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Electronic Energy Transfer and Quenching in Copolymers of Styrene and 2-(2′-Hydroxy-5′-vinylphenyl)-2*H*-benzotriazole: Photochemical Processes in Polymeric Systems. 10

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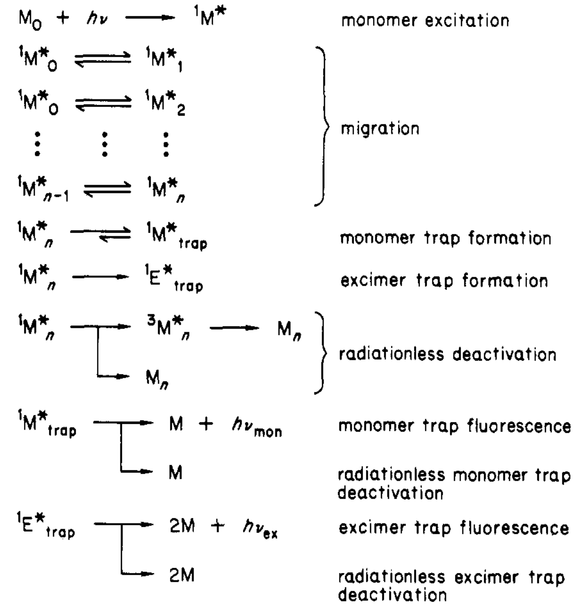
ABSTRACT: Intensity and lifetime quenching of the polystyrene monomer and excimer fluorescence emission by a pendant quencher have been studied in the solid state and in solution for a series of copolymers of styrene and 2-(2′-hydroxy-5′-vinylphenyl)-2*H*-benzotriazole. Two mechanisms of quenching have been identified. One involves interception of the migrating monomer excitation by the quencher, and the other involves a single-step Förster energy-transfer process from the excimer traps to a quencher. The relative efficiencies of these two quenching mechanisms in the solid state and in solution have been compared and related to the efficiency of electronic energy migration. An estimate of the excimer trap concentration in solid polystyrene is also reported.

Introduction

The critical issues related to electronic energy transfer and quenching phenomena in aromatic polymers have been delineated over the past few years through experimental studies of structure-photophysical property relationships[1-10] and through the development of theoretical models of electronic energy migration in idealized polymeric systems.[10-13] The pioneering work of Swank and Buck[14,15] demonstrated 30 years ago that long-range electronic energy transfer could occur between a site of electronic excitation and a luminescent quencher incorporated in a polymer via a dipole-dipole interaction. These and later studies on solid polymers did not have to invoke long-range multistep electronic energy migration in order to interpret the quenching data. More recently however, the importance of such processes in facilitating long-range energy transfer in polymers has been recognized. In light of this, Fredrickson and Frank[11] have proposed a simplified statistical model of long-range excitation transport via electronic energy migration in polystyrene (PS). This model assumes that a dipolar interaction with the nearest-neighbor chromophores underlies the electronic energy migration process. Short-range exchange and multipole interactions that may be important, particularly in solid films, have not been considered. While the exact mechanistic details of electronic energy migration in PS have not been addressed, the chief utility of the model lies in the fact that it can be used to define an experimental methodology to estimate distributions of conformational sequences that may serve as traps (e.g., dyads capable of forming excimers) and their role in the energy deactivation pathway.[16,17]

The basic features of PS photophysics have emerged from a considerable body of earlier work and are outlined in Scheme I.[18-24] In PS, as in a number of aromatic polymers, absorption of a photon by a particular chromophore producing an excited singlet state *may* be followed by an energy migration process where the excitation is no longer restricted to the original site of absorption but may be transported across a number of chromophores. During this process of migration, the mobile excitation may encounter trap sites in the polymer. Two types of intrinsic traps may be postulated. The first type, monomer traps, consists of isolated chromophores of slightly lower than the typical energy, which may be reversibly detrapped during their lifetime. These traps are the source of the weak "monomer emission" observed near 280 nm. Second, there are excimer traps, consisting of ring dyads oriented in such a way that they attain the excimer configuration during the residence time of excitation on one ring or the other. These traps are deeper than the monomer traps and once formed presumably do not dissociate to an appreciable extent during their lifetime. They are responsible for the broad, red-shifted "excimer emission" observed around 320 nm.

Scheme I
Photophysics and Excited-State Dynamics of Polystyrene



Time-resolved studies on PS in solution and in the solid state have shown that neither the monomer nor the ex-

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cimer emission have a resolvable rise time on the nanosecond time scale, thus placing a lower limit on the trapping rate of the order of $\sim 10^{10}$ s^{-1}.[22] The trap emission decays are well fitted to single-exponential decay functions, although a very weak delayed monomer emission has been reported in solution studies.[25] The chief rationale for the proposition that the monomer fluorescence is emitted by monomeric traps rather than the mobile monomeric excitation is that the radiative decay rate of the fluorescent state emitting at 280 nm ($\sim 5 \times 10^6$ s^{-1}) is at least 3 orders of magnitude lower than the rate of trapping of the mobile excitation at excimer sites. Consequently, the overall contribution to the monomer fluorescence quantum yield from the mobile "percursor states" is probably no more than 5×10^{-4}, or less than 10% of the observed monomer fluorescence.

The overlap between the monomer fluorescence and the electronic absorption spectrum of PS indicates a rather small Förster transfer radius ($R_0 \simeq 6$ Å),[26] thus rendering dipole–dipole energy transfer between adjacent chromophores on the same chain difficult. When other mechanisms of energy hopping (multipole processes and electron exchange) are discounted, intrachain migration is likely to be inefficient, and, consequently, the mobility of migrating excitation is presumed to be lower in dilute solution than in the solid state. In the PS homopolymer, it is difficult, if not impossible, to measure experimentally the efficiency of migration and trapping or the trap concentrations. However, if an extrinsic trap with known quenching characteristics can be incorporated into the polymer in a controlled fashion, then it should be possible, by studying the competition between the intrinsic and the extrinsic traps for the mobile excitation, to gain some insight into the excited-state dynamics in this system. These considerations have led us to prepare a series of random copolymers of styrene and a vinyl derivative of an electronic quencher and to study the luminescence properties of these copolymers in the solid state as well as in fluid solution. In the first part of this study carried out at room temperature, the relative contributions of static quenching of excited monomer and excimer traps via a one-step energy transfer to the quencher and dynamic quenching of the mobile excitation by stationary quencher traps will be evaluated as a function of the quencher concentration. Based on these results, certain conclusions related to the migration efficiency in solution and in the solid state are presented as well as an estimate of excimer trap concentration in copolymer films.

Experimental Section

Materials. 2-(2′-Hydroxy-5′-vinylphenyl)-2*H*-benzotriazole (2H5V) was synthesized by following a procedure published earlier.[27] Styrene was dried and vacuum-distilled twice prior to use. Mixtures of a free radical initiator (AIBN or peroxide), styrene, and 2H5V were made up in desired concentration ratios, placed in Pyrex tubes, deareated by bubbling in argon, and polymerized in a water bath. Earlier studies have indicated that the polymerization reactivity of 2H5V was close to that styrene and that random copolymers could be obtained by thermal copolymerization of the two monomers.[28] Subsequent to polymerization, the polymer mass was exhaustively extracted with methanol in a Soxhlet column for 168 h and then analyzed by high-performance liquid chromatography (HPLC) for unreacted monomer. Extraction was continued until no free styrene or vinyl-HPB could be detected. Following extraction, the polymer was further purified by two reprecipitations from methylene chloride solutions into methanol. The molecular weight of each polymer sample was determined by HPLC, employing a set of four ultramicro Styragel molecular exclusion columns (10-, 10^2-, 10^3-, 10^4-Å pore size), using narrow molecular weight polystyrene as the calibration standard. The concentration of pendant 2H5V groups in each copolymer was then determined by UV–vis absorption spectroscopy in methylene chloride solution. The extinction coefficient of the pendant 2H5V groups was assumed to be equal to that of the 2-(5′-methyl-2′-hydroxyphenyl)-2*H*-benzotriazole (5-methyl-HPB) derivative. In the films, quencher concentrations were calculated by assuming that the density of the copolymers is the same as that of pure PS, i.e., 1.06 g/cm^3. PS homopolymer was purchased from Polysciences, Inc., and exhaustively extracted and reprecipitated prior to use. Characterization data for all samples used in this work are provided in Table I.

Table I
Composition and Molecular Weight Data for Poly(styrene-*co*-2H5V) Copolymer Samples

2H5V, mol %	2H5V, mol/L	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	initiator
0.0	0.0	328 000	87 000	3.78	Polysciences
0.00155	1.55×10^{-4}	402 000	202 000	2.06	peroxide
0.00273	2.73×10^{-4}	463 000	218 000	2.12	peroxide
0.00616	6.16×10^{-4}	364 000	192 000	1.89	peroxide
0.0114	1.15×10^{-3}	410 000	200 000	2.05	peroxide
0.0285	2.88×10^{-3}	511 000	302 000	1.69	AIBN
0.0527	5.32×10^{-3}	511 000	302 000	1.69	AIBN
0.154	1.55×10^{-2}	480 000	280 000	1.71	AIBN
0.268	2.70×10^{-2}	240 000	133 300	1.80	AIBN
0.483	4.88×10^{-2}	242 600	132 500	1.83	AIBN
0.570	5.76×10^{-2}	306 000	167 200	1.83	AIBN
2.55	2.58×10^{-1}	241 700	116 400	2.08	peroxide
4.78	4.83×10^{-1}				peroxide

Solution studies were carried out by dissolving the polymers in requisite amounts of methylene chloride (Burdick and Jackson, glass distilled). Solid-state studies were performed on thin polymer films (25–75 μm) that were solution-cast from the same solvent under a nitrogen atmosphere and dried overnight in a vacuum oven.

Steady-State Fluorescent Studies. The steady-state fluorescence experiments were performed on a Perkin-Elmer MPF-3A spectrofluorimeter. The excitation wavelength was selected to be 260 nm, which corresponds to a maximum in the PS absorption spectrum and a minimum in the 2H5V absorption spectrum. The excitation bandwidth was typically 5 nm. A right-angle geometry was utilized for dilute solutions, and the optical density of these samples never exceeded 1.0. Concentrated solutions and solid films were examined at an angle of 35° in order to collect the maximum front-surface emission while minimizing the front-surface reflection.

Since HPB shows absorption in the range 250–350 nm, it has been necessary to correct the experimental data to account for this competitive absorption. Actually, two types of corrections have been made on the steady-state fluorescence data. One involves the competitive absorption by 2H5V groups with the PS phenyl groups at 260 nm. The second correction concerns reabsorption of the PS emission by 2H5V groups at 280 and 320 nm. For both corrections, the actual rate of extinction of exciting light was calculated as a function of sample thickness penetrated. Fluorescence intensity was then determined as a function of thickness, and the path of the fluorescent beam through the sample was mapped out by assuming isotropic light emission. The reabsorbed fluorescence flux was estimated by integration over this path. Again, in making these corrections, the extinction coefficients of the 5-methyl-HPB derivative have been used to approximate those of the copolymerized material. The estimated corrections for the films are given in Table II. For all but the highest 2H5V concentrations, the corrections are quite small, and thus any uncertainty associated with them should not materially alter the overall results and conclusions.

Time-Resolved Studies. Fluorescence lifetime studies were carried out by using the fourth harmonic of a Nd^{3+}:YAG laser at 266 nm as an excitation source. Approximately 1–5 mJ of energy were deposited per pulse and fresh samples were used to record each decay curve. Fluorescence was collected and monitored by a fast-rise (300 ps) silicon photodiode with matched amplifier. The signals were digitized on a Biomation 6500 transient recorder (2 ns/channel) and sent to a PDP-11/23 microcomputer for storage, averaging, and processing. While the

Table II
Correction Factors for Polystyrene Excimer Emission from Poly(styrene-*co*-2H5V) Films[a]

mol % 2H5V	correction factor for HPB screening at 260 nm (*S*)	correction factor for HPB reabsorption at 320 nm (*R*)	tot correction factor (*SR*)
0.0000	1	1	1
0.00155	1	1	1
0.00273	1	1	1
0.00616	1	1	1
0.0114	1	1.01	1.01
0.0285	1	1.02	1.02
0.0527	1	1.03	1.03
0.154	1.01	1.08	1.09
0.268	1.02	1.15	1.17
0.483	1.03	1.26	1.30
0.570	1.04	1.31	1.36

[a] Corrections assume ϵ_{PS}^{260} (in L m^{-1} cm^{-1}) = 207, ϵ_{HPB}^{260} = 1316, ϵ_{HPB}^{320} = 11483, and ϵ_{PS}^{320} = 0.

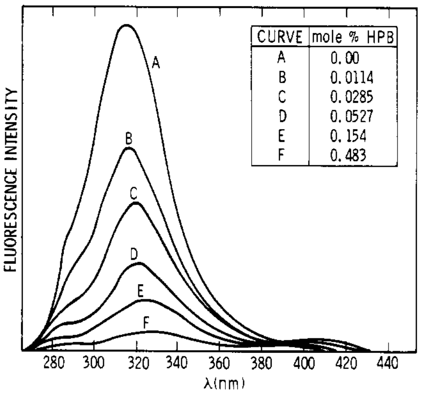


Figure 1. Steady-state emission spectra from selected poly(styrene-*co*-2H5V) films showing intensity quenching of the polystyrene monomer and excimer fluorescence. The excitation wavelength is 260 nm, and the spectra have been corrected for HPB absorption (see Tables II and III and associated text).

laser pulse width itself was 1 ns (FWHM), the overall system response function was somewhat slower (5 ns FWHM).

In some experiments, total fluorescence was monitored, including emission from the PS monomer and excimer traps. In order to isolate the excimer fluorescence, appropriate cutoff and band-pass filters were used. Time-resolved monomer fluorescence was difficult to detect due to its low intensity and short lifetime and the inherent insensitivity of the photodiode below 300 nm.

Results

Steady-State Emission. Front-surface emission spectra from representative PS–2H5V copolymer films recorded under steady-state irradiation conditions are shown (corrected for HPB absorption) in Figure 1. The strong band at $\lambda \simeq 320$ nm and the shoulder at $\lambda \simeq 285$ nm correspond to the well-known PS excimer and monomer fluorescence respectively. No other features are apparent except a very weak emission around 400 nm that seems to increase slightly with 2H5V content. This may be a weakly emitting PS–HPB exciplex or an impurity.

It is clear from Figure 1 that incorporation of 2H5V into the polymer results in quenching of the PS monomer and excimer emission. The PS excimer fluorescence intensities from the copolymer films relative to that of the PS homopolymer (and corrected for HPB absorption) are given in Table III.

Figure 2 is a plot of I_0/I vs. the quencher concentration, where I_0 is the unquenched excimer fluorescence intensity and I is the corrected excimer fluorescence intensity at a specified quencher concentration. Reliable quantitative estimates of monomer fluorescence intensities as a function of HPB concentration are difficult to obtain due to spectral overlap, low intensity, and scatter. It appears, however, that the monomer emission is quenched to a lesser extent than the excimer.

Table III
Relative Intensities of Polystyrene Excimer Fluorescence from Poly(styrene-*co*-2H5V) Films Corrected for HPB Absorption

mol % 2H5V	exptl intensity at 320 nm (*I*)	corrected intensity at 320 nm (*ISR*)
0.0000	1	1
0.00155	0.95	0.95
0.00273	0.88	0.88
0.00616	0.81	0.81
0.0114	0.61	0.62
0.0285	0.44	0.45
0.0527	0.26	0.27
0.154	0.14	0.15
0.268	0.09	0.11
0.483	0.057	0.075
0.570	0.045	0.062

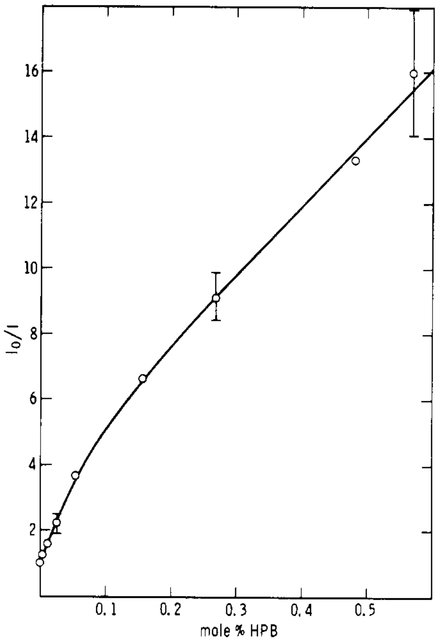


Figure 2. Dependence of the ratio of the unquenched polystyrene excimer fluorescence intensity (I_0) to the corrected quenched intensity (I) on the amount of 2H5V incorporated in the sample. Fluorescence was recorded in the steady-state mode, exciting at 260 nm and monitoring the excimer at 320 nm.

Steady-state emission spectra have also been recorded on the copolymer samples of up to 0.154 mol % 2H5V in dilute solutions of methylene chloride. Typical spectra are shown in Figure 3. These spectra have been recorded under conditions where the phenyl group concentration has been set to 5×10^{-3} M and thus the 2H5V concentration varied from zero to 7.5×10^{-6} M. Within experimental error, none of the copolymer samples examined showed quenching in dilute solution. Figure 4 shows steady-state fluorescence spectra from concentrated solutions of pure PS and from the 2.55 mol % 2H5V copolymer in methylene chloride. The pure PS spectrum (Figure 4a) recorded at a phenyl group concentration of 2 M looks very similar to that obtained in dilute solution. The uncorrected copolymer spectrum recorded at a phenyl group concentration of 2 M and thus an HPB concentration of 5.1×10^{-2} M (Figure 4b, curve i) is very weak. Due to the

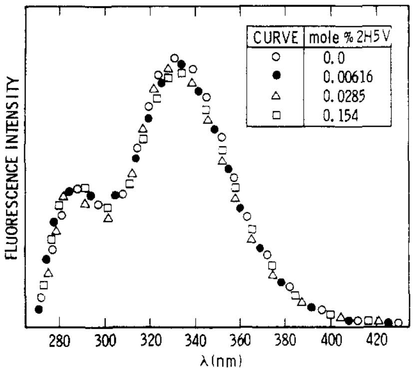


Figure 3. Steady-state emission spectra from dilute solutions of selected poly(styrene-*co*-2H5V) copolymers in methylene chloride. The phenyl group concentration in each case has been set to 5×10^{-3} M. The excitation wavelength is 260 nm. The data from the 0.154 mol % 2H5V copolymer sample has been corrected for HPB absorption as in the case of the films. The data from the other samples is reproduced as recorded.

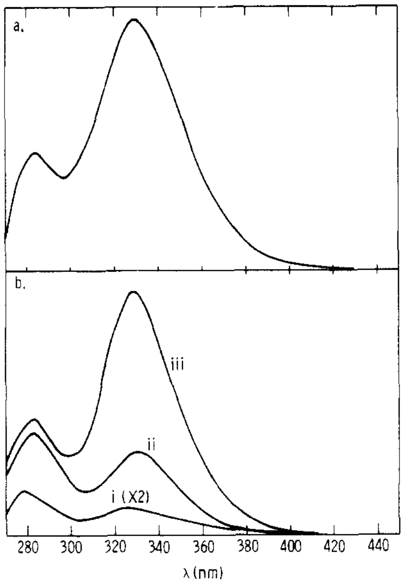


Figure 4. Steady-state emission spectra from concentrated solutions (200 gm/L) of (a) pure polystyrene and (b) PS-2H5V (2.55 mol % 2H5V) copolymer in methylene chloride. In 4b, curve i is the experimental data, curve ii is the experimental data corrected for HPB absorption showing that there is extensive quenching of the polystyrene excimer, and curve iii is the experimental data corrected for both absorption and Förster quenching of the monomer and excimer by HPB showing, by comparison to curve (a), that in concentrated solution the vast majority of quenching is accounted for by the Förster mechanism. The excitation wavelength in both cases is 260 nm and the Förster R_0 values for energy transfer from monomer and excimer to HPB used in correcting the copolymer data were 9.6 and 16 Å, respectively.

high concentration of 2H5V, the raw data must be corrected for HPB absorption, as in the case of the films. The corrected data shown in Figure 4b, curve ii indicate that the excimer fluorescence intensity has dropped 50–75% relative to the homopolymer while the monomer fluorescence has been only slightly affected. Thus the PS excimer fluorescence is quenched in highly concentrated solutions of the copolymer in contrast to the results obtained on dilute solutions; however, the quenching efficiency is ~ 5–10 times less than that found in films with equivalent 2H5V concentrations.

Time-Resolved Emission. Typical time-resolved excimer emission (300 nm < λ < 350 nm) traces for several PS–2H5V copolymer films are shown in Figure 5. In the case of pure PS (Figure 5a), the emission in the time domain 10–100 ns can be fit quite well by a single-exponential decay function with a decay time of 21.5 ± 0.5 ns, in good agreement with previous measurements in the solid state.[4,22] No change in the fluorescence decay behavior can be detected in films of up through 0.0527 mol % 2H5V (Figure 5b) even though, at this point, the steady-state excimer fluorescence intensity has dropped by 75% (see Figure 1).

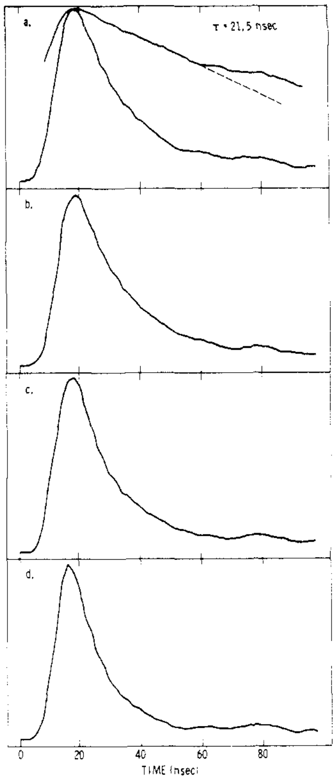


Figure 5. Time-resolved excimer emission (300–350 nm) from films of (a) pure polystyrene and selected PS–2H5V copolymers; (b) 0.0527 mol % 2H5V; (c) 0.268 mol % 2H5V; (d) 0.570 mol % 2H5V. No change is observed in the excimer decay up to a 2H5V content of 0.0527 mol % as shown in (b). Incorporation of further 2H5V does result in acceleration of the decay as shown in c and d. The excitation wavelength was 266 nm.

Excimer fluorescence decay accelerates in films with higher HPB content as shown in Figure 5, parts c and d. The decays, however, are no longer exponential but can be adequately fitted to the Förster quenching equation,[29] as follows:

$$I = I_0 \exp(-kt) \exp[-2\gamma(kt)^{1/2}] \qquad (1)$$

where k is the reciprocal of the fluorescence lifetime at zero quencher concentration and γ is the quenching efficiency. From least-squares fits of the experimental data to eq 1, it is possible to determine γ as a function of 2H5V content. Figure 6 shows a plot of this data from which C_0, the critical Förster concentration, or that quencher concentration at which the probability of quenching of the emissive species via the Förster mechanism is 0.5, can be calculated. The critical Förster radius, R_0, defined as the distance between a quencher and the emissive species at which the probability of quenching reaches 0.5, may then be calculated from C_0. The critical Förster parameters are related as follows:

$$\gamma = C/C_0 \qquad (2a)$$

$$C_0 = \frac{3000}{2\pi^{3/2}NR_0^{\,3}} \qquad (2b)$$

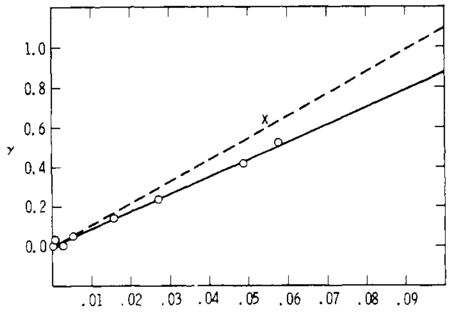


Figure 6. Dependence of γ on the HPB concentrations in copolymer films (○) and concentrated solution (×). The experimental γ values were determined by fitting the time-resolved excimer fluorescence decay data to eq 1. The calculated line (---) was derived by using an R_0 value of 17 Å determined from spectral overlap (eq 3). R_0 values determined from the experimental data of 16 Å in the solid state and 17.5 Å in solution are in excellent agreement with the theoretical value.

where C and C_0 are in units of mol/L, R_0 is in cm, and N is Avogadro's number.

The value of R_0 obtained from the slope of the line in Figure 6 is 16 Å. Using Förster theory, it is possible to calculate the critical Förster radius for the quenching of PS excimers by HPB groups following a method outlined by Berlman.[30] This method involves calculation of the overlap of the absorption spectrum of the quencher and the normalized emission spectrum of the donor. The relevant equation is

$$R_0 = \frac{9000\Phi_D k^2 \ln 10}{128\pi^5 n^4 N} \int F_D(\bar{\nu})\epsilon_Q(\bar{\nu}) \frac{d\bar{\nu}}{\bar{\nu}^4} \qquad (3)$$

where ν is the wavenumber, ϵ_Q is the molar extinction coefficient of the quencher, $\epsilon_D(\nu)$ is the normalized spectral distribution function of the donor, k^2 is an orientation factor equal to $^2/_3$ for a random distribution, Φ_D is the fluorescence quantum yield of the donor, and n is the index of refraction of the medium. The R_0 value calculated according to eq 3 for quenching of PS excimers by HPB is 17 Å, in good agreement with the experimental value. Calculated values of γ derived from the theoretical R_0 value are shown along with the experimental data in Figure 6. A theoretical determination of the R_0 value for PS monomer quenching by HPB has also been made by following the same method, and the calculated R_0 value in this case equals 9.6 Å. Thus Förster quenching of the monomer by HPB is considerably less efficient than that of the excimer.

A few transient measurements have been carried out on PS–2H5V copolymer films below 300 nm and beyond 360 nm. At wavelengths less than 300 nm a very weak, prompt emission with a lifetime of 1–2 ns is observed in all films. Based on its spectrum and lifetime, this emission is assumed to be the PS monomer emission.

At wavelengths greater than 360 nm, a weak prompt emission with a lifetime of 1 ns is observed in films with high 2H5V content. This is undoubtedly the 400-nm omission observed in the steady-state studies on copolymer films. Due to the weakness of the signal and its overlap with the tail of the PS excimer emission, it is impossible to characterize this feature any further.

Time-resolved measurements have also been made on fluid solutions of PS and the copolymers in methylene chloride. In dilute solution, at phenyl group concentrations of 5 × 10^{-3} M, the PS excimer fluorescence data in the region 10–50 ns can be fitted to a single-exponential decay function with a lifetime of 12.5 ± 0.5 ns for the homopolymer and all of the copolymers. No lifetime quenching of the PS excimer by HPB groups is observed in dilute solution. Representative data is shown in Figure 7. The observed lifetimes are in good agreement with that reported in the literature for the PS excimer in fluid solution.[22,24]

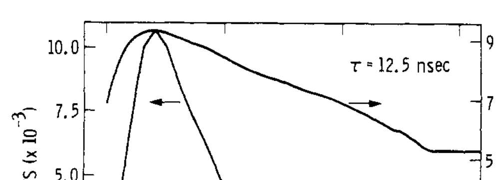


Figure 7. Time-resolved excimer emission (300–350 nm) from pure polystyrene in dilute solution of methylene chloride. Phenyl group concentration was 5 × 10^{-3} M, and the excitation wavelength was 266 nm. The measured lifetime is 12.5 ns.

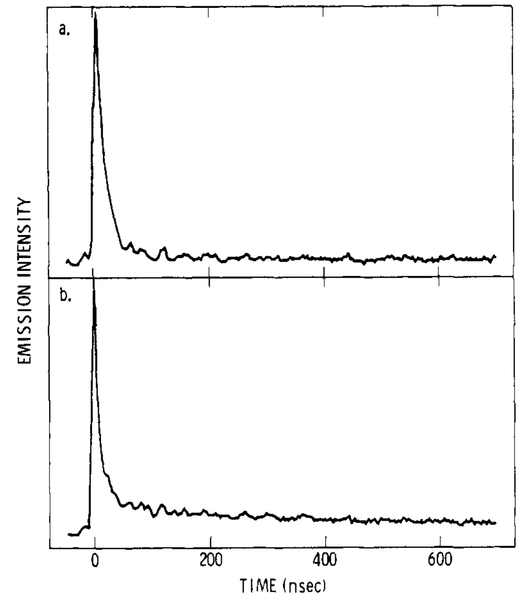
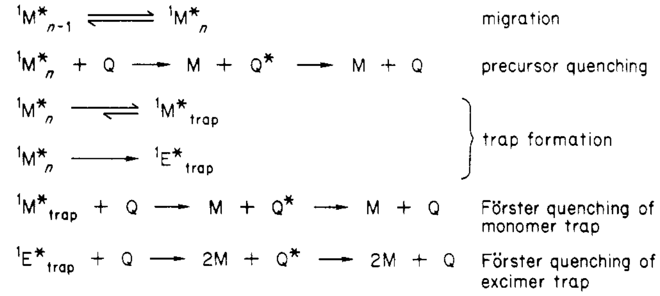


Figure 8. Time-resolved excimer emission (300–350 nm) from concentrated solutions (200 gm/L) of (a) pure polystyrene and (b) PS–2H5V copolymer (2.55 mol % 2H5V) in methylene chloride. The pure polystyrene decay is biexponential with decay times of 16 ns and ~2 μs. The copolymer decay shows a slow component with a decay time of ~1 μs, however, the fast component is not exponential and has been fit to the Förster decay expression (see text). The excitation wavelength in both cases was 266 nm.

A few time-resolved experiments have been carried out on the very concentrated solutions of the homopolymer and copolymers with high 2H5V content. Figure 8a shows the excimer fluorescence decay trace for pure polystyrene in methylene chloride at a phenyl group concentration of 2 M. The decay is biexponential, showing a fast component of 16.0 ± 0.5 ns, which is intermediate between the excimer lifetime found in dilute solution and in the solid state, and a weak, slow component of ~2 μs. Figure 8b shows the excimer fluorescence decay trace for the 2.55 mol % 2H5V copolymer in methylene chloride at a phenyl group concentration of 2 M and a 2H5V concentration of 0.051 M. Again, there is a weak, slowly decaying component that can be fit to a single-exponential decay of 1-μs lifetime. After subtracting the slowly decaying component from the trace, the prompt component is found to be no-

Scheme II
Quenching Mechanisms in Polystyrene



nexponential and adequately fitted by the Förster equation as described above. Thus we find that lifetime quenching of the PS excimer by the HPB groups does occur in concentrated solutions. The measured value of R_0 for quenching of PS excimers by HPB in concentrated solution is found to be 17.5 Å by fitting the data to eq 1. Thus, there is excellent agreement between the R_0 value for PS excimer quenching by HPB groups measured in concentrated solution and that measured in the solid state or calculated from eq 3.

Discussion

Combination of steady-state and transient data provides clear evidence of a dual quenching mechanism for the PS excimers in the copolymer films. The facile intensity quenching, unaccompanied by an acceleration of the fluorescence decay at low HPB levels, can only be explained in terms of interception and quenching of a precursor state, presumably the mobile monomer excitation, prior to its being trapped at the excimer sites. Subsequently, as the HPB level is increased, the excimers themselves are quenched via a static, long-range dipole–dipole interaction, resulting in a shortening of their lifetime as described by Förster kinetics. The quenching mechanisms are outlined below in Scheme II. The quantum efficiency of Förster static quenching is given by the expression[31]

$$f = \pi^{1/2}\gamma \exp(\gamma^2)[1 - \mathrm{erf}\ (\gamma)] \qquad (4)$$

Utilizing the experimentally determined γ's and eq 4, it is possible to decompose the overall excimer quenching curve (Figure 2) into its two constituent quenching components as shown in Figure 9. Förster quenching of the excimers is seen to contribute significantly only at high HPB levels. Even at the highest levels studied, the static (Förster) quenching contributes only ~15% to the total quenching efficiency. The precursor quenching or trapping of mobile excitation by HPB groups is the dominant quenching mechanism in the solid state.

The phenomenon of singlet energy migration in a number of aromatic polymers has generally been accepted in the literature. In the case of polystyrene, however, previous studies have provided only indirect or qualitative evidence of its existence, e.g., based on fluorescence depolarization measurements.[22] The finding of precursor quenching at very low quencher concentrations, based on the steady-state and time-resolved data reported here, presents strong "direct" evidence for the existence of mobile monomer excitation in solid polystyrene films.

Examination of the data in Figure 9 shows that the precursor quenching curve is not linear in the solid state, as would be expected if Stern–Volmer kinetics applied. Rather, there is a saturation effect (i.e., the curve flattens out) as the HPB level increases. There are at least four possible explanations to explain this behavior. First, all of the excitation sites may not be equivalent. Some of them may be so close to an excimer-forming site that the excimer is formed before any migration takes place, thus precluding the precursor quenching process. Webber has proposed the existence of these two types of excited monomers (migratory and nonmigratory) to explain the saturation effects observed in singlet–singlet annihilation studies on naphthalene and biphenyl polymers.[32] Second, it is possible that a third type of quencher (besides excimer traps and HPB groups), whose concentration varies in a *nonlinear* fashion with the HPB concentration, acts to intercept the migrating excitation. Such quenchers could be branch points or end groups created or altered due to the interaction of the initiators with the changing 2H5V monomer concentration during the polymerization process. Third, some of the HPB groups incorporated in the polymer may be atypical in the sense that they cannot intercept migrating excitation although they are still capable of acting as static (Förster) quenchers. Such a condition could arise from polymerization reactivity differences that may cause formation of nonrandom sequences at high HPB levels. The conformations associated with such sequences could be such that the efficiency of interception of migrating monomer would be lowered relative to the efficiency of Förster quenching of excimers. And finally, an intriguing, and somewhat speculative explanation may be offered, based on the observation that if the scale of electronic energy migration is comparable to van der Waals radii of the chromophores, it will not be possible to model the energy diffusion phenomenon as an isotropic three-dimensional random-walk process. The path of the migrating excitation may then describe finite compact clusters, and the quenching efficiency will depend

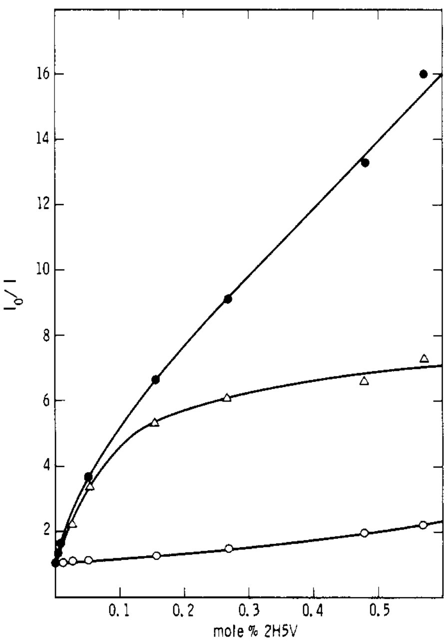


Figure 9. Dependence of total excimer quenching data (●) in films and its components, Förster quenching (○) and precursor quenching (△), on 2H5V content. The magnitude of the Förster quenching component was determined from eq 4 by using γ values measured in time-resolved emission studies. The magnitude of the precursor quenching component was determined by correcting the steady-state emission intensity data for Förster quenching. Thus, the lower curve is what would be observed if only Förster quenching was occurring, the middle curve is what would be observed if only precursor quenching was occurring, and the upper curve is what is observed experimentally with both quenching mechanisms active.

on the distribution of quenchers in these finite clusters.[36] Under these conditions, a certain fraction of the excitations may never encounter a quencher, leading to an experimental observation that a certain fraction of the mobile excitation is not amenable to dynamic quenching. While the experimental data cannot distinguish between these possibilities, it is clear that approximately 15–20% of the excitation is unavailable for quenching via singlet energy migration.

The quenching of the monomer emission in copolymer films by HPB is qualitatively similar to that observed for the excimer. It appears from the steady-state emission studies that the quenching rate is somewhat slower, perhaps simply reflecting the less efficient Förster quenching of monomer traps. Unfortunately, due to the low intensity of the monomer emission, its spectral overlap with the excimer and its short lifetime, it has been impossible to measure reliable quenching rate data.

The 400-nm emission, which has been observed to grow in the copolymer films at high HPB levels, is probably not from excited HPB groups. HPB is known to show vertical, "blue" emission at 405 nm and "red" emission from the proton-transferred zwitterionic state at 600 nm, depending on the nature of its environment.[34,35] However, direct excitation of the HPB at 355 nm in the copolymer films produces only the red emission. Furthermore, the 1-ns lifetime of the 400-nm emission in the copolymers is considerably longer than the 25–75 ps measured for the blue emission in various solvents.[33,34] The species responsible for this long-wavelength emission could be a phenyl–HPB exciplex or it could be simply an impurity or an end group whose concentration is related to that of HPB.

The precursor quenching data for the excimer provides a measure of the concentration of excimer-forming sites in the polymer. At the point where the excimer emission intensity has dropped by 50% (0.025 mol % or 2.5×10^{-3} M 2H5V), the probability of energy transfer from the migrating monomer to HPB or to an excimer site must be equal. At this point, the contribution of static quenching of excimer traps is negligible. If it is assumed that quenching or excimer formation involves migration, followed by a one-step Förster transfer to either an HPB moiety or an excimer trap site, respectively, then it follows that

$$C_E = C_{HPB}(R_0^{HPB}/R_0^E) \qquad (5)$$

where C^E and C^{HPB} are the concentrations of excimer trap sites and HPB groups and R_0^E and R_0^{HPB} are the critical distances for monomer to excimer and monomer to HPB energy transfer. The value of R_0^{HPB} calculated previously from Förster theory (eq 3) is 9.6 Å, while the value of R_0^E can be assumed to be equal to the R_0 value of PS transferring energy to itself, which is reported to be 6 Å.[30] This assumption is based on the fact that an excimer site cannot be distinguished from a typical monomer unit by migrating excitation. Substituting these R_0 values into eq 5 along with the HPB concentration at 50% quenching yields a value of 1.04×10^{-2} M for the concentration of excimer sites or approximately 1 per 950 monomer units. The above calculation assumes that energy transfer into an excimer site occurs via a dipole–dipole interaction. To our knowledge, this is the first experimental estimate of the concentration of excimer sites in solid polystyrene. Since R_0 is quite small, dipole–dipole interaction may no longer be a good approximation, as higher order terms may begin to dominate the transfer process. If this were the case, the true energy-transfer distance from monomer to excimer site would be longer than 6 Å, and thus the concentration of excimer trap sites calculated by this method actually represents an upper limit. The average number of hops prior to trapping cannot be calculated from our data unless an assumption is made concerning the dimentionality of the energy migration process. However, if a random distribution of excimer trap sites is assumed, a given excited monomer may be no more than 20 Å from the nearest excimer trap site at any given time and consequently, the *average* number of hops prior to trapping may be quite small.

The steady-state monomer and excimer emission spectra of the PS–2H5V copolymers in dilute solution show that there is little if any intensity quenching under these conditions. Furthermore, the time-resolved emission studies in dilute solution show no excimer lifetime quenching effects due to added HPB. The absence of significant lifetime quenching of the excimers under these conditions via one-step Förster transfer is not surprising since the bulk concentration of quencher is very low ($\sim 10^{-5}$ M). The absence of precursor quenching, however, is somewhat surprising. It seems that, in contrast to the solid state, there is little energy migration in dilute solution. The absence of any measurable precursor quenching in dilute solutions leads to the suggestion that *intrachain* energy migration may not be efficient and that the migration observed in the solid state is dominated by interchain processes. In highly concentration solutions of the copolymers, both intensity and lifetime quenching are observed. When the steady-state emission spectrum in Figure 4b, curve ii, is corrected for Förster quenching of the monomer and excimer by HPB groups, the spectrum in Figure 4b, curve iii, results. Comparison of the spectrum in Figure 4b, curve iii, with that in Figure 4a shows that even in highly concentrated solutions (2 M in PS) there is no evidence of precursor quenching. This observation is an indication that the phenomenon of electronic energy migration cannot be readily modeled as a three-dimensional percolation process[38] and may indeed follow fractal kinetics.[37] We propose to further investigate this possibility by studying the energy-transfer kinetics in PS solutions in the concentration range 2–10 M in PS and also as a function of temperature.

Conclusions

The results of this study of the emission spectra of films and solutions of PS–2H5V copolymers has led to three principal conclusions, which are summarized below:

(1) Chemical incorporation of small quantities of 2H5V into PS results in efficient quenching of the PS monomer and excimer fluorescence in the solid state.

(2) The excimer, and also the monomer fluorescence, is quenched via two mechanisms in the solid state. The first involves interception of migrating electronic excitation by energy transfer to HPB before it is trapped in fluorescent monomer and excimer traps, resulting in intensity quenching only. The second involves static (Förster) quenching of the excited trapped species, resulting in both intensity and lifetime quenching.

(3) Singlet-energy migration occurs in PS in the solid state but probably not in solution, thus limiting quenching to only the static mechanism in fluid media.

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Registry No. Poly(styrene-*co*-HPB) (copolymer), 81273-49-6.

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Ordered Structure in Aqueous Polysaccharide. 5. Cooperative Order–Disorder Transition in Aqueous Schizophyllan†

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ABSTRACT: Optical rotation and heat capacity measurements were made on aqueous solutions of schizophyllan, a triple-helical polysaccharide. The heat capacity data showed that aqueous schizophyllan, either isotropic or cholesteric, exhibited a sharp thermal transition located around 279 K, and the transition enthalpy per mole of the polysaccharide repeating unit (648.6 g) was (2.83 ± 0.1) kJ mol^{-1} in H_2O and 3.96 kJ mol^{-1} in D_2O. The corresponding change in optical rotation was observed in the same temperature range, indicating that both changes originated from some common molecular event, presumably an order–disorder transition in a relatively short range surrounding the triple helix of schizophyllan. The transition was found to occur cooperatively among the saccharide units on the helix between the ordered and disordered states, although it was not of the all-or-none type. It was concluded that at lower temperature side-chain glucose residues of schizophyllan, helped by the surrounding water molecules, form a well-organized structure developing over a large distance along the helix axis, which becomes disordered with increasing temperature in a highly cooperative manner.

Aqueous solutions of schizophyllan, a triple-helical polysaccharide, form a cholesteric mesophase at high concentration;[1-3] Figure 1 gives the chemical structure of schizophyllan. It was shown in our previous publication[4] that such cholesteric solutions underwent a thermal transition around 280 K, as revealed by sharp changes in optical rotation and cholesteric pitch with temperature. These changes were accompanied by endothermic DSC peaks in the same temperature range. It was suggested that this transition may be associated with solvation of schizophyllan triple helices with water followed by reori-

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