$
phenanthrene	62.0	$3.7 \times 10^6 \pm 0.4$
3-acetylphenanthrene	59.0	$2.9 \times 10^6 \pm 0.3$
chrysene	57.0	$9.1 \times 10^5 \pm 3.0$
fluoranthene	52.9	$< 9 \times 10^5$

[a] Average of determinations quoted in: Engle, P.; Monroe, B. *Adv. Photochem.* 1971, *8*, 245 (usually based on low-temperature phosphorescence). [b] Yokoyama, M.; Tamamura, T.; Nakano, T.; Mikawa, H. *J. Chem. Phys.* 1976, *65*, 272.

benzophenone T–T absorption disappears completely). We also note the work of Wagner and Scheve[8] on energy transfer from benzophenone to biphenyls in which back-transfer was relatively unimportant for benzophenone concentrations less than 10^{-2} M. Thus we believe that we can safely treat the data presented herein as a case of simple irreversible quenching.

In Figure 2 is a semilog log of k_Q (bimolecular rate constant) as a function of the energy of the triplet sensitizer. Like P2VN,[2] P4VBP has two distinct regions: at high energies k_Q falls off rapidly at approximately 67 kcal/mol while at low energies a second falloff occurs at about 56 kcal/mol. Unfortunately, we do not have available suitable higher energy sensitizers to test for a "plateau" in this plot (cf. the P2VN data in Figure 2). However, based on the behavior of small-molecule studies[9] it is reasonable to assume that our two highest energy sensitizers are very close to the diffusion-limited rate for small molecule–polymer pendent group reaction. (Table II lists the values of k_Q for the various sensitizers). The bimolecular rate constant with 3-acetylphenanthrene (e.g., an endothermic sensitizer for the biphenyl triplet) as the sensitizer for the P4VBP-1H is one-third the value of P4VBP-1. The log–log plot of k_Q vs. degree of polymerization (*P*) is shown in Figure 3 for the exothermic sensitizer benzophenone. It should be pointed out that the value of k_Q for benzophenone is not as large as a normal diffusion-limited rate constant. A linear least-squares fit of the data of Figure 3 yields a slope equal to −0.452.

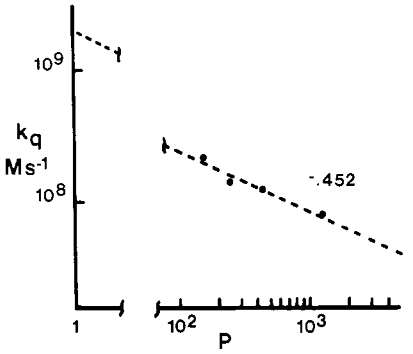

Figure 3. Molecular weight dependence of k_Q for benzophenone sensitizer. The dashed line is the least-squares fit to these points (slope −0.452) and also illustrates the extrapolation to *P* = 1.

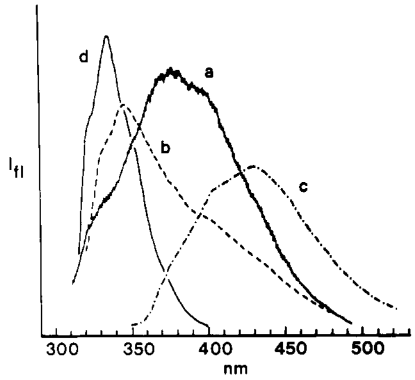

Figure 4. Fluorescence of P4VBP-1 in aerated CH_2Cl_2 with different λ_{exc} (intensity in arbitrary units): (a) λ_{exc} = 300 nm; (b) λ_{exc} = 310 nm; (c) λ_{exc} = 337.1 nm. Spectrum d is 4-vinylbiphenyl in aerated CH_2Cl_2 excited at 310 nm.

Figure 4 displays the fluorescence spectra of P4VBP-1 in aerated CH_2Cl_2. There is a profound effect in changing excitation wavelength. Figure 4a (excitation 300 nm) displays the typical biphenyl excimer emission (λ_{max} = 380 nm) along with the monomer component as has been shown by others.[10-12] When the excitation wavelength is changed to 310 nm, the P4VBP-1 emission is altered with the maximum emission now occurring at 348 nm and the retention of some structure (Figure 4b). For P4VBP-1H and 310-nm excitation, the peak at 348 nm is reduced to the point that the emission spectrum is quite similar to that using 300-nm excitation. The excitation spectra of both polymers monitored at 380 and 348 nm were essentially identical with the S_0–S_1 absorption of biphenyl. When the emission wavelength monitored is 430 nm, the excitation spectrum extends to the red of the biphenyl S_0–S_1 absorption, extending out to 400 nm. Excitation into this tail at 337 nm produces yet a third emission spectrum which is broad and featureless with λ_{max} at 430 nm (see Figure 4c). If the optical density at 300 nm is held constant for polymers PV4BP-1and P4VBP-1H (OD = 0.98 ± 0.01) the intensity at 430 nm for P4VBP-1H is 50% larger than that of P4VBP-1. For purposes of comparing with the other emission spectra, we have displayed in Figure 4d an emission spectrum of 4-vinylbiphenyl in aerated CH_2Cl_2. This spectrum is similar to that found by Berlman[13] except for diminution of the peak at 315 nm due to the trivial process of reabsorption caused by the relatively high concentration of solution. We will argue later that a species which is similar to 4-vinylbiphenyl is part of the P4VBP coil.

Discussion

(a) Sensitizer Energy Dependence of k_Q. In the Results it was shown that the semilog plot of k_Q as a function of the sensitizer triplet energy level indicated there were at least two triplet states in P4VBP. The higher energy triplet energy state is that of the biphenyl moiety on the polymer. This is verified from T–T absorption spectra obtained with benzophenone and phenanthrene as the sensitizers. The benzophenone-sensitized P4VBP solutions (Figure 1) display the transient absorption spectrum of only biphenyl triplet at long times. On the other hand, the phenanthrene–P4VBP solutions show only the triplet phenanthrene absorption spectrum at long times for the wavelength region 380–550 nm; i.e., no triplet biphenyl is produced. Evidently the phenanthrene triplet is quenched by a mechanism other than energy transfer to biphenyl.

From Figure 2 we estimate the triplet energy of the polymer-bound biphenyl chromophore as approximately 67 kcal/mol. This estimate is only approximate (±1 kcal/mol) because of the limited number of high-energy sensitizers, such that an accurate fit to the Sandros equation,[9] which includes back-transfer, is not possible. This value compares well with the earlier estimate by Wagner[14] of 68.5 kcal/mol of biphenyl in room-temperature solution and the more recent observation[8] that para substitution tends to lower the T_1–S_0 energy gap. According to Wagner,[15] the angle between the phenyl rings is 0° (i.e., planar) for the biphenyl triplet state in solution, while for the ground state the average angle lies between 20 and 25°. Thus, energy transfer to biphenyl occurs through a nonvertical transition. This nonplanarity of biphenyl plays an important part in the photophysics of this molecule. The relevance of this fact to triplet migration in P4VBP will be discussed in the following paper.[16]

From Figure 2 we can estimate the lower triplet state as ca. 56 kcal/mol. As stated previously, the T–T absorption spectrum at long times for endothermic sensitizers is composed of the sensitizer absorption only. The fact that k_Q for P4VBP-1H with 3-acetylphenanthrene as the sensitizer was reduced to one-third the value of P4VBP-1 implies that the low-energy triplet state is some reducible species that is part of the polymer coil. (This is similar to our findings for P2VN.[2]) This decrease in k_Q correlates well with the estimated 70–80% decrease in fluorescence intensity at 346 nm for P4VBP-1H compared to P4VBP-1. Thus, it is reasonable to suppose that the species that can be excited at 310 nm is also the one that produces the lower energy triplet state in the polymer.

(b) Nature of Polymer-Bound Impurities. The strong dependence of the polymer fluorescence spectrum on excitation wavelength and the ability of P4VBP to quench triplet sensitizers with energy much lower than 67 kcal/mol imply the existence of "abnormal" species on the polymer backbone. One obvious candidate would be a 4-vinylbiphenyl-like moiety, which would be left at chain ends by a disproportionation termination step. For the fluorescence spectrum of 4-vinylbiphenyl (Figure 4d), λ_{max} is at 335 nm, 11 nm to the blue of the polymer species excited at 310 nm. However, 310-nm radiation is weakly absorbed by the biphenyl moiety, such that the spectrum in Figure 4b may be a combination of biphenyl monomer, excimer, and "vinylbiphenyl" fluorescence.[17] Therefore we cannot unequivocally identify the intrinsic impurity species from fluorescence alone. There are three other observations that are consistent with the postulate that the intrinsic impurity is an "end group" that is like vinylbiphenyl. First, the intensity of the fluorescent component like that of Figure 4b is inversely proportional to the molecular weight of the P4VBP. Second, an independent experiment showed that 4-vinylbiphenyl quenched 3-acetylphenanthrene triplet with a rate constant of 3×10^9 M^{-1} s^{-1} (cf. 2.9×10^6 M^{-1} s^{-1}). Thus this kind of species, if present in the P4VBP chain, could give rise to the observed quenching of sensitizers that are endothermic with respect to the biphenyl triplet.[18] Third, reaction with TSPH reduces the relative intensity of this fluorescence component by an amount that corresponds to the decrease in k_Q (compare P4VBP-1 with P4VBP-1H). Since TSPH is known to reduce arylalkenes,[5] it is reasonable that this reduction procedure removes intrachain vinylbiphenyl moieties. A further "proof" of the end-group nature of the low-energy quenching group would be an inverse molecular weight dependec of k_Q, but for very endothermic sensitizers the values of k_Q were too small to be measured accurately.

When P4VBP was excited at 337 nm, the fluorescence spectra revealed a second "abnormal" species with λ_{max} at 430 nm. This emission feature was 50% more intense for P4VBP-1H than P4VBP-1 for two solutions with equal OD at 300 nm. The concentration of P4VBP-1H required to achieve this OD is higher than for P4VBP-1, which we interpret as arising from the diminution of the number of 4-vinylbiphenyl moieties.[17] Thus we assume that the species that emits at 430 nm is not reduced by TSPH and that the relative intensity of this fluorescence is increased because of (1) the higher concentration of the P4VBP-1H solution in the comparison cited above and (2) decreased absorption at 337 nm by the "tail" of the 4-vinylbiphenyl absorption. Once again this abnormal species seems to be associated with "end groups" because there is a consistent inverse molecular weight dependence of the 430-nm fluorescence.

Solomon has reviewed the possible abnormal groups that occur in radical polymerizations, including those initiated by AIBN.[19] For example, a mesomeric form of the usual cyanoisopropyl end group is a ketenimyl group that can hydrolyze to form an amide. We carefully compared the IR absorption of P4VBP-1 and P4VBP-1H films on KBr using a Nicolet Model 8000 FTIR and were not able to detect any significant difference between these two samples, within the signal-to-noise ratio of the data. In fact, the normal nitrile end group at 2220–2250 cm^{-1} was barely detectable. Thus it would seem that the IR absorption of the abnormal groups that we can detect by fluorescence spectroscopy is buried in the complex IR absorption of the aromatic and alkane groups.

(c) Molecular Weight Dependence of k_Q. In previous work it has been found that for the exothermic sensitizers the bimolecular rate constant k_Q is related to the intrinsic viscosity by eq 1. A relationship between k_Q and degree of polymerization P can be obtained[2] by using the Mark–Houwink relationship to give

$$k_Q \propto P^{(a-2)/3} \tag{2}$$

where a is the Mark–Houwink parameter. Utracki and Simha[4] have determined the a parameter for P4VBP at 20 °C to be 0.619, which, using eq 2, predicts that k_Q should be proportional to $P^{-0.46}$. This is in good agreement with the value obtained from the benzophenone sensitization experiment[20] (see Figure 3; least-squares slope is −0.45; cf. −0.41 for P2VN[2]). The least-squares intercept at $P = 1$ in Figure 3 is 1.9×10^9 s^{-1}. According to the model that is the basis of eq 2, this value should be half the k_Q value for the analogous reaction between two small molecules. We have experimentally determined the k_Q value for 4-methylbiphenyl quenching benzophenone to be 1.9×10^9 M^{-1} s^{-1}. (We note that Wagner and Scheve[8] using steady-state chemical quenching obtain the value of 6.2×10^8 M^{-1} s^{-1}.) Thus the extrapolation of the polymer data back to $P = 1$ overestimates the model compound bimolecular reaction rate. While one may argue that this extrapolation is numerically inaccurate, the direction of the error is consistent with the lowering of the triplet energy we have found in P4VBP. That is, 4-methylbiphenyl is not precisely a model compound for the polymer repeating unit. This is not surprising in view of the steric crowding found in polymer systems of this type.[21] A similar observation was made for P2VN,[2] in which the triplet state was lower by 1.5 kcal/mol than the model compound, 2-ethylnaphthalene.

We should point out a recent study by Lissi and coworkers[22] in which several carbonyl triplet-state sensitizers (biacetyl, benzil, and benzophenone) were quenched by naphthyl polymers and polystyrene, P4VBP (with benzil), and other polymeric alkenes and alkanes. For a diffusion-controlled reaction their results seem to be in essential agreement with our previous work,[1,2,23] including the molecular weight effect on k_Q. For endothermic quenching (e.g., the polystyrene derivatives) these workers propose a charge-transfer (CT) mechanism and relate k_Q to the ionization potential of the pendent group. The possibility of in-chain impurities was considered but assumed not to be important. However, no test of this assumption was provided (e.g., by carrying out a reduction reaction). Factors in favor of a CT mechanism are (1) a clear dependence of k_Q on the electron-donating ability of the pendent chromophore, (2) enhancement of k_Q by increasing the polarity of the solvent, and (3) (in the case of polystyrene) no dependence on molecular weight.

It seems to us that the most important points raised by the work of Lissi et al.[23] with respect to the present article are (1) there exists an alternative mechanism for endothermic quenching by polymers to that stressed herein and (2) "abnormal groups" that are part of a polymer chain do not necessarily have to quench via energy transfer but could act via a CT mechanism. This latter point enlarges the class of possible chemical species that might be active quenchers.

Summary

P4VBP polymerized with AIBN as the initiator has at least two triplet states in the polymer coil. The high-energy triplet state is due to the pendent biphenyl groups in the polymer, with an energy estimated as 67 kcal/mol. It is argued that the low-energy triplet state is due to a moiety from the disproportionation termination step in the polymerization which creates a vinylbiphenyl end group. The energy of this state is estimated as approximately 56 kcal/mol. The fluorescence spectra give evidence for two species in addition to normal biphenyl. One of these abnormal species is reducible by TSPH and it appears that this reducible species is responsible for the lower energy triplet state.

The relationship previously derived for an exothermic reaction between a small molecule and the pendent groups of a homologous polymer agrees with the molecular weight effect in k_Q for P4VBP, just as observed for P2VN.[2] Thus is seems likely that eq 1 (or eq 2) is a general relationship to describe the reaction kinetics of a small molecule and a pendent group of a homologous polymer when the reaction is intrinsically fast.

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Registry No. Poly(4-vinylbiphenyl), 25232-08-0; *N*-ethylcarbazole, 86-28-2; benzophenone, 119-61-9; triphenylene, 217-59-4; phenanthrene, 85-01-8; 3-acetylphenanthrene, 2039-76-1; chrysene, 218-01-9; fluoranthene, 206-44-0.

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(17) The molar extinction coefficient of 4-vinylbiphenyl at 310 nm is much greater than that of 4-methylbiphenyl, as is the quantum yield of fluorescence (0.61).[11]
(18) These observations are in contrast to our previous work on P2VN,[2] in which 2-vinylnaphthalene was not found to be an efficient quencher of sensitizers that are endothermic with respect to naphthalene.
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(21) It is not obvious that nearest-neighbor interactions will necessarily lower the T_1–S_0 energy gap. In the case of biphenyl this crowding could raise the energy by forcing the ground-state biphenyl into a more planar configuration and lower the T_1 state via weak triplet "excimer" formation.
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