

Intramolecular excimer formation and energy migration in head-to-head polystyrene

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Head-to-head polystyrene (HH-PS), in which the phenyl rings are separated by either two or four carbon atoms, displays predominantly fluorescence from monomeric units. No excimer emission is observable even when the polymer is dissolved in increasingly thermodynamically poorer solvents. This is strongly suggestive that excimer formation in normal head-to-tail polystyrene (HT-PS) occurs primarily between nearest-neighbouring chromophores. Intramolecular energy migration is shown to be negligible in both fluid and solid solutions of HH-PS. This is in direct contrast to the case with HT-PS in fluid solutions in which an energy migration coefficient of $7.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and an energy migration frequency of $4.1 \times 10^{11} \text{ s}^{-1}$ were determined.

(Keywords: excimer formation; energy migration; polystyrene, excimer emission, fluorescence)

INTRODUCTION

Intramolecular excimer formation and excitation energy migration in polymers have been intensively investigated¹⁻³. With dilute solutions, the results have led to somewhat contradictory conclusions about the relative importance of non-nearest- versus nearest-neighbouring chromophore interactions. For example, Fox *et al.*⁴ have shown that for alternating copolymers of styrene or vinyl naphthalene with methyl methacrylate, no excimer emission is observable. In addition, contracting the coil dimensions of the copolymers by dissolving them in increasingly thermodynamically poorer solvents led to no enhancement of excimer emission. These results were taken to demonstrate that nearest-neighbour interactions predominate in excimer formation in the homopolymers, the complexes being formed according to Hirayama's⁵ rule ($n=3$). The results of Irie *et al.*⁶ indicating that the ratio of excimer to monomer emission intensities for poly(1-vinyl naphthalene) decreases in poorer solvents, support this interpretation. Conversely, the observation⁷ of strong excimer fluorescence from dilute solutions of poly(acenaphthalene), in which nearest-neighbour contacts are impossible, argues strongly for the formation of non-nearest-neighbour complexes. Similarly, Somersall and Guillet⁸ have shown that for poly(naphthyl methacrylate), decreasing solvent goodness yields greatly enhanced excimer emission intensity, presumably due to an increasing number of across-loop contacts.

In the case of polystyrene, energy migration and excimer formation have been studied as a function of such parameters as tacticity^{9,10}, orientation in the bulk phase¹¹ and copolymerization^{12,13}. Inoue *et al.*¹⁴ have described the synthesis of head-to-head polystyrenes, HH-PS. In contrast to head-to-tail polystyrene, HT-PS, normally obtained via free-radical polymerization of

styrene monomer, the phenyl rings in this polymer are separated by either two or four carbon atoms. Excimer formation according to Hirayama's rule would thus be precluded. A comparison of the extent of intramolecular excimer formation and energy migration between HH-PS and HT-PS would then provide an indication of the relative importance of nearest versus non-nearest-neighbouring interactions in polystyrene. We wish to present here the full results of these studies, preliminary reports of which have appeared elsewhere^{1,5}.

EXPERIMENTAL

Ethyl benzene (EB) was washed with conc. H_2SO_4 until the acid layer was colourless. It was then washed with 0.1 N NaOH and water, dried over anhydrous MgSO_4 and distilled. Dibenzyl (DB) was recrystallized twice from warm methanol followed by drying for several days under a vacuum. 1,2-Dichloroethane (DCE) was washed with conc. H_2SO_4 , dilute KOH and then water. It was dried over CaCl_2 , refluxed over P_2O_5 and distilled prior to use. Cyclohexane (CH) (Fisher Spectranalyzed) and methanol (MeOH) (Fisher) were distilled prior to use. Tetrahydrofuran was refluxed for 4 to 5 h over LiAlH_4 , distilled and stored over sodium metal. Ethanol was dried with magnesium ethoxide and distilled prior to use. Acetophenone and isopropanol were also distilled.

Atactic, head-to-tail polystyrene (HT-PS) was prepared via free-radical polymerization at 60°C of the purified monomer in thoroughly degassed benzene solution using 0.1 mol% azobisisobutyronitrile (AIBN) as initiator. Purification was effected via multiple reprecipitation from dilute benzene solutions into a large excess of methanol.

The synthesis of head-to-head polystyrene (HH-PS) was accomplished by the free-radical polymerization of 2,3-diphenylbutadiene, using AIBN as initiator, as de-

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scribed by Inoue *et al.*¹⁴ The resultant poly(2,3-diphenylbutadiene) (PDPB) was reduced using potassium metal in dry THF. The reduction step was repeated five to six times until the u.v. absorbance spectrum of HH-PS no longer changed. The synthetic sequence is outlined in Figure 1 while Figure 2 illustrates the u.v. absorbance spectra of HH-PS and HT-PS. It can be seen that, while the spectra are very similar, HH-PS does exhibit a small absorbance tailing out above 300 nm. This tail is attributed to a small amount of 2,3-diphenyl-2-butene residues in the chain, the presence of which is not affected by additional hydrogenation steps. Attempts to reduce the polydiene using alternative reagents such as H₂/Pt/C, LiAlH₄-NiCl₂¹⁶ and diimide¹⁷⁻¹⁹ were completely unsuccessful.

Ultra-violet absorbance spectra were recorded using a Cary 219 ultra-violet-visible spectrophotometer. Fluorescence spectra were measured using either a Spex Fluorolog or SLM 8000S single-photon-counting fluorescence spectrometer. The latter instrument is equipped with a microprocessor capable of correcting the recorded fluorescence spectra for instrumental distortions. Unless otherwise specified, spectra were measured using right-angle viewing of solutions contained in 1 cm² quartz cells. The excitation wavelength was 255 nm and slit widths were kept at a 4 nm bandpass. The solutions were deaerated by thorough purging with oxygen-free argon.

Singlet lifetimes were determined with a single-photon-counting fluorescence lifetime apparatus (Photochemical

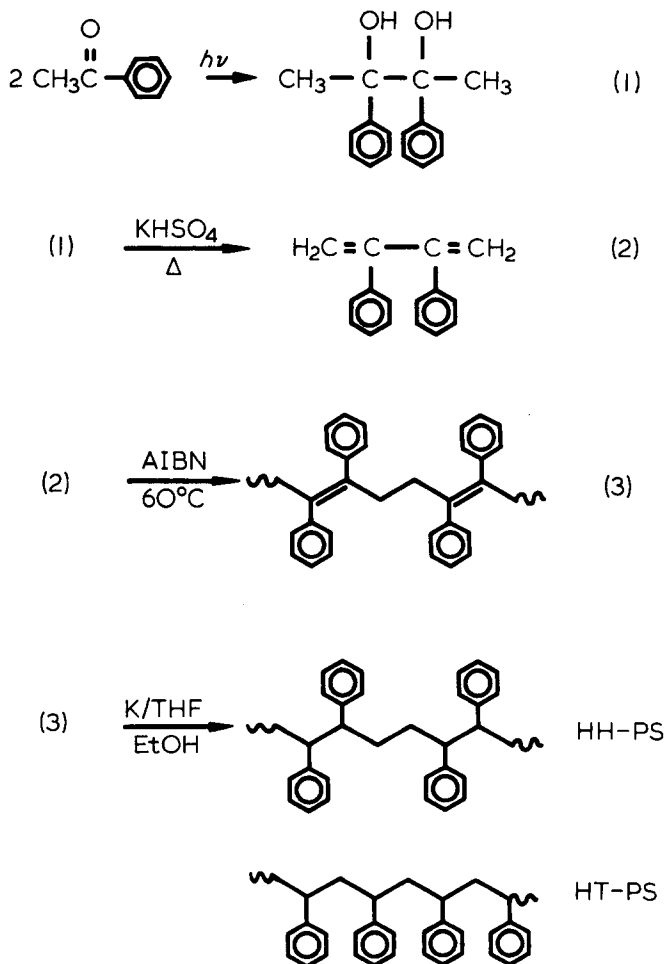


Figure 1 Synthesis of head-to-head polystyrene

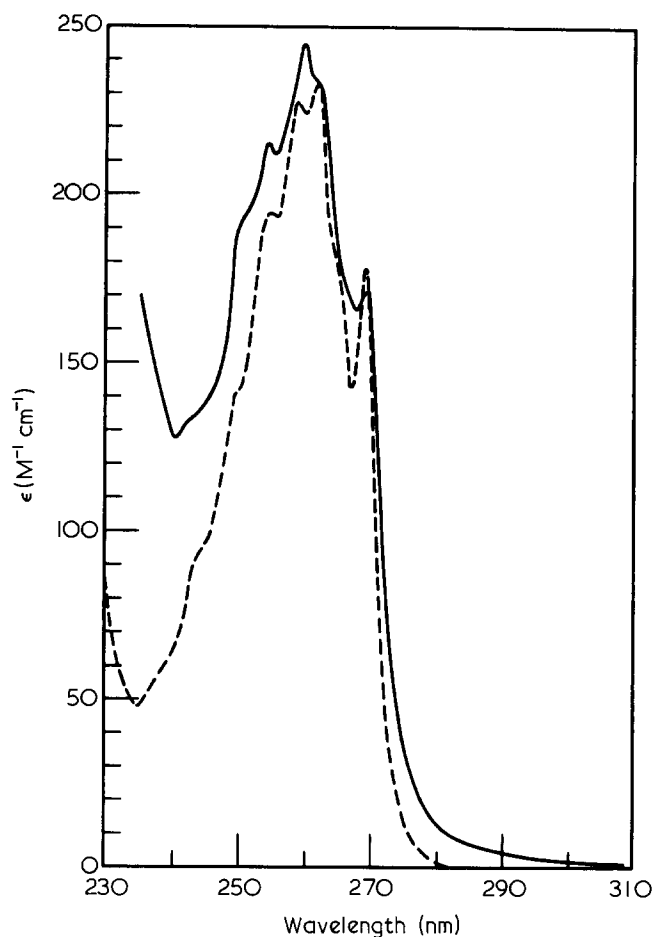


Figure 2 Absorbance spectra of HH-PS (—) and HT-PS (---) in DCE solutions

Research Associates Inc.) with its time-to-amplitude converter (TAC) output pulses passed through a fast analogue-to-digital (A/D) converter into a Terak 8510 microcomputer for temporary data storage and display. The Terak was in turn interfaced with a PDP 11/55 multiuser computer system for the subsequent analysis, long-term storage and hard-copy graphics of the acquired data.

RESULTS AND DISCUSSION

The fluorescence spectrum of HH-PS in deaerated DCE solution is shown in Figure 3 along with the spectra of EB, HT-PS and the PDPB precursor to HH-PS. The spectrum of DB was almost identical to that of EB. It can be seen that the fluorescence of HH-PS is primarily attributable to emission from monomeric phenyl rings, the 293 nm peak maximum being slightly red-shifted from the 284 nm maxima of the model compounds EB and DB. In contrast, the emission of HT-PS is dominated by a broad excimer band with a maximum at 335 nm with only a small shoulder at 285 nm representing fluorescence from monomeric species.

It can also be seen from Figure 3 that the spectrum of HH-PS displays a long tail extending out to about 460 nm. It possesses two weak maxima at 358 nm and 377 nm, wavelengths corresponding to the first two vibronic bands in the fluorescence spectrum of PDPB. The tail in HH-PS is therefore in all probability due to emission from residual 2,3-diphenyl-2-butene units in the

polymer, the presence of which are implied from the u.v. absorbance spectra in *Figure 2*. This precludes a definitive statement as to the complete absence or presence of a very small amount of excimer emission in HH-PS. Regardless, the major conclusion remains that fluorescence from HH-PS occurs primarily from uncomplexed monomeric phenyl rings and that excimer emission is extremely weak if not absent altogether. This behaviour is opposite to that observed for HT-PS and is strongly suggestive that the primary route to intramolecular excimer formation in polystyrene involves nearest-neighbour interactions.

In a good solvent, such as DCE, the HH-PS polymer coils are expanded, maximizing polymer-solvent interactions at the expense of polymer-polymer interactions. When successively larger aliquotes of a non-solvent, such as methanol, are added to the solution the coils will contract, thereby increasing the number of potential across-loop contacts of non-nearest-neighbouring chromophores. If such interactions contribute to excimer formation, their relative importance should be reflected in an increasing intensity of excimer emission at the expense of monomer fluorescence. Accordingly, the emission spectra of 10^{-3} M HH-PS and HT-PS in mixed DCE/MeOH solvents of composition 24:1, 11.5:1, 4:1 and 2:1 by volume were measured. The DCE/MeOH (2:1 v/v) solvent was so poor that only hazy solutions were obtained, indicating that the polymers were on the verge of precipitating out. The spectra of EB and DB in the same solvents were also recorded to ensure that the addition of MeOH did not result in noticeable wavelength shifts of monomer emission. In all cases, increasing the amount of MeOH in the solvent mix had no ascertainable effect on the shapes of the fluorescence spectra. This again strongly implies that the major excimer-forming site in polystyrene consists of two phenyl rings separated by three carbon atoms, complexation taking place according to Hirayama's rule.

While this study was in progress, Lindsell *et al.*²⁰ issued a report on the fluorescence of HH-PS. Their spectrum, recorded using methyltetrahydrofuran (MTHF) as solvent, was very similar to that shown in *Figure 3*. However, on decreasing solvent goodness by using solvent mixes containing increasingly larger proportions of the non-solvents methanol (MeOH) or cyclohexane (CH), these authors reported that the intensity of the emission attributable to residual 2,3-diphenyl-2-butene units greatly increased relative to that from monomer. This behaviour was attributed to significantly enhanced energy transfer from the excited phenyl chromophores to the 2,3-diphenyl-2-butene residues in the same chain. These observations are contrary to the results outlined above for the current study, using DCE/MeOH solvent mixes.

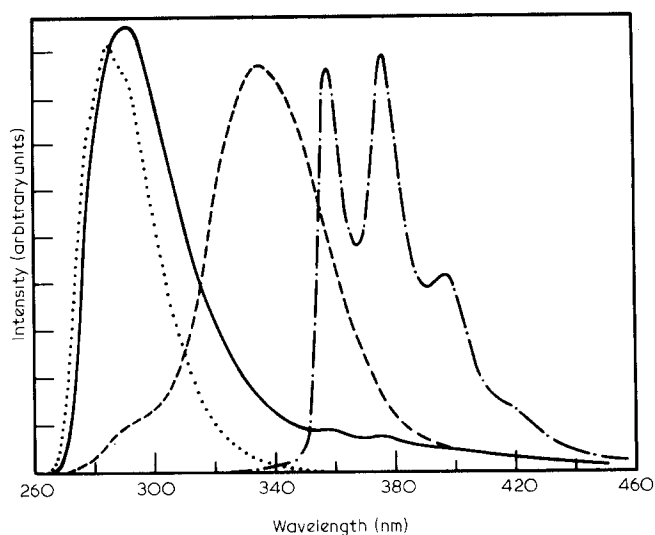


Figure 3 Fluorescence spectra in deaerated DCE solutions, 10^{-3} M in phenyl rings: ·····, EB; —, HH-PS; ---, HT-PS; - · - · -, PDPB

In order to examine these apparently contradictory results further, the spectrum of HH-PS in neat CH was measured. CH was a sufficiently poor solvent that maximum polymer solubility was reached at about 10^{-4} M and required gentle warming to effect dissolution. In deaerated CH solutions, the fluorescence of HH-PS was identical to that recorded in DCE (*Figure 3*). There was no noticeable increase in diphenylbutene residue emission intensity relative to that from monomeric phenyl rings.

If dissolving the HH-PS in increasingly poorer solvents indeed results in significant enhancement of energy transfer from the excited phenyl chromophores to the diphenylbutene residues, the effect should be noticeable by a marked reduction in the quantum yield of fluorescence, ϕ_F , of the donor groups. Quantum yields were therefore measured from the areas under the corrected fluorescence spectra, using a value of 0.18 for EB in CH as the standard²¹. The results are listed in *Table 1*. It can be seen that ϕ_F values for HH-PS are considerably reduced from those of the model compounds EB and DB. This is at least partially attributable to reabsorption of the HH-PS isolated phenyl ring emission by the diphenylbutene residues (see *Figures 2* and *3*). The magnitude of ϕ_F at 0.005 for HT-PS compares well with a literature value³ of 0.004. The major point, however, is that ϕ_F for HH-PS in the good solvent DCE was identical to that measured in CH, a poor solvent. In conjunction with the lack of any noticeable increase in emission intensity from diphenylbutene residues, as previously noted, this argues strongly

Table 1 Fluorescence parameters in fluid solutions^a

Compound	Solvent	ϕ_F	$k_q\tau_0$ (M^{-1})	τ_0 (s) $\times 10^9$	k_q ($M^{-1} s^{-1}$) $\times 10^{-9}$
EB	DCE	0.16	130	13.1	9.9
	CH	0.18 ^b		12.8	
DB	DCE	0.13	130	14.2	9.2
	CH	0.05		13.2	
HH-PS	DCE	0.05	25.7	14.4	2.0
	CH	0.05		14.4	
HT-PS	DCE	0.005	14.3	0.42 ^c	34.0

^a Deaerated by argon purging, 23°C

^b From ref. 21

^c From ref. 10

against enhanced intramolecular energy transfer as proposed by Lindsell *et al.*²⁰

It is not immediately clear why the results of the current study are not compatible with those of Lindsell *et al.*²⁰ in this respect. These authors report that their HH-PS sample showed no discernible trace of the 2,3-diphenyl-2-butene residues in its u.v. spectrum. This situation could not be achieved in this study (Figure 2) despite repeated attempts. However, a higher concentration of diphenylbutene trap sites within the polymer chain should lead to an enhancement of the extent of energy transfer to them from singlet excited monomeric phenyl rings. Reasonably, the effect should be even more noticeable with the polymer used in this study.

It should be noted, as well, that the MTHF solvent used by Lindsell *et al.*²⁰ shows significant u.v. absorbance at 260 nm, the excitation wavelength used by these authors. This raises the possibility of the occurrence of photosensitization by excited solvent molecules, in addition to direct excitation. The effect would be more important for monomeric phenyl rings than for diphenylbutene sites due to the much higher concentration of the former. As the MTHF is replaced by successively larger proportions of MeOH or CH₂ solvents which do not absorb at 260 nm, the extent of sensitization by solvent would decrease, leading to an enhancement of diphenylbutene emission intensity relative to that from monomeric phenyl rings. The temperature dependence of the fluorescence spectra of HH-PS in MTHF, reported by Lindsell *et al.*²⁰ can also perhaps be rationalized on the basis of photosensitization, when the decrease in the rate constant for material diffusion with decreasing temperature is taken into account.

Fluorescence quenching studies on DCE solutions of the compounds were carried out using CCl₄ as quencher. The results are shown in Figure 4 plotted according to the equation:

$$I_0/I_Q = 1 + k_q\tau_0[Q] \quad (1)$$

where I_0 and I_Q are the emission intensities of singlet excited monomeric phenyl rings in the absence and the presence of the quencher, Q, respectively. The bimolecular quenching rate constant is represented by k_q and τ_0 is the unquenched fluorescence lifetime. Values of $k_q\tau_0$, taken as the slopes of the lines in Figure 4 are listed in Table 1. Also listed are the fluorescent lifetimes, τ_0 , and the calculated magnitudes of the quenching rate constants, k_q .

The diffusion-controlled rate of quenching can be calculated from the Smoluchowski equation as modified by Ware and Novros²² and Yguerabide *et al.*²³:

$$k_{diff} = \frac{4\pi RDN}{1000} \left(1 + \frac{R}{(D\tau_0)^{1/2}} \right) \quad (2)$$

where R is the sum of donor and acceptor collisional radii and D is the sum of the acceptor+donor diffusion coefficients. N is Avogadro's number and τ_0 is the unquenched donor lifetime.

For the small molecule donor-acceptor pair EB and CCl₄, respectively, k_{diff} can be calculated from (2) using a value of $1.53 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for the diffusion coefficients of EB and CCl₄ as determined by Heisel and Laustriat²⁴. The sum of the collisional radii, R , is taken²⁵ as $5.0 \times 10^{-8} \text{ cm}$ and τ_0 as $13.1 \times 10^{-9} \text{ s}$ (Table 1), resulting in a value of $12.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for k_{diff} . If an efficiency of

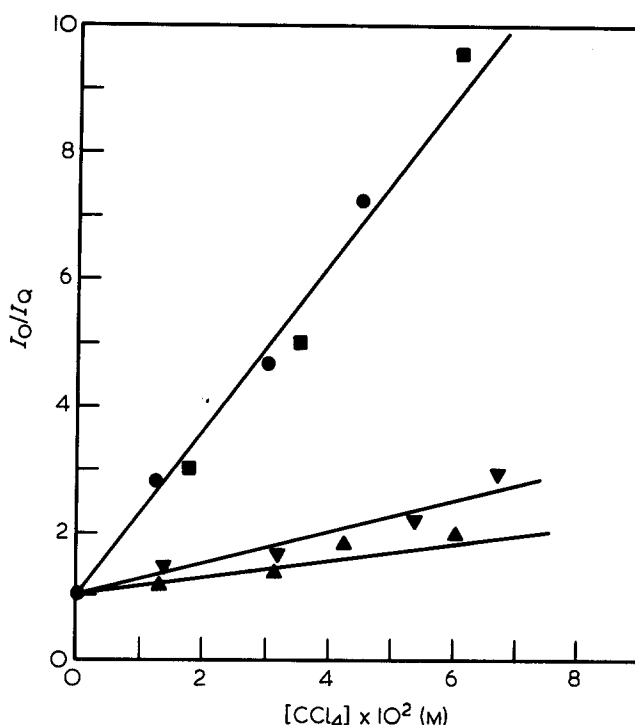


Figure 4 Fluorescence quenching in fluid solutions: ●, EB; ■, DB; ▼, HH-PS; ▲, HT-PS

energy transfer, α , is defined as the ratio k_q/k_{diff} , a value of 0.79 is obtained for the quenching of EB by CCl₄. This compares well with values reported by Ishii *et al.*²⁵ for a variety of alkyl benzenes quenched by CCl₄.

The assumption that is commonly made in the application of (2) to polymer-small molecule interactions is that the collisional radii are identical in donor and acceptor. This implies that the quencher can be considered to be interacting only with the excited phenyl ring and not the entire macromolecule. Furthermore, Heskins and Guillet²⁶ have suggested that the diffusion of the centre of mass of the polymer coil in solution is negligible in comparison to that of the small molecule quencher. Therefore, only the diffusion coefficient of the quencher CCl₄ enters into (2). Values of k_{diff} for HH-PS and HT-PS can thus be calculated as equal to $6.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $9.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively.

From Table 1, it is seen that CCl₄ quenches EB with a rate constant, $9.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, that approaches the diffusion-controlled limit, k_{diff} , of $12.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. For HT-PS, however, the value of $34.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for k_q is considerably higher than the calculated value of k_{diff} at $9.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The increased rate of quenching might be attributable²⁴ to intramolecular energy migration. In this case, equation (2) can be modified^{27,28} to include the possibility of an energy migrational term assuming some importance. The result is a rate constant, k_{diff} , which now reflects a collision rate arising from both diffusion and energy migration:

$$k_{diff} = \frac{4\pi RN(D+\Lambda)}{1000} \left(1 + \frac{R}{[(D+\Lambda)\tau_0]^{1/2}} \right) \quad (3)$$

where D represents the sum of the diffusion coefficients as before and Λ is the energy migration coefficient.

The value of k_{diff} can be determined as k_q/α if the value of α for the polymer-quencher pair is known. If the efficiency

of quenching of polymeric phenyl rings by CCl_4 is not greatly different from that of singlet EB, then $\alpha=0.79$ can be used in (3). This leads to $(D+\Lambda)=9.05 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Since D is taken as the diffusion coefficient of CCl_4 alone ($1.53 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) is obtained for the energy migration coefficient, Λ .

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

$$\omega = 6\Lambda/r^2 \quad (4)$$

where r is the separation between phenyl rings at which efficient energy transfer can occur. For planar, aromatic hydrocarbon rings this can be taken²⁹ to be no more than about $3.3 \times 10^{-8} \text{ cm}$. A value of $4.1 \times 10^{11} \text{ s}^{-1}$ is then obtained for ω .

For HH-PS, however, the value of k_{diff} is well below the calculated diffusion-controlled rate of quenching, $k_{\text{diff}}=6.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. There is no evidence for intramolecular energy migration in this polymer in fluid solutions of DCE at room temperature.

Intramolecular energy migration within solid solutions of polymers at 77 K has been demonstrated for a number of different systems^{8,30-34}. Accordingly, the quenching of the fluorescence of 10^{-3} M solutions of EB and HH-PS in solid solutions of α -methyltetrahydrofuran, MTHF, was studied using CCl_4 as quencher.

The results plotted according to equation (1), with the diffusional rate constant k_q being replaced⁸ by an energy migrational rate constant, k_{mig} , yielded non-linear plots. However, Figure 5 shows the results plotted according to the active-sphere model of Perrin³⁵ given by:

$$I_0/I_Q = \exp(VN'[Q]) \quad (5)$$

where I_0 and I_Q are unquenched and quenched fluorescence intensities, respectively, and VN' and $[Q]$ are the volume of the active sphere, Avogadro's number per millimole and the quencher concentration, respectively. It can be seen that reasonably linear plots are obtained. The quencher concentrations have been corrected for volume contraction on cooling the solutions to 77 K.

Values of the radii of the quenching spheres, R_Q , determined from the slopes of the lines in Figure 5 are 14.4 Å and 13.4 Å for EB and HH-PS, respectively. In the absence of material diffusion, a value of about 11 Å for R_Q is expected³⁶ for energy transfer from donor to quencher occurring by an exchange mechanism. The value of 14.4 Å for EB then, is attributable to a small amount of energy migration occurring by reabsorption of fluorescence due to the slight overlap of its absorbance and emission bands. Regardless, the value of R_Q for HH-PS at 13.4 Å is even smaller than that for its model compound, EB, and is good evidence again for the lack of intramolecular energy migration within this polymer. In comparison, Kilp and Guillet³³ have measured values of R_Q of 22.5 Å and 20.3 Å for naphthalene quenching of the phosphorescence of isotactic and atactic poly(acrylophenone), polymers in which intramolecular energy migration occurs with relative ease.

In conclusion, there is no evidence for intramolecular excimer formation or energy migration in HH-PS. This contrasts sharply with the situation in HT-PS and provides good evidence for the importance of nearest-versus non-nearest-neighbouring chromophore interactions for these photoprocesses.

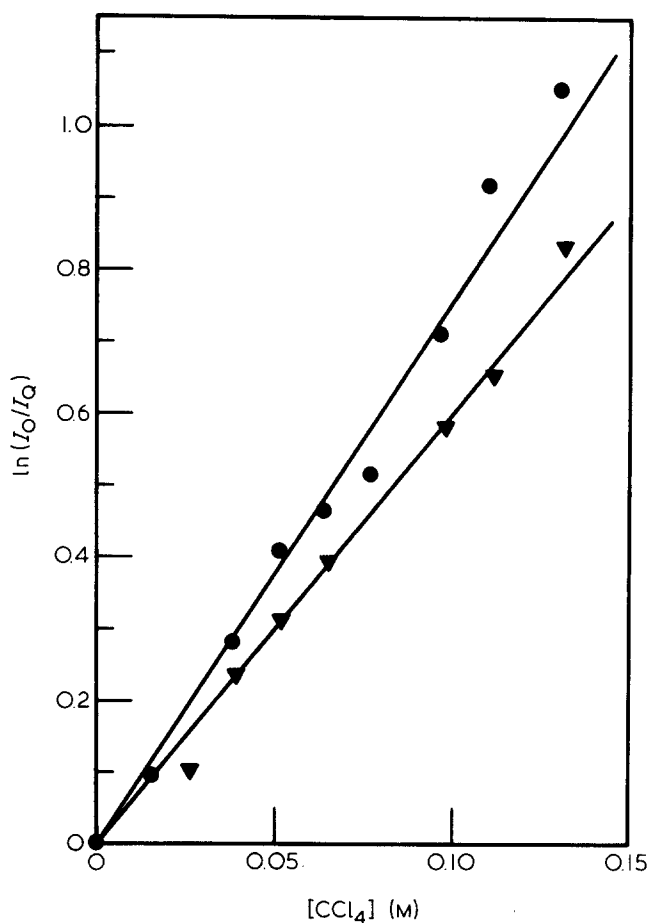


Figure 5 Fluorescence quenching in 77K solid solutions: ●, EB; ▼, HH-PS

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